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Noncovalent Interactions

Oligothiophene-Based Catenanes: Synthesis and Electronic Properties of a Novel Conjugated Topological Structure**

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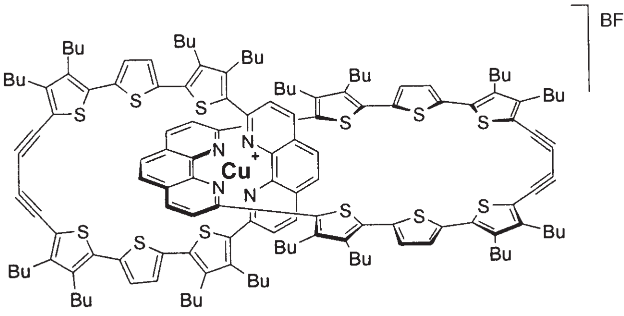
Dedicated to Professor Klaus Müllen on the occasion of his 60th birthday

Oligo- and polythiophenes are organic semiconductors that have important applications in organic electronics.[1] Various molecular shapes and dimensions, such as 1D linear,[2] 2D macrocyclic,[3] disk, and starlike,[4] as well as 3D dendritic,[5] have been developed. In particular, α-conjugated macrocyclic oligothiophenes have shown intriguing electronic[6] and self-assembling properties[7] as a result of their circular structure which makes them interesting as models for infinite, defect-free conjugated oligothiophene chains.[8]

Molecular topologies such as rotaxanes, catenanes, and knots have become a field of growing interest and underwent a transition from being laboratory curiosities[9] to more-accessible compounds.[10] Efficient synthesis procedures based on the supramolecular preorganization of relevant building blocks by directed metal–ligand complexation,[11] donor–acceptor π–π interactions,[12] hydrogen bonding,[13] chemically linked templates,[14] or routes which completely rely on self-assembly[15] led to very complex and sophisticated molecular structures. Interesting novel properties originating from the topology and independent motion, rotation, and translation of a ring[16] became the basis for applications as switchable devices in molecular electronics and machines.[17]

We aimed to prepare novel π-conjugated topologies based on oligothiophenes by combining their outstanding electronic benefits with the specific properties of the topological structure. In contrast to many already existing, quite flexible intertwined molecules, fully conjugated building blocks involve more rigid structural elements, which make their preparation a major unresolved synthetic challenge until now.

Our first attempt towards conjugated catenanes based on interlocked, conjugated terthienylphenanthroline macrocycles ended with a Cu^{I} catenate (Scheme 1).[18a] Mutual steric constraints between the relatively small macrocycles (28-membered rings) prevented demetalation and formation of the Cu-free catenane. Here, we report the synthesis and characterization of an expanded catenate **11** (Scheme 3) and the first demetalated conjugated catenane **12** consisting of quaterthiophene (4T), phenanthroline, and diacetylene units. The term “conjugated catenane” is used here not only because the mechanically bound catenane wheels are fully conjugated, but also to express that this novel topological structure may potentially offer very interesting and novel electronic and magnetic properties if one ring influences the other “through space”.



Scheme 1. Conjugated Cu^{I} catenate synthesized from terthienylphenanthrolines.

The well-known Cu^{I}-templated phenanthroline-based catenane synthesis developed by Sauvage and co-workers was utilized[10,11a,b] to provide a system with complete π conjugation, since 2,9-bis(oligothienyl)phenanthrolines are fully conjugated.[19] The synthesis of the enlarged system (Scheme 2) started from 2,9-diiodophenanthroline (**1**) which was subjected to a Neghishi-type coupling with zincated thiophene to form 2,9-di(thien-2-yl)phenanthroline (**2**, 92 %). Subsequent selective iodination with *N*-iodosuccinimide led

