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A Synthetic Approach Towards Interlocked π-Conjugated Macrocycles

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Dedicated to Prof. Dr. mult. Siegfried Hünig on the occasion of his 85th birthday

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A method for the synthesis of interlocked π-conjugated macrocycles is described. Starting from 2,9-bis(oligothienyl)-[1,10]phenanthrolines, (trimethylsilyl)acetylene groups were introduced at the terminal thiophene rings by selective iodination and subsequent Sonogashira–Hagihara coupling. Subsequently, we applied our recently developed metal-template approach to macrocyclization reactions by treating the deprotected acetylenes with *cis*-[Pt(dppp)Cl_2] to yield a platina-macrocycle. Based on this synthetic knowledge, by a multiple transition-metal-template protocol we accomplished the synthesis of a copper(I)–catenate consisting of two interlocked π-conjugated macrocycles which contain oligothiophene, diacetylene and phenanthroline units. Conclusive evidence for the new structures came from a detailed characterization of the platina-macrocycles and catenates by ESI-FT-ICR and tandem mass spectrometry experiments.

Introduction

Over the past two decades, α-conjugated oligothiophenes have become one of the best investigated classes of compounds for studying structure–property relationships in organic electronic materials of a defined structure.[1] In this context, we recently published a protocol for the synthesis of α-conjugated oligothiophene macrocycles.[2] Besides their unexpected properties due to their cyclic structure,[3] they represent a model of an ultimate, defect-free conjugated oligothiophene chain. In addition, they show excellent self-assembling properties on substrates[4] and form unique 1:1 π-donor–π-acceptor complexes with C_{60} fullerenes.[5] In the past few years, several attempts have been made towards the realization of individually addressable, switchable devices based on interlocked macrocyclic structures.[6] Catenanes have been intensively investigated and several synthetic approaches towards these compounds utilizing highly efficient templating strategies[7–12] and self-assembly processes[13,14] have been developed in the past few decades. The recent efficient synthesis of a Borromean ring, a topological structure of three interlocked rings, by self-assembly is a highlight of these studies.[15]

In this respect, it was our goal to prepare new conjugated supramolecular topologies based on oligothiophene macrocycles that combine their electronic material benefits and the properties of a defined supramolecular architecture in solution or on a surface. Nevertheless, threading of an oligothiophene chain through a conjugated macrocycle and the subsequent preparation of intertwined conjugated catenanes represents a yet unresolved major synthetic challenge. The design of interlocked π-conjugated macrocycles by an efficient strategy calls for the use of specific template binding sites that do not interrupt the molecule's entire π conjugation. Therefore, among all the available template methods, the well-known [1,10]phenanthroline-based catenane synthesis originally introduced by Sauvage and coworkers[8] appeared to be the most suitable approach and was the basis for our synthesis of the first conjugated catenates.

The synthesis of catenanes is still a considerable challenge, as is the identification of their intertwined topology. If no crystal structure is available, NMR experiments may provide some evidence. They often reveal up-field chemical shifts for the signals of those parts of a macrocycle that are inserted into the cavity of the other.[16] However, this is not necessarily the case for all catenanes because this effect is often caused by the anisotropy of aromatic rings incorporated in the two macrocycles of the catenane. Mass spectrometry represents a complementary method of investigation.[17] In addition to the analytical characterization with respect to the exact mass, charge state and isotope patterns,

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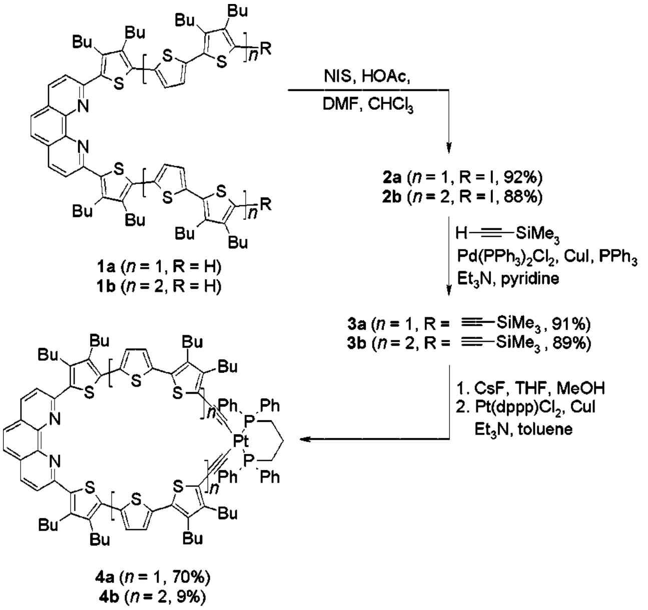
MS allows gas-phase experiments to be carried out in which molecules can be studied under environment-free conditions. Tandem mass spectrometric (MS/MS) experiments such as collision-induced dissociation (CID) provide an insight into a molecule's reactivity[18] and often indirectly into its structural features such as guest encapsulation[19] and intertwined topologies.[20] Consequently, tandem electrospray-ionization Fourier-transform ion-cyclotron-resonance (ESI-FT-ICR) mass spectrometry provides an insight into the structures of the compounds under study here and their reactivity in the gas phase.

Results and Discussion

Synthesis

Our synthesis started from the heteroaromatic chelating ligand [1,10]phenanthroline which had been substituted by alkylated terthiophene and quinquethiophene moieties at the 2- and 9-positions of the phenanthroline core (**1a**, **1b**).[21] A few attempts to use (oligothienyl)phenanthrolines as building blocks for supramolecular organic materials have previously been reported,[22] but no further transformations have been made starting from these materials. In our case, selective functionalization of the α-positions of the terminal oligothiophenes in (oligothienyl)phenanthrolines **1a** and **1b** could efficiently be achieved by reaction with *N*-iodosuccinimide in chloroform/DMF/acetic acid. The diiodinated 2,9-bis(oligothienyl)phenanthrolines **2a** and **2b** were isolated in 92 and 88% yields, respectively, after chromatographic workup (Scheme 1). Since two-fold iodination of **1a**,**b** proved to be crucial and the chromatographic behavior of the mono- and diiodo compounds was quite similar as compared with the starting materials, the reaction conditions were optimized by monitoring the reaction progress by ESI-MS. Subsequent Pd^0/Cu^I-catalyzed coupling[23] of iodinated compounds **2a** and **2b** with trimethylsilylacetylene in basic solvents gave the corresponding bis(ethynyl)-functionalized derivatives **3a** and **3b** in excellent yields (Scheme 1).

The formation of significant amounts of dehalogenated side-products, which are difficult to separate, could be suppressed when pyridine/Et$_3$N as solvent system was used instead of THF/Et$_3$N. TMS-protected bis(ethynyl) compounds **3a** and **3b** were quantitatively deprotected by CsF to give the less stable free acetylenes, which were allowed to react further in situ. Several methods for the cyclization of these compounds were applied in order to obtain macrocyclic (oligothienyl)phenanthrolines. Oxidative coupling of the acetylene units under modified Glaser conditions [CuCl/Cu(OAc)$_2$/pyridine, pseudo-high-dilution conditions] had been reported earlier to be an appropriate tool for the synthesis of oligothiophene-diacetylene macrocycles.[2a,2b] In our case, neither this procedure nor a transition-metal-catalyzed version of the Glaser coupling reaction [Pd(dppp)-Cl$_2$/CuI/Et$_3$N in THF] gave any detectable amounts of macrocyclic products. Nevertheless, we could successfully achieve intramolecular ring-closure of deprotected **3a**,**b** by applying our recently developed platinum-templated macrocyclization protocol[2c] (Scheme 1). Metalla-macrocycle **4a** was available in 70% yield by reaction of deprotected **3a** with 1 equiv. of platinum precursor complex *cis*-[Pt(dppp)-Cl$_2$] and 10% CuI in the toluene/Et$_3$N solvent system after preparative column chromatography. However, in the reaction of deprotected quinquethiophene-based compound **3b** with *cis*-[Pt(dppp)Cl$_2$] metalla-macrocycle **4b** was isolated in only 9% yield. In contrast to the efficient synthesis of the smaller macrocycle **4a**, in this case mainly polymeric material was obtained which remained on the column during chromatographic separation. This result led us to the conclusion that the platinum-templated macrocyclization of ethynylated 2,9-bis(oligothienyl)phenanthrolines may be limited by the overall chain length of the oligothiophene residue in the starting material. The resulting shape is connected to the probability of favorable conformations comprising *syn*-oriented thiophene units being adopted for the cyclization reaction. In their ^{31}P NMR spectra, compounds **4a** and **4b** showed chemical shifts typical of platinum metallacycles[2c] as well as typical P–Pt coupling constants of around 2250 Hz whilst the ^{1}H NMR spectra showed the absence of acetylenic proton signals. The efficient platinum-templated macrocyclization of open-chain ethynylated terthienyl-phenanthroline **3a** to metalla-macrocycle **4a** has led to the possibility of synthesizing more complicated, intertwined conjugated macrocycles.



