Dithienopyrroles:
Monomers, Oligomers, and Polymers

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Fakultät für Naturwissenschaften, Universität Ulm
“... and all the pieces matter” (Freamon, The Wire)
Danksagung

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The aim of this thesis was the synthesis and characterization of various dithienopyrroles and corresponding homopolymers. Especially with respect to their optoelectronic properties valuable structure-property relationships can thus be provided. Chapter 1 introduces selected examples of conjugated polymers and then deals with fused electron-rich heteroacenes, which are structurally related to dithienopyrroles. Moreover, literature-known monomeric, oligomeric, and polymeric dithienopyrrole derivatives are presented. In Chapter 2 own results regarding synthesis of N-functionalized dithieno[3,2-b:2′,3′-d]pyrroles by two complementary strategies, as well as oxidative polymerizations by electrochemical or chemical means are shown. The optoelectronic properties of both monomers and polymers are discussed and are correlated to the electronic distribution in the frontier molecular orbitals or to their chemical structures, respectively. Thus, the influence of substituents at the nitrogen is analysed in detail. Contrary to that, Chapter 3 is subsequently focused on the alteration of heteroatom positions in the conjugated backbone leading to a series of isomeric dithieno[2,3-b:3′,2′-d]pyrroles. Herein, consequences for the properties of monomers and polymers are elucidated. Chapter 4 deals with a series of dithieno[3,2-b:2′,3′-d]pyrrole derivatives bearing methyl residues in the two β-positions. The influence of these moieties on monomers and polymers is examined and entails the synthesis of two acceptor-donor-acceptor-type oligomers in Chapter 5. The latter compounds are suitable candidates for application in vacuum-processed organic solar cells.
List of abbreviations

A  acceptor
abs absorption
Ac  acyl
Anth anthracenyl
aq  aqueous
a.u. arbitrary unit
BHJ  bulk heterojunction
BINAP 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
Boc tert-butyloxy carbonyl
bp  boiling point
br  broad
Bu  butyl
Bz  benzyl
calc calculated
Cl  chemical ionization
CPDT cyclopenta[2,1-b;3,4-b′]dithiophene
CT  charge transfer
Cy  cyclohexyl
Cyclodec cyclodecyl
D  donor
dba  dibenzylideneacetone
dcc  N,N'-dicyclohexylcarbodiimide
DCTB trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile
DCV  dicyanovinylene
dec  decomposition
Dec  decyl
DFT  density functional theory
DIAD diisopropyl azodicarboxylate
DMAP N,N'-dimethylaminopyridine
DMC  dimethylethylene carbonate
DMEDA N,N'-dimethylethylenediamine
DMF  dimethylformamide
DMSO  dimethylsulfoxide
Dodec dodecyl
DPPA  diphenylphosphoryl azide
dppe 1,2-bis(diphenylphosphino)ethane
dppf 1,1′-bis(diphenylphosphino)ferrocene
dppp 1,3-bis(diphenylphosphino)propane
DSC  differential scanning calorimetry
DTP  dithieno[3,2-b:2′,3′-d]pyrrole
E  potential; energy
ecc  electrochemical
EC  ethylene carbonate
EDOT  3,4-ethylenedioxythiophene
El  electron ionization
<table>
<thead>
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<tr>
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<td>equivalents</td>
</tr>
<tr>
<td>exp</td>
<td>experimental</td>
</tr>
<tr>
<td>Fc</td>
<td>ferrocene</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier transformation</td>
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<td>g</td>
<td>gap</td>
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<td>gel permeation chromatography</td>
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<tr>
<td>Hexadec</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HPLC</td>
<td>high-performance liquid chromatography</td>
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<tr>
<td>HR</td>
<td>high resolution</td>
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<td>I</td>
<td>current</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>iso-DTP</td>
<td>dithieno[2,3-b:3',2'-d]pyrrole</td>
</tr>
<tr>
<td>iPr</td>
<td>isopropyl</td>
</tr>
<tr>
<td>J</td>
<td>coupling constant</td>
</tr>
<tr>
<td>LDA</td>
<td>lithium disopropylamide</td>
</tr>
<tr>
<td>lit</td>
<td>literature</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>M</td>
<td>molar; product molecule (mass spectrometry)</td>
</tr>
<tr>
<td>MALDI</td>
<td>matrix-assisted laser desorption/ionization</td>
</tr>
<tr>
<td>max</td>
<td>maximum</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
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<tr>
<td>Me-DTP</td>
<td>β,β'-dimethyl-substituted dithieno[3,2-b:2',3'-d]pyrrole</td>
</tr>
<tr>
<td>M_p</td>
<td>melting point</td>
</tr>
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<td>MS</td>
<td>mass spectrometry</td>
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<td>NBS</td>
<td>N-bromosuccinimide</td>
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<td>NIR</td>
<td>near infrared</td>
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<td>NIS</td>
<td>N-iodosuccinimide</td>
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<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>norm</td>
<td>normalized</td>
</tr>
<tr>
<td>Non</td>
<td>nonyl</td>
</tr>
<tr>
<td>Oct</td>
<td>octyl</td>
</tr>
<tr>
<td>Octadec</td>
<td>octadecyl</td>
</tr>
<tr>
<td>OFET</td>
<td>organic field effect transistor</td>
</tr>
<tr>
<td>OLED</td>
<td>organic light-emitting diode</td>
</tr>
<tr>
<td>opt</td>
<td>optical</td>
</tr>
<tr>
<td>OPV</td>
<td>organic photovoltaics</td>
</tr>
<tr>
<td>ox</td>
<td>oxidation</td>
</tr>
<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PC61BM</td>
<td>[6,6]-phenyl-C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PC71BM</td>
<td>[6,6]-phenyl-C71-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCC</td>
<td>pyridinium chlorochromate</td>
</tr>
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List of abbreviations

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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>PCE</td>
<td>power conversion efficiencies</td>
</tr>
<tr>
<td>Pent</td>
<td>pentyl</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>phen</td>
<td>phenanthroline</td>
</tr>
<tr>
<td>PMI</td>
<td>perylene monoimide</td>
</tr>
<tr>
<td>Pr</td>
<td>propyl</td>
</tr>
<tr>
<td>PSS</td>
<td>poly(styrene sulfonic acid)</td>
</tr>
<tr>
<td>red</td>
<td>reduction</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>RuPhos</td>
<td>2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl</td>
</tr>
<tr>
<td>sh</td>
<td>shoulder</td>
</tr>
<tr>
<td>t</td>
<td>reaction time</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>T$_d$</td>
<td>decomposition temperature</td>
</tr>
<tr>
<td>TA</td>
<td>thiazolyl</td>
</tr>
<tr>
<td>TBA</td>
<td>tetrabutylammonium</td>
</tr>
<tr>
<td>tBuXPhos</td>
<td>2-di-tert-butylphosphino-2′,4′,6′-triisopropylbiphenyl</td>
</tr>
<tr>
<td>Tetradec</td>
<td>tetradecyl</td>
</tr>
<tr>
<td>TGA</td>
<td>thermal gravimetric analysis</td>
</tr>
<tr>
<td>Th</td>
<td>thienyl</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TIPS</td>
<td>triisopropylsilyl</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
</tr>
<tr>
<td>TMEDA</td>
<td>$N,N,N',N'$-tetramethylethylenediamine</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>TOF</td>
<td>time of flight</td>
</tr>
<tr>
<td>Tol</td>
<td>tolyl</td>
</tr>
<tr>
<td>Tos</td>
<td>tosyl</td>
</tr>
<tr>
<td>$t_r$</td>
<td>retention time</td>
</tr>
<tr>
<td>Undec</td>
<td>undecyl</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>Vis</td>
<td>visible</td>
</tr>
<tr>
<td>ZSW</td>
<td>Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift</td>
</tr>
<tr>
<td>Δ</td>
<td>differential</td>
</tr>
<tr>
<td>ε</td>
<td>molar extinction coefficient</td>
</tr>
<tr>
<td>λ</td>
<td>wavelength</td>
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</table>
Aim of the work

The fascinating field of organic electronics combines the quite different industries of polymers and electronics in order to produce advanced high-performance materials. These compounds are intended to comprise typical optoelectronic properties of semiconductors, but are still easy to process into devices and have the potential to be more cost-effective than common inorganic materials like silicon.\textsuperscript{1-3} Increasingly, organic molecules find commercialization in light-emitting diodes,\textsuperscript{4} field-effect transistors,\textsuperscript{5} or solar cells,\textsuperscript{6} in which the chemical structure of the compounds determines the device performance to a major extent. Hence, structure-property relationships are the crucial foundation for the optimal and rational design of tailored materials for specific applications.

Dithienopyrroles are a popular class of building blocks because the structure exhibits a planar geometry, enabling an extended conjugation, low HOMO-LUMO energy gaps, and strong intermolecular interactions.\textsuperscript{7} Since the first report about dithienopyrroles,\textsuperscript{8} various derivatives have been synthesized which usually contain solubilizing alkyl substituents at the nitrogen. Homopolymers,\textsuperscript{9} co-polymers,\textsuperscript{10} or well-defined oligomers\textsuperscript{11} thereof have moreover been prepared (Scheme A1), whereas most commonly the electron-rich dithienopyrrole unit functions as the donor part in donor-acceptor-type compounds.

![Scheme A1: Homopolymers (left) and well-defined acceptor-donor-acceptor-type oligomers (right) comprising dithienopyrrole units (middle).](image)

In this thesis the aim was to synthesize and characterize different dithienopyrroles and corresponding homopolymers to provide further structure-property relationships particularly with regard to optoelectronic features. Therefore, the scope of \emph{N}-functionalizations of dithienopyrroles should be expanded and new synthetic pathways should be established.
Aim of the work

Comparing the properties of diverse substituted derivatives is supposed to shed light on the specific influence of functional groups attached at the nitrogen in both monomers and polymers. Secondly, the $\pi$-system itself should be altered by changing the relative positions of heteroatoms to each other. This might not only affect the conjugated backbone, but also change the influence of $N$-substituents. Finally, the two $\beta$-hydrogens of dithienopyrroles should be exchanged for methyls to impact the geometry of the corresponding monomers and polymers via steric interactions with bulky substituents or adjacent repeat units, respectively. Promising dithienopyrroles should also be used as the donor unit in acceptor-donor-acceptor-type oligomers for potential application in organic solar cells.

References

Synthesized compounds

Target compounds

Chapter 2:

Chapter 3:

Chapter 4:
Chapter 5:

**Synthesized compounds**

**Precursor**
Chapter 1

From conjugated polymers to dithienopyrroles and related heteroacenes
1.1 Conjugated polymers: polyacetylene, polythiophenes, and polypyrroles

Organic polymers can exhibit a huge range of different properties, but for a long time they had only been considered as insulating materials. This point of view changed with the discovery and development of electronically conducting polymers for which in the year 2000 Heeger, MacDiarmid, and Shirakawa were awarded the Nobel Prize in chemistry.[1-3] Hence, in the emerging field of organic electronics it was envisioned to combine the optoelectronic properties of metals or semiconductors with the ease of processing and low cost of polymers in order to manufacture so-called “synthetic metals”. [2] The structural requirements for these advanced materials are conjugated double or triple bonds and the structurally simplest polymeric representative thereof is polyacetylene (Figure 1.1). It can be prepared by Ziegler-Natta polymerization of acetylene and depending on the reaction conditions the configuration of the double bonds can be adjusted. Thus, at -78 °C in toluene the copper-coloured product contains about 98% cis double bonds, while at 150 °C in n-hexadecane the silver-coloured all-trans form is obtained.[4-6] Due to the Peierls distortion the double bonds are not delocalized and a bond length alternation is observed.[7-10] Therefore, the occupied π- and unoccupied π*-bands give rise to a non-zero band gap and render pristine polyacetylene a semiconductor.[1, 11] Intriguingly, by doping of the material, i.e. partial oxidation (p-type doping) or reduction (n-type doping), free charge carriers can be introduced which vastly increase the electrical conductivity up to the range of coinage metals.[12-16] However, as polyacetylene is insoluble and unstable under ambient conditions, it has remained fascinating only as a model for theoretical considerations, but not for practical applications.

![Figure 1.1: Structures of all-cis and all-trans polyacetylene.](image)

In order to yield environmentally more stable materials, aromatic compounds such as pyrrole[17] or thiophene[18] were polymerized after the pioneering work about polyacetylene. Early on polythiophenes gained much attention and were prepared by metal-catalysed cross-coupling,[19-20] Wurtz coupling,[21] or electropolymerization,[22] respectively. Yet, their low solubilities hampered characterization and processability and therefore solubilizing alkyl
chains were attached in the 3-positions. While this reduced the probability of β-coupling defects, regioisomerism became relevant. Thus, besides regioregular head-to-tail couplings also head-to-head or tail-to-tail linkages can be formed, leading to regioirregular poly(3-alkylthiophene)s (Scheme 1.1).

Scheme 1.1: Dimerization of 3-alkylthiophenes to different regioisomers.

In head-to-head connected thiophenes sterical repulsions between the rings cause a twist and hence a partial loss of conjugation between the repeat units in regioirregular poly(3-alkylthiophene)s. On the other hand, regioregular poly(3-alkylthiophene)s do not exhibit such detrimental interactions and can therefore self-assemble into highly ordered crystalline domains. This profoundly affects the optoelectronic properties and leads to decreased band gaps and bathochromically shifted maximum absorption wavelengths of regioregular poly(3-alkylthiophene)s. The regioselective connection between the repeat units is usually achieved by transition metal-catalysed cross-coupling polymerizations and one example known as the Grignard metathesis method by McCullough et al. is shown in Scheme 1.2. Initially, metallation of a 3-alkyl-2,5-dibromothiophene affords the required Grignard reagent. This precursor is then polymerized producing soluble regioregular polythiophenes due to the high selectivity of the applied nickel catalyst. Because of the quasi-living nature of the process the most popular derivative, poly(3-hexylthiophene) (P3HT), can be prepared in a wide range of polymerization degrees and varying polydispersities. Moreover, its synthesis can be conducted on kilogram scale, making it particularly attractive for the industrial use in optoelectronic devices.

Scheme 1.2: Grignard metathesis method for the synthesis of regioregular poly(3-alkylthiophene)s.
Substituting both $\beta$-positions of thiophene with alkyl moieties further increases the solubility of the corresponding polythiophenes, but also maximizes unfavourable steric repulsions between the repeat units. However, with attached carbocycles instead of linear residues steric hindrance can largely be reduced.[37] This has also been exploited in poly(3,4-ethylenedioxythiophene) (PEDOT), where additionally intramolecular interactions between oxygen and sulphur from adjacent repeat units planarize the $\pi$-conjugated system.[38] Due to the electron-donating influence of the alkoxy groups oxidative polymerizations of EDOT proceed very efficiently and have already been conducted in the first reports about PEDOT.[39-40] Because moreover no $\alpha$-$\beta$ or $\beta$-$\beta$ couplings can occur, a strictly linear defect-free polymer is obtained which has been correlated to the high stability of PEDOT.[41] Combining a moderate band gap (about 1.6 eV)[42] and a low oxidation potential (about -0.4 V vs. Ag/AgCl),[42] PEDOT exhibits an exceptional stability in the doped conducting state. Furthermore, it can be reversibly switched between the opaque dark blue neutral polymer and the oxidized form with a transparent light blue appearance.[43] Usually PEDOT is insoluble in any common organic solvent, yet by applying only small amounts of oxidant a short soluble polymer can be produced as well which on average exhibits between seven and eleven EDOT units.[44] Contrary to that, electropolymerization affords an insoluble material on the surface of the working electrode.[45] While just rather small amounts of the polymer can thus be synthesized, no purification steps after the polymerization are required and therefore no issues with the processing of insoluble fractions arise. Moreover, by electrochemical

![Scheme 1.3: Aqueous oxidative polymerization to PEDOT:PSS.](image)
means structuring on the nanometer scale\textsuperscript{[46]} and even polymerization in living tissue\textsuperscript{[47-48]} can be achieved. In industry, oxidative polymerization with peroxodisulfate and iron(III) sulfate in the presence of poly(styrene sulfonic acid) (PSS) as both template and dispersant is the method of choice to yield PEDOT:PSS polyelectrolyte complexes (Scheme 1.3). Herein, about every third or fourth monomer unit carries a positive charge in the relatively short PEDOT chains, which are electrostatically bound to the much larger PSS strings.\textsuperscript{[49]}

Commonly, aqueous dispersions of gelled particles are processed into thin films and are widely applied as antistatic or conductive coatings.\textsuperscript{[44, 49-51]} In order to tailor specific properties of PEDOT, functional groups can already be attached at the ethylene bridge of the monomer, but because of steric or electronic limitations especially electropolymerizations are sometimes inhibited. Hence, polythiophenes with bulky, respectively strongly electron-donating substituents at EDOT, are usually prepared by incorporating additional thiophenes in the monomer,\textsuperscript{[52]} copolymerization with another polymerizable compound,\textsuperscript{[53]} or post-functionalizations.\textsuperscript{[54-55]}

Concerning pendant groups at the conjugated $\pi$-system, pyrrole exhibits an advantage compared to thiophene, as in addition to the $\beta$-positions the nitrogen can also be functionalized via nucleophilic substitutions. Moreover, because of its symmetry with the nitrogen in the centre $N$-substituted polypyrroles do not possess regioisomers. Much effort has therefore been devoted to the modification of electrode surfaces with this polymer, although the conductivity usually decreases upon $N$-functionalization.\textsuperscript{[56]} The general goal in this approach is to promote certain electrochemical reactions either by accelerating a slow electron transfer between the electrode and the substrate or by direct involvement of an immobilized catalyst in the reaction.\textsuperscript{[57-58]} Thus, a large variety of ligands like bipyridine in pyrrole 1\textsuperscript{[59]} or phenanthroline in pyrrole 2\textsuperscript{[60]} can be attached at the nitrogen (Figure 1.2)

![Figure 1.2: Structures of pyrroles 1-3 bearing a bipyridine (left),\textsuperscript{[59]} phenanthroline (middle),\textsuperscript{[60]} or biotin (right)\textsuperscript{[61]} moiety attached at the nitrogen.](image-url)
after which a suitable metal is added and the respective catalytically active complex is obtained.\cite{62} Subsequently, electropolymerization not only permits the deposition of stable polypyrrole coatings, but also allows for precise control of the film thickness and hence the amount of incorporated active sites. Furthermore, besides inorganic complexes also organic moieties can be linked to polypyrrole and enable specific interactions. For example, immobilization of enzymes on biotin-substituted polypyrrole 3 (Figure 1.2) has been achieved, exploiting the high association constant of the biotin-avidin interaction \cite{63} and this concept can be applied in various sensing devices.\cite{64-65}
1.2 S,N-Heteroacenes

Combining both thiophenes and pyrroles in monodisperse fused systems leads to sulphur- and nitrogen-containing so-called S,N-heteroacenes. These molecules have raised attention, because the incorporation of heteroatoms often leads to a stabilization of large acenes,\(^{[66-71]}\) while the pyrrolic nitrogen moreover allows for the attachment of solubilizing alkyl chains. Already in 1957, unsubstituted SN2-derivative 4H-thieno[3,2-b]pyrrole was reported for the first time\(^{[72]}\) and was later electropolymerized to a thin film.\(^{[73]}\) The methyl-substituted analogue 9 is also literature-known and was prepared in five steps starting from commercially available aldehyde 4 (Scheme 1.4).\(^{[74-75]}\) Knoevenagel condensation of 4 with ethyl azidoacetate yielded 5, which was thermolyzed in xylene to close the pyrrole ring via intramolecular cyclization. Afterwards, N-functionalization of 6 was achieved in a nucleophilic substitution with methyl iodide by applying potassium tert-butoxide as base. The attached ester group in 7 was then hydrolysed under basic conditions and a copper-catalysed decarboxylation of 8 in the final step afforded target compound 9.

![Scheme 1.4: Synthesis of SN2-derivative 9.\(^{[74-75]}\)](image)

The next larger dithienopyrrole derivatives (SN3) with thiophenes at both edges are subject of the following Chapter 1.3 and Chapter 2 in this thesis. However, a whole series of further extended S,N-heteroacenes 10-25 up to SN13 bearing hexyl residues at the nitrogens was prepared in our institute and valuable structure-property relationships were derived (Figure 1.3).\(^{[76-81]}\) Thus, elongation of the conjugated backbone leads to a bathochromic and hyperchromic shift of the absorption maximum and a decrease of the optical HOMO-LUMO
energy gap. The emission maxima are also shifted to higher wavelengths and due to the rigid \( \pi \)-systems with little structural changes from the electronic ground state to the first excited state, very small Stokes shifts are observed. Additionally, the planar backbone enables strong S-S and S-\( \pi \) dipolar interactions in the solid state leading, for instance, to an unusual herringbone packing motif of SN7’.\(^{[78]}\) While the shortest S,N-heteroacenes exhibit an irreversible one-electron oxidation followed by their polymerization at the terminal positions, SN6 14 and the longer analogues 15-25 show two quasi-reversible or reversible oxidation waves. Herein, extension of the conjugated backbone and incorporation of more electron-rich pyrrole rings tend to destabilize the HOMO and facilitate the formation of radical cations and dications.

Figure 1.3: Structures of a series of hexyl-substituted S,N-heteroacenes 10-25.\(^{[76-82]}\)

Concerning the synthesis of these extended S,N-heteroacenes, Negishi- or Stille-type reactions were required to build up the carbon skeleton, whereas palladium-catalysed C-N or
C-S couplings were crucial for the incorporation of heteroatoms. In 2012, Suga et al. reported the preparation of a SN5-series in two steps starting from monothiophenes[83] and various substituted analogues have been prepared since then (Scheme 1.5).[76, 84-87] Firstly, tetrabromothiophene 26 was reacted with two equivalents of the zinc organyl 27 in a Negishi-type cross-coupling and terthiophene precursor 28 was obtained. Afterwards, twofold ring fusion was achieved by Buchwald-Hartwig amination with different alkyl or aryl amines and the corresponding substituted SN5-derivatives 12, 29-41 could be isolated.

![Scheme 1.5: Synthesis of precursor 28[83] and subsequent amination to SN5-derivatives 12, 29-41.](image)

Currently the longest representative of the S,N-heteroacene family is the tridecane 25 with overall thirteen fused thiophenes and pyrroles.[81] The remarkable synthesis involved the connection of two hexyl-substituted SN5-molecules in the peripheries with one thiophene in the middle as well as the final closure of two central thiophene rings (Scheme 1.6). More precisely, one α-position of SN5 12 was initially protected with a triisopropylsilyl (TIPS) group, which then enabled the selective monobromination of the second α-position of the obtained molecule 42 with NBS. A halogen dance reaction of 43 shifted this bromine to the β-position, whereas the free α-position in 44 could be brominated again. Subsequently, two equivalents of the dibromide 45 were cross-coupled with distannyl 46 in a Stille reaction to afford 47. This precursor already possessed the carbon skeleton of the desired SN13, but also contained the required bromines for following ring closure reactions. At first, Buchwald-Hartwig aminations with hexylamine were envisaged to incorporate further pyrrole moieties leading to a SN13-derivative with alternating thiophenes and pyrroles. However, already the shorter SN11'-analogue could not
be isolated, because more than four electron-rich pyrrole rings increased the HOMO energy level too strongly and thus render the respective S,N-heteroacene very unstable. As an alternative, palladium-catalysed C-S couplings with potassium thioacetate\cite{88} intriguingly afforded the completely fused system 48 exhibiting nine thiophenes and four pyrroles. Efficient cleavage of the TIPS protecting groups in the α-positions with tetrabutylammonium (TBA) fluoride finally yielded SN13-derivative 25.

Scheme 1.6: Synthesis of SN13-derivative 25.\cite{85}

Besides the novel structural features in extended S,N-heteroacenes revealing fascinating fundamental insights (\textit{vide supra}), electron-poor acceptor moieties have also been attached at the peripheries of several representatives and corresponding acceptor-donor-acceptor-type oligomers have successfully been implemented in high performance organic electronic devices.\cite{76-77, 84-86, 89-95} Yet, because of their tedious and time-consuming synthesis, in this respect the shorter S,N-heteroacenes, such as SN3, are much more convenient building blocks.
1.3 Monomeric dithienopyrroles

Thus, dithieno[3,2-b:2',3'-d]pyrroles (DTPs) comprising two thiophenes fused with one central pyrrole ring can be prepared in few steps and are widely used as precursors to build up larger conjugated systems. While the nitrogen in the centre provides planarization of DTPs and therefore ensures an improved π-orbital overlap compared to 2,2'-bithiophene, it also enables the attachment of functional groups without desymmetrization of the molecule (Figure 1.4). Hence, extending the conjugated system of DTP in both α- or β-positions does not cause regioirregularities, which, for example, are an issue with mono-functionalized thiophenes and can strongly affect the properties of the formed products (Chapter 1.1). In contrast to the longest derivatives of the S,N-heteroacene series, DTPs moreover do not form stable radical cations and can therefore be polymerized under oxidative conditions to poly(dithieno[3,2-b:2',3'-d]pyrrole)s (p(DTP)s, Figure 1.4).

![Figure 1.4: General structure of DTPs.](image)

For the synthesis of DTP monomers several different strategies have been applied and over the years product yields and scope have vastly improved. In 1983, the first report on DTPs by Zanirato et al. showed the synthesis of unsubstituted parent system 50 via thermolysis of 3-azido-2,2'-bithiophene 49 in a yield of 87% (Scheme 1.7). Later, nucleophilic substitutions with DTP 50 were carried out in order to attach various solubilizing alkyl residues at the nitrogen of DTP 51-56 (Scheme 1.7). Herein, a phase-transfer catalysis procedure was developed involving sodium hydroxide as base to deprotonate unsubstituted DTP 50. The same protocol also enabled the attachment of a 3,6,9-trioxadecyl moiety in DTP 57 or an ester residue in DTP 58. Although substitution reactions worked quite efficiently, the preparation of azide precursor 49 in several steps and only moderate overall yields for DTP 50 still limited the practical application of DTPs as building blocks for larger conjugated molecules.
Scheme 1.7: Synthesis of unsubstituted DTP 50 via thermolysis of azide 49\(^{[96]}\) and subsequent functionalizations via phase-transfer catalysis (X=Br, I, or Tos).

Therefore, a direct Buchwald-Hartwig amination of 3-bromothiophene 59 with several different primary amines was carried out to obtain a mixture of mono- and bis-aminated products (Scheme 1.8).\(^{[82]}\) The two compounds could be separated and in order to improve the yield of the desired bis-aminated product, the isolated aminothiophenes were coupled again with 3-bromothiophene 59.\(^{[102]}\) Afterwards, a twofold bromination with NBS was conducted and in the same pot the pyrrole ring was finally closed in a copper-catalysed Ullmann reaction.\(^{[82, 103-104]}\) This procedure yielded alkyl- or aryl-substituted DTPs 52-53, 60-69 in moderate overall yields and could be carried out on multi-gram scale. Nevertheless, the unselective amination step and the reactive nature of the isolated amine intermediates were a major drawback in this synthesis approach.

Scheme 1.8: Synthesis of alkyl- and aryl-substituted DTPs 52-53, 60-69 via Buchwald-Hartwig amination and subsequent bromination and Ullmann coupling.
It thus proved to be a superior strategy to reverse the coupling reactions, first building up a bithiophene unit by C-C bond formation and then closing the pyrrole ring via twofold amination. An important discovery in this respect was the efficient synthesis of the required starting material 3,3′-dibromo-2,2′-bithiophene 72 by Evenson and Rasmussen in 2010 (Scheme 1.9).\[^{105}\] The previous method involved bromination of 3-bromothiophene 59 with bromine to 2,3-dibromothiophene 70\[^{106}\] and in an additional step lithiation with \( n \)-BuLi followed by oxidative C-C coupling with CuCl\(_2\).\[^{107}\] In the new method, selective lithiation of 3-bromothiophene 59 in the 2-position was achieved with LDA and subsequent salt metathesis with zinc chloride gave the corresponding metal organyl 71. The latter could be coupled oxidatively with cupric chloride and oxygen gas in one pot and afforded dibromide 72 in 88% yield.

![Scheme 1.9: Synthesis of dibromide precursor 72.\[^{105-107}\]](image)

Using dibromide 72 as precursor, twofold aminations with R-NH\(_2\) were carried out and DTPs with various residues R at the nitrogen have been reported (Scheme 1.10).\[^{83, 105, 108-138}\] Initially, in the palladium-catalysed Buchwald-Hartwig amination of dibromide 72 with aniline phenyl-substituted DTP 65 was afforded in a yield of only 35% by applying the ligand P(tBu)\(_3\) at a reaction temperature of 80 °C.\[^{108}\] Afterwards, the bidentate ligands BINAP or dppf were mostly used in combination with Pd\(_2\)dba\(_3\) or Pd(dba)\(_2\) as palladium sources, because they force the bithiophene and the amine units in the required cis-configuration at the metal in the catalytic cycle. However, the most important aspect was to increase the reaction temperature to 110 °C\[^{114}\] and thus different alkyl- and aryl-substituted DTPs 52-55, 60, 63-65, 67, 73-89 were synthesized in excellent yields.\[^{109-110}\] The substrate scope was nevertheless quite limited and with further functional groups yields of the corresponding DTPs shrank drastically. Lutkenhaus et al., for instance, could prepare the 3,6,9-trioxa-}
substituted DTP 57 in a yield of just 35%.[131] Furthermore, by applying amides instead of primary amines, the coupling reaction with palladium catalysts was impeded and a copper catalyst had to be used instead.[105, 134] According to Evenson and Rasmussen, in the latter reactions the formed DTP products inhibited the catalyst which limited the conversion of the starting material 72.[105] Thus, the corresponding acyl- or benzyol-substituted DTPs 90-97 could be isolated in only moderate yields.

![Scheme 1.10: Synthesis of N-substituted DTPs 52-55, 57, 60, 63-65, 67, 73-110 via amination of dibromide 72 applying palladium or copper catalysts.](image)

When the DMEDA ligand at the copper catalyst was exchanged for L-proline, the amination of dibromide 72 with aryl diamines could be achieved, leaving one free NH₂ group at the phenyl or naphthyl residue in DTP 105 or 106, respectively.[126-127] Although a very long reaction time of eight days and even two equivalents of dibromide 72 were applied in the
coupling with 1,5-diaminonaphthalene, the second amino group did not react further after the ring closure to the dithienopyrrole unit and product \textbf{106} was obtained in a yield of 30%. However, when the reaction was carried out under palladium catalysis with other diamines, the analogous DTPs \textbf{104, 107, or 108} comprising a terminal NH$_2$-moiety could be isolated in 45% only by using equimolar amounts of the starting materials, respectively.$^{127-128, 137}$ Applying a 1:2 ratio of 1,10-decanediamine and dibromide \textbf{72}, on the other hand, \textit{bis}-DTP \textbf{111} was afforded in 78% yield in which two DTP units are connected through their nitrogens by an alkyl spacer (Figure 1.5). Later on, further examples of well-defined molecules comprising more than one DTP unit were synthesized by Ge \textit{et al.} (Figure 1.5).$^{139}$ They prepared the \textit{mono-}, \textit{bis-}, or \textit{tris}-amines of a truxene derivative and then carried out Buchwald-Hartwig aminations with dibromide \textbf{72} to obtain the corresponding DTPs \textbf{112-114} in yields of 35-83%, respectively.

![Figure 1.5: Chemical structures of the bis-DTP \textbf{111}$^{127}$ and DTP-substituted truxenes \textbf{112-114}$^{139}$](image)

While DTPs are by far the most common SN3-derivatives, isomeric dithieno[2,3-\textit{b}:3',2'-\textit{d}]-pyrroles (iso-DTPs) also comprise two terminal thiophenes with one pyrrole ring in the centre, but here all heteroatoms are located on the same side. In 2012, Nenajdenko \textit{et al.} reported the synthesis of iso-DTPs \textbf{123} and \textbf{124} with either ethyl or isopropyl residues at the nitrogen (Scheme 1.11).$^{140}$ Reacting first of all the corresponding \textit{N}-substituted succinimides \textbf{115} and \textbf{116} with the Vilsmeier reagent in a chloroformylation, pyrroles \textbf{117} and \textbf{118} were isolated in low yields.$^{141}$ Subsequently, two thiophenes were fused onto the central pyrrole via ring closure with ethyl thioglycolate. The ester groups in \textbf{119} and \textbf{120} were then hydrolysed and finally decarboxylation of the obtained \textbf{121} and \textbf{122} by pyrolysis under reduced pressure gave desired iso-DTPs \textbf{123} and \textbf{124} in overall yields of 3-4%, respectively.
The major disadvantage of this approach was the first step with quite low yields and harsh reaction conditions. Furthermore, the residue at the nitrogen was already attached in the beginning. Therefore, it was required to repeat and optimize each step in the sequence for the synthesis of iso-DTPs with different substituents. In this regard, a different approach involving substitution of the iso-DTP backbone at the nitrogen in the last step would be more convenient for the synthesis of a whole iso-DTP series. A suitable precursor for such a synthetic route would be unsubstituted iso-DTP 126. However, investigations of Zanirato et
al. showed that while unsubstituted DTP 50 could be prepared via thermolysis of 3-azido-2,2′-bithiophene 49 (vide supra), analogous iso-DTP 126 was not accessible in such a way. Instead the corresponding 2-azido-3,3′-bithiophene 125 already decomposed at ambient temperatures under release of dinitrogen and ring-opening (Scheme 1.12). The authors suggested that intermediate 127 was formed and dimerized in a hetero Diels-Alder-reaction. Analyses of the isolated products indicated the structure of the two isomers 128 and 129, but the compounds were too unstable to be fully characterized.

An alternative method for the substitution of parent iso-DTP 126 would be the amination of 2,2′-dibromo-3,3′-bithiophene 130. This strategy is analogous to the mostly applied preparation of DTPs (Scheme 1.10) and bears the advantage of attaching different residues in the final step. Following this approach, Buchwald et al. synthesized Boc-substituted iso-DTP 132 by applying a copper catalyst (Scheme 1.13), but other iso-DTP derivatives have not been reported, yet.

1.4 Cyclopentadithiophenes and dithienothiophenes

Compared to the nitrogen-bridged dithienopyrroles the analogous heterotriacene with carbon instead of nitrogen enables the attachment of two instead of just one substituent at the centre. The 2,2'-bithiophene-based system cyclopenta[2,1-\textit{b}:3,4-\textit{b}']dithiophene (CPDT) is therefore a widely used building block, but has to be synthesized in several steps (Scheme 1.14).\cite{143} First of all, bromothiophene 59 is lithiated in the 3-position and coupled to thiophene-3-carbaldehyde 133. In one pot the intermediate is then lithiated in the 2-positions and iodinated with elemental iodine. The afforded alcohol 134 is oxidized with pyridinium chlorochromate (PCC) to the corresponding ketone 135 in the next step.\cite{144} 

Subsequently, an intramolecular C-C coupling affords the annulated conjugated backbone in 136,\cite{144} which is then reduced to unsubstituted CPDT 137.\cite{145} Finally, functionalizations via deprotonation of CPDT 137 followed by nucleophilic reactions, e.g. with halides or ketones, yield either mono- or disubstituted CPDTs.\cite{146,147,148} Alternatively, Knoevenagel condensations\cite{149} or Wittig reactions\cite{150} can be carried out with ketone 136 to further elongate the conjugated \(\pi\)-system.

\textbf{Scheme 1.14:} Synthesis approach for functionalized cyclopenta[2,1-\textit{b}:3,4-\textit{b}']dithiophenes.\cite{143}
Thus, CPDT 138 bearing a strongly electron-withdrawing dicyanomethylene moiety at the central carbon was synthesized by Ferraris and Lambert.\[149\] Furthermore, in an analogous approach the isomers 139-141 were prepared as well and the influence of the relative positions of the sulphurs on the optoelectronic properties was investigated.\[151-152\] Altering the molecular structure led to a decreasing conjugation length going from CPDT 138 to 141 in Figure 1.6 resulting in decreasing HOMO and increasing LUMO energy levels. Moreover, only isomer 138 afforded smooth films upon electropolymerization,\[149, 153-156\] while the polymer growth with CPDT 139 and 140 was hampered by the slow electron transfer from the electrode through the thin film, respectively.\[151\]

![Figure 1.6: Structures of CPDT isomers 138-141 with dicyanomethylene substituents.](image)

Contrary to that, unsubstituted CPDT 137\[157\] and alkyl-substituted CPDTs\[146\] could readily be electropolymerized to stable films, although long alkyl chains rendered mono- and especially disubstituted derivatives soluble in chloroform. Further studies on alkyl-substituted p(CPDT)s revealed that much higher molecular weight materials could be obtained via chemical oxidative polymerizations with iron trichloride\[145, 147\] than by Kumada-,\[145, 147\] Negishi-,\[147\] or Yamamoto-type\[158\] polymerizations. Intriguingly, analyses via GPC and $^1$H NMR spectroscopy indicated average chain lengths exceeding 100 repeat units and a strictly linear constitution, as no $\beta$-coupling defects could be detected.\[145, 147\] The maximum absorption wavelengths in the UV-Vis spectra recorded in chloroform increased up to an average polymerization degree of 20 with the molecular weight of the polymer, whereas the dioctyl-substituted p(CPDT) showed a $\lambda_{\text{max}}$ of 595 nm and a $\lambda_{\text{onset}}$ of 700 nm.

However, the main disadvantage of cyclopentadithiophenes and their derivatives is the tedious preparation of the fused backbone which involves several steps. Bridging a bithiophene with a heteroatom instead of carbon, on the other hand, greatly facilitates the synthesis (Scheme 1.15). Thus, silicon\[159\] or germanium-bridged\[160\] analogues of CPDT can more conveniently be obtained by twofold lithiation of 3,3'-dibromo-2,2'-bithiophene 72 and
subsequent reaction with the corresponding dichloride. Similarly, the sulphur-bridged
dithieno[3,2-b:2',3'-d]thiophene 142 is afforded after quenching the lithiated species with
bis(phenylsulfonyl)sulphide.\textsuperscript{[161-162]} In 1985, this heterotriacene was electropolymerized for
the first time, giving a film of poly(dithienothiophene) on the working electrode with highly
reversible electrochromic behaviour.\textsuperscript{[163-164]} Upon oxidation the red polymer became dark
blue and only small degradation of the material was observed after 11000 switches.\textsuperscript{[165-166]}
While dithienothiophene 142 is the most commonly used derivative, all six dithienothiophene isomers 142-147 shown in Figure 1.7 have already been synthesized.\textsuperscript{[167]}

![Scheme 1.15: Synthesis of silolo[3,2-b:4,5-b']dithiophenes,\textsuperscript{[159]} germolo[3,2-b:4,5-b']dithiophenes,\textsuperscript{[160]} or dithieno[3,2-b:2',3'-d]thiophene\textsuperscript{[161-162]} starting from 3,3'-dibromo-2,2'-bithiophene 72.](image)

Figure 1.7: Structures of dithienothiophene isomers 142-147.

Their preparations involve successive C-C and C-S couplings, but different strategies have
been applied with variations in the order of these reactions. As an example, two approaches
for the synthesis of isomer 143 starting from commercially available 3-bromothiophene 59
are depicted in Scheme 1.16. In the first sequence,\textsuperscript{[168]} bromine-lithium exchange with n-BuLi
is followed by an oxidative homocoupling to 3,3'-bithiophene. Afterwards, twofold
bromination with N-bromosuccinimide (NBS) yields dibromide 130, which is lithiated and
quenched with (PhSO\textsubscript{2})\textsubscript{2}S. This strategy is analogous to the synthesis of isomer 142 shown in
Scheme 1.15, where first the bithiophene unit is built up to finally close the central ring via
twofold C-S couplings. However, in the complementary second approach this order is
reversed.\textsuperscript{[169]} Selective lithiation of 59 in the 2-position is achieved with lithium diisopropyl-
amide (LDA) and quenching with bis(phenylsulfonyl)sulphide affords intermediate 148. Lithium-bromine exchange with n-BuLi and oxidative C-C coupling with cupric chloride then gives target compound 143 in slightly higher overall yields and in just two instead of three steps.

Scheme 1.16: Two different strategies to synthesize dithieno[2,3-b:3',2'-d]thiophene 143 from 3-bromothiophene 59.\textsuperscript{[168-169]}

Dithienothiophenes are quite electron-rich and are thus suitable donor building blocks for donor-acceptor-type oligomers or polymers. The planar geometry enables close \(\pi-\pi\) stackings and strong S-\(\pi\) or S-S interactions in the solid state which is often favourable for application in optoelectronic devices.\textsuperscript{[170]} Yet, as no alkyl residues are attached, the solubility in common organic solvents quickly decreases when the conjugated backbone is elongated.\textsuperscript{[171-173]} This constitutes a major drawback and limits the access to extended \(\pi\)-systems to a certain extent.
1.5 Donor-acceptor-type oligomeric dithienopyrroles

A widely used concept in elongated π-systems involves the alternating incorporation of electron-rich (donor, D) and electron-poor (acceptor, A) units in polymers or monodisperse oligomers.\(^{[174]}\) The molecular orbitals of these components are mixed leading to decreased band gaps \(E_g\) in donor-acceptor-type compounds (Figure 1.8). This originates from the fact that the HOMO is mainly localized at the destabilized donor moieties, whereas the LUMO is dominated by the stabilized acceptors. Selecting suitable donor and acceptor building blocks with matching electron pushing, respectively pulling strengths, therefore allows to fine-tune the energy levels of the frontier molecular orbitals. Consequently, materials with adjusted band gaps for the application in optoelectronic devices can be designed which absorb light in the near-infrared (low \(E_g\)), visible (moderate \(E_g\)), or ultraviolet (high \(E_g\)) region.\(^{[175-177]}\)

![Figure 1.8: Orbital mixing in donor-acceptor-type compounds.](image)

While acceptors mostly exhibit electron-withdrawing units, such as imine, cyano, or carbonyl groups, donors are often derived from benzene or thiophene.\(^{[175-177]}\) A common design strategy for many donor moieties involves annulation of aromatic rings to prevent free rotation around carbon-carbon single bonds (Figure 1.9). Hence, these molecules exhibit a more planar geometry and a more extended conjugation, resulting in decreased HOMO-LUMO energy gaps and stronger intermolecular interactions. Ring fusion can be achieved by incorporation of carbon or a heteroatom, whereas solubilizing alkyl chains are often attached at these positions. Because thiophene exhibits a stronger electron-pushing ability than benzene, biphenyl- or terphenyl-derived systems are relatively weak donors in comparison to
On the other hand, the influence of the bridging atom also has to be taken into account. In this respect, nitrogen exhibits a very strong electron-donating effect due to its lone pair and good orbital overlap with carbon and therefore increases the donor strength further than carbon, silicon, germanium, or sulphur.\[176-177\]

![Figure 1.9: Common donor moieties derived from ring fusion of 1,1'-biphenyl (left), 1,1',4'1''-terphenyl (middle), or 2,2'-bithiophene (right).](image)

Thus, the nitrogen-bridged bithiophene-based DTPs represent quite strong donor building blocks and are widely applied in D-A-type copolymers (Chapter 1.6) or well-defined co-oligomers. Compared to various similar donors, such as 2,2'-bithiophene or carbazole, the incorporation of DTPs results in an increased charge-transfer character accompanied by a bathochromic shift of the lowest energy transition in the UV-Vis spectrum.\[178\] Hence, a larger part of the solar spectrum can often be utilized in photovoltaic devices. Yassin et al. functionalized 2-ethylhexyl-substituted DTP 64 at both α-positions by dicyanovinylene (DCV) acceptors, but the obtained A-D-A-type oligomer only yielded power conversion efficiencies (PCE) below 0.3% in planar heterojunction solar cells.\[179\] Subsequently, the same DTP was attached at both ends of several different acceptors in the centre to afford D-A-D-type oligomers instead (Figure 1.10). Bulk heterojunction (BHJ) solar cells with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PC_{61}BM) as electron acceptor were fabricated and gave PCEs of 0.19% with oligomer 149,\[180\] 0.88% with oligomer 150,\[181\] and 0.95% with oligomer 151\[182\] respectively.

Because in the D-A-D-type oligomers the DTP moieties are attached at the peripheries, one reactive α-position remains free at each side and therefore could participate in follow-up reactions or degradation processes during solar cell operation. Thus, in our institute the focus has laid on the opposite A-D-A-type approach for co-oligomers comprising DTP as donor unit.
in the centre. However, due to the poor solar cell performance of acceptor-substituted DTP 
(\textit{vide supra}), the energy levels of the frontier molecular orbitals had to be fine-tuned and an 
elongated $\pi$-system was required. Several DTPs bearing pheny\textsuperscript{[116, 183]} or thiény\textsuperscript{[183-186]} 
groups in both $\alpha$-positions have already been reported and have mostly been synthesized in 
a Stille-type cross-coupling of a DTP \textit{bis}-stannyl and the respective bromide or iodide. Hence, 
one thiophene was attached at each side of a DTP and because dicyanovinylene was proven 
to exhibit a balanced acceptor strength and favourable intermolecular interactions in the 
solid state,\textsuperscript{[187]} it was chosen as the acceptor function at the peripheries of oligomers \textbf{152-156} 
(Figure 1.11).\textsuperscript{[188-189]} Alkyl chains at the central nitrogen, respectively at the thiophenes, 
furthermore provided sufficient solubility for the processing into BHJ solar cells. PCEs of up to 
5.3\% with donor \textbf{155} and PC$_{61}$BM as acceptor have been achieved.\textsuperscript{[188]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{Structures of D-A-D-type oligomers \textbf{149-151} with 2-ethylhexyl-substituted DTP \textbf{64} as 
donor units at the peripheries and different acceptors A in the centre.\textsuperscript{[180-182]}}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{Structures of A-D-A-type oligomers \textbf{152-156} with one thiophene at both $\alpha$-positions of 
DTP intended for the application in solution-processed organic solar cells.\textsuperscript{[188-189]}}
\end{figure}
In another series, the \( \pi \)-system was further extended with a bithiophene instead of a monothiophene moiety (Figure 1.12). As a mimic of regioregular P3HT, hexyl chains were symmetrically attached at the \( \beta \)-positions of thiophenes. It was shown that the positions of the latter alkyl groups were quite important for the performance in photovoltaic devices, as hexyls pointing “inward” (160-162) exhibited a stronger sterical influence on the \( \pi \)-system than hexyls in the “outward” direction (157-159).\(^{190-192}\) Therefore, the maximum absorption of the isomers with “outer” alkyl side chains was hyperchromically and bathochromically shifted in solution. However, the oligomers with “inner” hexyls exhibited a larger solubility in chloroform and allowed for more diffusive reorientation in the corresponding films during solvent vapour annealing. Except for the two isomers incorporating a 2-ethylhexyl-substituted DTP (157 and 160), a higher efficiency could thus be obtained in BHJ solar cells.\(^{190-192}\)

Optimization of devices with donor 162 and PC\(_{71}\)BM as acceptor afforded a high open circuit voltage (0.84 V) and a high fill factor (72%) resulting in a PCE of 7.74%.\(^{193}\) Subsequently, the branching point of the hexyldecyl substituent at DTP was moved from the 2-position in 162 to the 4-position in 163, as previous studies with this concept suggested an improved charge carrier mobility due to a denser packing in the solid state.\(^{194-195}\) Indeed, this subtle alteration of the molecular structure led to slightly better devices with an internal “record” PCE of 8.2%.\(^{196}\) Additionally, the substituent at the central nitrogen was exchanged for

**Figure 1.12:** Structures of A-D-A-type oligomers 157-164 with bithiophenes at both \( \alpha \)-positions of DTP intended for the application in solution-processed organic solar cells.\(^{190, 190-191, 196}\)
3,6,9-trioxadecane in oligomer 164 to improve the solubility of the oligomer in non-halogenated solvents and BHJ solar cells with a PCE of up to 6.57% were obtained by processing from o-xylene and solvent vapour annealing with THF.\textsuperscript{[100]}

Besides the commonly applied processing from solution, photovoltaic devices can also be manufactured by sublimation of small molecules as active components\textsuperscript{[197-200]} and our cooperation partner Heliatek commercialized this concept. In order to be sublimable during vacuum-processing the molecular weight of the oligomer has to be low enough. Hence, insulating hexyl chains at the thiophenes were omitted, whereas at the central nitrogen only a phenyl (165) or propyl substituent (166)\textsuperscript{[201]} was attached (Figure 1.13).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13.png}
\caption{Structures of A-D-A-type oligomers 165 and 166 with one thiophene at both $\alpha$-positions of DTP intended for the application in vacuum-processed organic solar cells.}
\end{figure}
1.6 Polymeric dithienopyrroles

Apart from monodisperse DTP oligomers, polymeric derivatives have also gained interest. Thus, several different methods are suitable to polymerize DTP monomers at the thiényl ends and are depicted in Scheme 1.17. First of all, both α-positions can be iodinated with NIS\cite{111-112,185,202} or via successive treatment with t-BuLi and elemental iodine.\cite{110} Hence, with the help of a nickel catalyst Yamamoto-type polymerizations can be carried out.\cite{110} Alternatively, the α-positions can be metallated with a boronic ester or a trimethyl tin moiety and the obtained products can be reacted with the dihalogenated DTP species in Suzuki-\cite{99} respectively Stille-type cross-coupling reactions.\cite{110-112} Commonly the diiodides are used in these approaches, because the analogous dibromides are too unstable.\cite{114,116,183} Yet, in one report, Qin et al. could also successfully perform a Suzuki-type polymerization with an alkyl-substituted DTP dibromide.\cite{99} Due to the electron-rich nature of DTPs it can furthermore be difficult to lithiate both α-positions. Strong lithiating reagents, such as t-BuLi\cite{110,184,186,203} or n-BuLi in combination with TMEDA,\cite{183} are often required, but if the reaction is carried out in high concentration, n-BuLi alone can also be sufficient.\cite{100,190-191,196} For Stille-type polymerizations the purity of the DTP distannyl is of major importance. However, the abstraction of the stannyl groups can only be avoided, when prior to the purification via column chromatography the applied silica gel has been partially deactivated with triethylamine.\cite{183,203}

Scheme 1.17: General methods to polymerize DTPs.
Besides the mentioned cross-coupling reactions, DTPs can also be polymerized oxidatively. In order to form radical cations for the polymerization process different oxidants, such as FeCl$_3$ and RuCl$_3$, or electrochemical methods can be applied. Mechanistically, a DTP radical cation is formed at the beginning of the reaction which dimerizes to a dication (Scheme 1.18). The latter abstracts two protons, forming the neutral DTP dimer, which is subsequently oxidized again. The obtained cation can then couple to other radical cations and thus elongate the polymer chain successively. Mostly, the unpaired electron of the radical species is located in an α-position and therefore the DTP repeat units are connected in an α-α fashion. Nevertheless, the electron-donating nitrogens provide an increased stability of cationic species in comparison to thiophenes and the spin density can also shift to a β-position, resulting in α-β or β-β coupling defects in p(DTP)s.

![Scheme 1.18: Oxidative polymerization mechanism of DTPs.](image)

The first polymerization of DTPs was carried out in 1992 by Zotti et al., who reported the electropolymerization of unsubstituted and several alkyl-substituted DTPs (Scheme 1.19). The afforded polymers exhibited a HOMO-LUMO gap of 1.7 eV and an in situ conductivity of up to 40 S/cm. The same authors hydrolysed the ester functionality in DTP 58 to obtain the corresponding DTP with a carboxylic acid attached at the nitrogen which was required for pre-organizing the monomer onto an ITO working electrode. However, upon electropolymerization the coupling reactions in the monolayer only occurred to a limited extent and therefore relatively short p(DTP) chains were obtained. Later, Rasmussen et al. further
investigated the oxidative polymerization of DTPs including the first study of soluble p(DTP)\(_5\)\[^{103, 208-209}\]. To increase the yield of the soluble fraction just one equivalent of iron trichloride as oxidant was applied, but therefore the obtained materials exhibited rather low molecular weights corresponding to only about ten repeat units. Notably, Koeckelberghs et al. discovered that ruthenium trichloride was superior to the commonly applied oxidant FeCl\(_3\), giving alkyl-substituted p(DTP)s with a polymerization degree of up to 120\[^{110}\]. Moreover, Stille-type polymerizations turned out to yield larger p(DTP)s with a record average chain length of 673. Peculiarly, the materials possessed optical band gaps between 1.8 eV and 2.0 eV which were even increased compared to the reported values of Rasmussen et al.\[^{103, 209}\] and still largely deviated from the theoretically predicted band gap of an infinite p(DTP) by Roncali et al. (1.5 eV).\[^{117}\] This indicated a lower conjugation length of the obtained polymers and therefore the very high molecular weights might have rather been overestimated in the respective analyses by GPC.

\[
\begin{align*}
\text{Scheme 1.19: Polymerization of DTPs.}^{[97, 99, 101, 103, 105, 110-112, 131, 137, 207-211]} \\
\end{align*}
\]

In addition to various alkyl- and aryl-substituted DTPs, Evenson and Rasmussen also subjected octanoyl-substituted DTP \(91\) to electropolymerization.\[^{105}\] Due to the electron-withdrawing moiety at the nitrogens, the onset oxidation of the yielded p(DTP) \(P_{ec}91\) was increased by about 400 mV and the electrochemical band gap was decreased by about 0.1 eV compared to the octyl-substituted analogue. During several studies by another research group free NH\(_2\) moieties at the substituents in electropolymerized p(DTP)s \(P_{ec}104-P_{ec}107\) were used to immobilize glucose oxidase\[^{126, 128, 137}\] or folic acid\[^{211}\] for application as electrochemical sensors. Lutkenhaus et al. investigated the electropolymerized p(DTP)s \(P_{ec}61\) and \(P_{ec}57\) bearing decyl or trioxadecyl substituents at the nitrogens as potential cathode active materials for energy storage application by cycling the potential in a two electrode setup between 2.0 V and 4.0 V against Li/Li\(^+\) at a rate of 20 C (1 C corresponds to the current required to charge or discharge the material in 1 h).\[^{131}\] Specific capacities of 37 mAh/g and 42 mAh/g were measured in the first scan and after 1000 cycles 50% and 75% of the initial
capacity was retained. While decyl-substituted \( p(DTP) \) \( P_{ec}61 \) possessed a higher capacity, ether-functionalized polymer \( P_{ec}57 \) showed an improved mass transport during the doping and dedoping processes because of favourable interactions with lithium ions and the polar solvent. The functional group at the nitrogen thus provided a convenient means to fine-tune the properties of the corresponding \( p(DTP) \) homopolymer.

Various copolymers incorporating DTP units have also been investigated and selected examples are shown in Figure 1.14. Random copolymers like 167 can be obtained via electropolymerization of mixed solutions containing a DTP and another polymerizable building block.\(^{212-213}\) However, most commonly A-B-type copolymers have been prepared by means of Suzuki- or Stille-type cross-coupling reactions and have been applied, for instance, in OLEDs,\(^{124, 203}\) OFETs,\(^{115, 119, 123, 214-222}\) or OPV.\(^{120-123, 138, 216-218, 221-233}\) Because the DTP unit is usually only functionalized at the nitrogen, adjacent arylene or thiophene moieties can provide for additional sites to attach solubilizing alkyl chains as in copolymers 168-170.\(^{115, 203, 215}\) Thus, the solubility of copolymers is increased compared to DTP homopolymers and a larger degree of polymerization can be reached. This is in particular important as the polymer chain length directly influences the optoelectronic properties of the materials. Furthermore, due to their electron-rich nature, DTPs can be applied as donor component in donor-acceptor-type copolymers. Coupling DTP to an acceptor, such as benzothiadiazole in 171\(^{217}\) or perylene bisimide in 172,\(^{214}\) causes a charge-transfer character in the HOMO-LUMO transition and hence results in copolymers with decreased optical band gaps and red-shifted absorptions.

![Figure 1.14: Selected examples of copolymers 167-172 comprising DTP units.][1]

---

[1]: Chapter 1
1.7 References

Chapter 1


Chapter 1

Introduction


Introduction


Chapter 2

Dithieno[3,2-\textit{b}:2',3'-\textit{d}]pyrroles (DTPs)
Chapter 2

2.1 Introduction

The following chapter deals with the synthesis and characterization of various DTP monomers and homopolymers. First of all, various \(N\)-functionalizations using two complementary synthetic strategies for DTP monomers will be presented (Scheme 2.1). A comparison of the optoelectronic properties will elucidate the influence of substituents at the nitrogen in this respect. Furthermore, quantum chemical calculations will reveal the electronic distribution in the frontier molecular orbitals which can be correlated to the optoelectronic properties and thus help to rationalize observed trends in the series. Oxidative polymerizations by electrochemical or chemical means will yield the corresponding \(p\text{-}(DTP)\)s (Scheme 2.1). In this respect, the influence of \(N\)-substituents on the optoelectronic properties will also be analysed in detail.

\[
\begin{align*}
\text{Sulfur-aromatic} + R\cdot\text{NH}_2 & \rightarrow \text{Sulfur-aromatic} + R\cdot\text{X} + \text{Sulfur-aromatic} \\
\end{align*}
\]

Scheme 2.1: Two applied strategies to synthesize \(N\)-functionalized DTPs and subsequent polymerization to \(p\text{-}(DTP)\)s.
2.2 Synthesis of DTPs

2.2.1 C-N coupling with 3,3’-dibromo-2,2’-bithiophene

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In order to fine-tune the properties of the respective monomers and polymers, DTPs bearing several different residues R at the nitrogen were targeted. For the most common synthetic approach of an amination with R-NH₂, the required precursor 3,3’-dibromo-2,2’-bithiophene 72 thus had to be prepared in the first step (Scheme 2.2). Following the approach described in literature, 3-bromothiophene 59 was selectively lithiated in the 2-position with LDA and a salt metathesis with zinc chloride was carried out. Afterwards, an oxidative C-C coupling with cupric chloride gave the desired bithiophene 72 in 88% yield. As it has been discovered in our institute, treatment of the reaction mixture with dry oxygen gas is not necessary to complete the reaction and therefore the suspension was just stirred overnight. To subsequently remove the formed inorganic salts, an aqueous workup was moreover suggested in literature. However, on multi-gram scale this can be very tedious and hence it proved to be more convenient to directly adsorb the crude reaction mixture onto silica gel and purify dibromide 72 via column chromatography.

![Scheme 2.2: Synthesis of 3,3’-dibromo-2,2’-bithiophene 72.](image)

Additionally, the precursor 2-hexyldecyl amine 175 was not commercially available and had to be synthesized. It can, for example, be prepared in a nucleophilic substitution of the alkyl bromide with potassium phthalimide and subsequent reduction with hydrazine. Herein, however, another approach was carried out involving the reduction of an azide (Scheme 2.3). Thus, azide 174 was first of all synthesized in a Mitsonobu reaction of
2-hexyldecanol 173 with diphenylphosphoryl azide (DPPA) in 96% yield. Afterwards, azide 174 was reduced with lithium aluminium hydride and the raw product was distilled in a Kugelrohr apparatus to yield amine 175 in 81% yield.

**Scheme 2.3:** Synthesis of 2-hexyldecylamine 175.

Subsequently, Buchwald-Hartwig aminations of dibromide 72 with different alkyl amines or aniline were carried out under palladium catalysis (Scheme 2.4). The catalyst Pd$_2$dba$_3$ was used in combination with the bidentate ligand BINAP and after heating the reaction mixture under gentle reflux overnight, the raw products were purified via column chromatography. Hence, alkyl-substituted DTPs 60, 64, and 78, as well as phenyl-substituted DTP 65 could be obtained in excellent yields. Structure and purity of these literature-known products was confirmed by NMR spectroscopy. As a representative example the $^1$H NMR spectrum of hexyl-substituted DTP 60 is shown in Figure 2.1. Besides signals in the aliphatic region corresponding to the hexyl residue at the nitrogen, two characteristic doublets of the dithienopyrrole backbone appear at 7.14 and 7.01 ppm. These signals exhibit a pronounced roof effect and show a $^3$J$_{H,H}$ coupling constant of 5.3 Hz, which is in the typical range for the coupling between thienyl $\alpha$- and $\beta$-protons.

**Scheme 2.4:** Palladium-catalysed Buchwald-Hartwig amination of 3,3'-dibromo-2,2'-bithiophene 72.
Dithieno[3,2-\textbf{b}:2',3'-\textbf{d}]pyrroles (DTPs)

Figure 2.1: $^1$H NMR spectrum of hexyl-substituted DTP 60 recorded in CDCl$_3$.

The synthesis of benzoyl-substituted DTP 97 was then carried out as described in literature using a copper instead of a palladium catalyst (Scheme 2.5).\textsuperscript{[1]}

Herein, the bidentate ligand DMEDA complexed CuI and thus rendered it soluble in toluene which could be observed as a colour change of the suspension from colourless to green. Moreover, an important aspect was to apply the base potassium carbonate as a finely ground powder to enhance the reaction rate. After heating the mixture under gentle reflux for 24 h, the raw product was purified via column chromatography and the targeted product 97 was isolated in a yield of 37%. As proposed in literature, the moderate yields can be explained by the inhibition of the catalyst by the formed DTP product\textsuperscript{[1]} and therefore 19% of unreacted starting material 72 were recovered. Additionally, the formed water partially
hydrolysed the benzoyl moiety of DTP 97 to afford unsubstituted DTP 50 in 17% yield (more details see Chapter 2.2.2). Contrary to that, Boc-substituted DTP 176 was completely stable under the applied reaction conditions and the substituent at the nitrogen was not abstracted (Scheme 2.5). Most likely, the bulkier tert-butyl moiety protected the carbonyl group sterically and prevented a subsequent hydrolysis. The yield of DTP 176 (46%) was therefore slightly higher than the yield of benzoyl-substituted DTP 97, but due to the same inhibition of the catalyst the conversion was quite limited and large amounts of starting material 72 did not react. Peculiarly, adding more catalyst did not change the outcome of the Ullmann-type coupling reaction with dibromide 72 and thus the exact deactivation mechanism is still rather unclear. The moderate conversion was even decreased in the reaction of the dibromide with tosyl amide and after 24 hours only 14% of tosyl-substituted DTP 177 could be isolated (Scheme 2.5). Prolonging the reaction time to two days, a similar yield of 18% was obtained, while 61% of unreacted 72 were recovered. On the other hand, with thiobenzamide or 2-aminothiazole the coupling to the corresponding DTPs 178 and 179 did not work at all (Scheme 2.6). Neither with palladium, nor copper catalysts any conversion of dibromide 72 could be observed applying similar reaction conditions as depicted in Scheme 2.4, respectively Scheme 2.5. This clearly showed the limitation of the general approach involving C-N couplings with 3,3’-dibromo-2,2’-bithiophene 72 for the synthesis of N-substituted DTPs.

Scheme 2.6: Attempted synthesis of DTPs 178 and 179 via palladium- or copper-catalysed C-N couplings of 3,3’-dibromo-2,2’-bithiophene 72.
2.2.2 Several methods for the synthesis of unsubstituted DTP

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As already described in literature, besides from the amination of 3,3′-dibromo-2,2′-bithiophene [72], *N*-functionalized DTPs can also be obtained by substitution reactions of unsubstituted DTP 50 (Chapter 1.3). In this approach the DTP unit is built up initially and just in the final step substituents are attached at the nitrogen. The required DTP precursor 50 was firstly synthesized via thermolysis of azide 49 (Scheme 2.7).[5]

![Scheme 2.7: Synthesis of unsubstituted DTP 50 via azide thermolysis.](image)

Azide 49, on the other hand, was prepared starting from commercially available 3-bromo-thiophene 59. The latter compound was brominated in the 2-position with elemental bromine to afford dibromothiophene 70.[6] The raw product was distilled over a Vigreux column and the pure compound was obtained in 63% yield. Subsequently, the Grignard reagent of 2-bromothiophene (180) was synthesized and applied in a palladium-catalysed Kumada-type cross-coupling reaction with 70.[7] Purification of the product mixture via column chromatography using petroleum ether as eluent then gave bromobithiophene 181 in a yield of 86%. Prior to the next step, tosyl azide 182 had to be prepared in a nucleophilic substitution of tosyl chloride by sodium azide.[8] After the reaction was completed, the crude mixture was treated with water and product 182 could be extracted quantitatively with dichloromethane. Bromobithiophene 181 was subsequently lithiated with *n*-BuLi and reacted
with tosyl azide 182 to yield azidobithiophene 49 in 46% after purification via column chromatography.\[9\] Thermolysing the latter precursor led to the intramolecular closure of the pyrrole ring which involved the abstraction of dinitrogen and most likely the formation of a nitrene intermediate. Yet, the reported high yield of 87%\[5\] could not be reproduced and after purification via column chromatography unsubstituted DTP 50 could be isolated in only 38%. Due to the harsh reaction conditions and the highly reactive nature of the proposed nitrene intermediate several side-products were formed and significantly hampered the purification. Moreover, on large scale the product yield decreased very strongly and hence the reaction could just be carried out on a relatively small scale of few hundred milligrams. These drawbacks limited the practical use of DTP 50 as a precursor in N-functionalizations and thus a more convenient approach to prepare unsubstituted DTP 50 had to be found.

Considering synthetic efforts and atom economy, Buchwald-Hartwig or Ullmann-type amination of dibromide 72 with ammonia appeared to be a promising alternative (Scheme 2.8). With the preparation of dibromide 72 from bromothiophene 59 (vide supra), the strategy would overall require only two steps using commercially available starting materials.

\[
\begin{align*}
\text{Br} & & \text{Br} & + & \text{NH}_3 & \rightarrow \text{H} & + & \text{N} & & \text{NH}_2 \\
72 & & & & & 50 & & 183 & & 184
\end{align*}
\]

Scheme 2.8: Synthesis of unsubstituted DTP 50 via amination of dibromide 72 with ammonia. More details see Table 2.1.

