Synthesis and Characterization of Amorphous Cyclopentadithiophene- and Cyclopentadiene-based Organic Hole Transport Materials

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vorgelegt von
Michael Bauer

aus Ulm
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Amtierender Dekan: Prof. Dr. Thorsten Bernhardt
Erstgutachter: Prof. Dr. Peter Bäuerle
Zweitgutachter: Prof. Dr. Max von Delius
Drittgutachter: Prof. Dr. Marcel Mayor
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Fakultät für Naturwissenschaften, Universität Ulm
There is nothing intrinsically 'long' about redness. Knowing how red and blue look doesn't help us remember which wavelength is longer. I regularly have to look it up…

Richard Dawkins, Unweaving the Rainbow, p. 55
Danksagung

Der Inhalt dieser Seite wurde aus Gründen des Datenschutzes entfernt.
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<tr>
<td>a</td>
<td>acceptor</td>
</tr>
<tr>
<td>BF$_3$OEt$_2$</td>
<td>boron trifluoride diethyl etherate</td>
</tr>
<tr>
<td>BHJSC</td>
<td>bulk heterojunction organic solar cell</td>
</tr>
<tr>
<td>BINAP</td>
<td>2,2′-bis(diphenylphosphino)-1,1′-binaphthyl</td>
</tr>
<tr>
<td>CIGS</td>
<td>copper indium gallium selenide</td>
</tr>
<tr>
<td>CPDT</td>
<td>Cyclopentadithiophene</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammogram</td>
</tr>
<tr>
<td>d</td>
<td>donor</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>dd</td>
<td>doublet of doublet</td>
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<tr>
<td>ddd</td>
<td>doublet of doublet of doublet</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>Dis</td>
<td>disconnection</td>
</tr>
<tr>
<td>DFT</td>
<td>density-functional theory</td>
</tr>
<tr>
<td>diglyme</td>
<td>diethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>DMCC</td>
<td>dimethylcarbamoyl chloride</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DME</td>
<td>dichloroethane</td>
</tr>
<tr>
<td>dppf</td>
<td>1,1′-bis(diphenylphosphino)ferrocene</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>DSSC</td>
<td>dye-sensitized solar cells</td>
</tr>
<tr>
<td>DTP</td>
<td>dithienopyrrole</td>
</tr>
<tr>
<td>$E_{1/2}$</td>
<td>half-wave potential</td>
</tr>
<tr>
<td>EDOT</td>
<td>3,4-ethylenedioxythiophene</td>
</tr>
<tr>
<td>ETL</td>
<td>electron transport layer</td>
</tr>
<tr>
<td>equiv</td>
<td>equivalent</td>
</tr>
<tr>
<td>Fc/Fc$^+$</td>
<td>ferrocene/ferricenium</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>FGI</td>
<td>functional group interconversion</td>
</tr>
<tr>
<td>FMO</td>
<td>frontier molecular orbitals</td>
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<tr>
<td>FTICR</td>
<td>Fourier-transform ion cyclotron resonance</td>
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<tr>
<td>GC</td>
<td>gas chromatography</td>
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<tr>
<td>$H,H$-COSY</td>
<td>proton-proton correlation NMR spectroscopy</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
</tr>
<tr>
<td>HOAc</td>
<td>acetic acid</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HPLC</td>
<td>high-performance liquid chromatography</td>
</tr>
<tr>
<td>HTM</td>
<td>hole-transport material</td>
</tr>
<tr>
<td>HWE</td>
<td>Horner–Wadsworth–Emmons</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>ICl</td>
<td>iodine monochloride</td>
</tr>
<tr>
<td>$\dot{j}_c$</td>
<td>short-circuit current density</td>
</tr>
<tr>
<td>LDA</td>
<td>lithium diisopropylamide</td>
</tr>
<tr>
<td>LiTFSI</td>
<td>lithium bis(trifluoromethanesulfonyl)imide</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>MALDI</td>
<td>matrix-assisted laser desorption/ionization</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>matrix assisted laser desorption-ionization time-of-flight</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>$n$-BuLi</td>
<td>$n$-butyl lithium</td>
</tr>
<tr>
<td>NFA</td>
<td>non-fullerenic acceptor</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOE</td>
<td>nuclear Overhauser effect</td>
</tr>
<tr>
<td>NOESY</td>
<td>nuclear Overhauser effect NMR spectroscopy</td>
</tr>
<tr>
<td>PCBM[61]</td>
<td>[6,6]-phenyl-C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCE</td>
<td>power conversion efficiency</td>
</tr>
<tr>
<td>Pd$_2$dba$_3$</td>
<td>tris(dibenzylideneacetone)dipalladium(0)</td>
</tr>
<tr>
<td>PDI</td>
<td>perylenediimide</td>
</tr>
<tr>
<td>PE</td>
<td>petrol ether</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>poly(3,4-ethylenedioxythiophene) polystyrene sulfonate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>PESA</td>
<td>photoelectron spectroscopy in air</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>POCl$_3$</td>
<td>phosphoryl chloride</td>
</tr>
<tr>
<td>PSC</td>
<td>perovskite solar cells</td>
</tr>
<tr>
<td>$R_t$</td>
<td>retardation factor</td>
</tr>
<tr>
<td>SCLC</td>
<td>space-charge-limited-current</td>
</tr>
<tr>
<td>SEC</td>
<td>size exclusion chromatography</td>
</tr>
<tr>
<td>SET</td>
<td>single-electron transfer</td>
</tr>
<tr>
<td>spiro-biCPDT</td>
<td>spiro-bi[cyclopentadithiophene]</td>
</tr>
<tr>
<td>spiro-CPDTA</td>
<td>spiro-cyclopentadithiophene-$N$-phenylacridine</td>
</tr>
<tr>
<td>spiro-CPDTT</td>
<td>spiro-cyclopentadithiophene-thioxanthene</td>
</tr>
<tr>
<td>spiro-CPDTX</td>
<td>spiro-cyclopentadithiophene-xanthene</td>
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<tr>
<td>spiro-MeOTAD</td>
<td>$N,N,N',N',N'',N''',N'''$-Octakis(4-methoxyphenyl)-9,9'-spirobi[flourene]-2,2',7,7'-tetramine</td>
</tr>
<tr>
<td>SPhos</td>
<td>2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl</td>
</tr>
<tr>
<td>spiro-TAD</td>
<td>2,2',7,7'-tetrakis($N,N$-diphenylamino)-9,9'-spirobifluorene</td>
</tr>
<tr>
<td>$t$</td>
<td>triplet</td>
</tr>
<tr>
<td>TAA</td>
<td>triarylamine</td>
</tr>
<tr>
<td>TBAB</td>
<td>tetrabutylammonium bromide</td>
</tr>
<tr>
<td>TBAPF</td>
<td>tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>tBP</td>
<td>tert-butylpyridine</td>
</tr>
<tr>
<td>TFA</td>
<td>trifluoroacetic acid</td>
</tr>
<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>thin-layer chromatography</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>TMSCl</td>
<td>trimethylsilyl chloride</td>
</tr>
<tr>
<td>TPA</td>
<td>triphenylamine</td>
</tr>
<tr>
<td>TPD</td>
<td>$N,N$-diphenyl-$N,N$-di(m-tolyl)benzidine</td>
</tr>
<tr>
<td>tt</td>
<td>triplets of triplets</td>
</tr>
<tr>
<td>VB</td>
<td>valence-bond</td>
</tr>
<tr>
<td>VdW</td>
<td>Van-der-Waals</td>
</tr>
<tr>
<td>$V_{OC}$</td>
<td>open-circuit voltage</td>
</tr>
<tr>
<td>WF</td>
<td>work function</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
List of Structures
1 Cyclopentadithiophene-based Materials

1.1 Introduction

In this chapter, synthesis and characterization of 4H-cyclopenta[2,1-b:3,4-b']dithiophene-based molecular hole-transport materials (HTMs) is described. The design of the target structures was performed employing the spiro-concept\(^1\) on one hand and the knowledge about the optoelectronic properties of the triphenylamine (TPA)-capped cyclopentadithiophene (CPDT) that has been used in the HTM FK1 (Scheme 1-16), on the other hand\(^2\). The general structure of the planned spiro-CPDTs is illustrated in Figure 1-1. The structure can be divided into two parts. The lower part of the molecule, which consists of the central cyclopentadithiophene unit that remains unchanged for all target molecules substituted with triphenylamine groups attached at both thiophene α-positions to adjust the frontier molecular orbitals (FMO). The substituents “R” at the triphenylamines will be modified to achieve slight variations in the optoelectronic properties of the spiro-CPDTs. The upper part of the molecule, which should be electronically decoupled from the π-system of the lower part through the sp\(^3\)-spiro carbon atom, is responsible for the adjustment of the thermal-and morphological properties. The upper part is formed by two phenyl substituents, which are linked to the cyclopentadithiophene at the central sp\(^3\)-spiro carbon atom. The phenyl substituents are linked via the “X” substituent in the ortho-positions. This linkage of the phenyl substituents leads to a more rigid system, which should lead to a high glass transition temperature of the resulting spiro-CPDTs.\(^3\)-\(^4\) The properties of the planned HTMs are changed and optimized by the variation of the linkage “X” and the type of triarylamine (TAA) substituents used.

![Figure 1-1: General structure of the planned spiro-cyclopentadithiophene target molecules.](image)

Firstly, the state of the art of the design of amorphous organic electronic materials with high glass transition temperatures as well as the literature concerning fused cyclopentadithiophenes is discussed, followed by the planning and performing of the synthesis of the envisaged HTMs. The optical, electrochemical, and thermal analysis of the obtained CPDTs is presented afterwards.
1.2 State of the Art

The amorphous glassy state is of utmost importance for active materials in multiple organic electronics applications. The amorphous state ensures good reproducibility and is easier to achieve than a single crystalline state. In comparison to polycrystalline materials, an amorphous material does not form grain boundaries that can act as charge traps that are harmful to the device performance. A challenge has always been the low stability of the amorphous state in molecular organic electronic material-based devices. A possible solution was the incorporation of the molecular organic active material in a polymer matrix to stabilize the amorphous state. This approach was taken for example by the incorporation of HTM N,N-diphenyl-N,N-di(m-tolyl)benzidine (TPD) 1 in a polycarbonate matrix (Figure 1-2).

![Figure 1-2: Molecular structure of HTM TPD 1.](image)

In 1993 and 1994 Naito et al. conducted a quantitative and qualitative investigation of the relationship between thermal stability of the amorphous phase and the molecular structure. A stable amorphous state is given by a high glass transition temperature ($T_g$). According to Naito et al. a high $T_g$ is expected for molecules composed of a larger number of atoms, with a highly symmetric, globular, rigid, and dense structure. The amorphous state can be further stabilized if the phase transition enthalpy between the amorphous and crystalline state is small. This effect can be achieved by incorporating rigid and bulky substituents and by reducing the molecular cohesion. The findings of Naito et al. resulted in the development of various concepts for example the starburst or dendritic shaped molecular materials. This class of molecules was pioneered by Shirota. A small collection of triarylamine based starburst molecules is depicted in Figure 1-3. The effect of the structural modification on $T_g$ is interesting to see for all three HTMs. $4,4',4''$-Tris[N-(3-methylphenyl)-N-phenylamino]triphenylamine ($m$-TDATA) 2 exhibited a $T_g$ of only 75 – 80 °C. The fusing of the terminal triphenylamine (TPA) units to carbazoles results in the formation of $4,4',4''$-tri(N-carbazolyl)triphenylamine (TCTA) 3, which shows an elevated $T_g$ of 151 °C. The increased $T_g$ is attributed to the rigidification of the structure. The HTM $4,4',4''$-tris [bis(9,9-dimethylfluoren-2-yl)amino]triphenyl-benzene (TBFAPB) 4 comprises an elongated π-system com-
pared to $m$-TDATA and TCTA with terminal rigid fluorene units. This combination of a high molecular weight (1505 g/mol) and the rigidity results in a $T_g$ of 189 °C. All three molecules were employed as HTMs in organic electroluminescent devices.

![Figure 1-3: Structures of the starburst-shaped triphenylamine-based HTMs 2 ($m$-TDATA), 3 (TCTA), and 4 (TBFAPB).](image)

Any molecule with at least two cyclic moieties that are connected by one common sp$^3$-hybridized atom, is called a spiro compound.$^{[17]}$ The term was first proposed in 1900 by Adolf von Baeyer and was derived from the Latin word *spira* for pretzel.$^{[18]}$ In a spirocyclic molecule, two cyclic units are perpendicularly arranged due to the geometry of the linking sp$^3$-hybridized atom. The spiro-concept, *i.e.*, the linkage of two different (or similar) π-systems with different (or the same) functions over one common sp$^3$-hybridized atom, was developed as another means to achieve the stabilization of the amorphous state.$^{[5, 10]}$ The two parts are expected to be electronically independent from one another due to the sp$^3$-atom dividing them. In 1967, R. Hoffmann *et al.* first described the effect of spiroconjugation in spiro-linked π-systems as a special case of homoconjugation.$^{[20-21]}$ The effect on the FMOs was investigated and it was demonstrated that in all cases spiroconjugation increases the resonance stabilization.$^{[20]}$ It was further shown that the coupling of two conjugated radical fragments with (4$n$+3) π-electrons via a common sp$^3$-carbon atom can lead to a stable singlet ground state due to the interaction between formerly non-bonding states.$^{[21]}$ Further theoretical studies were performed, and it was shown, that spiroconjugation can occur between molecular orbitals, in which the 2p-orbitals next to the spiro-atom are antisymmetric to each other.$^{[22]}$ Spiroconjugation was directly experimentally confirmed in 1971 by Krapp *et al.* through
the observation of spiro-splitting in photoelectron spectra on spiro-bifluorene 5 and spiro-silabifluorene 6 (Figure 1-4).[23-24] It is now believed that electronic coupling in spiro-linked molecules mostly occurs through vibronic coupling or in vibration excited states.[25-27]

![Figure 1-4: Molecular structure of spiro-bifluorene 5 and spiro-silabifluorene 6.](image)

Spiro-bifluorene 5 was interestingly already synthesized in 1930 by Clarkson et al. starting from fluorenone 7 and biphenylmagnesium iodide 8 (Scheme 1-1). The reaction proceeds via a fluorenol intermediate 9 which is ring-closed using hydrochloric acid (HCl) in boiling acetic acid (HOAc) to afford spiro-bifluorene 5 in 53% isolated yield over two steps.[28]

![Scheme 1-1: First published synthesis of spiro-bifluorene 5.](image)

The spiro-concept was pioneered by Salbeck et al. and one of the first and most important HTMs was 2,2',7,7'-tetrakis(N,N-diphenylamino)-9,9'-spirobifluorene (spiro-TAD) 10, which is obtained by spiro-linking two tetraphenylbenzidine[29-30] moieties (Figure 1-5).[1, 31] The spiro-linkage increased the \( T_g \) from 60 °C[32] for the monomer to 133 °C for spiro-TAD. The increased \( T_g \) can be understood by comparing the initial structure of TPD 1 with the spiro-TAD 10 structure under consideration of the design rules for high \( T_g \) molecular materials discussed above. The spiro-linkage doubles the molecular weight and increases the symmetry from D\(_{2h}\) to T\(_d\), which results in a spherical structure of the HTM. The spiro-linkage additionally introduces a rigid element to the structure and decreases the possibility of the molecule to form \( \pi-\pi \)-interactions in the solid-state. All these combined effects explain the increase in \( T_g \) of more than 70 °C. The spiro-TAD structure was later slightly modified by the incorporation of methoxy substituents in all phenylamine \( \text{para} \)-positions to slightly adjust the highest occupied molecular orbital (HOMO) energy level resulting in the HTM \( N,N,N',N'',N''',N''''\)-Octakis(4-methoxyphenyl)-9,9'-spiro[fluorene]-2,2',7,7'-tetramine (spiro-MeOTAD) 11 (Figure 1-5).[33-34] The substitution of 10 decreased \( T_g \) again to 120 °C for 11 prob-
ably due to an increase in the molecular cohesion due to the eight methoxy groups. Spiro-MeOTAD 11 was initially used as a solid electrolyte in dye-sensitized solar cells (DSSC) comprising a ruthenium-based absorber material and TiO₂ as an electron transport layer (ETL).

Due to the success of spiro-MeOTAD as HTM in solid-state DSSC and later in Perovskite solar cells (PSC), many different structural variations have been designed and synthesized to optimize the molecules for their use as HTM in the respective device. Typical variations include the incorporation of more rigid substituents such as carbazoles in 2,2',7,7'-tetra(9H-carbazol-9-yl)-9,9'-spirobi[fluorene] (spiro-Carb) 12, phenoxazine in 2,2',7,7'-tetra(10H-phenoxazin-10-yl)-9,9'-spirobi[fluorene] (spiro-PhOx-TAD) 13, or phenothiazine in 2,2',7,7'-tetra(10H-phenothiazin-10-yl)-9,9'-spirobi[fluorene] (spiro-PhTh-TAD) 14 substituents (Figure 1-6). Spiro-Carb 12 can be seen as a fused version of spiro-TAD 10, while spiro-PhOx-TAD 13 is more similar to a fused version of a spiro-MeOTAD derivative with methoxy groups in the ortho-positions. The fusion of the substituents has again a large effect on T_g, spiro-Carb 12 exhibits the transition at 240 °C which is 107 °C higher than this of unfused spiro-TAD 10.
Spiro-MeOTAD has been synthesized with different substitution patterns of methoxy substituents on the terminal phenylamine units. A good overview of all synthesized derivatives can be found in a recent review by Martin et al.\textsuperscript{[35]}

The spiro-bifluorene unit is one of the most used building blocks in organic electronic materials. Depending on the substitution pattern, the molecule can act as HTM, ETL, or photoluminescent active material.\textsuperscript{[5, 31]} More than 50,000 spiro-bifluorene structures have been published to date.\textsuperscript{[38]} Besides the amino-substituted spiro-bifluorene cores, the class of spiro-linked oligophenyls is of importance due to their use as blue fluorescent emitters. The general structure of spiro-linked oligophenyls is illustrated in Figure 1-7 and they are systematically named after the number of spiro-linked oligo-para-phenyls. The general name for this class of molecules is therefore spiro-(2n+4)Φ. All spiro-(2n+4)Φ until spiro-10Φ have been synthesized by Salbeck et al.\textsuperscript{[1, 31, 34]} The oligo- para-phenyls are still well soluble despite their high molecular weight.

![Figure 1-7: General structure of spiro-linked oligophenyls spiro-(2n+4)Φ.](image)

The synthesis of T\textsubscript{d}-symmetrical spiro-bifluorene derivatives always starts from a tetrabrominated precursor 15, which can be obtained by fourfold bromination of spiro-bifluorene 5 with elemental bromine and iron(III) bromide as catalyst in quantitative yield (Scheme 1-2).\textsuperscript{[39]}

![Scheme 1-2: Synthesis of tetrabrominated spiro-bifluorene 15 by fourfold bromination of spiro-bifluorene 5.](image)

The thiophene analogues of fluorene, CPDT exists in six different isomers, which can be seen as the bridged analogous of 2,2-, 2,3-, and 3,3-bithiophene. The structures of all cyclopenta[b,b']di-thiophenes 16-18 are shown in Figure 1-8.
Figure 1-8: General structures of all three different cyclopenta[b,b']dithiophenes (16-18).

The unsubstituted 4H-cyclopenta[2,1-b:3,4-b']dithiophene 16 was first synthesized by Wynberg et al. starting from bis(3-thienyl)methanol 19 in three steps (Scheme 1-3). At first, the alcohol is reduced with LiAlH$_4$ in 80% to dithien-3-ylmethane 20, followed by a twofold α-bromination to bis(2-bromothien-3-yl)methane 21, lithiation, and oxidative coupling with copper(II) chloride to form CPDT 16. The three steps afforded 4H-cyclopenta[2,1-b:3,4-b']dithiophene 16 in 14% overall yield.[40]

Scheme 1-3: Synthesis of 4H-cyclopenta[2,1-b:3,4-b']dithiophene 16.[40]

The C$_s$-symmetrical 7H-cyclopenta[1,2-b:3,4-b']dithiophene 17 was similarly synthesized by the same group starting from 3-bromothiophenealdehyde 22 and 3-thienyllithium 23. The resulting alcohol 24 is oxidized with chromium(VI) oxide to the corresponding ketone 25, which in turn is reduced by a Wolff-Kishner reduction to 3-bromo-2-(thien-3-ylmethyl)thiophene 26. Bromination with elemental bromine led to 2-bromo-3-((3-bromothien-2-yl)methyldithiophene 27, which was lithiated and oxidative coupled to afford 7H-cyclopenta[1,2-b:3,4-b']dithiophene 17 in 10% overall yield over five steps (Scheme 1-4).

Scheme 1-4: Synthesis of 7H-cyclopenta[1,2-b:3,4-b']dithiophene 17.[40]

The missing C$_{2v}$-symmetric 7H-cyclopenta[1,2-b:4,3-b']dithiophene 18 was also synthesized by Wynberg et al. starting from (3-bromothien-2-yl)lithium 28 and 3-bromo-2-(chloromethyl)thiophene...
29 by nucleophilic substitution reaction to bis(3-bromothien-2-yl)methane 30 followed by lithiation and oxidative coupling in 6% isolated yield over two steps (Scheme 1-5).[41]

Scheme 1-5: Synthesis of 7H-cyclopenta[1,2-b:4,3-b’]dithiophene 18.[41]

The general synthetic strategy for all three cyclopentadithiophenes is hereby the same. At first, the alkyl-bridge is formed by the addition of a lithiated thiophene to the thiophene-carbaldehyde or halogenated alkylthiophene. The bithiophene moiety is ring-closed by an oxidative homocoupling of the respective lithiated thiophenes by copper(II) chloride afterwards. The low-yielding oxidative homocoupling in the last step is detrimental to the overall yield of this reaction sequence. Side-reactions are expected due to the unprotected thiophene α-positions.

A spiro-linkage of the three different cyclopenta[b,b’]dithiophenes 16, 20, and 27 with fluorene would result in the formation of three different spiro-cyclopentadithiophene-fluorenes 31, 32, and 33 (Figure 1-9).

Figure 1-9: Structure of all three possible spiro-linked combinations of cyclopenta[b,b’]dithiophene and fluorene.

The spiro-CPDT-fluorene 31 was first synthesized in 1970 by Wynberg et al. starting from fluorenone 34. Interestingly, lithiated 3,3’-dibromo-2,2’-bithiophene 35 was used for this reaction instead of lithiated 3-bromo-2,2’-bithiophene as expected. The fluorenol 36 was not isolated but directly treated with hydrochloric acid in glacial acid to achieve the ring-closure in 70% yield (Scheme 1-6).[42]

Scheme 1-6: Synthesis of spiro-cyclopentadithiophene-fluorene 31 by addition of lithiated bithiophene 35 to fluorenone 34.[42]
The synthesis has been modified by Bäuerle et al. starting from 4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one 37 and lithiated biphenyl 38 (Scheme 1-7). The ring-closure of the intermediate cyclopentadienol 39 was carried out with the Lewis-acidic boron trifluoride diethyl etherate (BF$_3$*OEt$_2$) instead of hydrochloric acid and acetic acid in 60% isolated yield. The spiro-cyclopentadithiophene-fluorene 31 was twofold brominated in the thiophene α-positions with N-bromosuccinimide (NBS) which afforded dibrominated spiro-CPDT-fluorene 40 in 92% yield.[43]

Scheme 1-7: Modified synthesis of spiro-cyclopentadithiophene-fluorene 31 and following bromination to dibromo-CPDT 40.[43]

The π-system of the brominated spiro-cyclopentadithiophene-fluorene 40 was extended with thiophene- and bithiophene units to obtain soluble quarter- and sexithiophene 41 and 42 with application as electroluminescent materials (Figure 1-10). The spiro-linkage increased the solubility in dichloromethane from 4.6 mg/ml to 12 mg/ml for the quaterthiophene 41, and from 1.1×10$^{-3}$ mg/ml to 3.8 mg/ml for the sexithiophene 42.[43]

Figure 1-10: Spiro-linked quaterthiophene 41 and sexithiophene 42.

A method to prepare spiro-cyclopentadithiophene-fluorene, comprising bromines at the 2- and 7-positions of the fluorine, 43 was reported by Leriche et al. in 2015. Trimethylsilyl (TMS)-protected 3-bromo-2,2'-bithiophene 44 and dibromo-fluorenone 45 were used as starting materials in the synthesis to form the fluorenol intermediate 46 after a lithium-bromine exchange at aryl halide 44 and subsequent addition to ketone 45. The ring-closure reaction towards dibrominated spiro-CPDT-fluorene 43 was again performed using hydrochloric acid in boiling acetic acid (Scheme 1-8).[44]
Scheme 1-8: Synthesis of 2',7'-dibromo-spiro-cyclopentadithiophene-fluorene 43.\(^{[44]}\)

Dibromo-spiro-cyclopentadithiophene-fluorene 43 was end-capped with 3,4-ethylenedioxythiophene (EDOT) in a Stille-type cross-coupling reaction and subsequently electropolymerized via the thiophene α-positions to form an electroactive polymer film (Figure 1-11).\(^{[44]}\)

Figure 1-11: Spiro-cyclopentadithiophene-fluorene-based monomers for electopolymerization.

The spiro-cyclopentadithiophene-fluorene HTM 2',7'-bis(bis(4-methoxyphenyl)amino)spiro[cyclopenta[2,1-b:3,4-b]dithiophene-4,9-fluorene] (FDT) 47 was designed and synthesized by Grätzel et al. also starting from TMS-protected 3-bromo-2,2'-bithiophene 44 and dibromo-fluorenone 45 but with an improved yield compared to the method of Leriche et al.\(^{[44]}\) The ring-closure reaction was performed with the Lewis-acid iron(III) chloride in chloroform and the following twofold palladium-catalyzed Buchwald-Hartwig amination with bis(4-methoxyphenyl)amine 48 afforded the desired material in 82% isolated yield (Scheme 1-9). The material was used as HTM in a mixed formamidinium (FA) and methylammonium (MA) cation \([\text{FA}]_{0.8}\text{(MA)}_{0.2}\text{Pb}_{2.4}\text{Br}_{0.6}\] PSC and achieved a power conversion efficiency (PCE) of 20.2%.\(^{[45]}\)

Scheme 1-9: Synthesis of the spiro-CPDT-fluorene-based HTM FDT 47.\(^{[45]}\)
The C₅-symmetric spiro-cyclopentadithiophene-fluorene 32 was also synthesized by Wynberg et al. in the same manner as its isomer 31, starting from [2,3'-bithiophen]-3-yllithium 49 and fluorenone 34. The fluorenol intermediate 50 was again ring-closed with hydrochloric acid and acetic acid. The isolated yield was slightly lower with 63% compared to 70% for spiro-CPDT 31 (Scheme 1-10).[42]

![Scheme 1-10: Synthesis of spiro-cyclopentadithiophene-fluorene 32.](image)

The third spiro-cyclopentadithiophene-fluorene 33 was synthesized by the same group of Wynberg using the same synthetic strategy as for spiro-CPDTs 31 and 32. The synthesis started from fluorenone 34 and [3,3'-bithiophen]-2-yllithium 51. The fluorenol intermediate 52 was this time isolated and obtained in 84% yield. In this case, the ring formation resulted in an isolated yield of 87%, the best for the series (Scheme 1-11).[42]

![Scheme 1-11: Synthesis of spiro-cyclopentadithiophene-fluorene 33.](image)

Further replacement of the remaining fluorene unit in spiro-CPDT-fluorene by CPDTs leads to seven different isomeric spiro-bi[cyclopentadithiophene]s (spiro-biCPDT)s (53-59) illustrated in Figure 1-12.

![Figure 1-12: Structure of all possible isomeric spiro-bi[cyclopentadithiophene]s 53-59 composed of cyclopenta[b,b']dithiophenes.](image)

Interestingly only, spiro-biCPDT 53 is described in literature. An explanation of the absence of the other isomers can probably be traced back to the paper of Wynberg et al. from 1970, where the
attempted synthesis of spiro-biCPDTs 53-56 have been described. The formation of the spiro-linkage proceeds via a carbocation intermediate, and the reactivity of the intermediate is depending on the substitution pattern. Wynberg et al. observed that the attachment of thienyl substituents, especially when α-linked, leads to a very high reactivity of the intermediate, which decomposes before ring-closure could be achieved.\textsuperscript{[42]} Therefore, it took another 37 years until a spiro-biCPDT 53 derivative was reported in 2007 by Salbeck et al.\textsuperscript{[46]} The tetrabrominated core 60 was coupled in a Suzuki-type cross-coupling with phenylboronic acid 61 (Scheme 1-12) to give the thiophene-analogues 2,2',6,6'-tetraphenyl-4,4'-spirobi[cyclopenta[2,1-b:3,4-b']dithiophene] (spiro-4P-CPDT) 62 of spiro-4Φ (see Figure 1-7).

\begin{center}
\textbf{Scheme 1-12:} Suzuki-type cross-coupling to form spiro-4P-CPDT 62.\textsuperscript{[46]}
\end{center}

Interestingly, no synthesis of the brominated spiro-biCPDT core 60 was given in this publication. The first synthesis of the spiro-biCPDT-core 53 was published six years later by Fungo et al.\textsuperscript{[47]} The tetrabrominated core 60 was synthesized starting from TMS-protected 3-bromo-2,2'-bithiophene 45 and dibrominated CPDT-one 63. An lithium-bromine exchange on aryl halide 45 was performed and the lithiated species was added to ketone 63 to afford 4-(5,5'-bis(trimethylsilyl)-[2,2'-bithien]-3-yl)-2,6-dibromo-4H-cyclopenta[2,1-b:3,4-b']dithien-4-ol 64 in 81% yield. The TMS-groups were ipso-substituted with NBS and the resulting tetrabrominated cyclopentadienol 65 was ring-closed with an iron(III) chloride mediated Friedel-Crafts alkylation reaction (Scheme 1-13).

\begin{center}
\textbf{Scheme 1-13:} Synthesis of tetrabrominated spiro-biCPDT 60.\textsuperscript{[47]}
\end{center}

The unsubstituted core 53 was obtained by dehalogenation via metal-halogen exchange with n-butyllithium (n-BuLi) and successive quenching of the organolithium intermediate with aqueous ammonium chloride solution (Scheme 1-14).
The central core 53 was formylated at the two thiophene α-positions by a twofold Vilsmeier-Haack formylation with N,N-dimethylformamide (DMF), phosphoryl chloride (POCl₃), and dichloroethane (DME) as the solvent. The remaining free thiophene α-positions of the dialdehyde 66 were brominated with NBS to further react the dibrominated spiro-biCPDT 67 by a Suzuki-type cross-coupling with TPA pinacol boronic ester. The spiro-biCPDT-based donor-acceptor (D-A) dye 68 was obtained after Knoevenagel condensation of the arylated spiro-biCPDT 69 with 2-cyanoacetic acid 70 (Scheme 1-15). The D-A dye 68 was employed as active material in a DSSC granting a PCE of 6%.[47]

A spiro-biCPDT-based HTM was synthesized by Mishra et al. in 2015. The spiro-biCPDT core was as well synthesized from TMS-protected 3-bromo-2,2'-bithiophene 45 and dibrominated CPDT-one 63 in three steps. The yield of the first step was slightly improved, but the second and third steps suffered from lower yields. The brominated core 60 was coupled with TAA boronic ester 71 in a fourfold Suzuki cross-coupling to tetrakis(triarylamine) capped spiro-biCPDT (FK1) 72 in 91% isolated yield (Scheme 1-16).[2]
The HTM FK1 exhibited a $T_g$ of 150 °C and has been employed in an n-i-p-type PSC exhibiting a PCE of 13.4% (reference cell with spiro-MeOTAD: 14.7%). Interestingly, this HTM did not require the addition of the otherwise used standard dopants and additives.

Spiro-linked sexithiophene (73) (Figure 1-13) was synthesized as another spiro-biCPDT-based HTM for the application in PSC.[48] The spiro-linkage resulted in an amorphous material with a $T_g$ of 137 °C. The HTM was employed together with the MAPbI$_3$-perovskite as an absorber in a n-i-p-type solar cell and resulted in a PCE of 10.4%.

The interest in spiro-biCPDT 53 as a central building block, which causes a cruciform structure in the molecule, has been sparked in the last years. The middle building block was used for the design of various non-fullerene acceptors (NFA) for the use in organic photovoltaics. Huang et al. synthesized a perylenediimide (PDI) functionalized spiro-biCPDT 74 (Figure 1-14). The rigid core resulted in a three-dimensional structure of the electron acceptor, which was employed together with donor polymer PTB7-Th in a bulk heterojunction organic solar cell (BHJSC) and resulted in a PCE of 7.11%.[49]
The NFA was further optimized by fusing the PDI substituents to the cyclopentadithiophene by a cyclodehydration reaction with iron(III) chloride and nitromethane to obtain the coupled molecule 75 (Figure 1-15). The NFA was implemented in a BHJSC together with donor polymer PTB7-Th. The cyclodehydration resulted in an improved performance of the NFA with a PCE of 8.89% compared to 7.11% for NFA 74. The increased performance was attributed to the better miscibility of the NFA with the polymer in the blend due to the prevention of overaggregation in the NFA.\cite{50}

Other spiro-b[cyclopentadithiophene]-based NFA materials were created by linking the core with acetylene-PDIs\cite{51} or diketopyrrolopyrrole.\cite{52}
1.3 Synthesis of Cyclopentadithiophene-based HTMs

1.3.1 Retrosynthesis

The synthesis of the envisaged spiro-cyclopentadithiophene-based hole transport materials was planned using a retrosynthetic approach. The introduction of TAA substituents by Suzuki-type cross-coupling in the last step of the synthesis has established itself as a modus operandi in HTM synthesis. For this reason, this procedure has already been taken into account and retrosynthesis has been carried out starting from the halogenated species 76. The aim of the retrosynthetic analysis was the development of a convergent synthetic approach that is applicable for various bridging groups “X”. Therefore, it was avoided to split a C-X bond. The retrosynthesis is shown in Scheme 1-17 with synthons and in Scheme 1-18 with synthetic equivalents.

Starting from the halogenated central building block 76 three different retrosynthetic operations are possible. The first one is a disconnection (Dis) of the six-membered heterocyclic ring (pathway A) which leads to a halogenated spiro-CPDT-core 77. The acceptor (a) is here assigned to the CPDT, the donor (d) to the electron-rich heteroatom substituted phenyl. The second step of pathway A is a functional group interconversion (FGI), where the halogens are cleaved off. This leads to cyclopentadithiophene 78, which can be further disconnected into a cyclopentadithiophene 79 and a diphenyl linked by “X” 80. This means that the heteroatom in the target molecule is determined in the first step by the choice of diphenyl compound 80. The second and third pathways, B and C, start with an FGI, which leads to the unsubstituted spiro-CPDT core 81. Pathway B continues again by the cleavage of the six-membered heterocycle which leads to 78. In pathway C the cyclopentadiene unit is cleaved which leads to bithiophene 82 with the fused heterocycle attached. The last step is then the dissociation into two building blocks, a heterocycle 83 with an acceptor function at the methylene-bridge and bithiophene 84 with donor functionality in the β-position.
Scheme 1-17: Retrosynthetic analysis of the general target-molecule structure 76. Synthons are used to indicate the reactivity.

The last considered retrosynthetic operation for 76 is the dissociation of the cyclopentadiene, which leads to pathway D. The obtained structure 85 is a halogenated bithiophene with the heterocycle attached. The problem with pathway D becomes apparent in the next step. The introduction of the halogens (FGI) could be difficult because the α- and α’-positions of the bithiophene are not equal. This results in different reactivity, which could render the selective introduction of the halogens difficult. Pathway D was therefore omitted in the planning of the synthesis.

The assignment of the synthetic equivalents to the synthons is shown in Scheme 1-18. The acceptor functionality of building blocks 79 and 83 is achieved by using a ketone functionality. Ketone 79 is known in literature and is easily accessible. The availability of ketone 83 depends on the choice of heteroatom “X”. The donor functionality of 80 and 84 should be ensured by the use of organolithium compounds, which can be easily prepared from n-BuLi and the corresponding aryl halide. The missing acceptor functionality of 76, 78, and 82 could be obtained by treating the respective alcohols with a Lewis acid forming a carbenium ion.

The key difference between pathway A and B on one hand and C on the other hand is whether the central five-membered or the attached six-membered ring will be formed during the synthesis. The implications of the chosen pathway on the reaction parameters will be discussed in the following.
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Figure 1-16: General structure of the first target molecule cyclopentadithiophene-N-phenylacridine 86.
The central spiro-cyclopentadithiophene-N-phenylacridine (spiro-CPDTA) was synthesized in a convergent multiple-step synthesis starting from commercially available starting materials according to pathway A. The synthesis of the necessary CPDT-one 87 starting from the commercially available 3-bromothiophene 88 is shown in Scheme 1-19.

Scheme 1-19: Synthesis of the TMS-protected cyclopentadithiophenone 87 according to a literature known procedure.

In the first step 3-bromothiophene 88 was oxidatively homocoupled with copper(II) chloride to 3,3'-dibromo-2,2'-bithiophene 89 according to a modified literature procedure. The 3-bromothiophene 88 was dissolved in dry tetrahydrofuran (THF) and lithiated with lithium diisopropylamide (LDA) in the 2-position at 0 °C. Zinc(II) chloride was added to perform the transmetallation of the lithiated thiophene to the organo-zinc compound. The solution was cooled to -60 °C and copper(II) chloride was added to oxidatively homocouple the thiophene to 3,3'-dibromo-2,2'-bithiophene 89. The crude product was purified by filtration in petrol ether (PE) through silica gel and following precipitation that afforded the bithiophene 89 in 78% isolated yield. In the next step, TMS-protecting groups were introduced at the thiophene α-positions according to another literature procedure, this additional step will simplify the following ring-closure reaction due to the suppression of side product formation. The dibromobithiophene 89 was dissolved in dry THF and the solution was added towards a LDA solution in THF at -78 °C. The reaction mixture was allowed to warm to -10 °C to ensure a full lithiation of the bithiophene. The mixture was cooled down again to -78 °C and trimethylsilyl chloride (TMSCl) was slowly added and the solution was warmed to room temperature. After aqueous processing, extraction, and drying, the TMS-protected bithiophene 90 was obtained as an orange solid in 95% yield. The last step consisted of the formation of the cyclic ketone 87. The TMS-protected bithiophene 90 was dissolved in dry THF, cooled to -78 °C and treated with n-BuLi to perform a twofold halogen-metal exchange. Freshly distilled dimethylcarbamoyl chloride (DMCC) in dry THF was slowly added to the lithiated solution. The lithiated thiophene 91 reacted at first with the DMCC to form the amide 92, which further reacted with the other lithiated thiophene α-position to form the hemiaminal intermediate 93 that is stable under the reaction conditions and does not react further (Scheme 1-20). The reaction mixture was quenched by the addition of saturated NH₄Cl-solution which instantly turned the solution dark red due to the hydrolysis of the hemiaminal to the ketone.
Scheme 1-20: Stepwise reaction of the twofold lithiated bithiophene with DMCC towards the ketone 87.

The organic phase was extracted with PE until the red color vanished, dried, and purified by flash column chromatography with silica gel to afford the ketone 87 as a red solid in 77% isolated yield.

The second building block for the convergent synthesis of the spiro-CPDTA core is 2-bromo-N,N-diphenylaniline 94. This aryl halide is not available via direct bromination of triphenylamine because the para-positions are more reactive in an electrophilic aromatic substitution. Therefore, the molecule was synthesized by Buchwald-Hartwig amination according to a literature-known procedure (Scheme 1-21).[65] Diphenylamine 95 and 2-bromoiodobenzene 96 were dissolved in dry toluene in a Schlenk-tube, 5 mol% palladium(II) acetate, 5 mol% of the bidental phosphane ligand 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) and sodium tert-butylate (NaOtBu) as a base were added under argon atmosphere, and heated to 100 °C. After cooling water was added, and the product was extracted, dried, and purified by column chromatography with silica gel. Recrystallization from methanol afforded the arylamine 94 as green crystals in 83% isolated yield. The green color indicated the presence of oxidized byproduct that was under the detection limit of the employed analysis methods.

Scheme 1-21: Synthesis of 2-bromo-N,N-diphenylaniline 94.

The two building blocks 87 and 94 were combined to form the spiro-CPDTA core. Aryl halide 94 was first lithiated and afterwards added to ketone 87 to form CPDT-ol 97. The next step was an ipso-substitution of the TMS-groups by iodine to allow the following functionalization by cross-coupling reactions. The formed iodinated CPDT-ol 98 was ring-closed in the last step by a Lewis-acid mediated intramolecular Friedel-Crafts alkylation to form the spiro-functionality in the halogenated spiro-CPDTA derivative 99. The synthetic steps are given in Scheme 1-22.
Aryl halide 94 was dissolved in dry THF and cooled to -78 °C under an argon atmosphere. A halogen-metal exchange was performed by slow addition of n-BuLi to the solution. Ketone 87 was dissolved in dry THF, cooled to -78 °C and slowly added towards the solution of lithiated 94. The reaction could easily be monitored by the vanishing red color of the ketone 87 upon addition. The reaction was warmed overnight to room temperature, quenched by the addition of saturated NH₄Cl and the organic phase was extracted and dried. The crude product was purified by flash column chromatography with silica gel that afforded the alcohol 97 as a slightly red solid in 66% yield. The slight red color indicated that traces of ketone 87 were still present but the amount was too small to be detected by nuclear magnetic resonance (NMR) spectroscopy. Ketone 87 and alcohol 97 possess similar polarities which made the purification tedious. The ipso-substitution of the TMS-protection groups was performed with iodine-monochloride (ICl) as iodination reagent. The high reactivity of the ICl required low reaction temperatures to ensure a high-selectivity of the reaction towards the substitution of the TMS-groups. Possible side reactions include the halogenation of the electron-rich arylamine moieties. Another problem was the exact dosage of the reagent due to the high density and air and moisture sensitivity. Therefore a 1 M solution in DCM was used, which was commercially available. The alcohol 98 was dissolved in DCM and cooled to -78 °C. A solution of ICl in DCM was slowly added and the resulting mixture was stirred at -78 °C. The reaction was quenched by the addition of saturated Na₂S₂O₅ solution to reduce the remaining ICl. The product was purified by flash column chromatography with silica gel, which resulted in the isolation of the iodinated CPDT-ol 98 as a yellow solid in 91% yield.
The instability of the C-I bond restricted the possibilities for the ring-closure reaction. An attempt with hydrochloric acid in boiling acetic acid led to the decomposition of the product and the formation of a violet iodine solution, which turned colorless after reduction with sodium disulfite. Therefore, milder reaction conditions using Lewis-acidic boron trifluoride diethyl etherate (BF₃*OEt₂) in DCM at room temperature were used. Alcohol 98 was dissolved in DCM Lewis-acid BF₃*OEt₂ was added, which turned to solution blue after a few seconds. The mixture was stirred for 5 minutes at room temperature before being quenched by the addition of saturated NaHCO₃ solution. The product was extracted and purified by flash column chromatography to afford the iodinated spiro-CPDTA 99 as a colorless solid in 81% isolated yield.

During repeated synthesis of CPDTA 99, a problem with the reproducibility of this reaction arose. The yield appeared to be very sensitive towards reaction parameters. Excess BF₃*OEt₂ and prolonged reaction times led to the formation of a variety of side-products. One side-product was a violet substance, which could be identified as iodine, because it lost its color after treatment with sodium disulfite. This result gave rise to the concern that the iodine group is too labile and is therefore the problematic functional group in this synthesis. The solution to the problem was the replacement of the iodide substituent by bromide. Compared to the C-I bond strength that is 220 kJ/mol the C-Br bond comprising a strength of 294 kJ/mol should lead to better stability of the molecule.[66] The pathway leading to corresponding brominated spiro-CPDTA 100 is illustrated in Scheme 1-23.

![Scheme 1-23: Synthetic route towards brominated spiro-CPDTA 100.](image)

The bromide substituents were introduced into alcohol 97 by ipso-substitution of the TMS-groups with NBS. Low temperatures were needed to ensure the selectivity of the reaction and avoid substitution at the arylamine. Alcohol 97 was dissolved in dry THF and cooled to -78 °C, NBS was added as solid under light-exclusion to avoid radical side-reactions. The mixture was slowly warmed to room temperature. This slow warming was necessary because the temperature where the bromination takes place on the TMS-groups but not on the arylamine is not known. The slow warming allowed the reaction to “find” the right temperature during the warming. The reaction was
quenched by the addition of Na₂SO₃ solution, extracted, and dried. The crude product was purified by flash column chromatography with silica gel and afforded the brominated CPDT-ol 101 as a yellow solid in 74% isolated yield. The ring-closure reaction was slightly optimized by stirring at lower temperatures for a longer period of time compared to the synthesis of 99. Alcohol 101 was dissolved in dry DCM and cooled to 0 °C. Lewis-acid BF₃·OEt₂ was added and the solution turned slightly green. The monitoring of the reaction by thin-layer chromatography (TLC) revealed a full conversion after 60 minutes at 0 °C. The reaction was again quenched, extracted, and purified by filtration through silica gel to afford brominated spiro-CPDTA 100 as a slightly yellow solid in 99% isolated yield without further purification.

The replacement of the iodide substituents with bromide not only increased the overall yield of the reaction sequence from 74% to 76% for the bromide derivatives, but also avoided one tedious purification step by column chromatography. The ring-closure reaction also showed good reproducibility leading to similar yields.

The aromatic excerpt of the NMR spectra of the three differently substituted CPDT-ols 97, 98, and 101, measured in CDCl₃, are depicted in Figure 1-17. The substitution at the thiophene α-positions affected the chemical shift of the different proton signals. The largest effect was visible for the thiophene β-proton signal, which is the singlet (s) at δ = 6.41 ppm for 101, δ = 6.53 ppm for 98, and δ = 6.58 ppm for 97 that are marked with red dots (●). The different TAA protons showed almost no change in chemical shift for the three different derivatives. The TPA ortho-protons are marked with the blue dots (●). They are for all three derivatives part of an AA'MM'X spin system and are therefore multiplets that are centered at δ = 6.75 ppm for 101, δ = 6.74 ppm for 98, and δ = 6.75 ppm for 97. The 3J-coupling constant of the AB spin-sub system amounts to 8.7 Hz for all three molecules. The triphenylamine meta-protons are marked with dark green dots (●) and are multiplets centered at δ = 7.15 ppm for 101 as well as 97, and at δ = 7.10 ppm for 98. They possess a 3J-coupling of 8.7 Hz to the ortho-proton and 7.4 Hz to the para-proton. The triphenylamino para-protons are marked with purple dots (●) and are centered at δ = 6.99 ppm for 101, δ = 7.00 ppm for 98, and δ = 6.92 ppm for 97. The phenyl that is attached to the CPDT unit revealed three different signals. The most deshielded signal for all investigated molecules is the proton ortho to the CPDT substituent. The signals are marked in maroon (●). The signals are doublets of a doublets (dd) which are centered at δ = 7.66 ppm for 101, δ = 7.65 ppm for 98, and δ = 7.72 ppm for 97. All three signals have a 3J-coupling of 7.5 Hz and another 4J-coupling of 2.1 Hz for 101, 1.9 Hz for 98, and 2.3 Hz for 97. The strong deshielding of the protons can be explained with the ring current effect of the CPDT in close proximity. The signals of the protons in meta- and para-position to the CPDT are marked in orange (●). Both signals overlap to form one multiplet.
with the center at $\delta = 7.31$ ppm for all three alcohols. The signal for 97 exhibited a strong roof effect, which is not that pronounced for the other two derivatives. The missing signals of the protons para to the diphenylamine are marked in cyan (●). The signals are centered at $\delta = 7.04$ ppm for 101 and 98 but at $\delta = 7.05$ ppm for 97 with a multiplet structure for all three derivatives. The invariance of most NMR signals to the substituent is expected because there should not be conjugation (in the ground state) between the CPDT core and the triarylamine substituent through the sp$^3$-carbon.

Figure 1-17: Aromatic excerpt of the NMR-spectra of alcohols 97, 98, and 101. All spectra were measured in CD$_2$Cl$_2$.

The improved synthesis of 100 and the necessity to up-scale its synthesis gave motivation to the development of another different, more effective route starting from ketone 87 and triarylamine 94 to yield spiro-CPDTA 100 via pathway C (see Scheme 1-17). In pathway C the sequence of ring-closure and bromination is the other way around, compared to the synthesis via pathway A. The intramolecular Friedel-Crafts alkylation was here performed directly with alcohol 97 and afforded the unsubstituted spiro-CPDTA core 102 (Scheme 1-24).
Scheme 1-24: Alternative, more efficient pathway towards brominated spiro-CPDTA 100.

The product mixture of the reaction of ketone 87 and triarylamine 94 to intermediate 97 was investigated using gas chromatography (GC) coupled with mass spectrometry (MS) to develop a viable synthetic procedure where purifications with column chromatography were limited to a minimum. The structures of all detected substances are provided in Figure 1-18 ordered by increasing polarity. Starting material 87 and desired product 97 possessed an almost similar polarity, which renders purification by column chromatography very tedious. The solution to the problem was a quick filtration of the product mixture with silica gel and a non-polar solvent to elute the triarylamines 94 and 94*. Subsequently, ketone 87 and products 97 and 97* were eluted with a more polar solvent (DCM).

Figure 1-18: Crude product mixture of the reaction towards alcohol 97.

The reaction mixture was afterwards treated with a large excess of BF$_3$*OEt$_2$ in DCM at 0 °C to afford unsubstituted spiro-CPDTA 102 and the deprotected ketone 87* (Scheme 1-25). The polarity of the desired product 102 was now significantly lower than that of starting material 87 and
side product 87'. Therefore, it was possible to separate the mixture by filtration with silica gel and a non-polar solvent. The deep-red color of ketone 87' served as an indicator to detect the impurity before collection.

Scheme 1-25: Treatment of the product mixture in the reaction of 87 and 94 via intermediate 97 with excess BF$_3$•OEt$_2$.

This reaction sequence yielded spiro-CPDTA 102 in 70% yield over two steps without time-consuming fractional purification by column chromatography. Spiro-CPDTA 102 was dissolved in dry DCM and cooled to 0 °C, NBS was added and the solution was stirred at 0 °C. The product was precipitated and washed with cold methanol to yield dibromo-CPDTA 102 as a white solid in quantitative yield.