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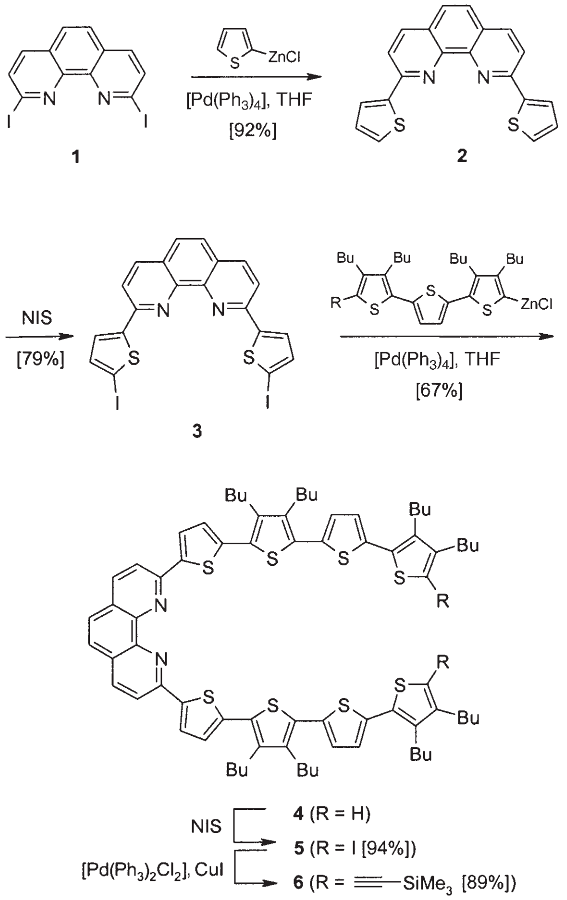


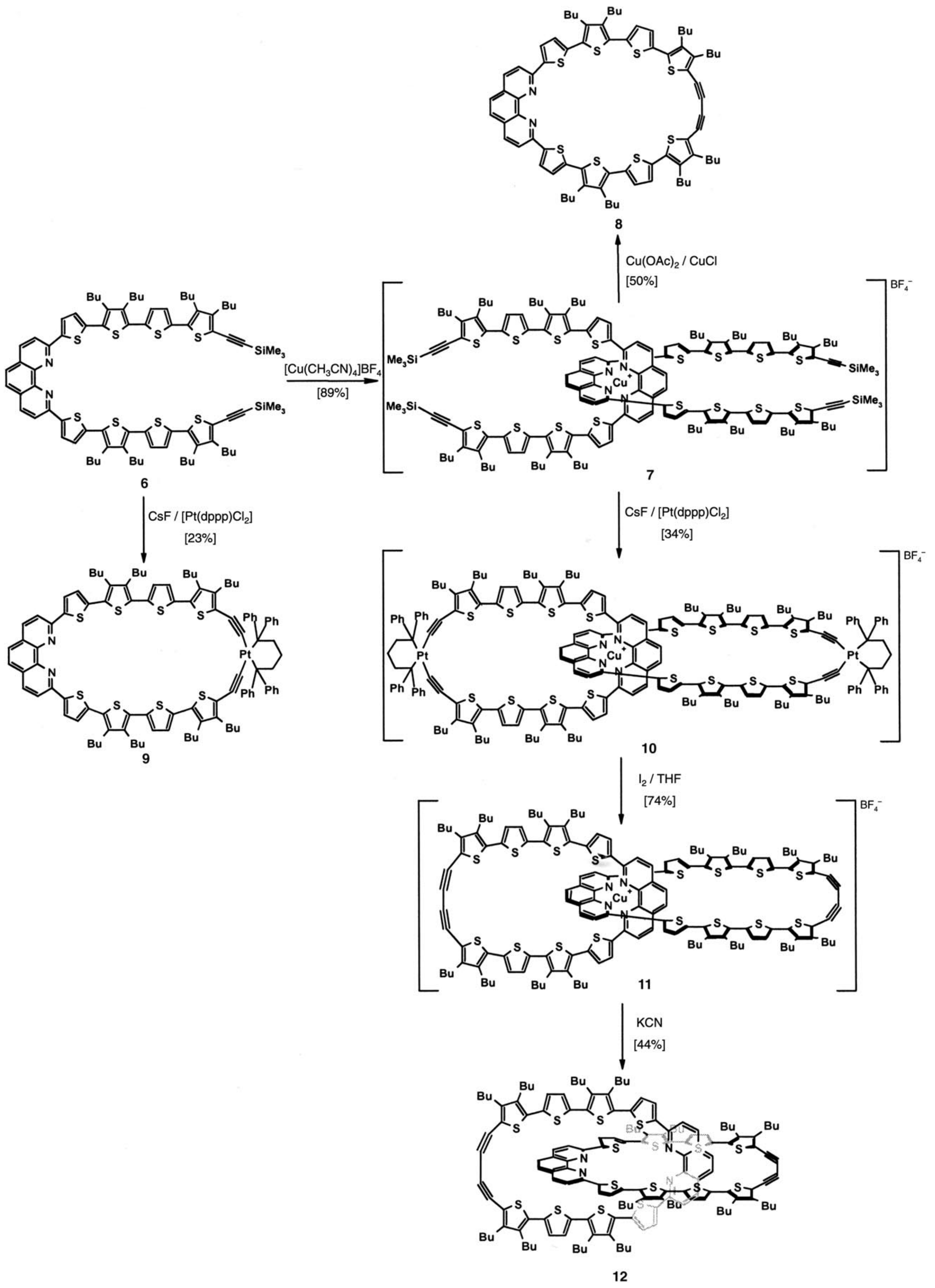
Scheme 2. Reaction sequence leading to crescent-shaped 2,9-bis-(quaterthienyl)phenanthroline (**6**) by Neghishi-type couplings, selective iodinations, and Sonogashira–Hagihara coupling. NIS = *N*-iodosuccinimide.

