Self-Complexing Tetrathiafulvalene-Based Donor–Acceptor Macrocycles

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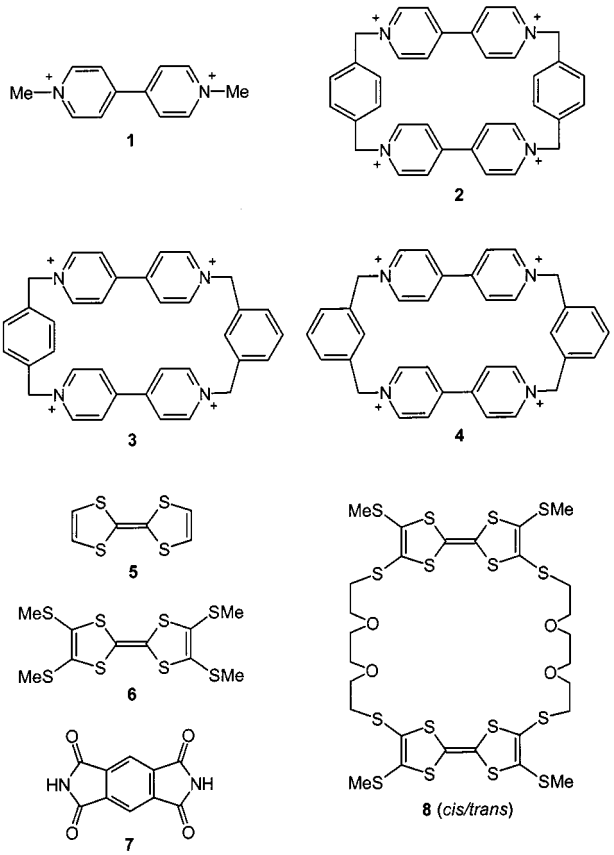
Two "self-complexing" macrocycles (**22ab** and **23ab**) based on a methylthio-substituted derivative of the electron donor tetrathiafulvalene (TTF) and a cyclic bipyridinium acceptor have been prepared.[1] When "decomplexed" by fractional crystallization, the rigid compound **22b** was not able to undergo "recomplexation" to any significant degree, whereas for the more flexible **23b**, an equilibrium between "complexed" (**23a**) and "uncomplexed" (**23b**) compounds was slowly re-established in solution according to UV/Vis measurements. **23ab** was thus seen to behave as a "thermo-switch", although with a rather slow response. Any complexation between the two separated components, i.e. the cyclic acceptor **3** and the tetrakis(methylthio)-tetrathiafulvalene **6**, was not observed by ^{1}H-NMR spectroscopy. However, **3** was able to bind unsubstituted TTF (**5**) in its cavity, albeit with a small association constant of only 60 M^{-1}. Taking advantage of the tetravalency of TTF, we also report the synthesis of a "self-complexing" pyromellitic diimide/TTF macrocycle (**33ab**). Whereas **22ab** and **23ab** were prepared employing the concept of template-assisted synthesis,[2] the synthesis of **33ab** did not rely on this technique.

Introduction

The construction of molecular devices which can operate as machines upon external energy transfer has recently been of great interest, particularly as such systems may be able to store and process information at the molecular level.[3] By exploiting non-covalent interactions between aromatic π-donors of the hydroquinone-type and π-acceptors based on derivatives of paraquat, Stoddart et al. have prepared a number of molecular shuttles and switches controllable by external stimuli.[4] An elegant example is provided by a "self-complexing" compound in which a naphthalene or hydroquinone π-donor and the π-acceptor cyclobis(paraquat-*p*-phenylene) (**2**) are covalently linked.[5a] A number of other "self-complexing" systems have recently been reported.[5b–5g]

The good π-electron donor tetrathiafulvalene (TTF, **5**) forms a strong complex with the cyclic acceptor cyclobis(paraquat-*p*-phenylene) (**2**).[6] We have utilized these donor–acceptor interactions in the self-assembly of a number of catenanes comprising **2** and bis(TTF) macrocycles (such as **8**) based on a tetramercapto-substituted TTF.[7] Systems in which the TTF unit and the bipyridinium unit (**1**) are linked, either in a rigid conformation, as a donor–acceptor cyclophane, or in a noncyclic system, have also been prepared.[8] In the present work, we have extended these concepts by directly linking the TTF unit to the cyclic acceptor. For synthetic reasons, we chose to attach the TTF unit (**6**) to the unsymmetrical *meta-para*-linked cyclophane of cyclobis(paraquat-phenylene) (**3**). The corresponding symmetrical *meta-meta*-linked cyclophane (**4**) was discarded on account of its poor ability to act as a host for 1,4-bis[2-(2-hydroxyethyloxy)ethyloxy]benzene, as reported by Stoddart et al.[9] Taking advantage of the tetravalency of TTF, it is also possible to prepare reversed systems, in which a π-acceptor, such as a derivative of the noncharged pyromellitic diimide **7** (PMDI), is linked to the cyclic TTF donor **8**.



The term "anchimeric assistance" is normally used to describe neighbouring-group participation in a reaction. Since the expression "complexation" is incorrect when used to describe an intramolecular reaction, we suggest using the

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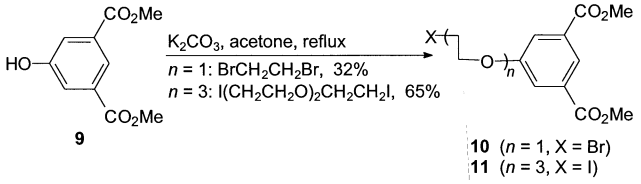
expression "anchimeric complexation" to describe "self-complexation" between two covalently linked groups.

Results and Discussion

To investigate the effect of the linker connecting the donor to the cyclic acceptor **3**, compounds with two different linker sizes were prepared. First, compounds **10** and **11** were prepared by *O*-alkylation of dimethyl 5-hydroxyisophthalate (**9**) (Scheme 1). The mono(cyanoethylated) TTF derivative **12** was deprotected with one equivalent of cesium hydroxide[10] (Scheme 2), and the resulting monothiolate was treated in situ with either **10** or **11**, affording compounds **13** and **14**, respectively. The ester groups were reduced with $LiAlH_4$, and then the respective hydroxy compounds **15** and **16** were mesylated in the presence of the nonnucleophilic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The mesylated compounds were converted directly to the corresponding chloro compounds by treatment with excess LiCl, giving moderate yields of compounds **17** and **18**. Subsequent Finkelstein reactions with LiBr gave the TTF-linked *m*-xylenedibromides **19** and **20**.



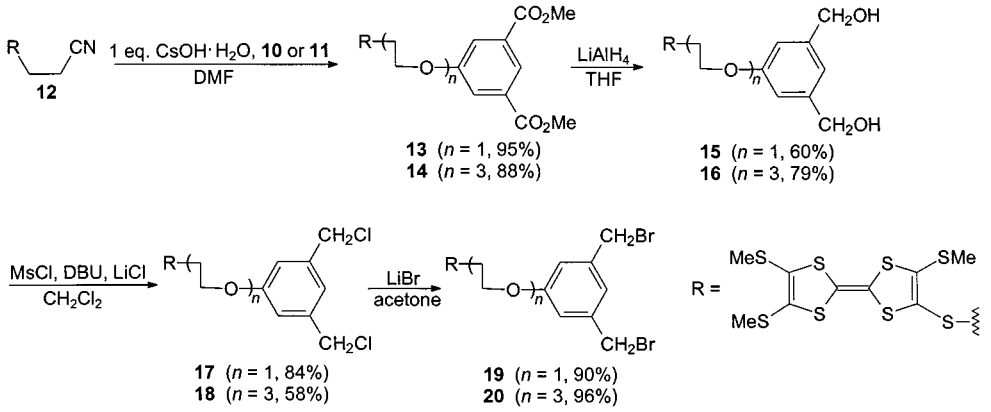
Scheme 1. Synthesis of **10** and **11**