In the amination attempts with ammonia various reaction conditions were investigated, applying either aqueous NH$_3$ or generating ammonia in situ from NH$_4$Cl and a base (Table 2.1). However, no profound differences were observed with regard to the ammonia source which is in accordance with reported results of other Buchwald-Hartwig reactions involving NH$_3$.\[10-17\] Moreover, under microwave irradiation the pressure could be set precisely to 6 bar, but debromination of the starting material 72 to bithiophene 183 occurred more quickly than with conventional heating. Palladium catalysts with BINAP (Table 2.1, entry 1) or dpff as ligand (Table 2.1, entry 2-4) led to a very fast decomposition of the dibromide and thus only bithiophene 183 was obtained. Even decreasing the reaction
temperature from 130 °C to 110 °C or 80 °C did not afford any product 50. Similarly to the palladium complexes, copper iodide in combination with DMEDA as ligand did not give a catalytically active species as well, although the dehalogenation of 72 proceeded much more slowly (Table 2.1, entry 5). In contrast to that, an active copper catalyst was formed with L-proline as ligand (Table 2.1, entry 6-8). Yet, according to analyses via GC/MS only trace amounts of unsubstituted DTP 50 were afforded even when the catalyst was applied in excess. The predominant reaction products were still bithiophene 183 originating from the debromination of 72 and monocoupled 3-amino-2,2′-bithiophene 184.

Table 2.1: Details of the applied reaction conditions for the synthesis of DTP 50 via Buchwald-Hartwig amination of dibromide 72 with NH₃ (Scheme 2.8).

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Pre-catalyst</th>
<th>Ligand</th>
<th>Base</th>
<th>Solvent</th>
<th>T [°C]</th>
<th>Time</th>
<th>Yield of 50 [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 NH₃ (2.00 eq)</td>
<td>Pd₂dba₃ (0.10 eq)</td>
<td>BINAP (0.40 eq)</td>
<td>NaOttBu (3.00 eq)</td>
<td>DMSO</td>
<td>130 (300 W)</td>
<td>4 h</td>
<td>0</td>
</tr>
<tr>
<td>2 NH₃ (2.00 eq)</td>
<td>Pd₂dba₃ (0.10 eq)</td>
<td>dppf (0.40 eq)</td>
<td>NaOttBu (2.40 eq)</td>
<td>toluene</td>
<td>130 (300 W)</td>
<td>4 h</td>
<td>0</td>
</tr>
<tr>
<td>3 NH₄Cl (2.00 eq)</td>
<td>Pd₂dba₃ (0.10 eq)</td>
<td>dppf (0.40 eq)</td>
<td>NaOttBu (4.40 eq)</td>
<td>toluene</td>
<td>110 (300 W)</td>
<td>4 h</td>
<td>0</td>
</tr>
<tr>
<td>4 NH₄Cl (2.00 eq)</td>
<td>Pd₂dba₃ (0.10 eq)</td>
<td>dppf (0.40 eq)</td>
<td>NaOttBu (4.40 eq)</td>
<td>toluene</td>
<td>80</td>
<td>2 d</td>
<td>0</td>
</tr>
<tr>
<td>5 NH₃ (2.00 eq)</td>
<td>CuL (0.20 eq)</td>
<td>DMEDA (0.40 eq)</td>
<td>K₂CO₃ (3.00 eq)</td>
<td>toluene</td>
<td>110 (300 W); 140 (300 W); 110</td>
<td>4 h; 4 h; 1 d</td>
<td>0</td>
</tr>
<tr>
<td>6 NH₃ (1.50 eq)</td>
<td>CuL (0.20 eq)</td>
<td>L-proline (0.40 eq)</td>
<td>K₂CO₃ (3.00 eq)</td>
<td>DMSO</td>
<td>80; 110</td>
<td>2 d; 1 d</td>
<td>traces</td>
</tr>
<tr>
<td>7 NH₄Cl (2.00 eq)</td>
<td>CuL (0.20 eq)</td>
<td>L-proline (0.80 eq)</td>
<td>K₂CO₃ (3.00 eq)</td>
<td>DMSO</td>
<td>100</td>
<td>2 d</td>
<td>traces</td>
</tr>
<tr>
<td>8 NH₃ (5.00 eq)</td>
<td>CuL (2.00 eq)</td>
<td>L-proline (4.00 eq)</td>
<td>K₂CO₃ (7.00 eq)</td>
<td>DMSO</td>
<td>100</td>
<td>1 d</td>
<td>traces</td>
</tr>
</tbody>
</table>

* Determined via GC/MS

Subsequently, lithium amide or sodium amide instead of ammonia were used in an attempted amination of dibromide 72 (Scheme 2.9). Applying lithium amide and a copper catalyst again only led to the slow abstraction of the bromine residues of the starting material under formation of bithiophene 183 (Table 2.2, entry 1). In contrast to that, when palladium catalysts were used, only minor amounts of bithiophene 183 were detected via GC/MS. However, no product 50 or any side-products were observed. This indicated the occurrence of a coupling reaction and the subsequent decomposition of the formed intermediate to insoluble undefined compounds. As unsubstituted DTP 50 is relatively stable
Chapter 2

Scheme 2.9: Attempted synthesis of unsubstituted DTP 50 via amination of dibromide 72 with lithium amide or sodium amide. More details see Table 2.2.

Table 2.2: Details of the applied reaction conditions for the attempted synthesis of DTP 50 via amination of dibromide 72 with lithium amide or sodium amide (Scheme 2.9). Reactions were carried out overnight.

<table>
<thead>
<tr>
<th>M-NH₂</th>
<th>Pre-catalyst</th>
<th>Ligand</th>
<th>Solvent</th>
<th>T [°C]</th>
<th>Base</th>
<th>Additives</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li-NH₂</td>
<td>Cu</td>
<td>DMEDA</td>
<td>110</td>
<td>Li-NH₂</td>
<td>-</td>
<td>Br cleavage</td>
</tr>
<tr>
<td></td>
<td>(4.00 eq)</td>
<td>(0.80 eq)</td>
<td>(0.80 eq)</td>
<td></td>
<td></td>
<td></td>
<td>dec.</td>
</tr>
<tr>
<td>2</td>
<td>Li-NH₂</td>
<td>Pd(dba)₂</td>
<td>dpff</td>
<td>110</td>
<td>NaOtBu</td>
<td>-</td>
<td>dec.</td>
</tr>
<tr>
<td></td>
<td>(1.00 eq)</td>
<td>(0.40 eq)</td>
<td>(0.40 eq)</td>
<td></td>
<td></td>
<td></td>
<td>dec.</td>
</tr>
<tr>
<td>3</td>
<td>Li-NH₂</td>
<td>Pd(dba)₂</td>
<td>dpff</td>
<td>110</td>
<td>Li-NH₂</td>
<td>-</td>
<td>dec.</td>
</tr>
<tr>
<td></td>
<td>(4.00 eq)</td>
<td>(0.40 eq)</td>
<td>(0.40 eq)</td>
<td></td>
<td></td>
<td></td>
<td>dec.</td>
</tr>
<tr>
<td>4</td>
<td>Li-NH₂</td>
<td>Pd(dba)₂</td>
<td>P(tBu)₃</td>
<td>110</td>
<td>NaOtBu</td>
<td>-</td>
<td>dec.</td>
</tr>
<tr>
<td></td>
<td>(1.00 eq)</td>
<td>(0.40 eq)</td>
<td>(0.40 eq)</td>
<td></td>
<td></td>
<td></td>
<td>dec.</td>
</tr>
<tr>
<td>5</td>
<td>Li-NH₂</td>
<td>Pd(dba)₂</td>
<td>P(tBu)₃</td>
<td>110</td>
<td>Li-NH₂</td>
<td>-</td>
<td>dec.</td>
</tr>
<tr>
<td></td>
<td>(4.00 eq)</td>
<td>(0.40 eq)</td>
<td>(0.40 eq)</td>
<td></td>
<td></td>
<td></td>
<td>dec.</td>
</tr>
<tr>
<td>6</td>
<td>Li-NH₂</td>
<td>Pd(dba)₂</td>
<td>dpff</td>
<td>100</td>
<td>NaOtBu</td>
<td>12-crown-4</td>
<td>dec.</td>
</tr>
<tr>
<td></td>
<td>(1.00 eq)</td>
<td>(0.20 eq)</td>
<td>(0.20 eq)</td>
<td>(2.00 eq)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Na-NH₂</td>
<td>Pd(dba)₂</td>
<td>dpff</td>
<td>100</td>
<td>KOrBu</td>
<td>15-crown-5</td>
<td>Br cleavage</td>
</tr>
<tr>
<td></td>
<td>(1.00 eq)</td>
<td>(0.20 eq)</td>
<td>(0.20 eq)</td>
<td>(2.00 eq)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Na-NH₂</td>
<td>Pd(dba)₂</td>
<td>dpff</td>
<td>110</td>
<td>Cs₂CO₃</td>
<td>15-crown-5</td>
<td>Br cleavage</td>
</tr>
<tr>
<td></td>
<td>(1.00 eq)</td>
<td>(0.20 eq)</td>
<td>(0.20 eq)</td>
<td>(1.00 eq)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

even at elevated temperatures, this intermediate was most likely the N-lithiated DTP. When the reaction temperature was then decreased from 110 °C to 80 °C, no reaction occurred anymore and only starting material 72 was retracted. Hence, relatively harsh reaction conditions were required to enable the Buchwald-Hartwig amination in the first place, yet the formed product was too unstable under these conditions. Bidentate dpff (Table 2.2, entry 2 and 3) and the monodentate P(tBu)₃ (Table 2.2, entry 4 and 5) were applied as ligand together with either sodium tert-butoxide or an excess of lithium amide as base. In order to coordinate the lithium cation of the amide and thus stabilize the formed reaction product or enable a direct formation of unsubstituted DTP 50, 12-crown-4 was added and dioxane was used as solvent (Table 2.2, entry 6). However, this did not change the outcome of the
reaction. Moreover, sodium amide was used instead of the lithium salt together with potassium tert-butoxide (Table 2.2, entry 7) or caesium carbonate (Table 2.2, entry 8) as base and 15-crown-5 to coordinate sodium cations. Nevertheless, opposed to the attempts with lithium amide no coupling reaction was observed, but only bromide cleavage of precursor 72 occurred.

Therefore, the direct synthesis of DTP 50 with ammonia or amide salts was not a viable synthesis route and other approaches involving ammonia surrogates R-NH₂ were subsequently investigated. Those surrogates had to bear a protecting group R, which first enabled the twofold C-N coupling with 3,3’-dibromo-2,2’-bithiophene 72 and afterwards could be readily cleaved off to yield targeted DTP 50. Firstly, this strategy was tested with benzylamine 185 as ammonia surrogate (Scheme 2.10).

![Scheme 2.10: Attempted synthesis of unsubstituted DTP 50 via benzyl cleavage of DTP 186. Details see Table 2.3.](image)

Due to the absence of functional groups in benzylamine 185 a palladium catalyst could be applied in the Buchwald-Hartwig amination of dibromide 72 and the resulting DTP 186 was isolated in a good yield of 86% after purification via column chromatography. Subsequently, it was attempted to split off the benzyl protecting group from DTP 186 with hydrogen and a Pd/C catalyst to afford unsubstituted DTP 50 (Table 2.3). Hydrogen gas was either continuously bubbled through the reaction mixture or a static hydrogen pressure was applied with an attached balloon, respectively. Different polar aprotic (ethyl acetate, anisole) or protic solvents (methanol, acetic acid, hydrochloric acid) and elevated temperatures of up to 100 °C were applied. Moreover, the reaction was also attempted in a microwave apparatus under a H₂-atmosphere. To exclude problems with the heterogeneous catalyst two different batches of Pd/C from Merck or Sigma Aldrich were tested and the reaction conditions in Table 2.3, entry 3 and 4, were also applied together with a Pt/C or a Rh/C catalyst. Nevertheless, in all attempts no formation of the targeted DTP 50 could be observed and only starting material
was quantitatively recovered. Hence, no suitable reaction condition for the hydrogenative benzyl cleavage of DTP 186 could be found. This was quite surprising, because usually benzyl protecting groups at a pyrrole ring can be split off with hydrogen in good yields.\textsuperscript{[18-28]} Furthermore, in the institute prior deprotections of benzyl ethers were performed successfully using the same setup and similar reaction conditions.

**Table 2.3:** Details of the applied reaction conditions for the synthesis of DTP 50 via deprotection of benzyl-substituted DTP 186 with \( \text{H}_2 \) and a Pd/C catalyst (Scheme 2.10). A static \( \text{H}_2 \) pressure was applied through a balloon filled with hydrogen or via purging the reaction mixture in a microwave tube, respectively. A dynamic inlet of \( \text{H}_2 \) was achieved by continuous purging of the reaction mixture.

<table>
<thead>
<tr>
<th>( \text{H}_2 ) inlet</th>
<th>Solvent</th>
<th>( T )</th>
<th>Reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>static</td>
<td>MeOH, EtOAc</td>
<td>RT</td>
</tr>
<tr>
<td>2</td>
<td>static</td>
<td>MeOH, EtOAc</td>
<td>65 °C</td>
</tr>
<tr>
<td>3</td>
<td>dynamic</td>
<td>EtOAc</td>
<td>RT</td>
</tr>
<tr>
<td>4</td>
<td>static</td>
<td>EtOAc</td>
<td>75 °C</td>
</tr>
<tr>
<td>5</td>
<td>dynamic</td>
<td>AcOH, anisole</td>
<td>RT</td>
</tr>
<tr>
<td>6</td>
<td>static (1.5 bar)</td>
<td>AcOH, anisole</td>
<td>100 °C</td>
</tr>
<tr>
<td>7</td>
<td>static (1.5 bar)</td>
<td>EtOAc</td>
<td>80 °C (100 W)</td>
</tr>
<tr>
<td>8</td>
<td>static (1.5 bar)</td>
<td>EtOAc, HCl</td>
<td>80 °C (100 W)</td>
</tr>
</tbody>
</table>

Instead of DTP 186 bearing a benzyl protecting group, Boc-substituted DTP 176 was subsequently applied as precursor for the synthesis of unsubstituted DTP 50 (Scheme 2.11).

```
\[
\text{O} - \text{N} - \text{C}\]
```

**Scheme 2.11:** Synthesis of unsubstituted DTP 50 via Boc cleavage of DTP 176.

The cleavage of the protecting group had to be carried out under mild conditions, as the targeted product 50 was found to quickly polymerize in acidic media. Thus, a reported procedure for the abstraction of Boc moieties involving a base and methanol was slightly adapted.\textsuperscript{[29]} After stirring a suspension of Boc-substituted DTP 176 and potassium carbonate for one day at room temperature, DTP 50 was purified via column chromatography and could be isolated in a yield of 81%. Hence, starting from commercially available 3-bromothiophene
Dithieno[3,2-b:2',3'-d]pyrroles (DTPs)

59, DTP 50 could be prepared in just three steps and with much less synthetic efforts than in the previously published method involving the potentially explosive azide 49 (vide supra).\cite{footnote}

Nevertheless, because Boc-substituted DTP 176 was only obtained in 46%, the overall yield of DTP 50 accounted for just 33%. In the critical step of the Ullmann-type C-N coupling of dibromide 72 with tert-butyl carbamate to DTP 176, the copper catalyst was most likely inhibited by the formed product limiting the conversion of the starting material (Chapter 2.2.1). Consequently, a direct in situ cleavage of the protecting group at the nitrogen of DTP would enable the reactivation of the catalyst and should allow for the complete conversion of dibromide 72.

During the synthesis of benzoyl-substituted DTP 97 in a similar Ullmann-type coupling, it was already discovered that also unsubstituted DTP 50 was formed (Chapter 2.2.1). This indicated the cleavage of the substituent at the nitrogen and stood in contrast to the observation of Evenson and Rasmussen, who observed “no significant side products”\cite{footnote} when they synthesized acyl- and benzoyl-substituted DTPs. As shown by TLC and the \textsuperscript{1}H NMR spectrum of the crude reaction mixture, DTP 50 was formed in situ and not during the workup or the purification procedure. Based on these findings, a plausible reaction sequence is proposed in Scheme 2.12.

\textbf{Scheme 2.12}: Proposed reaction sequence of the formation of unsubstituted DTP 50 during the copper-catalysed Ullmann-type C-N coupling of dibromide 72 with benzamide 187.
First of all, the Ullmann-type C-N coupling of dibromide 72 with benzamide 187 afforded benzoyl-substituted DTP 97 and formally two equivalents of HBr (A). The acid was directly neutralized by potassium carbonate, whereas carbonic acid was formed (B). Subsequently, the latter decomposed into water and carbon dioxide, which left this equilibrium as a gas and therefore provided a good driving force for the overall reaction (C). Under the applied alkaline conditions, the benzoyl moiety was finally hydrolysed and unsubstituted DTP 50 was afforded (D).

In order to elucidate the formation mechanism of DTP 50 in more detail, a suspension of isolated benzoyl-substituted DTP 97 and potassium carbonate in wet toluene with and without CuI and DMEDA was investigated. Herein, product 50 was only formed at elevated temperatures and in the presence of the copper complex. This indicated that the benzoyl substituent had to be coordinated to copper reducing the electron density at the carbonyl group and thus promoting a nucleophilic attack of hydroxide anions during hydrolysis. Nevertheless, amides are usually quite stable and two resonance structures can be formulated (Figure 2.2). However, in the case of pyrrole the second resonance structure with a C-N double bond leads to the loss of aromaticity and therefore contributes to a smaller extent to the properties of the molecule. This explains why benzoyl-substituted DTP 97 is less stable and more prone to hydrolysis than common amides. In combination with the activating copper species DTP 50 can therefore be generated from DTP 97.

\[
\begin{align*}
\text{N-alkyl amides} & \leftrightarrow \text{N-pyrrole amides} \\
\end{align*}
\]

*Figure 2.2: Resonance structures of N-alkyl amides (left) and N-pyrrole amides (right).*

As CuI and DMEDA are both required for the Ullmann-type coupling with benzamide and the following hydrolysis step, a one-pot procedure to directly produce DTP 50 from dibromide 72 was subsequently developed and optimized (Scheme 2.13, Table 2.4). Initially, under the reported reaction conditions of Evenson and Rasmussen,\(^\text{[1]}\) benzoyl-substituted DTP 97 was afforded as the main product in 37%, while unsubstituted DTP 50 was isolated in only 17% yield (Table 2.4, entry 1). By increasing the amount of catalyst and prolonging the reaction time to two days, the formed amide 97 hydrolysed completely and the yield of DTP
50 could therefore be increased to 50% (Table 2.4, entry 2). However, unreacted starting material 72 was observed as well. The amount of catalyst and the reaction time was subsequently further increased, yet, despite the full conversion of dibromide 72 leading only to lower yields of DTP 50 (Table 2.4, entry 3 and 4). Apparently, under the relatively harsh reaction conditions the product partially decomposed which made it necessary to complete the reaction as quickly as possible. Hence, few drops of water were added to the reaction mixture enhancing the hydrolysis of intermediate DTP 97 (Table 2.4, entry 5-7). Intriguingly, the additional water did not inhibit the catalyst, for instance by forming copper hydrate, and the best yield (59%) of DTP 50 was obtained by applying 0.2 equivalents of the catalyst and a reaction time of two days. The latter two parameters had to be finely adjusted, as decomposition of the product prevailed with extensive heating of the mixture. However, with too short reaction times DTP 97 and unreacted dibromide 72 were still present and had to be separated from product 50.

![Scheme 2.13: Synthesis of unsubstituted DTP 50 via Ullmann-type coupling of dibromide 72 with benzamide 187 as ammonia surrogate. The benzoyl-substituent of intermediate 97 is cleaved via in situ hydrolysis with the formed water. More details see Table 2.4.](image)

Because the solubility of the components might have been a limiting factor, different reaction conditions were furthermore investigated in this respect. First of all, DMF was applied as a more polar solvent than toluene (Table 2.4, entry 8). In this case, especially the solubility of benzamide was increased, but this did not improve the yield of DTP 50. Subsequently, 18-crown-6 ether was added to the reaction mixture in order to partly dissolve the base potassium carbonate (Table 2.4, entry 9). As again DTP 50 was isolated in only low amounts, triethylamine was applied as an alternative base to increase the yield of amide 97 (Table 2.4, entry 10). Herein, no water was formed during the reaction and therefore little amounts of DTP 50 were obtained due to the crude drying of the base before the reaction. At the same time only traces of DTP 97 were afforded showing the poor performance of the catalyst in combination with triethylamine. Previously, it was also disclosed that by applying...
Table 2.4: Details of the applied reaction conditions for the synthesis of unsubstituted DTP 50 via C-N couplings of dibromide 72 with benzamide 187 as ammonia surrogate (Scheme 2.13).

<table>
<thead>
<tr>
<th>Pre-catalyst</th>
<th>Ligand</th>
<th>Base</th>
<th>Solvent</th>
<th>T [°C]</th>
<th>Time [d]</th>
<th>Yield [%]</th>
<th>DTP 97</th>
<th>DTP 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cul</td>
<td>DMEDA</td>
<td>K₂CO₃</td>
<td>toluene</td>
<td>110</td>
<td>1</td>
<td>37</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>Cul</td>
<td>DMEDA</td>
<td>K₂CO₃</td>
<td>toluene</td>
<td>110</td>
<td>2</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>Cul</td>
<td>DMEDA</td>
<td>K₂CO₃</td>
<td>toluene</td>
<td>110</td>
<td>3</td>
<td>0</td>
<td>41</td>
</tr>
<tr>
<td>4</td>
<td>Cul</td>
<td>DMEDA</td>
<td>K₂CO₃</td>
<td>toluene</td>
<td>110</td>
<td>2</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>Cul</td>
<td>DMEDA</td>
<td>K₂CO₃</td>
<td>toluene/H₂O</td>
<td>110</td>
<td>3</td>
<td>0</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>Cul</td>
<td>DMEDA</td>
<td>K₂CO₃</td>
<td>toluene/H₂O</td>
<td>110</td>
<td>2</td>
<td>0</td>
<td>59</td>
</tr>
<tr>
<td>7</td>
<td>Cul</td>
<td>DMEDA</td>
<td>K₂CO₃</td>
<td>toluene/H₂O</td>
<td>110</td>
<td>2</td>
<td>0</td>
<td>46</td>
</tr>
<tr>
<td>8</td>
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<td>DMEDA</td>
<td>K₂CO₃</td>
<td>DMF</td>
<td>110</td>
<td>2</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>9</td>
<td>Cul</td>
<td>DMEDA</td>
<td>K₂CO₃</td>
<td>toluene</td>
<td>110</td>
<td>2</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>10</td>
<td>Cul</td>
<td>DMEDA</td>
<td>NEt₃ (3 eq)</td>
<td>toluene</td>
<td>110</td>
<td>2</td>
<td>1</td>
<td>5ᶜ</td>
</tr>
<tr>
<td>11</td>
<td>Cul</td>
<td>DMEDA</td>
<td>K₂CO₃</td>
<td>toluene</td>
<td>140</td>
<td>4 h</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>12</td>
<td>Cul</td>
<td>DMEDA</td>
<td>K₂CO₃</td>
<td>toluene</td>
<td>110</td>
<td>2</td>
<td>0</td>
<td>32</td>
</tr>
<tr>
<td>13</td>
<td>CuBr</td>
<td>DMEDA</td>
<td>K₂CO₃</td>
<td>toluene</td>
<td>110</td>
<td>2</td>
<td>0</td>
<td>47</td>
</tr>
<tr>
<td>14</td>
<td>Cul</td>
<td>phen</td>
<td>K₂CO₃</td>
<td>toluene</td>
<td>110</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>Cul</td>
<td>L-proline</td>
<td>K₂CO₃</td>
<td>toluene</td>
<td>110</td>
<td>2</td>
<td>0</td>
<td>traces</td>
</tr>
</tbody>
</table>

ᵃ Formation of DTP 50 due to residual water in the reaction mixture

potassium phosphate the reaction does not proceed at all.¹⁰ Hence, potassium carbonate seemed to be the optimal choice as base in this reaction. One reason for this is most likely that the carbonate forms carbonic acid, which decomposes into water and carbon dioxide. The latter is released as a gas and thus constitutes a good driving force for the overall reaction to DTP 50. Subsequently, instead of conventional heating the reaction was carried...
out under microwave irradiation with 300 W to reach a temperature of 140 °C (Table 2.4, entry 11). Even higher temperatures were avoided, because in the solid state DTP 50 decomposes at 167 °C. Microwave irradiation greatly decreased the necessary reaction time, yet also enhanced the decomposition of DTP 50. As a consequence, large amounts of an insoluble black solid were obtained besides still unreacted dibromide 72 and product 50 in 25% yield. In another attempt, a palladium complex was applied together with the copper catalyst, but the yield of DTP 50 could not be improved (Table 2.4, entry 12). Moreover, exchanging the counter anion of CuI to bromide did not have a major effect on the reaction and DTP 50 was isolated in a yield of 47% (Table 2.4, entry 13). Afterwards, phenanthroline (Table 2.4, entry 14) or L-proline (Table 2.4, entry 15) were tested as ligand for CuI. However, this only afforded copper complexes with no or very low catalytic activities in the Ullmann-type C-N coupling.

Finally, the reaction was carried out with benzamides bearing different substituents in the para-position (Scheme 2.14).

\[
\begin{align*}
\text{Br} & \quad \text{S} \\
& + \quad \text{NH}_2 \\
\text{H} & \quad \text{S} \\
\text{Br} & \quad \text{S}
\end{align*}
\]

**Scheme 2.14:** Synthesis of unsubstituted DTP 50 via Ullmann-type coupling of dibromide 72 with different benzamides as ammonia surrogates. The benzoyl-substituent of intermediates 188 or 189 is cleaved via *in situ* hydrolysis with the formed water. Stated yields refer to DTP 50.

It was suspected that altering the electronic structure of the benzamide precursor could accelerate either the Ullmann-type coupling of dibromide 72 or the hydrolysis of the substituted DTP leading to shorter reaction times with increased yields of product 50. Attaching an electron-donating ethoxy group to benzamide, substituted intermediate DTP 188 was not observed after a reaction time of one or two days. However, major amounts of unreacted starting material 72 were still present in the crude mixture and DTP 50 could only be isolated in 11% and 15%, respectively. This indicated that the rate of the initial C-N coupling was largely decreased accounting for a very low conversion of the starting
materials. Another attempt then involved the application of benzamide with an electron-withdrawing nitro group in the \textit{para}-position. After two days, substituted DTP 189 was isolated in 9% and the desired reaction product DTP 50 was afforded in a yield of 39%. Because precursor 72 was completely consumed, the Ullmann-type coupling was not largely inhibited and instead the subsequent hydrolysis step appeared to be slowed down. Most likely, the nitro group exhibited unfavourable interactions with the copper species and hampered the coordination of copper to the carbonyl group. Thus, no efficient activation could be achieved and even the combined yield of DTP 189 and unsubstituted DTP 50 did not surpass the optimized yield of 59% for DTP 50 in the reaction with unsubstituted benzamide 187.

In the latter approach unsubstituted DTP 50 could be synthesized in two steps starting from 3-bromothiophene 59 in an overall yield of 52% and therefore already represented a major improvement to all prior synthetic methods (\textit{vide supra}). Furthermore, the reaction could be carried out on multi-gram scale, the use of inert gas was not essential, full conversion of dibromide 72 was achieved, and the purification procedure was vastly simplified. Nevertheless, the moderate reaction rates demanded extensive heating of the mixture for two days. Under those relatively harsh conditions partial decomposition of DTP 50 still limited the product yield.

Hence, the application of another ammonia surrogate in the coupling with dibromide 72 which required milder reaction conditions appeared very promising to further increase the yield of DTP 50. In literature, the use of, for example, benzophenone imine,\textsuperscript{[30]} \textit{bis}(trimethylsilyl)amide,\textsuperscript{[31-32]} or triphenylsilyl amine 191\textsuperscript{[32]} has been reported for the monoamination of aryls to obtain mainly aniline derivatives. Due to the \textit{NH}\textsubscript{2} group, the latter precursor 191 could also enable a twofold Buchwald-Hartwig amination, which is needed to build up a dithienopyrrole unit. Although the amine was commercially available, it was synthesized in excellent yield by reacting triphenylsilyl chloride 190 with lithium amide at -78 °C (Scheme 2.15).\textsuperscript{[33-34]} The crude compound was extracted with ether, recrystallized from \textit{n}-hexane, and afterwards stored in the glovebox under an inert atmosphere. Subsequently, amine 191 was reacted with dibromide 72 under palladium catalysis in a Buchwald-Hartwig amination (Scheme 2.15). Initially, no reaction was observed using the bidentate dppf (Table 2.5, entry 1) or the modentate triphenylphosphine ligand (Table 2.5, entry 2). However, with \textit{tert}-butylphosphine a catalytically active palladium complex was obtained.
Dithieno[3,2-b:2',3'-d]pyrroles (DTPs)

Scheme 2.15: Synthesis of unsubstituted DTP 50 via Buchwald-Hartwig amination of dibromide 72 with ammonia surrogate 191. The substituent in 192 is cleaved via in situ reaction with tBuOH or NaOtBu to obtain Ph₃SiOtBu as by-product. More details see Table 2.5.

Table 2.5: Details of the applied reaction conditions for the synthesis of unsubstituted DTP 50 in a Buchwald-Hartwig amination of dibromide 72 with triphenylsilyl amine 191 as ammonia surrogate (Scheme 2.15). Reactions were carried out overnight.

<table>
<thead>
<tr>
<th>Pre-catalyst</th>
<th>Ligand</th>
<th>Solvent</th>
<th>T [°C]</th>
<th>Base</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(db)₂</td>
<td>dppf</td>
<td>toluene</td>
<td>NaOtBu</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(0.10 eq)</td>
<td>(0.40 eq)</td>
<td></td>
<td>(3.00 eq)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pd(Ph)₄</td>
<td>-</td>
<td>toluene</td>
<td>NaOtBu</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(0.10 eq)</td>
<td></td>
<td></td>
<td>(3.00 eq)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Pd₂(db)₃</td>
<td>P(tBu)₃</td>
<td>toluene</td>
<td>NaOtBu</td>
<td>72%</td>
</tr>
<tr>
<td></td>
<td>(0.05 eq)</td>
<td>(0.20 eq)</td>
<td></td>
<td>(3.00 eq)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Pd₂(db)₃</td>
<td>P(tBu)₃</td>
<td>toluene</td>
<td>NaOtBu</td>
<td>42%</td>
</tr>
<tr>
<td></td>
<td>(0.05 eq)</td>
<td>(0.20 eq)</td>
<td></td>
<td>(5.00 eq)</td>
<td></td>
</tr>
</tbody>
</table>

These findings were in agreement with the report of Barlow et al., who needed to apply P(tBu)₃ as ligand instead of BINAP for the synthesis of DTP 63 bearing a sterically demanding tert-butyl substituent at the nitrogen.\[^{35}\] Similarly, the conversion to DTP 192 already started at room temperature, yet after few hours the reaction did not progress further, because the catalyst was most likely inhibited by formed silyl side-products. Nevertheless, carrying out the reaction at 80 °C overnight led to the efficient formation of unsubstituted DTP 50, which was yielded in 72% (Table 2.5, entry 3). The intermediate, substituted DTP 192, could not be isolated and was only detected in the crude reaction mixture via MALDI mass spectrometry. Thus, cleavage of the silyl residue at the nitrogen occurred very quickly in situ with either the applied sodium tert-butoxide or the formed tert-butanol. The thermodynamic driving force
for this reaction was the formation of a Si-O bond, which is much stronger than a Si-N bond.\cite{36} The by-product tert-butoxytriphenylsilane could also be isolated and the analytical data was in accordance with literature.\cite{37} In attempting to optimize the reaction conditions, the amount of palladium was decreased to 0.03 equivalents, but in this case the reaction was not completed and more catalyst had to be added again. Also no full conversion could be achieved by applying only 2.2 equivalents of sodium tert-butoxide instead of 3.0 equivalents. The reaction rate was most likely decreased and the deactivation of the catalyst occurred already at an early stage. On the other hand, the yield of DTP 50 decreased to 42% using more base which indicated that the silyl residue of amine 191 was split off very quickly (Table 2.5, entry 4). Therefore, the relatively mild reaction conditions in Table 2.5, entry 3, gave the best results for the synthesis of unsubstituted DTP 50, which could thus prepared in an overall yield of 63% in two steps starting from 3-bromothiophene 59. However, considering the cheaper copper catalyst and the cheaper ammonia surrogate, the similar method using benzamide instead of triphenylsilyl amine 191 now also represents an attractive alternative \textit{(vide supra)}. 
2.2.3 N-functionalization of unsubstituted DTP

With unsubstituted DTP 50 readily available in large amounts, following substitution reactions were now more practical. Thus, DTP 50 was used as amine component in Buchwald-Hartwig aminations to attach aryl substituents at the nitrogen of DTP. Although phenyl-substituted DTP 65 can conveniently be prepared via amination of dibromide 72 with aniline (Chapter 2.2.1), the alternative synthesis with DTP 50 and a phenyl halide was investigated in detail to find the optimal conditions for this type of reaction (Scheme 2.16). Thus, other aryl- and heteroaryl-substituted DTPs could also be prepared (vide infra).

Scheme 2.16: Synthesis of phenyl-substituted DTP 65 via Buchwald-Hartwig amination with unsubstituted DTP 50. More details see Table 2.6.

In a patent it was claimed that the reaction of DTP 50 with bromobenzene gave phenyl-substituted DTP 65 in a yield of 88%. However, less than the stoichiometrically required one equivalent of base was used and very harsh reaction conditions were applied.\[^{38}\] Attempts to reproduce these results afforded DTP 65 in only 26% yield (Table 2.6, entry 1). However, when the palladium pre-catalyst was changed from Pd\(_2\)dba\(_3\) to Pd(OAc)\(_2\) and the reaction temperature was slightly decreased, the yield could be improved to 42% (Table 2.6, entry 2). Because precursor 50 is only moderately stable at elevated temperatures, milder reaction conditions seemed to be more promising and thus a yield of 51% was reached by further decreasing the temperature to 110 °C (Table 2.6, entry 3). Subsequently, phosphine P(o-Tol)\(_3\) possessing a Tolman cone angle of 194° was applied instead of P(tBu)\(_3\), which exhibits a cone angle of just 182° (Table 2.6, entry 4).\[^{39}\] With the increased sterical demand of the ligand, it was anticipated that the reductive elimination in the catalytic cycle would be facilitated. Instead the oxidative addition of the bromide was presumably hampered and therefore only trace amounts of phenyl-substituted DTP 65 were detected via GC/MS. Using the slightly modified tBuXPhos ligand, which comprises one biphenyl and only two tert-butyl residues at
the phosphorous, similar results as with the P(tBu)$_3$ ligand were obtained (Table 2.6, entry 5).

Yet, by decreasing the amount of palladium pre-catalyst, DTP 65 could be isolated in a much better yield of 76% (Table 2.6, entry 6). Because Pd(II) had to be reduced to Pd(0) in the beginning of the catalytic cycle, decreased amounts of catalyst also decreased the consumption of DTP 50 for the generation of the catalytically active species. Hence, besides the thermal decomposition of unsubstituted DTP 50 a limiting factor in the amination reaction was oxidation of DTP 50 to form Pd(0). In another attempt triethylamine was added to enable the reduction of Pd(II) to Pd(0), but only resulted in a decreased product yield (Table 2.6, entry 7).

Table 2.6: Details of the applied reaction conditions for the synthesis of phenyl-substituted DTP 65 via Buchwald-Hartwig amination with unsubstituted DTP 50 (Scheme 2.16).

<table>
<thead>
<tr>
<th>X</th>
<th>Pre-catalyst</th>
<th>Ligand</th>
<th>Solvent</th>
<th>T [°C]</th>
<th>Base</th>
<th>Time</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br</td>
<td>Pd$_2$dba$_3$ (0.05 eq)</td>
<td>P(tBu)$_3$ (0.10 eq)</td>
<td>o-xylene</td>
<td>NaO$t$Bu (0.60 eq)</td>
<td>2 d</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>Br</td>
<td>Pd(OAc)$_2$ (0.10 eq)</td>
<td>P(tBu)$_3$ (0.20 eq)</td>
<td>o-xylene</td>
<td>NaO$t$Bu (2.00 eq)</td>
<td>2 d</td>
<td>42</td>
</tr>
<tr>
<td>3</td>
<td>Br</td>
<td>Pd(OAc)$_2$ (0.10 eq)</td>
<td>P(tBu)$_3$ (0.20 eq)</td>
<td>toluene</td>
<td>NaO$t$Bu (2.00 eq)</td>
<td>2 d</td>
<td>51</td>
</tr>
<tr>
<td>4</td>
<td>Br</td>
<td>Pd(OAc)$_2$ (0.10 eq)</td>
<td>P(o-Tol)$_3$ (0.20 eq)</td>
<td>toluene</td>
<td>NaO$t$Bu (2.00 eq)</td>
<td>2 d</td>
<td>traces</td>
</tr>
<tr>
<td>5</td>
<td>Br</td>
<td>Pd(OAc)$_2$ (0.10 eq)</td>
<td>tBuXPhos (0.20 eq)</td>
<td>toluene</td>
<td>NaO$t$Bu (2.00 eq)</td>
<td>2 d</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>Br</td>
<td>Pd(OAc)$_2$ (0.03 eq)</td>
<td>P(tBu)$_3$ (0.06 eq)</td>
<td>toluene</td>
<td>NaO$t$Bu (2.00 eq)</td>
<td>2 d</td>
<td>76</td>
</tr>
<tr>
<td>7</td>
<td>Br</td>
<td>Pd(OAc)$_2$ (0.03 eq), NE$t$$_3$ (0.06 eq)</td>
<td>P(tBu)$_3$ (0.06 eq)</td>
<td>toluene</td>
<td>NaO$t$Bu (2.00 eq)</td>
<td>2 d</td>
<td>42</td>
</tr>
<tr>
<td>8</td>
<td>I</td>
<td>Pd(OAc)$_2$ (0.03 eq)</td>
<td>P(tBu)$_3$ (0.06 eq)</td>
<td>toluene</td>
<td>NaO$t$Bu (2.00 eq)</td>
<td>2 d</td>
<td>38</td>
</tr>
<tr>
<td>9</td>
<td>Cl</td>
<td>Pd(OAc)$_2$ (0.03 eq)</td>
<td>P(tBu)$_3$ (0.06 eq)</td>
<td>toluene</td>
<td>NaO$t$Bu (2.00 eq)</td>
<td>2 d</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>Tos</td>
<td>Pd(OAc)$_2$ (0.03 eq)</td>
<td>P(tBu)$_3$ (0.06 eq)</td>
<td>toluene</td>
<td>NaO$t$Bu (2.00 eq)</td>
<td>3 d</td>
<td>0</td>
</tr>
</tbody>
</table>

Afterwards, the optimized reaction conditions (Table 2.6, entry 6) were applied to other phenyl precursors. Using iodobenzene instead of bromobenzene gave phenyl-substituted DTP 65 in 38% yield (Table 2.6, entry 8). In general, Buchwald-Hartwig aminations with iodides mostly work less efficiently than the reaction with the corresponding bromides. According to Widenhoefer and Buchwald the main reason for this finding is that palladium
iodide dimers are more stable than the analogous bromide dimers.\textsuperscript{[40]} However, only the monomeric species can react further in the catalytic cycle. Additionally, in the coupling with bulky amines, the large size of iodide can lead to unfavourable steric interactions.\textsuperscript{[40]} On the other hand, with the smaller chloride these problems do not occur. Nevertheless, in the amination reaction of DTP 50 and chlorobenzene the yield of phenyl-substituted DTP 65 decreased to only 15\% (Table 2.6, entry 9). Most likely, this was due to the slow oxidative addition as a consequence of the stronger carbon-halogen bond. Finally, phenyl tosylate was applied as reactant, but no amination reaction occurred and after three days almost all of the starting material 50 was decomposed (Table 2, entry 10). Thus, coupling of DTP 50 with suitable bromides using the optimized reaction conditions (Table 2.6, entry 6) appeared to be most promising in order to attach other aryl residues at the nitrogen of DTP.

Bromobenzenes with an electron-donating methoxy or electron-withdrawing cyano group in the \textit{para}-position were subsequently applied in a Buchwald-Hartwig amination with DTP 50 using the conditions noted in Table 2, entry 6 (Scheme 2.17).

\begin{equation}
\text{Scheme 2.17: Synthesis of aryl-substituted DTPs 68 and 193 via Buchwald-Hartwig amination with unsubstituted DTP 50.}
\end{equation}

The reaction rates were lower than with unsubstituted bromobenzene and after a reaction time of two days starting material 50 could still be detected via GC/MS. Prolonging the reaction to three days finally gave target compounds 68 and 193 with full conversion of DTP 50, respectively. The purity of the isolated \textit{p}-methoxyphenyl-substituted DTP 68 and \textit{p}-cyanophenyl-substituted DTP 193 was confirmed by NMR spectroscopy, mass spectrometry, and elemental analyses, respectively. Similar yields of 54\% for DTP 68 and 59\% DTP 193 were achieved after purification via column chromatography and thus were considerably lower than the yield of 76\% for phenyl-substituted DTP 65. This result showed that functional groups rather hamper Buchwald-Hartwig aminations with DTP 50 as amine than increasing the reaction rate or the yield of the aryl-substituted DTP product.
For additional coupling reactions, TIPS-protected bromothiophene 195 was synthesized in quantitative yield from 2,5-dibromothiophene 194 after onefold lithiation with \( n \)-BuLi and subsequent quenching with TIPS chloride (Scheme 2.18).\(^{[41]}\)

![Scheme 2.18: Synthesis of bromothiophene 195](image)

Unsubstituted DTP 50 was then applied in Buchwald-Hartwig aminations with different heteroaryl bromides. To confirm structure and purity of the afforded substituted DTPs analyses via NMR spectroscopy, mass spectrometry, and elemental analyses were conducted, respectively. The reaction of 3-bromothiophene 59 with various alkyl- and arylamines has already been investigated and the best product yields were obtained with palladium acetate in combination with \( \text{P(tBu)}_3 \).\(^{[42]}\) While other palladium pre-catalysts showed a worse performance, several other phosphine ligands were tested and did not produce any active palladium species at all. Furthermore, by applying the \( \text{Pd(OAc)}_2/\text{P(tBu)}_3 \) catalyst, Watanabe et al. carried out a Buchwald-Hartwig amination of 2-bromothiophenes with diarylamines.\(^{[43]}\) The reaction conditions noted in Table 2.6, entry 6, therefore seemed quite suitable and were applied in the coupling of DTP 50 with 3-bromothiophene 59 (Scheme 2.19).

![Scheme 2.19: Synthesis of 3-thienyl-substituted DTP 196](image)

Whereas in the analogous coupling with bromobenzene lower amounts of palladium acetate were beneficial, because less DTP 50 was consumed for the generation of catalytically active \( \text{Pd}(0) \) (\textit{vide supra}), higher catalyst loadings and longer reaction times were required for the Buchwald-Hartwig aminations of heteroaryl bromides. Thus, amination of 3-bromothiophene 59 gave DTP 196 in only 4% yield after a reaction time of four days when only 0.03 equivalents of the catalyst were applied (Table 2.7, entry 1). Yet, increasing the
amount of palladium to 0.10 equivalents led to a much better yield of 34% (Table 2.7, entry 2). On the other hand, when the palladium source was changed to Pd$_2$dba$_3$, the yield decreased to 20% (Table 2.7, entry 3) being in accordance with similar reactions reported in literature (vide supra). Pyrrole exhibits a pK$_a$ value of 23.0 in DMSO which is only slightly lowered when one or two phenyl rings are fused to the structure (20.95 for indole; 19.9 for carbazole). Hence, unsubstituted DTP 50 should presumably also possess a pK$_a$ around 23 and is therefore acidic enough to be deprotonated by moderately strong bases. Nevertheless, under otherwise identical conditions 3-thienyl-substituted DTP 196 could only be detected in trace amounts via GC/MS in the reaction applying potassium carbonate as base instead of sodium tert-butoxide (Table 2.7, entry 4). Moreover, when lithium amide was used, the yield of DTP 196 with 27% was still quite low (Table 2.7, entry 5). However, as tert-butoxide is a weaker base than amide, the product yield did not directly correlate with the base strength and despite the moderate yield of 34%, sodium tert-butoxide still appeared to be the best choice in the Buchwald-Hartwig amination with DTP 50 as amine.

Table 2.7: Details of the applied reaction conditions for the synthesis of 3-thienyl-substituted DTP 196 via Buchwald-Hartwig amination with unsubstituted DTP 50 (Scheme 2.19).

<table>
<thead>
<tr>
<th>Pre-catalyst</th>
<th>Ligand</th>
<th>Solvent</th>
<th>T [°C]</th>
<th>Base</th>
<th>Time</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Pd(OAc)$_2$ (0.03 eq) P(tBu)$_3$ (0.06 eq)</td>
<td>toluene</td>
<td>110</td>
<td>NaOtBu (2.00 eq)</td>
<td>4 d</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>2 Pd(OAc)$_2$ (0.10 eq) P(tBu)$_3$ (0.20 eq)</td>
<td>toluene</td>
<td>110</td>
<td>NaOtBu (1.50 eq)</td>
<td>4 d</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>3 Pd$_2$dba$_3$ (0.10 eq) P(tBu)$_3$ (0.40 eq)</td>
<td>toluene</td>
<td>110</td>
<td>NaOtBu (1.20 eq)</td>
<td>4 d</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>4 Pd(OAc)$_2$ (0.10 eq) P(tBu)$_3$ (0.20 eq)</td>
<td>toluene</td>
<td>110</td>
<td>K$_2$CO$_3$ (2.00 eq)</td>
<td>4 d</td>
<td>traces</td>
<td></td>
</tr>
<tr>
<td>5 Pd(OAc)$_2$ (0.10 eq) P(tBu)$_3$ (0.20 eq)</td>
<td>toluene</td>
<td>110</td>
<td>LiNH$_2$ (2.00 eq)</td>
<td>4 d</td>
<td>27</td>
<td></td>
</tr>
</tbody>
</table>

The same reaction conditions were used for the amination of 2-bromothiazole with DTP 50 and thiazolyl-substituted DTP 179 was detected via GC/MS (Scheme 2.20). However, initial attempts of purifying the crude compound via column chromatography were not successful. Analyses of the isolated solids by GC/MS and $^1$H NMR spectroscopy indicated the complete decomposition of the product to undefined compounds. Most likely, the thiazole ring was opened due to interactions with silica gel. Therefore, in another attempt the product was
purified via column chromatography using partially deactivated aluminium oxide as stationary phase and finally DTP 179 could be isolated in 22%. This was especially intriguing as previous attempts of preparing thiazolyl-substituted DTP 179 via C-N coupling of dibromide 72 with the commercially available 2-aminothiazole failed (Chapter 2.2.1).

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{50} \\
\text{S} \\
\text{S} \\
\text{S}
\end{array} 
\begin{array}{c}
\text{+ Br-Ar} \quad \text{[Pd]}
\end{array} 
\begin{array}{c}
\text{0-22%}
\end{array} 
\begin{array}{c}
\text{Ar:}
\end{array} 
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{S} \\
\text{S}
\end{array} 
\begin{array}{c}
\text{(179), 22%}
\end{array} 
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{S} \\
\text{S}
\end{array} 
\begin{array}{c}
\text{(198), 0%}
\end{array} 
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{TIPS}
\end{array} 
\begin{array}{c}
\text{(199), 12%}
\end{array} 
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{Cl}
\end{array} 
\begin{array}{c}
\text{(200), 1%}
\end{array}
\]

**Scheme 2.20** Synthesis of heteroaryl-substituted DTPs 179, 198-200 via Buchwald-Hartwig amination of heteroaryl bromides with unsubstituted DTP 50.

However, while in the coupling of DTP 50 with 3-bromothiophene 59 the desired 3-thienyl-substituted DTP 196 was afforded, analogous amination of 2-bromothiophene 197 to 2-thienyl-substituted DTP 198 did not work at all (Scheme 2.20). This was similar to results reported in literature, where major difficulties concerning Buchwald-Hartwig aminations of thiophenes in the 2-position were mentioned.\(^{[42]}\) Applying TIPS-protected bromothiophene 195 in this reaction, formation of DTP 199 could be observed, but the reaction proceeded very slowly (Scheme 2.20). Although high catalyst loadings were used (0.20 equivalents), still large amounts of starting material 195 were reisolated indicating a slow oxidative addition of the bromide. In order to facilitate this step in the catalytic cycle, the sterical demand of the phosphine ligand was decreased and PPh\(_3\) with a Tolman cone angle of 143° was applied instead of tri-\textit{tert}-butylphosphine (182°).\(^{[39]}\) However, in this attempt no formation of DTP 199 could be observed and just small amounts of 2-TIPS-thiophene were afforded. Thus, relatively quick debromination of the starting material 195 occurred, which suggested that the limiting step of the catalytic reaction was not the oxidative addition anymore, but rather the amination or reductive elimination, respectively. Nevertheless, the reaction was subsequently carried out with the original catalytic system of Pd(OAc)\(_2\)/P\((\text{tBu})_3\) and the obtained DTP 199 was purified via column chromatography. The afforded raw product had to be further purified via HPLC using \(n\)-hexane as eluent and DTP 199 was isolated in 12% yield.
It was suspected that with an electron-withdrawing moiety at the thiophene unit the oxidative addition of 2-bromothiophene would be accelerated leading to higher product yields of the corresponding DTP. Chloride was chosen as the residue, because no inhibitive effect for the catalyst was expected and the amination would still mainly occur with the bromide. Thus, coupling of DTP 50 was carried out with 2-bromo-5-chlorothiophene and substituted DTP 200 was formed (Scheme 2.20). Unfortunately, the yield after purification via column chromatography was very low and traces of impurities were still detected. Further purification via HPLC using n-hexane as eluent was therefore conducted and the pure product could be isolated in just 1%.

Afterwards, 2-thienyl-substituted DTP 198, which could not be obtained from the amination with unsubstituted DTP 50 (vide supra), was synthesized by abstraction of the TIPS-protecting group in DTP 199 (Scheme 2.21). Thus, treatment with TBA fluoride and purification of the raw product via column chromatography yielded almost quantitatively targeted DTP 198.

Scheme 2.21: Synthesis of thienyl-substituted DTP 198.

Despite the low to moderate yields, coupling of small heterocycles such as thiophene or thiazole to the nitrogen of unsubstituted DTP 50 still represents an attractive method, because the corresponding products could not be directly obtained via Buchwald-Hartwig amination of dibromide 72 with heteroaryl amines. Thus, in the case of thiophenes, the respective amines are presumably too electron-rich and hence too unstable for application in Buchwald-Hartwig aminations. In contrast to that, other aromatic amines such as anilines are even commercially available and the corresponding DTPs can directly be prepared from dibromide 72 (Chapter 2.2.1). However, when the conjugated substituent is largely extended and functionalized, it might be difficult to obtain the corresponding amine thereof. In contrast to that, bromides of large aromatic compounds are often accessible in a more
straightforward synthetic route. It can therefore be more convenient to apply a Buchwald-Hartwig amination with unsubstituted DTP 50 for the preparation of DTPs bearing extended conjugated units with additional functional groups. An example of such a system is perylene monoimide, of which the 8-bromo derivative 201 had previously been synthesized in the institute. Amination with DTP 50 afforded perylene monoimide-substituted DTP 202, which was purified via column chromatography using dichloromethane as eluent (Scheme 2.22). Thereafter, product 202 was obtained in a good yield of 55% showing that aminations of phenyl moieties with DTP 50 gave much better yields than analogous reactions with heteroaryls. Thus, the method is a useful general approach for the synthesis of N-functionalized DTPs.

Dithieno[3,2-b:2′,3′-d]pyrroles (DTPs)

2.3 Quantum chemical calculations on DTPs

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DFT calculations were performed on DTPs bearing different residues R at the nitrogen in order to rationalize the influence of the structure to the electronic distribution in the frontier molecular orbitals (Figure 2.3-2.5). Previously, it was shown that in alkyl-substituted DTPs the HOMO is only located at the dithienopyrrole backbone with the nitrogen residing at a node. Herein, the same observation was made for almost all synthesized DTPs and thus substituents can influence the HOMO energy level just by inductive effects. The only exception in this regard is DTP 68, in which the attached 4-methoxyphenyl moiety also participates to a minor extent to the HOMO. Nevertheless, this does not profoundly affect the energy level of this frontier molecular orbital in comparison to, for example, phenyl-substituted DTP 65 (Chapter 2.4). Contrary to the HOMO, the LUMO of DTPs also extends to the nitrogen and the attached substituents. In the case of alkyl residues their contribution is very small and limited to the \( \alpha \)-carbon atom. Yet, with phenyls, benzoyl, Boc, tosyl, thienyls, or thiazolyln moieties the LUMO is located at the complete conjugated part of the molecule, respectively. Therefore, these residues have a significant impact on the LUMO energy levels. The electronic influence of the substituents is even more pronounced in DTPs 189 and 202 bearing a 4-nitrobenzoyl or a perylene monoimide residue at the nitrogen. In these derivatives, the LUMO is dominated by the substituent and only minor contributions of the pyrrole unit can be observed. In summary, functionalization of DTP at the nitrogen only indirectly affects the HOMO, whereas in particular conjugated moieties exhibit a major influence on the LUMO and therefore also affect the HOMO-LUMO energy gap.
Figure 2.3: Frontier molecular orbital surfaces of DTPs bearing hydrogen, alkyl, phenyls, or Boc at the nitrogen. Calculations were carried out with the Gaussian 09 program.\textsuperscript{[49]} Geometry optimizations and energy calculations were performed via DFT methods using the B3LYP correlation/exchange functional\textsuperscript{[50-51]} and the 6-311+G(d) basis set. Molecular orbital surfaces were generated utilizing the Gauss View 5.0 program with an isovalue of 0.02. & Alkyl chains were shortened to ethyl to save computational time.
Figure 2.4: Frontier molecular orbital surfaces of DTPs bearing benzoyle, tosylate, thienyls, or thiazolyl at the nitrogen. Calculations were carried out with the Gaussian 09 program. Geometry optimizations and energy calculations were performed via DFT methods using the B3LYP correlation/exchange functional and the 6-311+G(d) basis set. Molecular orbital surfaces were generated utilizing the Gauss View 5.0 program with an isovalue of 0.02.
Figure 2.5: Frontier molecular orbital surfaces of DTPs bearing thiienyls or perylene monoimide at the nitrogen. Calculations were carried out with the Gaussian 09 program.[49] Geometry optimizations and energy calculations were performed via DFT methods using the B3LYP correlation/exchange functional[50-51] and the 6-311+G(d) basis set. Molecular orbital surfaces were generated utilizing the Gauss View 5.0 program with an isovalue of 0.02.
2.4 Optoelectronic properties of DTPs

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The optoelectronic properties of all synthesized DTPs bearing different residues R at the nitrogen were determined. UV-Vis absorption spectra were recorded in THF solution and from the onset of the absorption band with the lowest energy the optical HOMO-LUMO gap $E_g$ was calculated. Additionally, the HOMO energy level was derived from the onset oxidation potential in the cyclic voltammogram. With $E_g$ and the HOMO energy level the LUMO energy level was then calculated. The cyclic voltammograms of DTPs bearing a hydrogen, alkyl, phenyl, benzoyl, or Boc residue at the nitrogen are depicted in Chapter 2.5 in context of their electropolymerization.

In Figure 2.6a the UV-Vis spectrum of hexyl-substituted DTP 60 is shown as a representative example for alkyl-substituted DTPs. It exhibits a global maximum at 298 nm with a local

![Figure 2.6: UV-Vis absorption spectra of DTPs with hydrogen, hexyl, or benzyl residues R attached at the nitrogen measured in THF solution (a) and cyclic voltammograms of DTP 186 (R=Bz; b) recorded in a solution of TBA-PF$_6$ (0.1 M) in acetonitrile with a scan rate of 100 mV/s.](image-url)
maximum at 310 nm and a shoulder at 289 nm corresponding to vibrational components of electronic $\pi-\pi^*$ transitions. The extinction coefficients slightly decrease with increasing bulkiness of the alkyl chains from hexyl in DTP 60 over 2-ethylhexyl in DTP 64 to 2-hexyldecyl in DTP 78 (Table 2.8). However, all alkyl-substituted DTPs possess an optical energy gap of 3.90 eV and the same HOMO and LUMO energy levels of -5.50 eV and -1.60 eV, respectively.

Similarly, benzyl-substituted derivative 186 is oxidized at 0.44 V corresponding to a HOMO energy level of -5.54 eV (Figure 2.6b). This formation of the DTP radical cation initialized the electropolymerization of DTP 186 and a p(DTP) film formed on the working electrode. Thus, in the second sweep the oxidation of the polymer at lower potentials could be observed as a new anodic signal and with increasing number of scans the continuous growth of the p(DTP) film was indicated by the increasing currents. In the UV-Vis spectrum monomer 186 exhibits the same features as the alkyl-substituted DTP analogues (Figure 2.6a) and the frontier molecular orbitals are only marginally stabilized (Table 2.8).

Table 2.8: Optoelectronic properties of DTPs 50, 60, 64, 78, and 186. The values of $E_{\text{pa}}$, $E_{\text{onset}}$, and the HOMO energy level were obtained via cyclic voltammetry. The values of $\lambda_{\text{max}}$, $\varepsilon$, $\lambda_{\text{onset}}$, and the energy gap $E_g$ were obtained via UV-Vis spectroscopy. The LUMO energy levels were obtained from the HOMO energy levels and $E_g$, respectively. Besides experimental results HOMO energy levels, energy gaps $E_g$, and LUMO energy levels derived from DFT calculations in Chapter 2.3 using the B3LYP functional and the 6-311+G(d) basis set are also stated.

<table>
<thead>
<tr>
<th>DTP</th>
<th>R</th>
<th>$E_{\text{pa}}^a$</th>
<th>$E_{\text{onset}}$</th>
<th>HOMO$^b$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon$</th>
<th>$\lambda_{\text{onset}}$</th>
<th>$E_g$</th>
<th>LUMO</th>
</tr>
</thead>
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<td></td>
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<td>0.40</td>
<td>-5.50</td>
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<td>3.90</td>
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<td>0.40</td>
<td>-5.50</td>
<td>298</td>
<td>24300</td>
<td>318</td>
<td>3.90</td>
<td>-1.60</td>
</tr>
<tr>
<td>186</td>
<td>Bz</td>
<td>0.55</td>
<td>0.44</td>
<td>-5.54</td>
<td>297</td>
<td>24600</td>
<td>317</td>
<td>3.91</td>
<td>-1.63</td>
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</table>

Potentials are referenced vs. Fc/Fc$^+$; $a$ $E_{\text{pa}}$: anodic peak potential (scan rate 100 mV/s); $b$ Redox potential of Fc/Fc$^+$ is -5.1 eV on the Fermi scale; $c$ R=Et

The absorption bands in the spectrum of unsubstituted DTP 50 are shifted hypsochromically by 3-4 nm with slightly decreased extinction coefficients (Figure 2.6a) and the shift of the absorption onset corresponds to a larger optical energy gap of 3.95 eV. Overall, the HOMO energy level of -5.49 eV and the LUMO energy level of -1.54 eV are nevertheless very similar to the respective values of alkyl-substituted DTPs (Table 2.8). Therefore, hydrogen
and different alkyl residues only have a marginal influence on the optoelectronic properties of DTPs which is in good agreement with the theoretical estimations of the frontier molecular orbitals (Chapter 2.3). Because of the node at the nitrogen in the HOMO the energy of this orbital is almost not affected by the latter substituents. On the other hand, the small contributions of hydrogen and alkyls to the LUMO lead to greater, but still small changes of the LUMO energies, respectively.

Boc-substituted DTP 176 shows an onset absorption at 321 nm in the UV-Vis spectrum due to an $E_b$ of 3.86 eV (Figure 2.7a). Additionally, the compound exhibits a global maximum at 284 nm accompanied by a local maximum at 299 nm and shoulders at 276 nm and 308 nm. Because of the electron-withdrawing influence of the Boc group the frontier molecular orbitals of DTP 176 are stabilized by 0.22 eV, respectively 0.31 eV, in comparison to the energy levels of unsubstituted DTP 50 (Table 2.9). The effect is larger for the LUMO than for the HOMO and therefore the optical energy gap of DTP 176 is also decreased by 0.09 eV.

![Figure 2.7](image)

**Figure 2.7:** UV-Vis absorption spectra of DTPs with benzyol, Boc, $p$-nitrobenzoyl (a), or tosyl (b) residues $R$ attached at the nitrogen measured in THF solution.

A more electron-withdrawing influence is exerted by benzyol and tosyl moieties and thus the HOMO with an energy level of -5.75 eV in benzyol-substituted DTP 97 and -5.86 eV in tosyl-substituted DTP 177 is further stabilized (Table 2.9). As the HOMOs are only localized at
the dithienopyrrole cores, these decreases originate from negative inductive effects of the substituents. In contrast to that, the residues at the nitrogen directly contribute to the LUMO. Hence, this molecular orbital is more affected, i.e., more stabilized to -2.18 eV for DTP 97 and -3.05 eV for DTP 177. Consequently, the electronic excitation from the HOMO to the LUMO also leads to a partial charge transfer from the dithienopyrrole unit to the conjugated benzoyl or tosyl substituent, respectively. This effect has as well been reported for acyl-substituted DTPs and can be observed in the UV-Vis spectra as a tailing absorption band at low energies and with decreased extinctions.\(^1\) In the spectrum of benzoyl-substituted DTP 97 thus a broad shoulder at 325 nm with an onset absorption at 347 nm appears and corresponds to a relatively low optical energy gap of 3.57 eV (Figure 2.7a). Similarly, tosyl-substituted derivative 177 exhibits a shoulder at 405 nm with a very low extinction coefficient besides the main absorption band with a maximum at 281 nm and a shoulder at 302 nm (Figure 2.7b). Hence, the tosyl moiety exhibits a particularly strong electronic influence and leads to a quite low HOMO-LUMO gap of 2.81 eV in DTP 177. Nevertheless, the compound can still be polymerized electrochemically as shown in Figure 2.8a and after few scans a thick dark blue p(DTP) film was afforded.

### Table 2.9: Optoelectronic properties of DTPs 97, 176, 177, and 189

The values of \(E_{\text{pa}}\), \(E_{\text{onset}}\), and the HOMO energy level were obtained via cyclic voltammetry. The values of \(\lambda_{\text{max}}\), \(\varepsilon\), \(\lambda_{\text{onset}}\), and the energy gap \(E_g\) were obtained via UV-Vis spectroscopy. The LUMO energy levels were obtained via cyclic voltammetry or from the HOMO energy levels and \(E_g\) respectively. Besides experimental results HOMO energy levels, energy gaps \(E_g\), and LUMO energy levels derived from DFT calculations in Chapter 2.3 using the B3LYP functional and the 6-311+G(d) basis set are also stated.

<table>
<thead>
<tr>
<th>DTP</th>
<th>(R)</th>
<th>(E_{\text{pa}}^a)</th>
<th>(E_{\text{onset}})</th>
<th>HOMO(^b)</th>
<th>(\lambda_{\text{max}})</th>
<th>(\varepsilon)</th>
<th>(\lambda_{\text{onset}})</th>
<th>(E_g)</th>
<th>LUMO</th>
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<td>COPh</td>
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<td>0.65 (exp.)</td>
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<td>-1.85</td>
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<tr>
<td>177</td>
<td>Tos</td>
<td>0.89 (DFT)</td>
<td>0.76 (exp.)</td>
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<td>281</td>
<td>15300</td>
<td>442</td>
<td>2.81</td>
<td>-3.05</td>
</tr>
<tr>
<td>189</td>
<td>COPh-NO(_2)</td>
<td>0.92 (DFT)</td>
<td>0.74 (exp.)</td>
<td>-5.84</td>
<td>283</td>
<td>24800</td>
<td>(c)</td>
<td>2.05(^d)</td>
<td>-3.79(^d)</td>
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</table>

Potentials are referenced vs. Fc/Fc\(^+\); \(a\) \(E_{\text{pa}}\): anodic peak potential (scan rate 100 mV/s); \(b\) Redox potential of Fc/Fc\(^+\) is -5.1 eV on the Fermi scale;\(^{[52]}\) \(c\) Could not be determined; \(d\) Determined electrochemically

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\(^1\) Valy et al., Chem. Sci. 2013, 4, 3754.
Dithieno[3,2-b:2',3'-d]pyrroles (DTPs)

Figure 2.8: Cyclic voltammograms of tosyl-substituted DTP 177 recorded in a solution of TBA-PF$_6$ (0.1 M) in acetonitrile (a) and $p$-nitrobenzoyl-substituted DTP 189 recorded in a solution of TBA-PF$_6$ (0.1 M) in dichloromethane with a scan rate of 100 mV/s (b and c). With DTP 189 a wide potential window was scanned (b) and several sweeps during the electropolymerization were conducted at higher potentials (c).

