Synthesis and Supramolecular Chemistry of Strained Carbon Nanohoops

Dissertation zur Erlangung des Doktorgrades Dr. rer. nat. der Fakultät für Naturwissenschaften der Universität Ulm

vorgelegt von

Youzhi Xu

geboren in Ruichang, Volksrepublik China

Ulm, 2019
Amtierender Dekan: Prof. Dr. Thorsten M. Bernhardt

1. Gutachter: Prof. Dr. Max von Delius

2. Gutachter: Prof. Dr. Alexander Kühne

Tag der Promotionsprüfung: 18.11.2019

Universität Ulm, Fakultät der Naturwissenschaften, 2019
Contents

Preface.............................................................................................................................................. I
List of Abbreviations.......................................................................................................................... III
1. State of the Art .............................................................................................................................. 1
   1.1. π-Conjugated Systems ............................................................................................................. 1
       1.1.1. Nonplanar Nanocarbons ............................................................................................... 3
       1.1.2. Conjugated Macrocycles ............................................................................................. 8
       1.1.3. Strained Carbon Nanohoops ................................................................................... 11
           1.1.3.1. [n]Cycloparaphenyleneacetylenes ..................................................................... 13
           1.1.3.2. [n]Cycloparaphenyles and Derivatives ................................................................. 16
           1.1.3.3. π-Extended Carbon Nanohoops ........................................................................... 23
           1.1.3.4. Cyclo-porphyrin Nanorings ................................................................................ 28
           1.1.3.5. Conjugated Carbon Nanocages ........................................................................ 31
           1.1.3.6. The Optoelectronic Properties of Strained Carbon Nanohoops .................... 34
   1.2. The Supramolecular Chemistry of Strained Carbon Nanohoops ......................................... 38
2. Aims and Achievements ............................................................................................................... 55
   2.2. Efficient Electron Transfer in Modular Porphyrin–[10]CPP Fullerene Complexes .......... 59
   2.3. Synthesis of Highly Strained, Radially π-Conjugated Porphyrinylene Nanohoops ......... 63
3. Publications .................................................................................................................................... 66
       phenylene-Fullerene [2]Rotaxanes ......................................................................................... 66
       Porphyrin-[10]CPP Fullerene Complexes .............................................................................. 124
   3.3. Highly Strained, Radially π-Conjugated Porphyrinylene Nanohoops ......................... 194
4. Summary and Outlook .................................................................................................................. 310
References......................................................................................................................................... 313
List of Publications and Patents ...................................................................................................... 318
List of Conference Contributions .................................................................................................. 319
Curriculum Vitae ............................................................................................................................ 320
Acknowledgements ........................................................................................................................ 321
Statement .......................................................................................................................................... 324
Preface

The central goal of this thesis was to tackle the challenging synthesis of strained carbon nanohoops and explore their applications in supramolecular chemistry as well as material science. Strained carbon nanohoops are macrocycles whose backbones are comprised only of sp$^2$- and/or sp-hybridized carbon atoms and that are particularly shape-persistent. [$n$]Cycloparaphenylene-acetylenes ([$n$]CPPAs) and [$n$]cycloparaphenylenes ([$n$]CPPs) are the most prominent examples of strained carbon nanohoops that are synthetically accessible. Following a decade of rapid progress on the synthesis of nanohoops, the research interest is shifting towards investigations of their properties and applications. [10]CPP is undoubtedly one of the most interesting family members of [$n$]CPPs, because it has a perfect ring size for the strong concave–convex π–π interaction with C$_{60}$/C$_{70}$. Therefore, the work of this thesis is focused on unleashing the supramolecular potential of [10]CPP derivatives and analogues (Figure 1).

Figure 1. Unleashing the supramolecular potential of [10]CPP derivatives and analogues.

The first chapter of this thesis introduces nonplanar π-conjugated systems, and mainly focuses on the synthesis and supramolecular chemistry of strained
carbon nanohoops (the last of these topics is presented in the form of a review article, which was recently published in *Angewandte Chemie*). Chapter 2 is a synopsis on the aims and achievements of each of the three research projects that have been carried out (Figure 1). Chapter 3 is presented in the form of articles that have recently been published or are under peer-review. Section 3.1 (Project I) describes the synthesis of two new [2]rotaxanes featuring [10]CPP. In these mechanically interlocked architectures, [10]CPP served as a supramolecular directing group to improve the regioselectivity of fullerene bisaddition. Section 3.2 (Project II) deals with an efficient modular electron transport system, in which [10]CPP plays the role of a rigid non-covalent bridge between zinc porphyrin and a range of fullerenes. Section 3.3 (Project III) presents the synthesis, optoelectronic properties and fullerene affinity (>10⁸ M⁻¹) of a series of highly strained porphyrinylene nanohoops ([10]CPP analogues). Chapter 4 contains closing remarks about the scope and significance of the presented work as well as further ideas that are currently being tested in the Delius lab.
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>CNTs</td>
<td>carbon nanotubes</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>COFs</td>
<td>covalent organic frameworks</td>
</tr>
<tr>
<td>cod</td>
<td>1,5-cyclooctadiene</td>
</tr>
<tr>
<td>COR</td>
<td>corannulene</td>
</tr>
<tr>
<td>CID</td>
<td>collision-induced dissociation</td>
</tr>
<tr>
<td>CS</td>
<td>charge separation</td>
</tr>
<tr>
<td>CR</td>
<td>charge recombination</td>
</tr>
<tr>
<td>dpff</td>
<td>1,1’-bis(diphenylphosphino)ferrocene</td>
</tr>
<tr>
<td>DABCO</td>
<td>1,4-diazabicyclo-[2.2.2]octane</td>
</tr>
<tr>
<td>DPV</td>
<td>differential pulsed voltammetry</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>EtOAc</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>FTO</td>
<td>fluorine-doped tin oxide</td>
</tr>
<tr>
<td>HPLC</td>
<td>high performance liquid chromatography</td>
</tr>
<tr>
<td>HBC</td>
<td>hexa-peri-hexabenzocoronene</td>
</tr>
<tr>
<td>HMB</td>
<td>hexamethylbenzene</td>
</tr>
<tr>
<td>HDTMA</td>
<td>hexadecyl trimethyl ammonium bromide</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>high-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>HOPG</td>
<td>highly oriented pyrolytic graphite</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>IMMS</td>
<td>ion-mobility mass spectrometry</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>LDA</td>
<td>lithium diisopropylamide</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>$m[n]$CPPs</td>
<td>meta-$[n]$cycloparaphenylenes</td>
</tr>
<tr>
<td>MIAs</td>
<td>mechanically interlocked architectures</td>
</tr>
<tr>
<td>MALDI</td>
<td>matrix-assisted laser desorption ionization</td>
</tr>
<tr>
<td>MINTs</td>
<td>mechanically interlocked carbon nanotubes</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>$[n]$CPPs</td>
<td>$[n]$cycloparaphenylenes</td>
</tr>
<tr>
<td>$[n]$CPPAs</td>
<td>$[n]$cycloparaphenyleneacetylenes</td>
</tr>
<tr>
<td>$[n]$CPY</td>
<td>$[n]$cyclo-2,7-pyrenlenes</td>
</tr>
<tr>
<td>$[n]$CPB</td>
<td>$[n]$cyclo-5,15-porphyrinylene-4,4'-biphenylenes</td>
</tr>
<tr>
<td>$[n]$CNs</td>
<td>$[n]$cyclo-1,4-naphthylenes</td>
</tr>
<tr>
<td>$[n]$CPTs</td>
<td>$[n]$cyclo-1,4-phenylene-2',5'-thienylenes</td>
</tr>
<tr>
<td>OLEDs</td>
<td>organic light-emitting diodes</td>
</tr>
<tr>
<td>OFETs</td>
<td>organic field-effect transistors</td>
</tr>
<tr>
<td>ODCB</td>
<td>ortho-dichlorobenzene</td>
</tr>
<tr>
<td>PAHs</td>
<td>polycyclic aromatic hydrocarbons</td>
</tr>
<tr>
<td>$p$TsOH</td>
<td>para-toluenesulfonic acid</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>single-walled carbon nanotubes</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SPAAC</td>
<td>strain-promoted azide–alkyne cycloaddition</td>
</tr>
<tr>
<td>TES</td>
<td>triethylsilyl</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetra-n-butylammonium fluoride</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultraviolet-visible</td>
</tr>
</tbody>
</table>

Note: conventional abbreviations for units and physical quantities are not included.
1. State of the Art

1.1. \( \pi \)-Conjugated Systems

\( \pi \)-Conjugated systems are molecules featuring atoms that are connected via neighbouring p orbitals with delocalized electrons, which typically leads to stabilization and bond length equalization.\(^1\) The simplest examples for \( \pi \)-conjugated systems are 1,3-butadiene and benzene. Graphene and carbon nanotubes (CNTs) can be considered as the largest \( \pi \)-conjugated systems. These carbon allotropes have exhibited many unique and useful properties in material sciences, for example, excellent electrical conductivity\(^2\), supercapacity\(^3\), exceptional tensile strength and mechanical stiffness\(^4\).

![Perpendicular \( \pi \)-Conjugation](image)

**Figure 2.** Schematic representation and selected examples of perpendicular and radial \( \pi \)-conjugation.

Regular graphene is a conductor (no band gap),\(^5,6\) whereas single-walled carbon nanotubes (SWCNTs) show either semiconducting (band gap: 0 to 2 eV) or metallic properties.\(^7-9\) The best way to explain and predict the properties of a new material is to understand the molecular structure. The excellent conductivity of graphene could be attributed to the formation of the larger delocalized \( \pi \) bond. One of the key differences between graphene and nanotubes is the orientation of p orbitals. As shown in Figure 2, graphene (nanoribbon) can be assigned to the perpendicularly linear \( \pi \)-conjugation, defected graphene can be assigned to the perpendicularly cyclic
π-conjugation, whereas carbon nanotubes must be assigned to the radial π-conjugation. The different inner and outside electron densities of radially π-conjugated systems responsible for a range of unique properties compared to the perpendicularly π-conjugated molecules. Furthermore, in order to systematically compare their differences, the study should start from the small and easily modifiable molecules.
1.1.1. Nonplanar Nanocarbons

Polycyclic aromatic hydrocarbons (PAHs) can be regarded as graphene segments composed of all fused aromatic rings.\cite{10,11} They are ubiquitously present in coal, tar and the combustion residues of organic compounds. The nature of their aromaticity and optoelectronic properties have long intrigued scientists. R. Scholl and E. Clar have contributed to the pioneering work on the synthesis and characterization of PAHs.\cite{12-14} In recent years, the efficient synthesis of well-defined and large π-extended PAHs (e.g. nanographenes and graphene nanoribbons) has enabled their investigation in nanoelectronics and spintronics.\cite{15} Corannulenes and helicenes as representative nonplanar PAHs were both first synthesized and studied half a century ago. However, the discovery of new carbon allotropes (e.g. fullerenes and CTNs) inspired further investigation of nonplanar PAHs. Within last two decades, the field of nonplanar PAHs has been significantly expanded and attracted widespread interest.

![Corannulene and derivatives](image)

Figure 3. Solid state structures of corannulene and derivatives, side chains omitted for clarity.

Corannulene is a $C_5$-symmetric bowl-shaped molecule consisting of a
cyclopentane fused with five benzene rings. It was first conceived and synthesized by W. Barth and R. Lawton in 1966.\cite{16} Interestingly, variable temperature NMR and computer calculations indicated that corannulene exhibits a fast bowl-to-bowl inversion at room temperature.\cite{17} The intrinsic concave/convex π-surfaces of corannulene can be used as a core of nonplanar PAHs. Scott and coworkers reported the synthesis of pentaindenocorannulene 1, using five-fold Pd-catalyzed intramolecular direct arylation of 1,3,5,7,9-pentakis (2-chlorophenyl)corannulene.\cite{18} Four years later, the same group successfully synthesized a fully hemispherical nanotube end-cap 2, which is the further cyclization product of 1.\cite{19} Furthermore, with Pd-catalyzed intramolecular direct arylation method, Itami and coworkers reported the synthesis of C$_5$-symmetric propeller-shaped quintuple [6]helicene 3.\cite{20} Before, they reported if treat the final cyclization step with Scholl reaction conditions, the main product was ten-fold intramolecular cyclization 4, a grossly warped nanographene.\cite{21} It is worth mentioning that bowl-shaped corannulenes can be used for the synthesis of molecular tweezers for fullerene encapsulation.\cite{22–24}

![Figure 4. Solid state structures of [7]helicene and derivatives, side chains omitted for clarity.](image)

[瑕疵]Helicenes are ortho-fused helical PAHs and were first reported a century
ago.\textsuperscript{[25]} The letter $n$ denotes the number of aromatic rings in the skeleton. There is a general relationship between the chirality and the absolute configuration: ($M$)-helicenes are levorotatory, while ($P$)-helicenes are dextrorotatory. Despite lacking chiral centers and asymmetric carbons, [$n$]helicenes have attracted continuing attention in chirality sensing, nonlinear optics, molecular machines and asymmetric catalysis.\textsuperscript{[26]} As the number of fused rings increases, π electrons start to form additional layers and the synthesis becomes much more difficult. Fujita and coworkers reported the one-step synthesis of [16]helicene using oxidative photocyclization, which is the longest [$n$]helicene synthesized to date.\textsuperscript{[27]}

Normally, π-extension often induces a significant change in electronic structure, while multihelicity provides molecular dynamics and multiple electronic states. Therefore, construction of nonplanar π-systems has been attracting chemists for many years.\textsuperscript{[28]} One prominent example is the synthesis of π-extended double helicene 5 described by Itami's group. Helicene 5 was obtained as a mixture of three isomers due to the two helical substructures (Figure 4). They could be isolated by chiral high performance liquid chromatography (HPLC) at room temperature due to the high isomerization barrier. Change in molecular geometry of 5 induces electronic state variation that was observed by UV-vis absorption and fluorescence spectroscopy.\textsuperscript{[29]} Bilayer graphene is somehow distinct from its single-layer relative in electronic properties such as band gap, exciton energies and spin-orbit interaction. Martin and coworkers reported the synthesis and characterization of a helical bilayer nanographene 6 by using [6]helicene as the chiral linker (Figure 4). X-ray structure indicated strong π-π interactions between the two hexa-peri-hexabenzocoronene (HBC) layers.\textsuperscript{[30]} Another important nanographene-helicene hybrid 7 was reported in the same year by Wang and coworkers. The alkyne cyclotrimerization product was directly converted to hexapole [7]helicene 7 by one-pot 18-fold Scholl dehydrocyclization. The propeller-shaped structure embeds six [7]helicenes
and comprises 150 conjugated carbon atoms. Helicene 7 was found to have eight reversible redox waves from -1.57 to 1.05 V by cyclic voltammetry (CV) measurement.[31]

**Figure 5.** Solid state structures of two twisted nanographenes, side chains omitted for clarity.

In addition to these well-known corannulenes and [n]helicenes, embedding pentagons, heptagons and octagons to PAHs allowed to construct twisted structures.[32] Unlike five-membered rings induce positive curvature, while seven- and eight-membered rings induce negative curvature. Since computational studies predicted carbon allotropes with negative curvature have various unique properties,[33] many chemists such as Miao, Itami and Scott have been working on the synthesis of negatively twisted PAHs. As shown in Figure 5, the negatively twisted C$_2$ symmetric nanographene 8 consisting of 30 phenyl rings and the dipleiadiene-embedded saddle-shaped nanographene 9 consisting of 26 phenyl rings have been synthesized by Miao and coworkers.[34,35] DFT calculations indicated that 8 is a flexible molecule and can be rapidly racemized through pseudorotation. Furthermore, 8 exhibited enhanced photoluminescence when water was added to its THF solution, which can be attributed to aggregation. The synthesis of 9 involves a ring expansion reaction as a key step to form the tetrabenzodipleiadiene.

Without changing the molecule size, heteroatomic doping (e.g. B, N, S, Si) in the hexagonal lattice can significantly change the electronic properties of nanographene and graphene nanoribbons.[15] For example, BN doping can increase the energy of electronic and optical band gap of HBC.[36] Porphyrin is
one of the most extensively studied heteroatomic doping macrocyclic systems. The electron rich structures are promising scaffolds to design a wide range of functional materials. The porphyrin oligomers directly fused by triple linkages to give planar porphyrin tapes.\cite{37,38} These large conjugated tapes give rise to various prominent attributes such as extraordinarily narrow HOMO-LUMO gaps, obviously red-shifted absorption bands and multicharge storage capabilities. However, Osuka and coworkers found that planar porphyrin tapes became arch-tapes 10 when the fused molecule was incorporated with heptagons (Figure 6). Furthermore, this U-shaped contorted structure can bind C<sub>60</sub> effectively.\cite{39} The wavelike structure 11 was obtained from meso,meso'-dibromosubphyrin dimer by intramolecular Yamamoto coupling. The anti-isomer was the sole product due to a large energetic stabilization compared to the syn-isomer. The fused dimer 11 displays a highly reversible reduction and oxidation waves, a short S<sub>1</sub>-state lifetime and a narrow HOMO-LUMO gap.\cite{40}

Figure 6. Solid state structures of porphyrin arch-tape 10 and fused subporphyrin dimer 11, side chains omitted for clarity.
1.1.2. Conjugated Macrocycles

With the development of synthetic methodologies in chemistry over the past few decades, many powerful C-C bond coupling methods have been introduced by organic chemists, such as Suzuki-Miyaura, Sonogashira and Yamamoto coupling reactions. This offered chemists great opportunities to design and build new and charming molecular structures, for example, fully conjugated macrocycles of trigonal (12), square (13), pentagonal (14), hexagonal (15), trefoil (16) and circular (17) shapes (Figure 7).

**Figure 7.** Examples of cyclic perpendicular π-conjugations.

Fully conjugated macrocyclic architectures with perpendicular p orbitals have drawn great attention due to their unique electronic structures and supramolecular properties. The shape-persistent backbones can be considered as building blocks for 1D nanotubes, 2D porous networks, 3D cages, covalent organic frameworks (COFs) and other kinds of (supra)molecular assemblies. For instance, the triangular compound 12 featuring three polar ethylene oxide side chains could self-assemble into vesicles when its chloroform solution was exposed to water. Such
multidimensional architectures with fully conjugated macrocycles as building blocks are fundamentally important due to their novel properties in organic electronics and energy storage materials. For example, trefoil-shaped 16 shows the most intense two-photon absorption compare to the related annulenes due to its exceptional planarity and edge-linkage.[46] Furthermore, Bäuerle and coworkers reported the interesting size-dependent photoelectric properties of fully α-conjugated cyclo[\(n\)]-thiophenes (e.g. 17).[47,49–51]

Before 2000, organic chemists were able to construct many kinds of unstrained carbon macrocycles and explore their unique optoelectronic properties. If you take a closer look at dodecaphenylenes 13, you will find that it is a slightly strained and nonplanar structure.[52] The strained cyclophane 17 was synthesized by using Cu-catalyzed coupling of 1,8-bis(4-(tributylstannyl)phenyl)naphthalene, perpendicular and radial \(\pi\)-conjugation are both present in this molecule.[52] The close biphenylenes have strong face-to-face \(\pi-\pi\) interaction, the optical properties of 18 are different to later reported [8]cycloparaphenylenes ([8]CPP, Figure 8a).[53]

**Figure 8.** a) Optical properties of 18 and [8]CPP. b) UV-Vis (solid) and fluorescence (dashed) spectra for [5]–[12]CPP, reproduced from ref. 54 with permission from the Royal Society of Chemistry, copyright (2015). c) Calculated HOMO and LUMO levels of cyclic (red) and linear (blue) \(p\)-phenylenes, adapted from ref. 55 with permission from the American Chemical Society, copyright (2015).
What are the differences in optoelectronic properties between the strained and unstrained molecules? To answer this question clearly, chemists not only performed quantum calculations, but they also tried to design and synthesize those molecules with different strain energy. For example, the radially π-conjugated \([n]\)CPPs were studied systematically in the last decade. All the absorption and fluorescence spectra of \([5]-[12]\)CPP are summarized in Figure 8b. Surprisingly, the absorption maximum of the nanohoops did not show obvious shift with increasing strain energy. However, the observed emission spectra have occurred significant blue shift with strain energies decreasing, and the meantime, the quantum efficiencies were increased. On the other hand, computer chemists were able to gain insight the molecules via DFT calculation (Figure 8c). The HOMO-LUMO gap of \([n]\)CPPs becomes narrower as the number of benzene ring decreases (the strain energy increases). This is in contrast to the open chain linear paraphenylenec oligomers which show narrowing band gap with increasing number of benzene rings. The narrow HOMO-LUMO gap gives \([n]\)CPPs great potential as new organic semiconducting materials.[54,55]
1.1.3. Strained Carbon Nanohoops

Figure 9. The development of strained carbon architectures.

Fullerene $C_{60}$ as a natural strained carbon allotrope was discovered by Kroto and coworkers in 1985.[56] This unique class of spherical molecules containing a large $\pi$-system has attracted enormous research interest from chemists and physicists. By now, different size, hetero[57] and endohedral fullerenes[58] have been successfully synthesized in macroscopic quantities. Outstanding electronic mobility and precise convexity of fullerenes enable important applications in organic solar cells and host-guest chemistry.[59–62]

CNTs as the second generation of natural strained carbon allotrope were reported by Iijima in 1991.[63] These long, cylindrical carbon structures exhibit exceptional mechanical stiffness, tensile strength and high electrical/thermal conductivity.[63] These properties are expected to be useful in many fields of material science, such as electronics, sensors, optics and composite materials.[64,65] $[n]$CPPAs as the analogue of $[n]$CPPs are the first artificial strained carbon nanohoops achieved by Kawase and coworkers in 1996.[66] $[n]$CPPs were envisioned as the shortest cross-section of armchair CNTs. Despite of great efforts of Vögtle and coworkers towards $[n]$CPPs synthesis,[67] these elusive nanohoops were successfully synthesized only in 2008 by Jasti and Bertozi.[68] Carbon nanobelts consisting solely of fused benzene rings were envisioned even before the discovery of CNTs. However, the groups of Vögtle, Stoddart, Cory, Herges and others have targeted carbon nanobelts synthesis not succeed.[69–71] Until 2017, Itami reported the bottom-up synthesis,
isolation and characterization of the first carbon nanobelt with a diameter of 0.8 nm whose strain energy reached to 119.5 kcal mol\textsuperscript{-1}.\textsuperscript{[72]}
1.1.3.1. \([n]\)Cycloparaphenyleneacetylenes

Phenylene-ethynylene macrocycles usually adopt noncollapsible and shape-persistent structures due to their backbones only comprised of benzene and acetylene. Consequently, these macrocycles can form various of supramolecular aggregates, such as 3D nanostructures, extended tubular channels, porous organic solids and host-guest complexes. The conjugated macrocycle backbones typically produce three types of cyclic phenylene-ethynylenes: ortho-cycle \((12, \text{Figure 7})^{[42]}\), meta-cycle and para-cycle \((20, \text{Scheme 1})^{[66]}\). We will only focus on discussing the synthesis and supramolecular properties \((\text{vide infra})\) of strained \([n]\)CPPAs and analogues.

**Scheme 1.** a) Synthetic strategy towards \([n]\)CPPAs reported by Kawase. b) Synthesis of CPPA derivative 25 reported by Tsuji. c) Synthesis of \([n]\)CPPA reported by Moore.
As the first type of fully conjugated hoop-shaped structures that was synthesized, \([n]\)CPPAs attracted particular interest because of their rigid structures and well-defined cavities. The syntheses of \([n]\)CPPAs and their 2,6- and 1,4-naphthalene analogues were reported by Kawase and coworkers.\(^{[73–75]}\) Compound 19 and related arylene-ethylene precursors were obtained through the McMurry coupling of 4,4’-diformyl-(Z)-stilbenes. The following bromination and dehydrobromination afforded a mixture of compounds 20 and 21 (4:1) in 85% yield, respectively (Scheme 1a).\(^{[66]}\) Moreover, the synthesis of \([7]\)CPPA, \([9]\)CPPA and the related compounds bearing two 1,4- and 2,6-naphthylene units was also accomplished by using a similarly synthetic route.\(^{[75]}\)

In 2001, Tsuji and coworkers reported the photochemical generation of \([n]\)CPPAs derivative \([4_8]\)paracyclophanedodecayne 25 from the corresponding Dewar benzene precursor 24. The macrocycle 23 was prepared in 15% yield via a modified Eglinton coupling of precursor 22 under pseudo-high-dilution conditions (Scheme 1b). Nanohoop 25 was isolated as an air-sensitive solid, which decomposed within several days no matter stored as solid or in solution at room temperature.\(^{[76]}\)

Fifteen years later, Moore and coworkers reported the synthesis and fullerene affinity of another \([n]\)CPPA derivative \([3]\)cycloparaterphenyleneacetylene (\([3]\)CPP\(^3\)A) by using alkyne metathesis (Scheme 1c). Surprisingly, the molybdenum(VI)-catalyzed alkyne metathesis of precursor 26 resulted in macrocycle 27 in quantitative yield. The reaction equilibrium was completely shifted toward the product formation due to the poor solubility of 27 in most organic solvents and precipitated out from the reaction solution, while the byproduct 2-butyne was removed by molecular sieves (5 Å). The final aromatization employed Jasti’s method (sodium naphthalenide, -78 °C) to give \([3]\)CPP\(^3\)A in 70% yield. \([3]\)CPP\(^3\)A was found to be unstable and decomposed into an insoluble yellow solid upon exposure to air. However, the authors found that \([3]\)CPP\(^3\)A could be stabilized by complexation of \(C_{70}\). Furthermore,
strain-promoted azide–alkyne cycloaddition (SPAAC) was investigated between azides and strained alkynes of [3]CPP$_3$A. The SPAAC reaction successfully afforded two isomers of triazoloparaterphenylene macrocycle.[77]
1.1.3.2. \([n]\)Cycloparaphenylenes and Derivatives

Even though the synthesis of \([2]\)CPP was envisioned by Parekh and coworkers in 1934, the structure of \([2]\)CPP looks too strained to be viable in the eyes of a modern chemist. Therefore, I think, the real history of the synthesis of cyclic oligoparaphenylenes featuring a radial \(\pi\)-conjugated system starts in 1993 when Vögtle and coworkers published the paper entitled “On the way to macrocyclic paraphenylenes”. At the beginning, Vögtle and coworkers failed to synthesize \([6]\)CPP and \([8]\)CPP by using desulfurization of macrocycle 28, but they have proposed more plausible targets than \([2]\)CPP (Scheme 2a). In addition, they have successfully prepared the ene-yne macrocycles 31 by using Wittig macrocyclization between dialdehyde 29 and diphosphonium 30. Unfortunately, the final intermolecular Diels-Alder reactions with 31 to obtain \([n]\)CPPs were unsuccessful.\(^{[67]}\)

![Scheme 2](image)

**Scheme 2.** a) Synthetic strategy towards \([n]\)CPPs proposed by Vögtle. b) Synthesis of picotube 33 reported by Herges. c) Synthetic strategy towards \([n]\)CPPs reported by Jasti and Bertozzi.

Following Vögtle’s report, Herges and coworkers have successfully synthesized a “picotube” 33 in 1996 (Scheme 2b). Tetradehydrodianthracene 32 was used as the
starting material to synthesize 33 by dimerizing metathesis. X-ray crystallographic investigation of 33 indicated that instead of forming a fully aromatic macrocycle, the picotube existed in the quinodimethane form. The cylindrical cavity of 33 suggests that this picotube could be used in host-guest chemistry. In a proof-of-concept study, it was shown that 33 could indeed encapsulate silver(I) salts.78

After many years of unsuccessful attempts, Jasti and coworkers published their landmark synthesis of three kinds of [n]CPPs (n = 9, 12 and 18, Scheme 2c). These three nanohoops were synthesized from the precursors 36, which contained 1,4-syn-dimethoxy-2,5-cyclohexadiene units. Syn-cyclohexadiene moiety 34 was synthesized by using p-diiodobenzene and 1,4-benzoquinone as starting materials. Subsequently, a portion of compound 34 was converted to the borylated precursor 35. The macrocycles 36 were generated in 22% combined yield by exposing a 1:1 mixture of 34 and 35 to Suzuki-Miyaura cross-coupling condition. At the end, the macrocycles could be converted to the corresponding CPPs in an acceptable yield by using lithium naphthalide as reducing agent.68

![Scheme 3. Synthetic strategy and properties of [5]CPP, adapted from ref. 81 with permission from the Nature Publishing Group, copyright (2014).](image_url)

By 2014, [n]CPPs were accessed in a variety of sizes (n = 6-16) since their first synthesis in 2008.79 Theoretical studies suggested the smaller ring size of [n]CPPs should display a range of appealing electronic properties compared to those hoops with larger sizes. However, the inherent strain in these distorted backbones makes
synthesis of the smaller \([n]CPPs\) very challenging. In 2000, a computational study indicated the highly strained \([5]CPP\) had a quinoid structure[^80]. However, fourteen years later, when \([5]CPP\) was synthesized by Jasti and Yamago, X-ray crystallographic analysis revealed its benzenoid structure. The precursor 37 was employed to prepare the 5-ring cyclic building block by palladium catalyzed boronate homocoupling (Scheme 3). However, when 5-ring macrocycle was treated with excess of sodium naphthalenide, a stable dianion was formed instead of \([5]CPP\). Then the moiety 38 was separated in 39% yield after quenching the dianion with methanol. Subsequently, 38 was treated with lithium diisopropylamide (LDA) giving \([5]CPP\) in 69% yield (Scheme 3). \([5]CPP\) can be envisaged as a fragment of \(C_{60}\), its calculated strain energy is 119 kal mol\(^{-1}\). \([5]CPP\) exhibits an absorption maximum at 335 nm, a very broad second band around 502 nm and no observable fluorescence.[^81][^82]

**Scheme 4.** Synthetic strategies towards \([n]CPPs\) developed by Itami.

The significance of Jasti’s first synthesis of \([n]CPPs\) was rapidly acknowledged by the scientific community. In 2009, Itami group contributed a new approach of \([n]CPPs\) synthesis (Scheme 4). Their building blocks consisted of 1,4-diphenylcyclohexanes and bis(methoxymethyl ether) protecting groups (39, 40). The 12-ring macrocycle 42 was synthesized using tandem Suzuki–Miyaura
couplings of 39 and 40. Finally, aromatization of 42 was accomplished using p-toluenesulfonic acid (pTsOH) in m-xylene, affording [12]CPP in 62% yield. High temperature (150 °C) and microwave irradiation were essential to the formation of [12]CPP.\textsuperscript{[83]} In the following years, Itami’s group and others successfully prepared \([n]CPPs\) of different sizes and their derivatives using the aforementioned approach.

Scheme 5. Two \([n]CPPs\) synthetic strategies developed by Yamago.

In 2010, Yamago and coworkers demonstrated the first synthesis of [8]CPP using an entirely new approach (Scheme 5a). It was based on the synthetic strategy towards π-conjugated macrocycles previously reported by Bäuerle and coworkers. This strategy relies on the formation of a “square-shaped” tetranuclear platinum complex followed by bromine-induced reductive elimination. The 4,4'-bis(stannylated) biphenyl 43 was easily prepared from commercially available 4,4'-dibromobiphenyl. Precursor 43 was treated with an equimolar amount of Pt(cod)Cl\(_2\) to give transmetallated macrocycle 44 (L = cod). Subsequently, the ligand exchange product 45 (L = dpff) formed effectively from 44 was treated with bromine to give the four-fold Ar-Ar bond formation product [8]CPP in 49% yield. Despite the use of expensive stoichiometric quantity of Pt source, the advantages of Yamogo’s approach are its exceedingly concise and high yielding compared to other methods developed so far.\textsuperscript{[53]}
Scheme 6. a) Synthesis of double cyclic nanohoop 51. Reaction conditions: i) xenon lamp, benzene, 30 °C, 12 h, 54%. ii) 54, Pd(OAc)$_2$, dpf, K$_2$CO$_3$, Ag$_2$O, PhMe/H$_2$O, 80 °C, 24 h, 54%. iii) Ni(cod)$_2$, 2,2′-bipyridyl, THF, 65 °C, 24 h, 95%. iv) sodium naphthalenide, THF, -78 °C, 1 h, 73%. v) ODCB, 175 °C, in the dark, 18 h, 72%. b) The synthesis of lemniscular nanohoop 56, adapted from ref. 88 with permission from the American Chemical Society, copyright (2019).

Prior to Jasti’s work, Yamago and coworkers developed another more efficient approach that employed different protecting groups and reducing agent. As shown in Scheme 5b, they developed a new 5-ring precursor 46 bearing triethylsilyl (TES) protecting groups. Macrocycle 47 was synthesized from 46 in 73% yield under Ni(0)-mediated Yamamoto coupling conditions. After removal of TES protecting groups, 47 was treated with 4.2 equiv tetra-$n$-butylammonium fluoride (TBAF) giving 48 in 96% yield. H$_2$SnCl$_4$ (SnCl$_2$:2HCl) was straightforwardly synthesized...
from SnCl\textsubscript{2} and two equivalents of HCl, which served as a stronger reducing agent than SnCl\textsubscript{2}. The key aromatization step of 48 using H\textsubscript{2}SnCl\textsubscript{4} took place under mild conditions and gave [5]CPP in 72\% yield.\textsuperscript{[84]} Furthermore, this approach was later widely used to synthesize strained carbon nanohoops by other chemists.\textsuperscript{[85]}

As the successful developed three types of L-shaped synthons (e.g. 34, 40 and 46) to overcome these molecular nontrivial strain energy, chemists are allowed to explore more properties by designing new types of nanohoops. Cong and coworkers reported on the synthesis of bis-macro cyclic nanohoop 51 using the anthracene photodimer synthon as a knot (Scheme 6a). 51 is a propeller-like, dual-curve and C\textsubscript{2} symmetric structure confirmed by X-ray crystallographic analysis. Interestingly, this figure-eight shaped nanohoop could be converted into anthracene containing CPP derivate 52 by thermally induced cycloreversion. The preliminary DFT calculations indicated that anthracene units could rapidly rotate at ambient temperature.\textsuperscript{[86]} Furthermore, a fascinating pentiptycene-derived chiral dual nanohoop was described by the same group in 2019.\textsuperscript{[87]}

Scheme 7. Synthesis of conjugated nanohoops 60 incorporating dibenzo[a,e]pentalenes.

Incorporation of plane and twist conjugations into the same molecule may provide fundamental insights into the relationship between \(\pi\)-electron conjugation and 3D structure. Stępień and coworkers have prepared the lemniscular dual nanohoop 56...
using carbazole-2,7-diyl synthon as a knot (Scheme 6b). Nanohoop 56 is a chiral molecule in which the twisted 9,9'-bicarbazole acts as a stereogenic center. Interestingly, the enantiomers of 56 did not racemize in solution at room temperature. The emission maximum of 56 was closest to [9]CPP, while the emission lifetime was much longer than the size matched [16]CPP.\[88\]

Since conjugated nanohoops incorporating antiaromatic units have not been studied before, Esser and coworkers reported the first hybrid aromatic nanohoop 60 by introducing two dibenzo[a,e]pentalenes (Scheme 7). Three different substituted dibenzo-[a,e]-pentalenes 57 were prepared for the macrocycles synthesis, and Itami’s approach was adopted to construct the fully conjugated nanohoop. DFT calculations indicated that 60 had a strain energy and diameter similar to [16]CPP. Furthermore, it was found that nanohoop 60 displayed ambipolar electrochemical behavior due to the presence of two dibenzo[a,e]pentalene units.\[89\]
1.1.3.3. $\pi$-Extended Carbon Nanohoops

Figure 10. Carbon nanohoops as the sidewall segments of armchair CNTs.

CNTs have found widespread applications in photonics and electronic materials. The optical and electronic properties of CNTs are determined by the sidewall structure (chirality) and diameter.\cite{90,91} However, the predictable and controlled synthesis of single-chirality, uniform-diameter SCNTs is a very difficult challenge in organic synthesis. CPPs and their $\pi$-extended derivatives were proposed as building blocks for armchair SCNTs (Figure 10). In 2013, Itami and coworkers reported a rational bottom-up approach to the synthesis of CNTs using CPPs as a template. The determined diameter of the formed CNTs was close to the corresponding carbon nanohoops.\cite{92} This finding has not only led to a new route to the programmable synthesis of uniform armchair CNTs, but it also actually inspired chemists to design and synthesize a variety of $\pi$-extended carbon nanohoops.

Scheme 8. a) Cyclacenes as sidewall segments of zigzag SCNTs. b) The proposed synthetic strategy of [6]$_{12}$cyclacene reported by Stoddart.
Since [6], cyclacenes are hoop-shaped macrocycles where phenyl moieties are fused together, they were proposed as the most promising building blocks for zigzag SCNTs (Scheme 8a). [6], Cyclacenes have drawn much attention since the 1980s due to their interesting structural and electronic properties as well as potential applications in host-guest chemistry. Many pioneering efforts were put into their challenging synthesis over past several decades. Unfortunately, these structures have not yet been synthesized due to their insuperable strain energy.

One of these examples is shown in Scheme 8b, Stoddart and coworkers successfully synthesized 63 by iterative Diels-Alder reactions. However, the fully conjugated [6]_{12} cyclacene has not been achieved yet.[69]


In 2011, Isobe and coworkers developed the synthetic strategy towards [4]cyclo-2,8-chrysenylenes ([4]CC) as a new type of π-extended carbon nanohoops, using the “platinum-square” methodology developed by Bäuerle and Yamago (Scheme 9). The bis(borylated) chrysene building block 64 was treated...
with Pt(cod)Cl₂ to give tetraplatinum complex 65. Macrocycle 65 could be transformed into four-fold reductive elimination product 66 by treating 65 with an excess of triphenylphosphine. Here, the differences to Yamago’s approach is that ligand exchange is unnecessary and use a different reductive agent. They found that the rotational isomers of [4]CC could be isolated by preparative HPLC and characterized by NMR and circular dichroism (CD) spectroscopies. The HPLC trace shows six peaks that corresponded to six possible isomers of [4]CC (Scheme 9). Two peaks were not observed in the corresponding CD chromatogram suggesting their assignment to achiral isomers A and C. For the four remaining isomers, the CD spectra suggested that D and F were enantiomeric, as were B and E. These isolated rigid tubular structures were suggested to serve as finite models for chiral (n, m)-SWNTs (n≠m).[93]


[n]Cyclo-2,7-pyrenlenes ([n]CPY) have an organized π surfaces larger than [n]CPPs, so they were supposed to be better precursors for the growth of structurally uniform armchair SCNTs. In 2014, Yamago and coworkers reported the synthesis of [4]cyclo-2,7-pyrenylene 70 ([4]CPY) using the “platinum-square” route developed by themselves four years ago (Scheme 10a). Precursor 67 was obtained from 2,7-dibromo-4,5,9,10-tetrahydropyrene in 85% yield. The following
platinum complex 68 was heated together with triphenylphosphine, giving [4]cyclo-4,5,9,10-tetrahydro-2,7-pyrenylene 46 ([4]CHPY) in 51% yield. Finally, [4]CHPY underwent oxidative aromatization with Pd/C at 150 °C giving [4]CPY in 97% yield. Interestingly, [4]CPY exhibited a concentration dependent fluorescence behavior, $\lambda_{\text{max}}$ significantly red-shifted with increase of concentration.$^{[94]}$

In recent years, extended PAHs or nanographenes have drawn widespread attention due to great potential applications in nanoelectronics, spintronics and optoelectronics. HBC as the simplest member of synthetic nanographenes has been extensively studied in material science. In 2017, Du and coworkers successfully constructed the largest $\pi$-conjugated nanohoop 72 using HBC as sole building block. The synthetic strategy was following Yamago's approach (Scheme 10b). Computational calculations indicated the strain energy of nanohoop 72 to be 49 kcal mol$^{-1}$. The author also found that this hoop-shaped molecule was able to selectively encapsulate C$_{70}$. $^{[95]}$

**Scheme 11.** The synthesis of carbon nanobelt 80 reported by Itami: i) PPh$_3$ (1.0 equiv), THF/MeOH, reflux, 3 h; 74, t-BuOK (1 M in THF), RT. ii) i-Pr$_2$NEt (1.4 equiv), (MeO)$_2$POH (1.3 equiv), RT, 3 h. iii) PPh$_3$ (1.0 equiv), THF/MeOH, reflux, 5 h; 4 M HCl, acetone, RT, 2 h; KPF$_6$. iv) t-BuOK (1.2 equiv), DCM, 0 °C→RT. v) 2,2-bipyridyl (12.0 equiv), Ni(cod)$_2$ (12.0 equiv), DMF, 70 °C, 15 min.

2017 was a milestone year to the chemistry for nanohoops. After decades of efforts and exploration by many chemists, Itami and coworkers reported the synthesis of the first artificial carbon nanobelt 80 (Scheme 11). Compound 80 represents a belt segment of (6,6)SCNT and has a strain energy as high as 119.5 kcal mol$^{-1}$. The dodeca-bromo macrocycle 79 was synthesized from starting materials 73 and 74.
by sequential Witting reactions. Finally, a subsequent nickel(0)-mediated aryl-aryl Yamamoto coupling gave carbon nanobelt 80 in 1% yield. X-ray crystallography confirmed that 80 has $C_{2h}$ symmetry and belt-shaped structure with a diameter of 8.3 Å. UV-vis spectrum of 80 showed two major bands at 284 nm and 313 nm as well as a following smaller peak at 412 nm. Furthermore, carbon nanobelt 80 exhibited deep red fluorescence ($\lambda_{\text{max}} = 630$ nm, $\Phi = 3\%$ in DCM). The fully conjugated fused belt structure was responsible for unusual optoelectronic properties, which encouraged chemists to investigate its applications in photonics and nanoelectronics.\textsuperscript{[72]}
1.1.3.4. Cyclo-porphyrin Nanorings

Porphydrin structure was first proposed over a century ago. Since then, porphyrins have found widespread applications in photocatalysis, molecular electronics, nonlinear optics and sensors due to their distinct structural and electronic properties. The optoelectronic properties of porphyrin can be easily regulated by peripheral substitution, metalation of the porphyrin core as well as scaffold deformation (ruffle/saddle deformation). In recent years, chemists have developed one more strategy to control the photoelectric properties of porphyrins, that is bending porphyrin to construct a porphyrin nanoring. The porphyrin nanorings exhibit completely different properties compared to the linear porphyrin oligomers, such as narrower HOMO-LUMO gaps, significantly red-shifted absorption and intriguing supramolecular properties.

Scheme 12. The synthesis of cyclo-porphyrin nanorings developed by Anderson, adapted from ref. 100 with permission from the American Chemical Society, copyright (2018).

Since 2007, Anderson’s group has designed and synthesized many kinds of alkyne-linked π-conjugated porphyrin nanorings using oligopyridines as templates. Here, template-directed synthesis can be understood as a given template organizes the reactants to promote formation of a specific product, and the template can be removed from the final product. As shown in Scheme 12,
[6]cyclo-porphyrin nanoring 83 was synthesized by template-directed cyclotrimerization of the linear porphyrin dimer 81, where the hexapyridyl 82 was employed as the template. Finally, the Glaser coupling product could be efficiently converted to [6]cyclo-porphyrin nanoring effectively by removal of the template with 1,4-diazabicyclo-[2.2.2]octane (DABCO). In addition, [12]cyclo-porphyrin nanoring complex 84 was synthesized in a moderate yield using hexapyridyl 82 as the Vernier template. X-ray crystallographic analysis confirmed that it was a figure-of-eight structure (instead of a large macrocycle). Now, with their developed templated-directed approach, Anderson and coworkers were able to successfully synthesize a conjugated porphyrin nanoball featuring fourteen porphyrins.

**Scheme 13.** a) The synthesis of [n]CPB reported by Osuka. b) The synthesis of porphyrin nanobelt 87 reported by Yamada, adapted from ref. 106 with permission from the American Chemical Society, copyright (2019).

Inspired by [n]CPPs synthesis, Osuka and coworkers reported another type of porphyrin nanoring using 4,4'-biphenyl as a linker instead of diacetylene. The synthetic strategy followed Yamago's platinum-mediated homocoupling approach (Scheme 13a). Finally, they were able to isolate four kinds of porphyrin nanorings, named [n]cyclo-5,15-porphyrinylene-4,4'-biphenylenes ([n]CPB, n = 3-6).
calculated strain energy of the smallest nan hoop [3]CPB (diameter: 16 Å) was 49.3 kcal mol\(^{-1}\). Decrease of the ring size led to a slight red shift of the absorption (Soret and Q bands) while the HOMO-LUMO gap became smaller according to cyclic voltammetry measurements\(^{[105]}\).

In 2019, Yamada and coworkers reported the synthesis of a much more strained porphyrin nanobelt 87 in 4% yield via condensation of precursor 86 and benzaldehydes (Scheme 13b). X-ray crystallographic analysis confirmed that 87 has a \(C_{3h}\) symmetry and belt-shaped structure. Compound 87 exhibited reversible reduction and oxidation with five electrons in each peak, indicating that this belt-shape structure could stabilize multianionic and cationic states. Furthermore, the authors found that one of belt-shaped molecule could encapsulate two \(C_{60}\) molecules according to UV-vis titrations\(^{[106]}\).
1.1.3.5. Conjugated Carbon Nanocages

3D nanocages are of great interest not only due to their sheer aesthetic appeal, but also because energy storage potential, molecular sensing, drug delivery and host-guest chemistry. In general, dynamic covalent bonds are typically utilized to construct thermodynamically stable 3D nanocages. Yet, most of 3D nanocages are not fully π-conjugated systems. After 2D hoop-shaped π-conjugated [n]CPPs were extensively studied, chemists moved forward and became interested in the synthesis and properties of strained hydrocarbon nanocages consisting of sp²- and/or sp-hybridized carbon atoms (Scheme 14).

Scheme 14. The synthesis of conjugated carbon nanocages of different sizes.

In 2013, Itami and coworkers reported the synthesis of carbon nanocage 92, using
a similar [n]CPPs synthetic strategy which had been developed in his group (Scheme 14a). The key intermediate node 90 was obtained in 53% yield via threefold Suzuki–Miyaura coupling reaction between 88 and 89. Compound 90 was then treated with Ni(cod)₂ to give cage 91 by a threefold homocoupling reaction. Subsequently, 91 was treated with NaHSO₄·H₂O and α-chloranil under reflux conditions to give fully conjugated carbon nanocage 92 in 69% yield. The optimized configuration showed distance between the two nodes is 18.4 Å.[111]

In the same year, Yamago and coworkers also reported a nanocage synthesis, using the platinum complex medium.[112] In 2018, by following Itami’s approach, Du and coworkers reported an even larger carbon nanocage 95 (Scheme 14c), where two HBC moieties were introduced as the cage nodes. Nanocage 95 allowed the selective encapsulation of C₇₀ fullerene. Furthermore, the authors envisioned that this cage could serve as a segment model for capped zigzag [12,0] carbon nanotubes.[113] In 2019, Tanaka and coworker successfully synthesized the smallest carbon nanocage 93 by regioselective alkyne cyclotrimerization (Scheme 14b). The strain energy of nanocage 93 is between [5]CPP and [6]CPP. Moreover, nanocage 93 had a significantly red-shifted emission maximum compared to nanocage 92.[114]

Scheme 15. Schematic synthetic route towards porphyrin nanocage 98 and absorption spectrum of complex 97, reproduced from ref. 104 with permission from the American Chemical Society, copyright (2018).
As π-conjugated molecules with high dimensionality are expected to have enhanced electronic delocalization compared to low dimensional molecular semiconductors, the precise size control and high yielding synthesis of 3D carbon nanostructures become more and more important. Instead of using an ultra-diluted reaction solution to improve the yield of cage formation (e.g. synthetic approach to 92), Anderson and coworkers developed a template-directed stepwise synthesis of π-conjugated 14-porphyrin nanocage 98 (Scheme 15). They first prepared the six-porphyrin nanoring template complex 96 consisting of four terminal alkyne substituents. Subsequently, they designed a four-legged template to direct the intramolecular Glaser coupling and obtained porphyrin nanocage complex 97 in 51% yield. The three coordinated templates could be removed by treatment with quinuclidine or DABCO giving 14-porphyrin nanocage 98 in quantitative yield. Fluorescence upconversion and fluorescence anisotropy measurements indicated that an ultrafast electronic delocalization as well as excitation rapidly migrates exist between the two perpendicular rings of cage 98.\textsuperscript{104}
1.1.3.6. The Optoelectronic Properties of Strained Carbon Nanohoops

After thorough discussion of the synthetic approaches towards strained carbon nanohoops in the previous sections, here we are going to focus on their optoelectronic properties. The subtle interplay of geometry, symmetry and strain plays a significant role in many of the interesting photoelectrical properties of \([n]\)CPPs. As shown in Table 1 and Figure 11a, the strain energies of \([n]\)CPPs increase dramatically as the hoop size becomes smaller. \([5]\)\-[13]CPP have similar absorption maxima between 335-340 nm, while fluorescence maxima shifts bathochromically and quantum yields drop significantly with the decreasing hoop size. The gradual fluorescent redshift can be explained by the enhancement of vibrational coupling and the reduction of \(S_1-S_0\) energy as the nanohoops become smaller. Theoretical calculations showed that the lowest excited state (\(S_1\)) of large \([n]\)CPPs (\(n \geq 8\)) has different symmetry from the ground state, thus allowing the \(S_1-S_0\) transition. However, complete delocalization was observed in the \(S_1\) state of \([n]\)CPPs (\(n \leq 7\)), conserving the symmetry of \(S_0\). Therefore, the rapid decrease of quantum yields was attributed to the symmetry conservation during \(S_1-S_0\) transition.\(^{54,55}\)

<table>
<thead>
<tr>
<th>([n])CPP</th>
<th>Strain Energy [kcal mol(^{-1})](^{115})</th>
<th>Absorption (\lambda_{\text{max}}) (nm)</th>
<th>(\varepsilon_{\text{max}})</th>
<th>Fluorescence (\lambda_{\text{max}}) (nm)</th>
<th>(\phi)</th>
<th>Singlet lifetime (ns)</th>
<th>Triplet lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>119</td>
<td>335</td>
<td>5.7 (\times) 10(^4)</td>
<td>NA</td>
<td>0</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>6</td>
<td>97</td>
<td>340</td>
<td>NA</td>
<td>NA</td>
<td>0</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>7</td>
<td>84</td>
<td>340</td>
<td>6.9 (\times) 10(^4)</td>
<td>587</td>
<td>0.01</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>8</td>
<td>72</td>
<td>340</td>
<td>1.0 (\times) 10(^5)</td>
<td>533</td>
<td>0.1</td>
<td>17.6</td>
<td>6.0 (\times) 10(^4)</td>
</tr>
<tr>
<td>9</td>
<td>66</td>
<td>340</td>
<td>1.2 (\times) 10(^5)</td>
<td>494</td>
<td>0.38</td>
<td>10.6</td>
<td>6.3 (\times) 10(^4)</td>
</tr>
<tr>
<td>10</td>
<td>58</td>
<td>338</td>
<td>1.3 (\times) 10(^5)</td>
<td>466</td>
<td>0.65</td>
<td>6.6</td>
<td>5.8 (\times) 10(^4)</td>
</tr>
<tr>
<td>11</td>
<td>54</td>
<td>340</td>
<td>1.3 (\times) 10(^5)</td>
<td>458</td>
<td>0.73</td>
<td>3.8</td>
<td>6.4 (\times) 10(^4)</td>
</tr>
<tr>
<td>12</td>
<td>48</td>
<td>339</td>
<td>1.4 (\times) 10(^5)</td>
<td>450</td>
<td>0.81</td>
<td>2.4</td>
<td>6.4 (\times) 10(^4)</td>
</tr>
<tr>
<td>13</td>
<td>46</td>
<td>338</td>
<td>1.6 (\times) 10(^5)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Itami and coworkers reported the synthesis and photophysical properties of various \([n]\)cyclo-1,4-naphthylenes ([\(n\)]CNs). As \(\pi\)-extended analogues of \([n]\)CPPs, they
have photophysical properties clearly different from same-sized $[n]$CPPs. For instance, the absorption maximum exhibits blue-shift with increase of the ring size. However, both $[n]$CPPs and $[n]$CNs displayed increased HOMO levels and decreased LUMO levels with decrease of the ring size (Table 2). Furthermore, the cyclic voltammetry measurements of $[n]$CPPs have provided the consistent experimental observations. Electrochemical data indicated that the smaller nanohoops become easier to oxidize and reduce.$^{[116,117]}$

![Figure 11](image_url)

**Figure 11.** a) UV-vis and fluorescence spectra of $[n]$CPP, reproduced from ref. 117 with permission from the American Chemical Society, copyright (2011). b) Optimized structure of $[8]$CN and UV-vis and fluorescence spectra of $[n]$CN, reproduced from ref. 116 with permission from the Royal Society of Chemistry, copyright (2017).

In 2019, inspired by previous nanohoop research, Jasti and coworker reported the synthesis of new meta-nanohoops $m[n]$CPPs with unusual symmetry (Figure 12). Since one benzene ring is linked to the rest of the nanohoop at meta-positions, there is no circular conjugation anymore, consequently, the symmetry of the molecular orbitals are different. Comparing optoelectronic properties of $m[n]$CPPs and $[n]$CPPs, it is easy to see how dramatic the effect of this small structural
perturbation in the nanohoop is. \( m[n] \)CPPs have similar absorption maxima at around 326 nm (Figure 12d). However, as hoop size decreases, another red shifted absorption band appears. In contrast to [5]CPP and [6]CPP, which have no fluorescence, \( m[5] \)CPPs and \( m[6] \)CPPs showed 0.01 and 0.22 fluorescence quantum yields, respectively. It is worth to mention that \( m[n] \)CPPs have shorter fluorescence lifetimes compared to \([n] \)CPPs.\\(^{[118]}\\)

**Table 2.** Computational and electrochemical properties of \([n] \)CPP.

<table>
<thead>
<tr>
<th>([n] )CPP</th>
<th>Diameter (nm)</th>
<th>Oxidation (V)</th>
<th>Reduction (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>7.1</td>
<td>0.25, 0.46</td>
<td>-0.27, -0.55</td>
<td>-4.67</td>
<td>-1.96</td>
</tr>
<tr>
<td>6</td>
<td>8.4</td>
<td>0.44, 0.30</td>
<td>NA</td>
<td>-4.92</td>
<td>-1.78</td>
</tr>
<tr>
<td>7</td>
<td>9.5</td>
<td>0.55</td>
<td>-0.27</td>
<td>-4.97</td>
<td>-1.80</td>
</tr>
<tr>
<td>8</td>
<td>11.1</td>
<td>0.59</td>
<td>NA</td>
<td>-5.11</td>
<td>-1.70</td>
</tr>
<tr>
<td>9</td>
<td>12.3</td>
<td>0.70</td>
<td>NA</td>
<td>-5.13</td>
<td>-1.72</td>
</tr>
<tr>
<td>10</td>
<td>13.9</td>
<td>0.74</td>
<td>NA</td>
<td>-5.20</td>
<td>-1.67</td>
</tr>
<tr>
<td>11</td>
<td>15.1</td>
<td>0.79</td>
<td>NA</td>
<td>-5.21</td>
<td>-1.68</td>
</tr>
<tr>
<td>12</td>
<td>16.6</td>
<td>0.83</td>
<td>NA</td>
<td>-5.26</td>
<td>-1.63</td>
</tr>
<tr>
<td>13</td>
<td>17.9</td>
<td>0.85</td>
<td>NA</td>
<td>-5.26</td>
<td>-1.635</td>
</tr>
</tbody>
</table>

**Figure 12.** Photophysical properties of \( m[n] \)CPP, adapted from ref.118 with permission from the
In recent years, thiophene-containing π-systems have drawn great attention due to their promising applications in organic solar cells, organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs), such as cyclothiophenes (e.g. 17), oligothiophenes and thiophene-incorporating PAHs.\(^{119,120}\) However, most of the reported thiophene-containing π-systems form linear/cyclic π-conjugation, where p orbitals are aligned perpendicularly to the molecular skeleton. Therefore, Itami and coworker prepared a series of \([n]\)cyclo-1,4-phenylene-2',5'-thienylenes (\([n]\)CPTs), a well-defined hybrid of cyclothiophene and CPP. X-ray crystallographic analysis showed that \([n]\)CPTs are highly strained and have radial π-conjugation (Figure 13a). Trends of spectral and electronic properties of \([n]\)CPTs, \([n]\)CPPs and cyclothiophenes are summarized in Figure 13b. As we can see, \([n]\)CPTs combine the features of both perpendicular and radial π-conjugation. For instance, the absorption maximum of \([n]\)CPTs are red-shifted while the emission maximum exhibits blue shift with increase of the ring size.\(^{121}\)

**Figure 13.** Computational and photoelectrical properties of \([n]\)CPT, adapted from ref. 121 with permission from Wiley-VCH, copyright (2015).
1.2. The Supramolecular Chemistry of Strained Carbon Nanohoops

Youzhi Xu, Max von Delius.*


Reproduced with permission of Wiley-VCH, copyright (2019).