Dibromides **19** and **20** were treated with **21** under ultra-high pressure (10 kbar) for 6 d. In this template-assisted ring-closure, the anchimeric complexes **22a** and **23a** (Scheme 3) were formed. The crude green reaction products, most likely containing intermolecular chains as well, were subjected to column chromatography and ion exchange. During workup of **23a**, partial "decomplexation" to the orange-coloured **23b** was observed. Repeated fractional crystallization by slow condensation of diisopropyl ether into acetonitrile solutions of **22a** and **23a** resulted in the removal of minor impurities. From these crystallizations, the orange compounds **22b** and **23b** were finally obtained, i.e. complete "decomplexation" had occurred. Redissolution of **23b** in acetonitrile initially gave an orange solution, which slowly turned pale-green on standing (room temp.) owing to partial "recomplexation". However, an acetonitrile solution of **22b** remained orange, and UV/Vis spectrophotometry showed that only a very small charge-transfer (CT) absorption was detectable after several days ($\lambda_{max} \approx 750$ nm, absorption ca. 0.015 at a conc. of 2.8×10^{-4} M). Thus, the short linker of **22b** essentially prevents the TTF unit from intramolecularly slipping back into the cyclic acceptor. Moreover, the persistent orange colour indicates the absence of any significant degree of intermolecular recomplexation.

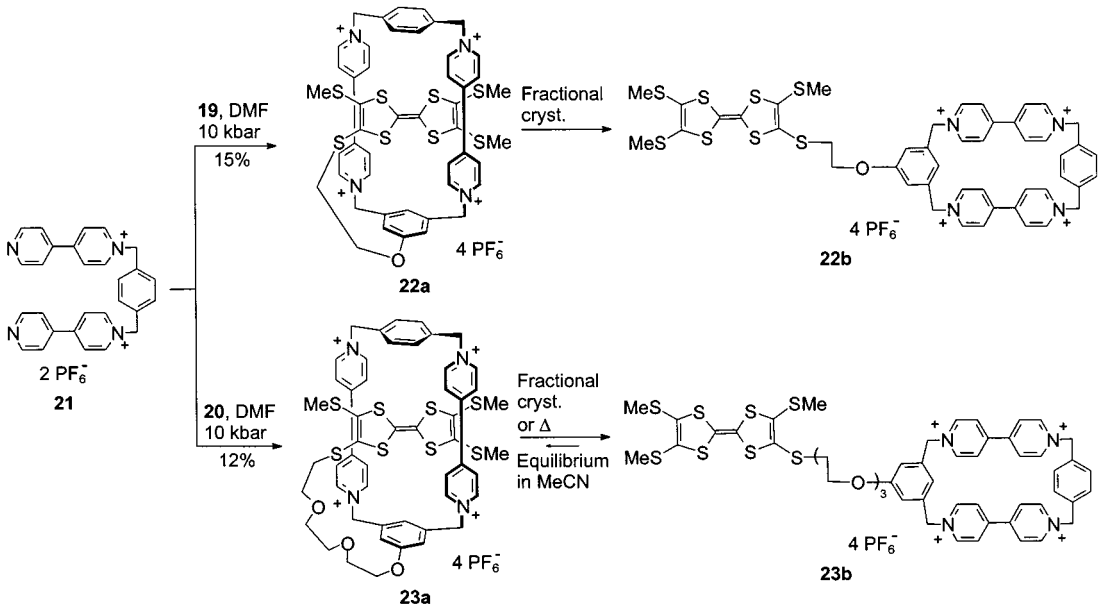
The UV/Vis absorption of a solution of the initially orange crystals of **23b** in acetonitrile was monitored with time (Figure 1a). The equilibrium between **23a** and **23b** was established after about 20 h, as indicated by the constant CT absorption ($\lambda_{max} \approx 785$ nm). The relatively small CT absorption indicates that only a small degree of "recomplexation" occurs, which was confirmed by ^1H NMR in CD_3CN (**23a**/**23b** ratio roughly 1:10). The small amount of **23a** gives rise to a displaced set of cyclophane proton signals and downfield-shifted SCH_3 proton signals (by about + 0.3−0.4 ppm). A downfield shift of the SCH_3 proton signals when the TTF is encircled by **2** has been observed previously for catenane compounds.[7d]

The question arises as to whether the "recomplexation" is truly of the anchimeric type. The absorption maxima at different times can be nicely fitted by a first-order equation[11] (Figure 1b), but of course this agreement does not give an unequivocal proof of exclusive anchimeric recomplexation. Nevertheless, since **22b** does not readily undergo intermolecular slippage in dilute solution, we would not expect this to be the case for **23b** either.[12]

Refluxing of the equilibrium solution of **23ab** in acetonitrile for 45 min resulted in almost complete conversion into **23b**, as indicated by a strong reduction of the CT band in the UV/Vis spectrum. However, the next day a CT absorption close to the starting equilibrium absorption at room temp. was re-established. This anchimeric decomplexation/recomplexation could be repeated.[13] Thus, **23ab**



Scheme 2. Synthesis of **19** and **20**



Scheme 3. Synthesis of **22ab** and **23ab**

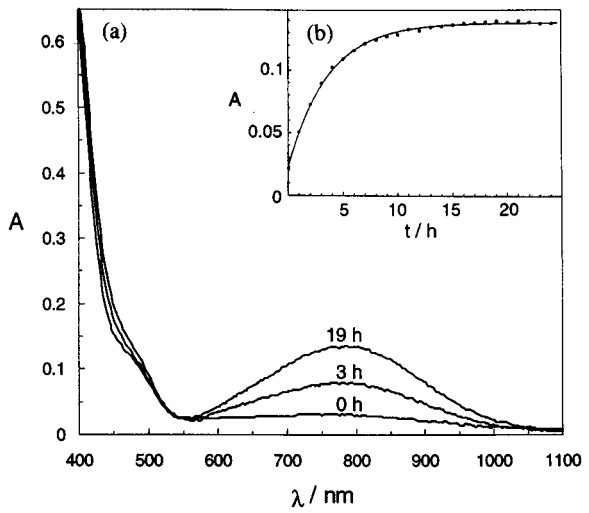


Figure 1a. The UV/Vis absorption spectrum of the initially "decomplexed" **23b** (2.4×10^{-4} M) in acetonitrile at three different times
Figure 1b. The time variation of the maximum absorbance ($\lambda_{max} \approx$ 785 nm) of initially "decomplexed" **23b** (2.6×10^{-4} M); a curve fit assuming first-order conditions is shown

behaves as a "thermo-switch". At higher temperatures, the gain in entropy associated with conversion of **23a** to **23b** outweighs the loss of donor−acceptor stabilization, and the equilibrium is displaced towards **23b**. As a final experiment, we subjected the solution of **23ab** to a pressure of 10 kbar once more (room temp., 4 d). However, this did not lead to any significant change in the absorption, i.e. the equilibrium was not displaced.

