Pyrrolo-Tetrathiafulvalenes and Their Applications in Molecular and Supramolecular Chemistry

Jan O. Jeppesen*[a] and Jan Becher*[a]

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Although tetrathiafulvalene and its derivatives have been extensively studied as π-electron donors in the fields of molecular organic metals and electrically conducting materials for more than 30 years, the intriguing potential of tetrathiafulvalene as a building block in molecular and supramolecular chemistry has only recently been developed. Progress in synthetic tetrathiafulvalene chemistry has enabled the preparation of elaborate molecular architectures and, in recent years, tetrathiafulvalene has been incorporated into a number of molecular and supramolecular systems. In this microreview we describe the background to our interest in the development of the parent pyrrolo-tetrathiafulvalenes, followed by a journey through their applications in macrocyclic, molecular, and supramolecular chemistry.
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1. Introduction

Among sulfur-containing heterocycles, tetrathiafulvalene[1] (TTF, **1**) and its derivatives have been intensively studied during the past three decades on account of their unique π-electron donor properties. Since the discovery of the first metallic charge transfer (CT) TTF complex,[2] the search for new TTF donor molecules suitable for the formation of molecular organic metals has occupied, and continues to occupy, a large section of the scientific community. During the past few years, however, the growing utility of TTF derivatives as building blocks in macrocyclic and supramolecular chemistry[3] has revealed that the TTF unit is useful[1k−1m] beyond the field of materials chemistry. Progress in synthetic TTF chemistry has allowed the preparation of elaborate molecular architectures and, in recent years, TTF has been incorporated into a number of molecular and supramolecular systems, such as cyclophanes, catenanes, rotaxanes, dendrimers, and polymers.[1k−1m]

This microreview describes the background to our interest in the development of the parent pyrrolo[3,4-*d*]-TTFs and highlights their applications in the fields of macrocyclic, molecular, and supramolecular chemistry.

1.1 Fundamental Properties of TTF

Although TTF is a planar 14π-electron system, it is nonaromatic according to the Hückel definition because the 14 π-electrons lack cyclic conjugation.[4] Its oxidation to the

[a] Department of Chemistry, University of Southern Denmark (Odense University),
Campusvej 55, 5230 Odense M, Denmark
Fax: (internat.) + 45/66158780
E-mail: joj@chem.sdu.dk
jbe@chem.sdu.dk

Jan. O. Jeppesen (left) was born in Esbjerg, Denmark in 1972. He received his B.Sc., M.Sc., and Ph.D. degrees in 1996, 1999, and 2001, respectively, from the University of Odense for work in molecular and supramolecular tetrathiafulvalene chemistry under the supervision of Professor Jan Becher. During his Ph.D. studies he spent 10 months in Professor Fraser Stoddart's group at the University of California, Los Angeles (UCLA) working on the design and synthesis of amphiphilic, bistable [2]rotaxanes for use in the fabrication of memory and logic circuits for a chemical computer. Currently he holds a position as research associate professor at the University of Odense, supported by the Carlsbergfondet.

Jan Becher (right) was born in Frederiksberg, Denmark, in 1939. Graduated from Professor Ole Buchardt's group, University of Copenhagen, 1966. Assistant professor at the University of Odense 1969−1989, awarded Dr. Scient. 1986 and appointed docent (professor) in 1989, also at the University of Odense. He was awarded the "Bjerrum Chemistry Award" and Gold Medal in 1992 as well as Docteur honoris causa (Université d'Angers, France) in 1998. His research interests cover heterocyclic chemistry, especially sulfur-containing heterocycles, macrocyclic chemistry, macrocyclic ligands, and supramolecular chemistry.

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radical cation **2** and dication **3** occurs (Figure 1) sequentially and reversibly at low potentials. In contrast to the neutral TTF unit, both the radical cation **2** and the dication **3** are aromatic in the Hückel sense, as a result of the 6π-electron heteroaromaticity of the 1,3-dithiolium cation. The key properties of TTF that make it an interesting building block in materials, macrocyclic, and supramolecular chemistry are:

(i) TTF is a strong π-electron donor.

(ii) Oxidation of the TTF^0 unit to the radical cation $TTF^{+\cdot}$ and dication TTF^{2+} occurs sequentially and reversibly (see Figure 1).

(iii) The oxidation potentials can be changed by attachment of electron-donating or electron-withdrawing substituents.

(iv) The TTF radical cation **2** and the TTF dication **3** are thermodynamically stable species.

(v) The UV/Vis absorption spectra of TTF^0, $TTF^{+\cdot}$, and TTF^{2+} are decisively different from one another.

(vi) TTF derivatives readily form dimers, highly ordered stacks, or two-dimensional sheets, which are stabilized by intermolecular π−π interactions and non-bonded sulfur−sulfur interactions.

(vii) TTF is stable to many synthetic transformations, although it is important to avoid strongly acidic conditions and strong oxidizing agents.

(viii) The contribution from 6π-electron heteroaromaticity in the 1,3-dithiolium cations explains the relative low oxidation potentials of the parent TTF ($E^1_{1/2}$ = 0.34 V, $E^2_{1/2}$ = 0.73 V vs. Ag/AgCl in MeCN).

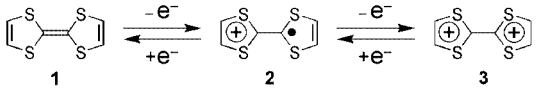

Figure 1. Sequential and reversible oxidation of TTF (**1**) affords stable cationic species **2** and **3**

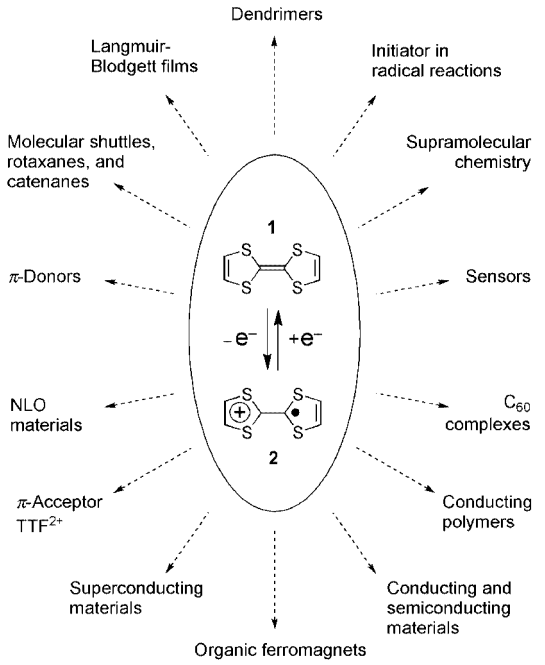

Figure 2. Some uses of the redox-active TTF unit in molecular, supramolecular, and materials chemistry

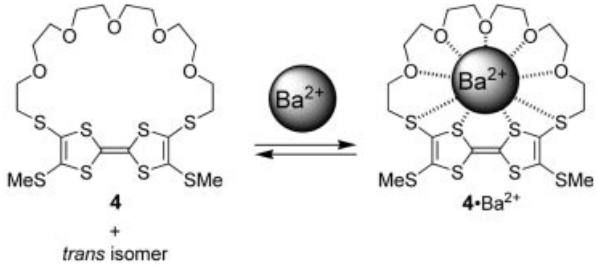

Figure 3. A *cis*/*trans* isomeric mixture of a TTF-crown **4** and the *cis* isomer's complexation with a Ba^{2+} ion; note that the *trans* isomer does not complex Ba^{2+} ions

1.2 Applications of TTFs

In recent years, different chemical modifications have been carried out on the TTF unit in order to prepare building blocks for macrocyclic and supramolecular chemistry at the molecular level. New TTF building blocks have been exploited in many areas of materials, macrocyclic, and supramolecular chemistry. Some examples in which TTFs have been used[5] are shown in Figure 2. The multitude of interesting properties of the TTF unit has prompted much research into the synthesis of new TTF derivatives, and excellent reviews have been published,[1] covering the use of TTFs in molecular, supramolecular, and materials chemistry up to the end of 1999. We therefore concentrate on recent examples of macrocyclic, molecular, and supramolecular systems based on pyrrolo-annulated TTFs.

2. Why Pyrrolo-TTFs?

The regioselective functionalization of TTF is a challenge, since TTF has D_{2h} symmetry with four identical potential attachment sites. Incorporation of the TTF unit into macrocyclic, molecular, and supramolecular systems therefore often results in mixtures of *cis* and *trans* isomers, as in the case (Figure 3) of the macrocyclic TTF derivative[6] **4**. The separation of the *cis* and *trans* isomers is often impossible, because TTF derivatives are prone to isomerization[7] in the presence of traces of acid[8] or on exposure to light[9] (Figure 4). The inherent *cis*/*trans* complication gives rise to a number of problems: (i) spectral data are difficult to interpret, (ii) physical studies on a mixture of the two isomers often become too complex, since the distribution of the isomers might change during the measurements, and (iii) preparation of single crystals for X-ray studies is more complicated, since an isomeric mixture is generally difficult to crystallize. For instance, it has been shown (Figure 3) by liquid solution ionization mass spectrometry (LSIMS) and ^{1}H NMR spectroscopy that only the *cis* isomer of the macrocyclic TTF derivative **4** is able to complex cations,[6] such as Ba^{2+} ions.

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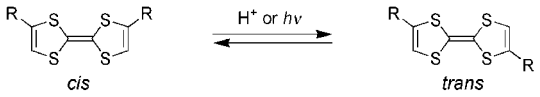


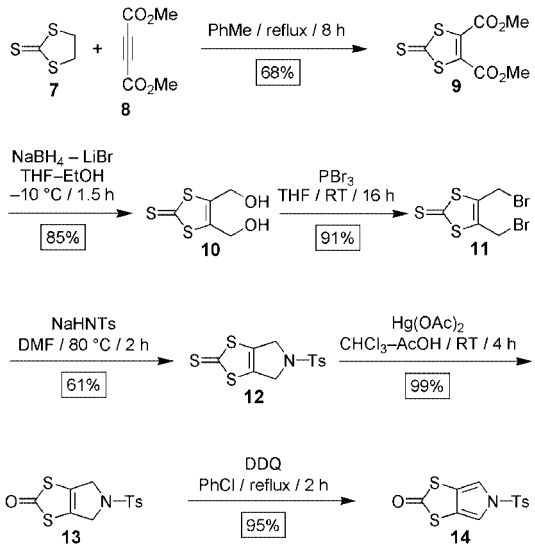
Figure 4. Isomerization of TTF derivatives in the presence of acid or on exposure to light

Some years ago, Cava and co-workers[10] presented a detailed study of bis(2,5-dimethylpyrrolo[3,4-*d*])-TTF (**5**) and their *N*-alkylated derivatives (Figure 5). The synthesis of **5** involves classical pyrrole chemistry, where the 1,3-dithiole-2-thione moiety is being built up from a 2,5-dimethylpyrrole core.[11] Annulation of TTF to two electron-rich 2,5-dimethylpyrrole rings produces a donor system with an oxidation potential lower than that of the parent TTF (**1**). Compound **5** has been used as a building block in macrocyclic, molecular, and supramolecular chemistry and produces systems devoid of *cis*/*trans* isomerism.[12] However, the four methyl groups in **5**, acting as protecting groups during the synthesis, block the α-positions in the pyrrole rings, excluding any possibility for further *C*-functionalization althoug *N*-alkylations are still possible. Furthermore, steric hindrance from the methyl groups has been observed when **5** is incorporated into macrocyclic, molecular, and supramolecular systems. In this context, the parent bis(pyrrolo[3,4-*d*])-TTF (**6**) appeared to be interesting (Figure 5), and a straightforward route to **6** and the related monopyrrolo-annulated TTFs by a simple, non-classical pyrrole synthesis[13] has recently been described.[14]

Figure 5. Structure of bis(2,5-dimethylpyrrolo[3,4-*d*])-TTF (**5**) and bis(pyrrolo[3,4-*d*])-TTF (**6**)

3. Synthesis of Pyrrolo-TTFs

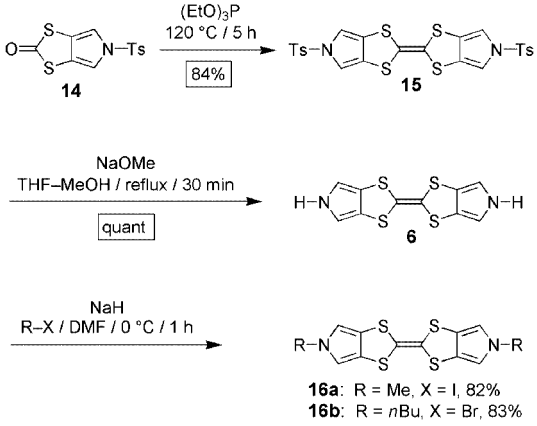
The bis(pyrrolo)-TTF **6** and its related monopyrrolo-TTFs were synthesized as illustrated in Schemes 1−3. The key starting material in the synthesis is the diester[15] **9** obtained (68%) from the reaction (Scheme 1) between 1,3-dithiolane-2-thione (**7**) and dimethyl acetylenedicarboxylate (**8**). The diol **10** can be prepared by a modification of a literature procedure reported by Fox and co-workers. The reported procedure[16] for reduction of the diester **9** with sodium borohydride in the presence of lithium chloride was not suitable for scale-up in our hands. However, by use of sodium borohydride in the presence of lithium bromide in a mixture of THF and EtOH at −10 °C, the reduction of **9** proceed smoothly (85%) to give the diol **10** in multigram quantities.[17] Dibromination of the diol **10** with phosphorus tribromide afford the dibromide **11** in 91% yield.[14]



Scheme 1. Preparation of the parent [*c*]-fused 1,3-dithiole-pyrrole ring system

The pyrrole ring is then constructed from this 1,3-dithiole-2-thione core, bearing two vicinal bromomethyl groups, in a few steps, the first being a ring-closure reaction with sodium tosylamide in DMF to afford the dihydropyrrolo compound **12** in 61% yield.[14] Transchalcogenation of the thione **12** with mercuric acetate in a mixture of $CHCl_3$ and AcOH gives the ketone **13** in quantitative yield. Dehydrogenation of the dihydropyrrole **13** by use of 2 equiv. of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in PhCl affords the *N*-tosylated (1,3)-dithiolo[4,5-*c*]pyrrol-2-one **14** in 95% yield.[14]

Self-coupling of the ketone **14**, to form the TTF derivative **15**, can be achieved (Scheme 2) in 84% yield with triethyl phosphite.[14] The tosyl protection groups of **15** can be cleanly removed by heating of a suspension of **15** and sodium methoxide at reflux in a 1:1 mixture of THF and MeOH, affording the bis(pyrrolo)-TTF **6** in quantitative yield. Finally, **6** can be dialkylated to give the *N*,*N*′-dialkyl derivatives **16** in 82−83% yields.