The synthesis of the three different spiro-CPDTA cores 99, 100, and 102 gave the possibility for a comparison of the NMR-spectra which are depicted in Figure 1-19 together with the molecular structures. The spectra were measured in CD$_2$Cl$_2$. Corresponding signals are marked in the same color for all three spiro-CPDTAs. The protons were assigned with the help of proton-proton correlation NMR spectroscopy (H,H-COSY) and nuclear Overhauser effect NMR spectroscopy (NOESY). There were eight signals visible for 99 and 100. The unsubstituted spiro-CPDTA 102 showed one additional signal corresponding to the thiophene-α-proton. This confirmed the expected C$_{2v}$-symmetry of the derivatives. The largest shift occurred for the thiophene-β-protons which are marked in dark green (●). For unsubstituted spiro-CPDTA 102, the proton gives a doublet centered at $\delta = 7.23$ ppm with a $^3J$-coupling constant of 4.9 Hz. The +M effect of the bromide or iodide substituents led to a shielding of the proton signal. The iodide derivative 99 shows the signal as a singlet at $\delta = 7.16$ ppm and the bromide as well at $\delta = 7.02$ ppm. The TPA protons form again an AA′MM′X-spin-system. The signals corresponding to the triphenylamine meta- and para-protons revealed an invariance to the substitution. The meta-protons have a multiplet structure centered at $\delta = 7.72$ ppm and are marked with grey dots (●). The para-proton is marked in maroon (●) and is centered at $\delta = 7.60$ ppm for all three derivatives. The ortho-protons are marked in orange (●) and show a multiplet structure, which is centered at $\delta = 7.48$ ppm for the spiro-CPDTA 102, and at $\delta = 7.44$ ppm for the bromide 100 and iodide derivatives 99. The AMX sub-
spin-system analysis gave a $^3J$-coupling constant of 8.4 Hz to the meta-proton and a $^4J$-coupling constant of 1.2 Hz to the para-proton. The acridine proton in 4-position is marked in red (●). The signal is split into a doublet of doublet of doublet (ddd) with $^3J$-coupling of 8.4 Hz, $^4J$-coupling of 1.2 Hz, and $^5J$-coupling of 0.5 Hz for all three derivatives. The signal is centered at $\delta = 6.38$ ppm for spiro-CPDTA 102, $\delta = 6.35$ ppm for iodinated derivative 99, and 6.37 ppm for brominated spiro-CPDTA 100. The signal of the acridine 3-position proton is marked in cyan (●). For spiro-CPDTA 102 and iodinated spiro-CPDTA 99, another signal with a ddd splitting was detected with the center being at $\delta = 6.97$ ppm for 102 and 6.98 ppm for the 99. The unsubstituted derivative has two $^3J$-couplings of 8.4 Hz and 6.5 Hz and one $^4J$-coupling of 2.3 Hz, the two halogenated derivatives two $^3J$-couplings of 8.4 Hz and 7.0 Hz and one $^4J$-coupling of 1.8 Hz. For brominated spiro-CPDTA 100, the signal is overlapping with the thiophene proton signal and it was therefore not analyzable. Regardless, the center could be estimated to be at $\delta = 6.99$ ppm. The signals of the protons in the acridine 2-position are marked in magenta (●), those of the 1-positions in blue (●). The signals could only be clearly discerned for iodide derivative 99 with the 2-position being centered at $\delta = 6.67$ ppm as a ddd with two $^3J$-couplings of 7.7 Hz and 7.0 Hz and one $^4J$-coupling of 1.2 Hz. The signal for the acridine 1-position is also a ddd centered at $\delta = 6.62$ ppm with $^3J$-coupling of 7.7 Hz, $^4J$-coupling of 1.8 Hz, and $^5J$-coupling of 0.4 Hz. For spiro-CPDTA 102 and brominated spiro-CPDTA 100, the two signals appeared as a higher-order multiplet because the difference in chemical shift is in the same range as the coupling constant between them. This can be concluded due to the roof effect of the signal. The multiplet is centered at $\delta = 6.66$ ppm for both derivatives. The spectra of all three derivatives are almost identical showing again the lacking conjugation through the spiro-linkage.
The halogenated spiro-CPDTAs 99 and 100 enabled further functionalization by palladium(0)-catalyzed cross-coupling reactions. As a possible coupling partner in a Suzuki-type cross-coupling reaction methoxy capped TPA boronic ester 103 was chosen and synthesized in three steps starting from aniline 104 and p-iodoanisole 105 (Scheme 1-26). The first step consisted of a twofold copper(I)-catalyzed hetero-Ullmann Reaction which was conducted according to a modified procedure of Kelkar et al.\cite{67} The second step was a bromination reaction in the free para-position with NBS according to a procedure of Nazeeruddin et al.\cite{68} followed by a palladium(0)-catalyzed borylation reaction.\cite{69}
The C-N coupling was carried out by dissolving aniline 104 in dry toluene and adding p-iodoanisole, 3.5 mol% 2,2'-bipyridine as ligand, 3.5 mol% copper(I) iodide as catalyst, potassium tert-butylate (KOtBu) as base, and refluxing the solution. After cooling down the aqueous workup was performed, and the crude product was purified by column chromatography with silica gel to afford the TAA 106 as a yellow solid in 35% (lit. 79%[67]) isolated yield. The lower yield can be explained by the changed reaction conditions compared to the literature where the reaction was performed in an autoclave at higher temperature and higher pressure. Another problem of this reaction was the amount of solids in the reaction mixture which made stirring problematic. However, the starting materials for this reaction are low-cost and commercially available and a large amount of the p-iodoanisole 105 (20% of initial) was isolated after the reaction. The bromination was performed by dissolving triarylamine 106 in dry THF and cooling the mixture down to 0 °C. NBS was added and the solution was stirred at 0 °C under light exclusion to prevent radical side reactions. The aqueous workup was performed, the product was extracted with DCM, dried, purified by column chromatography with silica gel to afford aryl bromide 107 as a white solid in 89% (lit. 91%[68]) isolated yield. Boronic ester 103 was synthesized by dissolving the triarylamine bromide 107, bis(pinacolato)diborane, potassium acetate (KOAc), and 5 mol% [1,1’-Bis(diphenylphosphino)ferrocene]dichloropalladium(II)-dichloromethane complex as catalyst in dry and degassed DMF in a Schlenk-tube. The tube was sealed and heated to 80 °C. The crude product was purified by column chromatography after the aqueous workup to obtain the boronic ester 103 as a solid in 73% (lit. 81%[69]) isolated yield.
A second boronic ester, namely non-methoxylated TPA boronic ester 108 was synthesized from commercially available 4-bromo-\(N,N\)-diphenylaniline 109 under the same reaction conditions as for boronic ester 103 (Scheme 1-27). The reaction yielded product 108 as a white solid in 87\% yield.

```
\begin{align*}
\text{Scheme 1-27: Synthesis of triphenylamine boronic ester 108.}
\end{align*}
```

With boronic esters 103 and 108 in hand, it was possible to further functionalize spiro-CPDTA 100 via Suzuki-type cross-coupling reactions. The first target HTM 109 was synthesized by coupling dibrominated spiro-CPDTA 100 to the methoxy-capped triphenylamine boronic ester 103 (Scheme 1-28).

```
\begin{align*}
\text{Scheme 1-28: Suzuki-type cross-coupling of dibromo spiro-CPDTA 100 and boronic ester 103 to form HTM 109.}
\end{align*}
```

Dibromo Spiro-CPDTA 100, boronic ester 103, and 10 mol\% tetrakis(triphenylphosphine)palladium(0) (Pd(PPh\(_3\))\(_4\)) as catalyst were dissolved in dry, degassed THF. A potassium phosphate (K\(_3\)PO\(_4\)) solution was added, and the reaction mixture was heated to 75 °C. The mixture was cooled down, water was added and the organic phase was extracted, dried and the crude product was purified by column chromatography with deactivated (triethylamine (NEt\(_3\))) silica gel, followed by precipitation from DCM/n-hexane to afford the spiro-CPDTA HTM 109 as an orange solid in 72\% isolated yield.

HTM 109 was characterized using NMR spectroscopy. In the aromatic region of the \(^1\)H-NMR-spectrum twelve unique signals were visible. The \(^1\)H-NMR-spectrum with the assignment is illustrated in Figure 1-20. Two-dimensional \(H,H\)-COSY NMR-spectroscopy was used to assign the
signals (Figure 1-21). Both spectra were measured in CDCl$_3$. Signals that couple with each other are connected by dotted lines in the COSY spectrum.

Figure 1-20: Aromatic excerpt of the $^1$H-NMR spectrum of HTM 109 with signal assignment.
Figure 1-21: Two-dimensional $H,H$-COSY-NMR-spectrum of HTM 109.
The phenylamine proton signals of the central $N$-phenylacridine were again the most deshielded ones. The phenylamine meta-proton signal in light grey (◯) is a multiplet centered at $\delta = 7.70$ ppm. The para-protons signal in maroon (●) results in another multiplet centered at $\delta = 7.57$ ppm while the ortho-protons signal in orange (●) has a multiplet structure with a strong dd character. The two coupling constants that could be extracted from the spectrum were a $^3J$-coupling of 8.4 Hz and a $^4J$-coupling of 1.3 Hz. The acridine moiety results in the expected four signals. The signal of the proton in 4-position is marked in dark grey (●). The signal is a dd centered at $\delta = 6.37$ ppm with $^3J$-coupling of 8.3 Hz and a $^4J$-coupling of 1.1 Hz. The signal for the 3-position is marked in magenta (●). The signal has a ddd splitting, which is centered at $\delta = 6.97$ ppm. Two $^3J$-couplings of 8.6 Hz and 7.1 Hz and a $^4J$-coupling of 1.6 Hz are visible. The 2-position in teal (●) has also a ddd splitting centered at $\delta = 6.68$ ppm. The coupling constants are $^3J = 7.7$ Hz, 7.1 Hz and $^4J = 1.2$ Hz. The last signal of the acridine moiety is marked in lime (●). The signal was unfortunately overlapping with another signal from the TAA substituents. However, with the help of the coupling constants from the neighboring protons of $^3J = 7.7$ Hz and $^4J = 1.6$ Hz a spin-simulation was performed resulting in a center position at $\delta = 6.80$ ppm. The CPDT moiety only shows one singlet for the $\beta$-thiophene protons centered at $\delta = 7.11$ ppm marked in olive (●). The triarylamine substituents consist of two separate AA’XX’ spin systems, from which each gave rise to two multiplet signals. The signal of the TAA proton ortho to the methoxy substituent is marked in red (●). The signal is centered at $\delta = 6.82$ ppm, the splitting between the largest peaks of the signal is 9.0 Hz, which doesn’t directly correspond to one coupling constant because it is part of a multiplet structure. The signal of the meta-protons is marked in cyan (●). It is shifted to higher ppm values due to the lower +M-effect of the methoxy substituent on the meta-position. The signal is centered at $\delta = 7.04$ ppm with a multiplet structure and again with a 9.0 Hz splitting between the two largest peaks. The last two unassigned signals belong to the phenylamine, which is directly connected to the CPDT core. The proton signal ortho to the amine is marked in blue (●) and shows the same multiplet structure as the other TAA protons. The signal is centered at $\delta = 6.89$ ppm and the splitting between the two largest peaks is 8.8 Hz. The meta-protons resulted in another multiplet centered at $\delta = 7.35$ ppm and a splitting of 8.8 Hz. The signal is marked in dark green (●).

The structure of the spiro-CPDTA 109 was confirmed by single-crystal X-ray structure analysis. The crystals were prepared by antisolvent-diffusion crystallization with DCM as solvent and $n$-hexane as antisolvent. The molecule crystallized as orange crystals with the monoclinic primitive space group $P2_1/c$ with four equivalent molecules per unit cell. The cell parameters are $a = 10.2586(1)$, $b = 18.1730(2)$, $c = 29.9845(3)$ Å; $\alpha = 90.00$, $\beta = 92.7628(9)$, and $\gamma = 90.00^\circ$, which
results in a volume of 5573.5 Å³. The structure of the asymmetric unit is illustrated in Figure 1-22.

The molecule has torsion angles of 173.1° and 147.5° between the central CPDT-core and the TAA substituents. The small deviation from planarity indicates strong conjugation between the CPDT-core and the TAA substituents. One of the terminal dianisylamines is twisted by 6.6° out of the plane formed by the CPDT-core, while the other one is twisted by 59.6° which results in a pseudo-three-dimensionality of the molecule. Interestingly, the expected tetrahedral geometry at the sp³-carbon of the CPDT cannot be observed. The acridine moiety is bent by 31° out of the expected perpendicular arrangement and shows a boat-conformation.

The C-C bond lengths of the conjugated backbone of molecule 109 are shown in Table 1-1 and the bond lengths are plotted in Figure 1-23 to show the bond length alternation. The terminal TAA units show C-C bond lengths between 138.2 pm and 139.7 pm. The low bond length alternation confirmed the expected aromatic character of the TAA units. The length of the TAA carbon-bonds is consistent with C-C bond lengths reported for crystalline spiro-MeOTad.⁷⁰ The longest C-C bonds were obtained for bonds 7 and 15. These bonds with a length of 147 pm connect the CPDT-backbone to the TAA substituents. The longer bond lengths indicate a weak aromatic character in the ground state of the molecule and the increased bond length could be beneficial to reduce steric strain in the molecule. However, the longer bond lengths could also possibly be due to packing effects.
Figure 1-23: Bond length-alternation in the single-crystal X-ray measurement of HTM 109.

The central bridged bithiophene shows the typical bond length alternation for thiophenes with 137 pm for thiophene α-β bonds and 141 pm for a β-β bonds. The α- α’ bond connecting the two thiophenes units shows a length of 144 pm. The bond is a part of the CPDT core which contributes to the single-bond character of this bond. It is slightly shorter than in the CPDT-based HTM FDT (Scheme 1-9, p. 10) where a length of 147 pm was reported.[45] The shorter bond length in acridine 109 could be due to the electron-donating effect of the TAA substituents.

Table 1-1: C-C bond-lengths in the solid HTM 109.

<table>
<thead>
<tr>
<th>C-C bond</th>
<th>Bond length [pm]</th>
<th>C-C bond</th>
<th>Bond length [pm]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>138.2</td>
<td>12</td>
<td>137.9</td>
</tr>
<tr>
<td>2</td>
<td>139.2</td>
<td>13</td>
<td>141.5</td>
</tr>
<tr>
<td>3</td>
<td>138.9</td>
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<td>137.3</td>
</tr>
<tr>
<td>4</td>
<td>139.5</td>
<td>15</td>
<td>147.0</td>
</tr>
<tr>
<td>5</td>
<td>138.1</td>
<td>16</td>
<td>139.7</td>
</tr>
<tr>
<td>6</td>
<td>139.3</td>
<td>17</td>
<td>138.2</td>
</tr>
<tr>
<td>7</td>
<td>146.7</td>
<td>18</td>
<td>138.4</td>
</tr>
<tr>
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<td>137.3</td>
<td>19</td>
<td>138.7</td>
</tr>
<tr>
<td>9</td>
<td>141.2</td>
<td>20</td>
<td>138.5</td>
</tr>
<tr>
<td>10</td>
<td>136.6</td>
<td>21</td>
<td>138.8</td>
</tr>
<tr>
<td>11</td>
<td>144.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The distortion of the acridine with respect to the CPDT core could be explained by a packing effect of the molecule and the resulting intermolecular interactions. Figure 1-24 illustrates an excerpt of the packing with short contacts marked in green. This distance between TAA of one molecule and an acridine carbon atom of an adjacent molecule is 3.367 Å, which is shorter than the sum of the Van-der-Waals (VdW) radii of the carbon atoms. It appears that the TAA substituent pushes the acridine moiety out of the expected conformation.

Figure 1-24: Packing of solid HTM 109. Short contacts between two carbon atoms are marked in green.

The interaction between the spiro-CPDTA-cores of multiple molecules is depicted in Figure 1-25. The planes formed by the CPDT-units are shown in red and the TAA substituents are faded out for improved clarity. The phenyl substituent of the acridine moiety shows a π-π interaction with the CPDT-core of a neighbor molecule with a distance of 3.583 Å. This interaction may be responsible for the short plane distance of 2.859 Å between two CPDT-cores.
Figure 1-25: Intermolecular π-π interaction between the N-phenylacridine-cores.

The unit cell of spiro-CPDTA HTM 109 is provided in Figure 1-26. The unit cell contains four equivalent molecules, whereby two molecules are always facing in the same and the other two in the opposite direction.

Figure 1-26: P2_1/c unit cell of HTM 109.
Another spiro-CPDTA-based HTM 110 was synthesized by coupling dibromo spiro-CPDTA 100 and triphenylamine boronic ester 108 in another Suzuki-type cross-coupling reaction (Scheme 1-29).

Scheme 1-29: Synthesis of TPA capped spiro-CPDTA HTM 110 by Suzuki-type cross-coupling.

Aryl bromide 100, boronic ester 108, and 12 mol% Pd(PPh₃)₄ catalyst were dissolved in dry THF. A K₃PO₄ solution was added and the mixture was heated to 75 °C. The reaction was cooled, water was added, and the product was extracted, dried, and purified by flash column chromatography with deactivated silica gel. The separation of the product from the side products was more complicated in this case compared to HTM 109. The mono-substitution and homo-coupled side products possessed a polarity which was not that different from the product 110. A good separation could have been achieved with a non-polar eluent mixture, but the solubility of the product 110 would have suffered. The solution was an eluent mixture of PE and Et₂O, where the percentage of Et₂O was gradually increased. This procedure afforded HTM 110 as a yellow solid in 74% isolated yield.

1.3.3 Synthesis of Spiro-Cyclopentadithiophene-Thioxanthene-based HTMs

The second central spiro-CPDT-core that was designed and synthesized was the spiro-cyclopentadithiophene-thioxanthene (spiro-CPDTT) 111, where substituent “X” is sulfur (Figure 1-27).

Figure 1-27: General structure of the second target molecule building block spiro-CPDT-thioxanthene 111.
Halogenated building block 111 was synthesized in a multi-step convergent synthesis starting from commercially available starting materials according to pathway A. The first step was the synthesis of monobromodiphenyl sulfide 112 in a C-S cross-coupling reaction of 2-bromothiophenol 113 and iodobenzene 114. Diphenyl sulfide 112 was lithiated and added to the previously synthesized ketone 87 to form TMS-protected CPDT-ol 115. The TMS-groups were then exchanged by bromide substituents to form aryl bromide 116. The last step was the ring-closure reaction to give the desired dibromo spiro-CPDTT 117. The reaction schematic is provided in Scheme 1-30.

Scheme 1-30: Convergent synthetic route according to pathway A towards dibromo spiro-CPDTT 117.

Aryl bromide 112 was synthesized according to a modified procedure of Rout et al. in a copper(I)-catalyzed C-S cross-coupling reaction. Ortho-bromothiophenol 113 and iodobenzene 114 were added to a solution of KOH in water. Tetrabutylammonium bromide (TBAB) was added as a phase-transfer catalyst and 6 mol% of copper(I)-iodide as catalyst. The resulting solution was heated to 80 °C. The organic phase was separated and the aqueous phase was extracted. The combined organic fractions were washed with hydrochloric acid and sodium bicarbonate solution, dried, and the solvent was removed. The crude product was purified by Kugelrohr-distillation to afford the monobromodiphenyl sulfide 112 as a colorless oil in 69% isolated yield.

The addition of aryl halide 112 to ketone 87 was performed similarly as for the acridine derivative 97. The aryl bromide 112 was dissolved in dry Et₂O and cooled to -78 °C and n-BuLi was slowly added to perform a lithium-halogen exchange. A solution of ketone 87 in dry THF was slowly
added to the lithiated solution and the reaction was directly quenched by the addition of -78 °C cold isopropyl alcohol (iPrOH). Saturated NH₄Cl solution was added and the organic phase was separated, dried, and the crude product was purified by column chromatography to afford CPDT-ol 115 as a yellow solid in 53% isolated yield. An additional 20% yield could be obtained after a high-performance liquid chromatography (HPLC) purification of the remaining fractions.

**Ipso**-substitution of the TMS-protection groups with bromide substituents was performed with NBS as bromination agent. Alcohol 115 was dissolved in dry DCM and cooled to -20 °C, NBS was slowly added and the solution was allowed to warm to 0 °C. The mixture was stirred for an additional hour at room temperature. Water was added and the organic phase was extracted, dried, and filtered through a short plug of silica to remove excess NBS. The crude product was purified by column chromatography to afford the brominated CPDT-ol 115 as a slightly grey solid in 55% isolated yield.

The intramolecular Friedel-Crafts alkylation, which leads to ring-closure of the alcohol 115, was performed with boron trifluoride diethyl etherate. Brominated CPDT-ol 115 was dissolved in dry DCM, cooled to 0 °C and BF₃*OEt₂ was added. The reaction was quenched by the addition of saturated sodium bicarbonate solution and the product was extracted, dried, and purified by flash column chromatography to afford dibromo spiro-CPDTT 117 as a slightly grey solid in 61% isolated yield.

The differences in the synthesis of dibromo spiro-CPDTT 117 compared to that of dibromo spiro-CPDTA 100 are visible for each step. The addition of monobromodiphenyl sulfide 112 to ketone 87 was carried out in diethyl ether, compared to THF for monobromo triarylamine 94. The choice of solvent was important, both reactions were carried out in THF and Et₂O and only one solvent resulted in a high conversion rate. Generally, yields for thioxanthene derivatives were lower. One problem could lay in the higher oxygen sensitivity of the thioether in comparison to the triphenylamine. This probably led to losses during the purification of the products. Another important difference between both derivatives lies in the Lewis acid-catalyzed Friedel-Crafts-alkylation of alcohols 99 and 116. Two equivalents (equiv) of BF₃*Et₂O were needed for the thioxanthene derivative, while only one was needed for the corresponding acridine. This is attributed to the higher basicity of the sulfide compared to the triphenylamine, which seems contra intuitive at first glance. However, the basicity of an amine is stepwise reduced by the addition of another phenyl group due to the good overlap of the phenyl sp²-carbons with the lone-pair of the nitrogen in a 2p-orbital. This leads to a decrease in basicity for every additional phenyl substituent added. The pKₐ decreases from 9.24 for NH₃ to 4.78 for aniline and 0.78 for diphenylamine. This effect is less pronounced...
for diphenyl sulfide because the energy difference between the 3p-orbital of the sulfur and the π-system of the phenyl rings is too large for a good overlap. The Lewis basicity of the triphenylamine is therefore too low for an attack by the BF$_3$-etherate.$^{[74]}

The low yields in the synthetic route towards the brominated spiro-CPDTT 117 as well as the sensitivity of the diphenyl sulfide moiety to oxygen led to the development of another synthesis route, which is based on pathway C in the retrosynthesis described in Scheme 1-17 on p. 17. In a first step 3-bromo-2,2'-bithiophene 118 was treated with n-BuLi to perform a lithium-halogen exchange. The lithiated intermediate was quenched by the addition of thioxanthone 119 to form alcohol 120 as an intermediate. The CPDT-ol 120 was directly treated with HCl in HOAc as solvent to initiate the intramolecular ring closure reaction forming unsubstituted spiro-CPDTT 121. In a last step, a twofold bromination, utilizing NBS was carried out to afford brominated spiro-CPDTT 117 (Scheme 1-31).

![Scheme 1-31: Synthetic route according to pathway C leading to dibromo spiro-CPDTT 117.](image)

Monobromo bithiophene 118 was dissolved in dry diethyl ether and cooled to -78 °C, n-BuLi (1.6 M in n-hexane) was slowly added and the solution turned yellow. Ketone 119 was added as a solid and the reaction was slowly warmed to room temperature. The reaction was quenched by the addition of a saturated NH$_4$Cl solution, the organic phase was extracted, dried, and the solvent was removed. The crude mixture was directly dissolved in acetic acid, concentrated hydrochloric acid was added and the solution was heated to 139 °C. Ice water was added, and the product was extracted and washed with saturated Na$_2$CO$_3$ solution to remove traces of acid. The crude product was filtered through a short plug of silica gel and purified by column chromatography to afford spiro-CPDTT 121 as a white solid in 24% isolated yield over two steps.
Spiro-CPDTT **121** was dissolved in DCM and cooled to 0 °C, NBS was added in one portion under light exclusion and the mixture was stirred at 0 °C before warming to room temperature. Saturated Na$_2$SO$_3$ solution was added to reduce the remaining NBS. The product was extracted, dried, and the solvent was removed to obtain dibromo spiro-CPDTT **117** in quantitative yield as a grey solid.

The moderate yield of the ring-closure reaction of intermediate CPDT-ol **120** needs to be put into perspective when discussing the advantages and disadvantages of pathway A or C. Pathway A required a series of four consecutive steps starting from CPDT-one **87** (which itself needs to be synthesized in three steps) and brominated diphenyl sulfide **112** (which is synthesized in a single step) for the formation of dibromo spiro-CPDTT **117**. The whole reaction sequence resulted in a yield of 24% over these steps. Three tedious purification steps by column chromatography were needed for the reaction via pathway A. In contrast, pathway C is a one-step synthesis and starts from cheap thioxanthone **119** and monobromo bithiophene **118**. The reaction sequence also resulted in an isolated yield of 24% over three steps but required only one purification step by column chromatography. This allows easier upscaling of the synthesis compared to pathway A. The different conditions and different yields for the reaction can be understood by taking a closer look at the structures, intermediates, and the mechanism of their formation. In both cases, the first step is the formation of the nucleophile by lithiation of the aryl halide. For pathway A, the lithiation takes place at a phenyl ortho to an electron-donating substituent. Pathway C required the lithiation of a thiophene-β-position. Both reactions work at low temperatures in very good conversion rates due to the fast kinetics of the halogen-lithium exchange. The thiophene required for pathway C could react further in an intermolecular acid-base reaction to form an α-lithiated thiophene due to the higher thermodynamic stability. Although this reaction would require higher temperatures and therefore does not take place at -78 °C. The acid-mediated ring-closure reaction is different for pathway A and C. The reactivity of the alcohol in the ring-closure reaction is dependent on the stability of the formed carbocation. (Figure 1-28) The carbocation **122** that is formed in pathway A comprises two β-thienyl and one phenyl substituent, while this in pathway C **123** has one β-thienyl and two phenyl substituents. The thienyl substituents have a stronger electron-donating effect and therefore stabilize the cation more effectively.

*Figure 1-28: Intermediates of the ring-closure reaction of pathway A (left) and pathway C (right).*
The other aspect that needed to be considered is the reactivity of the respective aromatic compounds that react as nucleophiles in this electrophilic aromatic substitution. The reactivity of thiophene in pathway C is here several orders of magnitude higher than that of the phenyl sulfide in pathway A. This coupled together with harsher reaction conditions for pathway C could lead to the formation of side products like cyclic ethers which further reduces the yield.\[44\]

The aromatic excerpts of the NMR spectra of spiro-CPDTT 121 and dibromo spiro-CPDTT 117 are depicted in Figure 1-29. The thioxanthene moiety showed four different signals in both cases. The signal of the proton in 4-position is marked in red (●). For 121 the signal has a dd-splitting that is centered at δ = 7.49 ppm with $^3$J-coupling of 7.7 Hz and $^4$J-coupling of 1.4 Hz. In spiro-CPDTT 121 the proton manifested itself as a ddd signal with $^3$J-coupling of 7.8 Hz, $^4$J-coupling of 1.3 Hz, and $^5$J-coupling of 0.5 Hz that is centered at δ = 7.49 ppm. The 2-position is marked in magenta (●). Dibromo spiro-CPDTT 117 gave a ddd signal with two $^3$J-couplings of 8.0 Hz and 7.3 Hz as well as one $^4$J-coupling of 1.4 Hz for this proton. The signal is centered at δ = 7.05 ppm.

The unsubstituted derivative shows the exact same splitting with the same coupling constants, but the proton is slightly more shielded and the center of the signal appeared at δ = 7.01 ppm. The signal for the protons in 1-position, marked in blue (●), is again a dd for 121 and a ddd for 117. The dd is centered at δ = 6.87 ppm and shows a $^3$J-coupling of 8.0 Hz and one $^4$J-coupling of 1.4 Hz. The ddd is centered at δ = 6.86 ppm and shows one $^3$J-coupling of 8.0 Hz, one $^4$J-coupling of 1.4 Hz, and a $^5$J-coupling of 0.5 Hz. The signal for the 3-position overlaps for both derivatives with the thiophene signal(s). The signal is marked in cyan (●) and was reconstructed with the help of the coupling constants obtained from the neighboring signals and a spin-simulation. For dibromo spiro-CPDTT 117 a ddd was obtained with coupling constants $^3$J of 7.7 Hz, 7.3 Hz, and $^4$J of 1.3 Hz with the center at δ = 7.25 ppm. The unsubstituted derivative showed a ddd centered at δ = 7.23 ppm with $^3$J-couplings of 7.8 Hz, 7.3 Hz, and, $^4$J-coupling of 1.4 Hz. The CPDT-core resulted in one singlet in the case of dibromo spiro-CPDTT 121 with a chemical shift of δ = 7.27 ppm. For spiro-CPDTT 117 two doublets were expected, but only one “doublet” was visible. This happened because the signal from the α- and β-H have coincidentally almost have the same chemical shift.
Figure 1-29: Excerpt of the aromatic part of the $^1$H-NMR spectra of spiro-CPDTTs 117 and 121.

Brominated spiro-CPDTT 117 was further functionalized in a twofold Suzuki-type cross-coupling reaction with TAA boronic esters 103 to obtain the spiro-CPDTT-based HTM 124 (Scheme 1-32).


Dibromo spiro-CPDTT 117 was dissolved in dry THF in a Schlenk-tube, boronic ester 103, 20 mol% of Pd(PPh$_3$)$_4$ catalyst, and 2 M K$_2$CO$_3$ solution was added. The reaction mixture was heated to 80 °C, cooled down and the organic phase was extracted, dried, and purified by column chromatography with deactivated silica gel. The HTM 124 was obtained after precipitated from PE/DCM as an orange solid in 80% isolated yield.

The excerpt of the aromatic part of the $^1$H-NMR spectrum of HTM 124 in CD$_2$Cl$_2$ is shown in Figure 1-31. The signals were assigned with the help of an $H,H$-COSY NMR spectrum which is depicted in Figure 1-30.
Figure 1-30: Two-dimensional $^1$H-$^1$H-COSY NMR spectrum of HTM 124.

Figure 1-31: Excerpt of the aromatic part of the $^1$H-NMR spectrum of HTM 124 with signal assignment.
The TAA substituents revealed four different signals which were overlapping. The signal for the protons ortho to the methoxy substituents are marked in red (●). The two largest peaks of the multiplet shows again a splitting of 9 Hz, which did not correspond to one coupling constant but was the result of four different coupling constants. The signal showed a chemical shift of δ = 6.84 ppm and is overlapping with the signal of the protons ortho to the CPDT substituent, marked in blue (●). These protons show a splitting of the signals with a distance of 8.9 Hz between the two main peaks. The protons from the para-methoxyphenyl substituents, in cyan (●), gave a signal at δ = 7.04 ppm. The signal also has two main peaks with a splitting of 9.0 Hz. The missing four-proton signal of the phenylamine substituent meta to the CPDT is marked in dark green (●). The signal is at δ = 7.35 ppm with an 8.9 Hz splitting and is overlapping with the singlet from the thiophene β-protons at δ = 7.34 ppm. From the four signals of the thioxanthene core, only two are clearly isolated and visible. The signal of the protons in 4-position, marked in dark grey (●), has a ddd structure centered at δ = 7.49 ppm with $^3$J-coupling of 7.8 Hz, $^4$J-coupling of 1.2 Hz, and $^5$J-coupling of 0.6 Hz. The proton in 3-position (●) shows again a ddd splitting with the center at δ = 7.23 ppm. The signal contains two $^3$J-couplings with 7.8 Hz and 6.4 Hz. The larger coupling is to the proton in 4-, the smaller in 2-position. One long-range $^4$J-coupling of 2.3 Hz is visible for the coupling to the proton in 1-position. From the H,H-COSY NMR spectrum and the integration it becomes clear that the center of the signals from the thioxanthene 2-(●), and 1-positions (●) are between δ = 7.00 ppm and 7.05 ppm. Additional information could unfortunately not be determined from the spectrum.

A second derivative without methoxy substituents at the TPA groups based on the spiro-CPDTT core was synthesized from aryl bromide 117 and corresponding boronic ester 108. HTM 125 was synthesized in a twofold Suzuki-type cross-coupling reaction (Scheme 1-33).

\[
\begin{align*}
\text{Br} & \quad \text{boronic ester 108} & \quad \text{Pd(PPh\textsubscript{3})\textsubscript{4}} \\
\text{117} & \quad \text{} & \quad \text{K\textsubscript{2}CO\textsubscript{3} (aq), THF, 80 °C} \\
& \quad \text{} & \quad [65\%]
\end{align*}
\]

**Scheme 1-33:** Synthesis of HTM 125 in a twofold Suzuki-type cross-coupling.

Aryl bromide 117, boronic ester 108, and 10 mol% Pd(PPh\textsubscript{3})\textsubscript{4} as a catalyst were dissolved in dry THF. A solution of K\textsubscript{3}PO\textsubscript{4} in water was added and the mixture heated to 75 °C. The reaction was cooled to room temperature and the product was extracted, dried, and purified by flash column
chromatography with deactivated silica gel. The purification of this reaction uncovered the same problems as with HTM 110, namely that the product is not easy to separate from the side products. This is due to the lower polarity of HTM 125 in comparison to methoxyphenyl-capped HTM 124. The lower polarity made it difficult to find a good eluent mixture, in which the material can be separated from the side products while still being soluble enough. An eluent mixture of DCM/PE and NEt3 was used for the purification and the amount of DCM was gradually increased to ensure a separation of the products. The product was precipitated from DCM/n-hexane to remove possible trace impurities and afforded the product as a yellow-orange solid. The product should be stored under argon because the surface of the solid tends to relative quickly turn green due to oxidation of the product. Interestingly, this did not happen with the more electron-rich HTMs 109 and 124 or with the other TPA-capped HTM 110.

### 1.3.4 Synthesis of Spiro-Cyclopentadithiophene-Xanthene-based HTM

A third spiro-CPDT-core was designed and synthesized. The general structure of the halogenated spiro-cyclopentadithiophene-xanthene (spiro-CPDTX) 126 where the “X” substituent is “O” is shown in Figure 1-32.

![General structure of the third target molecule cyclopentadithiophene-xanthene 126.](image)

After the good results with the alternative synthesis of spiro-CPDTT 117 according to pathway C, the same synthetic strategy was used to synthesize the spiro-CPDTX core starting from 3-bromobithiophene 118 and xanthone 127. 3-Bromobithiophene was treated with n-BuLi to perform a halogen-metal exchange reaction. The resulting lithiated bithiophene was reacted with xanthone to intermediate CPDT-ol 128. Alcohol 128 was not purified but directly refluxed with glacial acid and concentrated hydrochloric acid to perform the subsequent intramolecular ring-closing Friedel-Crafts alkylation. The obtained spiro-CPDTX 129 was brominated at the thiophene-α-positions using NBS to form dibromo spiro-CPDTX 130. All reactions are summed up in Scheme 1-34.
Alcohol 128 was synthesized by dissolving monobromo bithiophene 118 in dry Et₂O and cooling the reaction down to -78 °C before slowly adding n-BuLi in hexane to perform a halogen-metal exchange. The resulting mixture was stirred at -78 °C and xanthone 127 was added as a solid. An addition of the xanthone 127 in solution was unfortunately not possible due to the mediocre solubility of the ketone in Et₂O and THF. The reaction mixture was warmed, quenched, and the crude product was extracted. Alcohol 128 was not isolated but only partially purified by a filter column with silica gel and PE to first remove the bithiophene side-product and afterwards DCM to elute to the product mixture. This step was crucial because it substantially simplifies the purification of the next reaction step. The mixture now only contained alcohol 128, xanthone 127, and the alcohol 131 which was formed by the addition of n-BuLi to xanthone (Figure 1-33).

Ketone 127 should not react in the next reaction step and the alcohol 131 does not form a corresponding cation as easy as the product and should therefore not be a problem in the next reaction step. The yield of the reaction was determined by GC and GC-MS and the product was formed in 79%. The mixture was dissolved in glacial acid and hydrochloric acid was added. The mixture was heated to 130 °C for two hours. The solution was cooled to 0 °C, water was added, and the solution was neutralized with solid KOH. The crude product was extracted with Et₂O, dried and purified by column chromatography with silica gel, and precipitated from DCM/n-hexane to obtain spiro-
CPDTX 129 as a white solid in 27% yield with regard to 79% conversion in the previous step. In this step, column chromatography was easy to perform because all side products are significantly more polar than the product due to the separation of the bithiophene side product in the previous step. The bromination of spiro-CPDTX 129 was performed with NBS due to the good results with the spiro-CPDTT and spiro-CPDTA derivatives. Spiro-CPDTX 129 was dissolved in dry DCM and cooled to 0 °C, and NBS was added. The solution was stirred at 0 °C, methanol was added, and the precipitated product was filtered off. The precipitate was washed with cold methanol and dried in high vacuum to afford dibrominated spiro-CPDTX 130 as a white crystalline solid in 94% isolated yield.

The final Suzuki cross-coupling step of dibromo spiro-CPDTX 130 and boronic ester 103 was performed with the already established conditions using tetrakis(triphenylphosphine)palladium(0) as catalyst and potassium phosphate as base in THF at 80 °C overnight (Scheme 1-35). The product was purified by standard column chromatography and precipitation from DCM/MeOH afforded spiro-CPDTX-based HTM 131 as an orange solid in 74% isolated yield.

![Scheme 1-35: Synthesis of HTM 131 via Suzuki-type cross-coupling.](image)

**1.3.5 Synthesis of 4,4-Diphenyl-Cyclopentadithiophene-Based HTMs**

A class of materials without a spiro-linkage but still consisting of a CPDT-core was designed and synthesized to investigate and evaluate the influence of the spiro linkage on the properties of the materials. The missing rigidity of the phenyl substituents should lead to a lowering of $T_g$, but to which extend is open. This class of materials can be viewed as the general structure in Figure 1-1 without the linkage via the substituent “X”. The general structure of the halogenated diphenyl-cyclopentadithiophene (DP-CPDT) 132 is shown in Figure 1-34.
Dibromo diphenylcyclopentadithiophene 133 was synthesized in three steps starting from 3-bromo-2,2'-bithiophene 118 according to a procedure of Hanamura et al.\textsuperscript{[75]} In the first step, bithiophene 118 was treated with \textit{n}-BuLi to undergo a lithium-halogen exchange. The lithiated species attacked benzophenone 134 to form carbinol 135. Alcohol 135 was ring-closed with the Lewis-acid SnCl\textsubscript{4} to afford DP-CPDT 136. The thiophene α-positions were brominated by treatment of 136 with NBS to form dibromo DP-CPDT 133. The reaction sequence is illustrated in Scheme 1-36.

Scheme 1-36: Reaction sequence leading to the halogenated middle building block DP-CPDT 133.

3-Bromo-2,2'-bithiophene 118 was dissolved in Et\textsubscript{2}O, cooled to -78 °C and \textit{n}-BuLi in \textit{n}-hexane was added to perform the halogen-metal exchange. Benzophenone 134, dissolved in THF, was added and the solution was warmed to room temperature. The reaction was quenched by the addition of saturated NH\textsubscript{4}Cl-solution and the crude product was extracted with Et\textsubscript{2}O, dried and purified by column chromatography to obtain the product as a slightly blueish solid in 88% (lit.: 78%\textsuperscript{[75]}) isolated yield. Benzophenone was dissolved in THF for this reaction due to the mediocre solubility in Et\textsubscript{2}O. Alcohol 135 was again dissolved in DCM and the Lewis acid tin(IV) chloride was added. The reaction mixture was stirred at room temperature and quenched and neutralized by the addition of NaHCO\textsubscript{3} solution. The organic phase was separated, and the product extracted, dried, and purified by column chromatography to afford DP-CPDT 136 as a slightly yellow solid in 74% (lit.: 73%\textsuperscript{[75]}) isolated yield. DP-CPDT 136 was dissolved in DCM and cooled to -30 °C and
NBS was added portion-wise. The reaction mixture was stirred at -30 °C and was afterwards poured into a Na₂SO₃ solution to quench the reaction and reduce the remaining NBS. The product was extracted with DCM, dried and the solvent was removed. The crude product was purified by recrystallization from methanol (MeOH) to afford dibromo DP-CPDT 133 as a white solid in 72% (lit.: 84%[75]) isolated yield.

 Aryl bromide 133 was coupled to boronic ester 103 in a Pd(PPh₃)₄-catalyzed Suzuki-type cross-coupling reaction to form DP-CPDT-based HTM 137 (Scheme 1-37).

![Scheme 1-37: Twofold Suzuki-type cross-coupling of dibromo DP-CPDT 133 with boronic ester 103 to form the HTM 137.](image)

Aryl bromide 133, boronic ester 103, and 10 mol% Pd(PPh₃)₄ were dissolved in THF. A K₃PO₄ solution in water was added and the mixture was heated to 75 °C for 66 hours. The mixture was cooled down, water was added, and the product was extracted with Et₂O until the aqueous phase was no longer yellow. The crude product was dried and purified by flash column chromatography with silica gel deactivated with NEt₃. A gradient purification was used with a mixture of Et₂O and PE. The amount of Et₂O was slowly increased to make the solvent mixture more polar for an efficient separation of the products. The product was precipitated from Et₂O/ PE to afford a yellow solid in 75% isolated yield.

The triphenylamine-capped derivative 138 was synthesized in another Suzuki-reaction by coupling of aryl bromide 133 and boronic ester 108 (Scheme 1-38). The reaction time was prolonged to 90 h and the temperature was raised to 80 °C, while 2 M K₂CO₃ solution was used instead of K₃PO₄. After purification by column chromatography and precipitation from Et₂O/PE, the product was isolated in 78% yield as a yellow solid.
The first successful synthesis of DP-CPDT derivatives 137 and 138 were performed by Annika Schweinbeck during her Bachelor thesis.

It would be beneficial to have another option besides the methoxy-capped and the unsubstituted TPA substituents to fine-tune the optoelectronic properties of the synthesized HTMs. A possibility would be to utilize thiomethyl-capped TPA. The overlap between the 3p orbitals of the sulfur and the π-system of the TPA is smaller than for the 2p-orbitals of the oxygen and the TPA. The electron-donating ability is therefore less pronounced (σ = 0.00 ±0.1 for SMe and σ = -2.68 ±0.02 for OMe; σ: Hammett parameter) for the thiomethyl derivative (Figure 1-35).[76]

Additional benefits could arise if a thiomethyl-capped molecule is utilized as an HTM in a PSC. Surface interactions between mostly thiophene sulfur and solid-state dyes have been described in the literature.[45, 77] The interaction leads to another possible hole-transfer pathway from the dye to the HTM if sulfur atoms are present.[45] Synthesis of bis(4-thiomethylphenyl)aniline 139 is described in literature. A twofold nucleophilic substitution of bis(4-bromophenyl)anilnine with sodium methanethiolate is used to synthesize the thiomethyl-capped triphenylamine in 16% isolated yield.[78] The unsatisfactory literature yield led to the development of another synthetic route, based on the synthesis of TPA 106 but with a Pd⁰ instead of a Cu(I) catalyst. Bis(4-thiomethylphenyl)aniline 139 was synthesized starting from 4-bromothioanisole 140 and aniline 104 in a twofold Pd⁰-catalyzed Buchwald-Hartwig amination reaction with sodium tert-butylate (NaOtBu) as a base. Bis(4-thiomethylphenyl)aniline 139 was brominated with NBS in the free para-position to form 4-

**Scheme 1-38**: Twofold Suzuki-type cross-coupling of aryl bromide 133 with boronic ester 108 to form HTM 138.
bromo-\(N,N\)-bis[(4-methylthio)phenyl]aniline 141. Corresponding boronic ester 142 was obtained by a palladium-catalyzed borylation reaction with bis(pinacolato)diboron (Scheme 1-39).

Scheme 1-39: Synthetic route to the thiomethyl-capped triphenylamine boronic ester 142.

Synthesis of bis(4-thiomethylphenyl)aniline 139 was performed by dissolving aniline 104 together with 4-bromothioanisole 140, NaO\(\text{Bu}\), 5 mol\% tris(dibenzylideneacetone)dipalladium(0) (Pd\(_3\)db\(_3\)), and 10 mol\% 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) in toluene and heating the mixture to 120 °C. After cooling to room temperature, water was added, and the product was extracted, washed, dried, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography with silica gel to afford a colorless oil in 79\% isolated yield. The yield of 79\%, which was around five times that of the literature procedure\(^{[78]}\), with only 5 mol\% Pd\(_0\) per reaction made this reaction a very good pathway towards the desired TAA 139. The thiomethyl derivative should only be slightly less reactive than the methoxy-capped triphenylamine in an electrophilic aromatic substitution. Therefore, the same reaction conditions for the bromination that were used for methoxy-capped TPA 107 were used for the thiomethyl derivative 141. The reaction was carried out under light-exclusion to avoid radical side-reactions. Aromaticine 139 was dissolved THF, cooled to 0 °C, and NBS was slowly added to the solution and the reaction was stirred overnight at room temperature. The reaction was quenched with Na\(_2\)SO\(_3\)-solution, the product was extracted, dried, and purified by column chromatography to yield a colorless oil in 89\%. The yield was therefore the same for the methoxy- and the thiomethyl-capped triphenylamine which further showed the viability of this synthetic approach. Boronic ester 142 was synthesized by dissolving aryl bromide 42 together with bis(pinacolato)diboron as borination reagent, KOAc as a base, and 5 mol\% Pd(dppf)Cl\(_2\)*CH\(_2\)Cl\(_2\) catalyst in DMF. The reaction was
heated to 80 °C overnight, cooled down the product was extracted and purified by column chromatography with deactivated silica gel to afford the pure boronic ester 142 as a colorless oil in 90% yield.

The obtained boronic ester 142 was directly coupled to the diphenylcyclopentadithiophene core 133 in a palladium-catalyzed twofold Suzuki-cross-coupling reaction to form thiomethyl-phenyl-capped HTM 143 (Scheme 1-40).

Scheme 1-40: Twofold Suzuki-type cross-coupling of aryl bromide 133 and the thiomethyl-capped triphenylamine boronic ester 142 to form HTM 143.

Aryl bromide 133, boronic ester 142, and 10 mol% Pd(PPh₃)₄ were dissolved in THF. A K₃PO₄ solution was added and the mixture was heated to 80 °C for 62 hours. The product was extracted, dried, and purified by flash column chromatography with silica gel and an eluent mixture of PE/DCM and NEt₃. Further purification by size exclusion chromatography (SEC) was performed to remove the homocoupling side product. Another purification step utilizing HPLC was needed to remove the remaining traces of the homocoupling side product. In the end, the product was precipitated from DCM/n-hexane to afford thiomethyl-phenyl-capped HTM 143 as a yellow-orange solid in 66% isolated yield.

The aromatic excerpts of the ¹H-NMR spectra of HTMs 143 and 137 measured in THF-d₈ are displayed in Figure 1-36. Due to the C₂ᵥ symmetry of the molecules, nine different signals were expected, but only six isolated signals were visible for thiomethyl capped 143 and seven for methoxy capped 137. That means that three, respectively two signals are overlapping due to similar chemical shifts of the protons. For the anisyl and thioanisyl moiety, two signals with an integral of eight protons each were expected. The protons ortho to the thiomethyl gave one signal (●) with a center at δ = 7.19 ppm and a splitting of 8.8 Hz. The signal is overlapping with another signal. The methoxy derivative showed a more deshielded signal at δ = 7.02 ppm and a splitting of 8.9 Hz. The protons meta to the SMe-group gave a signal (●) at δ = 7.01 ppm with a splitting of 8.8 Hz. The methoxy derivative showed a multiplet at δ = 6.83 ppm with a splitting between the two largest peaks of 9.0 Hz. The two missing signals of the TPA substituent are multiplets located at
$\delta = 7.51$ ppm and $\delta = 7.41$ ppm for protons ortho to the amine (●) and at $7.01$ ppm, respectively. 6.86 ppm for the protons ortho to the thiophene (●). The signal for HTM 143 is completely overlapping with another arylamine-signal. For the CPDT-core one thiophene $\beta$-proton signal was observed. The singlet is marked in olive (●) and is located at $\delta = 7.39$ ppm for thiomethyl-capped 143 and $\delta = 7.30$ ppm for methoxy-capped 137. The phenyl substituents gave rise to three different signals with integrals of four, four, and two. The para-protons in magenta (●) gave a multiplet centered at $\delta = 7.18$ ppm for both derivatives, but the signal was only isolated visible for 137. The ortho-protons signal (●) is overlapping with the thiophene $\beta$-proton signal for thiomethyl-capped HTM 143 but visible for the methoxy derivative 137. Unfortunately, the signal was still obtained as a multiplet due to the AA’BB’M spin system. The missing meta-protons (●) gave a multiplet centered at $\delta = 7.22$ ppm for 143 and $\delta = 7.23$ ppm for 137. The aliphatic region is not shown here but the methoxy-signal gave a singlet at $\delta = 3.75$ ppm while the thiomethyl gave a singlet at $\delta = 2.44$ ppm. The comparison between the NMR spectra clearly showed the stronger -I effect of the methoxy group compared to the thiomethyl group. But the effect was only visible for the TAA-capped CPDT but not at the central phenyl substituents.
The results of the Suzuki-type cross-coupling reactions leading to eight different CPDT-based HTMs are summed up in Table 1-2. All Suzuki cross-coupling reactions were conducted under an argon atmosphere in a Schlenk-tube, employed the tetrakis(triphenylphosphine)palladium(0) catalyst and THF as a solvent. As a base either a 2 M aqueous K$_3$PO$_4$ or K$_2$CO$_3$ solution were used. The reactions were heated to 75 – 80 °C for 16 h to 90 h and resulted in isolated yields of 65% to 80%.

Figure 1-36: Aromatic section of the $^1$H-NMR spectra of HTMs 137 (top) and 143 (bottom) with the signal assignment.
Table 1-2: Overview of all performed Suzuki-type cross-coupling reactions leading to acridines 109 and 110, thioxanthenes 124 and 125, xanthene 131, and DP-CPDTs 137, 138, and 143.

<table>
<thead>
<tr>
<th>Amount of catalyst</th>
<th>Base</th>
<th>Temperature</th>
<th>Reaction time</th>
<th>Isolated yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>109</td>
<td>10 mol% K$_3$PO$_4$ (2 M)</td>
<td>75 °C</td>
<td>90 h</td>
<td>72%</td>
</tr>
<tr>
<td>110</td>
<td>12 mol% K$_3$PO$_4$ (2 M)</td>
<td>75 °C</td>
<td>90 h</td>
<td>74%</td>
</tr>
<tr>
<td>124</td>
<td>20 mol% K$_2$CO$_3$ (2 M)</td>
<td>80 °C</td>
<td>55 h</td>
<td>80%</td>
</tr>
<tr>
<td>125</td>
<td>20 mol% K$_2$CO$_3$ (2 M)</td>
<td>80 °C</td>
<td>16 h</td>
<td>65%</td>
</tr>
<tr>
<td>131</td>
<td>15 mol% K$_3$PO$_4$ (2 M)</td>
<td>80 °C</td>
<td>16 h</td>
<td>74%</td>
</tr>
<tr>
<td>137</td>
<td>10 mol% K$_3$PO$_4$ (2 M)</td>
<td>75 °C</td>
<td>66 h</td>
<td>75%</td>
</tr>
<tr>
<td>138</td>
<td>15 mol% K$_2$CO$_3$ (2 M)</td>
<td>80 °C</td>
<td>90 h</td>
<td>78%</td>
</tr>
<tr>
<td>143</td>
<td>10 mol% K$_3$PO$_4$ (2 M)</td>
<td>80 °C</td>
<td>62 h</td>
<td>66%</td>
</tr>
</tbody>
</table>

The usage of K$_2$CO$_3$ as a base seemed to give better yields but unfortunately, it also increased the formation of the side product formed by homocoupling of two CPDT-cores. This side product was difficult to separate from the main product due to a similar polarity. Therefore, it was chosen to sacrifice a few percent of yield for an easier purification by switching from K$_2$CO$_3$ to K$_3$PO$_4$ for later experiments. K$_3$PO$_4$ is a stronger base and should therefore form the tetravalent boronate intermediate faster, which reacts in the transmetallation step. This probably suppresses the formation of the homocoupled side products.