Cyclic voltammetry (vs. Ag/AgCl) confirmed the open structures of **22b** and **23b** [$E_{1,2}^{1/2}$(**22b**) = 0.55 V, 0.79 V; $E_{1,2}^{1/2}$(**23b**) = 0.54 V, 0.77 V; solvent MeCN] since no significant differences for the oxidation of the TTF unit were observed relative to **17** and **18**, respectively [$E_{1,2}^{1/2}$(**17**) = 0.53 V, 0.81 V; $E_{1,2}^{1/2}$(**18**) = 0.52 V, 0.78 V; solvent MeCN/CH_2Cl_2, 9:1]. We did not observe any difference between **23b** and the equilibrium solution of **23ab** upon electrochemical oxidation.[14]

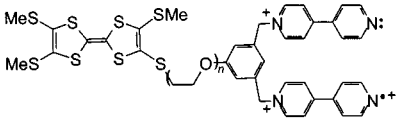
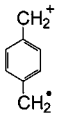
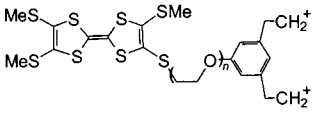
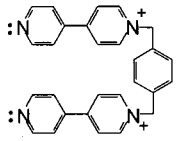
22ab and **23ab** were also characterized by electrospray mass spectrometry (ESMS), showing peaks attributable to $[M - n\ PF_6]^{n+}$ ($n = 1-4$), $[M - n\ PF_6]^{(n+1)+}$ ($n = 1-3$) and $[M - n\ PF_6]^{(n-1)+}$ (**22**, $n = 3,4$) (Table 1). Furthermore, a $[2\ M - 3\ PF_6]^{3+}$ ion was observed in the gas phase, but whether this was due to a real dimer or a dimeric cluster ion could not be established. Collisional activation (MS/MS) of the mass-selected $[M - 4\ PF_6]^{4+}$ ions resulted in similar fragmentations of the cyclic acceptor as previously observed for related TTF-based catenanes (Table 2).[7d]

By employing **6** as a template for the ring-closing reaction between **21** and **24** at 10 kbar, we obtained the *meta-para* cyclophane **3** in 12% yield (Scheme 4), i.e. in about the same yield as obtained with compounds **22** and **23**. The pseudorotaxane formation between unsubstituted TTF (**5**) and the *para-para* cyclophane **2** has previously been studied by X-ray analysis, UV/Vis and ^{1}H-NMR spectroscopy.[6] A high binding constant (K_a = 7000−10000 M^{-1}) in acetonitrile was determined for this complex. However, for the cyclophane **3**, the affinity for TTF is significantly decreased. A binding constant of 60 (± 15) M^{-1} (at 30°C) between **3** and **5** in acetonitrile was determined by NMR titration, the uncomplexed and complexed species being in rapid exchange with one another on the NMR time-scale (Scheme 5). The average chemical shift change of the two different cyclophane β-protons was plotted as a function of the TTF concentration, and the binding constant was determined by nonlinear curve-fitting of these data[15] (Figure 2). Mixing **1** and **5** in the same concentration range in acetonitrile did not alter the signals of the β-protons of **1** to any significant extent, confirming that external interactions do not contrib-

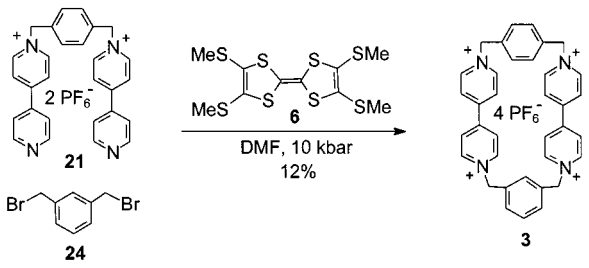
Table 1. ESMS data (*m*/*z*)

Compd.	$[M - 4\ PF_6]^{4+}$	$[M - 3\ PF_6]^{4+}$	$[M - 4\ PF_6]^{3+}$	$[M - 3\ PF_6]^{3+}$	$[M - 2\ PF_6]^{3+}$
22	234	270.3	312	360.3	408.7
23	256	292.3		389.7	438
	$[M - 3\ PF_6]^{2+}$	$[M - 2\ PF_6]^{2+}$	$[M - PF_6]^{2+}$	$[2\ M - 3\ PF_6]^{3+}$	$[M - PF_6]^{+}$
22	540.5	613		865.7	1371
23		657	729.5	924.3	1459

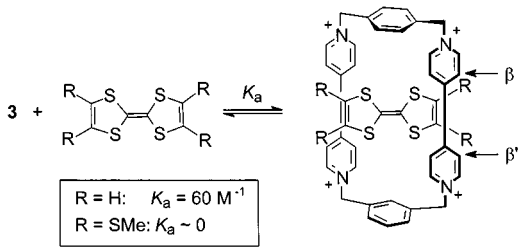
Table 2. ESMS/MS data (*m*/*z*)

Compd.	Parent ion	Daughter ions			
					
22	234	277.3	104	260	208
23	256	306.7	104	304	208

ute to the chemical shift changes observed for **3** upon addition of **5**. Not surprisingly, it was impossible to detect any complexation between **3** and the much weaker donor **6** by ^{1}H NMR, even after adding a ten-fold excess of **6** relative to **3** (at a conc. of ca. 4×10^{-4} M). The above equilibrium between **23a** and **23b** was strongly displaced towards **23b**, and disconnecting the host and the guest results in an even more unfavourable entropic contribution upon complexation. Moreover, this result supports the absence of intermolecular complexes of **23** at concentrations of 10^{-4} M.



Scheme 4. Template-assisted synthesis of **3**



Scheme 5. Complexation of TTF by **3**

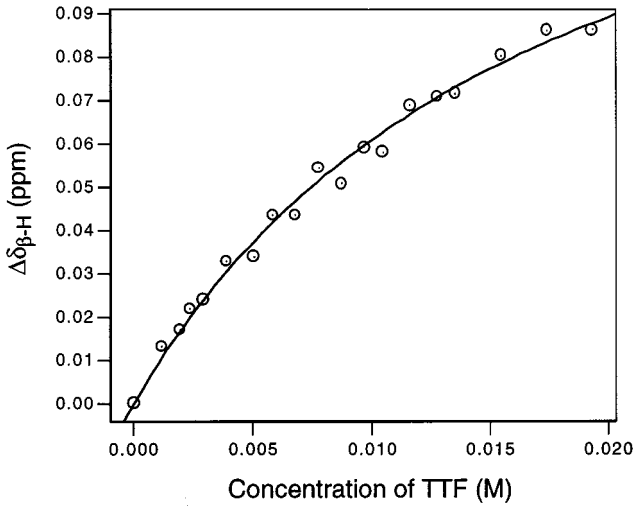
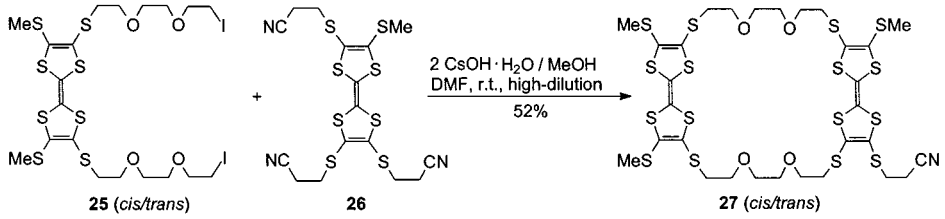


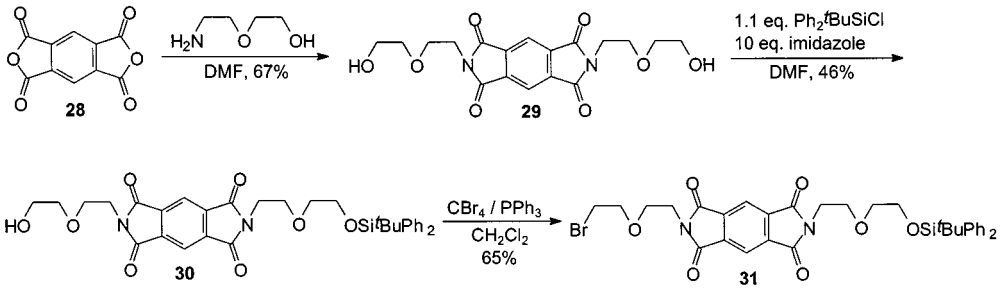
Figure 2. Average chemical shift change of the two different β-protons of **3** as a function of the concentration of TTF (**5**) in acetonitrile; $\Delta\delta_{\beta\text{-H}} = \delta_{\beta\text{-H}}(\text{uncomplexed}) - \delta_{\beta\text{-H}}$; the cyclophane **3** was kept at a constant concentration of 3.59×10^{-4} M[15]