Scheme 2. Preparation of the parent bis(pyrrolo)-TTF **6**

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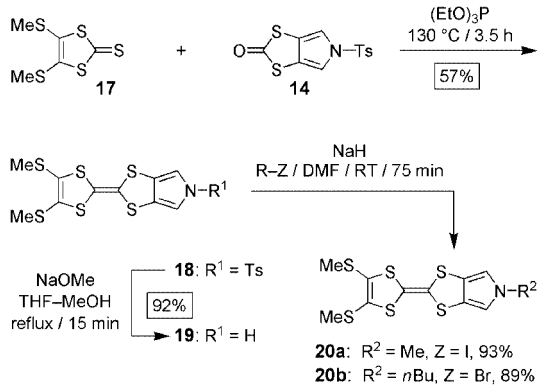
The asymmetric monopyrrolo-TTF **18** is obtained (Scheme 3) in optimum yield[14] by cross-coupling of **14** with the thione **17** in neat triethyl phosphite. Detosylation of **18** with sodium methoxide and subsequent *N*-alkylation proceed smoothly to give the *N*-alkylated derivatives **20**.



Scheme 3. Preparation of the parent monopyrrolo-TTF **19**

It should be noted that the tosyl group performs a triple function during the syntheses. Firstly, it activates the nitrogen atom in the ring-closure reaction. Secondly, it works as an excellent protecting group for the pyrrole nitrogen atom during the harsh triethyl phosphite coupling reaction. Finally, the tosyl group can be removed almost quantitatively from the aromatic pyrrole ring under mild conditions.

4. Fundamental Properties of Pyrrolo-TTFs

To shed more light on the fundamental redox behavior of this class of heterocycles, detailed electrochemical studies, together with some theoretical investigations, have been carried out on the pyrrolo-TTFs.[14]

4.1 Electrochemical Investigations

The electrochemical studies were carried out by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Solution oxidation potentials obtained from cyclic voltammograms (CVs) of the pyrrolo-TTF π-donors (D) are summarized in Table 1. The CVs of all compounds each showed two pairs of reversible redox waves, indicating good stabilities of their corresponding radical cations ($D^{+\cdot}$) and dications (D^{2+}). Compound **6** showed a higher (50 mV) first oxidation potential ($E^1_{1/2}$) than its α,α′,α′′,α′′′-tetramethylated analogue **5**, because of the electron-donating effect of the α-methyl groups. The first oxidation potential of **6** is higher (40 mV) than that of TTF (**1**), indicating that annulation of two pyrrole rings to the TTF unit results in a decrease in the electron-donating ability. A comparison of the CVs of the bis(pyrrolo)-TTF **6** and the *N*-tosylated bis(pyrrolo)-TTF **15** revealed significant shifts in both the first (+170 mV) and the second (+240 mV) oxidation potentials. Figure 6 shows a comparison of the CVs and of the differential pulse voltammograms (DPVs) of the *N*-tosylated monopyrrolo-TTF **18** and the monopyrrolo-TTF **19**. It is evident from the voltammograms that significant shifts in both the first (+150 mV) and the second (+110 mV) oxidation potentials are also observed in the monopyrrolo-TTF series. Attachment of an alkyl group to the nitrogen atom in the pyrrolo-TTFs (as in **16a**, **16b**, **20a**, and **20b**) resulted in a slight decrease (10−20 mV) in the oxidation potentials (both $E^1_{1/2}$ and $E^2_{1/2}$) relative to those of the pyrrolo-TTFs **6** and **19**. The anodic and cathodic shifts observed in the oxidation potentials for the pyrrolo-TTFs can be attributed to the inductive effects of the tosyl groups (strongly electron-withdrawing) and alkyl groups (slightly electron-donating).

Table 1. Oxidation potentials ($E^1_{1/2}$ and $E^2_{1/2}$) of pyrrolo-TTF derivatives **6**, **15**, **16a**, **16b**, **18**, **19**, **20a**, and **20b**, determined by cyclic voltammetry in MeCN [conditions: working and counter-electrodes were made of Pt, and the reference electrode was Ag/AgCl; the oxidation potentials for parent TTF (**1**) and bis(2,5-dimethylpyrrolo[3,4-*d*])-TTF (**5**) were measured for comparison under identical conditions]

Compd.	$E^1_{1/2}$ [V]	$E^2_{1/2}$ [V]	ΔE_p [V]
TTF (**1**)	+0.34	+0.73	+0.39
5	+0.33	+0.74	+0.41
6	+0.38	+0.72	+0.34
15	+0.55	+0.96	+0.41
16a	+0.36	+0.70	+0.34
16b	+0.36	+0.70	+0.34
18	+0.59	+0.86	+0.27
19	+0.44	+0.75	+0.31
20a	+0.42	+0.74	+0.32
20b	+0.42	+0.73	+0.31

4.2 Theoretical Investigations

NMR spectroscopic and electrochemical studies of the pyrrolo-TTFs indicate that a pronounced extension of the π-surface is present in the pyrrolo-TTFs.[14] To shed more light on the extension of the π-surface in the pyrrolo-TTFs, the characters of the highest occupied molecular orbitals (HOMOs) of the pyrrolo-TTFs **6** and **19** have been calculated by the semiempirical PM3 method.[14] Figure 7 (a) shows the electron distribution of **6**, and it is noteworthy that approximately 20% of the HOMO density is located on the outer two pyrrole rings − similarly to that in bis(ethylenedithio)-TTF (BEDT-TTF), in which the outer sulfur atoms have relatively large HOMO densities with the same phase as the inner sulfur atoms.[18] For the asymmetric monopyrrolo-TTF **19**, approximately 13% of the HOMO density is located on the outer pyrrole ring (Figure 7, b). Together with the NMR spectroscopic and electrochemical findings, these results clearly demonstrate that extensions of the π-surfaces exist in the pyrrolo-TTFs.

5. Applications of Pyrrolo-TTFs

The development of the new pyrrolo-TTFs has made it possible to prepare hitherto unknown molecular architec-

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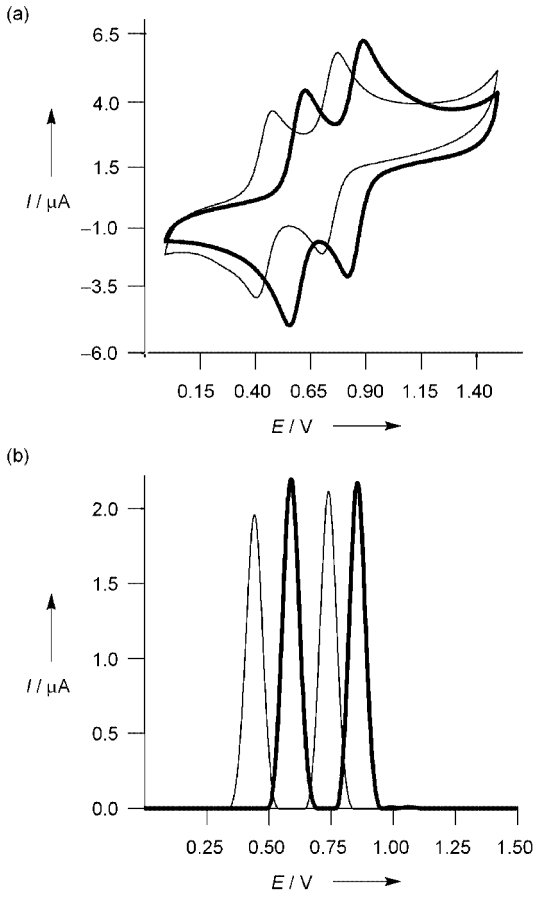


Figure 6. A comparison of the cyclic voltammograms (a) and the differential pulse voltammograms (b) for **18** (bold trace) and **19** (light trace)

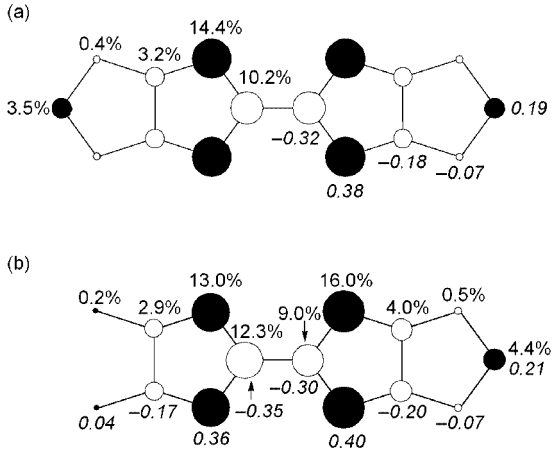
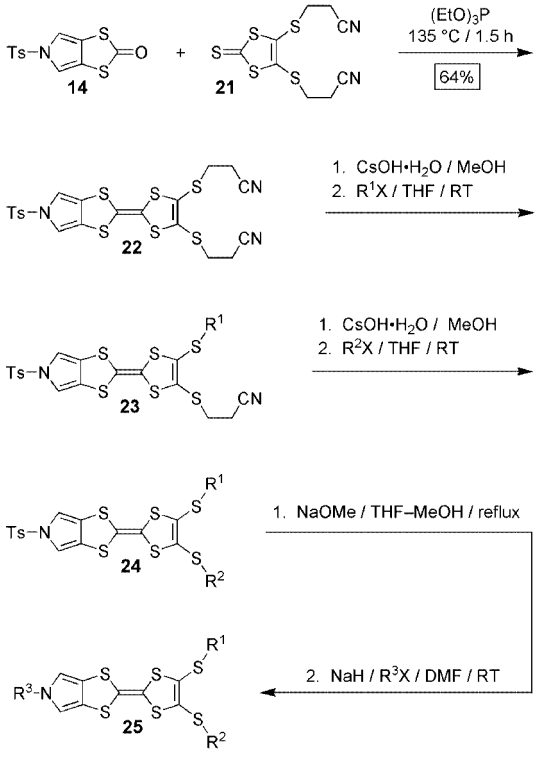


Figure 7. HOMO orbitals of (a) **6** and (b) **19**; plain numbers: HOMO electron density, italic numbers: HOMO coefficients

tures. Some recent applications of the pyrrolo-TTF system in macrocyclic, molecular, and supramolecular chemistry are described in the following sections.

5.1 Orthogonal Monopyrrolo-TTF Building Block

One of the major challenges in the chemistry of protecting groups is orthogonality, the possibility of selectively removing one group in the presence of others in any chronological sequence.[19] A perfect orthogonal TTF building block should possess two orthogonal sets of protecting groups,[20] thereby allowing the TTF unit to be functionalized regioselectively. Combination of the new pyrrolo-TTF ring system with conventional cyanoethyl thiolate TTF protection chemistry[21] produces an asymmetric TTF building block, which can be functionalized regioselectively and is devoid of *cis*/*trans* isomerism.[14b] The asymmetric TTF building block **22** can be synthesized as outlined in Scheme 4. Cross-coupling of the ketone **14** with 2 equiv. of the thione **21** in neat triethyl phosphite gives **22** (64%) in gram quantities after column chromatography. Compound **22** comprises two different sets of protecting groups − a tosyl and two cyanoethyl protecting groups − which can be deprotected in stepwise fashion, allowing the TTF unit to be functionalized regioselectively. Treatment of a THF solution of **22** with 1 equiv. of cesium hydroxide monohydrate selectively generates the TTF-monothiolate, without interfering with the tosyl protecting group. This TTF-monothiolate can then be alkylated with a variety of alkylating reagents (R^1X), affording (Scheme 4) the alkylthio-TTF derivatives **23** in high yields. Subsequently, the remaining cyanoethyl protecting group in **23** can be removed by use of 1 equiv. of cesium hydroxide monohydrate and the resulting thiolate can be alkylated by addition of appropriate alkylating reagents (R^2X), giving the dialkylated TTF derivatives



Scheme 4. Synthesis and potential of the asymmetric monopyrrolo-TTF building block **22**

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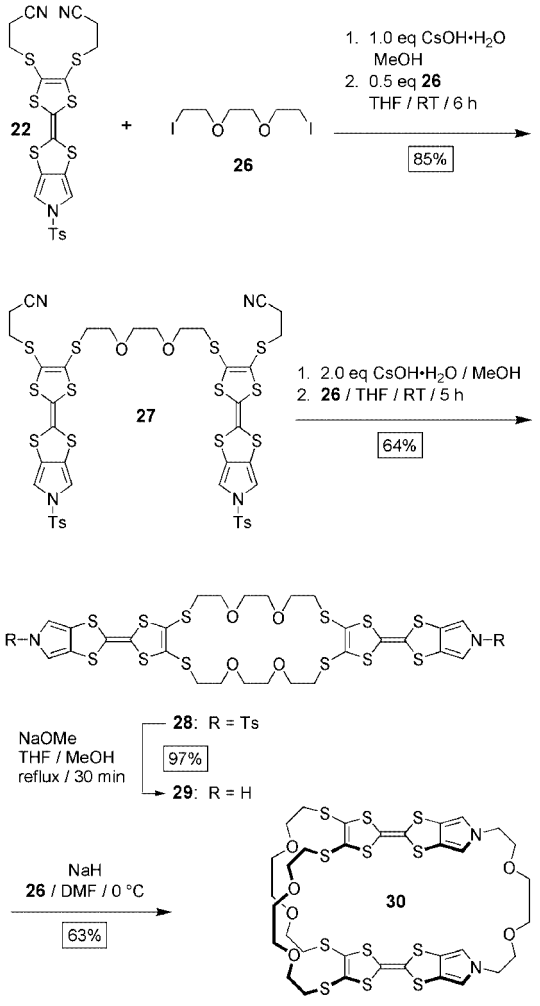
24. Removal of the tosyl protecting group can be carried out in near quantitative yield by heating **24** at reflux in a 1:1 mixture of THF and MeOH in the presence of an excess of sodium methoxide. Finally, *N*-alkylation of the pyrrole unit with different alkylating agents (R^3X) can be carried out in DMF containing sodium hydride, to afford (Scheme 4) the TTF derivatives **25**.