Scheme 1. Synthesis of linear and macrocyclic building blocks **2a**,**b** to **4a**,**b** from **1a**,**b**.

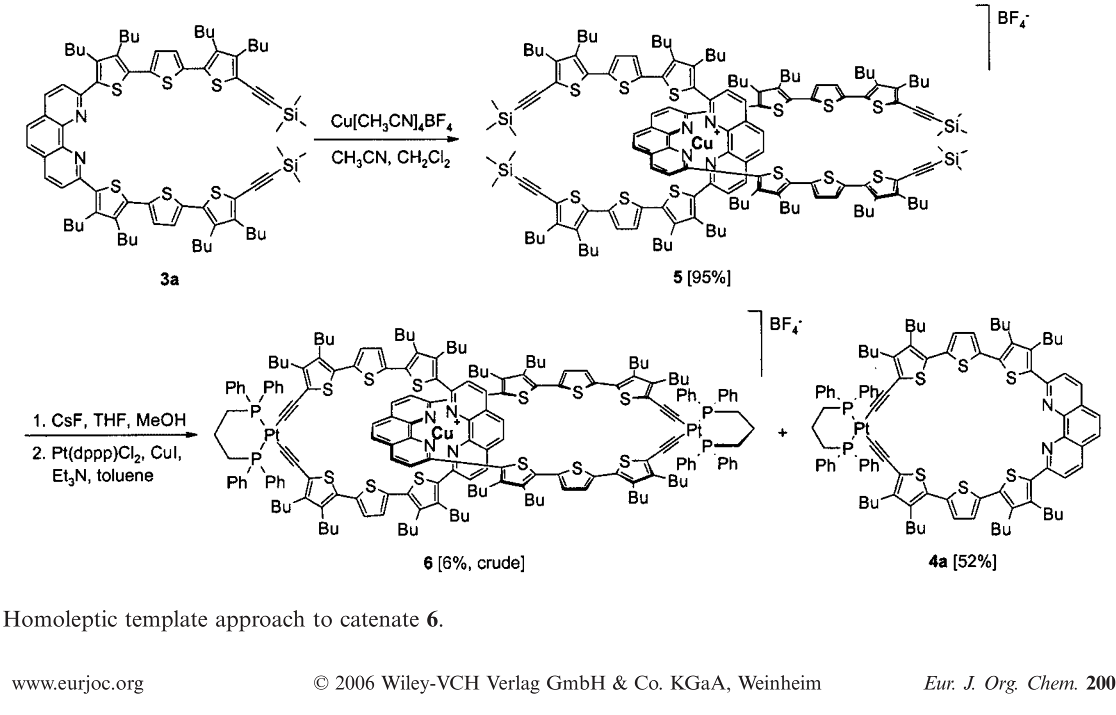
In this respect, we found that the reaction of **3a** with Cu$^+$ ions led to the formation of the homoleptic bis(phenanthroline) complex **5** in excellent yield (Scheme 2). Cu^I complex **5**, in which the two half-moon-shaped terthienyl-phenanthrolines are preorganized and fixed in a tetrahedral geometry, could be purified by column chromatography, and its ^{1}H NMR spectrum showed significant high-field shifts of the thiophene β-protons. This effect should be due to the close contact between the phenanthroline and thiophene subunits of the different ligands in **5** rather than a consequence of an angular distortion between the thiophene and phenanthroline subunits within the same ligand molecule. MALDI-TOF mass spectra revealed a base peak that corresponds to the complex **5** (m/z = 2691 Da $[M - BF_4]^+$) along with a peak at m/z = 1378 Da which could be assigned to the loss of one phenanthroline ligand. The TMS groups in complex **5** were removed with stoichiometric amounts of CsF in THF/MeOH, and the resulting acetylene groups were treated with 2 equiv. of *cis*-[Pt(dppp)Cl_2] (Scheme 2). The application of our metal-template approach was expected to lead directly to catenate **6**. In fact, only a small amount of rather impure catenate **6** was isolated along with a 52% yield of platina-macrocycle **4a**.

We assume that complex **5** exists in equilibrium with its free ligands in solution. However, along with the cyclization reaction using *cis*-[Pt(dppp)Cl_2], the equilibrium seems to be shifted towards the free ligands and the subsequent formation of macrocycle **4a** instead of the catenate **6**. This experimental outcome led us to the conclusion that platinum macrocyclization proceeds at a much higher rate for the deprotected free ligand **3a** than for the deprotected derivative of the Cu^I–phenanthroline complex **5**. Consequently we attempted to improve the yield of catenate **6** by utilizing a heteroleptic complexation strategy.

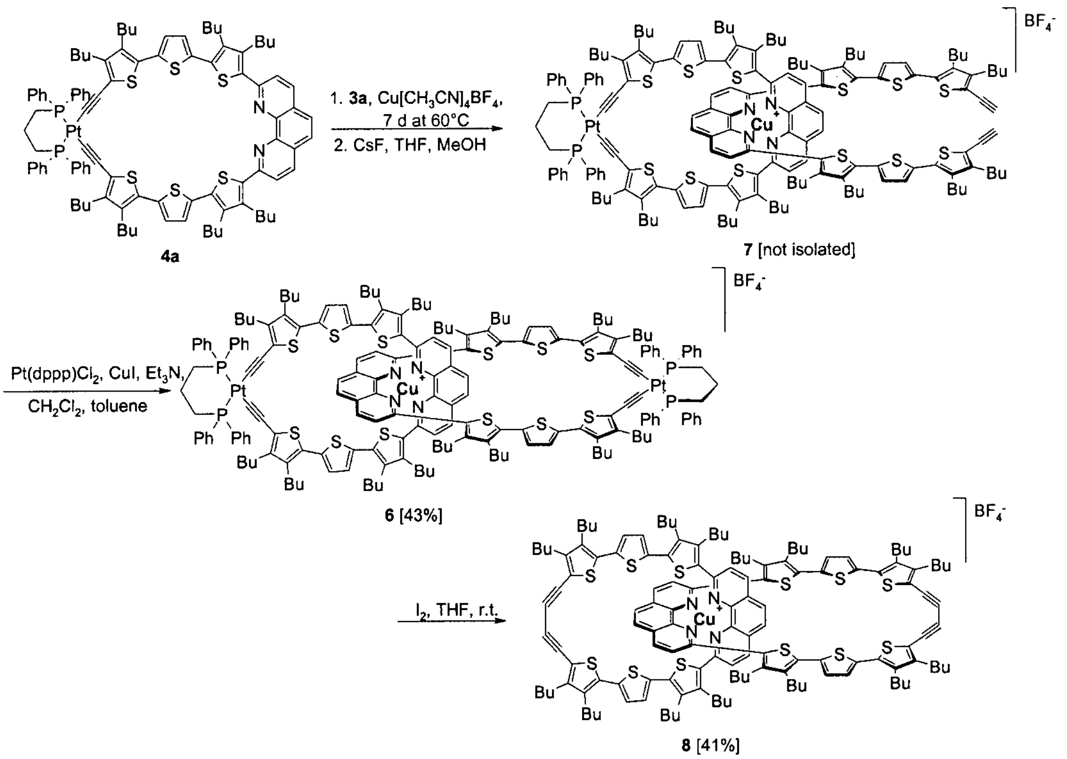
The complexation of platina-macrocycle **4a** with open-chain bis(terthienyl)phenanthroline **3a** and $[Cu(CH_3CN)_4]BF_4$ was achieved at an increased temperature under thermodynamic control indicating the increased steric demand of the heteroleptic complex system **7** which can be regarded as a conjugated pseudorotaxate (Scheme 3).