In the UV-Vis spectrum of $p$-nitrobenzoyl-substituted DTP 189 a global maximum at 283 nm appears and a close local maximum at 291 nm with a very long tailing can be observed (Figure 2.7a). To properly determine the onset absorption more concentrated solutions of DTP 189 were investigated, but the compound aggregated and the absorption shifted bathochromically. Thus, the optical HOMO-LUMO gap could not be determined from the spectrum. However, DFT calculations indicate a relatively small energy gap $E_g$ (Table 2.9). While the electronic distribution in the HOMO of DTP 189 is similar to most other DTPs, the LUMO is almost only located at the $p$-nitrobenzoyl substituent (Chapter 2.3). As a consequence, this molecular orbital is stabilized to a relatively large extent and with the reduction of the compound already starting at -1.31 V the LUMO energy level could be determined electrochemically to be -3.79 eV (Figure 2.8b). In the cyclic voltammogram two reversible one-electron reductions of the nitro group with redox potentials of -1.40 V and -1.80 V as well as the typical irreversible one-electron oxidation signal of the dithienopyrrole unit can
be observed. The latter starts at 0.74 V corresponding to a HOMO energy level of -5.84 eV (Table 2.9). Thus, with the nitro moiety at the benzoxy residue not only the LUMO is affected, but the substituent at the nitrogen of DTP 189 is also more electron-withdrawing than in benzoxy-substituted DTP 97 and further stabilizes the HOMO. After the oxidative formation of the radical cation, DTP 189 polymerized and within several scans a thick p(DTP) was obtained (Figure 2.8c).

Similarly to unsubstituted DTP 50, phenyl-substituted DTP 65 shows a global maximum at 310 nm and a local maximum at 299 nm, as well as a shoulder at 288 nm in the UV-Vis spectrum which correspond to π-π* transitions (Figure 2.9a). Furthermore, the phenyl residue leads to a slight decrease of the HOMO energy level to -5.60 eV and a more pronounced stabilization of the LUMO to -1.74 eV compared to unsubstituted DTP 50 (Table 2.10).

![Figure 2.9](image)

**Figure 2.9**: UV-Vis absorption spectra of DTPs with phenyl, p-methoxyphenyl, or p-cyanophenyl residues R attached at the nitrogen measured in THF solution (a) and cyclic voltammograms of p-methoxyphenyl-substituted DTP 68 (b), and p-cyanophenyl-substituted DTP 193 (c) recorded in a solution of TBA-PF₆ (0.1 M) in acetonitrile with a scan rate of 100 mV/s.
Attachment of an electron-donating methoxy group in the para-position of the phenyl substituent only marginally alters the optoelectronic properties of the DTP, so phenyl-substituted DTP 65 and p-methoxyphenyl-substituted DTP 68 show very similar UV-Vis spectra and cyclic voltammograms during the electropolymerization (Figure 2.9a and b, Table 2.10). On the other hand, the electron-withdrawing cyano moiety in the para-position of p-cyanophenyl-substituted DTP 193 leads to a bathochromically and hyperchromically shifted $\lambda_{\text{max}}$ of 318 nm with a shoulder at 293 nm (Figure 2.9a). The onset absorption of DTP 193 is also red-shifted to 340 nm corresponding to an energy gap of 3.65 eV. The HOMO is slightly stabilized to -5.66 eV, whereas the LUMO energy level is decreased to -2.07 eV (Table 2.10). Moreover, after the electrochemical formation of the radical cation in the first cycle, DTP 193 polymerized and, similarly to DTPs 65 and 68, formed a dark blue p(DTP) film (Figure 2.9c).

### Table 2.10: Optoelectronic properties of DTPs 65, 68, and 193.

<table>
<thead>
<tr>
<th>DTP</th>
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<th>$E_{\text{pa}}$</th>
<th>$E_{\text{onset}}$</th>
<th>HOMO$^b$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon$</th>
<th>$\lambda_{\text{onset}}$</th>
<th>$E_g$</th>
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<td>65</td>
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<tr>
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</tr>
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<td>193</td>
<td>Ph-CN</td>
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<tr>
<td></td>
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</tr>
</tbody>
</table>

Potentials are referenced vs. Fc/Fc$^+$; $a$ $E_{\text{pa}}$: anodic peak potential (scan rate 100 mV/s); $b$ Redox potential of Fc/Fc$^+$ is -5.1 eV on the Fermi scale.$^{[52]}$

In the UV-Vis spectra of 2-thienyl-substituted DTPs 198-200 slight differences can be observed depending on the residue at the 5-position of the thienyl moiety (Figure 2.10a). DTP 199 bearing a TIPS group exhibits a maximum at 309 nm with two shoulders at higher energies and an onset absorption at 344 nm. With chloride instead of the silyl residue DTP 200 shows a maximum at 307 nm and a shoulder at 295 nm. The onset absorption occurs at 377 nm due to a HOMO-LUMO gap of 3.68 eV, which is lower than the $E_g$ of 2-thienyl-substituted DTP 198 (3.77 eV), but slightly larger than the optical energy gap of 3.60 eV in
DTP 199 with TIPS at the 5-position of the 2-thienyl substituent (Table 2.11). The $\lambda_{\text{max}}$ of the former compound appears at 298 nm and the absorption band exhibits a shoulder at 306 nm.

![UV-Vis absorption spectra](image)

**Figure 2.10**: UV-Vis absorption spectra of DTPs with 2-thienyl, 5-TIPS-2-thienyl, or 5-chloro-2-thienyl residues R attached at the nitrogen measured in THF solution (a) and cyclic voltammograms of 2-thienyl-substituted DTP 198 (b), 5-TIPS-2-thienyl-substituted DTP 199 (c), and 5-chloro-2-thienyl-substituted DTP 200 (d) recorded in a solution of TBA-PF$_6$ (0.1 M) in acetonitrile with a scan rate of 100 mV/s.

The onset oxidation in the cyclic voltammogram of 2-thienyl-substituted DTP 198 occurs at 0.55 eV (Figure 2.10b) corresponding to a HOMO energy level of -5.65 eV (Table 2.11), which is thus very similar to the HOMO energy level of phenyl-substituted DTP 65 (-5.60 eV). However, the 2-thienyl residue exerts a slightly stronger electronic influence than phenyl and further stabilizes the LUMO to -1.88 eV. Although in DTP 198 a cross-linking during the polymerization could in principle occur at the thienyl substituent, the radical cation is most likely located at the dithienopyrrole unit and hence coupling reactions only occur at the $\alpha$- and
β-positions of DTP. Therefore, the cyclic voltammograms of 2-thienyl-substituted DTP 198 in Figure 2.10b and, for example, p-methoxyphenyl-substituted DTP 68 in Figure 2.9b and p-cyanophenyl-substituted DTP 193 in Figure 2.9c look very similar. Also with the 5-chloro-2-thienyl moiety in DTP 200 a p(DTP) film was obtained and the irreversible oxidation of the monomer started at 0.57 eV (Figure 2.10d). While the HOMO energy level was almost the same as in 2-thienyl-substituted DTP 198, due to the more electron-withdrawing influence of the substituent the LUMO was more stabilized to -1.99 eV (Table 2.11). Bearing a TIPS moiety instead of hydrogen or chloride in the 5-position of the thienyl residue, the LUMO energy level of DTP 199 was further decreased to -2.05 eV, whereas the HOMO was not affected (Table 2.11). However, during electropolymerization just a slight current increase could be observed after several cycles (Figure 2.10c). Hence, the sterical demand of the TIPS group most likely inhibited an effective C-C coupling and only a very thin p(DTP) film was afforded.

Table 2.11: Optoelectronic properties of DTPs 198-200. The values of $E_{pa}$, $E_{onset}$, and the HOMO energy level were obtained via cyclic voltammetry. The values of $\lambda_{max}$, $\varepsilon$, $\lambda_{onset}$, and the energy gap $E_g$ were obtained via UV-Vis spectroscopy. The LUMO energy levels were obtained from the HOMO energy levels and $E_g$, respectively. Besides experimental results HOMO energy levels, energy gaps $E_g$, and LUMO energy levels derived from DFT calculations in Chapter 2.3 using the B3LYP functional and the 6-311+G(d) basis set are also stated.

<table>
<thead>
<tr>
<th>DTP</th>
<th>R</th>
<th>$E_{pa}$</th>
<th>$E_{onset}$</th>
<th>HOMO</th>
<th>$\lambda_{max}$</th>
<th>$\lambda_{onset}$</th>
<th>$E_g$</th>
<th>LUMO</th>
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<td>198</td>
<td>2-Th exp.</td>
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<td>-5.65</td>
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<td>DFT</td>
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<tr>
<td>199</td>
<td>5-TIPS-2-Th</td>
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<td>23800</td>
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<tr>
<td>200</td>
<td>5-CI-2-Th</td>
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<td>307</td>
<td>25700</td>
<td>337</td>
<td>3.68</td>
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</table>

Potentials are referenced vs. Fc/Fc$^+$; $a$ $E_{pa}$: anodic peak potential (scan rate 100 mV/s); $b$ Redox potential of Fc/Fc$^+$ is -5.1 eV on the Fermi scale;[52]

Compared to 2-thienyl-substituted DTP 198, where the thienyl residue is bound at an α-position to the nitrogen, 3-thienyl-substituted DTP 196 shows similar features in the UV-Vis spectrum (Figure 2.11a). Thus, the derivative with a thienyl substituent attached in the β-position to the nitrogen also shows a maximum at 298 nm accompanied by a shoulder at higher wavelengths, but the onset absorption is blue-shifted to 323 nm due to a slightly larger $E_g$ of 3.84 eV (Table 2.12). Hence, the electronic influence of the thienyl moiety is less
pronounced in DTP 196 and the HOMO and LUMO energy levels are very similar to the respective values of phenyl-substituted DTP 65. As in 2-thienyl-substituted DTP 198 a cross-

![Chemical Structures](image)

**Figure 2.11:** UV-Vis absorption spectra of DTPs with 3-thienyl, 2-thiazolyl, or perylene monoimide residues R attached at the nitrogen measured in THF solution (a) as well as cyclic voltammograms of 3-thienyl-substituted DTP 196 (b) and 2-thiazolyl-substituted DTP 179 (c) recorded in a solution of TBA-PF$_6$ (0.1 M) in acetonitrile with a scan rate of 100 mV/s and cyclic voltammograms of perylene monoimide-substituted DTP 202 recorded in a solution of TBA-PF$_6$ (0.1 M) in dichloromethane with a scan rate of 100 mV/s (d and e). With DTP 202 a wide potential window was scanned (d) and several sweeps during the electropolymerization were conducted at higher potentials (e).
linking at the substituent could theoretically occur during the electropolymerization of 3-thienyl-substituted DTP 196. However, because the cyclic voltammograms in Figure 2.11b also look very similar to the plots of other aryl-substituted DTPs (e.g. p-methoxyphenyl-substituted DTP 68 in Figure 2.9b and p-cyanophenyl-substituted DTP 193 in Figure 2.9c), this does most likely not happen.

The voltammograms of thiazolyl-substituted DTP 179 indicate the same behaviour and after the formation of the radical cation had started at 0.61 V, it took just few scans to produce a dark blue p(DTP) film (Figure 2.11c). Due to the electron-withdrawing thiazolyl residue the frontier molecular orbitals are stabilized considerably, but not to such a high extent as, for instance, in benzoyl-substituted derivative 97 (Table 2.12). In the UV-Vis spectrum an absorption band with a $\lambda_{\text{max}}$ of 314 nm and a shoulder at 321 nm can be observed which is bathochromically shifted in comparison to unsubstituted DTP 50 or DTPs 196, 198-200 bearing thienyl residues at the nitrogen (Figure 2.11a). Furthermore, the onset absorption at 335 nm corresponds to an optical HOMO-LUMO gap of 3.70 eV.

Table 2.12: Optoelectronic properties of DTPs with different residues R attached at the nitrogen. The values of $E_{\text{pa}}$, $E_{\text{onset}}$, and the HOMO energy level were obtained via cyclic voltammetry. The values of $\lambda_{\text{max}}$, $\varepsilon$, $\lambda_{\text{onset}}$, and the energy gap $E_g$ were obtained via UV-Vis spectroscopy. The LUMO energy levels were obtained from the HOMO energy levels and $E_g$, respectively. Besides experimental results HOMO energy levels, energy gaps $E_g$, and LUMO energy levels derived from DFT calculations in Chapter 2.3 using the B3LYP functional and the 6-311+G(d) basis set are also stated.

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<thead>
<tr>
<th>DTP</th>
<th>R</th>
<th>$E_{\text{pa}}$</th>
<th>$E_{\text{onset}}$</th>
<th>HOMO</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon$</th>
<th>$\lambda_{\text{onset}}$</th>
<th>$E_g$</th>
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Potentials are referenced vs. Fc/Fc$^{\ddagger}$; $a$ $E_{\text{pa}}$: anodic peak potential (scan rate 100 mV/s); $b$ Redox potential of Fc/Fc$^{\ddagger}$ is -5.1 eV on the Fermi scale; $^{[52]}$ $c$ Determined electrochemically

With a perylene monoimide another electron-accepting group was attached at the nitrogen of DTP 202 and the compound shows a local maximum at 294 nm with two shoulders at 305 nm and 286 nm in the UV-Vis spectrum (Figure 2.11a). Because of the substituent an absorption band at 264 nm can be observed and further local maxima with relatively low
extinction coefficients appear at 338 nm and 355 nm. However, most prominently the broad band in the visible region with a \( \lambda_{\text{max}} \) of 508 nm gives rise to the dark red colour of the compound and, in contrast to the isolated perylene monoimide without DTP, does not exhibit a vibrational fine-structure.\(^{[53-54]}\) The onset absorption at 560 nm corresponds to a relatively low optical energy gap of 2.21 eV (Table 2.12). As DFT calculations indicate that the HOMO is only localized at the dithienopyrrole core, whereas mainly the perylene monoimide residue contributes to the LUMO (Chapter 2.3), this electronic transition is accompanied by a partial charge transfer from the DTP backbone to the substituent at the nitrogen. The HOMO is only slightly stabilized to -5.63 eV and therefore in this regard the electronic effect of the substituent in DTP 202 is similar to the influence of phenyls or thienyls (vide supra). On the other hand, the LUMO is much more affected by the perylene monoimide moiety and in the cyclic voltammogram a reversible one-electron reduction of the substituent starting at -1.32 V can be observed (Figure 2.11d). Due to differences in the analytic methods, the electrochemically determined HOMO-LUMO gap of 1.90 eV is even lower than the value obtained from UV-Vis spectroscopy (Table 2.12). Notably, the voltammogram of the monomer also reveals an irreversible oxidation signal of the dithienopyrrole backbone and despite the quite large sterical demand of the extended conjugated residue at the nitrogen the electropolymerization of DTP 202 is not prohibited (Figure 2.11e).

In Tables 2.8-2.12 the optoelectronic properties of all synthesized DTP monomers are summarized and besides experimental results HOMO energy levels, energy gaps \( E_g \), and LUMO energy levels derived from DFT calculations in Chapter 2.3 are also stated. While the energies of the HOMO are in quite good accordance with the values determined by cyclic voltammetry, the estimations for the LUMO energy level are too high, which is why the theoretical \( E_g \) is always considerably larger than the experimentally found energy gaps. The reason for these deviations is that the geometry of the molecule is optimized for the ground state, but not for the electronically excited state, respectively. Nevertheless, comparing the experimentally and theoretically determined values of different DTPs, the same trends can be observed and thus energetic variations of the frontier molecular orbitals were not profoundly caused by experimental conditions, such as temperature or solvent polarity. Hence, the described structure-property relationships can indeed be attributed to the inherent electronic influences of the various substituents at the nitrogen of DTP.
2.5. Electropolymerization of DTPs

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Several derivatives of the synthesized DTPs were potentiodynamically polymerized in an electrochemical cell on a platinum working electrode (Scheme 2.23). The respective monomers were used in millimolar concentrations in a solution of TBA-PF$_6$ as the supporting electrolyte. After the electropolymerization the obtained film was subjected to several scans in a monomer-free electrolyte solution until a stable current response was recorded. At this “conditioning” phase residual short polymers in the film were further polymerized. Subsequently, the respective film was characterized via cyclic voltammetry applying different scan rates between 10 mV/s and 100 mV/s and 30 cycles were measured with a scan rate of 100 mV/s in order to investigate the film stability.

\[ \text{Scheme 2.23: Electropolymerization of DTPs 50, 60, 64, 78, 65, 97, and 176.} \]

In Figure 2.12 the cyclic voltammograms of the electropolymerization and the following film characterization of unsubstituted DTP 50 are shown. From the first scan in the polymerization the onset oxidation potential of DTP 50 was determined to be 0.39 V corresponding to a HOMO energy level of -5.49 eV. The formed radical cations were, however, not stable and polymerized to form p(DTP) film P$_{ec}$50 on the working electrode. Therefore, in the backscan of the first scan a broad cathodic signal due to the reduction of the oxidized film and in the second cycle a new anodic signal at lower potentials due to the oxidation of the polymer could be observed. With increasing number of scans the currents increased and after ten scans a relatively thick dark blue film was obtained. During the electrochemical characterization of P$_{ec}$50 in a monomer-free electrolyte solution a broad oxidation wave
emerged due to the polydispersity of the polymer. The onset oxidation of p(DTP) $\text{P}_{\text{ec50}}$ occurred at -0.54 V corresponding to a HOMO energy level of -4.56 eV (Table 2.13). With regard to the HOMO $\text{p(DTP)s}$ can thus be located between the analogous polyheterotriacene with sulphur- instead of nitrogen-bridged bithiophene repeat units and the more electron-rich PEDOT. The latter exhibits a quite high HOMO energy level of about -4.3 eV\textsuperscript{[55-56]} whereas the HOMO of poly(dithieno[3,2-b:2',3'-d]thiophene) is more stabilized to about -4.9 eV\textsuperscript{[57-58]} Furthermore, $\text{p(DTP) P}_{\text{ec50}}$ showed a sharp peak at 0.17 V on top of the broad anodic signal which was also observed by Zotti et al.\textsuperscript{[4]} They attributed this signal to an unknown species adsorbed at the working electrode and only observed the peak during the polymerization in acetonitrile. However, during the characterization of $\text{P}_{\text{ec50}}$ in a blank electrolyte solution the peak was initially still visible and just disappeared when 30 cycles were measured to investigate the film stability. Herein, the exchanged charges only slightly decreased with the number of conducted scans and accounted for a 6% loss of electrophoric

![Graph](image_url)

**Figure 2.12:** Electropolymerization of DTP monomer 50 with a hydrogen residue at the nitrogen (a) and characterization of the obtained film $\text{P}_{\text{ec50}}$ using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents $I_{pa}$ and the cathodic peak currents $I_{pc}$ from the applied scan rate (d).
material. Moreover, the cycling stability of \( P_{\text{ec}50} \) was evidenced by the linear increase of the peak currents with increasing sweep rate. This indicated that the electron transfer in the redox process occurred very rapidly and hence the film was well adhered to the electrode.

Subsequently, the synthesized DTPs bearing a hexyl, 2-ethylhexyl, or 2-hexyldecyl chain at the nitrogen were also electropolymerized (Figure 2.13, 2.14, and 2.15). Independent from the alkyl group, DTP monomers 60, 64, and 78 exhibited an onset oxidation at 0.40 V corresponding to a HOMO energy level of -5.50 eV. As alkyl substituents increased the solubility of DTPs and the respective polymers in organic solvents, it was more difficult to obtain insoluble adhering p(DTP) films on the working electrode. Thus, applying negative potentials during the backsweeps, parts of the neutral polymer began to dissolve in all attempts. Nevertheless, after several scans stable polymer films were obtained from all three DTP monomers. The stability of \( P_{\text{ec}60}, P_{\text{ec}64}, \) and \( P_{\text{ec}78} \) was in particular evidenced by the small current changes after 30 cycles with material losses between 3% and 4%, respectively.

![Graph A](image1.png) ![Graph B](image2.png) ![Graph C](image3.png) ![Graph D](image4.png)

**Figure 2.13:** Electropolymerization of DTP monomer 60 with a hexyl residue at the nitrogen (a) and characterization of the obtained film \( P_{\text{ec}60} \) using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents \( I_{\text{pa}} \) and the cathodic peak currents \( I_{\text{pc}} \) from the applied scan rate (d).
Figure 2.14: Electropolymerization of DTP monomer 64 with a 2-ethylhexyl residue at the nitrogen (a) and characterization of the obtained film PEC64 using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents $I_{pa}$ and the cathodic peak currents $I_{pc}$ from the applied scan rate (d).

(Table 2.13). Furthermore, linear relationships between the scan rate and the peak currents were observed which showed that the films were well adhered at the surface of electrode. The onset oxidation of the polymers was very similar for all investigated p(DTP)s bearing alkyl residues and the HOMO energy level of hexyl-substituted derivative PEC60 with -4.52 eV only marginally varied from the HOMO energy level of 2-ethylhexyl- and 2-hexyldecyl-substituted derivatives PEC64 and PEC78 with -4.54 eV (Table 2.13). As observed for the monomeric DTPs, alkyl moieties therefore also exhibited very little influence on the optoelectronic properties of the corresponding polymers. Differences between these p(DTP)s, however, occurred as the consequence of an increased solubility of intermediates and the final polymers with increasing alkyl chain lengths or branching, respectively. Thus, the cyclic voltammograms in Figure 2.13, Figure 2.14, and Figure 2.15 varied depending on the alkyl residue at the nitrogen. The p(DTP) bearing hexyl chains (PEC60) exhibited a very broad oxidation and reduction curve with an anodic peak potential of 0.09 V and a cathodic peak potential of
0.05 V. While 2-ethylhexyl-substituted derivative $P_{ec64}$ showed similar curves with an increased anodic peak potential of 0.17 V and an increased cathodic peak potential of 0.14 V, $P_{ec78}$ with 2-hexyldecyl residues showed a relatively sharp anodic signal with a decreased peak potential of -0.03 V and a broad cathodic signal with a peak potential of -0.10 V.

**Figure 2.15:** Electropolymerization of DTP monomer 78 with a 2-hexyldecyl residue at the nitrogen (a) and characterization of the obtained film $P_{ec78}$ using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents $I_{pa}$ and the cathodic peak currents $I_{pc}$ from the applied scan rate (d).

**Table 2.13:** Electronic properties of electrochemically prepared p(DTP)s bearing different residues R at the nitrogen determined via cyclic voltammetry in a monomer-free electrolyte solution.

<table>
<thead>
<tr>
<th>p(DTP)</th>
<th>R</th>
<th>$E_{pa}$ [V]</th>
<th>$E_{pc}$ [V]</th>
<th>$E_{onset}$ [V]</th>
<th>HOMO$^c$ [eV]</th>
<th>Film loss$^d$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{ec50}$</td>
<td>H</td>
<td>0.18</td>
<td>0.19</td>
<td>-0.54</td>
<td>-4.56</td>
<td>6</td>
</tr>
<tr>
<td>$P_{ec60}$</td>
<td>Hex</td>
<td>0.09</td>
<td>0.05</td>
<td>-0.58</td>
<td>-4.52</td>
<td>4</td>
</tr>
<tr>
<td>$P_{ec64}$</td>
<td>2-EtHex</td>
<td>0.17</td>
<td>0.14</td>
<td>-0.56</td>
<td>-4.54</td>
<td>3</td>
</tr>
<tr>
<td>$P_{ec78}$</td>
<td>2-HexDec</td>
<td>-0.03</td>
<td>-0.10</td>
<td>-0.56</td>
<td>-4.54</td>
<td>4</td>
</tr>
<tr>
<td>$P_{ec65}$</td>
<td>Ph</td>
<td>0.34</td>
<td>0.31</td>
<td>-0.67</td>
<td>-4.43</td>
<td>5</td>
</tr>
<tr>
<td>$P_{ec97}$</td>
<td>COPh</td>
<td>0.17</td>
<td>-0.04</td>
<td>-0.23</td>
<td>-4.87</td>
<td>3</td>
</tr>
<tr>
<td>$P_{ec176}$</td>
<td>Boc</td>
<td>-0.12</td>
<td>-0.16</td>
<td>-0.53</td>
<td>-4.57</td>
<td>5</td>
</tr>
</tbody>
</table>

Potentials are referenced vs. Fc/Fc$^+$; $a$ $E_{pa}$: anodic peak potential (scan rate 100 mV/s); $b$ $E_{pc}$: cathodic peak potential (scan rate 100 mV/s); $c$ Redox potential of Fc/Fc$^+$ is -5.1 eV on the Fermi scale; $d$ Determined as the difference of exchanged charges during scan 2 and scan 30.
The oxidation of phenyl-substituted DTP 65 started at 0.50 V, which corresponded to a HOMO energy level of -5.60 eV and initialized the electropolymerization to $P_{ec}65$ (Figure 2.16). After few cycles, a stable and well adhered p(DTP)-film was obtained as evidenced by the linear current increase with increasing scan rate. Moreover, the exchanged charges only slightly decreased after 30 sweeps and only 5% of the material was lost (Table 2.13). In the cyclic voltammograms $P_{ec}65$ showed broad oxidation and reduction curves with a relatively high anodic peak potential of 0.34 V and a cathodic peak potential of 0.31 V. Although DTP monomer 65 exhibited a stabilized HOMO energy level in comparison to unsubstituted DTP 50, this trend was reversed in the respective electropolymers and the oxidation of $P_{ec}65$ already started at -0.67 V.

Benzoyl-substituted DTP 97 showed an onset oxidation at 0.65 V due to a HOMO energy level of -5.74 eV (Figure 2.17). In the subsequent electropolymerization $P_{ec}97$ was obtained exhibiting a HOMO energy level of -4.87 eV (Table 2.13). Thus, compared to the un-
substituted analogues DTP 50 and p(DTP) \( P_{ec}^{50} \) the HOMO of both the monomer and the polymer bearing an electron-withdrawing benzoyl residue was stabilized. In literature, the cyclic voltammogram of octanoyl-substituted p(DTP) \( P_{ec}^{91} \) with two relatively defined redox waves was shown as an example for acyl-substituted p(DTP)s.\(^1\) The same features were initially also observed for benzoyl-substituted p(DTP) \( P_{ec}^{97} \), but after few scans during the “conditioning” phase the two distinct redox waves merged together resulting in a very broad current response with an anodic peak potential of 0.17 V and a cathodic peak potential of -0.04 V. After 30 cycles, the current only slightly decreased showing the stability of the polymer film with just 3% material loss. Furthermore, p(DTP) film \( P_{ec}^{97} \) was well adhered on the working electrode as the peak currents linearly increased with the scan rate.

Due to the electron-withdrawing Boc substituent in DTP 176 this monomer showed an onset oxidation at a relatively high potential of 0.61 V corresponding to a HOMO energy level of -5.71 eV (Figure 2.18). However, Boc-substituted polymer \( P_{ec}^{176} \) possessed a HOMO energy level...
energy level of -4.57 eV, which was very similar to the HOMO energy levels of the analogous \(p\)(DTP)s with hydrogen or alkyl residues at the nitrogen (Table 2.13). Most likely, a partial abstraction of the Boc groups by the released protons occurred during electropolymerization and might have accounted for similarities to unsubstituted \(p\)(DTP) \(P_{ec} \, 50\). Such a cleavage of Boc residues was observed in the analogous oxidative chemical polymerization of DTP \(176\) with iron trichloride and evidenced by analyses of the obtained polymer \(P_{ox} \, 176\) via MALDI mass spectrometry and \(^1\)H NMR spectroscopy (Chapter 2.6). In the cyclic voltammograms of \(P_{ec} \, 176\) a relatively sharp additional peak at 0.44 V appeared on top of the broad anodic current response and after conducting 30 scans no significant changes could be observed. Thus, the oxidation of the polymer appeared to be chemically reversible and only 5% of the electrophoric material was lost. Moreover, the film was well adhered to the electrode and hence the anodic peak currents at -0.12 V and the cathodic peak currents at -0.16 V increased linearly with the sweep rate.

**Figure 2.18:** Electropolymerization of DTP monomer \(176\) with a Boc residue at the nitrogen (a) and characterization of the obtained film \(P_{ec} \, 176\) using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents \(I_{pa}\) at -0.2 V and the cathodic peak currents \(I_{pc}\) from the applied scan rate (d).
Afterwards, the electrochemically prepared p(DTP)s were characterized via UV-Vis-NIR spectroelectrochemistry using a three-electrode setup, which has been described in detail by Salbeck.\textsuperscript{[59]} Initially, the DTP monomers were polymerized onto a platinum disc working electrode and thus it was ensured that the same materials were obtained as for the electrochemical characterization. This was a great advantage in comparison to the widely used method of preparing films for spectroelectrochemical investigations on transparent conducting electrodes such as ITO. With the help of an optical fibre the light from the lamp of the spectrometer was then focused onto the working electrode, where it was partly absorbed by the covering polymer film, reflected, absorbed again, and guided back to the detector in the spectrometer. A solution of the supporting electrolyte TBA-PF\textsubscript{6} in acetonitrile provided electrical conductivity in the cell. In order to obtain the neutral polymer film without any oxidized parts a potential of -500 mV vs. Ag/AgCl was always applied in the beginning of the measurements. Subsequently, the voltage was gradually increased and UV-Vis-NIR spectra were recorded at various constant potentials (Figure 2.19, Table 2.14).

Neutral unsubstituted p(DTP) P\textsubscript{ec50} showed a band at 524 nm with an onset absorption at 665 nm. Hence, the HOMO-LUMO gap of the polymer was determined to 1.86 eV. All three alkyl-substituted derivatives P\textsubscript{ec60}, P\textsubscript{ec65}, and P\textsubscript{ec78} possessed a similar energy gap of about 1.8 eV, but the maximum absorption wavelength varied quite strongly between 481 nm and 558 nm. In previous publications on different electropolymerized p(DTP)s bearing hydrogen or alkyl substituents similar values of the $\lambda_{\text{max}}$ were reported, while band gaps were by about 0.1 eV lower.\textsuperscript{[4, 60-61]} These differences could be due to deviating polymerization procedures leading to slightly different materials or minor alterations in the UV-Vis-NIR spectra because of the recording in reflectance instead of transmission mode. Additionally, some reported spectra in literature were measured under ambient conditions causing a partial oxidation of the p(DTP) films.\textsuperscript{[60]} However, in our studies we often observed a slight bathochromic shift of the onset absorption in the visible range upon oxidation with which the energy gap of the neutral polymer would be estimated too low. In this respect, the used spectroelectrochemical setup was advantageous, as the reduction of the partially oxidized polymer films prior to the recording of the spectra could be accomplished and thus it could be ensured that the polymers were present in their completely neutral state.
Figure 2.19: UV-Vis-NIR spectra obtained from spectroelectrochemical measurements of p(DTP)s $P_{ec}50$ (R=H, a), $P_{ec}60$ (R=hexyl, b), $P_{ec}64$ (R=2-ethylhexyl, c), $P_{ec}78$ (R=2-hexyldecyl, d), $P_{ec}65$ (R=phenyl, e), $P_{ec}97$ (R=benzoyl, f), and $P_{ec}176$ (R=Boc, g). Applied voltages are stated vs. Ag/AgCl. Artefacts in the spectra are marked with *. Black arrows show the changes starting at low potentials. Blue arrows show the further changes at high potentials.
Phenyl-substituted p(DTP) $P_{ec}65$ exhibited a band at 439 nm with a pronounced shoulder at 500 nm and an onset at 647 nm, which corresponded to an energy gap of 1.92 eV. The spectrum of Boc-substituted $P_{ec}176$ was further blue-shifted with a $\lambda_{\text{max}}$ of 388 nm and also contained a shoulder at 485 nm. On the other hand, benzoyl-substituted p(DTP) $P_{ec}97$ showed just one absorption band at 481 nm, but the onset absorption was decreased to 599 nm due to an increased energy gap of 2.07 eV.

**Table 2.14:** Optical properties of electrochemically prepared p(DTP)s bearing different residues R at the nitrogens. The values of $\lambda_{\text{max}}$, $\lambda_{\text{onset}}$, and the energy gap $E_g$ were obtained from UV-Vis-NIR spectra of neutral polymer films measured in a spectroelectrochemical setup. The LUMO energy levels were calculated from the HOMO energy levels and the energy gaps $E_g$. The maxima $\lambda_{\text{max, p}}$ of the polaronic and $\lambda_{\text{max, bp}}$ of the bipolaronic species were obtained from spectroelectrochemical measurements.

<table>
<thead>
<tr>
<th>p(DTP)</th>
<th>R</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>$\lambda_{\text{onset}}$ [nm]</th>
<th>$E_g$ [eV]</th>
<th>LUMO [eV]</th>
<th>$\lambda_{\text{max, p}}$ [nm]</th>
<th>$\lambda_{\text{max, bp}}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{ec}50$</td>
<td>H</td>
<td>524</td>
<td>665</td>
<td>1.86</td>
<td>-2.70</td>
<td>688, 1064 (br)</td>
<td>1079 (br)</td>
</tr>
<tr>
<td>$P_{ec}60$</td>
<td>Hex</td>
<td>481</td>
<td>680</td>
<td>1.82</td>
<td>-2.70</td>
<td>673, 1290 (br)</td>
<td>1239 (br)</td>
</tr>
<tr>
<td>$P_{ec}64$</td>
<td>2-EtHex</td>
<td>558</td>
<td>680</td>
<td>1.82</td>
<td>-2.72</td>
<td>738, 1300 (br)</td>
<td>1240 (br)</td>
</tr>
<tr>
<td>$P_{ec}78$</td>
<td>2-HexDec</td>
<td>550</td>
<td>685</td>
<td>1.81</td>
<td>-2.73</td>
<td>738, 1380 (br)</td>
<td>1170 (br)</td>
</tr>
<tr>
<td>$P_{ec}65$</td>
<td>Ph</td>
<td>439</td>
<td>647</td>
<td>1.92</td>
<td>-2.51</td>
<td>518, 1008 (br)</td>
<td>971 (br)</td>
</tr>
<tr>
<td>$P_{ec}97$</td>
<td>COPh</td>
<td>481</td>
<td>599</td>
<td>2.07</td>
<td>-2.80</td>
<td>607 (sh), 1241 (br)</td>
<td>981 (br)</td>
</tr>
<tr>
<td>$P_{ec}176$</td>
<td>Boc</td>
<td>388</td>
<td>633</td>
<td>1.96</td>
<td>-2.61</td>
<td>485, 945</td>
<td>1281 (br)</td>
</tr>
</tbody>
</table>

By increasing the applied potential, neutral p(DTP) films were gradually oxidized and the formation of polaronic and finally bipolaronic states could be observed. Hence, the absorption band in the visible range decreased and initially two new bands at higher wavelengths appeared. Upon further oxidation, these two bands in the spectrum merged together to one broad band extending over a wide range in the NIR region. Similarly to PEDOT (Chapter 1.1), an electrochromic behaviour with a dark blue colour in the neutral form and a transparent appearance in the doped state was therefore observed.

In Figure 2.20 the energy diagram of the electrochemically prepared p(DTP)s is shown. Unsubstituted and alkyl-substituted polymers $P_{ec}50$, $P_{ec}60$, $P_{ec}64$, and $P_{ec}78$ possessed similar HOMO and LUMO energy levels, because these residues only had a small influence on the conjugated backbone. The HOMO energy level of phenyl-substituted p(DTP) $P_{ec}65$ was lifted by 0.13 eV compared to unsubstituted analogue $P_{ec}50$, while the LUMO energy level was
increased by 0.19 eV. $N$-substitution with the Boc residue in $P_{ec176}$ did not significantly alter the HOMO energy level, but the LUMO was also destabilized and thus the energy gap was increased further. However, the largest $E_g$ in the series was observed for benzoyl-substituted derivative $P_{ec97}$. Here, the HOMO was stabilized to a relatively large extent and exhibited an energy level of $-4.87$ eV, whereas the LUMO was only slightly decreased to $-2.80$ eV. Thus, the trend observed in the DTP monomers of decreased energy gaps with phenyl, benzoyl, or Boc moieties at the nitrogen instead of hydrogen was reversed for the corresponding electro-polymers. This showed that different substituents not only possess a direct electronic influence on p(DTP)s, but also impact the accessible chain lengths during polymerization which more profoundly affects the optoelectronic properties of the polymers.

Figure 2.20: Energy diagram showing the HOMO energy levels (blue), LUMO energy levels (red) and the energy gaps $E_g$ of electrochemically prepared p(DTP)s bearing different residues R at the nitrogens. As a representative example of the alkyl-substituted p(DTP)s only the energy levels of hexyl-substituted derivative $P_{ec60}$ are shown.
2.6 Chemical oxidative polymerization of DTPs

Electropolymerizations of DTPs afforded insoluble p(DTP) films on the working electrode which could directly be investigated electrochemically and spectroelectrochemically regarding their optoelectronic properties. However, due to their insolubility further investigations in solution concerning structural features of the polymers were not possible. Therefore, alkyl-substituted DTP monomers 60, 64, and 78 and Boc-substituted DTP 176 were chemically polymerized using iron trichloride as chemical oxidant (Scheme 2.24). Although this method differs from electropolymerization, the reaction mechanism is quite similar and thus from the obtained insights limited conclusions could also be drawn for the analogous electropolymerized p(DTP)s in Chapter 2.5.

\[
\begin{align*}
\text{Scheme 2.24: Chemical oxidative polymerization of DTPs 60, 64, 78, and 176.}
\end{align*}
\]

Applying too harsh reaction conditions in the chemical oxidative polymerization only yielded insoluble solids due to a relatively high polymerization degree. Hence, the amount of oxidant had to be optimized to afford large, but still soluble p(DTP)s (Table 2.15). Initially, the raw products were obtained in the oxidized state and were therefore first of all dedoped by treatment with aqueous hydrazine. This neutralization strongly increased the solubility of the polymers in organic solvents and small molecular weight fractions could be removed by washing with n-hexane. Finally, the larger soluble p(DTP)s were extracted with THF in a Soxhlett apparatus. Alkyl moieties led to the largest increase of the solubility, as they inhibited an efficient \( \pi-\pi \) stacking of the polymer and still soluble materials of \( P_{\text{ox}}60, P_{\text{ox}}64, \) and \( P_{\text{ox}}78 \) were isolated using four equivalents of FeCl\(_3\). On the other hand, with monomeric DTP 176 bearing a Boc group the amount of oxidant had to be decreased to just one equivalent. Nevertheless, in accordance with published results in literature for similar oxidative polymerizations\(^{[60, 62]} \) only moderate yields of soluble fractions were achieved for all derivatives. This was an inherent problem of p(DTP)s, because with just one solubilizing residue per repeat unit, they quickly became insoluble with increasing length of the polymer chain.
MALDI mass spectra of crude p(DTP)s were recorded to analyse the polymer chain length, but only trimers and tetramers could be detected. In contrast to that, analyses by GPC indicated relatively large average chain lengths of 24 to 36 repeat units in $\text{P}_{\text{ox}60}$, $\text{P}_{\text{ox}64}$, and $\text{P}_{\text{ox}78}$ bearing alkyl chains at the nitrogens (Table 2.15). As expected, with the bulkiest branched residue in the series the p(DTP) with the largest number of repeat units $n$ was obtained. Thus, the 2-hexyldecyl substituent in DTP 78 increased the solubility of the corresponding intermediates to the largest extent and enabled the highest degree of polymerization. Peculiarly, despite the branched alkyl groups in 2-ethylhexyl-substituted polymer $\text{P}_{\text{ox}64}$, a lower average molecular weight was obtained than in $\text{P}_{\text{ox}60}$ bearing linear hexyl residues. However, the latter polymer $\text{P}_{\text{ox}60}$ showed a larger polydispersity (1.4) than $\text{P}_{\text{ox}64}$ (1.1) indicating that larger as well as smaller polymer chains with hexyl substituents at the nitrogens were soluble in THF. Without solubilizing moieties attached at the nitrogens already the intermediate species of Boc-substituted p(DTP) $\text{P}_{\text{ox}176}$ precipitated from the reaction mixture preventing a further chain growth. Notably, because in the analyses via GPC polystyrene standards were used which adopt a coiled conformation in solution, the estimated molecular weights of the rather rod-like p(DTP)s could be too high. Such a tendency has been observed for polythiophenes,\textsuperscript{63-64} but due to the purification procedure including the prior removal of bright orange smaller p(DTP)s, the determined moderate chain lengths did not seem to be largely overestimated. In one publication about oxidatively prepared alkyl-substituted p(DTP)s, average chain lengths of 4.9-10.0 repeat units and similar low polydispersities were reported.\textsuperscript{60} As just one equivalent of FeCl$_3$ was applied by these authors and in the corresponding chromatograms soluble p(DTP)s with up to 30 repeat units
Dithieno[3,2-b:2′,3′-d]pyrroles (DTPs)

were detected, these results also indicated that the values shown in Table 2.12 were quite good estimations of the chain lengths.

In Figure 2.21 the $^1$H NMR spectrum of 2-hexyldecyl substituted polymer $P_{\alpha}78$ is shown as an example for alkyl-substituted p(DTP)s. Relatively broad signals were observed in the aliphatic range, whereas two sharper singlets of the dithienopyrrole protons at 8.02 ppm and 7.23 ppm appeared.

Figure 2.21: $^1$H NMR spectrum of the oxidatively prepared $P_{\alpha}78$ bearing 2-hexyldecyl residues at the nitrogens in THF-d$_8$.

All three polymers $P_{\alpha}60$, $P_{\alpha}64$, and $P_{\alpha}78$ with alkyl moieties exhibited such distinct signals in the aromatic region of the $^1$H NMR spectrum corresponding to thienyl $\alpha$- and $\beta$-protons. The downfield-shifted signal originated either from coupling defects in the polymer or from the end-group $\alpha$-protons, respectively. With the integral ratios of the two aromatic signals (0.29-0.48 to 2), in the latter case an average polymer chain length between 6.9 and 4.2 repeat units was implied. As the GPC measurements indicated much larger polymers (vide supra), the signal at about 8 ppm did most likely not originate from the end-group $\alpha$-protons. Instead $\alpha$-$\beta$ and $\beta$-$\beta$ coupling defects apparently occurred during the polymerization accounting for between 22-32% in alkyl-substituted p(DTP)s. However, it has to be stated that due to the very broad signals in the spectra of the polymers the deviations of the corresponding integrals were relatively high and the obtained values could only be rough estimations of structural features. While usually in thiophenes a relative reactivity of 95:5 is observed for the $\alpha$- and $\beta$-position, it was discovered that due to the electron-donating
ability of the nitrogen in DTP this difference is significantly decreased.\textsuperscript{60, 65-66} Hence, the more similar reactivities were responsible for more couplings in the β-position of DTP during polymerization and the relatively large extent of coupling defects in the obtained polymers.

Another important aspect was that, as indicated by the \textsuperscript{1}H NMR and MALDI mass spectra of polymer $P_{\text{ox}176}$, the Boc residues had partially been split off. In order to exclude the thermal cleavage of the substituent, in another polymerization attempt the dedoping of the raw polymer was carried out at ambient temperatures, yet again several Boc moieties in $P_{\text{ox}176}$ were abstracted. Hence, the cleavage occurred most likely due to the release of protons during the polymerization under liberation of isobutene and CO$_2$. This behaviour was also assumed for the electropolymerization of DTP 176, where the partial loss of Boc groups in $P_{\text{ec}176}$ was already suspected because of the unexpected optoelectronic properties (Chapter 2.5).

Furthermore, the trimer of ethyl-substituted DTP was used as model system for the corresponding alkyl-substituted polymer in DFT calculations. Geometry optimizations were carried out using the M06-2X correlation/exchange functional\textsuperscript{67} and the 6-311G basis set. Thus, the transoid configuration was shown to be slightly more stable than the cisoid geometry (Figure 2.22). Moreover, the repeat units are not coplanar, but slightly twisted by 18° relative to each other.

![Figure 2.22: Geometry optimized structure of the DTP trimer with ethyl residues at the nitrogens. Calculations were carried out with the Gaussian 09 program.\textsuperscript{49} Geometry optimizations were performed via DFT methods using the M06-2X correlation/exchange functional\textsuperscript{67} and the 6-311G basis set.](image)

To determine the optoelectronic properties of the soluble oxidatively prepared p(DTP)s $P_{\text{ox}60}$, $P_{\text{ox}64}$, $P_{\text{ox}78}$, and $P_{\text{ox}176}$ cyclic voltammograms and UV-Vis spectra were subsequently recorded (Figure 2.23) and the results are summarized in Table 2.16. Besides one or two absorption bands in the UV region, one broad band in the visible range was observed for all p(DTP)s corresponding to electronic π-π* transitions. Increasing the bulkiness of the attached alkyl residues from hexyl over 2-ethylhexyl to 2-hexyldecyl chains, the solubility of the
corresponding p(DTP)s also increased. Consequently, larger amounts of polymers with larger conjugation lengths could be dissolved and therefore the $\lambda_{\text{max}}$ slightly shifted to lower energies. Despite the larger average molecular weight of hexyl-substituted $\text{P}_{\text{ox}60}$ compared to 2-ethylhexyl-substituted $\text{P}_{\text{ox}64}$ (vide supra), the major fraction of $\text{P}_{\text{ox}60}$ therefore consisted of polymers with a shorter conjugation length. Most likely, this can be attributed to a larger extent of coupling defects in $\text{P}_{\text{ox}60}$ leading to a more pronounced cross-conjugation. From the onset oxidation potential in the cyclic voltammograms the HOMO energy levels were furthermore determined. The polymers $\text{P}_{\text{ox}60}$, $\text{P}_{\text{ox}64}$, and $\text{P}_{\text{ox}78}$ with alkyl residues at the nitrogens exhibited similar HOMO energy levels of about $4.8 \text{ eV}$, while the HOMO of Boc-substituted $\text{P}_{\text{ox}176}$ was slightly destabilized to $4.75 \text{ eV}$. Overall, all the three alkyl-substituted p(DTP)s $\text{P}_{\text{ox}60}$, $\text{P}_{\text{ox}64}$, and $\text{P}_{\text{ox}78}$ possessed very similar HOMO and LUMO energy levels and observed deviations are rather in the range of error in this respect.

![Figure 2.23](image)

**Figure 2.23:** Normalized UV-Vis absorption spectra in THF solutions of the oxidatively prepared p(DTP)s.

**Table 2.16:** Optoelectronic properties of soluble oxidatively prepared p(DTP)s bearing different residues R at the nitrogens. The onset oxidation potentials $E_{\text{onset}}$ and the HOMO energy levels were determined via cyclic voltammetry with TBA-PF$_6$ (0.1 M) as the supporting electrolyte in THF. The values of $\lambda_{\text{max}}$, $\lambda_{\text{onset}}$, and the energy gap $E_g$ were obtained from UV-Vis spectra measured in THF solution. The LUMO energy levels were calculated from the HOMO energy levels and the energy gaps $E_g$.

<table>
<thead>
<tr>
<th>p(DTP)</th>
<th>R</th>
<th>$E_{\text{onset}}$</th>
<th>HOMO</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\lambda_{\text{onset}}$</th>
<th>$E_g$</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{P}_{\text{ox}60}$</td>
<td>Hex</td>
<td>-0.24</td>
<td>-4.86</td>
<td>504</td>
<td>605</td>
<td>2.05</td>
<td>-2.81</td>
</tr>
<tr>
<td>$\text{P}_{\text{ox}64}$</td>
<td>2-EthHex</td>
<td>-0.28</td>
<td>-4.82</td>
<td>525</td>
<td>609</td>
<td>2.03</td>
<td>-2.79</td>
</tr>
<tr>
<td>$\text{P}_{\text{ox}78}$</td>
<td>2-HexDec</td>
<td>-0.26</td>
<td>-4.84</td>
<td>541</td>
<td>619</td>
<td>2.00</td>
<td>-2.84</td>
</tr>
<tr>
<td>$\text{P}_{\text{ox}176}$</td>
<td>Boc</td>
<td>-0.35</td>
<td>-4.75</td>
<td>461</td>
<td>532</td>
<td>2.33</td>
<td>-2.42</td>
</tr>
</tbody>
</table>

Potentials are referenced vs. Fc/Fc$^+$; a Redox potential of Fc/Fc$^+$ is $-5.1 \text{ eV}$ on the Fermi scale$^{[52]}$.
In comparison to the insoluble electropolymers, the smaller chain lengths accompanied by decreased conjugation lengths of the soluble p(DTP)s led to a decrease of the HOMO energy levels and an increase of the optical energy gaps by 0.2 to 0.4 eV, respectively (Figure 2.24). The solubilizing effect of the substituents was the most important structural aspect and with bulky 2-hexyldecyl chains the longest polymer \( P_{ox}78 \) was obtained. Similar to analogous electropolymers, the length of the conjugated backbone was the dominant feature determining the optoelectronic properties of soluble oxidatively prepared p(DTP)s, whereas direct electronic influences of the substituents were negligible.

![Figure 2.24](image_url)

**Figure 2.24**: Energy diagram showing the HOMO energy levels (blue), LUMO energy levels (red) and the energy gaps \( E_g \) of oxidatively prepared soluble p(DTP)s bearing different residues R at the nitrogens.
2.7 Ferrocenoyl-substituted p(DTP) for application in organic batteries

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Because of their high HOMO energy level and thus low oxidation potential, p(DTP)s represent suitable cathode active materials in secondary organic batteries. In such a device the p(DTP) in the cathode is oxidized during charging. The charged battery then contains the p(DTP) in its doped state and upon discharging the polymer is dedoped, i.e. reduced to its neutral form. However, due to just moderate doping levels of conducting polymers in general (Chapter 1.1), attached redox-active moieties are required to increase the low capacity of organic batteries. Similarly to polypyrrole the nitrogens of p(DTP)s are convenient sites for such functionalizations. Furthermore, with regard to redox-active substituents ferrocene was the first choice, because this prominent metallocene exhibits an excellent stability and very fast electrochemical response.\(^{[68-69]}\) Several ferrocene-containing polymers have already been applied as cathode active material in secondary organic batteries, but have suffered from capacity fading as a consequence of their dissolution in the electrolyte.\(^{[70-76]}\) By attaching ferrocene at p(DTP), we envisaged that the solubility of the material would be sufficiently low and thus the stability of the battery could be improved.

Therefore, unsubstituted DTP 50 was applied as precursor in a Steglich reaction to attach a ferrocenoyl moiety at the nitrogen (Scheme 2.25). Ferrocencarboxylic acid 203 was activated with \(N,N'\)-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) to facilitate the nucleophilic attack of DTP 50. Subsequently, ferrocenoyl-substituted DTP 204 was purified via column chromatography and was isolated in an excellent yield of 97%. The success of this strategy was also intriguing from a general synthetic point of view, because other DTPs bearing carbonyl groups could only be prepared in low to moderate yields by copper-catalysed C-N couplings of an amide with dibromide 72 (Chapter 2.2.1).\(^{[1]}\) Hence, with unsubstituted DTP 50 readily available (Chapter 2.2.2) \(N\)-functionalization of DTP via Steglich reaction represents a further adequate synthetic option.
Functionalized DTP 204 exhibits an absorption band at 293 nm accompanied by shoulders at 284 nm and 324 nm in the UV-Vis spectrum (Figure 2.25). Because of the ferrocenoyl residue at the nitrogen an additional band in the visible region appears with a much lower extinction resulting in the orange colour of the compound. Compared to isolated ferrocene with a HOMO energy level of -5.1 eV,\(^{[52]}\) the HOMO of DTP 204 is slightly stabilized to -5.25 eV due to the electron-withdrawing carbonyl group. Furthermore, the band at 453 nm in the UV-Vis spectrum is slightly red-shifted\(^{[77]}\) and corresponds to an \(E_g\) of 2.28 eV (Table 2.17).

![Figure 2.25: UV-Vis absorption spectrum of the DTP 204 with a ferrocenoyl residue attached at the nitrogen measured in THF solution.](image)

### Table 2.17: Optoelectronic properties of ferrocenoyl-substituted DTP 204. The values of \(E_{pa}\), \(E_{onset}\) and the HOMO energy level were obtained via cyclic voltammetry. The values of \(\lambda_{max}\), \(\varepsilon\), \(\lambda_{onset}\) and the energy gap \(E_g\) were obtained via UV-Vis spectroscopy. The LUMO energy level was obtained from the HOMO energy levels and \(E_g\).

<table>
<thead>
<tr>
<th>DTP</th>
<th>R</th>
<th>(E_{pa}) (^{[\text{a}]})</th>
<th>(E_{onset}) (^{[\text{a}]})</th>
<th>HOMO (^{[\text{b}]})</th>
<th>(\lambda_{max})</th>
<th>(\varepsilon)</th>
<th>(\lambda_{onset})</th>
<th>(E_g)</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>204</td>
<td>COFc</td>
<td>0.26(^{[\text{c}]})</td>
<td>0.15(^{[\text{c}]})</td>
<td>-5.25</td>
<td>293</td>
<td>25400</td>
<td>544</td>
<td>2.28</td>
<td>-2.97</td>
</tr>
</tbody>
</table>

\(\text{Potentials are referenced vs. } Fc/Fc^+; \ a \ E_{pa}: \text{ anodic peak potential (scan rate 100 mV/s); } b \text{ Redox potential of } Fc/Fc^+ \text{ is } -5.1 \text{ eV on the Fermi scale;}^{[52]} \ c \text{ Oxidation of the Fc moiety.}\)
Subsequently, DTP 204 with the redox-active ferrocenoyl moiety at the nitrogen was electropolymerized in dichloromethane (Scheme 2.26, Figure 2.26).

**Scheme 2.26: Electropolymerization of ferrocenoyl-substituted DTP 204.**

**Figure 2.26:** Electropolymerization of DTP monomer 204 with a ferrocenoyl residue at the nitrogen (a) and characterization of the obtained film $P_{\text{Fe}}204$ using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents $I_{\text{pa}}$ and the cathodic peak currents $I_{\text{pc}}$ from the applied scan rate (d).

First of all, the ferrocene residue was oxidized, because the HOMO of DTP 204 was apparently dominated by the substituent and not by the conjugated DTP core. At an onset potential of 0.73 V then the radical cation of the dithienopyrrole backbone was formed, initializing the polymerization of the monomer. The onset oxidation thus occurred in a similar range as for benzoyl- or Boc-substituted DTPs 97 and 176, which also possess a carbonyl
group at the nitrogen of the DTP moiety. In contrast to the forward sweeps with two distinct oxidation signals, in the backsweeps only one large reduction signal appeared. Moreover, with increasing number of cycles the currents steadily increased, as the polymer film \( P_{Fe204} \) grew on the electrode. During the electrochemical characterization of polymer \( P_{Fe204} \) the currents corresponding to the oxidation of the ferrocene residue were much larger than the anodic currents originating from the oxidation of the conjugated backbone. Therefore, in p(DTP) \( P_{Fe204} \) most attached ferrocenes were redox-active, whereas not every DTP repeat unit was oxidized. This is a common feature in conducting polymers (Chapter 1.1) and was also observed by Zotti \textit{et al.} for unsubstituted p(DTP), where on average about 0.6 anions per repeat unit were present in the fully oxidized state.\(^4\) The onset oxidation of ferrocenoyl-substituted p(DTP) \( P_{Fe204} \) at -0.21 V corresponded to a HOMO energy level of -4.89 eV (Table 2.18), which was similar to the HOMO energy level of benzoyl-substituted p(DTP) \( P_{Fe204} \) with -4.87 eV. Hence, in contrast to monomeric ferrocenoyl-substituted DTP 204, the HOMO of polymer \( P_{Fe204} \) was dominated by the conjugated poly(dithienopyrrole) backbone. However, the ferrocene residue showed distinct anodic and cathodic signals at 0.30 V and 0.08 V, which were shifted to higher potentials compared to isolated ferrocene. Similarly to monomer 204, this can be attributed to the electron-withdrawing effect of the carbonyl groups. Another important aspect was that the peak currents increased linearly with the sweep rate and after conducting 30 scans only 10% of the material was lost. A stable and well adhered polymer film of \( P_{Fe204} \) was therefore obtained which was subsequently also characterized spectroscopically (Figure 2.27).

**Table 2.18:** Optoelectronic properties of the electrochemically prepared p(DTP) \( P_{Fe204} \) bearing ferrocenoyl residues at the nitrogens. The peak potentials \( E_{pa} \) and \( E_{pc} \), the onset oxidation potential \( E_{onset} \), the HOMO energy level, and the film loss after 30 cycles were determined by cyclic voltammetry in a monomer-free electrolyte solution. The values of \( \lambda_{max} \), \( \lambda_{onset} \), and the energy gap \( E_g \) were obtained from the UV-Vis-NIR spectrum of the neutral polymer film measured in a spectroelectrochemical setup. The LUMO energy level was calculated from the HOMO energy level and the energy gap \( E_g \). The maxima \( \lambda_{max,p} \) of the polaron and \( \lambda_{max,bp} \) of the bipolaron species were obtained from spectroelectrochemical measurements.

<table>
<thead>
<tr>
<th>( E_{pa} ) (^a)</th>
<th>( E_{pc} ) (^b)</th>
<th>( E_{onset} )</th>
<th>HOMO (^c)</th>
<th>Film loss</th>
<th>( \lambda_{max} )</th>
<th>( \lambda_{onset} )</th>
<th>( E_g )</th>
<th>( E_{LUMO} )</th>
<th>( \lambda_{max,p} )</th>
<th>( \lambda_{max,bp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[V]</td>
<td>[V]</td>
<td>[V]</td>
<td>[eV]</td>
<td>[%]</td>
<td>[nm]</td>
<td>[nm]</td>
<td>[eV]</td>
<td>[eV]</td>
<td>[nm]</td>
<td>[nm]</td>
</tr>
<tr>
<td>0.30</td>
<td>0.08</td>
<td>-0.21</td>
<td>-4.89</td>
<td>10</td>
<td>570</td>
<td>761</td>
<td>1.63</td>
<td>-3.26</td>
<td>710, 1511</td>
<td>1115 (br)</td>
</tr>
</tbody>
</table>

Potentials are referenced vs. \( \text{Fc/Fc}^+ \); \( a \): \( E_{pa} \): anodic peak potential (scan rate 100 mV/s); \( b \): \( E_{pc} \): cathodic peak potential (scan rate 100 mV/s); \( c \): Redox potential of \( \text{Fc/Fc}^+ \) is -5.1 eV on the Fermi scale\(^{[52]} \).
In the UV-Vis-NIR spectrum of the neutral polymer film $P_{ec}204$ no distinct feature of the attached ferrocene residue could be observed in the visible region around 453 nm, because the extinction of the band originating from the conjugated p(DTP) backbone was orders of magnitude higher. It exhibited a maximum at 570 nm and an onset at 761 nm, which corresponded to a HOMO-LUMO energy gap of 1.63 eV (Table 2.18). Increasing the applied potential step by step led to the gradual oxidation of polymer $P_{ec}204$ and thus the band at 570 nm decreased continuously. Instead a new band at 710 nm and a broad band in the NIR range appeared due to the formation of polaronic states. Similarly to other p(DTP)s in Chapter 2.5 at higher potentials bipolaronic states were responsible for just one very broad band, which extended over the whole considered NIR range.

![Figure 2.27](image)

**Figure 2.27:** UV-Vis-NIR spectra obtained from spectroelectrochemical measurements of p(DTP) $P_{ec}204$ bearing ferrocenoyl residues at the nitrogens. Applied voltages are stated vs. Ag/AgCl. Artefacts are marked with * in the spectra. Black arrows show the changes starting at low potentials. The blue arrow shows the further changes at high potentials.

In order to have polymer $P_{ox}204$ available in large amounts for battery tests chemical oxidative polymerization of DTP monomer 204 was carried out (Scheme 2.27). According to previous experience of our cooperation partner Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW) Ulm, chloride ions in polymers often account for difficulties in organic batteries. Therefore, copper tetrafluoroborate instead of FeCl$_3$ was used as the oxidant. After a reaction time of two days, an excessive polymerization had occurred and the insoluble p(DTP) $P_{ox}204$ was obtained in its oxidized form. Undesirable soluble fractions as well as residual inorganic components were subsequently removed by thorough washings with different solvents and finally $P_{ox}204$ was afforded as a dark blue powder in 67% yield.
Scheme 2.27: Chemical oxidative polymerization of ferrocenoyl-substituted DTP 204.

Because of its insolubility the structure of P_{ox}204 could only be verified by FT-IR spectroscopy (Figure 2.28). In comparison to the spectrum of DTP monomer 204 the bands of the polymer were broader and less defined, yet characteristic stretching bands of the C-H bonds at 3111 cm\(^{-1}\) and the carbonyl feature at 1637 cm\(^{-1}\) were still visible. Moreover, a band of the ferrocene moiety at 488 cm\(^{-1}\) could also be observed. The thermal stability of p(DTP) P_{ox}204 was investigated both via differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA, Figure 2.28). In the DSC measurements the polymer was heated to 300 °C and no significant endothermic signal appeared. Similarly, less than 5% mass loss was detected by TGA up to 270 °C. At higher temperatures P_{ox}204 slowly degraded, leaving 67% of the originally subjected material at 800 °C. This approximately accounted for the cleavage of iron and one cyclopentadiene ring in each repeat unit.

Figure 2.28: Infrared spectra (a) of DTP monomer 204 and p(DTP) P_{ox}204 as well as TGA measurements of P_{ox}204 (b).
Subsequently, a mixture of ferrocenoyl-substituted p(DTP) \( \text{P}_{\text{ox}}204 \) (56.6%), carbon black (33.0%), and poly(tetrafluoroethylene) (10.4%) was processed into a composite electrode at ZSW Ulm. In a typical lithium ion battery environment consisting of a lithium counter electrode as anode and a solution of lithium hexafluorophosphate in a mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) galvanostatic cycling tests were carried out and cyclic voltammograms were recorded (Figure 2.29).

**Figure 2.29:** Cyclic voltammograms of a composite electrode containing ferrocenoyl-substituted p(DTP) \( \text{P}_{\text{ox}}204 \) in a solution of LiPF\(_6\) (1 M) in EC:DMC (1:1 by weight) at a scan rate of 0.1 mV/s and with a stepwise increase of the upper vertex potential. Measurements were performed at ZSW Ulm.

Cyclic voltammograms were conducted at a relatively low scan rate of 0.1 mV/s to ensure the complete reaction of the composite electrode and the upper vertex potential was increased step by step. A reversible redox wave corresponding to the ferrocene/ferricenium couple at 3.62 V (vs. Li/Li\(^+\)) appeared. Because of the electron-withdrawing amide linker this redox potential was increased in comparison to the isolated metallocene in the same electrolyte (3.24 V vs. Li/Li\(^+\)).\(^{[78]}\) Furthermore, the conjugated p(DTP) backbone was also reversibly oxidized accounting for low anodic and cathodic currents at potentials higher than 2.8 V. However, when the upper vertex potential reached 3.8 V, additional signals appeared below 3.0 V in the anodic and cathodic scans. Most likely, this indicated irreversible follow-up reactions due to a partial overoxidation of polymer \( \text{P}_{\text{ox}}204 \). Overoxidation has already been observed for other conducting polymers and can results in a disruption of the conjugated backbone.\(^{[79-81]}\)

Galvanostatic cycling tests shown in Figure 2.30 were performed using cut-off potentials of 3.9 V vs. Li/Li\(^+\) upon oxidizing the cathode (charging) and 2.5 V vs. Li/Li\(^+\) upon reducing the oxidized cathode (discharging). Moreover, a current rate of 6.88 mA/g was applied which
corresponded to 0.1 C, when a theoretical maximum capacity of 68.8 mAh/g was assumed. With the latter value only a one-electron redox process of the ferrocene substituents was taken into account, whereas small contributions from the conjugated polymer backbone were neglected.

Figure 2.30: Galvanostatic cycling performance of a composite electrode containing ferrocenoyl-substituted p(DTP) $P_{ox}204$ in a solution of LiPF$_6$ (1 M) in EC:DMC (1:1 by weight) at a current rate of 0.1 C. Measurements were performed at ZSW Ulm.

During galvanostatic cycling differences between charge and discharge capacities accounted for considerable irreversible capacities (Figure 2.30a). For example, in the first scan a charge capacity of 133 mAh/g and a discharge capacity of just 53 mAh/g were measured. Apart from the plateau in the potential profile between 3.50 V and 3.65 V related to the oxidation of ferrocenes, a second plateau at about 3.70 V to 3.90 V was observed. Because no counter-plateau was detected during discharge, it corresponded to an irreversible process. In contrast to many inorganic electrodes these irreversible capacities were not restricted to the first cycle. Nevertheless, with increasing number of scans they continuously decreased. One possible cause of irreversible capacities could be chemical follow-up reactions, which were also indicated in the cyclic voltammograms in Figure 2.29 (vide supra). Decreasing the cut-off potential below 3.9 V would avoid such processes, but would also lower the reversible capacity due to incomplete oxidation of the ferrocene moieties. Another possible explanation for irreversible capacities is the occurrence self-discharge phenomena. Herein, parts of the active material dissolved and acted as redox shuttles between the electrodes. This involved their oxidation at the cathode, diffusion to the anode, reduction at the anode, and diffusion back to the cathode. The results were increased charging and decreased discharging periods causing the observed irreversible capacities. In
general, the rate of self-discharge depends on the diffusion coefficient in the electrolyte solution and the concentration of dissolved molecules.\textsuperscript{[82]} As the irreversible capacity quickly decreased upon conducting several scans and a very high capacity retention was achieved (\textit{vide infra}), only minor parts of the active material were dissolved during galvanostatic cycling and overall the prepared composite electrode was quite stable.