In this concise review article (14 pages, 135 references), we focus on recent progress in the use of strained carbon nanohoops in a context of supramolecular chemistry. Following a brief history of synthetic milestones, we describe the use of nanohoops as hosts for different types of guests and give an overview on the exo binding of transition metals, the synthesis of mechanically interlocked architectures and efforts toward crystal engineering.

Comments on own contributions:

After deciding on the article layout together with Prof. Max von Delius, I focussed on the design of clear graphics and a thorough literature survey. The article was then jointly written up by myself and Prof. von Delius. Selina Hollstein contributed a frontispiece design. Dr. Sebastian Beil assisted in the proof-reading of the article.
The Supramolecular Chemistry of Strained Carbon Nanohoops
Youzhi Xu and Max von Delius*
Since 1996, a growing number of strained macrocycles, comprising only sp- or sp-hybridized carbon atoms within the ring, have become synthetically accessible, with the \( \text{[n]} \)cycloparaphenyleneacetylenes (CPPAs) and the \( \text{[n]} \)cycloparaphenylene (CPPs) being the most prominent examples. Now that robust and relatively general synthetic routes toward a diverse range of nanohoop structures have become available, the research focus is beginning to shift towards the exploration of their properties and applications. From a supramolecular chemistry perspective, these macrocycles offer unique opportunities as a result of their near-perfect circular shape, the unusually high degree of shape-persistence, and the presence of both convex and concave surfaces. In this Minireview, we give an overview on the use of strained carbon-rich nanohoops in host-guest chemistry, the preparation of mechanically interlocked architectures, and crystal engineering.

1. Introduction

1.1. Scope and Outline

Although the term “nanohoop” is somewhat ill-defined and emerged only recently,\(^1\) we believe that it adequately conveys the importance of topology and shape-persistence in the area of research covered in this Minireview. Moreover, the mental image of a “hula hoop” dance is helpful, because it illustrates the unique potential of this compound class in host-guest chemistry. To give a more precise definition of the scope of this Minireview, we focus on the supramolecular chemistry of macrocyclic compounds that mainly comprise carbon atoms within the ring and are relatively strained and shape-persistent as a consequence of “radial conjugation”\(^2\)-\(^4\) and have diameters of no more than about 25 Å.\(^5\) We make a few exceptions regarding these limitations, but only to discuss especially important compounds and concepts.

Following a concise history of relevant synthetic milestones, we describe the use of nanohoops as hosts for different types of guests (nido binding), which has been the area receiving most attention so far. More recent developments covered in this Minireview include studies on the exc binding of transition metals, the synthesis of mechanically interlocked architectures (MIAs), and efforts towards controlling and understanding the packing of nanohoops in the solid state.

1.2. Brief History of Strained Nanohoop Syntheses

Although the first attempts to prepare \( \text{[n]} \)cycloparaphenylenes (\( \text{[n]} \)CPPs) go back to 1934 and the \( \text{[n]} \)cyclohexanes were first proposed in 1954,\(^6\) it took until the 1980s before Vögtle\(^7\) and others\(^8\)-\(^10\) systematically attempted to prepare nanohoops such as the CPPAs and all-annelated macrocycles such as the “Vögtle belts”\(^11\). Although none of the synthetic attempts ultimately led to success, these early reports provided much conceptual inspiration and even included the preparation of the 1,4-disubstituted cyclohexanes\(^12\) that were later used by Iman and co-workers as intermediates in the preparation of CPPAs.\(^15\)

In 1996, Hedges and co-workers prepared a π-extended derivative of \( \text{[4]} \)CPP by ring-opening olefin metathesis (“picotube” I; Figure 1)\(^13\) and Kawase, Darabi, and Oda achieved the synthesis of \( \text{[r]} \)cycloparaphenyleneacetylenes \( \text{[6]} \)CPPA and \( \text{[8]} \)CPP (Figure 1) through a sequence of McMurry coupling reactions and subsequent bromination and elimination reactions.\(^16\) The difficult ring-closing step gave rise to relatively unstrained stilbene macrocycles and the ring strain was generated in exergonic reactions once the ring had formed. Other strategies to make CPPAs and their analogues include Sonogashira\(^17\) and Glaser/Eglinton\(^18\) coupling reactions as well as alkyne metathesis.\(^19\)

The first synthesis of prototypical \( \text{[r]} \)cycloparaphenyleneacetylenes \( \text{[19]} \)CPP, \( \text{[12]} \)CPP, and \( \text{[10]} \)CPP was reported by Bastl, Bertozzi et al. in 2006.\(^20\) Key to this milestone was a strategy to prepare a relatively unstrained macrocycle containing six to twelve sp\(^2\) carbon centres by Suzuki-Miyaura coupling and generate the ring strain subsequently by harnessing the free energy derived from the aromatization of three to six 1,4-cyclohexadiene moieties (mediated by Li-naphthalimide). A different strategy for the preparation of \( \text{[n]} \)CPPAs was disclosed by Yamaguchi and co-workers, who made use of platinum(II) metallacycles\(^21\)-\(^23\) that upon reductive elimination furnish \( \text{[n]} \)CPPAs. In recent years, several heteroatom-containing (e.g. \( \text{[aur]} \)CPP)\(^24\) and halogen-substituted (e.g. \( \text{[8F-6]} \)CPP; Figure 1)\(^25\) CPP derivatives were reported, thus indicating that the above-described synthetic routes are broadly applicable. For more detailed information on the syntheses and optoelectronic properties of \( \text{[n]} \)CPPAs the reader is referred to several recent review articles.\(^26\)-\(^28\)

Strained nanohoops of an entirely different design comprise meso-substituted porphyrins instead of the phenylene units found in CPPAs and CPPs. Anderson and co-workers have successfully used oligopyridine templates\(^29\)-\(^30\) to prepare porphyrin nanorings such as \( \text{c-PS} \) (Figure 1) by oxidative Glaser reactions. Since even a templated ring-closing step is typically not suitable for the generation of very high strain energies, \( \text{c-PS} \) may represent the limit of this approach. More strained porphyrin nanohoops were obtained by Osaka and co-workers using the platinum-mediated synthesis strategy commonly used to synthesize CPPAs.\(^31\)-\(^33\)
In 2017, after several research groups had already prepared CPPs containing annelated aromatic fragments (e.g. [4]CC, [4]CHBC, Figure 1),[19,36,37,42] Itami and co-workers achieved the first bulk synthesis of a “carbon nanobelt”. Compound 2 (Figure 1), for which a strain energy of 120 kcal mol\(^{-1}\) was estimated, was obtained from a deca-bromo precursor in a final Yamamoto coupling step in 1% yield.[6] Recent reports on the synthesis of armchair and chiral nanobelts[66] as well as a phenine nanocylinder[67] and a lamellar DPP derivative[68] suggest that this brief history of nanobelt synthesis is far from complete, which is good news for those who seek to make use of these compounds as supramolecular hosts and organic materials.[27]

2. Host–Guest Chemistry

2.1. Fullerene Guests

As a consequence of their unique convex structure and technological relevance, the fullerenes have long been studied as guests in various organic and metal-organic host architectures.[46–50] A unique advantage of strained carbon nanohoops in the context of previous research is that their concave cavities provide the shape-complementarity needed to achieve binding affinities and selectivities that could otherwise only be achieved in cages.

After the CPPs had become available in bulk around the turn of the millenium, these nanohoops were the first to be studied as supramolecular hosts.[51–53] Kawase et al. reported that the macrocycles [6]CPPA (Figure 1) and [8]CPPA have cavities of roughly 13 and 17 Å diameter.[54]
which is in the range required to accommodate C_{60} or higher fullerenes. In several solid-state structures, the authors observed evidence of interactions between two CPPAs and aromatic molecules such as hexamethylbenzene (HMB) and toluene (6[CPPA\_2\_HMB] \_1:1, [8]CPPA\_2\_toluene 1:4).

Stable 1:1 complexes of the smaller nanohoop [6]CPPA were observed with C_{60} (K_{\text{a}} = 1.6 \times 10^{3} \text{ M}^{-1}, benzene) and its derivative bis(ethoxycarbonyl)phenanthrofullerene (3). A drastic increase in the solubility of C_{60} in chloroform (5 mg mL^{-1}) was found as a consequence of complexation, and single-crystal X-ray diffraction confirmed the 1:1 stoichiometry as well as a “ball-on-bowl” structure (Figure 2a, left) with an offset of 2.0 Å, suggesting that the cavity of [6]CPPA may be too small to allow ideal concave–convex binding. The appearance of two singlets for the aromatic protons in the ^{1}H NMR spectrum upon cooling (Figure 2a, right) allowed the determination of a ΔG° value of 9.4 kcal mol^{-1} for the association/dissociation of [6]CPPA\_2\_C_{60}.{3,31}

An early example of “Russian doll” or “onion-type” complexes was reported by Kawase, Oda et al. in 2004 (Figure 2b).{35,56} The authors found that [6]CPPA fits into the cavity of [9]CPPA and they determined a binding constant of 1180 ± 140 M^{-1} (0 °C) for two π-extended analogues (4 and 5; Figure 2b) that are more soluble than the parent compounds. Upon addition of C_{60}, the formation of double-inclusion complexes was observed and for the case of [9]CPPA\_2\_6[CPPA\_2\_C_{60}] an association constant of 410 ± 80 M^{-1} was determined between the two nanohoops at −60°C, which is identical within error with the binding constant observed in the absence of C_{60}.

A variant of the CPPAs, in which phenylene and alkynyl linkers no longer strictly alternate, was recently reported by Moore and co-workers.{44} The combined use of the 1,4-dimethoxyphenylcyclohexadiene building blocks commonly found in CPPA syntheses with [Mo]-catalyzed alkyny metathesis enabled the gram-scale synthesis of strained macrocycle [3]CPPA, which features an odd number of alkynyl linkers. DFT studies predicted a diameter of approximately 15 Å, which should be well-suitable for the “induced-fit” binding of C_{60}. Indeed, UV-Vis titration experiments provided a K_{a} value of 1.0 \times 10^{5} \text{ M}^{-1} (toluene), which is very similar to the K_{a} value reported for the association of C_{60} with [11]CPPA (diameter 15.2 Å).{35} In the solid state, the [3]CPPA\_2\_C_{60} complex arranges into columnar stacks that are separated by 3.1 Å along the vertical axis (Figure 2c). This type of self-assembly is reminiscent of the nanopeapod assemblies observed when certain fullerenes are encapsulated within single-walled carbon nanotubes (SWCNTs),{49} thus suggesting potential applications in organic electronics.

Yamago and co-workers described the first example of a host–guest complex of an [n]CPPA nanohoop with a fullerene.{44} A binding constant of 3.6 \times 10^{5} \text{ M}^{-1} (toluene) was determined in a fluorescence-quench titration with C_{60}, which is two orders of magnitude higher than the one observed for [6]CPPA. Based on DFT calculations (M06-2X/6-31G^*) and low-temperature NMR spectroscopy, the authors proposed that C_{60} is located at the centre of the [10]CPPA cavity (diameter ca. 13.8 Å). A solid-state structure of [10]CPPA\_C_{60} (Figure 3a) obtained by Justi and co-workers{56} provided further support for this assumption. An interesting supramolecular aspect in Yamago’s study was the observed size-selectivity. An excess amount of solid C_{60} was added to a mixture of [8]CPP, [9]CPP, [10]CPP, [11]CPP, and [12]CPP in CDCl_{3}. This resulted in the ^{1}H NMR signal for [10]CPP shifting downfield, whereas the other chemical shifts...
remained unchanged (Figure 3b), and thus constitutes an impressively rapid qualitative tool to assess binding selectivities.

In similar experiments, the same authors studied the noncovalent interaction between C$_{60}$ and a mixture of [e]CPPs. As a result of the “North American football” shape of C$_{60}$, this fullerene is able to occupy the cavity in two fundamentally different orientations ("standing" or "lying") with a circular or oval cross-section, respectively, which explains why stable 1:1 complexes were observed with both [10]CPP (8.4 x 10$^{-2}$ M$^{-1}$, toluene) and [11]CPP (1.5 x 10$^{-2}$ M$^{-1}$, toluene). The size- and orientation-selectivity of binding was confirmed by two solid-state structures, DFT calculations, and the inclusion of a multifunctionalized C$_{60}$ derivative. Interestingly, Du and co-workers reported that the π-extended nonaromatic [4]CAPPB allowed the selective encapsulation of C$_{60}$ (1.1 x 10$^{-3}$ M$^{-1}$, toluene) but not C$_{70}$, which can be explained by the "standing" or "lying" orientations of C$_{60}$. [25,26]

Although there is typically no evidence for ground-state charge-transfer interaction between conventional fullerenes and [e]CPPs (see Section 2.2 for computational insights), the situation is different when endohedral metallofullerenes (EMFs) are encapsulated. The first evidence for a charge-transfer interaction between [11]CPP and the EMFs Ln@C$_{60}$ (Ln = La, Gd, Tb, and Lu; K$_{av}$ = 10$^{-2}$ M$^{-1}$, toluene) was reported by the groups of Itami and Yamago in 2014. [27,28] A case of particularly strong charge transfer was demonstrated by electrochemical (shift of E$_{onset}$) and spectroscopic (broadening of absorption bands) techniques in the 1:1 complex between [10]CPP and C$_{60}$-Li$^+$. [29] As illustrated in Figure 3c, the net positive charge is delocalized in a "layer-by-layer" fashion across the entire complex, making [10]CPP:C$_{60}$-Li$^+$ a cationic complex with an unusually diffuse charge distribution.

The use of [10]CPP as a supramolecular junction to generate modular dyads between a zinc porphyrin electron donor (6) and five representative fullerene electron acceptors (Figure 4a, left) was recently described by our own group in collaboration with Gold and Drews. [30] Fluorescence titrations confirmed binding constants higher than 10$^5$ M$^{-1}$ in toluene for all the studied fullerenes, which included the prototypical solar cell component PCBM, an arafullerene monooxadiazole, and the fullerene dimer C$_{60}$ (Figure 4a, right). Time-resolved transient absorption studies revealed efficient charge separation and recombination across the noncovalent [10]CPP junction. A particularly noteworthy finding was the observation of a lifetime of 0.5 μs, most likely due to charge delocalization, in the 2:1 complex between [10]CPP and the fullerene dimer (K$_{av}$ = 4.7 x 10$^{-7}$ M$^{-1}$, K$_{av}$ = 1.9 x 10$^{-7}$ M$^{-1}$, toluene).

In a related study, Wegner, Ewes, Tagmatarchis, and co-workers investigated the complex between the arafullerene dimer (C$_{60}$N$_2$) and [10]CPP. [31] The authors discovered that the two-step binding occurs with moderate cooperativity (α = 1.45), which indicates that a weak interaction is present between the two rings in the 2:1 complex (Figure 4b, left; K$_{av}$ = 8.4 x 10$^{-7}$ M$^{-1}$, K$_{av}$ = 3.0 x 10$^{-7}$ M$^{-1}$, 1,2-dichlorobenzene (ODCB)). DFT calculations on [10]CPP:C$_{60}$N$_2$ revealed insights into the geometry of the complex, the kinetic barriers for the binding of the first and second [10]CPP ring (Figure 4b, right), and predicted charge transfer from [10]CPP to C$_{60}$N$_2$. Evidence for such a ground-state charge transfer was indeed observed by differential pulsed voltammetry (DPV; E$_{onset}$ shift of 40 mV).

A strategy to further increase the binding affinity of [e]CPPs for fullerenes is to increase the π-surface by inserting annelated moieties into the ring. Du, Yang, and co-workers recently reported the gram-scale synthesis of compounds 7 and 8, which essentially represent π-extended [e]CPPs (Figure 5a,b). [32] The synthesis followed Jasti’s strategy, in which a Suzuki coupling reaction is used as the ring-closing step. The stepwise increase in the π-surface from [10]CPP to 7 and 8 was indeed reflected in the binding constants of the 1:1 complexes with C$_{60}$ (7:K$_{av}$ = 3.3 x 10$^{-4}$ M$^{-1}$, toluene; 8:K$_{av}$ = 2.3 x 10$^{-4}$ M$^{-1}$, toluene). As shown in Figure 5c, the authors were able to demonstrate that these complexes form photoconductive heterojunctions. Photocurrent measurements on fluorine-doped tin oxide (FTO) electrodes coated with different films as the working electrode showed stable anodic photocurrents and fully reversible ON/OFF behaviour. [33]

The molecular design of Ibose’s [4]pycyclo-2,5-chrysene (4C) π-extended nonaromatics deviates more significantly from the conventional [e]CPP structure. Using the P3-clinination synthesis strategy, the authors obtained macrocyclic tetramers of [4]phenacene, with only four C–C single bonds within the ring (Figure 6a). An interesting implication of the low symmetry of this structure is that six different stereomers of [4C] are generated, which the authors were able to isolate and identify. [34] When five compounds from the [4C] family were investigated regarding their affinity for fullerenes, association constants on an unprecedented scale.
State of the Art

Minireviews

State of the Art

Figure 5. a) Schematic and solid-state structure of 7-C8. b) Structure of the complex 8-C8. c) Photocurrent response of spin-coated films of 8-C8 (black), 9 (red), 7-C8 (dark blue), 7 (light blue), [10]CPP-κC8 (pink), and [10]CPP (purple) with and without photo-irradiation, adapted from Ref [67] with permission from Wiley-VCH. Copyright (2019).

State of the Art


State of the Art

NMR timescale and the rolling motion of the fullerene within the host is very rapid, even at −60°C.

Solid-state structures were obtained for both the 1:1 complex with C86 ((M)-[12,8]-HCC-CC. Figure 6b)[73] and the 2:1 complex with the fullerene dimer (9-[2]C86-9, 10-[2]C86-10. Figure 6c). A study of the thermodynamics of 2:1 complex formation revealed binding constants of $K_{d1}$ ≈ $10^{17}$ M$^{-1}$ and $K_{d2}$ ≈ $10^{9}$ M$^{-1}$, which means that in contrast to the 2:1 complexes based on [10]CPP (see above), the binding is anti-cooperative. This observation is likely a consequence of the wider rim of these nanoloops and/or an unfavourable interaction between the solubilizing hexyl chains. When two different members of the [4]CC family (9 and 10. Figure 6c) were added to C120, narcissistic self-sorting was observed.[73,74]

The same authors also reported that formation of the host-guest complex between C86 and (P)-[12,8]-HCC liberates the guest from motional restrictions in the solid state. In a detailed physical organic study, the authors could show that intermolecular contacts between the host and C86 maintained a tight association with an energy gain of approximately 14 kcal mol$^{-1}$, while the dynamic rotations of C86 within the host were subject to a small energy barrier of only 2 kcal mol$^{-1}$.[73]

To provide a suitable context for the association constants presented above, recent work on “saturn complexes” based on unstrained, disc-shaped macrocycles deserves a mention,[75,76,77,78] despite technically being beyond the scope of this Minireview. As a consequence of the smaller surfaces involved in noncovalent interactions, the association constants for these complexes with C86 (11:CC, $K_a$ = 23900 M$^{-1}$, toluene; 12:CC, $K_a$ = 580 M$^{-1}$, toluene) are three to four orders of magnitude lower than those for the [n]CPPs. Nevertheless, the topologies observed by single-crystal X-ray diffraction are certainly unique (Figure 7a) and provide an excellent testing ground for theoretical predictions (see Section 2.2). Another notable unstrained example is porphyrin nanobarrel 13, synthesized by Osuka and co-workers in 10% yield by consecutive cross-coupling reactions at multiple sites. Binding to C86 with 1:1 stoichiometry was confirmed by X-ray diffraction and an association constant of 5.3 x $10^{10}$ M$^{-1}$ (toluene) was determined by UV/Vis titrations.[77,78]

2.2. Computational Insights

Many of the experimental reports discussed in this Minireview are complemented by DFT calculations, typically with a focus on geometry optimizations and the calculation of HOMO/LUMO or strain energies. However, there have also been a number of dedicated theoretical studies, which we will discuss here. For example, Zhao and co-workers have investigated the nature of the noncovalent interaction in [n]CPP-CC$_n$ complexes ($n$ = 10, 11, 12), and a notable difference to the experimental and theoretical work by Yamago and co-workers[79] (see Section 2.1) was the consideration of an additional binding geometry (“half-lying”).[80] The same group also studied the potential energy experienced by C86 along a linear trajectory through the cavity of [8]CPP (strong
maximum at cavity centre), [9]CPP (unexpected three-wall diagram), and [10]CPP (strong minimum at cavity centre).\cite{9}

Grünie and co-workers included the complexes [10]CPP:C_{60}, and [11]CPP:C_{60} into a benchmark study on their DFT-D3 dispersion correction approach.\cite{10} The authors concluded that 1) the two-body dispersion energy ($\Delta E_D^{(2)}$) makes a particularly large contribution in these complexes, 2) there is a tendency to observe "over-binding" in calculations of systems with such large π-surfaces, and 3) although no general recommendation for specific solvation models can be given, solvation must not be ignored to obtain the best possible results. In another dispersion-corrected DFT study, Rodriguez-Oteia et al. studied the interaction of C_{60} and C_{70} with carbon nanohoops [10]CPP and [6]CPPA (Figure 9a).\cite{11}

A fundamental theoretical investigation into the nature of π-π interactions was recently carried out by Tskachenko and co-workers.\cite{12} The key proposal of this study, which included several [n]CPP and [n]CPPA fullerene complexes as examples, is that collective charge fluctuations are responsible for the interactions in nanohoop/fullerene complexes and that only computational approaches which take this into account are suited to provide accurate predictions (Figure 8b).

Finally, two recent articles cover theoretical aspects of the interaction of fullerenes with belt-shaped compounds such as the "belt"-shaped [n]CPPs and "clic"-shaped compounds that give rise to "saturn" complexes.\cite{13,14}

2.3. Non-Fullerene Guests

Concerning the inclusion of molecules other than fullerenes into the [n]CPPs, a particularly promising class of guests are the CPPs themselves. In two theoretical studies, the groups of Fomine and Bachrach predicted that CPPs differing by five phenylene units would be shape-complementary and form "Russian doll" complexes, in which two CPPs are aligned in a parallel manner.\cite{15,16} As shown in Figure 9a, Yanagisaka and co-workers demonstrated that these predictions are correct for a whole series of [n]CPPs (n = 5, 6, 7, 8, and 10) and that selective formation of complexes [n + 5]CPP : [n]CPP occurs, which represent the shortest possible analogues of double-walled armchair carbon nanotubes.\cite{17} The association constants in 1,1,2,2-[D]-tetrachloroethane were determined by 1H NMR titrations (ca. 10^{-4} M at 50°C) and a ternary complex, [15]CPP : [10]CPP : C_{60}, was also observed.

Anderson and co-workers described the self-assembly of "Russian doll" complexes based on two concentric porphyrin nanorings held in place by two types of templates.\cite{18} The action of the two templates was found to be highly cooperative and an energy transfer from the inner to the outer shell of the "Russian doll" complex was observed upon photoexcitation (Figure 9b). Moreover, a "shadow mask" approach allowed the replacement of magnesium centres by other metals, thus opening up a new route towards heterometalated porphyrin nanostructures.\cite{19} After template removal, Anderson's porphyrin nanorings represent a quite general interesting platform for studying the thermodynamics and kinetics of multivariant guest inclusion.\cite{20,21}

Going beyond π-π interactions, the Itoe group devised a "bowl-in-tube" host-guest complex that is based on surprisingly strong CH-π hydrogen bonds.\cite{22} Multivariant interactions of a bowl-shaped corannulene (Figure 9c: COR) with a [4]CPPC nanohoop gave rise to largely enthalpy-driven 1:1 binding ($K_A = 2.94 \times 10^4$ M^{-1}, DCM; isothermal titration
3. Metal Coordination

While the previous sections focused on the inclusion of organic guests within the cavity of strained carbon nanohoops (envelope binding), a number of studies has recently explored the reversible interaction of metals with the macrocyclic π-system or with heteroatoms inserted into the framework (mainly: enol binding).

In an organometallic tour de force, Jasti, Petrovskikhina, and co-workers investigated the multielectron reduction of [8]CPP. The complex 4K·[8]CPP<sup>−</sup> was isolated upon addition of an excess of elemental potassium in tetrahydrofuran in the presence of [18]crown-6 (Figure 10a). The reaction product exhibited a strongly red-shifted absorption band (λ<sub>max</sub> = 600 nm) and the solid-state structure revealed ionic interactions between the K<sup>+</sup> ions and both the concave and convex π-surfaces of [8]CPP<sup>−</sup>. More recently, the same authors reported the one- and twofold reduction of [6]CPP<sup>−</sup>, including evidence for the inclusion of THF in the cavity of the nanohoop.[18]

The reaction of nanohoops [9]CPP and [12]CPP with several transition-metal carbonyl complexes (Cr(CO)<sub>6</sub>, Mo(CO)<sub>6</sub>, W(CO)<sub>6</sub>) was investigated by Imai and co-workers.[19] In all three cases, evidence was observed for Ψ coordination, as expected for the formation of [a]CPP-M(CO)<sub>n</sub> complexes (n = 9, 12; M = Cr, Mo, W). X-ray crystallographic analysis of [9]CPP-Cr(CO)<sub>6</sub> (15) revealed that chromium-CPP coordination occurs at the convex surface of [9]CPP and that the a]CPP-Cr(CO)<sub>6</sub> complexes (Figure 10b) were good substrates for the selective introduction of silyl-, boryl-, and methoxycarbonyl substituents (n = 9, 10, 12). Related mono- and multinuclear complexes between rhenium(I) and the smaller, strongly curved nano-
hoops [5]CPP and [6]CPP were reported by Yamago and co-workers.\textsuperscript{[110]} Up to three Ru(cyclopentadienyl) fragments were found to be $\pi$-coordinated to alternating phenylene in [6]CPP, and DFT calculations shed light on the observed regioselectivity. An interesting question that remains open is whether the organometallic complexes are fluxional in solution, that is, whether the metallic motives are "walking" along the rings, as has been demonstrated in related planar systems.\textsuperscript{[102,105]}

Based on a Yamamoto coupling as the crucial ring-closing step, Jasti and co-workers succeeded in preparing a 2,2'-bipyridine-embedded [8]CPP (17). Figure 11.\textsuperscript{[104]} The authors demonstrated that the compound coordinates to both Pd$^{II}$ and Ru$^{II}$ metal centres, and the resulting [Pd$^{II}$(8CPPCl)$_{2}$] (18), [Pd$^{II}$([8CPP]$_{2}$)(BF$_{4}$)$_{2}$] (19), and [Ru$^{II}$(8CPP(bpy)$_{2}$)] (PF$_{6}$)$_{2}$ complexes were characterized in solution and the solid state. Although this new ligand class offers a rather unique steric environment, to the best of our knowledge it has not yet been tested in transition-metal-catalyzed transformations.

4.1. Catenanes

Two examples of the use of Sauvage’s strategy to prepare [2]catenanes featuring phenanthroline ligands are shown in Figure 12a,b. In 2007, Blüerfe et al. used a Cu$^{I}$ template to preorganize two U-shaped precursors and a Pd$^{II}$ template to furnish the diyne in a [2]catenane (20) comprising two identical rings featuring a total of four oligophenoxenes.\textsuperscript{[26]}

Optical spectroscopy and cyclic voltammetry revealed the presence of inter-ring as well as through-space donor-acceptor interactions in this compound (Figure 12a, right). In a more recent publication, Cong, Zhu, and co-workers described a phenanthroline-containing cyclopapharylenes [2]catenate.\textsuperscript{[116]}

The synthesis was based on ring closure by Suzuki–Miyaura coupling in the presence of a Cu$^{II}$ template and subsequent removal of the metal template and reorganization. The solid-state structure of catenate 21 provided evidence for a rare Möbius twist of the $n$-system,\textsuperscript{[117] which the authors rationalized computationally by stabilizing non-covalent interactions between the two rings (Figure 12b, right).}

The first observation of MILAs based on unaltered [n]CPPs was described by Mullén, Rücker, and co-workers in 2017.\textsuperscript{[118] The insoluble product mixture obtained as a side product during [n]CPP syntheses was analyzed by matrix-
assisted laser desorption ionization (MALDI), ion-mobility mass spectrometry (IMMS), and collision-induced dissociation (CID) mass spectrometry. Together, these gas-phase techniques provided evidence for the existence of different [2]catenanes, such as the interlocked dimer of [18]CPP shown in Figure 12c and perhaps even a trefoil knot. In their concluding remarks, the authors make the valid point that "the formation of significant amounts of CPP catenanes without targeted approaches of supramolecular preorganization [...] is certainly surprising and deserves further attention."

Taking advantage of an active metal template method earlier used to prepare [2]rotaxanes by Glaser coupling,[18,126] Anderson and co-workers described a spectacular [4]catenate, in which three phenanthroline-based macrocycles are interlocked with a large porphyrin nanoring (23: Figure 13). Interestingly, the synthesis first featured compound 22 as an intermediate, in which the smaller macrocycle is already mechanically interlocked as a consequence of the bulky meso substituents on the zinc porphyrins. Hence, it was possible to use the authors' standard template Glaser method in the next step, without having to worry about the detraining of the phenanthroline macrocycle, and the [4]catenate was obtained in 62% yield. Through a Vernier template effect,[22] the related [7]catenate porphyrin dodecamer complex was isolated as a by-product of this cyclization, albeit only in 6% yield.

4.3. Rotaxanes

Our group recently achieved the synthesis of two discrete [2]rotaxanes, in which [10]CPP serves as the macrocyclic component (Figure 14a).[20] The strong concave-convex interaction between C10 and [10]CPP was used to "trap" the macrocycle on a central fullerene bis-adduct binding site by conducting a carefully optimized Bingel-Hirsch reaction[22] in the final step. This crucial "covalent capture" event was surprisingly efficient (ca. 40% yield of rotaxane products) and furnished only two regiosymmetric [2]rotaxanes (trans-2, trans-3), strongly suggesting that [10]CPP acts as a template and inhibits the formation of other possible regiosymmetric products (e.g. e and cis isomers). Fullerene hexakis-adducts were chosen as stoppers, because the four equatorial cyclo-

propane substituents were judged to be ideally suited to prevent the large [10]CPP ring from delithiation. Conclusive evidence for the mechanically interlocked structure of compound 24 was indeed obtained by VT-NMR spectroscopy and CID mass spectrometry. When studying the two rotaxane isomers by transient absorption spectroscopy, Guidi and co-workers103 observed interesting differences between the charge separation (CS) and charge recombination (CR) kinetics (Figure 14a bottom; [10]CPP: electron donor; fullerene bisadduct: electron acceptor) of a “bound” and an “unbound” state of the nanohoop (the complexation/decomplexation process is slow on the timescale of the pump-probe experiments).

Two types of [2]rotaxanes based on small nanohoops featuring ortho-substituted pyridine moieties (Figure 14b, n = 1,3), were recently prepared by the Iaist group.225 The ortho substitution pattern alleviates much of the strain that would be present in the similarly sized nanohoops [6]CPP and [9]CPP and disrupts radial conjugation, which likely affects the photoluminescence of these macrocycles. Nevertheless, the nitrogen heterocenter of the pyridine ligand allowed the synthesis of rotaxanes 25 in an active metal template CuAAC reaction in yields of up to 70% (depending on the ring size and the stopper used). When a Pd2 salt was added to the rotaxane, a reversible fluorescence turn-off was observed (Figure 14b, red curve), thus suggesting possible uses of such compounds in ion sensing. To further demonstrate this potential, the authors prepared rotaxane 26, which is non-emissive as a result of an interaction between the nanohoop and a 3,5-dinitrophenyl stopper. The addition of fluoride ions, as a technologically relevant analyte, led to cleavage of the trispropyl (TIPS) stopper, release of the nanohoop, and a 123-fold fluorescence turn-on (Figure 14b, green curve).

Pérez and co-workers have recently developed a concept for synthesizing mechanically interlocked carbon nanotubes (“MINTs”)230–234 which is based on “clipping” rings around single-walled carbon nanotubes (SWCNTs) and represents an appealing approach for functionalizing and solution-processing of these nanomaterials. Osie and co-workers have reported a related “ring-toss” approach, which relies on the spontaneous interaction of Π-conjugated carbon nanohoops (Π-extended derivatives of [8]CPP, [9]CPP, and [10]CPP) with SWCNTs, which is why the resulting materials are perhaps best described as poly-pseudorotaxanes.235 Four different CPPs were combined with three SWCNT batches (differing in diameter, distribution) and the specificity of the interaction between the nanohoop and nanotubes was estimated by quantifying the amount of recovered nanohoop in UV/Vis. As no clear trend for size-selectivity was observed, the authors proposed that both “tube-in-ring”-type 27 and SWCNT complexes (Figure 14c) and “ring-on-tube”-type complexes were formed. MMTF94 calculations, high-resolution transmission electron microscopy (HR-TEM; Figure 14c, right), atomic force microscopy (AFM), and thermogravimetric analysis (TGA) studies were carried out to obtain a comprehensive picture of these two functionalization modes.

5. Self-Assembly and Crystal Engineering

Although evidence for the self-assembly of strained carbon nanohoops into discrete architectures in solution is still rare, the crystal structures of parent [n]CPPs provide valuable insights into the nature of intermolecular interactions (“herringbone” packing or channels).236 –238 In an elegant study making use of such porous channels in the solid state, Itami, Sakamoto, and co-workers co-crystallized iodine with nanohoops [9]CPP, [10]CPP, and [12]CPP and observed turn-on conductivity (ca. 10¹⁰ Ωcm resistivity at 500 mV bias voltage) and white-light emission for the solid-state material “[10]CPP·I₂”.239 Based on a combination of spectroscopic techniques, the authors concluded that the formation of polyiodide chains and ensuing charge transfer between the [10]CPP tubes and encapsulated iodine chains gives rise to these remarkable properties (Figure 15a).

![Figure 15](image)

Figure 15. a) Electric-stimulus-induced phase transition of the assembly of [10]CPP and iodine, adapted from Ref.235 with permission from Wiley-VCH, Copyright (2017). b) Self-assembly of [12]-[12]CPP into noncovalent nanotubes in the solid state, adapted from Ref.236 with permission from the American Chemical Society, Copyright (2018).

Equipping nanohoops such as the CPPs with polar functionalities is a promising strategy to enhance their intermolecular interactions in solution and the solid state. To this end, Yamago and co-workers have successfully prepared [8]-[6]CPP and [12]-[9]CPP, which represent the first fluorinated CPP derivatives.240 Starting from tetrafluoro-1,4-benzoquinone, the authors developed both a route based on a Yamamoto coupling step ([8]-[6]CPP and [12]-[9]CPP) and an unusual combination of the platinum metallacycle and 1,4-dihydroxy-2,5-cyclohexadiene approaches. When compared to the parent CPPs of the same size, the introduction
of eight and twelve fluorine atoms into the CPP framework led to a decrease in the LUMO level energies by 0.3 and 0.5 eV for 8F-[6]CPP and 12F-[9]CPP, respectively. X-ray crystallography revealed that the molecular structures of the two rings are similar to the analogous CPPs, and short distances between the fluorene and hydrogen atoms in the crystal packing indicate the presence of fluorine–hydrogen interactions. Based on the assumption that a fluorinated CPP would form a more stable “Russian doll” complex with a non-fluorinated CPP, titration experiments between 8F-[6]CPP and [11]CPP were performed. The observed association constant ($K_a = 1533 \pm 171 \text{W}^{-1}$) was indeed larger than that for the parent complex by a factor of three.

In a remarkable case of crystal engineering, Jasti, Alemin, and co-workers designed the larger, fluorinated nanohoop 12F-[12]CPP (Figure 15b) which, thanks to self-complementary fluorine–hydrogen interactions and a mild solution-casting technique, self-assembled into hexagonally packed bundles of supramolecular nanotubes that are reminiscent of SWCNTs.$^{[10]}$ A total of 36 C–H–F bonds per macrocycle was observed in the crystal packing of 12F-[12]CPP with H–F distances ranging from 2.53 to 2.62 Å (sum of van der Waals radii: 2.67 Å). The solid-state packing also revealed well-defined aren–perfluoroarene interactions between vertical columns, thereby resulting in an ideal 2D hexagonal circle packing morphology. When a solution of 12F-[12]CPP in chloroform was drop-cast onto a highly oriented pyrolytic graphite (HOPG) substrate, “forests” of hexagonal crystalline structures were observed by optical and scanning-electron microscopy (SEM; Figure 15b, bottom). The hexagonal structures were found to be on the order of approximately 1 μm in both height and width, and the observation of preferential orientations pointed towards epitaxial growth. The remarkable properties of these unusual noncovalent nanostructures include a high level of flexibility (out-of-plane elastic modulus: ca. 12 GPa) and bright photoluminescence in the solid state.

Iitami and co-workers were the first to explore the feasibility of an [η6]CPP as a molecular porous material.$^{[12,14]}$ [12]CPP was dried at 383 K in vacuo before gas adsorption measurements were performed with $N_2$, CO$_2$, H$_2$O, methanol, and ethanol. For the case of $N_2$, the authors concluded that the internal or interstitial spaces of the material are not sufficiently accessible to the guest molecule. For the case of CO$_2$, a type I isotherm was obtained and a specific surface area of 593 m$^2$ g$^{-1}$ was determined (Brunauer-Emmett-Teller (BET) method, 195 K). Whereas water was only adsorbed at relatively high partial pressures and without hysteresis (Figure 16a), the authors observed that [12]CPP adsorbed methanol and ethanol much more readily and in a two-step fashion, thus indicating the occurrence of structural transformations in the adsorption phase (Figure 16a). In situ powder XRD and IR measurements provided insights into these phase transformations and the formation of hydrogen bonds between guest molecules.

In 2013, the groups of Yamago and Iitami independently reported the synthesis of two different, three-dimensional “carbon nanocages”.$^{[13,14]}$ Whereas Iitami and co-workers prepared a macrocyclic CPP analogue (topologically equivalent to Lehn’s 2.2.2-cryptand$^{[10]}$) and observed interesting two-photon absorption cross-sections, Yamago and co-workers succeeded in converting an octahedral $\text{ML}_4$ Fujita-type complex$^{[14]}$ into macrocyclic CPP cage 28 (Figure 16b; topologically equivalent to the prototypical “soccer ball”

![Figure 15. a) Adsorption (filled circles), and desorption (open circles) isotherms of H$_2$O (green), MeOH (blue), and EtOH (red) in porous [12]CPP, measured at 298 K, reproduced from Ref. [137] with permission from the Royal Society of Chemistry, copyright (2016). b) Three-dimensional all-benzene n-conjugated molecule 28, adapted from Ref. [138] with permission from the Nature Publishing Group, copyright (2011). c) Simulated hole mobilities of [n]CPPs. d) Solid-state packing of [n]CPPs in different crystallographic directions. c) and d) reproduced from Ref. [139] with permission from the American Chemical Society, copyright (2019).](https://www.angewandte.org)
cystein reported by Weiss and co-workers. The strain energy of the most stable (DFT) isomer of 28 was calculated to be about 500 kJ mol⁻¹, which is comparable to that determined for [5]CPP (ca. 119 kJ mol⁻¹). In the solid state, a ball-shaped elliptic structure with pseudo-

Houk, Yowar, and co-workers carried out a comprehensive computational study with the aim of establishing links between the mesoscale morphologies of [n]CPPs (n = 5–12; Figure 16d) and the charge-transport properties of these nanohoops. A key finding was that hole mobilities increased with ring size and scaled in a well-behaved manner (ca. n⁷; Figure 16c). For disordered [n]CPPs, hole mobilities of up to 2 cm² V⁻¹ s⁻¹ were predicted and comparisons were drawn with calculations for the related fullerences. Since experiment and theory are in good agreement regarding the solid-state mobility of C₆₀ (5.3 cm² V⁻¹ s⁻¹ versus 3.1 cm² V⁻¹ s⁻¹, respectively), it will be interesting to see whether the predictions for the [n]CPPs are also accurate.

6. Conclusions and Outlook

Progress in the synthesis of new nanohoops and the generation of related supramolecular architectures has been very rapid during the past decade. Although the host-guest chemistry of known carbon nanohoops has been explored rather comprehensively and led to some unique findings, we expect that the synthesis of new compounds will lead to further opportunities. From a perspective of theory, the host-guest chemistry of strained nanohoops represents a valuable testing ground for dispersion correction methods, although the physical nature of the strong observed π-π interactions may remain a matter of controversial debate. Major research achievements and perhaps even concrete applications can be expected in nano hoop-based mechanically interlocked architectures and the design of nanohoop-based porous or semiconducting materials.

Acknowledgements

We are grateful for financial support from the Deutsche Forschungsgemeinschaft (DFG, 1826/419-4-SFB93 “Synthetic Carbon Allotropes”, project A1) and the University of Ulm. Sebastian B. Beil is acknowledged for providing helpful feedback. Selina Holstein is acknowledged for the design of the frontpiece graphic.

Conflict of interest

The authors declare no conflict of interest.
Macrocycles

Y. Xu, M. von Delius

The Supramolecular Chemistry of Strained Carbon Nanohoops

Curvy rings: Recent progress in strained nanohoops as well as their host–guest chemistry, mechanical interlocking, and self-assembly is summarized in this Minireview.
2. Aims and Achievements


![Mechanically Interlocked Architectures]

**Figure 14.** Schematic representations of mechanically interlocked architectures and our goals.

The first aim of this thesis was to design, synthesize and study the first example of a mechanically interlocked molecule based on a $[n]$CPP as the shuttle. $[n]$CPPs as a class of strained carbon nanohoops were first synthesized in 2008.\(^{[68]}\) Nowadays, relatively general and robust synthetic routes toward a range of $[n]$CPPs ($n = 5-16$) are available and some members of this family such as $[5]$CPP, $[8]$CPP and $[10]$CPP are even commercialized. Therefore, the research of this class of nanohoops is shifting towards the exploration of their properties and applications. From a perspective of supramolecular chemistry, these nanohoops offer great opportunities due to their near perfect circular shape. For instance, $[10]$CPP was found to selectively encapsulate $C_{60}$ fullerene with a binding constant of $10^6 \text{ M}^{-1}$.
due to the perfect concave−convex π-π interaction distances (3.4 Å) between the host and guest.\cite{122}

Mechanically interlocked architectures (MIAs) such as rotaxanes, catenanes and molecular knots are recognized as ideal components for the construction of molecular machines.\cite{123} The mechanical bond can be utilized to stabilize some highly reactive chemical motifs or to produce some unprecedented photoelectric properties. Following the first rotaxane synthesis by Schill and coworkers fifty years ago,\cite{124} the art of preparing MIAs has advanced significantly. However, since prototypical [n]CPPs lack heteroatoms, a unique synthetic challenge arises neither the classic active metal template strategy nor hydrogen bonding template approach can be employed for construction of based CPPs MIAs.

Figure 15. a) Retrosynthetic analysis of [2]rotaxane. b) Fluorescence titrations between [10]CPP and 101 in toluene. c) Partial 1H NMR spectra of [10]CPP (red), pseudorotaxane (light green), crude mixture of final Bingel reaction (dark green), and isolated [2]rotaxane isomers trans-2 (blue) and trans-3 (purple).

In this thesis, we aimed to perform the synthesis of the first [2]rotaxane featuring a fully conjugated macrocycle [10]CPP as a ring component by using a
Aims and Achievements

concave−convex π−π template strategy. Once the [10]CPP−fullerene [2]rotaxane is obtained, key aim was to gather fundamental insights on its photo/redox properties. Furthermore, owing to the ability of the mechanical bond to stabilize some highly reactive chemical motifs, [10]CPP was envisioned to be a supramolecular directing group to improve the regioselectivity of fullerene chemistry.

As shown in the retrosynthetic analysis, the synthesis of [2]rotaxane was divided into three key building blocks: [10]CPP, fullerene stopper and dimalonate macrocycle (Figure 15). [10]CPP was prepared according to a modified reported procedure. The solid-state structure of [10]CPP⊃C₆₀ shows the distance between the two π systems is roughly 3.4 Å, which is the optimal distance for π-π interactions. Therefore, we can quantify fullerene diethyl malonate pentakis adduct that possesses four rigid substituents along its equator should be effective at preventing [10]CPP from dethreading. It was prepared according to a modified three-step procedure starting from C₆₀. After the key compound 101 bears the central fullerene binding site was successfully transformed from half-thread 100, we proceeded to prepare the corresponding pseudorotaxane and to investigate the thermodynamics of the [10]CPP⊃fullerene inclusion complex. Interestingly, we could only obtain a near-perfect fitting for the experimental data, when 1:2 and 2:1 equilibria were considered in addition to the 1:1 mode of binding for schematic structures of the corresponding complexes and equilibria (Figure 15b). Furthermore, we found that [10]CPP signal in pseudorotaxane splits into two peaks at low temperature due to “freezing” of the complexation/decomplexation equilibrium. This discovery inspired us to start performing the final rotaxane formation reaction from low temperature. After screening reaction conditions, we were able to synthesize the [2]rotaxanes in total ca. 40% yield, where only two regioisomeric [2]rotaxanes had formed (Figure 15c).

With two [2]rotaxanes in hand, our collaborators carried out the electron transfer studies, which revealed that the mechanical bond leads to an interesting situation,
where a relatively well-defined “unbound” supramolecular state can be probed experimentally. Moreover, We have gained insights into the role of [10]CPP as supramolecular directing group in fullerene chemistry. Interestingly, we only observed three \textit{trans} regioisomers in fullerene bisaddition reaction. This means the modulation of reactivity leads to drastically improved regioselectivity in the present of [10]CPP. It is worth emphasizing that the costly [10]CPP template can be efficiently recycled in this reaction.
2.2. Efficient Electron Transfer in Modular Porphyrin–[10]CPP\(\rightarrow\) Fullerene Complexes

Inspired by the charge transport results of the first project, the second aim of this thesis was to design a modular donor-acceptor system for charge transfer study. A wide range of molecular donor-acceptor dyads and complex species that undergo intramolecular energy and photoinduced electron transfer have been prepared and studied in order to mimic natural photosynthesis and to create new photoactive devices.\cite{125} Many of these systems imitate photosynthetic reaction centers by using porphyrins as electron donors due to their rich and extensive absorptions, while \(\text{C}_6\text{0}\) and fullerene derivatives as effective electron acceptors owing to their small reorganization energy and readily accept multiple electrons in the electron transfer reactions.\cite{126}

![Figure 16. Representative examples of donor-acceptor dyads and our goals.](image)

Up to now, most porphyrin-fullerene dyads are based on the use of covalent linkages, which can mediate the distance, flexibility and spatial orientation between the donor and acceptor components.\cite{125,127} In addition, charge transfer studies
Aims and Achievements

were performed with noncovalently linked electron donor-acceptor systems, where porphyrin and fullerene were connected via hydrogen bonding or π-π interactions. However, no matter covalent bonding or hydrogen bonding, both donor and acceptor moieties have to be chemically functionalized (Figure 16).\textsuperscript{[128,129]} It is worth mentioning that selective and high yielding chemical modification of fullerenes as well as purification somehow are not so easy. For example, the fullerene dimer C\textsubscript{120} is impossible to functionalized selectively due to too many similar reactive double bonds and its overall thermodynamic instability. Therefore, so far there is no general way to study different fullerenes in a same donor-acceptor system.

Combining the literature and our previous research, we knew that [10]CPP can encapsulate a range size of fullerenes such as C\textsubscript{60} and C\textsubscript{70}. Therefore, we came up with the design of the modular porphyrin-[10]CPP dyad as an electron donor, in which [10]CPP was envisioned to be a molecular arm used to catch the electron acceptor fullerenes. There are several incomparable advantages of our system compared to the literature knew donor-acceptor systems:

- No functionalization is required on fullerene.
- With the preparation of iodo-[10]CPP, the electron donors can be easily replaced by efficient cross coupling reaction.
- Using unembellished fullerenes enables the facile method for authentic comparison of electron acceptors.
- Most importantly, the fullerene dimer C\textsubscript{120} also can serve as an electron acceptor in this modular donor-acceptor system.

The synthesis of porphyrin-[10]CPP dyad was divided into two building blocks: ethynylporphyrin and bromo/iodo-[10]CPP. The synthesis of ethynylporphyrin is very straightforward. However, we put enormous efforts and time into the synthesis of bromo/iodo-[10]CPP (Figure 17). At first we tried to functionalized [10]CPP directly by using BXS (X = Br, I), bromine or BXS/AuCl\textsubscript{3}. To our disappointment, we were either unable to transform [10]CPP directly into bromo/iodo-[10]CPP, or the
halogenation has not selectivity. Then we have tried to introduce the brominated precursor at the early stage. Unfortunately, the Suzuki-Miyaura reaction of macrocycle formation didn’t work very well. At the end, we decided to use a trimethylsilyl (TMS) group as a functional handle that would allow the late-stage introduction of an iodo substituent. TMS-[10]CPP was prepared in an acceptable yield, which can be converted into iodo-[10]CPP in 82% yield at low temperature (-78→-20 °C). With iodo-[10]CPP in hand, we found that porphyrin-[10]CPP dyad was synthesized in quantitative yield by using a copper-free Sonogashira reaction condition. It’s worth mentioning that the successful synthesis of iodo-CPPs is of great significance for the applications of CPPs in material science. Benefit from iodo-CPPs high activity, CPPs can be easily coupled with a range of groups to make hybrid materials.

![Figure 17](image_url)

**Figure 17.** Two key building blocks of porphyrin-[10]CPP dyad.

A range of fullerenes were prepared to preform host-guest and charge transport studies. We observed that porphyrin-[10]CPP dyad binds C_{60}, C_{70}, (C_{60})_{2}, PCBM and an azafullerene with binding constants exceeding $10^5$ M$^{-1}$ (toluene) in all cases. Independent support for the notion of strong fullerene binding was provided by electrospray ionization (ESI) mass spectrometry. Pump–probe spectroscopy revealed efficient charge separation between porphyrin and fullerenes, affording up
to 0.5 ms lifetime charge separated states. The advantage of this a modular donor-acceptor system is particularly evident in the case of dumbbell-shaped \((\text{C}_{60})_2\), which exhibited intricate charge-transfer behavior in 1:1 and 2:1 complexes.
2.3. Synthesis of Highly Strained, Radially \( \pi \)-Conjugated Porphyrinylene Nanohoops

After exploring the applications of \([10]\)CPP in supramolecular chemistry as well as material science, we aimed to design and synthesize porphyrinylene nanohoops, which can be regarded as the analogues of CPPs. \([n]\)CPPs have a similar absorption maxima between 335-340 nm, while the fluorescence maxima dramatically red shifts and HOMO-LUMO gap decreases with the hoop size becoming smaller.\[^{54,55}\] Furthermore, circularly shaped \([10]\)CPP and \([11]\)CPP were reported can encapsulate \(C_{60}\), \(C_{70}\) and fullerene derivatives by using concave−convex \(\pi\)-\(\pi\) interactions.\[^{130,131}\]

Porphyrin as an electron-rich pigment has been widely used in photocatalysis and molecular electronics. Making a strained porphyrin nanoring would be an effective way to regulate optoelectronic properties of porphyrin. For example, Osuka and coworkers found that \([n]\)cyclo-5,15-porphyrinylene-4,4′-biphenylenes (\([n]\)CPB) have a red-shifted absorption maximum and decreased HOMO-LUMO gap with the hoop size becoming smaller.\[^{105}\]

![Strained Carbon Nanohoops](image)

**Figure 18.** Representative examples of strained carbon nanohoops and our purpose.
Although small π-conjugated nanohoops are difficult to prepare, they offer an excellent platform for studying the interplay between strain and optoelectronic properties and increasingly find uses in host-guest chemistry and molecular self-assembly. However, neither template-directed porphyrin nanorings synthesis developed by Anderson nor the platinum-mediated porphyrin nanohoops synthesis developed by Osuka, the hoop size is hard to become too small. While the relatively large size of porphyrin nanohoops not only limits their applications in host-guest chemistry, but also they are not good enough platform to study the interplay between strain and optoelectronic properties.

On account of the significantly different photophysical properties of \([n]\text{CPPs}\) and \([n]\text{CPB}\), we designed an even smaller porphyrin nanohoop [2]cyclo-5,15-porphrinylene-4,4′,4″-terphenyl ([2]CPT). DFT calculations indicated that [2]CPT has a similar diameter and strain energy to [10]CPP. [2]CPT was envisioned to be the smallest porphyrin nanohoop at the time when the project was conceived. We believe it will not only exhibits unique optoelectronic properties due to the high strain energy, but also will show interesting supramolecular properties with respect to fullerenes due to the circular shape and similar size with [10]CPP. Furthermore, we could vary the linkers between the two porphyrins to make a range of different nanohoops.

In order to synthesize those porphyrinylene nanohoops, we chose the diboronate 103 and meso-porphyrin 104 as building blocks (Figure 19). The produces macrocyclic compounds were found until the Suzuki-Miyaura cross-coupling reaction temperature heated up to 125 °C with toluene as the sole solvent. Furthermore, we discovered that the addition of pyridine (100 equiv.) led to a significantly increased yield of the desired macrocycle and an unexpected ratio between [2]CPT-OTES and [3]CPT-OTES of ca. 2:1. The porphyrin macrocycles could be transformed smoothly into the corresponding alcohols \([n]\text{CPT-OH}\) by treatment with TBAF. The mild reagent \(\text{H}_2\text{SnCl}_4\) was employed in the final aromatization step, we able to isolate compounds [2]CPT and [3]CPT in reasonable
three-step yields of 10% and 6%, respectively.

**Figure 19.** Representative achievements in Project III.

In optoelectronic studies, we observed bathochromic shifts in the absorption spectrum and a narrowing of the HOMO/LUMO gap with the hoop size of \([n]CPT\) becomes small. Interestingly, strain-induced red-shifts are only observed in the emission spectra of \([n]CPPs\). By means of UV-Vis titrations in toluene, we were able to determine binding constants of \(2.5 \times 10^8 \text{ M}^{-1}\) for \(C_{60}\) and \(2 \times 10^7 \text{ M}^{-1}\) for \(C_{70}\). While [2]CPT binds the larger fullerene \(C_{70}\) slightly more strongly than \(C_{60}\) in the gas phase by collision-induced dissociation experiments. Furthermore, π-extended nanohoops [2]CPTN, [3]CPTN, and [3]CPTA were achieved by using the similar synthetic approach of [2]CPT. We failed to convert the small-ring precursor [2]CPTA-OH into [2]CPTA even at elevated temperature, which indicates that the aromatization energy no longer overcompensates the strain energy. These strained porphyrin nanohoops may prove useful for the regioselective synthesis or separation of fullerene bisadducts and in photoelectroactive devices.
3. Publications


Youzhi Xu, Ramandeep Kaur, Bingzhe Wang, Martin B. Minameyer, Sebastian Gsanger, Bernd Meyer, Thomas Drewello, Dirk M. Guldi,* and Max von Delius*

Reproduced with permission of the American Chemical Society, copyright (2018).

Abstract:

The cycloparaphenylenes (CPPs) are a class of strained macrocycles that until 2008 were considered beyond the reach of organic synthesis. With its cyclic array of ten para-substituted phenylene rings, [10]CPP possesses a concave π-system that is perfectly preorganized for the strong supramolecular association of convex fullerenes such as C_{60}. Although mechanically interlocked CPP architectures have been observed in the gas phase, the rational synthesis of bulk quantities has not been achieved yet, which is likely due to the fact that conventional template strategies are not amenable to CPP rings that lack heteroatoms. Here, we report the synthesis of two [2]rotaxanes, in which a [10]CPP ring binds to a central fullerene bis-adduct and is prevented from dethreading by the presence of two bulky fullerene hexakis-adduct stoppers. The final step in the rotaxane synthesis is surprisingly efficient (up to ca. 40% yield) and regioselective, because the fullerene acts as an efficient convex template, while [10]CPP acts as a supramolecular directing group, steering the reaction at the central fullerene exclusively towards two trans regioisomers. Comprehensive physicochemical studies confirmed the interlocked structure, shed light on the dynamic nature of the CPP-fullerene interaction, and revealed intriguing consequences of the mechanical bond on charge transfer processes. In light of recent advances in the synthesis of nanohoops and nanobelts, our concave-convex π-π templating strategy may be
broadly useful and enable applications in molecular electronics or complex molecular machinery.

**Comments on own contributions:**

This project took almost two years from the first synthesis to manuscript submission. Prof. Max von Delius had the original idea. More than 90% of synthesis and characterization experiments were carried out by myself, which includes the synthesis of main building blocks [10]CPP, malonates and fullerene hexakis-adduct stoppers, the supramolecular chemistry of pseudorotaxane, the optimization of synthetic approaches, HPLC purification and characterization of rotaxanes, as well as the study of [10]CPP as a supramolecular directing group in fullerene chemistry. All the NMR measurements, DNMR analysis, UV-vis absorption and fluorescence spectra were carried out by myself. Our collaborators in Erlangen carried out the transient absorption studies (photophysics). Furthermore, I participated in the manuscript preparation and wrote the supporting information.