The synthesis of all eight different TAA-capped CPDTs was confirmed by Fourier-transform ion cyclotron resonance matrix-assisted laser desorption/ionization (FTICR-MALDI) mass spectrometry. The normalized mass spectra of all molecules are shown in Figure 1-37. All methoxy-capped derivatives are shown blue, all unsubstituted triphenylamine-capped CPDTs in red, and the thiomethyl-capped triphenylamine derivative is in dark green. Acridine 109 appeared at m/z = 1025.330100 with a deviation to the calculated mass [M]$^+$ of 0.19 ppm. Acridine 110 appeared at m/z = 905.288169 ppm with a deviation of 1.84 ppm. Thioxanthene derivatives 124 and 125 showed signals at m/z = 966.259026 and m/z = 846.219208 with deviations of 0.45 ppm and 1.4 ppm. The only xanthene derivative 131 revealed one signal at m/z = 950.282828 with a deviation of 1.55 ppm. Diphenyl-CPDTs 137, 138, and 143 had signals at m/z = 936.304164, m/z = 816.260598 and m/z = 1000.21314 with deviations of 1.28 ppm, 1.33 ppm, and, 2.09 ppm.
The thiomethyl-capped HTM 143 showed another signal at m/z = 1016.207590 which corresponds to the oxidized species [M+O]. The oxidation was not observed when using different methods of analysis, therefore it probably oxidized during the sample preparation for the FTICR-MALDI mass spectrometry.

The deviations of the high-resolution mass spectra for all derivatives were below 4 ppm and therefore confirmed the structures of the described molecules.
1.4 Optoelectronic Characterization of CPDT-based HTMs

The optical properties of all newly synthesized HTMs were investigated using solution UV-vis absorption and emission spectroscopy. All spectra were measured in DCM to guarantee the comparability of the results. The oxidation behavior was investigated by cyclic voltammetry in solution. Photoelectron spectroscopy in air (PESA) was used as an additional method to determine the work function (WF) of the HTMs. In the following figures, all methoxyphenyl-capped HTMs are depicted in blue, the unsubstituted triphenylamine capped CPDTs in red and the thiomethyl-capped 143 is shown in green.

The UV-vis solution absorption and normalized emission spectra of spiro-CPDTAs 109 and 110 are illustrated in Figure 1-38. Acridines 109 and 110 both exhibited two absorption bands with the low energy maximum being the most intense one. For 109 one absorption band with a maximum at 293 nm and the other at 445 nm were observed. The maxima for 110 were with 287 nm and 436 nm blue-shifted compared to the methoxy-capped 109. This was expected because of the shorter π-system of acridine 110 and the missing +M effect of the methoxy substituents. The extinction coefficient (ε) of the low-energy absorption band for acridine 110 of 55 000 M⁻¹cm⁻¹ is around 20% smaller compared to 65 100 M⁻¹cm⁻¹ obtained for acridine 109. The high-energy absorption bands at 293 nm and 287 nm can be understood as overlapping absorptions of the TPA and the N-phenylacridine chromophores. The hypsochromic shift of 6 nm for acridine 110 can again be explained by the absence of methoxy substituents. An additional low-intensity transition was located at 361 nm for acridine 109 and 360 nm for acridine 110. The absorption band was attributed to an n-π* transition for both HTMs. With the help of the Planck-Einstein relation the optical gap \( E_{\text{opt}} \) was calculated. Here \( h \) is the Planck constant, \( c \) is the speed of light and \( \lambda_{\text{ons}} \) is the onset wavelength of the absorption.

\[
E_{\text{opt}} = \frac{hc}{\lambda_{\text{ons}}}
\]

For acridine 109 an optical gap of 2.45 eV and for acridine 110 of 2.51 eV was obtained. The smaller optical gap of acridine 109 is again due to methoxy substituents that extend the π-system. A closer look at the low-energy absorption band of both compounds revealed that they are not Gaussian-shaped but have two different slopes. This shows the composition of the absorption band from the different vibrionic transitions. The position of the 0-0 transition was estimated using the first and second-order derivative of the absorption curve with respect to the wavelength. The 0-0 transition for methoxy-capped 109 was located at 475 nm that for phenyl-capped 110 at
467 nm. The emission spectra of both materials showed a clear vibrionic splitting with two pronounced shoulders of the emission band. The emission maximum for methoxyphenyl-capped 109 was at 513 nm with a shoulder at 541 nm that for phenyl-capped 110 at 499 nm with the shoulder at 526 nm. The emission 0-0 transition for acridine 109 was at 507 nm resulting in a Stokes shift of 1329 cm\(^{-1}\), while the 0-0 transition of acridine 110 was at 494 nm which yielded a Stokes shift of 1170 cm\(^{-1}\). The magnitude of the Stokes shift for both acridines indicated a small reorganization energy upon photoexcitation which means that the ground state and the excited state are geometrically very similar.

The absorption spectra of thioxanthene-based HTMs 124 and 125, are shown below in Figure 1-39. The molecule with the larger π-system, 124, again showed a bathochromic shifted absorption with the global absorption maximum at 445 nm compared to 437 nm for the phenyl-capped 125. The extinction coefficients for 124 and 125 were similar with 68,100 M\(^{-1}\)cm\(^{-1}\) and 67,200 M\(^{-1}\)cm\(^{-1}\) respectively. The low-intensity n-π\(^*\) transition was located at 361 nm for 124 and 358 nm for 125. The high-energy absorption bands of 125 were located at 285 nm and 304 nm, while 124 showed a broad absorption at 290 nm. The region between 250 nm and 300 nm of the absorption spectra could again be understood by having a closer look at the different present chromophores. The absorption is made up of the individual absorptions of the TAA and thioxan-
Xanthene moieties. The unsubstituted TPA absorbs at shorter wavelengths than the methoxy-substituted TAA and is therefore not overlapping with the absorption of the spiro-thioxanthene. The optical gaps were calculated and xanthene 124 revealed the smaller optical gap with 2.44 eV compared to 2.51 eV for 125. The low energy absorption band could be deconstructed with regards to the vibrionic coupling. The 0-0 transition for methoxyphenyl-capped 124 was determined to be at 475 nm while that of phenyl-capped 125 was at 467 nm. The emission spectra showed again a strong vibrionic splitting of the emission band with the maximum at 516 nm for 124 and 502 nm for 125. The emission 0-0 transition for 124 was at 510 nm resulting in a Stokes shift of 1445 cm⁻¹, while the 0-0 transition of 125 was at 496 nm which yielded a Stokes shift of 1252 cm⁻¹.

![Graph](image)

**Figure 1-39:** Solution UV-vis absorption (solid line) and normalized emission (dotted line) spectra of thioxanthenes 124 (blue) and 125 (red).

The absorption and emission spectrum of the sole spiro xanthene-based HTM 131 is shown in **Figure 1-40**. The absorption spectrum showed again three absorption bands. The high energy absorption band was located at 299 nm and is again built up of the TAA and spiro-xanthene chromophores absorption. The low-energy absorption band had the absorption maximum at 445 nm with an extinction coefficient of 54 100 M⁻¹ cm⁻¹. The low-intensity n-π* transition absorption band was at 360 nm. The 0-0 transition of the low-energy absorption band was estimated to be at 480 nm. The optical gap was calculated to be 2.46 eV. The emission spectrum showed one emission band with a vibrionic splitting resulting in the emission maximum at 515 nm and the shoulder at 541 nm. The 0-0 transition of the emission was at 508 nm which and the Stokes shift was calculated to be 1109 cm⁻¹ which is consistent with the results of the other spiro-CPDTs.
The last series of HTMs 137, 138, and 143 contain a diphenylcyclopentadienothiophene core; their absorption spectra are compiled in Figure 1-41. DP-CPDTs 137 and 143 revealed two, 138 three absorption bands with the most red-shifted absorption at 443 nm for 137 and 435 nm for 138 and 442 nm for 143. All three CPDTs exhibited comparable extinction coefficients with 62,600 M⁻¹ cm⁻¹ for 137, 62,100 M⁻¹ cm⁻¹ for 138, and 64 100 M⁻¹ cm⁻¹ for 143. The high-energy region between 250 nm and 350 nm showed visible differences for the three different molecules. This region is shaped by the absorption of diphenylcyclopentadiene and the TAA chromophores. The absorption of the DP-CPDT core should not change throughout the series and the differences are therefore attributed to the different substituents at the TAAs. The methoxy-capped DP-CPDT 137 showed one peak at 290 nm. This is consistent with the absorption of the other methoxy-capped derivatives acridine 109, thioxanthene 124, and xanthene 131. The two bands of phenyl-capped DP-CPDT 138 were also consistent with the previously obtained results for acridine 110 and thioxanthene 125 and can be understood in the same manner. For 143 there does not exist a derivative with which it could be compared. But the results indicated that the thiomethyl-capped triphenylamine substituents absorb at 325 nm. This result was surprising because the thiomethyl groups are a weaker electron-donor than the methoxy groups and should therefore not lead to a stronger bathochromic shift. Although the stronger polarizability of the sulfur atoms could lead to the stabilization of excited states with diffuse electron density distribution. The weak n-π* transition was located at 362 nm for 137, 358 nm for 138, and 370 nm for 143. The optical gap was calculated to be 2.44 eV for 137, 2.50 eV for 138, and 2.47 eV for 143. The 0-0 transitions for the low-energy absorption bands were located at 472 nm for 137, 465 nm for 138, and 472 nm for 143. The emission spectra showed one emission band with a vibrionic splitting and the emission maxima at 513 nm for 137, 499 nm for 138, and 508 nm for the thiomethyl TAA-capped 143. The emission 0-0 transitions were determined to be at 506 nm, 493 nm, and 508 nm and resulted in Stokes shifts for the three HTMs of 1424 cm⁻¹, 1221 cm⁻¹, and 1266 cm⁻¹. The effect of the methoxy- and thiomethyl-substitution on the TAA become apparent in the changed optoelectronic properties
compared to unsubstituted TPA-capped derivative 138. The methoxy groups led to a batho-
chromic shift for the low-energy absorption, of 8 nm, the thiomethyl of 7 nm. The optical-gap was
decreased by 60 meV for 137 and 30 meV for 143 due to the extension of the π-system. A similar
effect was visible for the emission spectra, with the difference that the red-shift due to the thio-
ethyl substituents was more pronounced in the absorption- than in the emission spectrum. The
unsubstituted TPA-capped 138 showed the most hypsochromic shifted emission band at 493 nm.
The methoxy substituents led to a red-shift of 15 nm, the thiomethyl substituents of 13 nm. This
series of HTMs was the only series with a thiomethyl-capped triphenylamine therefore no refer-
ences were available. During the design of the HTMs, it was estimated, that the lower +M effect
of the SMe-group compared to the OMe-group will put 143 between 137 and 138 concerning the
optoelectronic properties. However, the UV-vis absorption and emission behavior seems to indi-
cate that the optoelectronic properties of 143 are closer related to methoxyphenyl-capped 137
than to the unsubstituted TPA-capped 138.

Figure 1-41: Solution UV-vis absorption (solid line) and normalized emission (dotted line) spectra of DP-CPDT 137
(blue), 138 (red) and 143 (green).

The optical properties of all CPDT-based HTMs are summed up in Table 1-3. All CPDTs showed
comparable optical behavior with only a slight variation in the absorption maxima between 435 nm
and 445 nm and extinction coefficients from 54,100 M\(^{-1}\)cm\(^{-1}\) to 68,100 M\(^{-1}\)cm\(^{-1}\). The absorption
onsets were in the range from 494 nm to 508 nm, which correspond to optical gaps between
2.51 eV to 2.44 eV. All molecules therefore possess a relatively large optical gap. Nevertheless,
it is possible to divide the materials into three categories depending on whether methoxy, thiomethyl, or no substituents were used on the TAA substituents. The first group, defined by the methoxy substituents, showed a more red-shifted absorption with maxima between 443 nm and 445 nm and energy gaps between 2.44 eV and 2.46 eV. The second group had more blue-shifted absorption maxima between 435 nm and 437 nm as well as larger optical energy gaps between 2.50 eV and 2.51 eV. Only one thiomethyl derivative was synthesized, therefore, it is not possible to see a systematic behavior.

| Table 1-3: Collected optical properties for all synthesized CPDT-based HTMs. |
|-----------------|-----|-----|-----|-----|-----|
| $\lambda_{\text{max}}$ | $\varepsilon$ | $E_{g}^{\text{opt}}$ | $\lambda_{\text{em}}^{\text{max}}$ | Stokes shift |
| [nm] | [M$^{-1}$cm$^{-1}$] | [eV] | [nm] | [cm$^{-1}$] |
| 109 | 445 | 65 100 | 2.45 | 513 | 1329 |
| 110 | 436 | 55 000 | 2.51 | 499 | 1170 |
| 124 | 445 | 68 100 | 2.44 | 516 | 1445 |
| 125 | 437 | 67 200 | 2.51 | 502 | 1252 |
| 131 | 445 | 54 100 | 2.46 | 515 | 1109 |
| 137 | 443 | 62 600 | 2.44 | 513 | 1424 |
| 138 | 435 | 62 100 | 2.50 | 499 | 1221 |
| 143 | 442 | 64 100 | 2.47 | 508 | 1266 |

Cyclic voltammetry was performed to determine oxidation potentials and energy levels of the FMO. This step was crucial to determine a possible applicability of the HTMs in state of the art perovskite solar cells. Cyclic voltammograms (CVs) were measured in DCM at room temperature and tetra-butylammonium hexafluorophosphate (TBAPF) as supporting electrolyte. Three cycles were measured at a scan speed of 100 mV/s if not stated otherwise. All potentials were internally referenced to the ferrocene/ ferricenium (Fc/Fc$^+$) redox pair. The half-wave potentials $E_{1/2}^{1/2}$ were calculated from the cathodic ($E_{\text{pc}}^{\text{c}}$) and anodic ($E_{\text{pa}}^{\text{a}}$) peak potentials. HOMO energy level was determined by the onset value of the oxidation ($E_{\text{ons}}^{\text{HOMO}}$, $E_{\text{HOMO}}^{\text{Fc}} = -5.1$ eV) [79]. LUMO energy levels were calculated from the HOMO energy and the optical gap.
The CVs of the acridine derivatives 109 and 110 are shown in Figure 1-42.

**Figure 1-42**: Cyclic voltammograms of acridines 109 (blue) and 110 (red). The positions of the oxidation potentials are marked with a cross.

Both molecules initially showed two successive reversible one-electron oxidation waves. The oxidation potentials of 109 at -0.01 V and 0.13 V were slightly more negative compared to that of 110 at 0.07 V and 0.22 V. The two oxidations were overlapping, and the exact positions were therefore evaluated with the help of a time-semi-derivative deconvolution of the current (Figure 1-43).
The third oxidation wave of acridine 109 was another reversible oxidation and located at 0.72 V. Integration of the current for each wave gave the information that the transferred charge of the first two oxidations is equal to that of the third oxidation. The third oxidation therefore corresponded to a transfer of two electrons under the assumption that the first two oxidations correspond to a one-electron oxidation. The first two oxidations corresponded therefore to the formation of the radical cation and dication, which should be delocalized on the arylamines and the CPDT-core through the π-system. The third oxidation was not that easy to attribute to a structural element in the molecule. The TPA-capped 110 showed a third oxidation at 0.68 V which was in the same region as the oxidation potential for the third oxidation of methoxy-phenyl capped 109. But the integrated current of this oxidation wave indicated that only one electron was transferred compared to the two electrons for the methoxy derivative 109. One possible explanation is that the third oxidation wave corresponds to the oxidation of the N-phenylacridine moiety for 110 and one of the two electrons transferred for 109 also corresponds to the oxidation of the N-phenylacridine. The oxidation waves overlap coincidentally with another oxidation process on the π-system. A fourth one-electron quasi-reversible oxidation wave at a potential of 1.02 V was visible for the methoxy derivative 109. This oxidation was again attributed to the TAA substituents and the central CPDT-core which were now fourfold positive charged. For methoxyphenyl-capped acridine 109 the HOMO energy level was calculated to be -5.03 eV against vacuum, for 110 a slightly
stabilized HOMO at -5.09 eV was obtained. The difference between the two molecules is again attributed to the electron-donating effect of methoxy groups and the extension of the π-system in the case of 109. The LUMO energy level for both acridine derivatives were calculated to be -2.58 eV.

The reversibility of the electron-transfer process was investigated for spiro-CPDTA 109 using cyclic voltammetry at different scan speeds. Linear sweep voltammograms (obtained from the cyclic voltammograms) at scan speeds of 100 mV/s, 50 mV/s, and 25 mV/s are illustrated in Figure 1-44. The electron transfer process for a reversible oxidation is a fast process and should therefore not be dependent on the scan speed of the measurement. The position of the anodic peak potentials $E_p^a$ for the second, third, and fourth oxidation waves are marked with dotted lines in the same color. The position for the first oxidation could not be determined, therefore, it was omitted. The position of the peak potentials for the second oxidation showed little variance with respect to the change in scanning speed. This confirmed the assumption that the formation of the dicationic species is a reversible process for this molecule. The dependence of $E_p^a$ on scan speed increased for the third oxidation, but not significantly. There was in particular no difference between $E_p^a(100 \text{ mV/s})$ and $E_p^a(50 \text{ mV/s})$. For the fourth oxidation, which has previously been classified as quasi-reversible, a clear dependence of the scan speed on the position of the peak potentials could be seen. The potentials shifted to more positive values with increasing scan speed. This behavior is in accordance with a partial irreversibility of the oxidation.
Figure 1-44: Linear-sweep voltammogram of 109 at 100 mV/s (top line), 50 mV/s (middle), and 25 (bottom) mV/s scan speed.

The CVs of the thioxanthene-based spiro-CPDTs 124 and 125 are shown in Figure 1-45. The CV of 124 showed two reversible and one quasi-reversible oxidation. The first two oxidations corresponded to the formation of the radical cation and dication, which are delocalized through the π-system. The oxidations occurred at 0.01 V and 0.14 V. The third quasi-reversible oxidation was located at 0.67 V. The integral is problematic to determine because the oxidation is not isolated and overlaps with the onset of a fourth oxidation. The oxidation corresponded again to the oxidation of the π-system. The onset of a fourth, irreversible oxidation was visible for methoxyphenyl-capped thioxanthene 124 which could be attributed to the oxidation of the thioxanthene moiety. The oxidized thioxanthene would most probably have spin-density at the sulfur atom which then could further react, making the oxidation irreversible. All redox potentials of phenyl-capped thioxanthene 125 are slightly shifted to more positive values. The initial formation of the radical cation and dication occurred at 0.17 V and 0.31 V. This was 0.16 V and 0.76 V more positive than for 124. The third oxidation occurred at 1.03 V which and is considerably shifted compared to the 0.67 V for the third oxidation of 124. Only one electron is transferred in this oxidation compared to the two electrons for the methoxy derivative. Determination of the HOMO energy level revealed -5.03 eV for 124 and -5.19 eV for 125. And the LUMO was -2.59 eV for 124 and -2.68 eV for 125.
The CV of the xanthene derivative 131 is displayed in Figure 1-46. The CV was measured with a scanning speed of 50 mV/s. The HTM showed the formation of the radical cation at 0.05 V and that of the dication at 0.18 V. Both oxidations were reversible processes where one electron each was transferred. A third and fourth oxidation appeared at 0.69 V and 1.05 V. Both oxidations could be classified as quasi-reversible one-electron oxidations of the π-system. The signal at 0.5 V during the scan in positive direction is a side product that was formed during the oxidation process and increased in intensity with the number of scans. The HOMO energy level was calculated to -5.07 eV which was slightly higher than expected compared to 109 and 124. The LUMO energy level is at -2.61 eV.
Figure 1-46: Cyclic voltammogram of 131. The positions of the oxidation potentials are marked with a cross.

The CVs of the last group of HTMs, DP-CPDTs 137, 138, and 143 are illustrated in Figure 1-47. For 137 three oxidation waves could be observed at 0.01 V, 0.14 V, and 0.69 V. The first two corresponded again to the reversible formation of the radical cation and dication and were therefore one-electron oxidations. The molecules are not spiro-linked and only consist of one delocalized π-system and two additional phenyl substituents that are distorted and not conjugated to the CPDT-backbone. That means that all oxidation processes either take place at the phenyl substituents or the TAA-substituted cyclopentadithiophene. The high oxidation potential required to oxidize benzene makes it unlikely that the phenyl substituents were oxidized here. That means that the third oxidation, which had a quasi-reversible character, also corresponded to the oxidation of the π-system consisting of the CPDT-core and TAA substituents. The onset of a fourth oxidation was visible but could not be determined due to the restrictions of the electrochemical window. The three oxidation potentials for 138 were slightly shifted to positive potentials and lie at 0.10 V, 0.20 V, and 0.98 V. All three oxidations are one-electron oxidations, the first two are again reversible and the third is quasi-reversible. The thiomethyl substituted triphenylamine-capped 143 exhibited a similar behavior than the other two derivatives and the obtained values were in the middle of those obtained for the unsubstituted and methoxy-substituted TAA-capped derivatives. The formation of the radical cation was at 0.07 V. This is between 0.01 V for 137 and 0.10 V for 138. The formation of the dication took place at 0.19 V. The third oxidation, which was again a quasi-reversible oxidation of the largest π-system took place at 0.68 V. The first two oxidation...
potentials are closer to the unsubstituted derivative, but the third oxidation is the same as for the methoxy derivative. The three diphenyl-cyclopentadithiophenes did not show an oxidation of the phenyl substituents in the measured electrochemical window due to the high oxidation potential required to oxidize benzene. From the oxidation onset, the HOMO energy levels were calculated to -5.03 eV for 137, -5.13 eV for 138, and -5.12 eV for 143. The thiomethyl derivative was again situated between unsubstituted triphenylamine capped 138 and electron-rich 137 but closer to the unsubstituted derivative. The LUMO energy levels are -2.59 eV for 137, -2.63 eV for 138, and -2.65 eV for 143.

![Figure 1-47: Cyclic voltammograms of DP-CPDTs 137 (blue), 138 (red), and 137 (green). The positions of the oxidation potentials are marked with a cross.](image)

The electrochemical properties of all CPDT-based HTMs are summed up in Table 1-4. The CPDTs can be divided into three groups, depending on whether methoxy, thiomethyl, or no substituents are attached to the TPA moieties. HTMs acridine 109, thioxanthene 124, xanthene 131, and DP-CPDT 137 comprising methoxy groups generally showed the highest HOMO energy levels between -5.03 eV and -5.07 eV and the first oxidation takes place at around 0 V vs Fc/Fc⁺. The methoxy capped derivatives of the spiro-linked HTMs could always be oxidized further than the phenyl-capped counterparts. Spiro-CPDTA 109 could be oxidized fivefold due to a combination of methoxy-groups and the redox-active acridine moiety (which can be seen as another TAA substituent). The methoxyphenyl capped DP-CPDT 137 exhibited only three oxidation waves during the electrochemical measurement and is therefore the exception of the methoxyphenyl capped
derivatives. This is due to the absence of a spiro-linked moiety. But the onset of a fourth oxidation wave, corresponding to another oxidation process at the \( \pi \)-system composed of the CPDT core and TAA substituents, was visible. This allowed to give general oxidation potentials for a generic methoxy-capped TAA substituted CPDT. The first oxidation wave occurs at around 0 V, the second at around 0.15 V, the third at 0.7 V and the fourth at approximately 1 V vs Fc/Fc\(^+\). The group consisting of acridine 110, thioxanthene 125, and DP-CPDT 138 lacking the methoxy groups showed deeper-lying HOMO energy levels between -5.09 eV and -5.19 eV. The first and second oxidation waves appear at around 0.1 V more positive values for this group of molecules and the third oxidation takes place at around 1 V (with the exception of acridine 110, where the third oxidation takes place at the acridine moiety). Thiomethyl derivative 143 forms a separate group with oxidation potentials and HOMO energy level between those of the other two groups. The HOMO energy level and the first two oxidation potentials are more comparable with the values obtained for the TPA capped derivatives while the third oxidation potential more resembles that of the methoxyphenyl capped derivatives.

**Table 1-4:** Collected electrochemical properties of all synthesized CPDT-based HTMs.

<table>
<thead>
<tr>
<th></th>
<th>( E_{ox1}^{1/2} )</th>
<th>( E_{ox2}^{1/2} )</th>
<th>( E_{ox3}^{1/2} )</th>
<th>( E_{ox4}^{1/2} )</th>
<th>( E_{ox5}^{1/2} )</th>
<th>( E_{HOMO} )</th>
<th>( E_{LUMO} )</th>
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</thead>
<tbody>
<tr>
<td>109</td>
<td>0.01</td>
<td>0.13</td>
<td>0.72</td>
<td>0.72</td>
<td>1.02</td>
<td>-5.03</td>
<td>-2.58</td>
</tr>
<tr>
<td>110</td>
<td>0.07</td>
<td>0.22</td>
<td>0.67</td>
<td>-</td>
<td>-</td>
<td>-5.09</td>
<td>-2.58</td>
</tr>
<tr>
<td>124</td>
<td>0.01</td>
<td>0.14</td>
<td>0.67</td>
<td>0.67</td>
<td>-</td>
<td>-5.03</td>
<td>-2.59</td>
</tr>
<tr>
<td>125</td>
<td>0.17</td>
<td>0.31</td>
<td>1.03</td>
<td>-</td>
<td>-</td>
<td>-5.19</td>
<td>-2.68</td>
</tr>
<tr>
<td>131</td>
<td>0.05</td>
<td>0.18</td>
<td>0.69</td>
<td>1.05</td>
<td>-</td>
<td>-5.07</td>
<td>-2.61</td>
</tr>
<tr>
<td>137</td>
<td>0.01</td>
<td>0.14</td>
<td>0.69</td>
<td>-</td>
<td>-</td>
<td>-5.03</td>
<td>-2.59</td>
</tr>
<tr>
<td>138</td>
<td>0.10</td>
<td>0.20</td>
<td>0.98</td>
<td>-</td>
<td>-</td>
<td>-5.13</td>
<td>-2.63</td>
</tr>
<tr>
<td>143</td>
<td>0.07</td>
<td>0.19</td>
<td>0.68</td>
<td>-</td>
<td>-</td>
<td>-5.12</td>
<td>-2.65</td>
</tr>
</tbody>
</table>

[a]: \( E^{1/2} = (E_p + E_p)/2 \) [b]: \( E_{HOMO} = -5.1 - E + \text{ons} \) [c]: \( E_{LUMO} = E_{HOMO} - E_{opt} \)

PESA was used as an alternative way to determine the HOMO-energy level of the HTMs by determination of the work function (WF). The measurement is based on the photoelectric effect and a photoelectron can only be detected if \( W_F \leq h\nu \) with \( \nu \) being the frequency of the incident light.
The HTMs were spin-coated on glass substrates and subsequently measured. Three samples were prepared and measured each. The work function was determined by the intersection between the baseline and a linear regression of the standardized photoelectron yield ratio.

PESA spectra of the acridines 109 and 110 are shown in Figure 1-48. For 109 a work function of 4.99 eV, for 110 of 5.10 eV was determined.

\[
\text{Standardized Photoelectron Yield Ratio} \quad \frac{\text{Yield}}{0.33}
\]

\[
\text{Energy [eV]} \quad 4.4 \quad 4.6 \quad 4.8 \quad 5.0 \quad 5.2 \quad 5.4 \quad 5.6
\]

\[
\begin{array}{c}
0 \\
5 \\
10 \\
15 \\
20 \\
\end{array}
\]

\[
\begin{array}{c}
\text{Standardized Photoelectron Yield Ratio} \\
\text{Energy [eV]} \\
4.4 \quad 4.6 \quad 4.8 \quad 5.0 \quad 5.2 \quad 5.4 \quad 5.6 \\
\end{array}
\]

\[
\begin{array}{c}
0 \\
5 \\
10 \\
15 \\
20 \\
\end{array}
\]

**Figure 1-48:** PESA-measurement of spiro-CPDTAs 109 (blue) and 110 (red).

A PESA spectrum of the thioxanthene-based material 125 is plotted in Figure 1-49, with the work function calculated to 5.12 eV.
Figure 1-49: PESA-measurement of spiro-CPDT 125.

The PESA spectra of DP-CPDTs 137 and 138 are shown in Figure 1-50. For the methoxy-substituted 137 a work function of 4.98 eV and for the unsubstituted TPA-capped 138 a work function of 5.10 eV was determined.

Figure 1-50: PESA-measurement of DP-CPDTs 137 and 138.
A comparison between the work function and onset oxidation potential was performed to gain insight into possible errors with the measurements. The energy levels of the onset oxidation and the negative work function vs the vacuum energy level of acridines 109 and 110, thioxanthene 125, and DP-CPDTs 137 and 138 are shown in Figure 1-51.

The methoxy-capped spiro-acridine 109 and DP-CPDT 137 showed consistent behavior with \( WF \) of 4.99 eV and 4.98 eV. The onset oxidation potentials are at -5.03 eV for both derivatives. The TPA capped acridine 110, thioxanthene 125, and DP-CPDT 138 did not show the same consistent behavior as the methoxy-capped derivatives. For thioxanthene 125 and DP-CPDT 138, the work function were calculated to be the highest once with 5.12 eV and 5.09 eV compared to oxidation onsets at -5.19 eV and -5.13 eV. Acridine 110 was the exception in that the oxidation onset is smaller (absolute) than the work function with -5.09 eV for the oxidation onset and 5.10 eV for the work function. The consistency of the work function obtained for the three investigated TPA-capped derivatives 110, 125, and 138 could potentially point to an error with the onset oxidation potential of acridine 110. The small deviation of the energy values calculated by electrochemistry from the directly measured work function revealed on the one hand that the electrochemical determination was surprisingly accurate and on the other hand the results indicated an amorphous character of the investigated compounds.
The optoelectronic properties of the DP-CPDT series HTMs 137, 138, and 143 were further investigated by UV-vis absorption spectroscopy of their oxidized species. A solution of the respective material was slowly titrated with tris(4-bromophenyl)ammonium hexachloroantimonate 144 as an oxidizing agent and an absorption spectrum was measured after each addition step. The oxidizing agent has an oxidation potential of 0.70 V vs Fc/Fc$^+$ in DCM which should be sufficient for at least a twofold oxidation of all three DP-CPDT derivatives (see Table 1-4).\textsuperscript{[80-81]} The oxidizing agent is a radical cation and therefore a single-electron transfer (SET) reagent (Scheme 1-41). The formed tris(4-bromophenyl)amine 145 can be detected with an absorption maximum at 309 nm in CH$_2$Cl$_2$.

\[ \text{144} \quad + \quad \text{M} \quad \xrightarrow{\text{SET}} \quad \text{145} \quad + \quad [\text{M}]^{+\cdot} \text{SbCl}_6^{-} \]

\textbf{Scheme 1-41:} Single-electron-transfer-reaction between oxidizing agent 144 and a substrate M.

It is noted that the reaction is an equilibrium reaction (if the formed radical cation is stable) and the equilibrium depends on the oxidation potential of the material via the Nernst equation shown below (at 25 °C). The standard cell potential ($E_0$) can be estimated from the $E^{1/2}$ obtained from CV and the number of electrons transferred is donated as $z$. The concentration of the reactants is noted using square brackets $c(x) := [x]$.

\[ E = E_0 - \frac{59 \text{ mV}}{z} \cdot \lg \left( \frac{[\text{Red}]}{[\text{Ox}]} \right) \]

For an electrochemical equilibrium, $\Delta E = 0$ is the prerequisite. This leads to the equations provided below.

\[ E_0(144) - \frac{59 \text{ mV}}{z} \cdot \lg \left( \frac{145}{144} \right) = E_0(M^+) - \frac{59 \text{ mV}}{z} \cdot \lg \left( \frac{[M]}{[M^+] \cdot [144]} \right) \]

\[ E_0(144) - E_0(M^+) = -\frac{59 \text{ mV}}{z} \cdot \lg \left( \frac{[M]}{[M^+] \cdot [144]} \right) + \frac{59 \text{ mV}}{z} \cdot \lg \left( \frac{145}{144} \right) \]

\[ E_0(144) - E_0(M^+) = \frac{59 \text{ mV}}{z} \cdot \left( \lg \left( \frac{145}{[144]} \right) - \lg \left( \frac{[M]}{[M^+] \cdot [144]} \right) \right) \]

\[ E_0(144) - E_0(M^+) = \frac{59 \text{ mV}}{z} \cdot \left( \lg \left( \frac{145}{[144]} \cdot [M^+] \right) \right) \]
\[ E_0(144) - E_0(M^+) = 59 \text{ mV} \cdot (\lg K) \]

This means that for an equilibrium constant \((K)\) of 10 a difference of 59 mV in the oxidation potential between the oxidant and the substrate is needed. Therefore, one can assume that molecules with an oxidation potential of 0.64 V vs. Fc/Fc\(^+\) can be oxidized to a satisfactory degree.

The first oxititration was carried out on methoxy arylamine capped DP-CPDT 137. The first oxidation potential of 137 is at 0.01 V, the second at 0.14 V, and the third at 0.69 V. DP-CPDT 137 can therefore be oxidized twice with 144 in a quantitative manner. A waterfall-diagram of the incremental-oxidation is shown in Figure 1-52. The amount of added oxidation agent is depicted on the z-axes. The addition was performed until 2.0 equivalents of oxidants were added. The absorption maximum of the neutral species at 443 nm slowly decayed as the absorption bands of the radical cation species at 757 nm and 1726 nm began to form. The addition of more than one equivalent of oxidant 144 led again to a decrease of absorption of the radical cation absorption bands and a formation of the dication absorption band at 1260 nm. The arising absorption band at 309 nm belongs to the reduced form of the oxidant 145.

![Waterfall-diagram of the stepwise oxidation of DP-CPDT derivative 137. The amount of added oxidant is shown on the z-axes.](image)

**Figure 1-52:** Waterfall-diagram of the stepwise oxidation of DP-CPDT derivative 137. The amount of added oxidant is shown on the z-axes.

The spectra of the neutral, radical cationic and dicationic species are displayed again in Figure 1-53 for better clarity. The signal at 1700 nm is an artifact that was caused by the change of a polarization filter in the UV-vis absorption spectrometer and could therefore not be avoided. The
initial absorption band at 301 nm shifted upon oxidation to 306 nm for the radical cation to 309 nm for the dication. This is due to the overlay with the reduced species of the oxidant 145 which absorbs at 309 nm in DCM.

![UV-vis absorption spectra](image)

**Figure 1-53:** UV-vis absorption spectra of the neutral (black), radical cationic (blue) and dicationic (red) species of 137.

A closer look at the different absorption bands allowed was needed to calculate the position of the energy levels of the radical cationic and dicationic state with the help of electrochemical data obtained by cyclic voltammetry. The different optical gaps were calculated from the onset absorptions of the radical cation and dication states. For the radical cation, the strong red-shifted absorption corresponds to the HOMO-SOMO gap with 0.53 eV, while the absorption at 753 nm corresponds to the SOMO-LUMO transition with an energy gap of 1.47 eV. For the dication, the absorption band at 1260 nm corresponds again to the HOMO-LUMO transition. All transitions are summed up in **Figure 1-54.** The position of the FMOs were calculated from the cyclic voltammetry and UV-vis absorption spectroscopy data. For the neutral species, the HOMO energy was calculated from the onset of the first oxidation obtained by cyclic voltammetry. The LUMO energy was calculated from the HOMO energy and the optical gap. In the case of the radical cation, it was possible to calculate the SOMO energy from the second oxidation potential obtained by cyclic voltammetry. The SOMO energy level is located at -5.16 eV and is therefore only slightly stabilized by the removal of one electron. The HOMO and LUMO energy levels were calculated with the help of the obtained optical gaps of the respective transitions. The HOMO energy level of the radical cation
was now at -5.69 eV while the LUMO energy level was at -3.69 eV. The HOMO of the radical cation was formerly the HOMO-1 in the uncharged oxidation state. The HOMO energy level of the dication was calculated from the third oxidation potential obtained in the CV and was located at -5.71 eV. The LUMO energy level was again calculated with the help of the optical gap and was at -4.89 eV. The LUMO of the dication was the SOMO of the radical cation respectively the HOMO of the neutral species.

![FMO levels of three different oxidation states of 137, calculated from the cyclic voltammetry and UV-vis-NIR data.](image)

**Figure 1-54:** FMO levels of three different oxidation states of 137, calculated from the cyclic voltammetry and UV-vis-NIR data.

Possible resonance structures of the radical cation are shown in **Figure 1-55**. In this Valence-Bond (VB) picture, the radical cation is delocalized through the whole π-system of the CPDT-core and attached triarylamines.
The spin-density of the radical cation state of 137 was calculated using density-functional theory (DFT) on a M062X/6-31+g(d) level of calculation.\textsuperscript{[83-84]} The plot of the isosurface (0.02) is illustrated in Figure 1-56. The calculation confirmed that the radical is delocalized through the molecule, with the highest spin-densities on the central CPDT-core and the phenylamine substituents attached to the core. Additional spin-density is located on the terminal diphenylamine and even extends to the lone-pair oxygen electrons of the methoxy groups. The spin-density on the terminal anisyl substituents is mostly located at the positions ortho and para to the amine and not on the meta-positions. This was also expected from VB theory because no resonance structures with the radical on the meta-positions can be drawn.
The FMOs were calculated with DFT on a M062X/6-31+g(d)-level for the unsubstituted methoxyphenyl capped DP-CPDT 137 in all three oxidation states. The calculated molecular orbitals are shown in Figure 1-57. The typical alternation between an aromatic and quinoidal character is visible between two neighboring orbitals in the same oxidation state. For the neutral species, the HOMO has an aromatic and the LUMO a quinoidal character. The HOMO is delocalized on the whole π-system of the arylamine substituents and the CPDT-core. The phenyl substituents (at the sp3-carbon atom) do not show any electron-density contribution to the HOMO. The LUMO is less delocalized than the HOMO with no contribution from the anisyl substituents. Interestingly, there is some electron density at the sp3-carbon atom of the cyclopentadiene. This could lead to some conjugation through the sp3-linkage in an excited state of the molecule. The different spatial extent of the HOMO and LUMO lead to a small charge-transfer character of the HOMO-LUMO transition.

In the radical cation species, the HOMO is the former HOMO-1, the SOMO is the former HOMO of the neutral species but is now only single occupied, and the LUMO of the radical cation is still the LUMO of the neutral species. The geometry change from the neutral to the radical cation species is easily visible. The left diphenylamine unit is less distorted in the radical cation than in the neutral species. This effect could be explained by having a look at the HOMO of the neutral and the SOMO of the radical cation species. Both molecular orbitals show a node between the nitrogen atom and the phenyl attached to the thiophene. The half vacancy of the SOMO orbital will therefore lead to a bond length shortening and a better conjugation between the central diphenyl-cyclopentadithiophene and the diphenylamine substituents. The electron probability density in the SOMO and LUMO of the radical cation is not visibly different from the HOMO and LUMO of the neutral molecule. The HOMO of the radical cation shows a high electron probability density on the TAAs and only a small density on the CPDT-core. The two transitions in the UV-vis-NIR spectrum of the radical cation are the SOMO-LUMO (at 757 nm) and HOMO-SOMO (at 1726 nm) transitions. The low-energetic HOMO-SOMO transition shows a charge transfer character where electron density is shifted from the TAA substituents to the central CPDT-core. The HOMO-LUMO transition is again a charge transfer from the diphenylamines to the central diphenylcyclopentadithiophene core with no more electron density on the terminal anisyl substituents in the LUMO. For the dication species, the LUMO again shows little difference to the HOMO of the neutral- and the SOMO of the radical cation species. The electron probability density is slightly decreased on the diphenylamine substituents and is therefore increased on the diphenyl-cyclopentadithiophene-core. The HOMO also has an enhanced electron density on the cyclopentadiene compared to the HOMO of the radical cation. The orbital shape leads again to a charge transfer character of the HOMO-LUMO transition. In this case, electron density is shifted from the anisyl substituents to the phenylamine-CPDT core.
Unsubstituted triphenylamine capped DP-CPDT derivative 138 was also characterized by redox titration with 144 and following UV-vis-NIR absorption spectroscopy. The absorption spectra of the stepwise oxidized 138 are shown in Figure 1-58. The oxidation was again carried out until the dication was obtained. The absorption band of the neutral species at 435 nm slowly decayed upon the addition of the oxidizing agent and two new absorption bands began to form. The first absorption band was located at 744 nm and corresponds to the SOMO-LUMO transition. This band also showed a vibrionic fine structure with a visible 0-0 and 0-1 transition. The second absorption band at 1503 nm corresponded to the HOMO-SOMO transition. The strong red-shift of this absorption is typical for polaron states. These absorption bands reached their highest intensity when one equivalent oxidizing agent was added. The intensity decreased upon the addition of another equivalent of 144 and another absorption band with a maximum at 1058 nm began to form. This band corresponded to the HOMO-LUMO transition of the dicationic state.

Figure 1-57: FMOs of neutral (left), radical cationic (middle), and dicationic (right) species of 137.
Figure 1-58: Waterfall-diagram of the stepwise oxidation of 138. The amount of added oxidant is shown on the z-axes.

The spectra of the neutral species, radical cation, and dication are displayed in Figure 1-59 for better clarity.

Figure 1-59: UV-vis-NIR absorption spectra of the neutral (black), radical cationic (blue), and dicationic (red) species of 138.
The calculated spin-density of DP-CPDT 138 radical cation is shown in Figure 1-60. A comparison between the spin-density of methoxy-capped 137 in Figure 1-56 and the unsubstituted TPA capped derivative 138 clearly revealed that the spin-density distribution does not change significantly. The only difference was that the methoxy groups were not present and there can therefore not be spin-density. The spin-density is still mostly localized on the diphenyl-CPDT and the neighboring nitrogen atoms. The terminal phenyl substituents show only substantial spin density on the ortho- and para-positions.

![Calculated spin-density on the radical cation of 138.](image)

**Figure 1-60:** Calculated spin-density on the radical cation of 138.

The FMO energy levels of the neutral molecule, radical cation, and dication were calculated from the absorption spectra and the oxidation potentials, which were obtained by cyclic voltammetry. The HOMO energy level of the neutral molecule is at -5.13 eV, the LUMO energy level at -2.63 eV. The HOMO energy level of the radical cation is at -5.88 eV, the SOMO energy level at -5.23 eV, and the LUMO energy level at -3.71 eV. The dication has the HOMO energy level at -6.01 eV and the LUMO energy level at -5.05 eV. The energy level diagram is shown in Figure 1-61.
The calculated FMOs of the three different oxidation states of material 138 are illustrated in Figure 1-62. The molecular orbitals closely resemble those of the methoxy-capped 137 shown in Figure 1-53. The HOMO of the neutral species has an aromatic character while the LUMO has a quinoidal character with additional electron density at the sp³-carbon of the cyclopentadiene. The HOMO is delocalized through the whole π-system, comprised of the CPDT-core and the TPA substituents, while the LUMO is only located on the central CPDT core and the attached aniline moiety. This difference results in a charge-transfer character of the HOMO-LUMO transition with electron density being shifted to the central core upon excitation. The SOMO of the radical cation is formed by the now half-vacant HOMO of the neutral species. No difference in electron probability density is visible between the two orbitals. The LUMO of the radical cation and the neutral species also closely resemble each other. The LUMO of the radical cation just shows a slightly smaller spatial electron distribution. In this oxidation state, the HOMO is strongly located on the TPA substituents with only a small electron probability density on the central core. The SOMO-LUMO transition (at 744 nm) and the HOMO-SOMO (at 1503 nm) transition have a charge-transfer character with electron density being shifted from the TPA substituents to the central core. The LUMO of the dication has arisen from HOMO of the neutral, and the SOMO of the radical cationic state. In contrast to the original orbital, the LUMO shows reduced electron density on the terminal phenyl substituents. The HOMO of the dication shows a quinoidal character with electron probability density on the whole π-system, comprised of TPA substituents and CPDT-core. This gives the HOMO-LUMO transition a charge-transfer character in which electron density is shifted from the terminal
phenyl substituents to the central core. The largest difference between the FMOs of 137 and 138 is manifested by the smaller π-system due to the missing methoxy substituents.

![Figure 1-62: FMOs of neutral (left), radical cationic (middle), and dicationic (right) species of 138.](image)

The final synthesized DP-CPDT derivative, thiomethyl-capped 143, was also characterized by UV-vis-NIR absorption spectroscopy as neutral, radical cationic, and dicationic species. The spectra are shown in Figure 1-63.
Figure 1-63: UV-vis-NIR absorption spectra of the neutral (black), radical cationic (blue) and dicationic (red) species of 143.

The absorption band of the neutral species at 442 nm slowly decayed upon the addition of oxidizing agent 144 and two new absorption bands began to form. The first absorption band was located at 754 nm and corresponded to the SOMO-LUMO transition. This band showed a vibrionic fine structure with a visible 0-0 and 0-1 transition. The second absorption band at 1760 nm, the most red-shifted band of the whole series, corresponded to the HOMO-SOMO transition. These absorption bands reached their highest intensity when one equivalent oxidizing agent was added. The intensity decreased upon the addition of another equivalent of 144 and another absorption band at 1362 nm began to form. This band corresponded to the HOMO-LUMO transition of the dicationic state. The FMO energy levels of all three oxidation states are shown in Figure 1-64. The neutral species has a HOMO energy level at -5.12 eV and a LUMO energy level at -2.65 eV. The radical cation has the HOMO energy level at -5.75 eV, the SOMO energy level at -5.24 eV, and the LUMO at -3.77 eV. In the dicationic state, the HOMO energy level is at -5.73 eV, while the LUMO energy level stabilizes to -5.00 eV.
The calculated spin-density of the radical cationic state of 143 is illustrated in Figure 1-65. The spin-density distribution is almost the same as in the case of methoxy-capped 137 (Figure 1-56). The spin-density here is extended onto the thiomethyl instead of the methoxy groups.

Figure 1-65: Calculated spin-density for the radical cation of 143.

The calculated FMOs are displayed in Figure 1-66. A comparison with the FMOs of 137 (Figure 1-54) revealed some interesting differences between the two derivatives. The LUMO of the neutral species does not change visibly, but for the HOMO there are differences due to the different heteroatom substituent on the TPA substituents. The HOMO extends towards the methoxy groups for the 137 but not onto the thiomethyl groups for 143. Interestingly, the effect on the SOMO of
the radical cation is the other way around and the electron density is larger on the sulfur atoms of 143 than on the oxygen atoms of the 137. This larger spatial extend of the SOMO of thiomethyl capped 143 could potentially lead to a better charge-extraction of the HTM when employed in a PSC compared to HTM 137. Another difference lies in the extension of the HOMO in the radical cation and dication state. For 143 the electron probability density is smaller on the CPDT-core compared to 137 in the HOMO of the cationic and dicationic state.

![Image: FMOs of neutral (left), radical cation (middle), and dication (right) species of 143.](image)

**Figure 1-66:** FMOs of neutral (left), radical cation (middle), and dication (right) species of 143.

The optoelectronic properties of the neutral, radical cationic, and dication species of all three DP-CPDT derivatives are summed up in **Table 1-5**. The different end groups at the TAA substituents are reflected in the varying optoelectronic properties of the three derivatives.

The unsubstituted triphenylamine-capped DP-CPDT 138 exhibited the strongest blue-shifted absorption bands in the neutral ($\lambda_{\text{max}} = 435$ nm), radical cationic ($\lambda_{\text{max}} = 744$ and 1503 nm), and dicationic state ($\lambda_{\text{max}} = 1058$ nm). The material additionally has the most stabilized HOMO in all three oxidation states with -5.13 eV for the neutral, -5.88 eV for the cationic, and -6.00 eV for the dicationic state. The introduction of electron-donating terminal methoxy groups at terminal TPA moieties in 137 led to a noticeable red-shift of all absorption bands. The absorption band in the neutral state is red-shifted by 8 nm (~ 51 meV) compared to 138. The two absorption bands in the radical cation state are shifted by 13 nm (29 meV) and 223 nm (106 meV) towards lower energies.

The large red-shift of the HOMO-SOMO transition in the radical cation of 137 compared to 138 is
mainly caused by the higher-lying HOMO energy level. The HOMO energy level of 137 is -5.69 eV which is 190 meV more destabilized than the HOMO of 138 which is at -5.88 eV. The SOMO energy level of the radical cation of 137 is only 70 meV more positive than the SOMO of 138 and the difference results in the described red-shift of the polaron absorption band. The different stabilizations of the HOMO and SOMO energy levels of the radical cation of 137 compared to 138 can be understood by having a closer look at the MO schemata (see Figure 1-57 and Figure 1-62). The orbital coefficient at the methoxy group is larger in the HOMO than in the SOMO in the radical cation of 137. This explains the stronger influence of the methoxy substitution on the HOMO energy level compared to the SOMO energy level. The smaller red-shift of the SOMO-LUMO transition (\(\lambda_{\text{max}} = 757 \text{ nm for } 137 \text{ and } \lambda_{\text{max}} = 744 \text{ nm for } 138\)) is caused by the invariance of the LUMO energy level to the methoxy substitution. This becomes evident when looking at the LUMOs of the radical cations of 137 and 138. The terminal phenyl or anisyl moieties have no contribution to the LUMOs. The dication of 137 exhibits an absorption band that is red-shifted by 202 nm (~188 meV) compared to that of 138. This red-shift is mainly caused by the elevation of the HOMO energy level from -6.00 eV for 138 to -5.71 eV for 137. The stronger lifting of the HOMO energy level compared to the LUMO energy level can be explained by the shape of the molecular orbitals. The LUMO is again mostly localized on the central core with weak contributions from the terminal TAA units, while the HOMO has strong contributions from the terminal anisyl moieties. The effects of the thiomethyl-substitution are not consistent in all three investigated oxidation states and therefore more difficult to evaluate. In the non-charged state, the FMO energy levels of 143 are almost like the ones of TPA capped DP-CPDT 138. This is very well explained by the calculated MOs (Figure 1-66). The HOMO and LUMO of 143 both show no contribution from the thiomethyl substituents. The two investigated absorption bands in the radical cation state are red-shifted by 14 nm (~30 meV) and 257 nm (~121 meV) compared to triphenylamine capped 138 and even red-shifted by 1 nm (~2 meV) and 34 nm (~14 meV) compared to the methoxyphenyl capped 137. The HOMO energy level in the 143 radical cation is located at -5.75 eV and is therefore shifted by 0.13 eV to more positive values compared to that of 138 radical cation. The SOMO of 143 is only shifted by 0.01 eV compared to that of 138. Interestingly the LUMO is stabilized to -3.77 eV which is 0.06 eV deeper than that of 138 and 0.08 eV deeper than that of 137. This underscores that the red-shift of the two absorption bands compared to TPA capped 138 is a consequence of an elevation of the HOMO energy level and a more negative LUMO energy level, while the red-shift compared to methoxyphenyl capped 137 is caused by deeper-lying SOMO and LUMO energy levels. The thiomethyl derivative 143 exhibited to smallest optical gap in the dication state with 0.73 eV compared to 0.82 eV to methoxyphenyl capped 137 and 0.96 eV to TPA capped 138. The absorption maximum is located at 1366 nm which means that a red-shift of 106 nm
(~76 meV) compared to 137 and 306 nm (~264 meV) compared to 138 takes place. The strong red-shift of the thiomethyl capped DP-CPDT 143 in the dication state can be explained by the differing effects of the thiomethyl groups on the HOMO and LUMO energy levels. The thiomethyl groups seem to elevate the HOMO energy level in the same manner as the methoxy groups in 137, while the LUMO energy level behaves like that of triphenylamine capped 138. The explanation lies in the difference between the sulfur atom of the thiomethyl group and the oxygen atom of the methoxy group. While the sulfur atom shows a smaller +M effect than the oxygen atom due to the weaker overlap between the 3p-orbitals and the π-system of the phenyl substituents, it is more polarizable. A comparison between the HOMO of 137 dication (Figure 1-57) and that of 143 dication (Figure 1-66) reveals that the orbital coefficient at the oxygen atom is much smaller than that at the sulfur atom. This larger coefficient is the manifestation of the good polarizability of the sulfur atoms, resulting in the elevated HOMO energy level.

