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A Chiral Macrocyclic Oligothiophene with Broken Conjugation – Rapid Racemization through Internal Rotation

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Dedication to *Prof. François Diederich* on the occasion of his retirement celebration.

A macrocyclic oligothiophene with an integrated pseudo-*para* substituted [2.2]paracyclophane has been achieved. The synthetic sequence relies on alternating steps of halogenation- and *Suzuki*-coupling conditions. By employing a modified *Eglinton* reaction under high dilution conditions, the macrocycle is closed and the obtained diacetylene is efficiently transferred to the corresponding thiophene. The molecule is fully characterized and its dynamic racemization is analysed by variable temperature NMR experiments. The racemization barrier hints with 38 kJ/mol at rapid enantiomerization at room temperature by *Mislow's* "Euclidian rubber glove" enantiomerization process. Macrocycle formation results in red-shifted absorption and emission spectra, hinting at increased conjugation through the oligothiophene versus the trough space conjugation through the [2.2]paracyclophane.

Keywords: Cyclophanes • Oligothiophenes • Macrocycles • Helical Chirality

Introduction

The ongoing miniaturization of electronic components approaches the nanometer scale, and novel concepts to fabricate objects in this range are a topic of high interest. One of the fabrication principles can be the bottom-up synthesis of molecules, profiting from the impressive achievements reported in the synthetic and macromolecular community. This assembly of tailor-made macromolecules from small reactive building blocks is approaching the nanoscale form the opposed direction than the scaling down of bulk materials in conventional inorganic silicon-based technology[1] and promising new research directions develop at the interface between both approaches.

Over the past decades, conjugated macrocycles have attracted high interest due to both, their structural integrity offering well-defined shapes and diameters, and their role as model compounds for infinitely conjugated π-systems.[2,3] Furthermore their physical and chemical features like their optical, electrochemical, and encapsulation properties moved into the focus of interest.[4–7] A synthetic milestone in the field of conjugated aromatic compounds was the synthesis and investigation of Kekulene by the young *François Diederich* in the labs of *Heinz Staab*.[8,9]

Various molecular motifs have been reported as subunits of conjugated macrocyclic compounds, like e.g. pyridines, benzenes, acetylenes as well as five-membered aromatic heterocycles, like furans and thiophenes.[10,11] We reported the assembly and investigation of a variety of macrocycles consisting of aromatic subunits in the past, among others structures comprising functional subunits like redox chromophores[12,13] or optically addressable azo-benzenes,[14] macrocycles designed as single molecule switches[15–17] or with pronounced π-stacking features,[18,19] and giant macrocycles as model compounds for persistent ring currents.[20] More recently, our focus moved to axial chiral systems like bicyclic "Geländer"-type structures[21] or the macrocyclization of the ligands assembled in a M(II) terpyridine complex resulting in a helical macrocycle with an arrangement resembling a propeller.[22]

Cyclo[*n*]thiophenes are an interesting class of conjugated macrocycles; they are model compounds for polythiophenes, with well-defined self-assembling and electronic features.[23] Initially, the synthesis of macrocyclic oligothiophenes was performed by reacting on both sides ethynyl-terminated ter- and quinquethiophenes under oxidative acetylene coupling conditions in the presence of a copper catalyst.[3] The resulting diethynyl linkers in the macrocycles were converted to thiophenes with sodium sulfide to form the corresponding cyclo[*n*]thiophenes. In this way, a library of macrocycles was obtained, where the smallest member of the series contained twelve thiophenes. In a later approach, strained oligothiophenic macrocycles were assembled, where only one diacetylene was formed oxidatively.[24] *Bäuerle* and coworkers also reported on catenanes,

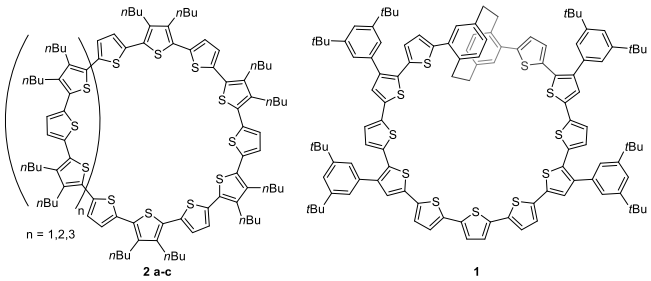


Figure 1. Series of oligothiophene macrocycles **2 a-c** (left side) developed by *Bäuerle* et al. as basis for the design of the target structure **1** (right side). The eleven thiophene subunits of the macrocycle are separated by a step due to the pseudo-*para* substituted PC subunit (top) which disturbs the conjugation. The four peripheral bis-3,5-(*tert*-butyl)phenyl substituents provide the solubility required for wet chemical processing.

where the synthesis of the target structure was achieved through complexation of platinum followed by reductive elimination to obtain the corresponding catenanes, comprising the diethynyl link in their oligothiophene macrocycles.[25]

The here presented structure is inspired by a split-ring resonator (SRR). This is the smallest possible realization of a circuit comprising a coil and a capacitor and thus displays interesting interactions with electromagnetic fields of suitable wavelength.[26] As an example, a negative refractive index at microwave frequencies was reported for a large array of equally micrometer sized metallic SRRs.[27,28]

The design of molecule **1** (Fig. 1) combines the conjugated periphery of an oligothiophene macrocycle with the conjugation altering pseudo-*para* [2.2]paracyclophane (PC). Using again the inspiring picture of a SRR, the macrocycle consisting of 2,5-interlinked thiophenes represent the "ring", while the PC acts as the "split". A particular appealing feature from the molecular design perspective is the helical chirality introduced by the step-like PC in the macrocycle, which might result in intriguing structural and chiroptical properties.[29]

The step in the macrocycle is realized due to the 3D-structure of pseudo-*para* [2.2]paracyclophane (PC).[30] It has attracted considerable attention due to the face-to-face orientation of its benzene rings, which are considerably closer than twice their individual *van-der-Waals* radii (typical ring distance: 3.09 Å), resulting in unusual optical, electronical and through-space charge-delocalization properties.[31–34] For example the comparison of annulene-PC hybrids with their benzannulene analogues displays typically a bathochromic shift in their absorption spectra, indicating an electronic conjugation throughout the PC building block.[35] Also, electrochemical investigations of dithienyl-substituted PC point at electronic coupling, as the oxidation wave is separated documenting the interdependence of both redox chromophores.[34,36] Self assembled molecular rods comprising a central PC unit displayed very comparable electronic transport features compared with their benzene analogues, such that the limited control over the number of molecules in the crossed-wire junctions did not allow to trace the origin of the observed subtle variations.[32] Very recent single molecule experiments with molecular rods comprising a central PC subunit in a mechanically controlled break junction experiment even displayed mechanically triggered quantum interference in the junctions transport behavior.[37]

Symmetrical disubstitution of PC leads to four different regioisomers.[38] Pseudo-*para* and *geminal* disubstitution leads to derivatives that are achiral due to internal symmetry elements.[39] However, pseudo-*ortho* and *meta* disubstitution leads to chiral products, separation of enantiomers of PCs with different substitution pattern have been accomplished.[40] Notably, pseudo-*ortho* disubstituted PC derivatives were incorporated in chiral thiophene-PC macrocycles, which showed pronounced chiroptical behavior.[41]

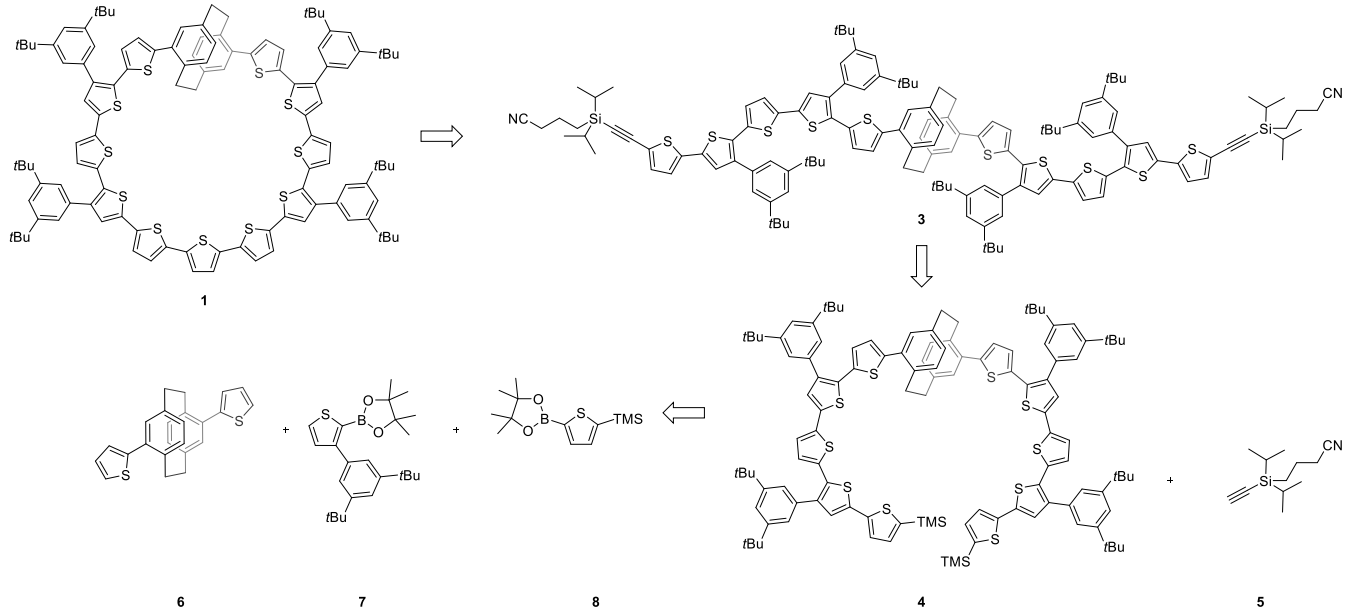
Here we report a novel approach making the pseudo-*para* disubstituted PC chiral by integrating it in the macrocyclic structure **1**. In **1** the macrocycle is complemented by eleven 2,5-diyl-thiophene subunits, which are introduced pairwise in a sequential synthetic strategy at both ends of the open oligomer in order to identify the number of thiophene subunits required for a successful macrocyclization. In addition, four bis-3,5-(*tert*-butyl)phenyl substituents provide the solubility in organic solvents required to enable wet chemical processing of both, the precursors and the target structure. The unique integration of the PC substitution pattern in the macrocyclic structure **1** leads, to the best of our knowledge, to the first chiral pseudo-*para* symmetrically disubstituted PC, as the introduction of the macrocycle leads to decreased symmetry. Interesting is the enantiomerization of **1**, which due to its 3D PC building block follows *Mislow*'s "Euclidean rubber glove" mechanism.[42,43] In other words, the molecule becomes its mirror image by rotations around single bonds without ever adapting a flat achiral conformation. The enantiomerization mechanism thus resembles the inversion of the chirality of a rubber glove, which is achieved by the complex movement of turning the glove inside out.