Furthermore, a maximum discharge capacity of 59.8 mAh/g was reached and accounted for 87\% of the theoretical capacity of the material (Figure 2.30b). This indicated that the redox-active ferrocenes were electronically well connected to the current collector in the electrode. Furthermore, a very good cycling stability was observed and the capacity retention of 97\% between cycle 10 and 50 ranked among the best performances reported for organic electrode materials, thus far.\textsuperscript{[83]} Hence, with the strategy to attach ferrocene groups at the conjugated p(DTP) a high stability of the cathode and a good electronic connection of the redox-active moieties was achieved. Nevertheless, the polymer backbone also increased the molecular weight of the material without significantly contributing to the capacity of the electrode. Therefore, the capacity of the battery was far too low for practical application and the conducted investigations can only be regarded as a proof of principle study involving the ferrocenoyl-functionalized p(DTP) \textbf{P}_{ec204} as cathode active material.
Chapter 2

2.8 Summary

N-functionalized DTPs 60, 64, 78, 65, 97, 176, 177, 186, and 189 with alkyl, phenyl, benzoyl, tert-butoxycarbonyl, tosyl, benzyl, or p-nitrobenzoyl residues (Figure 2.31) were prepared via amination of 3,3’-dibromo-2,2'-bithiophene in moderate to excellent yields. Moreover, several different methods for the synthesis of unsubstituted parent DTP 50 were developed and optimized involving Ullmann-type C-N couplings or Buchwald-Hartwig aminations to build up the central pyrrole ring. Using ammonia surrogates afforded the fused target heteroacene in overall yields of 33-63% in two to three steps starting from commercially available bromothiophene precursors and the developed methods are applicable on multi-gram scale. Whereas the amination with triphenylsilyl amine under palladium catalysis afforded the highest yield of unfunctionalized DTP 50, the coupling with the cheaper benzamide required a less expensive copper catalyst and could also be conducted without the use of inert gas. Intriguingly, the efficient preparation of unsubstituted DTP 50 as a precursor subsequently enabled the synthesis of other N-functionalized DTPs 68, 193, 196, 179, 198-200, 202, and 204 (Figure 2.31) via Buchwald-Hartwig amination of several aryl bromides or via Steglich reaction of ferrocene carboxylic acid.

![Figure 2.31: Structures of synthesized DTPs.](image)
The optoelectronic properties of DTPs shown in Figure 2.31 were determined by cyclic voltammetry and UV-Vis spectroscopy and were rationalized with the help of DFT calculations. Thus, the electron-withdrawing effect of conjugated substituents at the nitrogen is more pronounced in the LUMO because of the direct participation to this frontier molecular orbital, while in the HOMO a node at the nitrogen allows only for an indirect influence. Electropolymerizations of DTP monomers 50, 60, 64, 78, 65, 97, and 176 afforded very stable p(DTP) films on the working electrode which upon electrochemical doping switched their colour from dark blue to colourless. Chemical oxidative polymerizations of DTPs 60, 64, 78, and 176 yielded soluble p(DTP)s with estimated average chain lengths between 6 and 36 repeat units. On the other hand, in collaboration with the ZSW Ulm the insoluble p(DTP) \( P_{ox204} \) bearing redox-active ferrocenoyl moieties at the nitrogens was applied as cathode active material in an organic battery and exhibited a capacity of 59.8 mAh/g with an excellent capacity retention of 97%.
2.9 Experimental section

2.9.1 General methods

**Instruments and measurements**

A microwave reactor (CEM Discover) was used. Thin layer chromatography was carried out on aluminium plates, precoated with silica gel, Merck Si60 F254. Preparative column chromatography was performed on glass columns packed with silica gel (particle size 40–63 µm) from Macherey-Nagel or aluminium oxide, Merck 90 active basic, particle size 63-200 µm. HPLC was performed on a Shimadzu CBM-20A equipped with a SPD-20A UV-Vis detector and a LC-8A solvent delivery system using a Macherey-Nagel column (Nucleosil 100-5 NO2). Melting points were determined using a Büchi Melting Point B-545 or a Mettler Toledo DSC 823e under argon flow (heating rate 10 °C/min). Thermogravimetric analyses were carried out with a TGA/SDTA 851e from Mettler Toledo. UV-Vis absorption spectra were recorded in THF solutions on a Perkin Elmer Lambda 19 spectrometer. FT-IR spectra were measured with a Perkim Elmer Spectrum 2000. NMR spectra were recorded on an Avance 400 (1H NMR: 400 MHz, 13C NMR: 101 MHz) or a Bruker AMX 500 spectrometer (1H NMR: 500 MHz, 13C NMR: 125 MHz). Chemical shifts (δ) are reported in ppm using residual solvent protons (1H NMR: δH = 7.26 for CDCl3; δH = 5.32 for CD2Cl2; δH = 3.58 for THF-d8; δH = 6.00 for C2D2Cl4; 13C NMR: δC = 77.16 for CDCl3; δC = 53.84 for CD2Cl2; δC = 73.78 for C2D2Cl4) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). Coupling constants J relate to proton-proton couplings. Protons at the α- or β-positions of DTPs were assigned as Th-Hα or Th-Hβ, respectively. Elemental analyses were performed on an Elementar Vario EL. GC/EI-MS (70 eV) measurements were performed on a Shimadzu GCMS-QP2010 SE. Chemical ionisation (CI) mass spectra were measured on a Finnigan MAT SSQ-7000. MALDI-TOF mass spectra were recorded on a Bruker Daltonik Reflex III and high resolution MALDI mass spectra were performed on a Bruker SolariX using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix.

Cyclic voltammetry experiments were performed using a computer-controlled Autolab PGSTAT 30 potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. All
potentials were internally referenced to the ferrocene/ferricenium couple. Deoxygenated acetonitrile dried over molecular sieves or dichloromethane, respectively THF, dried via a MB SPS-800 solvent purifying system (MBraun) was used as the solvent. Solutions of tetrabutylammonium hexafluorophosphate (Sigma Aldrich) as the supporting electrolyte with a concentration of 0.1 M were applied and were blanketed with argon during the measurements. For electropolymerizations the respective monomer was used in a concentration of 0.01 M in acetonitrile (Chapter 2.5) or dichloromethane (Chapter 2.7). The obtained film was washed with dry acetonitrile or dichloromethane and subjected to several scans in a monomer-free electrolyte solution in acetonitrile until a stable current response was recorded ("conditioning"). Subsequently, the respective film was characterized by cyclic voltammetry using different scan rates between 100 mV/s and 10 mV/s. At every scan rate three scans were conducted. Additionally, 30 scans were measured with a scan rate of 100 mV/s.

Spectroelectrochemical measurements of the polymer films were carried out in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in dry acetonitrile. The applied setup has been described in detail in literature. A Princeton Applied Research PAR 363 potentiostat was used together with a platinum working electrode, a Ag/AgCl reference electrode, and a platinum sheet as the counter electrode. Polymer films were prepared electrochemically as stated above, including the "conditioning" phase. During the recording of the UV-Vis-NIR spectra the applied potential was kept constant. In order to obtain the UV-Vis-NIR spectrum of the neutral polymer film without any oxidized parts, a potential of -500 mV vs. Ag/AgCl was applied at the beginning of the spectroelectrochemical measurements. Instrumental artefacts were removed and marked in the spectra. Moreover, the absorption in the UV-Vis region below 860 nm was adjusted to the absorption at higher wavelengths to obtain continuous spectra.

GPC-UV analyses with THF as eluent were performed at 1 mL/min on a Merck Hitachi LaChrom GPC system equipped with an L-7100 HPLC pump, L-7420 UV-Vis detector, and three columns (PSS SDV 103 Å, 104 Å, and 105 Å). The columns were kept in a column heater at 35 °C and were calibrated with polystyrene standards (Polymer Standards Service).

Quantum chemical calculations were carried out with the Gaussian 09 program. Alkyl residues were shortened to ethyl in order to save computational time. Geometry optimizations and energy calculations were performed via DFT methods using the B3LYP
or the M06-2X\cite{67} correlation/exchange functional and the 6-311+G(d) or the 6-311G basis set. Molecular orbital surfaces were generated utilizing the Gauss View 5.0 program with an isovalue of 0.02.

**Electrode preparation with Pox204 and battery tests**

Composite electrodes with a composition of 56.6 wt.% active material Pox204, 33.0 wt.% carbon black, and 10.4 wt.% poly(tetrafluoroethylene) were prepared as follows: Approximately 100 mg active material and 60 mg carbon black (Imerys, Super P Li) were premixed by grinding in an agate mortar. Subsequently, the appropriate amount of poly(tetrafluoroethylene) powder (Dyneon, TF 2025Z) was added under further grinding to obtain a plastic mass, which was then processed into a free-standing film by roll pressing. Electrodes with 12 mm diameter and mass loadings between 6.5 g/cm\(^2\) and 7.5 g/cm\(^2\) were punched out, pressed onto aluminium expanded metal grid as current collector, and finally dried at 80 °C under dynamic vacuum (about 1 mbar) overnight. T-type 3-electrode cells were built from these electrodes using Li metal as counter and reference electrodes, 1 M LiPF\(_6\) in ethylene carbonate and dimethyl carbonate (Ube Industries, 1:1 by wt.) as electrolyte, and three layers of borosilicate glass microfiber non-wovens (Whatman, GF/A) as separator. Cyclic voltammograms were recorded with a VMP3 potentiostat from Biologic with a scan rate of 0.1 mV/s. Galvanostatic cycling tests were performed with a CTS-Lab cycler from Basytec using a current rate of 0.1 C and cut-off potentials of 2.5 V and 3.9 V vs. Li/Li\(^+\). The specific capacities refer to the mass of active material only.

**Materials**

Ether (VWR), toluene (VWR), and THF (Sigma Aldrich) were dried and purified by a MB SPS-800 (MBraun). Chlorobenzene, triethylamine, and diisopropylamine were purchased from VWR and dried over calcium hydride. THF, n-hexane, petroleum ether, dichloromethane, ether, isopropanol, dimethylsulfoxide, o-xylene, ethyl acetate, and methanol were purchased from VWR and distilled prior to use. A hydrogen gas bottle was purchased from VWR. An aqueous solution of ammonia (32%) and acetic acid were purchased from VWR. Hexylamine, 2-ethylhexylamine, and aniline were purchased from Merck and dried over calcium hydride. ZnCl\(_2\) and CuCl\(_2\) were purchased from Merck and dried in vacuo at 150 °C prior to use. Sodium tert-butoxide, bromobenzene, copper(I) iodide, sodium hydroxide,
sodium azide, triphenylphosphine, 2-bromothiophene, 4-bromoanisole, tosyl chloride, lithium aluminium hydride, Pd/C, Rh/C, Pt/C, and anhydrous iron trichloride were purchased from Merck. 4-(Dimethylamino)pyridine (DMAP), diisopropyl azodicarboxylate (DIAD), potassium tert-butoxide, and magnesium were purchased from Fluka. N,N’-Dimethyl-ethylenediamine (DMEDA), N,N’-dicyclohexylcarbodiimide (DCC), L-proline, copper(I) bromide, lithium amide, 12-crown-4, p-nitrobenzamide, ferrocenecarboxylic acid, p-toluene-sulfonamide, 2-aminothiazole, 4-bromobenzonitrile, 2-bromothiazole, and 2-bromo-5-chlorothiophene were purchased from Alfa Aesar. Potassium carbonate, tert-butyl carbamate, Pd(OAc)$_2$, Pd(dba)$_2$, Pd$_2$(dba)$_3$, Pd(dppf)Cl$_2$ x CH$_2$Cl$_2$, tBuXPhos, 2,2’-bis(diphenylphosphino)-1,1’-binaphthyl (BINAP), tri-tertbutylphosphine, tri(o-tolyl)phosphine, benzoic acid, 15-crown-5, 18-crown-6, p-ethoxybenzamide, thiobenzamide, copper(II) tetrafluoroborate, 2-hexyldecanol, diphenylphosphoryl azide (DPPA), iodobenzene, tetrabutylammonium fluoride trihydrate, Pd/C, and copper(II) tetrafluoroborate were purchased from Sigma Aldrich. Sodium amide, benzamide, and n-butyl lithium were purchased from Acros Organics. 1,1’-Bis(diphenylphosphino)ferrocene (dppf), 3-bromothiophene, triisopropylsilyl chloride, phenyl tosylate, and triphenylsilyl chloride were purchased from fluorochem. 8-Bromo-2-(2,6-diisopropylphenyl)-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione was internally provided. Unless stated otherwise, all synthetic steps were carried out under argon atmosphere.
2.9.2 Amination of dibromobithiophene

3,3’-Dibromo-2,2’-bithiophene (72)[1]

A solution of diisopropylamine (31.0 mL, 220 mmol, 1.10 eq) in THF (400 mL) was cooled to 0 °C and n-BuLi (1.6 M in n-hexane, 138 mL, 220 mmol, 1.10 eq) was slowly added. After stirring for 30 min, 3-bromothiophene 59 (18.7 mL, 200 mmol) was added and the reaction mixture was stirred for 3 h. Subsequently, ZnCl$_2$ (30.0 g, 220 mmol, 1.10 eq) was added in one portion and the suspension was stirred for 20 min. The reaction mixture was cooled to -78 °C and CuCl$_2$ (29.6 g, 220 mmol, 1.10 eq) was added. The suspension was stirred overnight, while slowly warmed to room temperature. After quenching with wet THF (100 mL), the crude product was purified via column chromatography (SiO$_2$, petroleum ether) and recrystallized from petroleum ether to yield dibromide 72 as a colourless solid (28.5 g, 88.0 mmol, 88%). The analytical data was in accordance with literature.

Mp.: 92-96 °C (lit.: 97-98 °C).[1]

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 7.41 (d, $J$ = 5.4 Hz, 2 H, H5), 7.08 (d, $J$ = 5.4 Hz, 2 H, H4) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ = 130.92, 128.99, 127.65, 112.75 ppm.

2-Hexyldecyl azide (174)[3]

To a solution of triphenylphosphine (3.75 g, 14.3 mmol, 1.30 eq) and 2-hexyldecanol 173 (3.19 mL, 11.0 mmol) in THF (150 mL) DIAD (2.81 mL, 14.3 mmol, 1.30 eq) and DPPA (3.08 mL, 14.3 mmol, 1.30 eq) were added. The solution was sonicated for 25 min. Subsequently, the solvent was removed under reduced pressure and the residue was extracted with n-hexane (5 $\times$ 100 mL). The raw product was purified via column chromatography (SiO$_2$, petroleum ether) to give azide 174 as a colourless liquid (2.82 g, 10.6 mmol, 96%). The analytical data was in accordance with literature.[3, 84]
Dithieno[3,2-b:2',3'-d]pyrroles (DTPs)

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 3.23$ (d, $J = 5.9$ Hz, 2 H, N-CH$_2$), 1.61 – 1.49 (m, 1 H, N-CH$_2$-CH), 1.36 – 1.21 (m, 24 H, N-CH$_2$-CH$_2$), 0.93 – 0.81 (m, 6 H, CH$_3$) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 55.41$, 38.35, 32.04, 31.95, 31.90, 30.06, 29.73, 29.70, 29.45, 26.75, 26.72, 22.83, 22.80, 14.26, 14.24 ppm.

2-Hexyldecyl amine (175)$^{[3]}$

LiAlH$_4$ (1.72 g, 45.3 mmol, 1.50 eq) was added in one portion to a solution of azide 174 (8.07 g, 30.2 mmol) in ether (600 mL) and the suspension was heated to reflux for 1 h. After cooling to room temperature, the reaction was quenched with aqueous NaOH (400 mL). The phases were separated and the organic phase was washed with brine (100 mL) and water (3 x 200 mL). Subsequently, the organic phase was dried over MgSO$_4$, filtrated, and the solvent was removed under reduced pressure. Distillation of the residue yielded amine 175 as a colourless liquid (5.91 g, 24.5 mmol, 81%). The analytical data was in accordance with literature.$^{[2-3]}$

Bp.: 141-146 °C/0.05 mbar.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 2.59$ (d, $J = 5.2$ Hz, 2 H, N-CH$_2$), 1.66 (s, 2 H, NH$_2$), 1.34 – 1.10 (m, 25 H, N-CH$_2$-CH, N-CH$_2$-CH$_2$), 0.87 (t, $J = 6.8$ Hz, 6 H, CH$_3$) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 45.03$, 40.42, 32.04, 32.02, 31.98, 31.59, 30.21, 29.87, 29.77, 29.47, 26.83, 26.79, 22.81, 14.24 ppm.

CI-MS: $m/z$ (%) = 242 (72) [M+H]$^+$, 484 (92) [M$_2$+H]$^+$.

Elemental analysis: calc. (%) for C$_{16}$H$_{35}$N: C 79.59, H 14.61, N 5.80; found: C 79.34, H 14.58, N 5.96.
4-Hexyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (60)

A suspension of 3,3'-dibromo-2,2'-bithiophene 72 (1.62 g, 5.00 mmol), NaOEtBu (1.06 g, 11.0 mmol, 2.20 eq), Pd(dbGa)₃ (137 mg, 0.15 mmol, 0.03 eq), and Binap (374 mg, 0.60 mmol, 0.12 eq) in toluene (12 mL) was purged with argon. Hexylamine (0.66 mL, 5.00 mmol, 1.00 eq) was added and the reaction mixture was heated at 110 °C overnight. After cooling to room temperature, water (40 mL) was added. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic phase was dried over MgSO₄, filtrated, and the solvent of the filtrate was removed under reduced pressure. The obtained residue was purified via column chromatography (SiO₂, petroleum ether) to yield DTP 60 as a colourless solid (1.18 g, 4.25 mmol, 85%). The analytical data was in accordance with literature.[48] 

Mp.: 43-45 °C (lit.: 42-43 °C).[48]

¹H NMR (CDCl₃, 400 MHz): δ = 7.14 (d, J = 5.3 Hz, 2 H, Th-Ηα), 7.01 (d, J = 5.3 Hz, 2 H, Th-Ηβ), 4.20 (t, J = 7.1 Hz, 2 H, N-CH₂), 1.90-1.83 (m, 2 H, N-CH₂-CH₂), 1.37-1.25 (m, 6 H, N-(CH₂)₂-, (CH₂)₃), 0.86 (t, J = 7.1 Hz, 3 H, CH₃) ppm.

¹³C NMR (CDCl₃, 101 MHz): δ = 145.06, 122.89, 114.72, 111.09, 47.57, 31.56, 30.48, 26.81, 22.65, 14.16 ppm.

UV-Vis (THF) λmax (ε): 310 (23 900), 298 (26 600), 289 (sh, 21 900) nm.

4-(2-Ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (64)

A suspension of 3,3'-dibromo-2,2'-bithiophene 72 (3.24 g, 10.0 mmol), NaOEtBu (2.31 g, 24.0 mmol, 2.40 eq), Pd₂(dbGa)₃ (0.46 g, 0.50 mmol, 0.05 eq), and Binap (1.25 g, 2.00 mmol, 0.20 eq) in toluene (24 mL) was purged with argon. 2-Ethylhexylamine (1.64 mL, 10.0 mmol, 1.00 eq) was added and the reaction mixture was heated at 110 °C overnight. After cooling to
room temperature, water (80 mL) was added. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 40 mL). The combined organic phase was dried over MgSO$_4$, filtrated, and the solvent of the filtrate was removed under reduced pressure. The obtained residue was purified via column chromatography (SiO$_2$, petroleum ether) to yield DTP 64 as a colourless oil (2.87 g, 9.85 mmol, 99%). The analytical data was in accordance with literature.$^{[60]}$

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.12 (d, $J$ = 5.3 Hz, 2 H, Th-$H_\alpha$), 6.98 (d, $J$ = 5.3 Hz, 2 H, Th-$H_\beta$), 4.06 (t, $J$ = 7.2 Hz, 2 H, N-CH$_2$), 2.01 – 1.88 (m, 1 H, N-CH$_2$-C$H$), 1.44 – 1.19 (m, 8 H, N-CH$_2$-CH-C$H_2$, N-CH$_2$-CH-(C$H_2$)$_3$), 0.96 – 0.79 (m, 6 H, CH$_3$) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ = 145.74, 123.02, 114.68, 111.65, 51.69, 40.82, 30.98, 29.02, 24.39, 23.39, 14.18, 10.83 ppm.

UV-Vis (THF) $\lambda_{\text{max}}$ (ε): 310 (22 800), 298 (25 400), 289 (sh, 20 800) nm.

4-(2-Hexyldecyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (78)$^{[85]}$

A suspension of 3,3'-dibromo-2,2'-bithiophene 72 (1.62 g, 5.00 mmol), NaOtfBu (1.15 g, 12.0 mmol, 2.40 eq), Pd$_2$(dba)$_3$ (0.23 g, 0.25 mmol, 0.05 eq), and BINAP (0.62 g, 1.00 mmol, 0.20 eq) in toluene (12 mL) was purged with argon. 2-Hexyldecylamine 175 (1.21 g, 5.00 mmol, 1.00 eq) was added and the reaction mixture was heated at 110 °C overnight. After cooling to room temperature, water (40 mL) was added. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic phase was dried over MgSO$_4$, filtrated, and the solvent of the filtrate was removed under reduced pressure. The obtained residue was purified via column chromatography (SiO$_2$, petroleum ether) to yield DTP 78 as a colourless oil (1.85 g, 4.58 mmol, 92%). The analytical data was in accordance with literature.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta$ = 7.14 (d, $J$ = 5.3 Hz, 2 H, Th-$H_\alpha$), 7.02 (d, $J$ = 5.3 Hz, 2 H, Th-$H_\beta$), 4.07 (d, $J$ = 7.4 Hz, 2 H, N-CH$_2$), 2.10 – 1.87 (m, 1 H, N-CH$_2$-CH), 1.40 – 1.14 (m, 24 H, N-CH$_2$-CH-(CH$_2$)$_3$, N-CH$_2$-CH-(CH$_2$)$_5$), 0.99 – 0.74 (m, 6 H, CH$_3$) ppm.
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\[ ^{13}\text{C NMR} \text{(CD}_2\text{Cl}_2, 101 MHz): \delta = 145.74, 122.99, 114.67, 111.65, 52.09, 39.38, 32.26, 32.16, 31.92, 30.26, 29.95, 29.87, 29.64, 26.74, 23.06, 23.00, 14.28, 14.24 \text{ ppm.} \]

\[ \text{UV-Vis (THF)} \lambda_{\text{max}} (\epsilon): 311 \text{ (22 000), 298 (24 300), 289 (sh, 19 700) nm.} \]

4-Phenyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (65)

A suspension of 3,3’-dibromo-2,2’-bithiophene 72 (1.62 g, 5.00 mmol), NaOtBu (1.15 g, 12.0 mmol, 2.40 eq), Pd\(_2\)(dba)\(_3\) (137 mg, 0.15 mmol, 0.03 eq), and BINAP (374 mg, 0.60 mmol, 0.12 eq) in toluene (12 mL) was purged with argon. Aniline (0.46 mL, 5.00 mmol, 1.00 eq) was added and the reaction mixture was heated at 110 °C overnight. After cooling to room temperature, water (25 mL) and dichloromethane (25 mL) were added. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 25 mL). The combined organic phase was dried over MgSO\(_4\), filtrated, and the solvent of the filtrate was removed under reduced pressure. The obtained residue was purified via column chromatography (SiO\(_2\), petroleum ether) to yield DTP 65 as a colourless solid (1.07 g, 4.19 mmol, 84%). The analytical data was in accordance with literature.\(^{[86]}\)

\[ \text{Mp.: 126-127 °C (lit.: 126-127 °C).}^{[87]} \]

\[ ^1\text{H NMR (CDCl}_3, 400 MHz): \delta = 7.62 – 7.58 \text{ (m, 2 H, o-Ph-H), 7.57 – 7.51 \text{ (m, 2 H, m-Ph-H), 7.34 \text{ (t, J = 7.3 Hz, 1 H, p-Ph-H), 7.18 \text{ (s, 4 H, Th-H), ppm.}} \]

\[ ^{13}\text{C NMR (CDCl}_3, 101 MHz): \delta = 144.09, 140.01, 129.91, 126.91, 126.13, 123.59, 122.74, 117.05, 112.39 \text{ ppm.} \]

\[ \text{UV-Vis (THF)} \lambda_{\text{max}} (\epsilon): 310 \text{ (25 500), 299 (28 400), 261 (10 000) nm.} \]

4-Benzoyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (97)\(^{[1]}\)

A suspension of CuI (95.2 mg, 0.50 mmol, 0.05 eq), DMEDA (0.22 mL, 2.00 mmol, 0.20 eq), and K\(_2\)CO\(_3\) (4.15 g, 30.0 mmol, 3.00 eq) in toluene (20 mL) was stirred for 30 min. Subsequently, benzamide (1.45 g, 12.0 mmol, 1.20 eq) and 3,3’-dibromo-2,2’-bithiophene 72
(3.24 g, 10.0 mmol) were added and the reaction mixture was heated at 110 °C for 24 h. After cooling to room temperature, water (60 mL) was added. The phases were separated and the aqueous phase was extracted with n-hexane (3 × 20 mL). The combined organic phase was dried over Na₂SO₄, filtrated, and the solvent of the filtrate was removed under reduced pressure. The obtained residue was purified via column chromatography (SiO₂, petroleum ether : dichloromethane = 3:1) to yield a fraction of unsubstituted DTP 50 as a colourless solid (298 mg, 1.66 mmol, 17%) and a fraction of benzoyl-substituted DTP 97 as a colourless solid (1.06 g, 3.74 mmol, 37%). The analytical data of DTP 50 and DTP 97 was in accordance with literature.¹,⁵

Analytical data of benzoyl-substituted DTP 97:
Mp.: 131-132 °C (lit.: 130-131 °C).¹

¹H NMR (CD₂Cl₂, 400 MHz): δ = 7.78 – 7.63 (m, 3 H, o-Ph-H, p-Ph-H), 7.60 – 7.52 (m, 2 H, m-Ph-H), 7.14 (d, J = 5.3 Hz, 2 H, Th-Hα), 6.84 (s, 2 H, Th-Hβ) ppm.
¹³C NMR (CD₂Cl₂, 101 MHz): δ = 167.10, 143.33, 134.80, 132.46, 129.11, 128.89, 124.52, 121.71, 116.60 ppm.
UV-Vis (THF) λₓₘᵡ (ε): 325 (sh, 5 500), 291 (22 300), 285 (sh, 20 600) nm.

4-Tert-butyloxycarbonyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (176)

A suspension of CuI (190 mg, 1.00 mmol, 0.10 eq), DMEDA (0.43 mL, 4.00 mmol, 0.40 eq), and K₂CO₃ (4.15 g, 30.0 mmol, 3.00 eq) in toluene (15 mL) was stirred for 30 min. Subsequently, tert-butyl carbamate (1.52 g, 13.0 mmol, 1.30 eq) and 3,3'-dibromo-2,2'-bithiophene 72 (3.24 g, 10.0 mmol) were added and the reaction mixture was heated at 110 °C for 24 h. After cooling to room temperature, the suspension was diluted with dichloromethane and filtered through a plug of celite. The raw product was purified via column chromatography (SiO₂, petroleum ether : dichloromethane = 3:1) to give DTP 176 as a yellow solid (1.30 g, 4.64 mmol, 46%).
Mp.: 89-90 °C.
¹H NMR (CDCl₃, 400 MHz): δ = 7.46 (s, 2 H, Th-Hβ), 7.20 (d, J = 5.2 Hz, 2 H, Th-Hα), 1.71 (s, 9 H, CH₃) ppm.
$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 148.83, 124.00, 120.03, 116.26, 84.09, 28.35$ ppm.

Cl-MS: $m/z$ (%) = 279 (31) [M$^+$], 224 (100) [(C$_8$H$_5$NS$_2$)COOH+H$^+$], 208 (6) [(C$_8$H$_5$NS$_2$)CO+H$^+$], 180 (22) [(C$_8$H$_5$NS$_2$)H+H$^+$].

Elemental analysis: calc. (%) for C$_{13}$H$_{13}$NO$_2$S$_2$: C 55.89, H 4.69, N 5.01, S 22.95; found: C 55.85, H 4.52, N 4.99, S 22.89.

UV-Vis (THF) $\lambda_{max}$ ($\epsilon$): 276 (sh, 19 800), 284 (26 400), 299 (20 700), 308 (sh, 16 100) nm.

4-Tosyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (177)

A suspension of CuI (38.1 mg, 0.20 mmol, 0.20 eq), DMEDA (0.09 mL, 0.80 mmol, 0.80 eq), K$_2$CO$_3$ (415 mg, 3.00 mmol, 3.00 eq), $p$-toluenesulfonamide (257 mg, 1.50 mmol, 1.50 eq), and 3,3'-dibromo-2,2'-bithiophene 72 (324 mg, 1.00 mmol) in toluene (2 mL) was heated at 110 °C for 2 d. After cooling to room temperature, the suspension was diluted with dichloromethane and filtered through a plug of celite. The raw product was purified via column chromatography (SiO$_2$, petroleum ether : dichloromethane = 3:1) to give DTP 177 as a green solid (58.7 mg, 0.18 mmol, 18%).

M.p.: 182-185 °C.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 7.71$ (d, $J = 8.4$ Hz, 2 H, $o$-Ph-H), 7.52 (d, $J = 5.3$ Hz, 2 H, Th-H$_{a}$), 7.27 (d, $J = 5.3$ Hz, 2 H, Th-H$_{b}$), 7.20 (dd, $J = 8.6$ Hz, 0.7 Hz, 2 H, $m$-Ph-H), 2.31 (s, 3 H, CH$_3$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): $\delta = 145.99, 142.69, 134.94, 130.27, 126.88, 125.63, 121.93, 115.21, 21.69$ ppm.

GC/EI-MS (70 eV): $t_s = 23.4$ min; $m/z$ (%) = 333 (44) [M$^+$], 178 (100) [M-SO$_2$C$_6$H$_4$CH$_3$]$^+$. 

Cl-MS: $m/z$ (%) = 334 (100) [M+H]$^+$.

Elemental analysis: calc. (%) for C$_{15}$H$_{13}$NO$_2$S$_3$: C 54.03, H 3.33, N 4.20, S 28.84; found: C 54.08, H 3.15, N 4.20, S 28.87.

UV-Vis (THF) $\lambda_{max}$ ($\epsilon$): 405 (sh, 100), 381 (sh, 200), 361 (sh, 200), 302 (sh, 8 700), 281 (15 300) nm.
Dithieno[3,2-b:2',3'-d]pyrroles (DTPs)

**Attempted synthesis of 4-thiobenzoyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (178)**

A suspension of CuI (95.2 mg, 0.50 mmol, 0.10 eq), DMEDA (0.22 mL, 2.00 mmol, 0.40 eq), K$_2$CO$_3$ (2.07 g, 15.0 mmol, 3.00 eq), thiobenzamide (1.05 g, 7.50 mmol, 1.50 eq), and 3,3'-dibromo-2,2'-bithiophene 72 (1.62 g, 5.00 mmol) in toluene (8 mL) was purged with argon and heated at 110 °C for 7 d. Analyses via TLC and GC/MS indicated the presence of unreacted starting material, but no product could be detected.

The procedure was repeated with a palladium catalyst. A suspension of Pd$_2$(dba)$_3$ (229 mg, 0.25 mmol, 0.05 eq), BINAP (623 mg, 1.00 mmol, 0.20 eq), NaO$_2$Bu (1.15 g, 12.0 mmol, 2.40 eq), thiobenzamide (1.05 g, 7.50 mmol, 1.50 eq), and 3,3'-dibromo-2,2'-bithiophene 72 (1.62 g, 5.00 mmol) in toluene (8 mL) was purged with argon and heated at 110 °C for 23 h. Again analyses via TLC and GC/MS indicated the presence of unreacted starting material, but no product could be detected.

**Attempted synthesis of 4-(2-thiazolyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (179)**

A suspension of 3,3'-dibromo-2,2'-bithiophene 72 (1.62 g, 5.00 mmol), NaO$_2$Bu (1.44 g, 15.0 mmol, 3.00 eq), Pd(dba)$_2$ (288 mg, 0.50 mmol, 0.10 eq), dppf (1.11 g, 2.00 mmol, 0.40 eq), and 2-aminothiazole (0.67 g, 6.50 mmol, 1.30 eq) in toluene (12 mL) was purged with argon and then heated at 110 °C for 20 h. Analyses via TLC and GC/MS indicated the presence of unreacted 72 and the side-products 3-bromo-2,2'-bithiophene 181 and 2,2'-bithiophene 183 from the dehalogenation of the starting material 72, but the targeted product could not be detected.

The procedure was repeated with a copper catalyst. A suspension of 3,3'-dibromo-2,2'-bithiophene 72 (972 mg, 3.00 mmol), K$_2$CO$_3$ (1.24 g, 9.00 mmol, 3.00 eq), CuI (114 mg, 0.60 mmol, 0.20 eq), DMEDA (0.27 mL, 2.40 mmol, 0.80 eq), and 2-aminothiazole (465 mg, 4.50 mmol, 1.50 eq) in toluene (5 mL) was heated at 110 °C for 3 d. However, analyses via TLC and GC/MS indicated the same results as with a palladium catalyst.
2.9.3 Synthesis of unsubstituted DTP

2,3-Dibromothiophene (70)[6]

To a solution of 3-bromothiophene 59 (163 g, 1.00 mol) in acetic acid (220 mL) a solution of bromine (54.0 mL, 1.05 mol) in acetic acid (100 mL) was slowly added at 0 °C. The orange solution was stirred overnight, while slowly warmed to room temperature. Afterwards, the reaction mixture was poured onto ice water (600 mL) and extracted with ether (4 × 200 mL). The combined organic phase was washed with aqueous sodium hydroxide (2 M, 3 × 250 mL), dried over MgSO₄, and filtrated. After removal of the solvent, the raw product was distilled over a Vigreux column (30 cm) to give dibromide 70 as a colourless liquid (153 g, 0.63 mol, 63%). The analytical data was in accordance with literature.

Bp.: 80-85 °C/9.5 mbar (lit.: 88-90 °C/13.3 mbar).[6]

¹H NMR (CDCl₃, 400 MHz): δ = 7.26 (dd, J = 5.7 Hz, 0.6 Hz, 1 H, H5), 6.92 (dd, J = 5.7 Hz, 0.6 Hz, 1 H, H4) ppm.

¹³C NMR (CDCl₃, 101 MHz): δ = 130.35, 127.17, 114.26, 111.39 ppm.

3-Bromo-2,2’-bithiophene (181)[7]

2-Bromothiophene 197 (18.7 g, 115 mmol) was added to a suspension of magnesium (4.47 g, 487 mmol) in ether (50 mL). The Grignard solution was heated to reflux for 45 min, cooled to room temperature, and filled in a dropping funnel. A suspension of Pd(dppf)Cl₂ × CH₂Cl₂ (735 mg, 0.90 mmol) and 2,3-dibromothiophene 70 (24.2 g, 100 mmol) in ether (120 mL) was cooled to 0 °C. The prepared Grignard solution was slowly added within 45 min and the reaction mixture was stirred for 3 h. After quenching with methanol (10 mL), the suspension was filtrated and the residue was washed with ether (50 mL). The raw product in the filtrate was purified via column chromatography (SiO₂, petroleum ether) to give 181 as a green oil (21.0 g, 85.7 mmol, 86%). The analytical data was in accordance with literature.
Dithieno[3,2-b:2',3'-d]pyrroles (DTPs)

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.43$ (dd, $J = 3.6$ Hz, 1.2 Hz, 1 H, H5'), 7.36 (dd, $J = 5.1$ Hz, 1.2 Hz, 1 H, H3'), 7.19 (d, $J = 5.4$ Hz, 1 H, H5), 7.09 (dd, $J = 5.2$ Hz, 3.7 Hz, 1 H, H4'), 7.02 (d, $J = 5.4$ Hz, 1 H, H4) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 134.46, 132.41, 131.96, 127.39, 126.91, 126.25, 124.53, 108.02$ ppm.

Tosyl azide (182)$^8$

![Tosyl azide](image)

Under ambient conditions a solution of NaN$_3$ (4.29 g, 66.0 mmol) in water (20 mL) was added to a suspension of tosyl chloride (10.5 g, 55.0 mmol) in isopropanol (35 mL). The reaction mixture was stirred at room temperature for 1 h and water (200 mL) was added. After stirring for 1 h, the product was extracted with dichloromethane (5 × 100 mL). The combined extract was dried over MgSO$_4$, filtrated, and the solvent was removed under reduced pressure to yield 182 as a colourless oil (10.8 g, 55.0 mmol, 100%). The analytical data was in accordance with literature.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.87 – 7.82$ (m, 2 H, H2), 7.43 – 7.39 (m, 2 H, H3), 2.49 – 2.48 (m, 3 H, CH$_3$) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 146.34, 135.64, 130.42, 127.69, 21.92$ ppm.

3-Azido-2,2'-bithiophene (49)$^9$

![3-Azido-2,2'-bithiophene](image)

A solution of 3-bromo-2,2'-bithienyl 181 (8.85 g, 36.1 mmol) in ether (40 mL) was added to a solution of n-BuLi (1.6 M in n-hexane, 22.6 mL, 36.1 mmol) in ether (10 mL) at -70 °C. More ether (100 mL) was added and the reaction mixture was stirred for 40 min. A solution of tosyl azide 182 (7.89 g, 40.0 mmol, 1.11 eq) in ether (40 mL) was slowly added and the reaction mixture was stirred for 5 h. After warming to -10 °C, a solution of Na$_2$P$_2$O$_7$ (9.60 g, 36.1 mmol) in water (150 mL) was added. The suspension was stirred at -10 °C for 1 h and subsequently left at 5 °C overnight. The phases were separated and the aqueous phase was extracted with dichloromethane (1 × 200 mL, 2 × 100 mL). The combined organic phase was washed with water (400 mL), dried over MgSO$_4$, and filtrated. The solvent of the filtrate was
removed under reduced pressure. The obtained residue was purified via column chromatography (SiO$_2$, petroleum ether) to give 49 as a brown solid (3.45 g, 16.6 mmol, 46%). The analytical data was in accordance with literature.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.28$ (m, 2 H, H$5'$, H$3'$), 7.20 (d, $J = 5.5$ Hz, 1 H, H$5$), 7.03 (dd, $J = 5.1$ Hz, 3.7 Hz, 1 H, H$4'$), 6.96 (d, $J = 5.5$ Hz, 1 H, H$4$) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 133.90$, 131.51, 127.34, 125.52, 125.12, 123.83, 122.54 ppm.

$4H$-Dithieno[3,2-$b$:2'$,3'$-$d$]pyrrole (50) by azide thermolysis

A solution of 3-azido-2,2'-bithiophene 49 (1.30 g, 6.27 mmol) in chlorobenzene (21 mL) was in equal measure added to three reaction flasks containing refluxing chlorobenzene (12 mL), respectively. The reaction mixtures were heated to reflux for 30 min. After cooling to room temperature, the reaction mixtures were united and the solvent was removed in vacuo. The raw product was purified via column chromatography (SiO$_2$, petroleum ether : ether = 9:2) to give DTP 50 as a colourless solid (430 mg, 2.40 mmol, 38%). The analytical data was in accordance with literature.

Mp.: 167 °C (dec.) (lit.: 167.168 °C).[5]

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.32$ (s, 1 H, NH), 7.15 (d, $J = 5.3$ Hz, 2 H, Th-$H_a$), 7.04 (d, $J = 5.3$ Hz, 2 H, Th-$H_b$) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 143.94$, 123.58, 116.58, 112.60 ppm.

GC/EI-MS (70 eV): $t_R = 16.4$ min; $m/z$ (%) = 179 (100) [M]$^+$. 

UV-Vis (THF) $\lambda_{max}$ (ε): 307 (sh, 18 200), 303 (18 700), 294 (22 500), 285 (sh, 18 700) nm.

$4H$-Dithieno[3,2-$b$:2'$,3'$-$d$]pyrrole (50) by amination with NH$_3$

In a typical attempt, a suspension of CuI (19.0 mg, 0.10 mmol, 0.20 eq), L-proline (23.0 mg, 0.20 mmol, 0.40 eq), K$_2$CO$_3$ (207 mg, 1.50 mmol, 3.00 eq), and 3,3'-dibromo-2,2'-bithiophene 72 (162 mg, 0.50 mmol) in DMSO (1 mL) was purged with argon. An aqueous solution of ammonia (25%, 0.06 mL, 0.75 mmol, 1.50 eq) was added and the reaction mixture was
heated at 80 °C for 2 d. Afterwards, additional aqueous solution of ammonia (25%, 0.30 mL, 3.75 mmol, 7.50 eq) was added and the reaction mixture was heated at 110 °C for 1 d. Analyses via TLC and GC/MS indicated the formation of trace amounts of unsubstituted DTP 50.

**Attempted synthesis of 4H-Dithieno[3,2-b:2',3'-d]pyrrole (50) by amination with lithium or sodium amide**

A suspension of CuI (76.2 mg, 0.40 mmol, 0.20 eq), DMEDA (0.18 mL, 1.60 mmol, 0.80 eq), lithium amide (193 mg, 8.00 mmol, 4.00 eq), and 3,3'-dibromo-2,2'-bithiophene 72 (648 mg, 2.00 mmol) in toluene (4 mL) was degassed and then heated at 110 °C for 2 d. Analyses via TLC and GC/MS indicated the presence of unreacted 72 and the side-products 3-bromo-2,2'-bithiophene 181 and 2,2'-bithiophene 183 from the dehalogenation of the starting material 72, but the targeted product could not be detected.

The procedure was repeated with a palladium catalyst. A suspension of Pd(dba)$_2$ (173 mg, 0.30 mmol, 0.10 eq), dppf (665 mg, 1.20 mmol, 0.40 eq), lithium amide (290 mg, 12.0 mmol, 4.00 eq), and 3,3'-dibromo-2,2'-bithiophene 72 (972 mg, 3.00 mmol) in toluene (5 mL) was degassed and then heated at 110 °C for 2 d. Analyses via TLC and GC/MS indicated the complete consumption of 72 and no presence of dehalogenated side-products. However, also no unsubstituted DTP 50 could be observed.

The reaction was also attempted with sodium amide instead of lithium amide. A suspension of Pd(dba)$_2$ (115 mg, 0.20 mmol, 0.10 eq), dppf (226 mg, 0.40 mmol, 0.20 eq), KOtBu (449 mg, 4.00 mmol, 2.00 eq), 15-crown-5 (450 mg, 2.00 mmol, 1.00 eq), sodium amide (46.4 mg, 2.00 mmol, 1.00 eq), and 3,3'-dibromo-2,2'-bithiophene 72 (648 mg, 2.00 mmol) in 1,4-dioxane (4 mL) was degassed and then heated at 100 °C overnight. Analyses via TLC and GC/MS indicated the presence of unreacted 72 and the dehalogenation side-products 3-bromo-2,2'-bithiophene 181 and 2,2'-bithiophene 183, but unsubstituted DTP 50 was not detected.
4-Benzyl-4\textit{H}-dithieno[3,2-\textit{b}:2',3'-\textit{d}]pyrrole (186)

A suspension of 3,3'-dibromo-2,2'-bithiophene 72 (1.62 g, 5.00 mmol), NaOtBu (1.44 g, 15.0 mmol, 3.00 eq), Pd(dba)$_2$ (288 mg, 0.50 mmol, 0.10 eq), dppf (1.11 g, 2.00 mmol, 0.40 eq), and benzylamine (0.71 mL, 6.50 mmol, 1.30 eq) in toluene (12 mL) was purged with argon and then heated at 110 °C overnight. After cooling to room temperature, water (40 mL) and dichloromethane (40 mL) were added. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 40 mL). The combined organic phase was dried over MgSO$_4$, filtrated, and the solvent of the filtrate was removed under reduced pressure. The obtained residue was purified via column chromatography (SiO$_2$, petroleum ether) to yield DTP 186 as a colourless solid (1.16 g, 4.31 mmol, 86%).

\textbf{Mp.:} 75-76 °C.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 7.38 - 7.29$ (m, 3 H, $m$-Ph-H, $p$-Ph-H), 7.22 (d, $J = 6.2$ Hz, 2 H, o-Ph-H), 7.15 (d, $J = 5.3$ Hz, 2 H, Th-H$_a$), 6.96 (d, $J = 5.3$ Hz, 2 H, Th-H$_b$), 5.38 (s, 2 H, CH$_2$) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 145.50$, 137.70, 129.09, 128.12, 127.39, 123.41, 115.45, 111.62, 51.22 ppm.

CI-MS: \(m/z\) (%) = 178 (18) [M–CH$_2$Ph]$^+$, 269 (100) [M]$^+$.

Elemental analysis: calc. (%) for C$_{15}$H$_{11}$NS$_2$: C 66.88, H 4.12, N 5.20, S 23.80; found: C 67.11, H 4.15, N 5.25, S 23.98.

UV-Vis (THF) $\lambda_{\text{max}}$ (\(\varepsilon\)): 309 (21 500), 297 (24 600), 288 (sh, 19 700) nm.

Attempted synthesis of 4\textit{H}-dithieno[3,2-\textit{b}:2',3'-\textit{d}]pyrrole (50) by benzyl cleavage

In a typical attempt, Pd/C (10%, 25.9 mg, 0.02 mmol, 0.20 eq) was added to a solution of benzyl-substituted DTP 186 (32.8 mg, 0.12 mmol) in ethyl acetate (5 mL). The setup was set under a dihydrogen atmosphere by evacuating and refilling with dihydrogen gas for five times. Subsequently, a balloon filled with dihydrogen was attached and under vigorous stirring the reaction mixture was heated at 75 °C for 24 h. The suspension was filtrated and
the volatile components of the filtrate were removed under reduced pressure. Yet, only starting material 186 was reisolated quantitatively as a colourless solid (32.8 mg, 0.12 mmol).

4H-Dithieno[3,2-b:2',3'-d]pyrrole (50) by Boc cleavage

A suspension of Boc-substituted DTP 176 (146 mg, 0.52 mmol) and K$_2$CO$_3$ (217 mg, 1.57 mmol, 3.00 eq) in methanol (10 mL) was stirred at room temperature for 1 d. After purification via column chromatography (SiO$_2$, petroleum ether : dichloromethane = 3:1) un-substituted DTP 50 was afforded as a colourless crystalline solid (75.3 mg, 0.42 mmol, 81%). The analytical data was in accordance with the data above and with literature.$^5$

4H-Dithieno[3,2-b:2',3'-d]pyrrole (50) by benzoyl cleavage

A suspension of isolated benzoyl-substituted DTP 97 (65.5 mg, 230 µmol), Cul (4.38 mg, 23.0 µmol, 0.10 eq), DMEDA (9.90 µL, 92.0 mmol, 0.40 eq), and K$_2$CO$_3$ (95.4 mg, 690 µmol, 3.00 eq) in wet toluene (2 mL) was heated at 110 °C overnight. After cooling to room temperature, the suspension was filtrated and the solvent of the filtrate was removed under reduced pressure. After purification via column chromatography (SiO$_2$, petroleum ether : dichloromethane = 3:1) unsubstituted DTP 50 was afforded as a colourless solid (35.9 mg, 200 µmol, 87%). The analytical data was in accordance with the data above and with literature.$^5$

4H-Dithieno[3,2-b:2',3'-d]pyrrole (50) by C-N couplings with benzamide

A suspension of Cul (1.14 g, 6.00 mmol, 0.20 eq), DMEDA (2.72 mL, 24.0 mmol, 0.80 eq), and K$_2$CO$_3$ (12.4 g, 90.0 mmol, 3.00 eq) in wet toluene (60 mL) was purged with argon. Subsequently, benzamide (4.36 g, 36.0 mmol, 1.20 eq) and 3,3'-dibromo-2,2'-bithiophene 72 (9.72 g, 30.0 mmol) were added and the reaction mixture was heated at 110 °C for 2 d. After
cooling to room temperature, the crude product was purified via column chromatography (SiO₂, petroleum ether : dichloromethane = 3:1) to yield unsubstituted DTP 50 as a colourless solid (3.19 g, 17.8 mmol, 59%). The analytical data was in accordance with the data above and with literature.⁵

4H-Dithieno[3,2-b:2′,3′-d]pyrrole (50) by C-N couplings with p-ethoxybenzamide

A suspension of CuI (114 mg, 0.60 mmol, 0.20 eq), DMEDA (0.27 mL, 2.40 mmol, 0.80 eq), K₂CO₃ (1.24 g, 9.00 mmol, 3.00 eq), p-ethoxybenzamide (766 mg, 4.50 mmol, 1.50 eq), and 3,3′-dibromo-2,2′-bithiophene 72 (972 mg, 3.00 mmol) in wet toluene (6 mL) was heated at 110 °C for 24 h. After cooling to room temperature, the suspension was diluted with dichloromethane and filtered through a plug of celite. The raw product was purified via column chromatography (SiO₂, petroleum ether : dichloromethane = 3:1) to give unsubstituted DTP 50 as a colourless solid (80.9 mg, 0.45 mmol, 15%). The analytical data was in accordance with the data above and with literature.⁵

4-(p-Nitrobenzoyl)-4H-dithieno[3,2-b:2′,3′-d]pyrrole (189)

A suspension of CuI (114 mg, 0.60 mmol, 0.20 eq), DMEDA (0.27 mL, 2.40 mmol, 0.80 eq), K₂CO₃ (1.24 g, 9.00 mmol, 3.00 eq), p-nitrobenzamide (748 mg, 4.50 mmol, 1.50 eq), and 3,3′-dibromo-2,2′-bithiophene 72 (972 mg, 3.00 mmol) in wet toluene (6 mL) was degassed and heated at 110 °C for 2 d. After cooling to room temperature, the suspension was diluted with dichloromethane and filtered through a plug of celite. The raw product was purified via column chromatography (SiO₂, petroleum ether : dichloromethane = 3:1) to give unsubstituted DTP 50 as a colourless solid (211 mg, 1.18 mmol, 39%) and p-nitrobenzoyl-substituted DTP 189 as a yellow solid (90.1 mg, 0.27 mmol, 9%).

The analytical data of DTP 50 was in accordance with the data above and with literature.⁵

Analytical data of DTP 189:

Mp.: 140 °C (dec.).
Dithieno[3,2-b:2',3'-d]pyrroles (DTPs)

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 8.43 - 8.39$ (m, 2 H, m-Ph-H), 7.94 - 7.90 (m, 2 H, o-Ph-H), 7.18 (d, $J = 5.3$ Hz, 2 H, Th-H$_{\alpha}$), 6.81 (s, 2 H, Th-H$_{\beta}$) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 164.97, 150.17, 142.80, 140.53, 130.05, 125.19, 124.45, 122.51, 116.28$ ppm.

CI-MS: $m/z$ (%) = 178 (16) [M–COPhNO$_2$]$^+$, 328 (91) [M+H]$^+$.

Elemental analysis: calc. (%) for C$_{15}$H$_8$N$_2$O$_3$S$_2$: C 54.87, H 2.46, N 8.53, S 19.53; found: C 54.77, H 2.57, N 8.71, S 19.48.

UV-Vis (THF) $\lambda_{\text{max}}$(E): 304 (sh, 20 000), 291 (24 700), 283 (24 800) nm.

Triphenylsilylamine (191) $^{[33-34]}$

![Triphenylsilylamine](image)

THF (30 mL) was added to lithium amide (532 mg, 22.0 mmol, 1.10 eq) and triphenylsilyl chloride (6.14 g, 20.0 mmol) at -78 °C and the suspension was stirred overnight, while slowly warmed to room temperature. The reaction was quenched with wet ether (200 mL), filtrated, and the solvent of the filtrate was removed under reduced pressure. Subsequently, the raw product was recrystallized from $n$-hexane to give 191 as a colourless solid (5.24 g, 19.0 mmol, 95%). The analytical data was in accordance with literature.

M.p.: 57-60 °C (lit.: 55-56 °C).$^{[88]}$

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.68 - 7.60$ (m, 6 H, o-Ph-H), 7.51 - 7.35 (m, 9 H, m-Ph-H, p-Ph-H), 1.30 (s, 2 H, NH$_2$) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 136.61, 135.27, 129.74, 127.93$ ppm.

GC/El-MS (70 eV): $t_R = 18.8$ min; $m/z$ (%) = 198 (100) [Ph$_2$SiNH$_2$]$^+$, 275 (21) [M]$^+$.

4H-Dithieno[3,2-b:2',3'-d]pyrrole (50) by amination with triphenylsilylamine

A suspension of 3,3'-dibromo-2,2'-bithiophene 72 (162 g, 0.50 mmol), NaOtBu (144 mg, 1.50 mmol, 3.00 eq), Pd$_2$(dba)$_3$ (22.9 mg, 0.03 mmol, 0.05 eq), tri-tert-butylphosphine (20.6 mg, 0.10 mmol, 0.20 eq), and triphenylsilylamine 191 (165 mg, 0.60 mmol, 1.20 eq) in toluene (1 mL) was purged with argon and heated at 80 °C overnight. After purification via
column chromatography (SiO$_2$, petroleum ether : dichloromethane = 3:1) unsubstituted DTP 50 was afforded as a colourless solid (64.2 mg, 0.36 mmol, 72%). The analytical data was in accordance with the data above and with literature.$^5$

The by-product tert-butoxytriphenylsilane was obtained as a colourless solid and the analytical data was in accordance with literature.$^{[17]}$

Analytical data of tert-butoxytriphenylsilane:

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.72 - 7.67$ (m, 6 H, o-Ph-H), 7.45 - 7.33 (m, 9 H, m-Ph-H, p-Ph-H), 1.29 (s, 9 H, CH$_3$) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 136.73, 135.63, 129.69, 127.77, 74.22, 32.27$ ppm.

GC/EI-MS (70 eV): $t_R = 18.9$ min; $m/z$ (%) = 199 (100) [Ph$_2$SiHO]$^+$, 259 (100)[Ph$_3$Si]$^+$, 317 (100) [M-CH$_3$]$^+$, 332 (28) [M]$^+$.
2.9.4 Amination of aryl halides with unsubstituted DTP

4-Phenyl-4H-dithieno[3,2-b:2’,3’-d]pyrrole (65)

A suspension of NaOtBu (192 mg, 20.0 mmol, 2.00 eq), P(tBu)₃ (12.4 mg, 0.06 mmol, 0.06 eq), Pd(OAc)₂ (6.7 mg, 0.03 mmol, 0.03 eq), unsubstituted DTP 50 (179 mg, 1.00 mmol), and bromobenzene (0.13 mL, 1.20 mmol, 1.20 eq) in toluene (2 mL) was purged with argon. The reaction mixture was heated at 110 °C for 2 d and then the crude product was purified via column chromatography (SiO₂, petroleum ether) to yield DTP 65 as a colourless solid (194 mg, 0.76 mmol, 76%). The analytical data was in accordance with the data stated in Chapter 2.9.2 and with literature.[86]

4-(p-Methoxyphenyl)-4H-dithieno[3,2-b:2’,3’-d]pyrrole (68)

A suspension of NaOtBu (192 mg, 20.0 mmol, 2.00 eq), P(tBu)₃ (12.4 mg, 0.06 mmol, 0.06 eq), Pd(OAc)₂ (6.7 mg, 0.03 mmol, 0.03 eq), unsubstituted DTP 50 (179 mg, 1.00 mmol), and 4-bromoanisole (0.15 mL, 1.20 mmol, 1.20 eq) in toluene (2 mL) was purged with argon. The reaction mixture was heated at 110 °C for 3 d and then the crude product was purified via column chromatography (SiO₂, petroleum ether) to yield DTP 68 as a colourless solid (155 mg, 0.54 mmol, 54%). The analytical data was in accordance with literature.[86]

**Mp.**: 133-134 °C.

**¹H NMR** (CD₂Cl₂, 400 MHz): δ = 7.50 (d, J = 8.8 Hz, 2 H, o-Ph-H), 7.19 (d, J = 5.3 Hz, 2 H, Th-Hₐ), 7.12 (d, J = 5.3 Hz, 2 H, Th-Hₐ), 7.06 (d, J = 8.8 Hz, 2 H, m-Ph-H), 3.87 (s, 3 H, CH₃) ppm.

**¹³C NMR** (CD₂Cl₂, 101 MHz): δ = 158.40, 144.83, 133.22, 124.59, 123.72, 116.49, 115.27, 112.45, 55.97 ppm.

**GC/EI-MS** (70 eV): tᵣ = 22.9 min; m/z (%) = 285 (100) [M⁺].

**Cl-MS**: m/z (%) = 286 (100) [M+H]⁺, 178 (2) [M-C₆H₄OCH₃]⁺.
**Elemental analysis**: calc. (%) for C₁₅H₁₁NOS₂: C 63.13, H 3.89, N 4.91, S 22.47; found: C 63.19, H 4.09, N 5.06, S 22.24.

**UV-Vis** (THF) $\lambda_{\text{max}} (\varepsilon)$: 309 (24 900), 297 (28 300), 253 (14 200) nm.

4-(p-Cyanophenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (193)

![Structure of 4-(p-Cyanophenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole](image)

A suspension of NaOtBu (192 mg, 20.0 mmol, 2.00 eq), P(tBu)$_3$ (12.4 mg, 0.06 mmol, 0.06 eq), Pd(OAc)$_2$ (6.7 mg, 0.03 mmol, 0.03 eq), unsubstituted DTP 50 (179 mg, 1.00 mmol), and 4-bromobenzonitrile (223 mg, 1.20 mmol, 1.20 eq) in toluene (2 mL) was purged with argon. The reaction mixture was heated at 110 °C for 3 d and then the crude product was purified via column chromatography (SiO$_2$, petroleum ether : dichloromethane = 6:1) to yield DTP 193 as a colourless solid (165 mg, 0.59 mmol, 59%).

**Mp.**: 243-245 °C.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 7.87 – 7.82$ (m, 2 H, o-Ph-H), 7.76 – 7.70 (m, 2 H, m-Ph-H), 7.27 (d, $J = 5.3$ Hz, 2 H, Th-H$_{\alpha}$), 7.24 (d, $J = 5.3$ Hz, 2 H, Th-H$_{\beta}$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): $\delta = 143.75$, 143.63, 134.43, 124.74, 122.57, 118.84, 118.80, 112.65, 109.22 ppm.

**GC/EI-MS** (70 eV): $t_R = 23.9$ min; $m/z$ (%) = 280 (100) [M]$^+$.  

**Cl-MS**: $m/z$ (%) = 281 (100) [M+H]$^+$.  

**Elemental analysis**: calc. (%) for C$_{15}$H$_8$N$_2$S$_2$: C 64.26, H 2.88, N 9.99, S 22.87; found: C 64.34, H 2.98, N 10.00, S 22.93.

**UV-Vis** (THF) $\lambda_{\text{max}} (\varepsilon)$: 318 (33 800), 293 (sh, 21 900) nm.

(5-Bromo-2-thienyl)(triisopropyl)silane (195)

![Structure of (5-Bromo-2-thienyl)(triisopropyl)silane](image)

At -70 °C n-BuLi (1.6 M in n-hexane, 38.8 mL, 62.2 mmol) was added to a solution of 2,5-dibromothiophene 194 (7.00 mL, 62.2 mmol) in THF (450 mL). After stirring for 30 min, triisopropylsilyl chloride (13.3 mL, 62.2 mmol) was added and the reaction mixture was
stirred overnight, while slowly warmed to room temperature. The suspension was diluted with n-hexane (600 mL), washed with water (500 mL) and brine (500 mL), dried over Na₂SO₄, filtrated, and the solvent of the filtrate was removed in vacuo to give 195 as a colourless oil (19.9 g, 62.2 mmol, 100%). The analytical data was in accordance with literature.

1H NMR (CDCl₃, 400 MHz): δ = 7.12 (d, J = 3.5 Hz, 1 H, H₄), 7.01 (d, J = 3.5 Hz, 1 H, H₃), 1.36 – 1.24 (m, 3 H, Si-CH₃), 1.09 (d, J = 7.3 Hz, 18 H, C₃H₃) ppm.

13C NMR (CDCl₃, 101 MHz): δ = 137.40, 136.21, 131.08, 116.63, 18.63, 11.79 ppm.

4-(3-Thienyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (196)

A suspension of unsubstituted DTP 50 (179 mg, 1.00 mmol), 3-bromothiophene 59 (0.19 mL, 2.01 mmol, 2.00 eq), NaOtBu (145 mg, 1.51 mmol, 1.50 eq), Pd(OAc)₂ (22.5 mg, 0.10 mmol, 0.10 eq), and P(tBu)₃ (40.6 mg, 0.20 mmol, 0.20 eq) in toluene (8 mL) was purged with argon and heated at 110 °C for 4 d. After cooling to room temperature, the suspension was diluted with dichloromethane and filtered through a plug of celite. The raw product was purified via column chromatography (SiO₂, petroleum ether) to give DTP 196 as a yellow solid (88.0 mg, 0.34 mmol, 34%).

Mp: 112-113 °C.

1H NMR (CD₂Cl₂, 500 MHz): δ = 7.51 (dd, J = 5.1 Hz, 3.2 Hz, 1 H, Th-H₄'), 7.41 (dd, J = 5.1 Hz, 1.4 Hz, 1 H, Th-H₅'), 7.34 (dd, J = 3.1 Hz, 1.4 Hz, 1 H, Th-H₂'), 7.22 (d, J = 5.3 Hz, 2 H, Th-H₆), 7.19 (d, J = 5.3 Hz, 2 H, Th-H₇) ppm.

13C NMR (CDCl₃, 101 MHz): δ = 144.30, 138.52, 126.54, 123.66, 122.69, 116.69, 113.24, 112.34 ppm.

GC/El-MS (70 eV): tᵣ = 21.2 min; m/z (%) = 261 (100) [M]+.

Cl-MS: m/z (%) = 261 (100) [M]+.

Elemental analysis: calc. (%) for C₁₂H₇NS₃: C 55.14, H 2.70, N 5.36, S 36.80; found: C 55.24, H 2.73, N 5.28, S 37.00.

UV-Vis (THF) λ_max (ε): 309 (22 600), 298 (25 200) nm.
4-(2-Thiazolyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (179)

A suspension of NaOtBu (192 mg, 20.0 mmol, 2.00 eq), P(tBu)$_3$ (41.3 mg, 0.20 mmol, 0.20 eq), Pd(OAc)$_2$ (22.5 mg, 0.10 mmol, 0.10 eq), unsubstituted DTP 50 (179 mg, 1.00 mmol), and 2-bromothiazole (199 mg, 1.20 mmol, 1.20 eq) in toluene (4 mL) was purged with argon. The reaction mixture was heated at 110 °C for 3 d and then the crude product was purified via column chromatography (Al$_2$O$_3$, petroleum ether : dichloromethane = 3:1) to yield DTP 179 as a yellow solid (57.1 mg, 0.22 mmol, 22%).

Mp.: 119-120 °C.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta$ = 7.70 (d, $J = 5.3$ Hz, 2 H, Th-$H_\alpha$), 7.61 (d, $J = 3.5$ Hz, 1 H, $H_4'$), 7.31 (d, $J = 5.3$ Hz, 2 H, Th-$H_\beta$), 7.12 (d, $J = 3.5$ Hz, 1 H, $H_5'$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): $\delta$ = 160.02, 142.86, 140.19, 124.60, 119.47, 114.99, 113.08 ppm.

GC/EI-MS (70 eV): $t_R = 21.5$ min; $m/z$ (%) = 262 (100) [M]$^+$.

Cl-MS: $m/z$ (%) = 263 (100) [M+H]$^+$.

Elemental analysis: calc. (%) for C$_{11}$H$_6$N$_2$S$_3$: C 50.36, H 2.31, N 10.68, S 36.66; found: C 50.39, H 2.38, N 10.64, S 36.52.

UV-Vis (THF) $\lambda_{max}$ ($\varepsilon$): 321 (sh, 25 800), 314 (30 600), 267 (8 400) nm.

Attempted synthesis of 4-(2-thienyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (198)

A suspension of unsubstituted DTP 150 (189 mg, 1.05 mmol), 2-bromothiophene 197 (0.21 mL, 2.11 mmol, 2.00 eq), NaOtBu (203 mg, 2.11 mmol, 2.00 eq), Pd(OAc)$_2$ (23.7 mg, 0.11 mmol, 0.10 eq), and P(tBu)$_3$ (85.3 mg, 0.42 mmol, 0.40 eq) in toluene (5 mL) was purged with argon and heated at 110 °C. After 7 d only unreacted starting material could be detected via TLC and $^1$H NMR spectroscopy.
Dithieno[3,2-\textit{b}:2',3'-\textit{d}]pyrroles (DTPs)

4-[2-(5-Triisopropylthienyl)]-4\textit{H}-dithieno[3,2-\textit{b}:2',3'-\textit{d}]pyrrole (199)

\[
\begin{array}{c}
\text{TIPS} \\
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{S} \\
\text{S} \\
\text{S}
\end{array}
\end{array}
\]

A suspension of unsubstituted DTP 50 (1.12 g, 6.25 mmol), 2-bromo-5-TIPS-thiophene 195 (2.99 g, 9.37 mmol, 1.50 eq), NaOtBu (1.20 g, 12.5 mmol, 2.00 eq), Pd(OAc)\textsubscript{2} (281 mg, 1.25 mmol, 0.20 eq), and P(tBu)\textsubscript{3} (1.01 g, 5.00 mmol, 0.80 eq) in toluene (12 mL) was purged with argon and heated at 110 °C for 2 d. After cooling to room temperature, the crude product was purified via column chromatography (SiO\textsubscript{2}, petroleum ether) and HPLC (\textit{n}-hexane) to give DTP 199 as a yellow solid (301 mg, 0.72 mmol, 12%).

\textbf{Mp.}: 105-106 °C.