to diiodo derivative **3** (79%), which was coupled analogously with zincated tetrabutylterthiophene to yield 2,9-bis(quaterthien-2-yl)phenanthroline (**4**, 67%) and finally diiodo compound **5** (94%). Sonogashira-type coupling of **5** with trimethylsilyl-protected acetylene gave crescent-shaped **6** (89%) in good overall yield as the precursor for cyclization experiments.

Complexation of **6** with $[Cu(CH_3CN)_4]BF_4$ led to the homoleptic bis-phenanthroline complex **7** (89%) in which the two phenanthroline units are preorganized in a pseudotetrahedral manner around a Cu^I center. After deprotection of the acetylene groups by cesium fluoride, complex **7** was treated under Eglington and pseudo-high-dilution conditions with $Cu(OAc)_2$/CuCl/pyridine to accomplish the ring closure. Surprisingly, macrocycle **8** was isolated in 50% yield instead of the expected catenate (Scheme 3).[20] Apparently, closure of the first macrocycle generates steric constraints, and thus results in the second open-chain unit disentangling. Since all typical procedures for double macrocyclization of **7** failed, we applied our recently developed Pt-templated macrocyclization protocol[3c] using crescent-shaped **6** as a model. Metallamacrocycle **9** was formed in 23% yield by reaction of desilylated **6** with one equivalent of *cis*-$[Pt(dppp)Cl_2]$ and 10% CuI in toluene/Et_3N. This yield is intermediate between that of homologous terthienylphenanthroline (70%) and quinquethiophenephenanthroline (7%).[19] This successful Pt-templated macrocyclization of **6** was then applied to Cu^I complex **7** after desilylation with CsF. The tetraethynylene was treated with two equivalents of *cis*-$[Pt(dppp)Cl_2]$ for three days at room temperature to give trismetalated Pt^{II}-Cu^I-Pt^{II}-catenate **10** (34%). Subsequent reaction with two equivalents of iodine in THF led to 1,1-reductive elimination of the Pt corners and simultaneous C–C bond formation to generate Cu^I catenate **11** (74%), which represents the higher homologue of the previously synthesized terthienylphenanthroline catenate (Scheme 1). In this case, because of the larger ring sizes (34-membered ring), decomplexation of the Cu^I center was achieved by reaction with KCN, and "conjugated catenane" **12** was isolated in pure form after chromatography (44%). Evidence for the interlocked structure of **12** comes from ^1H NMR spectroscopy as well as tandem mass spectrometry.[20]