Table 1-5: Optoelectronic properties of the neutral- radical cation (••+) and dication (+++)-species of 137, 138, and 143.

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1.5 Thermal Characterization of CPDT based HTMs

All newly developed triphenylamine- and methoxy-triphenylamine-based CPDTs were characterized by thermogravimetric analysis (TGA) to determine their thermal stability. Small samples (1-2 mg) of the HTMs were heated to 800 °C with a heating rate of 10 °C/min and the weight loss was determined. All measurements were carried out under nitrogen atmosphere. The decomposition temperatures were determined at 95% residual weight ($T_{d}^{95}$) and the onset of the decomposition ($T_{d}^{ons}$).[85]

The TGAs of spiro-CPDTAs 109 and 110 are shown in Figure 1-67. The samples exhibited a total weight loss of 40% for methoxy-triphenylamine-capped spiro-CPDTA 109 and 68% for triphenylamine-capped spiro-CPDTA 110 of the initial weight. The decomposition onset was calculated to be 417 °C for 109 and 442 °C for 110. The more conservative 5%-weight-loss decomposition temperature lies at 407 °C for 109 and 399 °C for 110.

![Figure 1-67: TGA measurements of spiro-CPDTAs 109 (blue) and 110 (red).](image)

TGAs of thioxanthene derivatives 124 and 125 are shown in Figure 1-68. The methoxy-capped 124 lost 37% of its initial weight at 800 °C while 125 showed a larger loss of 71%. The onset decomposition temperature of the two thioxanthene derivatives was 408 °C for 124 and 481 °C for 125. The 5% decomposition was at 408 °C for 124 and 439 °C for 125.
TGA of the xanthene based HTM 131 is illustrated in Figure 1-69. The xanthene derivative showed 5% weight-loss already at 352 °C and the onset of decomposition was at 357 °C. At 800 °C, the sample exhibited a total weight loss of 57%.

The TGAs of DP-CPDTs 137 and 138 are presented in Figure 1-70. Methoxy TPA-capped DP-CPDT 137 lost 50% of the initial weight while TPA-capped DP-CPDT 138 exhibited a weight loss...
of 67% at 800 °C. The onset of the decomposition was at 405 °C for 137 and 443 °C for 138. The 5% weight-loss threshold was at 384 °C for 137 and 410 °C for 138.

![Figure 1-70: TGA measurements of DP-CPDTs 137 (blue) and 138 (red).](image)

All investigated CPDT derivatives showed a high degree of thermal stability with a decomposition temperatures (95% initial weight left) above 350 °C. The thermal data is summarized in Table 1-6. All methoxy derivatives showed a smaller weight loss and a smaller decomposition temperature than their TPA-capped counterparts. The exceptions are the two spiro-CPDTA derivatives 109 and 110, which almost had the same decomposition temperature. Interestingly, the methoxy-capped spiro-CPDTA 110 and spiro-CPDTT 124 showed almost similar weight loss during the heating process. The shape of the curves also looked similar for both CPDTs. This could indicate that the weight loss does not happen at the spiro-cyclopentadithiophene unit, where the molecules are different, but on the TPA substituents. It could be possible that anisole is eliminated in this process. Anisole possesses a boiling point of around 150 °C and could therefore evaporate after formation. This explanation has a problem explaining the weight loss of the other two methoxy-triphenylamine derivatives 131 and 137. Both CPDTs exhibited greater weight loss than what would be expected for the cleavage of anisole, indicating a decomposition of the central core. The large weight loss of around 70% of TPA capped derivatives 110, 125, and 138 strongly indicates that their central core is decomposing during the heating process.
After the determination of the decomposition temperature, differential scanning calorimetry (DSC) was used to determine possible melting and glass transition temperatures for all synthesized HTMs. The DSC measurement of spiro-CPDTA 109 is shown in Figure 1-71. The sample underwent three heating and cooling cycles. The second and third cooling scan is enhanced by a factor of four. During the first heating cycle, there was one endothermal signal (●) with an onset at 244 °C and a peak at 250 °C. The signal could indicate a melting of the sample. But the relatively low temperature motivated to investigate the phase transition further. Another sample of acridine 109 was heated in a melting tube. At the temperature of the endothermal signal, no melting of the sample could be observed, instead the color of the material changed. The transition was therefore classified as a solid-solid phase transition. In the first cooling scan, no phase transitions were visible. At 75 °C the baseline of the measurement changed drastically. This effect is sometimes visible due to a delay in the measurement if the cooling rate cannot be achieved. In the second heating scan, two signals could be detected. The first signal (●) with an onset at 162 °C and a peak at 168 °C was characterized by a change in the baseline. This is typical for a glass transition. Here the transition is from the amorphous glassy to the amorphous rubbery state. The glass transition was here overlaid by an enthalpic recovery process. A second transition (●) was seen with an onset at 240 °C which was probably the same transition that was observed in the first heating scan. The phase transition enthalpies were calculated by integration of the signal in the first and

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**Table 1-6:** Summarized TGA data of spiro-acridines 109 and 110, spiro-thioxanthenes 124 and 125, spiro-xanthene 131, and diphenyl cyclopentadithiophenes 137 and 138.

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</tr>
<tr>
<td>138</td>
<td>443</td>
<td>410</td>
<td>67</td>
</tr>
</tbody>
</table>

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...
second heating cycles, and the ratio is approximately 10:1. This probably means that the acridine underwent another solid-solid transition in the first cooling cycle but the intensity is not high enough to be visible due to the uneven baseline. In the second cooling scan, an amorphous rubbery to glassy phase transition (●) was visible with an onset of 172 °C. This was slightly higher as the glass transition in the second heating scan. The third heating scan revealed the same two endothermal signals (● and ○) as in the second scan but the onset of the glass transition was shifted to 164 °C. The third cooling scan showed another weak glass transition in the same region as in the second cooling scan.

![Figure 1-71: DSC of acridine 109. Three heating- and cooling cycles are shown. The arrows indicate the measuring direction.](image)

The DSC data of acridine 110 is plotted in Figure 1-72. Three heating- and cooling cycles were measured. In the first heating scan, three different signals were visible. The problem is that the baseline here was not smooth and only one of the three signals also appeared in the second and third heating scans. The only signal that was present in all three heating scans was the signal at around 175 °C. The intensity of this endothermic transition increased in intensity going from the first to the second heating scan. At the second heating scan, the signal (●) had an onset of 171 °C and a peak at 177 °C. These signals were characterized by a change in baseline which indicates that a glass transition from the amorphous glassy to the amorphous rubbery state takes place. The signal was overlaid with a small enthalpic recovery. In the third heating scan, the onset of the glass transition (●) shifted to 168 °C and the peak to 175 °C. Interestingly, a closer look at the three different cooling scans revealed that in all three cycles the amorphous rubbery to glassy...
phase transition (●) takes place. The onset temperature in all three cycles was 171 °C and the intensity was always smaller than for the glassy to rubbery phase transition.

The DSC data of thioxanthene 124 is illustrated in Figure 1-73. As in the case of acridine 110, a variety of signals were visible with again only one small signal that was visible in all three scans. This endothermal phase transition was classified as glass transition. In the first scan, the glass transition (●) appeared at onset of 149 °C and a peak at 156 °C, in the second scan (●) at an onset of 152 °C and a peak at 158 °C and in the third scan (●) at an onset of 151 °C and a peak at 158 °C. No further consistent signal was visible in the heating scans. In the first cooling scan, a change in baseline was visible in the region of the glass transition at 150 °C (●), in the second at 156 °C (●), and in the third also at 156 °C (●). These baseline changes were again rubbery to glassy transitions.
The DSC of the second thioxanthene-based material 125 is shown in Figure 1-74. A large endothermic signal (●) was visible in the first heating scan. This signal was assigned to the melting of the sample. The large melting signal only appeared in the first heating scan with an onset value of 302 °C and a peak at 307 °C. In the first heating scan, no glass transition was visible. This strongly indicates that the thioxanthene was in a crystalline state after the precipitation from the solution and only changed into the amorphous state after the melting process. The absence of a cold crystallization peak in the heating scan supports this theory. A glass transition signal was afterwards visible in the second (●) and third (●) heating scan. The $T_g$ was determined from the onset to be 167°C for the second and 165 °C for the third heating scan. The peaks were located at 172 °C for the second, and at 169 °C for the third cycle.
The DSC data of xanthene based HTM 131 is shown in Figure 1-75. Two heating and cooling cycles were measured of this sample. The second heating scan is enhanced by a factor of four. In the first heating scan, an exothermal phase transition (●) took place with an onset at 154 °C and a peak at 171 °C. The exothermal transition was directly followed by an endothermal transition (●●) with a peak at 188 °C. This behavior indicates that first, a cold crystallization of the amorphous sample took place and afterwards the crystalline solid melted. However, the melting temperature appeared to be too low for the high molecular weight of the investigated compound. After the endothermal phase transition, the DSC curve started to become noisy. A repeated measurement with a different sample resulted in the same thermal behavior. A possible explanation can be found by having a look at the purification of xanthene 131. The solid was obtained by precipitation from a mixture of DCM and MeOH and afterwards dried in high vacuum. However, it appeared as if methanol keeps sticking to the solid. It could be possible that the methanol evaporates after the melting of the xanthene. This leads to a mass loss and a possible vibration of the crucible with the sample inside. At the end of the first heating scan, the baseline of the DSC measurement stabilized again. The first cooling scan did not result in any phase transitions. In the second heating scan, two small endothermal signals were visible. The first signal (●) with an onset at 142 °C and a peak at 154 °C is characterized by a baseline change and therefore corresponds to glass transition from the amorphous glassy to the amorphous rubbery state. The second signal (●●) with an onset at 233 °C and a peak at 246 °C was in a region where one would expect a possible melting of the sample. This signal coincides with the end of the large melting signal in the first heating scan. This
further supports the hypothesis that heavily with methanol contaminated solid melted during the first heating process.

The DSC data of methoxyphenyl-capped DP-CPDT 137 is plotted in Figure 1-76. The second and third cooling scans are enhanced by a factor of ten. In the first heating scan, an endothermal signal (●) was visible that was assigned to a melting of the crystalline solid. The onset of the melting point was at 263 °C and a peak at 265 °C. As in the case of thioxanthene 125, the sample was obtained by precipitation as a crystalline solid and after the melting and cooling an amorphous glassy material was formed. A glass transition (●) was visible in the second heating scan with an onset at 138 °C and a peak at 142 °C. The glass transition was overlaid with an enthalpic recovery. Another broad endothermal signal (●) with an onset at 215 °C and an endset at 264 °C was visible in the second heating scan. This phase transition could be the melting of some imperfect crystalline material, which usually has a melting point lower than the melting point of the crystalline material. But the same signal in the same temperature range can also be seen in the DSC of TPA-capped DP-CPDT 138 shown below in Figure 1-77. This could mean that the signal arose from a common impurity that was present if it is not from an inherent material property. The melting points of the common starting materials are not in this temperature range; therefore, they could be excluded as the source of this signal. No crystallization or melting of the amorphous compound was visible in the second heating scan. In the second cooling scan, a slight change in the baseline is visible in the region of the glass transition (●). The onset is 144 °C, but the signal was much less
pronounced than in the heating scan. In the third heating scan, the glass transition (○) was shifted to an onset of 141 °C and a peak at 145 °C. The same broad endothermal signal (●) as in the second heating scan was again visible. No phase transitions were visible in the third cooling scan.

![Figure 1-76: DSC of DP-CPDT 137. Three heating- and cooling cycles are shown. The arrows indicate the measuring direction.](image)

The DSC data of TPA-capped DP-CPDT 138 is depicted in Figure 1-77. The second and third cooling scans are enhanced by a factor of six. The exhibited thermal behavior was similar to that of methoxyphenyl-capped 137 but the phase transitions occurred at different temperatures. The melting point of the sample (○) had an onset at 284 °C and a peak at 288 °C. This is 21 degrees higher than for the methoxy-capped derivative 138. The glass transitions in the second (●) and the third (●) heating scan possessed both onsets at 150 °C and peaks at 154 °C. The broad endothermal signals in the second (●) and third (●) heating scan at temperatures slightly lower than the melting point were also visible for this material. The signals appeared in the same temperature range as for 138. An amorphous glassy to amorphous rubbery phase transition (●) appeared in the second cooling scan with an onset of 153 °C.
The DSC data of the final DP-CPDT derivate HTM 143 is given in Figure 1-78. The second and third heating and cooling cycles are enhanced by a factor of ten. No TGA measurement of the material was available therefore, the sample was only heated to 250 °C to prevent decomposition. In the first heating scan, an endothermal solid-solid transition (●) with an onset at 179 °C and a peak at 186 °C was encountered. The nature of the transition was investigated using a small sample in a melting tube and it was discovered that no melting took place in this temperature range but instead a color change of the sample occurred. In the second (●) and third (●) heating scans glass transitions were visible with an onset at 149 °C and a peak at 154 °C in the second, and 150 °C for the onset and 155 °C for a peak in the third scan. A low-intensity amorphous rubbery to amorphous glassy phase transition (●) with an onset at 154 °C was detectable in the second cooling scan. The melting point of the thiomethyl-capped HTM 143 was determined by heating a small crystalline sample in a melting tube. A melting region of 270 – 274 °C was determined.
Figure 1-78: DSC of material 143. Three heating- and cooling cycles are shown. The second and third heating and cooling cycles are enhanced by a factor of 10. The arrows indicate the measuring direction.

The DSC and TGA results can be better understood by categorizing the investigated CPDTs. The methoxy substituted HTMs always show a lower $T_g$ than their corresponding TPA-capped counterparts. This effect is between 6 degrees difference for the $N$-phenylacridine, 15 degrees for the thioxanthene, and 12 degrees for the DP-CPDT based HTMs. This influence of the methoxy substituents on $T_g$ can be divided into two parts. One part is that the molecular weight increases. According to Naito et al. an increased molecular weight should lead to an increased $T_g$. However, this effect is compensated by an increased molecular cohesion, which according to Naito et al. decreases $T_g$. The second trend is that $T_g$ increases if the size of the structural unit, which is spiro-linked to the CPDT, increases. The spiro-CPDTA-based HTMs 109 and 110 exhibited the highest glass transition temperatures of all investigated CPDTs, followed by the spiro-CPDTT- and spiro-CPDTX-based HTMs. The non-spiro-linked DP-CPDT-series had the lowest glass transition temperatures of all investigated materials. For this last class of CPDTs, a second effect on $T_g$ needs to be considered. The DP-CPDT-based class of HTMs consist of the only molecules that are not spiro-linked in this chapter. The spiro-linkage introduces rigidity and a spherical form, which both are beneficial for a high $T_g$. However, the geometry constraint due to the cyclopentadiene sp$^2$-carbon atom at the DP-CPDT core also results in rigidity and a spherical structure to a certain extend even when there is no spiro-linkage present. A comparison between the thermal properties of DP-CPDTs and spiro-CPDTTs is the closest we can get to estimate the influence of the spiro-linkage. The linkage therefore increases $T_g$ by around 10-15 degrees. A better estimate for the effect of the spiro-linkage could be obtained by synthesizing a spiro-cyclopentadithiophene-
fluorene-based HTM and determination of $T_g$. The thiomethyl capped HTM 143 showed a $T_g$ near that of the TPA capped 138. This result indicated that the thiomethyl substituents could be a viable alternative to methoxy groups to adjust the FMO energy levels of a material without jeopardizing the $T_g$. All thermal properties of the investigated CPDTs are summarized in Table 1-7. The reported $T_g$ values are taken as the smallest obtained onset of the amorphous glassy to amorphous rubbery phase transition and are therefore a conservative estimate. The melting point ($T_m$) were determined from the onset of the transition.

**Table 1-7: Thermal properties of CPDT-based HTMs.**

<table>
<thead>
<tr>
<th>$T_m$ [°C]</th>
<th>$T_g$ [°C]</th>
</tr>
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<tbody>
<tr>
<td>109</td>
<td>162</td>
</tr>
<tr>
<td>110</td>
<td>168</td>
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<td>150</td>
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<tr>
<td>143</td>
<td>149</td>
</tr>
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1.6 Summary

In summary, five new spiro-CPDT-, 109, 110, 124, 125, 131, and three new DP-CPDT-based materials, 137, 138, and 143 were prepared in a multi-step convergent synthesis starting from commercially available starting materials. All materials have been finalized by a twofold Pd-catalyzed Suzuki-type cross-coupling reaction of the corresponding brominated precursor and the respective TAA boronic ester in good yields. Three different TAA substituents were employed to induce slight changes in the electronic behavior of the materials. Three new spiro-CPDT-cores, spiro-cyclopentadithiophene-N-phenylacridine, spiro-cyclopentadithiophene-thioxanthenes and spiro-cyclopentadithiophene-xanthene were developed, have been synthesized, and the synthesis has been optimized to allow upscaling and avoid tedious purification steps by column chromatography. The synthesis of all materials was confirmed by high-resolution mass spectrometry and X-ray diffraction (XRD) structural analysis of spiro-CPDTA 109 was performed to confirm the spherical structure of the materials. The optoelectronic properties of all materials were investigated employing optical spectroscopy and electrochemistry. It was confirmed that the optoelectronic properties are mostly determined by the attached TAA substituents and not by the spiro-linked moiety. The methoxy-capped HTMs exhibited absorption maxima between 443 nm and 445 nm, while the maxima of the unsubstituted triphenylamine-capped materials were between 435 nm and 437 nm. The absorption maximum of the thiomethyl-capped material was in-between with 442 nm. The optical gaps were between 2.44 eV and 2.46 eV for the methoxy-capped, 2.50 eV and 2.51 eV for the unsubstituted triphenylamine-capped and 2.47 eV for the thiomethyl-capped material. For the methoxy-capped materials HOMO energy levels between -5.03 eV and -5.07 eV, for the unsubstituted triphenylamine-capped between -5.09 eV and -5.19 eV were obtained. The thiomethyl-capped TPA resulted in a material that has optoelectronic properties that are located between the methoxy- and unsubstituted triphenylamine-capped but leans more towards the unsubstituted triphenylamine-capped materials. All HTMs reversible form a radical cation and dication fulfilling a prerequisite for the application in PSC. The radical cations and dications of the DP-CPDT materials were prepared by chemical oxidation and the charged species were characterized by UV-vis-NIR absorption spectroscopy in order to determine the FMO energy levels. Ab-initio calculations were performed to investigate the neutral- radical cation and dication-states of all DP-CPDT materials with respect to the influence of the different TPA end groups. The thermal properties of all CPDTs were investigated with a focus on the influence of the spiro-linked moiety. All materials experienced high thermal stability with decomposition temperatures above 350 °C (except 143 where the decomposition temperature was not determined). An amorphous state was
obtained for all materials and the amorphous glassy to amorphous rubbery transition was investigated. All materials had relatively high glass transitions with temperatures between 162 °C and 168 °C for the spiro-CPDTA materials, 149 °C and 165 °C for the spiro-CPDTT materials, 142 °C for the spiro-CPDTEX material, and 138 °C to 150 °C for the non-spiro-linked DP-CPDT materials. It has been proven that all DP-CPDT-based materials as well as for acridine 109 and thioxanthenes 125 and 124 also can exist in a crystalline state and for the other materials this crystalline state seems possible.

An excerpt of the work on acridines has already been published.\[86\]
2 Synthesis and Structural Analysis of Tetrakis(triphenylamino)cyclopentadiene-derivatives

2.1 Introduction

In this chapter, the synthesis and characterization of two different tetrakis(triarylamine)-substituted 5,5-dimethoxycyclopentadienes and their transformation into cyclopentadienones and 6,6-dicyano pentafulvenes is described (Figure 1-1). For their synthesis, a convergent approach is planned with two building blocks, which are the halogenated central dimethoxycyclopentadiene and the boronic ester of the respective triarylamines. The transformation from dimethoxycyclopentadiene to cyclopentadienone allows for the synthesis of substituted cyclopentadienones that are not directly available due to the inherent instability of cyclopentadienone. The synthetic availability of substituted cyclopentadienones will open up the molecule to acceptor substitution on the core by Knoevenagel condensation of the respective cyclopentadienones with malononitrile to generate donor-acceptor (D-A)-structures. Structure-property relationship analysis will be performed to evaluate the influence of the different functional groups, dimethyl acetal, ketone, and dicyanovinylene on the optoelectronic properties of the cyclopentadiene derivatives. The focus will be laid on the influence of the substitution on the FMO energy levels. The steric demand of four TAA substituents on a small cyclopentadiene core will lead to an overcrowded molecule with a 3-dimensional, spherical structure. This will hopefully lead to amorphous materials with $T_g$ above 120°C.[87]

![Figure 2-1](image.png)

Figure 2-1: General structure of the planned cyclopentadiene derivatives.

Firstly, an introduction to the topic of non-fused cyclopentadienes is given. Then, the synthesis of cyclopentadiene acetics, cyclopentadienones, and the dicyanopentafulvenes is described. This is
followed by the structural identification of cyclopentadiene acetals by XRD and their packing properties. The optical and electrochemical characterization of all cyclopentadiene derivatives and finally, the thermal characterization of the cyclopentadienes is shown.
2.2 State of the Art

The carbocyclic cyclopentadiene 146, which can be seen as a bridged form of s-cis-butadiene, has always been of great interest due to its reactivity in various pericyclic reactions.\[88\] The diene nature of the compound opens it up towards [4+2] cycloadditions, also known as the Diels-Alder reaction. Cyclopentadiene can react with itself to form tricyclo[5.2.1.0\[2,6\]]deca-3,8-diene 147, also known as dicyclopentadiene (Scheme 2-1). This reaction already takes place at room temperature and is fully reversible. The retro-Diels-Alder reaction takes place upon heating 147 to higher temperatures and removing the monomeric 146 from the equilibrium.

![Scheme 2-1: Reversible dimerization of 146 by Diels-Alder cycloaddition.](image)

The second interesting pericyclic reaction that constantly takes place at cyclopentadiene 146 is a 1,5-sigmatropic hydrogen shift. In this reaction, a hydrogen atom (or more precisely a hydride group) moves along the π-system of the molecule, which results in the migration of the sp\(^3\)-position in the cyclopentadiene (Scheme 2-2). This sigmatropic reaction is not noticeable on an unsubstituted cyclopentadiene, but still takes place.\[89-90\]

![Scheme 2-2: 1,5-Sigmatropic H-shift in cyclopentadiene.](image)

The other interesting reactivity of cyclopentadiene concerns its relatively high C-H acidity at the sp\(^3\)-hybridized carbon atom. The acidity of the cyclopentadiene corresponds to a pK\(_a\) of 18 (in DMSO) and is therefore 26 orders of magnitude higher than for the allyl system (pK\(_a\) of 44 in DMSO).\[91-92\] This unusually high acidity is caused by the aromatic nature of the cyclopentadienyl anion. The anion has 6π electrons and therefore satisfies the Hückel-rule for aromaticity. Deprotonated cyclopentadiene reacts as a nucleophile and this reaction is used to introduce substituents into the cyclopentadiene core.

Extension of the π-system of cyclopentadiene through an exocyclic double bond at the formerly sp\(^3\)-hybridized carbon atom leads to the formation of the pentafulvene 148 depicted in Figure 2-2 on the left side. Cyclopentadienone 149, depicted on the right side in Figure 2-2, has a similar π-system and both molecules possess some similar reactivity. The unsubstituted parent compounds
both undergo dimerization through a Diels-Alder-reaction and are therefore not stable under ambient conditions. Both molecules possess some interesting reactivities due to their electronic structures. Both cyclopentadiene derivatives react with nucleophiles, but the reactive position is different for the two molecules and can be explained by resonance structures. The fulvene accepts nucleophiles at the exocyclic position because the resonance structure with a positive charge at this position is aromatic. The addition of nucleophiles at the cyclopentadienone takes place as in the case of other carbonyl groups at the carbonyl carbon but the reactivity is reduced because the resonance structure with the positive charge has some antiaromatic contribution.

![Figure 2-2: Resonance structures of pentafulvene 148 (left) and cyclopentadienone 149 (right).](image)

Cyclopentadienes and cyclopentadienones have been extensively used as moieties in organic materials. This section focuses only on non-fused systems so that the original moiety and its electronic structure are still prevalent.

Tetraphenylcyclopentadienone 150, also called tetracyclone, was first synthesized in 1925 by Löwenstein and Ulich starting from diphenylmaleic anhydride and phenylacetic acid. The now common synthesis, starting from benzil 151 and diphenylpropanone 152 (Scheme 2-3) was first published by Johnson et al. in 1943. Tetracyclone is here synthesized in 96% yield by a twofold crossed aldol-condensation in boiling ethanol.

![Scheme 2-3: Synthesis of tetracyclone 150 by twofold crossed Aldol-condensation](image)

The versatility of this reaction also allowed the synthesis of tetranaphtyl-,[98] diphenylpyridinyl-, [99] diphenylthiienyl-, [100] tetrapyridinyl,[101-102] and tetraethienyl-cyclopentadienone.[100] These tetra-substituted cyclopentadienones were used as building blocks in [4+2]-cycloadditions with substituted acetylenes to build up hexasubstituted benzenes in two steps. Hexaphenylbenzene 153 was first synthesized in this way in 1966 by Fieser (Scheme 2-4).[103] The synthesis starts with a Diels-Alder reaction of cyclopentadienone 150 as diene and diphenylacetylene 154 as dienophile. The formation of bicyclic ketone 155 is followed by an extrusion of carbon monoxide to form a stabilized
benzene ring (Scheme 2-4). In recent years his synthetic method has extensively been employed by Müllen et al. to synthesize various large polycyclic aromatic hydrocarbons.[104]

Scheme 2-4: Synthesis of hexaphenylbenzene 153 starting from cyclopentadienone 150 and diphenylacetylene 154.[104]

The reaction can also be used to synthesize polymeric structures if diacetylenes and dimeric-cyclopentadienones are used.[105]

The availability of tetracyclone also allowed synthesis of a tetraphenylocyclopentadienone dimethyl acetal 156 by reacting tetracyclone with dimethoxycarbene 157. The carbene reacts with the bicyclic intermediate 158 in a 1,4-addition and forms the dimethyl acetal of tetracyclone 156 after the loss of carbon monoxide in 23% isolated yield (Scheme 2-5).[106]

Scheme 2-5: Synthesis of acetal 156 from tetracyclone 150 and dimethoxycarbene 157.[106]

The obtained acetal 156 was characterized by UV-vis absorption spectroscopy and the absorption maximum is bathochromic shifted by 31 nm compared to tetraphenylocyclopentadiene 158. The bathochromic shift is attributed to spiro-conjugation between the methoxy groups and cyclopentadiene. The parent compound tetraphenylocyclopentadiene 158 can also be synthesized from tetracyclone 150 by reduction with lithium aluminum hydride (LiAlH₄) as a reducing agent and aluminum chloride (AlCl₃) as a Lewis-acid catalyst (Scheme 2-6).[107] This approach leads to an excellent yield of 93% which is a great improvement compared to the low yields that were obtained by the older preparation method of reducing cyclopentadienone with zinc powder.[108]
Tetraphenylcyclopentadiene is commonly deprotonated and employed as $\eta^5$- or $\eta^3$-ligand in metal complexes. Sandwich complexes have for example been prepared with yttrium, lanthanum, vanadium, chromium, cobalt, nickel, europium, samarium, or rhodium.

Cyclopentadiene has been used as a non-aromatic building block in organic electronic materials design as a means to decrease the optical gap without compromising the planar structure of the electronic materials. Pietrangelo et al. synthesized cyclopentadiene-fluorene polymer starting from 1,4-ditriflate cyclopentadiene and fluorene diboronic acid in a palladium-catalyzed Suzuki-type cross-coupling reaction (Scheme 2-7). This reaction afforded a polymer, in which aromatic (fluorene) and non-aromatic (cyclopentadiene) moieties are alternating. The obtained polymer showed a bathochromic shift of the absorption maximum of 15 nm compared to a corresponding fluorene-thiophene polymer with comparable molecular weight.

Dicyanovinylene-substituted tetraphenylpentafulvene 162 has been synthesized starting from tetracyclone, which was reacted with malonodinitrile, titanium(IV) chloride (TiCl$_4$) as Lewis-acid, and pyridine as base in a Knoevenagel condensation reaction (Scheme 2-8) to form 6,6-dicyano-2,3,4,5-tetraphenylpentafulvene 162 in 45% yield. The obtained polymer possessed the ability to undergo two reversible one-electron reductions making it a potential n-type semiconducting material for application in organic electronics.
The formation of stable radical anions enabled synthesis of a charge-transfer salt from 6,6-dicyano-2,3,4,5-tetraphenylpentafulvene 162 as electron acceptor and cobaltocene as electron donor.[115]

The synthesis of tetra-functionalized cyclopentadienones via twofold Aldol-condensation (Scheme 2-3) showed vastly different yields for different substitution patterns, which limits the availability of tetra substituted cyclopentadienones. One possibility to synthesize cyclopentadienones that are not accessible by condensation reaction is a detour via tetrasubstituted cyclopentadienone dimethyl acetal. This approach was used to synthesize the tetrakis[4-bis(N,N-dimethylaniline)]-6,6-dicyanopentafulvene 163 (Scheme 2-9). The synthesis starts from 1,2,3,4-tetrabromo-cyclopentadienone dimethyl acetal 164 and 4-N,N-dimethylaminophenyl boronic acid 165. Boronic acid 165 is fourfold coupled to acetal 164 in a Suzuki-type cross-coupling reaction with 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) as ligand to afford tetrakis[4-bis(N,N-dimethylaniline)]cyclopentadienone dimethyl acetal 166 in 47% isolated yield. In the second step, the obtained acetal 166 is deprotected with trifluoroacetic acid (TFA) to form tetrakis[4-bis(N,N-dimethylaniline)]cyclopentadienone 167. Ketone 167 was afterwards reacted in a Knoevenagel condensation with malonodinitrile to afford the acceptor-substituted pentafulvene 163 in only 4% isolated yield. The low yield cannot be attributed to an individual step because ketone 167 was not isolated. The authors attribute the low yield to the instability of ketone 167 under Knoevenagel condensation conditions, but the harsh treatment of the acetal with TFA could probably also explain the low yield for these transformations.
The introduction of electron-rich substituents at the acceptor-substituted pentafulvene leads to an amphoteric redox behavior. Fulvene 163 showed a two-electron oxidation at 0.15 V and a reduction at -1.19 V vs ferrocene/ferricinium (Fc/Fc⁺). This means that the reduction is shifted by 0.25 V to more negative potentials compared to fulvene 162. This effect is attributed to the electron-donating ability of the dimethyl amine groups.
2.3 Synthesis of Cyclopentadiene Derivatives

2.3.1 Synthesis of Cyclopentadienone Dimethyl Acetals

The synthesis of the tetrabrominated cyclopentadiene dimethyl acetal \(164\) started with six-fold bromination of cyclopentadiene \(146\) (Scheme 2-10). Hexabromocyclopentadiene \(168\) was afterwards substituted with sodium methoxide in a twofold S$_2$N$_2$-reaction to form acetal \(164\). Both reactions were carried out according to a modified literature procedure by Breslow et al.$^{[116]}$

\[\text{KOH, KOBr, H}_2\text{O, -5 °C [24%]} \xrightarrow{} \text{Br, Br} \xrightarrow{\text{Diglyme, MeONa [80%]}} \text{MeO, OMe} \]

Scheme 2-10: Synthesis of 1,2,3,4-tetrabromo-5,5-dimethoxycyclopenta-1,3-diene \(164\) starting from cyclopentadiene.

Cyclopentadiene \(146\) was hexabrominated using potassium hypobromite (KOBr) in the presence of potassium hydroxide. Potassium hypobromite was formed in-situ from bromine and potassium hydroxide because the hypobromite is not stable and therefore was not available for purchase (Scheme 2-11).

\[2 \text{KOH} + \text{Br}_2 \rightleftharpoons \text{KBr} + \text{KOBr} + \text{H}_2\text{O} \]

Scheme 2-11: Equilibrium for the hypobromite formation.

A solution of potassium hydroxide was cooled to -5 °C and bromine (Br$_2$) was slowly added while keeping the temperature below -5 °C. The low reaction temperature guarantees the stability of the formed hypobromite. Freshly cracked (see Scheme 2-1) and distilled cyclopentadiene \(146\) was added and the solution was allowed to warm to room temperature overnight. The crude product was extracted with PE and hexabromocyclopentadiene \(168\) was obtained after a series of recrystallizations from PE in 24% isolated yield.

The low yield of the reaction required to take a closer look at the mechanism of this reaction. The reaction can be split into three parts. In a first step, a deprotonation of the acidic C$_{sp3}$-H bond takes place and the aromatic cyclopentadienyl anion is formed. The anion attacks the hypobromite and is brominated. The next step is a 1,5-sigmatropic H-shift that leads to 1-bromocyclopentadiene. This series of deprotonation, substitution, and 1,5-sigmatropic H-shift takes place until 1,2,3,4,5-pentabromocyclopentadiene is obtained. No more sigmatropic rearrangements are possible and the final bromo substituent is introduced by another deprotonation and substitution. The proposed mechanism for the formation of hexabromocyclopentadiene \(168\) is shown in Scheme 2-12.
Scheme 2-12: Mechanism of hexabromocyclopentadiene formation by a series of deprotonations, nucleophilic substitutions, and 1,5-sigmatropic H-shifts.

A problem occurs when both sp\(^3\)-positions are substituted before all sp\(^2\)-positions are functionalized. This is the case if two deprotonation-substitution cycles take place before the sigmatropic rearrangement occurs. No more deprotonations or 1,5-sigmatropic H-shifts are possible from this point and the reaction cannot proceed further (Scheme 2-13). This problem could not only happen with the cyclopentadiene but on each bromination step, except for the last one.

Scheme 2-13: Possible mechanism of the undesired side reaction of the six fold bromination of cyclopentadiene that does not lead to the desired product.

Another problem for this reaction could occur if the temperature gets too high and the equilibrium for the hypobromite formation (Scheme 2-11) is shifted to the left side. The formed bromine will react with cyclopentadiene under electrophilic addition instead of substitution, this will lead to saturated side-products.

The twofold nucleophilic substitution reaction with sodium methoxide (NaOMe) was performed by dissolving hexabromocyclopentadiene 168 in dry diethylene glycol dimethyl ether (diglyme) and cooling down to -60 °C to avoid side reactions. A solution of NaOMe in dry MeOH was slowly added. The crude product, that was obtained after the aqueous workup and following extraction and precipitation from DCM/MeOH to afford dimethyl acetal 164 as a brown solid in 41% yield. The low yield of the reaction could be attributed to the used batch of sodium methoxide which was not fresh. Reactions with newer batches of sodium methoxide in the institute and literature resulted in isolated yields above 80%.[116]

The tetrabrominated dimethyl acetal 164 can be used to obtain tetrasubstituted cyclopentadienone acetals 169 or instead as a replacement of the unavailable tetrabromocyclopentadienone as a building block to obtain functionalized cyclopentadienones 170. The synthesis of tetrasubstituted cyclopentadienone 170 proceeds via two steps. In a first step, the substitution is performed by a
cross-coupling reaction with an organo-metal reagent (R-M) and a palladium catalyst. In the second step, the dimethyl acetal protection group can be cleaved off to yield the desired functionalized cyclopentadienone (Scheme 2-14).

Scheme 2-14: General synthetic route starting from dimethoxycyclopentadiene 164 towards tetra substituted cyclopentadienones or cyclopentadienone acetals.

Dimethyl acetal 164 was fourfold functionalized with two different triphenylamine substituents via palladium-catalyzed Suzuki cross-coupling reaction of the respective boronic ester. Tetrakis[N,N-bis(4-methoxyphenyl)]aniline]cyclopentadienone dimethyl acetal 171 was synthesized from acetal 164 and 4-methoxy-N-(4-methoxyphenyl)-N-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]aniline 103 (Scheme 2-15). The boronic ester 103 was synthesized according to the procedure given in Chapter 1 (Scheme 1-26, p. 29). The reaction was performed at 80 °C under an argon atmosphere in degassed THF with 20 mol% tetrakis(triphenylphosphine)palladium(0) as catalyst and aqueous potassium phosphate solution as a base. The crude acetal that was obtained after the aqueous workup, was purified by flash column chromatography with silica gel deactivated with NEt₃. A solvent mixture of petrol ether and diethyl ether with 3% of NEt₃ was initially used and later changed to a mixture of petrol ether, diethyl ether, and toluene to improve the solubility of the product in the eluent mixture. Acetal 171 was precipitated from DCM/PE to afford an orange solid in 74% isolated yield. The good yield of 74% corresponds to 92% effectiveness for each individual coupling step.

Scheme 2-15: Synthesis of tetrakisubstituted dimethyl acetal 171 by Suzuki-type cross-coupling reaction.

The good conversion and yield of the reaction might partially be explained by the electronic nature of dimethyl acetal 164. The 2- and 3-positions of the dimethyl acetal are more reactive in a Pd-
catalyzed cross-coupling reaction.[116] This means that the arylamine substituents in 1- and 4-position are introduced at the end of the reaction sequence after the 2- and 3-positions are already substituted. The strain that is introduced in the third and fourth coupling step is therefore not that high compared to a substitution of the 2- or 3-position if all the other three positions were already functionalized.

The structure of acetal 171 was confirmed by NMR spectroscopy. The $^1$H-NMR, $^{13}$C-NMR, and $H,H$-COSY spectra of acetal 171 are shown in Figure 2-3. Due to the C$_2$-symmetry of acetal 171 four signals with an integrated intensity of four protons each, four signals with an integrated intensity of eight protons each were expected in the aromatic region. Additionally, three different signals in the aliphatic region with intensities of six, 12, and 12 protons were expected for the methoxy groups. The spectrum contained three signals with an intensity of four protons each, four signals with an intensity of eight protons each, and one signal with 12 proton intensity in the aromatic region. The signal with the intensity of 12 was an overlap of a four proton and an eight-proton signal. The assignment of the protons is problematic for this acetal due to the similar chemical shifts of the four arylamine substituents. Nuclear Overhauser effect spectroscopy (NOESY) was performed to determine whether it is possible to see which aryl protons are in close proximity of the methoxy groups (●) at the cyclopentadiene. But due to the large distance between the methoxy groups and the high molecular mass of the molecule no nuclear Overhauser effect (NOE) was detected.[117] The large deshielding of the maroon (●) signal at $\delta = 7.39$ ppm is very interesting. The integral of four revealed that this signal corresponds to one of the phenyl rings directly attached to the cyclopentadiene core. The strong deshielding could be attributed to an additional ring-current effect that acts on the protons. The arylamine substituents in 2- and 3-position are encircled by two other arylamine substituents each which could lead to steric strain for the protons ortho to the cyclopentadiene substituents on these arylamine substituents. The close proximity of the protons to the neighboring phenyl ring could therefore introduce this second ring-current effect on the protons. The $^{13}$C-NMR spectrum gave further indications that this cannot be a normal electronic effect. The $^{13}$C-NMR signals, which can be assigned to the C-H groups of the arylamines, are located at $\delta = 130.87, 129.41, 127.55, 126.91, 120.54, 119.03, 115.12, and 115.10$ ppm. The signals always come in pairs of two, which correspond to the same carbon atom on substituents in 1- and 4- or 2- and 3-positon. If the large shift of the proton signal in maroon (●) would be due to the large difference in the electronic structure, this would also be visible for the $^{13}$C-NMR signals, which is not the case. From the $H,H$-COSY spectrum it can be extracted that the proton with the corresponding signal marked in maroon couples to the proton with the signal in orange (●). This would mean that the orange signal can be assigned to the protons ortho to the amine in positions

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The third signal with an integral of four protons is marked in teal (●). The signal showed a similar chemical shift as the protons ortho to the amine too, but for the substituents in 1- and 4-position. The missing four-proton signal is part of the multiplet with the integral of 12 protons and the center at $\delta = 6.80$ ppm marked in green (●). This signal can be attributed to the protons ortho to the cyclopentadiene for the substituents in 1- and 4-position. The four signals with an integral of eight protons each could not be assigned to their corresponding positions. From the $H, H$-COSY spectrum it becomes apparent that the protons with the signal marked in red (●), with a center at $\delta = 7.06$ ppm, couple with the protons that result in the signal marked in blue (●) with a center at $\delta = 6.84$ ppm. The protons with the signal marked in magenta (●), centered at $\delta = 7.00$ ppm, couple with the eight-proton signal marked in green (●). This means that each pair of signals red and blue or magenta and green correspond to protons on an anisyl unit either in 1- and 4-, or in 2- and 3-position. From the chemical shift, one would expect that the two deshielded signals in red and magenta correspond to protons meta to the methoxy substituent and the signals in blue and green correspond to protons ortho to the methoxy groups.

The aliphatic region showed the three expected signals corresponding to the different methoxy groups. The methoxy groups in 5-position at the cyclopentadiene and the arylamine substituents are expected to show noticeable different chemical shifts due to electronegativity differences between phenyl and cyclopentadiene. The dimethyl acetal group has an integrated intensity of six and corresponds therefore to the signal marked in dark green (●). The arylamine methoxy groups in 1- and 4-position gave different signals than those on the arylamines in 2- and 3-position as expected. The signals are marked in cyan (●) and in olive (●). Even in the $^{13}$C-NMR spectrum, two different signals were obtained at $\delta = 55.94$ ppm and 55.96 ppm for the arylamine methoxy groups. The signal at $\delta = 50.89$ ppm corresponds to the dimethyl acetal at the cyclopentadiene core. The difference in chemical shift between the aryl and cyclopentadiene methoxy groups can be understood by the electron-withdrawing effect of the phenyl groups which leads to a deshielding of the aryl methoxy protons and carbon atoms in the NMR.
Figure 2-3: $^1$H-NMR (top), $^{13}$C-NMR (middle), and $H,H$-COSY NMR (bottom, left) spectra of acetal 171 (bottom right) in deuterated dichloromethane.
The second triarylamine-substituted cyclopentadiene dimethyl acetal 172 was synthesized as well by fourfold palladium-catalyzed Suzuki-type cross-coupling of tetrabromocyclopentadiene dimethyl acetal 164 and triphenylamine boronic ester 108 (Scheme 2-16). Tetrabrominated acetal 164 and boronic ester 108, which was synthesized according to the procedure given in Chapter 1 (Scheme 1-27, p. 30), were dissolved in dry and degassed THF. The tetrakis(triphenylphosphine)palladium(0) catalyst was added in 20 mol% (5 mol% per coupling) and a degassed potassium carbonate solution was added as a base. The reaction tube was sealed under an argon atmosphere and heated to 80 °C.

Scheme 2-16: Synthesis of tetrasubstituted dimethyl acetal 172 by Suzuki-type cross-coupling reaction.

After aqueous workup, the crude product was purified by flash column chromatography with triethylamine-deactivated silica gel. An eluent gradient was used for this purification starting with a mixture of PE to Et₂O of 8:1 that was slowly changed to 5:1. Acetal 172 was precipitated from PE/Et₂O to afford an orange solid in 46% yield. The purification of acetal 172 was more complicated than that of methoxyphenyl-capped acetal 171. The impurities of this reaction included the two- and threefold-coupled side products. In the case of the methoxyphenyl-capped derivative 171, these side products possessed a much lower polarity due to two respectively four missing methoxy groups, compared to the main product. This allowed a clear separation of the side products by column chromatography. For the phenyl-capped acetal 172, this difference in polarity between the product and side-products was not that pronounced which made the separation much more difficult. The low yield of this reaction was addressed by Florian Stümpges in his Bachelor Thesis. He prolonged the reaction time and changed the base to K₃PO₄ which led to an isolated yield of 70% for this reaction[118].

The formation of both tetrasubstituted dimethyl acetals 171 and 172 was confirmed by FTICR-MALDI mass spectrometry. The mass spectra of acetals 171 and 172 are shown in Figure 2-4. Interestingly both spectra showed two sets of signals and their respective fine structures resulting from the elemental composition of the acetals.
The molecular peak appeared at $m/z = 1338.57162$ for 171 and at $m/z = 1098.48237$ for 172. These values are in good agreement with the expected values and result in a deviation of $\delta m/m = 0.12$ ppm and $\delta m/m = 3.94$ ppm. The second set of signals are always obtained at masses that are $\Delta m/z = 31$ smaller for both acetals. This corresponds to a cleavage of a methoxy group. The fact that both derivatives showed this behavior indicates that the methoxy group that is cleaved off in each molecule is one at the central dimethyl acetal unit and not to one at the arylamine groups. This is consistent with what is known about the stability of dimethyl acetal groups. It is noted that a closer look at the part of the spectra between the two sets of signals showed another set of signals with a very low intensity. This set of signals can be attributed to the cleavage of a methyl substituent.

The structures of both acetals 171 and 172 were further verified by single-crystal XRD. Both single crystals were obtained by an antisolvent diffusion crystallization. The single crystal of acetal 171 was obtained with chloroform as solvent and n-hexane as anti-solvent, while acetal 172 was obtained with DCM as solvent and n-hexane as antisolvent. The anisyl-capped acetal 171 crystallized in the triclinic primitive P1̅ space group with two equivalent molecules per unit cell ($a = 10.8185(2)$ Å, $b = 16.2139(5)$ Å, $c = 22.5926(6)$ Å; $\alpha = 107.709(3)^\circ$, $\beta = 95.339(19)^\circ$, $\gamma = 90.349(2)^\circ$). The structure of the asymmetric unit is illustrated in Figure 2-5, with the angles...
between the central cyclopentadiene and the phenyl substituents marked. The triarylamine substituents in 1- and 4-positions are twisted by 13° which means that they form an almost planar system relative to the cyclopentadiene unit. This fact hints towards a strong conjugation between the substituents and the core. The triphenylamine units in 2- and 3-position on the other hand showed a twist of 66° and 69°, respectively. This can be explained by steric hindrance. The triphenylamine units in 1- and 4-position only have one large neighboring triphenylamine substituent while triphenylamines in 2- and 3-position have two. The steric demand of the dimethyl acetal group is therefore not as large as for the triarylamino and does not result in a twist between the central cyclopentadiene and the adjacent triphenylamine units.

![Figure 2-5: Asymmetric unit of acetal 171 determined by single-crystal XRD measurement.](image)

The unit cell with two halves of the equivalent molecules of acetal 171 is shown in Figure 2-6. Both acetals are oriented anti to each other and are centered along the b-axis of the unit cell. The crystal structure additionally contains one molecule of chloroform per molecule of 171, but in Figure 2-6 the solvent molecule was omitted for clarity.
The analysis of short contacts, which means distances between atoms that are smaller than the sum of their VdW radii, showed that the packing in the crystal is dominated by two different types of interactions. One is represented by a CH-O interaction between the hydrogen atoms of the inner arylamine methoxy groups of the substituents in 2- and 3-position and the oxygen atoms of the dimethyl acetal. The distance between the interacting atoms amounts to 2.433 Å and 2.361 Å. This interaction leads to a stacking of the molecules perpendicular to the (-101) plane. Short contacts and the resulting stacking are shown in Figure 2-7.
Figure 2-7: Packing of acetal 171 perpendicular to the (-101) plane. The short contacts between the methoxy groups are marked in green.

The antiparallel stacking of the molecules along the (-101) plane is caused by CH-O interactions between arylamine methoxy groups and phenyl hydrogen atoms on molecules antiparallel to each other. The distances between interacting atoms are between 2.640 Å and 2.686 Å and four interactions are active per two molecules. The packing of acetal 171 along the (-101) plane is shown in Figure 2-8.

Figure 2-8: Packing of acetal 171 along the (-101) plane. The short contacts between the methoxy groups and the aryl hydrogen atoms are marked in green.
Phenyl-capped acetal 172 crystallized in the triclinic primitive P\(\overline{1}\) space group with two equivalent molecules per unit cell (\(a = 10.2785(4)\) Å, \(b = 15.4493(6)\) Å, \(c = 19.6524(7)\) Å; \(\alpha = 97.799(3)^\circ\), \(\beta = 98.067(3)^\circ\), \(\gamma = 90.493(3)^\circ\)). The angles between the phenyl substituents and the central cyclopentadiene are shown in Figure 2-9. Interestingly, the torsion angles are quite different compared to for the anisyl-capped acetal 171. The torsion between the triphenylamines in 1- and 4-position amount to 22° and 28°, respectively. These values are larger than the angle of 13° obtained for acetal 171. This finding indicates a weaker π-conjugation of the inner phenyl groups with the cyclopentadiene core than for methoxyphenyl derivative 171. On the other hand, the torsion angles between the cyclopentadiene moiety and the triphenylamine units in 2- and 3-position are 57° and 58°, respectively and smaller compared the acetal 171. This weaker distortion is probably enabled due to the larger angle between the substituents in 1- and 4-position which frees additional space for the substituents in 2- and 3-position.