Examples in which the asymmetric TTF building block **22** is incorporated into supramolecular and molecular systems are presented in the following sections.

5.2 Macrocyclic Systems

Cyclophanes are fundamentally important compounds in many aspects of macrocyclic and supramolecular chemistry, and research in this field has expanded rapidly in recent years.[22,23] Thanks to their rigid frameworks, primarily defined by aromatic units, these molecules, with very large cavities, are ready to accommodate charged or neutral guest molecules.[24] Incorporation of the redox-active TTF unit into such cyclophanes may serve a dual purpose, increasing the host−guest interaction with a complementary electroactive guest and at the same time electrochemically signaling the complexation event, making such molecules attractive components in, for example, sensor technology.[25]



Scheme 5. Synthesis of a TTF belt **30**, devoid of *cis*/*trans* isomerism

5.2.1 A Pyrrolo-TTF Belt

Dimeric TTF molecules[26] and TTF belts[27] in which two TTF units are linked by one or more spacer groups have received particular attention, on account of the potential to affect the formation, structure, and physical properties of their CT complexes and ion radical salts.[26] Most synthetic strategies employed for the preparation of this kind of molecules have so far resulted in mixtures of *cis* and *trans* isomers. This problem can be circumvented by use of the bis(cyanoethyl)-protected monopyrrolo-TTF building block[14b] **22**, possessing only three attachment sites. Through employment of this building block, a TTF belt **30** devoid of *cis*/*trans* isomerism has been prepared[28] in relatively few steps, as illustrated in Scheme 5. A solution of the monopyrrolo-TTF building block **22** was treated with 1 equiv. of cesium hydroxide monohydrate. This procedure generated the TTF-monothiolate, which was alkylated with 0.5 equiv. of 1,2-bis(2-iodoethoxy)ethane (**26**) to afford the bis-TTF **27** in 85% yield. Subsequently, the two remaining cyanoethyl protecting groups in **27** were removed by use of 2 equiv. of cesium hydroxide monohydrate, followed by the addition of 1 equiv. of the diiodide **26**, which effected the second deprotection/alkylation sequence, affording **28** in 64% yield. Removal of the tosyl groups in near quantitative yield was achieved by heating of **28** at reflux in a 1:1 mixture of THF and MeOH in the presence of an excess of sodium methoxide. Through the use of high-dilution conditions, a 63% yield of the TTF belt **30** was obtained after *N*-alkylation of the pyrrole units in **29** with the diiodide **26**. Figure 8 (a) shows the X-ray structure of the TTF belt **30**. The TTF belt **30** was designed to allow complexation of the electron-acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) inside its cavity. However, a solid-state X-ray crystal structure analysis (Figure 8, b) of the CT complex **30**·TCNQ revealed that the TCNQ was associated outside (alongside) one of the electron donors, reflecting the fact that the complicated and subtle balances between all the individual non-covalent forces acting in cooperation are difficult to predict. The efficient synthetic methodology developed, however, allows related TTF belts to be produced in a few steps, with variation of the spacers allowing optimization of the complexation properties of the macrocyclic host.

5.2.2 A Pyrrolo-TTF Cage

By extension of the synthetic methodology used for the preparation of TTF belts, we have developed[29] a general and efficient method for the synthesis of TTF cages employing the monopyrrolo-TTF building block **22**. The tris(TTF) cage **38** was designed to participate in host−guest chemistry,[3a] and Cory−Pauling−Koltun (CPK) modeling suggests that **38** has a cavity rather larger and more flexible than that of the TTF belt **30**, thereby increasing the probability that **38** might act as a host molecule for electron-deficient guests such as 1,3,5-trinitrobenzene. The tris(TTF)

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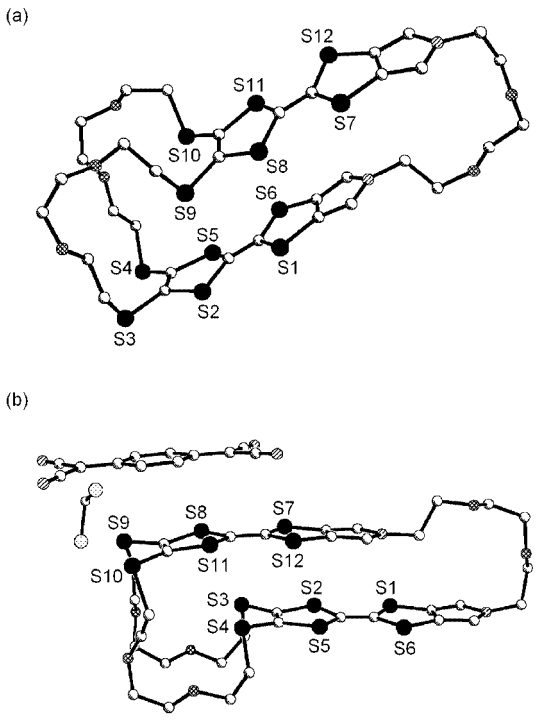
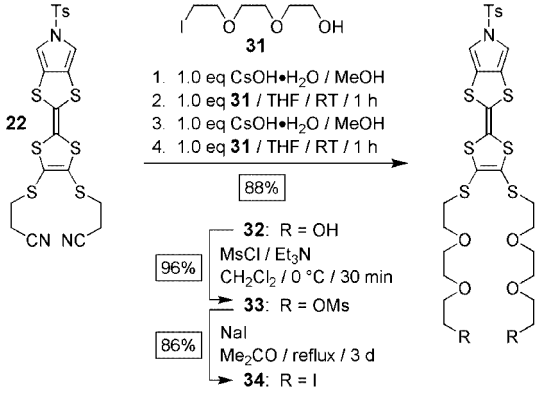


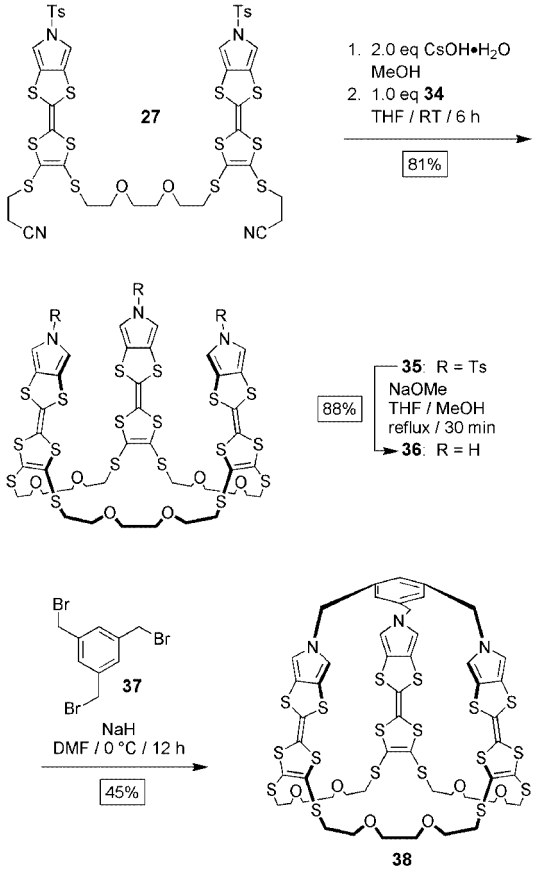
Figure 8. (a) Crystal structure (reprinted with permission from ref.[28] Copyright 2002 American Chemical Society) of the TTF belt **30**; hydrogen atoms are omitted for clarity; (b) crystal structure (reprinted with permission from ref.[28] Copyright 2002 American Chemical Society) of the CT complex **30**·TCNQ; hydrogen atoms are omitted for clarity

cage **38** was synthesized as illustrated in Schemes 6 and 7. A THF solution of the cyanoethyl-protected monopyrrolo-TTF building block **22** was treated with 1 equiv. of cesium hydroxide monohydrate. This procedure generated the TTF-monothiolate, which was alkylated with 1 equiv. of 2-[2-(2-iodoethoxy)ethoxy]ethanol (**31**). Subsequently, deprotection/alkylation with 1 equiv. of cesium hydroxide monohydrate and 1 equiv. of **31**, respectively, gave the TTF derivative **32** in 88% yield (Scheme 6). Mesylation of **32** in CH_2Cl_2 (96%), followed by treatment of **33** with sodium iodide in Me_2CO, gave the TTF derivative **34** (86%). Macrocyclization of the 36-membered ring system **35** was performed under high-dilution conditions. A THF solution of **27** was treated with 2 equiv. of cesium hydroxide monohydrate. This procedure generated the TTF-bis(thiolate), which was alkylated with 1 equiv. of the TTF derivative **34** under high-dilution conditions, to afford (Scheme 7) the tris(TTF) macrocycle **35** in 81% yield. Removal of the tosyl protecting groups was carried out in 88% yield by heating of **34** at reflux in the presence of an excess of sodium methoxide in a 1:1 mixture of THF and MeOH. Finally, the tris(TTF) cage **38** was obtained in 45% yield after *N*-alkylation of the three pyrrole units in **36** with 1,3,5-tris(bromomethyl)benzene (**37**) in DMF containing sodium hydride.

The structure of the tris(TTF) cage **38** was determined by mass spectrometry, NMR spectroscopy, and, above all, X-ray crystallography. The molecular structure of **38** is illustrated in Figure 9. The unit cell contains two TTF cage



Scheme 6. Synthesis of the TTF derivative **34**, starting from the monopyrrolo-TTF building block **22**



Scheme 7. Synthesis of the tris(TTF) cage **38**

molecules and six $CDCl_3$ molecules − three per tris(TTF) cage. Two of the $CDCl_3$ molecules reside inside the cavity of **38**, while the other is positioned outside the cage, indicating that the tris(TTF) cage is able to accommodate guest molecules. The fact that two $CDCl_3$ molecules reside inside the cavity of the solid-state structure of **38** give some promise that **38** may act as a host molecule for other guest molecules as well.

5.3 Tetrathiafulvaleno-Annulated Porphyrins

Porphyrins[30] play a central role in biological systems, and the development of modified porphyrins continues to

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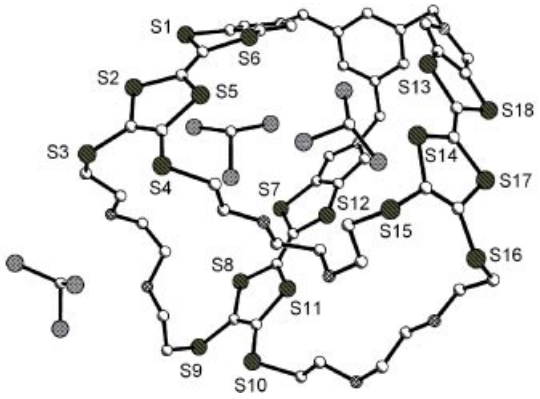
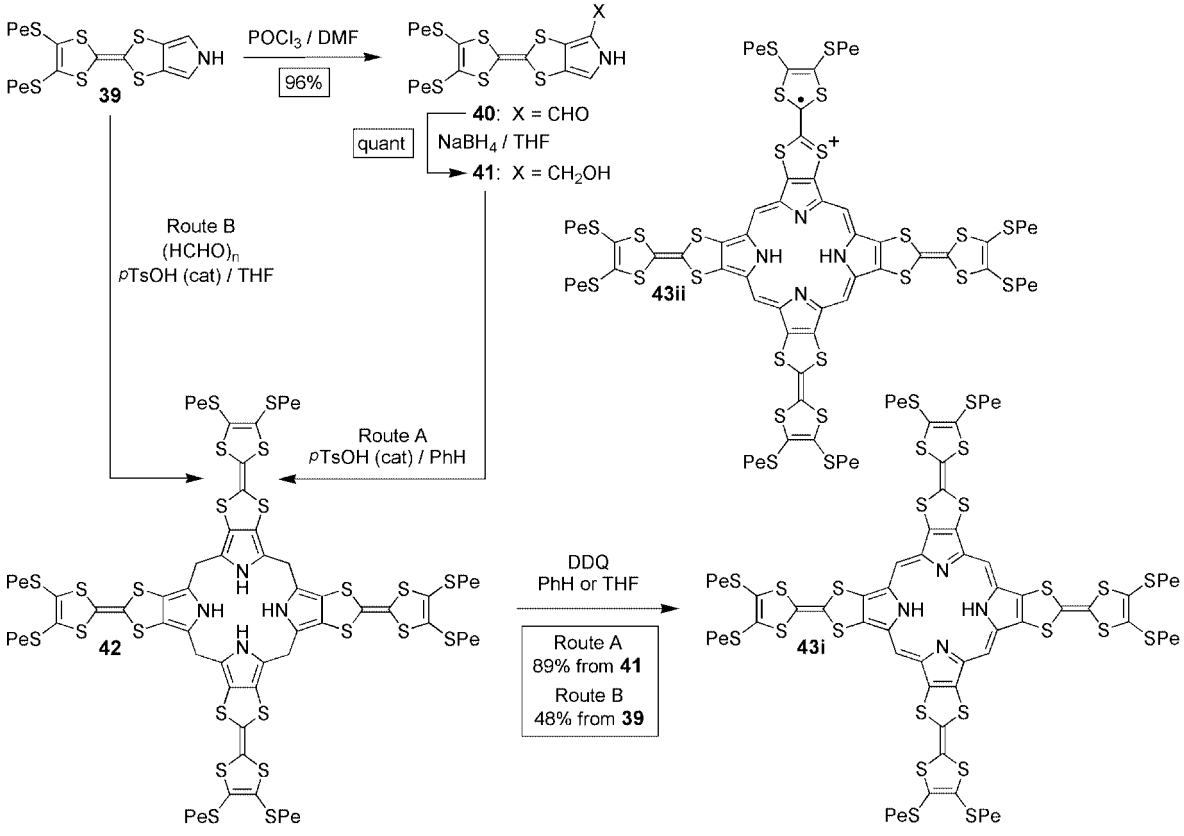