ESI-FTICR mass spectrometry of methanol solutions (with 0.5% CF_3CO_2H) of **8** and **12** generates ions corresponding to $[\mathbf{8}+H^+]$ and $[\mathbf{12}+H^+]$ at the expected m/z values of 1331.5 and 2662.1 Da, respectively. Experimental and calculated isotope patterns agree well, thus confirming the elemental compositions (Figure 1a). After careful mass-selection of $[\mathbf{12}+H^+]$, the protonated catenane was subjected to collision-induced dissociation (Figure 1b). The only fragment stemming from cleavage of a covalent bond within the macrocycle backbone corresponds to loss of one complete wheel. As observed earlier,[18a] a series of alkyl chain losses from the butyl groups on the thiophene rings originating from both the parent catenane and the macrocycle are also found. Macrocycle **8** shows the same series of alkyl side-chain fragmentations in an analogous MS/MS experiment. This fragmentation pattern is not in line with a weak (proton-bridged) complex of two non-intertwined wheels, because the extensive losses of alkyl groups cannot compete with dissociation of such a weak complex into two separate macrocycles. Neither does the fragmentation pattern support a single, large macrocycle with the elemental composition of the catenane, since the only backbone fragment (excluding the losses of alkyl groups) is the loss of one wheel. This behavior is typical of catenanes,[18] in which only one covalent bond within a macrocycle backbone needs to be broken, while a single macrocycle would require the cleavage of two covalent bonds and thus should lead to a number of different fragments. The only remaining topology is consequently that of a catenane.

The geometrical structure and preferred conformation of macrocycle **8** and catenane **12** were investigated by detailed analyses of ^1H and 2D NMR spectra in combination with semiempirical calculations. One set of signals in the NMR spectra of macrocycle **8**, a low-field shift of the β protons on the "inner" thiophene rings and a high-field shift of the closest phenanthroline protons (H3, H3′) relative to those of open-chained **6**, point to a symmetric over-all conformation of the macrocycle and to a distortion of the "inner" thiophene rings. This proposal agrees well with calculations which gave a symmetrical minimum energy conformation in which the "inner" thiophene rings are rotated by 95–100°, thus leading to a puckering of the phenanthroline unit by 27° from



Scheme 3. 2,9-Bis(quaterthienyl)phenanthroline **6** leads to homoleptic $\mathrm{Cu^I}$ complex **7** which can be used as a central building block for the synthesis of macrocycle **8** and catenane **12**. dppp = propane-1,3-diylbis(diphenylphosphane).

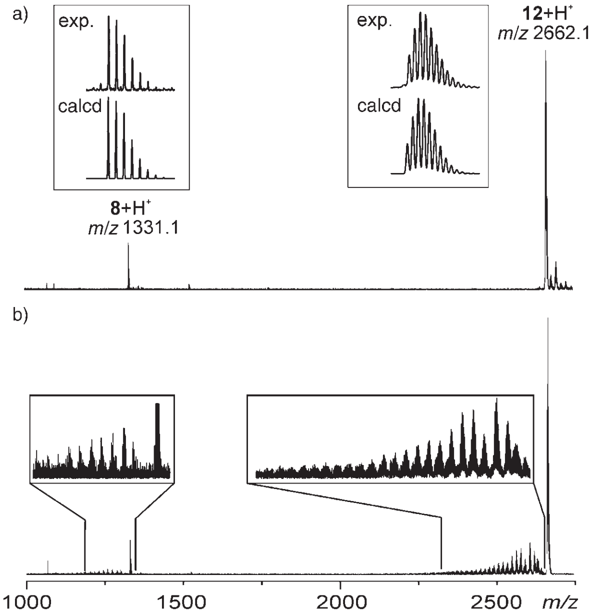


Figure 1. a) ESI-FTICR mass spectrum of a solution of catenane **12** in methanol (0.5% CF_3CO_2H). Insets: experimental and calculated isotope patterns. b) Collision-induced dissociation (collision gas: Ar) experiment conducted with mass-selected [**12**+H^+].

coplanarity.[21] Additionally, STM experiments on monolayers of **8** adsorbed on graphite display the symmetrical structure of the conjugated macrocycle (Figure 2).