Youzhi Xu, Ramandeep Kaur, Bingze Wang, Martin B. Minameyer, Sebastian Gsänger, Bernd Meyer, Thomas Drewello, Dirk M. Guldi, and Max von Delius

1Institute of Organic Chemistry and Advanced Materials, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany
2Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials, Friedrich-Alexander University Erlangen-Nürnberg, Egelandstrasse 3, 91058 Erlangen, Germany
3Interdisciplinary Center for Molecular Materials (ICMM) and Computer-Chemistry-Center (CCC), Friedrich-Alexander University Erlangen-Nürnberg, Nägelsbachstraße 25, 91052 Erlangen, Germany

Supporting Information

ABSTRACT: The cycloparaphenylenes (CPPs) are a class of strained macrocycles that until 2008 were considered beyond the reach of organic synthesis. With its cyclic array of ten para-substituted phenylene rings, [10]CPP possesses a concave π-system that is perfectly preorganized for the strong supramolecular association of convex fullerenes such as C80. Although mechanically interlocked CPP architectures have been observed in the gas phase, the rational synthesis of bulk quantities has not been achieved yet, which is likely due to the fact that conventional template strategies are not amenable to CPP rings that lack heteroatoms. Here, we report the synthesis of two [2]rotaxanes in which a [10]CPP ring binds to a central fullerene bis-adduct and is prevented from deheteroatomic by the presence of two bulky fullerene hexakis-adduct stoppers. The final step in the rotaxane synthesis is surprisingly efficient (up to ca. 40% yield) and regioselective because the fullerene acts as an efficient convex template, while [10]CPP acts as a supramolecular directing group, steering the reaction at the central fullerene exclusively toward two trans regioisomers. Physicochemical studies confirmed the interlocked structure, shed light on the dynamic nature of the CPP–fullerene interaction, and revealed intriguing consequences of the mechanical bond on charge transfer processes. In light of recent advances in the synthesis of nano hoops and nanobelts, our concave–convex π–π templating strategy may be broadly useful and enable applications in molecular electronics or complex molecular machinery.

INTRODUCTION

It is widely recognized that mechanically interlocked architectures such as catenanes and rotaxanes are ideal components for the construction of molecular machines. Yet, the mechanical bond can also be harnessed to stabilize otherwise highly reactive chemical motifs or to generate unprecedented functional properties and gather fundamental insights on photo/redox-active building blocks that the mechanical bond holds in dynamic spatial proximity. A class of macrocycles that seem predestined to give rise to such functional behavior are the cycloparaphenylenes (CPPs). These strained "nano hoops", which were first synthesized in 2008, exhibit highly unusual optoelectronic properties. For instance, a red-shifted emission is observed upon shortening the conjugation length, which is in stark contrast to the behavior observed in linear oligophenylenes. Moreover, [10]CPP strongly binds fullerenes and has been shown to mediate charge transport both in solution and in thin film.

A first step toward cycloparaphenylene-based mechanically interlocked molecules was recently achieved by Müller and coworkers who analyzed the insoluble remainder from a CPP synthesis by ion-mobility mass spectrometry (IMMS) and observed large macrocycles, as well as catenanes (Figure 1, top) and most likely also a trefoil knot. The rational synthesis of a mechanically interlocked compound based on one or more CPP rings and the study of the properties of such a compound is, however, still elusive. Herein, we report the use of a concave–convex π–π template strategy, which enabled us to achieve the synthesis of two [2]rotaxanes comprising a [10]CPP macrocycle, a fullerene bis-adduct binding site, and two fullerene hexakis-adduct stoppers (Figure 1, bottom).

Received: August 8, 2018
Published: September 20, 2018
RESULTS AND DISCUSSION

Synthesis Strategy and Preparation of Precursors. A key consideration for the synthesis of rotaxanes is the choice of reaction that forges the mechanical bond, i.e., the reaction that leaves the macrocycle kinetically trapped on the linear "thread". Due to the high strain energy present in [10]CPP (58 kcal/mol), the ring-closing step is not the final step in its synthesis, and the initially obtained macrocycle exhibits a rectangular rather than circular shape. As such, we chose to avoid a "clipping" approach, and instead opt for a "stoppering" strategy. Accordingly, our synthesis is based on the covalent capture of a pseudorotaxane by means of an addition reaction to the central fullerene in the final step of the synthesis (Scheme 1). A second strategic consideration relates to the choice of a "stopper", which needs to be sufficiently bulky to prevent the macrocycle from dethreading. With a chain of 40 carbon atoms constituting its macrocycle and a diameter of approximately 13.7 Å, [10]CPP represents an unusually large, albeit relatively shape-persistent nanoring, in comparison with the vast majority of reported [2]rotaxanes. As a result, we chose to utilize two fullerene hexakis-adducts as stoppers, based on the rationale that, in the supramolecular inclusion complex between [10]CPP and C<sub>60</sub>, the distance between the two π systems is roughly 3.4 Å, which is the optimal distance for π−π interactions. Hence, a fullerene that possesses four rigid substituents along its equator should be effective at preventing [10]CPP from dethreading. As a specific fullerene addition reaction, we chose the well-established Bingel reaction, both for functionalizing the fullerene stoppers and the central fullerene binding site because this reaction reliably generates octahedral hexakis-addition patterns, and most importantly, it can be carried out at low temperature, which we expected to be important for the crucial final reaction step.

The synthesis of key building blocks is shown in Scheme 1. Fullerene diethyl malonate pentakis adduct 1 was prepared according to a modified, three-step procedure starting from C<sub>60</sub>. Two "half-threads" (2, 3) were synthesized from 1 by means of high-yielding Bingel reactions with a symmetric dimalonate macrocycle (abbreviated as "Y") that, based on molecular modeling, would allow dynamic motion of [10]CPP along the thread of the final rotaxane. Half-thread 2 was transformed into key compound 4, which bears the central fullerene binding site, in a Bingel reaction whose selectivity for the monoaddition product was increased by utilization of excess C<sub>60</sub>. As a final building block, [10]CPP was prepared as illustrated in Scheme 1, according to a modified published procedure.

Rotaxane Synthesis and Characterization. With compound 4 in hand, we proceeded to prepare the corresponding pseudorotaxane and to investigate the thermodynamics of the [10]CPP⊂fullerene inclusion complex. As shown in Figure 2c (top), addition of one equivalent of [10]CPP to 4 resulted in a pronounced shift and slight broadening of the 'H NMR signal of [10]CPP, indicating that the two compounds are subject to a relatively strong noncovalent association (in CDCl<sub>3</sub>). The fluorescence of
[10]CPP with a maximum at 466 nm allowed us to carry out a quantitative study of this association by fluorescence quenching titration (in toluene; Figure 2b). When the titration data was fitted according to a 1:1 binding model, an association constant of $1.8 \times 10^6 \text{ M}^{-1}$ was obtained, which is in very good agreement with published data on [10]CPP complexes with other fullerene monoadducts. Upon close inspection, we noticed, however, that the fit did not optimally reproduce the experimental data. As a result, we tested whether a 2:1 or a 1:2 binding model would lead to better agreement. Interestingly, we could only obtain a near-perfect fit for the experimental data, when 1:2 and 2:1 equilibria were considered in addition to the 1:1 mode of binding (Figure 2b for schematic structures of the corresponding complexes and equilibria, as well as a summary of all binding constants). Although it is intriguing that both 2:1 and 1:2 complexes are ostensibly formed in highly dilute solution, it should be stressed that, at the more concentrated conditions used for the [2]rotaxane synthesis, the...
1:2 and 2:1 complexes are only present in very small amounts (<10%; Figure 53).

Having established that [10]CPP binds to 4 with $K_d = 10^6$ M$^{-1}$ in toluene, we turned our attention toward the conversion of 5 into [2]rotaxane 6 by means of a final Bingel reaction. When we subjected pseudorotaxane 5 to an equimolar amount of half-thread 2 under standard reaction conditions, we did indeed observe spectroscopic evidence that was indicative for the formation of the desired [2]rotaxane species, albeit in low yield. A thorough analysis of the corresponding MALDI mass spectra revealed that the low yield was primarily due to the formation of side products in which addition of CB$_2$ fragments to the central fullerene had occurred as a result of the large excess of CB$_2$. To alleviate this problem, we decided to circumvent the use of CB$_2$ by using brominated half-thread 3 (Figure 2) as a preactivated reagent for the addition reaction. To our delight, we found that an equimolar amount of this precursor led to a clean mixture of rotaxanes(s) 6 (ca. 16%) and unreacted [10]CPP (ca. 84%). By using a 2-fold excess of half-thread 3, we were able to increase the combined (NMR) yield of 6 to approximately 40% (H NMR stacked plot in Figure 2c).

Analysis of the crude mixture by $^1$H NMR, MALDI mass spectrometry, and HPLC suggested that a mixture of two regioisomeric [2]rotaxanes had formed. The observation of a mixture of isomers in such a reaction is not a surprising result because eight chemically distinct double bonds are available for the second addition step in 5.51 Purification of these two compounds by HPLC ($^1$H NMR stacked plot in Figure 2c) and extensive analysis of the corresponding UV-vis (Figure 2d) and $^1$H and $^{13}$C NMR spectra led us to conclude that the major product is the trans-3-6 (ca. 26% isolated yield) and the minor product is the trans-2-6 (ca. 10% isolated yield). This result is unusual in light of the literature on fullerene bis-addition reactions,52,62 owing to the fact that generally a more diverse isomeric mixture is observed, and the so-called $e$ isomer ($e$ for equatorial), whose formation we did not observe at all, is typically the major reaction product in Bingel reactions. The unexpected regioselectivity can be explained by considering the angle between the two substituents in different regioisomers. For instance, in the trans-1 regioisomer, the two addends are located diametrically opposed on the C$_{60}$ hence, the angle is 180°, which should be ideal for [10]CPP binding. As such, our inability to isolate the trans-1 rotaxane is likely a result of the statistical, steric, and electronic factors that have previously been invoked to explain the regioisomeric pathway of Bingel reactions.53 In the two isolated products, trans-2-6 and trans-3-6, the angle between substituents is 144° and 120° (Figure 2d,e for calculated structures), respectively, which evidently allows for the association of [10]CPP throughout the course of the Bingel reaction, whereas the 90° angle in the $e$ isomer presumably leads to steric repulsion and completely shuts down this regioisomeric pathway (vide infra for more results pertaining to the question of regioselectivity).

**Evidence for [2]Rotaxane Structure.** Not surprisingly for a molecule featuring a molecular weight of 5.3 kDa, as well as two flexible spacer groups, we were unable to grow single crystals for X-ray crystallography. Therefore, we aimed at providing evidence for the rotaxane structure of trans-2-6 and trans-3-6 by other means. The relative position and shape of the [10]CPP $^1$H NMR peaks corresponding to pseudorotaxane 5 and rotaxanes 6 are the first indications to this end (Figure 2c). More conclusive evidence was obtained by temperature NMR (VT-NMR). The [10]CPP signal in pseudorotaxane 5 splits into two peaks at low temperature due to “freezing” of the complexation/decomplexation equilibrium (Figure 3a; $\Delta f^G_{298K} = 57.3$ kJ mol$^{-1}$; $\tau_{1/2} = 1.2$ ms), whereas no such peak splitting is observed in rotaxane trans-3-6 (Figure S7). VT-NMR line-ship analysis54 allowed us to obtain a comprehensive kinetic picture of the interaction between [10]CPP and the fullerene monoadduct 4 (Figure 3b; $\Delta f^G = 33.0$ kJ mol$^{-1}$; $\Delta S^G = -81.5$ J mol$^{-1}$ K$^{-1}$), and we believe it is reasonable to assume that the dynamic [10]CPP translation in the rotaxanes will be on the same millisecond time scale. In contrast to pseudorotaxane 5, we were also unable to remove the [10]CPP ring from rotaxane trans-3-6 by addition of excess C$_{60}$ or silica gel chromatography.

The structural difference between the pseudorotaxane 5, on one hand, and the rotaxane isomer trans-3-6, on the other hand, is clearly reflected in the respective MALDI mass spectra (Figure 2f). In all cases, the molecular radical cation is observed. However, the molecular ion of the pseudorotaxane 5 is much less abundant than those ions, which correspond to decomposition products of 5, i.e., the radical cations of 4 and [10]CPP. This is indicative of the noncovalent bonding between 4 and [10]CPP. In the case of rotaxane 6, using trans-3-6 as example, the molecular ion produces the most intense signal, with only minor decomposition, as expected for the mechanically interlocked architecture in 6. We did not observe mass spectrometric evidence for the formation of [3]rotaxanes in which two CPP rings would be trapped on the thread. This finding may be due to the fact that the presence of two CPP rings in the corresponding pseudo[3]rotaxane (see Figure 2b) does not allow sufficient space for the Bingel reaction to proceed.

The most conclusive evidence for the rotaxane structure was provided by MS/MS spectra (Figure 2g). In MS/MS experiments, the chosen precursor ion was mass-selected and allowed to dissociate, producing a daughter ion mass spectrum.
of the individually selected precursor ion. While the molecular ion of pseudorotaxane S shows the efficient loss of the rather weakly bound CPP ring, the molecular ion of rotaxane 6 features the loss of malonate ligands, while the CPP ring remains attached to the fullerene thread. This behavior is fully consistent with a [2]rotaxane structure, where the CPP nanoring cannot dissociate without breaking a number of covalent bonds in the stopper (Figures S12 and S13).

To investigate to which extent the [10]CPP ring is mobile along the thread of the rotaxane, once it has dissociated from the central fullerene, we performed ROESY NMR experiments (Figure S8). In these spectra, we observed NOE contacts between the [10]CPP protons and various CH₃ groups of the macrocyclic spacer, indicating some mobility along the thread, at least in the vicinity of the central fullerene. However, we did not observe NOE contacts between the [10]CPP protons and the CH₃ protons within the ethyl ester substituents on the fullerene stoppers, indicating that there is most likely no local thermodynamic minimum for the macrocycle in the vicinity of the two stoppers.

Electron Transfer Studies with the Rotaxane Isomers.

All rotaxanes (Figure S14) exhibit in dichloromethane the characteristic absorption features of the fullerene monoadduct/ fullerene bis-adduct, on one hand, and of the fullerene hexakis-adduct, on the other hand, with prominent absorptions around 270 and 280 nm (ε ≈ 2.2 × 10⁴ M⁻¹ cm⁻¹), between 310 and 400 nm (ε ≈ 1.65 × 10⁴ M⁻¹ cm⁻¹), and around 700 nm (ε ≈ 1.0 × 10⁴ M⁻¹ cm⁻¹). In addition, the [10]CPP absorption is discernible at 340 nm (ε ≈ 1.3 × 10³ M⁻¹ cm⁻¹). In line with previous studies, the singlet excited state energies of the fullerene monoadduct, the fullerene bis-adduct, the fullerene hexakis-adduct, and [10]CPP are 1.76, 1.77, 1.89, and 3.46 eV, respectively.

To determine the energetics of charge transfer reactions between [10]CPP and the different fullerences in the pseudorotaxane S, trans-2-6, and trans-3-6, we recorded differential pulse voltammograms (Figure S15) in argon-saturated dichloromethane vs Fe/Fc. For pseudorotaxane S, the first and second reductions at −1.05 and −1.39 V, respectively, are centered on the monoadduct, while the third reduction due to the hexakis-adduct is noted at −1.55 V. The first [10]CPP centered oxidation is at +0.75 V. For trans-2-6 and trans-3-6, the first reduction at −1.23 V is centered on the bis-adduct and therefore shifted by 0.18 V relative to the monoadduct in the pseudorotaxane, followed by the second reduction and third reduction, which involve the hexakis- and bis-adducts, respectively, and coalesce at −1.59 V. Correspondingly, we derive energies of the charge-separated state of 1.82 eV for pseudorotaxane S and 1.98 eV for trans-2-6/trans-3-6.

To obtain insights into the photoproducts formed in the rotaxanes (trans-2-6/trans-3-6) upon photoexcitation, we turned to transient absorption spectroscopy on the femtosecond, pico- and nanosecond time scales (fs-TAS and ns-TAS). We selected an excitation wavelength of 320 nm (3.87 eV), where all fullerence adducts as well as [10]CPP absorb. Considering the extinction coefficients, the light partitioning at 320 nm is 1:1. Within a few picoseconds after excitation, an ultrafast evolution of the transient absorption features
characteristic of the one-electron oxidized [10]CPP and the one-electron reduced fullerene bis-adduct at around 540 and 1045 nm evolved (Figures 4 and S20-S22).\textsuperscript{39-61}

Multimwavelength and global target analyses\textsuperscript{39} of the fs-TAS and ns-TAS data necessitated five species and three species kinetic models, respectively, to fit the data for trans-2-6/ trans-3-6 (Figure S57). From the VT-NMR data, which are shown in Figure 3, we postulate that the dissociation of [10]CPP from the central fullerene bis-adduct and the microscopic reversibility of this process are very slow, that is, on the millisecond time scale, when compared to the electron transfer processes studied by fs-TAS and ns-TAS. Hence, we partitioned the data fitting into "bound" and "unbound" states, where [10]CPP is located on the central fullerene bis-adduct or somewhere along the thread, respectively. Based on the differences in association constants for [10]CPP in the two regioisomers, which infer that in trans-2-6 the "bound" state is less populated than in trans-3-6, we used a 9:1 ratio for trans-2-6 and a 7:3 ratio for trans-3-6.

For trans-2-6, the "bound" and "unbound" states transform in dichloromethane into two different [10]CPP**→C60**-charge-separated states in 0.84 ± 0.02 and 10.5 ± 0.3 ps, respectively. Notable is the fact that only the charge state originating from the "unbound" state features distinct fingerprints, while they are somewhat broadened in the case of the "bound" state as precursor. The difference is the appreciably stronger electronic coupling between [10]CPP and C60 in the "bound" relative to the "unbound" case. For trans-3-6, the corresponding Cs and CsC occur with 0.9 ± 0.02 and 12.9 ± 0.5 ps, respectively. Both [10]CPP**→C60**-charge-separated states, that is, "bound" and "unbound", are subject to a parallel decay (Figure S4b) and exhibit drastically different lifetimes. For trans-2-6 and trans-3-6, the two products are the triplet excited state of the fullerene bis-adduct, on one hand, and the ground state, on the other hand. As far as the first, short-lived component is concerned, it is constituted by the one-electron oxidized, "bound" [10]CPP, which is locked in close proximity to the fullerene bis-adduct, and decays with a time constant (CR) of 1.62 ± 0.2 ns. The second, long-lived component stems from "unbound" [10]CPP occupying a more distant location relative to the central fullerene bis-adduct, which is a unique consequence of the mechanically interlocked architecture (Figure 4f). From fs-TAS, only an upper limit of >6 ns was extrapolated for the underlying time constant (Cv). An accurate determination of CR was achieved by ns-TAS (Figures 4 and S20), where, next to the fast C, CV evolved with a lifetime of 20.3 ± 6 ns for trans-2-6. The lifetime values of trans-3-6 were 1.56 ± 0.2 and 26.9 ± 0.6 ns. On even longer time scales, only the triplet excited state absorption features of [10]CPP and the fullerene bis-adduct dominate the transient absorptions.

Further support for the notion of charge separation in a "bound" and "unbound" state came from changing the solvent dielectric constant from 89.3 for dichloromethane to 6.97 in 2-methyltetrahydrofuran. Considering that the charge recombination is placed in the normal region of the Marcus parabola as in fullerene-ferrrocene conjugates,\textsuperscript{62} CR is in 2-methy]tetrahydrofuran with 6.2 ± 3.4 and 8.3 ± 0.9 ns for trans-2-6 and trans-3-6, respectively, much faster than in dichloromethane (vide supra). In stark contrast, no differences between the two solvents are, however, seen for CR due to the close [10]CPP to C60 proximity in the "bound state": 1.75 ± 0.9 ns for trans-2-6 and 1.49 ± 0.3 ns for trans-3-6 (Figures S21 and S22).

**Preliminary Insights into the Role of [10]CPP as Supramolecular Directing Group.** Intrigued by the CPP-directed trans-3 and trans-2 regioselectivity during the final step of the rotaxane synthesis and inspired by recent progress toward regioselectivity using tethered reagents and endohedral fullerenes,\textsuperscript{63} we decided to investigate the generality of this effect with the help of model monomalonate 7. The addition of one equivalent of [10]CPP to 7 led to the corresponding inclusion complex 7C[10]CPP, which served as our starting material for a second addition reaction (Figure 5, top).

![Figure 5](image-url)

**Figure 5.** Model study on the effect of [10]CPP on the regioselectivity of fullerene bis-addition. (a) Reaction sequence for [10]CPP-directed bis-addition and subsequent removal of [10]CPP by addition of excess C60. Reaction conditions: (i) diethyl bromomalonate, DBU, CH3Cl, RT, 10 h, 46%. (b) Reaction outcome in the presence of [10]CPP (red bars) in comparison with published data\textsuperscript{63} in the absence of [10]CPP (black bars). (c) Structures of trans-2-8[10]CPP and trans-3-8[10]CPP, including corresponding substituent angle and binding constant Ks (fit according to 1:1 model). For further details, see Figures S23-S26.

analyzing the reaction outcome by HPLC, we observed the trans-3 bis-adduct (trans-3-8, ca. 24%) as major product and trans-2-8 as side product (ca. 20%), which is similar to the outcome of the rotaxane synthesis and confirms the generality of this effect. In addition to the trans-3 and trans-2 regioisomers, we also observed the trans-1 product, albeit in only ca. 2% yield. Presumably, this isomer was also formed in the rotaxane synthesis, but we failed to isolate trans-1-6 due to the smaller reaction scale. When these results are compared to published reports on the synthesis of 8 in the absence of [10]CPP,\textsuperscript{49} it is striking that the presence of [10]CPP completely suppresses the formation of the trans-4, e, cis-3, and cis-2 regioisomers, which in the absence of [10]CPP account for a total <50% of the product mixture.

Next, we proceeded to test our hypothesis that the altered regioselectivity in the presence of [10]CPP correlates with the ability of [10]CPP to maintain a strong noncovalent interaction once the bis-addition has occurred.\textsuperscript{64} Fluorescence titrations, in which [10]CPP was treated with trans-2-8 and trans-3-8, revealed that the association constant for the trans-2 isomer is approximately 20 times higher than for the trans-3 isomer. This finding explains why the trans-2/trans-3 ratio is higher in the presence of [10]CPP,\textsuperscript{64} and it also explains why...
the trans-1/trans-2 appears to be unchanged because CPP binding in these two products is already almost as strong as in monoadducts. In terms of the aforementioned substitution angles, these results imply that 180° (trans-1) and 144° (trans-2) allow for optimal reaction kinetics, whereas 120° (trans-3) does already lead to a decreased rate in the addition reaction, while 110° (trans-4), 90° (c), and <90° (isomers) seem to inhibit the addition reaction so dramatically that no observable quantities of the corresponding products are formed. The calculated geometries (DFT) of trans-2-6 and trans-3-6 shown in Figure 2e lend support to this reasoning because the [10]CPP ring appears to have a certain degree of freedom by rotation around the vertical axis in the trans-2 isomer, whereas there is not much room for such a rotation in the trans-3 isomer.

■ CONCLUSIONS

We have described the first synthesis of [2]rotaxanes featuring a shape-persistent cycloparaphenylene macrocycle devoid of heteroatoms. Key to the successful synthesis was the use of the strong concave–convex π–π interaction between [10]CPP and a fullereno monoadduct and the ability of the [10]CPP ring to significantly improve the outcome of the stopping reaction, which is reminiscent of Stoddart’s use of a cyclodextrin ring to enhance the rate of CuAAC “click” reactions67/68 or Leigh’s use of macrocyclic ligands in his “active metal template” approach.21/25 However, in the present example, the modulation of reactivity leads to drastically improved regioselectivity rather than reactivity enhancement or component preorganization. These findings may have technological importance because the most effective fullerenes in organic photovoltaics (PC_{71}BM, ICBA, and bis-PCBM)10/70 are employed as regioisomeric mixtures, despite recent evidence for significant differences in the performance between regioisomers.19 To this end, it is worth emphasizing that we developed a simple strategy for the efficient recycling of the costly [10]CPP template.

Our electron transfer studies revealed that the presence of the mechanically interlocked [10]CPP ring does not affect the reduction potential of the central fullerenic bis-adduct, as the observed ~1.21 V (vs Fe/Fe') is precisely what is expected for a fullerenic bis-adduct.21 However, transient absorption spectroscopy suggests that the mechanical bond leads to an interesting situation, where a relatively well-defined “unbound” supramolecular state can be probed experimentally. As one would expect based on the increased distance in the corresponding charge separated state, we found that charge recombination is much slower in the “unbound” state compared to the “bound” state and that the dielectric constant of the solvent strongly affects the kinetics of this recombination process. We anticipate that this apparent ability of the [10]CPP ring to act as a relay of (positive) charge, together with our new template strategy for the synthesis of carbon-rich rotaxanes, may lead to further advances in molecular electronics or machinery.

■ ASSOCIATED CONTENT

B Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b08244.

Synthesis and characterization data; details on mass spectrometry, variable-temperature NMR, transient absorption studies and DFT calculations (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*dirk.guld@fu.de
*max.vondelius@uni-ulm.de

ORCID

Bernd Meyer: 0000-0002-3481-8099
Dirk M. Guld: 0000-0002-3960-1765
Max von Delius: 0000-0003-1852-2969

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from the DFG (SFB953 “Synthetic Carbon Allotropes”, projects A7, B10, C1, and Z1), the University of Ulm, and FAU Erlangen-Nürnberg. Deepening Syngtan is acknowledged for precursor syntheses during a DAAD RISE project. Giorgio Baggi (University of Windsor) is acknowledged for helpful advice regarding NMR line-shape analysis. Dr. Harald Maid is acknowledged for recording ROESY NMR spectra.

■ REFERENCES

(51) These eight possible regioisomeric products are named with respect to the position of the second addend and with respect to the first addend: cis-1, cis-2, cis-3, trans-4, trans-3, cis-2, cis-1.
(53) The statistical difference results from the fact that there is only one trans-1 double bond, while there are four trans-2 double bonds, etc. See also ref. 51.
Supporting Information


Youzhi Xu,¹ Ramandeep Kaur,² Bingzhe Wang,³ Martin B. Minameyer,² Sebastian Gsänger,¹
Bernd Meyer,¹ Thomas Drewello,² Dirk M. Guldi*,² and Max von Delius*,¹

¹Institute of Organic Chemistry and Advanced Materials, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany
²Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials, Friedrich-Alexander University Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany
³Interdisciplinary Center for Molecular Materials (ICM) and Computer-Chemistry-Center (CCC), Friedrich-Alexander University Erlangen-Nürnberg, Nögelsbachstraße 25, 91052 Erlangen, Germany

Email: dirk.guldi@fau.de, max.vondelius@uni-ulm.de
Contents

1. General Experimental Section ................................................................. S3
2. Overview on Synthesis ........................................................................ S5
3. Synthetic Procedures and Characterization Data ................................. S6
   3.1. Synthesis of pentakisadduct 1 ......................................................... S6
   3.2. Synthesis of dibromo-cyclo-[2]-octylmalonate S4 ......................... S7
   3.3. Synthesis of ketone S7 ................................................................. S7
   3.4. Synthesis of S8 ........................................................................ S9
   3.5. Synthesis of S9 ........................................................................ S10
   3.9. Synthesis of 4 ........................................................................ S13
   3.10. Synthesis of pseudorotaxane 5 .................................................... S14
4. Fluorescence Titration and NMR Study on [10]CPP/Fullerene Binding in Pseudorotaxane 5 ... S17
5. Additional Data on Rotaxane Synthesis, Purification and Characterization .................................. S20
6. DFT Calculations ............................................................................. S25
7. MS-MS Study ................................................................................... S27
8. Electron Transfer Studies with the Rotaxane Isomers .......................... S28
10. Fluorescence Titration Study on 8⊂[10]CPP Binding Constant ........... S36
11. NMR Spectra ............................................................................... S38
12. References ..................................................................................... S48
1. General Experimental Section

Reagents and instruments

NMR spectra were recorded on a Bruker DRX 400 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz) or a Bruker AMX 500 (¹H NMR: 500 MHz, ¹³C NMR: 125 MHz) or a Bruker DRX 600 (¹H NMR: 600 MHz, ¹³C NMR: 150 MHz) spectrometer at 298 K and referenced to the residual solvent peak (¹H: 7.26 ppm for CDCl₃, 5.32 ppm for CD₂Cl₂; ¹³C: 77.16 ppm for CDCl₃, 53.84 ppm for CD₂Cl₂). Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. High resolution MALDI mass spectra were obtained on Bruker micro TOF II and Bruker Maxis 4G or Bruker SolariX (HRMS-ESI-TOF, Solvent: toluene or acetonitrile) instruments.

All commercially available reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros Organics or TCI and were used without further purification. Anhydrous THF, anhydrous DMF and n-butyl lithium (1.6 M in n-hexane and 2.5 M in n-hexane) were purchased from Sigma Aldrich. Molecular sieves were dried for 3 days at 150 °C under reduced pressure (10⁻² mbar) before use. Methyl iodide was dried over 5 Å molecular sieves and stored under N₂.

The steady state absorption spectroscopy was conducted in 10×10mm Cuvettes with a Perkin-Elmer Lambda 2 double beam instrument. Steady-State fluorescence spectra were recorded with a Fluoro Max 3 spectrophotometer Horiba Yobin Yvon.

To record the UV/Vis spectra Perkin Elmer Lambda 2 spectrometer was used. The data was collected at room temperature with the software UV WinLab using a slit width of 2nm and a scan rate of 480 nm/min.

Electrochemistry data was collected by performing differential pulse voltammetry at room temperature. Application of potential was controlled with µAutolab III/FRA2 potentiostat from METROHM. To record the current vs. the applied potential voltammograms, NOVA 1.10 software was used. A home-made cell was used to perform the measurements in Ar-saturated dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte in a three-electrode configuration. Glassy carbon was used as working electrode (3 mm diameter), Pt wire acting as the counter electrode, and Ag wire as the quasi-reference electrode. The Fe/Fc⁺ redox couple was used as an internal standard. The chemicals purchased from Acros Organics, Sigma Aldrich, and Alfa Aesar were used without any further treatment or purification.

Time-resolved absorption studies were performed by using the Clark MXR CPA 2101 and CPA2110 Ti:sapphire amplifier (775nm, 1 kHz, 150 fs pulse width) as the laser source. Ultrafast Systems HELIOS femtosecond transient absorption spectrometer was used to acquire time-resolved transient absorption spectra with 150 fs resolution and time delays from 0 to 5500 ps. By focusing a fraction of the fundamental 775 nm onto a 2 mm sapphire disk the probe-visible white light (~400–770 nm) was generated. And, the white light in (near) IR (780–1300 nm) region was generated by using a 1 cm sapphire disk. The excitation wavelength at 640 nm was generated using a non-collinear optical parameter (NOPA,
Clark MXR), which was then frequency doubled using a BBO crystal to obtain 320 nm. A long-pass filter was used to exclude the fundamental 775 nm. The measurements were performed in a 2 mm quartz cuvettes under argon atmosphere.

To measure transient absorption spectra with time delays of ~1 ns to 400 μs, an Ultrafast Systems EOS sub-nanosecond transient absorption spectrometer was employed. A built-in photonic crystal fiber supercontinuum laser source with a fundamental of 1064 nm at 2 kHz output frequency and pulse width of approximately 1 ns was used to generate the white light (~370 to >1600 nm).

Origin 2016 software was used to analyze the recorded data obtained from the pump-probe experiments. The kinetic traces, by picking the wavelengths which correspond to the characteristic absorption features, were fit using the mono- and multi-exponential functions in order to perform the multi-wavelength analysis. In addition to the multiwavelength analysis, global target analysis was also made. It involves usage of the R-package TIMP as well as the graphical user interface GloTarAn which is an open-source software. It is based on an excited state deactivation kinetic model, which helps to obtain the species associated spectra SAS and the population dynamics of the deconvoluted components.

As matrix for the MALDI mass spectra, trans-2-[3-(4-tet-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used. The mass spectrometer was a reflectron time-of-flight instrument (Reflex IV, Bruker) equipped with a nitrogen laser operating at 337 nm. Approximately 2 – 4 μL of the sample solution mixed with DCTB were dropped on a ground steel microtiter target plate (MTP 384, Bruker) and dried under atmosphere before entering the mass spectrometer.
2. Overview on Synthesis

Scheme S1. Reaction conditions: (a) 4-(N,N-Dimethylamino)benzaldehyde, pyridine, trimethylamine, N-chlorosuccinimide, 0 °C→RT, 12h, 40%; (b) diethyl malonate, CBr₃, DBU, toluene, RT, 12 h, 58%; (c) maleic anhydride, toluene, 15 °C, 12h, 76%; (d) S₃, CBr₃, DBU, CH₂Cl₂, RT, 12 h, 90%; (e) Br₂, p-TsOH, CH₂Cl₂, RT, 12h, 70%; (f) 1, DBU, CH₂Cl₂, RT, 10 h, 75%; (g) Co₆, CBr₃, BTTP, toluene, RT, 12 h, 56%; (i) n-BuLi, CH₃I, DMF, THF, -120 °C, 12 h, 62%; (j) n-BuLi, iso propyl pinacol borate, THF, -78 °C, 2 h, 90%; (k) Pd(OAc)₂, S-Phos, K₂PO₄, DMF/H₂O, 90 °C, 12 h; (l) sodium naphthalenide, THF, -78 °C, 2 h, 15% (two steps); (m) [10]CPP, CH₂Cl₂, quant.; (n) 3, BTTP, CH₂Cl₂, -50 °C→RT, 10h, 56%.
3. Synthetic Procedures and Characterization Data

3.1. Synthesis of pentakisadduct 1

\[ \text{C}_{60} \xrightarrow{\text{NCS, Pyridine, Et}_{3} \text{N, ODCB, 0°C}} \text{S1} \]

\[ \text{Diethyl maleate} \xrightarrow{\text{CBr}_{4}, \text{DBU, Toluene, r.t.}} \text{S2} \]

\[ \xrightarrow{400 \text{W Light, Toluene, 10°C}} 1 \]

1 was prepared according to a modified published procedure.\textsuperscript{51,52} Characterization data was consistent with the previous report.

**S1 (Isox-C\textsubscript{60}):** A 100 mL Schlenk flask was charged with 4-(N, N-Dimethylamino)benzaldoxime (0.82 g, 5.0 mmol), pyridine (1.0 mL, 12.5 mmol, 2.5 equiv) and chloroform (50 mL) under N\textsubscript{2} atmosphere. After cooling to 0 °C, N-chlorosuccinimide (0.81 g, 6.0 mmol, 1.2 equiv) was added to the stirred solution. The reaction mixture was stirred at 0 °C for 2 hours. Removal of the solvents under N\textsubscript{2} atmosphere gave a yellow oil. The oil was dissolved in dry 1, 2-dichlorobenzene (oDCB, 80 mL) and C\textsubscript{60}- Fullerene (3.6 g, 5.0 mmol) was added under N\textsubscript{2} atmosphere. Triethylamine (1.4 mL, 10.0 mmol, 1.2 equiv) was added at 0 °C and the reaction mixture was allowed to slowly warm up to room temperature for 12 hours. The crude mixture was directly purified by column chromatography (toluene) to give S1 (1.7 g, 2.0 mmol, 40%) as a dark brown solid.

**S2:** Under exclusion of light, a 250 mL Schlenk flask was charged with S1 (1.47 g, 1.65 mmol, 1 equiv), CBr\textsubscript{4} (10.0 g, 33.0 mmol, 20 equiv), diethyl maleate (1.5 mL, 9.9 mmol, 6 equiv) and anhydrous toluene (100 mL) under N\textsubscript{2} atmosphere. The mixture was stirred for 30 min at room temperature. DBU (2.7 mL, 18.1 mmol, 11 equiv) was diluted with 50 mL dry toluene and added dropwise to the reaction mixture over 30 min. The reaction mixture was stirred at room temperature for 2 days and filtered through a silica gel plug with toluene and ethyl acetate. After removal of the solvents under reduced pressure, the crude product was purified by column chromatography (toluene/ethyl acetate 93:7) to give S2 (1.6 g, 0.96 mmol, 58%) as an orange solid (the less polar adducts can be recycled).

1. A 250 mL Schlenk flask was charged with [5:1]hexakisadduct S2 (550 mg, 0.35 mmol, 1 equiv), maleic anhydride (955 mg, 9.70 mmol, 30 equiv) and dry toluene (200 mL) under N\textsubscript{2} atmosphere. The reaction mixture was irradiated with a halogen flood light (400 W) while the temperature was kept constant at 15 °C in a water bath over 24 h. The mixture was filtered through a silica gel plug with toluene and ethyl acetate. After removal of the solvents under reduced pressure, the crude product was purified by column chromatography (toluene/ethyl acetate 93:7) to give 1 (402 mg, 0.96 mmol, 76%) as a red solid. Spectroscopic data for 1 was in good agreement with literature data.\textsuperscript{53}

\[ ^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)} \delta = 4.49 - 4.36 (m, 16H, OCH}_3\text{), 4.28 (q, J = 7.1 Hz, 4H, OCH}_2\text{), 1.46 - 1.35 (m, 24H, CH}_3\text{), 1.29 (t, J = 7.1 Hz, 6H, CH}_3\text{).} \]
3.2. Synthesis of dibromo-cyclo-[2]-octylmalonate S4

![Chemical structure diagram]

A heat-gun dried 5 L Schlenk flask was charged with 1, 8-octanediol (14.6 g, 100.0 mmol, 1.0 equiv.), pyridine (16.0 mL, 200.0 mmol, 2.0 equiv.) and anhydrous dichloromethane (3 L). The malonyl dichloride (9.4 mL, 100.0 mmol, 1.0 equiv.) was diluted in dry dichloromethane and added to the reaction over 1 day. The reaction mixture was stirred at RT for 2 days. After removal of the solvent under reduced pressure, purification by column chromatography (CH$_2$Cl$_2$/EtOAc 20:1) gave S3 (3.3 g, 15% yield) as colourless solid. Characterization data was consistent with previous reports.$^{33}$

A heat-gun dried 100 mL Schlenk flask was charged with S3 (230 mg, 0.5 mmol, 1.0 equiv) and 50 mL anhydrous CH$_2$Cl$_2$. p-TsOH (228 mg, 1.2 mmol, 2.5 equiv) and Br$_2$ (65 $\mu$L, 1.2 mmol, 2.5 equiv) were added at room temperature. The reaction mixture was stirred for 12 hours, Na$_2$SO$_4$ (10 ml, 1M) was added carefully to quench the reaction, and the resulting mixture was extracted with CH$_2$Cl$_2$ (3 × 20 mL). The combined organic layers were concentrated under reduced pressure and purification by column chromatography (CH$_2$Cl$_2$) gave S4 (205 g, 70% yield) as a colourless solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 4.85 (d, $J = 1.3$ Hz, 2H, CHBr), 4.31 – 4.12 (m, 8H, OCH$_2$), 1.72 – 1.59 (m, 8H), 1.36 – 1.29 (m, 16H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 164.60 (C=O), 67.38 (OCH$_3$), 43.32 (CH), 43.30 (CH$_2$), 29.37 (CH$_2$), 28.55 (CH$_2$), 25.89 (CH$_3$).

HRMS (ESI$^+$) Calcd. for C$_{23}$H$_{24}$NaBr$_2$O$_4$ [M + Na$^+$] 609.0492; Found: 609.0495.

3.3. Synthesis of ketone S7

![Chemical structure diagram]
A 100 mL Schlenk flask was charged with 4-methoxyphenol (6.2 g, 50.0 mmol, 1.0 equiv) and anhydrous MeOH (60 mL) was added under N₂ atmosphere. The resulting solution was cooled to 0°C and iodobenzene diacetate (17.7 g, 55 mmol, 1.1 equiv) was added over 10 minutes. The reaction was allowed to stir at 0 °C for 3 hours and was quenched with saturated aq. NaHCO₃ (100 mL). The organic solvent was removed under reduced pressure and the resulting residue was diluted with CH₂Cl₂ (60 mL). The aqueous layer was extracted with CH₂Cl₂ (2 × 50 mL), and the combined organic layers were dried over Na₂SO₄. Removal of the solvent under reduced pressure afforded a mixture of quinone monoacetal and residual iodobenzene (1:1) as a pale red oil, which was used for the next step without further purification.

A 250 mL dry Schlenk flask was charged with 1,4-diiodobenzene (18.1 g, 55.0 mmol, 1.1 equiv) and 100 mL anhydrous THF. n-Butyllithium in n-hexane (24.0 mL, 2.5 mol/L, 60.0 mmol, 1.2 equiv) was added dropwise at -78 °C over 5 minutes under N₂ atmosphere. The reaction mixture was stirred for 50 minutes, then the crude quinone monoacetal in THF (20 mL) was added at -78 °C and the reaction temperature was slowly raised to -50 °C. MeOH (20 mL) was added to quench the reaction at -50 °C and the mixture was allowed to warm to room temperature. The solvents were removed under reduced pressure, the residue was diluted with acetone (100 mL) and 100 mL 10% aq. AcOH was added slowly. The solution was stirred for 12 hours, NaHCO₃ (50 mL, 1M) was added carefully to quench the reaction. The solvent was removed under reduced pressure before the aqueous layer was extracted with CH₂Cl₂ (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure. Purification by column chromatography (CH₂Cl₂/Et₂O 5:1) afforded ketone S6 (12.4 g, 80% yield) as pale yellow solid. Characterization data was consistent with previous reports.⁵⁴

A solution of ketone S6 (3.0 g, 9.5 mmol, 1.0 equiv) in 30 mL of dry THF was slowly added to a slurry of sodium hydride (450 mg, 11.4 mmol, 60% in mineral oil, 1.2 equiv) in 50 mL of dry THF that was kept at -50 °C. The reaction mixture was stirred for 2 hours while slowly warming from -50 °C to -30 °C. Methyl iodide (0.8 mL, 19.2 mmol, 2.0 equiv) and anhydrous DMF (5 mL) were added to quench the reaction at -50°C and the mixture was allowed to warm up to room temperature overnight. Water (20 mL) was added carefully to quench the methylation reaction, and the resulting mixture was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were concentrated under reduced pressure and purification by column chromatography (cyclohexane/ CH₂Cl₂ 1:2) gave S7 (2.3 g, 72% yield) as pale yellow solid.

¹H NMR (400 MHz, CDCl₃) δ = 7.68 (d, J = 8.6 Hz, 2H), 7.19 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 10.1 Hz, 2H), 6.41 (d, J = 10.1 Hz, 2H), 3.41 (s, 3H, OCH₃).

¹³C NMR (100 MHz, CDCl₃) δ = 185.4 (C=O), 150.1 (CH), 138.3 (C), 138.0 (CH), 130.5 (CH), 127.8 (C), 94.3 (C), 76.4 (C), 53.1 (CH₃).
3.4. Synthesis of S8

S5 was prepared according to a previously reported procedure. Characterization data was consistent with the previous report.

A 100 mL dry Schlenk flask was charged with S5 (1.6 g, 3.0 mmol, 1.0 equiv) and 60 mL anhydrous THF. n-Butyllithium in n-hexane (2.2 mL, 1.6 mol/L, 3.6 mmol, 1.2 equiv.) was added dropwise at -120 °C over 5 minutes under N2 atmosphere. The reaction mixture was stirred for 50 minutes, ketone S7 (1.0 g, 3.3 mmol, 1.1 equiv) was added at -78 °C and the temperature was slowly allowed to increase to -50 °C. Methyl iodide (0.3 mL, 4.5 mmol, 1.5 equiv) and anhydrous DMF (2 mL) were added to quench the reaction at -50 °C and the mixture was allowed to warm up to room temperature overnight. The solvent was removed under reduced pressure and the residue was diluted with CH2Cl2 (20 mL). The aqueous layer was extracted with CH2Cl2 (2 × 20 mL), and the combined organic layers were concentrated under reduced pressure. Purification by column chromatography (cyclohexane/CH2Cl2 1:2) gave S8 (1.4 g, 62% yield) as a colourless solid.

1H NMR (400 MHz, CDCl3) δ = 7.63 (d, J = 8.4 Hz, 4H), 7.33 (s, 4H), 7.12 (d, J = 8.5 Hz, 4H), 6.13 – 6.00 (m, 8H), 3.41 (s, 12H, OCH3).

13C NMR (100 MHz, CDCl3) δ = 143.3 (C), 142.8 (C), 137.5 (CH), 133.8 (CH), 133.1 (CH), 128.2 (CH), 128.2 (CH), 126.2 (CH), 93.5 (C), 74.7 (OCH3), 52.2 (C).

3.5. Synthesis of S9

A 50 mL dry Schlenk flask was charged with S8 (1.5 g, 2.0 mmol, 1.0 equiv) and 20 mL anhydrous THF. n-Butyllithium in n-hexane (2.8 mL, 1.6 mol/L, 4.4 mmol, 2.2 equiv) was added dropwise at −78 °C over 5 minutes under N₂ atmosphere. Isopropyl pinacol borate (1.6 mL, 8.0 mmol, 4.0 equiv) was added immediately, and the solution was stirred for 30 min at −78 °C. The reaction was warmed up to room temperature and water (20 mL) was added to the solution and the mixture was allowed to stir for 10 min before extracting with CH₂Cl₂ (2 × 20 mL). The crude product was washed with cold ethyl acetate to give compound S9 (1.4 g, 90% yield) as a colourless solid. Characterization data was consistent with previous reports.\(^{90}\)

\(^1\)H NMR (400 MHz, 298 K, CDCl₃) \(\delta = 7.75\) (d, \(J = 8.3\) Hz, 4H), 7.40 (d, \(J = 8.1\) Hz, 4H), 7.34 (s, 4H), 6.08 (s, 8H), 3.43 (d, \(J = 3.7\) Hz, 12H, OCH₃), 1.33 (s, 24H, CH₃).

\(^13\)C NMR (100 MHz, 298 K, CDCl₃) \(\delta = 146.58\) (C), 142.84 (C), 135.06 (CH), 133.51 (CH), 133.32 (CH), 126.20 (CH), 125.43 (CH), 83.89 (C), 75.05 (C), 74.77 (C), 52.10 (OCH₃), 25.01 (CH₃).


Under an Argon atmosphere, a 250 mL Schlenk flask was charged with diiodide S8 (758 mg, 1.0 mmol), diboronate S9 (758 mg, 1.0 mmol), Pd(OAc)₂ (20 mg, 0.1 mmol, 0.1 equiv), S-Phos (80 mg, 0.2 mmol,
0.2 equiv), K₂PO₄ (0.8 g, 4.0 mmol, 4 equiv), degassed DMF (100 mL) and degassed water (10 mL). The reaction mixture was stirred at 90 °C for 12 h under Argon. After cooling down to room temperature, the mixture was filtered through a short plug of Al₂O₃, and 100 mL water was added to the filtrate. After extraction with CH₂Cl₂ (3 × 60 mL), the combined organic layers were dried over Na₂SO₄. After removal of the solvent under reduced pressure, the crude mixture was used for the next step without further purification. The [10]macrocyclic crude mixture was dissolved in 60 mL THF under nitrogen and cooled down to –78 °C. At this point, freshly prepared sodium naphthalene (8.0 mL, 8.0 mmol, 1.0 M in THF) was added. The reaction mixture was stirred for 2 hours at –78 °C before MeOH (5 mL) was added and the resulting mixture was warmed up to room temperature. After removal of the solvents under reduced pressure, the crude yellow solid was purified by silica gel column chromatography (CH₂Cl₂/cyclohexane 1:2) to give [10]CPP (114 mg, 15% over two steps) as a yellow solid. Characterization data was consistent with previous reports.⁵⁶

¹H NMR (400 MHz, CDCl₃) δ = 7.56 (s, 40H).

¹³C NMR (100 MHz, CDCl₃) δ = 138.31(C), 127.51(CH).

3.7. Synthesis of [5:1]hexakisadduct 2

A 100 mL Schlenk flask was charged with 1 (206 mg, 0.14 mmol, 1 equiv.), CBr₄ (67 mg, 0.2 mmol, 1.5 equiv), malonate S3 (233 mg, 0.56 mmol, 4 equiv.) and dry CH₂Cl₂ (50 mL) under N₂ atmosphere. DBU (60.0 mL, 0.42 mmol, 3.0 equiv) was diluted with 10 mL dry CH₂Cl₂ and the solution was added dropwise to the reaction mixture over 20 min. The reaction mixture was stirred at room temperature for 12 hours. The crude product was purified by column chromatography (toluene/ethylic acetate 9:1) to give 2 (238 mg, 90%) as a yellow solid (the excess malonate can be recycled).

¹H NMR (400 MHz, CDCl₃) δ = 4.33 (q, J = 7.1 Hz, 20H, OCH₂), 4.24 (t, J = 6.8 Hz, 4H, OCH₂), 4.14 (t, J = 6.6 Hz, 4H, OCH₂), 3.56 (s, 2H, OCCH₂CO), 1.67 (dd, J = 23.2, 7.0 Hz, 8H, CH₂), 1.32 (t, J = 7.1 Hz, 48H).

¹³C NMR (100 MHz, CDCl₃) δ = 166.53 (C=O), 163.91 (C=O), 163.89 (C=O), 163.86 (C=O), 145.88 (C₁₈₆ sp2), 145.85 (C₁₈₆ sp2), 145.79 (C₁₈₆ sp2), 141.17 (C₁₈₆ sp2), 141.11 (C₁₈₆ sp2), 141.10 (C₁₈₆ sp2), 69.16 (OCCOCO), 69.12 (C₁₈₆ sp3), 67.05 (2 OCH₂), 65.63 (2 OCH₂), 62.92 (10 OCH₂), 45.39 (OCCOCO), 45.37 (OCCOCO), 45.34 (OCCOCO), 42.34 (OCCH₂CO), 29.76 (CH₂), 29.49 (CH₂), 28.64 (CH₂), 28.56 (CH₂), 26.03 (CH₂), 14.13 (10 CH₃).
HRMS (MALDI) Calcd. for C_{117}H_{64}O_{28} 1937.518; Found: 1937.511.


A 100 mL Schlenk flask was charged with 1 (71 mg, 0.05 mmol, 1 equiv.), dibromo-cyclo-[2]-octylmalonate S4 (138 mg, 0.25 mmol, 5 equiv.) and dry CH$_2$Cl$_2$ (40 mL) under N$_2$ atmosphere. DBU (9.3 uL, 0.06 mmol, 1.3 equiv) was diluted with 10 mL dry CH$_2$Cl$_2$ and added dropwise to the reaction mixture over 20 min at 0 °C. The mixture was allowed to warm up to room temperature over 10 hours. The crude product was purified by column chromatography (toluene/ethyl acetate 10:1) to give 3 (75 mg, 75%) as a yellow solid (the excess S4 can be recycled).

$^1$H NMR (400 MHz, CDCl$_3$) δ = 4.85 (s, 1H, CHBr), 4.39 – 4.11 (m, 28H, OCH$_3$), 1.68 (m, 8H, CH$_2$), 1.36 – 1.30 (m, 46H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 164.56 (C=O), 163.95 (C=O), 163.91 (C=O), 145.92 (C$_{6a}$ sp2), 145.90 (C$_{6a}$ sp2), 145.86 (C$_{6a}$ sp2), 145.83 (C$_{6a}$ sp2), 141.22 (C$_{6a}$ sp2), 141.17 (C$_{6a}$ sp2), 141.13 (C$_{6a}$ sp2), 69.20 (OCCCO), 69.15 (C$_{6a}$ sp3), 76.41 (2 OCH$_3$), 67.07 (2 OCH$_3$), 62.96 (10 OCH$_3$), 45.44 (OCCCO), 45.42 (OCCCO), 45.38 (OCCCO), 43.39 (OCCBrC), 29.52 (CH$_2$), 29.47 (CH$_2$), 28.60 (CH$_3$), 28.57 (CH$_2$), 26.07 (CH$_2$), 25.95 (CH$_3$), 14.17 (10 CH$_3$).

HRMS (MALDI) Calcd. for C$_{117}$H$_{64}$BrO$_{28}$ 2014.425; Found: 2014.422.
3.9. Synthesis of 4

A 100 mL Schlenk flask was charged with 2 (80 mg, 0.04 mmol, 1 equiv.), C₆₀ (128 mg, 0.16 mmol, 4 equiv.), CBr₄ (30 mg, 0.09 mmol, 2.2 equiv.) and dry toluene (50 mL) under N₂ atmosphere. Subsequently, tert-Butylimino-tri(pyrrolidino)phosphorene (BTTP, 25.0 µL, 0.12 mmol, 3.0 equiv.) was diluted with 10 mL anhydrous toluene and added dropwise to the reaction mixture over 20 min at 0 °C. The mixture was allowed to warm up to room temperature over 12 hours. The crude product was purified by column chromatography (toluene/ethyl acetate 10:1) to give 4 (70 mg, 63%) as a black solid (the excess C₆₀ can be recycled).

¹H NMR (400 MHz, CDCl₃) δ = 4.48 (t, J = 6.8 Hz, 4H, OCH₂), 4.33 (q, J = 7.1 Hz, 20H, OCH₂), 4.27 (t, J = 6.8 Hz, 4H, OCH₂), 1.88 (m, 4H, CH₂), 1.75 (m, 4H, CH₂), 1.56 – 1.38 (m, 16H, CH₂), 1.35 – 1.31 (m, 30H, CH₃).

¹³C NMR (100 MHz, CDCl₃) δ = 163.99 (C=O), 163.96 (C=O), 163.92 (C=O), 163.90 (C=O), 163.74 (C=O), 145.95 (C₆₀ sp²), 145.93 (C₆₀ sp²), 145.92 (C₆₀ sp²), 145.88 (C₆₀ sp²), 145.87 (C₆₀ sp²), 145.84 (C₆₀ sp²), 145.36 (C₆₀ sp²), 145.33 (C₆₀ sp²), 145.30 (C₆₀ sp²), 145.28 (C₆₀ sp²), 144.99 (C₆₀ sp²), 144.79 (C₆₀ sp²), 144.77 (C₆₀ sp²), 144.71 (C₆₀ sp²), 144.00 (C₆₀ sp²), 143.18 (C₆₀ sp²), 143.12 (C₆₀ sp²), 143.09 (C₆₀ sp²), 142.31 (C₆₀ sp²), 142.03 (C₆₀ sp²), 141.23 (C₆₀ sp²), 141.17 (C₆₀ sp²), 141.15 (C₆₀ sp²), 141.05 (C₆₀ sp²), 139.23 (C₆₀ sp²), 71.71 (OCCCCO), 68.23 (OCCCCO), 69.17 (C₆₀ sp³), 69.17 (C₆₀ sp³), 67.59 (2 OCH₂), 67.11 (2 OCH₂), 62.98 (10 OCH₂), 45.45 (OCCCCO), 45.43 (OCCCCO), 45.41 (OCCCCO), 29.66 (CH₂), 28.78 (CH₂), 28.66 (CH₂), 26.23 (CH₂), 26.16 (CH₂), 14.19 (10CH₂).

HRMS (MALDI) Calcd. for C₁₇₇H₁₂₂O₂₃: 2656.506; Found: 2656.503.
3.10. Synthesis of pseudorotaxane 5

A 50 mL round-bottom flask was charged with 4 (60 mg, 0.04 mmol, 1 equiv.) and toluene (50 mL). [10]CPP (30 mg, 0.04 mmol, 1 equiv.) was added and the solvent was removed under reduced pressure, affording 5 as a black solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.51 (s, 40H, [10]CPP), 4.58 (t, J = 6.8 Hz, 4H, OCH$_2$), 4.43 – 4.23 (m, 24H, OCH$_2$), 1.99 (m, 4H, CH$_2$), 1.89 – 1.72 (m, 4H, CH$_2$), 1.69 – 1.59 (m, 4H, CH$_2$), 1.56 – 1.46 (m, 12H, CH$_2$), 1.36 – 1.32 (m, 30H, CH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 163.89 (C=O), 163.86 (C=O), 163.80 (C=O), 163.78 (C=O), 163.54 (C=O), 145.85 (C$_{ax}$ sp$_2$), 145.84 (C$_{eq}$ sp$_2$), 145.83 (C$_{ax}$ sp$_2$), 145.77 (C$_{ax}$ sp$_2$), 145.76 (C$_{ax}$ sp$_2$), 145.73 (C$_{ax}$ sp$_2$), 143.77 (C$_{ax}$ sp$_2$), 143.67 (C$_{ax}$ sp$_2$), 143.57 (C$_{ax}$ sp$_2$), 143.41 (C$_{ax}$ sp$_2$), 143.37 (C$_{ax}$ sp$_2$), 143.33 (C$_{ax}$ sp$_2$), 143.06 (C$_{ax}$ sp$_2$), 142.71 (C$_{ax}$ sp$_2$), 142.20 (C$_{ax}$ sp$_2$), 141.42 (C$_{ax}$ sp$_2$), 141.19 (C$_{ax}$ sp$_2$), 141.14 (C$_{ax}$ sp$_2$), 141.07 (C$_{ax}$ sp$_2$), 141.05 (C$_{ax}$ sp$_2$), 140.81 (C$_{ax}$ sp$_2$), 140.23 (C$_{ax}$ sp$_2$), 139.52 (C$_{ax}$ sp$_2$), 137.97 (C$_{ax}$ sp$_2$), 137.68 (C), [10]CPP), 127.35 (CH, [10]CPP), 76.24 (OCCCO), 70.43 (OCCCO), 69.14 (C$_{ax}$ sp$_3$), 69.07 (C$_{eq}$ sp$_3$), 67.24 (2 OCH$_2$), 66.99 (2 OCH$_2$), 62.85 (10 OCH$_2$), 45.37 (OCCCO), 45.36 (OCCCO), 45.34 (OCCCO), 45.33 (OCCCO), 29.68 (CH$_2$), 29.63 (CH$_2$), 29.58 (CH$_2$), 28.86 (CH$_2$), 28.57 (CH$_2$), 26.23 (CH$_2$), 26.09 (CH$_2$), 14.05 (CH$_2$).