\textbf{\textsuperscript{1}H NMR} (CD\textsubscript{2}Cl\textsubscript{2}, 400 MHz): \(\delta = 7.31 - 7.29\) (m, 2 H, Th-H3', Th-H4'), 7.26 - 7.18 (m, 4 H, Th-H\textalpha, Th-H\textbeta), 1.46 - 1.32 (m, 3 H, Si-CH), 1.15 (d, \(J = 7.3\) Hz, 18 H, CH\textsubscript{3}) ppm.

\textbf{\textsuperscript{13}C NMR} (CD\textsubscript{2}Cl\textsubscript{2}, 101 MHz): \(\delta = 146.85, 144.94, 135.34, 128.92, 124.03, 118.88, 117.41, 113.06, 18.73, 12.13\) ppm.

\textbf{MALDI-MS (HR)}: \(m/z = \text{calc. for C}_{21}\text{H}_{27}\text{NS}_{3}\text{Si}: 417.10694; \text{found: 417.10653 [M]}^+; \delta_{m/m} = 0.98\) ppm.

\textbf{UV-Vis} (THF) \(\lambda_{\text{max}} (\varepsilon): 309 (23 800), 300 (\text{sh}, 22 000), 290 (\text{sh}, 18 700)\) nm.

4-[2-(5-Chlorothienyl)]-4\textit{H}-dithieno[3,2-\textit{b}:2',3'-\textit{d}]pyrrole (200)

\[
\begin{array}{c}
\text{Cl} \\
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{S} \\
\text{S} \\
\text{S}
\end{array}
\end{array}
\]

A suspension of unsubstituted DTP 50 (896 mg, 5.00 mmol), 2-bromo-5-chlorothiophene (1.22 g, 6.00 mmol, 1.20 eq), Pd(OAc)\textsubscript{2} (225 mg, 1.00 mmol, 0.20 eq), P(tBu)\textsubscript{3} (405 mg, 2.00 mmol, 0.40 eq), and NaOtBu (961 mg, 10.0 mmol, 2.00 eq) in toluene (20 mL) was purged with argon and then heated at 110 °C for 5 d. After cooling to room temperature, the crude product was purified via column chromatography (SiO\textsubscript{2}, petroleum ether) and subsequently via HPLC (\textit{n}-hexane) to afford DTP 200 as a yellow solid (21.6 mg, 0.07 mmol, 1%).

\textbf{Mp.}: 90-91 °C.
1H NMR (CD2Cl2, 400 MHz): δ = 7.22 (d, J = 5.3 Hz, 2 H, Th-Hα), 7.17 (d, J = 5.3 Hz, 2 H, Th-Hβ), 6.93 (s, 2 H, Th-H') ppm.

13C NMR (CD2Cl2, 101 MHz): δ = 145.24, 139.55, 125.64, 125.59, 124.43, 119.26, 117.57, 112.42 ppm.

GC/El-MS (70 eV): tR = 22.4 min; m/z (%) = 295 (100) [M]+, 260 (48) [M-Cl]+.

Elemental analysis: calc. (%) for C12H6ClNS3: C 48.72, H 2.04, N 4.74, S 32.51; found: C 48.13, H 2.18, N 5.04, S 32.57.

UV-Vis (THF) λmax (ε): 307 (25 700), 295 (sh, 25 000) nm.

4-(2-Thienyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (198)

Tetrabutylammonium fluoride trihydrate (293 mg, 900 µmol, 10.0 eq) was added to a solution of TIPS-protected DTP 199 (37.6 mg, 90.0 µmol) in THF (2 mL) and the reaction mixture was stirred for 2 d. The crude product was purified via column chromatography (SiO2, petroleum ether) to give DTP 198 as a yellow solid (23.3 mg, 89.0 µmol, 99%).

Mp.: 88-89 °C.

1H NMR (CD2Cl2, 400 MHz): δ = 7.23 (d, J = 5.4 Hz, 2 H, Th-Hα), 7.21 (d, J = 5.4 Hz, 2 H, Th-Hβ), 7.19 (dd, J = 5.5 Hz, 1.4 Hz, 1 H, Th-H5'), 7.14 (dd, J = 3.7 Hz, 1.4 Hz, 1 H, Th-H3'), 7.08 (dd, J = 5.5 Hz, 3.7 Hz, 1 H, Th-H4') ppm.

13C NMR (CD2Cl2, 101 MHz): δ = 145.28, 142.00, 126.54, 124.12, 120.94, 118.91, 117.28, 112.71 ppm.

CI-MS: m/z (%) = 262 (100) [M+H]+.

Elemental analysis: calc. (%) for C12H7NS3: C 55.14, H 2.70, N 5.36, S 36.80; found: C 55.34, H 2.78, N 5.39, S 37.04.

UV-Vis (THF) λmax (ε): 307 (sh, 25 000), 298 (24 600) nm.

A suspension of unsubstituted DTP 50 (143 mg, 0.80 mmol), 8-bromo-2-(2,6-diisopropylphenyl)-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione 201 (448 mg, 0.80 mmol, 1.00 eq), Pd(OAc)$_2$ (18.0 mg, 0.08 mmol, 0.10 eq), $t$(Bu)$_3$P (32.4 mg, 0.16 mmol, 0.20 eq), and NaOtBu (115 mg, 1.20 mmol, 1.50 eq) in toluene (6 mL) was purged with argon and then heated at 110 °C for 4 d. After cooling to room temperature, the crude product was purified via column chromatography (SiO$_2$, dichloromethane) to yield DTP 202 as a dark red solid (293 mg, 0.44 mmol, 55%).

**MP:** 187-205 (DSC).

$^1$H NMR (C$_2$D$_2$Cl$_4$, 400 MHz, 355 K): $\delta = 8.65$ (dd, $J = 8.0$ Hz, 2.0 Hz, 2 H, C4-H, C13-H), 8.56 – 8.48 (m, 4 H, C5-H, C6-H, C11-H, C12-H), 7.85 (dd, $J = 8.4$ Hz, 0.7 Hz, 1 H, C9-H), 7.77 (d, $J = 8.0$ Hz, 1 H, C7-H), 7.62 (dd, $J = 8.4$ Hz, 7.5 Hz, 1 H, C10-H), 7.48 – 7.39 (m, 1 H, p-Ph-H), 7.29 (d, $J = 7.8$ Hz, 2 H, m-Ph-H), 7.18 (d, $J = 5.3$ Hz, 2 H, Th-H$_{\alpha}$), 6.85 (d, $J = 5.3$ Hz, 2 H, Th-H$_{\beta}$), 2.79 – 2.72 (m, 2 H, CH-CH$_3$), 1.17 (d, $J = 6.8$ Hz, 12 H, CH$_3$) ppm.

$^{13}$C NMR (C$_2$D$_2$Cl$_4$, 125 MHz, 355 K): $\delta = 163.52$, 146.04, 145.73, 138.29, 136.98, 136.60, 131.70, 131.68, 131.26, 130.34, 130.01, 129.86, 129.68, 129.25, 129.03, 128.96, 127.64, 126.89, 126.46, 124.64, 124.26, 123.74, 123.69, 123.47, 121.57, 120.70, 120.60, 117.24, 112.25, 29.04, 23.76 ppm.

**MALDI-MS (HR):** $m/z =$ calc. for C$_{42}$H$_{30}$N$_2$O$_2$S$_2$: 658.17432; found: 658.17534 [M]$^+$; $\delta_{m/m} = 1.55$ ppm.

**UV-Vis (THF)** $\lambda_{\text{max}}$ (e): 508 (31 400), 355 (3 600), 338 (3 300), 305 (sh, 20 200), 294 (24 000), 286 (sh, 22 000), 264 (33 100) nm.
2.9.5 Chemical oxidative polymerizations

General procedure

The respective monomer (1.00 mmol) was dissolved in dichloromethane (50 mL). Anhydrous iron trichloride (4.00 eq) was added and the reaction mixture was stirred at ambient temperature for 24 h. The solvent was removed under reduced pressure and the residue was transferred into a Soxhlett apparatus, where the polymer was dedoped with aqueous hydrazine for 24 h, washed with n-hexane for 24 h, and extracted with THF. The solvent of the extract was removed under reduced pressure to yield the respective polymer.

Poly(4-hexyl-4H-dithieno[3,2-b:2′,3′-d]pyrrole) P_{ox}60

![Polymer structure](image)

Yield: 89.0 mg, 0.34 mmol, 34%.

\(^{1}\text{H NMR}\) (THF-d\(_8\), 400 MHz): \(\delta = 8.11 – 7.99\) (m, Th-H\(_{\alpha}\)), \(7.39 – 7.08\) (m, 2 H, Th-H\(_{\beta}\)), \(4.40 – 4.05\) (m, 2 H, N-CH\(_2\)), \(1.93 – 1.80\) (m, 2 H, N-CH\(_2\)-CH\(_2\)), \(1.49 – 1.19\) (m, 6 H, N-(CH\(_2\))\(_2\)-(CH\(_3\))\(_3\)), \(0.96 – 0.77\) (m, 3 H, CH\(_3\)) ppm.

IR (KBr): \(\nu = 2928, 2863\) (C-H), \(1631\) (C=C) cm\(^{-1}\).

Poly(4-(2-ethylhexyl)-4H-dithieno[3,2-b:2′,3′-d]pyrrole) P_{ox}64

![Polymer structure](image)

Yield: 39.0 mg, 0.13 mmol, 13%.

\(^{1}\text{H NMR}\) (THF-d\(_8\), 400 MHz): \(\delta = 7.95 – 7.89\) (m, Th-H\(_{\alpha}\)), \(7.26 – 7.07\) (m, 2 H, Th-H\(_{\beta}\)), \(4.24 – 4.13\) (m, 2 H, N-CH\(_2\)), \(2.07 – 2.01\) (m, 1 H, N-CH\(_2\)-CH\(_2\)), \(1.48 – 1.29\) (m, 8 H, N-CH\(_2\)-CH-CH\(_2\), N-CH\(_2\)-CH-(CH\(_3\))\(_3\)), \(0.98 – 0.88\) (m, 6 H, CH\(_3\)) ppm.

IR (KBr): \(\nu = 2960, 2928, 2869\) (C-H), \(1638\) (C=C) cm\(^{-1}\).
Poly(4-(2-hexyldecyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole) \( P_{ox78} \)

Yield: 119 mg, 0.29 mmol, 27%.

\(^1\)H NMR (THF-\(d_8\), 400 MHz): \( \delta = 8.08 - 7.95 \) (m, Th-\(H_\alpha\)), 7.35 – 7.06 (m, 2 H, Th-\(H_\beta\)), 4.32 – 4.03 (m, 2 H, N-CH\(\_2\)), 2.16 – 2.01 (m, 1 H, N-CH\(\_2\)-CH), 1.45 – 1.15 (m, 24 H, N-CH\(\_2\)-CH-(CH\(\_2\))^\(_5\)), N-CH\(\_2\)-CH-(CH\(\_2\))^\(_7\)), 0.91 – 0.81 (m, 6 H, CH\(\_3\)) ppm.

IR (KBr): \( \nu = 2921, 2850 \) (C-H), 1657 (C=C) cm\(^{-1}\).

Poly(4-tert-butyloxycarbonyl-4H-dithieno[3,2-b:2',3'-d]pyrrole) \( P_{ox176} \)

Only one equivalent of FeCl\(_3\) was used. Yield: 90.0 mg, 0.32 mmol, 32% (partial cleavage of Boc groups not considered).

\(^1\)H NMR (THF-\(d_8\), 400 MHz): \( \delta = 7.69 - 7.02 \) (m, Th-H), 1.78 (s, CH\(\_3\)), 1.43 (s, CH\(\_3\)) ppm.

IR (KBr): \( \nu = 3101, 3080, 2965 \) (C-H), 1734 (C=O), 1624, 1516 (C=C) cm\(^{-1}\).
2.9.6 Ferrocenoyl-substituted DTP and p(DTP)

4-Ferrocenoyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (204)

A suspension of unsubstituted DTP 50 (430 mg, 2.40 mmol), ferrocenecarboxylic acid 203 (732 mg, 3.12 mmol, 1.30 eq), N,N’-dicyclohexylcarbodiimide (644 mg, 3.12 mmol, 1.30 eq), and 4-dimethylaminopyridine (323 mg, 2.64 mmol, 1.10 eq) in dichloromethane (20 mL) was stirred at ambient temperature for 2 d. The reaction mixture was filtrated and the solvent of the filtrate was removed under reduced pressure. The obtained residue was purified via column chromatography (SiO\textsubscript{2}, petroleum ether : dichloromethane = 3:1) to afford DTP 204 as an orange solid (907 mg, 2.32 mmol, 97%).

\textbf{Mp.}: 122-124 °C.

\textbf{\textsuperscript{1}H NMR} (CD\textsubscript{2}Cl\textsubscript{2}, 400 MHz): \(\delta = 7.21 - 7.15 \text{ (m, 4 H, Th-H), 4.95 - 4.93 \text{ (m, 2 H, Cp-H), 4.55 - 4.54 \text{ (m, 2 H, Cp-H), 4.28 (s, 4 H, Cp-H) ppm.}}\)

\textbf{\textsuperscript{13}C NMR} (CD\textsubscript{2}Cl\textsubscript{2}, 101 MHz): \(\delta = 168.87, 143.43, 124.10, 120.72, 116.77, 76.64, 72.41, 71.23, 71.09 \text{ ppm.} \)

\textbf{Elemental analysis}: calc. (%) for C\textsubscript{19}H\textsubscript{13}FeNOS\textsubscript{2}: C 58.32, H 3.35, N 3.58, S 16.39; found: C 58.12, H 3.53, N 3.81, S 16.32.

\textbf{CI-MS}: \(m/z\) (%) = 391 (81) [M+H]\textsuperscript{+}.

\textbf{IR} (KBr): \(\tilde{\nu} = 3098 \text{ (C-H), 1669 \text{ (C=O, C=C), 505, 493 (Fe-Cp) cm}^{-1}.} \)

\textbf{UV-Vis} (THF) \(\lambda_{\text{max}} \text{ (e): 453 (400), 324 (sh, 7 300), 293 (25 400), 284 (sh, 22 900) nm.} \)

**Poly(4-ferrocenoyl-4H-dithieno[3,2-b:2',3'-d]pyrrole) P\textsubscript{ox}204**

Copper(II) tetrafluoroborate (1.61 g, 6.80 mmol, 4.00 eq) was added to a solution of ferrocenoyl-substituted DTP 204 (665 mg, 1.70 mmol) in dichloromethane (15 mL) and acetonitrile
Dithieno[3,2-b:2',3'-d]pyrroles (DTPs)

(15 mL). The reaction mixture was heated at 50 °C for 2 d. Afterwards, the suspension was filtrated and the filter residue was washed with methanol, water, petroleum ether, THF, dichloromethane, and ether to afford $P_{o204}$ as a dark blue solid (442 mg, 1.14 mmol, 67%).

IR (KBr): $\tilde{\nu} = 3111$ (C-H), 1637 (C=O, C=C), 488 (Fe-Cp) cm$^{-1}$.

$T_d$: 322 °C (TGA).
2.10 References

Dithieno[3,2-b:2',3'-d]pyrroles (DTPs)


[55] The HOMO energy level was calculated from the onset oxidation of PEDOT which occurred at about -0.4 V vs. Ag/AgCl = -0.8 V vs. Fc/Fc⁺.


[57] The HOMO energy level was calculated from the onset oxidation of poly(dithieno[3,2-b:2',3'-d]thiophene) which occurred at 0.37 V vs. Ag/Ag⁺ = 0.23 V vs. SCE = -0.15 V vs. Fc/Fc⁺ (V. V. Pavlishchuk, A. W. Addison, *Inorg. Chim. Acta* **2000**, *298*, 97-102).


Chapter 3

Dithieno[2,3-\textit{b}:3',2'-\textit{d}]pyrroles (iso-DTPs)

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3.1 Introduction

In Chapter 2 the influence of different substituents at the nitrogen of DTPs was examined. Another possibility to affect the properties of DTPs is to change the relative positions of the heteroatoms. This is, for instance, represented in isomeric dithieno[2,3-b:3',2'-d]pyrrole (iso-DTP), where the nitrogen in the centre and both sulphurs are located on the same side (Figure 3.1). The resulting structure of iso-DTPs exhibits a cross-conjugation in the backbone which will directly alter in particular the optoelectronic properties. Moreover, the influence of the residues R attached at the nitrogen will presumably also be changed. Therefore, with a series of iso-DTPs bearing different substituents comprehensive structure-property relationships can be derived in monomers and homopolymers.

![Figure 3.1: Structure of DTPs and isomeric iso-DTPs with different residues R attached at the nitrogen.](image)

Figure 3.1: Structure of DTPs and isomeric iso-DTPs with different residues R attached at the nitrogen.
3.2 Synthesis of iso-DTPs

3.2.1 Amination of 2,2′-dibromo-3,3′-bithiophene

Concerning the synthesis of N-functionalized iso-DTPs aminations of the corresponding dibromobithiophene appeared to be very promising. This approach is analogous to the mostly applied strategy for the preparation of DTPs (Chapter 2.2.1) and was already used by Buchwald et al. for the synthesis of Boc-substituted iso-DTP 132. Hence, 3,3′-bithiophene 205 was first of all prepared (Scheme 3.1). After lithiation of commercially available 3-bromo-thiophene 59 with n-BuLi in the 3-position, an oxidative coupling with CuCl₂ was conducted. Recrystallization of the formed product from n-hexane afforded bithiophene 205 in a yield of 72%. Twofold bromination with N-bromosuccinimide then gave dibromide 130, which is quite unstable in the solid state and can spontaneously decompose even at -20 °C under liberation of HBr. Nevertheless, in solution the dibromide is relatively stable and can be applied in reactions at elevated temperatures. Therefore, dibromide 130 was quickly purified via column chromatography and the clean precursor was directly reacted further. Boc-substituted iso-DTP 132 could thus be obtained in an Ullmann-type C-N coupling with tert-butyl carbamate. After purification via column chromatography the desired product was isolated in 37%. This yield refers to the amount of bithiophene 205, while in literature a yield of 78% relative to the amount of dibromide 130 was claimed. The differences can partly be explained by the partial decomposition of 130 during the workup. However, similarly to the synthesis of Boc-substituted DTP 176, even with prolonged reaction times no complete conversion could be achieved and large amounts of starting material 130 were reisolated. This indicated the inhibition of the copper catalyst by the formed iso-DTP 132, as it was proposed by Evenson and Rasmussen for the synthesis of acyl- and benzoyl-substituted DTPs.

Scheme 3.1: Synthesis of Boc-substituted iso-DTP 132 starting from 3-bromothiophene 59.
Subsequently, the synthesis of benzoyl-substituted iso-DTP 206 was attempted by using the same reaction conditions as for Boc-substituted iso-DTP 133 (Scheme 3.2). Because no reaction occurred, in another attempt toluene as the solvent was exchanged by mesitylene to carry out the reaction at 160 °C instead of 110 °C. Even under these very harsh conditions, however, still no product formation could be observed. This was quite surprising, as besides Boc-substituted iso-DTP 132 the same catalyst also enabled the synthesis of DTP isomers 97 and 176 with benzoyl and Boc substituents at the nitrogen (Chapter 2.2.1).

Scheme 3.2: Attempted synthesis of benzoyl-substituted iso-DTP 206 via C-N couplings of dibromide 130 with benzamide.

Nevertheless, amination of dibromide 130 with hexylamine to yield iso-DTP 207 was also attempted (Scheme 3.3). Different reaction conditions were investigated and are summarized in Table 3.1. Palladium catalysts together with BINAP, dppf, or PPh₃ as ligand were applied (Table 3.1, entry 1-3). In one attempt, mesitylene instead of toluene was used as the solvent to increase the reaction temperature to 160 °C (Table 3.1, entry 4). Finally, a copper catalyst together with different solvents and bases was tested (Table 3.1, entry 5-7), but in any case no hexyl-substituted iso-DTP 207 was formed.

Scheme 3.3: Attempted synthesis of hexyl-substituted iso-DTP 207 via amination of dibromide 130. More details see Table 3.1.
Table 3.1: Applied reaction conditions for the attempted synthesis of hexyl-substituted iso-DTP \(207\) (Scheme 3.3).

<table>
<thead>
<tr>
<th>Pre-catalyst</th>
<th>Ligand</th>
<th>Base</th>
<th>Solvent</th>
<th>T [°C]</th>
<th>Time</th>
</tr>
</thead>
</table>
| 1  | \(\text{Pd}_2(\text{dba})_3\)  
(0.03 eq) | BINAP   
(0.12 eq) | \(\text{NaOtfBu}\)  
(2.40 eq) | toluene | 110   | 23 h |
| 2  | \(\text{Pd}_2(\text{dba})_3\)  
(0.10 eq) | BINAP   
(0.40 eq) | \(\text{NaOtfBu}\)  
(2.40 eq) | toluene | 110   | 6 d  |
| 3  | \(\text{Pd}(\text{PPh}_3)_4\)  
(0.10 eq) | -       
( - )     | \(\text{NaOtfBu}\)  
(2.40 eq) | toluene | 110   | 2 d  |
| 4  | \(\text{Pd(dba)}_2\)  
(0.10 eq) | \(\text{dppf}\)  
(0.40 eq) | \(\text{NaOtfBu}\)  
(2.40 eq) | mesitylene | 160   | 3 d  |
| 5  | \(\text{Cul}\)  
(0.05 eq) | \(\text{DMEDA}\)  
(0.20 eq) | \(\text{K}_2\text{CO}_3\)  
(3.00 eq) | toluene | 110   | 4 d  |
| 6  | \(\text{Cul}\)  
(0.05 eq) | \(\text{DMEDA}\)  
(0.20 eq) | \(\text{K}_2\text{CO}_3\)  
(3.00 eq) | dioxane | 100   | 4 d  |
| 7  | \(\text{Cul}\)  
(0.05 eq) | \(\text{DMEDA}\)  
(0.20 eq) | \(\text{NaOtfBu}\)  
(2.40 eq) | dioxane | 100   | 2 d  |
3.2.2 Amination of 2-bromothiophenes

In contrast to the synthetic approach of closing the central pyrrole ring via amination of dibromide 130, an alternative ring fusion would involve a C-C coupling reaction (Scheme 3.4). Rasmussen et al. established this strategy for the synthesis of DTPs where they first carried out a Buchwald-Hartwig amination of two equivalents of 3-bromothiophene 59 with alkyl- or arylamines (Chapter 1.3). In a one-pot procedure, they subsequently brominated the afforded dithienylamine twice with NBS and an intramolecular oxidative C-C coupling with copper powder gave the targeted DTP products.

![Scheme 3.4: Retrosynthesis of an alternative strategy to synthesize iso-DTPs via C-C coupling in the final step.](image)

In order to synthesize substituted iso-DTPs via this approach, 2-bromothiophene 197 had to be applied instead of 3-bromothiophene 59 in the first step (Scheme 3.4). However, it has already been mentioned in literature that Buchwald-Hartwig aminations of 2-bromothiophenes only work with diarylamines, but not with monoaryl- or alkylamines. Therefore, we tested the more electron-deficient 2,5-dibromothiophene 194 in the coupling with hexylamine. Yet, no reaction was observed applying palladium catalysts with either the monodentate P(tBu)_3 or the bidentate BINAP ligand, respectively. Afterwards, TIPS-substituted bromothiophene 195 was used as precursor (synthesis see Chapter 2.2.3) and dithienylamine 208 was afforded (Scheme 3.5). Notably, for the purification via column chromatography n-hexane instead of petroleum ether had to be applied as eluent in order to achieve a sufficient separation from the contained impurities. Peculiarly, the same reaction of bromothiophene 195 with aniline or the slightly bulkier 2-ethylhexylamine did, however, not yield 209 or 210 under palladium catalysis with BINAP, P(tBu)_3, or dppf as ligand, respectively (Scheme 3.5).
Scheme 3.5: Amination of bromide 195 with hexylamine to product 208 and failed aminations with aniline to 209, respectively with 2-ethylhexylamine to 210.

Nevertheless, following the protocol of Rasmussen et al. for the synthesis of DTPs (vide supra), a twofold bromination of dithienylamine 208 with NBS in dry DMF and a subsequent Ullmann coupling with copper powder in one pot was attempted. While the bromination to yield dibromide 211 worked, no in situ C-C coupling to iso-DTP 212 was observed. The synthesis of dibromide 211 was then carried out in chloroform and the formed product was isolated (Scheme 3.6). It was anticipated that the bulky TIPS groups lead to a

Scheme 3.6: Attempted synthesis of hexyl-substituted iso-DTP 207 via ring closure of amine 208.
selective bromination in the 3- and 3’-position. However, at least two side-products were also observed in all attempts and separation of dibromide 211 from these impurities via column chromatography was not possible. From n-hexane minor amounts could be recrystallized, but analytical purity of dibromide 211 could not be achieved. Therefore, the raw product was used in the next step. Herein, dibromide 211 was lithiated with n-BuLi to give a bright yellow intermediate, which was further reacted in a C-C coupling reaction to close the pyrrole ring in the centre. Iso-DTP 212 was isolated as raw product and subsequently treated with tetrabutylammonium fluoride in order to cleave off the TIPS protecting groups. Hexyl-substituted iso-DTP 207 was identified in the obtained product mixture, but efforts to purify the compound via column chromatography were not successful. Hence, the targeted product could be synthesized, but no sufficient purification could be achieved. Moreover, due to the limited scope of the amination in the first step, alternative strategies had to be developed for the synthesis of a whole series of different iso-DTPs.
3.2.3 Attempted Cadogan reaction to synthesize unsubstituted iso-DTP

Another suitable precursor for the synthesis of a series of N-substituted iso-DTPs would be unsubstituted iso-DTP 126. Similarly to the approach for the synthesis of DTPs described in Chapter 2.2.3, the dithienopyrrole unit would be built up first and then different residues could be attached at the nitrogen via substitution reactions. Unfortunately, thermolysis of 2-azido-3,3'-bithiophene 125 does not yield the target product 126 (Chapter 1.3). Hence, instead of using azide precursor 125, a strategy involving a Cadogan reaction of nitrobithiophene 213 was chosen to obtain unsubstituted iso-DTP 126. This approach appeared quite promising, because carbazole, for example, can be synthesized from the reaction of 2-nitro-1,1'-biphenyl and triethylphosphite in very good yields.

In the first step, the required nitrobithiophene 213 was synthesized by nitration of 3,3'-bithiophene 205 (Scheme 3.7). For this reaction a slight excess of 0.2 equivalents of HNO₃ was used, but as the reaction worked better than anticipated about 20% of a dinitro side-product was obtained. After purification via column chromatography the desired precursor 213 could be isolated in a yield of 50% and the identity of 213 was confirmed by ¹H NMR spectroscopy. Here, the two doublets of the protons H4 and H5 at the thiophene ring with the nitro group possess a coupling constant ³J_H,H of 5.5 Hz, but isomers of 213 with the nitro group in the 4- or 5-position would exhibit coupling constants ⁴J_H,H with much lower values. For instance, in the second thiophene ring of 213 those ⁴J_H,H coupling constants were 2.9 and 1.2 Hz.

![Scheme 3.7](image)

**Scheme 3.7:** Attempted Cadogan reaction with nitrobithiophene 213 to afford unsubstituted iso-DTP 126. Formation of intermediate 214 was not observed, but cannot be excluded. More details see Table 3.2.

Precursor 213 was then used in a Cadogan reaction in order to synthesize unsubstituted iso-DTP 126 (Scheme 3.7). Different reaction conditions were tested and are summarized in Table 3.2. Generally, in Cadogan reactions a suitable reagent reduces the nitro group to form
a nitrene intermediate, which then rearranges to form a new N-C and N-H bond. First of all, P(OEt)$_3$ or PPh$_3$ were used as reductant under irradiation in the microwave (300 W) at a temperature of 210 °C (Table 3.2, entry 1 and 2). Subsequently, another attempt with PPh$_3$ and conventional heating at 165 °C was carried out (Table 3.2, entry 3). Yet, no product formation was observed by TLC, GC, or $^1$H NMR spectroscopy and only large amounts of an insoluble solid were afforded. A possible formation of unsubstituted iso-DTP 126 and its immediate decomposition under the harsh reaction conditions cannot be excluded but seems unlikely. Instead, the formed nitroso or nitrene intermediates probably reacted further, for example through ring cleavages or intermolecular couplings. In order to prevent such follow-up reactions, much milder conditions involving the Grignard reagent iPrMgBr and decreased temperatures of 0 °C or -70 °C were applied (Table 3.2, entry 4 and 5). However, this did also not change the outcome of the reaction and no product 126 could be detected. In our institute similar Cadogan reactions were investigated using mixed nitro-substituted thienyl-phenylene substrates and it was discovered that the position of the nitro group was very crucial. High yields of the respective products could be obtained with nitrophenyl precursors, but when nitrothiophenes were involved only low yields were afforded. Thus, unsubstituted DTP 50 was isolated in just 11% in a Cadogan reaction of corresponding precursor 3-nitro-2,2'-bithiophene which showed that this synthetic approach was very limited.

Table 3.2: Details of the applied reaction conditions for the attempted Cadogan reaction with nitro-bithiophene 213 to afford unsubstituted iso-DTP 126 (Scheme 3.7).

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Solvent</th>
<th>T [°C]</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P(OEt)$_3$</td>
<td>-</td>
<td>210 (300 W)</td>
</tr>
<tr>
<td>2</td>
<td>PPh$_3$</td>
<td>C$_6$H$_4$Cl$_2$</td>
<td>210 (300 W)</td>
</tr>
<tr>
<td>3</td>
<td>PPh$_3$</td>
<td>mesitylene</td>
<td>165</td>
</tr>
<tr>
<td>4</td>
<td>iPrMgBr</td>
<td>THF</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>iPrMgBr</td>
<td>THF</td>
<td>-70</td>
</tr>
</tbody>
</table>
3.2.4 N-functionalization of unsubstituted iso-DTP

An alternative method to the Cadogan reaction for the preparation of unsubstituted iso-DTP 126 was to split off the Boc residue in iso-DTP 132. In general, cleavage of Boc protecting groups are usually carried out either thermally or under acidic conditions, whereas the gaseous by-products isopropene and carbon dioxide are released from the reaction mixture. Analysis of Boc-substituted iso-DTP 132 via TGA, however, revealed a weight loss of 49% at 140 °C (Figure 3.2). This was much higher than the theoretical loss of the Boc residue (36%) and indicated the decomposition of iso-DTP 132 in the solid state starting already at relatively low temperatures. Therefore, a thermal cleavage appeared not to be very promising.

![Figure 3.2: Thermal gravimetical analysis of Boc-substituted iso-DTP 132.](image)

Instead Boc-substituted iso-DTP 132 was treated with trifluoroacetic acid and immediate gas formation indicated the successful removal of the Boc group. Yet, the quantitative formation of a dark blue insoluble solid showed that the formed unsubstituted iso-DTP 126 obviously polymerized. This reactivity under acidic conditions was similar to the instability of unsubstituted DTP 50. Nevertheless, both compounds were relatively stable in the isolated solid state and under mild basic conditions. Hence, the cleavage of the Boc group in iso-DTP 132 was carried out with potassium carbonate in methanol (Scheme 3.8) which already worked quite efficiently with Boc-substituted DTP analogue 176 (Chapter 2.2.2). Previously, a similar method to split off Boc protecting groups under basic conditions was reported and only very short reaction times were required under microwave irradiation. However, for
the synthesis of unsubstituted iso-DTP 126 it was found that increasing the temperature led to the major formation of insoluble side-products. Moreover, when the reaction time was increased to above five hours at room temperature, the product yield significantly decreased. These findings indicated that polymerization of iso-DTP 126 also occurred to some extent in the basic media and was the main factor for the limited yield of the product. Despite these drawbacks, the synthesis could be conducted on large scale and after purification via column chromatography unsubstituted iso-DTP 126 was isolated in a yield of 83%.


Having unsubstituted iso-DTP 126 available as a precursor, substitution reactions could then be carried out to synthesize a whole series of different iso-DTPs (Scheme 3.9). First of all, alkyl residues were attached at the nitrogen applying a procedure developed by Zotti et al. for the synthesis of alkyl-substituted DTP analogues.[16] In a biphasic water-toluene mixture with sodium hydroxide as base and tetrabutylammonium hydrogensulfate as phase-transfer catalyst iso-DTPs 207, 216, and 218 were prepared. For the synthesis of hexyl-substituted derivative 207 hexyl iodide was used as the alkylating reagent. However, to introduce 2-ethylhexyl and 2-hexyldecyl moieties only the corresponding bromides were commercially available. Unfortunately, in the reaction of unsubstituted iso-DTP 126 with the former alkyl halide 2-ethylhexyl-substituted iso-DTP 216 was afforded only in 45% yield. Therefore, alkyl tosylates 215 and 217 were prepared from p-toluenesulfonic chloride and 2-ethylhexano[17] or 2-hexyldecanol,[18] respectively. With the better leaving groups in these precursors the rate of the nucleophilic substitution was enhanced and the yield of 2-ethylhexyl-substituted iso-DTP 216 could be increased to 77%. Yet, with increasing steric demand of the alkyl residue the yield decreased from 91% for hexyl-substituted iso-DTP 207 to 37% for 2-hexyldecyl-substituted derivative 218. The purity of the synthesized iso-DTPs was confirmed by NMR spectroscopy, mass spectrometry, and elemental analyses.
respectively. As a representative example the $^1$H NMR spectrum of hexyl-substituted iso-DTP 207 is shown in Figure 3.3. Compared to hexyl-substituted DTP analogue 60 the signals of the aliphatic residue exhibited similar chemical shifts and in the aromatic region of the spectrum two doublets with a coupling constant of 5.2 Hz appeared. However, the latter two signals of the thienyl $\alpha$- and $\beta$-protons at 7.19 ppm and 6.86 ppm were slightly further separated from each other than usually observed in DTPs.

Scheme 3.9: Synthesis of alkyl-substituted iso-DTPs 207, 216, and 218 via nucleophilic substitution of alkyl iodides or alkyl tosylates by unsubstituted iso-DTP 126. Alk-X is Hex-I, 2-EtHex-Tos (215), or 2-HexDec-Tos (217).

Figure 3.3: $^1$H NMR spectrum of hexyl-substituted iso-DTP 207 recorded in CD$_2$Cl$_2$.

Subsequently, the reaction conditions for the synthesis of phenyl-substituted DTP 65 in a Buchwald-Hartwig amination with unsubstituted DTP 50 (Chapter 2.2.3) were applied for the
synthesis of phenyl-substituted iso-DTP analogue 219 (Scheme 3.10). Thus, bromobenzene was reacted with unsubstituted iso-DTP 126 under palladium-catalysis and after purification via column chromatography iso-DTP 219 was obtained in a yield of 51%.


Lastly, benzoyl-substituted iso-DTP 206 could be synthesized in a Steglich reaction of unsubstituted iso-DTP 126 (Scheme 3.11). Herein, benzoic acid was activated with \( N,N' \)-dicyclohexylcarbodiimide (DCC) and catalytic amounts of 4-dimethylaminopyridine (DMAP) in order to enable the nucleophilic substitution by amine 126. The reaction proceeded very efficiently and after purification via column chromatography benzoylated iso-DTP 206 was isolated in quantitative yields.

Scheme 3.11: Synthesis of benzoyl-substituted iso-DTP 206 via Steglich reaction of benzoic with unsubstituted iso-DTP 126.
3.3 Quantum chemical calculations on iso-DTPs

DFT calculations were performed on all synthesized iso-DTPs to elucidate the influence of the structure to the electronic distribution in the frontier molecular orbitals (Figure 3.4). In particular, observed relationships between the structure and the optoelectronic properties in Chapter 3.4 can thus better be rationalized. The HOMOs of iso-DTPs 126, 132, or 206 with hydrogen, Boc, or benzoyl substituents exhibit a node at the nitrogen atom and thus look similar to the orbitals of the corresponding DTP isomers, respectively (Chapter 2.3). However, the HOMOs of alkyl- and phenyl-substituted iso-DTPs 207, 216, 218, and 219 are also located at the nitrogen and the attached moiety. While the influence of alkyl groups is very low, the phenyl residue contributes considerably to the HOMO. Here, the most prominent change can be observed in comparison to the DTP series. The LUMOs of alkyl-substituted iso-DTPs are located at the dithienopyrrole unit with a node at the nitrogen, whereas the LUMO of unsubstituted iso-DTP 126 is mainly located at the residue. Similarly to the DTP analogues, the derivatives with conjugated substituents exhibit LUMOs, which extent from the dithienopyrrole unit to the phenyl, Boc, or benzoyl groups, respectively. However, whereas for the frontier molecular orbitals of all investigated DTPs very similar trends can be observed, the residues at the nitrogen of iso-DTPs appear to have a larger impact in this regard and the molecular orbitals of the various iso-DTPs differ more strongly.
Chapter 3

Calculations were carried out with the Gaussian 09 program. Geometry optimizations and energy calculations were performed via DFT methods using the B3LYP correlation/exchange functional and the 6-311+G(d) basis set. Molecular orbital surfaces were generated utilizing the Gauss View 5.0 program with an isovalue of 0.02. Alkyl chains were shortened to ethyl in order to save computational time.

**Figure 3.4:** Frontier molecular orbital surfaces of iso-DTPs bearing the residue R at the nitrogen.
3.4 Optoelectronic properties of iso-DTPs

The optoelectronic properties of the synthesized iso-DTPs 126, 132, 206, 207, 216, 218, and 219 bearing a hydrogen, Boc, benzoyl, hexyl, 2-ethylhexyl, 2-hexyldecyl, or phenyl residue at the nitrogen were determined. UV-Vis absorption spectra were recorded in THF solution and from the onset of the absorption band with the lowest energy the optical energy gap $E_g$ was calculated. Moreover, the HOMO energy level of iso-DTPs was derived from the onset oxidation potential in the cyclic voltammogram during their electropolymerization (Chapter 3.5). With $E_g$ and the HOMO energy level the LUMO energy level was then calculated.

With the exception of benzoyl-substituted iso-DTP 206, the absorption bands in the UV-Vis spectra of all prepared iso-DTPs are hypsochromically shifted compared to the spectra of respective DTP analogues (Figure 3.5, Figure 3.6, Table 3.3). This finding corresponds to increased optical energy gaps. Thus, alkyl-substituted iso-DTPs 207, 216, and 218 show an onset absorption at 291 nm due to an optical energy gap of 4.23 eV, which is increased by 0.33 eV compared to alkyl-substituted DTPs 60, 64, and 78. Furthermore, they exhibit only

![Figure 3.5: UV-Vis absorption spectra of iso-DTPs 126 and 207 measured in THF solution.](image-url)
one broad band without a vibrational fine-structure in the spectrum at a $\lambda_{\text{max}}$ of 271 nm. As a representative example for alkyl-substituted iso-DTPs the UV-Vis spectrum of iso-DTP 207 bearing a hexyl chain at the nitrogen is shown in Figure 3.5. Similarly to corresponding DTPs, the extinction coefficients slightly decrease with increasing bulkiness of the alkyl residue, but the shapes of the spectra are not affected. The HOMO of alkyl-substituted iso-DTPs with an energy level of -5.60 eV is stabilized by 0.10 eV compared to the HOMO of DTP analogues, while the LUMO is more destabilized by 0.22 eV to -1.37 eV. Unsubstituted iso-DTP 126 exhibits a HOMO energy level of -5.56 eV and a LUMO energy level of -1.30 eV. These values are little higher compared to alkyl-substituted iso-DTPs with similar deviations as observed in the DTP series. Moreover, the onset absorption of iso-DTP 126 is slightly shifted to 291 nm corresponding to an increased optical energy gap of -4.26 eV (Figure 3.5). Hence, regarding the optoelectronic properties the same trends with hydrogen and alkyl substituents at the nitrogen are observed for both DTPs and iso-DTPs. These residues, however, only exhibit a very limited influence on the optoelectronic properties. This is also confirmed by DFT calculations mostly showing little direct contributions of the substituents to the frontier

### Table 3.3: Optoelectronic properties of iso-DTPs with different residues R attached at the nitrogen.

<table>
<thead>
<tr>
<th>Iso-DTP</th>
<th>R</th>
<th>$E_{\text{pa}}$</th>
<th>$E_{\text{onset}}$</th>
<th>HOMO$^0$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon$</th>
<th>$\lambda_{\text{onset}}$</th>
<th>$E_{\text{g}}$</th>
<th>LUMO</th>
<th>Potential Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>126</td>
<td>H</td>
<td>0.70</td>
<td>0.46</td>
<td>-5.56</td>
<td>265</td>
<td>10700</td>
<td>291</td>
<td>4.26</td>
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</tr>
<tr>
<td></td>
<td>DFT</td>
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<tr>
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<td>-5.60</td>
<td>271</td>
<td>10600</td>
<td>293</td>
<td>4.23</td>
<td>-1.37</td>
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</tr>
<tr>
<td></td>
<td>exp.</td>
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<tr>
<td>216</td>
<td>2-EtHex</td>
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<td>0.50</td>
<td>-5.60</td>
<td>271</td>
<td>10500</td>
<td>293</td>
<td>4.23</td>
<td>-1.37</td>
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<tr>
<td></td>
<td>exp.</td>
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<tr>
<td>206</td>
<td>COPh</td>
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<tr>
<td>132</td>
<td>Boc</td>
<td>0.88</td>
<td>0.77</td>
<td>-5.87</td>
<td>235</td>
<td>20300</td>
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<td></td>
</tr>
</tbody>
</table>

Potentials are referenced vs. $\text{Fc/Fc}^+$; $a$ $E_{\text{pa}}$: anodic peak potential (scan rate 100 mV/s); $b$ Redox potential of $\text{Fc/Fc}^+$ is -5.1 eV on the Fermi scale$^{[22]}$; $c$ R=Et
molecular orbitals (Chapter 3.3). The observed differences between DTP and iso-DTP analogues bearing hydrogen or alkyls can therefore mostly be attributed to structural variations in the dithienopyrrole cores. Changing the relative positions of the two sulphurs and the nitrogen in iso-DTPs leads to a stabilization of the HOMO by about 0.1 eV and to a more pronounced destabilization of the LUMO by circa 0.2 eV. Consequently, the optical energy gap is increased by about 0.3 eV.

This trend in the two series can also be observed for the Boc-substituted derivatives, where iso-DTP 132 exhibits a HOMO energy level of -5.87 eV and a LUMO energy level of -1.71 eV (Table 3.3). In the UV-Vis spectrum an onset absorption at 298 nm corresponds to an $E_g$ of 4.16 eV (Figure 3.6). Furthermore, the compound shows one band at 235 nm and an adjacent band at 247 nm with a shoulder at 255 nm. As indicated by the electronic distributions in the frontier molecular orbitals (Chapter 3.3), upon HOMO-LUMO excitation electron density is shifted from the iso-DTP core of 132 to the Boc residue. Therefore, the relatively broad band at 277 nm with decreased extinction coefficients exhibits a partial charge transfer character. The same feature can be observed in the UV-Vis spectrum of benzoyl-substituted iso-DTP 206, because the compound exhibits a broad charge transfer band at 307 nm with an onset absorption at 349 nm (Figure 3.6, Table 3.3). Moreover, a band at 225 nm with a relatively broad shoulder at 256 nm appears. In comparison to the other

Figure 3.6: UV-Vis absorption spectra of iso-DTPs 132, 219, and 206 measured in THF solution.
prepared iso-DTP derivatives the strongly red-shifted onset absorption results in a decreased optical energy gap of 3.55 eV. Hence, the HOMO-LUMO gap of benzoyl-substituted iso-DTP 206 is even slightly lower than the $E_g$ of DTP analogue 97. This is in particular remarkable, as the change in the backbone rather causes an increase of the optical energy gap (vide supra).

With energy levels of -5.94 eV, respectively -2.39 eV, both HOMO and LUMO are, however, stabilized by about 0.2 eV compared to the frontier molecular orbitals of benzoyl-substituted DTP 97. Thus, the tendency of a stabilized HOMO energy level in iso-DTPs is more pronounced in benzoyl-substituted compound 206, but the stabilized LUMO stands in contrast to the trend of a destabilized LUMO for iso-DTPs bearing hydrogen, alkyls, or Boc substituents. Considering the electronic distribution in the frontier molecular orbitals derived from DFT calculations, these properties can be rationalized (Chapter 3.3). The HOMO is only located on the dithienopyrrole backbone and is therefore indirectly influenced by negative inductive effects of the benzoyl moiety. The LUMO, on the other hand, is affected to a greater extent by the benzoyl residue because of the major direct participation of the substituent to this frontier molecular orbital. In contrast to that, the phenyl residue in iso-DTP 219 directly contributes to both the HOMO and the LUMO. Therefore, upon HOMO-LUMO excitation no charge transfer occurs and no CT-band appears in the UV-Vis spectrum (Figure 3.6). Instead, the compound shows a band at 265 nm with a shoulder at 247 nm and a second band at 304 nm with a shoulder at 296 nm. Compared to unsubstituted iso-DTP 126, the absorption onset is red-shifted to 317 nm and corresponds to a decreased optical energy gap of 3.91 eV (Table 3.3), which is very similar to the HOMO-LUMO gap of phenyl-substituted DTP analogue 65. In accordance with the general trend in the series, compared to DTP analogue 65 the HOMO of phenyl-substituted iso-DTP 219 is stabilized by 0.08 eV to -5.68 eV.

Hence, the similar optical gap is due to the slightly stabilized LUMO energy level of -1.77 eV. As in benzoyl-substituted iso-DTP 206, in iso-DTP 219 the substituent at the nitrogen thus opposes the trend of destabilized LUMOs in iso-DTPs.

The experimentally determined values of the HOMO energy levels in the prepared iso-DTPs agree reasonably well with the values obtained from DFT calculations (Table 3.3) and the deviations are similarly small as in the DTP series (Chapter 2.4). Hence, the same trends can be observed in the experimental and theoretical properties and energetic variations of the frontier molecular orbitals were not profoundly caused by experimental conditions. The
described structure-property relationships can thus be attributed to the structure of iso-DTPs and constitute inherent features of these compounds. Yet, the calculated LUMO energy levels are again far too high. As in DTPs the best agreement between experimental and theoretical values is found for the benzoyl-substituted derivative 206 and the worst agreement is observed for iso-DTPs bearing alkyl residues. The respective differences of 0.54 eV and 1.07 eV are, however, far more pronounced. In Figure 3.7 the experimentally determined HOMO and LUMO energy levels of the synthesized iso-DTPs are summarized.

**Figure 3.7:** Experimentally determined HOMO (blue) and LUMO (red) levels of prepared iso-DTPs with different residues R attached at the nitrogen.
3.5 Electropolymerization of iso-DTPs

All prepared iso-DTPs bearing different residues at the nitrogen were potentiodynamically polymerized in an electrochemical cell on a platinum working electrode (Scheme 3.12). The respective monomers were used in millimolar concentrations in a solution of TBA-PF₆ as the supporting electrolyte. After the electropolymerization, the obtained films were subjected to several scans in a monomer-free electrolyte solution until a stable current response was recorded. At this “conditioning” phase residual short p(iso-DTP)s in the film were further polymerized. Subsequently, the respective films were characterized via cyclic voltammetry applying different scan rates between 10 mV/s and 100 mV/s. Finally, 30 cycles were measured with a scan rate of 100 mV/s to investigate the film stability.

\[ \text{Scheme 3.12: Electropolymerization of synthesized iso-DTPs 126, 207, 216, 218, 219, 206, and 132.} \]

In Figure 3.8 cyclic voltammograms of electropolymerization and following film characterization of unsubstituted iso-DTP 126 are shown. From the first scan in the polymerization the onset oxidation potential of iso-DTP 126 was determined to 0.46 V. This value corresponded to a HOMO energy level of -5.56 eV. Increasing the number of scans, the onset oxidation of the monomer continuously shifted to higher potentials and reached the frontier of the electrochemical solvent window after ten cycles. This indicated a slow ion diffusion through the p(iso-DTP) film \( P_{ec}^{126} \) on the working electrode. Therefore, only a thin polymer film could be obtained which did not grow further upon conducting more scans. In the monomer-free electrolyte solution unsubstituted \( P_{ec}^{126} \) exhibited a broad oxidation wave with an onset oxidation potential of 0.28 V (Table 3.4). This corresponded to a HOMO energy level of -5.38 eV. With increasing scan rate the anodic and cathodic peak currents increased linearly. However, when 30 cycles were recorded, the currents decreased considerably. The comparison of the released charges of the second and the 30th scan revealed a 31% loss of electrophoric material, clearly showing the moderate stability of the polymer film (Table 3.4).
Figure 3.8: Electropolymerization of iso-DTP monomer 126 with a hydrogen residue at the nitrogen (a) and the characterization of the obtained film $P_{ec126}$ using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents $I_{pa}$ at 0.63 V and the cathodic peak currents $I_{pc}$ from the applied scan rate (d).

The synthesized iso-DTPs 207, 216, and 218 bearing hexyl, 2-ethylhexyl, and 2-hexyldecyl chains were electropolymerized as well (Figure 3.9, 3.10, and 3.11). Independent from the alkyl group, monomers 207, 216, and 218 exhibited an onset oxidation of 0.50 V corresponding to a HOMO energy level of -5.60 eV. As in the case of unsubstituted iso-DTP 126, the onset oxidation potentials of alkyl-substituted iso-DTPs increased with increasing number of scans and reached the edge of the solvent window after ten scans. Hence, again only thin p(iso-DTP) films could be obtained. Because alkyl residues increase the solubility of iso-DTPs and the respective polymerization intermediates in organic solvents, it was more difficult to obtain insoluble p(iso-DTP) films on the working electrode. Similarly to the p(DTP) analogues (Chapter 2.5), the neutral polymers thus began to dissolve when negative potentials were applied during the backsweep. Nevertheless, after several scans films of alkyl-substituted p(iso-DTP)s $P_{e207}$, $P_{e216}$, and $P_{e218}$ were obtained from the respective iso-DTPs.
Chapter 3

Figure 3.9: Electropolymerization of iso-DTP monomer 207 with a hexyl residue at the nitrogen (a) and the characterization of the obtained film P_{ec}207 using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents I_{pa} and the cathodic peak currents I_{pc} from the applied scan rate (d).

Table 3.4: Optoelectronic properties of electrochemically prepared p(iso-DTP)s bearing different residues R at the nitrogens. The peak potentials E_{pa} and E_{pc}, the onset oxidation potentials E_{onset}, and the HOMO energy levels were determined via cyclic voltammetry in a monomer-free electrolyte solution. The values of λ_{onset} and the energy gap E_g were obtained from the UV-Vis-NIR spectra measured in a spectreochemical setup. The LUMO energy levels were calculated from the HOMO energy levels and the energy gaps.

<table>
<thead>
<tr>
<th>p(iso-DTP)</th>
<th>R</th>
<th>E_{pa}</th>
<th>E_{pc}</th>
<th>E_{onset}</th>
<th>HOMO</th>
<th>λ_{onset}</th>
<th>E_g</th>
<th>LUMO</th>
<th>Film loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_{ec}126</td>
<td>H</td>
<td>0.52</td>
<td>0.28</td>
<td>-5.38</td>
<td>490</td>
<td>2.53</td>
<td>-2.85</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>P_{ec}207</td>
<td>Hex</td>
<td>0.51</td>
<td>0.21</td>
<td>-5.31</td>
<td>562</td>
<td>2.21</td>
<td>-3.10</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>P_{ec}216</td>
<td>2-EtHex</td>
<td>0.51</td>
<td>0.20</td>
<td>-5.30</td>
<td>559</td>
<td>2.22</td>
<td>-3.08</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>P_{ec}218</td>
<td>2-HexDec</td>
<td>0.41</td>
<td>0.24</td>
<td>-5.34</td>
<td>560</td>
<td>2.21</td>
<td>-3.13</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>P_{ec}219</td>
<td>Ph</td>
<td>0.44</td>
<td>0.55</td>
<td>0.11</td>
<td>-5.21</td>
<td>738</td>
<td>1.68</td>
<td>-3.53</td>
<td>28</td>
</tr>
<tr>
<td>P_{ec}206</td>
<td>COPh</td>
<td>0.50</td>
<td>0.34</td>
<td>0.23</td>
<td>-5.33</td>
<td>782</td>
<td>1.59</td>
<td>-3.74</td>
<td>9</td>
</tr>
<tr>
<td>P_{ec}132</td>
<td>Boc</td>
<td>0.62</td>
<td>0.21</td>
<td>0.21</td>
<td>-5.31</td>
<td>628</td>
<td>1.97</td>
<td>-3.34</td>
<td>19</td>
</tr>
</tbody>
</table>

Potentials are referenced vs. Fc/Fc⁺; a E_{pa}: anodic peak potential (scan rate 100 mV/s); b E_{pc}: cathodic peak potential (scan rate 100 mV/s); c Redox potential of Fc/Fc⁺ is -5.1 eV on the Fermi scale; d Determined as the difference of exchanged charges during scan 2 and scan 30; e Could not be determined
Figure 3.10: Electropolymerization of iso-DTP monomer 216 with a 2-ethylhexyl residue at the nitrogen (a) and the characterization of the obtained film \( P_{ec216} \) using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents \( I_{pa} \) and the cathodic peak currents \( I_{pc} \) from the applied scan rate (d).

The onset oxidation potentials of the polymer films were very similar for all investigated \( p(iso-DTP) \)s with alkyl residues. Hexyl-substituted derivative \( P_{ec207} \) exhibited an onset oxidation of 0.21 V corresponding to a HOMO energy level of -5.31 eV (Table 3.4). 2-Ethylhexyl-substituted \( p(iso-DTP) \) \( P_{ec216} \) possessed an onset oxidation of 0.20 V and 2-hexyldecyl-substituted polymer \( P_{ec218} \) showed an onset oxidation of 0.24 V due to similar HOMO energy levels of -5.30 eV and -5.34 eV, respectively. With increasing scan rate the anodic and cathodic peak currents of all alkyl-substituted \( p(iso-DTP) \)s increased linearly. Nevertheless, the obtained films were quite unstable and after 30 cycles with a scan rate of 100 mV/s, the currents decreased very strongly. Comparing the released charges of the second and the 30th scan revealed that up to 63% of the material was lost (Table 3.4). This stood in contrast to the high stability of the \( p(DTP) \) analogues, which showed only minor degradations of 3-6% (Chapter 2.5).
During the electropolymerization of phenyl-substituted iso-DTP \( \text{P}_{\text{ec}} \text{219} \) an onset oxidation of 0.58 V was observed corresponding to a HOMO energy level of -5.68 eV (Figure 3.12). With increasing number of scans the oxidation signal of the monomer shifted to higher potentials, but the current still slightly increased. This indicated the growth of the p(iso-DTP) on the working electrode. The obtained polymer \( \text{P}_{\text{ec}} \text{219} \) showed an onset oxidation of 0.11 V due to a HOMO energy level of -5.21 eV (Table 3.4). This was far lower than the HOMO energy level of p(DTP) analogue \( \text{P}_{\text{ec}} \text{65} \), although phenyl-substituted DTP monomer 65 exhibits similar HOMO and LUMO energy levels as iso-DTP monomer 219. In the cyclic voltammograms of p(iso-DTP) \( \text{P}_{\text{ec}} \text{219} \) a very broad current response was visible with an anodic peak potential of 0.44 V and a cathodic peak potential of 0.55 V. Moreover, the linear dependency of the peak currents to the scan rate showed that the film was well adhered on the electrode. Nevertheless, after 30 cycles the current decreased considerably indicating that 28% of electrophoric material was lost (Table 3.4).
Figure 3.12: Electropolymerization of iso-DTP monomer 219 with a phenyl residue at the nitrogen (a) and the characterization of the obtained film $P_{ec}$219 using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents $I_{pa}$ and the cathodic peak currents $I_{pc}$ from the applied scan rate (d).

Iso-DTP 206 bearing a benzoyl residue at the nitrogen exhibited an onset oxidation of 0.84 V due to a HOMO energy level of -5.94 eV (Figure 3.13). Although the oxidation signal did not further shift to higher potentials with increasing number of scans, the currents only slightly increased. Hence, again just a very thin p(iso-DTP) film was obtained on the working electrode. The polymer $P_{ec}$206 exhibited an onset oxidation of 0.23 V corresponding to a HOMO energy level of -5.33 eV (Table 3.4). While the anodic peak currents showed slight deviations from the linear relationship to the scan rate, after 30 cycles only 9% of the material was lost (Table 3.4). Thus, benzoyl-substituted derivative $P_{ec}$206 was by far the most stable p(iso-DTP) in the investigated series.

Boc-substituted iso-DTP 132 possessed an oxidation onset of 0.77 V corresponding to a HOMO energy level of -5.87 eV (Figure 3.14). Similarly to most other iso-DTP monomers, the oxidation signal, however, continuously shifted to higher potentials reaching the frontier of
the solvent window after 20 scans. Therefore, electropolymerization of iso-DTP 132 just resulted in a thin film of $P_{ec}$132. This p(iso-DTP) showed an onset oxidation of 0.21 V due to a HOMO energy level of -5.31 eV (Table 3.4). The obtained polymer was well adhered to the electrode, as the peak currents linearly increased with the scan rate. Yet, the current decrease after 30 cycles was relatively large indicating the low stability of the film with a loss of 16% of electrophoric material (Table 3.4).

Subsequently, the electrochemically prepared p(iso-DTP) films were investigated via spectroelectrochemistry in a solution of TBA-PF₆ in acetonitrile using a previously described setup (Figure 3.15). Because herein a platinum working electrode was used, the same materials were obtained for both the electrochemical and the spectroelectrochemical characterizations. Moreover, in order to obtain the UV-Vis-NIR spectrum of the neutral polymer film without any oxidized parts a potential of -500 mV vs. Ag/AgCl was always applied prior to the spectroelectrochemical measurements.
Figure 3.14: Electropolymerization of iso-DTP monomer 132 with a Boc residue at the nitrogen (a) and the characterization of the obtained film P_{ec}132 using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents \( I_{pa} \) and the cathodic peak currents \( I_{pc} \) from the applied scan rate (d).

All neutral p(iso-DTP)s exhibited only a shoulder in the visible range of a band that extended to the UV region. The onset absorption was red-shifted from 490 nm for unsubstituted polymer P_{ec}126 to about 560 nm for alkyl-substituted P_{ec}207, P_{ec}216, and P_{ec}218 (Table 3.4). A further shift of the onset absorption to lower energies was observed for Boc-substituted P_{ec}132 with 628 nm, phenyl-substituted P_{ec}219 with 738 nm and benzoyl-substituted P_{ec}206 with 783 nm (Table 3.4). Applying relatively high potentials of up to 1500 mV vs. Ag/AgCl to oxidize the p(iso-DTP)s, the UV-Vis-NIR spectra barely changed. Thus, the polymers with hydrogen, hexyl, phenyl, and benzoyl residues just showed a new low energy shoulder with an increased extinction. The spectrum of Boc-substituted p(iso-DTP) did, however, not change considerably.
Figure 3.15: UV-Vis-NIR spectra obtained from spectroelectrochemical measurements of p(iso-DTP)s bearing hydrogen (Pec126, a), hexyl (Pec207, b), 2-ethylhexyl (Pec216, c), 2-hexyldecyl (Pec218, d), phenyl (Pec219, e), benzoyl (Pec206, f), or Boc (Pec132, f) residues at the nitrogens. Applied voltages are stated vs. Ag/AgCl. Artefacts are marked with * in the spectra.
In Figure 3.16 the energy diagram of the electrochemically prepared p(iso-DTP)s is shown. The HOMO energy levels of the polymers were very similar indicating that the different residues at the nitrogens only had a small influence in this regard. The slight increase of the HOMO energy level of benzoyl-substituted p(iso-DTP) $P_{ec}206$ stood in contrast to the influence of the benzoyl residue in p(DTP) analogue $P_{ec}97$, where the HOMO energy level was largely decreased by 0.31 eV (Chapter 2.5). On the other hand, the HOMO energy level of phenyl-substituted p(iso-DTP) $P_{ec}219$ was destabilized by 0.17 eV compared to unsubstituted analogue $P_{ec}126$. This trend could also be seen in the p(DTP) series between the analogues $P_{ec}65$ and $P_{ec}50$. Furthermore, the similar HOMO energy levels of the polymers bearing hydrogen, alkyl, or Boc units were also observed in both p(DTP)s and p(iso-DTP)s. Nevertheless, the influence of the different substituents on the LUMO was more pronounced in the p(iso-DTP) series. Whereas the LUMO energy levels of p(DTP)s bearing Boc, alkyl, or phenyl residues were increased compared to the LUMO energy of the unsubstituted polymer, the LUMO of p(iso-DTP) analogues $P_{ec}132$, $P_{ec}207$, $P_{ec}216$, $P_{ec}218$, and $P_{ec}219$ were considerably stabilized compared to unsubstituted p(iso-DTP) $P_{ec}126$. Moreover, the LUMO energy level of benzoyl-substituted $P_{ec}206$ was also largely decreased by 0.89 eV. Comparing p(DTP) and p(iso-DTP) series bearing the same residue at the nitrogens both the HOMO and the LUMO of the p(iso-DTP)s were stabilized, yet depending on the specific residue to a different extent. As a consequence, the energy gaps of the p(iso-DTP)s were larger with hydrogen or alkyl moieties, smaller with phenyl or benzoyl substituents, and almost the same with a Boc residue compared to the $E_g$ of the p(DTP) analogues.

![Energy Diagram](image)

**Figure 3.16:** Energy diagram showing the HOMO energy levels (blue), the LUMO energy levels (red) and the energy gaps $E_g$ of electrochemically prepared p(iso-DTP)s bearing different residues R at the nitrogens. Energy levels of all alkyl-substituted p(iso-DTPs) are similar to hexyl-substituted $P_{ec}207$. 

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3.6 Chemical oxidative polymerization of iso-DTPs

Subsequently, alkyl-substituted iso-DTP monomers 207, 216, and 218 were applied in chemical oxidative polymerizations with iron trichloride as the oxidant (Scheme 3.13). The thus obtained products were partly soluble in THF and could therefore be investigated in solution.

![Chemical oxidative polymerization of alkyl-substituted iso-DTPs](image)

**Scheme 3.13:** Chemical oxidative polymerization of alkyl-substituted iso-DTPs 207, 216, and 218.

However, application of more than one equivalent of iron trichloride afforded only insoluble solids. The polymers were dedoped with aqueous hydrazine, washed with n-hexane to remove small polymers, and finally extracted with THF. The obtained yields of the respective soluble fraction were considerably larger than for the analogous p(DTP)s (Chapter 2.6). Analyses by GPC indicated an average polymer chain length of only four to ten repeat units for the p(iso-DTP)s and relatively large polydispersities between 1.5 and 1.9 (Table 3.5). Moreover, in the $^1$H NMR spectra of p(iso-DTP)s $P_{ox207}$, $P_{ox216}$, and $P_{ox218}$ besides signals corresponding to the aliphatic residues only one broad signal in the aromatic region could be observed, respectively.

**Table 3.5:** Obtained yields of oxidatively polymerized p(iso-DTP)s with alkyl substituents at the nitrogens. Number average molar masses $M_n$, mass average molar masses $M_w$, polydispersities D, and average numbers of repeat units in the polymer chain n of p(iso-DTP)s according to GPC analyses in THF.

<table>
<thead>
<tr>
<th>p(iso-DTP)</th>
<th>Alk</th>
<th>Yield [%]</th>
<th>$M_n$ [g/mol]</th>
<th>$M_w$ [g/mol]</th>
<th>D</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{ox207}$</td>
<td>Hex</td>
<td>71</td>
<td>1300</td>
<td>2000</td>
<td>1.5</td>
<td>5.2</td>
</tr>
<tr>
<td>$P_{ox216}$</td>
<td>2-EtHex</td>
<td>49</td>
<td>1200</td>
<td>2200</td>
<td>1.9</td>
<td>4.2</td>
</tr>
<tr>
<td>$P_{ox218}$</td>
<td>2-HexDec</td>
<td>42</td>
<td>4000</td>
<td>6900</td>
<td>1.7</td>
<td>10.0</td>
</tr>
</tbody>
</table>

DFT calculations on ethyl-substituted iso-DTP trimer were subsequently carried out. Similarly to the DTP analogue the transoid configuration was shown to be slightly more
stable than the cisoid structure (Figure 3.17). However, the repeat units in the cross-conjugated iso-DTP trimer are twisted more strongly (33°) and considerably deviate from a coplanar geometry, where the overlap of the π-orbitals would be optimal. Thus, the effective conjugation length of p(iso-DTP)s is decreased compared to p(DTP)s. Considering respective polymers with the same chain lengths a blue-shifted absorption can be expected for p(iso-DTP)s. Nevertheless, the short chain lengths of the obtained p(iso-DTP)s were the dominating feature of the polymers and the geometry only played a minor role regarding the opto-electronic properties (vide infra).

Figure 3.17: Geometry optimized structures of the iso-DTP trimer with ethyl residues at the nitrogens. Calculations were carried out with the Gaussian 09 program[19]. Geometry optimizations were performed via DFT methods using the M06-2X correlation/exchange functional[24] and the 6-311G basis set.

The optoelectronic properties of soluble oxidatively prepared p(iso-DTP)s were then determined via UV-Vis spectroscopy and cyclic voltammetry (Table 3.6). Because Pox218 with the bulky 2-hexyldecyl substituent exhibited the longest polymer chain, it also possessed the lowest HOMO-LUMO energy gap in the series (Figure 3.18). The shorter polymers Pox207 and Pox216 bearing hexyl or 2-ethylhexyl residues showed an onset absorption at shorter wavelengths corresponding to a larger £g. Due to the very limited degree of polymerization, the soluble polymers exhibited much higher HOMO-LUMO energy gaps compared to the electrochemically prepared p(iso-DTP)s (Chapter 3.5). A similar trend could also be observed comparing electrochemically and oxidatively prepared p(DTP)s (Chapter 2.6).