The same trends are found in the ^1H NMR spectra of catenane **12**, and temperature-dependent measurements showed that the dynamic motion of the two interlocked macrocycles, which is frequently found for conventional catenanes,[16] is hindered up to 100 °C. Calculations predict a stable minimum energy conformation of catenane **12** consisting of two puckered, but intertwined symmetric macrocycles of **8**. In comparison to Cu^I catenate **11**, the distance between the two phenanthroline units in **12** has increased by approximately 1 Å during demetalation (Figure 2).

Catenane **12** is a unique molecular system in which the conjugated macrocycles are mechanically kept in proximity and may influence each other electronically "through space". Investigation of the optical and redox properties of **12** relative to those of macrocycle **8** gave clear evidence for a mutual interaction between its two rings.

The absorption spectra of both compounds showed a broad band arising from the π–π* transition of the conjugated system, with a maximum at nearly the same position and a tailing at lower energy, which is typical for cyclothiophenes[6] (Table 1, Figure 3). However, the molar extinction coefficient is doubled for catenane **12**, thus indicating an additive contribution of both rings in the intertwined system. If both spectra are normalized (same concentration of rings), a difference spectrum shows additional bands for catenane **12** from which the band at lower energy ($\lambda \approx 530$ nm) indicates an inter-ring charge-transfer (CT) transition. This finding is compatible with the conformation discussed above in which the (oligo)thiophene donor units in one ring are in proximity to the phenanthroline acceptor unit of the other ring (Figure 2). The decrease in the fluorescence quantum yield of catenane **12** ($\Phi = 2\,\%$) relative to that of macrocycle **8** ($\Phi = 6\,\%$) and open-chained **6** ($\Phi = 15\,\%$) is also consistent with a quenching arising from an "intermolecular" charge-transfer interaction in catenane **12**.

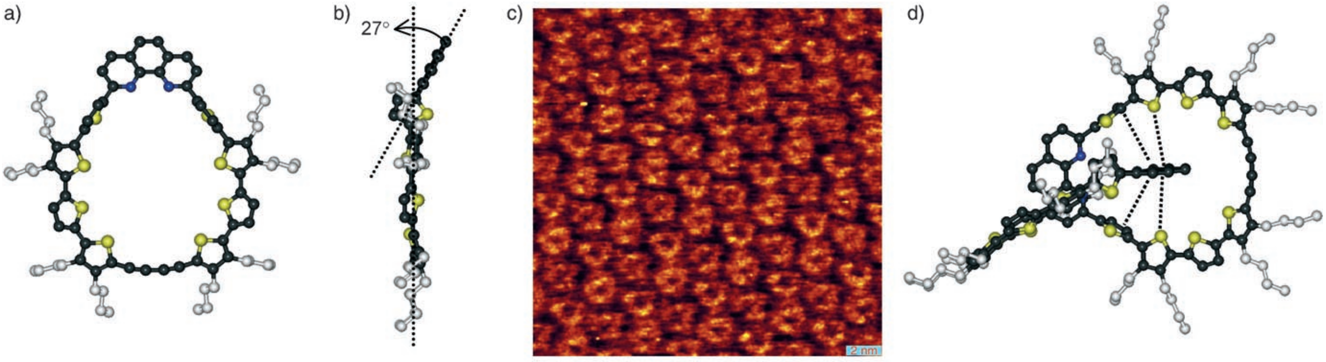


Figure 2. Calculated minimum energy conformation of macrocycle **8** (a: top view, b: side view). STM image of a monolayer of **8** at the solid (highly ordered pyrolytic graphite; HOPG)/liquid (1,2,4-trichlorobenzene) interface (c). Calculated minimum energy conformation of catenane **12** (d). The dashed lines illustrate "intermolecular" donor–acceptor interactions.

