Pergamon

Tetrahedron 57 (2001) 947–956

TETRAHEDRON

Tetrathiafulvalene-containing pseudorotaxanes formed between dibenzylammonium salts and crown ethers

Peter R. Ashton,[a] Jan Becher,[b,*] Matthew C. T. Fyfe,[c] Mogens Brøndsted Nielsen,[b,c,†] J. Fraser Stoddart,[c,*] Andrew J. P. White[d] and David J. Williams[d,*]

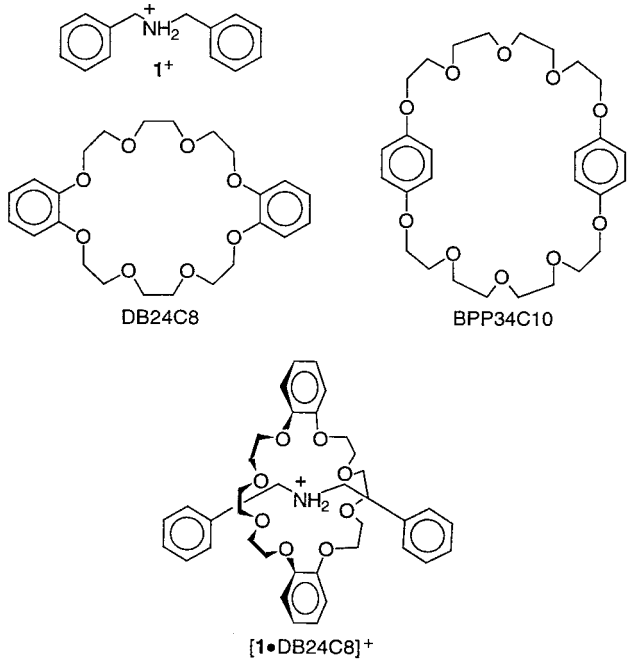
[a]*School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*
[b]*Department of Chemistry, University of Southern Denmark (Odense University), Campusvej 55, DK-5230 Odense M, Denmark*
[c]*Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, CA 90095, USA*
[d]*Department of Chemistry, Imperial College, South Kensington, London SW7 2AY, UK*

Received 21 September 2000; accepted 3 November 2000

Abstract—The synthesis of two tetrathiafulvalene (TTF) derivatives, one carrying arms incorporating four dibenzylammonium centers and the other encompassing two annulated crown ether rings—i.e., hydrogen bond donor and acceptor functions, respectively, is described. In the presence of macrocyclic polyethers—e.g., DB24C8 and BPP34C10—and dibenzylammonium hexafluorophosphate, these two TTF derivatives form pseudorotaxanes as evidenced by ^{1}H NMR spectroscopy, mass spectrometry, and differential pulse voltammetry.

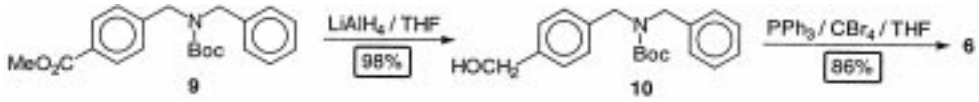
1. Introduction

The efficient π-electron donor, tetrathiafulvalene (TTF), has found wide application in many areas of macrocyclic[1] and supramolecular[2] chemistry. Nowadays, synthetic protocols are available for constructing elaborate multiply-bridged TTF macrocycles, some of which are able to form host–guest complexes with electron-deficient compounds as a result of donor-acceptor interactions. Also, considerable effort has been devoted[3] to employing hydrogen bonding for self-assembling supramolecular systems and networks based on TTF. Thus, the promotion of short intermolecular distances between TTF units in the crystal stacking is of crucial importance for the development of organic conductors. Moreover, the ability of TTF to switch reversibly between three redox states (0, +1, +2) upon oxidation/reduction, at potentials which are influenced by the presence of interacting molecules/ions, makes it a very good candidate for being incorporated into supramolecular assemblies.[2] Consequently, we decided to explore the ability of hydrogen bonds to govern the formation of TTF pseudorotaxanes and other supermolecules with interwoven architectures, employing the recognition motif that exists between secondary dialkylammonium ions and macrocyclic polyethers. Thus, the dibenzylammonium ion $\mathbf{1}^+$ and dibenzo[24]crown-8 (DB24C8) form a 1:1 complex $[\mathbf{1}\cdot DB24C8]^+$—in both the solution and solid states[4]—which is stabilized for the most part by hydrogen bonds between the electron-donating oxygen atoms of DB24C8 and (i) the NH_2^+ protons ($[^+N–H\cdots O]$) and (ii) the benzylic methylene protons ($[C–H\cdots O]$) of $\mathbf{1}^+$.



Keywords: crown ethers; dibenzylammonium salts; pseudorotaxanes; self-assembly; tetrathiafulvalene.
* Corresponding authors. Tel. +310-206-7078; fax: +310-206-1843; e-mail: stoddart@chem.ucla.edu
† Present address: Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule (ETH), Universitätsstrasse 16, CH-8092 Zürich, Switzerland.