In this paper the stepwise assembly of the macrocycle **1** is reported together with its full characterization. The molecular dynamics of **1** are investigated by variable temperature NMR (VT-NMR) experiments shining light on its unique racemization behavior. The extent of electronic conjugation through macrocycle **1** and its precursors is qualitatively investigated by UV-Vis absorption and emission spectroscopy.

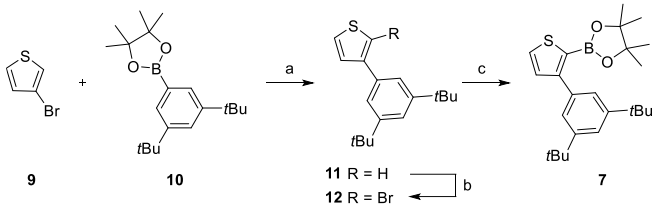
Results and Discussion

The synthesis of a complex structure as macrocycle **1** requires repetitive synthetic steps; mainly alternating halogenation and Pd-catalyzed carbon-carbon coupling reactions.

The linear and sequential synthetic strategy for macrocycle **1** involves a late stage macrocyclization and formation of a thiophene from the



Scheme 1. Synthetic strategy for the assembly of racemic macrocycle **1**.



Scheme 2. Synthesis of building block **7**. Reagents and conditions: (a) $Pd(PPh_3)_4$, Na_2CO_3, DMF, H_2O, 120 °C, 2 h, 88% (b) NBS, $CHCl_3$, AcOH, 40 °C, 1 h, 77%. (c) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF, -78 °C to room temp., 20 h, 90%.

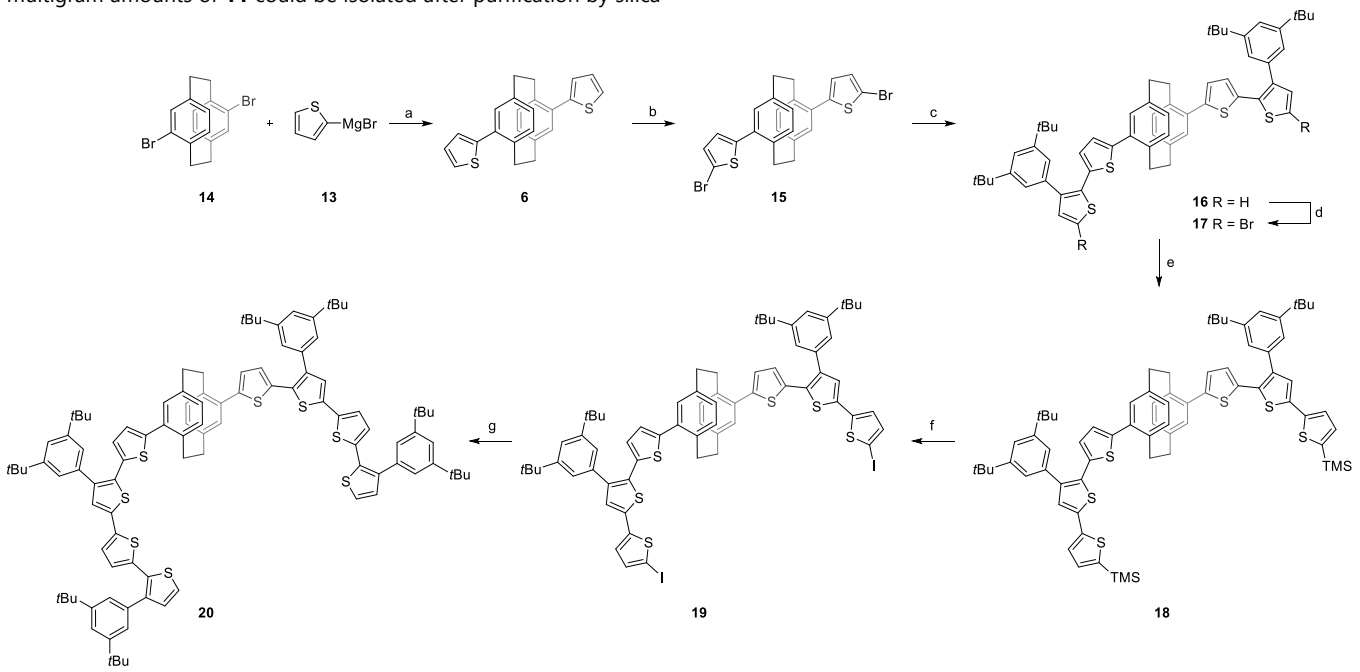
corresponding diacetylene, based on the linear protected intermediate **3**. Precedence for this strategy exists, as the cyclization of alkyne substituted oligothiophenes under oxidative acetylene coupling conditions[44] was employed by Bäuerle *et al*. for the synthesis of phenanthroline containing cyclic oligothiophenes of similar ring diameters.[24] Based on this concept, chiral carbon-rich macrocycles were also obtained in the labs of *François Diederich*, who produced alleno-acetylenic macrocycles with outstanding chiroptical properties.[45,46] The open-ring intermediate **3** is divided into two building blocks **4** and **5** which can be coupled in a *Sonogashira* reaction. This linear synthetic strategy allows for a step-by-step buildup of structure **4** through a series of halogenation and *Suzuki* coupling reactions without the need of excessive protecting-group strategies. Subunit **4** was assembled from highly functionalized building blocks **6**, **7** and **8** in a repetitive halogenation, Pd-catalyzed coupling chemistry sequence. Building block **7** and **8** were introduced to achieve reasonable solubility for all relevant intermediates during the course of the synthesis. While building blocks **6** and **8** are already literature-known, a strategy to form **7** had to be developed.[36,47]

The synthesis of building block **7**, that is introduced to increase the solubility, started from commercially available 3-bromothiophene (**9**) and literature-known 2-(3,5-di-tert-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**).[48]

The *Suzuki* coupling of both compounds afforded **11** in 88% yield and multigram amounts of **11** could be isolated after purification by silica gel chromatography. Next, **11** was reacted with one equivalent of *N*-bromosuccinimide (NBS) to selectively afford **12**. Excess of NBS lead to bromination also in the 5-position of the thiophene. Compound **12** was, after isolation by column chromatography (CC) in 77% yield, reacted with *n*-butyllithium (*n*-BuLi) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to yield **7**. During the course of the lithiation it is crucial that the temperature is kept at -78 °C, as at higher temperatures, deprotonation of **12** at the 5-position was observed, leading to the corresponding 2-bromo-5-pinacolboronato thiophene after work up. After addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and aqueous workup, **7** was isolated without purification in 90% yield as a yellow solid.

Having solubilizing building block **7** in hand, our focus moved towards the assembly of precursor **6**. While its synthesis is already literature known, we aimed to develop a higher yielding procedure than the one published previously. Collard *et al.* reported a procedure relying on a *Stille* coupling which was efficient yet difficult to purify.[36] More recently, a procedure developed by Martin *et al.* was reported which utilized *Suzuki* coupling conditions, however working with 5-alkyl-thiophene boronic acids.[34] Therefore, a procedure utilizing *Kumada* reaction conditions as developed by Rozenberg *et al.* was adapted.[49] Commercially available 2-thienyl magnesium bromide (**13**) was added dropwise to a suspension of pseudo-*para*-dibromo-PC (**14**) and $Pd(dppf)Cl_2$ in tetrahydrofuran (THF). After heating to 60 °C for two hours, building block **6** started to precipitate from the reaction mixture. Following aqueous workup and removal of the solvent, **6** could be isolated by washing the crude product with cyclohexane and cooled dichloromethane. Compound **6** was isolated in a yield of 87% as a white solid.