Figure 9. Crystal structure (reprinted with permission from ref.[29] Copyright 2002 American Chemical Society) of the tris(TTF) cage **38**·3$CDCl_3$; hydrogen atoms are omitted for clarity

provide a challenge for synthetic chemists. Modified porphyrins are useful for understanding of the fundamental functions of photosynthetic reaction centers, such as the antenna function, the stabilization of charge separation, and sequential electron-transfer processes.[31] In addition, porphyrins find expanding applications in materials science,[32] reaction catalysis,[33] molecular recognition,[34] and as diagnostic/therapeutic agents[35] and sensors.[36]

5.3.1 A Tetrakis(TTF)-Porphyrin

Although there have in the past been some attempts to combine TTF chemistry with porphyrin chemistry, the direct combination of those two major fields has only very recently been accomplished,[37] most probably because of the lack of an appropriate pyrrolo-TTF unit. With this building block to hand, we have prepared the first examples of single molecules in which the intriguing optical and metal ion binding abilities of the porphyrin ring system have been intimately coupled to the favorable redox properties of the TTF unit. The direct annulation of the porphyrin ring system with four TTF units situated at the periphery gives a porphyrin in which the annulene π-electron system is extended by direct conjugation with the TTF units. Through employment of the new pyrrolo-TTF unit, we have prepared[37,38] the first tetrathiafulvaleno-annulated fully conjugated porphyrin **43** ("**43**" refers to a mixture of **43i** and **43ii**) by two different synthetic routes, as illustrated in Scheme 8. Vilsmeier formylation of the monopyrrolo-TTF[14b] **39** under standard conditions produced the formylpyrrolo-TTF **40** in 96% yield. Reduction of the formyl group with sodium borohydride in THF proceeded quantitatively to give the alcohol **41**. Treatment of **41** with *p*-toluenesulfonic acid (*p*TsOH) in PhH afforded the porphyrinogen **42**, which was subsequently oxidized with DDQ in a one-pot reaction to give the porphyrin **43** as a pitch-black



Scheme 8. Synthesis of the tetrakis(TTF)-porphyrin **43**

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solid. Alternatively, the porphyrin **43** could be obtained as illustrated in Route B in Scheme 8. Stirring of the pyrrolo-TTF **39** with paraformaldehyde [$(HCHO)_n$] and a catalytic amount of *p*TsOH in THF at room temperature produced the porphyrinogen **42**. This intermediate could either be isolated and purified by chromatographic workup, or it could be directly oxidized with DDQ, yielding the porphyrin **43**.

Characterization[37] of the porphyrin **43** turned out to be a problem, since the ^{1}H NMR spectrum of compound **43**, recorded in $CDCl_3$ at 298 K, featured only very broadened peaks, which can be explained by the presence of radicals or slow tumbling resulting from aggregation in solution. Electron paramagnetic resonance (EPR) spectroscopy of **43** revealed a strong signal − arising from radicals − as a broad singlet without any detectable hyperfine structure at $g = 2.0084$, either when used neat or in CH_2Cl_2 solution. The linewidth and *g* value are consistent with the presence of a TTF radical cation.[39] Quantitative EPR measurements in CH_2Cl_2 showed that the isolated product **43** contained 19% unpaired spin, indicating that compound **43** consisted of a mixture of the neutral porphyrin (i.e., **43i**) and the radical cation porphyrin (i.e., **43ii**) in a ratio of approximately 4:1 (Scheme 8). All attempts to obtain the neutral porphyrin **43i** exclusively, by chemical reduction of the paramagnetic mixture of the neutral porphyrin **43i** and the radical cation porphyrin **43ii**, have so far been unsuccessful. A high-resolution matrix-assisted laser-desorption/ionization mass spectrum (MALDI-MS) of **43** showed the exact mass, $m/z = 1830.076$ corresponding to $C_{76}H_{94}N_4S_{24}^{+\cdot}$ (calcd. mass $M^{+\cdot} = 1830.077$) and, together with the elemental analysis of the isolated product, this proved to be the most unequivocal evidence[37] of the formation of **43**. The solution electrochemistry of **43** was studied by CV and by thin layer cyclic voltammetry (TLCV) and showed (Figure 10) that some of the TTF units in **43** do not exhibit normal electrochemical characteristics. The CV (vs. Ag/AgCl) of **43** showed two pairs of reversible oxidations at $E_{1/2}^1 = +0.63$ V and $E_{1/2}^2 = +1.10$ V. TLCV and deconvoluted voltammograms of **43** revealed that the first oxidation wave actually corresponds to two one-electron processes with $\Delta E < 100$ mV, whereas the second wave involves a one-step, two-electron process. Thus, first a radical cation is formed, which is then closely followed by the formation of a dication (probably as a biradical). Finally, a tetracation is formed. These results suggest the presence of an isolated electron-withdrawing 18π-electron porphyrin ring system in which the pyrrolo[*c*] bonds in two of the TTF units are included in the 18π-electron porphyrin ring system. Those two TTF units therefore do not show the electrochemical characteristics of a normal TTF unit and so only a total of four electrons are removed during oxidation of the neutral porphyrin. Furthermore, the deconvoluted voltammogram of compound **43** showed one reversible wave at $E_{1/2} = -1.30$ V (1 electron), which can be assigned to the first reduction of the porphyrin ring system. Finally, it has been demonstrated that compound **43** spreads readily from $CHCl_3$ solutions on H_2O, resulting in the formation of a well-defined Langmuir-Blodgett (LB) film. Information about the packing of the porphyrin **43** at an air-water interface was subsequently obtained from X-ray diffraction studies of this LB film.[37]

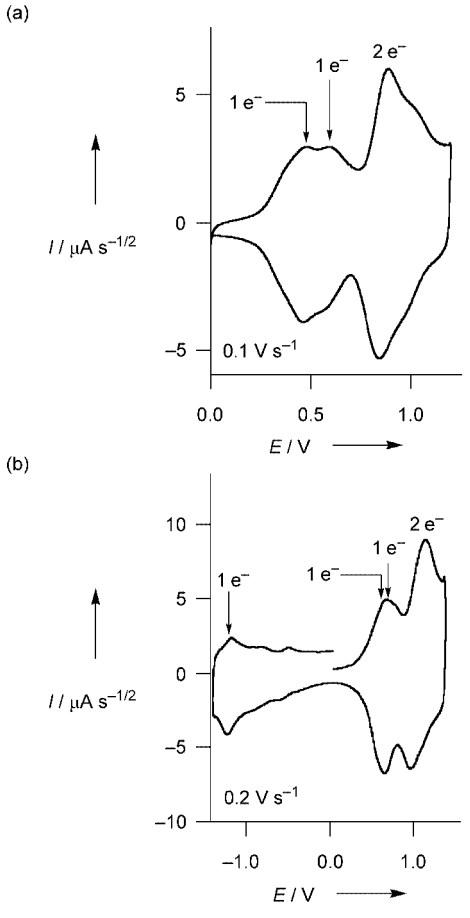

Figure 10. Deconvoluted voltammograms[37] (vs. Ag/AgCl) of a solution of the tetrakis(TTF)-porphyrin **43** (1.0 mM) in CH_2Cl_2/nBu$_4$NPF$_6$ (0.45 M) on a platinum electrode with a scan rate of (a) 0.1 V s^{-1} and (b) 0.2 V s^{-1}

5.3.2 A Mono(TTF)-Porphyrin

As demonstrated in the previous paragraph, the presence of radicals in the isolated tetrakis(TTF)-porphyrin **43** rendered ^{1}H NMR spectroscopic and photophysical characterization of this compound almost impossible. To elucidate the effect of annulation of a TTF unit directly onto the porphyrin ring system further, we have prepared[40] the mono(TTF)-porphyrin **46**. The synthetic approach to the mono(TTF)-porphyrin **46** is outlined in Scheme 9. The tripyrromethane **45** was obtained (not shown) in 25% yield by the condensation of *p*-cyanobenzaldehyde (**44**) with 5 equiv. of pyrrole. To obtain **46**, a cyclization reaction was carried out in CH_2Cl_2 at room temperature by addition of 2 equiv. of trifluoroacetic acid to equimolar quantities of the tripyrromethane **45** and the monopyrrolo-TTF **39** and 2 equiv. of *p*-cyanobenzaldehyde (**44**). The cyclization reaction was quenched by addition of 2 equiv. of triethylamine, whereupon the resulting red mixture was oxidized (porphyrinogen → porphyrin) with 1 equiv. of DDQ in a one-pot

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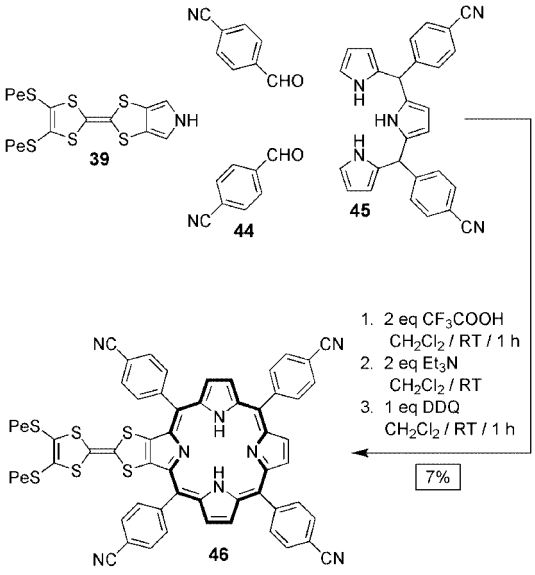

Scheme 9. Synthesis of the mono(TTF)-porphyrin **46**

reaction to afford the mono(TTF)-porphyrin **46** as a dark purple solid in 7% yield.

In contrast to the tetrakis(TTF)-porphyrin **43**, the mono-(TTF)-porphyrin **46** does not contain any radicals, as evidenced by the appearance of sharp peaks in its ^1H NMR spectrum. The electrochemical characterization of the mono(TTF)-porphyrin **46** was carried out by CV. As model compounds for **46**, the electrochemical behavior of the monopyrrolo-TTF derivative **39** and *meso*-tetrakis(*p*-cyanophenyl)porphyrin (TCPP) has also been investigated under similar conditions. The deconvoluted voltammogram (vs. Fc/Fc^+) of **46** revealed (Figure 11) four reversible redox waves. The processes at −1.39 and −1.65 V can be associated with the first and second reductions of the porphyrin ring system. They are both anodically shifted relative to the first (−1.51 V) and second (−1.83 V) reduction processes in the model compound TCPP (**47**), indicating that the LUMO orbital of **46** is located at a lower energy than the LUMO orbital of TCPP. The processes at +0.04 and +0.41 V can be associated with the first and second oxidation of the TTF unit, since they take place at potentials close to the first (−0.01 V) and second (+0.45) oxidation processes observed in the monopyrrolo-TTF model compound **39**. The first oxidation process associated with the TTF unit in **46** take place at a potential more positive (+50 mV) than that observed for the model compound **39**, an observation that can be accounted for by the presence of an electron-withdrawing 18π-electron porphyrin ring system. Since the TTF unit in **46** shows the electrochemical characteristics expected for a normal TTF unit, it can be concluded that **46** exists as the tautomer in which the pyrrolo[*c*] bond in the TTF unit is not included in the delocalization pathway (shown in bold in Scheme 9) for the 18-annulene system. The electrochemical investigation of **46** shows that the TTF unit and the porphyrin ring system can display their individual electrochemical characteristics and that there only are weak interactions between the two components. Furthermore, absorption spectroscopy carried out on the mono(TTF)-porphyrin **46** revealed that there are no significant electronic interactions among its chromophoric units in the ground state.[40] However, this is not the case in the excited state. Comparison of the emission spectra of the mono(TTF)-porphyrin **46** and the model compound TCPP revealed that the porphyrin fluorescence of **46** is quenched by 98% relative to the model compound TCPP, lacking the TTF unit. This observation clearly indicates that substantial electron transfer, from the TTF donor to the porphyrin chromophore, occurs in the emitting excited state of **46**. Removal of one electron from the TTF unit ($TTF \rightarrow TTF^{+\cdot}$) in the mono(TTF)-porphyrin **46** prevents the TTF unit from acting as an electron donor and from quenching the porpyrin emission. The outcome is a fluorescence switch consisting of the nonfluorescent mono(TTF)-porphyrin (OFF state) and the fluorescent mono($TTF^{+\cdot}$)-porphyrin (ON state) species and activated by oxidation of the TTF unit. Oxidation of the TTF unit was carried out by addition

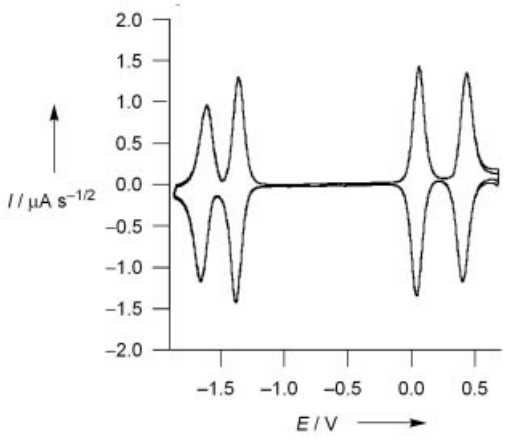

Figure 11. Deconvoluted voltammogram[40] (reproduced by permission of The Royal Society of Chemistry) (vs. Fc^+/Fc) recorded on a solution of the mono(TTF)-porphyrin **46** (0.5 mM) in CH_2Cl_2/nBu$_4$NPF$_6$ (0.1 M) on a platinum electrode with a scan rate of 0.1 V s^{-1}

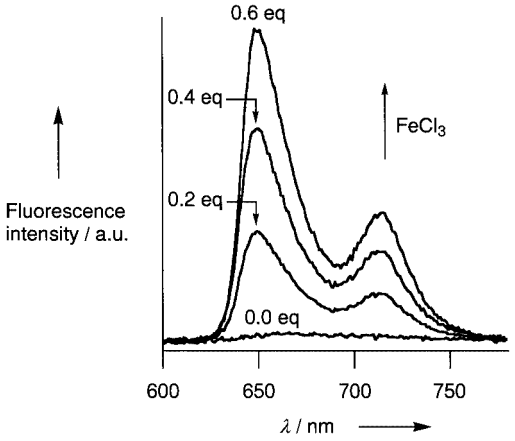

Figure 12. Emission spectra[40] (reproduced by permission of The Royal Society of Chemistry) (THF, 298 K) of the mono(TTF)-porphyrin **46** upon addition of increasing amounts of the oxidant $FeCl_3$; excitation was performed at 425 nm (Soret band).