Furthermore, in the cyclic voltammograms all three alkyl-substituted p(iso-DTP)s exhibited similar onset oxidation potentials corresponding to a HOMO energy level of about -5.5 eV (Table 3.6). Compared to the electrochemically prepared p(iso-DTP)s (Chapter 3.5) the soluble polymers possessed decreased HOMO and increased LUMO energy levels due to the relatively short chain lengths. Similarly to the p(DTP) series, the solubility determined the
possible polymerization degree of the soluble p(iso-DTP)s during the chemical oxidative polymerization. Thus, the solubilizing effect of the residues attached at the nitrogens was the most important structural aspect regarding the optoelectronic properties.

![Normalized UV-Vis absorption spectra of soluble oxidatively prepared p(iso-DTP)s](image)

**Figure 3.18:** Normalized UV-Vis absorption spectra of soluble oxidatively prepared p(iso-DTP)s $P_{ox}^{207}$, $P_{ox}^{216}$, and $P_{ox}^{218}$ bearing different alkyl residues at the nitrogens in THF solution.

**Table 3.6:** Optoelectronic properties of soluble oxidatively prepared p(iso-DTP)s bearing different alkyl residues at the nitrogens. The onset oxidation potentials $E_{onset}$ and the HOMO energy levels were determined via cyclic voltammetry with TBA-PF$_6$ (0.1 M) as the supporting electrolyte in THF. The values of $\lambda_{\text{max}}$, $\lambda_{\text{onset}}$, and the energy gap $E_g$ were obtained from UV-Vis spectra measured in THF solution. The LUMO energy levels were calculated from the HOMO energy levels and the energy gaps $E_g$.

<table>
<thead>
<tr>
<th>p(iso-DTP)</th>
<th>Alk</th>
<th>$E_{\text{onset}}$</th>
<th>HOMO$^a$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\lambda_{\text{onset}}$</th>
<th>$E_g$</th>
<th>LUMO $^b$</th>
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<tbody>
<tr>
<td>$P_{ox}^{207}$</td>
<td>Hex</td>
<td>0.34</td>
<td>-5.44</td>
<td>$^b$ 418</td>
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<tr>
<td>$P_{ox}^{216}$</td>
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<td>421</td>
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<td>-2.52</td>
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<tr>
<td>$P_{ox}^{218}$</td>
<td>2-HexDec</td>
<td>0.38</td>
<td>-5.48</td>
<td>$^b$ 455</td>
<td>2.73</td>
<td>-2.75</td>
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</table>

Potentials are referenced vs. Fc/Fc$^+$; $^a$ Redox potential of Fc/Fc$^+$ is -5.1 eV on the Fermi scale$^{22}$; $^b$ Could not be determined.
3.7 Summary

In this Chapter, first of all, several different methods for the synthesis of isomeric iso-DTPs (Figure 3.19) were investigated. Analogous to the mostly applied strategy for the preparation of DTPs, the amination of 2,2'-dibromo-3,3'-bithiophene afforded Boc-substituted iso-DTP 132. However, other derivatives bearing a hexyl or a benzoyl residue at the nitrogen were not accessible. Alternative strategies involving aminations of 2-bromothiophenes and a subsequent ring closure via C-C coupling as well as a Cadogan reaction of the corresponding nitrobithiophene precursor proved not to be viable synthetic routes either. Hence, the Boc substituent of prepared iso-DTP 132 was cleaved off to give unfunctionalized iso-DTP 126, which was then applied in various substitution reactions. Thus, three different alkyl-substituted iso-DTPs 207, 216, and 218 were prepared from the corresponding iodide or tosylate, phenyl-substituted derivative 219 was obtained in a Buchwald-Hartwig amination with bromobenzene, and finally benzoyl-substituted iso-DTP 206 was afforded in a Steglich reaction with benzoic acid. DFT calculations were performed on all synthesized iso-DTPs and indicated that the attached residues at the nitrogen mostly influence the HOMO only indirectly, while especially conjugated moieties directly contribute to the LUMO. Moreover, the electronic distributions in the frontier molecular orbitals are affected to a greater extent by the substituent at the nitrogen than for analogous DTPs. The experimental determination of the optoelectronic properties showed that in comparison to DTPs the cross-conjugated backbone in iso-DTPs leads to decreased HOMO and increased LUMO energy levels. Yet, the larger influence of the phenyl or benzoyl substituent on the LUMO results in similar energy gaps as in the DTP analogues.

![Figure 3.19: Structures of synthesized iso-DTPs.](image-url)
Electropolymerization of all prepared iso-DTPs afforded quite unstable p(iso-DTP) films, which upon oxidation only exhibited minor changes in the UV-Vis-NIR spectra. Compared to electrochemically prepared p(DTP)s both the HOMO and LUMO energy levels were decreased, but to a different extent depending on the residue at the nitrogens. Oxidative chemical polymerization of alkyl-substituted iso-DTPs 207, 216, and 218 afforded short polymers with an average chain length of up to ten repeat units. Here, the influence of substituents at the nitrogens on the optoelectronic properties could mostly be ascribed to the different solubilities of intermediate polymeric species. Thus, with the bulky 2-hexyldecyl moiety the longest p(iso-DTP) \( P_{\text{ox}218} \) was obtained exhibiting the lowest HOMO-LUMO energy gap in the series.
3.8 Experimental section

3.8.1 General methods

**Instruments and measurements**

Thin layer chromatography was carried out on aluminium plates, precoated with silica gel, Merck Si60 F254. Preparative column chromatography was performed on glass columns packed with silica gel (particle size 40–63 µm) from Macherey-Nagel. Melting points were determined using a Büchi Melting Point B-545. Thermogravimetric analyses were carried out with a TGA/SDTA 851e from Mettler Toledo. UV-Vis absorption spectra were recorded in THF solutions on a Perkin Elmer Lambda 19 spectrometer. FT-IR spectra were measured with a Perkim Elmer Spectrum 2000. NMR spectra were recorded on an Avance 400 spectrometer (1H NMR: 400 MHz, 13C NMR: 101 MHz). Chemical shifts (δ) are reported in ppm using residual solvent protons (1H NMR: δH = 7.26 for CDCl3; δH = 5.32 for CD2Cl2; δH = 3.58 for THF-d8; 13C NMR: δC = 77.16 for CDCl3; δC = 53.84 for CD2Cl2) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). Coupling constants J relate to proton-proton couplings. Protons at the α- or β-positions of iso-DTPs were assigned as Th-Hα or Th-Hβ, respectively. Elemental analyses were performed on an Elementar Vario EL. GC measurements were carried out using a Varian CP-3800 gas chromatograph. GC/EI-MS (70 eV) measurements were performed on a Shimadzu GCMS-QP2010 SE. Chemical ionisation (CI) mass spectra were measured on a Finnigan MAT SSQ-7000. High resolution MALDI mass spectra were performed on a Bruker SolariX using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix.

Cyclic voltammetry experiments were performed using a computer-controlled Autolab PGSTAT 30 potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferricenium couple. Deoxygenated acetonitrile dried over molecular sieves or THF dried via a MB SPS-800 solvent purifying system (M Braun) was used as the solvent. Solutions of tetrabutylammonium hexafluorophosphate (Sigma Aldrich) as the supporting electrolyte with a concentration of 0.1 M were applied and were blanketed with argon during the measurements. For electropolymerizations the respective monomer was used in a concentration of 0.01 M in acetonitrile. The
obtained film was washed with dry acetonitrile and subjected to several scans in a monomer-
free electrolyte solution until a stable current response was recorded (“conditioning”). Sub-
sequently, the respective film was characterized by cyclic voltammetry using different scan 
rates between 100 mV/s and 10 mV/s. At every scan rate three scans were conducted. 
Additionally, 30 scans were measured with a scan rate of 100 mV/s.
Spectroelectrochemical measurements of the polymer films were carried out in a 0.1 M 
solution of tetrabutylammonium hexafluorophosphate in dry acetonitrile. The applied setup 
has been described in detail in literature. A Princeton Applied Research PAR 363 
potentiostat was used together with a platinum working electrode, a Ag/AgCl reference 
electrode, and a platinum sheet as the counter electrode. Polymer films were prepared 
electrochemically as stated above, including the “conditioning” phase. During the recording 
of the UV-Vis-NIR spectra the applied potential was kept constant. In order to obtain the UV-
Vis-NIR spectrum of the neutral polymer film without any oxidized parts, a potential of -500 
mV vs. Ag/AgCl was applied at the beginning of the spectroelectrochemical measurements. 
Instrumental artefacts were removed and marked in the spectra. Moreover, the absorption 
in the UV-Vis region below 860 nm was adjusted to the absorption at higher wavelengths to 
obtain continuous spectra.
GPC-UV analyses with THF as eluent were performed at 1 mL/min on a Merck Hitachi 
LaChrom GPC system equipped with an L-7100 HPLC pump, L-7420 UV-Vis detector, and 
three columns (PSS SDV 103 Å, 104 Å, and 105 Å). The columns were kept in a column heater 
at 35 °C and were calibrated with polystyrene standards (Polymer Standards Service).
Quantum chemical calculations were carried out with the Gaussian 09 program. Alkyl 
residues were shortened to ethyl in order to save computational time. Geometry optimi-
izations and energy calculations were performed via DFT methods using the B3LYP or the 
M06-2X correlation/exchange functional and the 6-311+G(d) or the 6-311G basis set. 
Molecular orbital surfaces were generated utilizing the Gauss View 5.0 program with an 
isovalue of 0.02.
Materials

Ether (VWR), toluene (VWR), and THF (Sigma Aldrich) were dried and purified by a MB SPS-800 (MBraun). Mesitylene and dioxane were purchased from VWR and dried over calcium hydride. Chloroform, petroleum ether, dichloromethane, n-hexane, THF, dichlorobenzene, methanol, and pyridine were purchased from VWR and distilled prior to use. Acetic acid, acetic anhydride, and nitric acid (65%) were purchased from VWR. Hexylamine, 2-ethylhexylamine, and aniline were purchased from Merck and dried over calcium hydride. CuCl₂ was purchased from Merck and dried in vacuo at 150 °C prior to use. Sodium tert-butoxide, tetrabutylammonium hydrogensulfate, bromobenzene, copper(I) iodide, sodium hydroxide, triphenylphosphine, tosyl chloride, and anhydrous iron trichloride were purchased from Merck. 4-(Dimethylamino)pyridine (DMAP) was purchased from Fluka. Hexyl iodide, N,N'-dimethylhexylenediamine (DMEDA), N,N'-dicyclohexylcarbodiimide (DCC), and 2-ethylhexanol were purchased from Alfa Aesar. Potassium carbonate, tert-butyl carbamate, Pd(OAc)₂, Pd₂(dba)₃, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), tri-tert-butylphosphine, benzoic acid, 2-hexyldecanol, tetrabutylammonium fluoride trihydrate, and N-bromosuccinimide were purchased from Sigma Aldrich. Benzamide and n-butyl lithium were purchased from Acros Organics. 3-Bromothiophene was purchased from fluorochem. Pd(PPh₃)₄ was synthesized by S. Untch according to a published procedure. All synthetic steps were carried out under argon atmosphere.
3.8.2 Amination of dibromobithiophene

3,3’-Bithiophene (205)\(^{[2]}\)

\[
\begin{array}{c}
\text{S} & \text{S} \\
\text{C} & \text{C} \\
\text{C} & \text{C} \\
\text{C} & \text{C} \\
\text{C} & \text{C} \\
\text{S} & \text{S}
\end{array}
\]

A solution of 3-bromothiophene 59 (46.9 mL, 500 mmol) in ether (300 mL) was cooled to -70 °C. Within 30 min \(n\)-BuLi (1.6 M in \(n\)-hexane, 313 mL, 500 mmol) was added and the reaction mixture was stirred for 15 min. CuCl\(_2\) (67.9 g, 505 mmol, 1.01 eq) was added by portions and the resulting suspension was stirred for 1 h at -55 °C. Subsequently, the reaction mixture was stirred overnight, while slowly warmed to room temperature. After quenching with water (150 mL), the suspension was filtrated and the phases were separated. The organic phase was dried over MgSO\(_4\), filtrated, and the solvent was reduced \textit{in vacuo}. Afterwards, a colourless solid precipitated. The product 205 was separated and washed with \(n\)-hexane (29.9 g, 180 mmol, 72%). The analytical data was in accordance with literature.

\(\text{Mp.}:\ 124-127 ^\circ\text{C (lit.: 131-132 } ^\circ\text{C).}\)\(^{[2]}\)

\(\text{\textsuperscript{1}H NMR (CDCl}_3, 400 MHz): \delta = 7.39 (dd, J = 2.7 Hz, 1.5 Hz, 2 H, H2), 7.38 – 7.34 (m, 4 H, H4, H5) ppm.\)

\(\text{\textsuperscript{13}C NMR (CDCl}_3, 101 MHz): \delta = 137.37, 126.49, 126.22, 119.91 \text{ppm.}\)

2,2’-Dibromo-3,3’-bithiophene (130)\(^{[3]}\)

\[
\begin{array}{c}
\text{S} & \text{S} & \text{Br} & \text{Br} \\
\text{C} & \text{C} & \text{C} & \text{C} \\
\text{C} & \text{C} & \text{C} & \text{C} \\
\text{C} & \text{C} & \text{C} & \text{C} \\
\text{C} & \text{C} & \text{C} & \text{C} \\
\text{S} & \text{S}
\end{array}
\]

3,3’-Bithiophene 205 (3.33 g, 20.0 mmol) was dissolved in a 1:1 mixture of chloroform and glacial acetic acid (120 mL). NBS (7.12 g, 40.0 mmol, 2.00 eq) was added by portions and the reaction mixture was stirred at room temperature for 10 min. After quenching with saturated aqueous KOH (100 mL), the phases were separated and the organic phase was washed with water (50 mL). The solvent of the organic phase was evaporated under reduced pressure and the raw product was purified via column chromatography (SiO\(_2\), petroleum ether) to give 130 as a colourless solid. The analytical data was in accordance with literature. The product was stable in solution, but spontaneously decomposed in the solid state.

\(\text{\textsuperscript{1}H NMR (CDCl}_3, 400 MHz): \delta = 7.31 (d, J = 5.6 Hz, 2 H, H5), 7.09 (d, J = 5.6 Hz, 2 H, H4) \text{ppm.}\)

\(\text{\textsuperscript{13}C NMR (CDCl}_3, 101 MHz): \delta = 135.43, 129.28, 125.77, 111.30 \text{ppm.}\)
Dithieno[2,3-b:3',2'-d]pyrroles (iso-DTPs)

7-Tert-butyloxycarbonyl-7H-dithieno[2,3-b:3',2'-d]pyrrole (132) \[1\]

![Chemical Structure of 7-Tert-butyloxycarbonyl-7H-dithieno[2,3-b:3',2'-d]pyrrole (132)](image)

A suspension of CuI (3.85 g, 20.2 mmol, 0.20 eq), DMEDA (8.70 mL, 80.8 mmol, 0.80 eq), and K₂CO₃ (83.8 g, 606 mmol, 6.00 eq) in toluene (140 mL) was stirred for 30 min. Subsequently, tert-butyl carbamate (17.8 g, 152 mmol, 1.50 eq) and freshly prepared 2,2'-dibromo-3,3'-bithiophene 130 (32.7 g, 101 mmol) were added and the reaction mixture was heated at 110 °C for 2 d. After cooling to room temperature, the suspension was diluted with dichloromethane and filtered through a plug of celite. The raw product was purified via column chromatography (SiO₂, petroleum ether : dichloromethane = 3:1) to give iso-DTP 132 as a yellow solid (10.3 g, 37.0 mmol, 37%). The analytical data was in accordance with literature. 

Mp.: 72-74 °C (lit.: 72-73 °C). \[1\]

¹H NMR (CDCl₃, 400 MHz): δ = 7.17 (dd, J = 5.4 Hz, 1.3 Hz, 2 H, Th-Hₐ), 7.09 (d, J = 5.3 Hz, 1 H, Th-Hₐ), 7.03 (d, J = 5.3 Hz, 1 H, Th-Hₐ), 1.72 (s, 9 H, CH₃) ppm.

¹³C NMR (CDCl₃, 101 MHz): δ = 148.15, 137.79, 137.31, 126.42, 126.28, 121.45, 121.11, 117.34, 117.00, 85.78, 28.24 ppm.

UV-Vis (THF) λₘₐₓ (ε): 277 (sh, 3 200), 255 (sh, 13 500), 247 (17 000), 235 (20 300) nm.

Attempted synthesis of 7-benzoyl-7H-dithieno[2,3-b:3',2'-d]pyrrole (206)

![Chemical Structure of 7-benzoyl-7H-dithieno[2,3-b:3',2'-d]pyrrole (206)](image)

In a typical attempt, a suspension of CuI (776 mg, 4.08 mmol, 0.20 eq), DMEDA (1.76 mL, 16.3 mmol, 0.80 eq), and K₂CO₃ (19.7 g, 143 mmol, 7.00 eq) in toluene (40 mL) was stirred for 30 min. Subsequently, benzamide (5.59 g, 46.2 mmol, 2.26 eq) and freshly prepared 2,2'-dibromo-3,3'-bithiophene 130 (6.61 g, 20.4 mmol) were added and the reaction mixture was heated at 110 °C for 2 d. After cooling to room temperature, the suspension was diluted with dichloromethane and filtered through a plug of celite. Analyses via TLC and ¹H NMR spectroscopy indicated the presence of unreacted starting material 130, but the product could not be detected.
Attempted synthesis of 7-hexyl-7H-dithieno[2,3-b:3′,2′-d]pyrrole (207)

In a typical attempt, a suspension of Pd₂(db₃)₃ (0.46 g, 0.50 mmol, 0.10 eq), BINAP (1.25 g, 2.00 mmol, 0.40 eq), NaOtBu (1.15 g, 12.0 mmol, 2.40 eq), and freshly prepared 2,2′-dibromo-3,3′-bithiophene 130 (1.62 g, 5.00 mmol) in toluene (12 mL) was purged with argon. Subsequently, hexylamine (0.66 mL, 5.00 mmol, 1.00 eq) was added and the reaction mixture was heated at 110 °C. After 6 d still no product formation was observed. Only unreacted 130 and the side-products 2-bromo-3,3′-bithiophene and 3,3′-bithiophene 205 from the dehalogenation of dibromide 130 were detected via TLC, GC, and ¹H NMR spectroscopy.
3.8.3 Amination of bromothiophenes

\textbf{N-Hexyl-\textit{N},\textit{N-bis-}[2-[5-(triisopropylsilyl)thienyl]]amine (208)}

A suspension of 2-bromo-5-TIPS-thiophene 195 (13.4 g, 42.1 mmol, 2.00 eq), NaOtfBu (6.07 g, 63.1 mmol, 3.00 eq), Pd(OAc)$_2$ (0.47 g, 2.10 mmol, 0.10 eq), and BINAP (2.62 g, 4.21 mmol, 0.20 eq) in toluene (50 mL) was purged with argon. Hexylamine (2.77 mL, 21.0 mmol) was added and the reaction mixture was heated at 110 °C for 24 h. After cooling to room temperature, the suspension was diluted with dichloromethane and filtered through a plug of celite. The solvent of the filtrate was removed in vacuo and the obtained residue was purified via column chromatography (SiO$_2$, n-hexane) to yield 208 as a yellow solid (4.22 g, 7.30 mmol, 35%).

\textbf{Mp.:} 50-51 °C.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta$ = 6.99 (d, $J$ = 3.6 Hz, 2 H, H3), 6.58 (d, $J$ = 3.6 Hz, 2 H, H4), 3.70 – 3.65 (m, 2 H, N-CH$_2$), 1.78 – 1.67 (m, 2 H, N-CH$_2$-CH$_2$), 1.41 – 1.21 (m, 12 H, Si-CH, N-(CH$_2$)$_2$-(CH$_2$)$_3$), 1.09 (d, $J$ = 7.3 Hz, 36 H, Si-CH-C$_3$), 0.87 (t, $J$ = 7.0 Hz, 3 H, CH$_2$-CH$_3$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): $\delta$ = 158.94, 135.30, 123.51, 114.32, 57.69, 31.87, 27.64, 26.84, 22.97, 18.79, 14.17, 12.14 ppm.

MALDI-MS (HR): $m/z$ = calc. for C$_{32}$H$_{59}$NS$_2$Si$_2$: 577.36220; found: 577.36129 [M]$^+$; $\delta_{m/m}$ = 1.58 ppm.

\textbf{Attempted synthesis of N-phenyl-\textit{N},\textit{N-bis-}[2-[5-(triisopropylsilyl)thienyl]]amine (209)}

In a typical attempt, a suspension of 2-bromo-5-TIPS-thiophene 195 (2.42 g, 7.58 mmol, 2.00 eq), NaOtfBu (1.09 g, 11.4 mmol, 3.00 eq), Pd(OAc)$_2$ (85.1 mg, 0.38 mmol, 0.10 eq), BINAP (472 mg, 0.76 mmol, 0.20 eq), and aniline (0.35 mL, 3.79 mmol) in toluene (12 mL) was purged with argon. The reaction mixture was then heated at 110 °C for 23 h. After cooling to
room temperature, the suspension was diluted with dichloromethane and filtered through a plug of celite. Analyses via TLC and \(^1\)H NMR spectroscopy indicated the presence of unreacted starting material, but the target product could not be detected. The same result was obtained when Pd\(_2\)(dba)\(_3\) was applied as pre-catalyst instead of palladium acetate.

**Attempted synthesis of \(N\)-(2-ethylhexyl)-\(N,\)\(N\)-bis\(\{2\)-[5-(triisopropylsilyl)thienyl\}]amine (210)**

![Chemical structure of 210](image1)

In a typical attempt, a suspension of 2-bromo-5-TIP S-thiophene 195 (1.28 g, 4.01 mmol, 2.00 eq), NaO\(_t\)Bu (578 mg, 6.01 mmol, 3.00 eq), Pd(OAc)\(_2\) (45.0 mg, 0.20 mmol, 0.10 eq), and BINAP (250 mg, 0.40 mmol, 0.20 eq) in toluene (10 mL) was purged with argon. 2-Ethylhexylamine (0.33 mL, 2.00 mmol) was added and the reaction mixture was heated at 110 °C for 22 h. After cooling to room temperature, water (50 mL) and dichloromethane (30 mL) were added. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 50 mL). Analyses via TLC and \(^1\)H NMR spectroscopy indicated the presence of unreacted starting material, but the target product could not be detected. The same results were obtained when P(tBu)\(_3\) was applied as ligand instead of BINAP or when Pd\(_2\)(dba)\(_3\) as pre-catalyst together with dppf as ligand were applied, respectively.

**\(N\)-Hexyl-\(N,\)\(N\)-bis\(\{2\)-[3-bromo-5-(triisopropylsilyl)thienyl\}]amine (211)**

![Chemical structure of 211](image2)

A solution of \(N\)-bromosuccinimide (180 mg, 1.01 mmol, 2.10 eq) in chloroform (15 mL) was slowly added to a solution of amine 208 (279 mg, 0.48 mmol) in chloroform (25 mL) at 0 °C. After stirring for 3 h, the solvent of the reaction mixture was removed under reduced pressure and the obtained residue was purified via column chromatography (SiO\(_2\), petroleum ether) to give 211 as a colourless solid (345 mg). Part of the raw product could be re-crystallized from \(n\)-hexane (45 mg, 0.06 mmol, 13%).
Dithieno[2,3-b:3',2'-d]pyrroles (iso-DTPs)

Mp.: 62 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 6.90$ (s, 2 H, H3), $3.72 - 3.58$ (m, 2 H, N-CH$_2$), $1.79 - 1.68$ (m, 2 H, N-CH$_2$-CH$_2$), $1.42 - 1.21$ (m, 12 H, Si-CH, N-(CH$_2$)$_2$-(CH$_2$)$_3$), $1.09$ (d, $J = 7.3$ Hz, 36 H, Si-CH-CH$_3$), $0.87$ (t, $J = 7.0$ Hz, 3 H, CH$_2$-CH$_3$) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 151.57$, 137.12, 127.32, 103.47, 57.89, 31.58, 28.13, 26.54, 22.68, 18.68, 14.15, 11.73 ppm.

MALDI-MS (HR): $m/z$ = calc. for C$_{32}$H$_{57}$Br$_2$NS$_2$Si$_2$: 735.18139; found: 735.18111 [M]$^+$; $\delta_{m/m} = 0.38$ ppm.

7-Hexyl-2,5-bis(triisopropylsilyl)-7$H$-dithieno[2,3-b:3',2'-d]pyrrole (212)

![Chemical Structure]

To a solution of raw dibromide 211 (1.34 g, 1.82 mmol) in ether (60 mL) $n$-BuLi (1.6 M in $n$-hexane, 2.50 mL, 4.01 mmol, 2.20 eq) was slowly added at -70 °C. After stirring for 30 min, CuCl$_2$ (539 mg, 4.01 mmol, 2.20 eq) was added in one portion. The suspension was stirred overnight, while slowly warmed to room temperature. The reaction was quenched with wet ether (40 mL) and filtrated. The solvent of the filtrate was removed under reduced pressure and the obtained residue was purified via column chromatography (SiO$_2$, petroleum ether) to give 482 mg of the raw product 212 as a yellow solid. With further purification efforts no analytical purity of 212 could be reached.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 7.31$ (s, 2 H, H3), $4.09$ (t, $J = 7.2$ Hz, 2 H, N-CH$_2$), $2.02 - 1.94$ (m, 2 H, N-CH$_2$-CH$_2$), $1.42 - 1.30$ (m, 12 H, Si-CH, N-(CH$_2$)$_2$-(CH$_2$)$_3$), $1.14$ (d, $J = 7.4$ Hz, 36 H, Si-CH-CH$_3$), $0.87$ (t, $J = 7.1$ Hz, 3 H, CH$_2$-CH$_3$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): $\delta = 146.27$, 126.22, 124.79, 124.65, 50.00, 31.65, 28.84, 26.89, 22.95, 18.84, 14.13, 12.31 ppm.

MALDI-MS (HR): $m/z$ = calc. for C$_{32}$H$_{57}$NS$_2$Si$_2$: 575.34655; found: 575.34573 [M]$^+$; $\delta_{m/m} = 1.42$ ppm.
Chapter 3

7-Hexyl-7H-dithieno[2,3-b:3',2'-d]pyrrole (207)

A solution of raw TIPS-protected iso-DTP 212 (799 mg, 1.39 mmol) and tetrabutyl-ammonium fluoride (5.25 g, 16.6 mmol, 12.0 eq) in THF (35 mL) was stirred at room temperature overnight. Water (30 mL) and n-hexane (50 mL) were added, the phases were separated, and the aqueous phase was extracted with n-hexane (2 × 30 mL). The combined organic phase was dried over Na₂SO₄, filtrated, and the solvent of the filtrate was removed under reduced pressure. The obtained residue was purified via column chromatography (SiO₂, petroleum ether) to give 110 mg of a colourless oily mixture, which contained the target product 207. With further purification efforts no analytical purity of 207 could be reached.

¹H NMR (CDCl₃, 400 MHz): δ = 7.18 (d, J = 5.2 Hz, 2 H, Th-Hα), 6.84 (d, J = 5.2 Hz, 2 H, Th-Hβ), 4.09 (t, J = 7.1 Hz, 2 H, N-CH₂), 2.04 – 1.83 (m, 2 H, N-CH₂-CH₂), 1.43 – 1.25 (m, 6 H, N-(CH₂)₂-(CH₂)₃), 0.93 – 0.82 (m, 3 H, CH₃) ppm.

Further analytical data of pure iso-DTP 207 see Chapter 3.8.5.
3.8.4 Cadogan reaction with nitrobithiophene

2-Nitro-3,3'-bithiophene (213)\[11]\n
Fuming nitric acid (0.15 mL, 3.61 mmol, 1.20 eq) was slowly added to acetic anhydride (1 mL) at 5 °C and stirred for 10 min. Subsequently, the acidic mixture was slowly added to a suspension of 3,3'-bithiophene 205 (500 mg, 3.01 mmol) in acetic anhydride (3 mL) at 5 °C. After stirring for 1 h, the reaction mixture was poured onto ice water (20 mL) and dichloromethane (10 mL) was added. The phases were separated and the organic phase was washed with water (2 × 10 mL) and aqueous Na$_2$CO$_3$ (2 × 40 mL). Purification via column chromatography (SiO$_2$, petroleum ether : dichloromethane = 2:1) afforded 213 as a yellow solid (320 mg, 1.51 mmol, 50%).

Mp.: 88-89 °C (lit. 81-87 °C).\[26]\n
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.69 (dd, $J$ = 2.9 Hz, 1.2 Hz, 1 H, H2'), 7.48 (d, $J$ = 5.5 Hz, 1 H, H5), 7.39 (dd, $J$ = 5.1 Hz, 2.9 Hz, 1 H, H4'), 7.33 (dd, $J$ = 5.0 Hz, 1.2 Hz, 1 H, H5'), 7.11 (d, $J$ = 5.5 Hz, 1 H, H4) ppm.

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ = 137.31, 132.90, 131.13, 130.19, 128.78, 127.04, 125.46 ppm.

Cl-MS: m/z (%) = 212 (100) [M+H]$^+$.

Elemental analysis: calc. (%) for C$_8$H$_5$NO$_2$S$_2$: C 45.48, H 2.39, N 6.63, S 30.35; found: C 45.37, H 2.16, N 6.59, S 30.09.

Attempted synthesis of 7H-dithieno[2,3-b:3',2'-d]pyrrole (126)

In a typical attempt, 2-nitro-3,3'-bithiophene 213 (72.0 mg, 0.34 mmol) and triphenylphosphine (223 mg, 0.85 mmol, 2.50 eq) were put in a microwave tube and dissolved in dichlorobenzene (2 mL). The solution was purged with argon and then heated with 300 W at 210 °C for 45 min. Because no product was formed, the reaction mixture was heated again with 300 W at 210 °C for 45 min. However, only decomposition of the starting material 213 could be observed via TLC and GC.
3.8.5 N-substitution of unsubstituted iso-DTP

**7H-Dithieno[2,3-b:3',2'-d]pyrrole (126)**

A suspension of Boc-substituted iso-DTP 132 (3.80 g, 13.6 mmol) and K$_2$CO$_3$ (5.64 g, 40.8 mmol, 3.00 eq) in methanol (250 mL) was stirred at room temperature for 5 h. The solvent was removed under reduce pressure and the residue was dissolved in dichloromethane (200 mL) and water (150 mL). The phases were separated and the aqueous phase was extracted with dichloromethane (100 mL). The solvent of the combined organic phase was removed under reduced pressure and the obtained residue was purified via column chromatography (SiO$_2$, petroleum ether : dichloromethane = 3:1) to give iso-DTP 126 as a colourless solid (2.02 g, 11.3 mmol, 83%).

Mp.: 161 °C (dec.).

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta$ = 8.58 (s, 1 H, NH), 7.18 (d, $J$ = 5.3 Hz, 2 H, Th-$H_{\alpha}$), 6.89 (d, $J$ = 5.3 Hz, 2 H, Th-$H_{\beta}$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): $\delta$ = 139.40, 124.47, 117.30, 117.28 ppm.

Cl-MS: $m/z$ (%) = 180 (100) [M+H]$^+$.  
Elemental analysis: calc. (%) for C$_8$H$_5$NS$_2$: C 53.60, H 2.81, N 7.81, S 35.77; found: C 53.85, H 2.64, N 7.64, S 35.78.

UV-Vis (THF) $\lambda_{\text{max}}$ (e): 265 (10 700) nm.

**7-Hexyl-7H-dithieno[2,3-b:3',2'-d]pyrrole (207)**

A suspension of tetrabutylammonium hydrogensulfate (849 mg, 2.50 mmol, 2.50 eq) in toluene (25 mL) and aqueous NaOH (50%, 5 mL) was purged with argon for 15 min. Unsubstituted iso-DTP 126 (179 mg, 1.00 mmol) was added and the reaction mixture was stirred for 10 min. Subsequently, hexyliodide (0.30 mL, 2.00 mmol, 2.00 eq) was added dropwise and the reaction mixture was heated at 60 °C for 2 h. After cooling to room temperature,
water (25 mL) was added. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 30 mL). The combined organic phase was dried over MgSO₄, filtrated, and solvent of the filtrate was removed under reduced pressure. Purification via column chromatography (SiO₂, petroleum ether) afforded iso-DTP 207 as a colourless oil (241 mg 0.91 mmol, 91%).

\(^1\)H NMR (CD₂Cl₂, 400 MHz): \(\delta = 7.19\) (d, \(J = 5.3\) Hz, 2 H, Th-H\(\alpha\)), 6.86 (d, \(J = 5.3\) Hz, 2 H, Th-H\(\beta\)), 4.09 (t, \(J = 7.1\) Hz, 2 H, N-C\(\text{H}_2\)), 2.03 – 1.90 (m, 2 H, N-CH\(\text{H}_2\)-C\(\text{H}_2\)), 1.41 – 1.26 (m, 6 H, N-(CH\(\text{H}_2\))\(\text{C}_3\)), 0.88 (t, \(J = 7.1\) Hz, 3 H, CH\(\text{H}_3\)) ppm.

\(^{13}\)C NMR (CD₂Cl₂, 101 MHz): \(\delta = 140.64\), 122.83, 117.83, 116.37, 49.95, 31.69, 28.75, 26.87, 22.90, 14.16 ppm.

CI-MS: \(m/z\) (%) = 264 (100) [M+H]⁺.

Elemental analysis: calc. (%) for C\(_{14}\)H\(_{17}\)NS\(_2\): C 63.84, H 6.51, N 5.32, S 24.34; found: C 63.93, H 6.54, N 5.40, S 24.23.

UV-Vis (THF) \(\lambda_{\text{max}}\) (\(\varepsilon\)): 271 (10 600 nm).

2-Ethylhexyl tosylate (215)\(^{[17]}\)

Pyridine (5.70 mL, 70.0 mmol, 2.00 eq) was added to a solution of 2-ethylhexanol (5.49 mL, 35.0 mmol) in chloroform (37 mL) at 0 °C. Subsequently, tosyl chloride (10.0 g, 52.5 mmol, 1.50 eq) was added by portions and the reaction mixture was stirred for 3 h. After warming to room temperature, water (125 mL) and ether (125 mL) were added. The phases were separated and the organic phase was washed with hydrochloric acid (1 M, 4 × 50 mL), aqueous Na₂CO₃ (2 × 60 mL), and brine (2 × 60 mL). The solution was dried over MgSO₄, filtrated, and the solvent of the filtrate was removed under reduced pressure. The obtained residue was purified via column chromatography (SiO₂, petroleum ether) to yield 215 as a colourless oil (6.08 g, 21.4 mmol, 61%). The analytical data was in accordance with literature.

\(^1\)H NMR (CDCl₃, 400 MHz): \(\delta = 7.79\) (d, \(J = 8.3\) Hz, 2 H, o-Ph-H), 7.34 (d, \(J = 8.0\) Hz, 2 H, m-Ph-H), 3.91 (dd, \(J = 5.4\) Hz, 2.9 Hz, 2 H, N-CH₂), 2.45 (s, 3 H, Ph-CH₃), 1.57 – 1.47 (m, 1 H,
N-CH\textsubscript{2}-CH\textsubscript{2}), 1.38 – 1.06 (m, 8 H, N-CH\textsubscript{2}-CH\textsubscript{2}, N-CH\textsubscript{2}-CH-(CH\textsubscript{2})\textsubscript{3}), 0.83 (t, J = 7.2 Hz, 3 H, CH\textsubscript{2}-CH\textsubscript{3}), 0.78 (t, J = 7.5 Hz, 3 H, CH\textsubscript{2}-CH\textsubscript{3}) ppm.

\textsuperscript{13}C NMR (CD\textsubscript{2}Cl\textsubscript{2}, 101 MHz): \(\delta = 144.75, 133.22, 129.91, 128.06, 72.63, 39.16, 29.91, 28.78, 23.34, 22.97, 21.78, 14.11, 10.89\) ppm.

7-(2-Ethylhexyl)-7\textsubscript{H}-dithieno[2,3-\textit{b}:3',2'\textit{-d}]pyrrole (216)

A suspension of tetrabutylammonium hydrogensulfate (606 mg, 1.79 mmol, 2.00 eq) in toluene (25 mL) and aqueous NaOH (50%, 5 mL) was purged with argon for 15 min. Unsubstituted iso-DTP 126 (160 mg, 0.78 mmol) was added and the reaction mixture was stirred for 10 min. Subsequently, pure 2-ethylhexyl tosylate 215 (507 mg, 1.79 mmol, 2.00 eq) was added dropwise and the reaction mixture was heated at 60 °C for 3 h. After cooling to room temperature, water (25 mL) was added. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 25 mL). The combined organic phase was dried over MgSO\textsubscript{4}, filtrated, and solvent of the filtrate was removed under reduced pressure. Purification via column chromatography (SiO\textsubscript{2}, petroleum ether) afforded iso-DTP 216 as a colourless oil (176 mg, 0.60 mmol, 77%).

\textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 400 MHz): \(\delta = 7.18\) (d, J = 5.3 Hz, 2 H, Th-H\textsubscript{a}), 6.85 (d, J = 5.2 Hz, 2 H, Th-H\textsubscript{b}), 4.05 – 3.90 (m, 2 H, N-CH\textsubscript{2}), 2.23 – 2.05 (m, 1 H, N-CH\textsubscript{2}-CH), 1.43 – 1.21 (m, 8 H, N-CH\textsubscript{2}-CH-CH\textsubscript{2}, N-CH\textsubscript{2}-CH-(CH\textsubscript{2})\textsubscript{3}), 0.92 (t, J = 7.5 Hz, 3 H, CH\textsubscript{3}), 0.87 (t, J = 7.1 Hz, 3 H, CH\textsubscript{3}) ppm.

\textsuperscript{13}C NMR (CD\textsubscript{2}Cl\textsubscript{2}, 101 MHz): \(\delta = 141.08, 122.75, 117.81, 116.33, 39.18, 30.92, 28.88, 24.36, 23.34, 14.17, 10.73\) ppm.

CI-MS: \(m/z\) (%) = 292 (100) [M+H]\textsuperscript{+}.

Elemental analysis: calc. (%) for C\textsubscript{16}H\textsubscript{21}NS\textsubscript{2}: C 65.93, H 7.26, N 4.81, S 22.00; found: C 66.14, H 7.02, N 4.81, S 21.78.

UV-Vis (THF) \(\lambda_{\text{max}}\) (\(\epsilon\)): 271 (10 500) nm.
**Dithieno[2,3-b:3',2'-d]pyrroles (iso-DTPs)**

2-Hexyldecyl tosylate (217)

Pyridine (5.70 mL, 70.0 mmol, 2.00 eq) was added to a solution of 2-hexyldecanol (10.5 mL, 35.1 mmol) in chloroform (37 mL) at 0 °C. Subsequently, tosyl chloride (6.70 g, 35.1 mmol, 1.00 eq) was added by portions and the reaction mixture was stirred for 3 h. After warming to room temperature, water (125 mL) and ether (125 mL) were added. The phases were separated and the organic phase was washed with hydrochloric acid (1 M, 4 × 50 mL), aqueous Na₂CO₃ (4 × 75 mL), and brine (4 × 50 mL). The solution was dried over MgSO₄, filtrated, and the solvent of the filtrate was removed under reduced pressure. The obtained residue was purified via column chromatography (SiO₂, petroleum ether) to yield 217 as a colourless oil (13.9 g, 35.0 mmol, 100%). The analytical data was in accordance with literature.

**¹H NMR** (CDCl₃, 400 MHz): δ = 7.79 (d, J = 8.3 Hz, 2 H, o-Ph-H), 7.34 (d, J = 8.0 Hz, 2 H, m-Ph-H), 3.91 (d, J = 5.3 Hz, 2 H, N-CH₂), 2.45 (s, 3 H, Ph-CH₃), 1.37 – 1.03 (m, 25 H, N-CH₂-C-H, N-CH₂-CH-(CH₂)₅, N-CH₂-CH-(CH₂)₇), 0.88 (t, J = 7.0 Hz, 3 H, CH₂-CH₃), 0.87 (t, J = 7.0 Hz, 3 H, CH₂-CH₃) ppm.

**¹³C NMR** (CDCl₃, 101 MHz): δ = 144.71, 133.24, 129.90, 128.08, 72.99, 37.72, 32.02, 31.88, 30.71, 29.93, 29.64, 29.59, 29.42, 26.59, 26.54, 22.81, 22.76, 21.78, 14.27, 14.23 ppm.

7-(2-Hexyldecyl)-7H-dithieno[2,3-b:3',2'-d]pyrrole (218)

A suspension of tetrabutylammonium hydrogensulfate (2.75 g, 8.10 mmol, 2.50 eq) in toluene (100 mL) and aqueous NaOH (50%, 20 mL) was purged with argon for 15 min. Unsubstituted iso-DTP 126 (581 mg, 3.24 mmol) was added and the reaction mixture was stirred
for 10 min. Subsequently, pure 2-hexyldecyl tosylate 217 (2.57 g, 6.48 mmol, 2.00 eq) was added dropwise and the reaction mixture was heated at 60 °C for 3 h. After cooling to room temperature, water (100 mL) was added. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 100 mL). The combined organic phase was dried over MgSO$_4$, filtrated, and solvent of the filtrate was removed under reduced pressure. Purification via column chromatography (SiO$_2$, petroleum ether) afforded iso-DTP 218 as a colourless oil (478 mg, 1.18 mmol, 37%).

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta$ = 7.17 (d, $J = 5.2$ Hz, 2 H, Th-$H_\alpha$), 6.85 (d, $J = 5.3$ Hz, 2 H, Th-$H_\beta$), 3.96 (d, $J = 7.4$ Hz, 2 H, N-CH$_2$), 2.27 – 2.02 (m, 1 H, N-CH$_2$-CH), 1.40 – 1.12 (m, 24 H, N-CH$_2$-CH$_2$-$\text{C}(\text{C}_5\text{H}_5)$, N-CH$_2$-CH$_2$-$\text{C}(\text{C}_7\text{H}_5)$), 0.96 – 0.50 (m, 6 H, CH$_3$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): $\delta$ = 141.10, 122.75, 117.79, 116.31, 37.80, 32.26, 32.15, 31.86, 31.84, 30.22, 29.91, 29.87, 29.65, 26.62, 23.06, 23.01, 14.28, 14.25 ppm.

CI-MS: $m/z$ (%) = 403 (100) [M]$^+$, 179 (24) [(C$_8$H$_5$NS)$_2$H]$^+$.

Elemental analysis: calc. (%) for C$_{24}$H$_{37}$NS$_2$: C 71.41, H 9.24, N 3.47, S 15.88; found: C 71.39, H 9.11, N 3.48, S 15.86.

UV-Vis (THF) $\lambda_{\text{max}}$ ($\varepsilon$): 271 (9 800) nm.

7-Phenyl-7H-dithieno[2,3-b:3',2'-d]pyrrole (219)

A suspension of unsubstituted iso-DTP 126 (717 mg, 4.00 mmol), bromobenzene (0.84 mL, 8.00 mmol, 2.00 eq), NaOtBu (577 mg, 6.00 mmol, 1.50 eq), Pd(OAc)$_2$ (89.8 mg, 0.40 mmol, 0.10 eq), and P(tBu)$_3$ (162 mg, 0.80 mmol, 0.20 eq) in toluene (8 mL) was purged with argon and heated at 110 °C for 2 d. After cooling to room temperature, water (20 mL) and dichloromethane (20 mL) were added to the reaction mixture. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic phase was dried over MgSO$_4$, filtrated, and the solvent of the filtrate was removed under reduced pressure. Purification via column chromatography (SiO$_2$, petroleum ether) afforded iso-DTP 219 as a colourless solid (524 mg, 2.05 mmol, 51%).

Mp.: 137-140 °C.
Dithieno[2,3-b:3’,2’-d]pyrroles (iso-DTPs)

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 7.83 (dd, J = 8.5 Hz, 0.9 Hz, 2 H, o-Ph-H), 7.64 – 7.53 (m, 2 H, m-Ph-H), 7.32 (t, J = 7.5 Hz, 1 H, p-Ph-H), 7.28 (d, J = 5.3 Hz, 2 H, Th-H$_\alpha$), 6.98 (d, J = 5.3 Hz, 2 H, Th-H$_\beta$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): δ = 139.83, 138.65, 130.43, 125.74, 125.33, 118.65, 117.61, 116.54 ppm.

CI-MS: m/z (%) = 256 (100) [M+H]$^+$. 

Elemental analysis: calc. (%) for C$_{14}$H$_9$NS$_2$: C 65.85, H 3.55, N 5.49, S 25.11; found: C 65.84, H 3.34, N 5.50, S 25.32.

UV-Vis (THF) $\lambda_{\text{max}}$ ($\varepsilon$): 247 (sh, 13 400), 265 (18 400), 296 (sh, 9 000), 304 (9 600) nm.

7-Benzoyl-7H-dithieno[2,3-b:3’,2’-d]pyrrole (206)

Benzoic acid (271 mg, 2.22 mmol, 1.10 eq) was added to a suspension of unsubstituted iso-DTP 126 (361 mg, 2.01 mmol), N,N’-dicyclohexylcarbodiimide (457 mg, 2.22 mmol, 1.10 eq), and 4-dimethylaminopyridine (73.8 mg, 0.60 mmol, 0.30 eq) in dichloromethane (20 mL) at 0 °C. The reaction mixture was stirred overnight, while slowly warmed to room temperature. Then, the suspension was filtered and the solvent of the filtrate was removed under reduced pressure. The obtained residue was purified via column chromatography (SiO$_2$, petroleum ether : dichloromethane = 3:1) to afford iso-DTP 206 as a colourless solid (569 mg, 2.01 mmol, 100 %).

Mp.: 138-139 °C.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 7.79 – 7.74 (m, 2 H, o-Ph-H), 7.74 – 7.68 (m, 1 H, p-Ph-H), 7.64 – 7.58 (m, 2 H, m-Ph-H), 7.19 (d, J = 5.3 Hz, 2 H, Th-H$_\alpha$), 7.05 (s, 2 H, Th-H$_\beta$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): δ = 165.71, 138.42, 132.79, 132.67, 129.53, 128.22, 122.18, 116.82 ppm.

CI-MS: m/z (%) = 284 (100) [M+H]$^+$. 105 (76) [C$_6$H$_5$CO]$^+$. 

Elemental analysis: calc. (%) for C$_{15}$H$_9$NOS$_2$: C 63.58, H 3.20, N 4.94, S 22.63; found: C 63.53, H 3.05, N 4.98, S 22.64.

UV-Vis (THF) $\lambda_{\text{max}}$ ($\varepsilon$): 225 (27 000), 256 (sh, 12 800), 307 (4 400) nm.
3.8.6 Chemical oxidative polymerizations

**General procedure**

The respective iso-DTP monomer (1.00 mmol) was dissolved in dichloromethane (50 mL). Anhydrous iron trichloride (1.00 eq) was added and the reaction mixture was stirred at ambient temperature for 24 h. The solvent was removed under reduced pressure and the residue was transferred into a Soxhlett apparatus, where the polymer was dedoped with aqueous hydrazine for 24 h, washed with n-hexane for 24 h, and extracted with THF. The solvent of the extract was removed under reduced pressure to yield the respective polymer.

**Poly(7-hexyl-7H-dithieno[2,3-b:3',2'-d]pyrrole) Pox207**

Yield 145 mg, 0.56 mmol, 71%.

\(^1\text{H NMR}\) (THF-d\(_8\), 400 MHz): \(\delta = 7.59 – 6.83\) (m, Th-H), 4.24 – 3.77 (m, 2 H, N-CH\(_2\)), 2.05 – 1.83 (m, 2 H, N-CH\(_2\)-CH\(_2\)), 1.48 – 1.09 (m, 6 H, N-(CH\(_2\))\(_2\)-(CH\(_2\))\(_3\)), 0.93 – 0.75 (m, 3 H, CH\(_3\)) ppm.

\(\text{IR (KBr): } \tilde{\nu} = 2953, 2929, 2856\) (C-H), 1638 (C=C) cm\(^{-1}\).

**Poly(7-(2-ethylhexyl)-7H-dithieno[2,3-b:3',2'-d]pyrrole) Pox216**

Yield 136 mg, 0.47 mmol, 49%.

\(^1\text{H NMR}\) (THF-d\(_8\), 400 MHz): \(\delta = 7.74 – 6.60\) (m, Th-H), 4.10 – 3.72 (m, 2 H, N-CH\(_3\)), 2.20 – 1.88 (m, 1 H, N-CH\(_2\)-CH\(_2\)), 1.47 – 1.08 (m, 8 H, N-CH\(_2\)-CH-CH\(_2\), N-CH\(_2\)-CH-CH\(_2\)-CH\(_2\))\(_3\)), 0.98 – 0.75 (m, 6 H, CH\(_3\)) ppm.

\(\text{IR (KBr): } \tilde{\nu} = 2954, 2926, 2868\) (C-H), 1631 (C=C) cm\(^{-1}\).
Poly(7-(2-hexyldcyl)-7H-dithieno[2,3-b:3',2'-d]pyrrole) P_{ox.218}

Yield 124 mg, 0.31 mmol, 42%.

$^1$H NMR (THF-d$_8$, 400 MHz): $\delta = 7.35 - 6.44$ (m, 2 H, Th-H), 3.88 – 3.72 (m, 2 H, N-CH$_2$), 2.29 – 2.24 (m, 1 H, N-CH$_2$-CH), 1.44 – 1.16 (m, 24 H, N-CH$_2$-CH-(CH$_2$)$_5$, N-CH$_2$-CH-(CH$_2$)$_7$), 0.91 – 0.81 (m, 6 H, CH$_3$) ppm.

IR (KBr): $\tilde{\nu} = 2952, 2922, 2852$ (C-H), 1638 (C=C) cm$^{-1}$. 
3.9 References

[19] M. J. Frisch, **2013**, Gaussian, Inc., Wallingford CT.
Chapter 4

$\beta,\beta'$-Dimethyl-substituted dithieno[3,2-$b$:2',3'-$d$]pyrroles (Me-DTPs)
4.1 Introduction

In Chapter 2 oxidative chemical polymerizations of DTPs with iron trichloride afforded p(DTP)s, in which the repeat units were not always connected through the α-carbon atoms, but which contained 22-32% α-β or β-β coupling defects. The relatively large content of defects in the polymers has been ascribed to the more similar reactivity of the α- and β-positions in DTPs compared to thiophenes.\(^1\) However, coupling defects result in a bent structure with large sterical repulsions between the β-hydrogen and the adjacent N-R substituent and also lead to a cross-conjugation in the p(DTP) backbone (Figure 4.1). Thus, it is very likely that the properties of p(DTP)s are influenced to a significant extent by coupling defects.

![Figure 4.1: Structure of p(DTP)s without (left) or with α-β coupling defects (right). C-C single bonds are shown in blue. C-C double bonds are shown in red.](image)

Roncali et al. synthesized the monomer, dimer, and trimer of 2-ethylhexyl-substituted DTP and investigated the chain length dependence of their optoelectronic properties.\(^3\) In the UV-Vis spectra a red-shifted absorption could be observed with increasing chain length and extrapolation to an infinite defect-free polymer led to a theoretical \(\lambda_{\text{max}}\) of 645 nm (in solution) and a band gap \(E_g\) of 1.50 eV (Figure 4.2). 2-Ethylhexyl-substituted p(DTP) was synthesized via both oxidative chemical polymerization and electropolymerization and the chemically prepared polymer \(P_{\alpha 64}\) exhibited a \(\lambda_{\text{max}}\) of 525 nm and an \(E_g\) of 2.03 eV (Chapter 2.6), while electrochemically prepared polymer \(P_{\text{el 64}}\) showed a \(\lambda_{\text{max}}\) of 558 nm and an \(E_g\) of 1.82 eV (Chapter 2.5). In literature, similar values of a \(\lambda_{\text{max}}\) of 545 nm and an \(E_g\) of 1.76 eV have been reported for this p(DTP).\(^2\) Hence, relatively large deviations from the predicted properties for an infinite p(DTP) were observed. While only three values in the extrapolation in Figure 4.2c could account for a large error, in general, the existence of a finite effective conjugation length also leads to a convergence toward limiting values of the optoelectronic properties in conjugated polymers.\(^4\) Therefore, the predicted band gap of an
\(\beta,\beta'\)-Dimethyl-substituted dithieno[3,2-\(b\):2',3'-\(d\)]pyrroles (Me-DTPs)

infinite p(DTP) could be too low. On the other hand, another extrapolation from soluble oxidatively prepared p(DTP)s indicated an even lower minimal band gap of 1.25 eV\(^2\) and similar estimations about different polythiophenes were in rather good agreement with the experimentally determined properties.\(^{5-9}\) Hence, defects in p(DTP)s could also cause significant alterations. However, if the \(\beta\)-positions of DTP monomers were blocked by substituents, the polymerization could only occur in the free \(\alpha\)-positions and strictly linear p(DTP)s would be obtained. The role of coupling defects could thus be examined and if a similar degree of polymerization was reached, an increased conjugation length could be expected for the defect-free p(DTP)s. Nevertheless, residues in the \(\beta\)-positions presumably also exhibit an electronic and sterical influence of their own which has to be considered in this regard.

![Structure](image)

**Figure 4.2:** Structure of 2-ethylhexyl-substituted DTP monomer, dimer, and trimer (a) and their UV-Vis absorption spectra recorded in dichloromethane (copyright © 2010 WILEY-VCH Verlag GmbH & Co. KGaA) (b) Plot of band gap \(E_g\) against the reciprocal number of double bonds \(m\) (c).\(^3\)

Moreover, residues in the \(\beta\)-positions of DTP would not only affect the corresponding polymers, but would also impact structural and optoelectronic properties of the monomers. For instance, steric repulsions between the substituents in the \(\beta\)-positions and the residue at the nitrogen are likely to occur. Large aromatic \(N\)-substituents would therefore be forced to rotate out of the dithienopyrrole plane and a geometry with two perpendicular \(\pi\)-systems could be feasible in the DTP monomers. Such a structure is very intriguing as it potentially
enables a two-dimensional face-to-face $\pi-\pi$ stacking in the solid state, where electronic couplings between the molecules are maximized.$^{[10-11]}$ Thus, charge carrier mobilities would be improved and even an isotropic charge transport could be possible in devices, like OFETs$^{[12-13]}$ or organic solar cells.$^{[14]}$ In Figure 4.3 examples of three-dimensional conjugated molecules are depicted which show a two-dimensional $\pi-\pi$ stacking in the solid state.

![Structural examples of three-dimensional molecules with two-dimensional $\pi-\pi$ stacking in the solid state.](image)

Figure 4.3: Structural examples 220-222 of three-dimensional molecules with two-dimensional $\pi-\pi$ stacking in the solid state.$^{[12, 14-15]}$

The orthogonal geometries of compounds 220 and 221 originate from their spiro moieties in the centre,$^{[14-15]}$ while 222 exhibits a dihedral angle of 78° between the two pentacene units because of repulsive H-H interactions.$^{[12]}$ Although the $\pi$-systems in 222 are not perfectly perpendicular to each other, still only a weak intramolecular electronic coupling could be observed between the pentacenes. Therefore, with the design of an orthogonal cruciform structure two conjugated residues can be covalently linked and yet maintain electronically almost independent. For the application in OPV this might be a worthwhile strategy as two different chromophores can be connected to obtain new donors, non-
fullerenic acceptors, or donor-acceptor hybrids. Especially for non-fullerenic acceptors a twisted geometry concomitant with a three-dimensional structure could moreover be helpful to achieve sufficient phase separation in devices with a flat donor material. [16]

In this Chapter, synthesis and characterization of Me-DTP derivatives will be presented in which the \( \beta \)-positions were substituted by methyl groups. Because of the sterical demand of the methyl substituents in the monomers a twist of bulky moieties at the nitrogen out of the dithienopyrrole plane is expected. Furthermore, the blocking of the \( \beta \)-positions will lead to strictly linear p(Me-DTP)s without coupling defects.
4.2 Synthesis of Me-DTPs

The synthesis of Me-DTPs involved the preparation of dibromobithiophene precursor 226 according to literature procedures (Scheme 4.1).\textsuperscript{[17]} First of all, the commercially available 3-methylthiophene 223 was brominated in both α-positions with NBS. Instead of separating dibromide 224 from the mono- and triply brominated thiophene side-products via column chromatography as proposed in literature,\textsuperscript{[17]} the compound was distilled over a Vigreux column and could be obtained in a yield of 85%. Afterwards, dibromide 224 was specifically lithiated with LDA at the 4-position, as all other carbons of the thiophene ring were blocked by methyl or bromine substituents, respectively. The resulting lithium organyl was oxidatively coupled with CuCl₂ and the inorganic salts were removed in an aqueous workup. Finally, the product crystallized from chloroform, affording bithiophene 225 in a yield of 74%. The two bromine atoms in the α-positions were then cleaved off with zinc in a mixture of hydrochloric acid, acetic acid, and ethanol. After filtration of the reaction mixture, the crude product crystallized from the filtrate and was recrystallized from ethanol to afford dibromobithiophene 226 in 57% yield.

Scheme 4.1: Synthesis of dibromobithiophene 226.\textsuperscript{[17]}

This precursor was subsequently used to prepare Me-DTPs 227-232 bearing a hydrogen, propyl, hexyl, phenyl, 9-anthracenyl, or benzoyl residue at the nitrogen, respectively (Scheme 4.2). The latter compound 232 was obtained from an Ullmann-type coupling with benzamide using a copper catalyst. After 24 hours the desired benzoyl-substituted Me-DTP 232 was isolated in a yield of 36% besides unsubstituted analogue 227 originating from the \textit{in situ} hydrolysis of the benzoyl residue in Me-DTP 232. By increasing the reaction time to overall six days, the yield of unsubstituted Me-DTP 227 could be optimized from initially 22% to 63%. However, in the analogous synthesis of the unsubstituted DTP 50 without methyl groups a maximum yield of 59% could be achieved after two days (Chapter 2.2.2). There,
increasing the reaction time led to a decreased yield of DTP 50 because of its decomposition under the relatively harsh reaction conditions. In contrast to that, in Me-DTP 227 the two methyl groups in the β-positions apparently stabilized the compound and longer reaction times were beneficial. On the other hand, the cleavage of the benzoyl residue in Me-DTP 232 also proceeded much more slowly than the analogous hydrolysis of benzoyl-substituted DTP 97 without methyl residues. These findings indicated that the carbonyl moiety was more electron-rich and therefore less prone to a nucleophilic attack from water or hydroxide anions. Additionally, the methyl residues exhibited a pronounced sterical influence towards the substituent at the nitrogen, thus shielding the carbonyl group and decelerating the benzoyl cleavage.

![Scheme 4.2: Synthesis of Me-DTPs 227-232.](image)

Moreover, alkyl- and aryl-substituted Me-DTPs were synthesized in palladium-catalysed Buchwald-Hartwig aminations of dibromobithiophene 226 with the respective amines. For the synthesis of propyl-substituted Me-DTP 228 with propylamine the dead volume of the reaction flask had to be minimal, because the low boiling amine would otherwise have only been in the gas phase and no reaction could have occurred. After purification of the crude reaction mixture via column chromatography and a subsequent recrystallization from petroleum ether, the desired Me-DTP 228 was obtained in a yield of 85%. Similarly, the
hexyl- and phenyl-substituted compounds 229 and 230 were obtained in excellent yields of 79% and 95%, respectively. Hence, the methyl groups in the β-positions had no detrimental influence on the amination of dibromobithiophene and the same procedures as for the synthesis of the DTP analogues could be applied (Chapter 2.2.1). Consequently, 9-anthracenyl-substituted Me-DTP 231 was prepared according to the synthesis protocol for the corresponding DTP developed in our institute by A. Looser. The frequently used pre-catalyst Pd$_2$dba$_3$ was applied, but the bidentate dppf or BINAP ligands were exchanged for the monodentate RuPhos. As already discovered during the synthesis of unsubstituted DTP 50 via amination of dibromide 72 with triphenylsilyl amine, in general the use of monodentate ligands appeared to be beneficial for C-N couplings of dibromobithiophenes with sterically demanding amino components (Chapter 2.2.2). Furthermore, relatively large amounts of palladium catalyst were applied in order to enable short reaction times of only few hours. With longer reaction times, the 9-anthracenyl-substituted DTP analogue was found to be unstable and it eventually completely decomposed. Nevertheless, heating the reaction mixture for four hours, all starting material 226 was consumed and the crude Me-DTP 232 could be purified via column chromatography using a mixture of petroleum ether and dichloromethane as eluent. Recrystallization from toluene and n-hexane finally afforded pure 9-anthracenyl-substituted Me-DTP 232 in 74% yield.

Structure and purity of Me-DTPs 227-232 were confirmed by NMR spectroscopy, mass spectrometry, and elemental analysis. As an example, the $^1$H NMR spectrum of hexyl-substituted Me-DTP 229 is shown in Figure 4.4. Besides five signals of the hexyl moiety in the aliphatic region, a doublet of the two methyl residues at the dithienopyrrole core is observed at 2.49 ppm. This doublet arises due to the coupling of the CH$_3$ groups with the adjacent thienyl α-proton and exhibits a coupling constant $^4J_{\text{H-H}}$ of 1.1 Hz. The corresponding quartet of the two aromatic protons appears at 6.71 ppm and is thus shifted upfield compared to the doublet of the α-protons in hexyl-substituted DTP 60 without methyl residues (7.14 ppm). The other synthesized Me-DTPs show the same features of a quartet around 6.7 ppm and a doublet corresponding to the methyl residues. However, the latter signal exhibits a similar chemical shift of 2.38 ppm or 2.49 ppm only for unsubstituted Me-DTP 227 or propyl-substituted Me-DTP 228. In contrast to that, with conjugated N-substituents the doublet of the six methyl protons is shifted upfield to 1.84 ppm for phenyl-substituted Me-DTP 230 and
β,β’-Dimethyl-substituted dithieno[3,2-b:2’,3’-d]pyrroles (Me-DTPs)

Benzyol-substituted Me-DTP 232 and to 1.20 ppm for 9-anthracenyl-substituted derivative 231. These shifts have to be caused by influences of the substituent at the nitrogen and might be attributed to the aromatic ring current effect, respectively. Steric interactions with the adjacent methyl groups force the N-substituent in Me-DTP 230-232 to rotate out of the dithienopyrrole plane and revoke the coplanarity of the molecule (see also Chapter 4.3 and Chapter 4.4). Because of the bulky 9-anthracenyl residue in Me-DTP 231 this influence is pronounced to the largest extent and an orthogonal geometry is obtained with the methyls below and above the anthracene plane (Chapter 4.3). At these positions the aromatic ring current effect leads to an upfield shift of the signals in the 1H NMR spectrum. Hence, the largest shift of the aliphatic doublet compared to hexyl-substituted Me-DTP 229 is observed for Me-DTP 231 in the series.

Figure 4.4: 1H NMR spectrum of hexyl-substituted Me-DTP 229 recorded in CD2Cl2.
4.3 Quantum chemical calculations on Me-DTPs

The methyl groups in the β-positions of Me-DTPs are likely to exhibit sterical repulsions on residues attached at the nitrogen. However, the B3LYP functional does not account well for such non-covalent interactions and would most likely over- or underestimate the influence of the methyl substituents in this regard. DFT calculations on the synthesized series of Me-DTPs were therefore carried out using the M06-2X functional\textsuperscript{18} and the obtained frontier molecular orbital surfaces are depicted in Figure 4.5. Similarly to the investigated DTP analogues without methyl residues (Chapter 2.3), all derivatives possess a node at the nitrogen in the HOMO. Thus, only the dithienopyrrole unit contributes to the electronic distribution with minor participation of the methyls. In contrast to that, the LUMOs of unsubstituted and alkyl-substituted Me-DTPs \textsuperscript{227-229} are mainly localized at the N-substituent and thus differ strongly from the LUMOs of their DTP analogues. With a dihedral angle of 39° the benzoyl residue of Me-DTP \textsuperscript{232} is twisted out of the dithienopyrrole plane. Nevertheless, the LUMO of Me-DTP \textsuperscript{232} looks quite similar to the LUMO of DTP \textsuperscript{97} and still exhibits small contributions of the dithienopyrrole backbone. Due to more significant sterical interactions of the methyl groups with the phenyl residue in Me-DTP \textsuperscript{230} a dihedral angle of 67° can be observed in the calculated optimized geometry. Compared to the DTP analogue \textsuperscript{65} this altered structure leads to a more pronounced domination of the phenyl substituent in the LUMO. This trend is even stronger in Me-DTP \textsuperscript{231}, as almost only the 9-anthracenyl residue contributes to the LUMO. The latter exhibits a large sterical demand and therefore enforces an orthogonal geometry, where the π-orbitals of the dithienopyrrole unit and the conjugated anthracene substituent cannot overlap anymore.
**β,β’-Dimethyl-substituted dithieno[3,2-b:2’,3’-d]pyrroles (Me-DTPs)**

![Molecular Orbital Surfaces]

**Figure 4.5:** Frontier molecular orbital surfaces of Me-DTPs bearing different residues R at the nitrogen. Calculations were carried out with the Gaussian 09 program.\(^{[19]}\) Geometry optimizations and energy calculations were performed via DFT methods using the M06-2X correlation/exchange functional\(^{[18]}\) and the 6-311+G(d) basis set. Molecular orbital surfaces were generated utilizing the Gauss View 5.0 program with an isovalue of 0.02. Alkyl chains were shortened to ethyl in order to save computational time.
4.4 Structural and optoelectronic properties of Me-DTPs

Single crystals of phenyl-substituted derivative 230 were obtained for the analysis via X-ray crystallography. By cooling a solution of Me-DTP 230 in n-hexane to -20 °C colourless plate-shaped crystals were afforded and analysed by B. Müller (Institute of Inorganic Chemistry II, Ulm University). The structure (Figure 4.6) was then refined by Dr. E. Mena-Osteritz from our institute and the crystallographic data is compiled in Table 4.1. While phenyl-substituted DTP 65 without methyl residues crystallizes in the monoclinic space group P2₁/c, Me-DTP 230 crystallized in the orthorhombic Pnma group with four molecules per unit cell.