HRMS (MALDI) Calcd. for C$_{339}$H$_{122}$O$_{28}$: 3417.822; Found: 3417.807.

A 50 mL Schlenk flask was charged with 5 (40 mg, 0.02 mmol, 1 equiv.), 3 (80 mg, 0.04 mmol, 2.0 equiv.), and anhydrous CH₂Cl₂ (20 mL) under N₂ atmosphere. Subsequently, BTTP (13 μL, 0.06 mmol, 3.0 equiv.) was added at -50 °C and the mixture was allowed to warm to room temperature over 10 hours. The crude product was purified by HPLC (Cosmosil Buckyprep D) (toluene/ethyl acetate 20:1) to give the two rotaxane regioisomers as a black solids (trans-3-6: 28 mg, 26%; trans-2-6: 10 mg, 10%; combined yield: 36%).

trans-3-6

¹H NMR (500 MHz, CDCl₃) δ = 7.43 (s, 40H, [10](CPP), 4.65 – 4.44 (m, 8H, OCH₂), 4.40 – 4.26 (m, 8H, OCH₂), 2.03 – 1.93 (m, 8H, CH₂), 1.86 – 1.73 (m, 8H, CH₂), 1.68 – 1.61 (m, 8H, CH₂), 1.52 – 1.47(m, 16H, CH₂), 1.38 – 1.25(m, 68H).

¹³C NMR (125 MHz, CDCl₃) δ = 164.06 (C=O), 164.03 (C=O), 164.02 (C=O), 163.97 (C=O), 163.58 (C=O), 146.11 (C₆H₅ sp₂), 144.94 (C₆H₅ sp₂), 144.70 (C₆H₅ sp₂), 144.64 (C₆H₅ sp₂), 145.16 (C₆H₅ sp₂), 145.52 (C₆H₅ sp₂), 145.26 (C₆H₅ sp₂), 143.76 (C₆H₅ sp₂), 144.68 (C₆H₅ sp₂), 144.60 (C₆H₅ sp₂), 144.54 (C₆H₅ sp₂), 144.44 (C₆H₅ sp₂), 144.06 (C₆H₅ sp₂), 143.88 (C₆H₅ sp₂), 143.33 (C₆H₅ sp₂), 143.18 (C₆H₅ sp₂), 142.64 (C₆H₅ sp₂), 142.46 (C₆H₅ sp₂), 142.32 (C₆H₅ sp₂), 141.87 (C₆H₅ sp₂), 141.78 (C₆H₅ sp₂), 141.74 (C₆H₅ sp₂), 141.49 (C₆H₅ sp₂), 141.45 (C₆H₅ sp₂), 141.32 (C₆H₅ sp₂), 141.25 (C₆H₅ sp₂), 141.23 (C₆H₅ sp₂), 141.02 (C₆H₅ sp₂), 140.12 (C₆H₅ sp₂), 139.92 (C₆H₅ sp₂), 138.58 (C₆H₅ sp₂), 138.01 (C₆H₅ sp₂), 137.67 (C₆H₅ sp₂), 137.65 (C₆H₅ sp₂), 127.62 (CH, [10](CPP), 70.64 (OCCCO), 70.13 (OCCCO), 69.32 (OCCCO), 69.26 (C₆H₅ sp₂), 67.37 (OCH₂), 67.27 (OCH₂), 67.17 (OCH₂), 63.01 (20 OCH₂), 45.56 (OCCCO), 45.54 (OCCCO), 45.53 (OCCCO), 29.82 (CH₂), 29.79 (CH₂), 29.77 (CH₂), 29.09 (CH₂), 29.03 (CH₂), 28.76 (CH₂), 26.43 (CH₂), 26.39 (CH₂), 26.27 (CH₂), 14.23 (CH₃).

trans-2-6

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 7.44 (s, 40H, [10]CPP), 4.72 – 4.63 (m, 4H, OCH$_2$), 4.62 – 4.53 (m, 4H, OCH$_2$), 4.34 (q, $J = 6.5$ Hz, 48H, OCH$_2$), 2.09 – 1.95 (m, 8H, CH$_2$), 1.87 – 1.75 (m, 8H, CH$_2$), 1.73 – 1.62 (m, 8H, CH$_2$), 1.40 – 1.27 (m, 74H).

Note: due to the lower isolated amount of this regioisomer, a $^{13}$C NMR spectrum with good signal-to-noise could not be obtained. The $^1$H NMR, UV-Vis (trans-2l), HRMS and MS/MS (rotaxane!) data is however fully consistent with our structural assignment.

HRMS (MALDI) Calcd. for C$_{54}$H$_{26}$O$_{36}$ 5352.321; Found: 5352.507.


![Synthesis diagram](image)

A 100 mL Schlenk flask was charged with C$_{60}$ (150 mg, 0.2 mmol, 1 equiv.), diethyl malonate (45 uL, 0.24 mmol, 1.2 equiv.) and anhydrous toluene (40 mL) under N$_2$ atmosphere. DBU (600 uL, 0.4 mmol, 2.0 equiv) was added dropwise to the reaction mixture over 30 min. The reaction mixture was stirred at room temperature for 6 hours. The crude product was purified by column chromatography (toluene/petrol ether 1:1) to give 7 (79 mg, 45%) as a black solid. 7 (26 mg, 0.03 mmol, 1 equiv.) was dissolved in 20 mL CH$_2$Cl$_2$, 10[CPP] (23 mg, 0.03 mmol, 1 equiv.) was added affording complex 7c[10]CPP.

$^1$H NMR (400 MHz, CDCl$_3$/CS$_2$ 3:1) $\delta$ = 7.51 (s, 40H), 4.66 (q, $J = 7.1$ Hz, 4H), 1.62 (t, $J = 7.1$ Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$/CS$_2$ 3:1) $\delta$ = 163.47 (C=O), 143.87 (C$_{60}$ sp$^2$), 143.77 (C$_{60}$ sp$^2$), 143.65 (C$_{60}$ sp$^2$), 143.50 (C$_{60}$ sp$^2$), 143.39 (C$_{60}$ sp$^2$), 143.15 (C$_{60}$ sp$^2$), 142.28 (C$_{60}$ sp$^2$), 141.51 (C$_{60}$ sp$^2$), 141.28 (C$_{60}$ sp$^2$), 141.20 (C$_{60}$ sp$^2$), 140.91 (C$_{60}$ sp$^2$), 140.30 (C$_{60}$ sp$^2$), 139.64 (C$_{60}$ sp$^2$), 137.98 (C$_{60}$ sp$^2$), 137.80 (C, [10]CPP), 127.48 (CH, [10]CPP), 74.82 (OCCCO), 70.50 (C$_{60}$ sp$^3$), 63.19 (OCH$_3$), 14.56 (CH$_3$).

HRMS (MALDI) Calcd. for C$_{127}$H$_{56}$O$_4$ 1639.3743; Found: 1639.3729.
4. Fluorescence Titration and NMR Study on [10]CPP/Fullerene Binding in Pseudorotaxane 5

Fluorescence quenching was observed when 4 was added to [10]CPP in highly dilute toluene solution. To a solution of [10]CPP in toluene (7.2 × 10^{-7} M) was added a solution of 4 (6.5 × 10^{-6} M, prepared with [10]CPP solution at 7.2 × 10^{-7} M to keep [10]CPP concentration constant) at 25 °C. The changes in the fluorescent intensity of [10]CPP were measured at 466 nm.

Figure S1. (a) Fluorescence spectra and fluorescence titration of [10]CPP in the presence of 4 (0.0–2.5 × 10^{-6} M) in toluene, (b) Data fit in HypSpec Program according to a 1:1, 2:1 and 1:2 model (residuals are significantly lower than with only 1:1, 1:1/2:1 or 1:1/1.2 models (see Figure S2).
Figure S2. Fluorescence quenching experiment data fit in HypSpec Program. (a) According to a 1:1 model, (b) according to a 1:1 and 2:1 model, (c) according to a 1:1 and 1:2 model. All of the fitting deviation values are much higher than 1:1, 2:1 and 1:2 model.

Figure S3. Simulation of 1:2 (left) and 2:1 (right) binding isotherms at concentration of [2]rotaxane synthesis (c = M).
Complexation/decomplexation activation parameters were calculated from a line shape analysis of the VT-NMR spectra using the program Topspin 3.5 pl7. Free energies of activation ($\Delta G^2$) were estimated using the Eyring equation. $R$ is the ideal gas constant, $h$ is Plank’s constant and $k_b$ is Boltzmann’s constant. The enthalpic ($\Delta H^2$) and entropic ($\Delta S^2$) contributions to the transition state were calculated from Eyring plots. Errors associated $\Delta H^2$ and $\Delta S^2$ were elucidated from the standard deviations of the slopes and intercepts of each respective Eyring plot.

![Figure S4. Eyring plot: $\Delta G^2 = -RT[\ln(k/T) + \ln(h/k_B)]$, $\ln(k/T) = -\Delta H^2/RT + [\Delta S^2/R - \ln(h/k_B)]$. Plot of $\ln(k/T)$ versus $1/T$ is a straight line for which $\Delta H^2 = -(slope)R$ and $\Delta S^2 = [intercept + \ln(h/k_B)]R$.](image)
5. Additional data on rotaxane synthesis, purification and characterization

Figure S5. $^1$H NMR spectra (400 MHz, 298 K, CDCl$_3$) of crude products of rotaxane formation under three different conditions. (a) 2 (1 equiv.) reacted with 5 (1 equiv.) and CBr$_5$, affording many kinds of [10]CPP products, including trans-2-6, trans-3-6, but also CBr$_2$ addition to the central fullerene. (b) 3 (1 equiv.) reacted with 5 (1 equiv.) affording trans-2-6, trans-3-6 (16%) and pseudorotaxane, (c) 3 (2 equiv.) reacted with 5 (1 equiv.) affording trans-2-6, trans-3-6 (40%) and some free [10]CPP.

Figure S6. $^1$H NMR (500 MHz, 298 K, CDCl$_3$) spectra of purified trans-2-6 and trans-3-6 rotaxanes. For precise integrals, see the individual NMR spectra in section 11.
## Table S1. $^{13}$C NMR analysis of trans-3-6 central fullerene in comparison with other fullerene bisadducts

<table>
<thead>
<tr>
<th></th>
<th>trans-3-6 (125 MHz)</th>
<th>trans-3 (63 MHz ref$^{27}$)</th>
<th>trans-1 (100 MHz ref$^{39}$)</th>
<th>e (100 MHz ref$^{37}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(137.65, 137.67)</td>
<td>137.57</td>
<td>139.17</td>
<td>137.91</td>
</tr>
<tr>
<td>2</td>
<td>138.58</td>
<td>138.12</td>
<td>141.23</td>
<td>138.80</td>
</tr>
<tr>
<td>3</td>
<td>139.92</td>
<td>140.58</td>
<td>143.48</td>
<td>140.92</td>
</tr>
<tr>
<td>4</td>
<td>140.12</td>
<td>141.26</td>
<td>143.61</td>
<td>141.22</td>
</tr>
<tr>
<td>5</td>
<td>141.02</td>
<td>141.50</td>
<td>143.66</td>
<td>141.45</td>
</tr>
<tr>
<td>6</td>
<td>141.45</td>
<td>141.58</td>
<td>144.84</td>
<td>141.56</td>
</tr>
<tr>
<td>7</td>
<td>141.49</td>
<td>141.83</td>
<td>145.25</td>
<td>141.93</td>
</tr>
<tr>
<td>8</td>
<td>141.74</td>
<td>142.42</td>
<td></td>
<td>142.79</td>
</tr>
<tr>
<td>9</td>
<td>141.78</td>
<td>143.13</td>
<td></td>
<td>143.24</td>
</tr>
<tr>
<td>10</td>
<td>141.81</td>
<td>143.32</td>
<td></td>
<td>143.53</td>
</tr>
<tr>
<td>11</td>
<td>142.32</td>
<td>143.46</td>
<td></td>
<td>143.92</td>
</tr>
<tr>
<td>12</td>
<td>142.46</td>
<td>143.79</td>
<td></td>
<td>144.14</td>
</tr>
<tr>
<td>13</td>
<td>142.64</td>
<td>143.99</td>
<td></td>
<td>144.25</td>
</tr>
<tr>
<td>14</td>
<td>143.18</td>
<td>144.10</td>
<td></td>
<td>144.45</td>
</tr>
<tr>
<td>15</td>
<td>143.39</td>
<td>144.31</td>
<td></td>
<td>144.51</td>
</tr>
<tr>
<td>16</td>
<td>143.88</td>
<td>144.49</td>
<td></td>
<td>144.61</td>
</tr>
<tr>
<td>17</td>
<td>144.06</td>
<td>145.26</td>
<td></td>
<td>144.72</td>
</tr>
<tr>
<td>18</td>
<td>144.44</td>
<td>145.32</td>
<td></td>
<td>145.11</td>
</tr>
<tr>
<td>19</td>
<td>144.51</td>
<td>146.17</td>
<td></td>
<td>145.31</td>
</tr>
<tr>
<td>20</td>
<td>144.60</td>
<td>146.46</td>
<td></td>
<td>146.06</td>
</tr>
<tr>
<td>21</td>
<td>144.68</td>
<td>147.45</td>
<td></td>
<td>146.13</td>
</tr>
<tr>
<td>22</td>
<td>144.76</td>
<td>148.55</td>
<td></td>
<td>146.18</td>
</tr>
<tr>
<td>23</td>
<td>145.26</td>
<td>148.99</td>
<td></td>
<td>146.33</td>
</tr>
<tr>
<td>24</td>
<td>145.54</td>
<td>149.25</td>
<td></td>
<td>146.77</td>
</tr>
<tr>
<td>25</td>
<td>145.64</td>
<td>149.65</td>
<td></td>
<td>147.03</td>
</tr>
<tr>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td>147.32</td>
</tr>
<tr>
<td>27</td>
<td></td>
<td></td>
<td></td>
<td>147.54</td>
</tr>
<tr>
<td>28</td>
<td></td>
<td></td>
<td></td>
<td>150.53</td>
</tr>
</tbody>
</table>

Note: according to literature, the “fingerprint” part of the UV-Vis spectrum is indicative of either the trans-1, trans-3 or e regioisomer$^{37}$ but each regioisomer has different numbers of sp2 carbon signals. Hence, from the UV-Vis spectrum and $^{13}$C NMR results, we can confirm the main rotaxane is the trans-3 regioisomer. The structure of the trans-2 regioisomer was assigned based on its unique UV-Vis spectrum (see also Figure S24).
Figure S7. Variable-temperature $^1$H-NMR (500 MHz, CDCl$_3$) partial spectra of 5 (top) and trans-3-6 (bottom).
Figure S8. (a) $^1$H-NMR of *trans*-3-6 (600 MHz, 298 K, CDCl$_3$). (b) 1D-NOE experiment of *trans*-3-6 with selective excitation of the [10]CPP protons (7.4 ppm). (c) 1D-NOE experiment of *trans*-3-6 with selective excitation of the ethoxycarbonyl protons (4.3 ppm). Experimental details: All NOE experiments were performed in a Bruker 600 MHz spectrometer in CDCl$_3$ at 298 K. Selective excitation was done with an RSNOB of 80 Hz and the spins were allowed to mix for 0.2 s. The SPFGSENKO pulse sequence was used in the rotating frame (pulprog selrogp). The sample was not degassed.

**Conclusion:** there are clear NOE interactions between the [10]CPP ring and the aliphatic protons of the cyclic bismalonate spacer (those in vicinity of the central fullerene), but no NOE interactions between the [10]CPP ring and the ethoxycarbonyl protons (addends on the stopper fullerenes). This indicates that there is likely some degree of translational motion of [10]CPP near the central fullerene, but that [10]CPP does NOT occupy a position on the thread near the stoppers for a significant amount of time (i.e. there is no local thermodynamic minimum for [10]CPP near the stoppers).
Figure S9. $^{13}$C NMR analysis of purified *trans*-3-6 rotaxane.
6. DFT Calculations

Relaxed geometries were obtained from density-functional theory (DFT) calculations. These were carried out with the plane-wave code PWscf of the Quantum Espresso software package,\textsuperscript{810} using the PBE exchange-correlation functional.\textsuperscript{811} Grimme D3 dispersion corrections with Becke-Johnson damping\textsuperscript{812,813} and Vanderbilt ultrasoft pseudopotentials\textsuperscript{814} with a plane-wave kinetic energy cutoff of 30 Ry.

Figure S10. Calculated angle between addends in (a) trans-2, (b) trans-3, and (c) trans-4 fullerene bisadducts. Carbon, oxygen and hydrogen atoms are depicted in grey, red and white, respectively.
Figure S11. Two side views of (a, b) \textit{trans}-2-6 and (c, d) \textit{trans}-3-6. Carbon and oxygen atoms are depicted in grey and light red, with \{10\}CPP highlighted in dark red.
7. MS-MS Study

Figure S12. The MS/MS spectrum of the rotaxane trans-3-6 radical cation with an enlarged m/z-range compared to Figure 3g. Apart from the malonate ligand losses, further fragment ions can be assigned. For example, the signal at m/z 3840.0 indicates the loss of one neutral fullerene, which has five ligands attached, resulting in a pseudorotaxane-like fragment ion with the [10]CPP still located around the thread. Furthermore, two more signals are discernible at m/z 3237.3 and 3080.3. These signals are losses of the TetraC_{60} and PentaC_{60}, respectively, accompanied by the loss of [10]CPP, demonstrating that the nanoring can only be removed from the thread, if one of the stopper fullerenes has been eliminated.

Figure S13. MALDI ToF mass spectrum of the trans-2 rotaxane (top), displaying the radical cation of the rotaxane trans-2-6 and the radical cation of the [10]CPP. MS/MS spectrum of the rotaxane trans-2-6 radical cation (bottom), showing the identical fragmentation behavior as trans-3-6^{**} in Figure 3g.
8. Electron Transfer Studies with the Rotaxane Isomers

Figure S14. Ground state properties: Absorption spectra of pseudorotaxane 5 (black), trans-2-6 (red), trans-3-6 (blue), and [10]CPP (green) in dichloromethane recorded under ambient conditions.

Figure S15. Differential pulse voltammograms: a, Oxidation potential of pseudo rotaxane 5 (black), trans-2-6 (red), and trans-3-6 (blue). b, Reduction potentials of pseudo rotaxane 5 (black), trans-2-6 (red), and trans-3-6 (blue). Both a, and b were recorded at a scan rate of 0.05 V/sec by differential pulse voltammetry in argon-saturated dichloromethane with 0.1 M NBu4PF6 as the supporting electrolyte, Ag/Ag+ as a reference electrode, Pt as a counter electrode, glassy carbon as the working electrode, and Fe/Fe2+ redox couple as an internal standard.
Figure S16. Absorption features of oxidized [10]CPP: Differential absorption spectrum of electrochemically oxidized [10]CPP (green) recorded in argon-saturated dichloromethane with NBut₄PF₆ as supporting electrolyte, Ag/Ag⁺ as reference electrode, Pt as counter electrode, and Pt mesh as working electrode at an applied voltage of +1.2 V.

Figure S17. Kinetic model: Energy level diagram of trans-2-6 / trans-3-6 in dichloromethane and 2-methyltetrahydrofuran. CS: charge separation, CR: charge recombination, and GSR: ground state recovery.
Figure S18. Time-absorption profiles of \textit{trans}-2-6: Exponential fits of the time-absorption profiles of the characteristic absorption fingerprints of the [10]CPP cation at 520 nm (black), and \textit{C}_{60} radical anion at 1045 nm (red) of \textit{trans}-2-6 obtained by femtosecond pump-probe experiments ($\lambda_{exc} = 320$ nm, 140 nJ).

Figure S19. Time-absorption profiles of \textit{trans}-3-6: Exponential fits of the time-absorption profiles of the characteristic absorption fingerprints of the [10]CPP cation, at 520 nm (black), and \textit{C}_{60} radical anion at 1045 nm (red) of \textit{trans}-3-6 obtained by femtosecond pump-probe experiments ($\lambda_{exc} = 320$ nm, 140 nJ).
Figure S20. Electron transfer dynamics in trans-3-6: a, Differential absorption spectra obtained by fs-TAS pump-probe experiments ($\lambda_{exc} = 320$ nm, 140 nJ) of trans-3-6 in dichloromethane with several time delays between 1 to 5500 ps. b, Deconvoluted species associated spectra (SAS) in dichloromethane with bound $^1$([10]CPP$\supseteq$C$_{60}$) (SAS1 – black), unbound $^1$([10]CPP$\supseteq$C$_{60}$) (SAS2 – red), bound [10]CPP$^\supseteq$C$_{60}^-$ (SAS3 – blue), unbound [10]CPP$^\supseteq$C$_{60}^-$ (SAS4 – green) and $^3$([10]CPP) & $^3$(C$_{60}$) (SAS5 – pink) obtained via target analysis in GloTarAn. c, Population dynamics of SAS1, SAS2, SAS3, SAS4 and SAS5. d, Differential absorption spectra obtained by ns-TAS pump-probe experiments ($\lambda_{exc} = 320$ nm, 140 nJ) of trans-3-6 in dichloromethane with several time delays between 0.001 and 10 µs. e, Deconvoluted species associated spectra (SAS) in dichloromethane with bound [10]CPP$^\supseteq$C$_{60}^-$ (SAS3 – blue), unbound [10]CPP$^\supseteq$C$_{60}^-$ (SAS4 – green), and $^3$([10]CPP) & $^3$(C$_{60}$) (SAS5 – pink) obtained via target analysis in GloTarAn. f, Population dynamics of SAS3, SAS4, and SAS5.
Figure S21. Electron transfer dynamics in trans-2-6: a, Differential absorption spectra obtained by fs-TAS pump-probe experiments ($\lambda_{exc} = 320$ nm, $140$ nJ) of trans-2-6 in 2-methyltetrahydrofuran with several time delays between 1 to $5500$ ps. b, Deconvoluted species associated spectra (SAS) in 2-methyltetrahydrofuran with bound $^1$([10]CPP$\supset$C$_6$O) (SAS1 – black), unbound $^1$([10]CPP$\supset$C$_6$O) (SAS2 – red), bound [10]CPP$^{+}$$\supset$C$_6$O$^{-}$ (SAS3 – blue), unbound [10]CPP$^{+}$$\supset$C$_6$O$^{-}$ (SAS4 – green) and $^3$([10]CPP) & $^3$(C$_6$O) (SAS5 – pink) obtained via target analysis in GloTarAn. c, Population dynamics of SAS1, SAS2, SAS3, SAS4, and SAS5. d, Differential absorption spectra obtained by ns-TAS pump-probe experiments ($\lambda_{exc} = 320$ nm, $140$ nJ) of trans-2-6 in 2-methyltetrahydrofuran with several time delays between 0.001 and 10 ps. e, Deconvoluted species associated spectra (SAS) in 2-methyltetrahydrofuran with bound [10]CPP$^{+}$$\supset$C$_6$O$^{-}$ (SAS3 – blue), unbound [10]CPP$^{+}$$\supset$C$_6$O$^{-}$ (SAS4 – green), and $^3$(([10]CPP) & $^3$(C$_6$O) (SAS5 – pink) obtained via target analysis in GloTarAn. f, Population dynamics of SAS3, SAS4, and SAS5.
Figure S22. Electron transfer dynamics in trans-3-6: a, Differential absorption spectra obtained by fs-TAS pump-probe experiments ($\lambda_{exc} = 320$ nm, 140 nJ) of trans-3-6 in 2-methyltetrahydrofuran with several time delays between 1 to 5500 ps. b, Deconvoluted species associated spectra (SAS) in 2-methyltetrahydrofuran with bound $^{1^*}$(10)CPP$\rightleftharpoons$C$_{60}$ (SAS1 – black), unbound $^{1^*}$(10)CPP$\rightleftharpoons$C$_{60}$ (SAS2 – red), bound [10]CPP$\rightleftharpoons$C$_{60}$ (SAS3 – blue), unbound [10]CPP$\rightleftharpoons$C$_{60}$ (SAS4 – green) and $^{3^*}$(10)CPP & $^{3^*}$(C$_{60}$) (SAS5 – pink) obtained via target analysis in GloTarAn. c, Population dynamics of SAS1, SAS2, SAS3, SAS4, and SAS5. d, Differential absorption spectra obtained by ns-TAS pump-probe experiments ($\lambda_{exc} = 320$ nm, 140 nJ) of trans-3-6 in 2-methyltetrahydrofuran with several time delays between 0.001 and 10 µs. e, Deconvoluted species associated spectra (SAS) in 2-methyltetrahydrofuran with bound [10]CPP$\rightleftharpoons$C$_{60}$ (SAS3 – blue), unbound [10]CPP$\rightleftharpoons$C$_{60}$ (SAS4 – green), and $^{3^*}$(10)CPP & $^{3^*}$(C$_{60}$) (SAS5 – pink) obtained via target analysis in GloTarAn. f, Population dynamics of SAS3, SAS4, and SAS5.
9. Regiochemistry of Twofold Additions to [6,6] Bonds in 7\textsubscript{c}[10]CPP

A 50 mL Schlenk flask was charged with 7\textsubscript{c}[10]CPP (60 mg, 36.0 umol, 1 equiv.), diethyl bromomalonate (8.8 µL, 72.0 umol, 2.0 equiv.) and dry CH\textsubscript{2}Cl\textsubscript{2} (20 mL) under N\textsubscript{2} atmosphere. Subsequently, DBU (10.8 µL, 72.0 umol, 2.0 equiv) was diluted with 5 mL dry toluene and dropwisely to reaction over 10 min. The reaction mixture was stirred at room temperature for 10 hours. After removal of the solvent under reduced pressure, the crude products were purified by preparative TLC (toluene) to collect all fullerene bisadducts (32 mg, 46%). One part 8\textsubscript{c}[10]CPP bisadduct mixtures were added 7 to remove [10]CPP, then analyzed by HPLC (normal phase column) and UV-vis spectra. Another part 8\textsubscript{c}[10]CPP bisadduct mixtures were purified by preparative TLC (toluene/petrol ether 20:1) again, then analyzed by UV-vis spectra.

Figure S23. (a) The HPLC analysis after fullerene bisadducts remove [10]CPP, trans-1 (3.5%), trans-2 (44%) and trans-3 (52%), others less than 0.5%. (b) HRMS-MALDI of fullerene bisadduct mixture.
Figure S24. UV-vis spectra of fullerene bisadducts before (top) and after (bottom) removal of [10]CPP.$^{315}$
10. Fluorescence Titration Study on 8⊂[10]CPP Binding Constant

Fluorescence quenching experiment by the addition of 8 to [10]CPP. Binding constant $K_a$ in toluene. To a solution of [10]CPP in toluene ($6.0 \times 10^{-6} \text{ M}$) was added fullerene bisadducts ($trans$-2-8 is $1.35 \times 10^{-5} \text{ M}$, $trans$-3-8 is $2.7 \times 10^{-5} \text{ M}$, prepared with [10]CPP solution) in toluene at 25 °C. The changes in the fluorescent intensity of [10]CPP at 466 nm were measured. The $K_a$ were determined by using HypSpec Program.

Figure S25. (a) Fluorescence spectra and fluorescence titration of [10]CPP in the presence of $trans$-2-8 ($0.0$–$1.1 \times 10^{-5} \text{ M}$) in toluene, (b) Fluorescence quenching experiment data fit in HypSpec Program according to a 1:1 model.
Figure S26. (a) Fluorescence spectra and fluorescence titration of [10]CPP in the presence of trans-3-8 (0.0–2.6 × 10^3 M) in toluene, (c) Fluorescence quenching experiment data fit in HypSpec Program according to a 1:1 model.
11. NMR Spectra

\[ \text{^1H NMR (400 MHz, 298 K, CDCl}_3\text{)} \text{ of S4} \]

\[ \text{^13C NMR (100 MHz, 298 K, CDCl}_3\text{)} \text{ of S4} \]
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S7

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S7
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S8

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S8
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of 2
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 3

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of 3
$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of 4
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 5

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of 5
$^1$H NMR (500 MHz, 298 K, CDCl$_3$) of trans-3-6

$^{13}$C NMR (125 MHz, 298 K, CDCl$_3$) of trans-3-6
$^1$H NMR (400 MHz, 298 K, CDCl$_3$/CS$_2$ 3:1) of 7c-[10]CPP
$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$/CS$_2$ 3:1) of 7C[10]CPP
12. References

S8) http://supramolecular.org/

Youzhi Xu, Bingzhe Wang, Ramandeep Kaur, Martin B. Minameyer, Michael Bothe, Thomas Drewello, Dirk M. Guldi,* and Max von Delius*


Reproduced with permission of Wiley-VCH, copyright (2019).

Abstract:

In this publication, we report efficient photoinduced electron transfer across a [10]CPP moiety that serves as a modular, yet rigid, non-covalent bridge between a zinc porphyrin and a diverse range of fullerenes. The first preparation of iodo-[10]CPP is the cornerstone of our synthesis of a porphyrin-[10]CPP conjugate, which was found to bind C_{60}, C_{70}, (C_{60})_{2} and other fullerenes with association constants beyond 10^5 M^{-1}. Fluorescence and pump-probe spectroscopy revealed intramolecular energy transfer between CPP and porphyrin, as well as efficient charge separation between porphyrin and fullerenes, affording up to 0.5 µs lived charge-separated states. The advantage of our modular approach towards electron donor-acceptor dyads is particularly evident in the case of dumbbell-shaped (C_{60})_{2}, which gave rise to intricate charge transfer behaviour in unusual 1:1 and 2:1 complexes. In a broader context, our results suggest that [10]CPP and its cross-coupled derivatives could act as supramolecular mediators of charge transport in organic electronic devices.

Comments on own contributions:

This project took almost one and half years from the first synthesis to manuscript submission. I contributed the original idea, which Profs. Max von Delius and Dirk Guldi took up enthusiastically. 90% of synthesis experiments experiments were carried out by myself, which includes the labor-intensive synthesis of main building
blocks iodo-[10]CPP, porphyrin moiety and fullerene dimer $C_{120}$, the preliminary supramolecular chemistry study and all binding constant data fitting of porphyrin-[10]CPP dyad, the optimization of synthetic approaches, purification and characterization of all synthetic products. All the NMR measurements, computer calaculations, UV-vis absorption and fluorescence spectra were carried out by myself. The optoelectronic properties were carried by Bingzhe and Ramandeep. Furthermore, I participated in the manuscript preparation and wrote the supporting information.

Youzhi Xu*, Bingzhe Wang†, Ramandeep Kaur, Marini B. Minameyer, Michael Bothe, Thomas Drewello, Dirk M. Guldi,* and Max von Delius*

Abstract: Efficient photoinduced electron transfer was observed across a [10]cyclophaneperylenyl ([10]CPP) moiety that serves as a rigid non-covalent bridge between a zinc porphyrin and a range of fullerenes. The preparation of iodo-[10]CPP is the key to the synthesis of a porphyrin–[10]CPP conjugate, which binds C60, C60(C60)2, and other fullerenes (Kθ > 107 M−1). Fluorescence and pump-probe spectroscopy revealed intramolecular energy transfer between CPP and porphyrin and also efficient charge separation between porphyrin and fullerenes, affording up to 0.3 ns lifetime charge-separated states. The advantage of this approach towards electron donor–acceptor dyads is evident in the case of dumbbell-shaped (C60)2, which gave intricate charge-transfer behavior in 1:1 and 2:1 complexes. These results suggest that [10]CPP and its cross-coupled derivatives could act as supramolecular mediators of charge transport in organic electronic devices.

Following the first synthesis of a cyclophaneperylenyl (CPP) in 2008,[1] this compound class has been developed[2] and diversified[3] at a remarkable pace. Recently, even the synthesis of an elusive nanobelt was achieved,[4] indicating that strained aromatic macrocycles can now be prepared that were previously considered beyond the reach of organic synthesis. Recent work on the gas-phase identification of CPP catechines and the observation of Russian doll CPP–CPP complexes suggests that nanobelt offers rich opportunities in supramolecular chemistry.[5] [10]CPP is arguably the most interesting family member in this respect, because it has been shown to exhibit the perfect ring size for a strong concave–convex π-π interaction with C60[6] which raises the intriguing question whether [10]CPP could play a role as an additive in organic electronic devices.[1]

With the exception of one report on the formation of charge transfer complex [10]CPP–C60[7] under extremely high pressure (6 GPa),[8] the charge transport properties of [10]CPP–fullerene inclusion complexes,[9] are unexplored, which is in part due to the lack of precursors that would allow the general functionalization of [10]CPP by cross-coupling reactions. Hafiz has reported the synthesis of chloro-[10]CPP, along with its Ni-catalyzed homocoupling into [([10]CPP)2],[10] but the synthesis of more reactive and versatile iodinated or brominated [10]CPP substrates for cross-coupling reactions remains an unsolved problem.

Herein, we report the first synthesis of iodo-[10]CPP, based on a late-stage iodo substitution strategy (TMS−I). Starting from iodo-[10]CPP, we were able to carry out a highly efficient Sonogashira cross-coupling to afford conjugate I, in which [10]CPP (Figure 1, red) is covalently linked to a proto-

Figure 1. Structure of supramolecular electron donor–acceptor complex 1–PCBM and illustration of photoinduced electron transfer.

[1] Y. Xu, M. Bothe, Prof. Dr. M. von Delius
Institute of Organic Chemistry and Advanced Materials University of Ulm
Albert-Einstein-Allee 11, 89081 Ulm (Germany)
E-mail: max.vondelius@uni-ulm.de
[2] W. Wang, R. Kaur, M. B. Minameyer, Prof. Dr. T. Drewello, Prof. Dr. D. M. Guldi
Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials Friedrich-Alexander University Erlangen-Nürnberg
Egerlandstrasse 3, 91058 Erlangen (Germany)
E-mail: dirk.guldi@fau.de

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201802443.
As shown in Scheme 1 (top), our successful synthesis of iodo-[10]CPP follows Jasti’s reported synthesis of [10]CPP, with some crucial deviations, such as the use of a methoxymethyl protecting group (MOM) in the sixth step of the sequence (2, Scheme 1). In a Suzuki-Miyaura reaction, aryl dibromide 3 was coupled with aryl diboronic ester 4 and a subsequent reductive amination furnished TMS-[10]CPP in acceptable 30% yield over the challenging final two steps. Using iodine monochloride (ICl), we were able to convert TMS-[10]CPP into iodo-[10]CPP, and a copper-free Sonogashira reaction furnished conjugate 1 in quantitative yield. A qualitative 1H NMR titration provided evidence for selective binding of C₆₀ to the CPP ring, but not the porphyrin (Scheme 1, bottom).

With compound 1 in hand, we proceeded to explore its physicochemical properties. In the ground state, the typical Soret-band and Q-band absorptions of the porphyrin evolve at 425 and 551 nm, while absorptions of [10]CPP are discernable around 340 nm (Supporting Information, Figure S1). As shown in the 3D fluorescence spectrum (Figure 2), the excited state of conjugate 1 is dominated by an intramolecular energy transfer from the energy donating [10]CPP to the energy accepting porphyrin.

![3D Fluorescence Spectrum](image)

**Figure 2.** Room temperature 3D fluorescence spectrum of porphyrin-[10]CPP conjugate 1 upon 300 to 450 nm excitation in toluene and illustration of energy transfer. For a porphyrin reference, see the Supporting Information, Figure S2.

To gain insight into the formation of fullerene electron donor-acceptor complexes, we turned to C₆₀-C₈₅, aza-fullerene derivative C₆₀N-DPS, C₈₅, derive PCBM, and the fullerene dimer (C₆₀D₂), and conducted fluorescence titrations in toluene. The intensity of the porphyrin-centered fluorescence, with maxima at 600 and 650 nm, was found to decrease exponentially with increasing fullerene concentrations. Reaching the endpoint in the titrations the fluorescence intensity reduced to 18.6%, 18.4%, 19.5%, 30.0%, and 13.6% for C₆₀, C₈₅, C₆₀N-DPS, PCBM, and (C₆₀D₂), respectively. As such, the fluorescence intensities are in sound agreement with the electron acceptor strength of the fullerene, that is, C₆₀N-DPS > C₈₅ > C₆₀ > PCBM.

From fitting the data, we derived the association constants for the supramolecular electron donor-acceptor complexes (Figure 3: Supporting Information, Figures S14-S18). A remarkably high association constant of (1.6 ± 0.1) × 10⁶ M⁻¹ was found for the one-step binding of C₈₅ while (C₆₀D₂), is subject to two consecutive steps with underlying association constants of (4.7 ± 0.1) × 10⁶ and (1.9 ± 0.05) × 10⁶ M⁻¹. For C₆₀ and (aza)fullerene monoadducts C₆₀N-DPS and PCBM, the association constants are about one order of magnitude lower. These results suggest that for this set of fullerenes the relative binding affinities are mainly governed by the three-dimensional shape of the guest molecule (for example, C₆₀ is the only guest that can rotate freely within [10]CPP in all three dimensions). Independent support for the notion of strong fullerene binding was provided by electrospray ionization (ESI) mass spectrometry, including unprecedented MS/MS measurements of such complexes (Supporting Information, Figures S11, S12).

The nature of the singlet excited-state deactivation in fullerene complexes, that is, charge separation and charge
recombination, was corroborated by means of time-resolved transient absorption spectroscopy. 430 nm was chosen to excite the porphyrin in I and in the Π fullerene complexes exclusively despite a 10-fold excess of the fullerene in the latter case. In reference experiments with I, the porphyrin (second) singlet excited state features with its characteristic 630, 750, and 900 nm transient was seen to internally convert into the (first) singlet excited state and to intersystem cross to afford the triplet excited state; transient features include 500 and 850 nm fingerprints, respectively. Figure 4 documents in the case of Π:C₆₀ the prompt detection of only the same porphyrin (second) singlet excited state features (see above) and attests to its exclusive excitation. Following internal conversion, a fast decay of the porphyrin (first) singlet excited state goes hand-in-hand with the growth of maxima in the visible range at 530, 580, 620, and 660 nm as well as in the near-IR range at 1090 nm. The earlier maxima match the fingerprints absorptions of the one-electron oxidized form of the porphyrin,23 while the latter maximum is the known marker of the one-electron reduced form of C₆₀.24

Photoexcitation of Π:C₆₀ is followed by the formation of a metastable 1Π→C₆₀ charge-separated state. Figure 4 and the Supporting Information, Figure S21 document that in femto- and nanosecond pump-probe experiments, respectively, the charge-separated state decays in benzonitrile via the direct recovery of the ground state. Lowering the solvent-related stabilization of the 1Π→C₆₀ charge-separated state in, for example, toluene shifts its energy above that of the C₆₀ triplet excited state. As such, the 750 nm fingerprint absorption seen in reference experiments with C₆₀ (Supporting Information, Figure S25) evolves as a product of charge recombination.25 It is then the latter that reinitiates slowly the ground state. Similarly, we detected in Π fullerene the fingerprint absorptions of the well-known values of one-electron reduced forms for C₆₀ at 1380 nm,26 for C₆₀-N-DPS at 1050 nm,27 and for PCBM at 1040 nm.28

The case of (C₆₀)₂ is particularly interesting because, depending on stoichiometry and concentration, different molar ratios of a 1:1 (Π:(C₆₀)₂) and 2:1 (Π:(C₆₀)₂):C₆₀ complex are present in solution. Common to both is the one-electron oxidized form of the porphyrin with maxima in the visible range at 530, 580, 620, and 660 nm as well as the one-electron reduced form of (C₆₀), in the near-IR range at 1050 nm. As illustrated in Figure 5, however, the charge separation and recombination kinetics differed significantly from what has been seen for C₆₀, C₆₀-N-DPS, and C₆₀-PCBM (see above). For example, in Π:(C₆₀), the desymmetrization of the C₆₀ moieties results in two distinct charge recombination processes, that is a rapid process (Figure 5a) with a lifetime of 2.5 ± 0.4 ns and a slow process (Figure 5b) with a lifetime of 13.4 ± 2.3 ns involving the proximal and distant fullerene cores, respectively. Notably, the latter is longer-lived than any other Π:monofullerene charge-separated state that we observed in this study.

Only one electron-recombination process was observed in the more symmetric 2:3 complex (Π:(C₆₀)₂):C₆₀ (Figure 5c). However, by virtue of charge delocalization in the porphyrin·([10]CPP·([C₆₀]):[10]CPP·porphyrin charge-separated state, and in stark contrast to the 1Π→C₆₀ system, a lifetime of up to 541.8 ± 112.8 ns was observed,29 which is among the
longest-lived charge-separated states in fullereene/porphyrin containing electron donor-acceptor systems. This first study of intra(supramolecular) electron transfer to \((C_{60})_2\) attests to the unique potential of our modular, non-covalent approach. Nevertheless, it should be noted that, despite the conformational rigidity of our entire system and the high association constants, our results reflect average values, particularly in respect to fullerene rotation and translation (“shuffling” of \((C_{60})_2\)) within the CPP host.

In conclusion, we have successfully carried out the synthesis of a porphyrin-[10]CPP conjugate and studied its strong association with a range of fullerenes. Pump-probe spectroscopy demonstrated that [10]CPP as a supramolecular junction enables efficient charge transport between a porphyrin electron donor and unmodified fullerene electron acceptors. These results, together with Yamago’s recent report on the thin-film conductivity of [10]CPP and its alkyn derivatives imply that supramolecular complexes of [10]CPP and fullerenes may be a useful addition to the toolbox of organic electronics.

Acknowledgements

We are grateful for financial support from the DFG (SFB953: “Synthetic Carbon Allotropes”), the University of Ulm and FAU Erlangen-Nürnberg. Fabian Fritz and Pascal Frick are acknowledged for preparing a batch of \((C_{60})_2\).

Conflict of interest

The authors declare no conflict of interest.

Keywords: electron transfer · fullerenes · host–guest systems · strained molecules · time-resolved spectroscopy

How to cite: Angew. Chem. Int. Ed. 2018, 57, 11549–11553

Angew. Chem. 2018, 139, 11723–11727


[15] Owing to the energy transfer from CPP unit to porphyrin, the quantum yields of CPP unit in porphyrin-[10]CPP is only 0.44% when we use 340 nm excitation (see the Supporting Information, Figure S3).
[20] In the ground state absorption spectra, no significant shifts of the Soret and Q bands of I were observed upon fullerene binding (see the Supporting Information, Figure S13).
[23] a) H. Z. Yu, J. S. Biskin, A. H. Zewail, J. Phys. Chem. A 2002, 106, 9845–9854; b) for the spectroelectrochemistry results of conjugate I, see the Supporting Information, Figure S4.
[25] For \( 1^{(1)} \text{C}_{60} \), the light partitioning at the 430-nm excitation wavelength is 1/1 to 1 in benzotriazole and 56 to 1 in toluene as far as the porphyrin and \( \text{C}_{60} \), respectively, are concerned. Moreover, no notable \( \text{C}_{60} \) fluorescence, that is, \( < 10^{-3} \), is noted in the steady state fluorescence measurements. As such, we rule out the direct \( \text{C}_{60} \) excitation as the origin of \( \text{C}_{60} \) triplet formation.
[29] For charge separation and recombination rate constants, see the Supporting Information, Table S3.

Manuscript received: February 25, 2018
Revised manuscript received: May 10, 2018
Accepted manuscript online: July 9, 2018
Version of record online: August 6, 2018
Supporting Information

Youzhi Xu*, Bingzhe Wang*, Ramandeep Kaur, Martin B. Minameyer, Michael Bothe, Thomas Drewello, Dirk M. Guldi,* and Max von Delius*

anie_201802443_sm_misellaneous_information.pdf
## Contents

1. General Experimental Section ............................................................................ 3
2. Overview on Synthesis ......................................................................................... 4
3. Synthetic Procedures and Characterization Data .............................................. 5
   3.1 Synthesis of 2-TMS-4-methoxyphenol (S3) .................................................. 5
   3.2 Synthesis of ketone S5 ................................................................................ 6
   3.3 Synthesis of ketone 2 .................................................................................. 7
   3.4 Synthesis of S6 .......................................................................................... 7
   3.5 Synthesis of ketone S8 ................................................................................ 8
   3.6 Synthesis of 3 ............................................................................................ 9
   3.7 Synthesis of TMS-[10]CPP (S9) ................................................................ 10
   3.8 Synthesis of iodo-[10]CPP (S10) ................................................................. 11
   3.9 Synthesis of S11 ....................................................................................... 11
   3.10 Synthesis of porphyrin S12 ....................................................................... 12
   3.11 Synthesis of conjugate 1 .......................................................................... 13
   3.12 Synthesis of n-dodecylphenylsulfide azafullerene DPS-C$_{90}$N ............... 16
   3.13 Synthesis of fullerene dimer (C$_{90}$)$_2$ .................................................... 17
4. Molecular Modelling of Conjugate 1 ............................................................... 18
5. Characterization of Conjugate 1 ....................................................................... 19
   5.1 Intramolecular energy transfer ................................................................... 19
   5.2 Spectroelectrochemistry ............................................................................. 21
   5.3 Transient absorption spectra of conjugate 1 .............................................. 22
6. Characterization of Supramolecular 1$\rightarrow$Fullerene Complexes .................. 26
   6.1 Electrospray ionization mass spectra (ESI-MS) ......................................... 26
   6.2 Absorption spectra .................................................................................... 28
   6.3 Binding constants ..................................................................................... 29
   6.4 Transient absorption spectra of 1$\rightarrow$fullerene complexes .................... 32
7. NMR Spectra .................................................................................................... 50
8. References ......................................................................................................... 63
1. General Experimental Section

Reagents and instruments

NMR spectra were recorded on a Bruker DRX 400 (\(^1\)H NMR: 400 MHz, \(^{13}\)C NMR: 100 MHz) or a Bruker AMX 500 (\(^1\)H NMR: 500 MHz, \(^{13}\)C NMR: 125 MHz) spectrometers at 298 K and referenced to the residual solvent peak (\(^1\)H: 7.26 ppm for CDCl\(_3\), 5.32 ppm for CD\(_2\)Cl\(_2\); \(^{13}\)C: 77.16 ppm for CDCl\(_3\), 53.84 ppm for CD\(_2\)Cl\(_2\)). Coupling constants (J) are denoted in Hz and chemical shifts (\(\delta\)) in ppm. High resolution MALDI mass spectra were obtained on Bruker micro TOF II and Bruker Maxis 4G or Bruker Solarix (HRMS-ESI\(^+\)-TOF, Solvent: Toluene or Acetonitrile) instruments.

All commercially available reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros Organics or TCI and were used without further purification. Anhydrous THF, anhydrous DMF and \(n\)-Butyl lithium (1.6 M in n-hexane and 2.5 M in n-hexane) were purchased from Sigma Aldrich. Molecular sieves were dried for 3 days at 150 °C under reduced pressure (10\(^{-2}\) mbar) before use. Methyl iodide was dried in 5A molecular sieves and protected with N\(_2\). (C\(_{60}\))\(_2\) was prepared according to a published procedure.\(^{51}\)

The steady state absorption spectroscopy was conducted in 10x10mm Cuvettes with a Perkin-Elmer Lambda 2 double beam instrument. Steady-State fluorescence spectra were recorded with a Flouro Max 3 spectrofluorometer Horiba Yobin Yvon.

Transient absorption spectroscopy was performed using an amplified Ti:sapphire laser system (ModelCPA2110, Clark-MXR Inc.; output: 775 nm, 1 kHz, and <150 fs pulse width) in the Transient Absorption Pump/Probe System Helios from Ultrafast System. 430 nm excitation pulses were generated by frequency doubling 860 nm NOPA (Clark-MXR) output. All measurements were conducted at room temperature in deoxygenated solvents in 2 mm quartz cuvettes.

ESI mass spectra of the \(1 \Rightarrow\) fullerene complexes were recorded with a micrOTOF-Q II (Bruker, Bremen) equipped with an electrospray ion-source using nitrogen as nebulizing gas and a collision cell also utilizing nitrogen as collision gas. The capillary voltage was set to 6 kV to obtain sufficient oxidation of the dyad and its complexes. Mixtures of 1 and a given fullerene were diluted with acetonitrile and yielded best signal intensities upon further dilution with dichloromethane. For fragmentation of the host-guest complexes, the precursors were isolated and subsequently accelerated with 75 V prior to entering the collision cell.


Scheme S1. Reaction conditions: (a) Imidazole, TMSCl, DCM, 0 °C → RT, 12 h; (b) n-BuLi, TMSCl, THF, -78 °C, 2 h, 95 % (two steps); (c) 2 % HCl, DCM, MeOH, 1 h, 99 %; (d) Ph(OAc)$_2$, MeOH, 2 h, 0 °C; (e) 1,4-Diodobenzene, n-BuLi, THF, -78 °C, MeOH, 78 %; (f) NaH, THF, -60 °C → -40 °C, 2 h, MOMCl, 90 %; (g) 1,4-Dibromobenzene, n-BuLi, THF, -78 °C, CH$_3$I, DMF, 85 %; (h) 1,4-Dibromobenzene, n-BuLi, THF, -78 °C, quinone monoacetate, MeOH, 82 %; (i) NaH, THF, -60 °C → -50 °C, 2 h, CH$_3$I, DMF, 80 %; (j) n-BuLi, THF, -120 °C, CH$_3$I, DMF, 82 %; (k) Pd(OAc)$_2$, Cs$_2$CO$_3$, DMF, i-PrOH, 100 °C, 12 h; (l) Sodium naphthalenide, -78 °C, 2 h, 10 % (two steps); (m) ICl, -78°C → -20°C, 1 h, 82 %; (n) TMS acetylene, Pd(Ph$_3$P)$_2$Cl$_2$, CuI, THF, Et$_3$N, RT, 98 %; (o) n-BuLi, THF, -78 °C, 2 h, DMF, 72 %; (p) propionic acid, 150 °C, 3 h; (q) K$_2$CO$_3$, DCM, MeOH, RT, 4 h; (r) Zn(AC)$_2$, DCM, MeOH, RT, Overnight, 5 % (three steps); (s) Pd(Ph$_3$P)$_4$, Et$_3$N, DMF, RT → 40 °C, 4 h, quant.
3. Synthetic Procedures and Characterization Data

3.1 Synthesis of 2-TMS-4-methoxyphenol (S3)

2-Bromo-4-methoxyphenol (7.5 g, 37 mmol, 1.00 equiv) and imidazole (2.76 g, 40.6 mmol, 1.1 equiv) were added to a dry Schlenk flask under N₂. To this was added dry dichloromethane (DCM; 100 mL) and TMS-Cl (5.0 mL, 40.6 mmol, 1.0 equiv) was added dropwise to the stirring solution at 0°C. The solution was allowed to slowly warm up to room temperature overnight. Pentane (50 mL) was added to the crude reaction and the colorless solids were removed on a short alumina column under N₂ atmosphere. Removal of the solvents under N₂ atmosphere gave compound S1 as colorless oil (which is sensitive to moisture and directly used for the next step). Compound S1 was dissolved in dry THF (50 mL) and n-butyllithium in n-hexane (19.2 mL, 2.5 mol/L, 48.0 mmol, 1.3 equiv) was added dropwise at −78 °C over 5 min under N₂ atmosphere. The reaction mixture was stirred for 50 min, then TMS-Cl (6.4 mL, 51.8 mmol, 1.40 equiv) was added at −78 °C and the reaction mixture was allowed to slowly warm up to room temperature to give a pale yellow solution. After removal of the solvent under reduced pressure, water (100 mL) was added to the residue which was then extracted with DCM (3 x 50 mL). Removal of the solvents under reduced pressure gave compound S2 (9.43 g, 35 mmol, 95% yield) as a colorless solid.

¹H NMR (400 MHz, 298 K, CDCl₃): δ = 0.25 (s, 9H, Si(CH₃)₃), 0.30 (s, 9H, Si(CH₃)₃), 3.77 (s, 3H, OCH₃), 6.69 (dd, J₁ = 0.40 Hz, J₂ = 8.7 Hz, 1H), 6.77 (dd, J₁ = 3.2 Hz, J₂ = 8.7 Hz, 1H), 6.91 (d, J = 3.2 Hz, 1H).

¹³C NMR (100 MHz, 298 K, CDCl₃): δ = -0.85 (3CH₃), 0.76 (3CH₃), 55.78 (OCH₃), 114.93 (1CH), 116.99 (1CH), 120.98 (1CH), 131.22 (1C), 153.48 (1C), 154.36 (1C).

Compound S2 (9.43 g, 35 mmol) was dissolved in DCM (50 mL) and MeOH (50 mL), and 10 mL 2% aq. HCl was added and the mixture was stirred for 4h at room temperature. The solvent was removed under reduced pressure and the residue dissolved in Et₂O (60 mL) and washed with H₂O (3 x 50 mL). The organic layers were dried over Na₂SO₄ and removal of the solvent under reduced pressure gave pure compound S3 (6.7 g, 34.5 mmol, 99% yield) as a colourless solid without column chromatography. Spectroscopic data for S3 was in good agreement with literature data.²

¹H NMR (400 MHz, 298 K, CDCl₃): δ = 0.31 (s, 9H, Si(CH₃)₃), 3.74 (s, 3H, OCH₃), 4.41−4.55 (m, 1H, OH) 6.63 (d, J = 8.7 Hz, 1H), 6.77 (dd, J₁ = 3.1 Hz, J₂ = 8.7 Hz, 1H), 6.91 (d, J = 3.2 Hz, 1H).

¹³C NMR (100 MHz, 298 K, CDCl₃): δ = -0.16 (3CH₃), 55.81 (OCH₃), 115.19 (1CH), 115.21 (1CH), 120.73 (1CH), 126.87 (1C), 132.22 (1C), 154.38 (1C).
3.2 Synthesis of ketone S5

A 100 mL Schlenk flask was charged with 2-TMS-4-methoxyphenol (9.8 g, 50.0 mmol, 1.0 equiv) and MeOH (80 mL) was added under N₂ atmosphere. The resulting solution was cooled to 0 °C and iodobenzene diacetate (17.7 g, 55 mmol, 1.1 equiv) was added over 10 minutes. The reaction was allowed to stir at 0 °C for 2 hours, then quenched with saturated aq. NaHCO₃ (50 mL). The organic solvent was removed under reduced pressure, and the resulting residue was diluted with DCM (60 mL). The aqueous layer was extracted with DCM (2 × 50 mL), and the combined organic layers were dried over Na₂SO₄. Removal of the solvent under reduced pressure afforded a mixture of TMS-quinone monoacetal S4 and residual iodobenzene (1:1) as a pale yellow oil, which could be used for the next step without purification. A 250 mL dry Schlenk flask was charged with 1,4-diiobenzene (18.1 g, 55.0 mmol, 1.1 equiv) and 100 mL anhydrous THF. n-Butyllithium in n-hexane (24.0 mL, 2.5 mol/L, 60.0 mmol, 1.2 equiv) was added dropwise at −78 °C over 5 minutes under N₂ atmosphere. The reaction mixture was stirred for 50 minutes, then the crude TMS-quinone monoacetal S4 in THF (20 mL) was added at −78 °C, and the reaction temperature was slowly raised to −50 °C. MeOH (20 mL) was added to quench the reaction at −50 °C and the mixture was allowed to warm to room temperature. The solvents were removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with DCM (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure. Purification by column chromatography (DCM/Et₂O 5:1) afforded ketone S5 (15.0 g, 78% yield) as pale yellow solid.

³¹H NMR (400 MHz, 298 K, CDCl₃): δ = -0.03 (s, 9H, Si(CH₃)₃), 2.43 (s, 1H, OH), 6.08 (dd, J₁ = 1.9 Hz, J₂ = 9.9 Hz, 1H), 6.55 (d, J = 2.0 Hz, 1H), 6.79 (d, J = 9.9 Hz, 1H), 7.17 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H).

³¹C NMR (100 MHz, 298 K, CDCl₃): δ = -6.65 (3CH₃), 74.44 (1C), 93.61 (1CH), 125.24 (1CH), 127.54 (2CH), 135.56 (1CH), 137.73 (2CH), 138.41 (1C), 153.96 (1CH), 166.88 (1C), 184.21 (1C, C=O).

HRMS (ESI⁺) Calcd. for C₁₉H₁₈I₉O₃Si [M + H⁺] 385.0115; Found: 385.0111.
3.3 Synthesis of ketone 2

A solution of ketone S5 (7.7 g, 20 mmol, 1.0 equiv) in 30 mL of dry THF was slowly added to a slurry of sodium hydride (0.88 g, 22 mmol, 60% in mineral oil, 1.1 equiv) in 100 mL of dry THF that was kept at -60 °C. The reaction mixture was stirred for 2 hours while slowly warming from -60 °C to -40 °C. Methoxymethyl chloride (1.84 mL, 24.0 mmol, 1.2 equiv) was added and the solution was allowed to warm to room temperature. The solvent was removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with DCM (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure. Purification by column chromatography (DCM/EtO 100:1) gave 2 (7.7 g, 90% yield) as pale yellow solid.