Table 1: Spectroscopic and redox data for catenane **12**, macrocycle **8**, and open-chained **6**.

Compound	λ_{max}^{abs} [nm][a]	$\varepsilon \times 10^4$ [L mol^{-1} cm^{-1}]	E_g [eV][b]	λ_{max}^{em} [nm][a]	Φ^{em} [%][c]	E°_{ox1} [V][d]	E°_{ox2} [V][d]	E°_{ox3} [V][d]	E°_{ox4} [V][d]	E°_{red1} [V][e]
6	409	6.1	2.34	553	15	0.38	0.46	0.73	0.73	−2.40[f]
8	412	8.6	2.32	555, *598*	6	0.33	0.42	0.83	0.90	−2.14[f]
12	413	17.0	2.30	565, *602*	2	0.55	0.55	0.89	1.04	−2.13[f]

[a] In CH_2Cl_2. Strongest emission peak shown in italics.[b] The optical band gap was determined from the tangent at the low energy side of the main absorption band. [c] Standard 9,10-diphenylanthracene. [d] Redox potentials versus Fc/Fc$^+$ ($c = 5\times10^{-4}$ M for **8** and 2.5×10^{-4} M for **12** in CH_2Cl_2/0.1 M $TBAPF_6$ at 295 K, $\nu = 100$ mV s^{-1}. [e] In THF/0.1 M $TBAPF_6$ at 10^{-3} mol L^{-1}. [f] Irreversible redox process, E° at $I^{\circ} = 0.855\,I_p$.

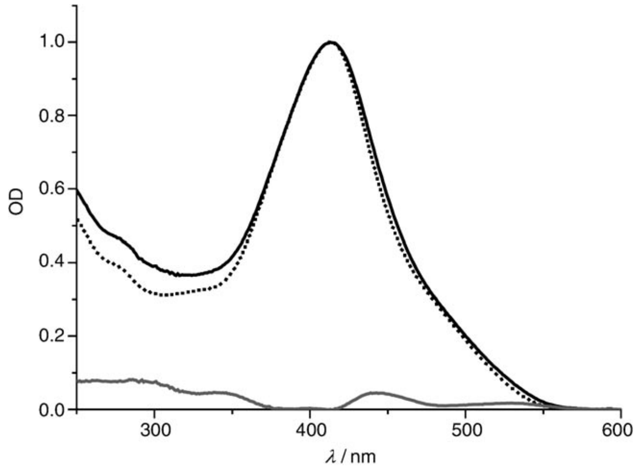


Figure 3. Normalized absorption spectra of catenane **12** (solid black line) in comparison to that of macrocycle **8** (dotted line) in dichloromethane and a difference spectrum comparing the two compounds (gray line).

Cyclic voltammetry studies show the remarkably different redox properties of **12**, **8**, and **6** (Table 1, Figure 4). The important electrophores in our systems are the 4T units which typically are oxidized reversibly to radical cations and dications by successive one-electron transfers. The corresponding potentials at which these processes occur generally depend on electronic influences in the vicinity of the electrophore. In this respect, macrocycle **8** shows first and second one-electron oxidation at potentials slightly negative of those of open-chained **6** (Table 1) and correspond to the formation of stable 4T radical cations. Further oxidation leads to tri- and tetracationic macrocycles at potentials which are more positive than those of **6**. All oxidation processes (of the 4T units) of intertwined catenane **12** are in general shifted to positive potentials because of the proximity of the electron-withdrawing phenanthroline unit. This effect is also due to inter-ring, through-space, donor–acceptor interactions, and strongly corroborates the symmetrical and puckered conformation discussed above.