Subsequently, **6** was dibrominated with NBS in dimethylformamide (DMF), and after aqueous workup and filtration through a plug of celite, **15** was obtained as a white solid. **15** could only be dissolved in substantial amounts of toluene after heating the suspension to 60 °C. Thus, compounds **15** and **7** were reacted in a *Suzuki* reaction with Pd-PEPPSI-IPr™ (PEPPSI: pyridine-enhanced precatalyst preparation stabilization and initiation, IPr: isopropyl) and K_2CO_3 in methanol (MeOH) and toluene in a procedure adapted from Nilsson *et. al.*[50] The



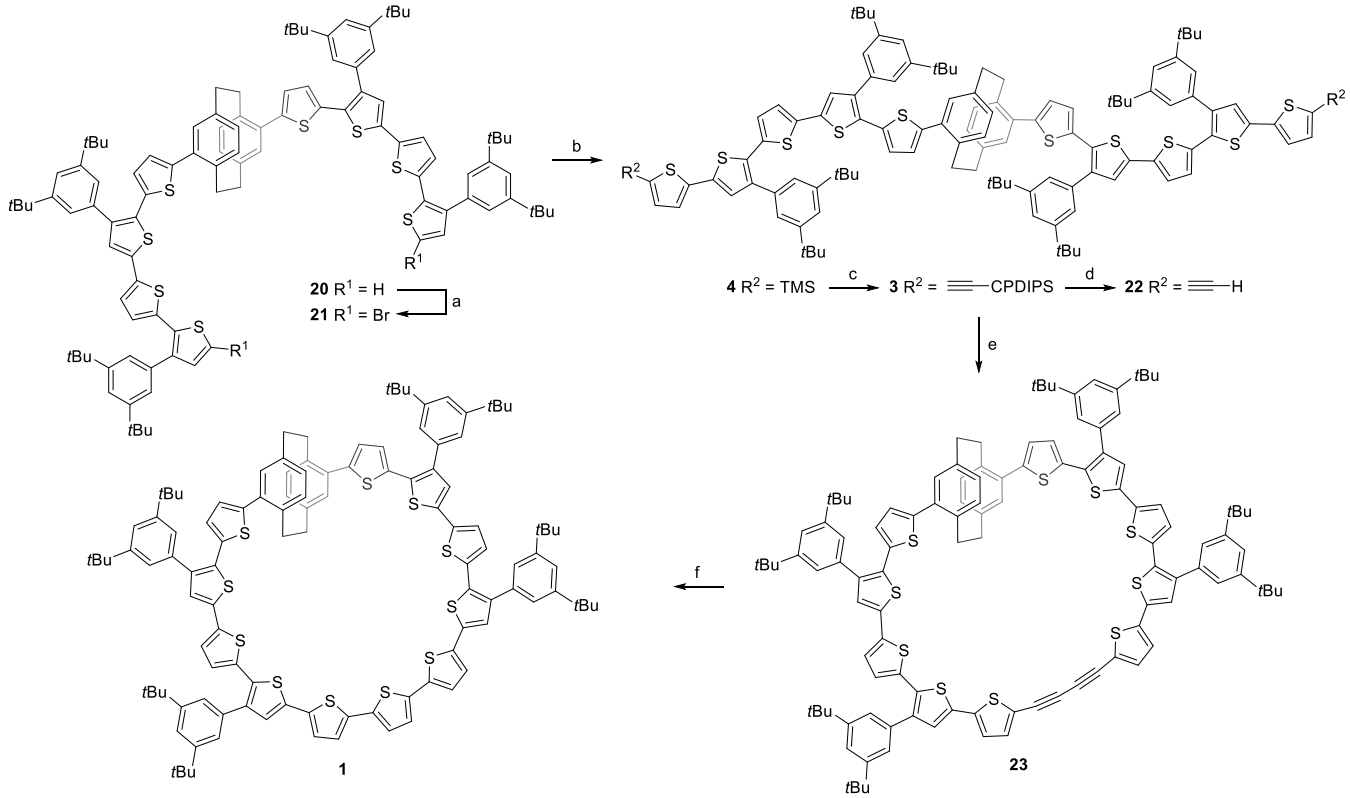
Scheme 3. Synthesis of fragment **20**. Reagents and conditions: (a) $Pd(dppf)Cl_2$, THF, 60 °C, 2 h, 87%. (b) NBS, $CHCl_3$, DMF, room temp., 20 h, 91%. (c) **7**, Pd-PEPPSI-IPr™, K_2CO_3, toluene, MeOH, 70 °C, 15 min, 95%. (d) NBS, DMF, room temp., 20 h, 92%. (e) **8**, Pd-PEPPSI-IPr™, K_2CO_3, toluene, MeOH, 70 °C, 20 min, 82%. (f) NIS, $CHCl_3$, AcOH, room temp., 1.5 h, 99%. (g) **7**, Pd-PEPPSI-IPr™, K_2CO_3, toluene, MeOH, 70 °C, 30 min, 83%.

reaction proceeded over the course of 15 minutes and **16** was obtained after CC in excellent yield as an off-white solid. To elongate the chain of thiophenes, **16** was brominated with NBS in DMF under exclusion of light. Aqueous work up and CC provided **17** as a yellow solid in 92% yield. Initial attempts to react **17** with thienyl boronic acid led to the hexathiophenic building block of very limited solubility that prevented its separation from the byproducts of the synthesis. Therefore, **17** was reacted in a Pd-PEPPSI-IPr™ catalyzed *Suzuki* reaction with trimethyl(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thien-2-yl)silane (**8**) to ensure improved solubility due to the presence of TMS groups, that can be easily transferred to an iodine with *N*-iodosuccinimide (NIS).[47]

After reacting **17** and **8** in a Pd-PEPPSI-IPr™ catalyzed *Suzuki* reaction for 20 minutes, **18** could be isolated after aqueous workup and CC as a yellow amorphous solid. Next, **18** was readily interconverted to compound **19** by dissolving it in a 1:1 mixture of chloroform and acetic acid and treatment with NIS. During the reaction, compound **19** precipitated from the solution, but was soluble enough to be purified by CC and was isolated in quantitative yield as a yellow wax. Subsequently, **19** was reacted with building block **7** with Pd-PEPPSI-IPr™ and K_2CO_3 in toluene and MeOH. After a reaction time of 30 minutes, followed by aqueous work up, **20** was isolated in good yield of 83% after CC as a yellow amorphous solid.

Compound **20** was dibrominated with NBS in $CHCl_3$ under the exclusion of light. After reacting the mixture for 20 hours, aqueous workup and CC lead to compound **21** in excellent yield as a yellow amorphous solid. Subsequently, **21** was reacted with building block **8** under the established *Suzuki* coupling conditions. Chromatography on silica gel and automated gel permeation chromatography (GPC) lead to the isolation of **4** in 72% yield. Unfortunately, all attempts to convert the TMS functionality of **4** to the corresponding dibromide or -iodide lead to a complex product mixture, which according to their MALDI-ToF MS analyses also contained mono- and trihalogenated species besides the desired material. Attempts to isolate the desired compound from those mixtures, either by silica gel chromatography or GPC were unsuccessful. Therefore, the mixture of bromides was directy reacted with CPDIPS acetylene in a *Sonogashira* reaction. The use of the polar protecting group introduced by Höger *et al*. lead to facile isolation of the desired protected diyne **3** by silica gel chromatography in toluene in 63% yield over two subsequent steps.[51] Deprotection of **3** to diyne **22** with tetrabutylammonium fluoride in THF proceeded in excellent yield.

The macrocyclization of **22** to **23** was achieved through a modified *Eglinton* coupling as published by Scott *et al.*[52] To facilitate selective formation of **23**, a 0.55 mM solution of **22** in pyridine was added by a syringe pump over the course of 48 hours to a solution of 15 equivalents CuCl and 21 equivalents $Cu(OAc)_2$ in 60 mL of pyridine. After aqueous workup, CC and size exclusion chromatography (BioBeads, SX-3) in toluene, the key intermediate **23** was isolated as a red amorphous solid in 33% yield. We also observed the twofold closed cyclic dimer of **22**, which was removed easily by size exclusion chromatography. It is noteworthy that the macrocyclization of a similar molecule with eight thiophenes instead of ten exclusively resulted in the formation of its twofold closed dimer. The final cyclization step to form the target compound **1** was performed using a procedure of Bäuerle *et al.*, where **23** was reacted with $Na_2S \cdot 9\ H_2O$ in a 1:1 mixture of DMF and 2-methoxyethanol.[25] To our delight, MALDI-TOF analysis of the reaction mixture after 1.5 hours showed only the mass of the target compound **1**. After acidic workup to remove excess reagent and solvent, and subsequent purification by CC, target compound **1** was isolated as a red amorphous solid in quantitative yield.



Scheme 4. Synthesis of target molecule **1**. Reagents and conditions: (a) NBS, $CHCl_3$, room temp., 20 h, 90%. (b) **8**, Pd-PEPPSI-IPr™, K_2CO_3, toluene, MeOH, 70 °C, 30 min, 72%. (c) NBS, $CHCl_3$, AcOH, room temp., 15 min; then CPDIPS acetylene, $Pd(PPh_3)_4$, CuI, toluene, diisopropylamine, 100 °C, 20 h, 63% (two steps). (d) TBAF, THF, room temp., 20 h, 97%. (e) CuCl, $Cu(OAc)_2$, pyridine, room temp., 48 h, 33%. (f) $Na_2S \cdot 9\ H_2O$, DMF, 2-methoxyethanol, 120 °C, 1.5 h, quant.

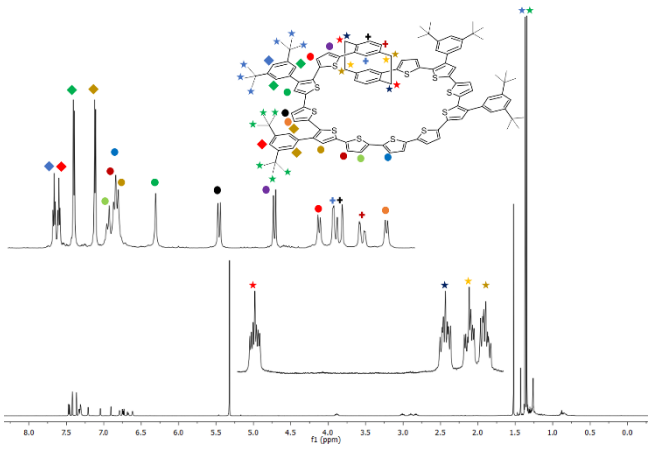


Figure 2. ^{1}H NMR spectrum of macrocycle **1** in CD_2Cl_2 at room temperature. Inlet: aromatic (top) and benzylic (bottom) protons of **1**.