![Figure 2-9: Asymmetric unit of acetal 172 determined by single-crystal XRD measurement.](image)

The repeating unit of acetal 172 is shown in Figure 2-10 (hydrogen atoms are omitted for better clarity). The repeating unit contains two anti-arranged molecules with the dimethyl acetal groups and the triphenylamine substituents at the 1- and 4-position pointing outwards. The triphenylamine substituents 2- and 3-position are pointing into the middle of the cell. The molecules are arranged along the b-axis of the unit cell and the planes formed by the cyclopentadiene units show a distance of 5.014 Å between each other.
The analysis of short contacts for acetal 172 resulted in O-H interactions between the methoxy groups. These interactions with distances of 2.386 Å and 2.536 Å are responsible for the arrangement of the molecules in a chain-like structure along the methoxy substituents (Figure 2-11). This behavior is different compared to acetal 171 where the O-H interactions are between the acetal methoxy groups and the arylamine methoxy groups. The absence of arylamine methoxy groups in acetal 172 therefore results in a very different packing behavior, where the molecules are anti-arranged due to the acetal-acetal interactions.
Figure 2-11: Chain-like arrangement of acetal 172 due to acetal-acetal OH-interactions. The short contacts are marked in green.

Another short contact, where the distance between the interacting atoms is smaller than the sum of the VdW radii, is visible in the packing. The interaction is a C-C interaction with a distance of 3.391 Å between phenylamine substituents. This interaction probably stabilizes the tail-to-tail arrangement of acetal 172 in the solid-state.
2.3.2 Synthesis of Tetrakis(triarylamine)cyclopentadienones

The successful synthesis of acetals 171 and 172 opened up the possibility to access corresponding cyclopentadienones by cleavage of the acetal to the ketone. This reaction is typically conducted using acid catalysis.\textsuperscript{[119]} In an attempt to avoid the harsh reaction conditions, a different approach using acetone and iodine was employed here. Tetrakis\{4-[N,N-bis(4-methoxy-phenyl)]aniline\}cyclopentadienone 173 was synthesized by dissolving acetal 171 in a mixture of acetone (Me\textsubscript{2}CO) and DCM (8:1) before a catalytic amount of iodine was added (Scheme 2-17). This reaction mixture was stirred at room temperature and afterwards a sodium sulfite solution was added to deactivate the remaining iodine by reduction. The product was extracted, dried, and purified by column chromatography with 1% ethyl acetate (EA) in DCM as eluent and silica gel as a stationary phase. The crude product was precipitated from DCM/PE which afforded ketone 173 as a violet solid in 61% isolated yield.

Scheme 2-17: Deprotection of acetal 171 to cyclopentadienone 173 using acetone and iodine.
In this case, dimethyl acetal 171 reacted as an acetalization reagent. Acetone was not only used as a reactant but also as a solvent (and therefore in large excess). In this reaction, acetone was converted to 2,2-dimethoxypropane. The addition of DCM to the mixture was necessary to increase the solubility of acetal 171. The reaction resulted in the formation of a yellow-colored side product with a lower retardation factor ($R_f$) than the product and the starting material. The mediocre yield of the reaction together with the color and the polarity of the side product could indicate that a [4+2]-cycloaddition follow-up reaction took place between two cyclopentadienones. This reaction could have been formed iodine catalyzed. Dimeric species were detected by matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry in the crude reaction mixture before purification, but it was not possible to detect whether the dimer was connected by a covalent bond or only an aggregate was formed.

Triphenylamine-capped dimethyl acetal 172 was as well deprotected using iodine in acetone. Tetrakis[4-(N,N-diphenylaniline)cyclopentadienone 174 was synthesized in the same manner as cyclopentadienone 173. Due to the lower polarity and solubility in acetone of acetal 172 compared to 171 a larger amount of DCM was necessary. A mixture of acetone to DCM in a ratio of 8:5 was therefore used as solvent. An elevated reaction temperature of 40 °C and a prolonged reaction time of 16 hours instead of 90 minutes were applied for the same reason (Scheme 2-18).

![Scheme 2-18: Deprotection of acetal 172 to the cyclopentadienone 174 using acetone and iodine.](image)

The reaction mixture was quenched by the addition of sodium sulfite solution and the organic phase was extracted with DCM and purified by column chromatography with an eluent mixture of PE:DCM of 2:1 and silica gel as stationary phase. The crude product was precipitated from DCM/PE to afford ketone 174 as a blackish solid in 69% isolated yield.

Both tetrakis(triarylamine)cyclopentadienones 173 and 174, were obtained in comparable yields of 61% and 69%, respectively. These yields are higher than the yield obtained for the TFA-catalyzed cleavage of dimethyl acetal of triarylamine-substituted dimethoxycyclopentadiene reported in literature (see Scheme 2-9 on p. 114). The low literature yield could be attributed to the high
basicity of the dimethylaniline substituents. The lower basicity of the triphenylamine substituent compared to that of dimethylaniline would probably also result in higher yields for an acid-catalyzed cleavage of the dimethyl acetal but the reaction was not attempted due to the good yield obtained with the employed method. Both reactions were first performed by Florian Stümpges during his Bachelor Thesis. He could obtain yields of 69% for ketone 173 and 75% for ketone 174.

2.3.3 Synthesis of Tetrakis(triarylamine)dicyanopentafulvenes

The formation of cyclopentadienones 173 and 174 from acetals 171 and 172, respectively, opened up further functionalization through condensation reactions of the keto group. In a first step, cyclopentadienones 173 and 174 were reacted with malonodinitrile in a Knoevenagel condensation reaction. These cyclopentadienones, which showed a weaker reactivity towards nucleophiles than other ketones, are further deactivated through the electron-rich arylamine substituents. Therefore, typical mild reaction conditions with ammonium acetate as a base and activating agent for the carbonyl group did not result in product formation. Therefore, another approach with a better activation of the carbonyl group was needed. As an alternative, the usage of Lewis acid TiCl₄ was chosen. The keto group attacked the Lewis acid in the first step which resulted in an increased electrophilicity of the carbonyl carbon. Pyridine was added as a base to deprotonate malonodinitrile. With these harsher reaction conditions, Knoevenagel condensation from ketone 173 with malonodinitrile to form 6,6-dicyano-tetrakis{4-(N,N-bis[4-methoxyphenyl])aniline}pentafulvene 175 was performed (Scheme 2-19). Ketone 173 and malonodinitrile were mixed and cooled to 0 °C, a solution of TiCl₄ and pyridine in DCM was added, and the mixture was stirred at room temperature. The mixture was washed with a 1 M HCl solution to remove pyridine and hydrolyze TiCl₄. The crude product was purified by flash column chromatography with silica gel as a stationary phase and DCM as eluent. The crude product was precipitated from DCM/MeOH to obtain pentafulvene 175 as a black solid in 49% isolated yield.

**Scheme 2-19**: Synthesis of pentafulvene 175 by Knoevenagel condensation of cyclopentadienone 173 and malonodinitrile.
Knoevenagel condensation to synthesize 6,6-dicyano-tetrakis[4-(N,N-diphenyl)aniline]pentafulvene 176 from cyclopentadienone 174 was performed under similar conditions (Scheme 2-20). Purification was performed with flash column chromatography on silica gel and an eluent mixture of DCM:PE (2:1). The solvent was removed, and the product was dispersed in MeOH and filtered. Pentafulvene 176 was isolated as a dark violet solid in 50% yield.

Scheme 2-20: Synthesis of pentafulvene 176 by Knoevenagel condensation of cyclopentadienone 174 and malononitrile.
### 2.4 Optoelectronic Characterization of Triarylamine-capped Cyclopentadiene-derivatives

The synthesized cyclopentadienone acetals, cyclopentadienones, and dicyanopentafulvenes were characterized by ultraviolet-visible (UV-vis) absorption spectroscopy. Dimethyl acetals 171 and 172 were additionally characterized by fluorescence spectroscopy. The fluorescence of cyclopentadienones 173 and 174 as well as that of pentafulvenes 175 and 176 was not investigated due to a very weak emission upon photoexcitation.

The absorption and emission spectra, measured in DCM, of acetals 171 and 172 are shown in Figure 2-13. Both spectra showed a strong high-energy absorption band at 304 nm, respectively 305 nm with extinction coefficients of 75 000 M⁻¹cm⁻¹ and 70 700 M⁻¹cm⁻¹. The position of the absorption band showed an invariance towards the substitution of methoxy groups on the TAA substituents. A second absorption band was located at 396 nm with an extinction coefficient of 27 300 M⁻¹cm⁻¹ for acetal 171 and at 378 nm with an extinction coefficient of 29 800 M⁻¹cm⁻¹ for acetal 172. This absorption band showed the expected bathochromic shift of 18 nm of the methoxyphenyl derivative 171 as well as an intensification. A low energy absorption band was located at 454 nm for acetal 171 with an extinction coefficient of 27 300 M⁻¹cm⁻¹ and at 446 nm with 24 000 M⁻¹cm⁻¹ for acetal 172. The bathochromic and hyperchromic shift of the methoxyphenyl derivative 171 was again explained by the electron-donating ability of the methoxy substituents and by the expansion of the π-system. The 0-0 transition was determined with the help of the first and second order derivative of the absorption spectrum with respect to the wavelength. For the low energy absorption band acetal 171 shows the 0-0 transition at 500 nm, acetal 172 at 488 nm.
It was difficult to determine which acetal showed the more intense low-energy absorption due to the variety of overlapping absorption bands. The absorption spectra were therefore integrated with respect to the wavelength in order to compare the intensity of the absorption bands. For the methoxyphenyl derivative 171, an integrated absorption of 0.908 M\(^{-1}\) and for phenyl derivative 172 of 0.813 M\(^{-1}\) was obtained. This confirmed that methoxy substitution indeed leads to a hyperchromic shift across all bands. The optical gap was determined by the onset wavelength (see p. 59) which yielded 2.37 eV for methoxyphenyl-capped acetal 171 and 2.41 eV for the triphenylamine-capped acetal 172. Both dimethoxy acetals 171 and 172 demonstrated a strong fluorescence upon photoexcitation. Methoxyphenyl capped cyclopentadiene 171 exhibited the emission maximum at 577 nm while triphenylamine capped 172 had a blueshifted maximum of 559 nm. The stokes shifts were 1270 cm\(^{-1}\) for 171 and 1190 cm\(^{-1}\) for 172 indicating similar reorganization energies in the photoexcited states.

To understand the complex absorption spectra of both acetals 171 and 172, a more detailed look into the structure of the acetals was necessary. The molecular structure can be divided into different chromophores, which possess a distinct absorption behavior. It should be possible to reconstruct the absorption spectra of acetals 171 and 172 with the help of the different chromophores and its absorption bands. The proposed chromophores of acetal 171 are shown in Figure 2-14. A literature search for molecules, which correspond to the chromophores, was performed to assemble the spectra piece by piece. Literature data for the first chromophore, which is represented by
bis(4-methoxyphenyl)aniline 177 gave an extinction coefficient of 23 000 M⁻¹cm⁻¹ and an absorption maximum at 298 nm. The second structure, vinyl-triphenylamine 178, is also known in literature. The UV-vis absorption spectrum of 178 in DCM gave two absorption bands at 308 nm and 336 nm. Another possible chromophore is represented by the 4,4′-bis(4-methoxyphenyl)aminostilbene 179 unit. Literature data for the trans-isomer is available and showed again two absorption bands at 398 nm with an extinction coefficient of 54 000 M⁻¹cm⁻¹ and 305 nm with 27 000 M⁻¹cm⁻¹. For the 1,2,3,4-tetrakis(triphenylamine)butadiene 180 chromophore only the non-methoxylated derivative is described in literature. The butadiene showed three absorption bands at 308 nm, 351 nm, and 381 nm. The extinction coefficients are unfortunately not reported, but the ratio of the absorption band intensities is 10:7:7.5 on going from the highest to the lowest energy absorption.

Figure 2-14: Acetal 171 with a triphenylamine- (177), vinyl-triphenylamine- (178), bis(N,N-diphenylamino)stilbene- (179), and tetrakis(triphenylamine)butadiene 180-chromophore marked in red.

The tetrasubstituted butadiene has the highest structural similarity to acetals 171 and 172. 1,3-Butadiene normally occurs in an s-trans conformation, but the ring-closure via the dimethyl acetal forces the butadiene structural unit in a planarized s-cis conformation in both acetals 171 and 172. This planarization of the π-system leads to an enhanced conjugation and therefore to a bathochromic shift of the absorption. The dimethyl acetal group shows another influence on the absorption behavior through spiro-conjugation. For tetraphenylcyclopentadienone dimethyl acetal 156 (Scheme 2-5, p. 111) the spiro-conjugation contributed to 31 nm bathochromic shift compared to tetraphenylcyclopentadiene 158 (Scheme 2-6, p. 112). Both effects, the planarization, and the electron-donation through spiro-conjugation, should be differently pronounced for different absorption bands. Only absorption bands that correspond to a chromophore that is delocalized along the cyclopentadiene core are affected. The low energy absorption band of acetal 171 is red-shifted by 65 nm compared to the low energy absorption of butadiene 180, while the low energy absorption band of acetal 172 is only red-shifted by 57 nm. The red-shifts of 65 nm and 57 nm, respectively,
compared to 1,3-butadiene 180, are the consequence of both the spiro-conjugation and the s-cis conformation.

The solution absorption spectra of cyclopentadienones 173 and 174 are illustrated in Figure 2-15. Both cyclopentadienones showed two different absorption bands. The high-energy absorption band was located at 307 nm and 308 nm for methoxyphenyl-capped ketone 173 and phenyl-capped ketone 174, respectively. Triphenylamine-substituted ketone 174 showed the more intense absorption with an extinction coefficient of 90 300 M⁻¹cm⁻¹ compared to 70 800 M⁻¹cm⁻¹ for methoxyphenyl-capped cyclopentadienone 173. The low-energy absorption bands of both ketones are relatively broad displaying a center at 499 nm with an extinction coefficient of 16 600 M⁻¹cm⁻¹ for ketone 173 and at 418 nm with 19 600 M⁻¹cm⁻¹ for ketone 174. This bathochromic shift of the absorption of ketone 173 is again explained by the electron-donating ability of the methoxy substitution at the TPA units.

![Figure 2-15: Solution UV-vis absorption spectra of cyclopentadienones 173 (blue) and 174 (red) in DCM.](image-url)

Both spectra showed a long tailing of the low energy absorption band which was at first attributed to the formation of aggregates in solution. A closer look at the concentration dependence of the absorbance revealed that the intensity behaved according to Beer-Lamberts-law. This means that the absorption band did not correspond to an aggregate because the formation should be largely concentration dependent. Another idea was to attribute the additional absorption to the partial oxidation of the ketone. But interestingly, this seems to be an inherent property of the cyclopentadienones.[123-124] The interesting electronic nature of the cyclopentadienone core resulted in the presence of two absorption bands that can be understood as a charge-transfer band from the
substituents into the ring and towards the oxygen (Figure 2-16). This effect is well-known and described in literature for the parent compound of all tetraphenyl-substituted cyclopentadienones, namely tetracyclone 150.\cite{123,125-126} The small-intensity charge-transfer transition was located at 651 nm and showed an extinction coefficient of 3 200 M\(^{-1}\)cm\(^{-1}\) for ketone 173 and is centered at 626 nm with 3 500 M\(^{-1}\)cm\(^{-1}\) for ketone 174. The zwitterionic Lewis structures, which describe the excited states, are shown in Figure 2-16. The zwitterionic part is marked in red. The delocalization of the positive charge on the para-methoxyphenyl units was omitted for viewability reasons. The structure on the left-hand side was attributed to the absorption band at 499 nm (for ketone 173) and on the right-hand side to the absorption band at 651 nm.\cite{125} The methoxyphenyl-capped cyclopentadienone 173 showed an onset wavelength of 828 nm which corresponds to an optical gap of 1.50 eV. The phenyl-capped cyclopentadienone 174 showed an onset wavelength of 782 nm which results in an optical gap of 1.59 eV. It is noted here that the determination of onset wavelengths from very diffuse absorption bands can be erroneous and should be treated with care.

![Figure 2-16: Zwitterionic states of the cyclopentadienone 173 after excitation by light. The Lewis-structure on the right side corresponds to the lowest energy absorption band due to the greater delocalization of the charges.](image)

The spectra of the dicyanomethylene-substituted pentafulvenes 175 and 176 are depicted in Figure 2-17. Both fulvenes showed two strong absorption bands each. The high-energy absorption band was centered at 308 nm with an extinction coefficient of 77 800 M\(^{-1}\)cm\(^{-1}\) for methoxyphenyl-capped pentafulvene 175 and at 310 nm with an extinction coefficient of 87 700 M\(^{-1}\)cm\(^{-1}\) for phenyl-capped pentafulvene 176. The second absorption band exhibited again a bathochromic shift for methoxyphenyl-capped pentafulvene 175 at 595 nm compared to 573 nm for phenyl-capped pentafulvene 176. Both bands possessed similar extinction coefficients of approximately 18 000 M\(^{-1}\)cm\(^{-1}\). The 0-0 transitions were determined for each absorption band. The high-energy absorption showed the 0-0 transition at 343 nm for pentafulvene 175 and 339 nm for pentafulvene 176. The second band showed the 0-0 transition at 656 nm for pentafulvene 175 and 623 nm for pentafulvene 176. Integration of the absorption spectra with respect to the wavelength confirmed that the methoxyphenyl-capped pentafulvene 175 has the more intense absorption through the
whole spectrum even if the extinction coefficients at the maxima are smaller. For the methoxyphenyl pentafulvene 175 1.015 M⁻¹ was obtained which is about 10% larger than 0.896 M⁻¹ for pentafulvene 176. The optical gap was determined to be 1.65 eV for pentafulvene 175 and 1.74 eV for pentafulvene 176.

![Graph showing UV-vis absorption spectra of pentafulvenes 175 (blue) and 176 (red).](image)

**Figure 2-17**: Solution UV-vis absorption spectra of pentafulvenes 175 (blue) and 176 (red).

The question of whether the same low-energy low-intensity charge-transfer band is present for the dicyanomethylene derivatives as for cyclopentadienones 173 and 174 needs to be answered. Theoretically, the same zwitterionic structures could be constructed (Figure 2-18), but for both derivatives, no hidden absorption bands could be detected beyond 700 nm. This could either mean that the absorption band does not exist or that the intensity is too low to be detected. An explanation for the absence of the band for the dicyanomethylene unit compared to the ketone could be the special electronic nature of the cyclopentadienone. The cyclopentadienone possesses a partial antiaromatic character due to the positive partial charge at the carbonyl carbon. This effect should not be that pronounced for the accepter-substituted pentafulvenes 175 and 176.
Figure 2-18: Hypothetical zwitterionic states of dicyanomethylene-pentafulvene 175.

The results of the optical characterization of dimethoxy cyclopentadienes 171 and 172, cyclopen
tadienones 173 and 174, and pentafulvenes 175 and 176 are compiled in Table 1-3.
Table 2-1: Collected optical properties of acetals 171, 172, ketones 173, 174, and pentafulvenes 175, 176.

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Electrochemical characterization of acetals 171 and 172, cyclopentadienones 173 and 174, and pentafulvenes 175 and 176 was performed by cyclic voltammetry to determine redox potentials and energy levels of the frontier molecular orbitals. This data is crucial to determine a possible applicability of the molecules as HTM in state of the art perovskite solar cells. Cyclic voltamograms were measured in DCM at room temperature and TBAPF as supporting electrolyte. Three
cycles were measured at a scan speed of 100 mV/s if not stated otherwise. All potentials were internally referenced to the Fc/Fc\* redox pair. The half-wave potentials $E^{1/2}$ were calculated from $E_p^C$ and $E_p^A$. HOMO energy level was determined by the onset value of the oxidation ($E_{\text{ons}}, E_{\text{HOMO}}^{\text{Fc}} = -5.1 \text{ eV}$) \cite{79}. The LUMO energy levels were calculated from the HOMO energy and the optical gap or the onset of the reduction if available.

Cyclic voltammograms of acetics 171 and 172 are shown in Figure 2-19. The intensity of the cyclic voltammogram of acetal 172 was enhanced by a factor of 2.5 for better comparability.

![Cyclic voltammograms of acetics 171 (blue) and 172 (red, scaled by 2.5). The positions of the oxidation potentials were marked with a cross.](image)

**Figure 2-19:** Cyclic voltammograms of acetics 171 (blue) and 172 (red, scaled by 2.5). The positions of the oxidation potentials were marked with a cross.

No reductions were detectable in the available electrochemical window for acetics 171 and 172. Methoxyphenyl-capped acetal 171 showed overlapping oxidation waves. A time semi-derivative deconvolution of the cyclic voltammogram was used to help to evaluate the exact positions of the oxidation potentials (Figure 2-20). From time semi-derivative deconvolution, it becomes evident that acetal 171 showed two successive reversible oxidation waves at 0.02 V and 0.08 V followed by a third reversible oxidation wave at 0.38 V. For phenyl-capped acetal 172 the oxidation potentials were shifted to more positive values for the first oxidation to 0.16 V and 0.65 V for the second. Evaluation of the transferred electrons by integration indicated that for acetal 171 one, one, and two electrons were transferred in the first three oxidation waves. For acetal 172 the integrals of
the first and second oxidation waves were the same and two electrons were expected to be transferred each. The splitting of the first two oxidation waves for acetal 171 indicated that electronic communication exists within the molecule that does not exist in acetal 172. The oxidation to the oxidation states +3 and +4 took place in one oxidation wave for both acetals. Methoxyphenyl-capped acetal 171 showed another oxidation wave at 1.00 V. The shape of the oxidation wave indicated a quasi-reversible process and the integral of the anodic process indicated that four electrons were transferred. For acetal 172 an onset of a third irreversible oxidation wave at approximately 1 V was visible. The HOMO energy level was calculated to -5.04 eV for acetal 171 and -5.17 eV for acetal 172. The higher-lying HOMO for acetal 171 was attributed to the electron-donating ability of the methoxy substituents. This HOMO and the optical gap resulted in LUMO energy levels of -2.67 eV and -2.76 eV for the two acetals 171 and 172.

![Graph](image)

**Figure 2-20:** Time semi-derivative deconvolution of the cyclic voltammogram of acetal 171 (Figure 2-19).

The assignment of the different oxidation processes to individual moieties of the molecule could be accomplished by having a closer look at the literature. Bis(4-methoxyphenyl)aniline 177 gives a reversible oxidation wave at 0.38 V.\(^{[127]}\) Trans-4,4'-bis(4-methoxyphenyl)aminostilbene 179 shows two oxidation waves at 0.08 V and 0.22 V.\(^{[121]}\) No electrochemical data for tetrakis(triphenyl-amine)butadiene 180 is reported in literature and was therefore not available for comparison. The first oxidation of acetal 171 took place at a slightly more negative potential compared to stilbene 179. This could be explained by the slightly longer π-system in the cyclopentadiene unit and due to the spiro-conjugation with the dimethyl acetal group. The first oxidation was expected to happen
at the triarylamine substituents in 1- and 4-position of the cyclopentadiene dimethyl acetal. The second oxidation at 0.08 V was expected to take place at the other triarylamine substituent in 1- or 4-position forming a dication. The third and fourth oxidation take place simultaneously at the triarylamine substituents in 2- and 3-positions at a potential of 0.38 V. This is the same potential at which the bis(4-methoxyphenyl)aniline 36 is oxidized. This indicates that the triarylamine substituents at 2- and 3-position are electronically isolated from each other in the dication state of the acetal 171. The oxidation state +4, therefore, has one positive charge located at each triarylamine substituent. The fourth and final oxidation of acetal 171 at 1.00 V transferred another four electrons from acetal 171 and now the molecule reaches oxidation state +8 with two positive charges at every triarylamine, although some positive charge will be localized on the cyclopentadiene backbone. A collection of proposed VB resonance structures of acetal 171 oxidation states +1, +2, +4, and +8 are illustrated in Figure 2-21. For the unsubstituted triphenylamine-capped acetal 172 only four electrons were transferred over two oxidation waves. This result indicates the acetal was only oxidized to the +4 oxidation state, which had one positive charge per triphenylamine substituent.
Figure 2-21: Incomplete collection of proposed VB resonance structures of acetal 171 oxidation states +1, +2, +4, and +8.
The oxidation process of acetal 171 was further investigated by UV-vis-NIR absorption spectroscopy of the different oxidation states. The molecule was reacted with SET reagent tris(4-bromophenyl)ammonium hexachloroantimonate 144 (Scheme 1-41, p. 76) as an oxidizing agent. The oxidation agent comprises an oxidation potential of 0.70 V vs. Fc/Fc+. The first oxidation potential of acetal 171 is at 0.02 V, the second at 0.08 V, and the third and fourth at 0.38 V vs. Fc/Fc+. These values indicate that acetal 171 can be fourfold quantitatively oxidized with 144. A waterfall diagram of the incremental oxidation until oxidation state +4 is shown in Figure 2-22. The amount of added oxidation agent is depicted on the z-axes. The addition was performed until 10 equiv of oxidants were added. The absorption spectra at 1, 2, 3, 4, and 10 equiv of added oxidant 144 are shown in Figure 2-23.

Figure 2-22: Waterfall-diagram of the stepwise oxidation of acetal 171 with oxidant 144. The amount of added oxidant is denoted on the z-axes.

The absorption maximum of the neutral species at 454 nm slowly decayed as the absorption bands of the radical cationic species began to appear at 542 nm, 851 nm, and 1801 nm. The absorption band at 851 nm showed a vibrionic splitting of 1500 cm⁻¹ with the 0-0 transition at 851 nm and the 0-1 transition at 749 nm. The isosbestic point for the addition of the first equivalent of oxidant 144 was found at 492 nm. The addition of more than one equivalent of 144 led again to a decrease of the most red-shifted absorption band of the radical cation at 1801 nm and the formation of the dication absorption bands at 659 nm and 945 nm. Another weak absorption was present in the low-energy region at around 1250 nm, the exact position could unfortunately not be determined due to the noisy signal in this region of the spectrum. The titration process from the +1 to the +2 oxidation state revealed three isosbestic points at 1407 nm, 425 nm, and 356 nm.
The arising absorption band at 309 nm belonged to the reduced species of the oxidant 144 which is tris(4-bromophenyl)amine 145. Further addition of oxidant towards the oxidation state +3 led to a red-shift of the absorption band at 945 nm to 954 nm. A new absorption band at 778 nm was also formed. The absorption band at 659 nm of the +2 state is slightly blue-shifted to 647 nm for the +3 state. Only one isosbestic point was found for this titration step at 1030 nm. The final titration step from +3 to +4 resulted again in three isosbestic points at 1063 nm, 705 nm, and 624 nm. The absorption bands at 954 nm and 778 nm of the oxidation state +3 experienced again a red-shift in the +4 oxidation state with the new bands being located at 966 nm and 783 nm. The absorption band at 647 nm underwent a larger blue-shift and was now located at 609 nm for the +4 state. The intensity of the low-energy absorption band at approximately 1250 nm has a maximum for the +2 oxidation state but the intensity decreased again in the +3 and +4 oxidation states. Even when a large excess (10 equiv) of oxidant 144 was added, the band was still present. The spectrum, that was measured after the addition of 10 equiv of oxidant 144 is depicted in Figure 2-23 to show that after 4 equiv of oxidant 144 were added, the positions of the absorption maxima did not change anymore. The new bands at 732 nm and 367 nm were the absorption bands of the unreacted oxidant 144. The titration with the oxidation confirmed the number of transferred electrons for each oxidation step in the CV of acetal 171.

Figure 2-23: UV-vis absorption spectra at the point of addition of 0 equiv (black), 1 equiv (blue), 2 equiv (red), 3 equiv (olive), 4 equiv (cyan) and 10 equiv (orange) 40 to acetal 171 in DCM.
The cyclic voltammograms of cyclopentadienones 173 and 174 are shown in Figure 2-24. Methoxyphenyl-capped derivative 173 showed two reversible oxidation waves at 0.13 V and 0.37 V. A third quasi-reversible oxidation wave was located at 0.97 V. The phenyl-capped ketone 174 only showed two oxidation waves at 0.23 V and 0.61 V. No reductions could be observed for both ketones in the available electrochemical window (≥ -2 V). The oxidation potentials of the ketones were shifted to more positive values compared to the corresponding acetals. For methoxyphenyl-capped acetal 171, the position of the first oxidation potential shifted from 0.02 V to 0.13 V for ketone 173. Interestingly no splitting of the first oxidation wave was visible for ketone 173. The second oxidation potential ketone 173, which was the third of the acetal 171, did not shift significantly. The ketone 173 showed this oxidation at 0.37 V and the acetal 171 at 0.38 V. This was expected because the second oxidation corresponds to the oxidation of an isolated triarylamine unit. The methoxyphenyl-capped ketone 173 had a third oxidation wave at 0.97 V. The shape indicated a quasi-reversible to irreversible process and the potential did not significantly change from the value obtained for acetal 171. Integration of the current indicated that the first two oxidation waves correspond to two electrons each and the third to four electrons which is consistent with the values obtained for acetal 171. Phenyl-capped cyclopentadienone 174 showed two reversible oxidation waves at 0.23 V and 0.61 V. This corresponds to a shift of \( \Delta E = 0.07 \) V and -0.04 V compared to acetal 172. The shift of the first oxidation potential was expected due to the destabilization of the positive charge through the introduction of the ketone functionality. The second oxidation potential was not expected to change, because this oxidation corresponded to the oxidation of an isolated TAA substituents. The HOMO energy levels were calculated to -5.13 eV for ketone 173 and to -5.31 eV for ketone 174. The difference can be attributed to the methoxy substituents. The LUMO energy levels are at -3.16 eV for methoxyphenyl-capped ketone 173 and -3.21 eV for phenyl-capped ketone 174.
**Figure 2-24:** Cyclic voltammograms of cyclopentadienones 173 (blue) and 174 (red). The positions of the oxidation potentials were marked with a cross.

The cyclic voltammograms of dicyanopentafulvenes 175 and 176 are shown in **Figure 2-25**. The influence of the stronger acceptor group on the electrochemical behavior became directly visible in the shape of the curve. The cyclic voltammogram now showed one reduction wave for fulvene 175 and two reduction waves for fulvene 176 besides the two oxidation waves that were present for both pentafulvenes. The formation of the radical anion of pentafulvene 175 is a quasi-reversible behavior and took place at -1.14 V. The process was a one-electron reduction. The oxidation behavior changed drastically and now only two different oxidation waves, one fewer than for ketone 173, and two fewer for acetal 171, are visible. The first oxidation wave at 0.28 V had a reversible shape and integration indicated that four electrons were transferred at once. The second oxidation wave had a quasi-reversible shape and was located at 0.95 V. The oxidation also corresponded to four transferred electrons. The merging of the first and second (respectively first, second, and third) oxidation wave in dicyanopentafulvene 175 can be understood by having a closer look at the influence of the acceptor unit. The acceptor substituent destabilizes a positive charge on the cyclopentadiene unit. This explains why no electronic communication between the TAA substituents takes place and all four triarylamine substituents were oxidized at the same potential. The result of this destabilization is the reason why the most stable cation that is possible for this system is localized at the TAA substituents without significant delocalization on the cyclopentadiene. Alt-
hough it is noted that the oxidation took place at a potential that is 0.1 V more negative in comparison to bis(4-methoxyphenyl)aniline 177. The second oxidation wave corresponded to a dication on each TAA unit and is therefore consistent with the expectations. The reversible reduction took place at -1.04 V and corresponded to the formation of the radical anion at the dicyanovinylene unit. The HOMO energy was calculated at -5.23 eV and the LUMO energy, calculated from the reduction onset, at -4.06 eV. These values result in an electrochemical gap ($E_{\text{g}}^{\text{ec}}$) of 1.17 eV. The phenyl-capped pentafulvene 176 showed two overlapping oxidation waves. The first one occurred at 0.40 V with two transferred electrons and a reversible shape. The second oxidation wave, which also included two transferred electrons, occurred at a potential of 0.62 V. The shape of the oxidation wave was not clearly visible but still indicated a reversible behavior. The main difference in the oxidation behavior between 175 and 176 was that the formation of the +4 oxidation state took place in one step for 175 and two steps for 176. The oxidation potential was positively shifted by $\Delta E = 0.12$ V and 0.34 V for pentafulvene 176 compared to pentafulvene 175. This effect is again attributed to the missing methoxy groups at the TPA substituents. The oxidation behavior of fulvene 176 was more reminiscent of that of ketone 174 than of fulvene 175. Phenyl-capped ketone 174 showed two separated oxidation waves at 0.23 V and 0.61 V. The first oxidation of the phenyl-capped pentafulvene 176 took place at 0.40 V which is shifted by 0.17 V to more positive potentials compared to ketone 174. The second oxidation potential did not significantly shift compared to that of the ketone. This was expected because the oxidation could be attributed to the oxidation of electronically isolated TAA substituents for ketone 174. And it is the same case for fulvene 176. Phenyl-capped pentafulvene 176 showed two reduction waves at -1.08 V and -1.58 V. The shape of the first reduction wave indicated a reversible behavior while the shape of the second reduction wave pointed to a quasi-reversible behavior. The two reduction waves of phenyl-capped pentafulvene 176, in contrast to the methoxyphenyl-capped pentafulvene 175 which only showed one reduction in the available electrochemical window, could be understood by the different electron-donating strength of the triphenylamine and bis(4-methoxyphenyl)aniline substituents. The stronger electron-donating group in pentafulvene 175 led to a destabilization of a negative charge with partial localization on the cyclopentadiene. The first reduction took place at the dicyanovinylene unit and was therefore in the same range as the reduction of pentafulvene 175. A second negative charge has to be delocalized through the cyclopentadiene and is therefore only visible for fulvene 176 and not for 175 in the available electrochemical window. The effect of different substituents on the reduction properties of 6,6-dicyanopentafulvenes is well described in literature.\textsuperscript{114} The HOMO energy level was calculated to be at -5.47 eV, which is shifted by 0.24 eV compared to methoxyphenyl-capped fulvene 175. The LUMO energy level was calculated to
-4.06 eV which is the same as for pentafulvene 175. This invariance of the LUMO energy level was consistent with what is expected from the chemical intuition. The LUMO should mostly be localized at the dicyanovinylene electron-accepting group, which is identical for both fulvenes. The difference in HOMO energy levels between the two fulvenes was as well attributed to the presence of methoxy groups in fulvene 175. The electrochemical gap amounted to 1.41 eV for pentafulvene 176.

Figure 2-25: Cyclic voltammograms of pentafulvenes 175 (blue) and 176 (red). The positions of the redox potentials were marked with a cross.

The electrochemical data of acetals 171 and 172, cyclopentadienones 173 and 174, and dicyano-pentafuvenes 175 and 176 are summarized in Table 2-2.
The optoelectronic characterization of cyclopentadienone acetals 171 and 172, cyclopentadienes 173 and 174, and pentafulvenes 175 and 176 showed certain structural property relationship trends. The methoxyphenyl-capped derivatives 171, 173, and 175 were oxidized up to oxidation state +8, while the phenyl-capped derivatives 172, 174, and 176 were only oxidizable up to oxidation state +4. Interestingly, the highest oxidation potential was almost invariant within the group of methoxyphenyl-capped and phenyl-capped cyclopentadiene derivatives. For the methoxyphenyl-capped cyclopentadienes the highest oxidation potential corresponds to the formation of a dication at each TAA substituent. The obtained values were between 0.95 V and 1.00 V. For the phenyl-capped cyclopentadienes the highest potential corresponds to the oxidation of isolated TAA units. The number of transferred electrons was verified for acetal 171 by redox-titration with radical cation salt 144. The energy level of the HOMO is highest for the respective acetal and decreases for the ketone and the lowest values were obtained for the dicyanopentafulvene. The methoxyphenyl-capped cyclopentadienes always showed lower-lying HOMO energy levels compared to their phenyl-capped counterparts. The obtained HOMO energy levels were between -5.04 eV and -5.47 eV. The LUMO energy level stabilizes through the introduction of an electron-accepting group. The most stabilized LUMO energy levels are obtained for the dicyanopentafulvenes, followed by the ketones, and the acetals. The difference between the LUMO energy levels obtained for the methoxyphenyl-capped and phenyl-capped derivatives is not that pronounced as for the HOMO energy levels. The LUMO energy levels were between -2.67 eV and -4.06 eV. The optical

### Table 2-2: Collected electrochemical properties of cyclopentadienone acetals 171 and 172, cyclopentadienes 173 and 174, and pentafulvenes 175 and 176. The number of transferred electrons is listed after the respective redox potentials.

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<td>-5.47</td>
<td>-4.06</td>
<td>1.41</td>
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[a]: $E_{1/2}^{ox} = (E_{p}^{ox} + E_{c}^{ox})/2$ [b]: $E_{HOMO} = -5.1 - E_{HOMO}^{ox}$ [c]: $E_{LUMO} = E_{LUMO} - E_{HOMO}^{ec}$ [d]: $E_{LUMO} = -5.1 - E_{LUMO}^{ox}$ [e]: $E_{HOMO}^{ec} = E_{LUMO}^{ec}$
behavior of all cyclopentadiene derivatives is dominated by the different TAA substituents on the cyclopentadienes. All derivatives showed one absorption band between 304 nm and 310 nm that is always attributed to the TAA absorption. These absorption bands showed the highest intensity in each absorption spectrum. The high intensity is due to the number of equivalent chromophores present. Acetals 171 and 172 showed broad absorptions with overlapping bands between 250 nm and 500 nm. The absorption behavior changed by the introduction of an electron-accepting unit. Ketones 173 and 174 showed three different absorption bands, whereby in each molecule the most red-shifted band had a charge-transfer character with low intensity. For dicyanopentafulvenes 175 and 176, two absorption bands were visible. The introduction of the dicyanovinylene groups led to another red-shift of the absorption in comparison to the cyclopentadienones. Pentafulvenes and cyclopentadienones showed broad absorption bands in solution indicating flexibility of the arylamine substituents. The most red-shifted absorption bands (ignoring the two low-intensity charge-transfer bands) are located between 446 nm and 595 nm with extinction coefficients between 16 600 M\(^{-1}\)cm\(^{-1}\) and 29 800 M\(^{-1}\)cm\(^{-1}\). The extinction coefficients are somehow a problematic indicator of the oscillator strengths for ketones 173 and 174 and as well as for fulvenes 175 and 176 due to the diffuse shape of the absorption bands. Integration of the absorption bands revealed that the intensity of the absorption bands of the methoxyphenyl-capped cyclopentadienes was always higher than for the phenyl-capped counterparts. The cyclopentadienes showed optical gaps between 2.41 eV and 1.65 eV. The largest optical gaps were obtained for the acetals, and the gap decreased for the ketones and the pentafulvenes. The fulvenes showed the smallest optical gap of the series due to the strongest electron-accepting unit.
2.5 Thermal Characterization of Triarylamine-capped Cyclopentadiene-derivatives

All cyclopentadiene derivatives were characterized by TGA to determine the decomposition temperature of the HTMs. The samples were heated to 700 °C under a nitrogen atmosphere. The decomposition temperature ($T_{d, 95}$) was determined at 95% residual weight. The threshold is marked with a horizontal grey dashed line and the respective decomposition temperatures are marked with vertical dashed lines. The methoxyphenyl derivatives are always shown in blue while the phenyl derivatives are shown in red.

The thermogravimetric analysis of dimethyl acetals 171 and 172 is displayed in Figure 2-26. Both acetals showed the same thermal behavior with a small initial weight loss of 2% with an onset at 282 °C for the methoxyphenyl-capped acetal 171 and 2.5% at 279 °C for the phenyl-capped acetal 172. A second weight loss occurred at an onset of 419 °C for both acetals. This second weight loss continued until acetal 171 showed a residual weight of 57% and acetal 172 of only 16%. The decomposition temperature was reached at 415 °C for acetal 171 and 413 °C for acetal 172. For these acetals, it becomes evident that the typically used 95% residual weight threshold is not a good indicator for the decomposition because both acetals exhibited a small 2%, respectively 2.5% weight-loss. These weight losses took place at temperatures that are already too high to attribute the weight loss to evaporation of solvents. The correctness of the results, as well as the nature of the small weight losses, will be discussed after the DSC results further down below.
The TGA results of cyclopentadienones 173 and 174 are shown in Figure 2-27. Both ketones exhibited one large weight loss with an onset temperature of 409 °C for ketone 173 and 429 °C for ketone 174. Methoxyphenyl-capped ketone 173 here showed the lower decomposition temperature with 399 °C compared to 419 °C for phenyl-capped cyclopentadienone 174. The total weight loss for phenyl-capped ketone 174 was larger with a residual weight of only 14% compared to 27% for the methoxyphenyl-substituted ketone 173.
The obtained values of phenyl-capped ketone 174 and dimethyl acetal 172 showed a surprising similarity. Both TGAs are again shown in Figure 2-28 for comparison. Acetal 172 is plotted in a red line while ketone 174 is shown as a red dotted line. Both cyclopentadienes exhibit the same thermal behavior except for a small initial drop for acetal 172.

![Figure 2-28: Comparison between the TGAs of the dimethyl acetal 172 (solid line) and the cyclopentadienone 174 (dotted line).](image)

This discovery might be a coincidence, but another possible explanation is that the acetal undergoes thermal elimination of dimethyl ether and forms ketone 174 at around 280 °C. The thermal decomposition of acetals to the corresponding carbonyl compounds is described in literature.\cite{128}

The problem with this explanation is that dimethyl ether has a molecular mass of 46 g/mol and the loss of dimethyl ether would correspond to a weight loss of 3.4% for the methoxy- and 4.2% for the unsubstituted acetal. These values are higher than the observed values of 2% and 2.5% which well corresponds to the loss of a methoxide or a methoxy radical with a molecular weight of 31 g/mol. The formation of the ketone could therefore happen over two steps, especially in the case of acetal 172. The methoxyphenyl-capped acetal 171 showed a very different thermal behavior than methoxyphenyl-capped ketone 173 which means that in this case the ketone is not formed from the acetal during the heating process and two different thermal decomposition pathways take place here.

TGA-measurements of dicyanopentafulvenes 175 and 176 are illustrated in Figure 2-29. Both fulvenes exhibited one weight-loss event with an onset at 402 °C for methoxyphenyl-capped pentafulvene 174 and 460 °C for phenyl-capped pentafulvene 175. The decomposition temperature
was at 420 °C for methoxyphenyl-capped pentafulvene 175 and at 459 °C for phenyl-capped pentafulvene 176. The phenyl-capped derivative had again the greater overall weight loss with a residual weight of 48% at 700 °C compared to 59% for methoxyphenyl-capped pentafulvene 175.

Figure 2-29: TGA-measurements of dicyanopentafulvenes 175 (blue) and 176 (red).

After determination of the decomposition temperatures, differential scanning calorimetry was measured to determine possible melting points and glass transition temperatures if an amorphous solid is present. The data points at the beginning and the end of each scan were removed to exclude signals that were obtained from the delay in the instrument. All heating scans were performed with a heating rate of 10 °C/min. The first cooling scan was performed with 10 °C/min, the second with 5 °C/min, and the third with 2 °C/min.

Two DSC measurements of acetal 171 are shown in Figure 2-30. In the diagram depicted on the left side, the acetal was heated to 360 °C, which is 55 degrees below the 5% weight loss decomposition temperature determined by TGA. The second and third heating and cooling scans are enhanced by a factor of two for better clarity. The second DSC measurement on the left depicts another sample of the same acetal 171 that was only heated to 290 °C. The second and third heating and cooling scans here are enhanced by a factor of five. The DSC diagram depicted on the left side showed a large endothermal signal (●) with an onset at 266 °C and a peak at 269 °C followed by a smaller exothermal signal (●) with an onset at 301 °C and a peak at 321 °C. This exothermal signal was in the same temperature range as the initial 2% weight loss of acetal 171 exhibited in the TGA measurement depicted above (Figure 2-26). Therefore, it can be concluded
that the decomposition of this acetal already took place at lower temperatures than obtained from
TGA by 5% weight loss. The different onset values of this decomposition temperature obtained by
DSC and TGA are due to the different methods of determination and the different shapes of the
curves obtained by these methods. This made the determination of comparable onset values dif-
ficult. In the second heating scan, two signals were visible. The first endothermal signal (●) is
assigned to a glass transition that is overlaid with an enthalpic recovery. The combined signal
showed an onset at 134 °C and a peak at 139 °C. A second small endothermal signal (●) showed
an onset at 249 °C and a peak at 257 °C. This signal corresponds to the melting of the product
obtained after the decomposition of the acetal in the first heating scan. In the second cooling scan,
there was no visible signal. The third heating scan showed again another glass transition with
overlaid enthalpic recovery (●) at an onset at 132 °C and a peak at 138 °C. The melting peak lost
substantially intensity and was almost not visible anymore. In the DSC measurement, depicted in
Figure 2-30 on the right side, the first heating scan only showed one endothermal signal (●) and
no exothermal signal. The endothermal melting peak showed an onset at 266 °C and a peak at
268 °C. The onset, which determines the melting point, was the same as for the measurement
depicted on the left. The first cooling scan again revealed no visible signals. In the second heating
scan, a glass transition superimposed with an enthalpic recovery (●) was visible with an onset at
115 °C and a peak at 120 °C. A second endothermal signal (●) with an onset of 247 °C and a
peak at 258 °C was observed in the same scan. This signal most probably corresponds to the
melting of acetal 171 in the crystalline state. No visible crystallization took place during the cooling
scans; therefore, it was expected that the melting signals are smaller in the second and third
heating scans and take place at lower temperatures due to imperfect or no crystallization of the
acetal. In the second cooling scan, a glass transition (●) from the amorphous rubbery to the amor-
phous glassy state was visible with an onset at 125 °C. The third heating scan resulted in a glass
transition (●) from the glassy to the rubbery state at an onset at 118 °C and a peak of the enthalpic
recovery at 123 °C. The signal in dark green (●) again corresponds to the melting of the acetal.
Figure 2-30: DSC data of acetal 171. Three heating and cooling scans are shown. The arrows indicate the measuring direction. The left diagram shows an excerpt of heating scans until 360 °C, while the right is from the sample that was heated to 290 °C.

The DSC measurements of the two acetal 171 samples (Figure 2-30) confirmed that a decomposition already takes place at 301 °C and that the 5% weight loss decomposition temperature in TGA is not a sufficient indicator for this acetal. The decomposition product showed a higher glass transition temperature than that of acetal 171.

DSC measurements of acetal 172 are shown in Figure 2-31. In the diagram on the left side, the material was again heated beyond the 2.3% weight loss temperature obtained by TGA. In the diagram on the right side, the sample was heated until 290 °C. The diagram on the right side depicts all scans besides the first one enhanced by a factor of three for better viewability. In the diagram on the left-hand side a melting point (●) was visible in the first heating scan at an onset of 260 °C and a peak at 265 °C. Afterwards, there was an exothermal signal (●) with an onset at 307 °C and a peak at 328 °C. This signal again corresponds to the decomposition of the acetal. In the first cooling scan, no signals were detected. The second heating scan showed two endothermal signals, the first one (●) with an onset at 136 °C and a peak at 140 °C, the second (●) with an onset at 239 °C and a peak at 252 °C. No signals were visible in the second cooling scan either. The third heating scan had one endothermal signal (●) at an onset at 135 °C and a peak at 139 °C. In the third cooling scan, an amorphous rubbery to amorphous glassy state transition (●) was detected with an onset at 137 °C. In the diagram on the right side, the first heating scan had a melting signal (●) with an onset at 260 °C and a peak at 264 °C. The onset of the melting point was the same as for the diagram on the left side, showing the identity of the used acetal samples. The first cooling scan exhibited a glass transition (●) with an onset at 123 °C. This glass
transition and the absence of a crystallization peak indicated that the material was in an amorphous state after the cooling process. In the second heating scan, the glass transition from the amorphous glassy to amorphous rubbery state (●) with an onset at 120 °C and a peak at 124 °C was visible. The second signal was exothermal (●) and had an onset at 187 °C and a peak at 204 °C. The exothermal signal was followed by another endothermal signal (●) with an onset at 234 °C and a peak at 250 °C. Another small endothermal signal (●) could be detected, but the onset could not be determined due to an overlap with the previous signal. The three peaks can be understood by a cold crystallization (exothermal) followed by the melting of the now crystalline acetal. The crystallinity of the material was not perfect due to the quick crystallization process and this led to a lower melting point in this heating scan compared to the melting signal in the first scan. The large melting signal was most probably overlaid by a crystal perfection process, which results in the last endothermal melting signal (●) at the same temperature region than the melting in the first heating scan. The second cooling scan resulted in a glass transition (●) at 124 °C. The third heating scan revealed another glass transition that is overlaid with an enthalpic recovery (●) with an onset at 121 °C and a peak at 126 °C. A second endothermal signal (●) was detected at an onset of 250 °C and a peak at 257 °C. This signal corresponded to the melting of the acetal. The results obtained for acetal 172 were consistent with those obtained for acetal 171. The decomposition of acetal 172 started with an onset at 307 °C and the glass transition of the decomposition product was higher than that of acetal 172. Interestingly, acetal 172 exhibited a cold crystallization process that was not visible for methoxyphenyl-capped acetal 171 under the same measurement conditions. The melting point of methoxyphenyl-capped acetal 171 was 6 degrees higher than that of phenyl-capped acetal 172. The glass transition temperature was higher for acetal 172 than for acetal 171.
DSC data of methoxyphenyl-capped cyclopentadienone 173 is plotted in **Figure 2-32**. The first heating scan revealed an interesting behavior of ketone 173 that has not been observed for any of the other cyclopentadiene derivatives. Ketone 173 first underwent an exothermal phase transition (●) with an onset at 163 °C and a peak at 171 °C. This transition was attributed to a cold crystallization process of amorphous cyclopentadienone 173. The ketone then underwent a series of phase transitions that gave overlapping signals in the DSC. An endothermal transition (●) was visible with an onset at 228 °C and a peak at 236 °C, followed by an exothermal transition (●) and yet another endothermal transition (●) with an onset at 258 °C and a peak at 262 °C. These three transitions might be understood by an initial melting of imperfect crystallized ketone (endothermic process), followed by a crystal perfection (exothermic) and the melting (endothermic) of the now proper crystalline ketone. In the first cooling scan, no crystallization or glass transition was detected. The second heating scan revealed a glass transition overlaid by an enthalpic recovery (●) with an onset at 136 °C and a peak at 142 °C. The second visible endothermal phase transition (●) showed an onset at 240 °C and a peak at 255 °C. This signal was caused by the melting of the crystalline fraction of the ketone 173. The second cooling scan did not show any additional signals. In the third heating scan, another glass transition with overlaid enthalpic recovery (●) was visible at an onset at 137 °C and a peak at 144 °C.
Figure 2-32: DSC data of cyclopentadienone 173. Three heating and cooling scans are shown. The arrows indicate the measuring direction.

The DSC data of phenyl-capped cyclopentadienone 174 is illustrated in Figure 2-33. Ketone 174 had an endothermal phase transition (●) at an onset at 287 °C and a peak at 294 °C in the first heating scan. The transition was attributed to the melting of the ketone. In contrast to methoxyphenyl capped ketone 173, no cold crystallization of was visible in this heating scan. This result proofed that phenyl-capped ketone 174 was in the crystalline state before the first heating scan. This contrasts with methoxyphenyl-capped ketone 173 that was in the amorphous state and first needs to crystallize before melting was possible. The second heating scan, which is enhanced by a factor of two, revealed two endothermal phase transitions. The transition (●) at an onset at 131 °C and a peak at 136 °C was again a glass transition from the amorphous glassy to the amorphous rubbery state. The transition was again overlaid by an enthalpic recovery. The second phase transition (●) exhibited an onset at 240 °C and a peak at 255 °C. This transition corresponded to melting of imperfect crystalline material. This imperfection was the reason why the melting point was 47 degrees lower compared to the crystalline material in the first heating scan. The third heating scan resulted in another glass transition (●) with overlaid enthalpic recovery at an onset at 135 °C and a peak at 139 °C. No signals could be detected during the first, second, and third cooling scans.
Figure 2-33: DSC data of cyclopentadienone 174. Three heating and cooling scans are shown. The second heating scan is enhanced by a factor of two. The arrows indicate the direction of measuring.