TLC monitoring of the reaction progress showed complete consumption of **4a** and **3a** after 7 d. Nevertheless, partial deprotection of the TMS-ethynyl residues due to the harsh reaction conditions was detected in the MALDI-TOF mass spectra and by-products could not be separated. We therefore decided to completely deprotect the product mixture with CsF to yield Cu^I–pseudorotaxate **7** which was subsequently treated with 1 equiv. of *cis*-[Pt(dppp)Cl_2] without further purification. After chromatographic purification, Cu^I–diplatina-catenate **6** was obtained in 43% yield. Although the MALDI-TOF mass spectra showed the molecular mass of catenate **6**, the NMR spectra revealed several nonseparable by-products. Subsequent reaction of the crude trimetallated catenate **6** with 4 equiv. of iodine in THF led to the 1,1-reductive elimination of the platinum corners with simultaneous C–C bond formation by coupling of the terminal ethynyl groups. Cu^I–catenate **8** was obtained in 41% yield in pure form after several chromatographic steps. MALDI-TOF MS proved the complete elimination of both platinum corners and the product showed no dissociation in mass spectrometry as we had observed for open-chain complex **5**. In the ^1H NMR spectrum the absence of acetylenic proton signals and the typical high-field shift of β-thiophene proton signals in interlocked structures are evident and speak for the structure of catenate **8**.

Unfortunately, all attempts to remove the Cu^+ ion from the interlocked complex and to obtain the corresponding catenane have failed so far. Neither reaction with KCN nor protonation of the phenanthroline moieties in different solvents led to detectable amounts of the decomplexed species. We rationalize that the high stability of catenate **8** against decomplexation is probably due to the rather small size of the sterically very demanding, two interlocked, 28-membered macrocycles which shield the Cu^+ ion well against attack of the decomplexation reagent. Indeed, it has been reported previously that the ease of ring-in-ring gliding plays a rate-determining role in the decomplexation of copper catenates.[24]



Scheme 2. Homoleptic template approach to catenate **6**.



Scheme 3. Heteroleptic template approach to catenates **6** and **8**.

Structural Proof of the Macrocycles and Catenates by Mass-Spectrometric Experiments

Macrocycles **4a** and **4b** as well as catenates **6** and **8** were investigated by ESI-FT-ICR mass spectrometry.[17c,17d] The macrocycles can be charged by two different methods. Spraying them from methanol solutions leads to the protonated species with signals at m/z = 1775.57815 Da [M + H]$^+$ for **4a** (Δm = 15 ppm) and m/z = 2328.78884 Da [M + H]$^+$ for **4b** (Δm = 8 ppm). Spraying these compounds from a nonacidic solvent gives rise to small contributions of radical cations which points to the ease of one-electron oxidation of the fully conjugated macrocycles. These radical cations could almost be completely suppressed in favor of the protonated compounds when trifluoroacetic acid was added to the solution. On the other hand, adding a small amount of [Cu(CH$_3$CN)$_4$]BF$_4$ to acetonitrile solutions leads to the corresponding copper adduct peaks which appear at m/z = 1837.327 Da [M + Cu]$^+$ for **4a** and at m/z = 2391.697 Da [M + Cu]$^+$ for **4b**. Catenates **6** and **8** are easily ionized by the loss of the counteranion (Figure 1). Electrospray ionization from acetonitrile solutions gave a peak at m/z = 3612.85458 Da [**6** – BF$_4$]$^+$ (Δm = 3 ppm) for catenate **6** and a peak at m/z = 2398.91162 Da [**8** – BF$_4$]$^+$ for catenate **8** (Δm = 8 ppm). Not only the exact masses, but also the isotope patterns agree excellently within the error margins with those calculated on the basis of natural abundances, thus confirming the elemental compositions.

While the ESI mass spectrum of **8** proves the presence of a pure sample and does not show any decomposition products, two major fragments are observed in the spectrum of

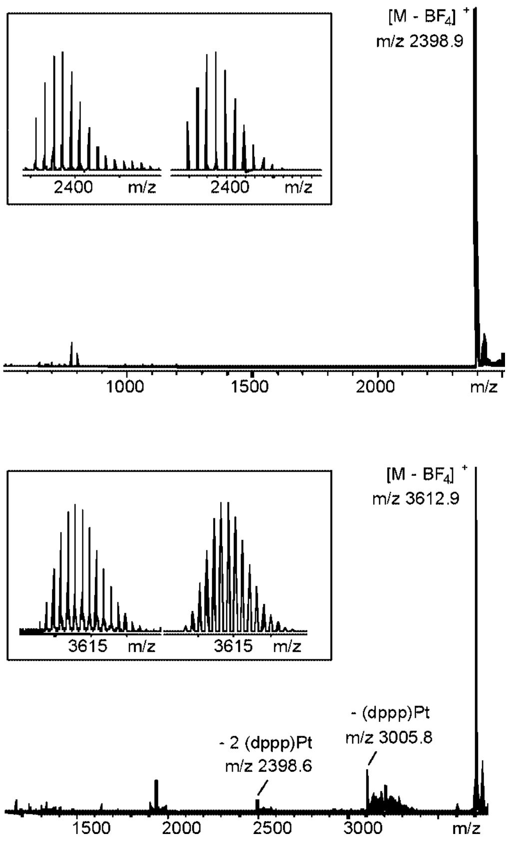


Figure 1. ESI-FT-ICR mass spectra of **6** (bottom) and **8** (top) (ca. 30 μM solutions in acetonitrile). Insets: isotope patterns (left: experimental; right: calculated on the basis of natural isotope abundances).

6 whose relative and absolute intensities vary with the spray conditions. One signal is observed at *m/z* = 3005.8 Da, which is more prominent than the second one at *m/z* = 2398.6 Da under soft ionization conditions, but still small relative to the parent-ion base peak. The second signal, which has the same mass as catenate **8**, increases in intensity with harsher ionization conditions at the expense of both the parent ion and the first signal at *m/z* = 3005.9 Da. The fact that the relative intensities vary with ionization conditions indicates that both are fragments of the parent catenate $[\mathbf{6} - BF_4]^+$ rather than impurities in the sample. We have therefore attributed these signals to consecutive losses of two neutral [(dppp)Pt] moieties (Δm = 607 Da) formed during the ionization process or subsequently in the gas phase. To confirm this, mass-selected $[\mathbf{6} - BF_4]^+$ was subjected to a tandem MS experiment in which it was collisionally activated with argon as the collision gas in the FT-ICR cell (collision-induced decay, CID). Again, the two major fragments were observed at *m/z* = 3005.9 Da (Δm = 607 Da) and *m/z* = 2398.9 Da (Δm = 1214 Da = 2 × 607 Da) (Figure 2). As these masses correspond to the loss of two [(dppp)Pt] units, we suggest that two consecutive reductive eliminations of [(dppp)Pt] lead to the formation of catenate **8** from catenate **6** in the gas phase. After the reductive eliminations, two fully conjugated, catenated macrocycles are obtained.