The identity of macrocycle **1** was fully corroborated by ^{1}H and ^{13}C NMR, as well as by 2D NMR spectroscopy, which enabled us to fully assign the observed resonances to the corresponding proton and carbon atoms. All recorded spectra of **1** are available in the supporting information (SI); its ^{1}H NMR spectrum recorded at 600 MHz is displayed in figure 2 to demonstrate both, purity and identity of the isolated target structure. The elemental formula of **1** was confirmed by high-resolution matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (HR MALDI-TOF MS, displayed in figure S57 in the SI). The signal observed for **1** showed an isotopic pattern matching the one expected for its elemental composition ($[M]^+$ $C_{116}H_{116}S_{11}$).

The macrocyclization of **22** to **23** yields the product as a racemic mixture. Both enantiomers for macrocycles **23** and **1** can readily interconvert through a concerted rotation around the C-C bonds between the benzene rings of the PC and the thiophene building blocks on each adjacent side (see figure 3). We investigated the racemization dynamics for macrocycle **1**. The rotation proceeds rapidly at room temperature, separation of the enantiomers by means of HPLC on a chiral stationary phase was not possible. It is worth to note that the racemization does not proceed through an achiral transition state, unlike in the cases of helicenes, twistacenes or banister- like molecules because the pseudo-*para* substituted PC does not allow for a symmetry element along the reaction coordinate that renders the transition state to be achiral .[53,54]

To further investigate the dynamics of the racemization, **1** was subjected to VT-NMR experiments in CD_2Cl_2. The most instructive picture of the dynamics is obtained when the resonances of the four CH_2-groups of the PC unit are analyzed at different temperatures. For

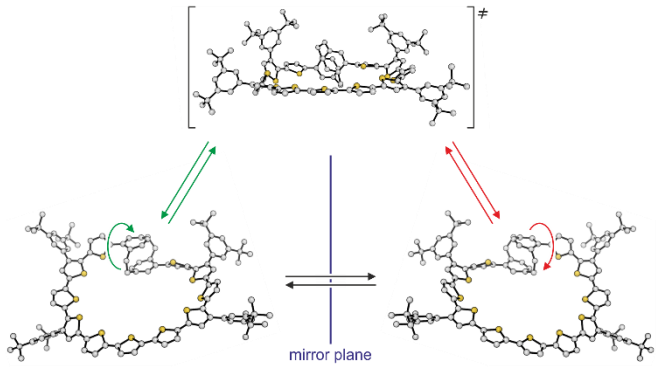


Figure 3. Graphical representation of both enantiomers of macrocycle **1** together with a transition state of the enantiomerization process. Rotation around the bonds between the oligothiophene-belt and the [2.2]paracyclophane interconverts one enantiomer into the other.

the static, chiral structure of **1**, these eight protons are all magnetically inequivalent, and, hence, eight resonances are expected. At room temperature, however, only four distinct complex multiplets are observed in the range between 2.5 and 4.0 ppm. This clearly demonstrates racemization kinetics that is fast on the ^{1}H-NMR time scale. Depending on the concentration of the sample, the resonances appear as sharp resolved signals (c.f. figure 2) or, at higher concentration, stacking of the extended aromatic ring systems leads to broadening which is not related to a dynamic process originating in the racemization. When the temperature was lowered to 218 K, severe line broadening occurs and after coalescence at approximately 213 K a splitting into eight, partially overlapping signals was observed indicating slow interconversion of the enantiomers by the rubber glove mechanism (see figure 4). The activation barrier for the racemization was determined from the shift difference of 417 Hz for H-41/H-41a and the coalescence temperature (213 K) to be 38 kJ mol^{-1}. The barrier for racemization is considerably lower than the barrier for similar ferrocene-based macrocycles with smaller ring sizes.[55] Further cooling of the sample to 183 K revealed a second dynamic process

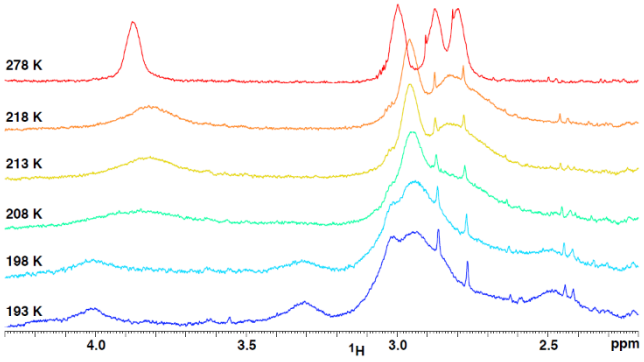


Figure 4. VT-NMR spectra of the resonances, corresponding to the benzylic protons of **1**.

that is most likely related to rotational restrictions in the di-tert-butylphenyl units.

To investigate the change in through-space vs. through-bond conjugation by the introduced macrocycle, the optoelectronical properties of macrocycles **23** and **1** were investigated by UV/Vis absorption and emission spectroscopy and compared to linear building block **22** (figure 5). The terminal alkyne substituted oligothiophene with a central PC subunit **22** has its absorption maximum at 438 nm. After macrocyclization, the absorption maxima of **23** and **1** are hypsochromically shifted with respect to **22**. The absorption maximum of **23** is found at 413 nm and the absorption maximum of **1** is at 420 nm. Both absorption spectra of the macrocyclic compounds display additional shoulders, one is found around 450 nm, which is more pronounced in the case of **23**, the other appears at wavelengths higher than 500 nm. The comparison of the absorption spectrum of **22** with reported electronic data from linear oligothiophenes points at through-space conjugation in the central PC subunit. Penta- and heptathiophenic oligomers have absorption maxima at 386 and 409 nm, respectively.[56] The absorption maximum of **22**, consisting of two pentathiophenes interlinked by PC, is at 438 nm. The bathochromic shift compared to the reported oligothiophenes confirms the through-space conjugation in the central PC subunit, as already reported for similar compounds.[34–36] Macrocyclic thiophenes of a given size have absorption maxima that correspond in energy to the absorption maxima of linear oligothiophenes of approximately half the number of thiophene subunits.[56] The hypsochromic shift of the absorption maxima of the macrocycles **23** and **1** compared to linear **22** was thus not surprising. Also, the rather small values of 25 nm and 18 nm of the recorded shifts for **23** and **1** respectively can be rationalized by the

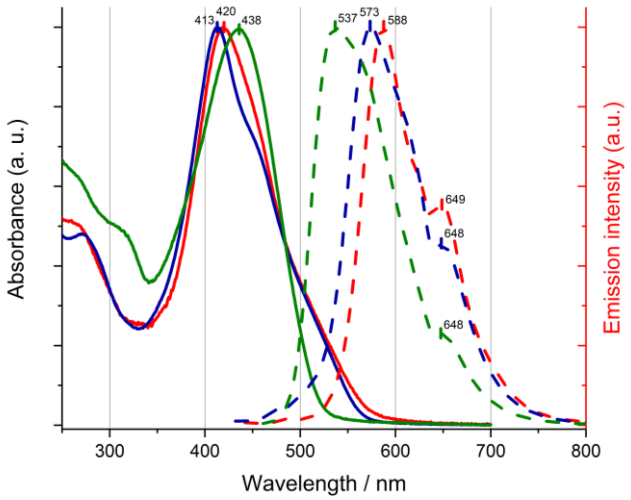


Figure 5. Absorption spectra of **22** (green line), **23** (blue line) and **1** (red line) and emission spectra (dotted lines of corresponding color). All spectra were recorded in dichloromethane at room temperature. The emission spectra were exited at 438 nm (**22**), 413 nm (**23**), and 420 nm (**1**).

through-space conjugation in the central PC unit of the linear precursor **22**. Compared with an oligomer of comparable length consisting exclusively of 2,5-interlinked thiophenes, the through-space conjugation is less effective than the delocalization in a thiophene, resulting in a larger separation of the frontier orbitals. The bathochromic shift of 7 nm of the absorption maximum of **1** compared to the signal of macrocycle **23** points at the increased delocalization through the sp^2 carbon atoms of the 2,5-diyl-thiophene linker in **1** (through-bond conjugation) compared with the *sp* centers of the diacetylene connection in **23**.

The emission spectra of all three samples **22**, **23**, and **1** have an intense maximum with a more or less pronounced shoulder at about 648-649 nm in common. While the maximum of the emission of **22** is at 537 with a *Stokes*' shift of 99 nm, the one of **23** is at 573 nm with a *Stokes'* shift of 160 nm and the emission maximum of **1** is at 588 nm with a *Stokes*' shift of 168 nm. Again, a bathochromic shift with increasing conjugation in the macromolecules' subunits is observed in the order of the emission signals.

Initial attempts to measure the HOMO-LUMO gap electrochemically failed due to irreversible behavior of **1** in the cyclic voltammetry experiment. As approximations of the HOMO-LUMO gaps, the electronic transitions between the vibrational ground states of the absorption and emission spectra were compared. For the linear precursor **22**, the absorption and emission bands intersect at 500 nm, corresponding to a transition energy of 2.48 eV. The intersection is bathochromically shifted to 528 nm (2.35 eV) for the cyclized **23** and shifts further to 542 nm (2.29 eV) upon replacing the diacetylene linkage with a thiophene subunit in **1**. The decrease of transition energies further corroborates the trend of increasing conjugation in the subunits of the investigated series.