The DSC measurement of pentafulvene 175 is depicted in Figure 2-34. In the first heating scan, two endothermal phase transitions were visible. The first transition (●) had an onset at 132 °C and a peak at 136 °C. The second phase transition (●) showed an onset at 250 °C and a peak at 255 °C. The first signal could be attributed to a glass transition with an overlaid enthalpic recovery, while the second signal corresponded to a melting of the pentafulvene. The second heating scan revealed the glass transition (●) at an onset at 145 °C, which was 13 degrees higher than in the first heating scan. The signal (●) in the range of 244-270 °C corresponds to a melting of the pentafulvene that was overlaid with a crystal perfection. In the first, second, third cooling scan, and the third heating scan no signals were detected.

Figure 2-34: DSC data of pentafulvene 175. Three heating and cooling scans are shown. The arrows indicate the direction of measuring.
The DSC data of pentafulvene 176 is presented in Figure 2-35. In the first heating scan, an endothermic phase transition (●) with an onset at 306 °C and a peak at 308 °C was visible. This transition was explained by the melting of the crystalline pentafulvene 176. The second heating scan, which is enhanced by a factor of two, revealed a glass transition overlaid by an enthalpic recovery (●) with an onset at 151 °C and a peak at 156 °C. In the third heating scan, that is also enhanced by a factor of two, the same glass transition with an overlaid enthalpic recovery (●) at an onset at 154 °C and a peak at 159 °C was detected. No signals were visible in the three cooling scans.

![Figure 2-35: DSC data of pentafulvene 176. Three heating and cooling scans are shown. The arrows indicate the direction of measuring.](image)

The results from all TGA and DSC measurements are summarized in Table 2-3. The cyclopentadiene derivatives 171-176 exhibited decomposition temperatures between 279 °C and 459 °C. All methoxyphenyl derivatives, except for the acetal 171, showed a lower decomposition temperature compared to that of the unsubstituted analogs. This could perhaps be attributed to the electron-donating effect of the methoxy groups, which could stabilize electron-deficient reaction intermediates with its +M effect. The exception is represented by phenyl-capped acetal 172, which had a lower decomposition temperature than the methoxyphenyl-capped acetal 171. This does not negate the general trend because the two acetals initially showed the same decomposition mechanism. The thermal stability of cyclopentadienones 173 and 174 was higher compared to corresponding acetals 171 and 172. Dicyanopentafulvenes 175 and 176 showed the highest thermal stability with decomposition temperatures above 420 °C. The phenyl-capped cyclopentadienes experienced a greater weight loss compared to the methoxy derivatives. This could be explained by two different thermal decomposition mechanisms for the two differently substituted arylamines. All cyclopentadienes were brought into an amorphous state with a high stability of the amorphous
glassy state due to glass transition temperatures above 120 °C. The glass transition temperature increased from acetals 171 and 172 to cyclopentadienes 173 and 174, and the highest values were obtained for dicyanofulvenes 175 and 176. The phenyl-capped cyclopentadiene derivatives always showed the higher glass transition temperatures than the corresponding methoxyphenyl-capped counterparts. This effect of the methoxy groups on $T_g$ must be divided into two parts. The first effect is that the molecular weight of the material is increased. According to Naito et al., an increased molecular weight should lead to an increased $T_g$ of the material. However, this effect is compensated by the increased molecular cohesion, which according to Naito et al. decreases $T_g$.[3]

The transformation from the acetal to the keto group in cyclopentadienes led to an increase in the glass transition temperature of 11 degrees, respectively 9 degrees. The increased glass transition temperature could be attributed to an increased rigidity of the cyclopentadienones compared to the acetals. The introduction of the dicyanovinylene group led to a further increase of the glass transition temperatures by 14 degrees and 19 degrees compared to the cyclopentadienones. The higher glass transition temperatures could be attributed to the increased molecular mass of the pentafulvenes compared to that of the ketones.

Table 2-3: Thermal properties of cyclopentadienone acetals 171 and 172, cyclopentadienones 173 and 174, and pentafulvenes 175 and 176 obtained from TGA and DSC measurements.

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2.6 Summary

In this chapter, the design and synthesis of a series of overcrowded tetrakis(triarylamine)-substituted cyclopentadienone dimethyl acetals, cyclopentadienones, and dicyanopentafulvenes was presented. Dimethyl acetals 171 and 172 were obtained in three steps starting from cheap, commercially available cyclopentadiene 146. The key-step involved a palladium-catalyzed fourfold Suzuki-type cross-coupling reaction of tetrabromocyclopentadienone dimethyl acetal 164 and triarylamine boronic esters 103 and 108 in 74% and 54% isolated yield, respectively. The synthesis and structures of acetals 171 and 172 were confirmed by single-crystal X-ray crystal diffraction analysis and high-resolution FTICR-MALDI mass spectrometry. Deprotection of the cyclopentadienone dimethyl acetals 171 and 172 to the corresponding cyclopentadienones 173 and 174 was performed under mild reaction conditions with acetone and iodine catalysis in 61% and 69% isolated yield, respectively. The Knoevenagel-condensations of the respective cyclopentadienones, performed by Florian Stümpges during his Bachelor Thesis, resulted in the formation of dicyanopentafulvenes 175 and 176 in 49 and 50% isolated yield, respectively. All cyclopentadienone derivatives were electrochemically characterized by cyclic voltammetry and optical properties were determined with UV-vis absorption spectroscopy. All methoxy-capped cyclopentadienone derivatives were eightfold oxidized, while all phenyl-capped cyclopentadienone derivatives were fourfold oxidized in the available electrochemical window. The obtained HOMO energy levels are between -5.04 eV and -5.17 eV for acetals 171 and 172, -5.13 eV and -5.31 eV for cyclopentadienones 173 and 174, and -5.23 eV and -5.47 eV for pentafulvenes 175 and 176. The obtained HOMO energy levels allow to use acetals 171 and 172, and cyclopentadienone 173 as HTM in perovskite solar cells. On the other hand, the HOMO energy levels of cyclopentadienone 174 and pentafulvenes 175 and 176 are too low and could lead to a bad charge extraction. Investigation of the thermal behavior revealed that acetals 171 and 172 showed a significantly lower decomposition temperature than the other cyclopentadienones 173 and 174 or pentafulvenes 175 and 176. The decomposition temperatures of 282 °C and 279 °C could be directly linked to the dimethyl acetal group. The decomposition temperatures of the other cyclopentadienes were all above 399 °C. All investigated cyclopentadiene derivatives have been shown to be existent in both a crystalline and an amorphous state. All phenyl-capped cyclopentadienes showed a higher glass transition temperature than their methoxyphenyl-capped counterparts. All obtained glass transition temperatures are above 120 °C rendering the cyclopentadienes as good candidates for applications, in which thermal stability is required such as HTMs in Perovskite solar cells.
3 Perovskite Solar Cells

3.1 Introduction

In this chapter, the application of the synthesized CPDTs and the cyclopentadienone dimethyl acetal 171 in state of the art perovskite solar cells is described. The design rules for thermal stable materials with fitting FMO energy levels that were created in Chapter 1 and 2 are examined here through the use of the synthesized molecules as HTMs. By identifying structure-property relationships, it is anticipated that suggestions for improvements for the next generation of HTMs can be derived. This step is very important because the prediction of material properties from molecular properties is still very difficult.

At first a short introduction into the field of perovskite solar cells and their historical development from DSSCs is given. The developments that improved the PCE from 3.8% in 2009 to over 25% today are shown. An overview about the most commonly applied HTM spiro-MeOTAD 11 and its problems are discussed. This is followed by an overview about the most efficient organic HTMs that have been published together with their thermal characterization.

The electrochemical characterization of the “gold-standard” HTM spiro-MeOTAD 11 is discussed to ensure comparability with the data obtained in Chapter 1 and 2. This is followed by the exemplary full characterization of spiro-CPDTA 109 based PSCs including long-term stability and thermal stability data. The results will be discussed with respect to the spiro-MeOTAD reference devices. The PSC results of spiro-CPDTA 109, spiro-CPDTT 124, and DP-CPDT 137 and 138 are shortly discussed. This is followed by the characterization of a cyclopentadienone dimethyl acetal 171 based PSC. The chapter is concluded by the summary of the results.
3.2 State of the Art

The original perovskite mineral calcium titanate CaTiO$_3$ was discovered in 1839 and named for Russian mineralogist Lev Perovski. All perovskites are defined by their AMX$_3$-type composition and the perovskite crystal structure. In the ideal perovskite crystal structure, the cation “A” occupies a twelfold coordination site and is flanked by eight MX$_6$ octahedra.[131] The first methylammonium (MA) lead halide perovskites were first synthesized in 1978 by Dieter Weber.[132] The perovskite structures were obtained by mixing an aqueous methylamine solution with the respective hydrohalic acid and adding Pb(NO$_3$)$_2$ as lead-source at temperatures of around 100 °C. The synthesis of the deeply colored lead halide perovskites was confirmed by XRD. Nowadays hybrid organic-inorganic lead perovskite materials are highly interesting as light-absorbing materials in solar cells. These perovskite absorber materials possess desirable properties such as high extinction coefficients, high charge carrier diffusion length and low exciton binding energies.[133-135] The first PSC was created by Miyasaka et. al. who employed two hybrid perovskites MA$\text{PbBr}_3$ and MA$\text{PbI}_3$ in the form of nanocrystals as light sensitizer on TiO$_2$ in a DSSC.[130] The MA$\text{PbI}_3$ perovskite absorber possesses the smaller optical gap of the two perovskite materials and could harvest photons up to 800 nm. This led to a high short-circuit current density ($J_{SC}$) of 11.0 mA/cm$^2$ and a modest open-circuit voltage ($V_{OC}$) of 0.61 V resulting in a PCE of 3.81% of the PSC. The second perovskite absorber MA$\text{PbBr}_3$ exhibited a lower $J_{SC}$ with 5.6 mA/cm$^2$ but a higher $V_{OC}$ of almost 1 V due to its larger optical gap when employed in a PSC. This resulted in a PCE of 3.13% of the device. The liquid electrolyte containing acetonitrile or methoxyacetonitrile led unfortunately to a dissolving of the perovskite sensitizer and therefore to solar cell lifetimes in the range of minutes. But the excellent optoelectronic properties of the lead halide perovskite sparked further interest in the material. The design and stability of the PSC was improved by Park et.al. in 2011 through the employment of MA$\text{PbI}_3$ nanocrystals and an electrolyte containing the iodide-triiodide redox-shuttle in a mixture of EA, tert-butylpyridine and urea.[136] The PSC exhibited now a higher $J_{SC}$ of 16 mA/cm$^2$ and higher $V_{OC}$ of 0.63 V resulting in a PCE of 6.2%. But the liquid electrolyte proofed to be a problem because the perovskite nanocrystals still dissolved in it leading to a solar cell lifetime of around 10 minutes. The solution to the dissolution of the perovskite absorber material was the use of solid-state electrolytes. The use of spiro-MeOTAD (11, Figure 1-5 p. 5) as a HTM together with MA$\text{PbI}_3$ as absorber resulted in an impressive PCE of 9.7% at a $J_{SC}$ of 17 mA/cm$^2$ and a $V_{OC}$ of 0.89 V.[137] The solid state electrolyte spiro-MeOTAD led to a dramatic increase in the solar cell lifetime with long term stability of over 500 hours. The threshold of 10% PCE was first exceeded by Snaith et. al. who demonstrated that the perovskite absorber does not
have to be in the form of nanoparticles. The highly crystalline MAPbI$_2$Cl perovskite was formed directly by spin coating of a precursor solution of 3:1 MAI to PbCl$_2$ in DMF on a mesoporous TiO$_2$ or Al$_2$O$_3$ layer. The replacement of the mesoporous n-type semiconductor TiO$_2$ with the mesoporous insulator Al$_2$O$_3$ lead to the best PCE of 10.9%. Spiro-MeOTAD was again used as HTM leading to a device structure of fluorine-doped tin oxide (FTO)/compact TiO$_2$ (c-TiO$_2$)/mesoporous Al$_2$O$_3$ (m-Al$_2$O$_3$), MAPbI$_2$Cl, spiro-MeOTAD/Ag.$^{[138]}$ The improved PCE upon the use of the insulator Al$_2$O$_3$ lead to the discovery that the lead halide perovskite can also act as a n-type semiconductor material. In 2013 Snaith et. al. demonstrated that the mesoporous metal oxide layer (defining the mesoscopic PSC) is not necessary for the functionality of a PSC. A simplified planar architecture of FTO/c-TiO$_2$/perovskite absorber/spiro-MeOTAD/Au led to a $J_{SC}$ of 20.3 mA/cm$^2$, $V_{OC}$ of 0.89 V and a PCE of 11.4%. This planar architecture could potentially lead to easier and cheaper manufacturing of larger scale PSCs.$^{[139]}$ Since the PSC was developed from the DSSC, its n-i-p structure is usually used. An alternative is the inverted planar PSC based on the p-i-n structure of organic solar cells. In this p-i-n structure poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is coated on a FTO substrate as a HTM, followed by the perovskite absorber and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM[61]) as electron transport material. A small layer of titanium oxide was introduced between the PCBM[61] and the aluminum top electrode for better contacting. The inverted planar PSC resulted in a $J_{SC}$ of 15.8 mA/cm$^2$, $V_{OC}$ of 0.94 V and a PCE of 9.8%.$^{[140]}$ Replacement of MA cations with formamidinium (FA) cations led to the development of perovskite absorber materials with bandgaps as low as 1.48 eV. This perovskite material was employed in a planar p-i-n PSC and achieved a high PCE of 14.2%. The good performance was mainly attributed to an enhanced $J_{SC}$ of 23.3 mA/cm$^2$ due to the lower bandgap.$^{[141]}$ However the FA based perovskite proofed to be instable at room temperature and slowly converts to a yellow δ-phase. This problem was addressed by the development of a mixed “A”-cation perovskite. The FA cations were partially replaced by Cs$^+$ and MA resulting in a perovskite composition of Cs$_{0.2}$FA$_{0.8}$PbI$_{2.84}$Br$_{0.16}$. This mixed cation perovskite showed excellent stability at room temperature and even at elevated temperatures of up to 250 °C under nitrogen atmosphere or up to 150 °C in air. The increased stability was attributed to mixing entropy gains. The mixed cation perovskite absorber was employed in an FTO/c-TiO$_2$/mesoporous titanium dioxide (m-TiO$_2$), perovskite, Spiro-MeOTAD/Au device structure and revealed a $J_{SC}$ of 23.3 mA/cm$^2$, $V_{OC}$ of 1.07 V, a fill factor (FF) of 73.3%, and a PCE of 18.0% beating pure FAPbI$_3$ (PCE: 10.4%).$^{[142]}$ The incorporation of different cations into the perovskite structure was taken one step further by Saliba et. al. Rubidium was added as another non-oxidizable cation into the mixture. The rubidium, which does not form a perovskite phase by itself in a RbPbI$_3$ composition, interestingly further stabilized the
perovskite phase in the mixed cation perovskite. The replacement of 5% “A”-cation by Rb+ seemed to achieve the best results in a mesoscopic PSC structure with PCE of 21.6% and stabilized performance of 95% of the initial value over 500 hours at 85 °C and maximum power point tracking under nitrogen atmosphere.\textsuperscript{143} Inorganic HTMs have been investigated as an alternative to spiro-MeOTAD. The most efficient inorganic HTM is copper thiocyanate (CuSCN) which led to a PCE of 20.3% in a PSC. Although a layer of reduced graphene oxide was needed as a spacer between the HTM and the top gold electrode to prevent degradation.\textsuperscript{144} It is noted here that HTM-free PSCs are also possible because the hybrid organic-inorganic lead perovskite is not only a n-type but also a p-type semiconducting material. However, HTM-free PSCs do not reach the efficiencies of that HTM-containing do.\textsuperscript{145-147}

Perovskite solar cells now have surpassed a PCE of 25% beating multi-crystalline silicon solar cells.\textsuperscript{129} In recent years the development of silicon/perovskite or copper indium gallium selenide (CIGS)/perovskite solar cells has seen a lot of progress.\textsuperscript{148} This tandem architecture is seen as a method to surpass the Shockley-Queisser limit of around 33% PCE for a single-junction solar cell.\textsuperscript{149} Silicon/perovskite tandem solar cells have now surpassed single-crystalline silicon solar cells and are approaching PCEs of 30%.\textsuperscript{129, 148}

The dramatic increase of the stability of the perovskite absorber material revealed the HTM spiro-MeOTAD as new “Achilles’ Heel” of the PSC.\textsuperscript{143} The problems of spiro-MeOTAD include its low \( T_g \) at 120 °C, its permeability for the metal electrode diffusion at elevated temperatures, and harmful changes to the perovskite/spiro-MeOTAD layer upon heating.\textsuperscript{33, 150-151} Other problems with spiro-MeOTAD are its high cost, environmental impact, and the need for dopants and additives.\textsuperscript{152-154} These shortcomings of spiro-MeOTAD led the a necessity to synthesize and investigate new HTMs. There are certain requirements for a good HTM which need to be met.\textsuperscript{155-156} The HTM should possess a HOMO energy level that is higher than the edge of the perovskite valence band to allow efficient charge-carrier extraction. The hole mobility of the HTM should be in the range of \( 10^{-3} - 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) without the use of dopants or additives if possible. The HTM should further possess a thermal stable amorphous state with the \( T_g \) above 120 °C. The optical gap of the HTM should be relatively large if an application in a tandem solar cell is planned. However, small gap HTMs have been successfully employed in PSCs and are usable if no tandem structure is planned.\textsuperscript{57}

The range of newly synthesized HTMs used in PSC is summarized in two new and several old reviews.\textsuperscript{35, 154-158} This section here will focus on organic HTMs with PCEs > 20% and reported \( T_g \).
The most common employed molecular HTM is still spiro-MeOTAD 11. Spio-MeOTAD is usually doped with tert-butylpyridine (tBP), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and Co(III) salts. The tBP additive interacts with the perovskite surface and leads to a greater selectivity towards holes through p-doping of perovskite film surface.\(^{[159]}\) LiTFSI is attributed with promoting the oxidation (and therefore p-doping) of the spiro-MeOTAD by oxygen.\(^{[160]}\) Cobalt(III) salts directly oxidize the HTM. The problem is that all additives lead to a faster degradation of the perovskite solar cell through a variety of mechanisms.\(^{[157]}\) LiTFSI is a hygroscopic salt that accelerates the degradation of the PSC through hydrolysis of the perovskite layer in humid environments. The salt is additionally to blame for a decreased adhesion at the perovskite/HTM interface.\(^{[161]}\) The tBP can either degrade the perovskite layer directly through the formation of complexes with PbI\(_2\) or it can act as plasticizer and can reduce the \(T_g\) of spiro-MeOTAD to around 70 °C.\(^{[162}-163\) The reported HOMO energy level of spiro-MeOTAD has a large fluctuation range dependent on the method used. A common reported value is -5.16 eV.\(^{[35]}\)

In the following the absence of the two additives tBP and LiTFSI and not the presence is noted due to their prevalence in preparation of HTMs for PSCs.

The TAA capped thiophene based HTM (Z26) 181 in Scheme 3-1 was synthesized by a twofold Horner–Wadsworth–Emmons (HWE) reaction of thiophene dicarboxaldehyde 182 and TAA phosphonic ester 183 in 53% isolated yield. This makes the synthesis of the HTM one of the few which did not require a transition metal catalyst cross-coupling step. The HTM 182 with an HOMO energy level at -5.16 eV was employed in a n-i-p mesoscopic PSC with FA\(_{0.81}\)Pb\(_{0.85}\)I\(_{2.51}\) (MAPbBr\(_{3}\))\(_{0.15}\) mixed cation perovskite and resulted in a PCE of 20.1% with a \(J_{SC}\) of 23.5 mA/cm\(^2\), \(V_{OC}\) of 1.13 V, and an FF of 75%. The disadvantage of this simple HTM is its low \(T_g\) of 98 °C due to the low molecular weight and planar structure.\(^{[164]}\)

\[
\begin{align*}
\text{MeO} &+ \text{MeO} \quad \text{H}_2\text{O} \quad \text{H}_2\text{CO} \quad \text{N} \\
\text{O} &+ \text{O} \quad \text{N} \quad \text{O} \quad \text{O} \\
\text{O} &+ \text{O} \quad \text{N} \quad \text{O} \\
\text{O} &+ \text{O} \quad \text{N} \quad \text{O} \\
\text{O} &+ \text{O} \quad \text{N} \quad \text{O} \\
\text{O} &+ \text{O} \quad \text{N} \quad \text{O} \\
\end{align*}
\]

**Scheme 3-1:** Synthesis of the HTM Z26 181 by a HWE reaction.\(^{[164]}\)

The planarized starburst HTM DCZ-O\text{MeTAD} 184 (Figure 3-1) is mentioned due to its relatively high \(T_g\) of 130 °C. The HTM with a HOMO energy level of -5.27 eV was successful used in a planar
n-i-p PSC with the mixed FA/MA cation perovskite. The HTM resulted in a device performance with a PCE of 21.6% with an excellent FF of 81% at $J_{SC}$ of 25.1 mA/cm$^2$ and a $V_{OC}$ of 1.06 V.$^{[165]}$

![Figure 3-1: Structure of the planar starburst HTM DCZ-OMeTAD 184.\[165]\]

The CPDT-based HTM FDT 47 (Scheme 1-9 p. 10) is mentioned here again because it was one of the first alternatives to spiro-MeOTAD with a PCE > 20%. The HTM with a $T_g$ of 110 °C and a HOMO energy level of -5.16 was employed in a mesoscopic PSC with a (FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$ perovskite absorber. The HTM reached a PCE of 20.2% with an FF of 76% a $J_{SC}$ of 22.7 mA/cm$^2$ and a $V_{OC}$ of 1.14 V. The advantages of the FDT 47 are the lower cost and the possibility to process the HTM from toluene instead of chlorobenzene. However, the lower $T_g$ compared to spiro-MeOTAD could lead to stability problems.$^{[45]}$

Another low-cost HTM is the spiro-xanthene based X55 185. It was synthesized in a “one-pot” Buchwald-Hartwig reaction by first mixing dibrominated spiro-xanthene-fluorene 186 with 4-methoxyaniline 187 with a palladium(0) catalyst, 1,1′-bis(diphenylphosphino)ferrocene (dppf) as ligand and NaOtfBu as base (Scheme 3-2). The monobromo spiro-xanthene-fluorene 188 was added afterwards and the mixture was heated again to afford the HTM 185 in 84% yield. The HTM exhibited a very high $T_g$ of 174 °C due to the high molecular weight and the three spiro-functionalities. The HTM with a HOMO energy level of -5.23 eV was used in a mesoscopic n-i-p type PSC with the mixed-cation (FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$ perovskite absorber material. A PCE of 20.8% with an FF of 77% a $J_{SC}$ of 23.4 mA/cm$^2$ and a $V_{OC}$ of 1.15 V was obtained. The PSC also showed an enhanced stability compared to that of a spiro-MeOTAD reference device. The increases stability was attributed to an enhanced hydrophobicity of the HTM 185.$^{[166]}$
Scheme 3-2: One-pot synthesis of spiro-xanthene based HTM X55 185.[166]

The dithienopyrrole (DTP) based HTM DTP-C6Th 189 (Scheme 3-3) was synthesized starting from DTP bisstannate 190 and 2-bromo-4-TAA-thiophene 191 in a palladium-catalyzed Stille-type cross-coupling reaction in 85% yield. The DTP based HTM was used with an FTO/SnO₂/C₆₀-SAM/MA₀.7FA₀.3Pb(I₀.925Br₀.075)/HTM/Au device architecture. The PSC resulted in a PCE of 21% with \( J_{SC} \) of 22.7 mA/cm² and a \( V_{OC} \) of 1.15 V. The solar cell exhibited stability over 60 days in the glove-box and retained 85% of the initial PCE after 60 days under ambient conditions. The HTM had a HOMO energy level of -5.03 eV (determined by photoelectron spectroscopy) and a low \( T_g \) of only 84.5 °C. The poor stability of the amorphous phase is explained by the planar structure of the molecule.[167]
The bis(thienothiophene) based D-A-D HTM MPA-BTTI 192 was synthesized starting from anhydride 193 (Scheme 3-4). The anhydride was converted to the imide 194 with \textit{n}-dodecylamine, followed by twofold bromination with NBS to form aryl bromide 195, cross-coupling to TAA boronic ester 103 (Scheme 1-26, p. 29) to afford the HTM 192 in 31\% yield over three steps. MPA-BTTI 192 exhibited remarkable thermal stability with a $T_g$ of 256 °C. The HOMO energy level of -5,24 eV and an optical gap of 1.92 eV put this HTM in between the small-gap and large-gap materials. The HTM was used in an inverted planar p-i-n structure PSC together with C60 as electron transport material. The characterization of the PSC revealed a PCE of 21.19\% at a $J_{SC}$ of 23.2 mA/cm$^2$, a $V_{OC}$ of 1.12 V, and an FF of 81.4\%. Interestingly neither dopants nor additives were needed despite the relatively low mobility of $2 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ (determined by charge space-charge-limited-current (SCLC)) of HTM 192. The device kept 90\% of its initial PCE after 500 hours at maximum power point under ambient conditions. HTM 192 is the current record holder for dopant-free HTMs in inverted planar PSC.$^{168}$
Another low-cost HTM which did not require dopants nor additives is the spiro-fluorene based HTM DFH 196 (Scheme 3-5). The HTM was synthesized in two steps starting from dibrominated fluorenone 45. The aryl bromide 45 was coupled to ditolylamine 197 in a Buchwald-Hartwig cross-coupling reaction in 89% yield. The ketone 198 was reacted with ethylene glycol under acid catalysis to introduce the spiro functionality in 82% isolated yield. The HTM exhibited a similar thermal stability as spiro-MeOTAD with \( T_g \) at 120 °C. DFH was employed in an inverted planar p-i-n PSC with C\(_{60}\) as electron transport material and resulted in a PCE of 20.6% with a \( J_{SC} \) of 22.6 mA/cm\(^2\), a \( V_{OC} \) of 1.10 V, and an FF of 82.9%.\textsuperscript{169}

### 3.3 Application of Cyclopentadithiophene and Cyclopentadiene HTMs in Perovskite Solar Cells

The application of the in Chapter 1 and 2 synthesized organic HTMs in state of the art PSCs were performed at EPFL Lausanne in the group of Prof. Michael Grätzel.

A CV of spiro-MeOTAD was measured as a prerequisite to obtain comparable FMO energy levels to discuss the performance of the synthesized HTMs with respect to spiro-MeOTAD. Cyclic volt-
symmetry was performed with the same conditions applied in Chapter 1 (p. 59) to ensure comparability of the results. The CV of spiro-MeOTAD 11 is illustrated in Figure 3-2. The oxidation was measured until 1 V vs Fc/Fc⁺. It is clearly visible that spiro-MeOTAD 11 exhibited three oxidation waves at potentials of -0.01 V, 0.12 V and 0.33 V. The onset of a fourth oxidation at around 1 V could also be detected. For spiro-MeOTAD 11 the oxidation waves could be attributed to one, one, two and four transferred electrons. The HOMO energy level of spiro-MeOTAD was calculated from the onset of the oxidation and it is located at -5.04 eV vs. vacuum. The discrepancy between the obtained value of -5.04 eV and the literature value of -5.16 eV needs to be considered when discussing the $V_{oc}$ of PSC with the HTMs employed.

![Figure 3-2: Cyclic voltammogram of HTM spiro-MeOTAD 11. The positions of the redox potentials were marked with a cross.](image)

PESA was used to obtain another value for the HOMO energy level trough the determination of the work function. The calculated value should help to evaluate whether the electrochemical measurement is accurate or not. The PESA data is depicted in Figure 3-3. The work function was determined in the same manner as in Chapter 1 (p. 73) with the help of linear interpolation. The measurement revealed a work function of 5.01 eV for spiro-MeOTAD 11. This value is close to the one obtained through electrochemical characterization. The spiro-MeOTAD exhibits the same trend as the investigated CPDTs namely that the obtained work function is smaller (in absolute values) than the obtained HOMO energy level.
The spiro-cyclopentadithiophene-acridine 109 was employed in a state of art mesoscopic n-i-p PSC with the triple cation (CsI)$_{0.05}$(FAPbI$_3$)$_{0.90}$(MAPbBr$_3$)$_{0.10}$ perovskite absorber.$^{[86]}$ The performance of HTM 109 was compared to that of a reference spiro-MeOTAD 11 PSC and the long-term stability with and without thermal stress was investigated. The hydrophobicity of the employed HTMs was investigated using contact angle measurements between the perovskite films that were coated with the respective HTMs. The contact angles after 0 minutes, 15 minutes, and 30 minutes are illustrated in Figure 3-4 (a) for spiro-MeOTAD 11 and (b) for spiro-CPDTA 109. The initial contact angle of 70.8° for the water droplet on the spiro-MeOTAD film quickly decreased to 54.1° after 15 minutes and to 38.9° after 30 minutes. This revealed the susceptibility of the spiro-MeOTAD based device to humidity. The spiro-CPDTA 109 toped perovskite on the other hand only showed a moderate decay of the contact angle from 73.1° at 0 minutes, to 68.2° at 15 minutes, and 60.6° at 30 minutes underscoring the higher hydrophobicity of HTM 109 compared to spiro-MeOTAD. This could possibly lead to a reduced vulnerability of the PSC towards moisture. Time-integrated and time-resolved photoluminescence (PL) was used to investigate the hole-extraction properties of spiro-MeOTAD and spiro-CPDTA 109. The time-integrated PL is depicted in Figure 3-4 (c) and the time-resolved in Figure 3-4 (d). The perovskite film revealed a strong PL that was quenched when either spiro-MeOTAD or HTM 109 was deposited. The time-resolved PL
showed alike PL lifetimes of around 15 ns for both HTMs hinting towards similar charge extraction kinetics.

Figure 3-4: (a) Contact angle of water on a spiro-MeOTAD toped perovskite film. (b) Contact angle of water on a HTM 109 toped perovskite film. (c) Time-integrated PL spectra of the perovskite with and without HTMs. (d) Time-resolved PL decays from perovskite films with and without HTMs. Adapted with permission from S. Akin, M. Bauer, R. Uchida, N. Arora, G. Jacopin, Y. Liu, D. Hertel, K. Meerholz, E. Mena-Osteritz, P. Bäuerle, S. M. Zakeeruddin, M. I. Dar, M. Grätzel, ACS Appl. Energy Mater. 2020, 3, 7456-7463. Copyright 2020 American Chemical Society.

The fabricated PSC were characterized through their current-voltage characteristics (Figure 3-5 (a,d,e)), their external quantum efficiency (Figure 3-5 (b)), and stabilized output power (SOP) (Figure 3-5 (c)). The current-voltage characteristics revealed a $J_{SC}$ of 24.7 mA/cm$^2$, a $V_{OC}$ of 1.10 V, an FF of 77%, and a resulting PCE of 21.0% for spiro-CPDTA 109, while the spiro-MeOTAD reference device showed a $J_{SC}$ of 24.4 mA/cm$^2$, a $V_{OC}$ of 1.14 V, an FF of 76%, and a resulting PCE of 21.1%. The spiro-CPDTA 109 revealed the better $J_{SC}$ and FF and only had the lower PCE due to the 0.04 V lower $V_{OC}$. Interestingly the $V_{OC}$ of HTM 109 is lower by around the same amount by which the HOMO energy level is higher than that of spiro-MeOTAD 11. The $J_{SC}$ obtained by integration of the EQE spectra (Figure 3-5 (b)) showed no differences between the two HTMs and was in good agreement with the previously obtained values. The same can be said for the SOP where stabilized PCEs of 20.6% respectively 20.7% were obtained for spiro-CPDTA 109 and spiro-MeOTAD 11 (Figure 3-5 (c)). The shape of the forward and reverse current-voltage scans did not show a hysteresis effect for both HTMs (Figure 3-5 (d,e)). The reproducibility of the results
was verified by the preparation of 25 cells with each HTM. The histogram of the obtained PCEs is depicted in Figure 3-5 (f). The low spread of the obtained PCEs underscores the good reproducibility of the results.

![Figure 3-5](image)

**Figure 3-5:** (a) Current-voltage characteristics of the top PSC with spiro-MeOTAD 11 and spiro-CPDTA 109. (b) Integrated EQE spectra for both HTMs. (c) SOP tracking of both devices. (d) Current-voltage characteristics of the top PSC with spiro-MeOTAD 11. (e) Current-voltage characteristics of the top PSC with spiro-CPDTA 109. (f) Histogram of the PCEs obtained from 25 cells each. Adapted with permission from S. Akin, M. Bauer, R. Uchida, N. Arora, G. Jacopin, Y. Liu, D. Hertel, K. Meerholz, E. Mena-Osteritz, P. Bäuerle, S. M. Zakeeruddin, M. I. Dar, M. Grätzel, *ACS Appl. Energy Mater.* 2020, 3, 7456-7463. Copyright 2020 American Chemical Society.

The long-term device stability of the PSCs was investigated by 400 hours continuous illumination at maximum power point under nitrogen atmosphere (**Figure 3-6 (a)**). The spiro-CPDTA 109 based device exhibited a small initial drop of 10% of the initial PCE after 40 hours and stabilizes at this value for the whole duration of the measurement. The spiro-MeOTAD 11 based device lost almost 50% of its initial PCE after 30 hours but regained some of the initial PCE and stabilized at
around 65% of the initial PCE. The differences in the stability of the spiro-MeOTAD and spiro-CPDTA based devices become even more apparent under thermal stress (Figure 3-6 (b)). The PSCs were heated at first to 60 °C for around 50 hours, then to 70 °C for around 60 hours and finally to 80 °C for another 60 hours. At 60 °C the normalized PCE of the spiro-MeOTAD and spiro-CPDTA 109 based devices began to diverge at a temperature of 70 °C. The spiro-MeOTAD based device fell to around 60% of the initial PCE during the 70 °C phase while the spiro-CPDTA based device only fell to around 90%. In the 80 °C temperature phase the spiro-MeOTAD device experienced accelerated deterioration and dropped to 10% of the initial PCE. The spiro-CPDTA based device retained around 75% of the initial PCE even after 60 hours at 80 °C.

Figure 3-6: (a) Maximum power point tracking of the PSC over 400 hours at room temperature. (b) Maximum power point tracking of the PSC at elevated temperature. Adapted with permission from S. Akin, M. Bauer, R. Uchida, N. Arora, G. Jacopin, Y. Liu, D. Hertel, K. Meerholz, E. Mena-Osteritz, P. Bäuerle, S. M. Zakeeruddin, M. I. Dar, M. Grätzel, ACS Appl. Energy Mater. 2020, 3, 7456-7463. Copyright 2020 American Chemical Society.

The excellent result of the HTM spiro-CPDTA 109 in a PSC validates the design strategy of the HTMs with stable amorphous state that was employed in Chapter 1. The excellent long-term and thermal stability of the spiro-CPDTA 109 based device can be directly linked to the higher \( T_g \) of the HTM in comparison to that of spiro-MeOTAD. The good hole-extraction of HTM 109 can partially be attributed to the optimized HOMO energy level with an offset to the perovskite valence band at -5.4 eV. The lower \( V_{OC} \) of the spiro-CPDTA 109 based device could possibly be fixed by
the application of phenyl-capped spiro-CPDTA 110 which has a lower HOMO energy level. However, the HTM 110 based device did only show initial PCEs of around 10% and was therefore not further optimized.

Spiro-thioxanthene based HTM 124 was employed in a triple-cation PSC. The device showed a good performance with a $J_{sc}$ of 23.70 mA/cm$^2$, a $V_{oc}$ of 1.25 V, an FF of 75%, and a PCE of 18.3% in the reverse scan. The device showed unfortunately a large hysteresis reducing the FF and resulting in a weak performance of a $J_{sc}$ of 23.88 mA/cm$^2$, a $V_{oc}$ of 1.21 V, an FF of 60%, and a PCE of 14.8% in the forward scan. Further optimization is necessary to enhance to performance of the xanthene 124 as HTM in a PSC.

The DP-CPDT based HTMs 137 and 138 were also employed in n-i-p mesoscopic PSC together with a triple-cation perovskite absorber.$^{[170]}$ Methoxyphenyl capped 137 revealed a $J_{sc}$ of 24.5 mA/cm$^2$, a $V_{oc}$ of 1.11 V, an FF of 78%, and a PCE of 21.1%. The phenyl-capped DP-CPDT 138 showed a $J_{sc}$ of 22.9 mA/cm$^2$, a $V_{oc}$ of 1.08 V, an FF of 75%, and a PCE of 18.5%. The weaker performance of DP-CPDT 138 can be seen in all parameters. The lower $V_{oc}$ is especially interesting because the phenyl capped 138 has a HOMO energy level of -5.13 eV and is therefore 0.1 eV lower than that of methoxyphenyl capped 137. The lower offset between the HOMO energy level of the HTM and the edge of the valence band of the perovskite absorber material in the HTM 138 based device should theoretically lead to a higher $V_{oc}$. However, the absence of this effect demonstrates once again that a simple correlation between the HOMO energy level of the HTM and $V_{oc}$ of the PSC does not exist. But the lower HOMO energy level of HTM 138 could lead to a poorer hole extraction due to the lower offset, which could explain the lower $J_{sc}$ of the PSC compared to the 137 based PSC. The presence of methoxy groups in a HTM are known to passivate defects at the perovskite interface and to provide a beneficial interaction between the perovskite and the HTM.$^{[171-173]}$ In this context it appears to always be a beneficial to introduce methoxy groups into a HTM molecular structure as long as the FMO energy levels do not shift to much into an unfavorable region.

Of the cyclopentadiene based HTMs synthesized in Chapter 2, only the methoxyphenyl capped cyclopentadienone dimethoxy acetal 171 was employed as a HTM in PSC.$^{[174]}$ A triple cation FA$_{0.85}$MA$_{0.1}$Cs$_{0.05}$Pb(I$_{0.97}$Br$_{0.03}$)$_3$ absorber material with high iodide content was used together with HTM 171. The champion PSC showed an impressive PCE of 23.1% with a $J_{sc}$ of 25.6 mA/cm$^2$, a $V_{oc}$ of 1.10 V, and an FF of 82%, beating the spiro-MeOTAD 11 reference device that had a PCE of 22.6%. The device based on HTM 171 exhibited the greater thermal stability and showed only a drop of 10% in the PCE after 250 hours at 80 °C compared to a 30% drop for the spiro-MeOTAD
based device. This behavior seems strange at first glance because both spiro-MeOTAD and HTM
171 show glass transition temperatures at around 120 °C and should therefore possess similar
thermal stabilities. But the situation drastically changed when dopants and additives were added.
The $T_g$ of spiro-MeOTAD was reduced by around 40 degrees while the $T_g$ of acetal 171 only mar-
ginally decreased. The HTM 171 was the only investigated HTM that could beat the spiro-Me-
OTAD reference device. The great performance, its straight-forward low-cost synthesis, and the
high thermal stability could make acetal 171 a very good candidate to replace spiro-MeOTAD in
PSCs.
3.4 Summary

In this chapter the performance of spiro-CPDTAs 109 and 110, spiro-CPDTT 124, DP-CPDTs 137 and 138, and cyclopentadienone dimethyl acetal 171 as HTMs in PSCs was described. Acridine 109 and DP-CPDT 137 both showed performances that were comparable to that of spiro-MeOTAD with a PCE of around 21%, while acetal 171 even surpassed it with a PCE > 23%. Acridine 110, thioxanthene 124 and DP-CPDT 138 demonstrated performances that were worse than that of spiro-MeOTAD. The hysteresis effect in the measurement of spiro-CPDTT 124 indicated an insufficient hole extraction from the material. The long-term and thermal stability of the PSCs employing acridine 109, acetal 171, and DP-CPDTs 137 and 138 was always superior to that of the spiro-MeOTAD reference device. This validated the approach to synthesize HTMs with high thermal stability through the stabilization of the amorphous state in Chapters 1 and 2. However, the increased thermal stability of the acetal 171 based device compared to that of the spiro-MeOTAD despite their similar glass-transition temperatures, indicates the necessity to determine the stability of the amorphous state not only in the pure HTM but also when mixed with additives. The weaker performance of the phenyl capped derivatives 110 and 138 compared to their methoxy-phenyl capped counterparts demonstrated the need for methoxy groups on the terminal arylamine moieties. This is supported by the excellent performance of acetal 171 which possess eight methoxy groups on the TAA substituents. The tradeoff for the improved performance of methoxy groups is the lower $T_g$ of the HTMs. However, this effect is only around 10 degrees and the device stability does not suffer as long as the $T_g$ is still over 120 °C.
Summary

The aim of this work was the design and synthesis of novel hole transport materials with a stable amorphous state. This goal was achieved with two different strategies.

In Chapter 1 the spiro-concept i.e., the linkage of two different \( \pi \)-systems with different functions over one common \( sp^3 \)-hybridized atom was used. One \( \pi \)-system was represented by a triarylamine-flanked cyclopentadithiophene unit. The use of this unit allowed to tune the optoelectronic properties of the molecules towards their planned application purpose. The second \( \pi \)-system is electronically disconnected from the first one and can therefore independently be tuned and optimized. Three new spiro-cyclopentadithiophene middle building blocks, containing a spiro-linked acridine, thioxanthene, or xanthene have been synthesized and described (Figure S1).

![Figure S1](image1.png)

**Figure S1**: Newly developed and synthesized spiro-cyclopentadithiophenes.

The three spiro central building blocks were substituted with triarylamine units in the free thiophene \( \alpha \)-positions by palladium-catalyzed Suzuki-type cross-coupling reactions to obtain five different spiro-cyclopentadithiophene based hole transport materials. Three additional hole transport materials were obtained by coupling three different triarylamine substituents to non-spiro diphenylcyclopentadithiophene building blocks. These non-spiro hole transport materials were used as reference to evaluate the influence of the spiro-linkage.

All hole transport materials were electrochemically characterized to validate their applicability in perovskite solar cells. The success of the spiro-concept in the synthesis of the hole transport materials was checked through thermal analysis by differential scanning calorimetry. All materials showed high glass transition temperatures above 135 °C providing evidence for a stable amorphous state.

In Chapter 2 the concept of overcrowding was used to obtain molecules with spherical structures. This force 3-dimensional structure should also lead to a material with a stable amorphous state. The small cyclopentadiene moiety was chosen as a central building block. Substitution of the small
cyclopentadiene derivative by Suzuki-type cross-coupling with four sterically demanding triarylamine substituents led to the desired overcrowding (Figure S2).

![Diagram](Image)

**Figure S2:** Overcrowded triarylamine-flanked dimethoxy cyclopentadiene.

Two different triarylamine substituents were used. The central dimethoxy cyclopentadiene was transformed into a cyclopentadienone to open the molecule up to further functionalization. This possibility was used to introduce a dicyanovinylene group into the molecule by a Knoevenagel condensation. The influence of the different cyclopentadiene derivatives on the optoelectronic properties was investigated with optical spectroscopy and electrochemistry. It was discovered that the central building block has a large influence on the redox behavior and on the optical spectrum. The concept of overcrowding to achieve hole transport materials with a stable amorphous state was here again verified by differential scanning calorimetry. All six hole transport materials showed glass transition temperatures of 120 °C and higher, confirming the design philosophy.

In Chapter 3 a selection of the synthesized hole transport materials was employed in perovskite solar cells. The materials were investigated for their performance in the solar cells but also for their thermal stability. From the solar cell results it could be concluded that methoxy groups on the triarylamines increase the performance of the device. All of the methoxy capped hole transport materials surpassed the performance of their phenyl capped counterparts. One of the spiro-acridine and one of the diphenyl-cyclopentadiene hole transport materials both achieved very good results of 21% power conversion efficiencies in perovskite solar cells. The best result was obtained for the methoxyphenyl-capped cyclopentadienone acetal. The material could beat the spiro-MeOTAD reference device and could achieve an outstanding PCE of 23% (Figure S3).
The long-term and thermal stability of the investigated hole transport materials proofed to be better than that of spiro-MeOTAD. This validated the employed design strategy for hole transport materials of Chapter 1 and 2.
Experimental

Physical Measurements and Instrumentation

Nuclear magnetic resonance (NMR) spectra were either recorded on a Bruker Avance 400 Spectrometer (\(^1\)H-NMR: 400 MHz, \(^1^3\)C-NMR: 101 MHz) or a Bruker AMX 500 Spectrometer (\(^1\)H-NMR: 500 MHz, \(^1^3\)C-NMR: 126 MHz). Chemical shifts (\(\delta\)) are given in parts per million (ppm) against tetramethyl silane. Residual proton signals of the deuterated solvents were used as internal standard (\(\delta = 7.26\) ppm (CDCl\(_3\)), 5.32 ppm (CD\(_2\)Cl\(_2\)), 3.85 ppm (THF-d8), and 7.17 ppm (C\(_6\)D\(_6\)) for \(^1\)H-NMR spectroscopy and \(\delta = 77.16\) ppm (CDCl\(_3\)), 54.0 ppm (CD\(_2\)Cl\(_2\)), 67.57 ppm (THF-d8), 7.16 ppm (C\(_6\)D\(_6\)), and 73.78 ppm (TCE-d2) for \(^1^3\)C-NMR spectroscopy.[175-176] Coupling constants \(J\) are given for proton-proton couplings whenever possible. The splitting of the NMR signals is given as doublet (d), doublet of doublet (dd), doublet of doublet of doublet (ddd), triplet (t) triplet of triplet (tt), or multiplet (m). Higher order spin systems are always denoted as multiplets without coupling constants. Signals are assigned to the respective carbon or hydrogen atoms whenever possible. Carbon signals that could not be assigned but could be attributed to quaternary carbon atoms are denoted with C\(_q\) and primary carbon atoms with C-H.

UV-vis-NIR absorption spectra were recorded on a Perkin Elmer Lambda 19 spectrometer. Fluorescence spectra were recorded on a Perkin Elmer LS 55 fluorescence spectrometer. All optical solution measurements were performed in 1 cm quartz cuvettes from Hellma Analytics in uvasol-grade dichloromethane (Merck). Photoelectron spectroscopy in air was measured on an RKI Instruments model AC-II photoelectron spectrometer.

Electrochemical measurements were performed with a computer-controlled Autolab PGSTAT30 potentiostat in a three-electrode setup in an electrochemical cell under argon atmosphere with a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. All potentials were internally referenced against the ferrocene/ferricenium redox pair. The measurements were performed with concentrations of the redox active species between 0.5 – 1 mM in dichloromethane. Tetrabutylammonium hexafluorophosphate (0.1 M) was added as a supporting electrolyte.

Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry was measured on a BrukerDaltonik Reflex III while high-resolution Fourier-transform ion cyclotron resonance (FTICR) MALDI mass spectra were recorded on a Bruker SolariX mass spectrometer. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was employed as matrix. Gas chromatography-mass spectrometry (GC-MS) was recorded on a Shimadzu GC-2010.
Plus coupled with a Shimadzu GCMS-QP2010 SE mass spectrometer with electron ionization (EI). Gas chromatography (GC) was measured on a Varian CP-3800 gas chromatograph.

Melting points were determined using a Büchi Melting Point M-565 or a Mettler Toledo DSC 823e under an argon flow. DSC data was baseline corrected by subtraction of a polynomial fit. Thermo-gravimetric analysis (TGA) was measured either on a TG 209 F1 Libra from Netzsch or on a Perkin Elmer. TGA 8000 under nitrogen atmosphere.

The diffraction data of al crystals were collected in a stream of nitrogen at temperatures between 140 and 150K on an Agilent SuperNova, Cu at zero, Atlas CCD using graphite-monochromated Cu Kα radiation. Data collection strategy was performed with the APEX2 software, data reduction, absorption correction and cell refinement with CrysAlisPro171.

Thin-layer chromatography was carried out on Merck Si60 F254 aluminum plates coated with silica gel. Preparative column chromatography was performed with silica gel 60 (Macherey-Nagel GmbH & Co. KG) particle size 0.063 – 0.2 mm for standard column chromatography or silica gel 60 M (Macherey-Nagel GmbH & Co. KG) particle size 0.04 – 0.063 mm for flash column chromatography. High-performance liquid chromatography (HPLC) was performed on a Shimadzu CBM-20A with an SPD-20A UV/VIS detector and a Macherey-Nagel Nucleosil 100-5 NO2 column.

Quantum chemical calculations were performed with Gaussian 16 or 9 and the results were visualized with GaussView 5.[177-179]

Materials

Toluene (PhMe), tetrahydrofuran (THF), petrol ether (PE), ethyl acetate (EA), dichloromethane (DCM), diethyl ether (Et2O), n-Hexane, isopropyl alcohol (iPrOH), methanol (MeOH), chloroform (CHCl3), and acetone were purchased from VWR International in technical grade and purified by distillation prior to usage. Diethylene glycol dimethyl ether (diglyme) was purchased from Sigma Aldrich and dried with calcium hydride. The anhydrous solvents THF (Carl Roth), Et2O (VWR International), DCM (VWR International), toluene (VWR International), and DMF (VWR International) were purified by a MB SPS-800 solvent purification equipment from MBraun. Inorganic salts sodium sulfate (Na2SO4), sodium chloride (NaCl), sodium hydrogen carbonate (NaHCO3), sodium carbonate (Na2CO3), sodium sulfite (Na2SO3), zinc chloride (anhydrous, dried in high vacuum before use) (ZnCl2), ammonium chloride (NH4Cl), and potassium hydroxide (KOH) were purchased from VWR International, potassium carbonate (K2CO3), copper(I) iodide (CuI), copper(II) chloride (CuCl2), and potassium acetate (KOAc) were purchased from Merck, potassium phosphate (K3PO4) and tin(IV) chloride (SnCl4) from Sigma Aldrich. N-Butyllithium (n-BuLi, 1.6 M in n-hexane)
and boron trifluoride diethyl etherate (BF₃·OEt₂, solution in diethyl ether) were purchased from Acros Organics. The chemicals aniline, bromine (Br₂), diisopropylamine, diphenylamine, iodobenzene, N-bromosuccinimide (NBS), potassium tert-butoxide (KOtBu), sodium tert-butoxide (NaOtBu), triethylamine (NEt₃), and trimethylsilyl chloride (TMSCl) were purchased from Merck. Benzophenone, 2,2’-bis(diphenylphosphino)-1,1’-binaphthyl (BINAP), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos), dimethyl carbamoyl chloride (distilled prior to use), iodine (I₂), sodium methoxide (solution in methanol), palladium(II) acetate (PdOAc₂), tetrabutyl ammonium bromide (TBABr), and triis(dibenzylideneacetone)dipalladium(0) (Pd₂dba₃) were purchased from Sigma Aldrich. 2-Bromo-N,N-diphenylaniline, thioxanthone, and xanthone purchased from Tokyo Chemical Industry. 2,2’-Bipyridin, bis(pinacolato) diborane, 2-bromothiophene, and 4-bromo-N,N-diphenylaniline were purchased from Fluorochem. 4-Bromothioanisole, iodine monochloride (1 M solution in DCM), and 4-iodoanisole were purchased from Alfa Aeser. The catalyst [1,1’-bis(diphenylphosphino)ferrocene]dichloropalladium(II) complex with dichloromethane (Pd(dppf)Cl₂·CH₂Cl₂) was purchased from OxChem. 3-Bromo-2,2’-bithiophene (118) and tetrakis(triphenylphosphine) palladium(0) (Pd(PPh₃)₄) were synthesized in the Institute of Organic Chemistry 2 according to modified literature procedures.