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of increasing amounts of the chemical oxidant $FeCl_3$ to a solution of **46**. Emission spectra (Figure 12) recorded on this solution revealed that the fluorescence intensity increased upon addition of increasing amounts of $FeCl_3$.

5.4 Cation and Anion Sensors Based on Pyrrolo-TTFs

The advent of supramolecular chemistry[3] has stimulated contemporary chemists' interest in the development of chemosensors capable of recognizing specific chemical species.[25,41] Electrochemically active sensors designed to permit the detection of substrates through binding-induced changes in the redox properties can be produced (Figure 13) from the covalent association of a substrate-recognition functionality (receptor unit) and an electrochemical-signaling capacity (redox-active unit).

5.4.1 A Bis(pyrrolo)-TTF Macrocycle as a Cation Sensor

In the context of redox-responsive receptors the TTF unit is an ideal redox-active unit, in view of its unique π-electron-donating properties. Its oxidation to the radical cation ($TTF^{+\cdot}$) and dication (TTF^{2+}) occurs sequentially and reversibly at low potentials and such a reversibility in its redox processes can allow electrochemical control of trapping (neutral TTF) or releasing (cationic TTF) of a given cation, simply by changing the redox state of the TTF unit. Incorporation of the TTF unit into macrocycles containing a crown ether recognition motif has been well documented[1k−1m,6,42] in recent years and has allowed the electrochemical recognition of various metal cations. Until now, essentially for synthetic reasons, the TTF unit has mainly been introduced into such systems as a tetrathio-TTF unit[6,42] resulting in the isolation of *cis*/*trans* isomeric[43] mixtures, as in the case (Figure 3) of the TTF crown[6] **4**. This problem has recently[44] been circumvented by incorporation of the bis(pyrrolo)-TTF unit into a macrocycle containing polyether subunits. The bis(pyrrolo)-TTF crown **48** was synthesized as outlined in Scheme 10. *N*,*N*′-Functionalization of the bis(pyrrolo)-TTF unit **6** with the catechol derivative **47** was carried out under high-dilution conditions in DMF with sodium hydride as base, producing the macrocyclic compound **48** in 37% yield. This kind of bis(substitution) ensures a close proximity between the coordinating unit and the central part of the electroactive TTF unit, which is necessary in order to optimize the response of the electroactive part upon complexation of a metal cation.

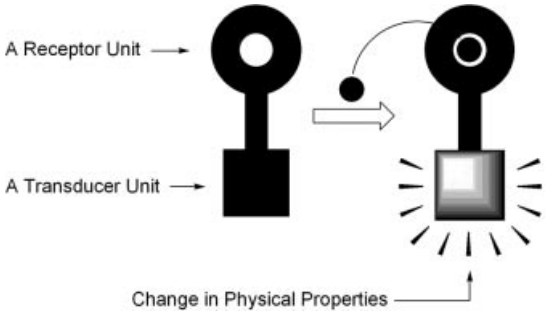
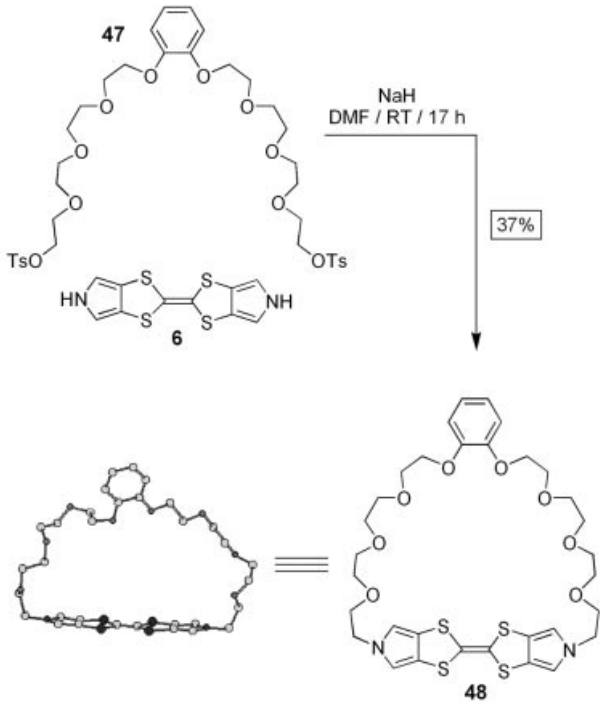


Figure 13. The concept of a molecular sensor



Scheme 10. Synthesis of the macrocyclic receptor **48** and its geometrical optimization (PM3, Hyperchem)

^1H NMR and UV/Vis spectroscopy showed[44] that metallic cations can be complexed (Scheme 11) within the macrocyclic receptor **48** and that **48** exhibits remarkably high binding affinities − in its neutral state − toward Pb^{2+} and Ba^{2+} ions. Binding constants (K_a) in the range of 100000 to 1000000 M^{-1} in a 1:1 mixture of CD_3CN and $CDCl_3$ at 298 K were obtained from titration studies, which correspond to the highest binding constants reported so far for a TTF-based cation receptor. Furthermore, CV was used to demonstrate that the binding properties of **48** can be modified (Scheme 11) simply by changing the redox state of the bis(pyrrolo)-TTF unit, thereby allowing a controlled uptake (neutral TTF) and release (TTF^{2+}) of the cation from the receptor cavity. The progressive addition of Pb^{2+} ions to solution of **48** (CH_3CN/CH_2Cl_2, 1:1) caused significant modifications in the CVs (Figure 14) and the emergence of a new redox wave. Thus, for addition of molar equivalents between 0 and 1, the first oxidation process associated with the bis(pyrrolo)-TTF unit is divided into two different redox waves as a result of the coexistence of the free receptor **48** (E^1_{ox} = 0.38 V) and the complex **48**·Pb^{2+} (E^1_{ox} = 0.52 V). The corresponding ΔE^1_{ox} is 140 mV, the highest value so far observed for cation receptors based on TTF, and can be attributed to the remarkable binding properties of **48** toward Pb^{2+} ions. Furthermore, it should be noted that the potential associated with the second oxidation of the bis(pyrrolo)-TTF unit remains unaltered after the addition of Pb^{2+} ions, which gives indirect confirmation of the release of the metal cation when the bis(pyrrolo)-

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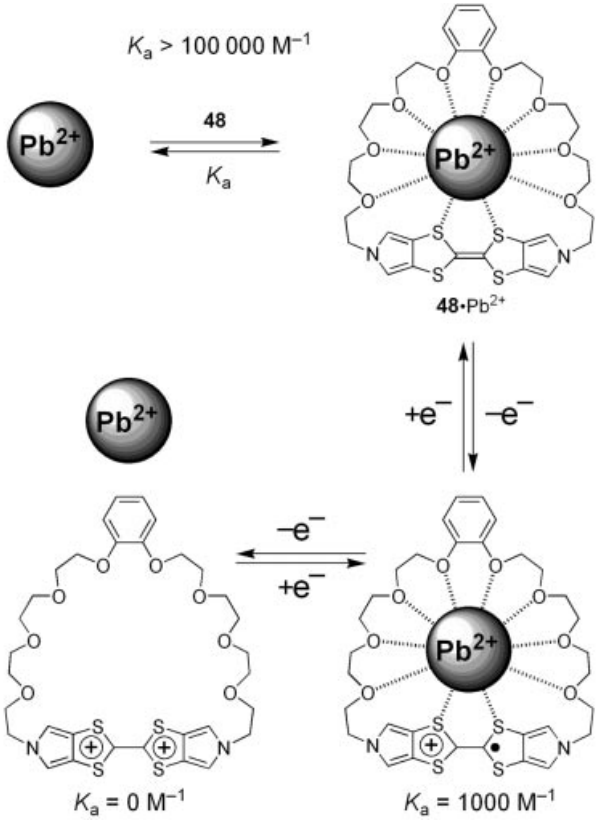


Scheme 11. Complexation of the Pb^{2+} ion by the macrocyclic receptor **48** and its electrochemically driven expulsion

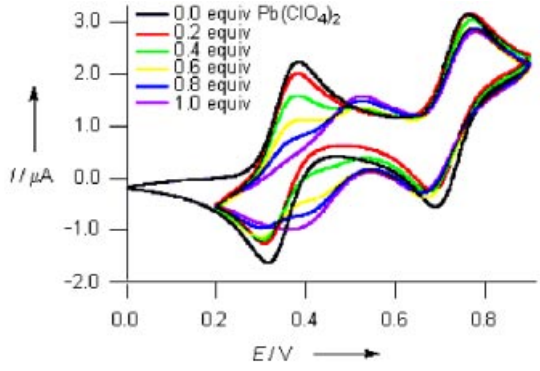
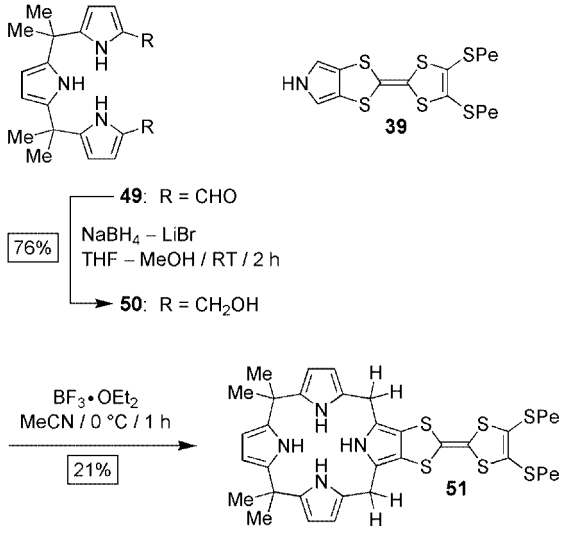


Figure 14. Cyclic voltammograms[44] (reprinted with permission from ref.[44] Copyright 2002 American Chemical Society) of the bis(pyrrolo)-TTF-crown **48** (1.0 mM) recorded in a mixture of CH_2Cl_2 and CH_3CN and nBu_4NPF_6 (0.1 M) as the supporting electrolyte in the presence of increasing amounts of Pb^{2+} ions

TTF unit is oxidized to the dicationic stage. Binding constants of the **48**·Pb^{2+} complex have also been evaluated[44] on the basis of a square scheme, by simulation with a fitting program (DIGISIM 2.1 by BAS Inc.). The binding properties of **48** are directly correlated to the oxidation state of the bis(pyrrolo)-TTF unit. Firstly, a very strong affinity is observed (Scheme 11) for the neutral state (K_a^0 = 100000 M^{-1}), secondly, a decrease in the complexation ability is observed for the radical cation $TTF^{+\cdot}$ state ($K_a^{+\cdot}$ = 1000 M^{-1}), and finally, the total expulsion of the Pb^{2+} ion from **48** is seen at the dicationic TTF^{2+} state ($K_a^{2+} \approx 0$ M^{-1}).