Conclusions

We present an efficient synthesis of chiral macrocycle **1** and its full characterization by ^{1}H, ^{13}C and 2D NMR spectroscopy as well as high resolution mass spectrometry. Suitable precursors to incorporate PC as a key building block to break the conjugation of the macrocycle were designed and synthesized. The assembly of the achiral linear precursors is based on Pd- catalyzed coupling chemistry combined with halogenation sequences of the corresponding thiophenes. A linear synthetic strategy allowed to determine the required length of the precursor for a successful macrocyclization. The ring closing as key step of the synthesis provided the target molecule in reasonable yields, considering both its size and structural flexibility. The macrocyclization yielded a racemic mixture that could not be resolved due to the low racemization barrier at room temperature. The racemization barrier was investigated with VT-NMR experiments and was found to be 38 kJ mol^{-1}, indicating unhindered rotation of the central PC unit versus the oligothiophenic chain at room temperature. Investigation of the optical properties of the obtained macrocycles and comparison with the open-ring precursor allowed to determine the change of electronic features upon macrocyclization. All spectra of the macrocycles were considerably red-shifted compared to the open-ring precursor. We obtained rare insights into the through-space versus through-bond conjugation through the comparison of the considerable lowered transition energies between vibrational ground states.

In summary, two unique conjugated macrocycles have been prepared and investigated, elucidating the influence of a prochiral building block with broken conjugation on structural and electronical properties.

We are currently advancing the concept of helical chiral oligothiophene macrocycles comprising a PC subunit by designing model compounds of increased stability due to sterically hindered enantiomerization processes.

Experimental Section

General

Instruments, materials and methods are described in detail in the Supporting Information.

Previously Described Compounds

4,16-Dibromo[2.2]paracyclophane, trimethyl(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thien-2-yl)silane, 2-(3,5-di-tert-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and CPDIPS-acetylene were prepared according to reported procedures.[47,48,51,57]

Experimental

3-(3,5-Di-*tert*-butylphenyl)thiophene (11): 2-(3,5-Di-*tert*-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[48] (12.9 g, 40.7 mmol, 1.05 eq.), 3-bromothiophene (3.64 mL, 38.8 mmol, 1.00 eq.), Na_2CO_3 (20.5 g, 194 mmol, 5.00 eq.) and $Pd(PPh_3)_4$ (1.12 g, 970 µmol, 2.5 mol%) were suspended in a mixture of DMF (54 mL) and H_2O (6 mL). The reaction mixture was degassed by bubbling a stream of argon through the solution and was heated to 120 °C for two hours. The reaction was allowed to reach room temperature, toluene was added, and the organic phase was washed with 2 M HCl and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude was purified by column chromatography (pentane), yielding **11** as a colorless oil (9.35 g, 34.3 mmol, 88%). ^{1}H NMR (250 MHz, CD_2Cl_2) δ = 7.47 – 7.38 (m, 6H), 1.37 (s, 18H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 151.88, 135.76, 127.89, 127.29, 126.52, 122.00, 121.49, 120.56, 35.39, 31.79 ppm. MS (EI, 70 eV): *m/z* (%) = 272.20 (48.90), 257.20 (100), 57.10 (73.16). HRMS (EI): *m/z* calcd. for: $C_{18}H_{24}S^+$ [M^+]: 272.1594; found 272.1598.

2-Bromo-3-(3,5-di-*tert*-butylphenyl)thiophene (12): 3-(3,5)-Di-*tert*-butylphenyl)thiophene (**11**) (9.33 g, 34.3 mmol, 1.00 eq.) was

dissolved in $CHCl_3$ (100 mL) and AcOH (100 mL). To this was added, under exclusion of light, NBS (6.11 g, 34.3 mmol, 1.00 eq) and the reaction was heated to 40 °C for one hour. The reaction was allowed to reach room temperature, CH_2Cl_2 was added and the reaction was neutralized with sat. aq. $NaHCO_3$. It was dried over $MgSO_4$ and the solvent was removed in vacuo. The crude was purified by column chromatography (cyclohexane), yielding **12** as a colorless oil (9.27 g, 26.4 mmol, 77%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.45 (t, ^4J = 1.8 Hz, 1H), 7.41 (d, ^4J = 1.8 Hz, 2H), 7.35 (d, ^3J = 5.6 Hz, 1H), 7.08 (d, ^3J = 5.6 Hz, 1H), 1.37 (s, 18H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 151.48, 142.81, 134.60, 129.88, 126.45, 123.63, 122.27, 108.62, 35.45, 31.77 ppm. MS (EI, 70 eV): *m/z* (%) = 352.20 (28.89), 350.15 (28.84), 337.15 (75.23), 335.15 (72.64), 57.10 (100). $C_{18}H_{23}BrS$ (351.346): calcd. C 61.53 H 6.60; found C 61.65 H 6.87.

2-(3-(3,5-Di-*tert*-butylphenyl)thien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7): 2-Bromo-3-(3,5-di-*tert*-butylphenyl)thiophene (**12**) (3.45 g, 9.83 mmol, 1.0 eq.) was dissolved in THF (60 mL) and was degassed with argon. The reaction mixture was cooled to -78 °C and *n*-BuLi (1.6 M in hexane, 6.14 mL, 9.83 mmol, 1.0 eq.) was added dropwise. The reaction was stirred for two hours and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.21 mL, 10.8 mmol, 1.10 eq.) was added dropwise. The reaction was allowed to reach room temperature and 2 M HCl was added. The crude was taken up in toluene and filtered through a plug of celite. The solvent was removed, and **7** was obtained as brown oil, which solidified upon standing (3.51 g, 8.86 mmol, 90%). M.p.: 69 – 71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (d, ^3J = 4.8 Hz, 1H), 7.47 (d, ^4J = 1.8 Hz, 2H), 7.40 (t, ^4J = 1.8 Hz, 1H), 7.31 (d, ^3J = 4.8 Hz, 1H), 1.39 (s, 18H), 1.31 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.02, 149.96, 136.33, 131.64, 131.36, 123.82, 121.37, 83.99, 35.05, 31.69, 24.94 ppm. The carbon, to which the boron is bound is not observed. HRMS (EI): *m/z* calcd. for: $C_{24}H_{35}BO_2S^+$ [M^+]: 398.2450; found 398.2452.

4,16-Dithienyl[2.2]paracyclophane (6): 4,16-Dibromo[2.2]paracyclophane (4.58 g, 12.5 mmol, 1.0 eq.) and $Pd(dppf)Cl_2$ (229 mg, 313 µmol, 2.5 mol%) were suspended in THF (100 mL) and degassed with argon. To this was added thienyl magnesium bromide (1.0 M in THF,50.0 mL 50.0 mmol, 4.0 eq.) and the reaction was heated to 60 °C for two hours. The reaction was allowed to reach room temperature and sat. aq. NH_4Cl was added. The organic phase was diluted with CH_2Cl_2 and was washed with 2 M HCl. The solvent was removed under reduced pressure and the crude was washed with cyclohexane and cold CH_2Cl_2 and dried. **6** was obtained as a white solid (4.06 g, 10.9 mmol, 87%). The analytical data agreed with the values reported in literature.[36] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (dd, ^3J = 4.9 Hz, ^4J = 1.4 Hz, 2H), 7.16 – 7.11 (m, 4H), 6.74 (dd, ^3J = 7.8 Hz, ^4J = 2.0 Hz, 2H), 6.66 (d, ^4J = 2.0 Hz, 2H), 6.59 (d, ^3J = 7.8 Hz, 2H), 3.77 – 3.69 (m, 2H), 3.01 – 2.85 (m, 4H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 144.35, 140.26, 137.35, 135.08, 135.05, 133.66, 129.77, 127.74, 126.13, 125.38, 34.54, 34.17 ppm. MS (EI, 70 eV): *m/z* (%) = 373.20 (13.43), 372.25 (48.76), 187.10 (100), 185.10 (68.51), 171.10 (48.12), 141.15 (24.68), 115.15 (14.17).

4,16-Di-(5-bromothienyl)[2.2]paracyclophane (15): 4,16-Dithienyl[2.2]paracyclophane (**6**) (4.06 g, 10.9 mmol, 1.00 eq.) was suspended in $CHCl_3$ (75 mL) and DMF (75 mL) and under exclusion of light NBS (3.98 g 22.3 mmol 2.05 eq.) was added. The reaction was allowed to proceed for 20 hours and 2 M HCl was added. The organic layer was washed with 2 M HCl and dried over $MgSO_4$. The solvent was removed under reduced pressure, the crude was taken up in toluene and filtered through a plug of celite. **15** was obtained as a white solid after solvent removal (5.23 g, 9.86 mmol, 91%). M.p.: 240 – 242 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.09 (d, ^3J = 3.8 Hz, 2H), 6.86 (d, ^3J = 3.8 Hz, 2H), 6.74 (dd, ^3J = 7.8 Hz, ^4J = 2.0 Hz, 2H), 6.57 – 6.53 (m, 4H), 3.72 – 3.64 (m, 2H), 3.00 – 2.86 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.83, 140.36, 137.30, 135.13, 134.40, 133.39, 130.64, 130.06, 126.39, 111.80, 34.47, 34.03 ppm. HRMS (EI): *m/z* calcd. for: $C_{24}H_{18}Br_2S_2^+$ [M^+]: 527.9212; found 527.9216.