Further support for this structural assignment comes from three additional experiments. (i) When the collision energy was increased in the CID experiment with $[\mathbf{6} - BF_4]^+$, a series of fragmentations of the *n*-butyl side-chains was observed from the $[\mathbf{6} - BF_4 - 2\ (dppp)Pt]^+$ ion following the two-fold reductive elimination [i.e., –30 Da ($-C_2H_6$), –42 Da ($-C_3H_6$), –44 Da ($-C_3H_8$), –58 Da ($-C_4H_{10}$), etc. relative to the fully deplatinated ion peak at *m/z* = 2398.9 Da]. Instead, the loss of one of the ligands of the copper ion almost vanishes within the noise. (ii) Under the same collision conditions, catenate **8** shows the same series of fragmentations of the butyl side-chains. Owing to the completely conjugated nature of the intertwined macrocycles, all bonds within the macrocycle are difficult to cleave. In addition, simple bond cleavage within the macrocycle backbone alone would not give rise to fragmentation because both halves are still connected through coordination to the Cu^I ion. Consequently, the cleavage of C–C single bonds in the *n*-butyl side-chains represents the lowest-energy processes. (iii) As a control experiment, intermediate **5**, a copper-bridged dimer of **3a** $[(\mathbf{3a})_2 + Cu]^+$, was subjected to a CID experiment. Since it is an open-chain analogue of **8**, it can either give fragments of the *n*-butyl chains or decompose with the loss of one of the ligands from the central copper ion. We isolated the monoisotopic ions of **5** (*m/z* = 2687.1 Da) and upon collisional activation the only fragment observed was *m/z* = 1375.1 Da, which corresponds to the loss of one ligand leaving a $[\mathbf{3a} + Cu]^+$ adduct. As no further fragments between the parent ion and $[\mathbf{3a} + Cu]^+$ were observed, the weakest bonds are now the two dative N–Cu bonds. Because the structure is not mechanically bound, one ligand can easily be removed. This is in marked contrast to the fragmentation of $[\mathbf{8} - BF_4]^+$ and $[\mathbf{6} - BF_4 - 2\ (dppp)Pt]^+$ in which ligand loss would require an additional bond cleavage within one of the fully conjugated macrocycles to permit the loss of one ligand from the copper ion.

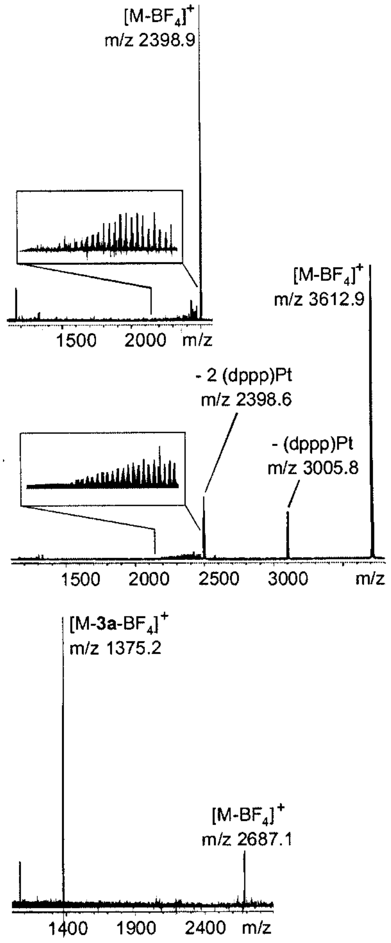


Figure 2. Tandem mass spectra (CID) of **8** (top), **6** (center) and open-chain analogue **5** (bottom). Insets: fragmentations stemming from bond cleavages in the *n*-butyl chains. Note that in the case of **6** the whole isotope pattern was isolated (*m/z* > 3600 Da), while for **5** and **8** the monoisotopic peak was isolated exclusively.

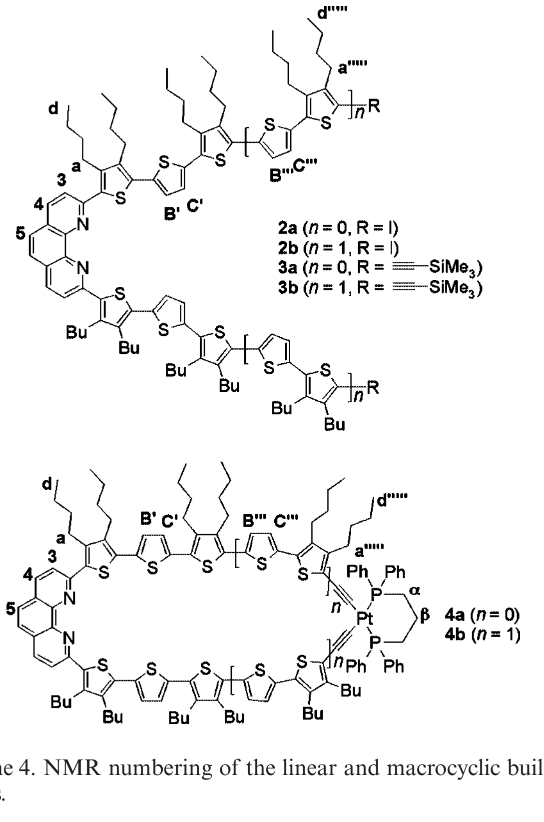
These three observations provide definitive and independent evidence (i) for the catenated structure[20] of both **6** and **8** and (ii) for the feasibility of the reductive elimination processes leading to ring-closure in the gas phase,[18] in which this reaction takes place, when the ions are collisionally activated, which basically means that their internal energy is increased. Since no oxidant is present in the high vacuum of the mass spectrometer, ring-closure occurs without oxidation of the [(dppp)Pt] moieties. This difference in reactivity between the condensed and gas phases may well be due to the fact that the ions are isolated in the high vacuum of the mass spectrometer while they might react with other molecules in their environment in the condensed phase when just heated. This would give rise to the observed side-products. The environment-free conditions of the gas phase can thus be regarded as the ideal dilution experiment for macrocycle formation. Side-reactions such as oligomerizations, which are often observed in solution, can be completely suppressed in the gas phase.

Conclusion

We have been able to develop a synthetic strategy for the synthesis of interlocked π-conjugated macrocycles. The protocol is based on the high-yielding synthesis of ethynyl-functionalized 2,9-bis(oligothienyl)phenanthrolines **3a** and **3b** which are the key building blocks in the synthesis of the novel conjugated topologies described herein. Their successful transformation to the macrocyclic platinum bis(acetylides) **4a** and **4b** allowed us to overcome the difficulties that arise when these substrates are subjected to conventional C–C coupling macrocyclization reactions. Heteroleptic Cu^I complexation of open-chain ligand **3a** and platina-macrocycle **4a** under thermodynamic control and subsequent ring-closure to the second platina-macrocycle provided access to the interlocked trimetallated catenate **6**. Subsequent 1,1-reductive elimination of the platinum corners with iodine led to the Cu^I–catenate **8** which represents the first member in a novel family of interlocked π-conjugated macrocycles. However, owing to the small ring size of the individual macrocycles of the Cu^I–catenate **8**, removal of the templating Cu^I failed. A detailed characterization of macrocycles **4a** and **4b** and catenates **6** and **8** by ESI-FT-ICR mass spectrometry yielded exact masses and isotope patterns which agree well with calculated ones. In addition, collision-induced decay experiments on catenates **6** and **8** as well as on open-chain analogue **5** were performed. The fragmentation patterns provide independent evidence for the interlocked structure of the catenates. Comparison of these spectra show that two successive reductive eliminations of the platinum(II) species in **6** occur in the gas phase leading to ring-closure reactions that generate the fully conjugated catenates from their metal-organic precursors. Further attempts to synthesize metal-free interlocked conjugated macrocycles by utilizing different types of (oligothienyl)phenanthrolines as starting materials are currently under investigation in our laboratory.