![Figure 4.6](image)

**Table 4.1:** Crystallographic data of Me-DTP 230 with R’=CH₃ and phenyl-substituted DTP 65 with R’=H.

<table>
<thead>
<tr>
<th></th>
<th>R’=CH₃</th>
<th>R’=H²⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C₁₆H₁₃NS₂</td>
<td>C₁₆H₁₀NS₂</td>
</tr>
<tr>
<td>formula weight</td>
<td>283.39</td>
<td>255.34</td>
</tr>
<tr>
<td>temperature</td>
<td>293(2) K</td>
<td>100(2) K</td>
</tr>
<tr>
<td>crystal system</td>
<td>orthorhombic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>Pnma</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>a</td>
<td>14.1117(3) Å</td>
<td>9.9552(11) Å</td>
</tr>
<tr>
<td>b</td>
<td>14.1998(3) Å</td>
<td>14.2894(16) Å</td>
</tr>
<tr>
<td>c</td>
<td>6.88772(14) Å</td>
<td>8.1057(9) Å</td>
</tr>
<tr>
<td>α</td>
<td>90°</td>
<td>90.00°</td>
</tr>
<tr>
<td>β</td>
<td>90°</td>
<td>101.783(2)°</td>
</tr>
<tr>
<td>γ</td>
<td>90°</td>
<td>90.00°</td>
</tr>
<tr>
<td>V</td>
<td>1380.18(5) Å³</td>
<td>1128.8(2) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρcalc</td>
<td>1.364 g/cm³</td>
<td>1.503 g/cm³</td>
</tr>
<tr>
<td>μ</td>
<td>3.350 mm⁻¹</td>
<td>0.443 mm⁻¹</td>
</tr>
<tr>
<td>radiation</td>
<td>CuKα(λ=1.54184 Å)</td>
<td>MoKα(λ=0.71073 Å)</td>
</tr>
<tr>
<td>reflections collected</td>
<td>9007</td>
<td>9952</td>
</tr>
<tr>
<td>independent reflections</td>
<td>1462 [Rviron=0.0332, Rsigma=0.0171]</td>
<td>2707 [Rviron=0.0167]</td>
</tr>
<tr>
<td>goodness-of-fit on F²</td>
<td>1.067</td>
<td>1.035</td>
</tr>
<tr>
<td>final R indices [I&gt;2σ(I)]</td>
<td>R₁=0.0309, wR₁=0.0881</td>
<td>R₁=0.0267, wR₁=0.0699</td>
</tr>
<tr>
<td>final R indices (all data)</td>
<td>R₁=0.0354, wR₁=0.0916</td>
<td>R₁=0.0298, wR₁=0.0721</td>
</tr>
<tr>
<td>R-factor</td>
<td>3.21%</td>
<td>2.67%</td>
</tr>
</tbody>
</table>

Compared to phenyl-substituted DTP 65, the bond angles and bond lengths of the central dithienopyrrole unit in Me-DTP 230 are very similar (Table 4.2). The exterior C1-C2 bonds
exhibit a pronounced double bond character, whereas the inner carbon-carbon bonds of the fused system show a reduced bond length alternation. In Me-DTP 230 the N-C8 bond to the phenyl ring is slightly longer, whereas the C-C bonds in the phenyl ring are shorter and vary between 1.368 and 1.390 Å. Thus, the bond lengths are less similar indicating that the π-electrons in the phenyl ring are slightly less delocalized. The most prominent change, however, is the increased dihedral angle between the dithienopyrrole and the phenyl units (Table 4.2). While calculations on phenyl-substituted DTP 65 using the B3LYP functional indicated co-planarity of the two conjugated moieties (Chapter 2.3), by applying the M06-2X functional a dihedral angle of 43° was observed. Thus, with the latter functional the experimentally determined value of 37° was quite well predicted. In contrast to that, analogous calculations on Me-DTP 230 indicated only a dihedral angle of 67° (Chapter 4.3). The experimentally found twist of 88° is therefore largely due to repulsive interactions of the

Figure 4.6: Crystal structure of Me-DTP 230: molecular structure (a), unit cell (b), intermolecular close contacts of one molecule (c), and packing diagram with top view (d) and side view (e). The thermal ellipsoids are set at a 50% probability level. Hydrogens are omitted for clarity. Close contacts are depicted in green. The distance of the two dithienopyrrole planes in (e) is 1.0 Å.
methyl groups with the phenyl residue, but packing effects also play a certain role. Hence, even with the relatively small phenyl substituent at the nitrogen the steric demand of the methyl units is sufficient to enforce the rotation out of the dithienopyrrole plane and an almost orthogonal geometry is obtained in the solid state. As with larger acenes, such as naphthalene or anthracene, steric repulsions involving the methyl groups are increased, calculations on 9-anthracenyl-substituted Me-DTP already indicate a dihedral angle of 90° (Chapter 4.3). Thus, although no single crystals of derivative could be obtained, it can be expected that 9-anthracenyl-substituted Me-DTP possesses a similar cruciform structure as phenyl-substituted Me-DTP in the solid state.

Table 4.2: Bond distances, bond angles, and selected torsion angles in crystalline Me-DTP with R'\(=\)CH\(_3\) and phenyl-substituted DTP with R'\(=\)H.

<table>
<thead>
<tr>
<th>Bond</th>
<th>R'(=)CH(_3) [Å]</th>
<th>R'(=)H [Å](^{[20]})</th>
<th>Angle</th>
<th>R'(=)CH(_3) [°]</th>
<th>R'(=)H [°](^{[20]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-C1</td>
<td>1.735(2)</td>
<td>1.736(1)</td>
<td>S1-C1-C2</td>
<td>115.0(1)</td>
<td>113.6(1)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.357(2)</td>
<td>1.365(2)</td>
<td>C1-C2-C3</td>
<td>108.9(1)</td>
<td>110.3(1)</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.428(2)</td>
<td>1.425(2)</td>
<td>C2-C3-C4</td>
<td>115.1(1)</td>
<td>114.2(1)</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.390(2)</td>
<td>1.393(2)</td>
<td>C3-C4-S1</td>
<td>110.4(1)</td>
<td>110.66(9)</td>
</tr>
<tr>
<td>C4-S1</td>
<td>1.724(2)</td>
<td>1.721(1)</td>
<td>C4-S1-C1</td>
<td>90.57(8)</td>
<td>91.18(6)</td>
</tr>
<tr>
<td>C2-C9</td>
<td>1.499(3)</td>
<td>-</td>
<td>C3-C2-C9</td>
<td>125.9(1)</td>
<td>-</td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.421(2)</td>
<td>1.416(2)</td>
<td>N-C3-C4</td>
<td>109.3</td>
<td>109.5(1)</td>
</tr>
<tr>
<td>C3-N</td>
<td>1.389</td>
<td>1.392(1)</td>
<td>C3-C4-C5</td>
<td>107.1(1)</td>
<td>107.2(1)</td>
</tr>
<tr>
<td>N-C11</td>
<td>1.430</td>
<td>1.420(1)</td>
<td>C3-N-C6</td>
<td>107.2</td>
<td>106.68(9)</td>
</tr>
<tr>
<td>C11-C12</td>
<td>1.377</td>
<td>1.395(2)</td>
<td>C3-N-C11</td>
<td>126.3</td>
<td>126.4(1)</td>
</tr>
<tr>
<td>C12-C13</td>
<td>1.386</td>
<td>1.390(2)</td>
<td>N-C11-C12</td>
<td>119.6</td>
<td>120.3(1)</td>
</tr>
<tr>
<td>C13-C14</td>
<td>1.374</td>
<td>1.391(2)</td>
<td>C11-C12-C13</td>
<td>119.4</td>
<td>119.5(1)</td>
</tr>
<tr>
<td>C14-C15</td>
<td>1.375</td>
<td>1.391(2)</td>
<td>C12-C13-C14</td>
<td>120.7</td>
<td>120.5(1)</td>
</tr>
<tr>
<td>C15-C16</td>
<td>1.390</td>
<td>1.393(2)</td>
<td>C13-C14-C15</td>
<td>119.5</td>
<td>119.6(1)</td>
</tr>
<tr>
<td>C16-C11</td>
<td>1.368</td>
<td>1.394(2)</td>
<td>C14-C15-C16</td>
<td>120.2</td>
<td>120.4(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C15-C16-C11</td>
<td>119.9</td>
<td>119.7(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C16-C11-C12</td>
<td>120.4</td>
<td>120.3(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C3-N-C11-C12</td>
<td>88.0</td>
<td>37.0</td>
</tr>
</tbody>
</table>

Despite the almost orthogonal geometry of the dithienopyrrole and the phenyl units in Me-DTP no two-dimensional \(\pi-\pi\) stacking can be observed in the solid state. Instead the diagrams in Figure 4.6d and 4.6e show a herringbone packing of Me-DTP with sulphur-sulphur close contacts of 3.534 Å. Moreover intermolecular edge-to-face interactions of the phenyl residue with adjacent pyrrole units are also present. Thus, each molecule interacts with six neighbouring molecules (Figure 4.6c).
The optoelectronic properties of the synthesized Me-DTPs 227-232 bearing a hydrogen, propyl, hexyl, phenyl, 9-anthracenyl, or benzoyl residue at the nitrogen were determined. UV-Vis absorption spectra were recorded in THF solution and from the onset of the absorption band with the lowest energy the optical HOMO-LUMO gap $E_g$ was calculated. Furthermore, the HOMO energy level was derived from the onset oxidation potential in the cyclic voltammogram during the electropolymerization of the respective monomer (Chapter 4.5). With $E_g$ and the HOMO energy level the LUMO energy level was subsequently calculated.

Me-DTPs 227-230 bearing a hydrogen, alkyl, or phenyl substituent show almost identical UV-Vis spectra (Figure 4.7). These spectra consist of one absorption band with a vibrational fine-structure and exhibit very similar maximum absorption wavelengths $\lambda_{\text{max}}$, extinction coefficients $\varepsilon$, and onset absorptions $\lambda_{\text{onset}}$ (Table 4.3). Hence, these substituents only have a marginal influence in this respect. Furthermore, Me-DTPs 227-230 possess almost the same energy gaps $E_g$ as the DTP analogues without methyl substituents in the $\beta,\beta'$-positions. This is the consequence of a very similar influence of the electron-donating methyl substituents in Me-DTPs 227-230 on both the HOMO and the LUMO energy levels, which are increased by 0.07-0.20 eV, respectively.

![Figure 4.7: UV-Vis absorption spectra of Me-DTPs 227, 229, and 230 measured in THF solution.](image-url)
### Table 4.3: Optoelectronic properties of Me-DTPs 227-232 with different residues R attached at the nitrogen.

The values of $E_{pa}$, $E_{onset}$, and the HOMO energy level were obtained by cyclic voltammetry (Chapter 4.5). The values of $\lambda_{max}$, $\varepsilon$, $\lambda_{onset}$, and the energy gap $E_g$ were obtained via UV-Vis spectroscopy. The LUMO energy levels were obtained from the HOMO energy levels and the energy gaps $E_g$. Besides experimental results HOMO energy levels, energy gaps $E_g$, and LUMO energy levels derived from DFT calculations in Chapter 4.3 using the M06-2X functional and the 6-311+G(d) basis set are also stated.

<table>
<thead>
<tr>
<th>Me-DTP</th>
<th>R</th>
<th>$E_{pa}$</th>
<th>$E_{onset}$</th>
<th>HOMO$^a$</th>
<th>$\lambda_{max}$</th>
<th>$\varepsilon$</th>
<th>$\lambda_{onset}$</th>
<th>$E_g$</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTP</td>
<td></td>
<td>[V]</td>
<td>[V]</td>
<td>[eV]</td>
<td>[nm]</td>
<td>[M$^{-1}$ cm$^{-1}$]</td>
<td>[nm]</td>
<td>[eV]</td>
<td>[eV]</td>
</tr>
<tr>
<td>227</td>
<td>H</td>
<td>0.43</td>
<td>0.31</td>
<td>-5.41</td>
<td>292</td>
<td>23700</td>
<td>315</td>
<td>3.94</td>
<td>-1.47</td>
</tr>
<tr>
<td></td>
<td>DFT</td>
<td></td>
<td></td>
<td></td>
<td>-7.11</td>
<td></td>
<td></td>
<td>3.13</td>
<td>-3.98</td>
</tr>
<tr>
<td>228</td>
<td>Pr</td>
<td>0.43</td>
<td>0.32</td>
<td>-5.42</td>
<td>296</td>
<td>20310</td>
<td>317</td>
<td>3.91</td>
<td>-1.51</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td></td>
<td></td>
<td></td>
<td>-7.06</td>
<td></td>
<td></td>
<td>3.10</td>
<td>-3.96</td>
</tr>
<tr>
<td>229</td>
<td>Hex</td>
<td>0.43</td>
<td>0.33</td>
<td>-5.43</td>
<td>296</td>
<td>25200</td>
<td>317</td>
<td>3.91</td>
<td>-1.52</td>
</tr>
<tr>
<td></td>
<td>DFT</td>
<td></td>
<td></td>
<td></td>
<td>-7.08</td>
<td></td>
<td></td>
<td>2.47</td>
<td>-4.61</td>
</tr>
<tr>
<td>230</td>
<td>Ph</td>
<td>0.46</td>
<td>0.35</td>
<td>-5.45</td>
<td>295</td>
<td>25200</td>
<td>317</td>
<td>3.91</td>
<td>-1.54</td>
</tr>
<tr>
<td></td>
<td>DFT</td>
<td></td>
<td></td>
<td></td>
<td>-7.08</td>
<td></td>
<td></td>
<td>2.47</td>
<td>-4.61</td>
</tr>
<tr>
<td>231</td>
<td>9-Anth</td>
<td>0.52</td>
<td>0.44</td>
<td>-5.54</td>
<td>255</td>
<td>131400</td>
<td>406</td>
<td>3.05</td>
<td>-2.49</td>
</tr>
<tr>
<td></td>
<td>DFT</td>
<td></td>
<td></td>
<td></td>
<td>-6.54</td>
<td></td>
<td></td>
<td>4.95</td>
<td>-1.59</td>
</tr>
<tr>
<td>232</td>
<td>COPh</td>
<td>0.64</td>
<td>0.55</td>
<td>-5.65</td>
<td>289</td>
<td>24600</td>
<td>373</td>
<td>3.32</td>
<td>-2.33</td>
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<td></td>
<td></td>
<td>-7.26</td>
<td></td>
<td></td>
<td>2.05</td>
<td>-5.21</td>
</tr>
</tbody>
</table>

Potentials are referenced vs. Fc/Fc$^+$; $a$ $E_{pa}$: anodic peak potential (scan rate 100 mV/s); $b$ Redox potential of Fc/Fc$^+$ is -5.1 eV on the Fermi scale$^{[21]}$; $c$ R=Et

In contrast to that, benzoyl-substituted Me-DTP 232 exhibits a low energy shoulder extending to an onset absorption wavelength of 373 nm in the UV-Vis spectrum (Figure 4.8). Benzoyl-substituted DTP analogue 97 without methyl residues in the $\beta,\beta'$-positions shows a similar shoulder, yet with a shorter onset absorption wavelength of 347 nm (Chapter 2.4). Due to the electronic transition from the HOMO to the LUMO this band has been ascribed to possess a partial charge transfer character from the DTP donor unit to the weak acceptor moiety at the nitrogen.$^{[22]}$ DFT calculations were in accordance with this claim, as the HOMO is only localized at the dithienopyrrole backbone, but the whole conjugated part including the benzoyl residue participates to the LUMO (Chapter 2.3). Because the LUMO in Me-DTP 232 is slightly more dominated by the substituent than in DTP analogue 97 (Chapter 4.3), the bathochromic shift of the low energy band can be rationalized. However, in order to fully exclude that this band originated from oxidized fractions of Me-DTP 232, UV-Vis spectra of the same solution were measured immediately and after one day, after two days, and after four days, respectively. Identical spectra were recorded and therefore the partial oxidation of Me-DTP 232 did not occur. Secondly, the benzoyl residue lowers the HOMO energy level of
\(\beta,\beta'\)-Dimethyl-substituted dithieno[3,2-b:2',3'-d]pyrroles (Me-DTPs)

Me-DTP 232 by 0.24 eV with respect to unsubstituted parent Me-DTP 227 (Table 4.3). The oxidation of Me-DTP 232 consequently starts at higher potentials and is therefore unlikely to occur already under ambient conditions. Hence, the low energy band indeed originates from the HOMO-LUMO transition of the neutral compound 232. Notably, in comparison to benzoyl-substituted DTP analogue 97 the energy gap \(E_g\) of Me-DTP 232 is decreased by 0.25 eV. This decrease is partly due to an increased HOMO energy level by 0.10 eV as a result of the electron-donating influence of the methyl substituents. However, opposed to the trend in the series, the LUMO energy level of Me-DTP 232 is not increased, but decreased by 0.15 eV compared to DTP 97 which can again be attributed to the more pronounced influence of the benzoyl group on this frontier molecular orbital.

\[
\begin{align*}
\text{Figure 4.8: UV-Vis absorption spectra of Me-DTPs 231 and 232 measured in THF solution.}
\end{align*}
\]

In the UV-Vis spectrum of 9-anthracenyl-substituted Me-DTP 231 similar absorption bands appear in the region around 300 nm as in the spectra of the other derivatives in the series (Figure 4.8). The anthracene unit, however, accounts for two distinct additional features at lower and higher wavelengths which are very characteristic and are also observed in the spectrum of pure anthracene. The intense higher energy band has been ascribed to an electronic transition, which is polarized along the longer molecular axis in the anthracene plane.\(^{[23]}\) The lower energy bands with a vibrational fine-structure, on the other hand,
correspond to a transition with polarization along the shorter molecular axis.\cite{24-25} Herein, the onset absorption occurs at 406 nm due to a relatively low $E_g$ of 3.05 eV (Table 4.3). Compared to the phenyl substituent in Me-DTP 230, the 9-anthracenyl group is slightly more electron-withdrawing and causes a decreased HOMO energy level of -5.54 eV. Because the LUMO is, however, largely dominated by the substituent at the nitrogen, the influence of the anthracene unit is here much more pronounced and leads to the lowest LUMO energy level in the series.

Applying the M06-2X functional in the quantum chemical calculations, non-covalent interactions were taken much better into account than with the B3LYP functional and therefore more accurate geometric estimations of the compounds were obtained. However, the calculated values of the frontier molecular orbital energy levels in Me-DTPs 227-232 largely deviate from the experimentally determined values (Table 4.3). In this respect much better estimations for the DTP analogues were obtained using the B3LYP functional (Chapter 2.4). In Figure 4.9 the experimentally determined HOMO and LUMO energy levels of the synthesized Me-DTPs are summarized.

![Figure 4.9](image_url)

**Figure 4.9:** Experimentally determined HOMO (blue) and LUMO (red) levels of Me-DTPs with different residues attached at the nitrogen. The energy levels of propyl-substituted Me-DTP 228 are almost identical to the values of hexyl-substituted Me-DTP 229 (Table 4.3).
4.5 Electropolymerization of Me-DTPs

Me-DTPs 227 and 229-232 bearing different residues at the nitrogen were potentiodynamically polymerized in a three-electrode electrochemical cell on a platinum working electrode (Scheme 4.3). The respective monomers were used in millimolar concentrations in a solution of TBA-PF₆ as the supporting electrolyte. After the electropolymerization the obtained film was subjected to several scans in a monomer-free electrolyte solution until a stable current response was recorded. At this “conditioning” phase residual short p(Me-DTP)s in the film were further polymerized. Subsequently, the respective film was characterized via cyclic voltammetry applying different scan rates between 10 mV/s and 100 mV/s. Finally, 30 cycles were measured with a scan rate of 100 mV/s to investigate the film stability.

Unsubstituted Me-DTP monomer 227 showed an onset oxidation potential of 0.31 V in the first scan of the cyclic voltammograms which corresponded to a HOMO energy level of -5.41 eV (Figure 4.10). Because the p(Me-DTP) film Pₑₑ₂₂₇ continuously grew with increasing number of cycles during the polymerization, the currents also increased and after ten scans a thick green film was obtained. Moreover, the polymer exhibited an anodic peak potential of 0.26 V, a cathodic peak potential of -0.07 V, and an onset oxidation of 0.07 V (Table 4.4). The latter corresponded to a relatively low HOMO energy level of -5.17 eV, which accounted for a strong decrease of 0.61 eV compared to analogous p(DTP) Pₑₑ₂₅₀ without methyl substituents in the β,β’-positions. Nevertheless, with increasing scan rate the peak currents increased linearly indicating that the redox process was not hampered by a slow electron transfer and that the film was well adhered to the surface of the electrode. Furthermore, the loss of electrophoric material after conducting 30 cycles only accounted for 4% and thus a quite stable polymer film was obtained.
Figure 4.10: Electropolymerization of Me-DTP monomer 227 with a hydrogen residue at the nitrogen (a) and the characterization of the obtained film $P_{\text{ec,227}}$ using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents $I_{pa}$ and the cathodic peak currents $I_{pc}$ from the applied scan rate (d).

Table 4.4: Electronic properties of electrochemically prepared p(Me-DTP)s $P_{\text{ec,227}}$, $P_{\text{ec,229}}$, $P_{\text{ec,230}}$, and $P_{\text{ec,232}}$ determined via cyclic voltammetry in a monomer-free electrolyte solution.

<table>
<thead>
<tr>
<th>p(Me-DTP)</th>
<th>R</th>
<th>$E_{pa}$ [V]</th>
<th>$E_{pc}$ [V]</th>
<th>$E_{onset}$ [V]</th>
<th>HOMO$^c$ [eV]</th>
<th>Film loss$^d$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{ec,227}}$</td>
<td>H</td>
<td>0.26</td>
<td>-0.07</td>
<td>0.07</td>
<td>-5.17</td>
<td>4</td>
</tr>
<tr>
<td>$P_{\text{ec,229}}$</td>
<td>Hex</td>
<td>0.24</td>
<td>-0.07</td>
<td>0.13</td>
<td>-5.23</td>
<td>5</td>
</tr>
<tr>
<td>$P_{\text{ec,230}}$</td>
<td>Ph</td>
<td>0.17</td>
<td>-0.05</td>
<td>-0.05</td>
<td>-5.05</td>
<td>6</td>
</tr>
<tr>
<td>$P_{\text{ec,232}}$</td>
<td>COPh</td>
<td>0.57</td>
<td>0.38</td>
<td>0.28</td>
<td>-5.38</td>
<td>6</td>
</tr>
</tbody>
</table>

Potentials are referenced vs. Fc/Fc$^+$; $a$ $E_{pa}$: anodic peak potential (scan rate 100 mV/s); $b$ $E_{pc}$: cathodic peak potential (scan rate 100 mV/s); $c$ Redox potential of Fc/Fc$^+$ is -5.1 eV on the Fermi scale; $d$ Determined as the difference of exchanged charges during scan 2 and scan 30.

In Figure 4.11 the cyclic voltammograms of the electropolymerization and the following film characterization of Me-DTP 229 bearing a hexyl residue are shown. In the first scan of the polymerization, the onset oxidation of Me-DTP 229 occurred at 0.33 V due to a HOMO energy level of -5.43 eV. The cyclic voltammogram of propyl-substituted derivative 228
looked almost the same, but the obtained polymer film of $P_{ec228}$ was not further investigated. In contrast to that, the thick green film of $P_{ec229}$ was characterized in a monomer-free electrolyte solution and a relatively sharp oxidation wave could be observed with an anodic peak potential of 0.24 V followed by a broader reduction wave with a cathodic peak potential of 0.07 V (Table 4.4). The onset oxidation of the polymer occurred at 0.13 V, because the HOMO energy level of -5.23 eV was similarly low as in unsubstituted polymer $P_{ec227}$. A stable well adhered polymer film of $P_{ec229}$ was obtained and hence the peak currents increased linearly with the sweep rate and after 30 cycles just 5% of the material was lost.

Figure 4.11: Electropolymerization of Me-DTP monomer 229 with a hexyl residue at the nitrogen (a) and the characterization of the obtained film $P_{ec229}$ using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents $I_{pa}$ and the cathodic peak currents $I_{pc}$ from the applied scan rate (d).

Me-DTP 230 bearing a phenyl residue was also electropolymerized (Figure 4.12). The monomer exhibited an onset oxidation of 0.35 V corresponding to a HOMO energy level of -5.45 eV. Thus, the same trend of a slightly stabilized HOMO with a phenyl instead of an alkyl substituent at the nitrogen was observed as in the DTP series without methyl groups in
the β,β'-positions. Carrying out few scans, a stable well adhered p(Me-DTP) film of $P_{ec}230$ was obtained as evidenced by the minor loss (6%) of electrophoric material after 30 cycles and the linear relationship between the scan rate and the anodic and cathodic peak currents, respectively. Furthermore, the obtained polymer possessed an onset oxidation potential of -0.05 V corresponding to a HOMO energy level of -5.05 eV (Table 4.4). As in the p(DTP) series, the HOMO of phenyl-substituted polymer $P_{ec}230$ was thus destabilized compared to alkyl-substituted analogue $P_{ec}229$. However, in comparison to p(DTP) $P_{ec}65$ without methyl groups, the HOMO energy level of phenyl-substituted p(Me-DTP) $P_{ec}230$ was still significantly decreased by 0.62 eV.

![Graphs showing electropolymerization and characterization results](image)

**Figure 4.12:** Electropolymerization of Me-DTP monomer 230 with a phenyl residue at the nitrogen (a) and the characterization of the obtained film $P_{ec}230$ using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents $I_{pa}$ and the cathodic peak currents $I_{pc}$ from the applied scan rate (d).

Monomer 231 with a 9-anthracenyl residue at the nitrogen exhibited an onset oxidation of 0.44 V due to a HOMO energy level of -5.54 eV (Figure 4.13). However, in contrast to the other synthesized Me-DTP monomers, only a thin polymer film of $P_{ec}231$ was obtained, as
only small new signals at lower potentials could be observed after the first cycle. The peak currents at 0.52 V corresponding to the oxidation of the monomer decreased with increasing number of scans, whereas the peak potential stayed constant. Thus, the polymerization process was most likely hampered by the significant steric demand of the anthracene substituent and the obtained unstable film was not further characterized.

Figure 4.13: Electropolymerization of Me-DTP monomer 231 with a 9-anthracenyl residue at the nitrogen.

During the electropolymerization of benzoyl-substituted Me-DTP 232 an onset oxidation of 0.55 V was observed corresponding to a HOMO energy level of -5.65 eV (Figure 4.14). After ten scans, a stable blue film of P_{ec}232 was obtained and after 30 cycles only 6% of the material was lost. Moreover, there was a linear relationship between the sweep rate and the anodic and cathodic peak currents, because a quick electron transfer between the film and the working electrode was ensured by the good adherence of the film. The polymer possessed an onset oxidation potential of 0.28 V and a HOMO energy level of -5.38 eV (Table 4.4), which was decreased by 0.51 eV compared to p(DTP) analogue P_{ec}97.

In addition to the electrochemical characterization, the obtained polymer films were also investigated via spectroelectrochemistry in a solution of tetrabutylammonium hexafluorophosphate in acetonitrile using a recently described setup (Figure 4.15)\textsuperscript{[26]} Neutral polymer films without any oxidized parts could be investigated by applying a potential of -500 mV vs. Ag/AgCl prior to the measurements, respectively. Furthermore, an important aspect was the use of a platinum working electrode, as it ensured that the same materials were obtained for both the electrochemical and the spectroelectrochemical characterizations.
Figure 4.14: Electropolymerization of Me-DTP monomer 232 with a benzoyl residue at the nitrogen (a) and the characterization of the obtained film P_{ec}232 using different scan rates (b) and carrying out 30 cycles at a rate of 100 mV/s (c). Dependency of the anodic peak currents I_{pa} and the cathodic peak currents I_{pc} from the applied scan rate (d).

The neutral films of P_{ec}227, P_{ec}229, and P_{ec}230 with hydrogen, hexyl, or phenyl substituents exhibited one absorption band with a maximum between 409 and 414 nm as well as an onset absorption between 475 and 516 nm, respectively (Table 4.5). The latter corresponded to energy gaps in the range of 2.40 to 2.61 eV, which were largely increased compared to the analogous p(DTP)s without methyls in the β,β'-positions. In contrast to that, polymer P_{ec}232 with a benzoyl moiety attached at the nitrogens possessed the same energy gap of 2.07 eV (Table 4.5) as corresponding p(DTP) analogue P_{ec}97. Nevertheless, the maximum of the absorption band was located at 459 nm compared to 481 nm for P_{ec}97 and like the decreased HOMO energy level of P_{ec}232 the LUMO was also largely stabilized. In accordance with the spectroelectrochemical investigations on the p(DTP) analogues, gradually increasing the applied potential then led to the oxidation of the films and thus the formation of polarons and finally bipolarons could be observed. The former possessed two absorption bands in the visible and near-infrared region, while the latter showed one broad
Figure 4.15: UV-Vis-NIR spectra obtained from spectroelectrochemical measurements of p(Me-DTP)s bearing hydrogen (P_{pec}227, a), hexyl (P_{pec}229, b), phenyl (P_{pec}230, c), or benzoyl (P_{pec}232, d) residues at the nitrogens, respectively. Applied voltages are stated vs. Ag/AgCl. Black arrows show the changes starting at low potentials. The blue arrow shows the further changes at high potentials. Artefacts are marked with * in the spectra.

Table 4.5: Optical properties of electrochemically prepared p(Me-DTP)s P_{pec}227, P_{pec}229, P_{pec}230, and P_{pec}232 bearing different residues R at the nitrogens. The values of \( \lambda_{\text{max}} \), \( \lambda_{\text{onset}} \), and the energy gap \( E_g \) were obtained from UV-Vis-NIR spectra of the neutral polymer films measured in a spectroelectrochemical setup. The LUMO energy levels were calculated from the HOMO energy levels and the energy gaps \( E_g \). The maxima \( \lambda_{\text{max}, p} \) of the polaron and \( \lambda_{\text{max}, bp} \) of the bipolaron species were obtained from spectroelectrochemical measurements.

<table>
<thead>
<tr>
<th>p(Me-DTP)</th>
<th>R</th>
<th>( \lambda_{\text{max}} )</th>
<th>( \lambda_{\text{onset}} )</th>
<th>( E_g )</th>
<th>LUMO</th>
<th>( \lambda_{\text{max}, p} )</th>
<th>( \lambda_{\text{max}, bp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_{pec}227</td>
<td>H</td>
<td>409</td>
<td>516</td>
<td>2.40</td>
<td>-2.77</td>
<td>628, 1320 (br)</td>
<td>1200 (br)</td>
</tr>
<tr>
<td>P_{pec}229</td>
<td>Hex</td>
<td>400</td>
<td>475</td>
<td>2.61</td>
<td>-2.62</td>
<td>704, 1330 (br)</td>
<td>a</td>
</tr>
<tr>
<td>P_{pec}230</td>
<td>Ph</td>
<td>414</td>
<td>494</td>
<td>2.51</td>
<td>-2.66</td>
<td>648, a</td>
<td>a</td>
</tr>
<tr>
<td>P_{pec}232</td>
<td>COPh</td>
<td>459</td>
<td>600</td>
<td>2.07</td>
<td>-3.31</td>
<td>664, a</td>
<td>a</td>
</tr>
</tbody>
</table>

* Maximum was outside of the measured range
band extending over a wide range of the NIR region. These changes in the UV-Vis-NIR spectra were accompanied by the decrease of the original band of the neutral polymers in the visible region. The energy diagram in Figure 4.16 summarizes the determined HOMO and LUMO energy levels of electrochemically prepared p(Me-DTP)s.

Figure 4.16: Energy diagram showing the HOMO energy levels (blue), LUMO energy levels (red) and the energy gaps $E_g$ of electrochemically prepared p(Me-DTP)s bearing different residues R at the nitrogens.

In electopolymers $P_{eC227}$, $P_{eC229}$, $P_{eC230}$, and $P_{eC232}$ the strongly decreased HOMO energy levels compared to the analogous p(DTP)s indicated a decreased conjugation length. On the one hand, this could have been caused by the presence of only short polymer chains in the obtained films. Herein, the absence of any $\alpha$-$\beta$ or $\beta$-$\beta$ coupling defects considerably decreased the solubility, so already species with low molecular weight precipitated at the working electrode and were not polymerized further. However, because the hexyl substituent at the nitrogens in $P_{eC229}$ only had a marginal influence on the optoelectronic properties compared to unsubstituted $P_{eC227}$, the limited solubility of intermediate species was certainly not the only factor. Additionally, the methyl groups probably interacted with the methyls or the sulphur atoms of the adjacent DTP core leading to an increased twist between the repeat units. DFT calculations on the Me-DTP trimer with ethyl moieties at the nitrogens were therefore conducted and indicated a cisoid-like geometry to be slightly more stable than a transoid-like structure in this model system (Figure 4.17). While for the analogous DTP trimer the transoid geometry is more favourable, the repeat units are only twisted by 18° relative to each other (Chapter 2.6). In contrast to that, the Me-DTP trimer
...dimethyl-substituted dithieno[3,2-b:2',3'-d]pyrroles (Me-DTPs) exhibits a dihedral angle of 60° due to sterical repulsions of adjacent methyl residues. This results in an interruption of the conjugation, because the overlap of the π-orbitals in neighbouring dithienopyrroles is impeded. However, in comparison to the respective monomers the electopolymers exhibited decreased LUMO and slightly increased HOMO energy levels indicating that the conjugation between the repeat units was not fully interrupted and the π-orbitals could still overlap to a certain extent. This was also an important aspect concerning the optoelectronic properties of acceptor-donor-acceptor-type oligomers involving Me-DTPs as the central unit (Chapter 5).

**Figure 4.17:** Geometry optimized structures of Me-DTP trimer with ethyl residues at the nitrogens. Calculations were carried out with the Gaussian 09 program.\textsuperscript{19} Geometry optimizations were performed via DFT methods using the M06-2X correlation/exchange functional\textsuperscript{18} and the 6-311G basis set.
4.6 Chemical oxidative polymerization of Me-DTPs

While the optoelectronic properties of electropolymerized Me-DTPs indicated a small polymerization degree in $P_{\text{ec}227}$, $P_{\text{ec}229}$, $P_{\text{ec}230}$, and $P_{\text{ec}232}$, the insolubility of the obtained materials impeded the analysis of their molecular weights via GPC. Furthermore, in the MALDI mass spectra of p(DTP)s in Chapter 2.6 only the shortest chains could be detected. Hence, Me-DTP $229$ with a solubilizing hexyl residue at the nitrogen was oxidatively polymerized applying four equivalents of iron trichloride as oxidant (Scheme 4.4). The resulting raw polymer was dedoped by treatment with aqueous hydrazine, washed with $n$-hexane to remove short polymers, and extracted with THF to afford $P_{\text{ox}229}$ in a yield of 21%.

![Scheme 4.4: Chemical oxidative polymerization of Me-DTP 229.](image)

With the THF-soluble fraction structural information of the polymer could be gained by investigations in solution. Thus, analysis by GPC indicated a number average molar mass of only 2600 g/mol corresponding to an average chain length of 9.0 repeat units (Table 4.6). Compared to analogous $P_{\text{ox}60}$ without methyl substituents in the $\beta,\beta'$-positions, this result meant a decrease of more than two thirds, while the polydispersity was even increased. Due to the small polymer chain length of $P_{\text{ox}229}$ in the $^1\text{H}$ NMR spectrum a singlet of the endgroup $\alpha$-protons at 6.80 ppm could be observed besides the signals of the alkyl moieties (Figure 4.18). In agreement with the results from GPC, the integral of the singlet indicates a chain length of 8.7 repeat units in the polymer. Hence, the analyses of the electropolymerized analogues was confirmed (Chapter 4.5) and both electropolymerizations and chemical oxidative polymerizations of Me-DTPs could only afford quite short polymers.
\textbf{Table 4.6:} Number average molar masses $M_n$, mass average molar masses $M_w$, polydispersities $D$, and average numbers $n$ of repeat units in the polymer chain of $N$-hexyl-substituted $p(DTP)$ $P_{ox60}$ and $p(\text{Me-DTP})$ $P_{ox229}$ according to GPC analyses in THF.

\begin{tabular}{|c|c|c|c|c|}
\hline
polymer & $M_n$ [g/mol] & $M_w$ [g/mol] & $D$ & $n$ \\
\hline
$P_{ox60}$ & 8100 & 11300 & 1.4 & 31.0 \\
$P_{ox229}$ & 2600 & 4300 & 1.7 & 9.0 \\
\hline
\end{tabular}

\textbf{Figure 4.18:} $^1$H NMR spectrum of the soluble oxidatively prepared $p(\text{Me-DTP})$ $P_{ox229}$ bearing hexyl residues at the nitrogens recorded in THF-d$_8$.

On the one hand, the coupling of DTPs in the $\alpha$-positions might be impeded due to the sterical demand of the methyls in the $\beta$-positions and could account for the limited polymerization degree of $p(\text{Me-DTP})$s. Furthermore, the absence of any $\alpha$-$\beta$ or $\beta$-$\beta$ coupling defects in the polymers could also be an important factor. However, in Stille-type polymerizations Koeckelberghs \textit{et al.} obtained defect-free $p(DTP)$s, which were larger than the analogues obtained from chemical oxidative polymerizations.\textsuperscript{[27]} Nevertheless, the polymerization method seems to be far more important in this respect, because in palladium-catalysed cross-couplings the obtained polymers stay in solution during the whole reaction, whereas in oxidative polymerizations intermediates and products are present in their less soluble doped state and often precipitate from the reaction mixture. Moreover, Ogawa and Rasmussen found that oxidatively prepared $p(DTP)$s containing $\alpha$-$\beta$ and $\beta$-$\beta$ coupling defects were more soluble than their linear defect-free analogues and thus could mostly be removed by washing with chloroform.\textsuperscript{[2]} Hence, coupling defects increase the solubility of $p(DTP)$ intermediates during oxidative polymerizations preventing their precipitation at an early
stage, and finally enabling a much higher polymerization degree. Because these defects are not possible in p(Me-DTP)s bearing methyl substituents in the β-positions, the obtained polymer P_{ox}229 consequently exhibited only a low average molecular weight.

Subsequently, the optoelectronic properties of p(Me-DTP) P_{ox}229 were determined by cyclic voltammetry and UV-Vis spectroscopy. In Figure 4.19 and Table 4.7 they are compared to the properties of analogous hexyl-substituted p(DTP) P_{ox}60 without methyl residues. The onset oxidation of p(Me-DTP) P_{ox}229 occurred at 0.02 V corresponding to a HOMO energy level of -5.12 eV. In comparison to the UV-Vis spectrum of p(DTP) P_{ox}60, the absorption was blue-shifted exhibiting a maximum absorption wavelength $\lambda_{\text{max}}$ of 383 nm and an onset absorption at 444 nm. This was due to a larger energy gap $E_g$ of 2.79 eV with a lower HOMO and a higher LUMO energy level of P_{ox}229. These trends can unambiguously be explained by the shorter polymer chain and thus a smaller conjugation length of P_{ox}229 compared to the analogous p(DTP) P_{ox}60.

Figure 4.19: Normalized UV-Vis absorption spectra of the soluble oxidatively prepared p(DTP) P_{ox}60 and p(Me-DTP) P_{ox}229 with hexyl residues at the nitrogens in THF solution.

<table>
<thead>
<tr>
<th>polymer</th>
<th>$E_{\text{onset}}$ [V]</th>
<th>HOMO$^\alpha$ [eV]</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>$\lambda_{\text{onset}}$ [nm]</th>
<th>$E_g$ [eV]</th>
<th>LUMO [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_{ox}60</td>
<td>-0.24</td>
<td>-4.86</td>
<td>504</td>
<td>605</td>
<td>2.05</td>
<td>-2.81</td>
</tr>
<tr>
<td>P_{ox}229</td>
<td>0.02</td>
<td>-5.12</td>
<td>383</td>
<td>444</td>
<td>2.79</td>
<td>-2.33</td>
</tr>
</tbody>
</table>

Potentials are referenced vs. Fc/Fc$^+$; a Redox potential of Fc/Fc$^+$ is -5.1 eV on the Fermi scale$^{[21]}$
4.7 Summary

In summary, a series of Me-DTPs 227-232 with attached methyl groups in the two β-positions and a hydrogen, propyl, hexyl, phenyl, 9-anthracenyl, or benzoyl substituent at the nitrogen was synthesized via C-N couplings of 3,3′-dibromo-4,4′-dimethyl-2,2′-bithiophene with corresponding amines or benzamide in the final step (Figure 4.20). The methyl groups in the β,β′-positions slightly increase the HOMO energy levels of the corresponding Me-DTPs due to their electron-donating ability, but almost do not change the shape of this frontier molecular orbital. However, because of sterical interactions with bulky residues at the nitrogen, the latter are forced to rotate out of the dithienopyrrole plane. Consequently, the LUMO is mainly influenced by the conjugated substituent at the nitrogen and to a lesser extent by the dithienopyrrole backbone. Intriguingly, even with the relatively small phenyl attached at the nitrogen of Me-DTP 230 an almost orthogonal geometry is obtained in the solid state, but instead of a two-dimensional face-to-face π-π stacking this derivative exhibits a herringbone stacking motif.

Moreover, an important feature of Me-DTPs is that both β-positions are blocked and therefore strictly linear homopolymers without coupling defects are obtained. The absence of these defects considerably decreased the solubility of short p(Me-DTP) intermediates during oxidative polymerizations and thus accounted for a low polymerization degree. Furthermore, steric repulsions of the methyls led to an increased twist between the repeat units which additionally contributed to a relatively short conjugation length in the polymer. Nevertheless, except for the bulky 9-anthracenyl-substituted Me-DTP monomer 231, all derivatives afforded quite stable electropolymerized films, which were very well adhered on the working electrode.
4.8 Experimental section

**Instruments and measurements**

Thin layer chromatography was carried out on aluminium plates, precoated with silica gel, Merck Si60 F254. Preparative column chromatography was performed on glass columns packed with silica gel (particle size 40–63 µm) from Macherey-Nagel. Melting points were determined using a Büchi Melting Point B-545 or a Mettler Toledo DSC 823e under argon flow (heating rate 10 °C/min). UV-Vis absorption spectra were recorded in THF solutions on a Perkin Elmer Lambda 19 spectrometer. NMR spectra were recorded on an Avance 400 spectrometer (\(^{1}\text{H} \text{NMR:} 400 \text{ MHz}, \ ^{13}\text{C} \text{NMR:} 101 \text{ MHz}\)). Chemical shifts (δ) are reported in ppm using residual solvent protons (\(^{1}\text{H} \text{NMR:} \delta_H = 7.26 \text{ for } \text{CDCl}_3; \delta_H = 5.32 \text{ for } \text{CD}_2\text{Cl}_2; \delta_H = 3.58 \text{ for } \text{THF-d}_8\); \(^{13}\text{C} \text{NMR:} \delta_C = 77.16 \text{ for } \text{CDCl}_3; \delta_C = 53.84 \text{ for } \text{CD}_2\text{Cl}_2\)) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants \(J\) relate to proton-proton couplings. Protons at the α-positions of DTP were assigned as Th-\(H_\alpha\). Elemental analyses were performed on an Elementar Vario EL. GC/EI-MS (70 eV) measurements were performed on a Shimadzu GCMS-QP2010 SE. Chemical ionisation (CI) mass spectra were measured on a Finnigan MAT SSQ-7000.

X-ray diffraction data of a colourless plate-shaped single crystal of Me-DTP 230 were collected in a stream of nitrogen at 150 K on an Agilent SuperNova, Cu at zero, Atlas CCD using graphite-monochromated Cu K\(_\alpha\) radiation. Data collection, data reduction, and cell refinement were performed using the CrysAlisPro software.\(^{28}\) An absorption correction based on the semi-empirical “multi-scan” approach was performed using the SCALE3 ABSPACK scaling algorithm.\(^{28}\) The structure was solved by charge flipping using Superflip.\(^{29-31}\) For the final model all non-hydrogen atoms were refined anisotropically using SHELXL.\(^{32}\)

Cyclic voltammetry experiments were performed using a computer-controlled Autolab PGSTAT 30 potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferricenium couple. Deoxygenated acetonitrile dried over molecular sieves or THF dried via a MB SPS-800 solvent purifying system (MBraun) was used as the solvent. Solutions of tetrabutylammonium hexafluoro-
phosphate (Sigma Aldrich) as the supporting electrolyte with a concentration of 0.1 M were applied and were blanketed with argon during the measurements. For electropolymerizations the respective monomer was used in a concentration of 0.01 M in acetonitrile. The obtained film was washed with dry acetonitrile and subjected to several scans in a monomer-free electrolyte solution until a stable current response was recorded ("conditioning"). Subsequently, the respective film was characterized by cyclic voltammetry using different scan rates between 100 mV/s and 10 mV/s. At every scan rate three scans were conducted. Additionally, 30 scans were measured with a scan rate of 100 mV/s.

Spectroelectrochemical measurements of the polymer films were carried out in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in dry acetonitrile. The applied setup has been described in detail in literature. A Princeton Applied Research PAR 363 potentiostat was used together with a platinum working electrode, a Ag/AgCl reference electrode, and a platinum sheet as the counter electrode. Polymer films were prepared electrochemically as stated above, including the "conditioning" phase. During the recording of the UV-Vis-NIR spectra the applied potential was kept constant. In order to obtain the UV-Vis-NIR spectrum of the neutral polymer film without any oxidized parts, a potential of -500 mV vs. Ag/AgCl was applied at the beginning of the spectroelectrochemical measurements. Instrumental artefacts were removed and marked in the spectra. Moreover, the absorption in the UV-Vis region below 860 nm was adjusted to the absorption at higher wavelengths to obtain continuous spectra.

GPC-UV analysis with THF as eluent was performed at 1 mL/min on a Merck Hitachi LaChrom GPC system equipped with an L-7100 HPLC pump, L-7420 UV-Vis detector, and three columns (PSS SDV 103 Å, 104 Å, and 105 Å). The columns were kept in a column heater at 35 °C and were calibrated with polystyrene standards (Polymer Standards Service).

Quantum chemical calculations were carried out with the Gaussian 09 program. Alkyl residues were shortened to ethyl in order to save computational time. Geometry optimizations and energy calculations were performed via DFT methods using the M06-2X correlation/exchange functional and the 6-311+G(d) or the 6-311G basis set. Molecular orbital surfaces were generated utilizing the Gauss View 5.0 program with an isovalue of 0.02.
Chapter 4

Materials

Toluene (VWR) and THF (Sigma Aldrich) were dried and purified by a MB SPS-800 (MBraun). Chloroform, ethanol, petroleum ether, toluene, dichloromethane, and \( n \)-hexane were purchased from VWR and distilled prior to use. Diisopropylamine was purchased from VWR and dried over calcium hydride. Propylamine, hexylamine, and aniline were purchased from Merck and dried over calcium hydride. \( \text{CuCl}_2 \) was purchased from Merck and dried in vacuo at 150 °C prior to use. Sodium tert-butoxide, copper(I) iodide, acetic acid, 3-methylthiophene, and anhydrous iron trichloride were purchased from Merck. \( N,N' \)-Dimethyl-ethylenediamine (DMEDA) was purchased from Alfa Aesar. Potassium carbonate, Pd(dbta)\(_2\), Pd\(_2\)(dba)\(_3\), \( N \)-bromosuccinimide, hydrochloric acid (35%), and 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (RuPhos) were purchased from Sigma Aldrich. Benzamide, zinc, and \( n \)-butyl lithium were purchased from Acros Organics. 1,1'-Bis(diphenylphosphino)ferrocene (dppf) was purchased from fluorchem. 9-Aminoanthracene was synthesized by A. Looser according to published procedures.\(^{[33]} \) All synthetic steps were carried out under argon atmosphere.

2,5-Dibromo-3-methylthiophene (224)\(^{[17]} \)

![Structure of 2,5-Dibromo-3-methylthiophene](image)

3-Methylthiophene 223 (38.1 g, 0.39 mol) was dissolved in a 1:1 mixture of chloroform and glacial acetic acid (400 mL). \( N \)-Bromosuccinimide (145 g, 0.82 mol, 2.10 eq) was added by portions and the reaction mixture was heated at 80 °C for 8 h. After quenching with saturated aqueous KOH (300 mL), the phases were separated. The organic phase was washed with water (3 \( \times \) 200 mL), dried over MgSO\(_4\), filtrated, and the solvent of the filtrate was evaporated under reduced pressure. The raw product was distilled over a Vigeux column (30 cm) to give dibromide 224 as a yellow oil (84.9 g, 0.33 mol, 85%). The analytical data was in accordance with literature.

\(^{1}H\) NMR (CDCl\(_3\), 400 MHz): \( \delta = 6.77 \) (s, 1 H, \( H4 \)), 2.15 (s, 3H, \( CH3 \)) ppm.

\(^{13}C\) NMR (CDCl\(_3\), 101 MHz): \( \delta = 138.21, 132.02, 110.27, 108.51, 15.29 \) ppm.
β,β'-Dimethyl-substituted dithieno[3,2-b:2',3'-d]pyrroles (Me-DTPs)

\[3,3',5,5'-\text{tetrabromo-4,4'-dimethyl-2,2'-bithiophene (225)}^{[17]}\]

A solution of diisopropylamine (15.4 mL, 109 mmol, 1.20 eq) in THF (200 mL) was cooled to 0 °C and \(n\)-BuLi (1.6 M in \(n\)-hexane, 68.3 mL, 109 mmol, 1.20 eq) was added. After stirring for 30 min, the solution was cooled to -78 °C, 2,5-dibromo-3-methylthiophene 224 (23.3 g, 91.0 mmol) was added, and the reaction mixture was stirred for 2 h. Subsequently, CuCl\(_2\) (14.7 g, 109 mmol, 1.20 eq) was added in one portion and the reaction mixture was stirred overnight, while slowly warmed to room temperature. Aqueous hydrochloric acid (2 M, 150 mL) and chloroform (150 mL) were added, the phases were separated, and the aqueous phase was extracted with chloroform (2 × 100 mL). The product crystallized from the combined organic phase to afford bithiophene 225 as a beige solid (17.1 g, 33.5 mmol, 74%). The analytical data was in accordance with literature.

\(\text{Mp.: 180-182 °C.}\)

\(^{1}\text{H NMR (CDCl}_3\), 400 MHz): \(\delta = 2.26\) (s, 3 H, \(CH_3\)) ppm.

\(^{13}\text{C NMR (CDCl}_3\), 101 MHz): \(\delta = 137.42, 128.40, 115.07, 111.22, 16.45\) ppm.

\[3,3'-\text{dibromo-4,4'-dimethyl-2,2'-bithiophene (226)}^{[17]}\]

A suspension of 3,3’,5,5’-tetrabromo-4,4’-dimethyl-2,2’-bithiophene 225 (4.33 g, 8.50 mmol) in ethanol (25 mL), aqueous hydrochloric acid (0.3 M, 5 mL), and acetic acid (5 mL) was heated at 110 °C and zinc dust (1.33 g, 20.4 mmol, 2.40 eq) was added by portions. After 3 h the reaction mixture was filtrated hot and a brown precipitate formed from the filtrate. The isolated solid was recrystallized from ethanol to afford dibromide 226 as a colourless solid (1.71 g, 4.85 mmol, 57%). The analytical data was in accordance with literature.

\(\text{Mp.: 65-68 °C.}\)

\(^{1}\text{H NMR (CDCl}_3\), 400 MHz): \(\delta = 7.13\) (q, \(J = 1.0\) Hz, 2 H, Th-\(H_\alpha\)), 2.28 (d, \(J = 1.1\) Hz, 6 H, \(CH_3\)) ppm.

\(^{13}\text{C NMR (CDCl}_3\), 101 MHz): \(\delta = 137.77, 129.54, 122.43, 115.99, 16.84\) ppm.
3,5-Dimethyl-4H-dithieno[3,2-\textit{b}:2',3'-\textit{d}]pyrrole (227)

A suspension of Cul (57.1 mg, 0.30 mmol, 0.10 eq), DMEDA (0.13 mL, 1.20 mmol, 0.40 eq), K$_2$CO$_3$ (1.24 g, 9.00 mmol, 3.00 eq), benzamide (545 mg, 4.50 mmol, 1.50 eq), and 3,3'-dibromo-4,4'-dimethyl-2,2'-bithiophene 226 (1.06 g, 3.00 mmol) in wet toluene (6 mL) was purged with argon and heated at 110 °C for 6 d. After cooling to room temperature, the suspension was diluted with dichloromethane and filtered through a plug of celite. The raw product was purified via column chromatography (SiO$_2$, petroleum ether : dichloromethane = 3:1) to yield Me-DTP 227 as a colourless solid (391 mg, 1.89 mmol, 63%).

\textbf{Mp.}: 160-163 °C.

\textbf{¹H NMR} (CD$_2$Cl$_2$, 400 MHz): \(\delta = 8.30\) (s, 1 H, NH), 6.77 (q, \(J = 1.1\) Hz, 2 H, Th-\(H_d\)), 2.38 (d, \(J = 1.2\) Hz, 6 H, \(CH_3\)) ppm.

\textbf{¹³C NMR} (CD$_2$Cl$_2$, 101 MHz): \(\delta = 143.89, 122.69, 118.92, 116.52, 13.36\) ppm.

\textbf{Cl-MS}: \(m/z\) (%) = 207 (100) [M]$^+$.  

\textbf{Elemental analysis}: calc. (%) for C$_{30}$H$_9$NS$_2$: C 57.94, H 4.38, N 6.76, S 30.93; found: C 57.70, H 4.58, N 6.67, S 30.95.

\textbf{UV-Vis} (THF) \(\lambda_{\text{max}}\) (\(\varepsilon\)): 301 (sh, 19 800), 292 (23 700), 281 (sh, 18 700) nm.

4-Propyl-3,5-dimethyl-4H-dithieno[3,2-\textit{b}:2',3'-\textit{d}]pyrrole (228)

A suspension of 3,3'-dibromo-4,4'-dimethyl-2,2'-bithiophene 226 (352 mg, 1.00 mmol), NaOtBu (288 mg, 3.00 mmol, 3.00 eq), Pd(db)$_2$ (28.8 mg, 0.05 mmol, 0.05 eq), dppf (111 mg, 0.20 mmol, 0.20 eq), and propylamine (0.12 mL, 1.50 mmol, 1.50 eq) in toluene (3 mL) was purged with argon and was then heated at 110 °C overnight. After cooling to room temperature, the crude product was purified via column chromatography (SiO$_2$, petroleum ether) to yield Me-DTP 228 as a colourless solid (212 mg, 0.85 mmol, 85%).

\textbf{Mp.}: 122-124 °C (DSC).

\textbf{¹H NMR} (CD$_2$Cl$_2$, 400 MHz): \(\delta = 6.71\) (q, \(J = 1.1\) Hz, 2 H, Th-\(H_d\)), 4.40 – 4.30 (m, 2 H, N-\(CH_3\)),

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2.49 (d, J = 1.1 Hz, 6 H, Th-CH₃), 1.90 – 1.74 (m, 2 H, N-CH₂-CH₂), 0.96 (t, J = 7.4 Hz, 3 H, CH₂-CH₃) ppm.

¹³C NMR (CD₂Cl₂, 101 MHz): δ = 143.60, 123.09, 119.52, 115.75, 47.50, 26.80, 14.93, 11.00 ppm.

GC/EI-MS (70 eV): tᵣ = 19.3 min; m/z (%) = 249 (100) [M]⁺, 220 (92) [M-C₂H₅]⁺, 206 (18) [M-C₃H₅]⁺.

CI-MS: m/z (%) = 250 (100) [M+H]⁺, 220 (5) [M-C₂H₅]⁺.

Elemental analysis: calc. (%) for C₁₃H₁₂NS₂: C 62.61, H 6.06, N 5.62, S 25.71; found: C 62.81, H 6.14, N 5.82, S 25.59.

UV-Vis (THF) λₘₐₓ (ε): 308 (17 200), 296 (20 300), 286 (sh, 16 100) nm.

4-Hexyl-3,5-dimethyl-4H-dithieno[3,2-b:2′,3′-d]pyrrole (229)

A suspension of 3,3′-dibromo-4,4′-dimethyl-2,2′-bithiophene 226 (1.06 g, 3.00 mmol), NaOtBu (865 mg, 9.00 mmol, 3.00 eq), Pd(dba)₂ (86.3 mg, 0.15 mmol, 0.05 eq), dppf (333 mg, 0.60 mmol, 0.20 eq), and hexylamine (0.51 mL, 3.90 mmol, 1.30 eq) in toluene (8 mL) was purged with argon and was then heated at 110 °C overnight. After cooling to room temperature, the crude product was purified via column chromatography (SiO₂, petroleum ether) to yield Me-DTP 229 as a colourless solid (691 mg, 2.37 mmol, 79%).

Mp.: 103-104 °C.

¹H NMR (CD₂Cl₂, 400 MHz): δ = 6.71 (q, J = 1.1 Hz, 2 H, Th-H₆), 4.40 – 4.35 (m, 2 H, N-CH₂), 2.49 (d, J = 1.1 Hz, 6 H, Th-CH₃), 1.86 – 1.73 (m, 2 H, N-CH₂-CH₂), 1.43 – 1.35 (m, 2 H, N-(CH₂)₂-CH₂), 1.34 – 1.28 (m, 4 H, N-(CH₂)₃-(CH₂)₂), 0.91 – 0.85 (m, 3 H, CH₂-CH₃) ppm.

¹³C NMR (CD₂Cl₂, 101 MHz): δ = 143.51, 123.07, 119.48, 115.73, 46.17, 33.60, 31.90, 26.70, 22.97, 14.93, 14.14 ppm.

CI-MS: m/z (%) = 291 (100) [M]⁺.

Elemental analysis: calc. (%) for C₁₆H₁₅NS₂: C 65.93, H 7.26, N 4.81, S 22.00; found: C 65.88, H 7.14, N 4.74, S 21.95.

UV-Vis (THF) λₘₐₓ (ε): 308 (sh, 21 400), 296 (25 200), 286 (sh, 19 700) nm.
4-Phenyl-3,5-dimethyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (230)

A suspension of 3,3′-dibromo-4,4′-dimethyl-2,2′-bithiophene 226 (528 mg, 1.50 mmol), NaOtBu (432 mg, 4.50 mmol, 3.00 eq), Pd(dba)₂ (43.1 mg, 0.08 mmol, 0.05 eq), dppf (166 mg, 0.30 mmol, 0.20 eq), and aniline (0.18 mL, 1.95 mmol, 1.30 eq) in toluene (5 mL) was purged with argon and was then heated at 110 °C overnight. After cooling to room temperature, the crude product was purified via column chromatography (SiO₂, petroleum ether) to yield Me-DTP 230 as a colourless solid (403 mg, 1.42 mmol, 95%).

Mp.: 162-165 °C.

¹H NMR (CD₂Cl₂, 400 MHz): δ = 7.52 – 7.47 (m, 5 H, Ph-H), 6.71 (q, J=1.1 Hz, 2 H, Th-Hα), 1.84 (d, J = 1.1 Hz, 6 H, CH₃) ppm.

¹³C NMR (CD₂Cl₂, 101 MHz): δ = 144.63, 138.53, 129.49, 128.98, 128.93, 123.71, 119.57, 116.10, 14.28 ppm.

CI-MS: m/z (%) = 283 (100) [M⁺].

Elemental analysis: calc. (%) for C₁₆H₁₃NS₂: C 67.81, H 4.62, N 4.94, S 22.62; found: C 67.79, H 4.71, N 5.01, S 22.73.

UV-Vis (THF) λ_max (ε): 305 (21 400), 295 (25 200), 285 (sh, 20 300) nm.

4-(9-Anthracenyl)-3,5-dimethyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (231)

A suspension of 3,3′-dibromo-4,4′-dimethyl-2,2′-bithiophene 226 (352 mg, 1.00 mmol), NaOtBu (577 mg, 6.00 mmol, 6.00 eq), Pd₂(dba)₃ (93.4 mg, 0.10 mmol, 0.10 eq), RuPhos (196 mg, 0.40 mmol, 0.40 eq), and 9-aminoanthracene (290 mg, 1.50 mmol, 1.50 eq) in toluene (5 mL) was purged with argon and was then heated at 115 °C for 4 h. After cooling to room temperature, the crude product was purified via column chromatography (SiO₂, petroleum ether : dichloromethane = 6:1) and recrystallized from n-hexane and toluene to yield Me-DTP 231 as a yellow solid (284 mg, 0.74 mmol, 74%).
**β,β’-Dimethyl-substituted dithieno[3,2-b:2’,3’-d]pyrroles (Me-DTPs)**

**Mp.:** 301-305 °C (DSC).

**1H NMR** (CD$_2$Cl$_2$, 400 MHz): δ = 8.68 (s, 1 H, H10’), 8.14 (d, J = 8.4 Hz, 2 H, H1’, H8’), 7.55 – 7.50 (m, 2 H, H4’, H5’), 7.45 – 7.38 (m, 4 H, H2’, H3’, H6’, H7’), 6.67 (q, J = 1.1 Hz, 2 H, Th-Hδ), 1.20 (d, J = 1.2 Hz, 6 H, CH$_3$) ppm.

**13C NMR** (CD$_2$Cl$_2$, 101 MHz): δ = 145.87, 131.49, 131.28, 130.24, 128.85, 128.58, 127.80, 126.21, 123.70, 123.43, 119.47, 119.44, 119.42 ppm.

**GC/EI-MS** (70 eV): $t_{r}$ = 27.9 min; m/z (%) = 383 (100) [M]+.

**EI-MS:** m/z (%) = 384 (100) [M]+.

**Elemental analysis:** calc. (%) for C$_{24}$H$_{17}$NS$_2$: C 75.16, H 4.47, N 3.65, S 16.72; found: C 75.29, H 4.55, N 3.79, S 16.61.

**UV-Vis** (THF) $\lambda_{\text{max}}$ (ε): 388 (6 400), 368 (7 200), 351 (4 900), 334 (sh, 2 300), 303 (19 100), 292 (23 100), 282 (sh, 19 400), 255 (131 300), 250 (sh, 109 700) nm.

**4-Benzoyl-3,5-dimethyl-4H-dithieno[3,2-b:2’,3’-d]pyrrole (232)**

A suspension of CuI (28.6 mg, 0.15 mmol, 0.05 eq), DMEDA (68.0 µL, 0.60 mmol, 0.20 eq), K$_2$CO$_3$ (1.24 g, 9.00 mmol, 3.00 eq), benzamide (545 mg, 4.50 mmol, 1.50 eq), and 3,3’-dibromo-4,4’-dimethyl-2,2’-bithiophene 226 (1.06 g, 3.00 mmol) in toluene (6 mL) was purged with argon and heated at 110 °C for 24 h. After cooling to room temperature, the suspension was diluted with dichloromethane and filtered through a plug of celite. The raw product was purified via column chromatography (SiO$_2$, petroleum ether : dichloromethane = 3:1) to yield unsubstituted Me-DTP 227 as a colourless solid (135 mg, 0.65 mmol, 22%) and benzoyl-substituted Me-DTP 232 as a yellow solid (337 mg, 1.08 mmol, 36%). The analytical data of unsubstituted Me-DTP 227 was in accordance with the data above.

**Analytical data of unsubstituted Me-DTP 227:**

**Mp.:** 123-124 °C.

**1H NMR** (CD$_2$Cl$_2$, 400 MHz): δ = 7.84 – 7.80 (m, 2 H, o-Ph-H), 7.70 – 7.64 (m, 1 H, p-Ph-H), 7.53 – 7.48 (m, 2 H, m-Ph-H), 6.79 (q, J = 1.1 Hz, 2 H, Th-Hδ), 1.84 (d, J = 1.1 Hz, 6 H, CH$_3$) ppm.

**13C NMR** (CD$_2$Cl$_2$, 101 MHz): δ = 167.61, 143.09, 135.57, 134.25, 131.22, 129.27, 125.74, 121.62, 120.88, 15.89 ppm.
**CI-MS:** \(m/z \) (%) = 311 (52) \([M]^+\).

**Elemental analysis:** calc. (%) for C\textsubscript{17}H\textsubscript{13}NOS: C 65.57, H 4.21, N 4.50, S 20.59; found: C 65.41, H 4.05, N 4.65, S 20.59.

**UV-Vis** (THF) \(\lambda_{\text{max}} \) (\(\varepsilon\)): 324 (sh, 7 200), 297 (sh, 21 000), 289 (23 000), 241 (sh, 16 700) nm.