4,16-Di-(3′-(3,5-di-*tert*-butylphenyl))-[2,2′-bithien]-5-yl-[2.2]paracyclophane 16: 4,16-Di-(5-bromothienyl)[2.2]paracyclophane **15** (340 mg, 640 µmol, 1.00 eq.), boronic ester **7** (770 mg, 1.93 mmol, 3.00 eq.) and K_2CO_3 (532 mg, 3.85 mmol, 6.00 eq.) were suspended in toluene (10 mL) and MeOH (10 mL). The reaction mixture was degassed with argon and Pd-PEPPSI-IPr™ (22.2 mg, 32.1 µmol, 5 mol%) was added. The reaction mixture was placed in a preheated oil bath and the reaction was stirred at 70 °C for 15 minutes. The reaction was allowed to reach room temperature and the organic layer was washed with 2 M HCl. It was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by column chromatography (cyclohexane/CH_2Cl_2 4:1) and **16** was obtained as an off-white solid (557 mg, 610 µmol, 95%). M.p.: >250 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.44 (t, ^4J = 1.9 Hz, 2H), 7.34 (d, ^3J = 5.2 Hz, 2H), 7.32 (d, ^4J = 1.8 Hz, 4H), 7.16 (d, ^3J = 5.2 Hz, 2H), 7.00 (d, ^3J = 3.7 Hz, 2H), 6.93 (d, ^3J = 3.7 Hz, 2H), 6.61 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2H), 6.51 (d, ^4J = 1.9 Hz, 2H), 6.43 (d, ^3J = 7.8 Hz, 2H), 3.69 – 3.60 (m, 2H), 2.92 – 2.78 (m, 6H), 1.33 (s, 36H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 151.47, 144.82, 140.77, 140.69, 137.69, 136.65, 135.89, 135.48, 135.22, 133.65, 132.11, 131.21, 130.17, 127.64, 126.66, 124.40, 124.29, 121.92, 35.40, 34.77, 34.48, 31.80 ppm. HRMS (MALDI TOF, DCTB): *m/z* calcd for $C_{60}H_{64}S_4^+$ [M^+]: 912.3885, found: 912.3882.

4,16-Di-(5′-bromo-3′-(3,5-di-*tert*-butylphenyl))-[2,2′-bithien]-5-yl-[2.2]paracyclophane 17: Tetrathiophene **16** (400 mg, 440 µmol, 1.00 eq) was dissolved in DMF (25 mL) and to this was added in the dark NBS (160 mg, 900 µmol, 2.05 eq.). The reaction was stirred at room temperature for 20 hours and toluene was added to the reaction mixture. The organic layer was washed with 2 M HCl and was dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2/cyclohexane 1:9). **17** was isolated as a yellow solid (432 mg, 400 µmol, 92%). M.p.: 250 – 252 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.44 (t, ^4J = 1.9 Hz, 2H), 7.27 (d, ^4J = 1.9 Hz, 4H), 7.14 (s, 2H), 6.98 (d, ^3J = 3.8 Hz, 2H), 6.92 (d, ^3J = 3.8 Hz, 2H), 6.58 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2H), 6.48 (d, ^4J = 1.9 Hz, 2H), 6.40 (d, ^3J = 7.8 Hz, 2H), 3.65 – 3.57 (m, 2H), 2.91 – 2.78 (m, 6H), 1.32 (s, 36H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 151.64, 145.36, 141.13, 140.70, 137.72, 135.48, 135.05, 134.82, 133.86, 133.65, 133.56, 131.92, 130.26, 127.99, 126.67, 124.17, 122.36, 110.97, 35.41, 34.75, 34.43, 31.77 ppm. HRMS (MALDI TOF, DCTB): *m/z* calcd for $C_{60}H_{62}Br_2S_4^+$ [M^+]: 1068.2096, found: 1068.2095.

4,16-Di-(3′-(3,5-di-*tert*-butylphenyl))-5′′-trimethylsilyl-[2,2′:5′,2′′-terthien]-5-yl-[2.2]paracyclophane 18: Dibromide **17** (800 mg, 750 µmol, 1.00 eq.), boronic ester **8** (845 mg, 2.99 mmol, 4.00 eq.) and K_2CO_3 (619 mg, 4.48 mmol, 6.00 eq.) were suspended in toluene (25 mL) and MeOH (25 mL). The reaction mixture was degassed with argon and Pd-PEPPSI-IPr™ (25.9 mg, 37.4 µmol, 5 mol%) was added. The reaction mixture was placed in a preheated oil bath and the reaction was stirred at 70 °C for 20 minutes. The reaction was allowed to reach room temperature and the organic layer was washed with 2 M HCl. It was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by column chromatography (cyclohexane/CH_2Cl_2 9:1) and **18** was obtained as a yellow wax (744 mg, 610 µmol, 82%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.27 (t, ^4J = 1.9 Hz, 2H), 7.14 (d, ^4J = 1.9 Hz, 4H), 7.12 (d, ^3J = 3.5 Hz, 2H), 7.03 (s, 2H), 7.00 (d, ^3J = 3.5 Hz, 2H), 6.82 (d, ^3J = 3.8 Hz, 2H), 6.72 (d, ^3J = 3.8 Hz, 2H), 6.39 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2H), 6.29 (d, ^4J = 1.9 Hz, 2H), 6.21 (d, ^3J = 7.8 Hz, 2H), 3.48 – 3.38 (m, 12H), 2.71 – 2.60 (m, 6H), 1.14 (s, 36H), 0.15 (s, 18H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 151.63, 144.83, 142.34, 141.37, 141.00, 140.68, 137.70, 136.37, 135.70, 135.53, 135.49, 135.17, 133.65, 131.13, 130.20, 127.79, 127.77, 127.42, 126.70, 125.69, 124.27, 122.23, 35.44, 34.75, 34.51, 31.82, 0.12 ppm. HRMS (MALDI TOF, DCTB): *m/z* calcd for $C_{74}H_{84}S_6Si_2^+$ [M^+]: 1220.4430, found: 1220.4422.

4,16-Di-(3′-(3,5-di-*tert*-butylphenyl))-5′′-iodo-[2,2′:5′,2′′-terthien]-5-yl-[2.2]paracyclophane 19: TMS-thienyl derivative **18** (752 mg, 620 µmol, 1.00 eq.) was dissolved in $CHCl_3$ (50 mL) and AcOH (50 mL). After degassing the reaction mixture with argon, NIS (314 mg, 1.35 mmol, 2.20 eq.) was added in one portion. It was stirred at room

temperature for 1.5 hours and to the crude was added sat. aq. $NaHCO_3$. The organic layer was washed with sat. aq. $NaHCO_3$ and brine and was dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude was purified by column chromatography (cyclohexane/CH_2Cl_2 4:1) and **19** was obtained as a yellow wax (812 mg, 610 µmol, 99%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.48 (t, ^4J = 1.8 Hz, 2H), 7.33 (d, ^4J = 1.8 Hz, 4H), 7.23 (d, ^3J = 3.7 Hz, 2H), 7.18 (s, 2H), 7.03 (d, ^3J = 3.7 Hz, 2H), 6.95 (d, ^3J = 3.8 Hz, 2H), 6.92 (d, ^3J = 3.8 Hz, 2H), 6.59 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2H), 6.49 (d, ^4J = 1.9 Hz, 2H), 6.41 (d, ^3J = 7.8 Hz, 2H), 3.66 – 3.61 (m, 2H), 2.90 – 2.77 (m, 6H), 1.35 (s, 36H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 151.10, 144.46, 142.86, 140.74, 140.09, 138.00, 137.12, 135.47, 134.91, 134.90, 134.53, 133.57, 133.07, 131.12, 129.64, 127.62, 127.01, 126.13, 125.21, 123.67, 121.76, 72.07, 34.86, 34.16, 33.92, 31.24 ppm. HRMS (MALDI TOF, DCTB): *m/z* calcd for $C_{68}H_{62}I_2S_6^+$ [M^+]: 1328.1573, found: 1328.1570.

4,16-Di-(3′,3‴-bis(3,5-di-*tert*-butylphenyl))-[2,2′:5′,2″:5″,2‴-quarterthien]-5-yl-[2.2]paracyclophane 20: Diiodo compound **19** (800 mg, 620 µmol, 1.00 eq). boronic ester **7** (982 mg, 2.46 mmol, 4.00 eq.) and K_2CO_3 (511 mg, 3.70 mmol, 6.00 eq.) were suspended in toluene (30 mL) and MeOH (30 mL). The reaction mixture was degassed with argon and Pd-PEPPSI-IPr™ (42.6 mg, 61.6 µmol, 5 mol%) was added. The reaction mixture was placed in a preheated oil bath and the reaction was stirred at 70 °C for 30 minutes. The reaction was allowed to reach room temperature and the organic layer was washed with 2 M HCl. It was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by column chromatography (cyclohexane/CH_2Cl_2 4:1) and **20** was obtained as a yellow wax (827 mg, 511 µmol, 83%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.52 (t, ^{4}J = 1.8 Hz, 2H), 7.48 (t, ^4J = 1.8 Hz, 2H), 7.38 – 7.34 (m, 10H), 7.20 (d, ^3J = 5.2 Hz, 2H), 7.12 – 7.10 (m, 4H), 7.06 (d, ^3J = 3.8 Hz, 2H), 7.04 (d, ^3J = 3.8 Hz, 2H), 6.97 (d, ^3J = 3.8 Hz, 2H), 6.65 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2H), 6.54 (d, ^4J = 1.9 Hz, 2H), 6.46 (d, ^3J = 7.8 Hz, 2H), 3.67 – 3.62 (m, 2H), 2.96 – 2.82 (m, 6H), 1.39 (s, 36H), 1.38 (s, 36H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 151.62, 151.43, 144.88, 141.31, 141.01, 140.68, 137.70, 137.27, 136.28, 136.11, 135.58, 135.48, 135.45, 135.29, 135.15, 133.65, 131.47, 131.32, 131.07, 130.20, 127.98, 127.51, 127.49, 126.72, 124.71, 124.35, 124.30, 124.22, 122.23, 121.99, 35.44, 35.40, 34.75, 34.51, 31.82, 31.76 ppm. HRMS (MALDI TOF, DCTB): *m/z* calcd for $C_{104}H_{112}S_8^+$ [M^+]: 1616.6524, found: 1616.6526.