5.4.2 A Mono(pyrrolo)-TTF Calix[4]pyrrole as an Anion Sensor

Calix[4]pyrroles[45] – first synthesized in the 19th century by Baeyer[46] – contain four pyrrole NH hydrogen bond functionalities and have recently received extensive attention as receptors for anionic and neutral substrates.[47] They have been used to prepare optical anion sensors[48] and anion-selective high-performance liquid chromatography (HPLC) supports.[49] However, only a very few electrochemically active sensors based on calix[4]pyrroles have been reported.[50] As shown in the previous paragraph, TTF has already been used as the redox-active unit in a number of cation-responsive receptors.[42,44] However, no anion receptor incorporating TTF as the redox-active unit had been described in the literature prior to the publication of a communication[51] in 2003 describing the first example of a single molecule in which the anion receptor abilities of the calix[4]pyrrole system had been coupled to the favorable redox properties of the TTF unit through direct annulation of one TTF unit onto the upper rim of the calix[4]pyrrole skeleton. The mono(TTF)-calix[4]pyrrole **51** was synthesized as outlined in Scheme 12. The tripyrranedicarbaldehyde **49** can be prepared[52] by condensation of pyrrole and acetone, followed by a Clezy formylation. Reduction of the formyl groups in **49** with sodium borohydride/lithium bromide in anhydrous THF/MeOH produced the bis(hydroxymethyl)tripyrrane **50** in 76% yield. Treatment of equal quantities of **50** and the mono(pyrrolo)-TTF derivative **39** with a catalytic amount of boron trifluoride–diethyl ether (BF_3·Et_2O) in anhydrous MeCN, gave the mono(TTF)-calix[4]pyrrole **51** in 21% yield.[51]



Scheme 12. Synthesis of the mono(TTF)-calix[4]pyrrole **51**

The mono(TTF)-calix[4]pyrrole **51** was shown[51] by ^1H NMR spectroscopy and CV to form 1:1 complexes (Scheme 13) with Br^-, Cl^-, and F^- ions. ^1H NMR spectro-

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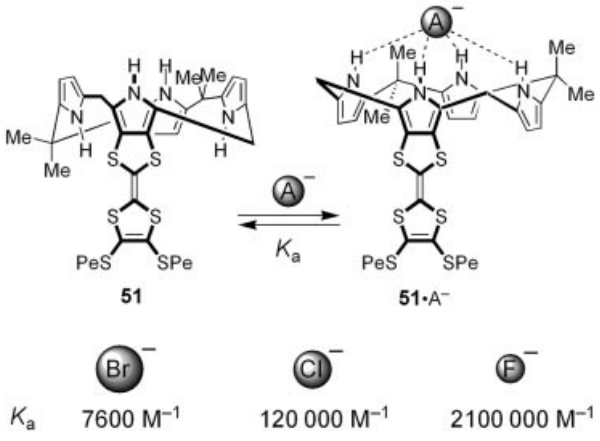

Scheme 13. Complexation of the Br^-, Cl^-, and F^- ions by the mono(TTF)-calix[4]pyrrole **51** and their K_a values in CD_3CN/0.5% v/v D_2O at 300 K

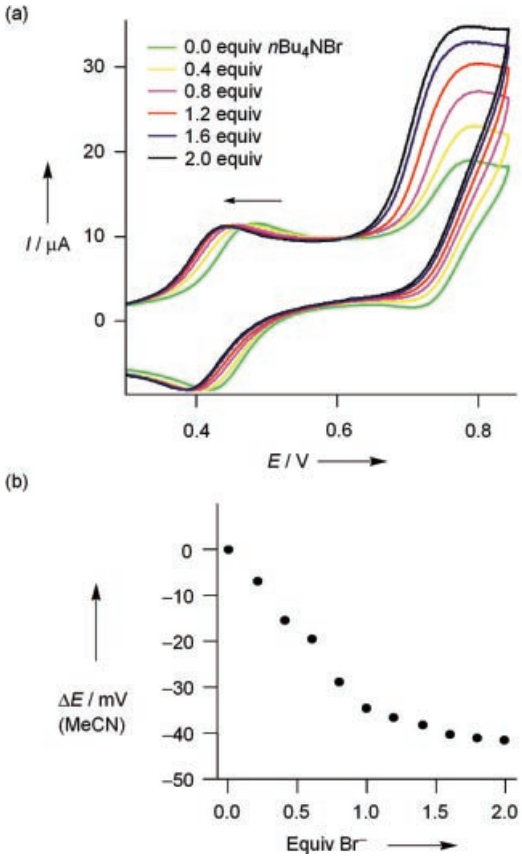

Figure 15. (a) Cyclic voltammograms[51] of the receptor **51** (0.5 mM) recorded in MeCN at 298 K with nBu_4NPF_6 (0.4 M) as the supporting electrolyte; the receptor **51** was titrated by addition of a concentrated MeCN solution of nBu_4NBr that, to account for dilution effects, also contained receptor **51** at the initial concentration; the potentials were referred to Ag/AgCl; (b) CV titration curves[51] showing the cathodic shift of the first oxidation potential of the receptor **51** upon addition of Br^- ions; note that the cathodic shift of the first oxidation potential is independent of the second oxidation process

scopic titration and competitive binding studies between the receptor **51** and Br^-, Cl^-, and F^- ions have been carried out in CD_3CN containing 0.5% v/v D_2O at 300 K. The receptor **51** displays the strongest anion-binding affinities yet recorded for calix[4]pyrrole receptors and the binding constants obtained (Scheme 13) between **51** and Br^-, Cl^-, and F^- ions are two orders of magnitude higher than those reported for *meso*-octamethylcalix[4]pyrrole.[53,54] The stronger affinity of **51** toward anions is presumably a direct consequence of the stronger acidity of the pyrrolo-TTF NH proton, as compared to the other NH protons in **51**. This implies that the pyrrolo-TTF NH proton is able to form a stronger hydrogen bond with anions upon complexation, in relation to NH protons in the parent *meso*-octamethylcalix[4]pyrrole. The receptor **51** was designed to permit the detection of anions through binding-induced changes in the electrochemical properties of the TTF unit. CV was used to probe the changes in the oxidation potentials of the receptor **51** upon complexation of anions. As can be seen by inspection of Figure 15, the progressive addition of Br^- ions to a solution of **51** in MeCN at 298 K resulted in a cathodic displacement of the first oxidation potential ($E^1_{1/2}$) of the TTF unit. It should be noted (Figure 15, a) that the current intensity associated with the second oxidation wave increases when the concentration of Br^- ions increases. This unexpected growth in current intensity is a consequence of the oxidation of the anion.[55] It transpires from Figure 15 (b) that the displacement of the first oxidation potential reached a limit ($\Delta E^1 = -40$ mV) when approximately stoichiometric amounts of Br^- ions were added to the receptor **51**, which provides further evidence of the high stability of the **51**·Br^- complex. Similar cathodic displacements were observed when the receptor **51** was titrated with a solution of Cl^- ions. The electrochemical results reveal that complexation of the anions inside the cavity of **51** shift the first oxidation of the TTF unit to more cathodic potentials, which can be accounted for by delocalization of the negative charge from the binding site N−H···X^- to the TTF unit.[56] The annulation of the TTF unit onto the upper rim of the calix[4]pyrrole skeleton, not only transduces the binding event to an electrochemical output signal, but also substantially increases the binding abilities toward anionic substrates as compared to other calix[4]pyrrole receptors, such as *meso*-octamethylcalix[4]pyrrole.

5.5 Catenanes and Rotaxanes Incorporating Pyrrolo-TTFs

The emergence of supramolecular chemistry[3] has aroused the interest of chemists of many different persuasions in compounds such as catenanes and rotaxanes.[57] The chemistry of the non-covalent bond has transformed these interlocked molecular systems from chemical curiosities into a flourishing field of modern-day research. During the last decade it has thus become possible to construct these kinds of intricate, yet highly ordered molecules by recognition of the role that mechanical bonds[58] can play alongside covalent and non-covalent bonds, and catenanes and rotaxanes are now prime candidates for the construction of artificial molecular machines[59,60] and the fabrication of molecular electronic devices.[61]

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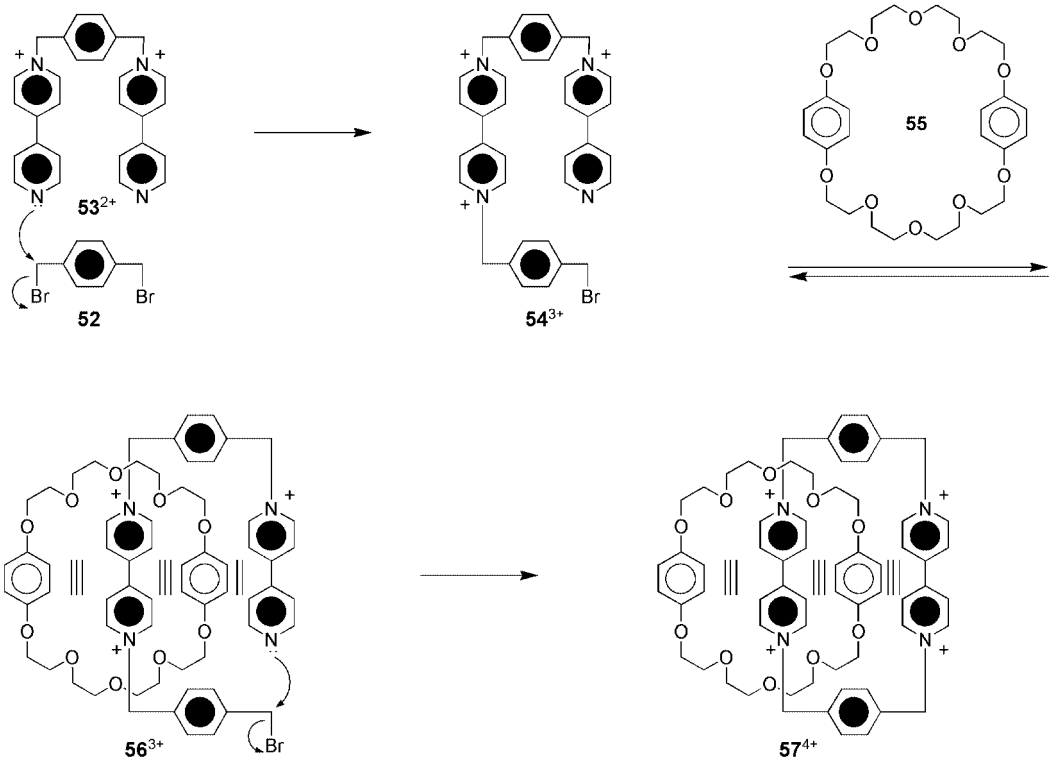
A [2]catenane[62,63] is a molecule (Figure 16) composed of two interlocked macrocyclic components.[57] The two macrocycles are not linked covalently to each other: rather, a mechanical bond serves to hold them together and prevents their dissociation. A [2]rotaxane[63,64] is a molecule (Figure 16) consisting of a ring component and a dumbbell-shaped component.[57] The ring component encircles the linear, rod-like portion of the dumbbell-shaped component and is trapped mechanically around it by two bulky stoppers. The two components can therefore not dissociate from one another, even though they are not linked covalently to each other. In contrast, in a [2]pseudorotaxane,[57,65] at least one of the stoppers on the dumbbell-shaped component is absent (Figure 16) with the consequence that dissociation of the [2]pseudorotaxane into its components can occur, and the equilibrium between the species is controlled by the free energy of complexation (i.e., a [2]pseudorotaxane is a supramolecular species).

Figure 16. Schematic representations of a [2]catenane, a [2]rotaxane, and a [2]pseudorotaxane

Stoddart and co-workers[66] have developed a strategy for the formation of both catenanes and rotaxanes based on molecular recognition between π-electron donors and acceptors assisted by hydrogen bonding. The first catenane[66] synthesized in Stoddart's laboratories was the [2]catenane **57**$^{4+}$, which was prepared, in an extraordinary 70% yield, from 1,4-bis(bromomethyl)benzene (**52**), the dication **53**$^{2+}$, and the macrocyclic polyether bis(*p*-phenylene)-34-crown-10 (**55**). The high yield can be explained in terms of the mechanism of the catenane's formation, illustrated in Scheme 14. Most probably, one of the free nitrogen atoms in **53**$^{2+}$ first quaternizes upon reaction with the dibromide **52** to afford the π-electron-accepting tricationic intermediate **54**$^{3+}$. This intermediate can thread its way through the cavity of the macrocyclic polyether **55** to form a [2]pseudorotaxane **56**$^{3+}$ (pre-catenane), which is stabilized by π−π stacking, CT interactions, electrostatic interactions between the 4,4′-bipyridinium moiety and the two hydroquinone units, and by hydrogen-bonding interactions between the α-H protons in the 4,4′-bipyridinium moiety and the oxygen atoms in the macrocyclic polyether **55**. The tricationic intermediate **56**$^{3+}$ is ideally disposed to form the [2]catenane **57**$^{4+}$ by an intramolecular nucleophilic attack of the residual free nitrogen atom on the carbon atom of the remaining benzyl bromide group. This so-called clipping approach for the preparation of [2]catenanes is a good example of supramolecular assistance to covalent synthesis. This strategy can also be employed for the preparation of [2]rotaxanes, and an illustrative example carried out by Becher and



Scheme 14. Mechanism for the formation of the [2]catenane **57**$^{4+}$

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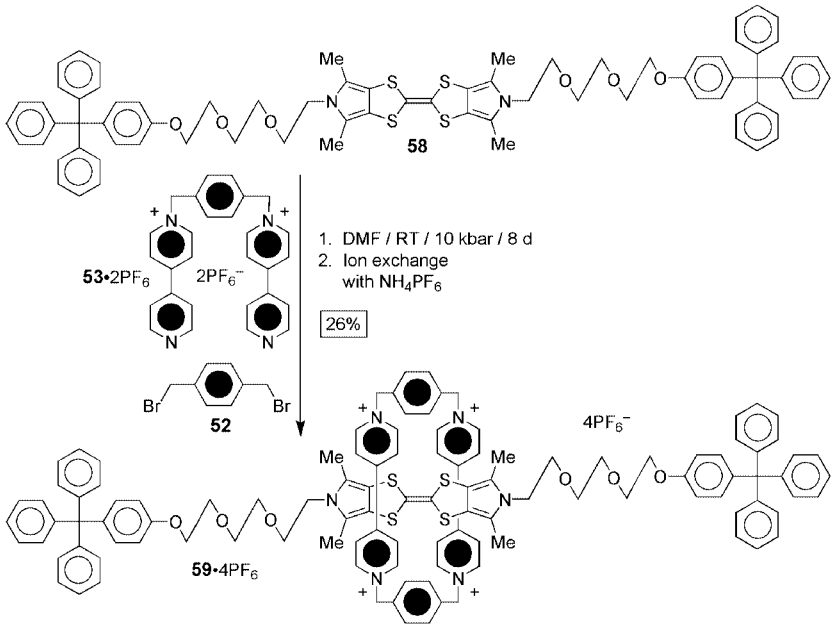
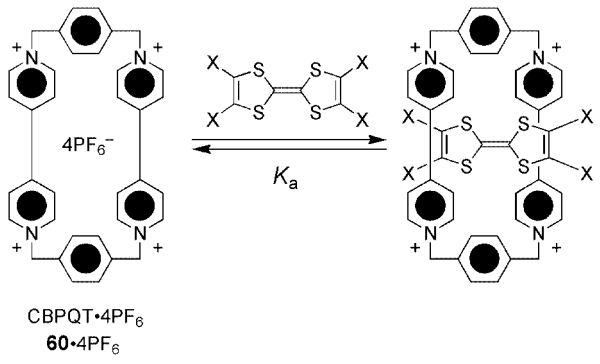


Scheme 15. Synthesis of the [2]rotaxane **59**·4PF_6 by use of the clipping methodology

co-workers[67] is shown in Scheme 15. The dumbbell-shaped compound **58** − containing a bis(pyrrolo)-TTF unit as the π-electron donor in its rod section − was used as the template[68] for the production of cyclobis(paraquat-*p*-phenylene) tetracation (CBPQT^{4+}) from the dicationic precursor **53**·2PF_6 and the dibromide **52**, affording the [2]rotaxane **59**·4PF_6 in 26% yield.