\(^1\)H NMR (400 MHz, 298 K, CDCl\(_3\)): \(\delta = -0.07\) (s, 9H, Si(CH\(_3\))\(_3\)), 3.51 (s, 3H, OCH\(_3\)), 4.70 (dd, \(J_1 = 7.2\) Hz, \(J_2 = 29.2\) Hz, CH\(_2\)), 6.15 (dd, \(J_1 = 2.0\) Hz, \(J_2 = 10.1, 1H\)), 6.70 (d, \(J = 2.0\) Hz, 1H), 6.85 (d, \(J = 10.1\) Hz, 1H), 7.17 (d, \(J = 8.6\) Hz, 2H), 7.67 (d, \(J = 8.6\) Hz, 2H).

\(^{13}\)C NMR (100 MHz, 298 K, CDCl\(_3\)): \(\delta = -0.70\) (3CH\(_3\)), 56.12 (1CH\(_3\)), 79.65 (1C), 93.41 (1CH\(_2\)), 93.68 (1C), 125.75 (1CH), 127.86 (2CH), 137.75 (2CH), 137.95 (1C), 138.69 (1CH), 154.09 (1CH), 165.12 (1C), 184.33 (1C, C=O).

HRMS (ESI\(^+\)) Calcd. for C\(_{17}\)H\(_{21}\)INaO\(_2\)Si [M + Na\(^+\)] 451.0197; Found: 451.0193.

3.4 Synthesis of S6

A 250 mL dry Schlenk flask was charge with 1,4-dibromobenzene (5.6 g, 24.0 mmol, 1.2 equiv) and 100 mL anhydrous THF. n-Butyllithium in n-hexane (9.6 mL, 2.5 mol/L, 24.0 mmol, 1.2 equiv) was added dropwise at -78 °C over 5 minutes under N\(_2\) atmosphere. The reaction mixture was stirred for 50 minutes, then 2 (8.6 g, 20.0 mmol, 1.0 equiv) was added at -78 °C and the temperature was increased to -50 °C. Methyl iodide (1.9 mL, 30.0 mmol, 1.5 equiv) and anhydrous DMF (10 mL) were added to quench the reaction at -50°C and the mixture was allowed to warm up to room temperature overnight. Water (50 mL) was added carefully to quench the reaction, and the resulting mixture was
extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were concentrated under reduced pressure and purification by column chromatography (cyclohexane/DCM 1:2) gave S6 (9.5 g, 85% yield, mixture of diastereomers) as pale yellow solid.

1H NMR (400 MHz, 298 K, CDCl₃): δ = -0.15 (s, 9H, Si(CH₃)₂), 3.34 (s, 3H, OCH₃), 3.49 (s, 3H, OCH₃), 4.58 (dd, J₁ = 8.0 Hz, J₂ = 44.0 Hz, CH₂), 5.89 (dd, J₁ = 2.5 Hz, J₂ = 10.3, 1H), 6.07 (d, J = 10.2 Hz, 1H), 6.37 (d, J = 2.5 Hz, 1H), 7.27 – 7.32 (m, 2H), 7.38 – 7.45 (m, 2H), 7.46 – 7.51 (m, 2H), 7.64 – 7.70 (m, 2H).

13C NMR (100 MHz, 298 K, CDCl₃): δ = 0.05 (3CH₂), 51.97 (1C), 56.05 (OCH₃), 73.55 (OCH₃), 78.44 (1C), 92.78 (CH₂), 93.03 (1C), 121.96 (1C), 128.1 (1CH), 128.17 (4CH), 131.75 (2CH), 137.83 (2CH), 142.72 (1C), 143.93 (1C), 143.96 (2CH), 143.81 (1C), 144.83 (1C).


3.5 Synthesis of ketone S8

A 250 mL dry Schlenk flask was charged with 1,4-dibromobenzene (13.0 g, 55.0 mmol, 1.1 equiv) and 120 mL anhydrous THF. n-Butyllithium in n-hexane (22.0 mL, 2.5 mol/L, 55.0 mmol, 1.1 equiv) was added dropwise at -78 °C over 5 minutes under N₂ atmosphere. The reaction mixture was stirred for 50 minutes, then quinone monoacetal (7.7 g, 50.0 mmol, 1.0 equiv) was added at -78 °C and the temperature was slowly increased to -50 °C. MeOH (20 mL) was added to quench the reaction at -50°C and the mixture was allowed to warm up to room temperature. The resulting mixture was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were concentrated under reduced pressure and purification by column chromatography (DCM/ErOAc 5:1) gave S7 (10.6 g, 82% yield) as pale yellow solid. Characterization data was consistent with previous reports. 33

A solution of ketone S7 (10.6 g, 40 mmol, 1.0 equiv) in 30 mL of dry THF was slowly added to a slurry of sodium hydride (1.6 g, 40 mmol, 60% in mineral oil, 1.0 equiv) in 100 mL of dry THF that was kept at -60 °C. The reaction mixture was stirred for 2 hours while slowly warming from -60 °C to -50 °C. Methyl iodide (3.8 mL, 60.0 mmol, 1.5 equiv) and anhydrous DMF (20 mL) were added to quench the reaction at -50°C and the mixture was allowed to warm up to room temperature overnight. Water (20 mL) was added carefully to quench the methylation reaction, and the resulting mixture was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were concentrated under reduced pressure and purification by column chromatography (cyclohexane/DCM 2:1) gave S8 (8.9 g, 80% yield) as pale yellow solid.

1H NMR (400 MHz, 298 K, CDCl₃): δ = 3.42 (s, 3H, OCH₃), 6.37 – 6.46 (m, 2H), 6.69 – 6.79 (m, 2H), 7.37 – 7.28 (m, 2H), 7.44 – 7.52 (m, 2H).
SUPPORTING INFORMATION

${^13}C$ NMR (100 MHz, 298 K, CDCl$_3$): $\delta$ = 53.07 (OCH$_3$), 76.34 (1C), 122.58 (1C), 127.63 (2CH), 130.49 (2CH), 132.02 (2CH), 137.55 (1C), 150.06 (2CH), 185.42 (1C, C=O).

HRMS (ESI$^+$) Calcd. for C$_{13}$H$_{11}$NaBrO$_2$ [M + Na$^+$] 300.9835; Found: 300.9848.

3.6 Synthesis of 3

A 100 mL dry Schlenk flask was charged with S6 (2.4 g, 4.0 mmol, 1.0 equiv) and 60 mL anhydrous THF. n-Butyllithium in n-hexane (2.8 mL, 1.6 mol/L, 4.4 mmol, 1.1 equiv) was added dropwise at -100°C over 5 minutes under N$_2$ atmosphere. The reaction mixture was stirred for 50 minutes, then ketone S8 (1.2 g, 4.0 mmol, 1.0 equiv) was added at -78°C and the temperature was slowly increased to -50°C. Methyl iodide (0.4 mL, 6.0 mmol, 1.5 equiv) and anhydrous DMF (2 mL) were added to quench the reaction at -50°C and the mixture was allowed to warm up to room temperature overnight. The solvent was removed under reduced pressure and the residue was diluted with DCM (50 mL). The aqueous layer was extracted with DCM (2 x 50 mL), and the combined organic layers were concentrated under reduced pressure. Purification by column chromatography (DCM) gave 3 (1.9 g, 62% yield, mixture of two diastereomers) as pale yellow oil.

${^1}H$ NMR (400 MHz, 298 K, CDCl$_3$): $\delta$ = 0.15 (s, 9H, Si(CH$_3$)$_3$), 3.36 (s, 3H, OCH$_3$), 3.42 (s, 3H, OCH$_3$), 3.43 (s, 3H, OCH$_3$), 4.60 (dd, J$_1$ = 8.0 Hz, J$_2$ = 44.0 Hz, 2H), 5.87 (dd, J$_1$ = 2.5 Hz, J$_2$ = 10.3, 1H), 6.08 – 6.01 (m, 2H), 6.11 (d, J = 10.3 Hz, 1H), 6.20 – 6.14 (m, 2H), 6.37 (d, J = 2.6 Hz, 1H), 7.21 (s, 2H), 7.46 – 7.32 (m, 6H), 7.52 – 7.47 (m, 4H).

${^{13}}C$ NMR (100 MHz, 298 K, CDCl$_3$): $\delta$ = -0.09 (3CH$_3$), 52.13 (OCH$_3$), 52.14 (OCH$_3$), 52.17 (OCH$_3$), 55.90 (OCH$_3$), 73.76 (1C), 74.87 (1C), 74.75 (1C), 78.03 (1C), 92.27 (1CH$_3$), 121.61 (1C), 121.69 (1C), 125.92 (2CH), 126.38 (2CH), 127.91 (2CH), 127.94 (1CH), 128.13 (2CH), 131.47 (2CH), 131.71 (2CH), 133.01 (1CH), 133.19 (1CH), 133.69 (1CH), 133.85 (1CH), 138.56 (1CH), 142.24 (1C), 142.58 (1C), 142.97 (1C), 143.36 (1C), 143.53 (1CH), 145.78 (1C).

HRMS (MALDI) Calcd. for C$_{38}$H$_{42}$NaBr$_2$O$_6$Si [M + Na$^+$] 789.1045; Found: 789.1054.
3.7 Synthesis of TMS-[10]CPP (S9)

4 was prepared according to a previously reported procedure. Characterization data was consistent with the previous report. Under an Argon atmosphere, a 250 mL Schlenk flask was charged with dibromide 3 (632 mg, 0.8 mmol), diboronate 4 (607 mg, 0.8 mmol), Pd(OAc)$_2$ (108 mg, 0.16 mmol, 0.2 equiv), Cs$_2$CO$_3$ (1.0 g, 3.2 mmol, 4 equiv), degassed DMF (100 mL) and 2-propanol (10 mL). The reaction mixture was stirred at 100 °C for 12 h under Argon. After cooling down to room temperature, the mixture was filtered through a short plug of Al$_2$O$_3$, and 100 mL water was added to the filtrate. After extraction with DCM (3 x 60 mL), the combined organic layers were dried over Na$_2$SO$_4$. After removal of the solvent under reduced pressure, the crude mixture was used for the next step without further purification. The [10]macrocycle crude mixture was dissolved in 60 mL THF under nitrogen and cooled down to -78 °C. At this point, freshly prepared sodium naphthalenide (10 mL, 10 mmol, 1.0 M in THF) was added. The reaction mixture was stirred for 2 h at -78 °C before MeOH (5 mL) was added. Then the resulting mixture was warmed up to room temperature. After removal of the solvent under reduced pressure, the crude yellow solid was purified by silica gel column chromatography (CH$_2$Cl$_2$/cyclohexane = 1:2) to give TMS-[10]CPP S9 (66 mg, 10% two steps) as a yellow solid.

$^1$H NMR (400 MHz, 298 K, CDC$_3$): $\delta = 0.33$ (s, 9H, Si(CH$_3$)$_3$), 6.87 (d, J = 8.0 Hz, 1H), 7.12 (dd, $J_1 = 1.6$ Hz, $J_2 = 8.4$ Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.42 - 7.62 (m, 32H), 7.96 (d, J = 2.0 Hz).

$^{13}$C NMR (100 MHz, 298 K, CDC$_3$): $\delta = 1.38$ (3CH3), 127.25 (CH), 127.30 (CH), 127.34 (CH), 127.46 (CH), 127.48 (CH), 127.54 (CH), 127.61 (CH), 127.64 (CH), 127.81 (CH), 127.91 (CH), 129.74 (CH), 131.64 (CH), 132.79 (CH), 137.35 (CH), 137.93 (C), 138.02(C), 138.04(C), 138.06(C), 138.24(C), 138.29(C), 138.32(C), 138.44(C), 138.49(C), 138.63(C), 139.10(C), 139.19(C), 142.73(C), 147.05(C).

HRMS (MALDI) Calcd. for C$_{53}$H$_{48}$Si: 832.3525; Found: 832.3522.
3.8 Synthesis of Iodo-[10]CPP (S10)

A 25 mL Schlenk flask was charged with TMS-[10]CPP S9 (40 mg, 24.0 umol, 1.0 equiv) and anhydrous DCM (20 mL) under N₂ atmosphere. The resulting solution was cooled to -78 °C and ICl (1 mL, 28.0 umol/mL in DCM, 1.2 equiv) was added over 10 minutes. The reaction was slowly warmed up to -20 °C and then quenched with aq. Na₂SO₃ (10 mL, 1M). The mixture was extracted with DCM (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure. Purification by preparative TLC (DCM/n-hexane 1:2) gave S10 (15 mg, 72% yield (82% yield based on recovered TMS-[10]CPP)) as pale yellow solid.

¹H NMR (400 MHz, 298 K, CDCl₃): 6 = 6.84 (d, J = 7.8 Hz, 1H), 7.11 (dd, J₁ = 1.6 Hz, J₂ = 8.4 Hz, 1H), 7.48 – 7.64 (m, 36H), 8.24 (d, J = 2.0 Hz).

¹³C NMR (125 MHz, 298 K, CDCl₃): 6 = 94.27 (C), 127.31 (CH), 127.35 (CH), 127.39 (CH), 127.46 (CH), 127.48 (CH), 127.50 (CH), 127.51 (CH), 127.54 (CH), 127.59 (CH), 127.64 (CH), 127.72 (CH), 127.84 (CH), 128.13 (CH), 129.65 (CH), 133.19 (CH), 136.51 (CH), 137.39 (C), 137.74 (C), 138.04 (C), 138.29 (C), 138.31 (C), 138.33 (C), 138.34 (C), 138.36 (C), 138.47 (C), 138.51 (C), 138.65 (C), 138.71 (C), 138.84 (C), 139.71 (C), 140.29 (C), 141.57 (C), 143.86 (C).

HRMS (MALDI) Calcd. for C₅₆H₃₃I 886.2096; Found: 886.2092.

3.9 Synthesis of S11

4-(4'-bromo)biphenylethynyl-trimethylsilane was prepared according to a previously reported procedure. Characterization data was consistent with the previous report.

A 100 mL dry Schlenk flask was charged with 4-(4'-bromo)biphenylethynyl-trimethylsilane (1.0 g, 3.0 mmol, 1.0 equiv) and 60 mL anhydrous THF. n-Butyllithium in n-hexane (2.5 mL, 1.6 mol/L, 4.0 mmol, 1.3 equiv) was added dropwise at -78 °C under N₂ atmosphere. The reaction mixture was stirred for 30 minutes, then DMF (460 ul, 6.0 mmol, 2.0 equiv) was added at -78 °C and the mixture was allowed
SUPPORTING INFORMATION

1H NMR (400 MHz, 298 K, CDCl3): δ = 0.27 (s, 9H, Si(CH3)3), 7.55 – 7.60 (m, 4H), 7.77 – 7.71 (m, 2H), 7.99 – 7.90 (m, 2H), 10.05 (s, 1H, CHO).

13C NMR (125 MHz, 298 K, CDCl3): δ = 0.09 (3CH3), 96.02 (1C), 104.65 (1C), 123.48 (1C), 127.25 (2CH), 127.70 (2CH), 130.44 (2CH), 132.71 (2CH), 135.52 (1C), 139.65 (1C), 146.32 (1C), 191.95 (CHO).

HRMS (ESI) Calcd. for C18H19O3Si [M + H]+ 279.1200; Found: 279.1202.

3.10 Synthesis of porphyrin S12

Fresh pyrrole (0.63 mL, 12.0 mmol), 4-tert-Butylbenzaldehyde (1.5 mL, 9.0 mmol) and Aldehyde S11 (0.84 g, 3.0 mmol) were dissolved in propionic acid (100 mL). The reaction mixture was stirred at 150°C for 3 h and methanol (4 x 50 mL) was added after cooling to room temperature. The purple solid was filtered off, dried under reduced pressure and redissolved in DCM (200 mL) and MeOH (50 mL). The reaction mixture was stirred for 4 hours and K2CO3 (0.83 g, 6.0 mmol) was added. The solvents were removed under reduced pressure and the residue was diluted with DCM (50 mL). The aqueous layer was extracted with DCM (2 x 100 mL) and the combined organic layers were concentrated under reduced pressure. The residue was dissolved in DCM (300 mL) and MeOH (100 mL) and Zn(OAc)2 was added and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and purification by silica gel column chromatography (CH2Cl2/cyclohexane = 1:2) gave porphyrin S12 (142 mg, 5% yield) as a purple solid.

1H NMR (400 MHz, 298 K, CDCl3/C2D2 2:1): δ = 1.64 (s, 27H), 3.25 (s, 1H), 7.71 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.1 Hz, 6H), 7.92 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 8.1 Hz, 2H), 8.15 (d, J = 8.1 Hz, 6H), 8.31 (d, J = 8.1 Hz, 2H), 9.08 – 8.93 (m, 8H).
SUPPORTING INFORMATION

$^{13}$C NMR (125 MHz, 298 K, CDCl$_3$/CS$_2$: 2:1): δ = 31.96, 35.12, 78.48, 84.02, 120.64, 121.72, 121.74, 121.84, 124.03, 125.63, 127.65, 132.13, 132.38, 132.46, 132.50, 132.63, 133.23, 134.74, 135.52, 139.55, 140.18, 141.74, 142.93, 150.42, 150.61, 150.67, 150.71, 150.76, 150.78, 150.82.

HRMS (MALDI) Calcd. for C$_{64}$H$_{69}$N$_4$Zn 944.3796; Found: 944.3788.

3.11 Synthesis of conjugate 1

Under an Argon atmosphere, a 25 mL Schlenk flask was charged with iodo-[10]CPP S10 (8.8 mg, 10.0 μmol), porphyrin S12 (11.5 mg, 12.0 μmol, 1.2 equiv), degassed DMF (10 mL) and Et$_3$N (2 mL). Pd(Ph$_3$P)$_4$ (5 mg, 0.4 equiv) was added at room temperature and the mixture was heated to 40 °C for 4 hours. The mixture was filtered through a short plug of Al$_2$O$_3$. After removal of the solvent under reduced pressure, the crude yellow solid was purified by preparative TLC (CH$_2$Cl$_2$/cyclohexane = 2:1) to give conjugate 1 (17 mg, quant.) as a purple solid.

$^1$H NMR (500 MHz, 298 K, CDCl$_3$): δ = 1.62 – 1.63 (m, 27H), 7.14 (d, J = 8.5 Hz, 1H), 7.24 (dd, J = 2.1 Hz, J = 8.0 Hz, 1H), 7.64 – 7.49 (m, 34H), 7.72 (d, J = 8.2 Hz, 2H), 7.76 – 7.78 (m, 6H), 7.84 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.3 Hz, 2H), 7.98 (d, J = 1.9 Hz, 1H), 8.01 (d, J = 8.1 Hz, 2H), 8.15 – 8.17 (m, 6H), 8.33 (d, J = 8.0 Hz, 2H), 9.01 (d, J = 14.5 Hz, 8H).

$^{13}$C NMR (125 MHz, 298 K, CDCl$_3$): δ = 29.86 (C), 31.88 (CH$_2$), 35.05 (CH$_3$), 66.57 (C), 90.70 (C), 92.48 (C), 120.37 (C), 121.47 (C), 121.57 (C), 122.65 (C), 123.61 (CH), 123.63 (CH), 125.22 (CH), 127.17 (CH), 127.20 (CH), 127.28 (CH), 127.33 (CH), 127.37 (CH), 127.39 (CH), 127.44 (CH), 127.46 (CH), 127.51 (CH), 127.53 (CH), 127.54 (CH), 127.55 (CH), 127.60 (CH), 127.64 (CH), 127.82 (CH), 129.23 (CH), 129.25 (CH), 129.30 (CH), 130.46 (CH), 131.80 (CH), 132.05 (CH), 132.20 (CH), 132.24 (CH), 132.36 (CH), 134.46 (CH), 135.26 (CH), 137.88 (C), 137.93 (C), 138.11 (C), 138.22 (C), 138.24 (C), 138.26 (C), 138.28 (C), 138.32 (C), 138.36 (C), 138.41 (C), 138.48 (C), 138.60 (C), 138.82 (C), 139.27 (C), 139.93 (C), 140.87 (C), 141.08 (C), 142.64 (C), 150.13 (C), 150.40 (C), 150.46 (C), 150.51 (C), 150.56 (C).

HRMS (MALDI) Calcd. for C$_{124}$H$_{169}$N$_4$Zn 1703.6804; Found: 1703.6796.
SUPPORTING INFORMATION

HRMS (MALDI) of conjugate 1:

Variable-Temperature $^1$H-NMR spectrum (400 MHz, CDCl$_3$):

Note: At room temperature, any conformers of conjugate 1 (CPP ring in relation to porphyrin; see also section 4) are subject to rapid equilibration.
2D-^1^H/^1^H-COSY-NMR spectrum (400 MHz, CDCl₃, 298 K):

2D-^1^H/^1^3^C-HSQC-NMR spectrum (CDCl₃, 298 K):
3.12 Synthesis of \( n \)-dodecylphenylsulfide azafullerene DPS-C\(_{29}\)N

\( C_{60} \)-N-MEM-ketolactam (S13)\(^{36} \) was synthesized according to a published procedure. Characterization data was consistent with the previous report.

In oven-dried round bottom flasks (50 mL), S13 (60 mg, 70 \( \mu \)mol) was dissolved in 1,2-dichlorobenzene (15 mL, analytical purity). Subsequently, S14 (195 mg, 700 \( \mu \)mol) and \( p \)-toluenesulfonic acid (133 mg, 700 \( \mu \)mol) was added and the reaction mixtures were stirred at 150 \( ^\circ \)C on a preheated heat-on block until no \( C_{60} \)-N-MEM-ketolactam S13 could be detected by TLC (ca. 15 to 30 minutes). Alternatively, the reaction progress can be monitored by analytical HPLC (COSMOSIL BUCKYPREP, toluene, 1 mL/min). After quick cooling to room temperature by means of an ice bath, the reaction mixtures were combined and directly subjected to flash column chromatography (silica gel, toluene (HPLC grade)). The solvent was removed under reduced pressure and the residues were purified by preparative HPLC (COSMOSIL, toluene, 18 mL/min). The crude product should never be completely dried prior to HPLC purification in order to reduce losses caused by filtration with syringe filter. Finally, the product was dissolved in a minute amount of CS\(_{2}\) and reprecipitated from \( n \)-pentane. The target compound DPS-C\(_{29}\)N was isolated as back solid (43 mg, 43\% yield).

\(^1\)H NMR (400 MHz, 298 K, CDCl\(_3\)): \( \delta = 0.88 \) (t, \( J = 4.0 \) Hz, 3 H), 1.25 – 1.53 (m, 18 H), 1.80 – 1.87 (m, 2 H), 3.14 (t, \( J = 7.6 \) Hz, 2 H) 7.81 (d, \( J = 8.0 \) Hz, 2H), 8.78 (d, \( J = 8.0 \) Hz, 2H).

\(^{13}\)C NMR (100 MHz, 298 K, CDCl\(_3\)/CS\(_2\), 2:1): \( \delta = 14.39, 23.00, 29.31, 29.38, 29.55, 29.62, 29.88, 29.91, 29.95, 32.15, 33.37, 82.81, 124.22, 127.82, 129.22, 133.15, 137.68, 138.22, 139.95, 140.12, 141.04, 141.16, 141.59, 141.63, 141.95, 142.23, 142.91, 143.29, 144.14, 144.46, 144.70, 145.18, 145.19, 145.82, 146.01, 146.38, 146.56, 146.76, 147.31, 147.42, 147.71, 147.72, 147.95, 148.75, 154.53.

3.13 Synthesis of fullerene dimer (C$_{60}$)$_2$

Fullerene dimer (C$_{60}$)$_2$ was synthesized by ball milling technique. 100 mg of C$_{60}$ and 20 mg (2 molar equiv) of KCN were placed in a capsule in glovebox filled with nitrogen, then vigorous mixing in ball milling reactor (conditions: 400 r/min, 20 min and RT). Analysis of the reaction mixture by high-pressure liquid chromatography (HPLC) indicated the presence of only one product (retention time of 14.1 min over a Buckyprep column eluted with toluene; 1 mL/min). Separation by flash chromatography (n-hexane/toluene 1:1 → toluene/oDCB 1:1) reprecipitation from oDCB/ hexane gave C$_{120}$ (26 mg, 26% yield). Characterization data was consistent with the previous report.$^{58}$

HPLC chromatogram of C$_{120}$ (purity > 98%)
4. Molecular Modelling of Conjugate 1

Software: Spartan '14 V 1.14; Semi-empirical, method: PM6
5. Characterization of Conjugate 1

5.1 Intramolecular energy transfer

Figure S1. Normalized room temperature absorption (black, solid) and emission (red, dash) spectra of conjugate 1 in toluene upon 340 nm excitation.

Figure S2. Room temperature 3D fluorescence spectra of ZnP upon 300 to 460 nm excitation in toluene. A concentration of $10^{-6}$ M was used.
Figure S3. Linear plot of room temperature fluorescence intensity of [10]CPP (black) and conjugate 1 (red) vs. absorbance upon 340 nm excitation in toluene. The integrated fluorescence intensity was recorded the emission of [10]CPP unit around 470 nm. 97
Figure S4. Differential absorption spectrum (visible and near-infrared) obtained upon electrochemical oxidation of conjugate 1 with an applied potential of +0.7 V in toluene/Acetonitrile (4:1 v/v) with 0.1 M TBAPF₆ vs. Ag-wire.
5.3 Transient absorption spectra of conjugate 1

Figure S5. (a) Differential absorption spectra obtained upon femtosecond pump probe experiments at room temperature (430 nm / 500 nJ) of conjugate 1 in toluene with time delays between 2, 10 and 500 ps – for time delays see Figure legend. (b) the time-absorption profiles and corresponding fits of intersystem crossing at 840 and 1300 nm, that is, the characteristic absorption features of triplet excited states and singlet excited states of ZnP. (c) Differential absorption spectra obtained upon nanosecond pump probe experiments at room temperature (430 nm / 500 nJ) of conjugate 1 with time delays between 0.001 to 100 μs – for time delays see Figure legend. (d) the time-absorption profiles and corresponding fits of intersystem crossing at 840 and 1300 nm, that is, the characteristic absorption features of triplet excited states and singlet excited states of ZnP.

Table S1 Second singlet state, first singlet state, and triplet excited state lifetimes of 1 in toluene, chlorobenzene and benzonitrile at room temperature obtained from exponential fittings of the time profiles upon femtosecond / nanosecond pump probe experiments (430 nm / 500 nJ).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(S_2 - S_1)</th>
<th>(S_1 - T_1)</th>
<th>(T_1 - T_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzonitrile</td>
<td>2.74 ± 0.57 ps</td>
<td>1.90 ± 0.04 ns</td>
<td>136.62 ± 19.58 μs</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>3.33 ± 0.52 ps</td>
<td>1.90 ± 0.09 ns</td>
<td>95.73 ± 7.92 μs</td>
</tr>
<tr>
<td>toluene</td>
<td>1.63 ± 0.34 ps</td>
<td>2.19 ± 0.08 ns</td>
<td>85.30 ± 5.77 μs</td>
</tr>
</tbody>
</table>
5.4 Transient absorption spectra of fullerenes

Figure S6 (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments at room temperature (430 nm / 500 nJ) of C$_{60}$ in toluene with time delays of 2 ps (black) and 5000 ps (red) correlating with the absorption spectra of the C$_{60}$ singlet excited state and C$_{60}$ triplet excited state, respectively, at room temperature. (b) Time-absorption profiles of the characteristic absorption fingerprints of the C$_{60}$ singlet excited state at 970 nm (black) and the C$_{60}$ triplet excited state at 750 nm (red) to illustrate the intersystem crossing with a rate constant of 5.1 x 10$^3$ s$^{-1}$.

Figure S7 (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments at room temperature (430 nm / 500 nJ) of C$_{70}$ in toluene with time delays of 2 ps (black) and 5000 ps (red) correlating with the absorption spectra of the C$_{70}$ singlet excited state and C$_{70}$ triplet excited state, respectively, at room temperature. (b) Time-absorption profiles of the characteristic absorption fingerprints of the C$_{70}$ singlet excited state at 615 nm (black) and the C$_{70}$ triplet excited state at 1000 nm (red) to illustrate the intersystem crossing with a rate constant of 1.7 x 10$^5$ s$^{-1}$. 
**Figure S8** (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments at room temperature (430 nm / 500 nJ) of PCBM in toluene with time delays of 2 ps (black) and 5000 ps (red) correlating with the absorption spectra of the PCBM singlet excited state and PCBM triplet excited state, respectively, at room temperature. (b) Time-absorption profiles of the characteristic absorption fingerprints of the PCBM singlet excited state at 1000 nm (black) and the PCBM triplet excited state at 706 nm (red) to illustrate the intersystem crossing with a rate constant of $9.3 \times 10^8$ s$^{-1}$.

**Figure S9** (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments at room temperature (430 nm / 500 nJ) of C$_{60}$-DPS in toluene with time delays of 2 ps (black) and 5000 ps (red) correlating with the absorption spectra of the C$_{60}$-DPS singlet excited state and C$_{60}$-DPS triplet excited state, respectively, at room temperature. (b) Time-absorption profiles of the characteristic absorption fingerprints of the C$_{60}$-DPS singlet excited state at 505 nm (black) to illustrate the intersystem crossing with a rate constant of $1.3 \times 10^9$ s$^{-1}$. 
Figure S10 (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments at room temperature (430 nm / 500 nJ) of (C$_{60}$)$_2$ in toluene with time delays of 2 ps (black) and 5000 ps (red) correlating with the absorption spectra of the (C$_{60}$)$_2$ singlet excited state and (C$_{60}$)$_2$ triplet excited state, respectively, at room temperature. (b) Time-absorption profiles of the characteristic absorption fingerprints of the (C$_{60}$)$_2$ singlet excited state at 1000 nm (black) and the (C$_{60}$)$_2$ triplet excited state at 720 nm (red) to illustrate the intersystem crossing with a rate constant of 9.1 x 10$^4$ s$^{-1}$. 
6. Characterization of Supramolecular 1$\supset$Fullerene Complexes

6.1 Electrospray ionization mass spectra (ESI-MS)

Figure S11. ESI-MS$^1$ spectra of 1 with various fullerenes (from top to bottom: C$_{60}$, C$_{70}$, PCBM, C$_{59}$N-DPS). All spectra display 1 as its radical cation together with a signal of the complex of 1 and the respective fullerene also as the radical cation. The insets are the measured (top) and the simulated (bottom) isotope patterns of the given 1$\supset$fullerene complex. Small features of a doubly charged complex-dimer are also discernible in all four spectra. A signal for the complex 1$\supset$(C$_{60}$)$_2$ could not be obtained during ESI-MS (spectrum not shown) due to instability of the weak covalent bond between the two C$_{60}$ moieties under the given electrospray conditions.\textsuperscript{58}
Figure S12. ESI-MS\(^2\) fragmentation mass spectra of the host-guest complexes of 1 with the respective fullerenes (from top to bottom: \(C_{60}\), \(C_{70}\), PCBM, \(C_{59}\)-N-DPS). In all spectra the \(1^{**}\) is the sole fragment ion with no sign of the respective fullerene ion, indicating that the charge is exclusively localized on 1. Furthermore, since all fragmentations yield the conjugate as fragment ion, these MS\(^2\) experiments are a definite proof of complex formation between 1 and the fullerene derivatives.
6.2 Absorption spectra

Figure S13. Room temperature absorption spectra of complexes 1\(\supseteq C_{60}\) in toluene (a), 1\(\supseteq C_{69}\) in BN (b) 1\(\supseteq C_{70}\) in toluene (c), 1\(\supseteq\)PCBM in toluene (d), 1\(\supseteq C_{90}\)N-DPS in toluene (e) and 1\(\supseteq (C_{60})_{2}\) in toluene (f). The black curves are Conjugate 1 absorption spectra. \(C_{(1)} = 4 \times 10^{-8}\) M; \(C_{(fullerene)} = 4 \times 10^{-7}\) M.
6.3 Binding constants

Figure S14. Fluorescence spectra (a) and the emission intensity changes (b) and (c) of conjugate 1 (4 x 10⁸ M) upon complexation with C₆₀ (0 – 1.4 x 10⁸ M) with photoexcitation at 425 nm in toluene at room temperature, (b) red crosses represent a fit according to only a 1:1 model (see Table S2, entry 1), (c) red crosses represent a fit according to a 1:1, 2:1 and 1:2 model (slightly better agreement between fit and data), but the binding constants Kₐ₂ and Kₐ₃ are three orders of magnitude lower than Kₐ₁, which describes the formation of the 1:1 complex, which is why the transient absorption measurements are only negligibly affected by these two additional equilibria (see also Table S2, entry 2 for the transient absorption data that shows no evidence for significant quantities of the 2:1 or 1:2 complexes).

Figure S15. Fluorescence spectra (a) and the emission intensity changes (b) of conjugate 1 (4 x 10⁸ M) upon complexation with C₁₀ (0 –1.8 x 10⁶ M) with photoexcitation at 425 nm in toluene at room temperature. Red crosses represent a fit according to a 1:1 model (see Table S2, entry 3).
Figure S16. Fluorescence spectra (a) and the emission intensity changes (b) of conjugate 1 (4 x 10⁻⁸ M) upon complexation with PCBM (0 – 1.4 x 10⁻⁵ M) with photoexcitation at 425 nm in toluene at room temperature. (c, d) Repetition of fluorescence titration and data fitting under identical conditions to ascertain reproducibility. Red crosses represent a fit according to a 1:1 model (see Table S2, entries 4a and 4b).

Figure S17. Fluorescence spectra (a) and the emission intensity changes (b) of conjugate 1 (4 x 10⁻⁸ M) upon complexation with C₅₉N-DPS (0 – 1.4 x 10⁻⁵ M) with photoexcitation at 425 nm in toluene at room temperature. Red crosses represent a fit according to a 1:1 model (see Table S2, entry 5).
Figure S18. Fluorescence spectra (a) and the emission intensity changes (b) of conjugate 1 (1 x 10^{-7} M) upon complexation with (C_{60})_2 (0 – 2.7 x 10^{-6} M) with photoexcitation at 425 nm in toluene at room temperature. Red crosses represent a fit according to a 1:1 and 2:1 model (see Table S2, entry 6).

Table S2. Summary of the fluorescence intensity quenched reaching the endpoint in the titration experiments and the observed binding constants

<table>
<thead>
<tr>
<th>Entry</th>
<th>Fullerene</th>
<th>Fluorescence quenched</th>
<th>$K_a$ (M^{-1})</th>
<th>Error (M^{-1})</th>
<th>Data Fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C_{60}</td>
<td>81.4 %</td>
<td>$1.6 \times 10^{-6}$</td>
<td>$\pm 0.1 \times 10^{-6}$</td>
<td>1:1 model</td>
</tr>
<tr>
<td>2</td>
<td>C_{60}</td>
<td></td>
<td>$K_{A1} = 1.7 \times 10^{5}$ (1:1)</td>
<td>$\pm 0.4 \times 10^{-4}$</td>
<td>1:1, 2:1 and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_{A2} = 1.0 \times 10^{3}$ (2:1)</td>
<td>$\pm 0.6 \times 10^{-3}$</td>
<td>1:2 model</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_{A3} = 1.0 \times 10^{3}$ (2:1)</td>
<td>$\pm 0.7 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C_{70}</td>
<td>81.6 %</td>
<td>$2.6 \times 10^{-5}$</td>
<td>$\pm 0.4 \times 10^{-4}$</td>
<td>1:1 model</td>
</tr>
<tr>
<td>4a</td>
<td>PCBM</td>
<td>70.0 %</td>
<td>$3.7 \times 10^{-5}$</td>
<td>$\pm 0.1 \times 10^{-5}$</td>
<td>1:1 model</td>
</tr>
<tr>
<td>4b</td>
<td>PCBM</td>
<td>70.3 %</td>
<td>$3.8 \times 10^{-5}$</td>
<td>$\pm 0.1 \times 10^{-5}$</td>
<td>1:1 model</td>
</tr>
<tr>
<td>5</td>
<td>C_{60}-N-DPS</td>
<td>80.5 %</td>
<td>$4.8 \times 10^{-5}$</td>
<td>$\pm 0.1 \times 10^{-4}$</td>
<td>1:1 model</td>
</tr>
<tr>
<td>6</td>
<td>(C_{60})_2</td>
<td>87.0 %</td>
<td>$K_{A1} = 4.7 \times 10^{5}$ (1:1)</td>
<td>$\pm 0.1 \times 10^{5}$</td>
<td>1:1 and 2:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_{A2} = 1.9 \times 10^{5}$ (2:1)</td>
<td>$\pm 0.5 \times 10^{5}$</td>
<td></td>
</tr>
</tbody>
</table>

All fits were performed with HypSpec 2014 (error corresponds to goodness of fit). Equilibrium constants for 2:1 and 1:2 complexes are typically associated with relatively large uncertainties, which is not due to poor control of experimental conditions, but inherent to such systems, especially if $K_{A1}$ is larger than $K_{A2}$ and/or $K_{A3}$, see ref. S9.
6.4 Transient absorption spectra of 1→ fullerene complexes

Figure S19. Differential absorption changes in (a) the visible and in (b) the near-infrared obtained upon femtosecond pump-probe experiments (430 nm / 500 nJ) of 1→C60 (C1 = 1 x 10⁻⁵ M; C1C60 = 1 x 10⁻⁴ M) in benzonitrile at room temperature.

Figure S20. (a) Evolution associated spectra (visible and near-infrared) of ZnP second singlet excited state (black), the ZnP first singlet excited state (red), and the charge separated state (blue), respectively at room temperature obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1→C60 (C1 = 1 x 10⁻⁵ M; C1C60 = 1 x 10⁻⁴ M) in benzonitrile. The insert shows the zoom in between 900 and 1200 nm. (b) Population-time profiles as obtained from Global and Target analysis, showing internal conversion from ZnP second singlet excited state (black) to the ZnP first singlet excited state (red), the charge separation from ZnP first singlet excited state and the charge recombination from the charge separated state (blue).
Figure S21. (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump probe experiments at room temperature (430 nm / 500 nJ) of $1\rightarrow C_{60}$ ($C_{f1} = 1 \times 10^{-5}$ M; $C_{C_{60}} = 1 \times 10^{-4}$ M) in benzonitrile with time delays between 0.001 and 100 µs – see Figure legend for details – at room temperature. (b) Time–absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C$_{60}$ radical anion at 1100 nm (black) and the ZnP radical cation at 630 nm (red) to illustrate the charge recombination with a rate constant of $2.3 \times 10^{8}$ s$^{-1}$.

Figure S22. (a) Evolution associated spectra (visible and near-infrared) of charge separated state (black) and the ZnP triplet excited state (red) stems from the free 1, respectively at room temperature obtained upon nanosecond pump probe experiments (430 nm / 500 nJ) of $1\rightarrow C_{60}$ ($C_{f1} = 1 \times 10^{-5}$ M; $C_{C_{60}} = 1 \times 10^{-4}$ M) in benzonitrile. (b) Population-time profiles as obtained from Global and Target analysis, showing charge recombination from charge separated state (black) and the internal conversion from the triplet excited state of free 1 (red).
Figure S23. (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1→C60 (C_i = 1 x 10^-5 M; C_C60 = 1 x 10^-4 M) in toluene with time delays of 1.5, 5, and 240 ps correlating with the absorption spectra of the ZnP second singlet excited state, the ZnP first singlet excited state, and the charge separated state, respectively, at room temperature. The insert shows the zoom in between 900 and 1200 nm. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C60 radical anion at 1080 nm (black) and the ZnP radical cation at 630 nm (red) to illustrate the internal conversion, the charge separation, and the charge recombination with rate constants of 1.1 x 10^{12}, 2.1 x 10^{10}, and 8.5 x 10^{8} s^{-1}.

Figure S24. (a) Evolution associated spectra (visible and near-infrared) of ZnP second singlet excited state (black), the ZnP first singlet excited state (red), and the charge separated state (blue), respectively at room temperature obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1→C60 (C_i = 1 x 10^-5 M; C_C60 = 1 x 10^-4 M) in toluene. The insert shows the zoom in between 900 and 1200 nm. (b) Population-time profiles as obtained from Global and Target analysis, showing internal conversion from ZnP second singlet excited state (black) to the ZnP first singlet excited state (red), the charge separation from ZnP first singlet excited state and the charge recombination from the charge separated state (blue).
**Figure S25.** (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump probe experiments at room temperature (430 nm / 500 nJ) of 1$\rightarrow$C$_{60}$ ($C_{(1)}$ = $1 \times 10^{-5}$ M; $C_{(C_{60})}$ = $1 \times 10^{-4}$ M) in toluene with time delays between 0.001 and 100 μs — see Figure legend for details — at room temperature. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C$_{60}$ radical anion at 1080 nm (black), the ZnP radical cation at 630 nm (red), and the C$_{60}$ triplet excited state at 750 nm (blue) to illustrate the charge recombination and recovery of the ground state with rate constants of $7.6 \times 10^8$ and $7.3 \times 10^4$ s$^{-1}$.

**Figure S26.** (a) Evolution associated spectra (visible and near-infrared) of charge separated state (black), the C$_{60}$ triplet excited state (red) and the ZnP triplet excited state (blue) stems from the free 1, respectively at room temperature obtained upon nanosecond pump probe experiments (430 nm / 500 nJ) of 1$\rightarrow$C$_{60}$ ($C_{(1)}$ = $1 \times 10^{-5}$ M; $C_{(C_{60})}$ = $1 \times 10^{-4}$ M) in toluene. (b) Population-time profiles as obtained from Global and Target analysis, showing charge recombination from charge separated state (black) to the C$_{60}$ triplet excited state (red) and the internal conversion from triplet excited state of free 1 (blue).
Figure S27. Differential absorption changes in (a) the visible and in (b) the near-infrared obtained upon femtosecond pump-probe experiments (430 nm / 500 nJ) of 1$\cdots$C$_{70}$ ($C_{(i)} = 1 \times 10^{-5}$ M; $C_{(c70)} = 1 \times 10^{-4}$ M) in benzonitrile at room temperature.

Figure S28. (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump-probe experiments (430 nm / 500 nJ) of 1$\cdots$C$_{70}$ ($C_{(i)} = 1 \times 10^{-5}$ M; $C_{(c70)} = 1 \times 10^{-4}$ M) in benzonitrile with time delays of 2, 5, and 120 ps correlating with the absorption spectra of the ZnP second singlet excited state, the ZnP first singlet excited state, and the charge separated state, respectively, at room temperature. The insert shows the zoom in between 900 and 1500 nm. (b) Time- absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C$_{90}$ radical anion at 1380 nm (black) and the ZnP radical cation at 630 nm (red) to illustrate the internal conversion, the charge separation, and the charge recombination with rate constants of $1.2 \times 10^{12}$, $2.2 \times 10^{10}$, and $6.2 \times 10^{8}$ s$^{-1}$. 
**Figure S29.** (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump probe experiments at room temperature (430 nm / 500 nJ) of 1\(\rightarrow\)C\(_{70}\) (C\(_{1}\) = 1 \(\times\) 10\(^{-6}\) M; C\(_{C_{70}}\) = 1 \(\times\) 10\(^{-4}\) M) in benzonitrile with time delays between 0.001 and 100 \(\mu\)s – see Figure legend for details – at room temperature. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C\(_{70}\) radical anion at 1380 nm (black) and the ZnP radical cation at 630 nm (red) to illustrate the charge recombination with a rate constant of 2.5 \(\times\) 10\(^{9}\) s\(^{-1}\).

**Figure S30.** (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1\(\rightarrow\)C\(_{70}\) (C\(_{1}\) = 1 \(\times\) 10\(^{-6}\) M; C\(_{C_{70}}\) = 1 \(\times\) 10\(^{-4}\) M) in toluene with time delays of 2, 5, and 85 ps correlating with the absorption spectra of the ZnP second singlet excited state, the ZnP first singlet excited state, and the charge separated state, respectively, at room temperature. The insert shows the zoom in between 900 and 1500 nm. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C\(_{70}\) radical anion at 1380 nm (black) and the ZnP radical cation at 655 nm (red) to illustrate the internal conversion, the charge separation, and the charge recombination with rate constants of 1.4 \(\times\) 10\(^{12}\), 2.0 \(\times\) 10\(^{10}\), and 1.6 \(\times\) 10\(^{8}\) s\(^{-1}\).
Figure S31. (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump–probe experiments at room temperature (430 nm / 500 nJ) of 1→C70 (C(1) = 1 × 10^{-3} M; C_{C70} = 1 × 10^{-4} M) in toluene with time delays between 0.001 and 100 μs – see Figure legend for details – at room temperature. (b) Time–absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C70 radical anion at 1380 nm (black), the ZnP radical cation at 630 nm (red), and the C70 triplet excited state at 1000 nm (blue) to illustrate the charge recombination and recovery of the ground state with rate constants of 1.5 × 10^9 and 7.1 × 10^8 s^{-1}.

Figure S32. Differential absorption changes (a) in the visible and (b) in near-infrared obtained upon femtosecond pump-probe experiments (430 nm / 500 nJ) of 1→PCBM (C(1) = 1 × 10^{-6} M; C_{PCBM} = 1 × 10^{-8} M) in benzonitrile at room temperature.
Figure S33. (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1:PCBM (C(1) = 1 × 10^{-3} M; C(PCBM) = 1 × 10^{-4} M) in benzonitrile with time delays of 2, 5, and 200 ps correlating with the absorption spectra of the ZnP second singlet excited state, the ZnP first singlet excited state, and the charge separated state, respectively, at room temperature. The insert shows the zoom in between 900 and 1200 nm. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the PCBM radical anion at 1045 nm (black) and the ZnP radical cation at 675 nm (red) to illustrate the internal conversion, the charge separation, and the charge recombination with rate constants of 1.0 × 10^{12}, 1.8 × 10^{10}, and 3.1 × 10^{8} s^{-1}.

Figure S34. (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump probe experiments at room temperature (430 nm / 500 nJ) of 1:PCBM (C(1) = 1 × 10^{-5} M; C(PCBM) = 1 × 10^{-4} M) in benzonitrile with time delays between 0.001 and 100 µs – see Figure legend for details – at room temperature. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the PCBM radical anion at 1010 nm (black) and the ZnP radical cation at 630 nm (red) to illustrate the charge recombination with a rate constant of 3.0 × 10^{8} s^{-1}.
Figure S35. (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1-PBCM (C(_t) = 1 \times 10^{-5} M; C(PCBM) = 1 \times 10^{-4} M) in toluene with time delays of 2, 5, and 200 ps correlating with the absorption spectra of the ZnP second singlet excited state, the ZnP first singlet excited state, and the charge separated state, respectively, at room temperature. The insert shows the zoom in between 900 and 1200 nm. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the PCBM radical anion at 1045 nm (black) and the ZnP radical cation at 630 nm (red) to illustrate the internal conversion, the charge separation, and the charge recombination with rate constants of 1.1 \times 10^{10}, 2.0 \times 10^{10}, and 7.6 \times 10^{9} \text{s}^{-1}.

Figure S36. (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump probe experiments at room temperature (430 nm / 500 nJ) of 1-PBCM (C(_t) = 1 \times 10^{-5} M; C(PCBM) = 1 \times 10^{-4} M) in toluene with time delays between 0.001 and 100 \mu s – see Figure legend for details – at room temperature. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the PCBM radical anion at 1010 nm (black), the ZnP radical cation at 615 nm (red), and the PCBM triplet excited state at 730 nm (blue) to illustrate the charge recombination and recovery of the ground state with rate constants of 6.3 \times 10^{5} and 4.5 \times 10^{4} \text{s}^{-1}.
Figure S37. Differential absorption changes (a) in the visible and (b) in the near-infrared obtained upon femtosecond pump-probe experiments (430 nm / 500 nJ) of 1→C_{S9}N-DPS (C_{(1)} = 2 × 10^{-5} M; C_{(C_{S9}N-DPS)} = 2 × 10^{-5} M) in benzonitrile at room temperature.

Figure S38. (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1→C_{S9}N-DPS (C_{(1)} = 2 × 10^{-5} M; C_{(C_{S9}N-DPS)} = 2 × 10^{-5} M) in benzonitrile with time delays of 2, 10, and 200 ps correlating with the absorption spectra of the ZnP second singlet excited state, the ZnP first singlet excited state, and the charge separated state, respectively, at room temperature. The insert shows the zoom in between 900 and 1200 nm. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C_{S9}N-DPS radical anion at 1050 nm (black) and the ZnP radical cation at 620 nm (red) to illustrate the internal conversion, the charge separation, and the charge recombination with rate constants of 3.6 × 10^{11}, 8.3 × 10^{5}, and 8.9 × 10^{5} s^{-1}. 

41
Figure S39. (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump probe experiments at room temperature (430 nm / 500 nJ) of 1:1C_{60}N-DPS (C_{11} = 2 \times 10^{-6} \text{ M};
C_{(C_{60}N-DPS)} = 2 \times 10^{-5} \text{ M}) in benzonitrile with time delays between 0.001 and 100 \mu s – see Figure legend for details – at room temperature. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C_{60}N-DPS radical anion at 1000 nm (black) and the ZnP radical cation at 608 nm (red) to illustrate the charge recombination with a rate constant of 2.9 \times 10^5 \text{ s}^{-1}.

Figure S40. (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1:1C_{60}N-DPS (C_{11} = 2 \times 10^{-6} \text{ M};
C_{(C_{60}N-DPS)} = 2 \times 10^{-5} \text{ M}) in toluene with time delays of 2, 8, and 90 ps correlating with the absorption spectra of the ZnP second singlet excited state, the ZnP first singlet excited state, and the charge separated state, respectively, at room temperature. The insert shows the zoom in between 900 and 1200 nm. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C_{60}N-DPS radical anion at 1050 nm (black) and the ZnP radical cation at 630 nm (red) to illustrate the internal conversion, the charge separation, and the charge recombination with rate constants of 6.7 \times 10^{11}, 8.4 \times 10^8, and 1.0 \times 10^9 \text{ s}^{-1}.
**Figure S41.** (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump-probe experiments at room temperature (430 nm / 500 nJ) of $1 \rightleftharpoons \text{C}_{60}$N-DPS ($C_{111} = 2 \times 10^{-5}$ M; $C_{(\text{C}_{60}N-\text{DPS})} = 2 \times 10^{-5}$ M) in toluene with time delays between 0.001 and 100 μs – see Figure legend for details – at room temperature. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C$_{60}$N-DPS radical anion at 1010 nm (black), the ZnP radical cation at 630 nm (red), and the C$_{60}$N-DPS triplet excited state at 750 nm (blue) to illustrate the charge recombination and recovery of the ground state with rate constants of $9.8 \times 10^3$ and $7.2 \times 10^4$ s$^{-1}$.

**Figure S42.** Differential absorption changes (a) in the visible and (b) in the near-infrared obtained upon femtosecond pump-probe experiments (430 nm / 500 nJ) of $1 \rightleftharpoons (\text{C}_{60})_2 \rightleftharpoons 1$ ($C_{111} = 2 \times 10^{-4}$ M; $C_{(\text{C}_{60})_2} = 1 \times 10^{-4}$ M) in benzonitrile at room temperature.
**Figure S43.** (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1×(C60)2 < 1 (C11 = 2 × 10^{-4} M; C_{(C60)2} = 1 × 10^{-4} M) in benzonitrile with time delays of 2, 10, and 200 ps correlating with the absorption spectra of the ZnP second singlet excited state, the ZnP first singlet excited state, and the charge separated state, respectively, at room temperature. The inset shows the zoom in between 900 and 1200 nm. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the (C60)2 radical anion at 1060 nm (black) and the ZnP radical cation at 612 nm (red) to illustrate the internal conversion, the charge separation, and the charge recombination with rate constants of 8.7 × 10^{11}, 1.1 × 10^{10}, and 4.8 × 10^{8} s^{-1}.

**Figure S44.** (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump probe experiments at room temperature (430 nm / 500 nJ) of 1×(C60)2 < 1 (C11 = 2 × 10^{-4} M; C_{(C60)2} = 1 × 10^{-4} M) in benzonitrile with time delays between 0.001 and 100 μs – see Figure legend for details – at room temperature. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the (C60)2 radical anion at 1010 nm (black) and the ZnP radical cation at 615 nm (red) to illustrate the charge recombination with a rate constant of 2.3 × 10^{5} s^{-1}.
Figure S45. (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1→(C_{60})_{2}→1 (C_{t}) = 1 × 10^{-3} M; C_{(C_{60})_{2}} = 1 × 10^{-4} M) in toluene with time delays of 1, 5, and 100 ps correlating with the absorption spectra of the ZnP second singlet excited state, the ZnP first singlet excited state, and the charge separated state, respectively, at room temperature. The insert shows the zoom in between 900 and 1200 nm. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the (C_{60})_{2} radical anion at 1040 nm (black) and the ZnP radical cation at 630 nm (red) to illustrate the internal conversion, the charge separation, and the charge recombination with rate constants of 8.0 × 10^{11}, 9.6 × 10^{9}, and 4.9 × 10^{8} s^{-1}.

Figure S46. (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump probe experiments at room temperature (430 nm / 500 nJ) of 1→(C_{60})_{2}→1 (C_{t}) = 2 × 10^{-4} M; C_{(C_{60})_{2}} = 1 × 10^{-4} M) in toluene with time delays between 0.001 and 100 μs – see Figure legend for details – at room temperature. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the (C_{60})_{2} radical anion at 1010 nm (black), the ZnP radical cation at 615 nm (red), and the (C_{60})_{2} triplet excited state at 750 nm (blue) to illustrate the charge recombination and recovery of the ground state with rate constants of 3.0 × 10^{6} and 1.7 × 10^{6} s^{-1}.
Figure S47. Differential absorption changes (a) in the visible and (b) in the near-infrared obtained upon femtosecond pump-probe experiments (430 nm / 500 nJ) of 1→(C₆₀)₂ (C₁ = 2 × 10⁻⁶ M; C(C₆₀O₂) = 1 × 10⁻⁴ M) in benzonitrile at room temperature.

Figure S48. (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1→(C₆₀)₂ (C₁ = 2 × 10⁻⁶ M; C(C₆₀O₂) = 1 × 10⁻⁴ M) in benzonitrile with time delays of 2, 10, and 200 ps correlating with the absorption spectra of the ZnP second singlet excited state, the ZnP first singlet excited state, and the charge separated state, respectively, at room temperature. The insert shows the zoom in between 900 and 1200 nm. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the (C₆₀)₂ radical anion at 1050 nm (black) and the ZnP radical cation at 620 nm (red) to illustrate the internal conversion, the two charge separations, and the first charge recombination with rate constants of 1.1 x 10¹², 2.3 x 10¹¹, 8.4 x 10⁸, and 4.0 x 10⁶ s⁻¹.
Figure S49. (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump probe experiments at room temperature (430 nm / 500 nJ) of 1≥(C₆H₅)₂ (C₁), = 2 x 10⁻⁵ M; C₅(C₆H₅)₂ = 1 x 10⁻⁴ M) in benzonitrile with time delays between 0.001 and 100 µs – see Figure legend for details – at room temperature. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the (C₆H₅)₂ radical anion at 1020 nm (black) and the ZnP radical cation at 615 nm (red) to illustrate the two charge recombinations with rate constants of 3.9 x 10⁶ and 8.7 x 10⁷ s⁻¹.

Figure S50. (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (430 nm / 500 nJ) of 1≥(C₆H₅)₂ (C₁), = 2 x 10⁻⁵ M; C₅(C₆H₅)₂ = 1 x 10⁻⁴ M) in toluene with time delays of 2, 5, and 100 ps correlating with the absorption spectra of the ZnP second singlet excited state, the ZnP first singlet excited state, and the charge separated state, respectively, at room temperature. The insert shows the zoom in between 900 and 1200 nm. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the (C₆H₅)₂ radical anion at 1020 nm (black) and the ZnP radical cation at 630 nm (red) to illustrate the internal conversion, the two charge separations, and the first charge recombination with rate constants of 2.0 x 10¹², 7.6 x 10¹⁰, 1.0 x 10¹⁰ and 3.7 x 10⁸ s⁻¹.
Figure S51. (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond pump probe experiments at room temperature (430 nm / 500 nJ) of 1≠C60 (C60 = 2 × 10⁻⁷ M; C(C60) = 1 × 10⁻⁴ M) in toluene with time delays between 0.001 and 100 μs – see Figure legend for details – at room temperature. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the (C60)₂ radical anion at 1020 nm (black), the ZnP radical cation at 630 nm (red), and the (C60)₂ triplet excited state at 760 nm (blue) to illustrate the two charge recombinations and recovery of the ground state with rate constants of 2.1 × 10⁸, 8.8 × 10⁷ and 1.1 × 10⁶ s⁻¹.