Experimental Section

General: Solvents and reagents were purchased from Aldrich, Merck and ABCR, unless otherwise stated, and purified and dried by standard methods prior to use. $[Pt(dppp)Cl_2]$[25] and $[Cu(CH_3CN)_4]BF_4$[26] were synthesized according to known procedures. 2,9-Bis(oligothienyl)phenanthrolines **1a** and **1b** were synthesized from 2,9-diiodophenanthroline and the corresponding oligothiophene–zincate by a Negishi coupling protocol.[21] Preparative column chromatography was performed on glass columns packed with silica gel (Merck Silica 60, particle size 0.04–0.063 mm). Thin-layer chromatography was carried out on silica gel Si60 F_{254} (Merck). NMR spectra were recorded with Bruker Avance 400 and AMX 500 spectrometers. The atom numbering used in NMR characterization is outlined in Scheme 4. Mass spectra (cited as monoisotopic masses) were recorded with a Bruker Daltonics Reflex III (MALDI-TOF, matrix: dithranol) and a Waters-Micromass ZMD (ESI^+, sprayed from THF/15% water/1% TFA solutions) instrument. Elemental analysis was performed with an Elementar Vario EL device. High-resolution ESI mass spectra and MS/MS spectra were recorded with a Bruker APEX IV Fourier-transform ion-cyclotron-resonance (FT-ICR) mass spectrometer with an Apollo electrospray ion source equipped with an off-axis 70° spray needle. Methanol and acetonitrile typically served as the spray solvent and 30 μM analyte solutions were used. Analyte solutions were introduced into the ion source with a syringe pump (Cole-Palmers Instruments, Series 74900) at flow rates of around 3–4 μL/min. Ion transfer into the first of three differential pumping stages in the ion source was performed through a glass capillary with 0.5 mm internal diameter and nickel coatings at both ends. Ionization parameters, some with a significant effect on signal intensities, were adjusted as follows: capillary voltage: –4.1 to –4.4 kV; end-plate voltage: –2.8 to –3.5 kV; cap-exit voltage: +200 to +300 V; skimmer voltages: +8 to +12 V; temperature of drying gas: 200 °C. The flow of the drying and nebulizer gases were kept in a medium range (ca. 10 psi). The ions were accumulated in the instrument's hexapole for 0.5–1 s, introduced into the FT-ICR cell, which was operated at pressures below 10^{-10} mbar, and detected by a standard excitation and detection sequence. For each measurement 16–256 scans were averaged to improve the signal-to-noise ratio. For MS/MS experiments, the complete isotope patterns of the ion of interest were isolated by applying correlated sweeps followed by shots to remove the higher isotopes (owing to the high *m/z* value of 3612.9 Da the complete isotope pattern of **6** was isolated and subjected to the CID experiment). After isolation, argon was introduced into the ICR cell as the collision gas through a pulsed valve at a pressure of around 10^{-8} mbar. The ions were accelerated by a standard excitation protocol and detected after a 2 s pumping delay. Several dif-



Scheme 4. NMR numbering of the linear and macrocyclic building blocks.

ferent spectra were recorded at different excitation pulse attenuations in order to obtain at least a rough and qualitative idea of the effects of different collision energies on the fragmentation patterns.

2,9-Bis(3,4,3′′,4′′-tetrabutyl-5′′-iodo-[2,2′:5′,2′′]terthien-5-yl)[1,10-]phenanthroline (2a) and 2,9-Bis(3,4,3′′,4′′,3′′′′,4′′′′-hexabutyl-5′′′′-iodo-[2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′]quinquethien-5-yl)[1,10]phenanthroline (2b): The corresponding starting material, 2,9-bis(oligothienyl)phenanthroline **1a** (3.27 g, 2.91 mmol) or **1b** (0.65 g, 0.34 mmol), was dissolved in chloroform and acidified with a few droplets of glacial acetic acid. Subsequent addition of a solution of 2.5 equiv. of NIS in DMF was followed by stirring at room temp. under the exclusion of light. ESI-MS monitoring showed complete diiodination after 2–4 d. The organic solutions were washed with aqueous Na$_2$CO$_3$ and Na$_2$S$_2$O$_5$ solutions, concentrated to dryness and purified by chromatography on silica (hexanes/THF, 90:10). The resinous products crystallized upon addition of MeOH and ultrasonication. Amorphous orange solids with yields of 3.68 g (92%) (**2a**) and 0.57 g (88%) (**2b**) were obtained. **2a:** ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.20 (d, ^{3}J = 8.4 Hz, 2 H, 4-H), 7.89 (d, ^{3}J = 8.4 Hz, 2 H, 3-H), 7.70 (s, 2 H, 5-H), 7.23 (d, ^{3}J = 3.8 Hz, 2 H, B′-H), 7.01 (d, ^{3}J = 3.8 Hz, 2 H, C′-H), 3.31 (t, ^{3}J = 8.0 Hz, 4 H, a-H), 2.85 (t, ^{3}J = 8.1 Hz, 4 H, a′-H), 2.78 (t, ^{3}J = 8.1 Hz, 4 H, a′′-H), 2.56 (t, ^{3}J = 7.8 Hz, 4 H, a′′′-H), 1.43–1.65 (m, 32 H, b-H to b′′′-H and c-H to c′′′-H), 0.86–1.02 (m, 24 H, d-H to d′′′-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 153.4, 147.6, 145.9, 143.0, 140.8, 138.7, 138.3, 137.3, 136.4, 136.3, 135.6, 132.9, 127.3, 126.5, 126.1, 125.7, 121.2, 74.3, 33.15, 33.08, 32.2, 31.2, 28.5, 28.1, 27.9, 23.2, 23.1, 23.07, 23.04, 14.1, 14.07, 14.0 ppm. ESI-MS: *m*/*z* = 1373 [M + H]$^+$. C$_{68}$H$_{82}$I$_2$N$_2$S$_6$ (1373.62): C 59.46, H 6.02, N 2.04; found C 59.33, H 5.95, N 1.93. **2b:** ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.18 (d, ^{3}J = 8.4 Hz, 2 H, 4-H), 7.91 (d, ^{3}J = 8. 4 Hz, 2 H, 3-H), 7.67 (s, 2 H, 5-H), 7.31 (d, ^{3}J = 3.8 Hz, 2 H, B′-H), 7.15 (d, ^{3}J = 3.8 Hz, 2 H, C′-H), 7.08 (d, ^{3}J = 3.8 Hz, 2 H, B′′′-H), 7.01 (d, ^{3}J = 3.8 Hz, 2 H, C′′′-H), 3.36 (t, ^{3}J = 7.8 Hz, 4 H, a-H), 2.92 (t, ^{3}J = 7.9 Hz, 4 H, a′-H), 2.76–2.82 (m, 12 H, a′′-H to a′′′′-H), 2.58 (t, ^{3}J = 7.8 Hz, 4 H, a′′′′′-H), 1.43–1.72 (m, 48 H, b-H to b′′′′′-H and c-H to c′′′′′-H), 0.89–1.06 (m, 36 H, d-H to d′′′′′-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 153.3, 147.6, 145.9, 143.0, 140.7, 140.3, 140.2, 138.6, 138.2, 136.9, 136.5, 136.3, 136.2, 136.0, 135.5, 133.1, 130.2, 129.8, 127.2, 126.3, 126.2, 126.16, 126.0, 125.6, 121.1, 74.2, 33.13, 33.1, 33.02, 33.0, 32.2, 32.0, 31.7, 31.2, 28.4, 28.1, 27.9, 27.0, 23.2, 23.1, 23.04, 22.99, 22.8, 22.76, 14.1, 14.04, 14.03, 14.0, 13.99, 13.97 ppm. ESI-MS: *m*/*z* = 1927 [M + H]$^+$. C$_{100}$H$_{122}$I$_2$N$_2$S$_{10}$ (1926.55): C 62.35, H 6.38, N 1.45; found: C 62.45, H 6.40, N 1.35.