5.5.1 Binding Studies between TTF Derivatives and Cyclobis(paraquat-p-phenylene)

Thanks to the ability of the π-electron-accepting tetracationic cyclophane[69] CBPQT^{4+} (**60**$^{4+}$, Scheme 16) to include π-electron donors within its cavity as a result of stabilizing non-covalent interactions, it has been employed for the construction of a number of mechanically interlocked compounds, such as catenanes and rotaxanes. However, Mirzoian and Kaifer[70] have observed that the best electron donors do not always exert the largest binding affinities with CBPQT^{4+}. Thus, indole (K_a = 100 M^{-1}, Me_2CO) forms a stronger complex than catechol (K_a = 68 M^{-1}, Me_2CO), even though indole is a weaker π-electron donor than catechol. The relatively better inclusion of indole is probably the consequence of its larger π-surface. Stoddart and co-workers, and later Bryce and co-workers investigated[71] the green 1:1 complex formed between CBPQT^{4+} and TTF (**1**) and found their association to be very strong indeed. Although a considerable range of catenanes, rotaxanes, and pseudorotaxanes, incorporating different TTF units, and employing CBPQT^{4+} as the encircling component, have been reported,[72] the binding affinities between differently substituted TTF derivatives and CBPQT^{4+} have not been investigated in detail. Recently,[73] some binding studies have been carried out to shed more light on the factors influencing the inclusion of different TTF derivatives inside the cavity of CBPQT^{4+}. The TTFs investigated are displayed in Figure 17. All of these TTFs are devoid of polyether substituents capable of forming hydrogen bonds[74] with the α-bipyridinium hydrogen atoms on the tetracationic cyclophane CBPQT^{4+}. Compounds **5** and **61**−**63**



Scheme 16. Equilibrium for the formation of 1:1 complexes between CBPQT·4PF_6 (**60**·4PF_6) and TTF derivatives

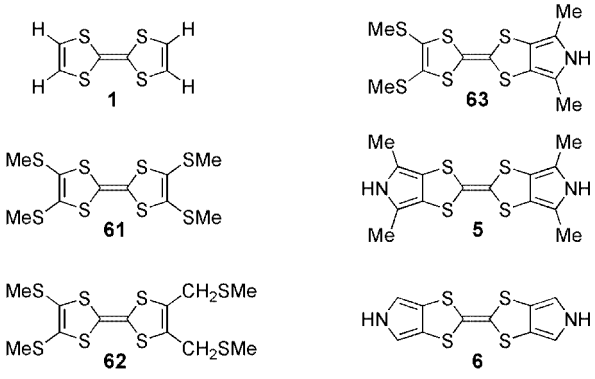


Figure 17. TTF (**1**) and the TTF derivatives **5**, **6**, and **61**−**63** investigated

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were observed to be in slow exchange with their $CBPQT^{4+}$ complexes on the ^1H NMR timescale (250 MHz, 303 K), since both complexed and uncomplexed $CBPQT^{4+}$ resonances were present in the ^1H NMR spectra. The cyclophane protons show significant shifts in their resonances upon complexation, which made it possible to determine binding constants (K_a) by employing the ^1H NMR single-point method.[73] The K_a values and derived free energies for complexation ($-\Delta G°$) by $CBPQT^{4+}$ of the TTF derivatives **5** and **61**−**63** are listed in Table 2. In contrast, the TTFs **1** and **6** were found to be in fast exchange with their $CBPQT^{4+}$ complexes on the ^1H NMR timescale (250 MHz, 303 K). Binding constants for the complexation of $CBPQT^{4+}$ with the bis(pyrrolo)-TTF derivatives **5** and **6** have been determined by the UV/Vis dilution method. The binding constants and derived $-\Delta G°$ values, obtained from the two UV/Vis experiments, are recorded in Table 3. The K_a values listed in Table 2 reveal a significant trend. As the first oxidation potential ($E^1_{1/2}$) for the TTF derivatives decreases, the binding constant increases. Thus, the better the π-electron donor, the stronger the complex formed with $CBPQT^{4+}$. The data recorded in Table 3, however, show that the first oxidation potential is not the only factor of importance. Note that, even though the bis(pyrrolo)-TTF derivative **6** is a slightly weaker donor than TTF (**1**), it nevertheless exhibits a stronger association with $CBPQT^{4+}$. It seems that the extended π-surface of the bis(pyrrolo)-TTF derivative **6** is exerting a stabilizing influence upon the complex relative to the parent TTF (**1**). When four electron-donating methyl groups are attached to the pyrrole units, as in the TTF derivative **5**, the binding constant increases even further, so the thermodynamic data clearly demonstrate that the strength of the complexation is governed both (i) by the π-electron-donating properties (measured by the first oxidation potential $E^1_{1/2}$), and (ii) by the area of the π-surface. It transpires that, for donor−acceptor interactions, Equation (1) (see Figure 18) is obeyed,[75] where k_1 and k_2 are constants and β is the overlap integral between donor and acceptor, while E^1_{don} and E^1_{acc} are the first redox potentials of the donor (TTF derivative) and acceptor ($CBPQT^{4+}$) entities. Figure 18 shows a plot of $-\Delta G°$ in Me_2CO vs. the reciprocal difference $1/(E^1_{don} - E^1_{acc})$ in redox potentials for the TTFs **1**, **5**, **6**, and **61**−**63**, with $E^1_{acc} = -0.25$ V (vs. Ag/AgCl in MeCN) used for the cyclic $CBPQT^{4+}$ acceptor.[76] Deviations from a straight line originate mainly from different overlap integrals β. Note that the overlap is smaller for unsubstituted TTF (**1**), containing neither sulfur-containing nor pyrrolo substituents, and larger for the bis(pyrrolo)-TTF **6**.

$$-\Delta G^o = k_1 + T\Delta S^o + \frac{k_2\beta^2}{E^1_{don} - E^1_{acc}} \quad (1)$$

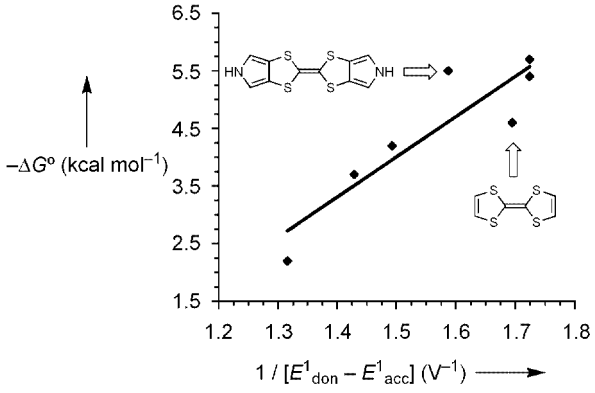

Figure 18. Plot of $-\Delta G°$ in Me_2CO vs. the reciprocal difference in redox potentials between π-electron donor (TTF derivative) and π-electron acceptor ($CBPQT^{4+}$) units; the seven data points have been fitted by a best straight line

Table 2. Comparison of binding constants (K_a) and derived free energies of complexation ($-\Delta G°$) between different TTFs and $CBPQT^{4+}$ determined by ^1H NMR single-point method with the first oxidation potential ($E^1_{1/2}$) for different TTFs; temperature 303 K, unless otherwise stated

Compd.	K_a [M^{-1}] (Me_2CO)[a]	$-\Delta G°$ [kcal mol^{-1}] (Me_2CO)	$E^1_{1/2}$ [V] (MeCN)[b]
5	7900	5.4	+0.33
63	1000	4.2	+0.42
62	490	3.7	+0.45
61	40	2.2	+0.51

[a] Estimated error on $K_a = \pm 10\%$. [b] Oxidation potentials $E^1_{1/2}$ (vs. Ag/AgCl) were obtained from cyclic voltammograms.

Table 3. Comparison of binding constants (K_a) and derived free energies of complexation ($-\Delta G°$) between different TTFs and $CBPQT^{4+}$ determined by UV/Vis spectroscopy with the first oxidation potential $E^1_{1/2}$ for different TTFs; temperature 295 K, unless otherwise stated

Compd.	K_a [M^{-1}] (Me_2CO)[a]	$-\Delta G°$ [kcal mol^{-1}] (Me_2CO)	$E^1_{1/2}$ [V] (MeCN)[b]
5	18 000	5.7	+0.33
6	12 000	5.5	+0.38
1	2 600[c]	4.6	+0.34

[a] Estimated error on $K_a = \pm 15\%$. [b] Oxidation potentials $E^1_{1/2}$ (vs. Ag/AgCl) were obtained from cyclic voltammograms. [c] At 294 K, see ref.[71c]

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Whether or not a TTF derivative and the cyclophane $CBPQT^{4+}$ are in fast exchange with their complex on the ^1H NMR timescale, is influenced largely by the bulkiness of the TTF derivative. Hence, when the TTF unit is substituted with four bulky SMe groups, as in the case of **61** − or with two SMe and two CH_2SMe groups, as in the case of **62** − the kinetics for the complexation/decomplexation process are in slow exchange on the 250 MHz timescale (303 K). The bis(pyrrolo)-TTF derivative **6**, however, undergoes fast exchange with its $CBPQT^{4+}$ complex, but attachment of four Me substituents, as in the case of **5**, changes the kinetics to slow exchange on the 250 MHz timescale (303 K). The exchange rate is hence a function of a fine balance between electronic and steric factors.

In summary, three major conclusions can be drawn:

(i) The stronger the donor, the higher the binding constant.

(ii) Extension of the π-system of the TTF derivative increases the extent of the binding.

(iii) The kinetics for complexation/decomplexation are related to the bulkiness of the TTF derivative.

These findings are of fundamental importance in the designing of (bistable) molecular switches[61] based on catenanes, rotaxanes, and pseudorotaxanes in which one of the π-electron-donating sites in one component is a derivatized TTF unit and the other recognition component is $CBPQT^{4+}$.

5.5.2 A Bistable [2]Rotaxane Incorporating a Mono(pyrrolo)-TTF Unit

Since the mechanically interlocked components of nondegenerate catenanes and rotaxanes can be induced to change their relative positions as a result of some carefully chosen external stimulus, they are ideally suited for the construction of artificial molecular machines[59][60] and the fabrication of molecular electronic devices,[61] because large-amplitude motion can be envisaged within such architectures without the risk of damaging the chemical structure of the system. The relative movements of the interlocked components (Figure 19) can be triggered by chemical, electrochemical, and photochemical stimuli (input signal), forcing the molecule to switch between its two nondegenerate states (State 0 and State 1), which can be distinguished spectroscopically (output signal).

Many catenanes and rotaxanes have been synthesized by template-directed methods and characterized in solution. However, it is the integration of these molecules into the device setting that has been receiving much attention over the last few years.[61] Among the desirable features for the redox-controllable, amphiphilic [2]rotaxanes that have been employed for the fabrication of single-molecule thick electrochemical junctions in electronic devices are: (i) the siting of redox-active units along the rod section of the dumbbell component, and (ii) the presence of both hydrophobic and hydrophilic groups as stoppers at the ends of the dumbbell component. TTF's unique π-electron donor properties, together with its ability to form a strong green 1:1 complex with the tetracationic cyclophane $CBPQT^{4+}$, have been responsible for TTF's incorporation into a considerable range[72] of catenanes and pseudorotaxanes. Although a TTF unit and a 1,5-dioxynaphthalene (DNP) moiety have been incorporated[72n] into the crown ether ring component of a redox-switchable [2]catenane − a compound already previously employed in the fabrication of a solid-state electronically reconfigurable switch[61d] − no rotaxanes employing these two recognition sites for a $CBPQT^{4+}$ component had been described in the literature prior to the publication of a communication[77] in 2001 describing an amphiphilic bistable [2]rotaxane. In addition, rotaxanes incorporating TTF units in dumbbell components incorporating two different stoppers had hitherto been unknown, most probably because of the lack of an appropriate TTF building block. Now that such a building block is available, in the form of the mono(pyrrolo)-TTF unit, amphiphilic bistable [2]rotaxanes have been designed with $CBPQT^{4+}$ as the ring component and with the dumbbell component − containing a mono(pyrrolo)-TTF unit and a DNP moiety within its rod section − terminated by a hydrophilic dendritic stopper at one end and a hydrophobic tetraarylmethane stopper at the other.[77,78]

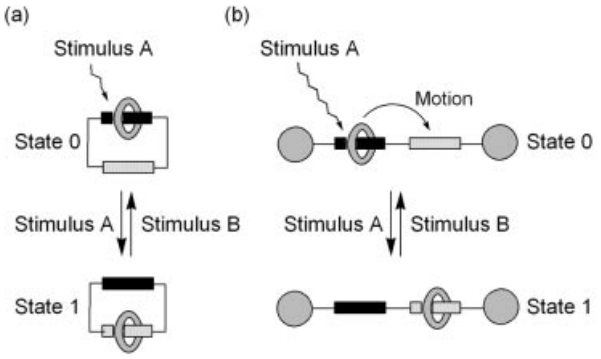

Figure 19. Schematic representations of the mechanical movements relating to States 0 and 1 in non-degenerate (a) [2]catenanes and (b) [2]rotaxanes