Figure S52. Energy level diagram for 1≠C60 complexes. IC: internal conversion, CS: charge separation, CR: charge recombination, BN: benzonitrile.
**Table S3. Summary of charge separation and recombination rate constants in toluene and benzonitrile (BN).**

<table>
<thead>
<tr>
<th>Fullerene /porphyrin stoichiometry</th>
<th>$k_{cs}$ ($s^{-1}$)</th>
<th>$k_{cr}$ ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Toluene</td>
<td>BN</td>
</tr>
<tr>
<td>$C_{60}$</td>
<td>$2.1 \times 10^{10}$</td>
<td>$1.1 \times 10^{10}$</td>
</tr>
<tr>
<td>$C_{70}$</td>
<td>$2.0 \times 10^{10}$</td>
<td>$2.2 \times 10^{10}$</td>
</tr>
<tr>
<td>PCBM</td>
<td>$2.0 \times 10^{10}$</td>
<td>$1.8 \times 10^{10}$</td>
</tr>
<tr>
<td>$C_{60}$N-DPS</td>
<td>$8.4 \times 10^{6}$</td>
<td>$8.3 \times 10^{6}$</td>
</tr>
<tr>
<td>$(C_{60})_2$</td>
<td>$7.6 \times 10^{10}$</td>
<td>$2.3 \times 10^{11}$</td>
</tr>
<tr>
<td></td>
<td>$1.0 \times 10^{10}$</td>
<td>$8.4 \times 10^{9}$</td>
</tr>
<tr>
<td></td>
<td>$9.6 \times 10^{6}$</td>
<td>$1.1 \times 10^{10}$</td>
</tr>
</tbody>
</table>

*a*: under these conditions, the mixture consists of roughly 92% of the 1:1 complex and 8% of the 2:1 complex.

*b*: under these conditions, the mixture consists of roughly 5% of the 1:1 complex and 90% of the 2:1 complex (plus 5% free 1).
7. NMR Spectra

$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S2

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S2
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S3

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S3
SUPPORTING INFORMATION

$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S5

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S5
SUPPORTING INFORMATION

$^{1}H$ NMR (400 MHz, 298 K, CDCl$_3$) of 2

$^{13}C$ NMR (100 MHz, 298 K, CDCl$_3$) of 2
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S6

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S6
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S8

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S8
**SUPPORTING INFORMATION**

$^1$H NMR (400 MHz, 298 K, CDCl₃) of 3

$^{13}$C NMR (100 MHz, 298 K, CDCl₃) of 3
$^{1}H$ NMR (400 MHz, 298 K, CDCl$_3$) of S9

$^{13}C$ NMR (100 MHz, 298 K, CDCl$_3$) of S9
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S10

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S10
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S11

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S11
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S12

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S12
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 1

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of 1
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of DPS-$C_{60}$N

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$/CS$_2$ 2:1) of DPS-$C_{60}$N
8. References

S1) Hashiguchi, M.; Inada, H.; Matsuo, Y. Carbon, 2013, 61, 418-422.
3.3. Highly Strained, Radially π-Conjugated Porphyrinylene Nanohoops

Youzhi Xu, Sebastian Gsanger, Martin B. Minameyer, Inhar Imaz, Daniel Maspoch, Oleksandr Shyshov, Fabian Schwer, Xavi Ribas, Thomas Drewello, Bernd Meyer,* Max von Delius.*

*J. Am. Chem. Soc. 2019, 141, 18500–18507. (Front cover)

Reproduced with permission of the American Chemical Society, copyright (2018).

Abstract:

Small π-conjugated nanohoops are difficult to prepare, but offer an excellent platform for studying the interplay between strain and optoelectronic properties and increasingly, these shape-persistent macrocycles find uses in host-guest chemistry and self-assembly. Here, we report the synthesis of a new family of radially π-conjugated porphyrinylene/phenylene nanohoops. The strain energy in the smallest nanohoop [2]CPT is approximately 54 kcal mol$^{-1}$, which results in a narrowed HOMO-LUMO gap and a red shift in the visible part of the absorption spectrum. Due to its high degree of preorganization and a diameter of ca. 13 Å, [2]CPT was found to accommodate C$_{60}$ with a binding affinity exceeding $10^8$ M$^{-1}$ despite off-center binding (X-Ray crystallography). Moreover, the π-extended nanohoops [2]CPTN, [3]CPTN and [3]CPTA (N for naphthyl; A for anthracenyl) have been prepared using the same strategy, and [2]CPTN has been shown to bind C$_{70}$ five times more strongly than [2]CPT. Our failed synthesis of [2]CPTA represents an interesting negative result, because here the sum of strain and aromatization energies is no longer favourable in the final reaction step. These results indicate that forcing ring strain onto organic semiconductors is a viable strategy to fundamentally influence both optoelectronic and supramolecular properties.

Comments on own contributions:

This project took almost one and half years from the first synthesis to manuscript
submission. I had the original idea andProf. Max von Delius provided valuable
guidance. 95% of experiments were carried out by myself, which includes the
synthesis of main building blocks porphyrin moieties, syn-cyclohexadiene moieties,
all the supramolecular chemistry studies and all binding constant data fitting of
[2]CPT and [2]CPTN, the optimization of synthetic approaches, purification and
characterization of all synthetic products, as well as the single crystal growing of
[2]CPT and [2]CPT\(\supseteq\)C\(_{60}\). All the NMR measurements, DNMR analysis, UV-vis
absorption spectra, cyclic voltammetry and differential pulse voltammetry were
carried out by myself. DFT calculations were carried out by Sebastian Gsänger.
X-ray single crystal structural analyses were carried out by Inhar Imaz, Daniel
Maspoch and Oleksandr Shyshov. Energy-dependent fragmentation experiments
were carried out by Martin Minameyer. Furthermore, I participated in the
manuscript preparation and wrote the supporting information.
Highly Strained, Radially π-Conjugated Porphyrinylene Nanohoops

Youzhi Xu,\textsuperscript{1} Sebastian Gsänger,\textsuperscript{2} Martin B. Minameyer,\textsuperscript{8} Inhar Imaz,\textsuperscript{7} Daniel Maspoch,\textsuperscript{3,7} Oleksandr Shyshov,\textsuperscript{2} Fabian Schwer,\textsuperscript{7} Xavi Ribas,\textsuperscript{1} Thomas Drewello,\textsuperscript{8} Bernd Meyer,\textsuperscript{2,4} and Max von Delius\textsuperscript{5,6,7}

\textsuperscript{1}Institute of Organic Chemistry, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany
\textsuperscript{2}Interdisciplinary Center for Molecular Materials (ICMM) and Computer- Chemistry-Center (CCC), Friedrich-Alexander University Erlangen-Nürnberg, Nägelsbachstrasse 25, 91052 Erlangen, Germany
\textsuperscript{3}Department of Chemistry and Pharmacy, Friedrich-Alexander University Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany
\textsuperscript{4}Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and the Barcelona Institute of Science and Technology, Campus UAB, 08193 Bellaterra, Barcelona, Catalonia, Spain
\textsuperscript{5}ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain
\textsuperscript{6}Institut de Química Computacional i Catalisi and Departament de Quimica, Universitat de Girona, Campus Montilivi, 17003 Girona, Catalonia, Spain

Supporting Information

ABSTRACT: Small π-conjugated nanohoops are difficult to prepare, but offer an excellent platform for studying the interplay between strain and optoelectronic properties, and, increasingly, these shape-persistent macrocycles find uses in host–guest chemistry and self-assembly. We report the synthesis of a new family of radially π-conjugated porphyrinylene/phenylene nanohoops. The strain energy in the smallest nanohoop \([2]\text{CPT}\) is approximately 54 kcal mol\(^{-1}\), which results in a narrowed HOMO–LUMO gap and a red shift in the visible part of the absorption spectrum. Because of its high degree of preorganization and a diameter of ca. 13 Å, \([2]\text{CPT}\) was found to accommodate \(\text{C}_{60}\) with a binding affinity exceeding \(10^9\) M\(^{-1}\) despite the fullerene not fully entering the cavity of the host (X-ray crystallography). Moreover, the π-extended nanohoops \([2]\text{CPTN}, [3]\text{CPTN}, and [3]\text{CPTA} (N for 1,4-naphthyl; A for 9,10-anthracenyl) have been prepared using the same strategy, and [2]CPTN has been shown to bind \(\text{C}_{60}\) 5 times more strongly than \([2]\text{CPT}\). Our failed synthesis of [2]CPTA highlights a limitation of the experimental approach most commonly used to prepare strained nanohoops, because in this particular case the sum of aromatization energies no longer outweighs the buildup of ring strain in the final reaction step (DFT calculations). These results indicate that forcing ring strain onto organic semiconductors is a viable strategy to fundamentally influence both optoelectronic and supramolecular properties.

INTRODUCTION

Carbon-rich “nanohoops” exhibiting radial π-conjugation (Figure 1), such as the \([n]\) cycloparaphenylene, have attracted much attention recently due to their challenging synthesis, intriguing optoelectronic properties, and vast potential in supramolecular chemistry.\(^1\) Macrocycles containing porphyrins have been pursued for several decades,\(^2\) leading to important advances in host–guest chemistry\(^3\) and catalysis.\(^4\) Most reported compounds, however, do not exhibit an uninterrupted conjugation pathway or significant ring strain. An exception regarding conjugation is Anderson’s work on large porphyrin nanorings,\(^5,6\) which has produced new concepts of template synthesis\(^7\) and spectacular insights into global (anti)aromaticity\(^8\) as well as charge delocalization.\(^9\) The smallest nanoring synthesized by Anderson features five porphyrin moieties linked by butadiyne spacers that appear to bear most of the moderate ring strain.\(^7\) Osaka’s porphyrinylene/phenylene hybrids featuring three to six porphyrins within the macrocycle are subject to significant strain energies (up to 49 kcal mol\(^{-1}\)).\(^7\) However, with a diameter of 16 Å, the smallest nanohoop of this series is still too large to effectively accommodate fullerenes.\(^8\)

We wondered whether a smaller variant of Osaka’s macrocycles would be accessible based on recent progress in the synthesis of highly strained macrocycles.\(^9\) Specifically, we...
anticipated that [2]cyclo-5,15-porphyrinylene-4,4',4'-terphenyl ([2]CPT) would have a diameter similar to [10]-cycloparaphenylenec (10)CPP, which has recently been shown to be an excellent host for C80, enabling studies on noncovalent charge transfer and the synthesis of [2]- rotaxanes. Herein, we report that [2]CPT as highly strained porphyrinylene/phenylene nanohoop can be synthesized in seven linear steps. Although the calculated ring strain of 54 kcal mol⁻¹ in this compound is not as high as in the smallest CPP ([5]CPP: 119 kcal mol⁻¹), we observed a strong influence of strain on the absorption, and in contrast to the CPPs the bathochromic shift affects the visible part of the spectrum. We also prepared several π-extended analogues of [n]CPT and found that members of the [2]CPT nanohoop family are extremely effective receptors for C80 and C70 (e.g., Figure 1).

RESULTS AND DISCUSSION

Synthesis of Precursors. The key steps in the synthesis of [n]CPT are shown in Figure 2a. Diboronate 1 and meso-porphyrin 2 are accessible on a multigram scale in four and three linear steps, respectively. Under standard conditions for Suzuki–Miyaura cross-coupling (125 °C, toluene, Cs₂CO₃), we found that the crucial ring-closing step only gave minuscule quantities of the desired small nanohoop [2]CPT-OTES. In a parameter optimization study for this reaction step, we discovered that the addition of pyridine (100 equiv) led to a significantly increased yield of the desired macrocycle and an unexpected ratio between [2]CPT-OTES and [3]CPT-OTES of ca. 2:1. We initially attributed this effect to the binding of pyridine to the nickel center, but, on the basis of the Ni–Ni distance of 7.4 Å in the solid-state structure of [2]CPT-OH (vide infra) and the highly successful use of pyrazine in preliminary experiments, we believe that a π–π template effect between the electron-deficient heteroarene and the electron-rich porphyrin may be more likely. As shown in Figure 2b, compound [2]CPT-OTES exhibits a broad peak in the 1H NMR spectrum for the signal corresponding to the tert-butyl groups, indicating that the rotation of the meso-aryl in [2]CPT-OTES is relatively slow on the NMR timescale. Variable-temperature (VT) NMR spectroscopy and line-shape analysis allowed us to determine the kinetic parameters (e.g., ΔG°₂⁰ = 14.1 kcal mol⁻¹, Figures S3–S5) for this process.

which we attribute to hindered di(tert-butyl)phenyl rotation due to steric clash between the ortho-aryl protons and the pyrrole protons.

The isolated compounds [n]CPT-OTES underwent a smooth transformation into the corresponding alcohols [n]CPT-OH upon addition of a suitable fluoride reagent. Typically, we converted these intermediates immediately into the target compounds, but in one instance we attempted to purify compound [2]CPT-OH and were able to grow single crystals suitable for X-ray crystallography. The solid-state structure (Figure 2a) of this compound reveals a rectangular (slightly oval) shape with a Ni−Ni distance of 7.4 Å and two porphyrin macrocycles with a “ruffle” geometry and an offset angle of 80°, which likely helps in avoiding an unfavorable interaction between two tert-butyl groups. Because this compound could be of interest as a bimetallic catalyst, it is worth noting that in this solid-state structure the cavity is populated by (masked) solvent molecules and that DFT studies point toward negligible ring strain (Table 1), as well as the ability to adopt a variety of conformations, including some with small cavity volumes (Figure S40).

Nanohoop Synthesis and Characterization. We found that the final aromatization step (Figure 2a) required rigorously optimized reaction conditions, which is presumably a result of the large amount of ring strain generated and the risk of porphyrin degradation. Only when we used the mild reagent H2SnCl4,11c we were able to isolate compounds [2]CPT and [3]CPT in reasonable three-step yields of 10% and 6%, respectively. With pure compounds [2]CPT-OH, [2]CPT, and [3]CPT in hand, we proceeded to compare key properties by NMR and UV–vis spectroscopy, cyclic voltammetry, and DFT calculations (Table 1). The 1H NMR spectra (Figure 2b) indicate that, in contrast to the rectangular precursor (vide supra), the rotation of di(tert-butyl)phenyl groups is not hindered at room temperature in both [2]CPT and [3]CPT, which is likely a consequence of the strain-induced conical arrangement of these groups. Other notable features in the NMR spectra include significant differences in the chemical shifts of aromatic protons (red in Figure 2b) and two sets of signals for pyrrole protons (“F” and “E”), pointing toward a “ruffle” rather than “saddle” geometry of the porphyrin moieties, which are bent out-of-plane by ca. 35° (C−C−Ni−C). A VT-NMR study further revealed that the barrier for the meso-aryl C−C bond rotation decreases with increasing nonplanarity of the porphyrin (trend for ΔG°calc [2]CPT-OTES > [3]CPT > [2]CPT; Figures S4, S9, and S12).

A solid-state structure of [2]CPT could be obtained by synchrotron X-ray diffraction (Figure 3). Single crystals of [2]CPT were prepared by slow evaporation of a solution in CH3CN and CHCl3 (1:1). As shown in Figure 3, [2]CPT has an oval shape (approximately C3 symmetry) with an average diameter of ca. 13.2 Å. The average torsional angle (θ, Figure 3e, bottom) between neighboring pyrene units is 41°, and the phenylene-phenylene bond lengths as well as phenylene-porphyrin bond lengths are shortened by ca. 0.05 Å upon reductive aromatization, suggesting radial conjugation similar to that of the larger [n]CPPs.10 Furthermore, excessive ring strain seems to be avoided, at least in the solid state, by placing the two face-to-face porphyrins out of a horizontal line. The packing diagram reveals evidence for intermolecular π-π interactions between the terphenyl bridges (3.5 Å, Figure 3c), which leads to “sideways” stacking of the molecules. In the third dimension, this packing leads to uniform pores with “walls” composed

*Homodesmotic DFT calculations (B3LYP/6-31G(d,p); 1,2-EDZP). Measured in CH2Cl2; CH3CN, Trisolv favorite (0.1 M), 295 K, γ = 100 mV s-1, vs Fe/C. Set Fe/C/Fe EFe/Fe = −5.1 eV. Calculated by the difference of the values of E(EHOMO) and E(EVOC).
nearly exclusively of sp^3-hybridized carbon atoms, which could be of interest for future porous energy storage materials.\textsuperscript{21}

**Optoelectronic Properties.** While the unstrained precursor [2]CPT-OH exhibits an absorption spectrum typical for tetraaryl nickel porphyrins (Table 1), we observed significant red shifts for both the Soret (30 nm) and the Q (40 nm) bands for the smallest nanohoop [2]CPT when compared to the unstrained reference compound. These red shifts are more pronounced than those found in Osaka’s smallest nanohoop\textsuperscript{10} (Soret λ\textsubscript{max} with 435 nm is comparable to [3]CPT), which is likely a result of a larger deviation from planarity of the porphyrins. Of note, strain-induced red-shifts are limited to the emission spectra and the ultraviolet part of the spectrum for the related [n]CPPs.\textsuperscript{14} Interestingly, there is an inversion in the intensity of the Q bands of the most strained nanohoop [2]CPT. Compounds [3]CPT and [2]CPT were found to be essentially nonfluorescent, which is typical for nickel porphyrins.\textsuperscript{22} Data gathered independently by cyclic voltammetry (Figure S26) and DFT calculations (Figures S48–S52, including calculated UV–vis spectra) indicate that the observed bathochromic shifts in the absorption spectrum are due to a narrowing of the HOMO/LUMO gap with increasing ring strain. DFT calculations of the frontier molecular orbitals reveal that for both the HOMO and the LUMO the orbitals are delocalized over the entire ring, yet dominant on the porphyrin moieties (Figure 3d). These results suggest that the incorporation of a dye into a small nanohoop is a viable strategy to exert strain onto the dye and thus change its optoelectronic properties.\textsuperscript{23}

**Fullerene Complexation.** We next turned our attention to the inclusion of fullerene guests into the small nanohoop [2]CPT. As shown in Figure 2b, addition of 1 equiv of C\textsubscript{60} led to dramatic changes in all signal sets of the ^1H NMR spectrum as well as a splitting of the pyrrole signals. By means of UV–vis titrations in toluene (Figure 4a; carried out in triplicate), we were able to determine binding constants of ca. 3 × 10\textsuperscript{4} M\textsuperscript{−1} for C\textsubscript{60} and ca. 2 × 10\textsuperscript{5} M\textsuperscript{−1} for C\textsubscript{70}. It is worth noting that the strength of fullerene binding is so high that in the MALDI mass spectrum, where noncovalent interactions are typically broken during ionization, the signal for the radical cation of complex [2]CPT\textsuperscript{+}C\textsubscript{60} is of the same intensity as that for the parent compound [2]CPT (Figure 4b). MS/MS experiments revealed that the nanohoop carries the positive charge in the radical cations of the complexes [2]CPT\textsuperscript{+}C\textsubscript{60} (Figures S55 and S56). Collision-induced dissociation experiments at variable collision energies allowed direct comparison of gas-phase relative dissociation energies of fullerene complexes with a monomeric porphyrin (dissociation onset at E\textsubscript{onset} = 0.15 eV), [10]CPP (onset at E\textsubscript{on} = 0.49 eV), and [2]CPT, which in the gas phase binds the larger fullerene C\textsubscript{70} slightly more strongly than C\textsubscript{60} (onset at E\textsubscript{on} = 0.78 and 0.76 eV, respectively).

Single crystals of the [2]CPT\textsuperscript{+}C\textsubscript{60} complex were grown by slow diffusion of CH\textsubscript{2}CN into a mixture of CHCl\textsubscript{3} and 1,2-dichlorobenzene (1:1). The solid-state structure clearly shows that a complex between [2]CPT and C\textsubscript{60} with 1:1 stoichiometry is present. As shown in Figure 5a, the carboxylation of C\textsubscript{60} is clearly facilitated by convex–concave π–π interactions (3.4–3.7 Å) and induces the nanohoop to adopt a more spherical shape. The torsional angle between neighboring phenylene units decreases to 35° (average value), and the ring adopts a conical shape to allow for π–π interactions between terphenyl bridges and C\textsubscript{60}. According to the solid-state structure, the ^1H NMR data, and DFT calculations (Figure S41), the diameter of [2]CPT is slightly too small for a "perfect" (symmetric) encapsulation of C\textsubscript{60}, which results in “off-center” binding with an offset of 1.9 Å (X-ray). Nevertheless, the calculated deformation energy (upon binding of C\textsubscript{60}, see Table S12) is less than 1 kcal mol\textsuperscript{−1}, indicating that [2]CPT is an outstanding host for C\textsubscript{60}.

The structure of [2]CPT\textsuperscript{+}C\textsubscript{60} was studied using DFT calculations, because high-quality single crystals could not be obtained in this particular case. The calculations once more indicate that the fullerene cannot fully enter into the cavity with an offset distance of 2.3 Å, which, as expected, is larger than the corresponding offset for C\textsubscript{60} (Figure S41). This finding provides an evident opportunity to design related fullerene receptors with even higher binding affinities (vide infra). For both the [2]CPT\textsuperscript{+}C\textsubscript{60} and the [2]CPT\textsuperscript{+}C\textsubscript{70} complexes, the HOMO orbital is localized exclusively on porphyrin moieties, while the LUMO orbital is localized dominantly, but not exclusively, on the fullerene (Figures Sd, SS3, and SS4). Hence, the DFT calculations suggest that charge transfer plays a role in the noncovalent complexes, which is in agreement with the bathochromatic shifts observed during the host–guest titrations (Figure 4a).

**π-Extension of NanoHoops.** Several π-extended CPPs, which can be considered intermediate structures on the way...
Figure 5. X-ray crystal structure of [2]CPT@C60: (a) ORTEP drawing with 30% probability. (b) Top view with distances and dihedral angles labeled. (c) Packing in the unit cell. Hydrogen atoms are omitted for clarity. (d) Frontier molecular orbitals of [2]CPT@C60 calculated at the B3LYP/6-31G* level of theory (isovalue 0.018 au).


from CPPs to armchair carbon nanotubes, have been prepared in recent years.\textsuperscript{24-26} We wondered whether the inclusion of naphthalene or anthracene moieties would be possible within the [n]CPT architecture. To this end, we start our synthesis from commercially available α-naphthoquinone and anthraquinone to synthesize the diborane precursors on a multigram scale. Macrocyclic compounds [n]CPTN-OTES and [n]CPTA-OTES (n = 2, 3) were prepared successfully using the same Suzuki–Miyaura cross-coupling conditions with results comparable to those of the parent system. The porphyrin macrocycles could also be transformed smoothly into the corresponding alcohols [n]CPTN-OH and [n]CPTA-OH by treatment with tetrabutylammonium fluoride (TBAF). Strong deviations from the parent system were found in the final step of the synthesis. In case of the naphthyl system, we found that for the small-ring precursor [2]CPTN-OH the final aromatization reaction only proceeded at 70 °C and gave only 32% yield of [2]CPTN after 12 h, whereas the larger [3]CPTN-OH could be easily transformed into [3]CPTN in 82% yield at room temperature (6 h). In case of the anthracenyl system, we failed to convert the small-ring precursor [2]CPTA-OH into [2]CPTA (Figure S24) even at elevated temperature, which indicates that the aromatization energy no longer overcompensates the strain energy. This interpretation is not only in agreement with Clar’s “sexist” theory,\textsuperscript{27} but was corroborated by DFT calculations, which indeed show that there is a difference of about 20 kcal mol\textsuperscript{-1} (two moieties per ring) in the aromatization enthalpy gain between neighboring compounds in this series (Figure S6b). Hence, by moving from phenyl (reaction efficient at room temperature) to naphthyl (reaction inefficient at elevated temperature) to anthracenyl (reaction impossible), we seem to have probed the limitations of the aromatization versus strain-generation approach that is so commonly used in this field of research.\textsuperscript{28} Of note, we can rule out an electronic, and with some confidence also a steric, effect, because the larger precursor [3]CPTA-OH could be converted to [3]CPTA in nearly quantitative yield under mild conditions.

The absorption spectra of the two naphthyl-bridged nanohoops ([2]CPTN and [3]CPTN) are similar to the corresponding [n]CPT nanohoops, but the Soret-band and Q-band absorptions are slightly blue-shifted (Table 1 and Figure 6c). The [3]CPTA absorption maximum was further blue-shifted (428 nm, Table 1), but the most striking observation for this compound is the high molar absorption coefficient of the Soret band (ε = 6.2 × 10\textsuperscript{5} cm\textsuperscript{-1} M\textsuperscript{-1}), which significantly exceeds those determined for all other nanohoops. Differential-pulse voltammetry and cyclic voltammetry experiments of [n]CPTN and [3]CPTA (Figure S26) revealed that these nanohoops exhibit a slightly increased HOMO/LUMO gap when compared to their CPT analogues.\textsuperscript{29}

Depending on the rotation frequency of the phenyl–naphthyl C–C bonds, the π-extended nanohoops of type [n]CPTN can in principle exist as two different stereoisomers,
which is why we conducted an NMR study to shed light on this issue. The $^1$H NMR spectra of [2]CPTN and [3]CPTN showed only one set of signals at room temperature, indicating either fast rotation of the C–C bonds or the presence of only one stereoisomer. Conclusive evidence to this end was obtained by variable-temperature NMR (VT-NMR). The $t$-Bu group signal of [2]CPT, [2]CPTN, and [3]CPTN splits into two peaks at low temperature (ca. 240, 230, and 250 K, respectively), which we attribute to the slow rotation of the porphyrin–(tBu)$_2$phenyl C–C bond (see Figures S9, S16, S20, and S21 for VT-NMR spectra and Eyring analyses). Evidence for a restricted rotation of the naphthalene units within the nanohoop was not observed in the investigated temperature range (minimum temperature: 250 K).

To test the limits of fullerene affinity in these new nanohoop architectures, we studied the thermodynamics of [2]CPTNC$_{60}$fullerene complexes. UV–vis titrations revealed an association constant of 3.0 × 10$^8$ M$^{-1}$ (toluene) for [2]CPTN>C$_{60}$ (Figure S32), which is essentially identical to the association constant observed for the [2]CPT>C$_{60}$ complex. We propose that this unexpected result is due to the cancellation of two effects: π-extension indeed leads to a larger "contact area" and hence stronger association between fullerene and nanohoop, but is offset by a higher energy of deformation, which we determined to be ca. 7 kcal mol$^{-1}$ (DFT; Table S12). When the [2]CPTN>C$_{60}$ complex was studied in the same way, an increase of the binding constant (1.0 × 10$^7$ M$^{-1}$, toluene) by a factor of 5 was observed in comparison to the parent system (Figure 7c). Thanks to the large VUV surface of C$_{60}$ in this case, the increased interaction between C$_{60}$ and nanohoop outweighs the deformation of the ring (ca. 8 kcal mol$^{-1}$, DFT; Table S12).

**CONCLUSIONS**

We developed a concise synthesis of a series of strained porphyrin macrocycles, which due to their unique molecular design offer opportunities for uses in bimetallic catalysis and crystal engineering. The two nanohoops [2]CPT and [2]CPTN can be considered porphyrinogen equivalents to [10]CPP, albeit with ca. 100-fold increased affinity for fullerenes, which may prove useful for the regioselective synthesis or separation of fullerene bisadducts$^{69}$ and in photovoltaic devices.$^{50}$ We also observed unusual optical properties, most importantly, a strain-induced red-shift of absorption in the visible range of the spectrum, which may inspire further studies on the use of nanohoops for binding organic semiconductors$^{31}$ or molecular switches out-of-plane.$^{52}$

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b08584.

Synthesis and characterization data; details on mass spectrometry, variable-temperature NMR, UV–vis titrations, and theoretical calculations (PDF)


X-ray crystallographic data for [2]CPT (CIF)

X-ray crystallographic data for [2]CPT>C$_{60}$ (CIF)

**AUTHOR INFORMATION**

Corresponding Authors

*max.rondelius@uni-ulm.de

*bernd.meyer@fau.de

**ORCID**

Inhar Ilmaz: 0000-0002-0278-1141

Daniel Marschel: 0000-0001-3325-9161

Xavi Rubas: 0000-0002-2850-4409

Bernd Meyer: 0000-0002-3481-8009

Max von Delius: 0000-0003-1852-2969

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We are grateful for financial support from the Deutsche Forschungsgemeinschaft (DFG, project number 18249149-SF68953 "Synthetic Carbon Allotropes"), the University of Ulm, and FAU Erlangen-Nürnberg. I.M. thanks the Severo Ochoa Center of Excellence Program (ICCN2, Grant SEV-2017-0706), and X.R. is thankful for the ICREA-Academia award.

**REFERENCES**


Supporting Information

Highly Strained, Radially $\pi$-Conjugated Porphyrinylene Nano hoops

Youzhi Xu,¹ Sebastian Gutanger,¹ Martin B. Minameyer,¹ Inhar Imaz,² Daniel Maspooh,¹,² Oleksandr Shyshov,³ Fabian Schorer,¹ Xavi Ribas,⁴ Thomas Dreuschl,⁵ Bernd Meyer,⁵,⁺ and Max von Delius¹,⁺

¹Institute of Organic Chemistry, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany.
²Interdisciplinary Center for Molecular Materials (ICMM) and Computer-Chemistry-Center (CCC), Friedrich-Alexander University Erlangen-Nürnberg, Nägelsbachstrasse 25, 91052 Erlangen, Germany.
³Department of Chemistry and Pharmacy, Friedrich-Alexander University Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany.
⁴Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and the Barcelona Institute of Science and Technology, Campus UAB, 08193 Bellaterra, Barcelona, Catalonia, Spain.
⁺ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain.
⁵Institut de Química Computacional i Catalisi and Departament de Química, Universitat de Girona, Campus Montilivi, 17003 Girona, Catalonia, Spain.
Email: max.vondelius@uni-ulm.de
bernd.meyer@fau.de
Contents
1. General Experimental Section ................................................................. S3
2. Overview on Synthesis ........................................................................... S4
3. Synthetic Procedures and Characterization Data .................................... S5
  3.1 Synthesis of S2 .................................................................................. S5
  3.2 Synthesis of S4 .................................................................................. S6
  3.3 Synthesis of 1 ................................................................................. S7
  3.4 Synthesis of 2 ................................................................................. S8
  3.7 Synthesis of [3]CPT-OH ................................................................. S15
  3.8 Synthesis of [2]CPT ........................................................................ S17
  3.9 Synthesis of [3]CPT ........................................................................ S20
  3.10 Synthesis of S8 ........................................................................ S24
  3.11 Synthesis of S9 ........................................................................ S25
  3.12 Synthesis of S12 ........................................................................ S26
  3.16 Synthesis of [2]CPTN ................................................................. S31
  3.18 Synthesis of [n]CPTNA-OH ............................................................. S37
  3.19 Synthesis of [n]CPTNA ............................................................... S39
4. Redox Properties .................................................................................. S41
6. X-Ray Crystalllographic Details .......................................................... S48
7. DFT Calculations .................................................................................. S68
8. MS Study ............................................................................................ S86
9. NMR Spectra ....................................................................................... S89
10. References .......................................................................................... S106
1. General Experimental Section

Reagents and instruments

NMR spectra were recorded on a Bruker DRX 400 (\(^1\)H NMR: 400 MHz, \(^13\)C NMR: 100 MHz) or a Bruker AMX 500 (\(^1\)H NMR: 500 MHz, \(^13\)C NMR: 125 MHz) spectrometers at 298 K and referenced to the residual solvent peak (\(^1\)H: 7.26 ppm for CDCl\(_3\), 5.32 ppm for CD\(_2\)Cl\(_2\); \(^13\)C: 77.16 ppm for CDCl\(_3\), 53.84 ppm for CD\(_2\)Cl\(_2\)). Coupling constants (\(J\)) are denoted in Hz and chemical shifts (\(\delta\)) in ppm. High resolution MALDI mass spectra were obtained on Bruker micro TOF II and Bruker Maxis 4G or Bruker SolariX (HRMS-ESI\(^{-}\)-TOF, solvent: toluene or acetonitrile) instruments. Single-crystal diffraction analysis data were collected at \(-180^\circ\text{C}\) with a Rigaku XtaLAB P200 by using graphite monochromated Cu-K\(\alpha\) radiation.

All commercially available reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros Organics or TCI and were used without further purification. Anhydrous THF, anhydrous DMF and \(n\)-Butyl lithium (1.6 M in n-hexane and 2.5 M in n-hexane) were purchased from Sigma Aldrich. Molecular sieves were dried for 3 days at 150 \(^\circ\text{C}\) under reduced pressure (10\(^{-7}\) mbar) before use.
2. Overview on Synthesis

Scheme S1. Reaction conditions: (i) 4,4-Dimethoxy-2,5-cyclohexadien-1-one, n-BuLi, THF, -78 °C, MeOH, 85%; (ii) Imidazole, TESCl, DMF, RT, 12 h, 96%; (iii) 1-Chloro-4-bromobenzene, n-BuLi, THF, -78 °C, MeOH; (iv) Imidazole, TESCl, DMF, RT, 12 h, 93%; (v) Bis(pinacolato)diboron, Pd(OAc)$_2$, S-Phos, K$_2$PO$_4$, 1,4-dioxane, 90 °C, 48 h, 98%; (vi) Ni(OAc)$_2$·4H$_2$O, DMF, 140 °C, 10 h, 97%; (vii) NBS, pyridine, CHCl$_3$, 30 min, 95%; (viii) Pd(PPh$_3$)$_4$, Cs$_2$CO$_3$, pyridine, toluene, 125 °C, 12 h, 16%; (ix) TBDMS, THF, RT, 1 h, 98%; (x) H$_2$SO$_4$, THF, RT, 12 h, 62%; (xi) Pd(PPh$_3$)$_4$, Cs$_2$CO$_3$, 125 °C, toluene, 12 h; (xii) TBAF, THF, RT, 1 h, 8%; (two steps); (xiii) H$_2$SO$_4$, THF, RT, 12 h, 70%; (xiv) Quinone, n-BuLi, THF, -78 °C, MeOH; (xv) Imidazole, TESCl, DMF, 100 °C, 12 h; (xvi) Bis(pinacolato)diboron, Pd(OAc)$_2$, S-Phos, K$_2$PO$_4$, 1,4-dioxane, 90 °C, 48 h; (xvi) Pd(PPh$_3$)$_4$, Cs$_2$CO$_3$, pyridine, toluene, 125 °C, 12 h. TBAF, THF, RT, 1 h; (xvii) H$_2$SO$_4$, RT, 12 h, 82% (1:1JCPPTN). NaI, Na$_2$PO$_4$, AcOH, 100 °C, 6 h, 95% (1:1:1JCPPTA).
3. Synthetic Procedures and Characterization Data

3.1 Synthesis of S2

A 100 mL dry Schlenk flask was charged with 1-Chloro-4-bromobenzene (4.2 g, 22.0 mmol, 1.1 equiv) and 60 mL anhydrous THF. n-Butyllithium in n-hexane (8.8 mL, 2.5 mol/L, 22.0 mmol, 1.1 equiv) was added dropwise at -78 °C over 5 minutes under N2 atmosphere. The reaction mixture was stirred for 50 minutes, then 4,4-Dimethoxy-2,5-cyclohexadien-1-one (3.0 g, 20.0 mmol, 1.0 equiv) was added at -78 °C, and the reaction temperature was slowly raised to -50 °C. MeOH (10 mL) was added to quench the reaction at -50 °C and the mixture was allowed to warm to room temperature. The solvents were removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with DCM (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure. Purification by column chromatography (DCM/Et2O 5:1) afforded ketone S1 (3.8 g, 85% yield) as pale yellow solid.

A 50 mL dry Schlenk flask was charged with ketone S1 (2.2 g, 10 mmol, 1.0 equiv), Imidazole (816 mg, 12 mmol, 1.2 equiv) and 30 mL dry DMF. The Chlorotriethylsilane (2.0 mL, 12 mmol, 1.2 equiv) was slowly added to solution at room temperature, the reaction mixture was stirred for 12 hours. The solvent was removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with DCM (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure gave pure S2 (3.3 g, 98% yield) as light brown oil. Characterization data was consistent with previous reports.21
3.2 Synthesis of S4

A 100 mL dry Schlenk flask was charged with 1-Chloro-4-bromobenzene (2.1 g, 11.0 mmol, 1.1 equiv) and 60 mL anhydrous THF. n-Butyllithium in n-hexane (4.4 mL, 2.5 mol/L, 11.0 mmol, 1.1 equiv) was added dropwise at -78 °C over 5 minutes under N2 atmosphere. The reaction mixture was stirred for 50 minutes, then the ketone S2 (3.4 g, 10.0 mmol, 1.0 equiv) was added at -78 °C, and the reaction temperature was slowly raised to -50 °C. MeOH (10 mL) was added to quench the reaction at -50 °C and the mixture was allowed to warm to room temperature. The solvents were removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with DCM (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure, S3 was collected without further purification.

A 50 mL dry Schlenk flask was charged with ketone S3. Imidazole (816 mg, 12 mmol, 1.2 equiv) and 30 mL dry DMF. The Chlorotriethylsilane (2.0 mL, 12 mmol, 1.2 equiv) was slowly added to solution at room temperature, the reaction mixture was stirred for 12 hours. The solvent was removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with DCM (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure gave pure S4 (5.2 g, 93% yield) as colourless solid.

$^1$H NMR (400 MHz, 298 K, CDCl3): δ = 7.23 (s, 8H), 5.95 (s, 4H), 0.93 (t, J = 7.9 Hz, 18H), 0.59 (q, J = 7.9 Hz, 12H).

$^{13}$C NMR (100 MHz, 298 K, CDCl3): δ = 144.55 (C), 133.22 (C), 131.55 (CH), 128.43 (CH2), 127.37 (CH), 71.17 (C), 7.17 (CH2), 6.53 (CH2).

HRMS (ESI) Calcd. for C_{20}H_{23}Cl_2O_Si [M + H$^+$] 561.2173; Found: 561.2115.
3.3 Synthesis of 1

![Chemical reaction diagram]

1 was prepared according to a modified published procedure.\textsuperscript{21}

Under an Argon atmosphere, a 50 mL dry Schlenk flask was charged with S4 (5.6 g, 10.0 mmol, 1.0 equiv), Bis(pinacolato)diboron (7.6 g, 30 mmol, 3 equiv), K$_3$PO$_4$ (12.6 g, 60 mmol, 6 equiv), S-Phos (0.53 mg, 1.3 mmol, 1.3 equiv), Pd(OAc)$_2$ (0.1 g, 0.5 mmol, 0.05 equiv) and anhydrous 1,4-dioxane (20 mL). The reaction mixture was stirred at 90 °C for 48 h under Argon. After cooling down to room temperature, the mixture was filtered through a short plug of active charcoal, the solvent was removed under reduced pressure and the residue was washed with MeOH (300 mL) gave pure 1 (7.3 g, 98% yield) as white solid.

$^1$H NMR (400 MHz, 298 K, CDCl$_3$): $\delta$ = 7.74 – 7.65 (m, 4H), 7.38 – 7.29 (m, 4H), 5.96 (s, 4H), 1.34 (s, 24H), 0.92 (t, $J$ = 7.9 Hz, 18H), 0.63 – 0.55 (m, 12H).

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$): $\delta$ = 149.21 (C), 134.83 (CH), 131.53 (CH), 125.31 (CH), 83.86 (C), 71.68 (C), 25.03 (CH$_3$), 7.20 (TES), 6.57 (TES).

HRMS (MALDI) Calcd. for C$_{32}$H$_{32}$B$_4$O$_6$Si$_2$: 744.4584; Found: 744.4531.
3.4 Synthesis of 2

S5 was prepared according to a modified published procedure. Characterization data was consistent with the previous report.

S5 (2.7 g, 4 mmol) and Ni(OAc)₂·4H₂O (1.1 g, 6 mmol, 1.5 equiv) were dissolved in DMF (100 mL). The reaction mixture was stirred at 140 °C for 10 h. After cooling down to room temperature, the solvent was removed under reduced pressure and the residue was washed with MeOH (300 mL) gave pure S6 (2.6 g, 97% yield) as red solid.

Under an Argon atmosphere, a 100 mL dry Schlenk flask was charged with S6 (1.6 g, 2.2 mmol, 1.0 equiv), anhydrous CHCl₃ (50 mL) and pyridine (0.6 mL, 3 equiv), the N-bromosuccinimide (0.89 g, 5.0 mmol, 2.3 equiv) was added the reaction in 10 min. After stirring in the dark for 30 min, the reaction was quenched with acetone (5.0 mL), the solvent was removed under reduced pressure and the residue was washed with MeOH (200 mL) gave pure 2 (1.8 g, 90% yield) as red solid.

¹H NMR (400 MHz, 298 K, CDCl₃); δ = 9.45 (d, J = 5.0 Hz, 8H), 8.77 (d, J = 5.0 Hz, 8H), 7.80 (d, J = 1.8 Hz, 8H), 7.74 (t, J = 1.8 Hz, 4H), 1.49 (s, 72H).


Under an Argon atmosphere, a 100 mL dry Schlenk tube was charged with 1 (82 mg, 0.11 mmol, 1.0 equiv), 2 (100 mg, 0.11 mmol, 1.0 equiv), Cs₂CO₃ (0.14 g, 0.44 mmol, 4.0 equiv), Pd(PPh₃)₄ (25 mg, 0.02 mmol, 0.2 equiv), pyridine (1 mL) and degassed toluene (50 mL). The reaction mixture was stirred at 125 °C for 12 h under Argon. After cooling down to room temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography (DCM/petroleum ether 1:3) afforded compound [2]CPT-OTES (23 mg, 16% yield) as red solid. From the reaction monitoring with HRMS (Figure S1), there is small ratio of [3]CPT-OTES formed in this reaction, unfortunately, but it can’t be purified at this step due to its unstable in silica gel.

¹H NMR (400 MHz, 298 K, CDCl₃): δ = 8.52 – 8.35 (m, 16H), 7.59 (t, J = 1.8 Hz, 4H), 6.29 (s, 8H), 1.35 (s, 72H), 1.12 (t, J = 7.9 Hz, 36H), 0.83 (q, J = 7.9 Hz, 24H).

¹³C NMR (100 MHz, 298 K, CDCl₃): δ = 148.87 (CH), 143.28 (C), 141.93 (CH₂), 141.47 (CH), 139.70 (CH), 133.11 (C), 132.36 (CH), 131.56 (CH), 128.71 (C), 124.91 (CH₂), 120.94 (C), 119.54 (C), 117.40 (C), 72.97 (C), 35.01 (C, t-Bu), 31.75 (CH₃, t-Bu), 7.36 (CH₃, TES), 6.85 (CH₂, TES).

HRMS (MALDI) Calcd. for C₁₉₇H₃₄N₆O₁₀Si; 2461.2219. Found: 2461.2207.
Figure S1. Reaction monitoring by HRMS (MALDI, DCTB as the matrix), with pyridine (left) and without pyridine (right).

Figure S2. HRMS of [2]CPT-OTES (MALDI, DCTB as the matrix).
Figure S3. Variable-Temperature $^1$H-NMR spectrum (500 MHz. CDCl$_3$) partial of [2]CPT-OTES.
Figure S4. Experimental (left) and simulated (right) $^1$H NMR spectra of [2]CPT-OTES at various temperature.

Figure S5. Eyring plot: \( \Delta G^\ddagger = -RT[\ln(k/T) + \ln(h/k_B)] \), \( \ln(k/T) = -\Delta H^\ddagger/RT + [\Delta S^\ddagger/R - \ln(h/k_B)] \). Plot of \( \ln(k/T) \) versus \( 1/T \) is a straight line for which: \( \Delta H^\ddagger = -(\text{slope})R \) and \( \Delta S^\ddagger = \text{[intercept + ln(h/k_B)]R} \).

\[
\begin{align*}
\Delta H^\ddagger &= 38.4 \text{ kJ mol}^{-1} \\
\Delta S^\ddagger &= -62.8 \text{ J mol}^{-1}\text{K}^{-1} \\
\Delta G^\ddagger_{298} &= 58.9 \text{ kJ mol}^{-1} \quad (14.1 \text{ kcal mol}^{-1})
\end{align*}
\]

Under an N₂ atmosphere, a 50 mL dry Schlenk tube was charged with [2]CPT-OTES (30 mg, 0.012 mmol, 1.0 equiv) and anhydrous THF (20 mL). TBAF in THF (0.12 mL, 1.0 mol/L, 0.12 mmol, 10.0 equiv) was added dropwise at room temperature. H₂O (5 mL) was added to quench the reaction after reaction mixture was stirred at room temperature for 1 h. The solvents were removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with DCM (2 x 20 mL), and the combined organic layers was filtered through a short plug of silica gel and washed out the product with pure ethyl acetate afforded [2]CPT-OH (23 mg, 98% yield) as red solid.

¹H NMR (400 MHz, 298 K, THF-d₈): δ = 8.53 – 8.34 (m, 16H), 7.70 (t, J = 1.8 Hz, 4H), 6.24 (s, 8H), 5.24 (s, 4H), 1.51 – 1.26 (m, 72H).

¹³C NMR (100 MHz, 298 K, THF-d₈): δ = 149.52 (CH), 144.57 (C), 142.41 (CH₃), 142.14 (CH₂), 140.51 (C), 139.98 (C), 133.19 (CH), 132.48 (CH), 131.92 (CH), 129.14 (CH), 125.75 (C), 121.58 (C), 119.88 (C), 118.10 (C), 70.76 (C), 35.38 (C, t-Bu), 31.75 (CH₃, t-Bu).

Figure S6. HRMS of [2]CPT-OH (MALDI, DCTB as the matrix).

Figure S7. Variable-Temperature $^1$H-NMR spectrum (500 MHz, CDCl$_3$) partial of [2]CPT-OH.

Under an Argon atmosphere, a 100 mL dry Schlenk tube was charged with 1 (82 mg, 0.11 mmol, 1.0 equiv), 2 (100 mg, 0.11 mmol, 1.0 equiv), Cs₂CO₃ (0.14 g, 0.44 mmol, 4.0 equiv), Pd(PPh₃)₄ (25 mg, 0.02 mmol, 0.2 equiv), pyridine (1 mL) and degassed toluene (80 mL). The reaction mixture was stirred at 125 ℃ for 12 h under Argon. After cooling down to room temperature, the mixture was filtered through a short plug of Al₂O₃, the solvent was removed under reduced pressure, the crude product was used to next step without further purification.

Under an N₂ atmosphere, a 50 mL dry Schlenk tube was charged with the crude product and anhydrous THF (40 mL). TBAF in THF (2.0 mL, 1.0 mol/L) was added dropwise at room temperature. H₂O (5 mL) was added to quench the reaction after reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (DCM/EtOAc 2:1) afforded compound [3]CPT-OH (10 mg, 8% yield) as red solid.

¹H NMR (500 MHz, CDCl₃): δ = 8.64 (s, 24H), 7.97 (d, J = 8.0 Hz, 12H), 7.84 (d, J = 8.0 Hz, 12H), 7.74 (d, J = 1.7 Hz, 12H), 7.59 (t, J = 1.8 Hz, 6H), 6.44 (s, 12H), 1.32 (s, 108H).

¹³C NMR (100 MHz, CDCl₃): δ = 148.92, 143.63, 142.97, 142.62, 140.51, 139.98, 133.92, 132.88, 132.75, 132.44, 132.38, 132.28, 132.23, 132.21, 131.95, 131.84, 128.99, 128.78, 128.66, 124.04, 121.06, 120.36, 118.47, 69.52, 35.02, 31.72.

HRMS (MALDI) Calcd. for C₇₉H₇₀N₁₂Ni₄O₁₂: 3007.315; Found: 3007.314.

S15
Figure S8. HRMS of [β]CPT-OH (MALDI, DCTB as the matrix).
3.8 Synthesis of [2]CPT

The H$_2$SnCl$_4$ was prepared according to a published procedure.$^{33}$ To a solution of SnCl$_2$·2H$_2$O (0.22 g, 1.0 mmol) in THF (10 mL) was added conc. HCl (0.18 mL, 2.2 mmol, 2.2 equiv) at room temperature. After stirring for 0.5 h at this temperature, the resulting solution (0.44 mL, 0.044 mmol, 4.4 equiv) was added to [2]CPT-OH (20 mg, 0.01 mmol) in THF (20 mL), and the resulting mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (DCM/petroleum ether 1:3) afforded compound [2]CPT (12 mg, 62%).

$^1$H NMR (500 MHz, 298 K, CDCl$_3$): $\delta$ = 9.05 (d, $J$ = 4.9 Hz, 8H), 8.55 (d, $J$ = 4.9 Hz, 8H), 7.70 – 7.64 (m, 16H), 7.30 – 7.28 (m, 16H), 7.26 – 7.22 (m, 8H), 1.42 (s, 72H).$^{13}$C NMR (125 MHz, 298 K, CDCl$_3$): $\delta$ = 149.31 (C$_{CH}$), 140.73 (C$_{CH}$), 139.90 (C), 139.79 (C$_{CH}$), 139.14 (C), 138.98 (C), 138.38 (C), 133.86 (C$_{CH}$), 133.80 (C), 132.26 (C$_{CH}$), 128.39 (C$_{CH}$), 128.30 (C), 127.38 (C$_{CH}$), 121.30 (C), 121.09 (C), 115.17 (C), 35.09 (C, t-Bu), 31.78 (C$_{CH}$, t-Bu).

HRMS (MALDI) Calcd. for C$_{137}$H$_{312}$N$_4$Si$_3$: 1936.866; Found: 1936.860.
Figure S9. Variable-Temperature $^1$H-NMR spectrum (500 MHz, CDCl$_3$) partial of [2]CPT.

$$
\Delta G^\circ = 19.1 \times 10^3 \times T_c \left(9.97 + \log T_c - \log \nu_{\text{av}} \nu_{\text{gl}}\right)
$$

$$
\Delta G^\circ ([2]CPT) = 48 \text{ kJ mol}^{-1} (11.5 \text{ kcal mol}^{-1})
$$
Figure S10. (a) $^1$H-NMR of [2]CPT (400 MHz, 298K, CDCl$_3$). (b) 1D-NOE experiment of [2]CPT with selective excitation of the protons at 9.09 ppm. (c) 1D-NOE experiment of [2]CPT with selective excitation of the protons at 8.57 ppm. (d) 1D-NOE experiment of [2]CPT with selective excitation of the protons at 7.73 ppm. (e) 1D-NOE experiment of [2]CPT with selective excitation of the protons at 7.67 ppm. Experimental details: All NOE experiments were performed in a Bruker 400 MHz spectrometer in CDCl$_3$ at 298K. The sample was not degassed.
3.9 Synthesis of [3]CPT

The H₂SnCl₄ was prepared according to a modified published procedure. To a solution of SnCl₄·2H₂O (0.22 g, 1.0 mmol) in THF (20 mL) was added conc. HCl (0.18 mL, 2.2 mmol, 2.2 equiv) at room temperature. After stirring for 0.5 h at this temperature, the resulting solution (0.24 mL, 0.021 mmol, 7.0 equiv) was added to [3]CPT·OH (10 mg, 0.003 mmol) in THF (20 mL), and the resulting mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (DCM/petroleum ether 1:3) afforded compound [3]CPT (6.7 mg, 70%).

¹H NMR (400 MHz, 298 K, CDCl₃): δ = 8.99 (d, J = 5.0 Hz, 12H), 8.70 (d, J = 5.0 Hz, 12H), 7.89 – 7.65 (m, 18H), 7.31 (t, J = 4.2 Hz, 24H), 7.53 (d, J = 8.3 Hz, 12H), 1.43 (s, 108H).

¹³C NMR (125 MHz, 298 K, CDCl₃): δ = 149.25 (CH), 141.15 (CH), 141.01 (CH), 140.34 (C), 140.19 (C), 139.29 (C), 138.73 (C), 133.76 (CH), 133.48 (C), 132.26 (C), 128.63 (CH), 128.20 (CH), 126.79 (CH), 121.29 (C), 120.32 (C), 116.40 (C), 35.10 (C, t-Bu), 31.78 (CH₃, t-Bu).

HRMS (MALDI) Calcd. for C₆₅H₄₆N₁₀N₄: 2905.298; Found: 2905.301.
Figure S11. HRMS of 3JCPT (MALDI, DCTB as the matrix).
Figure S12. Variable-Temperature $^1$H-NMR spectrum (500 MHz, CDCl$_3$) partial of [3]CPT.

$\Delta G^\circ = 19.1 \times 10^3 \times T_c (9.97 \times \log T_c - \log \Delta H_{\text{vap}})$

$\Delta G^\circ (\text{[3]CPT}) = 50.8 \text{ kJ mol}^{-1} (12.1 \text{ kcal mol}^{-1})$
Figure S13. (a) $^1$H-NMR of [3]CPT (400 MHz, 298K, CDCl3). (b) 1D-NOE experiment of [3]CPT with selective excitation of the protons at 9.01 ppm. (c) 1D-NOE experiment of [3]CPT with selective excitation of the protons at 8.72 ppm. (d) 1D-NOE experiment of [3]CPT with selective excitation of the protons at 7.61 ppm. (e) 1D-NOE experiment of [3]CPT with selective excitation of the protons at 7.52 ppm. Experimental details: All NOE experiments were performed in a Bruker 400 MHz spectrometer in CDCl3, at 298K. The sample was not degassed.
3.10 Synthesis of S8

A 250 mL dry Schlenk flask was charged with 1-Chloro-4-bromobenzene (5.8 g, 30.0 mmol, 3.0 equiv) and 100 mL anhydrous THF. n-Butyllithium in n-hexane (12.0 mL, 2.5 mol/L, 30.0 mmol, 3.0 equiv) was added dropwise at -78 °C over 5 minutes under N₂ atmosphere. The reaction mixture was stirred for 50 minutes, then the 2-Naphthoquinone (1.6 g, 10.0 mmol, 1.0 equiv) was added at -78 °C, and the reaction temperature was slowly raised to 0 °C. MeOH (10 mL) was added to quench the reaction. The solvents were removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with DCM (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure. Purification by column chromatography (DCM/ElOAc 10:1) afforded S7 (2.8 g, 75% yield) as colourless solid.

A 50 mL dry Schlenk flask was charged with ketone S7 (1.9 g, 5 mmol, 1.0 equiv), Imidazole (816 mg, 12 mmol, 2.4 equiv) and 30 mL dry DMF. The Chloroacetylilysilane (2.0 mL, 12 mmol, 2.4 equiv) was slowly added to solution at room temperature, the reaction mixture was stirred for 12 hours at 100 °C. The solvent was removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with DCM (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure gave pure S8 (3.0 g, 95% yield) as light brown oil.

¹H NMR (400 MHz, 298 K, CDCl₃): δ = 7.52-7.48 (m, 2H), 7.30-7.22 (m, 4H), 7.19-7.09 (m, 8H), 6.13 (s, 2H), 0.90 (t, J = 7.9 Hz, 13H), 0.61-0.46 (m, 12H).

¹³C NMR (100 MHz, 298 K, CDCl₃): δ = 146.26 (C), 139.38 (C), 132.98 (C), 132.05 (CH), 128.08 (CH₂), 128.03 (CH), 127.52 (CH), 127.70 (CH), 73.61 (C), 7.21 (CH₂), 6.57 (CH₃).

HRMS (ESI⁺) Calcd. for C₃₆H₄₆Cl₂O₂Si₂ [M + H⁺] 611.2323; Found: 611.2372.
3.11 Synthesis of S9

Under an Argon atmosphere, a 50 mL dry Schlenk flask was charged with S8 (3.0 g, 5.0 mmol, 1.0 equiv), Bis(pinacolato)diboron (3.68 g, 15 mmol, 3 equiv), K2PO4 (6.3 g, 30 mmol, 6 equiv), S-Phos (0.26 mg, 0.6 mmol, 1.3 equiv), Pd(OAc)2 (0.1 g, 0.5 mmol, 0.1 equiv) and anhydrous 1,4-dioxane (30 mL). The reaction mixture was stirred at 90 °C for 48 h under Argon. After cooling down to room temperature, the mixture was filtered through a short plug of active charcoal, the solvent was removed under reduced pressure and the residue was washed with MeOH (300 mL) gave pure S9 (3.9 g, 99% yield) as white solid.

1H NMR (400 MHz, 298 K, CDCl3): δ = 7.68 - 7.61 (m, 4H), 7.46 (dd, J = 6.0, 3.4 Hz, 2H), 7.32 - 7.27 (m, 4H), 7.17 (dd, J = 6.0, 3.4 Hz, 2H), 6.11 (s, 2H), 1.33 (s, 24H), 0.89 (t, J = 7.9 Hz, 18H), 0.63 - 0.43 (m, 12H).

13C NMR (100 MHz, 298 K, CDCl3): δ = 151.10, 139.53, 134.58, 131.85, 128.15, 127.42, 125.90, 83.83, 77.48, 77.16, 76.84, 74.02, 25.01 (CH3), 7.24 (CH3), 6.58 (SiCH2).

HRMS (MALDI) Calcd. for C86H58B6O14Si2: 794.4741; Found: 794.4701.

S25
3.12 Synthesis of S12

A 250 mL dry Schlenk flask was charged with 1-Chloro-4-bromobenzene (5.8 g, 30.0 mmol, 3.0 equiv) and 100 mL anhydrous THF. n-Butyllithium in n-hexane (12.0 mL, 2.5 mol/L, 50.0 mmol, 3.0 equiv) was added dropwise at -78 °C over 5 minutes under N₂ atmosphere. The reaction mixture was stirred for 50 minutes, then the Anthraquinone (2.1 g, 10.0 mmol, 1.0 equiv) was added at -78 °C, and the reaction temperature was slowly raised to 0 °C. MeOH (10 mL) was added to quench the reaction. The solvents were removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with EtOAc (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure. The residue was washed with DCM (100 mL) gave pure S10 (3.9 g, 90% yield) as colourless solid.