An acceptor covalently attached to a donor TTF macrocycle constitutes a complementary system. In order to achieve this goal, we required a TTF macrocycle with a reactive "handle". This was accomplished by treating the bis(iodide) **25**[7d] with the 2,7(6)-bis(thiolate) generated from **26** by selectively removing the two cyanoethyl groups in the 2,7(6) positions using two equivalents of cesium hydroxide (Scheme 6). The resulting macrocycle **27** (*cis*/*trans*) containing one protected thiolate group may be considered as a key building block for the synthesis of oligomeric

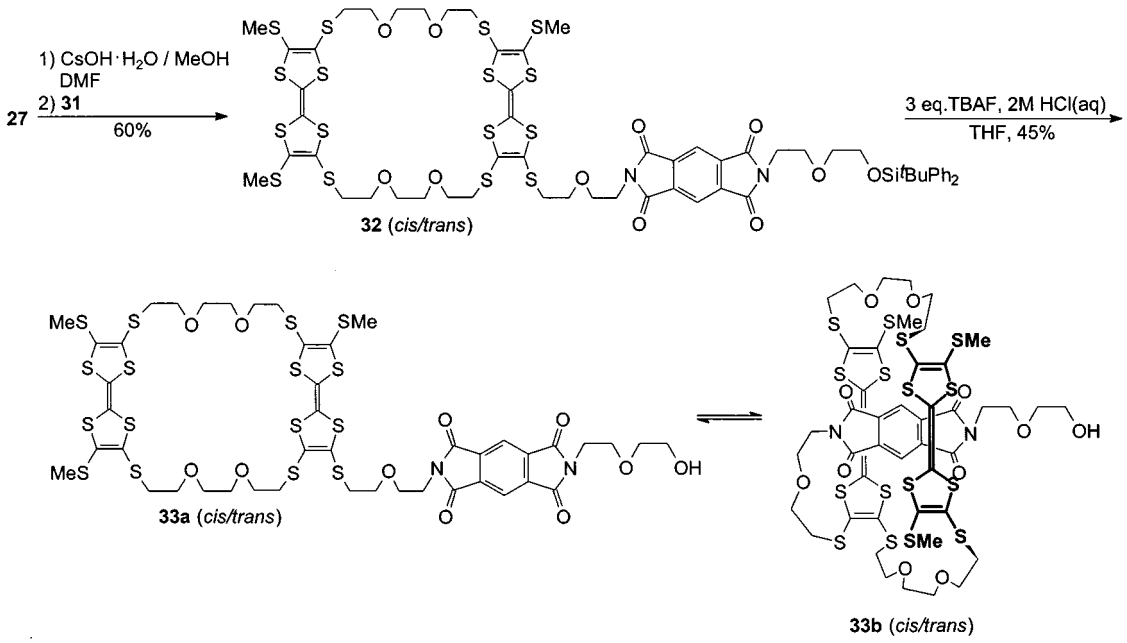
macrocyclic systems. Sanders et al. have successfully used a pyromellitic diimide acceptor for the construction of donor–acceptor catenanes.[16] In order to investigate an alternative noncharged system, we prepared the pyromellitic diimide **31** containing an electrophilic CH_2Br group (Scheme 7). First, pyromellitic bis(anhydride) (**28**) was converted into the diimide **29** by reaction with 2-(2-aminoethyloxy)-ethanol.[17] Protection of one of the two hydroxy groups with a *tert*-butyldiphenylsilyl group followed by bromination of the other hydroxy group using CBr_4/PPh_3 afforded the monobromide **31**. Treatment of the TTF macrocycle **27** with one equivalent of cesium hydroxide and alkylation of the generated thiolate with **31** gave compound **32** (*cis*/*trans*) in good yield (Scheme 8). The yield of the reaction is remarkably high considering the fact that pyromellitic diimide derivatives have shown instability towards strong nucleophiles. The only explanation for the high yield is the very fast nature of the thiolate alkylation. Finally, the OH protecting group was removed with tetrabutylammonium fluoride affording a greenish-brown equilibrium mixture of **33ab** (*cis*/*trans*). Whereas **22** and **23** were formed by template-assisted ring closure, the synthesis of **33** was not dependent on donor–acceptor interactions, the crucial step being nucleophilic attack of a reactive thiolate on CH_2Br. A comparison of the UV/Vis spectra of **32** and **33ab** in CH_2Cl_2 confirms the "self-complexing" ability of **33**. A shoulder on the usual TTF absorption was observed at about 580 nm for both compounds (Figure 3), but the extinction coefficient was much higher for **33ab** than for **32**. The bulky *tert*-butyldiphenylsilyl group in **32** most probably



Scheme 6. Synthesis of **27**



Scheme 7. Synthesis of **31**



Scheme 8. Synthesis of **33ab**

prevents the pyromellitic diimide from slipping into the cyclic donor. However, in the absence of this group, compound **33b** can be formed without any hindrance. ^{1}H-NMR spectroscopy offers evidence for an equilibrium between **33a** and **33b** (fast exchange). Thus, the two PMDI proton signals are shifted downfield by about + 0.07 ppm in $CDCl_3$ relative to those in **32**. However, in cyclic voltammetric studies we were not able to detect any difference between **33ab** and **8** (or **32**), suggesting that the equilibrium is displaced towards **33a**.

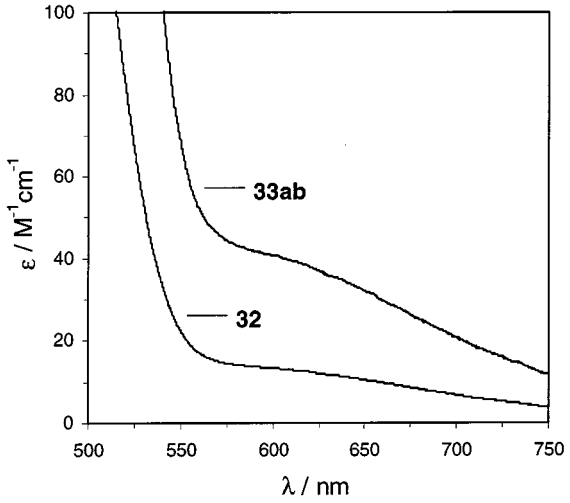


Figure 3. UV/Vis absorption spectra of **32** and **33ab** in dichloromethane

In conclusion, the two "self-complexing" macrocycles **22a** and **23a** were seen to "decomplex" upon fractional crystallization, even though their formation was dependent on the template effect provided by the TTF donor. An equilibrium "visible to the eye" between **23b** and **23a** was established in dilute solution, but favouring **23b**, which possesses higher degrees of freedom. The "complexation" could be switched "off" and "on" by subsequent heating and cooling, although the response was rather slow. The nature of the "recomplexation" observed seems to be of the intramolecular (anchimeric) type in dilute solution (10^{-4} M), whereas the synthetic step involving the ring closure may be assisted both intra- and intermolecularly. Mixing the separate components **3** and **6** did not result in complexation, thus indicating the importance of the linker present in **23a**. However, **3** was able to bind the better donor **5** with an association constant of 60 M^{-1}. Moreover, a pyromellitic diimide has been covalently attached to a bis(TTF) macrocycle (**33ab**) without relying on the template effect in the synthesis. An equilibrium between **33a** and **33b** has been observed by both UV/Vis and ^{1}H-NMR spectroscopy.