2,9-Bis(3,4,3′′,4′′-tetrabutyl-5′′-trimethylsilylethynyl[2,2′:5′,2′′]terthien-5-yl)[1,10]phenanthroline (3a) and 2,9-Bis(3,4,3′′,4′′,3′′′′,4′′′′-hexabutyl-5′′′′-trimethylsilylethynyl[2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′]-quinquethien-5-yl)[1,10]phenanthroline (3b): Iodo compound **2a** (3.57 g, 2.60 mmol) or **2b** (0.51 g, 0.26 mmol) was dissolved in pyridine/triethylamine (1:1) in a pressure-resistant Schlenk tube and the mixture purged with argon. [Pd(PPh$_3$)Cl$_2$] (5 mol%), CuI (10 mol%), PPh$_3$ (10 mol%) and TMS-acetylene (3 equiv.) were added. The sealed tube was heated to 70 °C whilst stirring. ESI-MS monitoring showed complete conversion after 6 h. After evaporation of the solvent, the residue was taken up in CH$_2$Cl$_2$ and filtered through a short bed of silica. Analytically pure products were available after preparative column chromatography on silica (hexanes/THF, 90:10). The resinous products crystallized upon addition of MeOH and ultrasonication. Amorphous orange solids with yields of 3.11 g (91%) (**3a**) and 0.44 g (89%) (**3b**) were obtained. **3a:** ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.20 (d, ^{3}J = 8.5 Hz, 2 H, 4-H), 7.89 (d, ^{3}J = 8.4 Hz, 2 H, 3-H), 7.70 (s, 2 H, 5-H), 7.23 (d, ^{3}J = 3.8 Hz, 2 H, B′-H), 7.10 (d, ^{3}J = 3.8 Hz, 2 H, C′-H), 3.37 (t, ^{3}J = 8.0 Hz, 4 H, a-H), 2.86 (t, ^{3}J = 8.1 Hz, 4 H, a′-H), 2.74 (t, ^{3}J = 8.1 Hz, 4 H, a′′-H), 2.68 (t, ^{3}J = 7.9 Hz, 4 H, a′′′-H), 1.40–1.69 (m, 32 H, b-H to b′′′-H and c-H to c′′′-H), 0.94–1.02 (m, 18 H, a-H to a′′-H), 0.86 (t, ^{3}J = 7.3 Hz, 6 H, d′′′-H), 0.28 (s, 18 H, SiMe$_3$-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 153.5, 149.7, 146.0, 143.3, 140.1, 138.5, 138.0, 137.2, 136.4, 135.9, 132.7, 132.0, 127.3, 126.4, 126.2, 125.7, 121.4, 117.4, 102.0, 98.1, 33.2, 33.1, 32.9, 32.4, 28.6, 28.1, 27.9, 27.8, 23.2, 23.1, 23.0, 14.1, 14.06, 14.0, 0.12 ppm. ESI-MS: *m*/*z* = 1315 [M + H]$^+$. C$_{78}$H$_{100}$N$_2$S$_6$Si$_2$ (1314.24): C 71.29, H 7.67, N 2.13; found: C 71.16, H 7.67, N 2.17. **3b:** ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.20 (d, ^{3}J = 8.5 Hz, 2 H, 4-H), 7.90 (d, ^{3}J = 8.5 Hz, 2 H, 3-H), 7.70 (s, 2 H, 5-H), 7.27 (d, ^{3}J = 3.8 Hz, 2 H, B′-H), 7.12 (d, ^{3}J = 3.8 Hz, 2 H, C′-H), 7.07 (d, ^{3}J = 3.8 Hz, 2 H, B′′′-H), 7.06 (d, ^{3}J = 3.8 Hz, 2 H, C′′′-H), 3.34 (t, ^{3}J = 7.9 Hz, 4 H, a-H), 2.89 (t, ^{3}J = 8.1 Hz, 4 H, a′-H), 2.66–2.80 (m, 16 H, a′′-H to a′′′′′-H), 1.42–1.69 (m, 48 H, b-H to b′′′′′-H and c-H to c′′′′′-H), 0.84–1.03 (m, 36 H, d-H to d′′′′′-H), 0.29 (s, 18 H, SiMe$_3$-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 153.4, 149.7, 145.9, 143.0, 140.7, 140.3, 140.2, 138.4, 138.1, 136.9, 136.5, 136.4, 136.0, 135.7, 133.1, 131.9, 130.2, 129.8, 127.2, 126.4, 126.2, 126.1, 126.0, 125.7, 121.2, 117.2, 102.0, 98.0, 33.15, 33.09, 33.05, 33.0, 32.9, 32.4, 28.5, 28.1, 27.9, 23.22, 23.20, 23.11, 23.08, 22.9, 14.13, 14.09, 14.05, 0.10 ppm. ESI-MS: *m*/*z* = 1868 [M + H]$^+$. C$_{110}$H$_{140}$N$_2$S$_{10}$Si$_2$ (1867.17): C 70.76, H 7.56, N 1.50; found: C 70.76, H 7.67, N 1.43.

Platina-macrocycle 4a: Bis(ethynyl) compound **3a** (673 mg, 512 µmol) was dissolved in THF (10 mL). CsF (172 mg, 1.13 mmol) in MeOH (1 mL) was then added and the mixture stirred at room temp. for 1 h. Solvent evaporation, filtration through silica (CH$_2$Cl$_2$) and removal of the solvent gave the deprotected compound which was dissolved in toluene (10 mL). After subsequent purging with argon and addition of [Pt(dppp)Cl$_2$] (347 mg, 512 µmol), CuI (9.75 mg, 51.2 µmol) and Et$_3$N (0.28 mL, 2.05 mmol), the reaction mixture was stirred at 70 °C for 20 h. Evaporation of the solvent followed by column chromatography on silica (CH$_2$Cl$_2$) gave 636 mg of an amorphous yellow-orange powder **4a**; yield 70%. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.20 (d, ^{3}J = 8.6 Hz, 2 H, 4-H), 7.94 (d, ^{3}J = 8.6 Hz, 2 H, 3-H), 7.87–7.93 (m, 8 H, Ph-H), 7.68 (s, 2 H, 5-H), 7.41 (d, ^{3}J = 3.9 Hz, 2 H, B′-H), 7.35–7.40 (m, 12 H, Ph-H), 7.17 (d, ^{3}J = 3.9 Hz, 2 H, C′-H), 2.86–2.95 (m, 8 H, a-H and a′-H), 2.67–2.71 (m, 4 H, a′′-H), 2.42 (m, 4 H, α-H), 2.00 (t, ^{3}J = 7.7 Hz, 4 H, a′′′-H), 1.20–1.17 (m, 26 H, b-H to b′′-H, c-H to c′′-H and β-H), 1.08–1.15 (m, 4 H, b′′′-H), 0.93–1.08 (m, 18 H, d-H to d′′-H), 0.79–0.85 (m, 4 H, c′′′-H), 0.57 (t, ^{3}J = 7.3 Hz, 6 H, d′′′-H) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ = –5.54 ($J_{\text{P–Pt}}$ = 2.25 kHz) ppm. HRMS (ESI-FT-ICR): calcd. 1775.60492 [M + H]$^+$; found 1775.57815.

Platina-macrocycle 4b: Bis(ethynyl) compound **3b** (160 mg, 85.6 µmol) was dissolved in THF (5 mL). CsF (52.0 mg, 343 µmol) in MeOH (1 mL) was added and the mixture stirred at room temp. for 2 h. Solvent evaporation, filtration through silica (CH$_2$Cl$_2$) and removal of the solvent gave the deprotected compound which was dissolved in toluene (6 mL). After purging with argon and subsequent addition of [Pt(dppp)Cl$_2$] (58.1 mg, 85.6 µmol), CuI (2.00 mg, 10.5 µmol) and Et$_3$N (0.10 mL, 721 µmol), the reaction mixture was stirred at room temp. for 24 h. Evaporation of the solvent followed by column chromatography on silica (CH$_2$Cl$_2$) gave 17 mg of an amorphous orange-brownish powder **4b**; yield 9%. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.22 (d, ^{3}J = 8.4 Hz, 2 H, 4-H), 7.90–7.94 (m, 10 H, 3-H and Ph-H), 7.70 (s, 2 H, 5-H), 7.36–7.42 (m, 12 H, Ph-H), 7.33 (d, ^{3}J = 3.8 Hz, 2 H, B′-H), 7.04 (d, ^{3}J = 3.8 Hz, 2 H, C′-H), 7.02 (d, ^{3}J = 3.8 Hz, 2 H, B′′′-H), 6.95 (d, ^{3}J = 3.8 Hz, 2 H, C′′′-H), 3.00 (t, ^{3}J = 8.3 Hz, 4 H, a-H), 2.85 (t,

${}^3J$ = 8.3 Hz, 4 H, a′-H), 2.68–2.72 (m, 8 H, a″-H and a‴-H), 2.61 (t, ${}^3J$ = 8.1 Hz, 4 H, a′′′′-H), 2.44 (m, 4 H, H-α), 1.96 (t, ${}^3J$ = 7.8 Hz, 4 H, a′′′′′-H), 1.34–1.70 (m, 50 H, b-H to b′′′′′-H, c-H to c′′′′′-H and β-H), 0.89–1.01 (m, 30 H, d-H to d′′′′-H), 0.58 (t, ${}^3J$ = 7.5 Hz, 6 H, d′′′′′-H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –5.60 ($J_{P–Pt}$ = 2.25 kHz) ppm. HRMS (ESI-FT-ICR): calcd. 2328.80729 $[M + H]^+$; found 2328.78884.