**Synthetic Procedures**

### 3,3’-Dibromo-2,2’-bithiophene (89).[^62]

![Bithiophene 89](image)

The reaction was carried out in a flame-dried three-necked flask under argon atmosphere. A fresh solution of LDA was prepared by dissolving 22.3 g diisopropylamine (29.6 ml, 0.22 mol) in 1.5 l dry THF. The solution was cooled to 0 °C and n-BuLi (1.6 M in hexane, 139 ml, 0.22 mol) was slowly added. The solution was stirred for an additional 30 min at 0 °C. 3-Bromothiophene (34.8 g, 19.0 ml, 0.20 mol) was added in one portion and the resulting solution was stirred for additional 2 h at 0 °C. Dried ZnCl₂ (30.1 g, 0.22 mol) was added and the solution was stirred for 15 min. The solution was then cooled to -60 °C and CuCl₂ (32.3 g, 0.24 mol) was added. The solution was stirred overnight and allowed to warm to room temperature. Silica gel was added, and the solvent was removed under reduced pressure. The product was filtered over a short silica gel plug and washed down with PE. The solvent was evaporated, and the resulting white precipitate was washed with cold PE and dried in high vacuum. Bithiophene 89 was obtained as a white crystalline solid (25.45 g, 78.5 mmol, 78%, lit. 85-90%[^62]).
$T_m = 96.5 - 98.0 \, ^\circ\text{C} (2 \, ^\circ\text{C/min}), \text{lit.} \ 96.8 - 98.0 \, ^\circ\text{C}.^{[62]}$

$^1\text{H-NMR} \ (400 \, \text{MHz, CDCl}_3): \delta \ [\text{ppm}] \ 7.41 \ (d, \ 3J_{(H_4,H_5)} = 5.4 \, \text{Hz,} \ 1\text{H}, \ H_4), \ 7.09 \ (d, \ 3J_{(H_5,H_4)} = 5.4 \, \text{Hz,} \ 1\text{H}, \ H_5)$.

$^{13}\text{C-NMR} \ (101 \, \text{MHz, CDCl}_3): \delta \ [\text{ppm}] \ 130.92 \ (\text{C}_4), \ 128.99 \ (\text{C}_2), \ 127.55 \ (\text{C}_5), \ 112.75 \ (\text{C}_3)$.

$(3,3'-\text{Dibromo-[2,2'-bithiophene]-5,5'-diyl})\text{bis(trimethylsilane)} \ (90).^{[63]}$

A solution of LDA was prepared by dissolving freshly distilled diisopropylamine (3.75 ml, 2.81 g, 27.8 mmol) in 100 ml dry THF. The solution was cooled to -78 °C and n-BuLi (1.6 M in hexane, 16.50 ml, 26.4 mmol) was slowly added. The solution was slowly warmed to -50 °C and afterwards stirred at 0 °C for 30 minutes. The solution was again cooled to -78 °C and 3,3'-dibromo-2,2'-bithiophene 89 (3.80 g, 11.7 mmol) in 50 ml dry THF was added over 30 minutes. The resulting mixture was slowly warmed to -10 °C and stirred for an additional 30 minutes before being cooled to -78 °C again. Trimethylsilyl chloride (4.3 ml, 33.8 mmol) was slowly added and the solution was warmed to room temperature overnight. The reaction was quenched by the addition of water and the organic phase was twice extracted with Et$_2$O. The combined organic fractions were washed with brine, dried with Na$_2$SO$_4$ and the solvent was removed under reduced pressure and dried under high vacuum. An orange oil was obtained which solidified in the freezer. TMS-protected bithiophene 90 was acquired as a slightly orange solid (5.30 g, 11.09 mmol, 98% purity, 94.5%, lit. 90%$^{[180]}$). Further purification by recrystallization from PE or methanol is possible.

$T_m = 83.1 - 84.8 \, ^\circ\text{C} (2 \, ^\circ\text{C/min}), \text{lit.} \ 86 - 88 \, ^\circ\text{C}.^{[180]}$

$^1\text{H-NMR} \ (400 \, \text{MHz, CDCl}_3): \delta \ [\text{ppm}] = 7.15 \ (s, \ 2\text{H}, \ H_4), \ 0.34 \ (s, \ 18\text{H}, \ Si-(\text{CH}_3)_3)$.

$^{13}\text{C-NMR} \ (101 \, \text{MHz, CDCl}_3): \delta \ [\text{ppm}] = 143.07 \ (\text{C}_5), \ 137.15 \ (\text{C}_4), \ 134.07 \ (\text{C}_2), \ 113.08 \ (\text{C}_3), -0.23 \ (\text{Si}-(\text{CH}_3)_3)$.

$2,6$-Bis(trimethylsilyl)$-4\text{H-cyclopenta[2,1-}b3,4-b\text{]}$dithiophen-4-one$ \ (87).^{[64]}$
The reaction was carried out in a flame dried three-necked flask under argon atmosphere. 3,3'-Dibromo-[2,2'-bithiophen]-5,5'-diyl)bis(trimethylsilane) 90 (2.0 g, 4.3 mmol) was dissolved in 50 ml dry THF and cooled to -78 °C. N-Butyl lithium (1.6 M in hexane, 5.4 ml, 8.6 mmol) was slowly added. The solution was stirred for an additional 15 min at -78 °C. A solution of N,N-dimethyl carbamoyl chloride (462 mg, 390 µl, 4.3 mmol) in 4 ml dry THF was cooled to -78 °C and slowly added to the reaction mixture. The solution was allowed to warm to 0 °C and afterwards quenched by addition of saturated NH₄Cl solution. The organic phase was twice extracted with PE, dried with Na₂SO₄, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography with an eluent mixture of PE:DCM of 3:1. The ketone 87 was obtained as 1.11 g (3.30 mmol, 77%, lit. 86%) of a red solid.

\[ T_m = 71.0 - 72.2 \, ^\circ\text{C} \, (2 \, ^\circ\text{C/min}) \]

\[ ^1\text{H-NMR} \, (400 \, \text{MHz, CDCl}_3): \delta \, [\text{ppm}] = 7.06 \, (s, 2H, H3), 0.31 \, (s, 18H, Si-(CH}_3)_3). \]

\[ ^{13}\text{C-NMR} \, (101 \, \text{MHz, CDCl}_3): \delta \, [\text{ppm}] = 183.35 \, (C4), 154.56 \, (Cq), 145.12 \, (Cq), 144.37 \, (Cq), 128.13 \, (C3), 0.00 \, (Si-(CH}_3)_3). \]

\[ \text{FTICR-MALDI: } m/z: \text{ calcd. for C}_{15}\text{H}_{20}\text{OSSi}_2: 336.04941; \text{ found: 336.04833 [M]}^+ (\delta m/m= 3.21 \, \text{ppm}). \]

**2-Bromo-N,N-diphenylaniline (94).*[^65]**

The reaction was carried out in a flame-dried Schlenk-tube under argon atmosphere. Diphenylamine 95 (158 mg, 934 µmol), palladium(II)-acetate (9 mg, 39 µmol), Xantphos (23 mg, 39 µmol, 5 mol%) and NaOtBu (112, 1.2 mmol) were evacuated for 15 minutes. Dry toluene (1 ml) and 220 mg 2-bromiodobenzene 96 (100 µl, 779 µmol) were added, the tube was sealed and heated to 100 °C for 16 hours. Water was added and the product was extracted with DCM, dried with Na₂SO₄ and the solvent was evaporated under reduced pressure. The product was purified using column chromatography with silica gel and an eluent mixture of PE:DCM 3:1. The triarylamine 94 was recrystallized from methanol to afford the product as slightly green crystals (209 mg, 0.64 mmol, 83%, lit. 87%[^181]).

\[ T_m = 62.7 - 63.9 \, ^\circ\text{C} \, (3 \, ^\circ\text{C/min}), \text{ lit 63 } \, ^\circ\text{C}.[^181] \]

[^65]: Reference or note for the 2-Bromo-N,N-diphenylaniline (94).
[^181]: Reference or note for the melting point of the triarylamine 94.
1H-NMR (400 MHz, CD2Cl2): δ [ppm] = 7.66 (dd, 3J(H3,H4) = 8.0 Hz, 4J(H3,H5) = 1.5 Hz, 1H, H3), 7.36 (ddd, 3J(H,H) = 8.0, 7.3 Hz, 1J(H5,H3) = 1.5 Hz, 1H, H5), 7.28 – 7.19 (m, 5H, H2', H6), 7.15 (ddd, 3J(H,H) = 8.0, 7.2 Hz, 1J(H4,H6) = 1.7 Hz, 1H, H4), 7.01 – 6.92 ppm (m, 6H, H3', H4').

13C-NMR (101 MHz, CD2Cl2): δ [ppm] = 147.36 (Cq), 145.79 (Cq), 134.85 (C-H), 132.15 (C-H), 129.42 (C3'), 129.38 (C-H), 127.90 (C-H), 124.14 (Cq), 122.39 (C4'), 122.24 (C2').


4-(2-(Diphenylamino)phenyl)-2,6-bis(trimethylsilyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-ol (97).

2-Bromo-N,N'-diphenylaniline (898 mg, 2.77 mmol) was dissolved in 17 ml dry THF and cooled to -78 °C under an argon atmosphere. A solution of n-BuLi in hexane (1.6 M, 1.8 ml, 2.9 mmol) was slowly added and the solution was stirred for an additional hour at -78 °C. 2,6-Bis(trimethylsilyl)-4H-cyclopenta[2,1-b:3,4-b']dithien-4-one 87 (932 mg, 2.77 mmol) was dissolved in 15 ml dry THF and cooled to -78 °C and added to the lithiated arylamine. The solution was stirred for another hour at -78 °C and then warmed overnight to room temperature. The reaction was quenched by the addition of saturated NH4Cl solution and the product was extracted with DCM. The combined organic phases were dried with Na2SO4 and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography with silica gel and PE:DCM 1:1 as eluent. Alcohol 97 was obtained as 1065 mg (1.83 mmol, 66%) of slightly red solid.

T_m = 152.0 – 156.0 °C (2 °C/min).

1H-NMR (400 MHz, CD2Cl2): δ [ppm] = 7.72 (dd, 3J(H6,H5) = 7.5 Hz, 4J(H6,H4) = 2.3 Hz, 1H, H6), 7.36 – 7.25 (m, 2H, H4, H5), 7.15 – 7.07 (m, 4H, H3'), 7.07 – 7.03 (m, 1H, H3), 6.95 – 6.88 (m, 2H, H4'), 6.78 – 6.69 (m, 4H, H2'), 6.57 (s, 2H, H3''), 4.64 (br, 1H, OH), 0.20 (s, 18H, Si-(CH3)3).

13C-NMR (101 MHz, CD2Cl2): δ [ppm] = 159.64 (Cq), 147.90 (C-H), 144.63 (Cq), 143.17 (Cq), 142.15 (Cq), 139.85 (Cq), 132.91 (C-H), 129.98 (C-H), 129.38 (C-H), 129.08 (C-H), 128.70 (C-H), 127.59 (C-H), 122.84 (C-H), 122.76 (C-H), 79.09 (C-OH), 0.14 (Si-(CH3)3).
**FTICR-MALDI:** $m/z$: calcd. for $C_{33}H_{35}NO_{2}S_{2}$: 581.16986; found: 581.16895 [M]$^+$ ($\delta m/m= 1.57$ ppm).

4-(2-(Diphenylamino)phenyl)-2,6-diiodo-4$H$-cyclopenta[2,1-$b$;3,4-$b'$]dithiophen-4-ol (98).

[Chemical structure diagram]

4-(2-(Diphenylamino)phenyl)-2,6-bis(trimethylsilyl)-4$H$-cyclopenta[2,1-$b$;3,4-$b'$]dithiophen-4-ol 97 (200 mg, 344 µmol) was dissolved in 10 ml dry DCM under argon atmosphere. The mixture was cooled to -78 °C and an iodine monochloride (0.68 ml, 390 µmol, 1 M in DCM) was slowly added. The solution was stirred for 10 min at -78 °C and afterwards quenched by the addition of Na$_2$S$_2$O$_5$ solution. Water was added and the organic phase was extracted with DCM, dried with Na$_2$SO$_4$, and the crude product was purified by flash column chromatography with silica gel and a solvent mixture of PE:DCM of 2:3 to afford aryl iodide 98 as a yellow solid (215 mg, 312 µmol, 90.8%).

$T_m = 262.7$ °C, decomposition (2 °C/min).

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = 7.65 (dd, $^3J_{(H_6,H_5)} = 7.8$ Hz, $^4J_{(H_6,H_4)} = 1.8$ Hz, 1H, H6), 7.38 – 7.26 (m, 2H, H4, H5), 7.19 – 7.11 (m, 4H, H3'), 7.04 (dd, $^3J_{(H_3,H_4)} = 7.8$ Hz, $^4J_{(H_3,H_5)} = 1.5$ Hz, 1H, H3), 7.02 – 6.97 (m, 2H, H4'), 6.80 – 6.66 (m, 4H, H2'), 6.53 (s, 2H, $\beta$-H), 4.78 (s, 1H, OH).

$^{13}$C-NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = 157.45 (C$_q$), 148.10 (C$_q$), 144.89 (C$_q$), 142.18 (C$_q$), 138.17 (C$_q$), 133.05 (C-H), 131.95 (C-H), 129.87 (C-H), 129.47 (C-H), 129.30 (C-H), 127.79 (C-H), 123.17 (C-H), 122.91 (C-H), 79.68 (1C, C4''), 73.38 (2C, C2'').

**FTICR-MALDI** $m/z$: calcd. for $C_{27}H_{17}I_{2}NO_S$: 688.88409; found: 688.88335 [M]$^+$ ($\delta m/m= 1.07$ ppm).

4-(2-(Diphenylamino)phenyl)-2,6-diiodo-4H-cyclopenta[2,1-b:3,4-b]dithiophen-4-ol 98 (227 mg, 329 μmol) was dissolved in dry DCM under an argon atmosphere. BF₃·OEt₂ (75 μl, 350 μmol, 50% solution) was added and the solution was stirred for 5 minutes. The reaction mixture was quenched by the addition of saturated NaHCO₃ solution and the product was extracted with DCM, dried with Na₂SO₄ and the solvent was evaporated. The crude product was purified by flash column chromatography with silica gel and an eluent mixture of PE:DCM 6:1 to afford spiro acridine 99 as an orange solid (179 mg, 267 μmol, 81.0%).

T_m = 262.7 °C, decomposition (2 °C/min).

¹H-NMR (400 MHz, CD₂Cl₂): δ [ppm] = 7.76 – 7.67 (m, 2H, H3'), 7.64 – 7.55 (m, 1H, H4'), 7.44 (dd, ³J(H₂,H₃)= 8.4 Hz, ⁴J(H₂,H₄)=1.2 Hz, 2H, H2'), 7.16 (s, 2H, H3''), 6.67 (ddd, ³J(H₃,H₄)=1.8 Hz 2H, H3), 7.16 (s, 2H, H3''), 6.67 (ddd, ³J(H₂,H₃)=7.8, 7.0 Hz, ⁴J(H₂,H₄)=1.2 Hz, 2H, H2), 6.62 (dd, ³J(H₁,H₂)= 7.7 Hz, ⁴J(H₁,H₃)=1.7 Hz, 2H, H1), 6.36 (ddd, ³J(H₄,H₃)= 8.4 Hz, ⁴J(H₄,H₂)=1.2 Hz, ⁵J(H₄,H₃)=0.5 Hz. 2H, H4).

¹³C-NMR (126 MHz, CDCl₃): δ [ppm] = 162.85 (C₉), 141.63 (C₈), 140.83 (C₇), 140.29 (C₆), 132.01 (C-H), 131.24 (C-H), 131.19 (C-H), 128.78 (C₅), 128.07(C-H), 126.23(C-H), 121.08 (C-H), 115.08 (C-H), 73.66 (C2''), 53.85 (C4'').

FTICR-MALDI: m/z: calcd. for C₂⁷H₁₅I₂NS₂: 670.87299; found: 670.87355 [M]+ (δm/m= 0.84 ppm).
2,6-Dibromo-4-(2-(diphenylamino)phenyl)-4\textit{H}-cyclopenta[2,1-\textit{b}:3,4-\textit{b}]di thiophen-4-ol (101).

TMS-protected cyclopentadienol 97 (1.44 g, 2.47 mmol) was dissolved in 200 ml THF and cooled to -78 °C under light exclusion. N-bromosuccinimide (881 mg, 4.95 mmol) was added and the solution was stirred for 16 hours while allowing to warm to room temperature. The reaction mixture was quenched by the addition of saturated Na\textsubscript{2}SO\textsubscript{3} solution and the organic phase was extracted with Et\textsubscript{2}O, washed with water, and dried with MgSO\textsubscript{4}. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography with silica gel and an eluent mixture of PE:DCM 1:1 which afforded aryl bromide 101 as a yellow solid (1.08 g, 1.81 mmol, 74%).

\[ T_m = 98.2 - 99.9 \, ^\circ\text{C} (2 \, ^\circ\text{C/min}). \]

\textbf{\textsuperscript{1}H-NMR} (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}): δ [ppm] = 7.66 (dd, \[ ^3J_{(H6,H5)} = 7.5 \, \text{Hz}, \, ^4J_{(H6,H4)} = 2.1 \, \text{Hz}, \, 1\, \text{H}, \, H6), \, 7.38 - 7.25 \, (m, \, 2\, \text{H}, \, H4; \, H5), \, 7.20 - 7.10 \, (m, \, 4 \, \text{H}, \, H3'), \, 7.08 - 7.02 \, (m, \, 1 \, \text{H}, \, H3), \, 7.02 - 6.93 \, (m, \, 2\, \text{H}, \, H4'), \, 6.80 - 6.72 \, (m, \, 4\, \text{H}, \, H2'), \, 6.41 \, (s, \, 2\, \text{H}, \, H3''), \, 4.77 \, (s, \, 1\, \text{H}, \, -\text{OH}).

\textbf{\textsuperscript{13}C NMR} (101 MHz, CD\textsubscript{2}Cl\textsubscript{2}): δ [ppm] = 155.39 (C\textsubscript{1}), \, 148.14 (C\textsubscript{2}), \, 144.89 (C\textsubscript{3}), \, 138.03 (C\textsubscript{4}), \, 137.48 (C\textsubscript{5}), \, 133.04 (C-H), \, 129.91 (C-H), \, 129.52 (C-H), \, 129.31 (C3'), \, 127.80 (C-H), \, 125.55 (C-H), \, 123.16 (C-H), \, 122.91 (C2'), \, 112.49 (C2''), \, 80.74 (C4'').

\textbf{FTICR-MALDI}: \textit{m/z}: calcd. for C\textsubscript{27}H\textsubscript{17}Br\textsubscript{2}NOS\textsubscript{2}: 592.91183; found: 592.91215 [M]\textsuperscript{+} (δm/m= 0.54 ppm).
2',6'-Dibromo-10-phenyl-10H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b]dithiophene] (100).

Starting from Cyclopentadienol 97 (pathway A)
2,6-Dibromo-4-(2-(diphenylamino)phenyl)-4H-cyclopenta[2,1-b:3,4-b]dithiophen-4-ol 97 (1.00 g, 1.68 mmol) was dissolved in 400 ml dry DCM and cooled to 0 °C. BF$_3$·OEt$_2$ (750 µl, 3.38 mmol, 50% solution) was added and the resulting solution was stirred for 1 hour at 0 °C. The reaction was quenched by the addition of saturated NaHCO$_3$ solution and the product was extracted with DCM, dried with MgSO$_4$, and directly filtered through silica gel. The dibrominated acridine 100 was obtained as a slightly yellow solid without further purification (957 mg, 1.66 mmol, 98.7%).

Starting from Acridine 102 (pathway B)
10-Phenyl-10H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b]dithiophene] 102 (500 mg, 1.19 mmol) was dissolved in 45 ml dry DCM and was cooled to 0 °C. NBS (424 mg, 2.38 mmol) was added in one portion and the solution was stirred for 4 hours at 0 °C. The precipitate was filtered, and PE was added to the filtrate. The filtrate was reduced and filtered again. The solid was washed with cold methanol to afford dibrominated acridine 100 as a slightly grey solid after drying in high vacuum (673 mg, 1.17 mmol, 97.8%).

$T_m$ = 296.9 – 300.0 °C (3 °C/min).

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$): δ [ppm] = 7.75 – 7.68 (m, 2H, H3'), 7.63 – 7.56 (m, 1H, H4'), 7.46 – 7.42 (m, 2H, H2'), 7.03 – 6.96 (m, 4H, H3'', H3), 6.72 – 6.62 (m, 1H, H1, H2), 6.37 (ddd, $^3$J$_{H4,H3}$ = 8.3 Hz, $^4$J$_{H4,H2}$ = 1.1 Hz, $^5$J$_{H4,H1}$ = 0.7 Hz, 2H, H4).

$^{13}$C-NMR (101 MHz, CDCl$_3$): δ [ppm] = 160.58 (C$_q$), 141.63 (C$_q$), 140.73 (C$_q$), 135.53 (C$_q$), 131.24 (C3'), 131.16 (C2'), 128.79 (C4'), 128.10 (C3), 124.69 (C1), 125.65(C3''), 121.09 (C2), 120.94 (C$_q$), 115.07 (C4), 112.76(C2''), 53.58 (C4').

FTICR-MALDI: m/z: calcd. for C$_{27}$H$_{15}$Br$_2$NS$_2$: 574.90127; found: 574.90075 [M]$^+$ (δm/m= 0.90 ppm).
10-Phenyl-10H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b]dithiophene] (102).

The reaction was carried out under argon in a flame-dried three-necked flask. 2-Bromo-N,N-diphenylaniline (1.00 g, 3.08 mmol) was dissolved in 130 ml dry THF, cooled to -78 °C and n-BuLi (1.6 M in hexane, 2.51 ml, 4.02 mmol) was slowly added. The solution was stirred at -78 °C for a further 60 min. 2,6-Bis(trimethylsilyl)-4H-cyclopenta[2,1-b:3,4-b]dithiophen-4-one 87 (1.12 g, 3.30 mmol) was dissolved in 20 ml dry THF, cooled to -78 °C and slowly added to the lithiated aryl bromide solution until the red color of the ketone did not vanish anymore. Then, the reaction was stopped by adding 2 ml -78 °C cold isopropanol, ammonium chloride solution was added, and the product was removed under vacuum. The crude product was purified by a short filter column with silica gel and an eluent mixture of PE:DCM 2:1. All fractions that were eluted before the elution of the red ketone were discarded. The eluent mixture was changed to PE:DCM 1:4 to elute the product. The purification resulted in the isolation of 1.46 g (2.4 mmol, 95% pure, 77.4%) of a slightly yellow solid of 4-(2-(diphenylamino)phenyl)-2,6-bis(trimethylsilyl)-4H-cyclopenta[2,1-b:3,4-b]dithiophen-4-ol 97. The product mixture was dissolved in 50 ml dry DCM, cooled to 0 °C and BF₃•OEt₂ (50% in Et₂O, 3.3 ml, 15.1 mmol) was quickly added. The solution was stirred for 1 h at 0 °C and the reaction mixture was quenched by the addition of saturated NaHCO₃ solution. The organic phase was extracted three times with DCM, dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography with silica gel and PE:DCM 8:1. Subsequently, the acridine 102 was recrystallized from DCM/PE to obtain 0.91 g (2.2 mmol, 72%) of a white solid.

Tₘ = 260.0 – 262.0 °C (2 °C/min).

¹H-NMR (400 MHz, CD₂Cl₂): δ [ppm] = 7.75 – 7.66 (m, 2H, H3'), 7.63 – 7.55 (m, 1H, H4'), 7.50 – 7.41 (m, 2H, H2'), 7.22 (d, 3J(H₃',H₂') = 4.9 Hz, 1H, H3''), 7.01 (d, 3J(H₂',H₃'') = 4.9 Hz, 1H, H2''), 6.96 (ddd, 3J(H₃,H₄;H₃,H₂) = 8.3, 6.5, Hz, 4J(H₃,H₁) = 2.3 Hz, 2H, H3), 6.72 – 6.57 (m, 4H, H1, H2), 6.37 (ddd, 3J(H₄,H₃) = 8.3 Hz, 4J(H₄,H₂) = 1.1 Hz, 5J(H₄,H₁) = 0.5 Hz, 1H, H4).
**Synthesis of \(N,N\)-bis(4-methoxyphenyl)aniline (106).\[^{67}\]**

The reaction was carried out in a flame-dried three-necked flask under argon atmosphere. 4-iodoanisole 105 (70.0 g, 299 mmol), 13.3 g aniline 104 (13.0 ml, 142 mmol), 2,2'-bipyridine (0.78 g, 5.00 mmol) and copper(I) iodide (0.95 g, 5.0 mmol) were dissolved in 200 ml dry toluene. The solution was degassed with argon before potassium tert-butylate (47.93 g, 427 mmol) was added and the reaction mixture was stirred for 3.5 h at 115 °C. The solution was allowed to cool down to room temperature. The organic phase was separated, filtered and the residue was treated with Et₂O. The organic phase was again separated, and the combined organic phases were washed with water and dried with MgSO₄. The product mixture was separated with silica gel column chromatography with an eluent mixture of PE:EA 10:1 which afforded triarylamine 106 as a slightly yellow solid (15.16 g, 49.7 mmol, 35%, lit. 73%).

\(T_m = 103.5 - 104.7 \, ^\circ\text{C} (1 \, ^\circ\text{C/min}), \text{lit.} \, 104 - 105 \, ^\circ\text{C}.\[^{182}\]

\(^1\text{H-NMR} (400 MHz, CDCl₃): \delta [ppm] = 7.17 (dd, \(J_{(H3,H4);H3,H2}) = 8.7, 7.3 \, Hz, 2H, H3), 7.05 (d, \(J_{(H2,H3}) = 8.9 \, Hz, 4H, H2'), 6.97 - 6.91 (m, 2H, H2), 6.89 - 6.84 (m, 1H, H4), 6.82 (d, \(J_{(H3,H2}) = 9.0 \, Hz, 4H, H3'), 3.79 (s, 6H, OCH₃).

\(^{13}\text{C-NMR} (101 MHz, CDCl₃): \delta [ppm] = 155.80 (C₉), 148.90 (C₃), 141.29 (C₆), 129.05 (C₃), 126.51 (C₂'), 121.04 (C₂), 120.69 (C₄), 114.76 (C₃'), 55.61 (O-CH₃).

\(\text{GC-MS: } m/z: \text{ calcd. for } C_{20}H_{19}NO₂: 305; \text{ found: } 305 \, [M]^+, 290 \, [M-CH₃]^+.

[^{1}]: The carbon sp³-signal could not be detected most probably due to the slow relaxation.
Synthesis of 4-Bromo-$N,N'$-bis(4-methoxyphenyl)aniline (107).\[68\]

\[
\text{Br} \quad \text{3} \quad \text{2} \quad \text{1} \quad \text{4} \\
\text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{OMe} \\
\text{OMe} \quad \text{OMe} \\
\]

$N,N'$-Bis(4-methoxyphenyl)aniline (3.08 g, 10.1 mmol) was dissolved in 20 ml dry THF and cooled to 0 °C. NBS (1.80 g, 10.1 mmol) was added in one portion and the mixture was stirred for an additional 3 h at 0 °C. Water was added and the product was extracted using DCM. The combined organic fractions were dried with MgSO$_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography with silica gel and an eluent mixture of PE:DCM of 4:1 which afforded the triarylamine 107 as a white solid (3.44 g, 8.94 mmol, 89%, lit. 91\%\[68\]).

$T_m = 99.1 – 100.1$ °C (1 °C/min), lit. 96 – 98 °C.\[183\]

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$): δ [ppm] = 7.26 – 7.18 (m, 2H, H3), 7.09 – 6.95 (m, 4H, H2'), 6.90 – 6.79 (m, 4H, H3'), 6.79 – 6.71 (m, 2H, H2), 3.77 (s, 6H, O-CH$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$): δ [ppm] = 156.80 (C4'), 148.63 (C6), 140.92 (C7), 132.16 (C-H), 127.27 (C2'), 122.11 (C-H), 115.25 (C3'), 112.40 (C4), 55.97 (O-CH$_3$).

FTICR-MALDI: m/z: calcd. for C$_{29}$H$_{18}$BrNO$_2$: 383.05209; found: 383.05151 [M]$^+$ (δm/m= 1.51 ppm).

4-Methoxy-$N$-(4-methoxyphenyl)-$N'$(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (103).\[69\]

\[
\text{OMe} \quad \text{OMe} \\
\text{2} \quad \text{3} \\
\text{1} \quad \text{2} \quad \text{3} \\
\text{OMe} \quad \text{OMe} \\
\]

4-Bromo-$N,N'$-bis(4-methoxyphenyl)aniline (1.08 g, 2.81 mmol), bis(pinacolato)diborane (0.86 g, 3.37 mmol), KOAc (0.83 g, 8.43 mmol) and Pd(dppf)Cl$_2$*CH$_2$Cl$_2$ (115 mg, 0.14 mmol, 5 mol%) were dissolved in 10 ml dry, degassed DMF under argon atmosphere. The resulting solution was
degassed for a further 5 minutes and afterwards heated to 80 °C for 12 h. The reaction mixture was cooled to room temperature and water and diethyl ether was added. The organic phase was separated and the aqueous phase was extracted with diethyl ether. The combined organic fractions were dried with MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified using column chromatography with silica gel and an eluent mixture of PE:EA of 9:1. Boronic ester 103 was obtained as a white solid (0.89 g, 2.06 mmol, 73%, lit. 81%[69]).

\[ T_m = 129.1 - 131.2 \degree C (2 \degree C/min). \]

\(^1\)H-NMR (400 MHz, CDCl₃): \( \delta \) [ppm] = 7.63 - 7.58 (m, 2H, H2), 7.09 - 7.04 (m, 4H, H2'), 6.89 - 6.85 (m, 2H, H3), 6.85 - 6.81 (m, 4H, H3'), 3.80 (s, 6H, OCH₃), 1.32 (s, 12H, CH₃).

\(^{13}\)C-NMR (101 MHz, CDCl₃): \( \delta \) [ppm] = 156.30 (C4'), 151.49 (C4), 140.52 (C1'), 135.88 (C2), 127.25 (C2'), 118.74 (C3), 114.83 (C3'), 83.52 (C4''), 55.60 (O-CH₃), 24.98 (CH₃).

FTICR-MALDI: \( m/z \) calcld. for C₂₆H₃₀BₙN₄O₄: 431.22671; found: 431.22548 \([M]^{+} (\delta m/m= 2.85 \text{ ppm}). \]

4,4'-(10-Phenyl-10H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b]dithiophene]-2',6'-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (109).

A 2 M potassium phosphate solution was freshly prepared and degassed with argon for 2 h. Dry THF was degassed for 1 h with argon. 2',6'-Dibromo-10-phenyl-10H-spiro[acridin-9,4'-cyclopenta[2,1-b:3,4-b]dithiophene] 100 (25 mg, 31 µmol), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline 103 (47 mg, 108 µmol) and tetrakis(triphenylphosphine)palladium(0) (5 mg, 3 µmol, 10 mol%) were filled into a Schlenk-tube and were evacuated for 1 h. THF (2.5 ml, dry, degassed) was added and the obtained solution was degassed for an additional 5 min. The 2 M potassium phosphate solution (130 µl, 0.26 mmol) was added and the solution was degassed for 2 min. The tube was sealed and the solution was heated to 75 °C for 90 h. The reaction was cooled down, water and Et₂O was added and the product was
three times extracted with Et₂O. The collected organic fractions were dried with MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography with silica gel (deactivated with NEt₃). An eluent gradient was utilized from PE:Et₂O 3:1 to 1:1. The triarylamine capped spiro acridine 109 was isolated (32 mg, 31 µmol, 72%) as an orange-yellow solid.

¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.74 – 7.67 (m, 2H, H3'), 7.60 – 7.53 (m, 1H, H4'), 7.46 (dd, ³J(H₂',H₃') = 8.4 Hz, ⁴J(H₂',H₄') = 1.3 Hz, 2H, H2'), 7.35 (d, ³J(H₃'',H₂'') = 8.8 Hz, 4H, H3''), 7.11 (s, 2H, H3'''), 7.04 (d, ³J(H₂''',H₃''') = 9.0 Hz, 8H, H2'''), 6.97 (ddd, ³J(H₃,H₄; H₃,H₂) = 8.6, 7.1 Hz, 4J(H₄,H₂) = 1.2 Hz, 2H, H4'), 6.89 (d, ³J(H₂',H₃') = 8.8 Hz, 4H, H₂'), 6.86 – 6.78 (m, 10H, H₃'''), 6.68 (ddd, ³J(H₂,H₁; H₂,H₃) = 7.7, 7.1 Hz, 4J(H₄,H₃) = 1.2 Hz, 2H, H2'), 6.37 (dd, ³J(H₄,H₃) = 8.3 Hz, 4J(H₄,H₂) = 1.0 Hz, 2H, H₄'), 3.80 (s, 12H, OCH₃).

¹³C-NMR (101 MHz, CDCl₃): δ [ppm] = 162.72 (C₄'''), 156.01 (C₄'''), 148.06 (C₉), 145.89 (C₉), 141.81 (C₉), 141.05 (C₉), 140.81 (C₁'''), 134.15 (C₉), 131.27 (C₃'), 131.18 (C₂'), 128.63 (C₄'), 127.62 (C₃), 127.34 (C₉), 126.64 (C₂'''), 126.46 (C₁), 125.87 (C₂''), 122.61 (C₉), 121.02(C₂), 120.92 (C₃'''), 117.30 (C₃'''), 114.82 (C₃'''), 114.75 (C₄), 55.63 (O-CH₃), 54.21 (C₄''').

FTICR-MALDI: m/z: calcld. for C₆₇H₅₁N₃O₄S₂: 1025.33155; found: 1025.33136 [M]+ (δm/m= 0.19 ppm).

N,N-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (108).

4-Bromo-N,N-diphenylaniline (5.00 g, 15.4 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (4.70 g, 18.5 mmol), KOAc (4.54 g, 46.3 mmol) and Pd(dppf)Cl₂*CH₂Cl₂ (0.63 mg, 0.77 mmol, 5 mol%) were put in a dried Schlenk-tube and evacuated for one hour. Freshly degassed DMF (20 ml) was added and the resulting solution was degassed for 5 minutes. The tube was sealed and heated to 80 °C for 12 hours. Water was added and the product was extracted with DCM, dried with MgSO₄, and the crude product was purified by flash column chromatography with silica gel and an eluent mixture of PE:EA of 16:1 to afford boronic ester 108 as a white solid (5.00 g, 13.4 mmol, 87%).
\( T_m = 88.5 - 92.6 \text{ (2 °C/min)} \), lit. 89 – 91 °C.\(^{[184]}\)

\(^1\)H-NMR (400 MHz, CD\(_2\)Cl\(_2\)): \( \delta \text{ [ppm]} = 7.64 - 7.57 \text{ (m, 2H, H2)}, 7.31 - 7.24 \text{ (m, 4H, H3')}, 7.13 - 7.04 \text{ (m, 6H, H3, H2')}, 7.04 - 6.95 \text{ (m, 2H, H4')}. \)

\(^{13}\)C-NMR (101 MHz, CD\(_2\)Cl\(_2\)): \( \delta \text{ [ppm]} = 151.14 \text{ (C4)}, 147.93 \text{ (C1')}, 136.25 \text{ (C2)}, 129.89 \text{ (C3')}, 125.66 \text{ (C2')}, 124.05 \text{ (C4')}, 121.96 \text{ (C3)}, 84.10 \text{ (C4'')}, 25.22 \text{ (CH3)}. \)

4,4'-((10-Phenyl-10'H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b]dithiophene]-2',6'-diyl)bis(\( N,N \)-diphenylaniline) (110).

A 2 M potassium phosphate solution was freshly prepared and degassed with argon for 2 h. Dry THF was degassed for 1 h with argon. 2',6'-Dibromo-10-phenyl-10'H-spiro[acridin-9,4'-cyclopenta[2,1-b:3,4-b]dithiophene] 100 (255 mg, 442 \( \mu \)mol), \( N \)-phenyl-\( N \)-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline 108 (492 mg, 1.33 mmol) and tetrakis(triphenylphosphine)palladium(0) (61 mg, 53 \( \mu \)mol, 12 mol\%) were filled into a Schlenk-tube and were evacuated for 30 min. THF (5 ml, dry, degassed) was added and the obtained solution was degassed for an additional 5 min. The 2 M potassium phosphate solution (1.33 ml, 2.65 mmol) was added and the solution was degassed for 2 min. The tube was sealed and the solution was heated to 75 °C for 90 h. The reaction was cooled down, water and Et\(_2\)O was added and the product was three times extracted with Et\(_2\)O. The collected organic fractions were dried with MgSO\(_4\) and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography with silica gel (deactivated with 3% NEt\(_3\)). An eluent gradient from PE:Et\(_2\)O 12:1 to 10:1 was used. Triphenylamine capped spiro acridine 110 was isolated as a yellow solid (296 mg 327 \( \mu \)mol, 74\%).

\(^1\)H-NMR (500 MHz, CD\(_2\)Cl\(_2\)): \( \delta \text{ [ppm]} = 7.50 \text{ (d, } ^3 J = 7.7 \text{ Hz, 2H)}, 7.44 \text{ (d, } ^3 J = 8.6 \text{ Hz, 2H)}, 7.40 \text{ (s, 2H, H3''')}, 7.30 - 7.22 \text{ (m, 12H)}, 7.12 - 6.98 \text{ (m, 23H)}. \)
$^{13}$C-NMR (UDEFT) (126 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = 158.38, 148.01, 147.89, 146.32, 136.37, 136.07, 132.84, 129.88 (C-H), 129.25, 128.21, 127.34, 127.32, 127.00, 126.54, 125.13 (C-H), 124.08, 123.78, 118.84, 59.12 (C$^{4''''}$).$^2$

FTICR-MALDI: m/z: calcd. for C$_{63}$H$_{43}$N$_3$S$_2$: 905.28984; found: 905.28817 ($[M]$+ (δm/m= 1.84 ppm).

Synthesis of 1-Bromo-2-(phenylsulfanyl)benzene (112).$^{[71]}$

A solution of KOH (1.57 g, 28.0 mmol) in 25 ml water was prepared. Iodobenzene 114 (4.19g, 2.3 ml, 20.5 mmol), o-bromothiophenol 113 (3.53 g, 2.20 ml, 18.7 mmol), tetrabutylammonium bromide (6.02 g, 18.7 mmol) and copper(I) iodide (196 mg, 1.03 mmol, 5.5 mol%) were added to the solution under an argon atmosphere. The solution was heated to 80 °C for 60 hours. After cooling to room temperature, the organic phase was separated, and the product was extracted with Et$_2$O. The organic fractions were washed with HCl, saturated NaHCO$_3$ solution, and the solvent was removed. The crude product was purified by a filtration column with silica gel and DCM as eluent. The product was further purified by Kugelrohr-distillation (140 – 170 °C, 1 mbar), followed by a column chromatography with silica gel and a solvent mixture of PE:DCM of 4:1 to afford diphenyl sulfide 112 as a colorless oil (3.40 g, 12.8 mmol, 69%, lit.: 96%$^{[71]}$).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = $\delta$ 7.56 (ddd, $^3$J$_{(H6,H5)}$ = 7.9 Hz, $^4$J$_{(H6,H4)}$ = 1.4 Hz, $^5$J$_{(H6,H4)}$ = 0.3 Hz, 1H, H6), 7.49 – 7.36 (m, 5H, H2', H3', H4'), 7.15 (ddd, $^3$J$_{(H4,H3)}$ = 7.9 Hz, $^3$J$_{(H4,H5)}$ = 7.4 Hz, $^4$J$_{(H4,H6)}$ = 1.4 Hz, 1H, H4), 7.03 (ddd, $^3$J$_{(H5,H6)}$ = 7.9 Hz, $^3$J$_{(H5,H4)}$ = 7.3 Hz, $^4$J$_{(H5,H3)}$ = 1.6 Hz, 1H, H5), 6.92 (ddd, $^3$J$_{(H3,H4)}$ = 8.0 Hz, $^4$J$_{(H3,H5)}$ = 1.6 Hz, $^5$J$_{(H3,H4)}$ = 0.3 Hz, 1H, H3).

$^{13}$C-NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = 138.97 (C$_q$), 133.72 (C-H), 133.40 (C-H), 133.27 (C$_q$), 130.37 (C-H), 130.06 (C-H), 128.86 (C-H), 128.32 (C-H), 127.83 (C-H), 123.42 (C$_q$).

$^2$ The carbon atoms C$^{1'-4'}$ give the same signal as the carbon atoms at C$^{1''''-4''''}$ due to the same chemical environment.
4-(2-(Phenylthio)phenyl)-2,6-bis(trimethylsilyl)-4\textit{H}-cyclopenta[2,1-\textit{b}:3,4-\textit{b}]dithiophen-4-ol (115).

2-Bromophenyl-phenylsulfide 112 (1.58 g, 5.94 mmol) was dissolved in 150 ml dry Et\textsubscript{2}O and cooled to -78 °C. A solution of \textit{n}-BuLi (1.6 M, 4.46 ml) in \textit{n}-hexane was slowly added and the resulting mixture was stirred for two hours while keeping the temperature between -75 and -80 °C. 2,6-Bis(trimethylsilyl)-4\textit{H}-cyclopenta[2,1-\textit{b}:3,4-\textit{b}]dithien-4-one 87 (2.00 g, 5.94 mmol) was dissolved in 50 ml dry THF and was slowly added to the aryllithium solution. The reaction was quenched by the addition of 10 ml -78 °C cold isopropanol. The solution was allowed to warm to room temperature and saturated NH\textsubscript{4}Cl-solution was added. The organic phase was separated, and the aqueous phase was extracted with 50 ml Et\textsubscript{2}O. The collected organic fractions were dried with MgSO\textsubscript{4} and the solvent was removed under reduced pressure. The crude product was purified by column chromatography with silica gel and an eluent mixture of PE:EA of 10:1 which afforded 1.23 g of pure product. An additional 0.51 g of product was obtained after HPLC (hexane: DCM 1:1) purification of the remaining mixture. A total of 1.74 g (4.30 mmol, 72.5%) of the yellow TMS-protected cyclopentadienol 115 was isolated.

\[ T_m = 62.1 - 64.3 \, ^\circ \text{C} \text{ (2 \, ^\circ \text{C/min}).} \]

\textbf{\textsuperscript{1}H-NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2})}: \[ \delta \text{ [ppm]} = 7.64 \, \text{ (br, 1H), 7.28 - 7.17 \, \text{ (m, 6H), 7.13 \, (br, 4H), 3.53 \, (br, OH), 0.28 \, (s, 18H, Si(CH}_3)_3}. \]

\textbf{\textsuperscript{13}C-NMR (101 MHz, CD\textsubscript{2}Cl\textsubscript{2})}: \[ \delta \text{ [ppm]} = 159.14 \, (\text{C}_4), 144.17 \, (\text{C}_6), 142.97 \, (\text{C}_a), 142.60 \, (\text{C}_b), 137.67 \, (\text{C}_9), 135.53 \, (\text{C}-\text{H}), 134.43 \, (\text{C}_q), 130.90 \, (\text{C}-\text{H}), 129.39 \, (\text{C}-\text{H}), 129.17 \, (\text{C}-\text{H}), 128.87 \, (\text{C}-\text{H}), 127.83 \, (\text{C}-\text{H}), 127.29 \, (\text{C}-\text{H}), 79.60 \, (\text{C}_4'), 0.00 \, (\text{Si}(\text{CH}_3)_3). \]

\textbf{FTICR-MALD}: \[ m/z : \text{ calcd. for C}_{27}H_{30}OS_3Si_2: 522.09918; \text{ found: } 522.09930 \, \text{ [M]}^+ \, (\delta m/m= 0.23 \text{ ppm}). \]
2,6-Dibromo-4-[2-(phenylthio)phenyl]-4H-cyclopenta[2,1-b:3,4-b]dithiophen-4-ol (116).

4-(2-(Phenylthio)phenyl)-2,6-bis(trimethylsilyl)-4H-cyclopenta[2,1-b:3,4-b]dithien-4-ol 115 (584 mg, 1.12 mmol) was dissolved in 125 ml dry DCM and cooled to -20 °C. NBS (417 mg, 2.35 mmol) was slowly added and the solution was stirred for 2.5 hours while the solution was allowed to warm to 0 °C. The reaction mixture was stirred for an additional hour at room temperature. The reaction mixture was quenched by the addition of water and the organic phase was extracted with DCM, dried with MgSO₄, and filtered over silica gel. The crude product was purified by column chromatography with silica gel and an eluent mixture of PE:DCM 1:2. Dibrominated cyclopentadithiophene 116 was isolated as a slightly grey solid (332 mg, 0.62 mmol, 55%).

Tₘ = 60.0 – 60.9 °C (2 °C/min).

¹H-NMR (400 MHz, CD₂Cl₂): δ [ppm] = 7.69 (br, 1H), 7.32 – 7.20 (m, 6H), 7.07 (br, 2H), 7.00 (s, 2H, β-H), 3.52 (s, 1H, OH).

¹³C-NMR (101 MHz, CD₂Cl₂): δ [ppm] = 154.89 (C₃), 141.04 (C₄), 138.77 (C₂), 136.91 (C₀), 135.88 (C-H), 133.68 (C₃), 130.68 (C-H), 129.63 (C-H), 129.47 (C-H), 129.39 (C-H), 127.55 (C-H), 127.37 (C-H), 125.96 (C-H), 113.11 (C₂”), 80.98 (C₄”).

FTICR-MALDI: m/z: calcd. for C₂₁H₁₂Br₂OS₃: 533.84170; found: 533.84221 [M]+ (δm/m= 0.96 ppm).

2,6-Dibromospiro[cyclopenta[2,1-b:3,4-b]dithiophene-4,9’-thioxanthene] (117).
Starting from Cyclopentadienol 116 (pathway A)

2,6-Dibromo-4-[2-(phenylthio)phenyl]-4H-cyclopenta[2,1-b:3,4-b]dithien-4-ol 116 (189 mg, 0.35 mmol) was dissolved in 50 ml dry DCM and cooled to 0 °C. BF$_3$·OEt$_2$ (170 µl, 0.78 mmol, 50% in Et$_2$O) was slowly added and the solution was stirred for one hour. The reaction was quenched by the addition of saturated NaHCO$_3$-solution. The product was extracted with DCM, dried with Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The product was purified by column chromatography with flash column chromatography with silica gel and an eluent mixture of PE:DCM of 9:1. Spiro thioxanthene 117 was isolated as a greyish solid (111 mg, 0.21 mmol, 60.7%).

Starting from Cyclopentadienol 97 (pathway C)

Spiro[cyclopenta[2,1-b:3,4-b]dithiophene-4,9'-thioxanthene] 121 (50 mg, 0.14 mmol) was dissolved in 50 ml dry DCM and cooled to 0 °C under argon atmosphere. NBS (49 mg, 0.28 mmol) was added in one portion and the solution was stirred for 1 h at 0 °C. The ice bath was removed, and the solution was allowed to warm to room temperature. Saturated Na$_2$SO$_3$ solution was added and the product was extracted with DCM (3x), washed with water, and dried with MgSO$_4$. The product was obtained as a slightly grey solid (72 mg, 0.14 mmol, quantitative).

$T_m = 259.2$ °C, decomposition (3 °C/min).

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = 7.41 (dd, $^3$J$_{(H4,H3)} = 7.7$ Hz, $^4$J$_{(H4,H2)} = 1.4$ Hz, 2H), 7.22 – 7.13 (m, 4H, H3', H3), 6.97 (ddd, $^3$J$_{(H2,H1;H2,H3)} = 8.0$, 7.3 Hz, $^4$J$_{(H2,H4)}$ 1.3 Hz, 2H, H2), 6.79 (dd, $^3$J$_{(H1,H3)} = 8.0$ Hz, $^4$J$_{(H1,H3)} = 1.3$ Hz, 2H, H1).

$^{13}$C-NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = 155.79 (C$_q$), 137.33 (C$_q$), 135.25 (C$_q$), 132.69 (C$_q$), 128.51 (C-H), 127.40 (C-H), 127.38 (C-H), 126.68 (C-H), 126.56 (C-H), 113.20 (C3'), 59.56 (C4').

FTICR-MALDI: m/z: calcd. for C$_{21}$H$_{10}$Br$_2$S$_3$: 515.83114; found: 515.83088 [M]$^+$ (δm/m= 0.50 ppm).

Spiro[cyclopenta[2,1-b:3,4-b]dithiophene-4,9'-thioxanthene] (121).

3-Bromo-2,2'-bithiophene 118 (1.00 g, 4.08 mmol) was dissolved in 100 ml dry THF and cooled to -78 °C and n-BuLi (3.31 ml, 5.30 mmol, 1.6 M in hexane) was slowly added. The solution was stirred for one additional hour at -78 °C. Thioxanthone 119 (1.04 g, 4.89 mmol) was added in one
portion as a solid and the solution was allowed to warm to room temperature overnight. The reaction was quenched by the addition of saturated NH₄Cl-solution and the organic phase was extracted with Et₂O and dried over MgSO₄. The solvent was removed and the residue was again dissolved in 100 ml acetic acid and 4 ml of HCl (35%) was added and the solution was heated to 130 °C for 4 hours. Ice water was added, and the product was extracted with DCM, washed with saturated Na₂CO₃ solution, dried with MgSO₄, and filtered through a short plug of silica gel. The crude product was purified by column chromatography with an eluent mixture of PE:DCM of 10:1 to afford spiro thioxanthene 121 as a white solid (352 mg, 0.98 mmol, 24%).

Tₘ = 260.1 – 262.0 °C (2 °C/min).