The systems described here may be viewed as first-generation model compounds. They all suffer from a relatively poor ability to undergo anchimeric complexation. This problem may be solved by using better electron donors than the present MeS-substituted TTF. Also, as in the case of **33**, by introducing more rigidity into the linkers connecting the two TTFs, a better preorganization of the donor and acceptor may lead to increased recognition abilities. Thus, in this way, the TTF macrocycle may constitute a better host for the linked acceptor. Alternatively, by oxidation of the TTF macrocycle generating TTF^{2+}, a host for a covalently linked electron donor may be obtained. The reversible conversion of TTF to TTF^{2+} has successfully been exploited by Stoddart et al. in the construction of a redox-controlled catenane switch[18] and of a three-pole supramolecular switch.[6d]

Experimental Section

All reactions were carried out under N_2. Acetone was dried by standing over Drierite; methanol was distilled from Mg; DMF was allowed to stand over molecular sieves (4 Å) for at least 3 d prior to use; THF was distilled from sodium/benzophenone. High-pressure experiments were performed in a Psika (20 kbar) instrument. Melting points were determined with a Büchi melting-point apparatus and are uncorrected. UV experiments were performed with Shimadzu UV160A and UV3100 instruments. NMR spectra were recorded with Bruker 250 MHz and Varian 300 MHz spectrometers; all chemical shifts are quoted in ppm relative to TMS or the solvent as internal standards. Electron impact (EI), fast-atom bombardment (FAB), and plasma desorption (PD) mass spectra were obtained with a Varian MAT 311A, a Kratos MS 60 TC, and a Bio-ion 20R, respectively. Electrospray (ES) mass spectra were recorded using a Finnigan MAT TSQ 700 triple-quadrupole mass spectrometer. The compounds were electrosprayed from acetonitrile solution. ESMS/MS experiments were performed using argon typically at a pressure of 0.7 mTorr. The ion of interest was selected by the first quadrupole, collisionally activated in the second (actually an octapole), and the products were analysed by the third quadrupole. CV experiments were performed at a scan rate of 100 mVs^{-1} using Bu_4NPF_6 as supporting electrolyte. Counter and working electrodes were made of Pt and the reference electrode was Ag/AgCl. Elemental analyses were performed at the Microanalytical Laboratory, University of Copenhagen, and at Atlantic Microlab, Inc., Norcross, Georgia.

Compound 10: A mixture of **9** (2.5 g, 12 mmol), 1,2-dibromoethane (7 mL, d = 2.17 g/mL, 81 mmol), and K_2CO_3 (2.0 g, 15 mmol) in anhydrous acetone (150 mL) was stirred under reflux overnight. The solvent was then removed in vacuo and the residue was extracted with CH_2Cl_2 (250 mL). The organic phase was washed with water and saturated aqueous NaCl solution, dried with anhydrous $MgSO_4$, and the solvent was removed in vacuo. The residue was subjected to column chromatography (silica, CH_2Cl_2), affording **10** (1.20 g, 32%) as a white solid; m.p. 71 °C. – ^{1}H NMR ($CDCl_3$): δ = 3.68 (t, J = 6.2 Hz, 2 H, $BrCH_2$), 3.95 (s, 6 H, CO_2CH_3), 4.39 (t, J = 6.2 Hz, 2 H, OCH_2), 7.77 (d, J = 1.6 Hz, 2 H, Ar), 8.32 (t, J = 1.6 Hz, 1 H, Ar). – ^{13}C NMR ($CDCl_3$): δ = 28.56 ($BrCH_2$), 53.40 (CH_3), 68.27 (OCH_2), 120.03, 123.71, 132.03, 158.32 (Ar), 166.07 (C=O). – MS (FAB); *m/z*: 316 [M^+]. – $C_{12}H_{13}BrO_5$ (317.1): calcd. C 45.45, H 4.13; found C 45.14, H 3.96.

Compound 11: A mixture of **9** (2.0 g, 9.5 mmol), 1,2-bis(2-iodoethyloxy)ethane (17.6 g, 47.6 mmol), and K_2CO_3 (1.4 g, 10 mmol) in anhydrous acetone (100 mL) was stirred under reflux overnight. The solvent was then removed in vacuo and the residue was extracted with CH_2Cl_2 (300 mL). The organic phase was washed with water and saturated aqueous NaCl solution, dried with anhydrous $MgSO_4$, and the solvent was removed in vacuo. The residue was subjected to column chromatography [silica, (i) CH_2Cl_2/petroleum

ether, 1:1, (ii) CH_2Cl_2/EtOAc, 10:1] affording **11** (2.80 g, 65%) as a pale-yellow oil. – ^{1}H NMR ($CDCl_3$): δ = 3.26 (t, *J* = 6.9 Hz, 2 H, ICH_2), 3.68–3.79 (m, 6 H, OCH_2), 3.89–3.94 (m, 8 H, OCH_2, CO_2CH_3), 4.23 (t, *J* = 4.8 Hz, 2 H, OCH_2), 7.78 (d, *J* = 1.4 Hz, 2 H, Ar), 8.28 (t, *J* = 1.4 Hz, 1 H, Ar). – ^{13}C NMR ($CDCl_3$): δ = 2.68 (ICH_2), 52.33 (CO_2CH_3), 68.01, 69.57, 70.23, 70.85, 71.96 (OCH_2), 120.00, 123.20, 131.80, 158.97 (Ar), 166.19 (C=O). – MS (EI); *m/z*: 452 [M^+]. – $C_{16}H_{21}IO_7$ (452.2): calcd. C 42.49, H 4.68; found C 42.65, H 4.69.

Compound 13: To a solution of **12** (1.33 g, 3.1 mmol) in dry DMF (100 mL) was added a solution of $CsOH·H_2O$ (0.57 g, 3.4 mmol) in dry MeOH (10 mL) and the reaction mixture was stirred for 30 min. Compound **10** (1.12 g, 3.7 mmol) in dry DMF (10 mL) was added, and the resulting mixture was stirred for a further 3 h. The solvent was then removed in vacuo and CH_2Cl_2 (150 mL) was added. The organic phase was washed with water and saturated aqueous NaCl, and dried with $MgSO_4$. The solvent was removed, and the residue was chromatographed (silica, CH_2Cl_2) affording **13** (1.8 g, 95%) as an orange oil. – ^{1}H NMR ($CDCl_3$): δ = 2.41–2.43 (3 s, 9 H, SCH_3), 3.21 (t, *J* = 6.4 Hz, 2 H, SCH_2), 3.95 (s, 6 H, CO_2CH_3), 4.26 (t, *J* = 6.4 Hz, 2 H, OCH_2), 7.77 (d, *J* = 1.4 Hz, 2 H, Ar), 8.30 (t, *J* = 1.4 Hz, 1 H, Ar). – MS (PD); *m/z*: 610.1 [M^+]. – $C_{21}H_{22}O_5S_8$ (610.9): calcd. C 41.29, H 3.63; found C 41.45, H 3.60.

Compound 14: Compound **14** was prepared in a similar manner from **11** and **12** in 88% yield as an orange oil. – ^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 9 H, SCH_3), 3.00 (m, 2 H, SCH_2), 3.69–3.73 (m, 8 H, OCH_2), 3.94 (s, 6 H, CO_2CH_3), 4.22 (m, 2 H, OCH_2), 7.78 (br, 2 H, Ar), 8.28 (br, 1 H, Ar). – ^{13}C NMR ($CDCl_3$): δ = 18.96, 19.02 (SCH_3), 35.27 (SCH_2), 52.31 (CO_2CH_3), 67.98, 69.54, 70.02, 70.51, 70.78 (OCH_2), 110.77, 110.90 (TTF fulvene C=C), 119.93, 123.15 (Ar), 124.45, 127.36, 127.54, 130.83 (TTF cyclic C=C), 131.75, 158.92 (Ar), 166.14 (C=O). – MS (PD); *m/z*: 697.7 [M^+]. – $C_{25}H_{30}O_7S_8$ (699.0): calcd. C 42.96, H 4.33; found C 43.25, H 4.40.