4,16-Di-(5‴-bromo-3′,3‴-bis(3,5-di-*tert*-butylphenyl))-[2,2′:5′,2″:5″,2‴quarterthien]-5-yl-[2.2]paracyclophane 21: Octathiophene **20** (385 mg, 240 µmol, 1.00 eq) was dissolved in $CHCl_3$ (70 mL) and to this was added in the dark NBS (84.7 mg, 480 µmol, 2.00 eq.). The reaction was stirred at room temperature for 20 hours. The organic layer was washed with 2 M HCl and was dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2/cyclohexane 1:9). **21** was isolated as a yellow wax (381 mg, 210 µmol, 90%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.46 (t, ^4J = 1.8 Hz, 2H), 7.43 (t, ^4J = 1.8 Hz, 2H), 7.30 (d, ^4J = 1.8 Hz, 4H), 7.25 (d, ^4J = 1.8 Hz, 4H), 7.12 (s, 2H), 7.09 – 7.08 (m, 4H), 7.00 (d, ^3J = 3.7 Hz, 2H), 6.96 (d, ^3J =3.8 Hz, 2H), 6.91 (d, ^3J = 3.7 Hz, 2H), 6.58 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2H), 6.48 (d, ^4J = 1.9 Hz, 2H), 6.40 (d, ^3J = 7.8 Hz, 2H), 3.66 – 3.60 (m, 2H), 2.90 – 2.74 (m, 6H), 1.33 (s, 36H), 1.31 (s, 36H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 151.64, 151.60, 144.94, 141.36, 141.33, 140.67, 137.85, 137.69, 136.20, 135.51, 135.47, 135.12, 135.00, 134.70, 134.37, 133.94, 133.63, 132.86, 131.31, 130.20, 128.33, 127.70, 127.52, 126.72, 124.25, 124.21, 124.20, 122.42, 122.26, 111.30, 35.43, 35.41, 34.74, 34.50, 31.80, 31.71 ppm. HRMS (MALDI TOF, DCTB): *m/z* calcd for $C_{104}H_{110}Br_2S_8^+$ [M^+]: 1772.4734, found: 1772.4743.

4,16-Di-(3′,3‴-bis(3,5-di-*tert*-butylphenyl))-5⁗-trimethylsilyl-[2,2′:5′,2″:5″,2‴:5‴,2⁗qinquethien]-5-yl-[2.2]paracyclophane 4: Dibromide **21** (160 mg, 90.0 µmol, 1.00 eq), boronic ester **8** (153 mg, 540 µmol, 6.00 eq.) and K_2CO_3 (74.8 mg, 540 µmol, 6.00 eq.) were suspended in toluene (10 mL) and MeOH (10 mL). The reaction mixture was degassed with argon and Pd-PEPPSI-IPr™ (6.15 mg, 9.02 µmol, 10 mol%) was added. The reaction mixture was placed in a preheated oil bath and the reaction was stirred at 70 °C for 30 minutes. The reaction was allowed to reach room temperature and the organic layer was washed with 2 M HCl. It was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by column chromatography (cyclohexane/CH_2Cl_2 4:1) as well as GPC. **4** was obtained as a yellow wax (125 mg, 65.0 µmol, 72%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.46 (t, ^4J = 1.8 Hz, 2H), 7.45 (t, ^4J = 1.8 Hz, 2H), 7.32 – 7.30 (m, 10H), 7.21 (s, 2H), 7.20 (d, ^3J = 3.5 Hz, 2H), 7.10 – 7.08 (m, 4H), 7.01 – 6.99 (m, 4H), 6.92 (d, ^3J = 3.7 Hz, 2H), 6.59 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2H), 6.49 (d, ^4J = 1.9 Hz, 2H), 6.41 (d, ^3J = 7.8 Hz, 2H), 3.66 – 3.61 (m, 2H), 2.90 – 2.77 (m, 6H), 1.34 – 1.33 (m, 72H), 0.35 (s, 18H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 151.61, 151.56, 142.16, 142.15, 141.59, 141.58, 141.31, 141.14, 140.67, 137.69, 137.22, 137.21, 136.25, 135.82, 135.74, 135.53, 135.52, 135.46, 135.22, 135.12, 133.63, 130.40, 130.19, 127.83, 127.71, 127.51, 127.49, 126.71, 125.80, 124.29, 124.28, 124.20, 122.28, 122.23, 35.43, 35.42, 34.73, 34.49, 31.80, 31.75, 0.10 ppm. HRMS (MALDI TOF, DCTB): *m/z* calcd for $C_{118}H_{132}S_{10}Si_2^+$ [M^+]: 1924.7069, found: 1924.7068.

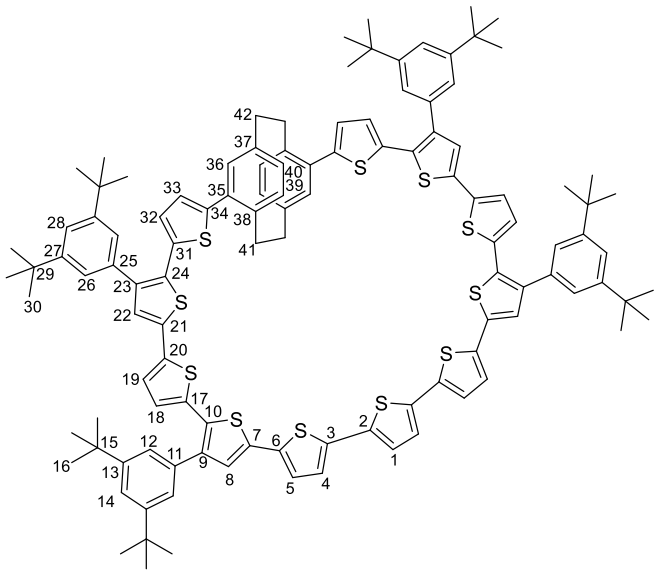
4,16-Di-((3′,3‴-bis(3,5-di-*tert*-butylphenyl))-5⁗-((4-cyanopropyl)diisopropyl)silylethynyl-[2,2′:5′,2″:5″,2‴:5‴,2⁗-qinquethien]-5-yl)-[2.2]paracyclophane 3: Decathiophene **4** (125 mg, 65.0 µmol, 1.00 eq.) was suspended in $CHCl_3$ (5 mL) and AcOH (5 mL) and was degassed with argon. NBS (24.3 mg, 137 µmol, 2.10 eq.) was added in one portion and the reaction was stirred at room temperature for 15 minutes. The crude was poured into sat. aq. $NaHCO_3$ and the organic layer was washed with brine. The solvent was removed under reduced pressure and the crude was passed through a plug of silica gel in toluene. After removal of the solvent, the crude was dissolved in toluene (5 mL) and diisopropylamine (2 mL). To this was added CPDIPS acetylene (27.3 mg, 131 µmol, 3.00 eq.) and the mixture was degassed with argon. $Pd(PPh_3)_4$ (2.53 mg, 2.20 µmol, 5.0 mol%) and CuI (0.21 mg, 1.10 µmol, 2.5 mol%) were added to the reaction mixture and it was heated to 100 °C for 20 hours. After completion of the reaction, it was diluted with toluene, and the organic layer was washed with 2 M HCl. It was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude was purified by column chromatography in toluene and **3** was obtained as an orange wax (92.6 mg, 43.8 µmol, 63%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.48 – 7.46 (m, 4H), 7.32 (d, ^4J = 1.8 Hz, 8H), 7.22 (s, 2H), 7.20 (d, ^3J = 3.8 Hz, 2H), 7.12 (d, ^3J = 3.8 Hz, 2H), 7.10 – 7.09 (m, 4H), 7.02 – 7.00 (m, 4H), 6.92 (d, ^3J = 3.8 Hz, 2H), 6.60 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2H), 6.49 (d, ^4J = 1.9 Hz, 2H), 6.41 (d, ^3J = 7.8 Hz, 2H), 3.67 – 3.61 (m, 2H), 2.92 – 2.77 (m, 6H), 2.44 (t, J = 7.0 Hz, 4H), 1.91 – 1.81 (m, 4H), 1.35 (s, 72H), 1.12 – 1.09 (m, 24H), 0.89 – 0.83 (m, 4H). ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 151.66, 151.64, 144.94, 141.66, 141.35, 140.68, 138.95, 137.70, 137.54, 136.23, 135.54, 135.49, 135.43, 135.14, 135.02, 134.75, 134.41, 133.65, 131.36, 131.24, 130.21, 128.47, 127.94, 127.61, 127.53, 126.73, 124.30, 124.21, 124.16, 122.50, 122.44, 122.265, 122.258, 120.30, 100.36, 96.66, 35.46, 35.44, 34.75, 34.51, 31.82, 31.77, 30.28, 21.86, 21.27, 18.55, 18.32, 12.32, 10.15 ppm. Two aliphatic carbon signals do not correspond to a signal from compound **A**. HRMS (MALDI TOF, DCTB): *m/z* calcd for $C_{136}H_{154}N_2S_{10}Si_2^+$ [M^+]: 2190.8852, found: 2190.8816.