¹H-NMR (400 MHz, CD₂Cl₂): δ [ppm] = 7.48 (ddd, 3J(H₄,H₃) = 7.8 Hz, 4J(H₄,H₂) = 1.4 Hz, 5J(H₄,H₁) = 0.5 Hz, 2H, H₄), 7.25 – 7.19 (m, 6H, H₂', H₃', H₃), 7.01 (ddd, 3J(H₂,H₁; H₂,H₃) = 8.0, 7.3 Hz, 4J(H₂,H₄) = 1.4 Hz, 2H, H₂), 6.86 (ddd, 3J(H₁,H₂) = 8.0 Hz, 4J(H₁,H₃) = 1.4 Hz, 5J(H₁,H₄) = 0.5 Hz, 2H, H₁).

¹³C-NMR (101 MHz, CDCl₃): δ [ppm] = 157.59 (C_q), 137.04 (C_q), 136.19 (C_q), 132.47 (C_q), 127.63 (C-H), 126.87 (C-H), 126.79 (C-H), 126.36 (C-H), 126.04 (C-H), 123.59 (C-H), 58.00 (C₄').

FTICR-MALDI: m/z: calcd. for C₂₁H₁₂S₃: 360.01011; found: 360.00939 [M]+ (δm/m= 2.00 ppm).

4,4'-{Spiro[cyclopenta[2,1-b:3,4-b]dithiophe-4,9'-thioxanthene]-2,6-diyl}bis(N,N-bis(4-methoxyphenyl)aniline) (124).

A 2 M potassium carbonate solution was freshly prepared and degassed with argon for 2 h. Dry THF was degassed for 1 h with argon. 2,6-Dibromospiro(cyclopenta[2,1-b:3,4-b]dithiophe-4,9'-thioxanthene) 117 (100 mg, 193 µmol), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline 103 (250 mg, 579 µmol), tetrakis(triphenylphosphine)palladium(0) (45 mg, 39 µmol, 20 mol%) were filled into a Schlenk-tube and were evacuated for 1 h. THF (5 ml) was added and the solution was degassed for 5 minutes, K₂CO₃ (580 µl, 2 M, 1.16 mmol) was added and the solution was degassed for another minute. The Schlenk-tube was sealed and the solution was heated to 80 °C for 55 h. The reaction mixture
was cooled to room temperature, extracted with DCM, and dried with MgSO₄. The crude product was purified by column chromatography with deactivated (NEt₃) silica gel. An eluent mixture of PE:Et₂O of 5:1, which was gradually changed to 1:1, was used. Triarylamine capped spiro thiioxanthene 124 was precipitated from DCM/PE and was isolated as an orange solid (149 mg, 0.15 mmol, 80%).

\[\text{H-NMR} (400 MHz, CD}_2\text{Cl}_2): \delta [ppm] = 7.49 (ddd, \; \text{J}_{(H4,H3)} = 7.8 \text{ Hz}, \; \text{J}_{(H4,H2)} = 1.3 \text{ Hz}, \; \text{J}_{(H4,H1)} = 0.6 \text{ Hz, 2H, H4}), 7.38 – 7.32 (m, 6H, H3', H3''), 7.23 (ddd, \; \text{J}_{(H3,H4,H2)} = 7.8, \; 6.4 \text{ Hz, 2J}_{(H3,H1)} = 2.3 \text{ Hz, 2H, H3}), 7.08 – 6.99 (m, 12H, H2'', H2, H1), 6.88 – 6.80 (m, 12H, H3'', H2'), 3.78 (s, 12H, OCH₃).

\[\text{C-NMR} (101 MHz, CD}_2\text{Cl}_2): \delta [ppm] = 158.11 (C_q), 156.74 (C_H), 148.80 (C_q), 146.47 (C_q), 140.98 (C_H), 136.42 (C_q), 135.52 (C_q), 132.76 (C_q), 128.11 (C_q), 127.27 (C_H), 127.24 (C_H), 127.15 (C_q), 126.98 (C_H), 126.30(C-H), 120.72 (C-H), 118.17 (C-H), 115.20 (C-H), 59.01 (C_4'''), 55.97 (O-CH₃).

\[\text{FTICR-MALDI:} \; m/z: \text{calcd. for C}_{61}H_{46}N_{2}O_{4}S_{3}: 966.26142; \text{found: 966.26185 [M]+ (δm/m= 0.45 ppm).}

\[4,4'-(Spiro[cyclopenta[2,1-b:3,4-b]dithiophene-4,9'-thioxanthene]-2,6-diyl)bis(N,N-diphenylaniline) (125).

A 2 M potassium carbonate solution was freshly prepared and degassed with argon for 2 h. Dry THF was degassed for 1 h with argon. 2,6-Dibromospiro(cyclopenta[2,1-b:3,4-b]dithiophene-4,9'-thioxanthene) 117 (50 mg, 193 µmol), N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (107 mg, 289 µmol) 108, and tetrakis(triphenylphosphine)palladium(0) (22 mg, 19 µmol, 20 mol%) were filled into a Schlenk-tube and were evacuated for 1 h. THF (5 ml) was added and the solution was degassed for 5 minutes, K₂CO₃ (290 µl, 2 M, 579 µmol) was added and the solution was degassed for another minute. The Schlenk-tube was sealed and the solution was heated to 80 °C overnight. The reaction mixture was cooled to room temperature, extracted with DCM, and dried with MgSO₄. The crude product was purified by column chromatography with
deactivated (NEt₃) silica gel. An eluent mixture of PE:Et₂O:NEt₃ of 5:1:0.06 was used. Triphenylamine capped spiro cyclopentadithiophene 125 was precipitated from DCM/PE and was isolated as an orange solid (53 mg, 63 µmol, 65%).

\[ T_m = 302 \, ^\circ C \text{ (onset, DSC).} \]

**\(^1\)H-NMR** (400 MHz, THF-d₈): \( \delta [ppm] = 7.51 – 7.43 \) (m, 8H), 7.28 – 7.19 (m, 10H), 7.10 – 6.97 (m, 20H).

**\(^{13}\)C-NMR** (101 MHz, THF-d₈): \( \delta [ppm] = \) 159.38 (Cq), 148.68 (C-H), 148.44 (Cq), 146.86 (Cq), 137.04 (Cq), 136.36 (Cq), 133.29 (Cq), 130.26 (C-H), 130.13 (Cq), 128.56 (C-H), 127.77 (C-H), 127.66 (C-H), 127.58 (C-H), 126.98 (C-H), 125.42 (C-H), 124.82 (C-H), 124.08 (C-H), 119.63 (Cq), 59.68 (C4‴).

**FTICR-MALDI:** \( m/z \): calcd. for C₅₇H₃₈N₂S₃: 846.21971; found: 846.21855 [M]+ (\( \delta m/m = 1.37 \) ppm).

**Spiro(cyclopenta[2,1-b:3,4-b′]dithiophene-4,9′-xanthene) (129).**

3-Bromo-2,2′-bithiophene 118 (3.65 g, 87% purity (GC), 12.9 mmol) was dissolved in 150 ml dry Et₂O, cooled to -78 °C and n-BuLi (11.6 ml, 18.6 mmol, 1.6 M in hexane) was slowly added. The solution was stirred for one additional hour at -78 °C. Xanthone 127 (3.65 g, 18.6 mmol) was added in one portion as a solid and the solution was allowed to warm to room temperature overnight. The reaction was quenched by the addition of a saturated NH₄Cl solution and the organic phase was extracted with Et₂O and dried with MgSO₄. The solvent was removed and the crude product was purified by a filtration column with silica gel and at first with a mixture of PE:DCM of 9:1 as eluent to remove bithiophene impurities and afterwards with DCM to elute the intermediate alcohol 128 (5.95 g, 62% purity, 10.2 mmol, 79%). The mixture was directly dissolved in 175 ml acetic acid and 4 ml of HCl (35%) was added and the solution was heated to 130 °C for 4 hours. Ice water was added, and the solution was neutralized by the addition of KOH. Diethyl ether was added, and the organic phase was separated, and the aqueous phase was twice more extracted with diethyl ether. The combined organic fractions were dried with MgSO₄ and the solvent was removed. The crude product was purified by column chromatography on silica gel with an eluent mixture of PE:DCM of 10:1 to afford spiro xanthene 129 as a white solid (956 mg, 2.78 mmol, 27%) after precipitation from DCM/n-hexane.
$T_m = 228.5 - 231.2 \, ^\circ\text{C} (2 \, ^\circ\text{C/min})$.

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = 7.26 – 7.19 (m, 4H, H4, H3), 7.18 (d, $^3J_{(H3,H2')} = 4.9 \, \text{Hz}$, 2H, H3'), 6.85 (ddd, $^3J_{(H2,H1,H2',H3')} = 7.8, 6.5 \, \text{Hz}$, $^4J_{(H2,H4)} = 2.0 \, \text{Hz}$, 2H, H2), 6.77 (d, $^3J_{(H2,H3')} = 4.9 \, \text{Hz}$, 2H, H2'), 6.59 (ddd, $^3J_{(H1,H2)} = 7.8 \, \text{Hz}$, $^4J_{(H1,H2)} = 1.5 \, \text{Hz}$, $^5J_{(H1,H4)} = 0.6 \, \text{Hz}$, 2H, H1).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ [ppm] = 162.13 (C$_{q}$), 151.84 (C$_{q}$), 136.54 (C$_{q}$), 128.53 (C-H), 126.82 (C-H), 126.40 (C-H), 123.51 (C-H), 122.76 (C$_q$), 122.48 (C-H), 117.08 (C-H), 50.49 (C$_4'$).

FTICR-MALDI: m/z: calcd. for C$_{21}$H$_{12}$O$_2$S$_2$: 344.03296; found: 344.03225 [M]$^+$ ($\delta m/m = 2.06 \, \text{ppm}$).

$2,6$-Dibromospiro(cyclopenta[2,1-$b$:3,4-$b$]dithiophene-4,9'-xanthene) (130).

$\begin{align*}
\text{Spiro(cyclopenta[2,1-$b$:3,4-$b$]dithiophene-4,9'-xanthene) 129} & \text{ (300 mg, 871 $\mu$mol) was dissolved in 200 ml dry DCM and was cooled to 0 \, ^\circ\text{C} under argon atmosphere. NBS (310 mg, 1.74 mmol) was added and the solution was stirred for 1 h at 0 \, ^\circ\text{C}. The solution was slowly warmed to room temperature and poured into methanol. The solvent was partially removed under mild vacuum until a precipitate formed. After cooling, the precipitate was filtrated and the crude product was dried under high vacuum to afford the dibrominated xanthene 130 as a white crystalline solid (412 mg, 0.82 mmol, 94%).}
\end{align*}$

$T_m = 266.4 - 268.2 \, ^\circ\text{C} (2 \, ^\circ\text{C/min})$.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 7.28 – 7.24 (m, 2H, H4), 7.28 – 7.17 (m, 2H, H3), 6.88 (ddd, $^3J_{(H2,H1,H2',H3')} = 7.9, 7.0 \, \text{Hz}$, $^4J_{(H2,H4)} = 1.5 \, \text{Hz}$, Hz, 2H, H2), 6.79 (s, 2H, H3'), 6.61 (dd, $^3J_{(H1,H2)} = 7.9 \, \text{Hz}$, $^4J_{(H1,H3')} = 1.6 \, \text{Hz}$, 2H, H1).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ [ppm] = 160.01 (C$_{4a}$), 151.59 (C$_q$), 136.20 (C$_q$), 129.03 (C-H), 126.68 (C-H), 125.37 (C-H), 123.72 (C-H), 121.19 (C$_q$), 117.37 (C-H), 113.03 (C$_q$), 51.71 (C$_4'$).

FTICR-MALDI: m/z: calcd. for C$_{21}$H$_{10}$Br$_2$O$_2$: 499.84343; found: 499.84329 [M]$^+$ ($\delta m/m = 0.28 \, \text{ppm}$).
4,4’-{Spiro(cyclopenta[2,1-b:3,4-b]dithiophene-4,9'-xanthene)-2,6-diyl}-bis(N,N-bis(4-methoxyphenyl)aniline) (131).

A 2 M potassium phosphate solution was freshly prepared and degassed with argon for 4 h. Dry THF was degassed for 2 h with argon. 2,6-Dibromospiro(cyclopenta[2,1-b:3,4-b]dithiophene-4,9’-xanthene) 130 (300 mg, 597 µmol), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline 103 (618 mg, 1.43 mmol) and tetrakis(triphenylphosphine)palladium(0) (104 mg, 90 µmol, 15 mol%) were filled into a Schlenk-tube and evacuated for 1 h. THF (25 ml) was added and the solution was degassed for 5 minutes, K₃PO₄ (1.8 ml, 2 M in H₂O, 3.6 mmol) was added and the solution was degassed for another minute. The Schlenk-tube was sealed and the solution was heated to 80 °C for 16 h. The reaction mixture was cooled to room temperature, extracted with DCM, and dried with MgSO₄. The crude product was purified by flash column chromatography with deactivated (NET₃) silica gel. An eluent mixture of PE:DCM of 9:1 with 1% NET₃ was used and the product was crystallized from DCM/methanol to afford triarylamine capped spiro xanthene 131 as an orange solid (418 mg, 439 µmol, 73.6%).

¹H-NMR (400 MHz, CD₂Cl₂): δ [ppm] = 7.37 – 7.31 (m, 4H, H3’), 7.30 – 7.22 (m, 4H, H3, H4), 7.09 – 7.02 (m, 8H, H2”), 6.95 – 6.89 (m, 4H, H3, H3’”), 6.89 – 6.83 (m, 12H, H2’, H3’”), 6.81 – 6.74 (m, 2H, H1).

¹³C-NMR (101 MHz, CD₂Cl₂): δ [ppm] = 162.65 (C₉), 156.59 (C-H), 152.02 (C₉), 148.62 (C₉), 146.65 (C₉), 140.82 (C₉), 134.90 (C₉), 128.86 (C₉), 127.24 (C-H), 127.12 (C-H), 126.93 (C₉), 125.99 (C-H), 123.81 (C-H), 122.96 (C₉), 120.52 (C-H), 117.29 (C-H), 116.85 (C-H), 115.04 (C-H), 55.81 (O-CH₃), 46.58 (C4’”).

FTICR-MALDI: m/z: calcd. for C₆₁H₄₆N₂O₅S₂: 950.28427; found: 950.28280 [M]+ (δm/m= 1.55 ppm).
Synthesis of [2,2'-Bithiophen]-3-yl-diphenylmethanol (135).[75]

3-Bromo-2,2'-bithiophene 118 (5.17 g, 21.1 mmol) was dissolved in 150 ml dry Et_2O and cooled to -78 °C. A solution of n-BuLi (13.2 ml, 21.1 mmol, 1.6 M in n-hexane) was slowly added and the resulting mixture was stirred for 2 hours at -78 °C. Benzophenone (3.20 g, 17.6 mmol) was dissolved in 50 ml dry Et_2O and slowly added to the reaction mixture. The reaction was allowed to warm to room temperature overnight and was quenched by the addition of saturated NH_4Cl solution. The product was extracted with Et_2O, washed with H_2O, dried with MgSO_4 and the crude product was purified by column chromatography with silica gel and an eluent mixture of PE:EA of 8:1 to afford carbinol 135 as a slightly blue solid (5.38 g, 15.4 mmol, 88%, lit. 78%[75]).

T_m = 120.2 – 121.2 °C (1 °C/min), lit. 121 – 123 °C.[75]

^1H-NMR (400 MHz, CD_2Cl_2): δ [ppm] = 7.34 – 7.22 (m, 11H, H2'', H3'', H4'', H5), 7.15 (d, 3J(H5',H4') = 5.3 Hz, 1H, H5'), 6.86 (dd, 3J(H5',H4') = 5.2 Hz, 4J(H3',H3') = 3.5 Hz, 1H, H5'), 6.68 (dd, 3J(H3',H4') = 3.6 Hz, 4J(H3',H5') = 1.2 Hz, 1H, H3'), 6.39 (d, 3J(H4,H5) = 5.3 Hz, 1H, H4), 3.35 (s, 1H, OH).

^13C-NMR (101 MHz, CDCl_3): δ [ppm] = 147.41 (C_4), 145.42 (C_5), 135.03 (C_3), 131.54 (C_2), 131.39 (C-H), 128.74 (C-H), 127.98 (C-H), 127.62 (C-H), 127.60 (C-H), 127.40 (C-H), 127.32 (C-H), 123.64 (C-H), 80.56 (C1'''').

CI-MS: m/z: calcd. for C_{21}H_{16}OS_2: 348; found: 348 [M]^*.

4,4-Diphenyl-4H-cyclopenta[2,1-b:3,4-b]dithiophene (136).[75]

[2,2'-Bithiophen]-3-yl-diphenylmethanol 135 (3.80 g, 10.9 mmol) was dissolved in 200 ml dry DCM under argon atmosphere and SnCl_4 (1.53 ml, 13.1 mmol) was added. The resulting mixture was stirred for 80 minutes at room temperature. The reaction was quenched upon addition of saturated NaHCO_3 solution and the organic phase was extracted with DCM (3x) washed with water and dried with MgSO_4. The crude product was purified by column chromatography with silica gel and
an eluent mixture of PE:DCM 9:1 to afford diphenyl cyclopentadithiophene 136 as a slightly yellow solid (2.68 g, 8.12 mmol, 74%, lit. 73%\[^75\]).

\[ T_m = 156.6 – 157.7 \, ^\circ C \text{ (1 \, ^\circ C/min)}, \text{lit.} \, 158 – 160 \, ^\circ C.\[^75\] \]

\[^1H\]-NMR (400 MHz, CD\(_2\)Cl\(_2\)): δ [ppm] = 7.27 – 7.19 (m, 12H, H2’, H2, H3, H4), 7.07 (d, \( J_{H3',H2'} = 5.0 \, \text{Hz}, 2H, H3' \)).

\[^13C\]-NMR (101 MHz, CDCl\(_3\)): δ [ppm] = 157.35 (C\(_q\)), 143.93 (C\(_q\)), 136.55 (C\(_q\)), 128.39 (C-H), 127.70 (C-H), 126.82 (C-H), 125.58 (C-H), 123.42 (C-H), 62.09 (C4').

\[ 2,6\text{-Dibromo-4,4-diphenyl-4\text{H}-cyclopenta[2,1-b:3,4-b]}\text{dithiophene (133).}\[^75\] \]

4,4-Diphenyl-4\text{H}-cyclopenta[2,1-b:3,4-b]dithiophene 136 (2.11 g, 6.37 mmol) was dissolved in 200 ml dry DCM and cooled to -30 °C. NBS (2.28 g, 12.8 mmol) was added portion-wise and the solution was stirred for 3 h at -30 °C. The reaction mixture was poured into a saturated Na\(_2\)SO\(_3\) solution, extracted with DCM (3x) and the combined organic fractions were washed with brine and dried with MgSO\(_4\). The solvent was removed, and the crude product was recrystallized in 1.05 l methanol to afford dibrominated cyclopentadithiophene 133 as a white solid (2.25 g, 4.61 mmol, 72%, lit. 84%\[^75\]).

\[ T_m = 288 – 288.5 \, ^\circ C \text{ (1 \, ^\circ C/min)}, \text{lit.} \, 289 – 291 \, ^\circ C.\[^75\] \]

\[^1H\]-NMR (400 MHz, CD\(_2\)Cl\(_2\)): δ [ppm] = 7.28 – 7.24 (m, 6H, H3, H4), 7.19 – 7.14 (m, 4H, H2), 7.07 (s, 2H, H3').

\[^13C\]-NMR (101 MHz, TCE-d\(_2\)): δ [ppm] = 155.55 (C\(_q\)), 142.31 (C\(_q\)), 136.30 (C\(_q\)), 128.45 (C-H), 127.35 (C-H), 127.05 (C-H), 126.26 (C-H), 112.02 (C1), 63.5 (C4').

FTICR-MALDI: \( m/z \): calcd. for C\(_{21}\)H\(_{12}\)Br\(_2\)S\(_2\): 485.87472; found: 485.87329 [M]* (δm/m= 2.94 ppm).
4,4’-(4,4-Diphenyl-4\text{H}-cyclopenta[2,1-\text{b}:3,4-\text{b}]dithiophene-2,6-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (137).

\[
\begin{align*}
\text{MeO} & \quad \text{N} & \quad \text{MeO} \\
\text{MeO} & \quad \text{N} & \quad \text{MeO}
\end{align*}
\]

2,6-Dibromo-4,4-diphenyl-4\text{H}-cyclopenta[2,1-\text{b}:3,4-\text{b}]dithiophene 133 (75 mg, 0.15 mmol), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline 103 (166 mg, 0.38 mmol), and tetrakis(triphenylphosphine)palladium(0) (18 mg, 15 µmol, 10 mol%) were filled in a Schlenk-Tube and evacuated for 1 h. Dried THF (8.0 ml) was added and the solution was degassed for 4 min with argon. A 2 M solution of K\textsubscript{3}PO\textsubscript{4} (461 µl, 0.92 mmol) was added and the mixture was degassed for another minute. The tube was sealed and the reaction mixture was heated to 75 °C for 66 h. Water was added and the product was extracted with Et\textsubscript{2}O, dried with MgSO\textsubscript{4}, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel deactivated with NEt\textsubscript{3}. A solvent mixture of PE:Et\textsubscript{2}O of 3:1, which was gradually changed to 1:1, was used. Triarylamine capped cyclopentadithiophene 137 was precipitated from Et\textsubscript{2}O/PE and was isolated as a yellow solid (108 mg, 0.12 mmol, 75%).

\[T_{m} = 264 \degree C \text{ (onset, DSC)}\]

\textbf{\textsuperscript{1}H-NMR} (500 MHz, THF-d\textsubscript{8}): \[\delta [\text{ppm}] = 7.45 - 7.37 \text{ (m, 4H, H3‘)}, 7.34 - 7.28 \text{ (m, 6H, H2, H3’’’)}, 7.25 - 7.13 \text{ (m, 6H, H3, H4)}, 7.06 - 6.98 \text{ (m, 8H, H2’’)}, 6.91 - 6.80 \text{ (m, 12H, H3’’, H2’)}, 3.75 \text{ (s, 12H, OCH\textsubscript{3})}.\]

\textbf{\textsuperscript{13}C-NMR (UDEFT)} (126 MHz, THF-d\textsubscript{8}): \[\delta [\text{ppm}] = 159.03 \text{ (C1)}, 157.51 \text{ (C4’’’)}, 149.37 \text{ (Cq)}, 146.54 \text{ (Cq)}, 145.09 \text{ (Cq)}, 141.76 \text{ (C-H)}, 135.59 \text{ (Cq)}, 129.25 \text{ (C-H)}, 128.96 \text{ (C3)}, 128.32 \text{ (Cq)}, 127.59 \text{ (C-H)}, 127.49 \text{ (C2’’)}, 126.77 \text{ (C2)}, 121.66 \text{ (C-H)}, 119.36 \text{ (C-H)}, 115.64 \text{ (C3’’’)}, 64.07 \text{ (C4’’’)}, 55.76 \text{ (O-CH\textsubscript{3})}.\]

\textbf{FTICR-MALDI}: \[m/z: \text{ calcd. for } C_{61}H_{48}N_{2}O_{4}S_{2}: 936.30555; \text{ found: } 936.30435 [M]\textsuperscript{+} (\delta m/m = 1.28 \text{ ppm})].
4,4’-(4,4-Diphenyl-4H-cyclopenta[2,1-b:3,4-b]dithiophene-2,6-diyl)bis(N,N-diphenylaniline) (138).

2,6-Dibromo-4,4-diphenyl-4H-cyclopenta[2,1-b:3,4-b]dithiophene 133 (200 mg, 0.41 mmol), N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline 108 (492 mg, 1.33 mmol) were dissolved in dry, degassed THF (4.0 ml) and the solution was degassed for 2 min with argon. A 2 M solution of degassed K$_2$CO$_3$ (1.23 ml, 2.46 mmol) was added and the mixture was degassed for another two minutes before adding the catalyst tetrakis(triphenylphosphine)palladium(0) (71 mg, 61 µmol, 15 mol%) and degassing for additional 30 seconds. The tube was sealed and the reaction was heated to 80 °C for 90 h. Water was added and the product was extracted with DCM, dried with MgSO$_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography with silica gel deactivated with NEt$_3$. A solvent mixture of PE:Et$_2$O of 7:1 with 1% NEt$_3$ was used as eluent. Triphenylamine capped cyclopentadithiophene 138 was precipitated from Et$_2$O/PE and was isolated as a yellow solid (260 mg, 0.32 mmol, 78%).

$T_m = 281$ °C (onset, DSC).

$^1$H-NMR (400 MHz, C$_6$D$_6$): δ [ppm] = 7.48 – 7.43 (m, 4H, H2), 7.24 – 7.19 (m, 6H, H3', H3''), 7.14 – 7.04 (m, 22H, H2'', H3'', H3, H4), 6.99 – 6.94 (m, 4H, H2'), 6.87 (tt, $^3$J$_{H4''-H3''}$ = 6.8 Hz, $^4$J$_{H4''-H2''}$ = 1.6 Hz, 4H, H4'').

$^{13}$C-NMR (126 MHz, THF-d$_8$): δ [ppm] = 159.25 (C$_q$), 148.72, 148.32 (C$_q$), 146.25 (C$_q$), 144.92 (C$_q$), 136.10 (C$_q$), 130.38 (C$_q$), 130.25 (C-H), 129.30 (C-H), 128.92 (C-H), 127.68, 127.00 (C-H), 125.36 (C-H), 124.90 (C-H), 124.03 (C-H), 120.06, 64.09 (C4'').

FTICR-MALDI: m/z: calcd. for C$_{57}$H$_{40}$N$_2$S$_2$: 816.26274; found: 816.26165 [M]$^+$ (δm/m= 1.33 ppm).
4-Bromo-\(N,N\)-bis(4-methylthiophenyl)aniline (139).

The reaction was carried out in a flame-dried Schlenk-tube under argon atmosphere. 4-Bromothiоanisole 140 (12.0 g, 59.2 mmol), aniline 104 (2.06 g, 2.00 ml, 21.9 mmol), NaO\(\text{tBu}\) (8.42 g, 87.6 mmol), Pd\(\text{2dba}_3\) (1.00 g, 1.1 mmol, 10 mol%), and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) (1.36 g, 2.2 mmol, 10 mol%) were dissolved in dry degassed toluene and heated to 120 °C for 16 hours. After cooling to room temperature, water was added and the product was extracted with Et\(_2\)O. The combined organic fractions were washed with water, dried with MgSO\(_4\) and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography with silica gel and a solvent mixture of PE:DCM of 3:1 to afford triarylamine 139 as a colorless oil (5.86 g, 17.4 mmol, 79%).

\(T_m = 60.1 – 62.8 \, ^\circ\text{C} (3 \, ^\circ\text{C/min}).\)

\(^1\text{H-NMR}\) (400 MHz, CD\(_2\)Cl\(_2\)): δ [ppm] = 7.31 - 7.26 (m, 2H, H3), 7.22 - 7.19 (m, 4H, H3'), 7.10 - 7.06 (m, 2H, H2), 7.06 - 7.02 (m, 5H, H2', H4), 2.46 (s, 6H, S-CH\(_3\))

\(^{13}\text{C-NMR}\) (101 MHz, CD\(_2\)Cl\(_2\)): δ [ppm] = 148.0 (C\(_q\), 145.8 (C\(_q\), 132.4 (C\(_q\), 129.8 (C-H), 128.8 (C-H), 125.1 (C-H), 124.3 (C-H), 123.3 (C-H), 17.1 (S-CH\(_3\)).

\text{FTICR-MALDI}: m/z: calcd. for C\(_{20}\)H\(_{19}\)NS\(_2\): 337.09589; found: 337.09521 [M]\(^+\) (δm/m= 2.01 ppm).

4-Bromo-\(N,N\)-bis(4-methylthiophenyl)aniline (141).

The reaction was carried out under light-exclusion. 4-(Methylthio)-\(N\)-(4-(methylthio)phenyl)-\(N\)-phenylaniline 139 (5.30 g, 15.7 mmol) was dissolved in dry THF and cooled to 0 °C. \(N\)-Bromosuccin-
imid (2.80 g, 15.7 mmol) was slowly added to the solution. The reaction was stirred for an additional 20 hours at room temperature. The reaction was quenched by the addition of saturated Na₂SO₃-solution and the organic phase was extracted with Et₂O, washed with water, and dried with MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography with silica gel and a solvent mixture of PE:DCM of 6:1 which afforded triarylamine bromide 141 as a colorless oil (5.81 g, 14.0 mmol, 89%).

\[ T_m = 83.4 - 85.0 \, ^\circ\mathrm{C} \, (3 \, ^\circ\mathrm{C/min}). \]

\(^1\text{H}-\text{NMR} \, (400 \, \text{MHz, CD}_2\text{Cl}_2): \delta \, [\text{ppm}] = 7.35 - 7.30 \, (\text{m, 2H, H3}), \, 7.20 - 7.14 \, (\text{m, 4H, H3'}), \, 7.05 - 6.96 \, (\text{m, 4H, H2'}), \, 6.95 - 6.87 \, (\text{m, 2H, H2}), \, 2.46 \, (\text{s, 6H, S-CH}_3). \]

\(^{13}\text{C}-\text{NMR} \, (101 \, \text{MHz, CD}_2\text{Cl}_2): \delta \, [\text{ppm}] = 147.28 \, (\text{C}_q), \, 145.19 \, (\text{C}_q), \, 133.23 \, (\text{C}_q), \, 132.62 \, (\text{C-H}), \, 128.71 \, (\text{C-H}), \, 125.44 \, (\text{C-H}), \, 125.16 \, (\text{C-H}), \, 115.02 \, (\text{C}_q), \, 16.88 \, (\text{S-CH}_3). \]

\text{FTICR-MALDI: m/z: calcd. for C}_{20}\text{H}_{18}\text{BrNS}_2: 415.00640; \text{found: 415.00577} \, [\text{M}]^+ \, (\delta m/m = 1.51 \, \text{ppm}). \]

\textbf{4-(Methylthio)-N-(4-(methylthio)phenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (142).[^69]}

![Chemical structure of 4-(Methylthio)-N-(4-(methylthio)phenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (142).

The reaction was carried out in a flame-dried Schlenk-tube under argon atmosphere. 4-Bromo-\textit{N,N}-bis(4-(methylthio)phenyl)aniline 141 (2.57 g, 6.20 mmol), bis(pinacolato)diboron (1.88 g, 7.40 mmol) Pd(dppe)Cl₂*CH₂Cl₂ (0.25 g, 0.3 mmol, 5 mol%), and potassium acetate (1.82 g, 18.5 mmol) were dissolved in 15 ml dry DMF. The tube was sealed and heated to 80 °C for 16 hours. The crude product was extracted with DCM, washed with water, and dried with MgSO₄. The solvent was removed, and the product was again dissolved in DCM and purified by filtration over silica gel deactivated with NEt₃. Boronic ester 142 was obtained as a colorless oil, which solidified in the freezer (2.59 g, 5.6 mmol, 90%).

\[ T_m = 47.3 - 50.2 \, ^\circ\mathrm{C} \, (3 \, ^\circ\mathrm{C/min}). \]
\textbf{1H-NMR} (400 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = 7.71 – 7.53 (m, 2H, H2), 7.28 – 7.14 (m, 4H, H3'), 7.04 – 7.00 (m, 4H, H2'), 6.99 – 6.95 (m, 2H, H3), 2.46 (s, 6H, S-CH$_3$), 1.31 (s, 12H, CH$_3$).

\textbf{13C-NMR} (101 MHz, CD$_2$Cl$_2$): $\delta$ [ppm] = 150.74 (C$_q$), 145.18(C$_q$), 136.27 (C-H), 133.48 (C$_q$), 128.64 (C-H), 126.06 (C-H), 121.69 (C-H), 84.10 (C4''), 25.20 (CH$_3$), 16.85 (S-CH$_3$).

\textbf{FTICR-MALDI}: $m/z$: calcd. for C$_{26}$H$_{30}$BNO$_2$S$_2$: 463.18110; found: 463.18001 [M]$^+$ ($\delta$m/m= 2.35 ppm).

\textbf{4,4'-(4,4-Diphenyl-4H-cyclopenta[2,1-b:3,4-b]dithiophene-2,6-diyl)bis(N,N-bis(4-(methylthio)phenyl)aniline) (143)}.  

![Chemical structure](image)

Dry THF was degassed for 1 hour with argon, a fresh solution of K$_3$PO$_4$ in H$_2$O was prepared, and degassed with argon for 2 hours. 2,6-Dibromo-4,4-diphenyl-4H-cyclopenta[2,1-b:3,4-b]dithiophene 133 (240 mg, 0.49 mmol), 4-(methylthio)-N-(4-(methylthio)phenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline 142 (706 mg, 1.52 mmol), and tetrakis(triphenylphosphine)palladium(0) (71 mg, 61 µmol, 12 mol%) were dissolved in 12 ml dry and degassed THF and the solution was degassed for 5 minutes. K$_3$PO$_4$ solution (1.48 ml, 2.95 mmol, 2 M in water) was added and the reaction mixture degassed for another 2 minutes. The Schlenk tube was sealed and the mixture was heated to 80 °C for 62 hours. The solution was cooled and water was added. The organic phase was twice extracted with DCM, dried with MgSO$_4$, and the crude product was purified by flash column chromatography with silica gel and an eluent mixture of PE:DCM of 1:1 and 1% NEt$_3$. The cyclopentadiene was further purified by size exclusion chromatography in DCM, followed by a purification with HPLC on a nitrophenyl column with n-hexane/DCM 1:1 and 0.1% NEt$_3$. Triarylamine capped cyclopentadithiophene 143 was precipitated from n-hexane/DCM and was isolated as a yellow-orange solid (323 mg, 0.32 mmol, 65.6%).

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3 One $^{13}$C-NMR signal is missing. The C1 atom which is directly bound to the boron atom could be missing due to the quadrupole relaxation between the two atoms.
\( T_m = 270 \, ^\circ \text{C} \) (onset, DSC).

\(^1\text{H-NMR}\) (500 MHz, THF-\(d_8\)): \( \delta \,[\text{ppm}] = 7.53 - 7.48 \,(m, \, 4\, H, \, H3') , \, 7.39 \,(s, \, 2H, \, \beta-H), \, 7.34 - 7.30 \,(m, \, 4H, \, H2), \, 7.25 - 7.21 \,(m, \, 4H, \, H3), \, 7.21 - 7.16 \,(m, \, 10H, \, H4, \, H3''), \, 7.03 - 6.99 \,(m, \, 12H, \, H2', \, H2''), \, 2.44 \,(s, \, 12H, \, S-CH_3).

\(^{13}\text{C-NMR}\) (126 MHz, THF-\(d_8\)): \( \delta \,[\text{ppm}] = 159.31 \,(C_q), \, 148.00 \,(C_q), \, 146.22 \,(C_q), \, 146.03 \,(C_q), \, 144.91 \,(C_q), \, 136.10 \,(C_q), \, 134.01 \,(C-H), \, 130.39 \,(C_q), \, 129.35 \,(C-H), \, 129.29 \,(C-H), \, 128.94 \,(C-H), \, 127.68 \,(C_q), \, 127.02 \,(C-H), \, 125.84 \,(C-H), \, 124.54 \,(C-H), \, 120.07 \,(C_q), \, 64.11 \,(C4''), \, 16.62 \,(S-CH_3).

\text{FTICR-MALDI:} \, m/z: \, \text{calcd. for } C_{61}H_{48}N_2S_6: \, 1000.21417; \, \text{found: } \, 1000.21208 \,[M]^+ \,(\delta m/m= \, 2.09 \, \text{ppm}).

\text{Hexabromocyclopentadiene (168).}\text{[116, 186]}

A solution of potassium hypobromite was prepared by dissolving potassium hydroxide (306 g, 5.45 mol) in 1.36 l water, cooling to -5 °C, and slow addition of bromine (93 ml, 1.82 mol) while keeping the temperature below -5 °C. Freshly distilled cyclopentadiene 146 (15 ml, 182 mmol) was added and the solution was stirred at -5 °C for two additional hours. The reaction was allowed to warm to room temperature overnight. The organic phase was extracted with PE and hexabromocyclopentadiene 168 was obtained after a series of recrystallizations from PE as a slightly brown solid (22.99 g, 43 mmol, 23.5%).

\( T_m = 82.3 - 84.5 \, ^\circ \text{C} \,(2 \, ^\circ \text{C/min}), \, \text{lit. } 86 - 87 \, ^\circ \text{C}.\text{[187]}

\(^{13}\text{C-NMR}\) (101 MHz, CDCl₃): \( \delta \,[\text{ppm}] = 130.44 \,(C1), \, 123.48 \,(C2), \, 57.30 \,(C5).

\text{1,2,3,4-Tetrabromo-5,5-dimethoxycyclopenta-1,3-diene (164).}\text{[116]}

Hexabromocyclopentadiene 168 (3.61 g, 6.69 mmol) was dissolved in 16 ml dry diglyme under an argon atmosphere and cooled to -60 °C. Sodium methoxide (3.213 ml, 25% in MeOH, 14.05 mmol) was slowly added and the solution was stirred for 2 hours at -30 °C and additional 3 hours at room temperature before pouring the solution on ice. The organic phase was extracted with DCM, dried

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with Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The crude product was purified by precipitation from DCM/MeOH and the acetal 164 was obtained as a slightly brown solid (1.22 g, 2.75 mmol, 41%).

$T_m = 103.2 - 104.4 \, ^\circ C (2 \, ^\circ C/min), \text{lit. } 104 - 105 \, ^\circ C.^[188]

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 3.27 (s, 6H, OCH$_3$).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ [ppm] = 126.1 (C$_a$), 124.4 (C$_a$), 107.1 (C$_a$), 51.6 (OCH$_3$).

4,4',4'',4'''-(5,5-Dimethoxycyclopenta-1,3-diene-1,2,3,4-tetrayl)tetrakis-[$N,N$-bis(4-methoxyphenyl)aniline] (171).

A 2 M potassium phosphate solution was freshly prepared and degassed with argon for 2 h. Dry THF was degassed for 1 h with argon. 1,2,3,4-Tetrabromo-5,5-dimethoxycyclopenta-1,3-diene 164 (50 mg, 113 µmol), 4-methoxy-$N$-(4-methoxyphenyl)-$N$-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]aniline 103 (195 mg, 452 µmol), tetrakis(triphenylphosphane)palladium(0) (20 mg, 17µmol, 15 mol%) were filled into a Schlenk-tube and were evacuated for 1 h. THF (3 ml) was added and the solution was degassed for 5 minutes with argon, K$_2$PO$_4$ (850 µl, 2 M, 1.70 mmol) was added and the solution was degassed for another minute. The Schlenk-tube was sealed and the solution was heated to 80 °C for 72 h. The reaction mixture was cooled to room temperature, water was added, and the organic phase was extracted with Et$_2$O and dried with MgSO$_4$. The crude product was purified by flash column chromatography with trimethylamine-deactivated silica gel. An eluent mixture of PE:Et$_2$O of 1:1 and 3% NEt$_3$ which was later changed to PE:Et$_2$O:PhMe 2:2:1 was used. Acetal 171 was precipitated from DCM/PE and was isolated as an orange solid (112 mg, 84 µmol, 73.9%).

$T_m = 266 \, ^\circ C \, (\text{DSC, onset})$. 

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\[ ^1H-NMR \text{ (400 MHz, CD}_2\text{Cl}_2): \delta [ppm] = 7.42 – 7.36 (m, 4H, H2'''), 7.10 – 7.02 (m, 8H), 7.03 – 6.96 (m, 8H), 6.88 – 6.79 (m, 8H), 6.83 – 6.76 (m, 12H), 6.78 – 6.69 (m, 4H, H2'), 6.73 – 6.65 (m, 4H, H3'''), 3.78 (s, 6H, OCH}_3, 3.76 (s, 6H, OCH}_3), 3.19 (s, 6H, OCH}_3). \]

\[ ^{13}C-NMR \text{ (101 MHz, CD}_2\text{Cl}_2): \delta [ppm] = 156.71 (Cq), 156.40 (Cq), 148.08 (Cq), 147.78 (Cq), 144.02 (Cq), 141.36 (Cq), 141.02 (Cq), 133.88 (Cq), 130.87 (C-H), 129.41 (C-H), 128.94 (Cq), 127.55 (C-H), 126.91 (C-H), 125.79 (Cq), 120.54 (C-H), 119.03 (C-H), 115.49 (Cq), 115.12 (C-H), 115.10 (C-H), 55.96 (OCH}_3), 55.94 (OCH}_3), 50.89 (OCH}_3). \]

FTICR-MALDI: \( m/z: \) calcd. for \( C_{87}H_{78}N_{4}O_{10}: 1338.57179; \) found: 1338.57156 [M]\(^+\) (\( \delta m/m = 0.12 \) ppm).

4,4',4'',4'''-(5,5-Dimethoxycyclopenta-1,3-diene-1,2,3,4-tetrayl)tetrakis-(N,N-diphenylaniline) \((172)\).

A 2 M potassium carbonate solution was freshly prepared and degassed with argon for 3 h. Dry THF was degassed for 30 min with argon. 1,2,3,4-Tetrabromo-5,5-dimethoxycyclopenta-1,3-diene \( 164 \) (150 mg, 339 \( \mu \)mol) was filled into a Schlenk-tube and evacuated for 30 min. \( N,N\)-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline \( 108 \) (857 mg, 2.31 mmol) and 6 ml THF were added and the solution was degassed for 10 min. Tetrakis(triphenylphosphine)palladium(0) (78 mg, 67 \( \mu \)mol, 20 mol\%) and 2.0 ml \( K_2CO_3 \) (4.1 mmol, 2 M in \( H_2O \)) were added and the solution was degassed for additional five minutes. The Schlenk-tube was sealed and the solution was heated to 80 °C for 64 h. The reaction mixture was cooled to room temperature, water was added and the organic phase was extracted with DCM and dried with MgSO\( _4 \). The crude product was purified by flash column chromatography with trimethylamine-deactivated silica gel. An eluent mixture of PE:Et\(_2\)O of 8:1 and which was gradually changed to PE:Et\(_2\)O 5:1, was used. Acetal \( 172 \) was precipitated from PE/Et\(_2\)O and was isolated as an orange solid (171 mg, 156 \( \mu \)mol, 45.8%).

\( T_m = 260 \) °C (DSC, onset).
^1H-NMR (500 MHz, CD$_2$Cl$_2$): δ [ppm] = 7.53 – 7.46 (m, 4H, H2'''), 7.31 – 7.24 (m, 8H), 7.24 – 7.18 (m, 8H), 7.15 – 7.09 (m, 8H), 7.08 – 6.98 (m, 16H), 6.95 – 6.86 (m, 12H), 3.26 (s, 6H, OCH$_3$).

$^{13}$C-NMR (126 MHz, CD$_2$Cl$_2$): δ [ppm] = 148.18, 148.07, 147.45, 147.07, 144.46, 134.67, 131.18 (C-H), 130.73, 130.24, 129.82 (C-H), 129.71 (C-H), 128.71, 127.66, 125.38 (C-H), 124.79, 123.74 (C-H), 123.46 (C-H), 51.04 (OCH$_3$).

FTICR-MALDI: m/z: calcd. for C$_{79}$H$_{62}$N$_4$O$_2$: 1098.48673; found: 1098.48237 [M$^+$] (δm/m= 3.97 ppm).

2,3,4,5-Tetrakis[4-[bis(4-methoxyphenyl)amino]phenyl]cyclopenta-2,4-dien-1-one (173).

4,4',4'',4'''-(5,5-Dimethoxycyclopenta-1,3-diene-1,2,3,4-tetrayl)tetrakis[N,N-bis(4-methoxyphenyl)aniline] (88 mg, 66 µmol) 171 was dissolved in 4 ml acetone and 0.5 ml DCM. Iodine (2 mg, 16 µmol) was added and the solution was stirred for 90 min at room temperature. The reaction was quenched by the addition of a saturated Na$_2$SO$_3$ solution and the product was extracted with DCM and dried with MgSO$_4$. The crude product was purified by column chromatography with 1% EA in DCM as eluent and silica gel as a stationary phase. Cyclopentadienone 173 was precipitated from PE/DCM and afforded the product as a violet solid (52 mg, 40 µmol, 61%).

$T_m$ = 258 °C (DSC, onset).

$^1$H-NMR (500 MHz, CD$_2$Cl$_2$): δ [ppm] = 7.13 – 7.09 (m, 4H), 7.07 – 7.01 (m, 16H), 6.86 – 6.81 (m, 16H), 6.80 – 6.73 (m, 4H), 6.70 – 6.67 (m, 4H), 3.78 (s, 12H, OCH$_3$), 3.78 (s, 12H, OCH$_3$).

$^{13}$C-NMR (126 MHz, CD$_2$Cl$_2$): δ [ppm] = 202.24 (C1), 156.95 (Cq), 156.78 (Cq), 153.39 (Cq), 149.18 (Cq), 148.21 (Cq), 141.15 (Cq), 140.85 (Cq), 131.19 (C-H), 131.07 (C-H), 128.72 (Cq), 127.58 (C-H), 127.53 (C-H), 125.86 (Cq), 124.09 (Cq), 123.88 (Cq), 119.52 (C-H), 118.83 (C-H), 115.26 (C-H), 115.22 (C-H), 56.01 (OCH$_3$).
**FTICR-MALDI**: \( m/z \): calcd. for \( C_{85}H_{72}N_{4}O_{9} \): 1292.52993; found: 1292.528833 [M\(^+\)] (\( \delta m/m = 0.85 \) ppm).

**2,3,4,5-Tetrakis(4-(diphenylamino)phenyl)cyclopetana-2,4-dien-1-one (174).**

![Chemical structure diagram]

\( 4',4'',4'''-\)((5,5-Dimethoxycyclopenta-1,3-diene-1,2,3,4-tetrayl)tetrakis(\( N,N \)-diphenylaniline) \quad 172 

(76 mg, 69 \( \mu \)mol) was dissolved in 4 ml acetone and 2.5 ml DCM. Iodine (3.5 mg, 28 \( \mu \)mol) was added and the solution was stirred heated to 40 °C for 16 hours. The reaction was quenched by the addition of saturated \( \text{Na}_2\text{SO}_3 \) solution and the product was extracted with DCM and dried with \( \text{MgSO}_4 \). The crude product was purified by column chromatography with PE:DCM of 2:1 as eluent and silica gel as a stationary phase. Cyclopentadienone 174 was precipitated from PE/DCM and afforded the product as a dark violet solid (52 mg, 40 \( \mu \)mol, 61%).

\( T_m = 287 \) °C (DSC, onset).  

\( ^1H\text{-NMR} \) (500 MHz, \( \text{CD}_2\text{Cl}_2 \)): \( \delta \) [ppm] = 7.29 – 7.19 (m, 20H), 7.12 – 7.02 (m, 20H), 6.95 – 6.91 (m, 4H), 6.90 – 6.84 (m, 8H).

\( ^{13}C\text{-NMR} \) (126 MHz, \( \text{CD}_2\text{Cl}_2 \)): \( \delta \) [ppm] = 201.76 (C1), 153.83 (Cq), 148.48 (Cq), 148.08 (Cq), 147.83 (Cq), 147.42 (Cq), 131.40 (C-H), 131.17 (C-H), 129.92 (C-H), 129.85 (C-H), 127.59 (Cq), 125.80 (Cq), 125.48 (Cq), 125.35 (C-H), 124.24 (C-H), 124.03 (C-H), 123.75 (C-H), 122.74 (C-H), 122.05 (C-H).

**FTICR-MALDI**: \( m/z \): calcd. for \( C_{77}H_{56}N_{4}O \): 1052.44541; found: 1052.443570 [M\(^+\)] (\( \delta m/m = 1.75 \) ppm).


References


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Appendix

Single Crystal X-Ray Structure Data

Single Crystal X-Ray Analysis of 4,4',4'',4'''- (5,5-Dimethoxycyclopenta-1,3-diene-1,2,3,4-tetrayl)tetrakis-[N,N-bis(4-methoxyphenyl)aniline] (171)

Bond precision: C-C = 0.0030 Å  Wavelength=1.54184
Cell: 
a= 10.8185 (2) Å  b= 16.2139 (5) Å  c = 22.5926 (6) Å
α = 107.709 (3)  β= 95.3396 (19)  γ = 90.349 (2)
Temperature: 150 K

Volume  Calculated  Reported
3756.33 (18)  3756.34 (18)
Space group  P -1  P -1
Hall group  -P 1  -P 1
Moiety formula  C87 H78 N4 O10, C H Cl3  C H Cl3, C87 H78 N4 O10
Sum formula  C88 H79 Cl3 N4 O10  C88 H79 Cl3 N4 O10
Mr  1458.91  1458.90
Dx,g cm-3  1.290  1.290
Z  2  2
Mu (mm-1)  1.619  1.619
F000  1532.0  1532.0
F000'  1538.42
h,k,lmax  13,20,28  13,20,28
Nref  15305  14756
Tmin,Tmax  0.646,0.823  0.714,1.000
Tmin'  0.521
Correction method= # Reported T Limits: Tmin = 0.714 Tmax = 1.000
AbsCorr = MULTI-SCAN

Data completeness = 0.964  Theta(max)= 74.161
R(reflections)= 0.0535( 11931)  wR2(reflections)= 0.1544( 14756)
S = 1.032  Npar= 993

Single Crystal X-Ray Analysis of 4,4',4'',4'''- (5,5-Dimethoxycyclopenta-1,3-diene-1,2,3,4-tetrayl)tetrakis-[N,N-diphenylaniline] (172)

Bond precision: C-C = 0.0019 Å  Wavelength=1.54184
Cell: 
a= 10.2785 (4) Å  b= 15.4493 (6) Å  c = 19.6524 (7) Å
α = 97.799 (3)  β= 98.067 (3)  γ = 90.493 (3)
Temperature: 150 K

Volume  Calculated  Reported
3060.0 (2)  3060.04 (19)
Space group  P -1  P -1
### Single Crystal X-Ray Analysis of 4,4'-(10-Phenyl-10H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b]dithiophene]-2',6'-diyl)bis(N,N-bis(4-methoxy-phenyl)aniline) (109)

The structure of molecule 4,4'-(10-Phenyl-10H-spiro[acridine-9,4'-cyclopenta[2,1-b:3,4-b]dithiophene]-2',6'-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) 109 obtained from single crystal X-ray structural analysis was entered into the database of the Cambridge Crystallographic Data Centre (CCDC) under CCDC number 1979010.

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Correction method= # Reported T Limits: Tmin = 0.812 Tmax = 1.000
AbsCorr = MULTI-SCAN

Data completeness = 0.966
Theta(max)= 74.085
R(reflections)= 0.0418( 10389)

wR2(reflections)= 0.1186( 12008)
S = 1.033
Npar= 769
Nref 11344 11024
Tmin,Tmax 0.871,0.910 0.594,1.000
Tmin' 0.709
Correction method= # Reported T Limits: Tmin = 0.594 Tmax = 1.000
AbsCorr = MULTI-SCAN

Data completeness = 0.972
Theta(max)= 74.117
R(reflections)= 0.0431(9103)
wr2(reflections)= 0.1225(11024)
S = 1.067
Npar= 785
Publications


Presentations


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Curriculum Vitae

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