Compound 15: $LiAlH_4$ (0.15 g, 4.0 mmol) was suspended in dry THF (15 mL). Then, **13** (1.04 g, 1.7 mmol) in dry THF (15 mL) was added over a period of 5 min with stirring, and the resulting mixture was refluxed for 2 h. After cooling to room temp., water (50 mL) was carefully added, and the solution was extracted with CH_2Cl_2 (3 × 200 mL). The organic phase was dried ($MgSO_4$) and the solvent was evaporated in vacuo. Column chromatography (silica, EtOAc) gave **15** (0.57 g, 60%) as an orange solid; m.p. 108–109 °C. – ^{1}H NMR ($CDCl_3$): δ = 2.40–2.44 (3 s, 9 H, SCH_3), 3.18 (t, *J* = 6.6 Hz, 2 H, SCH_2), 4.21 (t, *J* = 6.6 Hz, 2 H, OCH_2), 4.68 (d, *J* = 5.2 Hz, 4 H, CH_2OH), 6.85 (br., 2 H, Ar), 6.97 (br., 1 H, Ar). – MS (PD); *m/z*: 554.2 [M^+]. – $C_{19}H_{22}O_3S_8$ (554.9): calcd. C 41.13, H 4.00; found C 41.36, H 3.86.

Compound 16: Compound **16** was obtained in a similar manner from **14** in 79% yield as an orange solid; m.p. 77–78 °C. – ^{1}H NMR ($CDCl_3$): δ = 2.19–2.41 (br., 2 H, OH), 2.43 (2 s, 9 H, SCH_3), 3.00 (t, *J* = 6.7 Hz, 2 H, SCH_2), 3.67–3.73 (m, 6 H, OCH_2), 3.86 (t, *J* = 4.6 Hz, 2 H, OCH_2), 4.14 (t, *J* = 4.6 Hz, 2 H, OCH_2), 4.63 (s, 4 H, CH_2OH), 6.84 (br., 2 H, Ar), 6.91 (br., 1 H, Ar). – MS (PD); *m/z*: 641.7 [M^+]. – $C_{23}H_{30}O_5S_8$ (643.0): calcd. C 42.97, H 4.70; found C 43.28, H 4.69.

Compound 17: To a solution of **15** (0.38 g, 0.68 mmol) in CH_2Cl_2 (50 mL) were added $MeSO_2Cl$ (0.6 mL) and DBU (1.4 mL). The reaction mixture was stirred for 2 1/2 h at room temp., and then further portions of $MeSO_2Cl$ (0.5 mL) and DBU (1.4 mL) were added. After stirring for a further 2 1/2 h, LiCl (1.2 g, 28 mmol) was added, and the mixture was left overnight under stirring. It was subsequently diluted with CH_2Cl_2 (100 mL), washed with water, and dried ($MgSO_4$). The solvent was removed, and the residue was chromatographed (silica, CH_2Cl_2/EtOAc, 1:1), affording **17** (0.34 g, 84%) as an orange solid; m.p. 78–80 °C. – ^{1}H NMR ($CDCl_3$): δ = 2.39–2.45 (3 s, 9 H, SCH_3), 3.17 (t, *J* = 4.9 Hz, 2 H, SCH_2), 4.21 (m, 2 H, OCH_2), 4.55 (s, 4 H, $ClCH_2$), 6.89 (d, *J* = 1.2 Hz, 2 H, Ar), 7.02 (br., 1 H, Ar). – MS (PD); *m/z*: 590.4 [M^+]. – $C_{19}H_{20}Cl_2OS_8$ (591.8): calcd. C 38.56, H 3.41; found C 38.85, H 3.33.

Compound 18: Compound **18** was obtained in a similar manner from **16** in 58% yield as an orange oil. – ^{1}H NMR ($CDCl_3$): δ = 2.39–2.45 (3 s, 9 H, SCH_3), 3.00 (t, *J* = 6.8 Hz, 2 H, SCH_2), 3.67–3.74 (m, 6 H, OCH_2), 3.87 (t, *J* = 4.8 Hz, 2 H, OCH_2), 4.16 (t, *J* = 4.6 Hz, 2 H, OCH_2), 4.54 (s, 4 H, $ClCH_2$), 6.92 (br., 2 H, Ar), 6.99 (br., 1 H, Ar). – MS (PD); *m/z*: 677.2 [M^+]. – $C_{23}H_{28}Cl_2O_3S_8$ (679.9): calcd. C 40.63, H 4.15; found C 41.05, H 4.20.

Compound 19: A solution of **17** (0.32 g, 0.54 mmol) and LiBr (6.0 g, 69 mmol) in dry acetone (100 mL) was refluxed overnight. The solvent was then removed in vacuo, and the residue was dissolved in CH_2Cl_2 (150 mL). The resulting solution was washed with water and dried ($MgSO_4$). Evaporation of the solvent followed by column chromatography of the residue (silica, CH_2Cl_2) afforded **19** (0.33 g, 90%) as an orange solid. According to PDMS, the product contained a small amount of the monosubstituted compound (Cl,Br), which could not be removed by chromatography. – ^{1}H NMR ($CDCl_3$): δ = 2.39–2.44 (3 s, 9 H, SCH_3), 3.17 (t, *J* = 6.5 Hz, 2 H, SCH_2), 4.20 (t, *J* = 6.5 Hz, 2 H, OCH_2), 4.43 (s, 4 H, $BrCH_2$), 6.86 (d, *J* = 1.1 Hz, 2 H, Ar), 7.02 (br., 1 H, Ar). – MS (PD); *m/z*: 680.2 [M^+]. – Isotope pattern; *m/z* (% calcd./% found): 678 (42.7/42.3), 679 (12.0/11.5), 680 (100/100), 681 (27.5/27.8), 682 (76.3/72.6), 683 (20.4/20.1), 684 (22.2/22.6), 685 (5.5/5.9), 686 (3.5/3.8).

Compound 20: Compound **20** was obtained in a similar manner from **18** in 96% yield as an orange oil containing a small amount of the monosubstituted compound (Cl,Br). – ^{1}H NMR ($CDCl_3$): δ = 2.44 (br., 9 H, SCH_3), 3.01 (t, *J* = 6.6 Hz, 2 H, SCH_2), 3.66–3.75 (m, 6 H, OCH_2), 3.87 (t, *J* = 4.8 Hz, 2 H, OCH_2), 4.16 (t, *J* = 4.8 Hz, 2 H, OCH_2), 4.44 (s, 4 H, $BrCH_2$), 6.90 (d, *J* = 1.2 Hz, 2 H, Ar), 7.01 (br., 1 H, Ar). – MS (PD); *m/z*: 767.7 [M^+].

Compound 22ab: A mixture of **19** (0.29 g, 0.43 mmol) and **21** (0.27 g, 0.38 mmol) in DMF (12 mL) was transferred to a Teflon tube and subjected to a pressure of 10 kbar for 6 d. The solvent was then removed in vacuo to leave a green residue, which was subjected to column chromatography (silica, MeOH/2 M aqueous NH_4Cl/$MeNO_2$, 7:2:1). The green fraction obtained was concentrated in vacuo. The product was redissolved in the minimum amount of water, and then saturated aqueous NH_4PF_6 was added until precipitation was complete. Filtration and washing with water afforded **22ab** as a green compound (0.086 g, 15%). Fractional crystallization by condensation of diisopropyl ether into an acetonitrile solution of **22ab** afforded the uncomplexed orange compound **22b**. – ^{1}H NMR (CD_3CN) of **22b**: δ = 2.40/2.41 (2 s, 9 H, SCH_3), 3.28 (t, *J* = 6.0 Hz, 2 H, SCH_2), 4.34 (t, *J* = 6.0 Hz, 2 H, OCH_2), 5.69 (s, 4 H, NCH_2), 5.76 (s, 4 H, NCH_2), 6.89 (s, 1 H, Ar), 7.30 (d, *J* = 1.3 Hz, 2 H, Ar), 7.60 (s, 4 H, Ar), 8.05 (d, *J* = 6.9 Hz, 4 H, β-H), 8.07 (d, *J* = 6.9 Hz, 4 H, β-H), 8.74 (d, *J* = 6.9 Hz, 4 H, α-H), 8.85 (d, *J* = 6.9 Hz, 4 H, α-H). – $C_{47}H_{44}F_{24}N_4OP_4S_8$ (1517.2): calcd. C 37.21, H 2.92, N 3.69; found C 36.85, H 3.01, N 3.63.