**Poly(4-hexyl-3,5-dimethyl-4H-dithieno[3,2-b:2',3'-d]pyrrole) \(P_{\text{ox}229}\)**

Hexyl-substituted Me-DTP monomer \(229\) (291 mg, 1.00 mmol) was dissolved in dichloromethane (50 mL). Anhydrous iron trichloride (649 mg, 4.00 mmol, 4.00 eq) was added and the reaction mixture was stirred at ambient temperature for 24 h. The solvent was removed under reduced pressure and the residue was transferred into a Soxhlett apparatus, where the polymer was dedoped with aqueous hydrazine for 24 h, washed with \(n\)-hexane for 24 h, and extracted with THF. The solvent of the extract was removed under reduced pressure to yield polymer \(P_{\text{ox}229}\) as an orange solid (62.0 mg, 0.21 mmol, 21%).

**\(^1\text{H NMR}\)** (THF-\(d_8\), 400 MHz): \(\delta = 6.80 \) (s, Th-H\(a\)), 4.62 – 4.47 (m, 2 H, N-CH\(_2\)), 2.55 – 2.43 (m, Th-CH\(_3\)), 2.02 – 1.81 (m, 2 H, N-CH\(_2\)-CH\(_3\)), 1.52 – 1.31 (m, 6 H, N-(CH\(_2\))\(_2\)-(CH\(_2\))\(_3\)), 0.95 – 0.89 (m, 3 H, CH\(_2\)-CH\(_3\)) ppm.

**IR** (KBr): \(\tilde{\nu} = 2952, 2926, 2854\) (C-H), 1684 (C=C) cm\(^{-1}\).
4.9 References

Chapter 5

Acceptor-donor-acceptor-type oligomers
5.1 Introduction

Organic solar cells are most commonly processed from solution, but with small organic molecules the active layers can also be produced by sublimation under reduced pressure (vacuum processing).\(^{[1-4]}\) Hence, the applied components do not need to be soluble and insulating alkyl chains can be omitted. Vacuum-processed organic solar cell devices are commercialized by our cooperation partner Heliatek and usually contain C\(_{60}\) as acceptor and an A-D-A-type oligomer as donor material. In this respect, oligothiophenes with DCV acceptor groups at the peripheries gained much interest. Thus, quarterthiophenes with hydrogens in methyls in 234, or ethyls in 235 were utilized in BHJ solar cells (Figure 5.1).\(^{[5-6]}\) The attachment of methyl residues in quarterthiophene 234 led to stronger intermolecular interactions in the solid state compared to its ethyl- or unsubstituted analogues 233 and 235 and therefore the highest PCE of 3.8% in the series was obtained.\(^{[6]}\)

\[\text{Figure 5.1: Structures of DCV-substituted quarterthiophenes 233-235 intended for the application in vacuum-processed organic solar cells.}\]

With the larger DCV-substituted quinquethiophenes 236-238 a similar favourable ordering was observed and depended on the position of attached methyl residues (Figure 5.2).\(^{[7]}\) Vacuum-processed photovoltaic cells incorporating oligomer 238 with two CH\(_3\) groups at the central thiophene unit showed the best performance in this series. Thus, in optimized devices applying derivative 238 relatively high PCEs of up to 8.3% in single junction and 9.7% in triple junction solar cells could be reached.\(^{[8]}\)

These intriguing results with DCV-substituted oligothiophenes indicated an important role of methyl residues concerning intermolecular interactions in the active layer of vacuum-processed organic solar cells. Consequently, the synthesized Me-DTPs described in Chapter 4 appeared to be promising building blocks as central donor units in A-D-A-type oligomers.
Analogous oligomers 165 and 166\textsuperscript{[9]} without methyls at the DTP donor unit have already been prepared and incorporate one thiophene spacer at each side between the central DTP moiety and DCV acceptor groups in the peripheries (Chapter 1.5).

\textbf{Figure 5.2:} Structures of DCV- and methyl-substituted quinquethiophenes 236-238 intended for the application in vacuum-processed organic solar cells.
5.2 Synthesis of A-D-A-type oligomers

As a reference compound for similar oligomers with different DTP units in the centre, phenyl-substituted oligomer 165 was first of all synthesized (Scheme 5.1). Thus, phenyl-substituted DTP 65 was lithiated in the two α-positions with n-BuLi and the reaction mixture was stirred at -78 °C for one hour and then at 0 °C for another hour. Herein, the high DTP concentration of 0.3 M was an important factor to ensure the twofold reaction and avoid the mono-lithiated side-product. After quenching with trimethyltin chloride at -78 °C and aqueous workup, distannyl 239 was extracted and used without further purification. A twofold Stille-type cross-coupling reaction with DCV-substituted bromothiophene 240 finally gave A-D-A-type oligomer 165 in a yield of 89%. For further purification a small sample of compound 165 was sublimed at a tube-based vacuum sublimation unit allowing sublimations at controlled temperatures and at high vacuum. Only minor amounts of solid residues remained at the source and a sublimation yield of 88% was achieved. The purity of oligomer 165 was confirmed by 1H NMR spectroscopy and high-resolution MALDI mass spectrometry. In order to dissolve larger amounts of the hardly soluble compound, the NMR spectrum was recorded at 82 °C in C2D2Cl4 and a sufficiently improved signal-to-noise ratio was obtained.

![Scheme 5.1: Stannylation of phenyl-substituted DTP 65 and subsequent Stille-type coupling to oligomer 165.](image)
The corresponding twofold stannylation of phenyl-substituted Me-DTP 230 was subsequently attempted (Scheme 5.2, Table 5.1). However, under identical conditions mostly mono-stannylated side-product 241 and starting material 230 were obtained (Table 5.1, entry 1). Steric shielding of the α-positions in Me-DTP 230 by the adjacent methyl residue could be one reason for the limited conversion during stannylation. However, electronic effects seemed to be a more important factor. Due to the electron-donating influence of the methyl groups the dithienopyrrole unit in Me-DTP 230 is more electron-rich than in the analogous phenyl-substituted DTP 65. This hampered the twofold deprotonation of phenyl-substituted Me-DTP 230 and made it necessary to apply harsher reaction conditions. Thus, by increasing the reaction time, respectively the temperature during lithiation with n-BuLi, the product ratio could be shifted in favour of the desired distannyl 242 (Table 5.1, entry 2-3). Relatively large amounts of monostannyl 241 and also starting material 230 were yet still afforded. Therefore, the stronger lithiating reagent t-BuLi was applied, but the yield of distannyl 242 could only be improved to 63% (Table 5.1, entry 4-5).

Scheme 5.2: Twofold stannylation of phenyl-substituted Me-DTP 230. Details see Table 5.1.

<table>
<thead>
<tr>
<th>Lithiating reagent</th>
<th>-78 °C</th>
<th>0 °C</th>
<th>RT</th>
<th>Yield of 230</th>
<th>Yield of 241</th>
<th>Yield of 242</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 n-BuLi</td>
<td>1 h</td>
<td>1 h</td>
<td>-</td>
<td>40%</td>
<td>45%</td>
<td>15%</td>
</tr>
<tr>
<td>2 n-BuLi</td>
<td>1 h</td>
<td>2 h</td>
<td>-</td>
<td>5%</td>
<td>43%</td>
<td>52%</td>
</tr>
<tr>
<td>3 n-BuLi</td>
<td>1 h</td>
<td>-</td>
<td>2 h</td>
<td>4%</td>
<td>36%</td>
<td>60%</td>
</tr>
<tr>
<td>4 t-BuLi</td>
<td>1 h</td>
<td>2 h</td>
<td>-</td>
<td>13%</td>
<td>26%</td>
<td>61%</td>
</tr>
<tr>
<td>5 t-BuLi</td>
<td>1 h</td>
<td>-</td>
<td>3 h</td>
<td>7%</td>
<td>31%</td>
<td>63%</td>
</tr>
</tbody>
</table>
Using a mixture of Me-DTP 230, monostannyl 241, and distannyl 242 in a subsequent Stille-type cross-coupling reaction with DCV-substituted bromothiophene 240 would most likely have yielded major amounts of undesired side-products. Therefore, the stannyl groups in products 241 and 242 were abstracted again after each attempt by subjecting the mixture to column chromatography with silica gel and starting material 230 could be recovered. However, considerable overall losses of Me-DTP 230 during this procedure of stannylation and stannyl abstraction as well as the colour change of the stannyl mixture from orange to blue-green upon storage at -20 °C under argon atmosphere indicated the partial decomposition of stannylated Me-DTP 230. Most likely a C-C coupling to polymeric DTP species occurred showing the increased reactivity of methyl-substituted distannyl 242 compared to the quite stable analogue 239 without methyl residues.

Hence, the stannylation attempts of Me-DTP 230 gave unsatisfactory results and alternative strategies were investigated. Instead of preparing distannyl 242 via lithiation of Me-DTP 230 and subsequent quenching with trimethylstannyl chloride, the dibromide or diiodide of Me-DTP 230 could have been reacted with a bis(trialkyltin) reagent under palladium catalysis. Dibromides of DTPs without methyl groups in the two β-positions quickly polymerize, if the pyrrole is substituted by an alkyl chain with a CH group in α-position to the nitrogen, but are reasonably stable, if the nitrogen is aryl-substituted.[10-12] Moreover, a higher stability is observed for diiodides and also N-alkyl DTPs thereof can be isolated.[13] Their synthesis can either be carried out via lithiation of a DTP with t-BuLi and subsequent quenching with iodine,[13] or via direct iodination of a DTP with NIS.[14-17] The latter approach was carried out applying phenyl-substituted Me-DTP 230 and after purification via column chromatography diiodide 243 could be isolated in quantitative yields (Scheme 5.3). Analysis by high-resolution MALDI mass spectrometry still indicated the presence of minor impurities, but diiodide 243 was reacted further without additional purification steps. Coupling with bis(tributyltin) under palladium catalysis afforded the targeted distannyl 245. However, excess of the applied bis(tributyltin) could not be removed in an aqueous workup. Efforts to isolate distannyl 245 by column chromatography with largely deactivated silica gel moreover led to the partial abstraction of stannyl groups and only a mixture of Me-DTP 230, monostannyl 244, and distannyl 245 could be isolated.
Acceptor-donor-acceptor-type oligomers

\[
\begin{array}{c}
\text{H}_2\text{C} \quad \text{N} \quad \text{CH}_3 \\
\text{S} \quad \text{S} \quad \text{230} \\
\end{array}
\quad
\begin{array}{c}
\text{H}_2\text{C} \quad \text{N} \quad \text{CH}_3 \\
\text{S} \quad \text{S} \quad \text{I} \\
\end{array}
\quad
\begin{array}{c}
\text{H}_2\text{C} \quad \text{N} \quad \text{CH}_3 \\
\text{S} \quad \text{S} \quad \text{I} \\
\end{array}
\quad
\begin{array}{c}
\text{Bu}_3\text{Sn} \quad \text{Pd} \\
\text{SnBu}_3 \\
\text{244} \\
\end{array}
\quad
\begin{array}{c}
\text{H}_2\text{C} \quad \text{N} \quad \text{CH}_3 \\
\text{S} \quad \text{S} \quad \text{SnBu}_3 \\
\text{245} \\
\end{array}
\]

**Scheme 5.3:** Iodination of phenyl-substituted Me-DTP 230 and subsequent stannylation.

Therefore, instead the stannyl component of dicyanovinylene-substituted thiophene was prepared\(^{[18-19]}\) in order to couple it in a Stille reaction with diiodide 243. Following this approach, 2-(tributylstannyl)thiophene 246 was lithiated in the S-position with LDA and then quenched with DMF (Scheme 5.4). After aqueous workup, the raw product was purified via column chromatography to give aldehyde 247 in a yield of 67%. Subsequently, Knoevenagel condensation with malonodinitrile afforded DCV-substituted stannylthiophene 248, which was purified by column chromatography with dichloromethane as eluent. The product was isolated in a yield of 86% and could then be used in Stille-type cross-coupling reactions for the synthesis of the targeted A-D-A-type oligomers.

\[
\begin{array}{c}
\text{Bu}_3\text{Sn} \\
\text{S} \\
\text{246} \\
\end{array}
\quad
\begin{array}{c}
1) \text{LDA} \\
2) \text{DMF} \\
\text{Bu}_3\text{Sn} \\
\text{S} \quad \text{O} \\
\text{247} \\
\end{array}
\quad
\begin{array}{c}
\text{CH}_2(\text{CN})_2 \\
\text{Bu}_3\text{Sn} \\
\text{S} \quad \text{CN} \quad \text{CN} \\
\text{248} \\
\end{array}
\]

**Scheme 5.4:** Synthesis of DCV-substituted stannylthiophene 248\(^{[18-19]}\)

Firstly, phenyl-substituted derivative 249 was prepared by reacting diiodide 243 with stannyl 248 (Scheme 5.5). After precipitation with methanol, A-D-A-type oligomer 249 was isolated as a mixture with several side-products, which mostly originated from homo-coupling of precursor 243. Pure oligomer 249 was obtained by gradient high vacuum sublimation, but with this method only a low yield could be achieved. Most likely the high molecular weight side-products hampered a more efficient sublimation and thus large amounts of decomposed sample remained at the source.
Scheme 5.5: Synthesis of oligomer 249 via Stille-type cross-coupling.

Hence, the synthetic procedure for propyl-substituted derivative 251 was slightly adapted (Scheme 5.6). Twofold iodination of Me-DTP 228 with NIS initially gave diiodide 250 containing only minor impurities and the product was used without further purification. However, in order to avoid a large extent of homo-coupling in the Stille reaction of diiodide 250 and stannyl 248, the less active palladium catalyst Pd(PPh₃)₂Cl₂ was applied instead of Pd(PPh₃)₄. Propyl-substituted oligomer 251 could subsequently be purified via column chromatography and was obtained in 63% yield. Moreover, high vacuum sublimation worked much more efficiently than for the raw phenyl-substituted analogue 249 and a sublimation yield of 73% for oligomer 251 was reached.

Scheme 5.6: Synthesis of diiodide 250 and subsequent Stille-type cross-coupling to oligomer 251.

Similarly to analogue 165, the purity of oligomers 249 and 251 was confirmed by ¹H NMR spectroscopy (measured at 82 °C in C₂D₂Cl₄) and high-resolution MALDI mass spectrometry. The ¹H NMR spectrum of propyl-substituted oligomer 251 is shown in Figure 5.3. As expected, the propyl residue and the two methyl groups of the central Me-DTP donor unit give rise to four different signals in the aliphatic region of the ¹H NMR spectrum. Furthermore,
two doublets at 7.78 ppm and 7.36 ppm with a coupling constant $^3J_{HH}$ of 4.1 Hz appear due to the four protons of the two thiophene moieties. Herein, the downfield shifted doublet overlaps with the singlet of the two DCV protons at 7.77 ppm. The $^1$H NMR spectrum of phenyl-substituted derivative 249 looks very similar to the spectrum of 251, but instead of aliphatic signals of the propyl substituent contains two aromatic multiplets corresponding to the phenyl protons. Additionally, the singlet of the two methyl groups attached at the Me-DTP unit is further shifted upfield from 2.78 ppm for propyl-substituted oligomer 251 to 2.09 ppm. A similar effect was also observed for propyl- and phenyl-substituted Me-DTPs 228 and 230 and can most likely be explained by the aromatic ring current effect of the phenyl-substituent in oligomer 249 (compare Chapter 4.2). In the MALDI mass spectra of both oligomers only one set of signals appeared indicating their high respective purity. The $m/z$ value of 599.03588 for oligomer 249 deviated by 0.42 ppm from the calculated theoretical mass, whereas a deviation of 0.12 ppm with the value of 565.05185 was observed for oligomer 251.

\[ \text{Figure 5.3: } ^1\text{H NMR spectrum of co-oligomer 251 recorded in C}_2\text{D}_2\text{Cl}_4 \text{ at } 82 \, ^\circ\text{C.} \]
5.3 Thermal and optoelectronic properties of A-D-A-type oligomers

The thermal properties of the synthesized oligomers 165, 249, and 251 were determined (Figure 5.4, Table 5.2). Melting points $M_p$ were obtained by differential scanning calorimetry (DSC) and the decomposition temperatures $T_d$ were estimated from thermal gravimetric analysis (TGA). In the DSC curve of phenyl-substituted oligomer 165 an exothermic signal at 394-396 °C appears due to the melting of the compound. Upon heating to 800 °C during TGA, oligomer 165 decomposes and the accompanied mass losses approximately correspond to the successive cleavage of the two DCV groups starting at 407 °C. Similarly, the analogous co-oligomer 166 with a propyl instead of a phenyl substituent at the central nitrogen melts at 367 °C and also decomposes when the temperature is further increased. The higher melting point of phenyl-substituted derivative 165 in comparison to propyl-substituted oligomer 166 indicates stronger intermolecular interactions due to the participation of the phenyl residue in $\pi-\pi$ stackings and the same trends can be observed for analogous oligomers incorporating selenophene instead of thiophene rings.

![Figure 5.4: DSC (a) and TGA (b) measurements of oligomers 165, 249, and 251 at a heating rate of 10 °C/min under argon (a) or nitrogen (b) flow.](image_url)
In contrast to that, the melting point of phenyl-substituted oligomer 249 (305-310 °C) is decreased compared to analogue 251 (323-325 °C), which bears a propyl chain at the central nitrogen. Similarly to corresponding Me-DTP precursor 230 (Chapter 4.4), the phenyl ring in oligomer 249 is presumably almost perpendicularly distorted to the dithienopyrrole plane and therefore cannot contribute to the same π-π stackings. Other interactions of the phenyl moieties apparently do not play a major role and the relatively low melting point rather indicates that the phenyl substituent even prevents stronger π-π stackings of the conjugated backbone. At elevated temperatures above 350 °C both phenyl-substituted oligomer 249 and propyl-substituted derivative 251 degrade and therefore an endothermic signal in the DSC curves can be observed, respectively. Similarly to the analogous oligomers without methyl residues, the mass losses during TGA approximately account for the successive cleavage of the two DCV acceptors. Further comparison of the thermal properties of the four A-D-A-type oligomers 165, 166, 249, and 251 leads to the trend that melting points significantly decrease upon incorporating Me-DTPs instead of DTPs. Thus, the intermolecular interactions are weakened as a consequence of distorted π-systems in methyl-substituted oligomers 249 and 251. Moreover, their sublimation is possible at slightly lower temperatures. It should, however, be stated that sublimation of phenyl-substituted derivative 249 at 290 °C and of propyl-substituted oligomer 251 at 300 °C at a pressure of 10^{-6} mbar was conducted relatively close to the respective melting temperatures. Therefore, the exact process could rather have been a distillation than a sublimation.

Table 5.2: Thermal and optical properties of co-oligomers 165, 166, 249, and 251. Melting points were determined via DSC analyses. The optical properties were obtained from UV-Vis absorption and fluorescence spectra recorded in dichloromethane solution. The optical HOMO-LUMO gaps $E_g^{opt}$ were determined from $\lambda_{onset,\,abs}$. The Stokes shifts were calculated as the difference between $\lambda_{max,\,abs}$ and $\lambda_{max,\,em}$. Values for oligomer 166 were taken from literature.^[9]

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>$M_p$ [°C]</th>
<th>$T_d$ [°C]</th>
<th>$\lambda_{max,,abs}$ [nm]</th>
<th>$\varepsilon$ [M^{-1} cm^{-1}]</th>
<th>$\lambda_{onset,,abs}$ [nm]</th>
<th>$E_g^{opt}$ [eV]</th>
<th>$\lambda_{max,,em}$ [nm]</th>
<th>Stokes shift [cm^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>165</td>
<td>394-396</td>
<td>407</td>
<td>583</td>
<td>68400</td>
<td>643</td>
<td>1.93</td>
<td>665</td>
<td>2115</td>
</tr>
<tr>
<td>166</td>
<td>367</td>
<td>370^b</td>
<td>598</td>
<td>93600</td>
<td>657</td>
<td>1.89</td>
<td>668</td>
<td>1752</td>
</tr>
<tr>
<td>249</td>
<td>305-310</td>
<td>356</td>
<td>573</td>
<td>73400</td>
<td>646</td>
<td>1.92</td>
<td>670</td>
<td>2527</td>
</tr>
<tr>
<td>251</td>
<td>323-325</td>
<td>351</td>
<td>573</td>
<td>64100</td>
<td>649</td>
<td>1.91</td>
<td>676</td>
<td>2659</td>
</tr>
</tbody>
</table>

[a] Decomposition temperature $T_d$ determined from the onset of the mass loss in the TGA curves; [b] Value estimated from DSC analysis in literature^[9]
Chapter 5

The optical properties of oligomers 165, 249, and 251 were determined via UV-Vis absorption and fluorescence spectroscopy in dichloromethane solution (Figure 5.5) and the results are summarized in Table 5.2.

![Figure 5.5: UV-Vis absorption (solid lines) and normalized fluorescence spectra (dotted lines) of co-oligomers 165, 249, and 251 recorded in dichloromethane solution. For the fluorescence spectra the compounds were excited at 576 nm (165) or 560 nm (249, 251) and concentrations of 10^{-7} M were used, respectively.]

In the UV-Vis spectra of the synthesized co-oligomers 165, 249, and 251 three relatively small bands in the UV region can be observed. Additionally, one main absorption band in the visible range without a vibrational fine-structure appears and corresponds to π-π* transitions. The onset absorptions occur in the range of 643 nm to 657 nm due to similar optical HOMO-LUMO energy gaps $E_{\text{g, opt}}$ (1.89-1.93 eV). Compared to the spectrum of the same oligomer without terminal dicyanovinylene acceptor groups (recorded in acetonitrile solution) $\lambda_{\text{max, abs}}$ of phenyl-substituted co-oligomer 165 is bathochromically shifted by 187 nm and the extinction coefficient is strongly increased by 23300 M^{-1} cm^{-1}.\cite{10} This effect is due to the increased polarization of acceptor-donor-acceptor-type oligomer 165. The absorption maximum of analogue 166 with a propyl instead of a phenyl residue in the centre is further red-shifted to 598 nm and exhibits an even higher extinction. Nevertheless, the emission maximum of the two compounds 165 and 166 (665 nm and 668 nm) are very similar. The emission maximum $\lambda_{\text{max, em}}$ of 670 nm for phenyl-substituted oligomer 249 and 676 nm for propyl-substituted analogue 251 with methyl groups in the β-positions are slightly shifted to higher wavelengths and the difference between phenyl- and propyl-substituted oligomers is increased to a minor extent. However, the absorption maximum
λmax, abs of both compounds is located at 573 nm. In this series, the oligomer bearing a phenyl moiety possesses a higher extinction coefficient. Furthermore, the moderate Stokes shifts in the four co-oligomers indicate that little reorganization energy upon photoexcitation is required and thus the electronic ground state and the first excited state exhibit similar rod-like structural geometries. With methyl residues in the β-positions of the central DTP unit the Stokes shifts of phenyl-substituted oligomer 249 (2527 cm⁻¹) and propyl-substituted oligomer 251 (2659 cm⁻¹) are slightly larger than in the corresponding analogues 165 (2115 cm⁻¹) and 166 (1752 cm⁻¹). Most likely, this can be explained by the sterical repulsions between the methyls and the adjacent thiophenes which lead to a twist of the conjugated moieties and thus a relatively large deviation from a planar geometry. A similar effect has been observed for oligomers 160-162 with “inner” hexyl side chains (Chapter 1.5) or in the homopolymers of Me-DTPs (Chapter 4.5 and 4.6). Because such a twist hampers the overlap of the π-orbitals, it also accounts for the slightly blue-shifted λmax, abs in the oligomer series with methyl substituents. Overall, the optical properties of phenyl-substituted derivative 249 and propyl-substituted oligomer 251 differ less strongly than in the series of analogues 165 and 166. Hence, in this regard the phenyl or propyl residues at the central nitrogen exhibit a much less pronounced influence.

Because of their poor solubility the electrochemical properties of the prepared co-oligomers 165, 249, and 251 were determined using the relatively sensitive square wave voltammetry method (Figure 5.6). The redox potentials were determined and from the onset of the oxidation, respectively reduction, the energy levels of the frontier molecular orbitals

![Figure 5.6](image-url)
were estimated (Table 5.3). In addition to that, the amount of exchanged electrons and the electrochemical reversibility were investigated via cyclic voltammetry. In the voltammograms two reversible one-electron oxidations of the donor unit to the corresponding radical cation and subsequently to the dication, as well as an irreversible two-electron reduction of the DCV acceptor groups can be observed, respectively. Due to the electron-withdrawing character of the phenyl moiety, oligomer 165 possesses higher reduction and first oxidation potentials than propyl-substituted analogue 166. This corresponds to decreased HOMO (-5.58 eV) and LUMO (-3.89 eV) energy levels. Because the LUMO is slightly more stabilized, the electrochemical energy gap $E_{\text{g,ec}}$ of co-oligomer 165 is decreased from 1.75 eV in oligomer 166 to 1.69 eV. Contrary to that, both phenyl- and propyl-substituted oligomers 249 and 251 with methyl residues in the $\beta$-positions exhibit a similar $E_{\text{g,ec}}$. As discussed for the optical properties (vide supra), the substituent at the nitrogen does not significantly influence the electrochemical properties as well. Thus, independent from the propyl or phenyl group the oligomers possess HOMO energy levels of about -5.5 eV and LUMO energy levels of about -3.9 eV. However, in comparison to propyl-substituted analogue 166 the electron-donating methyls in oligomer 251 should lead to a lower reduction potential (increased LUMO energy) and lower first oxidation potential (increased HOMO energy). Nevertheless, the opposite trend is observed and can be explained by the twisted conjugated backbone as a consequence of steric repulsions between methyls and adjacent thiophenes. Therefore, the electron-donating influence of the Me-DTP donor unit in oligomers 249 and 251 is less pronounced. This results in a stabilized LUMO of 249 and 251 compared to propyl-substituted oligomer 166. Furthermore, the hampered overlap of the $\pi$-orbitals in Me-DTP containing oligomers 249 and 251 leads to a lower HOMO energy level than in analogue 166.

Table 5.3: Electronic properties of co-oligomers 165, 166, 249, and 251. Values for co-oligomer 166 were taken from literature.[9, 18]

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>$E_{\text{ox1}}$ $^a$ [V]</th>
<th>$E_{\text{ox2}}$ $^b$ [V]</th>
<th>$E_{\text{red}}$ $^c$ [V]</th>
<th>HOMO $^d$ [eV]</th>
<th>LUMO $^d$ [eV]</th>
<th>$E_{\text{g,ec}}$ $^e$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>165</td>
<td>0.58</td>
<td>0.88</td>
<td>-1.31</td>
<td>-5.58</td>
<td>-3.89</td>
<td>1.69</td>
</tr>
<tr>
<td>166</td>
<td>0.47</td>
<td>1.01</td>
<td>-1.53</td>
<td>-5.47</td>
<td>-3.72</td>
<td>1.75</td>
</tr>
<tr>
<td>249</td>
<td>0.55</td>
<td>1.10</td>
<td>-1.38</td>
<td>-5.55</td>
<td>-3.86</td>
<td>1.69</td>
</tr>
<tr>
<td>251</td>
<td>0.54</td>
<td>1.12</td>
<td>-1.36</td>
<td>-5.54</td>
<td>-3.84</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Potentials are referenced vs. Fc/Fc$^+$; $^a$ $E_{\text{ox1}}$: first oxidation potential; $^b$ $E_{\text{ox2}}$: second oxidation potential; $^c$ $E_{\text{red}}$: reduction potential; $^d$ Redox potential of Fc/Fc$^+$ is -5.1 eV on the Fermi scale$^{[22]}$; $^e$ Difference of electrochemically determined HOMO and LUMO energy levels.
Propyl-substituted oligomer 251 was applied as donor component in vacuum-processed organic solar cells by Heliatek. However, obtained results are confidential and are therefore not part of this thesis.
5.4 Summary

In this Chapter, acceptor-donor-acceptor-type co-oligomer 165 as well as novel co-oligomers 249 and 251 comprising a Me-DTP donor unit with methyl residues in the β-positions were synthesized for application in vacuum-processed organic solar cells (Figure 5.7). Due to the electron-donating influence of methyl groups, Me-DTP distannyls were too reactive. Therefore, corresponding Me-DTP diiodides were used in Stille-type cross-couplings with a DCV-substituted stannylthiophene. The targeted oligomers 249 and 251 bearing a phenyl or propyl substituent at the central nitrogen were isolated and purified by high vacuum sublimation. Similarly to Me-DTP precursor 230, the methyl residues enforce a rotation of the phenyl moiety out of the dithienopyrrole plane in oligomer 249 which diminishes the influence of the N-substituent on the optoelectronic properties. Furthermore, steric repulsion between methyls and adjacent thiophenes cause a twist of the conjugated backbone in oligomers 249 and 251. Compared to the analogous compounds without CH₃ groups at the DTP donor unit, this geometry leads to weaker intermolecular interactions, increased Stokes shifts, and a decreased overlap of the π-orbitals.

![Figure 5.7: Structures of synthesized acceptor-donor-acceptor-type co-oligomers.](image-url)
5.5 Experimental section

Instruments and measurements

Thin layer chromatography was carried out on aluminium plates, precoated with silica gel, Merck Si60 F254. Preparative column chromatography was performed on glass columns packed with silica gel (particle size 40–63 µm) from Macherey-Nagel. Purification by gradient vacuum sublimation was performed at a CreaPhys tube-based vacuum sublimation unit DSU05. Melting points were determined using a Mettler Toledo DSC 823e under argon flow (heating rate 10 °C/min). Thermogravimetric analyses were carried out with a TGA/SDTA 851e from Mettler Toledo. UV-Vis absorption spectra were recorded in dichloromethane solutions on a Perkin Elmer Lambda 19 spectrometer and corrected fluorescence spectra were recorded on a Perkin Elmer LS 55 fluorescence spectrometer. NMR spectra were recorded on an Avance 400 (\(^1\)H NMR: 400 MHz, \(^{13}\)C NMR: 101 MHz) or a Bruker AMX 500 spectrometer (\(^1\)H NMR: 500 MHz). Chemical shifts (δ) are reported in ppm using residual solvent protons (\(^1\)H NMR: δ\(_H\) = 5.32 for CD\(_2\)Cl\(_2\); δ\(_H\) = 6.00 for C\(_2\)D\(_2\)Cl\(_4\); \(^{13}\)C NMR: δ\(_C\) = 53.84 for CD\(_2\)Cl\(_2\)) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants \(J\) relate to proton-proton couplings. Protons at DTP were assigned as DTP-\(H\), whereas protons at the attached thiophenes were assigned as Th-\(H\). MALDI-TOF mass spectra were recorded on a Bruker Daltonik Reflex III and high resolution MALDI mass spectra were performed on a Bruker SolariX using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. Cyclic voltammetry and square wave voltammetry experiments were performed using a computer-controlled Autolab PGSTAT 30 potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferricenium couple. Deoxygenated dichloromethane dried via a MB SPS-800 solvent purifying system (MBraun) was used as the solvent. Solutions of tetrabutylammonium hexafluorophosphate (Sigma Aldrich) as the supporting electrolyte with a concentration of 0.1 M were applied and were blanketed with argon during the measurements.
Materials

DMF (VWR), toluene (VWR), and THF (Sigma Aldrich) were dried and purified by a MB SPS-800 (MBraun). Petroleum ether, n-hexane, dichloromethane, ether, methanol, dichloro-ethane, and chloroform were purchased from VWR and distilled prior to use. Diisopropyl-amine and triethylamine were purchased from VWR and dried over calcium hydride. Ammonium acetate was purchased from Merck. Bis(triphenylphosphine)palladium dichloride was purchased from fluorochem. Trimethyltin chloride, N-iodosuccinimide, bis(tributyltin), 2-(tributylstannyl)thiophene, malonodinitrile, and hydrochloric acid (35%) were purchased from Sigma Aldrich. n-Butyl lithium and t-butyl lithium were purchased from Acros Organics. Pd(PPh₃)₄[23] was synthesized by S. Untch and 2-((5-bromothiophen-2-yl)methylene)malonodinitrile 240[24] was prepared by D. Popovic according to published procedures. All synthetic steps were carried out under argon atmosphere.

4-Phenyl-2,6-bis(trimethylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (239)

A solution of phenyl-substituted DTP 65 (128 mg, 0.50 mmol) in THF (1.5 mL) was cooled to -78 °C and n-BuLi (1.6 M in n-hexane, 0.94 mL, 1.50 mmol, 3.00 eq) was added dropwise. The reaction mixture was stirred for 1 h at -78 °C and subsequently 1 h at 0 °C. After cooling the suspension again to -78 °C, a solution of trimethyltin chloride (308 mg, 1.50 mmol, 3.00 eq) in THF (1.5 mL) was added and the reaction mixture was stirred overnight, while slowly warmed to room temperature. The suspension was poured on ice-cold aqueous NaHCO₃ (50 mL), ether (100 mL) was added, and the phases were separated. The aqueous phase was extracted with ether (2 × 50 mL), the combined organic phase was dried over MgSO₄, filtrated, and the volatile components of the filtrate were removed under reduced pressure to give distannyl 239 as a slightly orange solid (288 mg, 0.50 mmol, 100%). The product was used without further purification.

¹H NMR (CD₂Cl₂, 400 MHz): δ = 7.66-7.62 (m, 2 H, o-Ph-H), 7.58-7.53 (m, 2 H, m-Ph-H), 7.37-7.31 (m, 1 H, p-Ph-H), 7.21 (s, 2 H, DTP-H), 0.40 (s, 18 H, CH₃) ppm.
Acceptors-donor-acceptor-type oligomers

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): $\delta = 147.21$, $140.65$, $137.29$, $130.14$, $126.07$, $123.03$, $122.65$, $119.59$, -8.08 ppm.

MALDI-MS (HR): $m/z = \text{calc. for } C_{20}H_{25}NS_{2}Sn_2: 580.94655$; found: $580.94777$ [M]$^+$; $\delta_{m/m} = 2.10$ ppm.

2,2'{-[(4-Phenyl-4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)bis(thiophene-5,2-diyl)]-bis-(methaneylelylidene)}dimalononitrile (165)

A solution of stannyl 239 (223 mg, 0.38 mmol), 2-{[5-bromothiophen-2-yl]methylene}malononitrile 240 (211 mg, 0.88 mmol, 2.30 eq), and Pd(PPh$_3$)$_4$ (22.2 mg, 0.02 mmol, 0.05 eq) in DMF (10 mL) was thoroughly degassed and heated at 80 °C overnight. Methanol (15 mL) was added and the obtained suspension was filtrated. The filter residue was washed with methanol (50 mL) and $n$-hexane (25 mL) to yield oligomer 165 as a dark blue solid (196 mg, 0.34 mmol, 89%). Part of the product (30.0 mg) was further purified via gradient high vacuum sublimation at a temperature of 310 °C and at a pressure of $10^{-6}$ mbar to yield 26.4 mg of the sublimed product (88%).

$M_p$: 394-396 °C (DSC).

$T_d$: 407 °C (TGA).

$^1$H NMR (CD$_2$Cl$_2$, 500 MHz, 355 K): $\delta = 7.75$ (s, 2 H, DCV-H), 7.71 – 7.67 (m, 2 H, o-Ph-H), 7.69 (d, $J = 4.0$ Hz, 2 H, Th-H), 7.64 – 7.61 (m, 2 H, m-Ph-H), 7.56 – 7.51 (m, 1 H, p-Ph-H), 7.45 (s, 2 H, DTP-H), 7.38 (d, $J = 4.2$ Hz, 2 H, Th-H) ppm.

MALDI-MS (HR): $m/z = \text{calc. for } C_{30}H_{13}N_5S_4: 571.00483$; found: $571.00460$ [M]$^+$; $\delta_{m/m} = 0.40$ ppm.

UV-Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (ε): 583 (68 800), 340 (10 100), 298 (12 200), 261 (16 800) nm.
3,5-Dimethyl-4-phenyl-2,6-bis(trimethylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (241)

In a typical attempt, a solution of phenyl-substituted Me-DTP 230 (142 mg, 0.50 mmol) in THF (1.5 mL) was cooled to -78 °C and t-BuLi (1.7 M in n-pentane, 0.88 mL, 1.50 mmol, 3.00 eq) was added dropwise. The reaction mixture was stirred for 1 h at -78 °C and subsequently 3 h at ambient temperature. After cooling the suspension again to -78 °C, a solution of trimethyltin chloride (360 mg, 1.75 mmol, 3.50 eq) in THF (1.5 mL) was added and the reaction mixture was stirred overnight, while slowly warmed to room temperature. The suspension was poured on ice-cold aqueous NaHCO₃ (50 mL), ether (100 mL) was added, and the phases were separated. The aqueous phase was extracted with ether (2 × 50 mL), the combined organic phase was dried over MgSO₄, filtrated, and the volatile components of the filtrate were removed under reduced pressure to give a yellow oily solid (293 mg). Analysis via ¹H NMR spectroscopy revealed a mixture of starting material 230 (7%), mono-stannylated side product 241 (31%), and the desired distannyl 242 (63%).

Monostannyl 241:

¹H NMR (CD₂Cl₂, 400 MHz): δ = 7.50-7.46 (m, 5 Ph-H), 6.68 (q, 1 H, DTP-H), 1.83-1.82 (m, 3 H, DTP-CH₃), 1.81-1.80 (m, 3 H, DTP-CH₃), 0.37 (s, 9 H, Sn-CH₃) ppm.

MALDI-TOF-MS: m/z = calc. for C₁₉H₂₁NS₂Sn: 447.0; found: 446.7 [M]⁺.

Distannyl 242:

¹H NMR (CD₂Cl₂, 400 MHz): δ = 7.50-7.46 (m, 5 H, Ph-H), 1.82 (s, 6 H, DTP-CH₃), 0.37 (s, 18 H, Sn-CH₃) ppm.

MALDI-TOF-MS: m/z = calc. for C₂₂H₂₉NS₂Sn₂: 609.0; found: 609.8 [M]⁺.

2,6-Diido-3,5-dimethyl-4-phenyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (243)

Under exclusion of light and at 0 °C N-iodosuccinimide (465 mg, 1.96 mmol, 2.20 eq) was added to a solution of phenyl-substituted Me-DTP 230 (253 mg, 0.89 mmol) in chloroform...
Acceptor-donor-acceptor-type oligomers

(9 mL). After the addition, the reaction mixture was warmed to room temperature and stirred for 3 h. Subsequently, an aqueous solution of \( \text{Na}_2\text{S}_2\text{O}_3 \) (2 M, 30 mL) and dichloromethane (10 mL) were added. The phases were separated and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic phase was dried over \( \text{MgSO}_4 \), filtrated, and the raw product was purified via column chromatography (SiO\(_2\), petroleum ether) to afford diiodide 243 as a yellow solid (475 mg, 0.89 mmol, 100%). The product was used without further purification.

\( \text{Mp}: 172 \text{°C (dec.; DSC)} \).

\( ^1\text{H-NMR} \) (CD\(_2\)Cl\(_2\), 400 MHz): \( \delta = 7.58 - 7.48 \) (m, 3 H, \( m\)-Ph-\( H \), \( p\)-Ph-\( H \), \( 7.46 - 7.42 \) (m, 2 H, \( o\)-Ph-\( H \)), \( 1.74 \) (s, 6 H, \( \text{C}_8\text{H}_3 \)) ppm.

\( ^{13}\text{C-NMR} \) (CD\(_2\)Cl\(_2\), 101 MHz): \( \delta = 141.84 \), \( 137.54 \), \( 129.70 \), \( 129.62 \), \( 129.26 \), \( 127.97 \), \( 119.31 \), \( 74.14 \), \( 16.23 \) ppm.

MALDI-MS (HR): \( m/z = \text{calc. for C}_{16}\text{H}_{11}\text{NS}_2\text{I}_2: 534.84169; \text{found: 534.84139 [M]}^+; \delta_{m/m} = 0.56 \text{ppm.} \)

3,5-Dimethyl-4-phenyl-2,6-bis(tributylstannyl)-4\( H \)-dithieno[3,2-b:2',3'-d]pyrrole (245)

![Image of 3,5-Dimethyl-4-phenyl-2,6-bis(tributylstannyl)-4\( H \)-dithieno[3,2-b:2',3'-d]pyrrole](image)

A solution of diiodide 243 (214 mg, 0.40 mmol), \( \text{bis(tributyl)tin} \) (1.10 g, 1.80 mmol, 4.50 eq), and \( \text{Pd(PPh}_3)_4 \) (46.2 mg, 0.04 mmol, 0.10 eq) in toluene (3 mL) was purged with argon and heated at 110 °C for 26 h. The reaction mixture was poured on ice-cold aqueous NaHCO\(_3\) (50 mL), ether (100 mL) was added, and the phases were separated. The aqueous phase was extracted with ether (2 × 50 mL), the combined organic phase was dried over Na\(_2\)SO\(_4\), filtrated, and the volatile components of the filtrate were removed under reduced pressure. Analysis via MALDI-TOF mass spectrometry indicated the formation of the product. However, the attempted purification via column chromatography (SiO\(_2\), petroleum ether) using silica gel, which was largely deactivated with triethylamine, led to the partial abstraction of the stannyl groups. Thus, the formed product could not sufficiently be purified.

MALDI-TOF-MS: \( m/z = \text{calc. for C}_{40}\text{H}_{65}\text{NS}_2\text{Sn}_2: 861.3; \text{found: 862.0 [M]}^+ \).
5-(Tributylstannyl)thiophene-2-carbaldehyde (247)$^{[18-19]}$

A solution of diisopropylamine (6.64 mL, 47.0 mmol, 1.10 eq) in THF (15 mL) was cooled to 0 °C and n-BuLi (1.6 M in n-hexane, 29.4 mL, 47.0 mmol, 1.10 eq) was slowly added. The solution was stirred for 30 min and then added dropwise to a solution of 2-(tributylstannyl)-thiophene 246 (14.0 mL, 42.8 mmol) in THF (42 mL) at -78 °C. After stirring for 1 h, DMF (3.81 mL, 49.2 mmol, 1.15 eq) was added in one portion and the reaction mixture was stirred for 2 h, while slowly warmed to room temperature. Aqueous hydrochloric acid (1 M, 100 mL) was added, the phases were separated, and the aqueous phase was extracted with dichloromethane (3 × 200 mL). The combined organic phase was dried over Na$_2$SO$_4$, filtrated, and the raw product was purified via column chromatography (SiO$_2$, petroleum ether : dichloromethane = 3:1) to yield aldehyde 247 as an orange oil (11.5 g, 28.7 mmol, 67%).

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 9.93 – 9.90$ (m, 1 H, CO-H), 7.86 – 7.84 (m, 1 H, C3-H), 7.29 (d, J = 3.5 Hz, 1 H, C4-H), 1.63 – 1.52 (m, 6 H, Sn-CH$_2$), 1.39 – 1.29 (m, 6 H, Sn-CH$_2$-CH$_2$), 1.20 – 1.14 (m, 6 H, Sn-(CH$_2$)$_2$-CH$_2$), 0.89 (t, J = 7.3 Hz, 9 H, CH$_3$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): $\delta = 182.20, 151.72, 149.56, 137.15, 136.75, 29.24, 27.61, 13.78, 11.35$ ppm.

2-{{[5-(Tributylstannyl)thiophen-2-yl]methylene}malononitrile (248)$^{[18-19]}$

Malonodinitrile (659 mg, 9.97 mmol) and ammonium acetate (961 mg, 12.5 mmol) were added to a solution of aldehyde 247 (1.00 g, 2.49 mmol) in dichloroethane (10 mL) and the reaction mixture was heated at 80 °C for 3 h. After cooling to room temperature, water (20 mL) and dichloromethane (20 mL) were added. The phases were separated, the aqueous phase was extracted with dichloromethane (2 × 20 mL), the combined organic phase was dried over Na$_2$SO$_4$, filtrated, and the raw product was purified via column chromatography (SiO$_2$, dichloromethane) to give DCV-substituted stannylthiophene 248 as an orange oil (966 mg, 2.15 mmol, 86%).
$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 7.92 - 7.88$ (m, 1 H, DCV-H), 7.85 (dd, $J = 3.7$, 0.6 Hz, 1 H, C3-H), 7.33 (d, $J = 3.7$ Hz, 1 H, C4-H), 1.63 - 1.50 (m, 6 H, Sn-CH$_2$), 1.39 - 1.29 (m, 6 H, Sn-CH$_2$-CH$_2$), 1.24 - 1.11 (m, 6 H, Sn-CH$_2$-CH$_2$), 1.08 - 0.96 (m, 6 H, Sn-CH$_2$-CH$_2$), 0.89 (t, $J = 7.3$ Hz, 9 H, CH$_3$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): $\delta = 156.56$, 150.46, 141.15, 138.80, 137.32, 114.86, 113.99, 76.93, 29.22, 27.58, 13.77, 11.59 ppm.

2,2'-[(3,5-Dimethyl-4-phenyl-4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)]bis(thiophene-5,2-diyl)]bis(methanyleylidene)dimalonodinitrile (249)

![Chemical structure of 249]

A solution of diiodide 243 (166 mg, 0.31 mmol), stannyl 248 (418 mg, 0.93 mmol, 3.00 eq), and Pd(PPh$_3$)$_4$ (17.9 mg, 0.02 mmol, 0.05 eq) in DMF (10 mL) was thoroughly degassed and heated at 80 °C overnight. After cooling to room temperature, methanol (15 mL) was added and the obtained suspension was filtrated. The filter residue was washed with methanol (80 mL) to yield 141 mg of raw oligomer 249 as a dark blue solid. Part of the product (76.5 mg) was further purified via gradient high vacuum sublimation at a temperature of 290 °C and at a pressure of $10^{-6}$ mbar to yield the sublimed pure product (8.7 mg, 15.0 µmol, 5%).

$M_p$: 305-310 °C (DSC).

$T_d$: 356 °C (TGA).

$^1$H NMR (C$_2$D$_2$Cl$_4$, 500 MHz, 355 K): $\delta = 7.75$ (d, $J = 4.6$ Hz, 2 H, Th-H), 7.75 (s, 2 H, DCV-H), 7.66 - 7.60 (m, 3 H, α-Ph-H, β-Ph-H), 7.60 - 7.55 (m, 2 H, m-Ph-H), 7.34 (d, $J = 4.2$ Hz, 2 H, Th-H), 2.09 (s, 6 H, CH$_3$) ppm.

MALDI-MS (HR): $m/z =$ calc. for C$_{32}$H$_{17}$N$_3$S$_4$: 599.03613; found: 599.03588 [M]$^+$; $\delta_{m/m} = 0.42$ ppm.

UV-Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (ε): 573 (73 400), 346 (16 300), 295 (sh, 15 100), 273 (18 500) nm.
2,6-Diiodo-3,5-dimethyl-4-propyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (250)

Under exclusion of light and at 0 °C N-iodosuccinimide (331 mg, 1.47 mmol, 2.10 eq) was added to a solution of propyl-substituted Me-DTP 228 (175 mg, 0.70 mmol) in chloroform (7 mL). After the addition, the reaction mixture was warmed to room temperature and stirred for 4 h. Subsequently, an aqueous solution of Na$_2$S$_2$O$_3$ (2 M, 20 mL) and dichloromethane (20 mL) were added. The phases were separated and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic phase was dried over Na$_2$SO$_4$, filtered, and the raw product was purified via column chromatography (SiO$_2$, petroleum ether) to afford diiodide 250 as a yellow solid (316 mg, 0.63 mmol, 90%). The product was used without further purification.

M$_p$: 144 °C (dec.; DSC).

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta = 4.34 - 4.28$ (m, 2 H, N-CH$_2$), 2.46 (s, 6 H, DTP-CH$_3$), 1.84 – 1.73 (m, 2 H, N-CH$_2$-CH$_2$), 0.94 (t, $J = 7.5$ Hz, 3 H, CH$_2$-CH$_3$) ppm.

$^{13}$C NMR (CD$_2$Cl$_2$, 101 MHz): $\delta = 140.75$, 127.11, 119.04, 74.28, 47.07, 26.58, 17.18, 10.89 ppm.

MALDI-MS (HR): $m/z = \text{calc. for } C_{13}H_{13}NS_2I_2$: 500.85734; found: 500.85933 [M]$^+$; $\delta_{m/m} = 3.97$ ppm.

2,2'{-[[3,5-Dimethyl-4-propyl-4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl]bis(thiophene-5,2-diyl)]bis(methaneylylidene)]dimalonodinitrile (251)

A solution of diiodide 250 (296 mg, 0.59 mmol), stannyl 248 (796 mg, 1.77 mmol, 3.00 eq), and Pd(PPh$_3$)$_2$Cl$_2$ (20.7 mg, 0.03 mmol, 0.05 eq) in DMF (14 mL) was thoroughly degassed and heated at 80 °C for two days. After cooling to room temperature, methanol (20 mL) was added and the obtained suspension was filtrated. The filter residue was washed with methanol (250 mL) and then purified via column chromatography (SiO$_2$, dichloromethane) to
yield oligomer 251 as a dark blue solid (211 mg, 0.37 mmol, 63%). Part of the product (60.7 mg) was further purified via gradient high vacuum sublimation at a temperature of 300 °C and at a pressure of $10^{-6}$ mbar to yield 44.5 mg of the sublimed product (73%).

$\mathbf{M_p}$: 323-325 °C (DSC).

$\mathbf{T_d}$: 351 °C (TGA).

$^1\text{H} \text{ NMR} \ (\text{CD}_2\text{Cl}_2, \ 500 \text{ MHz}, \ 355 \text{ K}): \ \delta = 7.78 \ (d, \ J = 4.1 \text{ Hz}, \ 2 \text{ H}, \ \text{Th-H}), \ 7.77 \ (s, \ 2 \text{ H}, \ \text{DCV-H}), \ 7.36 \ (d, \ J = 4.1 \text{ Hz}, \ 2 \text{ H}, \ \text{Th-H}), \ 4.51 \ (t, \ J = 9.3 \text{ Hz}, \ 2 \text{ H}, \ \text{N-CH}_2), \ 2.78 \ (s, \ 6 \text{ H}, \ \text{DTP-CH}_3), \ 2.01 - 1.91 \ (m, \ 2 \text{ H}, \ \text{CH}_2-\text{CH}_2), \ 1.07 \ (t, \ J = 7.4 \text{ Hz}, \ 3 \text{ H}, \ \text{CH}_2-\text{CH}_3) \text{ ppm.}$

**MALDI-MS (HR):** $m/z = \text{calc. for C}_{29}\text{H}_{19}\text{N}_5\text{S}_4$: 565.05178; found: 565.05185 [M]$^+$; $\delta_m/m = 0.12$ ppm.

**UV-Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}} (\varepsilon)$:** 573 (64 100), 344 (15 000), 298 (12 400), 275 (12 100) nm.
5.6 References

Summary

The aim of this thesis was the synthesis and characterization of various dithienopyrroles and their corresponding homopolymers in order to derive structure-property relationships in both monomers and polymers. Structural alterations of the commonly applied dithieno-[3,2-b:2',3'-d]pyrrole (DTP) involved functionalizations at the nitrogen with different substituents, the change of the relative heteroatom positions to isomeric DTPs (iso-DTPs), and the attachment of methyl groups in both β-positions to Me-DTPs (Scheme S1).

![Scheme S1: Structural alterations of dithienopyrrole to N-functionalized DTPs (left), iso-DTPs (middle), and Me-DTPs (right).](image)

The preparation of many N-functionalized DTPs can most conveniently be carried out by twofold amination of 3,3'-dibromo-2,2'-bithiophene with a primary amine or amide under palladium, respectively copper catalysis (Scheme S2). Thus, a series of substituted DTPs 60, 64, 78, 65, 97, 176, 177, 186, and 189 was synthesized in moderate to excellent yields. Nevertheless, the scope of this approach was quite limited, especially with regard to heteroaryl substituents. Therefore, an alternative strategy using unsubstituted DTP 50 as starting material was subsequently pursued (Scheme S2). Herein, a more efficient synthesis of this important precursor 50 than the literature-known thermolysis of the corresponding azide was first of all developed and optimized. Out of various C-N couplings of 3,3'-dibromo-2,2'-bithiophene with ammonia or ammonia surrogates, the copper-catalysed reaction with benzamide (59% yield) and the palladium-catalysed reaction with triphenylsilyl amine (72% yield) gave the best results. Afterwards, unsubstituted DTP 50 was applied in Buchwald-Hartwig aminations with different aryl bromides, respectively in a Steglich reaction with ferrocenecarboxylic acid, and functionalized DTPs 65, 68, 193, 196, 179, 198-200, 202, and
were obtained. This synthetic approach thus represents a useful alternative to the direct amination of 3,3’-dibromo-2,2’-bithiophene and enables the preparation of DTPs bearing sophisticated functional groups at the nitrogen.

Conjugated residues exhibit an electron-withdrawing effect in the synthesized DTPs leading to decreased energy levels of the frontier molecular orbitals in comparison to non-functionalized parent compound 50. As indicated by DFT calculations, a node at the nitrogen in the HOMO only allows for an indirect electronic influence of the substituents, whereas the direct participation of conjugated moieties to the LUMO results in a larger impact. Consequently, depending on the electron-withdrawing effect of the specific functional group at the nitrogen, the HOMO-LUMO energy gap is reduced to a different extent. Electropolymerization of DTPs 50, 60, 64, 78, 65, 97, and 176 yielded very stable p(DTP) films on the working electrode and an electrochromic behaviour with a dark blue colour in the neutral state and a colourless appearance in the fully oxidized state was observed. Because of only one solubilizing residue per repeat unit p(DTP)s quickly become insoluble during polymerization and only relatively short polymer chains are accessible. This was confirmed by oxidative chemical polymerizations of alkyl- or Boc-substituted DTPs 60, 64, 78, and 176, where soluble p(DTP)s with an estimated average chain length of up to 36 monomer units were obtained. Hence, the length of the conjugated backbone determines the optoelectronic properties of
the polymer and mainly solubilizing effects rather than direct electronic influences of the substituents at the nitrogens are relevant. However, in the case of ferrocenoyl-substituted p(DTP) \( \text{P}_{\text{ox}} \) the redox activity of the residue at the nitrogen is also an important aspect and in collaboration with ZSW Ulm this polymer was successfully applied as cathode active material in organic batteries.

Afterwards, a series of iso-DTPs 126, 207, 216, 218, 219, 206, and 132 with altered relative positions of the nitrogen and the sulphur atoms was synthesized (Figure S1). Yet, the direct C-N couplings of 2,2′- dibromo-3,3′-bithiophene with the corresponding amine or amide only worked for Boc-substituted derivative 132. Hence, the Boc residue was split off and unsubstituted iso-DTP 126 was afforded. This precursor was subsequently functionalized at the nitrogen with different alkyl moieties in 207, 216, and 218 via nucleophilic substitution of the corresponding iodide or tosylate, with a phenyl residue in 219 via Buchwald-Hartwig amination of bromobenzene, and in 206 with a benzoyl substituent via Steglich reaction of benzoic acid. Similarly to analogous DTPs, the nitrogen of most iso-DTPs resides at a node in the HOMO, while the whole conjugated part of the molecule contributes to the LUMO. However, the specific distribution of the electron density in the frontier molecular orbitals of iso-DTPs is more strongly affected by the substituent. Additionally, the cross-conjugated structure of the backbone results in stabilized HOMOs and destabilized LUMOs. In contrast to DTPs, electropolymerization of all prepared iso-DTPs only gave quite instable films, which did not show any electrochromism. Moreover, the degree of polymerization was further decreased compared to p(DTP)s. Thus, soluble p(iso-DTP) obtained from polymerization of alkyl-substituted iso-DTPs 207, 216, and 218 with iron(III) chloride exhibited a relatively short average chain length of up to ten repeat units.

Figure S1: Structures of synthesized iso-DTPs.
Subsequently, a series of Me-DTPs 227-232 with attached methyl groups in the two β-positions of DTP was synthesized via C-N couplings of 3,3′-dibromo-4,4′-dimethyl-2,2′-bithiophene (Figure S2). The methyl residues possess an electron-donating effect and thus slightly destabilize the HOMO. Furthermore, they enforce a twist of bulky substituents at the nitrogen out of the dithienopyrrole plane as a result of sterical interactions. This altered geometry not only affects the packing in the solid state, but also increases the influence of conjugated substituents on the LUMO. In the homopolymers sterical repulsions between the methyls cause a twist between the repeat units leading to shorter conjugation lengths. Moreover, because both β-positions are blocked, no coupling defects during polymerizations can occur and strictly linear p(Me-DTP)s are obtained. However, this led to a major decrease in solubility and therefore only short polymers were afforded, whereas the soluble hexyl-substituted derivative Pox229 possessed an average chain length of about nine repeat units.

![Figure S2: Structures of synthesized Me-DTPs.](image)

Me-DTPs 228 and 230 with propyl or phenyl residues at the nitrogen were then used as donor component in acceptor-donor-acceptor-type co-oligomers for application in vacuum-processed organic solar cells. Stille-type cross-coupling of the respective Me-DTP diiodide with a DCV-substituted stannylthiophene afforded the corresponding sublimable co-oligomers 249 and 251 shown in Figure S3. Due to the sterical demand of the methyls, the conjugated backbone is twisted and the rotation of the phenyl substituent out of the dithienopyrrole plane in co-oligomer 249 is enforced. Compared to the analogous derivatives without methyl groups at the DTP donor unit, the co-oligomers exhibited weaker intermolecular interactions, increased Stokes shifts, and a decreased overlap of their π-orbitals.
In conclusion, three series of DTPs, iso-DTPs, and Me-DTPs with different substituents at the nitrogen, as well as two acceptor-donor-acceptor-type co-oligomers with central Me-DTP donor units were synthesized and characterized in this thesis.
Zusammenfassung


![Schema Z1: Strukturelle Modifikationen von Dithienopyrrol zu N-funktionalisierten DTPs (links), iso-DTPs (Mitte) und Me-DTPs (rechts).](image)

Die Herstellung vieler N-funktionalisierter DTPs kann am einfachsten über doppelte Aminierung von 3,3′-Dibrom-2,2′-bithiophen mit einem primären Amin oder Amid unter Palladium-beziehungsweise Kupferkatalyse durchgeführt werden (Schema Z2). So wurde eine Serie der substituierten DTPs 60, 64, 78, 65, 97, 176, 177, 186 und 189 in moderaten bis exzellenten Ausbeuten hergestellt. Jedoch war der Anwendungsbereich dieser Methode insbesondere im Hinblick auf Heteroarylsubstituenten sehr eingeschränkt. Daher wurde eine alternative Strategie verfolgt, welche vom unsubstituierten DTP 50 ausging (Schema Z2). Hierbei wurde zuerst eine effizientere Synthese als die literaturbekannte Thermolyse des entsprechenden Azids für dieses wichtige Edukt 50 entwickelt und optimiert. Aus einer Reihe verschiedener C-N Kupplungen von 3,3′-Dibrom-2,2′-bithiophen mit Ammoniak oder Ammoniakäquivalenten erzielten die kupferkatalysierte Reaktion mit Benzamid (59% Ausbeute) sowie die palladiumkatalysierte Reaktion mit Triphenylsilylamin (72% Ausbeute) die
Zusammenfassung

besten Resultate. Danach wurde das unsubstituierte DTP 50 in Buchwald-Hartwig-Aminierungen mit unterschiedlichen Arylbromiden, beziehungsweise in einer Steglich Reaktion mit Ferrocencarbonsäure eingesetzt und die funktionalisierten DTPs 65, 68, 193, 196, 179, 198-200, 202 sowie 204 wurden so erhalten. Dieser Syntheseweg repräsentiert daher eine nützliche Alternative zur direkten Aminierung von 3,3'-Dibrom-2,2'-bithiophen und ermöglicht die Darstellung weiterer DTPs mit ausgeklügelten funktionellen Gruppen am Stickstoff.

\[ \begin{align*}
\text{Schaum Z2: Angewandte Strategien für die Synthese von } N\text{-funktionalisierten DTPs.}
\end{align*} \]

Konjugierte Reste üben eine elektronenziehenden Wirkung in den hergestellten DTPs aus, die im Vergleich zur unsubstituierten Verbindung 50 abgesenkte Energieniveaus der Grenzorbitale zur Folge hat. Wie DFT Rechnungen zeigten, erlaubt ein Knotenpunkt am Stickstoff im HOMO nur einen indirekten elektronischen Einfluss der Substituenten, wohingegen die direkte Beteiligung von konjugierten Resten am LUMO größere Auswirkungen hat. Somit ist je nach elektronenziehender Eigenschaft der jeweiligen funktionellen Gruppe am Stickstoff die HOMO-LUMO Energielücke in unterschiedlichem Ausmaß verringert. Elektropolymerisation der DTPs 50, 60, 64, 78, 65, 97 und 176 erbrachte sehr stabile p(DTP)-Filme auf der Arbeitselektrode und ein elektrochromes Verhalten mit einer dunkelblauen Farbe im Neutralzustand sowie einer farblosen Erscheinung im vollständig oxidierten Zustand wurde beobachtet. Auf Grund von lediglich einem löschlichkeitsvermittelnden Rest pro Wiederholeinheit

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werden p(DTP)s während der Polymerisation schnell unlöslich und nur relative kurze Ketten sind zugänglich. Dies wurde durch chemisch oxidative Polymerisation der alkyl- oder Boc-substituierten DTPs 60, 64, 78 und 176 bestätigt, wo lösliche p(DTP)s mit einer geschätzten durchschnittlichen Kettenlänge von bis zu 36 Monomereinheiten erhalten wurden. Dadurch bestimmt die Länge des konjugierten Rückgrats die optoelektronischen Eigenschaften des Polymers und löslichkeitsvermittelnde Effekte der Substituenten am Stickstoff sind eher relevant, als direkte elektronische Einflüsse. Die Redoxaktivität des Restes am Stickstoff im Ferrocenoyl-substituierten p(DTP) P_{ox}204 ist jedoch auch ein bedeutender Aspekt und in Zusammenarbeit mit dem ZSW Ulm wurde dieses Polymer erfolgreich als Aktivmaterial der Kathode in organischen Batterien eingesetzt.


Abbildung Z1: Strukturen der synthetisierten iso-DTPs.
Zusammenfassung

kreuzkonjugierte Struktur des Rückgrats eine Stabilisierung der HOMOs und Destabilisierung der LUMOs. Im Gegensatz zu DTPs lieferte die Elektropolymerisation aller hergestellten iso-DTPs nur recht instabile Filme, welche keine Elektrochromie zeigten. Der Polymerisationsgrad war im Vergleich zu p(DTP)s kleiner und lösliche p(iso-DTP)s, die durch Polymerisation der alkyl-substituierten iso-DTPs 207, 216 und 218 mit Eisen(III)-chlorid erhalten wurden, wiesen eine relativ kurze durchschnittliche Kettenlänge von bis zu zehn Wiederholeinheiten auf.


![Abbildung Z2: Strukturen der synthetisierten Me-DTPs.](image)

Die Me-DTPs 228 und 230 mit Propyl- oder Phenylresten am Stickstoff wurden dann als Donorkomponente in Akceptor-Donor-Akceptor-Oligomeren für die Anwendung in vakuum-prozessierten organischen Solarzellen eingesetzt. Stille-Kreuzkupplungen der jeweiligen Me-
Zusammenfassung

DTP-Diiodide mit einem DCV-substituierten Stannythiophen lieferten die entsprechenden sublimierbaren Co-Oligomere 249 und 251, die in Abbildung Z3 gezeigt sind. Wegen des sterischen Anspruchs der Methylgruppen ist das konjugierte Rückgrat verdrillt und die Rotation des Phenylrestes in Co-Oligomer 249 aus der Dithienopyrrol-Ebene heraus wird erzwungen. Im Vergleich zu den analogen Derivaten ohne Methylgruppen wiesen die Oligomer schwächere intermolekulare Wechselwirkungen, größere Stokes-Verschiebungen und eine geringere Überlappung ihrer π-Orbitale auf.

Abbildung Z3: Strukturen der synthetisierten Akzeptor-Donor-Akzeptor-Oligomere.

Zusammenfassend kann festgestellt werden, dass es in dieser Arbeit gelungen ist, drei Serien von DTPs, iso-DTPs und Me-DTPs mit unterschiedlichen Substituenten am Stickstoff sowie zwei Akzeptor-Donor-Akzeptor-Oligomere mit zentralen Me-DTP Donoreinheiten herzustellen und zu charakterisieren.
Der Lebenslauf wurde aus Gründen des Datenschutzes entfernt.
The CV was removed due to reasons of data protections.
Publications

“Ferroocene-functionalized polyheteroacenes for the use as cathode active material in rechargeable batteries”

“New methods for the synthesis of 4H-dithieno[3,2-b:2',3'-d]pyrrole”

“Synthesis and characterization of two isomeric dithienopyrrole series and the corresponding electropolymers”

“Carbon-rich ruthenium allenylidene complexes bearing heteroscorpionate ligands”

Presentations

GDCh-Wissenschaftsforum 2017 in Berlin:
10/09/2017 – 14/09/2017
Poster presentation
“Isomeric dithienopyroles: monomers and electropolymers”
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Ulm-Erlangen Symposium on Functional Organic Materials in Ulm:
10/07/2017 – 11/07/2017
Poster presentation
“Isomeric dithienopyroles: monomers and electropolymers”

20th European Symposium on Organic Chemistry (ESOC) in Cologne:
02/07/2017 – 06/07/2017
Poster presentation
“Synthesis and characterization of isomeric dithienopyrrole series and corresponding electropolymers”
Teile dieser Dissertation wurden bereits in folgenden Fachartikeln veröffentlicht:


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