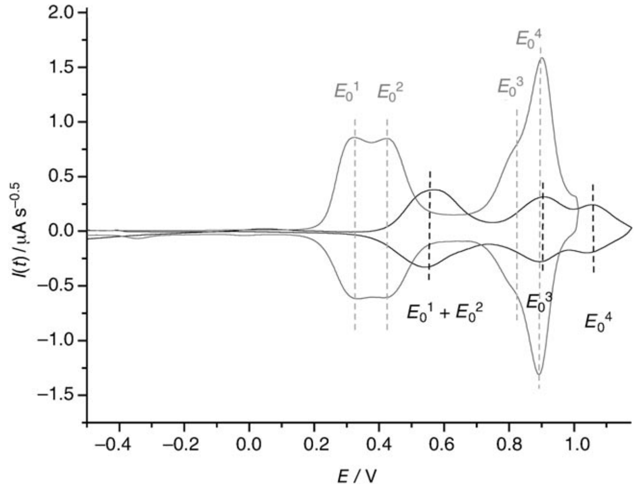


Figure 4. Deconvoluted cyclic voltammogram of catenane **12** (black line) in comparison to that of macrocycle **8** (gray line) (**12**: 2.5×10^{-4} M, **8**: 5×10^{-4} M, in CH_2Cl_2/0.1 M $TBAPF_6$ at 295 K, $\nu = 100$ mV s^{-1}, potentials versus the ferrocene/ferrocenium (Fc/Fc^+) couple. TBA = tetrabutylammonium.

In conclusion, we have prepared a unique "π-conjugated catenane" consisting of intertwined oligothiophene–phenanthroline macrocycles as a novel topological structure in the field of conjugated oligomers and polymers by a double metal template strategy. The interesting optical and redox properties found are in line with the structural and conformational analyses, which gave clear evidence that the two macrocycles in catenane **12** influence each other by through-space donor–acceptor interactions. Investigations on the Arahonov–Bohm effect on a single molecule, for example, would be possible with these types of molecules.[22]

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Keywords: catenanes · conjugation · noncovalent interactions · oligothiophenes · template synthesis

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[20] Analytical data for macrocycle **8**: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.30$ (d, $^3J = 8$ Hz, 2H), 8.25 (d, $^3J = 4$ Hz, 2H), 7.82 (d, $^3J = 8$ Hz, 2H), 7.75 (s, 2H), 7.36 (d, $^3J = 4$ Hz, 2H), 7.05 (s, 4H), 2.60–2.82 (m, 16H), 1.79 (brs), 1.69–1.43 (m, 32H), 0.89–0.99 ppm (m, 24H); *m/z* calcd for $[M+H]^+$ ($C_{80}H_{87}N_2S_8$): 1331.4629; found: 1331.6 $[M+H]^+$ (MALDI-TOF-MS); 1331.4693 $[M+H^+]$ (HRMS (ESI-FTICR)); UV/Vis (CH_2Cl_2): $\lambda_{max} = 413$ nm ($\varepsilon = 8.9 \times 10^4$ L mol^{-1} cm^{-1}). Analytical data for catenane **12**: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.22$ (d, $^3J = 4$ Hz, 4H), 8.13 (d, $^3J = 8$ Hz, 4H), 7.79 (d, $^3J = 8$ Hz, 4H), 7.48 (s, 4H), 7.21 (d, $^3J = 4$ Hz, 4H), 7.06 (d, $^3J = 4$ Hz, 4H), 7.03 (d, $^3J = 4$ Hz, 4H), 2.60–2.78 (m, 32H), 1.35–1.61 (m, 64H), 0.89–0.99 ppm (m, 48H); *m/z* calcd for $[M+H]^+$ ($C_{160}H_{173}N_4S_{16}$): 2661.9186; found: 2661.9 $[M+H]^+$ (MALDI-TOF-MS), 2661.9387 $[M+H^+]$ (HRMS (ESI-FTICR)); UV/Vis (CH_2Cl_2): $\lambda_{max} = 412$ nm ($\varepsilon = 1.7 \times 10^5$ L mol^{-1} cm^{-1}).

[21] According to calculations, a fully coplanar conformation of macrocycle **8** could be achieved by an *anti* arrangement of one “inner” thiophene ring, thus leading to a nonsymmetric structure.

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