A 50 mL dry Schlenk flask was charged with ketone S10 (2.2 g, 5 mmol, 1.0 equiv), Imidazole (816 mg, 12 mmol, 2.4 equiv)) and 30 mL dry DMF. The Chlorotriethylsilane (2.0 mL, 12 mmol, 2.4 equiv) was slowly added to solution at room temperature, the reaction mixture was stirred for 12 hours at 100 °C. The solvent was removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with DCM (2 × 50 mL), and the combined organic layers were concentrated under reduced pressure gave pure S11 (3.2 g, 98% yield) as light brown oil.

Under an Argon atmosphere, a 50 mL dry Schlenk flask was charged with S11 (3.2 g, 5.0 mmol, 1.0 equiv), Bis(pinacolato)diboron (3.68 g, 15 mmol, 3 equiv), K₂PO₃ (6.3 g, 30 mmol, 6 equiv), S-Phos (0.26 mg, 0.6 mmol, 1.3 equiv), Pd(OAc)₂ (0.1 g, 0.5 mmol, 0.1 equiv) and anhydrous 1,4-dioxane (30 mL). The reaction mixture was stirred at 90 °C for 48 h under Argon. After cooling down to room temperature, the mixture was filtered through a short plug of active charcoal, the solvent was removed under reduced pressure and the residue was washed with MeOH (300 mL) gave pure S12 (4.0 g, 95% yield) as white solid.

¹H NMR (400 MHz, 298 K, CDCl₃): δ = 7.65 – 7.57 (m, 4H), 7.50 (dd, J = 6.0, 3.4 Hz, 4H), 7.31 – 7.26 (m, 4H), 7.18 (dd, J = 6.1, 3.4 Hz, 4H), 1.30 (s, 24H), 0.86 (t, J = 7.9 Hz, 18H), 0.39 (q, J = 9.7 Hz, 12H).

¹³C NMR (100 MHz, 298 K, CDCl₃): δ = 154.30, 139.53, 134.25, 129.25, 127.72, 126.27, 83.77, 76.29, 24.99, 7.42, 6.65.

HRMS (MALDI) Calcd. for C₁₂H₁₂B₂O₆Si₂: 844.4897, Found: 844.4824.

S26

Under an Argon atmosphere, a 250 mL dry Schlenk tube was charged with 89 (87 mg, 0.11 mmol, 1.0 equiv), 2 (100 mg, 0.11 mmol, 1.0 equiv), Cs₂CO₃ (0.14 g, 0.44 mmol, 4.0 equiv), Pd(P₆P₅)₂ (25 mg, 0.02 mmol, 0.2 equiv), pyridine (1 mL) and degassed toluene (120 mL). The reaction mixture was stirred at 125 °C for 12 h under Argon. After cooling down to room temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography (DCM/petroleum ether 1:4) afforded compound [2]CPTN-OTES (25 mg, 18% yield) as red solid. The [3]CPTN-OTES can’t be purified at this step.

¹H NMR (400 MHz, 298 K, CDCl₃): δ = 8.46 – 8.33 (m, 14H), 8.31 (d, J = 4.9 Hz, 2H), 8.29 (d, J = 4.9 Hz, 2H), 7.98 (dt, J = 5.9, 3.5 Hz, 4H), 7.59 (tt, J = 8.0, 1.8 Hz, 4H), 7.49 (dt, J = 5.7, 3.9 Hz, 4H), 6.52 (s, 4H), 6.09 (s, 6H), 1.35 (s, 72H), 1.07 (t, J = 7.9 Hz, 36H), 0.81 – 0.67 (m, 24H).

¹³C NMR (100 MHz, 298 K, CDCl₃): δ = 148.82, 145.05, 142.06, 142.01, 141.93, 141.62, 141.57, 141.45, 140.45, 139.75, 139.69, 139.41, 133.01, 132.28, 132.23, 131.80, 131.75, 131.40, 131.38, 128.77, 127.82, 127.11, 120.89, 119.54, 117.54, 74.82(C), 35.00(t-Bu, C), 31.75(t-Bu, CH₃), 7.41(CH₃), 6.91(SiCH₂).

HRMS (MALDI) Calcd. for C₆₅H₆₁N₁₂Si₂O₂S₁: 2561.2538; Found: 2561.2604.

Under an N₂ atmosphere, a 50 ml dry Schlenk tube was charged with [2]CPTN-OTES (20 mg, 0.008 mmol, 1.0 equiv) and anhydrous THF (20 mL). TBAF in THF (0.1 mL, 1.0 mol/L, 0.10 mmol) was added dropwise at room temperature. H₂O (5 mL) was added to quench the reaction after reaction mixture was stirred at room temperature for 1 h. The solvents were removed under reduced pressure and the residue was diluted with DCM (100 mL). The aqueous layer was extracted with DCM (2 × 20 mL), and the combined organic layers was filtered through a short plug of silica gel and washed out the product with pure ethyl acetate afforded [2]CPTN-OH (16 mg, 99% yield) as red solid.

1H NMR (500 MHz, 298K, THF-d₈) δ = 8.45 (dd, J = 10.5, 4.9 Hz, 4H), 8.40 – 8.31 (m, 6H), 8.30 – 8.23 (m, 6H), 8.02 (dd, J = 6.3, 3.4 Hz, 4H), 7.67 (t, J = 9.4, 1.8 Hz, 4H), 7.49 – 7.40 (m, 4H), 6.44 (s, 4H), 5.59 (s, 4H), 1.56 – 1.18 (m, 72H).

13C NMR (126 MHz, 298K, THF) δ = 149.45, 145.87, 142.59, 142.48, 142.44, 142.43, 142.31, 142.23, 142.16, 142.02, 140.55, 140.51, 139.82, 134.28, 133.48, 132.34, 132.00, 131.92, 131.68, 129.15, 128.01, 127.36, 121.46, 119.89, 119.82, 118.22, 118.18, 72.64, 35.36, 31.76.

HRMS (MALDI) Calcd. for C₁₆H₁₃₂N₄O₄ 2104.9079; Found: 2104.9051.
Figure S14a. HRMS of [2]CPTN-OH (MALDI, DCTB as the matrix)
3.15 Synthesis of [3]CPTN-OH

Under an N₂ atmosphere, a 50 mL dry Schlenk tube was charged with the crude product (ca. 60 mg) and anhydrous THF (40 mL). TBAF in THF (2.0 mL, 1.0 mol/L, 0.12 mmol) was added dropwise at room temperature. H₂O (5 mL) was added to quench the reaction after reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (DCM/EtOAc 4:1) afforded compound [3]CPTN-OH (21 mg, 12% yield of two steps) as red solid. Since there are several isomers together, so they can’t be characterized by ¹H/¹³C NMR.

HRMS (MALDI) Calcd. for C₁₁₀H₁₉₉N₁₂N₃O₆: 3157.3618; Found: 3157.4105

Figure S14b. HRMS of [3]CPTN-OH (MALDI, DCTB as the matrix).

The $\text{H}_2\text{SnCl}_4$ was prepared according to a modified published procedure. To a solution of $\text{SnCl}_4\cdot2\text{H}_2\text{O}$ (0.22 g, 1.0 mmol) in THF (20 mL) was added conc. $\text{HCl}$ (0.18 mL, 2.2 mmol, 2.2 equiv) at room temperature. After stirring for 0.5 h at this temperature, the resulting solution (0.2 mL, 0.05 mmol, 5.0 equiv) was added to [2]CPTN-OH (20 mg, 0.01 mmol) in THF (20 mL), and the resulting mixture was stirred at 70 °C for 12 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (DCM/petroleum ether 1:4) afforded compound [2]CPTN (6.5 mg, 32%).

$^1\text{H}$ NMR (500 MHz, 298 K, CDCl$_3$) $\delta$ = 9.08 (d, $J=4.9$ Hz, 8H), 8.58 (d, $J=4.9$ Hz, 8H), 8.20 (dd, $J=6.3$, 3.4 Hz, 4H), 7.72 (s, 8H), 7.66 (t, $J=1.9$ Hz, 4H), 7.42 (dd, $J=6.1$, 3.6 Hz, 4H), 7.29 (s, 16H), 6.90 (s, 4H), 1.43 (s, 72H).

$^{13}\text{C}$ NMR (125 MHz, 298 K, CDCl$_3$) $\delta$ = 149.29, 140.78, 139.99, 139.05, 138.81, 138.45, 133.78, 133.40, 132.52, 132.27, 128.90, 128.52, 128.42, 121.29, 120.81, 115.64, 35.11, 31.79.

HRMS (MALDI) Calcd. for $\text{C}_{146}\text{H}_{122}\text{Ni}_3\text{N}_8$: 2036.8969; Found: 2036.8961
Figure S15. HRMS of [2]CPTN (MALDI, DCTB as the matrix).

Figure S16. Variable-Temperature $^1$H-NMR spectrum (500 MHz, CDCl$_3$) partial of [2]CPTN.

The H$_2$SnCl$_4$ was prepared according to a modified published procedure. To a solution of SnCl$_4$·2H$_2$O (0.22 g, 1.0 mmol) in THF (20 mL) was added conc. HCl (0.18 mL, 2.2 mmol, 2.2 equiv) at room temperature. After stirring for 0.5 h at this temperature, the resulting solution (1.4 mL, 0.07 mmol, 7.0 equiv) was added to [3]CPTN-OH (63 mg, 0.02 mmol) in THF (20 mL), and the resulting mixture was stirred at room temperature for 6 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (DCM/petroleum ether 1:4) afforded compound [3]CPTN (50 mg, 82%).

$^1$H NMR (500 MHz, 298 K, CDCl$_3$) $\delta$ = 9.04 (d, $J$ = 5.0 Hz, 12H, D), 8.73 (d, $J$ = 5.0 Hz, 12H, C), 8.25 (dd, $J$ = 6.4, 3.3 Hz, 6H, G), 8.06 - 7.67 (m, 18H, A+B), 7.65 (d, $J$ = 8.0 Hz, 12H, E), 7.53 (t, $J$ = 8.6 Hz, 18H, F), 7.41 (s, 6H), 1.45 (s, 108H, t-Bu).

$^{13}$C NMR (1265 MHz, 298 K, CDCl$_3$) $\delta$ = 149.26, 141.24, 141.18, 140.29, 139.36, 138.97, 133.44, 133.24, 132.56, 132.29, 128.85, 128.64, 127.58, 126.90, 126.16, 121.30, 120.29, 116.58, 35.12, 31.80.

HRMS (MALDI) Calcd. for C$_{216}$H$_{252}$N$_{12}$Ni$_3$: 3055.3453; Found: 3055.3449
Figure S17. HRMS of [3]CPTN (MALDI DCTB as the matrix).

Figure S18. $^1$H-$^1$H NOESY of [3]CPTN in CDCl$_3$ at room temperature.
Figure S19. 1H-1H COSY of [3]CPTN in CDCl₃ at room temperature.

Figure S20. Variable-Temperature 1H-NMR spectrum (500 MHz, CDCl₃) partial of [3]CPTN.

S35
Figure S21. Eyring plot: $\Delta G^\ddagger = -RT[\ln(k/T) + \ln(h/k_B)]$, $\ln(k/T) = -\Delta H^\ddagger / R T + [\Delta S^\ddagger / R - \ln(h/k_B)]$. Plot of $\ln(k/T)$ versus $1/T$ is a straight line for which: $\Delta H^\ddagger = -(slope)R$ and $\Delta S^\ddagger = [intercept + \ln(h/k_B)]R$.

$\Delta H^\ddagger = 58.9 \text{ kJ mol}^{-1}$

$\Delta S^\ddagger = 31.6 \text{ J mol}^{-1} \text{K}^{-1}$

$\Delta G^\ddagger_{298} = 49.5 \text{ kJ mol}^{-1}$

$\tau_{1/2, 298} = 53.0 \text{ ms}$
3.18 Synthesis of [n]CPTNA-OH

Under an Argon atmosphere, a 250 mL dry Schlenk tube was charged with S12 (82 mg, 0.22 mmol, 1.0 equiv), 2 (200 mg, 0.22 mmol, 1.0 equiv), Cs₂CO₃ (0.28 g, 0.88 mmol, 4.0 equiv), Pd(PPh₃)₄ (50 mg, 0.04 mmol, 0.2 equiv), pyridine (1 mL) and degassed toluene (150 mL). The reaction mixture was stirred at 125 °C for 12 h under Argon. After cooling down to room temperature, the mixture was filtered through a short plug of Al₂O₃, the solvent was removed under reduced pressure, the crude product was used to next step without further purification.

Under an N₂ atmosphere, a 50 mL dry Schlenk tube was charged with the crude product and anhydrous THF (40 mL), TBAF in THF (2.0 mL, 1.0 mol/L.) was added dropwise at room temperature. H₂O (5 mL) was added to quench the reaction after reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (DCM/EtOAc 8:1) afforded compounds [2]CPTA-OH (41 mg, 17% yield) and [3]CPTA-OH (43 mg, 12% yield) as red solid.

[2]CPTA-OH:

HRMS (MALDI) Calcd. for C₁₄H₁₆N₂Ni₅O₄: 2204.9392; Found: 2204.9392

Figure S22. HRMS of [2]CPTA-OH (MALDI, DCTB as the matrix).
[^JCPTA-OH:]

^1^H NMR (400 MHz, 298 K, THF-d$_6$) δ = 8.56 (d, J = 5.0 Hz, 12H), 8.43 (d, J = 5.0 Hz, 12H), 7.92 – 7.78 (m, 36H), 7.63 (d, J = 1.8 Hz, 12H), 7.53 (t, J = 1.8 Hz, 6H), 7.41 (dd, J = 6.0, 3.4 Hz, 12H), 5.68 (s, 6H), 5.51 (s, 6H), 1.18 (s, 108H). 

^1^3^C NMR (100 MHz, 298 K, THF-d$_6$) δ = 149.85, 149.34, 143.59, 143.33, 142.10, 140.82, 139.99, 133.47, 132.34, 132.12, 129.52, 129.49, 128.21, 126.33, 121.40, 120.76, 119.27, 73.91, 35.18, 31.54.

HRMS (MALDI) Calcd. for C$_{22}$H$_{26}$N$_{12}$Ni$_{8}$O$_{8}$: 3307.4082; Found: 3307.4787

**Figure S23.** HRMS of [3]CPTA-OH (MALDI, DCTB as the matrix).
3.19 Synthesis of [n]CPTNA

The [n]CPTA-OH were treated with different reducing agents, temperatures and solvents, the Figures S24 has shown the representative results by HR-MALDI-MS. [2]CPTA-OH seems impossible be aromatized to [2]CPTA with so high strain energy, but [3]CPTA-OH was easily aromatized to [3]CPTA with mild condition.

Figure S24. Reaction monitoring by HRMS (MALDI, DCTB as the matrix).
Under an Argon atmosphere, a 50 mL dry Schlenk tube was charged with [3]CPTA-OH (40 mg, 0.012 mmol, 1.0 equiv), NaI (18 mg, 0.12 mmol, 10.0 equiv), NaH₂PO₄ (11 mg, 0.12 mmol, 10.0 equiv), degassed AcOH (20 mL). The reaction mixture was stirred at 100 °C for 6 h under Argon. After cooling down to room temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography (DCM/petroleum ether 1:5) afforded compound [3]CPTA (37 mg, 95%).

¹H NMR (400 MHz, 298 K, CDCl₃) δ = 9.08 (d, J = 5.0 Hz, 12H), 8.78 (d, J = 4.9 Hz, 12H), 7.82 (d, J = 6.3, 3.1 Hz, 24H), 7.74 – 7.53 (m, 18H), 7.40 (d, J = 7.9 Hz, 12H), 7.31 (dd, J = 6.7, 3.4 Hz, 12H), 1.46 (s, 108H).

¹³C NMR (125 MHz, 298 K, CDCl₃) δ = 149.34, 141.22, 141.11, 139.32, 139.19, 138.68, 137.07, 133.62, 132.26, 130.53, 130.35, 128.68, 127.04, 125.26, 121.35, 120.44, 116.36, 35.14, 31.82.

HRMS (MALDI) Calcd. for C₂₂H₂₆N₈N₃²⁺ 3205.3917; Found: 3205.3912.

Figure S25. HRMS of [3]CPTA (MALDI, DCTB as the matrix).
4. Redox Properties


S41

\( K_{\text{asso}} \) values were evaluated by applying a nonlinear curve-fitting method to absorbance changes (\( \Delta \text{Abs} \)) observed for the host molecules upon titration with \( C_{\text{hs}} \) or \( C_{\text{ho}} \):

\[
\Delta \text{Abs} = (L(1 + K_{\text{asso}}X + K_{\text{asso}}A) - (L^2(K_{\text{asso}}X + K_{\text{asso}}A + 1)^2 - 4K_{\text{asso}}^2AX)^{1/2})/2K_{\text{asso}}A
\]

where \( X \) and \( A \) represent \([\text{Guest}]_{\text{host}}\) and \([\text{Host}]_{\text{host}}\), respectively; \( L \) denotes \( \Delta \text{Abs} \) at 100% complexation; \( L \) and \( K_{\text{asso}} \) are parameters.

Figure S27. Absorption spectral change upon titration of [2]CPT with \( C_{\text{ho}} \) in toluene at 298K (left). Change in \( \Delta \text{Abs} \) at 446 nm, the data was fitted by 1:1 equation (right).

Table S1. UV-vis Titration between [2]CPT and \( C_{\text{ho}} \)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>([H] )</th>
<th>([G] )</th>
<th>( K_{\text{A}} )</th>
<th>fit error</th>
<th>stat. error</th>
<th>( K_{\text{A}} ) (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.75 x 10^{-6}</td>
<td>0.186 x 10^{-6}</td>
<td>2.65 x 10^{7}</td>
<td>5.30 x 10^{7}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>0.40 x 10^{-6}</td>
<td>0.132 x 10^{-6}</td>
<td>2.67 x 10^{7}</td>
<td>4.03 x 10^{7}</td>
<td>3.4 x 10^{7}</td>
<td>2.54 ± 0.3 x 10^{7}</td>
</tr>
<tr>
<td>c</td>
<td>1.25 x 10^{-6}</td>
<td>0.180 x 10^{-6}</td>
<td>2.31 x 10^{7}</td>
<td>7.80 x 10^{7}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{1}\)To estimate a confidence interval at 95% probability for \( n = 3 \) repeat measurements standard uncertainty \( u = s/\sqrt{n} \), where \( s \) is the sample standard deviation, was multiplied by the Student \( t \)-value for the degrees of freedom \( (n - 1) \).\(^{31}\)
Figure S28. a) $^1$H NMR (500 MHz) spectrum of [2]CPT (top) and $^3$H NMR (400 MHz) spectrum of [2]CPT-$C_{60}$ (bottom). b) 2D $^1$H-$^1$H-COSY-NMR spectrum (400 MHz, CDCl$_3$, 298 K) of [2]CPT-$C_{60}$. 

S43
Figure S29. Variable-Temperature $^1$H-NMR spectrum (500 MHz, CDCl$_3$) partial of [2]CPT$\Rightarrow$C$_{60}$.

**Conclusion:** Figure S28 has shown that the pyrrolo moieties of [2]CPT split into two sets after binding with C$_{60}$ (likely due to offset binding), while most other proton signals are not visible (at r.t.). Figure S29 demonstrates that the proton signals appear below room temperature NMR.
Figure S30. Absorption spectral change upon titration of [2]CPT with C₉ in toluene at 298K (left). Change in ΔA₆56 at 446 nm, the data was fitted by 1:1 equation (right). To a solution of [2]CPT in toluene (7.2 x 10⁻⁵ M) was added a solution of C₉ (1.2 x 10⁻⁵ M), prepared with [2]CPT solution at 7.2 x 10⁻⁵ M to keep [2]CPT concentration constant 0–2.0 equiv at 25°C.

Figure S31. MALDI Fourier transform ion-cyclotron resonance mass spectrum of [2]CPT and C₉ with DCTB as the matrix. The Spectrum shows the radical cation of [2]CPT⁺⁺ and the radical cation of the host-guest-complex [[2]CPT−C₉]⁺⁺. Insets display the measured (top, red) and the simulated (bottom, black) isotope pattern of the free molecule and the complex.
Figure S32. Absorption spectral change upon titration of [2]CPTN with C_{60} in toluene at 298 K (left). Change in ΔΔAbs at 442 nm, the data was fitted by 1:1 equation (right). To a solution of [2]CPTN in toluene (4.2 x 10^{-7} M) was added a solution of C_{60} (2.8 x 10^{-6} M, prepared with [2]CPTN solution at 4.2 x 10^{-7} M to keep [2]CPTN concentration constant) 0–2.4 equiv at 25 °C.
Figure S33. Absorption spectral change upon titration of [2]CPTN with C_{70} in toluene at 298K (left). Change in ΔAbs at 442 nm, the data was fitted by 1:1 equation (right). To a solution of [2]CPTN in toluene (4.2 × 10^{-7} M) was added a solution of C_{70} (2.2 × 10^{-4} M), prepared with [2]CPTN solution at 4.2 × 10^{-7} M to keep [2]CPTN concentration constant) 0–1.9 equiv at 25 °C.
6. X-Ray Crystallographic Details

The crystallographic data of [2]CPT and [2]CPT$_{2}$C$_{80}$ were collected at the XALOC beamline of the ALBA synchrotron at 100 K using a MD2M single-axis diffractometer (Mastel, France) and a Pilatus 6 M detector (Dectris, Switzerland). The data set was collected on omega single-axis scans with 1s per frame exposures at \( \lambda = 0.82653 \) Å. The data were collected in single-axis rotation leading to a low theta fraction value. The crystal was diffracting at a low resolution with very weak peaks and showed degradation due to radiation damage. This poor density and fast degradation is attributed to the solvent loss and severe motions of the solvents (volatile toluene). The structure was solved using SHELXT$^{35}$ refined by the full matrix least-squares based of \( F^2 \) using SHELXL97.\(^{36}\) Although the limited quality of the data, we have been able to locate the fullerene inside the cage. Due to the disorder of fullerene some positions were refined imposing restraints. Attempts to identify and model the disordered solvent molecules were unsatisfactory; therefore, the PLATON/SQUEEZE routine was applied to mask out the disordered electron density (543 electrons per unit cell for [2]CPT and 1154.6 electrons per unit cell for [2]CPT$_{2}$C$_{80}$).\(^{37}\)
Figure S34. Solid state structure of [2]CPT-OH. Thermal ellipsoids are shown at the 50% probability level (top), representation of the packing structure after removing t-Bu groups (bottom). The cif-file was deposited in the Cambridge Structural Database under identifier CCDC 1881890.

Table S2. Crystal data and structure refinement for [2]CPT-OH.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₆H₆N₂NiO₂</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1044.97</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>150.00(14)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>14.9071(5)</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>a/Å</td>
<td>15.8745(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>18.8299(6)</td>
</tr>
<tr>
<td>α°</td>
<td>94.574(3)</td>
</tr>
<tr>
<td>β°</td>
<td>103.809(3)</td>
</tr>
<tr>
<td>γ°</td>
<td>110.373(3)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>3991.1(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>ρ calc/g/cm³</td>
<td>0.870</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.621</td>
</tr>
<tr>
<td>F(000)</td>
<td>1108.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.291 × 0.189 × 0.115</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54184)</td>
</tr>
<tr>
<td>2θ range for data collection</td>
<td>6.036 to 148.972</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-17 ≤ h ≤ 18, -19 ≤ k ≤ 16, -23 ≤ l ≤ 23</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>28109</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>15606 [R_{wp} = 0.0607, R_{fwp} = 0.0716]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>15606/10/728</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.080</td>
</tr>
<tr>
<td>Final R indexes [I = 2σ (I)]</td>
<td>R₁ = 0.0764, wR₂ = 0.2374</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0999, wR₂ = 0.2569</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>1.12/-0.36</td>
</tr>
</tbody>
</table>
Figure S35. Solid state structure of [2]CPT. Thermal ellipsoids are shown at the 30% probability level (top), representation of the packing structure (bottom). The cif-file was deposited in the Cambridge Structural Database under identifier CCDC 1909920.
### Table S3. Crystal data and structure refinement for [2]CPT.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>[2]CPT</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{12}H_{22}N_{4}N_{6}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1939.77</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>15.450(5)</td>
</tr>
<tr>
<td>b/Å</td>
<td>17.790(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>18.180(5)</td>
</tr>
<tr>
<td>α°</td>
<td>115.78(8)</td>
</tr>
<tr>
<td>β°</td>
<td>93.59(8)</td>
</tr>
<tr>
<td>γ°</td>
<td>114.36(8)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>3916.3(10)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
</tr>
<tr>
<td>ρ_{calc}/cm³</td>
<td>0.822</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.278</td>
</tr>
<tr>
<td>F(000)</td>
<td>1196.0</td>
</tr>
<tr>
<td>Crystal size/mm²</td>
<td>0.06 × 0.05 × 0.05</td>
</tr>
<tr>
<td>Radiation</td>
<td>synchrotron (λ = 0.71073)</td>
</tr>
<tr>
<td>2θ range for data collection</td>
<td>2.604 to 57.676</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-20 ≤ h ≤ 20, -23 ≤ k ≤ 23, -22 ≤ l ≤ 1 ≤</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>50250</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>14451 [R_{int} = 0.1035, R_{exp} = 0.1033]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>14451/0/641</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.240</td>
</tr>
<tr>
<td>Final R indexes [I=2σ(I)]</td>
<td>R₁ = 0.1290, wR₂ = 0.3720</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.2121, wR₂ = 0.4417</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.67/-1.24</td>
</tr>
</tbody>
</table>

### Table S4. Fractional Atomic Coordinates (× 10⁵) and Equivalent Isotropic Displacement Parameters (Å² × 10⁶) for [2]CPT. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>3464.4(5)</td>
<td>1126.4(6)</td>
<td>911.2(8)</td>
<td>103.3(5)</td>
</tr>
<tr>
<td>N4</td>
<td>4660(4)</td>
<td>1827(5)</td>
<td>1762(6)</td>
<td>107(2)</td>
</tr>
</tbody>
</table>

- 255 -
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>2260(4)</td>
<td>468(4)</td>
<td>57(5)</td>
<td>98(2)</td>
</tr>
<tr>
<td>C101</td>
<td>8243(5)</td>
<td>4108(5)</td>
<td>687(6)</td>
<td>101(3)</td>
</tr>
<tr>
<td>C102</td>
<td>8098(4)</td>
<td>3172(5)</td>
<td>314(5)</td>
<td>101(2)</td>
</tr>
<tr>
<td>N3</td>
<td>4108(3)</td>
<td>735(5)</td>
<td>93(5)</td>
<td>110(2)</td>
</tr>
<tr>
<td>C103</td>
<td>322(5)</td>
<td>-4099(6)</td>
<td>-3222(7)</td>
<td>121(3)</td>
</tr>
<tr>
<td>C110</td>
<td>2642(5)</td>
<td>-569(6)</td>
<td>-1135(8)</td>
<td>125(4)</td>
</tr>
<tr>
<td>C104</td>
<td>2527(6)</td>
<td>-1886(6)</td>
<td>-4208(7)</td>
<td>120(3)</td>
</tr>
<tr>
<td>C1</td>
<td>1107(5)</td>
<td>-3063(5)</td>
<td>-2998(6)</td>
<td>99(2)</td>
</tr>
<tr>
<td>C3</td>
<td>1513(4)</td>
<td>-2299(5)</td>
<td>-2230(6)</td>
<td>102(3)</td>
</tr>
<tr>
<td>C4</td>
<td>1094(5)</td>
<td>-485(5)</td>
<td>-1328(6)</td>
<td>106(3)</td>
</tr>
<tr>
<td>C5</td>
<td>-40(4)</td>
<td>2294(5)</td>
<td>70(5)</td>
<td>97(2)</td>
</tr>
<tr>
<td>C6</td>
<td>9292(4)</td>
<td>5774(5)</td>
<td>984(6)</td>
<td>103(3)</td>
</tr>
<tr>
<td>C7</td>
<td>8787(4)</td>
<td>4772(5)</td>
<td>397(7)</td>
<td>108(3)</td>
</tr>
<tr>
<td>C8</td>
<td>2231(4)</td>
<td>-1385(5)</td>
<td>-2034(6)</td>
<td>103(3)</td>
</tr>
<tr>
<td>C9</td>
<td>3639(9)</td>
<td>1209(9)</td>
<td>5300(9)</td>
<td>159(5)</td>
</tr>
<tr>
<td>N1</td>
<td>2822(3)</td>
<td>1524(4)</td>
<td>1733(6)</td>
<td>117(3)</td>
</tr>
<tr>
<td>C11</td>
<td>5866(5)</td>
<td>2610(5)</td>
<td>3082(6)</td>
<td>108(3)</td>
</tr>
<tr>
<td>C12</td>
<td>6342(5)</td>
<td>2704(5)</td>
<td>2494(6)</td>
<td>106(3)</td>
</tr>
<tr>
<td>C13</td>
<td>5625(4)</td>
<td>2186(5)</td>
<td>1695(8)</td>
<td>123(4)</td>
</tr>
<tr>
<td>C14</td>
<td>439(4)</td>
<td>3598(5)</td>
<td>-668(7)</td>
<td>108(3)</td>
</tr>
<tr>
<td>C15</td>
<td>2023(5)</td>
<td>1638(6)</td>
<td>1577(7)</td>
<td>107(3)</td>
</tr>
<tr>
<td>C16</td>
<td>-621(5)</td>
<td>-4350(6)</td>
<td>-3850(8)</td>
<td>152(4)</td>
</tr>
<tr>
<td>C17</td>
<td>2010(4)</td>
<td>-256(5)</td>
<td>-799(6)</td>
<td>101(3)</td>
</tr>
<tr>
<td>C18</td>
<td>2163(5)</td>
<td>-2053(5)</td>
<td>-3515(6)</td>
<td>104(2)</td>
</tr>
<tr>
<td>C19</td>
<td>141(5)</td>
<td>1670(5)</td>
<td>266(6)</td>
<td>103(2)</td>
</tr>
<tr>
<td>C20</td>
<td>5180(6)</td>
<td>3584(6)</td>
<td>5226(8)</td>
<td>128(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>C22</td>
<td>6763(5)</td>
<td>2684(5)</td>
<td>896(6)</td>
<td>107(3)</td>
</tr>
<tr>
<td>C23</td>
<td>4276(4)</td>
<td>2371(5)</td>
<td>3951(6)</td>
<td>102(2)</td>
</tr>
<tr>
<td>C24</td>
<td>7385(5)</td>
<td>2490(5)</td>
<td>439(6)</td>
<td>109(3)</td>
</tr>
<tr>
<td>C26</td>
<td>1787(5)</td>
<td>1979(5)</td>
<td>2383(7)</td>
<td>113(3)</td>
</tr>
<tr>
<td>C27</td>
<td>665(6)</td>
<td>-4807(6)</td>
<td>-3667(9)</td>
<td>176(6)</td>
</tr>
<tr>
<td>C28</td>
<td>5277(5)</td>
<td>701(6)</td>
<td>-539(8)</td>
<td>124(3)</td>
</tr>
<tr>
<td>C29</td>
<td>2391(8)</td>
<td>-2803(8)</td>
<td>-4996(8)</td>
<td>157(4)</td>
</tr>
<tr>
<td>C30</td>
<td>2454(5)</td>
<td>2087(6)</td>
<td>2988(7)</td>
<td>113(3)</td>
</tr>
<tr>
<td>C31</td>
<td>642(4)</td>
<td>3266(5)</td>
<td>506(5)</td>
<td>96(2)</td>
</tr>
<tr>
<td>C32</td>
<td>8672(5)</td>
<td>4472(6)</td>
<td>-458(7)</td>
<td>103(3)</td>
</tr>
<tr>
<td>C33</td>
<td>1985(8)</td>
<td>-1506(10)</td>
<td>-4559(10)</td>
<td>182(6)</td>
</tr>
<tr>
<td>C34</td>
<td>4793(5)</td>
<td>2117(5)</td>
<td>2609(7)</td>
<td>101(3)</td>
</tr>
<tr>
<td>C35</td>
<td>3645(6)</td>
<td>-1157(8)</td>
<td>-3928(8)</td>
<td>154(4)</td>
</tr>
<tr>
<td>C36</td>
<td>2556(5)</td>
<td>-1284(6)</td>
<td>-2693(7)</td>
<td>106(3)</td>
</tr>
<tr>
<td>C37</td>
<td>1028(4)</td>
<td>1981(5)</td>
<td>787(6)</td>
<td>97(2)</td>
</tr>
<tr>
<td>C38</td>
<td>851(5)</td>
<td>170(6)</td>
<td>-794(7)</td>
<td>119(3)</td>
</tr>
<tr>
<td>C39</td>
<td>661(4)</td>
<td>3908(5)</td>
<td>189(6)</td>
<td>98(2)</td>
</tr>
<tr>
<td>C40</td>
<td>4072(5)</td>
<td>2071(5)</td>
<td>3039(6)</td>
<td>106(3)</td>
</tr>
<tr>
<td>C41</td>
<td>47(8)</td>
<td>-4085(7)</td>
<td>-2441(7)</td>
<td>170(5)</td>
</tr>
<tr>
<td>C42</td>
<td>3872(6)</td>
<td>1700(6)</td>
<td>4216(8)</td>
<td>122(3)</td>
</tr>
<tr>
<td>C44</td>
<td>1462(5)</td>
<td>-2934(5)</td>
<td>-3685(7)</td>
<td>109(3)</td>
</tr>
<tr>
<td>C45</td>
<td>3965(17)</td>
<td>468(17)</td>
<td>4884(18)</td>
<td>377(18)</td>
</tr>
<tr>
<td>C46</td>
<td>8943(5)</td>
<td>5102(5)</td>
<td>-771(7)</td>
<td>116(3)</td>
</tr>
<tr>
<td>C47</td>
<td>4408(5)</td>
<td>-109(5)</td>
<td>-1127(6)</td>
<td>101(2)</td>
</tr>
<tr>
<td>C48</td>
<td>6985(5)</td>
<td>3622(5)</td>
<td>1325(7)</td>
<td>122(3)</td>
</tr>
<tr>
<td>C49</td>
<td>7701(5)</td>
<td>4293(6)</td>
<td>1200(6)</td>
<td>113(3)</td>
</tr>
</tbody>
</table>

- 257 -
C50  4105(6)  1960(7)  5063(8)  130(3)
C52  4770(6)  2925(7)  5646(7)  129(3)
C53  5103(5)  1215(6)  209(7)  104(3)
C54  3139(5)  1823(5)  2549(7)  106(3)
C55  5993(8)  4643(8)  6088(9)  164(5)
C56  3632(4)  -42(5)  -707(5)  98(3)
C57  6799(8)  4665(9)  6609(10)  221(7)
C58  1666(5)  2967(5)  1262(6)  117(3)
C59  5848(5)  2002(5)  922(7)  109(3)
C60  1471(5)  3581(5)  1105(6)  115(3)
C61  5487(11)  5168(10)  6603(12)  259(9)
C62  4912(6)  3313(6)  4550(6)  118(3)
C63  386818  1560(17)  6193(18)  334(14)
C64  1485(4)  1409(5)  817(6)  97(2)
C65  2475(8)  605(10)  4856(11)  220(7)
C67  6589(12)  5216(9)  5611(12)  256(9)
C69  1528(5)  739(5)  95(7)  112(3)

Table S5. Anisotropic Displacement Parameters (Å²×10⁶) for [2]CPT. The Anisotropic displacement factor exponent takes the form: -2π²[bh²U₁₁+bk²U₁₂+...].

<table>
<thead>
<tr>
<th>Atom</th>
<th>U₁₁</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₂₂</th>
<th>U₂₃</th>
<th>U₃₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>56.1(5)</td>
<td>72.8(6)</td>
<td>166.7(11)</td>
<td>69.8(7)</td>
<td>5.1(5)</td>
<td>13.9(4)</td>
</tr>
<tr>
<td>N4</td>
<td>82(4)</td>
<td>94(4)</td>
<td>160(7)</td>
<td>85(5)</td>
<td>32(4)</td>
<td>34(3)</td>
</tr>
<tr>
<td>N2</td>
<td>63(3)</td>
<td>63(3)</td>
<td>162(6)</td>
<td>62(4)</td>
<td>19(3)</td>
<td>21(2)</td>
</tr>
<tr>
<td>C101</td>
<td>59(3)</td>
<td>79(4)</td>
<td>150(7)</td>
<td>70(5)</td>
<td>5(4)</td>
<td>11(3)</td>
</tr>
</tbody>
</table>

S55
<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C102</td>
<td>58(3)</td>
<td>82(4)</td>
<td>146(7)</td>
<td>66(5)</td>
<td>7(4)</td>
</tr>
<tr>
<td>N3</td>
<td>47(2)</td>
<td>115(5)</td>
<td>204(8)</td>
<td>115(6)</td>
<td>46(4)</td>
</tr>
<tr>
<td>C103</td>
<td>68(4)</td>
<td>81(5)</td>
<td>181(9)</td>
<td>68(6)</td>
<td>9(5)</td>
</tr>
<tr>
<td>C110</td>
<td>59(3)</td>
<td>101(6)</td>
<td>248(12)</td>
<td>120(7)</td>
<td>43(5)</td>
</tr>
<tr>
<td>C104</td>
<td>85(4)</td>
<td>83(5)</td>
<td>177(9)</td>
<td>71(6)</td>
<td>17(5)</td>
</tr>
<tr>
<td>C1</td>
<td>64(3)</td>
<td>74(4)</td>
<td>129(6)</td>
<td>53(5)</td>
<td>4(4)</td>
</tr>
<tr>
<td>C3</td>
<td>58(3)</td>
<td>72(4)</td>
<td>162(8)</td>
<td>69(5)</td>
<td>10(4)</td>
</tr>
<tr>
<td>C4</td>
<td>65(3)</td>
<td>63(4)</td>
<td>154(8)</td>
<td>45(5)</td>
<td>0(4)</td>
</tr>
<tr>
<td>C5</td>
<td>59(3)</td>
<td>74(4)</td>
<td>152(7)</td>
<td>64(4)</td>
<td>15(4)</td>
</tr>
<tr>
<td>C6</td>
<td>61(3)</td>
<td>75(4)</td>
<td>157(7)</td>
<td>66(5)</td>
<td>10(4)</td>
</tr>
<tr>
<td>C7</td>
<td>56(3)</td>
<td>77(4)</td>
<td>181(9)</td>
<td>74(6)</td>
<td>7(4)</td>
</tr>
<tr>
<td>C8</td>
<td>52(3)</td>
<td>65(4)</td>
<td>154(7)</td>
<td>54(5)</td>
<td>-2(4)</td>
</tr>
<tr>
<td>C9</td>
<td>157(9)</td>
<td>167(10)</td>
<td>191(12)</td>
<td>141(10)</td>
<td>34(9)</td>
</tr>
<tr>
<td>N1</td>
<td>40(2)</td>
<td>92(4)</td>
<td>220(9)</td>
<td>96(5)</td>
<td>18(4)</td>
</tr>
<tr>
<td>C11</td>
<td>69(4)</td>
<td>78(4)</td>
<td>139(7)</td>
<td>55(5)</td>
<td>-12(4)</td>
</tr>
<tr>
<td>C12</td>
<td>58(3)</td>
<td>75(4)</td>
<td>153(7)</td>
<td>53(5)</td>
<td>12(4)</td>
</tr>
<tr>
<td>C13</td>
<td>41(3)</td>
<td>78(4)</td>
<td>228(11)</td>
<td>86(6)</td>
<td>7(5)</td>
</tr>
<tr>
<td>C14</td>
<td>57(3)</td>
<td>75(4)</td>
<td>180(9)</td>
<td>73(5)</td>
<td>3(4)</td>
</tr>
<tr>
<td>C15</td>
<td>64(4)</td>
<td>87(5)</td>
<td>167(9)</td>
<td>76(6)</td>
<td>22(5)</td>
</tr>
<tr>
<td>C16</td>
<td>72(4)</td>
<td>109(6)</td>
<td>230(12)</td>
<td>97(8)</td>
<td>-15(6)</td>
</tr>
<tr>
<td>C17</td>
<td>55(3)</td>
<td>74(4)</td>
<td>159(8)</td>
<td>70(5)</td>
<td>4(4)</td>
</tr>
<tr>
<td>C18</td>
<td>77(4)</td>
<td>69(4)</td>
<td>146(7)</td>
<td>61(5)</td>
<td>19(5)</td>
</tr>
<tr>
<td>C19</td>
<td>68(3)</td>
<td>71(4)</td>
<td>154(7)</td>
<td>62(5)</td>
<td>9(4)</td>
</tr>
<tr>
<td>C20</td>
<td>91(5)</td>
<td>86(5)</td>
<td>171(10)</td>
<td>53(7)</td>
<td>13(6)</td>
</tr>
<tr>
<td>C22</td>
<td>59(3)</td>
<td>78(4)</td>
<td>152(7)</td>
<td>55(5)</td>
<td>12(4)</td>
</tr>
<tr>
<td>C23</td>
<td>68(3)</td>
<td>73(4)</td>
<td>135(7)</td>
<td>58(5)</td>
<td>-15(4)</td>
</tr>
</tbody>
</table>

- 259 -

556
<table>
<thead>
<tr>
<th>Publication Code</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>C24</td>
<td>58(3) 70(4) 170(8) 64(5) 9(4) 7(3)</td>
</tr>
<tr>
<td>C26</td>
<td>88(3) 86(5) 174(9) 68(6) 3(5) 21(5)</td>
</tr>
<tr>
<td>C27</td>
<td>89(5) 85(6) 320(17) 99(8) 20(7) 25(4)</td>
</tr>
<tr>
<td>C28</td>
<td>65(4) 94(6) 195(10) 85(7) 15(5) 14(4)</td>
</tr>
<tr>
<td>C29</td>
<td>147(8) 126(8) 181(10) 93(8) 56(8) 35(7)</td>
</tr>
<tr>
<td>C30</td>
<td>63(3) 107(5) 167(8) 98(6) 5(4) 15(3)</td>
</tr>
<tr>
<td>C31</td>
<td>69(3) 77(4) 131(6) 59(4) 4(4) 23(3)</td>
</tr>
<tr>
<td>C32</td>
<td>74(4) 80(4) 148(8) 70(5) 5(5) 23(3)</td>
</tr>
<tr>
<td>C33</td>
<td>129(7) 215(13) 259(15) 176(13) 31(9) 76(8)</td>
</tr>
<tr>
<td>C34</td>
<td>60(3) 83(4) 173(9) 84(6) 26(5) 26(3)</td>
</tr>
<tr>
<td>C35</td>
<td>88(5) 174(9) 218(11) 147(9) 33(6) 28(5)</td>
</tr>
<tr>
<td>C36</td>
<td>67(3) 98(5) 175(9) 97(7) 37(5) 29(4)</td>
</tr>
<tr>
<td>C37</td>
<td>61(3) 77(4) 155(7) 65(5) 21(4) 29(3)</td>
</tr>
<tr>
<td>C38</td>
<td>63(3) 94(5) 191(9) 91(6) 3(5) 15(4)</td>
</tr>
<tr>
<td>C39</td>
<td>66(3) 70(4) 137(7) 56(5) -10(4) 18(3)</td>
</tr>
<tr>
<td>C40</td>
<td>67(4) 72(4) 158(8) 67(5) -15(4) 13(3)</td>
</tr>
<tr>
<td>C41</td>
<td>138(8) 115(7) 174(10) 81(7) 45(7) -15(6)</td>
</tr>
<tr>
<td>C42</td>
<td>79(4) 96(5) 185(10) 84(7) 17(6) 25(4)</td>
</tr>
<tr>
<td>C43</td>
<td>65(3) 86(5) 163(8) 68(5) 18(4) 23(3)</td>
</tr>
<tr>
<td>C44</td>
<td>490(30) 490(30) 730(50) 560(40) 500(40) 410(30)</td>
</tr>
<tr>
<td>C45</td>
<td>72(4) 70(4) 177(8) 64(5) 6(5) 15(5)</td>
</tr>
<tr>
<td>C46</td>
<td>67(4) 80(4) 129(6) 50(5) 17(4) 18(3)</td>
</tr>
<tr>
<td>C47</td>
<td>71(4) 66(4) 190(9) 58(5) 8(5) 10(3)</td>
</tr>
<tr>
<td>C48</td>
<td>67(4) 89(5) 164(8) 78(5) 18(5) 10(3)</td>
</tr>
<tr>
<td>C49</td>
<td>97(5) 111(7) 164(9) 82(7) 12(6) 27(5)</td>
</tr>
<tr>
<td>C50</td>
<td>109(6) 115(7) 140(8) 66(6) -8(6) 43(5)</td>
</tr>
<tr>
<td>C51</td>
<td>557</td>
</tr>
<tr>
<td>Atom</td>
<td>Atom</td>
</tr>
<tr>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>N1</td>
<td>N4</td>
</tr>
<tr>
<td>N1</td>
<td>N2</td>
</tr>
<tr>
<td>N1</td>
<td>N3</td>
</tr>
<tr>
<td>N1</td>
<td>N1</td>
</tr>
<tr>
<td>N4</td>
<td>C34</td>
</tr>
<tr>
<td>N4</td>
<td>C13</td>
</tr>
<tr>
<td>N2</td>
<td>C69</td>
</tr>
</tbody>
</table>

Table S6. Bond Lengths for [2]CPT.
<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>C17</td>
<td>1.412(11)</td>
<td>C18</td>
<td>C44</td>
</tr>
<tr>
<td>C101</td>
<td>C49</td>
<td>1.318(12)</td>
<td>C18</td>
<td>C36</td>
</tr>
<tr>
<td>C101</td>
<td>C102</td>
<td>1.404(10)</td>
<td>C19</td>
<td>C37</td>
</tr>
<tr>
<td>C101</td>
<td>C7</td>
<td>1.469(11)</td>
<td>C20</td>
<td>C62</td>
</tr>
<tr>
<td>C102</td>
<td>C24</td>
<td>1.380(9)</td>
<td>C20</td>
<td>C52</td>
</tr>
<tr>
<td>N3</td>
<td>C56</td>
<td>1.359(10)</td>
<td>C20</td>
<td>C55</td>
</tr>
<tr>
<td>N3</td>
<td>C53</td>
<td>1.362(8)</td>
<td>C22</td>
<td>C24</td>
</tr>
<tr>
<td>C103</td>
<td>C1</td>
<td>1.520(9)</td>
<td>C22</td>
<td>C48</td>
</tr>
<tr>
<td>C103</td>
<td>C41</td>
<td>1.521(4)</td>
<td>C22</td>
<td>C59</td>
</tr>
<tr>
<td>C103</td>
<td>C16</td>
<td>1.533(11)</td>
<td>C23</td>
<td>C62</td>
</tr>
<tr>
<td>C103</td>
<td>C27</td>
<td>1.552(14)</td>
<td>C23</td>
<td>C42</td>
</tr>
<tr>
<td>C110</td>
<td>C56</td>
<td>1.363(9)</td>
<td>C23</td>
<td>C40</td>
</tr>
<tr>
<td>C110</td>
<td>C17</td>
<td>1.365(12)</td>
<td>C26</td>
<td>C30</td>
</tr>
<tr>
<td>C110</td>
<td>C8</td>
<td>1.493(14)</td>
<td>C28</td>
<td>C47</td>
</tr>
<tr>
<td>C104</td>
<td>C18</td>
<td>1.506(12)</td>
<td>C28</td>
<td>C53</td>
</tr>
<tr>
<td>C104</td>
<td>C33</td>
<td>1.531(13)</td>
<td>C30</td>
<td>C54</td>
</tr>
<tr>
<td>C104</td>
<td>C35</td>
<td>1.547(10)</td>
<td>C31</td>
<td>C60</td>
</tr>
<tr>
<td>C104</td>
<td>C29</td>
<td>1.551(15)</td>
<td>C31</td>
<td>C39</td>
</tr>
<tr>
<td>C1</td>
<td>C3</td>
<td>1.315(11)</td>
<td>C32</td>
<td>C46</td>
</tr>
<tr>
<td>C1</td>
<td>C44</td>
<td>1.464(12)</td>
<td>C34</td>
<td>C40</td>
</tr>
<tr>
<td>C3</td>
<td>C8</td>
<td>1.401(8)</td>
<td>C37</td>
<td>C58</td>
</tr>
<tr>
<td>C4</td>
<td>C38</td>
<td>1.366(12)</td>
<td>C37</td>
<td>C64</td>
</tr>
<tr>
<td>C4</td>
<td>C17</td>
<td>1.452(9)</td>
<td>C38</td>
<td>C69</td>
</tr>
<tr>
<td>C5</td>
<td>C31</td>
<td>1.389(9)</td>
<td>C39</td>
<td>C46</td>
</tr>
<tr>
<td>C5</td>
<td>C19</td>
<td>1.423(9)</td>
<td>C40</td>
<td>C54</td>
</tr>
<tr>
<td>C6</td>
<td>C14</td>
<td>1.399(10)</td>
<td>C42</td>
<td>C50</td>
</tr>
</tbody>
</table>

559
Publications

\begin{align*}
\text{C6} & \quad \text{C7} & \quad 1.421(11) & \quad \text{C47} & \quad \text{C56} & \quad 1.478(11) \\
\text{C7} & \quad \text{C32} & \quad 1.378(12) & \quad \text{C48} & \quad \text{C49} & \quad 1.370(10) \\
\text{C8} & \quad \text{C36} & \quad 1.380(12) & \quad \text{C50} & \quad \text{C52} & \quad 1.397(13) \\
\text{C9} & \quad \text{C63} & \quad 1.42(3) & \quad \text{C53} & \quad \text{C59} & \quad 1.367(11) \\
\text{C9} & \quad \text{C50} & \quad 1.495(13) & \quad \text{C55} & \quad \text{C57} & \quad 1.494(17) \\
\text{C9} & \quad \text{C45} & \quad 1.51(2) & \quad \text{C55} & \quad \text{C61} & \quad 1.514(18) \\
\text{C9} & \quad \text{C65} & \quad 1.585(16) & \quad \text{C55} & \quad \text{C67} & \quad 1.609(19) \\
\text{N1} & \quad \text{C54} & \quad 1.315(11) & \quad \text{C58} & \quad \text{C60} & \quad 1.376(10) \\
\text{N1} & \quad \text{C15} & \quad 1.365(9) & \quad \text{C64} & \quad \text{C69} & \quad 1.365(12)
\end{align*}

\[1\text{-X,1-Y, Z}\]

\textbf{Table S7. Bond Angles for [2]CPT.}

\begin{tabular}{cccccc}
Atom & Atom & Atom & Angle$^\circ$ & Atom & Atom & Angle$^\circ$ \\
N4 & Ni1 & N2 & 177.6(2) & C36 & C18 & C104 & 118.0(6) \\
N4 & Ni1 & N3 & 89.4(5) & C37 & C19 & C5 & 121.0(6) \\
N2 & Ni1 & N3 & 91.2(3) & C62 & C20 & C52 & 121.5(9) \\
N4 & Ni1 & N1 & 90.5(3) & C62 & C20 & C55 & 127.1(10) \\
N2 & Ni1 & N1 & 89.0(3) & C52 & C20 & C55 & 111.4(11) \\
N3 & Ni1 & N1 & 179.8(2) & C24 & C22 & C48 & 115.9(7) \\
C34 & N4 & C13 & 104.2(8) & C24 & C22 & C59 & 127.5(8) \\
C34 & N4 & Ni1 & 127.2(5) & C48 & C22 & C59 & 116.3(8) \\
C13 & N4 & Ni1 & 128.7(8) & C62 & C23 & C42 & 119.5(9) \\
C69 & N2 & C17 & 106.0(7) & C62 & C23 & C40 & 119.4(7) \\
C69 & N2 & Ni1 & 125.3(6) & C42 & C23 & C40 & 121.0(7) \\
C17 & N2 & Ni1 & 127.4(5) & C22 & C24 & C102 & 121.4(7)
\end{tabular}