4,16-Di-((3′,3‴-bis(3,5-di-*tert*-butylphenyl))-5⁗-ethynyl-[2,2′:5′,2″:5″,2‴:5‴,2⁗qinquethien]-5-yl)-[2.2]paracyclophane 22: Compound **3** (150 mg, 70.0 µmol, 1.00 eq.) was dissolved in wetted THF (25 mL). The reaction mixture was degassed with argon and TBAF (1.0 M in THF, 0.21 mL, 210 µmol, 3.00 eq.) was added dropwise. The reaction was stirred at room temperature for 20 hours and the reaction mixture was diluted with toluene. The organic layer was washed with brine and dried over $MgSO_4$. After column chromatography (cyclohexane/CH_2Cl_2 4:1), **22** was received as an orange wax (124 mg, 68.0 µmol, 97%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.47 – 7.45 (m, 4H), 7.31 (d, J = 1.8 Hz, 8H), 7.23 (d, ^3J = 3.9 Hz, 2H), 7.22 (s, 2H), 7.12 (d, ^3J = 3.8 Hz, 2H), 7.10 – 7.08 (m, 4H), 7.01 – 7.00 (m, 4H), 6.92 (d, ^3J = 3.8 Hz, 2H), 6.59 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2H), 6.49 (d, ^4J = 1.9 Hz, 2H), 6.40 (d, ^3J = 7.8 Hz, 2H), 3.66 – 3.60 (m, 2H), 3.50 (s, 2H), 2.91 – 2.76 (m, 6H), 1.35 – 1.33 (m, 72H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 151.47, 151.45, 144.74, 141.98, 141.45, 140.48, 138.96, 137.50, 137.35, 136.03, 135.33, 135.21, 134.93, 134.81, 134.55, 134.39, 133.44, 133.07, 131.25,

131.04, 130.03, 128.37, 128.33, 127.74, 127.42, 127.33, 126.53, 124.09, 124.00, 123.91, 122.25, 122.06, 121.19, 120.85, 82.83, 76.95, 35.25, 35.24, 34.55, 34.31, 31.61, 31.56 ppm. HRMS (MALDI TOF, DCTB): *m/z* calcd for $C_{116}H_{116}S_{10}^+$ [M^+]: 1828.6279, found: 1828.6274.

Macrocycle 23: Diyne **22** (60.0 mg, 32.8 µmol, 1.00 eq.) was dissolved in pyridine (60 mL) and degassed with argon. CuCl (48.7 mg, 490 µmol, 15.0 eq.) and $Cu(OAc)_2$ (125 mg, 690 µmol, 21.0 eq.) were dissolved in pyridine (60 mL) and degassed with argon. The solution of diyne **22** was added dropwise via syringe pump over the course of 48 hours. After completed addition, the crude was diluted with toluene, and 2 M HCl was added. The organic layer was washed with 2 M HCl and brine and the solvent was removed under reduced pressure. The crude was filtered through a plug of celite and purified by size exclusion chromatography (BioBeads SX-3, toluene) and column chromatography (pentane/CH_2Cl_2 4:1). **23** was obtained as a red wax (19.8 mg, 10.8 µmol, 33%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ = 7.47 – 7.40 (m, 4H), 7.40 (d, ^4J = 1.8 Hz, 4H), 7.37 (d, ^4J = 1.8 Hz, 4H), 7.29 (s, 2H), 7.25 (d, ^3J = 3.8 Hz, 2H), 7.22 – 7.21 (m, 4H), 7.05 (d, ^3J = 3.8 Hz, 2H), 6.90 (d, ^3J = 3.7 Hz, 2H), 6.76 (d, ^3J = 3.7 Hz, 2H), 6.73 – 6.72 (m, 2H), 6.69 – 6.68 (m, 4H), 6.66 (d, ^3J = 3.9 Hz, 2H), 3.90 – 3.86 (m, 2H), 3.04 – 2.98 (m, 6H), 1.36 (s, 36H), 1.35 (s, 36H) ppm. ^{13}C NMR (151 MHz, CD_2Cl_2) δ = 151.66, 151.50, 143.75, 141.07, 141.03, 140.82, 140.52, 136.89, 136.26, 135.68, 135.65, 135.48, 135.40, 134.78, 134.75, 134.16, 134.13, 133.05, 131.66, 131.14, 129.99, 129.98, 128.18, 126.91, 126.47, 126.27, 125.24, 123.87, 123.77, 123.69, 123.07, 122.16, 121.98, 121.01, 80.05, 78.62, 35.29, 35.28, 34.93, 34.85, 31.59, 31.58 ppm. HRMS (MALDI TOF, DCTB): *m/z* calcd for $C_{116}H_{114}S_{10}^+$ [M^+]: 1826.6122, found: 1826.6110.

Macrocycle 1: Macrocycle **23** (4.00 mg, 2.19 µmol, 1.00 eq.) was suspended in DMF (2 mL) and 2-methoxyethanol (2 mL). It was degassed with argon and $Na_2S \cdot 9\ H_2O$ (5.26 mg, 21.9 µmol, 10.0 eq.) was added to the reaction mixture. The reaction was placed in a preheated oil bath and was stirred for 1.5 hours at 120 °C. It was allowed to reach room temperature, diluted with toluene and washed with 2 M HCl, repeatedly. The solvent was removed under reduced pressure and the crude was purified by column chromatography (pentane/CH_2Cl_2 4:1). **1** was obtained as a red wax (4.00 mg, 2.18 µmol, 99%).



^{1}H NMR (600 MHz, CD_2Cl_2) δ = 7.47 (t, ^4J = 1.9 Hz, 2H, H-28/H-28a), 7.46 (t, ^4J = 1.8 Hz, 2H, H-14/H-14a), 7.42 (d, ^4J = 1.9 Hz, 4H, H-26/H-26a), 7.37 (d, ^4J = 1.8 Hz, 4H, H-12/H-12a), 7.34 – 7.30 (m, 8H, H-1/H-1a, H-4/H-4a, H-5/H-5a, H-8/H-8a), 7.21 (s, 2H, H-22/H-22a), 7.05 (d, ^3J = 3.8 Hz, 2H, H-19/H-19a), 6.90 (d, ^3J = 3.7 Hz, 2H, H-33/H-33a), 6.79 (d, ^3J = 3.7 Hz, 2H, H-32/H-32a), 6.76 – 6.72 (m, 4H, H-36/H-36a, H-39/H-39a), 6.68 (dd, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 2H, H-40/H-40a), 6.62 (d, ^3J = 3.9 Hz, 2H, H-18/H-18a), 3.91 – 3.86 (m, 2H, H-41/H-41a), 3.03 – 2.98 (m, 2H, H-41/H-41a), 2.92 – 2.88 (m, 2H, H-42/H-42a), 2.85 – 2.80 (m, 2H, H-42/H-42a), 1.37 (s, 36H, H-30/H-30a), 1.35 (s, 36H, H-16/H-16a) ppm. ^{13}C NMR (151 MHz, CD_2Cl_2) δ = 151.77 (2 C, C-13/ C-13a), 151.64 (2 C, C-27/C-27a), 143.90 (2 C, C-34/C-34a), 143.75, (2 C, C-37/C37a), 141.43 (2 C, C-9/C-9a), 140.47 (2 C, C-23/C-23a), 138.00 (2 C, C-38/C-38a), 137.19 (2 C, C-31/C-31a), 136.58 (2 C, C-2/C-2a), 136.55 (2 C, C-7/C-7a), 136.45 (2 C, C-3/C-3a), 136.23 (2 C, C-20/C-20a or C-21/C-21a), 135.88 (2 C, C-17/C-17a), 135.68 (2 C, C-24/C-24a), 135.54 (2 C, C-39/C-39a), 135.40 (2 C, C-11/C-11a), 135.16 (2 C, C-6/C-6a), 135.15 (2 C, C-36/C-36a), 134.97 (2 C, C-20/C-20a or C-21/C-21a), 134.92 (2 C, C-35/C-35a), 131.14 (2 C, C-25/C-25a), 130.70 (2 C, C-10/C-10a), 130.09 (2 C, C-40/C-40a), 128.02 (2 C, C-8/C-8a), 126.94 (2 C, C-22/C-22a), 126.79 (2 C, C-18/C-18a), 126.24 (2 C, C-33/C-33a), 125.18 (2 C, C-5/C-5a), 125.16 (2 C, C-1/C-1a), 125.01 (2 C, C-4/C-4a), 124.87 (2 C, C-32/C-32a), 124.03 (2 C, C-19/C-19a), 123.93 (2 C, C-12/C-12a), 123.91 (2 C, C-26/C-26a), 122.17 (4 C, C-28/C-28a and C-14/C-14a), 35.46 (2 C, C-29/C-29a), 35.43 (2 C, C-15/C-15a), 35.29 (2 C, C-41/C-41a), 35.16 (2 C, C-42/C-42a), 31.76 (2 C, C-30/C-30a), 31.75 (2 C, C-16/C-16a) ppm. HRMS (MALDI TOF, DCTB): *m/z* calcd for $C_{116}H_{116}S_{11}^+$ [M^+]: 1860.5999, found: 1860.5977.

Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.

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Author Contribution Statement

K. J. W. performed the synthesis and characterization of all materials and co-wrote the manuscript. D. H., N. M., and W. G. performed NMR analyses of the macrocyclic compounds. M. M. supervised the work and wrote the manuscript. All authors commented on the manuscript.

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