Compound 23ab: A mixture of **20** (0.16 g, 0.21 mmol) and **21** (0.13 g, 0.18 mmol) in DMF (12 mL) was subjected to a pressure of 10 kbar for 6 d. The solvent was then removed in vacuo to leave a green residue, which was subjected to column chromatography (silica, MeOH/2 M aqueous NH_4Cl/$MeNO_2$, 7:2:1). The green frac-

tion obtained was concentrated in vacuo. The product was redissolved in the minimum amount of water, and saturated aqueous NH_4PF_6 was added until precipitation was complete. Filtration and washing with water afforded **23ab** as a solid containing both green and orange compounds (0.035 g, 12%). Fractional crystallization by condensation of diisopropyl ether into an acetonitrile solution of **23ab** afforded the uncomplexed orange compound **23b**. – ^{1}H NMR (CD_3CN) of **23b**: δ = 2.39/2.42 (2 s, 9 H, SCH_3), 3.01 (t, *J* = 6.1 Hz, 2 H, SCH_2), 3.57–3.68 (m, 6 H, OCH_2), 3.85 (m, 2 H, OCH_2), 4.24 (t, *J* = 4.5 Hz, 2 H, OCH_2), 5.69 (s, 4 H, NCH_2), 5.76 (s, 4 H, NCH_2), 6.89 (s, 1 H, Ar), 7.32 (d, *J* = 1.4 Hz, 2 H, Ar), 7.60 (s, 4 H, Ar), 8.05 (d, *J* = 6.9 Hz, 4 H, β-H), 8.07 (d, *J* = 6.9 Hz, 4 H, β-H), 8.75 (d, *J* = 6.9 Hz, 4 H, α-H), 8.85 (d, *J* = 6.9 Hz, 4 H, α-H). – $C_{51}H_{52}F_{24}N_4O_3P_4S_8$ (1605.3): calcd. C 38.16, H 3.26, N 3.49; found C 38.46, H 3.16, N 3.26.

Compound 3: A mixture of **21** (0.219 g, 0.31 mmol), **24** (0.082 g, 0.031 mmol) and **6** (0.301 g, 0.77 mmol) in DMF (12 mL) was subjected to a pressure of 10 kbar for 6 d. The solvent was then removed in vacuo to leave a green residue, which was washed with CH_2Cl_2 and subjected to column chromatography (silica, MeOH/H_2O/saturated aq. NH_4Cl, 6:3:1). The cyclophane fraction was concentrated in vacuo and the residue was dissolved in the minimum amount of water. Saturated aqueous NH_4PF_6 was then added until precipitation was complete. Filtration and washing with water afforded **3** (0.040 g, 12%) as a white solid. – ^{1}H NMR (CD_3CN): δ = 5.76 (s, 8 H, NCH_2), 7.34 (s, 1 H, Ar), 7.60 (s, 4 H, Ar), 7.67 (m, 1 H, Ar), 7.76 (m, 2 H, Ar), 8.06 (2 d, *J* = 6.9 Hz, 8 H, β-H), 8.75 (d, *J* = 6.9 Hz, 4 H, α-H), 8.84 (d, *J* = 6.9 Hz, α-H). – MS (FAB); *m*/*z*: 665 [M – 3 PF_6]$^+$, 810 [M – 2 PF_6]$^+$, 955 [M – PF_6]$^+$.

Compound 27 (*cis*/*trans*): To a stirred solution of **26** (0.51 g, 1.0 mmol) in DMF (50 mL) at room temp., a solution of $CsOH·H_2O$ (0.36 g, 2.1 mmol) in methanol (10 mL) was added dropwise over a period of 30 min. The solution was stirred for 1 h. Then, this solution and a solution of **25** (0.86 g, 1.0 mmol) in DMF (60 mL) were added simultaneously, over a period of 20 h at room temp., to DMF (100 mL) under high-dilution conditions by means of a perfusor pump. Stirring was continued for a further 3 h, and then the reaction mixture was concentrated in vacuo. CH_2Cl_2 (100 mL) was added, and the organic solution was washed with water, and dried ($MgSO_4$). The solvent was removed and the residue was purified by column chromatography (silica, CH_2Cl_2/EtOAc, 10:1), affording **27** (0.52 g, 52%) as an orange semicrystalline oil. – ^{1}H NMR ($CDCl_3$): δ = 2.44–2.46 (3 s, 9 H, SCH_3), 2.70–2.77 (m, 2 H, CH_2CN), 2.98–3.10 (m, 10 H, SCH_2), 3.61–3.76 (m, 16 H, OCH_2). – MS (PD); *m*/*z*: 986.3 [M$^+$]. – $C_{30}H_{37}NO_4$ (988.6): calcd. C 36.45, H 3.77, N 1.42; found C 36.62, H 3.55, N 1.55.

Compound 29: A solution of pyromellitic bis(anhydride) **28** (4.36 g, 0.02 mol) and 2-(2-aminoethyloxy)ethanol (5.3 g, 0.05 mol) in DMF (170 mL) was refluxed overnight. After cooling to room temperature, the mixture was concentrated to a volume of ca. 50 mL, and then water was added in order to precipitate the product. The flask was placed in a refrigerator overnight to complete the precipitation. The product was subsequently collected by filtration, washed with water, and dried in vacuo at 60°C, affording **29** (5.28 g, 67%) as a white solid; m.p. 184–184.5°C. – ^{1}H NMR ($CDCl_3$): δ = 2.22 (s, 2 H, OH), 3.50–4.00 (m, 16 H, CH_2), 8.29 (s, 2 H, PMDI). – ^{13}C NMR ($CDCl_3$): δ = 38.16 (CH_2OH), 61.65 (NCH_2), 67.94, 72.21 (OCH_2), 118.48 (PMDI CH), 137.29 (PMDI C–C), 166.39 (C=O). – MS (FAB); *m*/*z* (%): 393 [M + H$^+$] (59), 331 (26), 307 (100), 289 (65). – $C_{18}H_{20}N_2O_8$ (392.4): calcd. C 55.10, H 5.14, N 7.14; found C 54.84, H 4.99, N 7.16.

Compound 30: To a solution of **29** (3.00 g, 7.63 mmol) and imidazole (5.21 g, 76.5 mmol) in dry DMF was slowly added *t*$BuPh_2SiCl$ (2.31 g, 8.41 mmol) and the resulting mixture was stirred overnight. It was subsequently diluted with CH_2Cl_2 (125 mL), washed with 4 M HCl (3 × 100 mL) and water (2 × 100 mL), and dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was subjected to column chromatography (silica, 2% MeOH in CH_2Cl_2), affording **30** (2.22 g, 46%) as a clear, colourless oil. – ^{1}H NMR ($CDCl_3$): δ = 0.97 (s, 9 H, CH_3), 2.30 (s, 1 H, OH), 3.60 (2 t, *J* = 5.3 Hz, 4 H, CH_2), 3.77 (m, 8 H, CH_2), 3.96 (2 t, *J* = 5.3 Hz, 4 H, CH_2), 7.36 (m, 6 H, Ph), 7.63 (dd, *J* = 7.5 Hz, 1.8 Hz, 4 H, Ph), 8.22 (s, 2 H, PMDI). – ^{13}C NMR ($CDCl_3$): δ = 18.83 [Si*C*(CH_3)$_3$], 26.44 (CH_3), 37.67 (NCH_2), 61.41 (CH_2OH), 63.16 (CH_2OSi), 67.39, 67.71, 71.94, 72.09 (OCH_2), 118.13 (PMDI CH), 127.54, 129.52, 133.45, 135.41 (Ph), 136.99, 137.16 (PMDI C–C), 166.05, 166.25 (C=O). – MS (EI); *m*/*z* (%): 573 [M$^+$ – *t*Bu] (13), 393 (25), 331 (100), 287 (29), 269 (47), 256 (31), 199 (32), 173 (29).