\textbf{S60}
<table>
<thead>
<tr>
<th>C49</th>
<th>C101 C102</th>
<th>115.2(7)</th>
<th>C30</th>
<th>C26</th>
<th>C15</th>
<th>109.1(8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C49</td>
<td>C101 C7</td>
<td>120.9(8)</td>
<td>C47</td>
<td>C28</td>
<td>C53</td>
<td>111.1(8)</td>
</tr>
<tr>
<td>C102</td>
<td>C101 C7</td>
<td>122.7(9)</td>
<td>C26</td>
<td>C30</td>
<td>C54</td>
<td>104.8(9)</td>
</tr>
<tr>
<td>C24</td>
<td>C102 C101</td>
<td>121.3(8)</td>
<td>C60</td>
<td>C31</td>
<td>C5</td>
<td>117.7(6)</td>
</tr>
<tr>
<td>C56</td>
<td>N3 C53</td>
<td>111.0(8)</td>
<td>C60</td>
<td>C31</td>
<td>C39</td>
<td>117.3(6)</td>
</tr>
<tr>
<td>C56</td>
<td>N3 N11</td>
<td>124.2(4)</td>
<td>C5</td>
<td>C31</td>
<td>C39</td>
<td>122.7(6)</td>
</tr>
<tr>
<td>C53</td>
<td>N3 N11</td>
<td>124.7(7)</td>
<td>C7</td>
<td>C32</td>
<td>C46</td>
<td>122.9(8)</td>
</tr>
<tr>
<td>C1</td>
<td>C103 C41</td>
<td>112.1(8)</td>
<td>N4</td>
<td>C34</td>
<td>C40</td>
<td>127.3(7)</td>
</tr>
<tr>
<td>C1</td>
<td>C103 C16</td>
<td>108.3(7)</td>
<td>N4</td>
<td>C34</td>
<td>C11</td>
<td>111.3(8)</td>
</tr>
<tr>
<td>C41</td>
<td>C103 C16</td>
<td>107.5(8)</td>
<td>C40</td>
<td>C34</td>
<td>C11</td>
<td>121.1(9)</td>
</tr>
<tr>
<td>C1</td>
<td>C103 C27</td>
<td>111.3(7)</td>
<td>C18</td>
<td>C36</td>
<td>C8</td>
<td>120.8(6)</td>
</tr>
<tr>
<td>C41</td>
<td>C103 C27</td>
<td>109.8(9)</td>
<td>C19</td>
<td>C37</td>
<td>C58</td>
<td>117.1(6)</td>
</tr>
<tr>
<td>C16</td>
<td>C103 C27</td>
<td>107.7(9)</td>
<td>C19</td>
<td>C37</td>
<td>C64</td>
<td>128.0(7)</td>
</tr>
<tr>
<td>C56</td>
<td>C110 C17</td>
<td>119.6(10)</td>
<td>C58</td>
<td>C37</td>
<td>C64</td>
<td>114.1(6)</td>
</tr>
<tr>
<td>C56</td>
<td>C110 C8</td>
<td>122.6(8)</td>
<td>C4</td>
<td>C38</td>
<td>C69</td>
<td>111.2(7)</td>
</tr>
<tr>
<td>C17</td>
<td>C110 C8</td>
<td>116.9(7)</td>
<td>C14</td>
<td>C39</td>
<td>C46</td>
<td>118.0(7)</td>
</tr>
<tr>
<td>C18</td>
<td>C104 C33</td>
<td>112.7(9)</td>
<td>C14</td>
<td>C39</td>
<td>C31</td>
<td>121.3(7)</td>
</tr>
<tr>
<td>C18</td>
<td>C104 C35</td>
<td>114.5(8)</td>
<td>C46</td>
<td>C39</td>
<td>C31</td>
<td>120.0(8)</td>
</tr>
<tr>
<td>C33</td>
<td>C104 C35</td>
<td>105.3(7)</td>
<td>C34</td>
<td>C40</td>
<td>C54</td>
<td>114.2(9)</td>
</tr>
<tr>
<td>C18</td>
<td>C104 C29</td>
<td>113.5(7)</td>
<td>C34</td>
<td>C40</td>
<td>C23</td>
<td>123.6(6)</td>
</tr>
<tr>
<td>C33</td>
<td>C104 C29</td>
<td>105.4(10)</td>
<td>C54</td>
<td>C40</td>
<td>C23</td>
<td>121.7(8)</td>
</tr>
<tr>
<td>C35</td>
<td>C104 C29</td>
<td>104.6(9)</td>
<td>C50</td>
<td>C42</td>
<td>C23</td>
<td>121.7(9)</td>
</tr>
<tr>
<td>C3</td>
<td>C1 C44</td>
<td>116.3(6)</td>
<td>C18</td>
<td>C44</td>
<td>C1</td>
<td>120.2(9)</td>
</tr>
<tr>
<td>C3</td>
<td>C1 C103</td>
<td>125.4(8)</td>
<td>C32</td>
<td>C46</td>
<td>C39</td>
<td>118.9(9)</td>
</tr>
<tr>
<td>C44</td>
<td>C1 C103</td>
<td>118.2(8)</td>
<td>C28</td>
<td>C47</td>
<td>C56</td>
<td>104.0(8)</td>
</tr>
<tr>
<td>C1</td>
<td>C3 C8</td>
<td>124.8(9)</td>
<td>C22</td>
<td>C48</td>
<td>C49</td>
<td>121.3(10)</td>
</tr>
<tr>
<td>C38</td>
<td>C4</td>
<td>C17</td>
<td>103.5(8)</td>
<td>C101</td>
<td>C49</td>
<td>C48</td>
</tr>
<tr>
<td>------</td>
<td>-----</td>
<td>-----</td>
<td>----------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>C31</td>
<td>C5</td>
<td>C19</td>
<td>119.8(6)</td>
<td>C42</td>
<td>C50</td>
<td>C52</td>
</tr>
<tr>
<td>C14</td>
<td>C6</td>
<td>C7</td>
<td>119.1(9)</td>
<td>C42</td>
<td>C50</td>
<td>C9</td>
</tr>
<tr>
<td>C32</td>
<td>C7</td>
<td>C6</td>
<td>117.5(7)</td>
<td>C52</td>
<td>C50</td>
<td>C9</td>
</tr>
<tr>
<td>C32</td>
<td>C7</td>
<td>C101</td>
<td>121.7(7)</td>
<td>C50</td>
<td>C52</td>
<td>C20</td>
</tr>
<tr>
<td>C6</td>
<td>C7</td>
<td>C101</td>
<td>119.6(10)</td>
<td>N3</td>
<td>C53</td>
<td>C59</td>
</tr>
<tr>
<td>C36</td>
<td>C8</td>
<td>C3</td>
<td>117.6(8)</td>
<td>N3</td>
<td>C53</td>
<td>C28</td>
</tr>
<tr>
<td>C36</td>
<td>C8</td>
<td>C110</td>
<td>122.3(6)</td>
<td>C59</td>
<td>C53</td>
<td>C28</td>
</tr>
<tr>
<td>C3</td>
<td>C8</td>
<td>C110</td>
<td>120.1(8)</td>
<td>N1</td>
<td>C54</td>
<td>C40</td>
</tr>
<tr>
<td>C63</td>
<td>C9</td>
<td>C50</td>
<td>114.4(13)</td>
<td>N1</td>
<td>C54</td>
<td>C30</td>
</tr>
<tr>
<td>C63</td>
<td>C9</td>
<td>C45</td>
<td>108.4(14)</td>
<td>C40</td>
<td>C54</td>
<td>C30</td>
</tr>
<tr>
<td>C50</td>
<td>C9</td>
<td>C45</td>
<td>108.5(11)</td>
<td>C57</td>
<td>C55</td>
<td>C61</td>
</tr>
<tr>
<td>C63</td>
<td>C9</td>
<td>C65</td>
<td>112.3(15)</td>
<td>C57</td>
<td>C55</td>
<td>C67</td>
</tr>
<tr>
<td>C50</td>
<td>C9</td>
<td>C65</td>
<td>110.1(9)</td>
<td>C61</td>
<td>C55</td>
<td>C67</td>
</tr>
<tr>
<td>C45</td>
<td>C9</td>
<td>C65</td>
<td>102.3(15)</td>
<td>C57</td>
<td>C55</td>
<td>C20</td>
</tr>
<tr>
<td>C54</td>
<td>N1</td>
<td>C15</td>
<td>110.6(9)</td>
<td>C61</td>
<td>C55</td>
<td>C20</td>
</tr>
<tr>
<td>C54</td>
<td>N1</td>
<td>N11</td>
<td>125.0(5)</td>
<td>C67</td>
<td>C55</td>
<td>C20</td>
</tr>
<tr>
<td>C15</td>
<td>N1</td>
<td>N11</td>
<td>124.0(8)</td>
<td>N3</td>
<td>C56</td>
<td>C110</td>
</tr>
<tr>
<td>C12</td>
<td>C11</td>
<td>C34</td>
<td>103.7(6)</td>
<td>N3</td>
<td>C56</td>
<td>C47</td>
</tr>
<tr>
<td>C11</td>
<td>C12</td>
<td>C13</td>
<td>108.5(7)</td>
<td>C110</td>
<td>C56</td>
<td>C47</td>
</tr>
<tr>
<td>N4</td>
<td>C13</td>
<td>C59</td>
<td>124.1(9)</td>
<td>C60</td>
<td>C58</td>
<td>C37</td>
</tr>
<tr>
<td>N4</td>
<td>C13</td>
<td>C12</td>
<td>111.6(10)</td>
<td>C53</td>
<td>C59</td>
<td>C13</td>
</tr>
<tr>
<td>C59</td>
<td>C13</td>
<td>C12</td>
<td>124.2(7)</td>
<td>C53</td>
<td>C59</td>
<td>C22</td>
</tr>
<tr>
<td>C39</td>
<td>C14</td>
<td>C61</td>
<td>122.7(7)</td>
<td>C13</td>
<td>C59</td>
<td>C22</td>
</tr>
<tr>
<td>C64</td>
<td>C15</td>
<td>N1</td>
<td>128.2(10)</td>
<td>C31</td>
<td>C60</td>
<td>C58</td>
</tr>
<tr>
<td>C64</td>
<td>C15</td>
<td>C26</td>
<td>125.6(8)</td>
<td>C20</td>
<td>C62</td>
<td>C23</td>
</tr>
</tbody>
</table>
### Table S8. Hydrogen Atom Coordinates (Å×10^6) and Isotropic Displacement Parameters (Å^2×10^3) for [2]CPT.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H102</td>
<td>8489.27</td>
<td>3008.85</td>
<td>-24</td>
<td>121</td>
</tr>
<tr>
<td>H3</td>
<td>1308.9</td>
<td>-2370.65</td>
<td>-1782.86</td>
<td>123</td>
</tr>
<tr>
<td>H4</td>
<td>754.05</td>
<td>-963.44</td>
<td>-1895.68</td>
<td>127</td>
</tr>
<tr>
<td>H5</td>
<td>-613.17</td>
<td>2052.12</td>
<td>-347.92</td>
<td>116</td>
</tr>
<tr>
<td>H6</td>
<td>9442.05</td>
<td>6009.1</td>
<td>1569.87</td>
<td>124</td>
</tr>
<tr>
<td>H11</td>
<td>6145.63</td>
<td>2807.51</td>
<td>3645.32</td>
<td>129</td>
</tr>
<tr>
<td>H12</td>
<td>7025.75</td>
<td>3052.07</td>
<td>2602.78</td>
<td>128</td>
</tr>
<tr>
<td>H14</td>
<td>95.59</td>
<td>2942.51</td>
<td>-1055.46</td>
<td>129</td>
</tr>
<tr>
<td>H16A</td>
<td>-1125.96</td>
<td>-4977.99</td>
<td>-3998.41</td>
<td>227</td>
</tr>
<tr>
<td>H16B</td>
<td>-853.11</td>
<td>-3900.64</td>
<td>-3587.62</td>
<td>227</td>
</tr>
<tr>
<td>H16C</td>
<td>-474.19</td>
<td>-4354.08</td>
<td>-4356.29</td>
<td>227</td>
</tr>
<tr>
<td>H19</td>
<td>-356.96</td>
<td>1038.76</td>
<td>32.36</td>
<td>123</td>
</tr>
<tr>
<td>H24</td>
<td>7328.29</td>
<td>1885.73</td>
<td>205.99</td>
<td>131</td>
</tr>
<tr>
<td>H26</td>
<td>1261.19</td>
<td>2102.7</td>
<td>2467.48</td>
<td>136</td>
</tr>
</tbody>
</table>

^1-\times \text{X,1-Y,-Z}
<table>
<thead>
<tr>
<th>H27A</th>
<th>156.44</th>
<th>-5427.22</th>
<th>-3799.74</th>
<th>264</th>
</tr>
</thead>
<tbody>
<tr>
<td>H27B</td>
<td>785.85</td>
<td>-4825.51</td>
<td>-4184.26</td>
<td>264</td>
</tr>
<tr>
<td>H27C</td>
<td>1266.1</td>
<td>-4632.45</td>
<td>-3291.33</td>
<td>264</td>
</tr>
<tr>
<td>H28</td>
<td>5896.97</td>
<td>878.59</td>
<td>-632.96</td>
<td>149</td>
</tr>
<tr>
<td>H29A</td>
<td>2635.93</td>
<td>-2650.46</td>
<td>-5412.63</td>
<td>236</td>
</tr>
<tr>
<td>H29B</td>
<td>2753.75</td>
<td>-3054.41</td>
<td>-4821.94</td>
<td>236</td>
</tr>
<tr>
<td>H29C</td>
<td>1697.57</td>
<td>-3273.41</td>
<td>-5241.56</td>
<td>236</td>
</tr>
<tr>
<td>H30</td>
<td>2476.86</td>
<td>2284.85</td>
<td>3557.81</td>
<td>135</td>
</tr>
<tr>
<td>H32</td>
<td>8402.62</td>
<td>3821.34</td>
<td>-844.52</td>
<td>123</td>
</tr>
<tr>
<td>H33A</td>
<td>2242.58</td>
<td>-1411.98</td>
<td>-4997.08</td>
<td>273</td>
</tr>
<tr>
<td>H33B</td>
<td>1286.71</td>
<td>-1959.88</td>
<td>-4795.14</td>
<td>273</td>
</tr>
<tr>
<td>H33C</td>
<td>2085.16</td>
<td>-907.77</td>
<td>-4105.03</td>
<td>273</td>
</tr>
<tr>
<td>H35A</td>
<td>3818.86</td>
<td>-1091.08</td>
<td>-4402.24</td>
<td>232</td>
</tr>
<tr>
<td>H35B</td>
<td>3778.12</td>
<td>-548.39</td>
<td>-3468.03</td>
<td>232</td>
</tr>
<tr>
<td>H35C</td>
<td>4032.57</td>
<td>-1380.32</td>
<td>-3739.03</td>
<td>232</td>
</tr>
<tr>
<td>H36</td>
<td>3046.08</td>
<td>-689.9</td>
<td>-2580.43</td>
<td>127</td>
</tr>
<tr>
<td>H38</td>
<td>329.9</td>
<td>251.15</td>
<td>-962.79</td>
<td>143</td>
</tr>
<tr>
<td>H41A</td>
<td>-448.65</td>
<td>-4723.14</td>
<td>-2608.34</td>
<td>255</td>
</tr>
<tr>
<td>H41B</td>
<td>627.34</td>
<td>-3891.99</td>
<td>-2028.76</td>
<td>255</td>
</tr>
<tr>
<td>H41C</td>
<td>-211.63</td>
<td>-3655.06</td>
<td>-2192.25</td>
<td>255</td>
</tr>
<tr>
<td>H42</td>
<td>3435.12</td>
<td>1062.85</td>
<td>3808.16</td>
<td>147</td>
</tr>
<tr>
<td>H44</td>
<td>1208.13</td>
<td>-3453.7</td>
<td>-4239.05</td>
<td>131</td>
</tr>
<tr>
<td>H45A</td>
<td>3803.58</td>
<td>223.34</td>
<td>4278.77</td>
<td>566</td>
</tr>
<tr>
<td>H45B</td>
<td>4670.43</td>
<td>758.38</td>
<td>5118.28</td>
<td>566</td>
</tr>
<tr>
<td>H45C</td>
<td>3628.71</td>
<td>-46.08</td>
<td>4991.25</td>
<td>566</td>
</tr>
<tr>
<td>H46</td>
<td>8865.07</td>
<td>4875.16</td>
<td>-1351.47</td>
<td>139</td>
</tr>
<tr>
<td>H47</td>
<td>4328.99</td>
<td>-585.62</td>
<td>-1662.81</td>
<td>122</td>
</tr>
<tr>
<td>H48</td>
<td>6642.95</td>
<td>3807.98</td>
<td>1708.75</td>
<td>148</td>
</tr>
<tr>
<td>H49</td>
<td>7811.51</td>
<td>4917.33</td>
<td>1495.55</td>
<td>136</td>
</tr>
<tr>
<td>H52</td>
<td>4949.96</td>
<td>3144.46</td>
<td>6228.22</td>
<td>155</td>
</tr>
<tr>
<td>H57A</td>
<td>7079.79</td>
<td>4317.76</td>
<td>6236.35</td>
<td>332</td>
</tr>
<tr>
<td>H57B</td>
<td>7307.82</td>
<td>5316.5</td>
<td>6987.17</td>
<td>332</td>
</tr>
<tr>
<td>H57C</td>
<td>6528.37</td>
<td>4374.51</td>
<td>6937.89</td>
<td>332</td>
</tr>
<tr>
<td>H58</td>
<td>2231.76</td>
<td>3214.13</td>
<td>1690.48</td>
<td>141</td>
</tr>
<tr>
<td>H60</td>
<td>1921.31</td>
<td>4233.12</td>
<td>1421.25</td>
<td>138</td>
</tr>
<tr>
<td>H61A</td>
<td>4981.53</td>
<td>5119.94</td>
<td>6222.53</td>
<td>376</td>
</tr>
<tr>
<td>H61B</td>
<td>5190.3</td>
<td>4887.65</td>
<td>6931.54</td>
<td>376</td>
</tr>
<tr>
<td>H61C</td>
<td>5969.75</td>
<td>5829.63</td>
<td>6980.83</td>
<td>376</td>
</tr>
<tr>
<td>H62</td>
<td>5151.16</td>
<td>3760.32</td>
<td>4374.79</td>
<td>142</td>
</tr>
<tr>
<td>H63A</td>
<td>3560.75</td>
<td>1038.8</td>
<td>6294.08</td>
<td>501</td>
</tr>
<tr>
<td>H63B</td>
<td>4592.79</td>
<td>1857.43</td>
<td>6423.74</td>
<td>501</td>
</tr>
<tr>
<td>H63C</td>
<td>3670.87</td>
<td>2021.7</td>
<td>6465.43</td>
<td>501</td>
</tr>
<tr>
<td>H65A</td>
<td>2342.44</td>
<td>382.97</td>
<td>4254.8</td>
<td>330</td>
</tr>
<tr>
<td>H65B</td>
<td>2196.71</td>
<td>66.77</td>
<td>4939.71</td>
<td>330</td>
</tr>
<tr>
<td>H65C</td>
<td>2179.17</td>
<td>1000.91</td>
<td>5104.25</td>
<td>330</td>
</tr>
<tr>
<td>H67A</td>
<td>6133.29</td>
<td>5245.34</td>
<td>5283.98</td>
<td>383</td>
</tr>
<tr>
<td>H67B</td>
<td>7083.04</td>
<td>5853.7</td>
<td>6072.94</td>
<td>383</td>
</tr>
<tr>
<td>H67C</td>
<td>6907.18</td>
<td>4891.58</td>
<td>5298.51</td>
<td>383</td>
</tr>
</tbody>
</table>

565
Figure S36. Solid state structure of [2]CPT₃C₆0. Thermal ellipsoids are shown at the 30% probability level (top), representation of the packing structure (bottom). The cif-file was deposited in the Cambridge Structural Database under identifier CCDC 1909921.
Table S9. Crystal data and structure refinement for [2]CPT\(\supseteq\)C_{80}.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>[2]CPT(\supseteq)C_{80}</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{18}H_{12}N_{2}Ni_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>2660.38</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(_1)/n</td>
</tr>
<tr>
<td>a/Å</td>
<td>15.830(5)</td>
</tr>
<tr>
<td>b/Å</td>
<td>34.130(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>30.670(5)</td>
</tr>
<tr>
<td>(\alpha^\circ)</td>
<td>90</td>
</tr>
<tr>
<td>(\beta^\circ)</td>
<td>90.14(8)</td>
</tr>
<tr>
<td>(\gamma^\circ)</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å(^3)</td>
<td>16570.3(10)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}/\text{cm}^3)</td>
<td>1.066</td>
</tr>
<tr>
<td>(\mu/\text{mm}^{-1})</td>
<td>0.400</td>
</tr>
<tr>
<td>F(000)</td>
<td>6144.0</td>
</tr>
<tr>
<td>Crystal size/mm(^3)</td>
<td>0.08 × 0.06 × 0.06</td>
</tr>
<tr>
<td>Radiation</td>
<td>synchrotron ((\lambda = 0.72656))</td>
</tr>
<tr>
<td>2(\Theta) range for data collection/(\text{°})</td>
<td>4.16 to 41.628</td>
</tr>
<tr>
<td>Index ranges</td>
<td>(-15 \leq h \leq 15, -34 \leq k \leq 34, -30 \leq l \leq 30)</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>106778</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>16657 (\left[R_{\text{rel}} = 0.0727, R_{\text{merge}} = 0.0489\right])</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>16657/174/1759</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>2.346</td>
</tr>
<tr>
<td>Final R indexes ([D=\sigma(D)])</td>
<td>(R_1 = 0.1632, wR_2 = 0.4829)</td>
</tr>
<tr>
<td>Final R indexes ([\text{all data}])</td>
<td>(R_1 = 0.1915, wR_2 = 0.5189)</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å(^{-1})</td>
<td>1.01/-2.12</td>
</tr>
</tbody>
</table>
7. DFT Calculations

a) Computational methods

Relaxed geometries were obtained from density-functional theory (DFT). The calculations were carried out with the plane-wave code PWscf of the Quantum Espresso software package,\(^5,8\) using the gradient-corrected Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional,\(^9\) Grimme D3 dispersion corrections with Becke-Johnson damping,\(^5,5,1,5\) Vanderbilt ultrasoft pseudopotentials\(^9\) and a plane-wave basis set with a kinetic energy cutoff of 30 Ry. The tert-butyl groups were replaced by H atoms to reduce the complexity and computational cost. In the geometry optimizations structures were assumed to be relaxed when a force convergence threshold of 3 meV/Å was reached.

Electronic properties and absorption spectra were determined with the ORCA code,\(^3,1,3\) using the B3LYP hybrid exchange-correlation functional,\(^5,4,5,4,5,5\) the triple-zeta def2-TZVP basis set\(^5,1,6\) and the RIJCOSX approximation with def2/J auxiliary basis functions.\(^5,7\) The calculations were done for the optimized PBE+D3 geometries from PWscf. In addition, for the calculation of the strain energy of the rings, all structures were re-optimized by including Grimme D3 dispersion corrections (B3LYP+D3) and without using the RIJCOSX approximation. Time-dependent density-functional theory (TD-DFT) was used for the calculation of absorption spectra. Solvation effects in THF were taken into account with the implicit conductor-like continuum polarization model (C-PCM) using a dielectric constant of 7.25 and a refractive index of 1.407.

b) Structures of the tetraphenyl porphyrin and the terphenyl bridge

In the gas phase, Ni-tetraphenyl-porphyrins (Ni-TPP) adopt the ruffled configuration with \(S_4\) symmetry. In this structure, the pyrrole rings are alternately rotated clockwise and anticlockwise by about 16.5° and the meso carbon atoms (C\(_\text{meso}\)) are displaced alternately 0.486 Å above and below the mean porphyrin plane (see Figure S37). This leads to a wave-like bending of the porphyrin core with an out-of-plane tilt of the line connecting the central Ni and the C\(_\text{meso}\) atoms of 4.2° (10.8° for the line connecting Ni and the outer atom C\(\alpha\) of the phenyl ring, see Figure S37). Simultaneously, the phenyl rings are alternately rotated clockwise and anticlockwise out of a vertical orientation with respect to the mean plane of the porphyrin core by about 30°.

The saddle configuration of Ni-TPP (D\(_{5d}\) symmetry), in which the pyrrole rings are not rotated but alternately tilted up and down, is higher in energy by 0.8 kcal/mol (3.2 kJ/mol, PBE+D3). Rotating all phenyl rings into the same orientation (propeller-like structure with D\(_3\) symmetry) increases the energy by 2.0 kcal/mol (8.4 kJ/mol) compared to the ruffled ground state (PBE+D3).

In the terphenyl bridge neighboring phenyl rings are rotated out of a common plane with a dihedral angle \(β\) of 35.7° between pairs of carbon atoms on the neighboring phenylene units (see Figure S37). This rotation can be in alternate directions (shown in Figure S37) or in the same direction along the chain. Both conformers have the same energy within the accuracy of the calculations (PBE+D3). The carbon atoms C\(_1\),
C₂, C₃ and C₄ (see Figure S37) strictly stay on one line, i.e. the angles between the C₁-C₂-C₃ and C₂-C₃-C₄ atoms do not deviate from 180° degree.

The OH groups at the (1,4) position of the central p-phenylene unit change the hybridization of the carbon atoms C₁ and C₄ from sp² to sp³. Accordingly, the angles between C₁-C₂-C₃ and C₂-C₃-C₄ become 123.2° and 177.5°, i.e. they deviate by θ₁=56.8° and θ₂=2.5° from 180°, respectively, see Figure S37. The OH groups are oriented outwards. Rotating the OH groups to an inward orientation increases the energy by 2.7 kcal/mol (11.3 kJ/mol, PBE+D3).

Figure S37. Top: Ruffled ground state structure of Ni-TPP in the gas phase (top and two side views). Bottom: Structure of the terphenyl bridges with and without OH groups.

c) Structure of the ring molecules

The [2]CPT ring is rather rigid and has only a small number of flexible degrees of freedom. In our geometry optimizations we probed different orientations of the free phenyl rings at the porphyrins and different inward/outward tilts of the phenyl rings in the terphenyl bridges. Depending on the combination of the different rotations, the [2]CPT ring can have D₅, C₃, C₁ (only one axis from the D₅ group remains) or C₁ symmetry. The lowest energy is found for the D₅ conformer (PBE+D3, see Figure S38). However, the energy of most conformers is within a range of 1 kcal/mol. In the D₅ structure, all phenyl rings next to the porphyrin core maintain the same orientation as in the ruffled gas phase conformation, though the ruffling amplitude is now significantly enlarged due to the bending of the ring. We characterize the
bending of C-C bonds in the ring by the two angles $\theta_1$ and $\theta_2$ within the terphenyl bridge (see Figure S37) and we introduce the angles $\theta_3$ and $\theta_4$ as the deviation of the angles between the atoms C$_{5}$-C$_{6}$-C$_{7}$ and C$_{1}$-C$_{2}$-Ni from 180°, respectively. The calculated values are summarized in Table S10 together with the ring diameters $d$ and $D$.

**Figure S38.** Optimized structures (PBE+D3) of the [2]CPT and [3]CPT rings in the gas phase.

**Table S10.** Summary of structural parameters of the nanorings from the PBE+D3 calculations. The diameters $d$ are the Ni-Ni distances and $D$ are the distances between midpoints of the middle p-phenylene, (for [2]CPT) or between a p-phenylene midpoint and a Ni ion (for [3]CPT, see Figure S38). $\beta$ and $\alpha$ are the dihedral angles between neighboring p-phenyles (within the bridge) and between porphyrins and p-phenyles, see Figure S38. The angles $\theta$ describe the bending of conjugated C-C bonds (deviations of angles from 180°, see text).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>43.0°</td>
<td>45.0°</td>
<td>48.6°</td>
<td>49.4°</td>
<td>63.1°</td>
</tr>
<tr>
<td>$\beta$</td>
<td>38.3°</td>
<td>43.6°</td>
<td>64.4°</td>
<td>42.6°</td>
<td>23.6°</td>
</tr>
<tr>
<td>$\theta_1$</td>
<td>18.6°</td>
<td>21.5°</td>
<td>20.7°</td>
<td>11.1°</td>
<td>66.7°</td>
</tr>
<tr>
<td>$\theta_2$</td>
<td>15.1°</td>
<td>16.6°</td>
<td>14.1°</td>
<td>9.0°</td>
<td>6.2°</td>
</tr>
<tr>
<td>$\theta_3$</td>
<td>14.8°</td>
<td>15.1°</td>
<td>14.1°</td>
<td>8.7°</td>
<td>3.3°</td>
</tr>
<tr>
<td>$\theta_4$</td>
<td>27.1°</td>
<td>28.1°</td>
<td>27.2°</td>
<td>18.7°</td>
<td>8.6°</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(d(C-C)) [(\AA)]</td>
<td>1.478</td>
<td>1.477</td>
<td>1.478</td>
<td>1.531</td>
<td></td>
</tr>
<tr>
<td>(d(C-C_{\text{peripheral}})) [(\AA)]</td>
<td>1.487</td>
<td>1.486</td>
<td>1.478</td>
<td>1.486</td>
<td></td>
</tr>
</tbody>
</table>

The bond lengths of the C₅-C₅ and the C₆-C₆ peripheral bonds within the ring plane are given in Table S11. The value for the C₅-C₅ bond within the relaxed, unstrained gas phase terphenyl molecule is shorter than a typical C-C single bond, indicating the \(\pi\)-conjugation between the phenyl units. The same holds for the C₆-C₆ peripheral bond within the gas phase Ni-TPP molecule. In the P2 fragment, which is obtained by opening the [2]CPT ring and performing a full relaxation (see homodesmotic reaction model below), the same C₅-C₅ and C₆-C₆ peripheral bond lengths are found as in the gas phase building blocks. Within the [2]CPT ring, the length of the C₅-C₅ bonds remain unchanged and the C₆-C₆ peripheral bonds become even slightly shorter so that both are now basically identical in length (see Table S11). This shows that the \(\pi\)-conjugation of the terphenyl and Ni-TPP building blocks is fully maintained within the strained [2]CPT ring. On the other hand, in [2]CPT-OH, i.e. before aromatization, the C₅-C₅ bond length is significantly larger. Further evidence for the persistence of the \(\pi\)-conjugation in the [2]CPT rings is given by the hybridization of the HOMO and LUMO orbitals of the Ni-TPP units across the terphenyl bridges (see below).

Based on the results for the [2]CPT ring we performed calculations for [3]CPT only for the conformation with full D₃ symmetry. The optimized structure is shown in Figure S38 and the structural parameters are listed in Table S10. All phenyl rings have maintained the same orientation as in the ruffled conformation of Ni-TPP in the gas phase.

The naphthyl units in the [2]CPTN rings introduce an additional degree of freedom: the naphthyl units can point to the same side or to opposite sides of the ring. Both break the \(D_2\) symmetry of the [2]CPT ring. Altogether we probed 10 different conformations of the [2]CPTN ring in our geometry optimizations, with different symmetry and different orientations of the naphthyl units. The lowest energy is found for the same-side orientation of the naphthyl units and a remaining \(C_2\) symmetry axis perpendicular to the ring plane (PBE+D3, see Figure S39). However, the energy of most of the other conformers is within a range of 4 kcal/mol. For the [2]CPTA ring we find that the conformer with \(C_1\) symmetry is now lower in energy by 1.7 kcal/mol (7.1 kJ/mol, PBE+D3) than the \(D_2\) conformer (see Figure S39). However, in all low-energy [2]CPTN and [2]CPTA structures all phenyl rings next to the porphyrin core maintain the same orientation as in the ruffled gas phase Ni-TPP conformation.

Figure S40. Optimized structure (PBE+D3) of the [2]CPT-OH ring in the gas phase. Left: more open conformer with similar ring diameter as in the crystal structure. Right: Collapsed conformer, which is predicted to be the global energy minimum in the gas phase.

The [2]CPT-OH ring is much more flexible. Altogether we performed geometry optimizations for 14 conformers, differing in their orientation of the free phenyl rings at the porphyrins and the orientation of
the phenyl rings and OH groups in the bridge. We obtain two different types of relaxed structures. The first type has a more open ring with structural parameters very similar as in the crystal structure. However, note that the X-ray crystal structure shows additional THF molecules in the center of the ring. The structure with lowest energy of this type has again D$_2$ symmetry and is shown in Figure S40. In the second type of structures the ring has collapsed. The most stable conformer has inversion symmetry and is shown in Figure S40. It has a lower energy of 11 kcal/mol (46.0 kJ/mol) in the gas phase than the open configuration. The two porphyrins are stacked on-top of each other, but shifted off-center to reduce overlap of the phenyl rings.

d) Structure of the fullerene complexes

For each combination of ring and fullerene geometry optimizations were performed for about 10 different initial configurations with varying orientation of the fullerene with respect to the ring. Also rotations of the p-phenylene units within the ring were taken into account.

![Figure S41](image_url)

**Figure S41.** Optimized structure (PBE+D3) of [2]CPT:$\equiv$C$_{68}$ and [2]CPT:$\equiv$C$_{70}$ with off-center binding distance.
Figure S42. Optimized structures (PBE+D3) of [2]CPTN\(\leq C_{60}\) and [2]CPTN\(\leq C_{70}\) with off-center binding distance.

The energetically most favorable structures from this search are shown in Figures S41–S42. Without fullerene, the four phenylene units within the [2]CPT and [2]CPTN rings, which are connected to the porphyrins, are tilted alternately inwards and outwards (see Figures S38, S39 and S43). However, upon binding of a fullerene, in the lowest-energy conformer two phenylene rings change their orientation and all phenylene rings now point outwards (as seen from top, see Figure S43). The ring adopts a conical-like shape, which allows optimization of the \(\pi-\pi\)-interactions with the fullerene. Simultaneously, the ring bends so that the upper phenyl rings of the porphyrins come closer together and the lower phenyl rings are farther apart (see Figure S43). The tilt of the \(p\)-phenylene units and the bending of the ring are clearly visible in the X-ray structure (see Figure 5 in the manuscript). After rotation of the phenylene units the porphyrins are no longer in a strict ruffled configuration. Nevertheless, the rings with rotated phenylenes are stable conformers, though with a slightly higher energy. Table S12 shows the energy difference between the gas-phase relaxed conformer with rotated phenylenes and the global optimum structure. However, rotating the phenylene rings is an activated process with a considerable energy barrier due to the steric repulsion between the \(H\) atoms of the phenylene units. The rotation of the phenylene rings breaks the \(D_2\) symmetry of [2]CPT ring. Only a \(C_2\) axis perpendicular to the ring plane as in [2]CPTN remains.
**Figure S43.** Reorientation of the \( p \)-phenylene units within the ring upon binding of a fullerene. Left: Energetically most favorable \([2]\text{CPT}\) gas phase structure (see also Figure S38). The four phenylene units of the ring connected to the porphyrin are tilted alternately inwards and outwards. Right: Gas-phase relaxed ring structure after rotation of two phenylene units. This conformation is adopted upon adsorption of a fullerene.

The total deformation energy of the \([2]\text{CPT}\) and \([2]\text{CPTN}\) rings upon binding of a fullerene has been decomposed into two contributions (see Table S12): the energy change by rotation of the phenylene rings as described above (which can be regarded as a "binding preparation" process) and the subsequent deformation energy of the pre-prepared rings. The second contribution was calculated by removing the fullerene from the relaxed ring/fullerene complex structure and performing a total energy calculation without relaxation. This energy was then subtracted from the total energy of the gas-phase relaxed ring with rotated phenylenes. As shown in Table S12, the total deformation energy for \([2]\text{CPT}\) is very small: 0.8 kcal/mol for \([2]\text{CPT}\)=C\(_{90}\) and 1.0 kcal/mol for \([2]\text{CPT}\)=C\(_{30}\). It is considerably larger for \([2]\text{CPTN}\): 6.8 kcal/mol for \([2]\text{CPTN}\)=C\(_{90}\) and 7.7 kcal/mol for \([2]\text{CPTN}\)=C\(_{30}\). The reasons are the larger dihedral angles in the phenylene-naphthalene-phenylene bridges, which makes the rotation of the phenylene units energetically more expensive, and the larger deformation of the rings due to the enhanced dispersion interactions. In the end, the energy gain due to the larger contact area in the \([2]\text{CPTN}\) complexes is mostly counterbalanced by the larger ring strain, leading to rather similar binding affinities.

**Table S12.** Energy change of the \([2]\text{CPT}\) and \([2]\text{CPTN}\) rings upon rotation of the phenylene rings (binding preparation) and subsequent deformation by binding of a fullerene.

<table>
<thead>
<tr>
<th>( \Delta E [\text{kcal/mol}] )</th>
<th>([2]\text{CPT})</th>
<th>([2]\text{CPTN})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation of phenylene rings</td>
<td>0.2</td>
<td>4.5</td>
</tr>
<tr>
<td>Deformation upon C(_{90}) binding</td>
<td>0.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Deformation upon C(_{30}) binding</td>
<td>0.8</td>
<td>3.2</td>
</tr>
</tbody>
</table>
The conical shape of the inner part of the $[2]CPT$ and $[2]CPTN$ rings after rotation of the phenylene units is also responsible for the slightly off-center binding of the fullerences with respect to the Ni atoms of the porphyrins. The off-center distances of all complexes are indicated in Figures S41-S42. The $[2]CPT\subset C_{60}$ and $[2]CPTN\subset C_{60}$ complexes maintain the $C_{3}$ symmetry with a rotation axis perpendicular to the plane of the (phenylene-rotated) rings. This symmetry is lost for the $C_{60}$ complexes. The calculated displacement of 1.62 Å for $[2]CPT\subset C_{60}$ (gas phase relaxation, PBE+D3) is in excellent agreement with the offset of 1.9 Å found in the X-ray structure (solid phase). In $[2]CPTN\subset C_{60}$ the offset is slightly larger since the fullerene is now centered with respect to the naphthyl units (see Figure S42).

One of our geometry optimizations for $[2]CPT\subset C_{60}$ was started from the global optimum $[2]CPT$ conformation with alternately tilted phenylene units and $D_{3h}$ symmetry. The $C_{60}$ was added in the center of the ring and the $D_{3h}$ symmetry was maintained in the relaxation. In particular, enforcing the $C_{3}$ rotation axis through the midpoints of the central $p$-phenylene rings of the terphenyl bridges guarantees that the fullerene stays in the center of the ring. The relaxed structure can be regarded as an approximation of the transition state for the movement of the fullerene through the central plane of the ring. The energy of this conformer is 16.5 kcal/mol (68.9 kJ/mol) higher than the global optimum, which represent a rough estimate for the activation barrier.

e) Analysis of the strain energy

The strain in the nanohoops is analyzed in two different ways. The first method relies on our observation that the porphyrins maintain their ruffled gas phase conformation in the rings, however now with larger amplitude. To illustrate this we cut the porphyrins out of their rings and saturated the broken C-C bonds by hydrogen (the symmetries of the rings guarantee that the porphyrins within each ring are equivalent). Only those additional H atoms were relaxed, all other atoms were kept at their positions as in the ring. Overlays of these distorted porphyrins from the rings with their optimized gas phase structure are shown in Figures S44-S46. The calculated energy difference between the distorted porphyrin from the rings and the relaxed gas phase structure is a good measure for the ring strain. The results in Table S13 show in particular that the $[2]CPT\cdot OH$ ring is basically unstrained.

**Table S13.** Energy difference $\Delta E$ (in kcal/mol) between the strained Ni-TPP molecule in the ring and the fully optimized gas phase structure. In addition, the deviation $\gamma$ of the angle between the meso carbons in the ring and the central Ni ion from 180° is given, see Figures S44-S46. For the optimized ruffled gas phase conformation of Ni-TPP the angle $\gamma$ is 16.4°.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$</td>
<td>15.4</td>
<td>6.5</td>
<td>0.6</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>35.2°</td>
<td>32.0°</td>
<td>19.2°</td>
</tr>
</tbody>
</table>
**Figure S44.** Overlaid structures of Ni-TPP in the constrained geometry as cut out of the [2]CPT ring (solid, black/blue) and the optimized ruffled gas phase structure (translucent, red). The top phenyl units stick into the vacuum and the bottom phenyl units are part of the ring structure.
Figure S45. Overlayed structures of Ni-TPP in the constrained geometry as cut out of the [3]CPT ring (solid, black/blue) and the optimized ruffled gas phase structure (transparent, red). The top phenyl units stick into the vacuum and the bottom phenyl units are part of the ring structure.
Figure S46. Overlaid structures of Ni-TPP in the constrained geometry as cut out of the [2]CPT-OH ring (solid, black/blue) and the optimized ruffled gas phase structure (transparent, red). The top phenyl units stick into the vacuum and the bottom phenyl units are part of the ring structure.

In the second approach we characterize the ring strain by the homodesmotic reaction model. In this method the \([n]\) ring is decomposed into \(n\) monomeric units \(P_1\). The broken bonds of the monomeric units are saturated by H atoms. The strain energy is calculated as the energy difference between the ring, \(E([n]\text{ring})\), and the \(n\) monomeric units, \(nE(P_1)\). The energy contribution from breaking \(n\) bonds in the ring and saturating them with H atoms is taken into account by subtracting for each bond the binding energy of an unstrained dimer \(P_2\) built out of two monomers \(P_1\). The energy expression for the strain energy is then given by

\[
E_{\text{str}} = E([n]\text{ring}) - nE(P_1) - n \left( E(P_2) - 2E(P_1) \right)
\]

The structures of the optimized monomer and dimer fragments are shown in Figure S47, and the calculated strain energies are summarized in Table S14.
Figure S47. Optimized structures (PBE+D3) of the monomer (P1) and dimer (P2) fragments of the nanorings.

Table S14. Calculated ring strain energies $E_{strain}$ (in kcal/mol) using the homodesmotic reaction model.\textsuperscript{518}

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{strain}$ @ PBE+D3</td>
<td>44.5</td>
<td>43.5</td>
<td>44.5</td>
<td>26.9</td>
<td>2.4</td>
</tr>
<tr>
<td>$E_{strain}$ @ B3LYP+D3</td>
<td>54.3</td>
<td>53.1</td>
<td>54.4</td>
<td>34.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

f) Electronic structure

In Figure S48 we compare the positions of the HOMO and LUMO levels between our different Ni-TPP structures, i.e. the gas-phase relaxed ruffled conformer and the three cut-outs from the [2]CPT-OH, [3]CPT and [2]CPT rings. In the gas phase structure, the LUMO is two-fold degenerate. This degeneracy is lifted by the deformation of the porphyrin. The positions of the HOMO and LUMO levels for the Ni-TPP from the untrained [2]CPT-OH ring and the gas-phase relaxed ruffled conformer are basically identical. With increasing deformation, however, the HOMO rises and the LUMO is lowered, resulting in a significant reduction of the HOMO-LUMO gap. This leads to a strong red-shift of the UV-vis absorption spectra with increasing ring strain, as demonstrated by the TD-DFT calculated spectra shown in Figure S51. Nevertheless, the character of the HOMO and LUMO orbitals remains very similar (see Figure S48).
Figure S48. Wavefunction isosurface plots of the HOMO, LUMO and LUMO+1 states (the same isovalue of 0.018 au is used in all figures) and selected energy levels of different Ni-TPP structures (gas-phase relaxed ruffled conformer and the deformed porphyrins from the ring structures shown in Figures S44-S46).
In Figures S49-S50 the electronic structures of the cut-out porphyrins and the full rings are compared. The orbital plots show that the HOMO and the LUMO of the rings are delocalized over the bridges and are formed by bonding and antibonding linear combinations of the HOMO and LUMO of the individual porphyrin building blocks. This is further evidence for the extended π-conjugation within the rings. The energy split between the bonding and antibonding linear combinations is evident in the energy level diagrams. This split is a measure for the overlap of the porphyrin HOMO and LUMO orbitals when the molecular orbitals of the rings are formed. The bonding linear combination of the porphyrin HOMOs has almost the same energy as the HOMO of the individual porphyrins, whereas the antibonding combination, which becomes the HOMO of the rings, is shifted upwards in energy. In contrast, the bonding linear combination of the porphyrin LUMOs, forming the LUMO of the rings, moves down in energy, whereas the antibonding combinations remain similar in energy as the LUMO of the individual porphyrins (see Figures S49-S50). Thus, the extended π-conjugation leads to a further reduction of the HOMO-LUMO gap, in addition to the contributions coming from the deformation of the porphyrin cores. As a consequence, the UV-vis absorption spectrum is even more red-shifted when two deformed porphyrins are combined to a 2CPT ring (see TD-DFT calculated spectra in Figure S52).

Finally, in Figures S53-S54 the HOMO and LUMO levels of the 2CPT ring with incorporated fullerenes are analyzed. While the HOMO of the fullerene-ring complex is mainly located on the ring, the LUMO mostly resides on the fullerene. This is not surprising considering the HOMO/LUMO positions of the individual 2CPT ring and the fullerenes. The Figures S53-S54 also show that the fullerenes have almost no impact on the position of the HOMO of the ring, whereas the ring significantly raises the LUMO of the fullerenes.

**Figure S51.** Calculated UV-vis absorption spectra for different Ni-TPP structures (gas-phase relaxed ruffled conformer and the deformed porphyrins from the ring structures shown in Figures S44-S46).

**Figure S52.** Calculated UV-vis absorption spectra for the deformed Ni-TPP unit from the [2]CPT ring and the full [2]CPT ring structure.
**Figure S53.** Frontier orbital analysis of [2]CPT:$\supset$C$_{60}$.

**Figure S54.** Frontier orbital analysis of [2]CPT:$\supset$C$_{70}$. 

- 288 -
8. MS Study

The mass spectrometer utilized was a quadrupole time-of-flight (qToF) hybrid, namely the microTOF-Q II (Bruker, Germany) equipped with an electrospray ionization (ESI) or an atmospheric pressure photoionization (APPI) ion source. For collision-induced dissociation experiments mass-selected ions were accelerated through a collision cell. Nitrogen was used as the collision gas. Energy dependent fragmentation experiments can be conducted by varying the acceleration potential (E_{ab}) and plotting the survival yield (SY) of the precursor ion against the collision energy in the center of mass range (E_{com}). SY and E_{com} are given by equation 1 and 2, respectively.

\[
SY = \frac{\sum f_{Int(Prev)}}{\sum f_{Int(Prev)} + \sum f_{Int(Frag)}} \quad \text{(Eq. 1)}
\]

\[
E_{com} = \frac{m(n_2)}{m(n_2) + m(Prev)} \times E_{ab} \quad \text{(Eq. 2)}
\]

The data points are then fitted with a sigmoidal Boltzmann fit:

\[
f(x) = \frac{A_1 - A_2}{1 + e^{-\frac{x-x_0}{s}} + A_2}
\]

\(A_1\) and \(A_2\) are the beginning and ending value, respectively, and \(s_0\) refers to the width of the steepest part of the sigmoid curve. The inflection point is given by \(x_0\). As a measure for the relative dissociation energy we extracted the onset energies of the complexes from the crossing point of the \(SY = 1\) line with the tangent through the inflection point.\(^{229}\)

The sample solutions contained [2]CPT and either C_{40} or C_{50}. All components had a concentration of 5 x 10^{-4} M in DCM:Tol (1:1; V:V) with 0.5 % TFA to expand the electrochemical oxidation window of the ESI source.\(^{230}\)
**Figure S55.** ESI-MS results for [2]CPT and C_{60}. Isotope pattern of the measured [2]CPT$\rightleftharpoons$C_{60}$^{+}$ complex (top) and the simulated pattern (middle). MS/MS-spectrum of the [2]CPT$\rightleftharpoons$C_{60}$^{+}$ complex showing the loss of the neutral fullerene, yielding the [2]CPT$^{+}$ radical cation (bottom).

The MS results for [2]CPT with either C_{60} or C_{70} are displayed in the figures S55 and S56, respectively. Both fullerenes yield similar results as the radical cation of the complex [2]CPT$\rightleftharpoons$C_{60/70}$^{+}$ is detected. In either case evidence for the formation of a host/guest-complex between the nanoloop and the fullerenes is provided. The measured isotope pattern for the complexes is shown in the top trace of the respective figure together with the simulated pattern for comparison below it. MS/MS experiments provide definite proof of the complex, since the precursor complex loses the neutral fullerene and [2]CPT$^{+}$ retains the change as displayed in the bottom part of either figure.
Figure S56. ESI-MS results for [2]CPT and C\textsubscript{70}. Isotope pattern of the measured [[2]CPT\textendash C\textsubscript{70}]\textsuperscript{**} complex (top) and the simulated pattern (middle). MS/MS-spectrum of the [[2]CPT\textendash C\textsubscript{70}]\textsuperscript{**} complex showing the loss of the neutral fullerene, yielding the [2]CPT\textsuperscript{**} radical cation (bottom).
9. NMR Spectra

$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S4

$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S4
$^1$H NMR (400 MHz, 298 K, CDCl₃) of 1

$^1$C NMR (100 MHz, 298 K, CDCl₃) of 1
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 2

$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of [2]CPI-OTES

591
$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of [2]CPT-OTES

$^1$H NMR (400 MHz, 298 K, $d$-THF) of [2]CPT-OH
$^{13}$C NMR (100 MHz, 298 K, $d$-THF) of [2]CPT-OH

$^1$H NMR (500 MHz, 298 K, CDCl$_3$) of [2]CPT
$^1$C NMR (125 MHz, 298 K, CDCl₃) of [2]CPT

$^1$H NMR (400 MHz, 298 K, CDCl₃) of [3]CPT OH (with pyridine)
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 3CPT

$^1$C NMR (100 MHz, 298 K, CDCl$_3$) of [3]CPT-OH (with pyridine)
$^{13}$C NMR (125 MHz, 298 K, CDCl$_3$) of [3]CPT

$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of 88
$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S8

$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S9
$^1$H NMR (400 MHz, 298 K, CDCl$_3$) of S12

$^1$C NMR (100 MHz, 298 K, CDCl$_3$) of S9
$^{13}$C NMR (100 MHz, 298 K, CDCl$_3$) of S12

$^1$H NMR (500 MHz, 298 K, CDCl$_3$) of [2]CPTN-OTES
$^{13}$C NMR (125 MHz, 298 K, CDCl$_3$) of $[\text{2}][\text{CPTN-OTES}$

$^1H$ NMR (500 MHz, 298 K, d$_2$-THF) of $[\text{2}][\text{CPTN-OH}$
$^{13}$C NMR (125 MHz, 298 K, d-THF) of [2]CPTN-OH

$^1$H NMR (500 MHz, 298 K, CDCl₃) of [2]CPTN
$^{13}$C NMR (125 MHz, 298 K, CDCl$_3$) of [2]CPTN

$^1$H NMR (500 MHz, 298 K, CDCl$_3$) of [3]CPTN
$^{13}$C NMR (125 MHz, 298 K, CDCl$_3$) of [3]CPTN

$^1$H NMR (500 MHz, 298 K, d$_2$-THF) of [3]CPTA-OH
$^{13}$C NMR (500 MHz, d-THF) of [3]CPTA-OH

$^1$H NMR (500 MHz, 298 K, CDCl$_3$) of [3]CPTA
$^{13}$C NMR (125 MHz, 298 K, CDCl$_3$) of [3]CPTA
10. References


4. Summary and Outlook

As a “young” compound class, strained carbon nanohoops have attracted much attention recently due to their challenging synthesis, appealing optoelectronic properties and enormous potential in supramolecular chemistry. Therefore, progress in the synthesis of new strained carbon nanohoops and in generation of related supramolecular architectures has been very rapid over the past five years. This thesis summarizes two novel applications of strained carbon nanohoops in supramolecular chemistry based on known molecule [10]CPP (Chapters 3.1 and 3.2) as well as the synthesis of a series of new strained porphyrinylene/phenylene nanohoops (Chapter 3.3).

In Project I, we have described the first synthesis of [2]rotaxanes featuring a shape-persistent nanohoop [10]CPP. Strong concave–convex π–π interactions between [10]CPP and a fullerene monoadduct were the key to successful synthesis of these mechanically interlocked molecules. Moreover, insights into the role of [10]CPP as a supramolecular directing group indicated that the modulation of reactivity leads to drastically improved regioselectivity of fullerene bisaddition. Recent evidence showed that different regioisomers of fullerenes exhibit dramatically different performances in organic photovoltaics. Our findings might have technological importance to fullerene-containing organic solar cell. The electron transfer studies showed that the mechanical bond leads to an interesting phenomenon, a relatively well-defined “unbound” supramolecular state was detected by experiment. Based on the decreased distance in the corresponding charge separated state, we found that charge recombination was much faster in the “bound” state compared to the “unbound” state. Moreover, the dielectric constant of the experiment solvent strongly affected the kinetics of this charge recombination process. These interesting charge transport properties suggest that mechanically interlocked molecules may be used for the shuttling of charges (e.g. to prevent undesired recombination events in photocatalysis).
In **Project II**, we have successfully synthesized a porphyrin–[10]CPP conjugate and investigated its strong association with a range of fullerenes. Fluorescence spectroscopy revealed intramolecular energy transfer from [10]CPP to zinc porphyrin. Transient absorption spectroscopy demonstrated that [10]CPP as a supramolecular junction allows efficient charge transport between a zinc porphyrin electron donor and a series of unmodified fullerene electron acceptors. These promising results indicated that supramolecular complexes of [10]CPP with fullerenes may be a useful addition to the toolbox of organic electronics (e.g. to stabilize film morphologies in organic transistors or solar cells).

As a continuation of **Project II**, we propose to prepare a porphyrin equipped with two [10]CPP rings in the two trans meso positions (Scheme 16). To achieve this goal, we will make use of our previously developed synthesis of iodo-[10]CPP and the subsequent copper-free Sonogashira coupling reaction. We will then combine this compound with (C$_{60}$)$_2$ at different concentrations. At low concentrations, we expect formation of soluble oligomers. While higher concentrations or slow evaporation of solvent, we expect that intriguing supramolecular polymers will form. Due to the expected anisotropy of charge carrier transport, these supramolecular assemblies are worth being investigated in organic field effect transistors.

![Scheme 16. Example of a one-dimensional supramolecular assembly based on the interaction between (C$_{60}$)$_2$ and [10]CPP.](image)

**Scheme 16.** Example of a one-dimensional supramolecular assembly based on the interaction between (C$_{60}$)$_2$ and [10]CPP.

In **Project III**, we have successfully carried out a concise synthesis of a series of strained porphyrin macrocycles, which due to their unique molecular design offer opportunities for uses in bimetallic catalysis and crystal engineering. Two
nanohoops [2]CPT and [2]CPTN can be considered porphyrinogenic equivalents of [10]CPP, albeit with ca. 100-fold increased affinity to fullerenes. This may prove useful for the regioselective synthesis or separation of fullerene bisadducts as well as for construction of photoelectroactive devices. We also observed unusual optoelectronic properties of the synthesized nanohoops, most importantly, a strain-induced red-shift of absorption in the visible range of the spectrum, which may inspire further studies on the bending of organic semiconductors or molecular switches.

As a continuation of Project III, we plan to replace the central phenylene group within the strained macrocycle by pentacene and anthracene moieties (Scheme 17). Importantly, this change of design does not make the underlying synthesis significantly more challenging and we expect that each of the two key starting materials can be prepared in gram scale. Once the pentacene and anthracene containing target nanohoops are obtained, they can be used to carry out intramolecular singlet fission and charge transfer studies.

Scheme 17. The synthetic strategy towards pentacene and anthracene containing nanohoops.
References

References


References

Int. Ed. 2015, 54, 15197–15201.


List of Publications and Patents


List of Conference Contributions


3. 1st Ulm Symposium on Solar-Driven Chemistry, 08-10/10/2017: poster presentation.

4. 2nd From Carbon-Rich Molecules to Carbon-Based Materials Conference, Bahamas, 06-10/06/2018: poster presentation. (J. Mater. Chem. C Poster Prize)


7. 14th International Symposium on Macrocyclic and Supramolecular Chemistry (ISMSC2019), Lecce, Italy, 02-06/06/2019: poster presentation. (MDPI poster prize)

8. The 18th International Symposium on Novel Aromatic Compounds (ISNA-18), Sapporo, Hokkaido, Japan, 21-26/07/2019: poster presentation. (ChemLett poster prize)
Curriculum Vitae

Personal Information
Name: Youzhi Xu (徐尤智)
Date of birth: July 1990
Place of birth: Ruichang
Nationality: Chinese

Education
Ph.D University of Ulm, Germany (06/2016 –)
University of Erlangen-Nürnberg, Germany (01/2016–06/2016)
Organic Chemistry (Synthesis and Supramolecular Chemistry of Curved π-Systems)
Advisor: Prof. Dr. Max von Delius

M.Sc International Phosphorus Laboratory, Zhengzhou University, China (09/2012.09 – 07/2015)
Organic Chemistry (Cycloaddition of Organophosphorus Compounds with Alkyne)
Advisor: Prof. Dr. Zheng Duan

B.Sc East China Institute of Technology, China (09/2008 – 07/2012)
Biotechnology (Study on Preparation and Stability of High Color Value Gardenia Blue)
Advisor: Prof. Huazheng Liang

Awards and Scholarships
2019 ChemLett poster prize at ISNA-18
2019 MDPI poster prize at ISMSC2019
2018 "Journal of Materials Chemistry C" Poster Prize at the 2nd From Carbon-Rich Molecules to Carbon-Based Materials Conference
2011 "Science and Technology Innovation" the Third Award of Jiangxi Province
2010 "Tiaozhan cup" Excellence Award of Jiangxi Province, Grand Prize of University
2012 -2015 National Scholarship (A1)
Acknowledgements

How time flies! It is a wonderful experience to work and live in Germany, especially to be a member of Delius’s group. First of all, I would like to thank my supervisor Prof. Max von Delius for giving me the opportunity to join his research group four years ago and his unremitting support throughout my Ph.D study. He not only taught me how to be better for carrying out scientific research, writing and presentation, but also taught me how to better handle interpersonal relationships with cooperators and colleagues. I really enjoyed and benefited a lot from such an international and young research group. It is my great pleasure to grow up together with Delius’s group.

Many thanks to all the members of Delius group (Oleg, Michael, Oleksandr, Henrik, Lizzy, Sebastian, Bala, Xiang, Selina, Julian, Medina, Fabian, René, Jing, Jie, Philipp, Anna, Mario, Dominik and Deepsing) who have given me great support in daily work and life during the past four years. Particularly, deeply appreciate Oleg and Michael for their kind help in my thesis correction and giving helpful suggestions.

I would like to thank Prof. Dr. Peter Bäuerle for sharing several key instruments with our group. Many thanks to all the members of Bäuerle and Pammer groups for offering great discussions during the joint institute seminar.

Here, I also want to express my great thanks to our cooperators Prof. Dr. Dirk M. Guldi, Prof. Dr. Thomas Drewello, Prof. Dr. Bernd Meyer, Bingzhe Wang, Martin B. Minameyer, Ramandeep Kaur and so on, who have given my research projects great help. Your participation makes our studies much more interesting and fruitful.

As a member of a Chinese rural family, it isn’t an easy thing to receive high education and study abroad. Herein, I am really grateful to my family members who have given me continued counsel and support during the past 29 years. Particularly, I appreciate my wife Linlin for abandoning her career and coming to ten thousand miles away in Germany to live together with me.

Vielen Dank an alle Mitglieder der Delius-Gruppe (Oleg, Michael, Oleksandr, Henrik, Lizzy, Sebastian, Bala, Xiang, Selina, Julian, Medina, Fabian, René, Jing, Jie, Philipp, Anna, Mario, Dominik und Deepsing), die mich in den letzten vier Jahren bei der täglichen Arbeit und im Leben großartig unterstützt haben. Besonders danke ich Oleg und Michael für ihre freundliche Unterstützung bei der Korrektur meiner Abschlussarbeit und für hilfreiche Vorschläge.

Ich möchte Prof. Dr. Peter Bäuerle für die gemeinsame Nutzung seiner Forschungsgeräte danken. Vielen Dank an alle Mitglieder der Gruppen Bäuerle und Pammer für die hilfreichen Diskussionen während des Institutsseminars.

Ein großes Dankeschön gilt auch unseren Kollaborationspartnern Prof. Dr. Dirk M. Guldi, Prof. Dr. Thomas Drewello, Prof. Dr. Bernd Meyer, Bingzhe Wang, Martin B. Minameyer, Ramandeep Kaur und so weiter. die mir in meinen Forschungsprojekten sehr geholfen haben. Ihre Teilnahme macht unser Studium viel interessanter und fruchtbarer.

bist, um mit mir zusammenzuleben.

时光荏苒，四年德国留学时光就如白驹过隙。初踏入德国时的兴奋和彷徨恍若昨天。这四年美好又充实的留学时光注定是我生命中浓墨重彩的一笔。走出国门，开拓眼界，接受不同文化、价值观的碰撞和洗礼。在这里的每一份经历都已成为我人生中宝贵的财富。

值此完成博士毕业论文之际，首先我想感谢我的导师、朋友 Max。感谢您这四年一直给予我的指导和帮助！至始至终的尊重学生的选择、想法和意见，我已经深深的被您的人格魅力吸引和影响。希望有朝一日为人师，我也能成为一个像您这样的人。同时，我也非常感谢课题组同事四年来给予的帮助与关心。

转眼已是三十而立的年纪，感谢父母三十年来茹苦含辛的养育和教导！感谢家人一如既往的理解与支持！至此，特别想感谢我的妻子琳琳，感谢你在我一无所有时嫁给我，并且放弃自己的事业和远离家人来到我的身边。感谢你一直以来无微不至的照顾，有你的生活是那么的多姿多彩。人生就是一场旅行，无论以后我们身处世界的哪个角落，你我同行！
Statement

Die vorliegende Arbeit entstand im Zeitraum von Januar 2016 bis Juli 2019 zunächst am Institut für organische Chemie der FAU-Erlangen-Nürnberg und danach am Instituten für Organische Chemie II und I Universität Ulm (durchgehend jedoch im Arbeitskreis von Prof. Dr. Max von Delius). Hiermit erkläre ich, dass ich die vorliegende Arbeit selbstständig angefertigt und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt sowie die wörtlich oder inhaltlich übernommenen Stellen als solche kenntlich gemacht und die Satzung der Universität Ulm zur Sicherung guter wissenschaftlicher Praxis in der aktuell gültigen Fassung vom 08.03.2012 beachtet habe.

Ulm, Nov. 2019

Youzhi Xu