Homoleptic Copper(I)–Bis(phenanthroline) Complex 5: Bis(terthienyl)phenanthroline **3a** (1.19 g, 905 µmol) was dissolved in CH_2Cl_2 (10 mL) and the mixture degassed with argon. $Cu(CH_3CN)_4BF_4$ (157 mg, 500 µmol) was dissolved in degassed CH_3CN (6 mL) and added to the solution of the phenanthroline derivative using a double cannula technique. A deep-red solution formed immediately which was stirred overnight. After evaporation of the solvent, purification was achieved by flash chromatography on silica gel (CH_2Cl_2/MeOH, 97:3) to yield 1.19 g of **5** as a black-red solid; yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, ${}^3J$ = 8.3 Hz, 4 H, 4-H), 7.81 (d, ${}^3J$ = 8.4 Hz, 4 H, 3-H), 7.79 (s, 4 H, 5-H), 6.78 (d, ${}^3J$ = 3.8 Hz, 4 H, B′-H), 6.04 (d, ${}^3J$ = 3.8 Hz, 4 H, C′-H), 2.67 (t, ${}^3J$ = 7.8 Hz, 8 H, a-H), 2.61 (t, ${}^3J$ = 7.8 Hz, 8 H, a′-H), 2.34 (t, ${}^3J$ = 8.2 Hz, 8 H, a″-H), 2.17 (t, ${}^3J$ = 8.0 Hz, 8 H, a‴-H), 1.13–1.63 (m, 64 H, b-H to b‴-H and c-H to c‴-H), 1.00 (t, ${}^3J$ = 7.3 Hz, 12 H, d-H), 0.87–0.92 (m, 24 H, d′-H to d″-H), 0.80 (t, ${}^3J$ = 7.3 Hz, 12 H, d‴-H), 0.29 (s, 36 H, $SiMe_3$-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 149.9, 143.7, 142.8, 138.8, 138.6, 136.9, 136.0, 135.2, 134.4, 132.1, 131.0, 128.7, 126.9, 126.1, 126.0, 125.4, 117.7, 102.6, 97.7, 33.0, 32.8, 32.6, 32.4, 28.6, 28.1, 27.8, 27.6, 23.1, 23.02, 22.99, 22.94, 14.07, 14.05, 13.98, 13.75, 0.11 ppm. MS (MALDI-TOF): m/z = 2691 $[M – BF_4]^+$, 1378 $[M – BF_4 – 39]^+$.

Cu^I–Diplatina-catenate 6: Platina-macrocycle **4a** (280 mg, 158 µmol) was dissolved in CH_2Cl_2 (15 mL) and the mixture purged with argon, followed by subsequent addition of a solution of $[Cu(CH_3CN)_4]BF_4$ (106 mg, 337 µmol) in degassed CH_3CN (2 mL). After 5 h at room temp., compound **3a** (207 mg, 158 µmol), dissolved in CH_2Cl_2 (5 mL), was added. The solution was refluxed at 60 °C for 7 d until TLC showed no more uncomplexed material (silica; CH_2Cl_2/MeOH, 95:5). The solution was concentrated to dryness, the residue taken up in THF (10 mL) and the mixture stirred at room temp. for 2.5 h upon addition of CsF (48 mg, 316 µmol) in MeOH (1 mL). After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (10 mL) and toluene (10 mL), $[Pt(dppp)Cl_2]$ (107 mg, 158 µmol), CuI (3 mg, 15.8 µmol) and Et_3N (0.2 mL) were added. The mixture was purged with argon and stirred at 70 °C for 24 h. Flash chromatography (silica; CH_2Cl_2/MeOH, 97:3) gave 249 mg of crude **6**; yield 43%. The product was used in the next step without further purification. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –5.29 (impurity), –6.73 ($J_{P–Pt}$ = 2.24 kHz), –8.84 (impurity) ppm. HRMS (ESI-FT-ICR): calcd. 3612.86429 $[M – BF_4]^+$; found 3612.85458.

Cu^I–Catenate 8: Diplatina-catenate **6** (72 mg, 19.4 µmol) was dissolved in THF (10 mL) and the mixture stirred with iodine (19.6 mg, 77.6 µmol) at room temp. MALDI-TOF MS showed complete elimination of the platinum after 7 d. Repeated separation attempts by preparative flash chromatography (silica; CH_2Cl_2 to CH_2Cl_2/2-propanol, 97:3) gave 20 mg of **8**; yield 41%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.70 (d, ${}^3J$ = 8.5 Hz, 4 H, 4-H), 8.31 (s, 4 H, 5-H), 7.88 (d, ${}^3J$ = 8.3 Hz, 4 H, 3-H), 6.94 (d, ${}^3J$ = 3.7 Hz, 4 H, B′-H), 6.84 (d, ${}^3J$ = 3.7 Hz, 4 H, C′-H), 2.62–2.67 (m, 16 H, a-H and a′-H), 2.41 (m, 8 H, a″-H), 2.28–2.31 (m, 8 H, a‴-H), 0.65–1.70 (m, 112 H and solvent residues, b-H to b‴-H, c-H to c‴-H and d-H to d‴-H) ppm. HRMS (ESI-FT-ICR): calcd. 2398.89248 $[M – BF_4]^+$; found 2398.91162.

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[1] P. Bäuerle, “Oligothiophenes” in *Electronic Materials: The Oligomeric Approach*, (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**.

[2] a) J. Krömer, I. Rios-Carreras, G. Fuhrmann, C. Musch, M. Wunderlin, T. Debaerdemaeker, E. Mena-Osteritz, P. Bäuerle, *Angew. Chem. Int. Ed.* **2000**, *39*, 3481–3486; b) G. Fuhrmann, J. Krömer, P. Bäuerle, *Synth. Met.* **2001**, *119*, 125–126; c) G. Fuhrmann, T. Debaerdemaeker, P. Bäuerle, *Chem. Commun.* **2003**, 948–949.

[3] M. Bednarz, P. Reineker, E. Mena-Osteritz, P. Bäuerle, *J. Lumin.* **2004**, *110*, 225–231.

[4] a) E. Mena-Osteritz, P. Bäuerle, *Adv. Mater.* **2001**, *13*, 243–246; b) E. Mena-Osteritz, *Adv. Mater.* **2002**, *14*, 609–616.

[5] E. Mena-Osteritz, P. Bäuerle, *Adv. Mater.*, in press; DOI: 10.1002/adma.200501575.

[6] a) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem. Int. Ed.* **2000**, *39*, 3348–3391; b) A. R. Pease, J. O. Jeppesen, J. F. Stoddart, Y. Luo, C. P. Collier, J. R. Heath, *Acc. Chem. Res.* **2001**, *34*, 433–444; c) Y. Luo, C. P. Collier, J. O. Jeppesen, K. A. Nielsen, E. Delonno, G. Ho, J. Perkins, H.-R. Tseng, T. Yamamoto, J. F. Stoddart, J. R. Heath, *ChemPhysChem* **2002**, *3*, 519–525; d) C. A. Schalley, K. Beizai, F. Vögtle, *Acc. Chem. Res.* **2001**, *34*, 465–476; e) V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, **2003**; f) C. A. Schalley, A. Lützen, M. Albrecht, *Chem. Eur. J.* **2004**, *10*, 1072–1080.

[7] For general reviews on template effects, see: a) D. H. Busch, N. A. Stephensen, *Coord. Chem. Rev.* **1990**, *100*, 119–154; b) R. Cacciapaglia, L. Mandolini, *Chem. Soc. Rev.* **1993**, *22*, 221–231; c) S. Anderson, H. L. Anderson, J. K. M. Sanders, *Acc. Chem. Res.* **1993**, *26*, 469–475; d) N. V. Gerbeleu, V. B. Arion, J. Burgess, *Template Synthesis of Macrocyclic Compounds*, Wiley-VCH, Weinheim, **1999**; e) F. Diederich, P. J. Stang (Eds.), *Templated Organic Synthesis*, Wiley-VCH, Weinheim, **2000**; f) T. J. Hubin, D. H. Busch, *Coord. Chem. Rev.* **2000**, *200*, 5–52.