The synthetic approach to this kind of complicated molecules is based (Scheme 17) on *S*- and *N*-alkylation of the mono(pyrrolo)-TTF unit **68**. The mono(pyrrolo)-TTF building block **68** was synthesized (not shown) by a triethyl phosphite mediated cross-coupling of the ketone **14** and 4-(2-cyanoethylthio)-5-methylthio-1,3-dithiole-2-thione.[78,79] By employment of this building block the amphiphilic bistable [2]rotaxane **73**·$4PF_6$ was synthesized as shown in Schemes 17 and 18. A condensed version of the synthesis of the linear dumbbell component is outlined in Scheme 17. In order to complete the synthesis (Scheme 18) of the amphiphilic bistable [2]rotaxane **73**·$4PF_6$, the cyclophane $CBPQT^{4+}$ was introduced by means of a clipping reaction, which gave an analytically pure compound.[77,78] The bistable [2]rotaxanes **73**·$4PF_6$ was isolated as a brown solid, and ^1H NMR and UV/Vis spectroscopy and CV revealed the presence of both stable translational isomers, in an approximately ratio of 1:1 at ambient temperature. It turned out that the SMe group situated between the TTF and the

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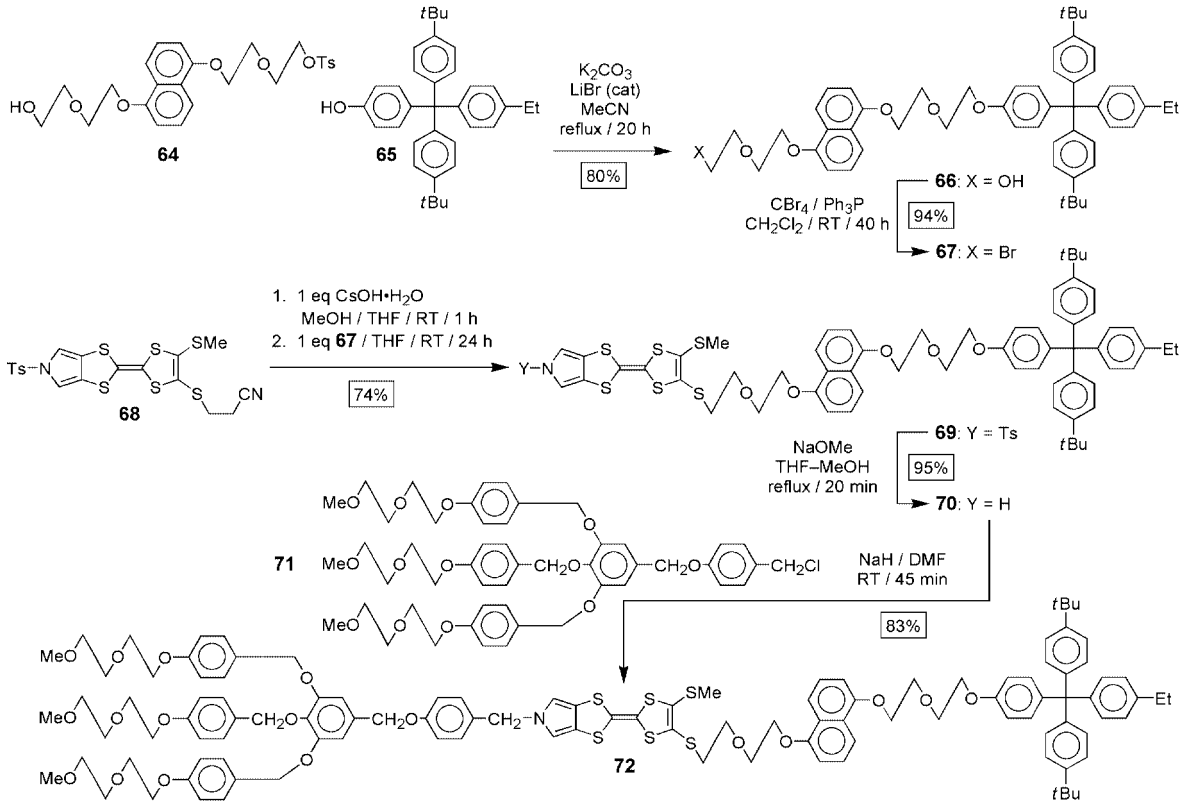
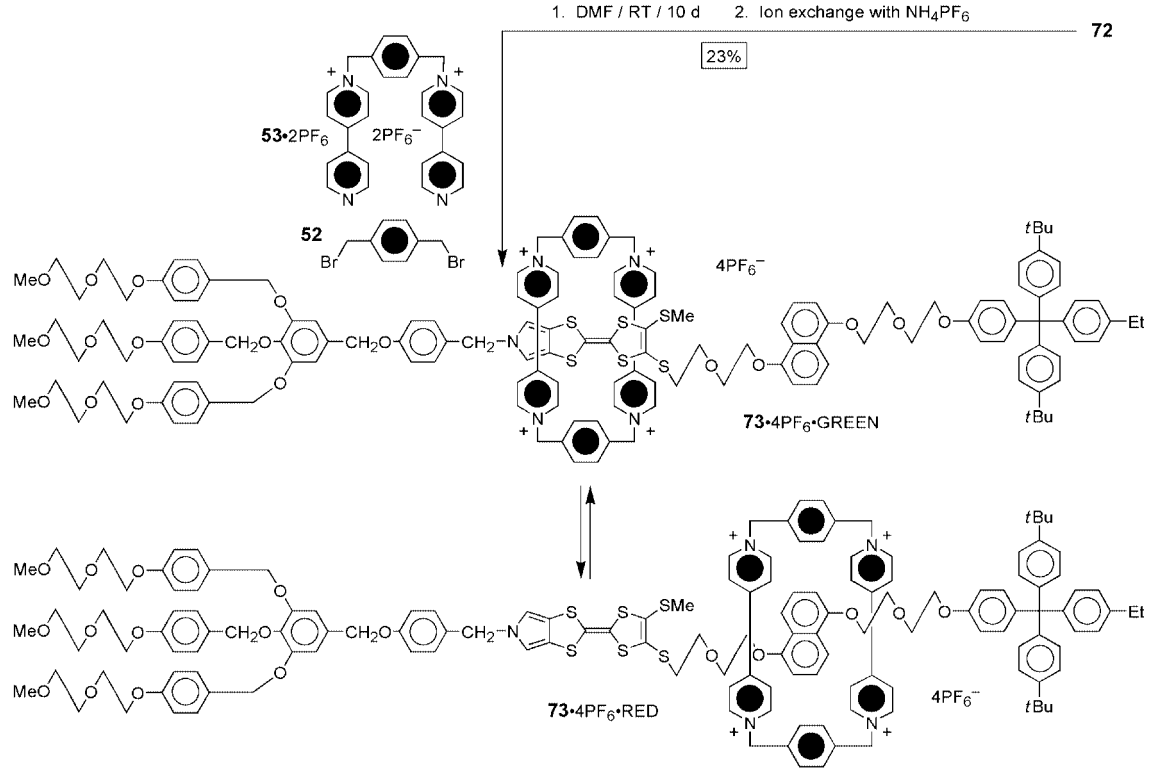


Scheme 17. The synthesis of the dumbbell-shaped component **72** of the amphiphilic bistable [2]rotaxane **73**·4PF$_6$



Scheme 18. The clipping reaction to give a mixture of translational isomers of the bistable [2]rotaxane **73**·4PF$_6$

DNP recognition sites adds a considerable activation barrier for the shuttling of the tetracationic cyclophane CBPQT^{4+} between the two recognition sites. In fact, the steric hindrance exhibited by the SMe group made it possible to isolate (Figure 20, a) the translational isomers **73**·4PF$_6$·RED and **73**·4PF$_6$·GREEN and to study the kine-

tics of the shuttling of $CBPQT^{4+}$ between the two recognition sites. These processes, which are accompanied by clearly detectable color changes, can be monitored by ^1H NMR and UV/Vis spectroscopy, allowing the determination of the rate constants (k) and the associated energies of activation ($\Delta G^{\ddagger}$) both for the shuttling (Figure 20, b) of $CBPQT^{4+}$ from the DNP recognition site in **73**·$4PF_6$·RED to the TTF recognition site in **73**·$4PF_6$·GREEN, and also for the shuttling of $CBPQT^{4+}$ from the TTF recognition site in **73**·$4PF_6$·GREEN to the DNP recognition site in **73**·$4PF_6$·RED.[77,78]

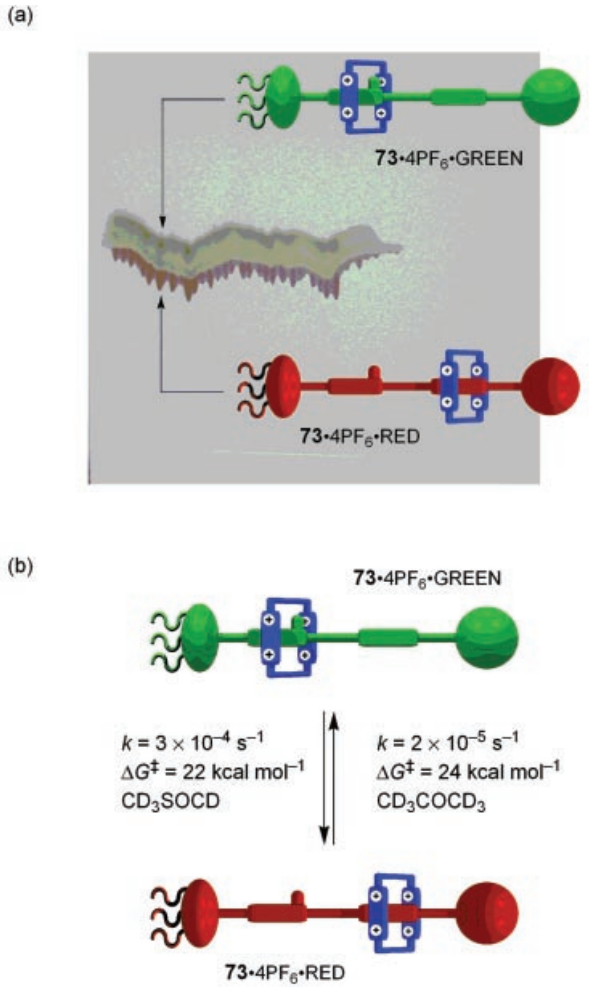


Figure 20. (a) A preparative thin layer chromatogram,[77] showing the separation of **73**·$4PF_6$·RED from **73**·$4PF_6$·GREEN; (b) rate constants (k) and associated energies of activation ($\Delta G^{\ddagger}$) for the shuttling processes in the bistable [2]rotaxane **73**·$4PF_6$

Finally, it should be mentioned that the performance of the bistable [2]rotaxane **73**·$4PF_6$ and closely related molecules in a device setting are currently under investigation and are not discussed further here, except to highlight the fact that solid-state switches fabricated from this kind of amphiphilic [2]rotaxanes[61f][61g][61i][61k][61l] are far superior to the switch[61d] fabricated from a TTF-based [2]catenane.[72n]

6. Summary and Outlook

The aim of this microreview has been to illustrate the fact that the parent pyrrolo-TTFs offer considerable scope as versatile building blocks for a number of applications in macrocyclic, molecular, and supramolecular chemistry. They have oxidation potentials in an attractive range, and are therefore stable in air. Furthermore, the pyrrolo-TTFs have their 2- and 5-positions unsubstituted, allowing easy introduction of new functionalities as demonstrated in Schemes 8, 9, and 12. A fundamental understanding of redox-responsive receptors, such as the bis(pyrrolo)-TTF crown **48** and the mono(TTF)-calix[4]pyrrole **51**, can aid the design of more complicated systems that may find applications as new sensors or as novel drug delivery systems. The preparation of amphiphilic bistable [2]rotaxanes such as **73**·$4PF_6$, described in Section 5.5.2, and their incorporation into solid-state devices is very promising. However, the field of molecular computing is still in its infancy and serious challenges lie ahead. On the assumption that such molecular devices really do exhibit operations based on intrinsic molecular properties, they need to be scaled down to dimensions of only a few molecules. Without any doubt, the future of molecular electronics lies in the hands of people of disparate backgrounds, including chemists (both synthetic and physical), physicists, materials scientists, electronics engineers, and, of course, computer scientists.

Acknowledgments

We thank the many colleagues and co-workers whose names appear alongside ours in those references to our own research, for their crucial inputs and key outputs, especially Prof. J. F. Stoddart, Dr. K. Takimiya, Prof. M. Sallé, and Dr. E. Levillain. Financial support from the Carlsbergfondet and the Danish Natural Science Research Council (SNF) in Denmark is gratefully acknowledged.

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[55] Indeed, in the absence of the receptor **51**, Br^- ions undergo oxidation in solution at a potential close to the second oxidation potential of **51**. As a consequence of the overlapping nature of these two oxidation processes, it is not possible to obtain any information as to whether complexation, of anions to the receptor **51**, also affects the second oxidation potential of the TTF unit in **51**, see ref.[51]

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[62] The term *catenane* is derived from the Latin word *catena*, meaning *chain*.

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[65] The distinction between rotaxanes and pseudorotaxanes is far from a straightforward one. When size-complementarity between the stoppers and the macrocyclic component is achieved, certain "rotaxanes" behave as pseudorotaxanes and can dissociate into their constituent components under appropriate conditions. Thus, a species that is a rotaxane at ambient temperature might well be a pseudorotaxane at elevated temperatures. Even a change in solvent can turn a rotaxane into a pseudorotaxane at the same temperature; see: [65a] F. M. Raymo, J. F. Stoddart, *Chem. Rev.* **1999**, *99*, 1643−1663. [65b]

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