Compound 31: To a stirred solution of **30** (0.98 g, 1.6 mmol) and CBr_4 (0.8 g, 2.3 mmol) in CH_2Cl_2, PPh_3 (0.61 g, 2.3 mmol) was added in three portions. The resulting mixture was stirred overnight and then the solvent was evaporated in vacuo. **31** (0.72 g, 65%) was obtained after column chromatography (silica, 5% EtOAc in CH_2Cl_2) as a clear, yellowish oil. – ^{1}H NMR ($CDCl_3$): δ = 0.97 (s, 9 H, CH_3), 3.39 (t, *J* = 6.0 Hz, 2 H, $BrCH_2$), 3.58 (t, *J* = 5.0 Hz, 2 H, CH_2), 3.79 (m, 8 H, CH_2), 3.97 (t, *J* = 5.3 Hz, 4 H, CH_2), 7.38 (m, 6 H, Ph), 7.62 (dd, *J* = 7.7 Hz, 1.9 Hz, 4 H, Ph), 8.23 (s, 2 H, PMDI). – ^{13}C NMR ($CDCl_3$): δ = 18.99 [Si*C*(CH_3)$_3$], 26.59 (CH_3), 30.17 (CH_2Br), 37.79, 38.12 (NCH_2), 63.30 (CH_2OSi), 67.37, 67.56, 70.44, 72.05 (OCH_2), 118.28 (PMDI CH), 127.68, 129.66, 135.58 (Ph), 137.18, 137.30 (PMDI C–C), 166.21, 166.26 (C=O). – MS (EI); *m*/*z* (%): 635 [M$^+$ – *t*Bu] (1), 393 (100), 256 (31), 173 (32), 135 (12). – $C_{34}H_{37}BrN_2O_7Si$ (693.7): calcd. C 58.87, H 5.38, N 4.04; found C 58.71, H 5.37, N 3.87.

Compound 32 (*cis*/*trans*): To a solution of **27** (0.92 g, 0.93 mmol) in dry, degassed DMF (20 mL) was added $CsOH·H_2O$ (0.17 g, 1.00 mmol) in dry MeOH (5 mL). After stirring for 30 min, **31** (1.10 g, 1.59 mmol) was added. The resulting mixture was stirred overnight and then concentrated in vacuo. The residue was redissolved in CH_2Cl_2, and this solution was washed with brine and water, dried ($MgSO_4$), and the solvent was evaporated. Chromatographic workup (silica, 5% EtOAc in CH_2Cl_2) gave **32** (0.86 g, 60%) as a greenish-brown glass. – ^{1}H NMR ($CDCl_3$): δ = 0.98 (s, 9 H, CH_3), 2.43/2.44 (2 s, 9 H, SCH_3), 3.00 (m, 10 H, SCH_2), 3.64 (m, 26 H, CH_2), 3.95 (t, *J* = 4.2 Hz, 4 H, CH_2), 7.38 (m, 6 H, Ph), 7.62 (dd, *J* = 1.6 Hz, 7.5 Hz, 4 H, Ph), 8.22 (s, 2 H, PMDI). – ^{13}C NMR ($CDCl_3$): δ = 18.98 [Si*C*(CH_3)$_3$], 26.59 (SCH_3), 35.14, 35.29 (SCH_2), 37.88, 38.08 (NCH_2), 63.29 (CH_2OSi), 67.40, 67.55, 69.25, 70.05, 70.15, 70.44, 70.52, 72.03 (OCH_2), 110.52, 111.03 (TTF fulvene C=C), 118.25 (PMDI CH), 124.19, 124.90 (TTF cyclic C=C), 127.67 (Ph), 129.64 (Ph), 130.15, 130.23 (TTF cyclic C=C), 133.58 (Ph), 135.56 (Ph), 137.14, 137.25 (PMDI C–C), 166.18, 166.23 (C=O). – MS (FAB); *m*/*z* (%): 1546 [M$^+$]. – $C_{61}H_{70}N_2O_{11}S_{16}Si$ (1548.3): calcd. C 47.32, H 4.56, N 1.81, S 33.13; found C 47.20, H 4.48, N 1.78, S 33.34.

Compound 33ab (*cis*/*trans*): To a solution of **32** (100 mg, 0.065 mmol) in THF (5 mL) were added a 1 M solution of tetrabutylammonium fluoride (TBAF) in THF (0.2 mL, 0.2 mmol) and 2 M HCl (0.1 mL, 0.2 mmol) and the resulting mixture was stirred overnight. The solvent was then evaporated, and the residue was redissolved in CH_2Cl_2. This solution was washed with water and dried ($MgSO_4$). Column chromatography (silica, 5% MeOH in CH_2Cl_2) gave **33ab** (0.038 g, 45%) as a greenish glass. – ^{1}H NMR

($CDCl_3$): δ = 2.42 (2 s, 9 H, SCH_3), 2.97 (m, 10 H, SCH_2), 3.63 (m, 26 H, CH_2), 3.96 (t, J = 5.1 Hz, 4 H, CH_2), 8.29 (s, 2 H, PMDI). − ^{13}C NMR ($CDCl_3$): δ = 19.04 (SCH_3), 35.12, 35.32, 35.49 (SCH_2), 37.97, 38.14 (NCH_2), 61.62, 67.34, 67.94, 69.22, 70.11, 70.47, 72.14 (OCH_2), 118.26 (PMDI CH), 137.03, 137.19 (PMDI C−C), 166.00, 166.19 (C=O); signals from the TTF core were not detected. − MS (FAB); *m/z* (%): 1308 [M^+]. − $C_{45}H_{52}N_2O_{11}S_{16}$ (1309.9): calcd. C 41.26, H 4.00, N 2.14; found C 41.16, H 3.92, N 2.04.

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[11] For first-order equilibria the following relationship between absorbance A and time t can be evaluated: $A = A_0\exp[-(k_+ + k_-)t]$ + constant·{1 − $\exp[-(k_+ + k_-)t]$}, where k_+ and k_- denote the rate constants for the forward and backward processes, and A_0 is the initial absorption.

[12] Owing to the limited amount of **23b** available, we were not able to measure the extinction coefficient at several different concentrations in order to ascertain whether anchimeric complexation is still dominant at high concentrations, i.e. to check whether the Lambert−Beer law is satisfied over a broad concentration range. Moreover, the fact that the equilibrium disfavours **23a**, which is responsible for the CT absorption, renders such a determination uncertain.

[13] A small decrease in the equilibrium CT absorption (ca. 5%) was observed after each experiment, which may be accounted for by chemical decomposition upon refluxing.

[14] Anodic shifts are generally observed for TTFs encircled by **2** in either catenanes or rotaxanes.[6][7]

[15] The data were fitted (Ultra-Fit 2.11) using the following expression relating the chemical shift change (Δδ) of the host (i.e. **3**) and the concentration c of the guest (i.e. TTF):

$$\Delta\delta = \frac{\Delta\delta(\text{sat})}{c(\text{host})} \cdot \frac{K_a\{c(\text{host}) + c(\text{guest})\} + 1 - \left\{K_a\{c(\text{host}) + c(\text{guest})\} + 1\right)^2 - 4K_a^2 c(\text{host})c(\text{guest})\}^{0.5}}{2K_a}$$

The concentration of host was kept constant at c(host); Δδ(sat) denotes the saturated chemical shift change, i.e. when all of the host is present in its complexed form.

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