[8] a) C. O. Dietrich-Buchecker, J.-P. Sauvage, J. P. Kintzinger, *Tetrahedron Lett.* **1983**, *24*, 5095–5098; b) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Rev.* **1987**, *87*, 795–810; c) J.-P. Sauvage, *Acc. Chem. Res.* **1990**, *23*, 319–327; for a book on mechanically interlocked molecules, see: d) J.-P. Sauvage, C. O. Dietrich-Buchecker (Eds.), *Molecular Catenanes, Rotaxanes, and Knots*, Wiley-VCH, Weinheim, **1999**.

[9] a) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725–2828; b) D. Philp, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196; c) S. A. Nepogodiev, J. F. Stoddart, *Chem. Rev.* **1998**, *98*, 1959–1976; d) F. M. Raymo, J. F. Stoddart, *Chem. Rev.* **1999**, *99*, 1043–1063.

[10] a) C. A. Hunter, *J. Am. Chem. Soc.* **1992**, *114*, 5303–5311; b) H. Adams, F. J. Carver, C. A. Hunter, *J. Chem. Soc., Chem. Commun.* **1995**, 809–810.

[11] a) A. G. Johnston, D. A. Leigh, L. Nezhat, J. P. Smart, M. D. Deegan, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1212–1216; b) D. A. Leigh, K. Moody, J. P. Smart, K. J. Watson, A. M. Z. Slawin, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 306–310.

[12] a) F. Vögtle, S. Meier, R. Hoss, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1619–1622; b) R. Hoss, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 375–384; c) F. Vögtle, T. Dünnwald, T. Schmidt, *Acc. Chem. Res.* **1996**, *29*, 451–460; d) R. Jäger, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 930–944; e)

G. M. Hübner, J. Gläser, C. Seel, F. Vögtle, *Angew. Chem. Int. Ed.* **1999**, *38*, 383–386; f) C. Reuter, F. Vögtle, *Org. Lett.* **2000**, *2*, 593–595; g) C. A. Schalley, G. Silva, C. F. Nising, P. Linnartz, *Helv. Chim. Acta* **2002**, *85*, 1578–1596; h) P. Ghosh, O. Mermagen, C. A. Schalley, *Chem. Commun.* **2002**, 2628–2629; for a review, see: i) M. Kogej, P. Ghosh, C. A. Schalley, "How to thread a string into the eye of a molecular needle: Template-directed synthesis of mechanically interlocked molecules" in *Strategies and Tactics in Organic Synthesis* (Ed.: M. Harmata), Elsevier, Amsterdam, **2004**, vol. 4, pp. 171–210.

[13] a) M. Fujita, *Acc. Chem. Res.* **1999**, *32*, 53–61; b) K. Biradha, M. Fujita, *Adv. Supramol. Chem.* **2000**, *6*, 1–39; c) A. Hori, K. Kumazawa, T. Kusukawa, D. K. Chand, M. Fujita, S. Sakamoto, K. Yamaguchi, *Chem. Eur. J.* **2001**, *7*, 4142–4149.

[14] a) C. P. McArdle, M. J. Irwin, M. C. Jennings, R. J. Puddephatt, *Angew. Chem. Int. Ed.* **1999**, *38*, 3376–3378; b) C. P. McArdle, M. C. Jennings, J. J. Vittal, R. J. Puddephatt, *Chem. Eur. J.* **2001**, *7*, 3572–3583.

[15] a) K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G. W. V. Cave, J. L. Atwood, J. F. Stoddart, *Science* **2004**, *304*, 1308–1312; b) S. J. Cantrill, K. S. Chichak, A. J. Peters, J. F. Stoddart, *Acc. Chem. Res.* **2005**, *38*, 1–9.

[16] a) T. Felder, C. A. Schalley, *Angew. Chem. Int. Ed.* **2003**, *42*, 2258–2260; b) P. Linnartz, S. Bitter, C. A. Schalley, *Eur. J. Org. Chem.* **2003**, 4819–4829; c) P. Linnartz, C. A. Schalley, *Supramol. Chem.* **2004**, *16*, 263–267.

[17] a) M. Przybylski, M. O. Glocker, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 806–826; b) J. S. Brodbelt, *Int. J. Mass Spectrom.* **2000**, *200*, 57–69; c) C. A. Schalley, *Int. J. Mass Spectrom.* **2000**, *194*, 11–39; d) C. B. Lebrilla, *Acc. Chem. Res.* **2001**, *34*, 653–661; e) C. A. Schalley, *Mass Spectrom. Rev.* **2001**, *20*, 253–309.

[18] For an example of a supramolecular neighboring group effect in the fragmentation of metallosupramolecular squares, see: C. A. Schalley, T. Müller, P. Linnartz, M. Witt, M. Schäfer, A. Lützen, *Chem. Eur. J.* **2002**, *8*, 3538–3551.

[19] a) C. A. Schalley, R. K. Castellano, M. S. Brody, D. M. Rudkevich, G. Siuzdak, J. Rebek Jr, *J. Am. Chem. Soc.* **1999**, *121*, 4568–4579; b) C. A. Schalley, T. Martín, U. Obst, J. Rebek Jr, *J. Am. Chem. Soc.* **1999**, *121*, 2133–2138; c) B. M. O'Leary, T. Szabo, N. Svenstrup, C. A. Schalley, A. Lützen, J. Rebek Jr, *J. Am. Chem. Soc.* **2001**, *123*, 11519–11533; d) H. Mansikkamäki, M. Nissinen, C. A. Schalley, *New J. Chem.* **2003**, *27*, 88–97; e) R. Zadmard, M. Junkers, T. Schrader, T. Grawe, A. Kraft, *J. Org. Chem.* **2003**, *68*, 6511–6521; f) R. Zadmard, T. Schrader, U. Linne, *Chem. Eur. J.* **2004**, *10*, 4233–4239; g) I. Müller, D. Möller, C. A. Schalley, *Angew. Chem. Int. Ed.* **2005**, *44*, 480–484.

[20] a) C. A. Schalley, J. Hoernschemeyer, X.-Y. Li, G. Silva, P. Weis, *Int. J. Mass Spectrom.* **2003**, *228*, 373–388; b) C. A. Schalley, P. Ghosh, M. Engeser, *Int. J. Mass Spectrom.* **2004**, *232–233*, 249–258.

[21] M. Ammann, P. Bäuerle, *Org. Biomol. Chem.* **2005**, *3*, 4143–4152.

[22] a) P.-L. Vidal, B. Divisia-Blohorn, G. Bidan, *Inorg. Chem.* **1999**, *38*, 4203–4210; b) P.-L. Vidal, B. Divisia-Blohorn, G. Bidan, J.-L. Hazemann, J.-M. Kern, J.-P. Sauvage, *Chem. Eur. J.* **2000**, *6*, 1663–1673; c) J.-P. Sauvage, J.-M. Kern, G. Bidan, B. Divisia-Blohorn, P.-L. Vidal, *New J. Chem.* **2002**, *26*, 1287–1290.

[23] a) R. Rossi, A. Carpita, C. Bigelli, *Tetrahedron Lett.* **1985**, *26*, 523–526; b) N. G. Kundu, M. Pal, C. Chowdhury, *J. Chem. Res. (S)* **1993**, 432–433.

[24] C. O. Dietrich-Buchecker, A. Edel, J. P. Kitzinger, J.-P. Sauvage, *Tetrahedron* **1987**, *43*, 333–344.

[25] T. G. Appleton, M. A. Bennett, I. B. Tomkins, *J. Chem. Soc., Dalton Trans.* **1976**, 439–446.

[26] C. O. Dietrich-Buchecker, J.-P. Sauvage, J.-M. Kern, *J. Am. Chem. Soc.* **1989**, *111*, 7791–7800.

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