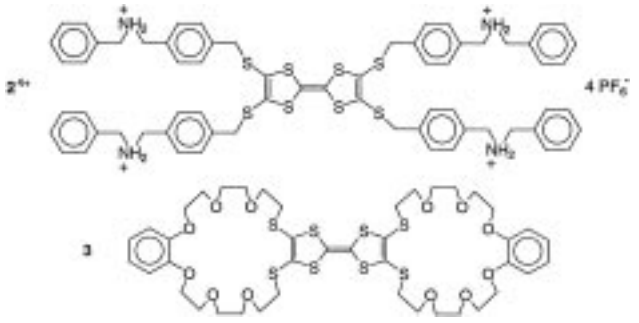
0040–4020/01/$ - see front matter
PII: S0040-4020(00)01062-0



Scheme 1. Synthesis of Boc-protected dibenzylamine building block containing a benzylic bromide.

To date, a number of pseudorotaxane superstructures involving secondary dialkyl- or dibenzylammonium ions and crown ethers, such as DB24C8 or bis-*p*-phenylene[34]-crown-10 (BPP34C10), have been reported,[4,5] including both singly- and multiply-stranded pseudorotaxanes, in addition to interlocked molecular compounds with interwoven architectures formed from branched oligoammonium cations. Thus, by employing a porphyrin as the central core, an analog resembling the photosynthetic special pair has been self-assembled as a 4+2 interwoven complex.[5h]

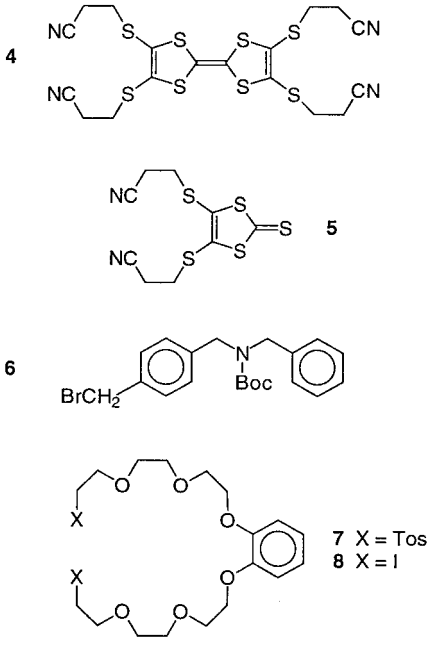
We now describe the first examples of such supramolecular systems containing the redox responsive unit TTF. Combining TTF with the functions in either $\mathbf{1}^{+}$ or DB24C8 leads to the two complementary compounds $\mathbf{2}^{4+}$ and **3**, i.e., a TTF tetracation and a TTF-catechol biscrown. The syntheses of these target molecules are described and their abilities to form complexes with DB24C8, BPP34C10 and $\mathbf{1}^{+}$, in turn, are discussed.



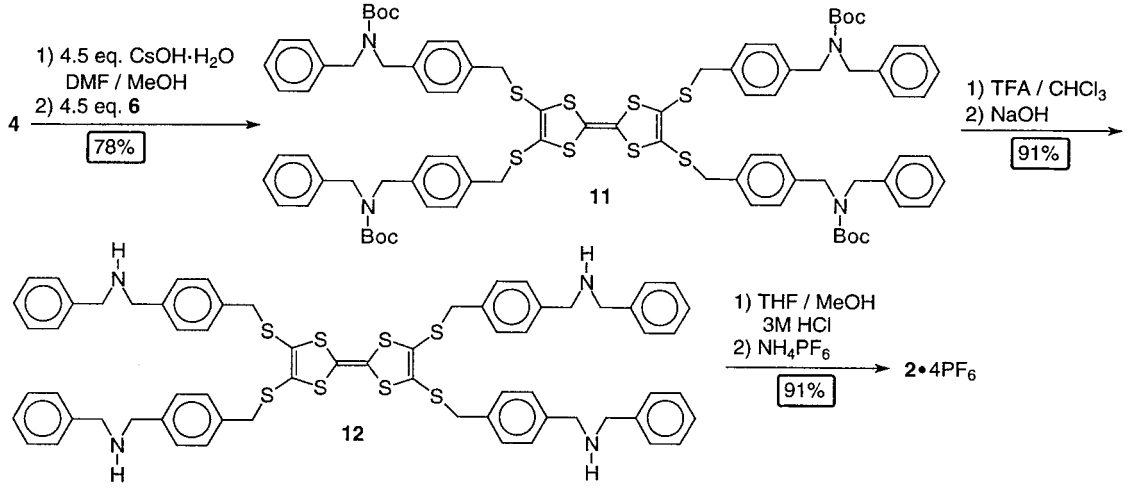
2. Results and discussion

2.1. Synthesis

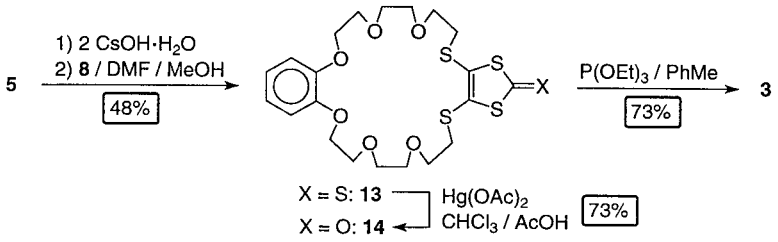
Retrosynthetic analyses suggest **4**–**8** as possible presursors for $\mathbf{2}^{4+}$ and **3**. The cyanoethyl-protected TTF-thiolate **4** and its 'half-unit', 1,3-thiole-2-thione (**5**), are easily deprotected using CsOH as base.[6] The thiolate functions, which are generated in this fashion, can then be realkylated with the alkylating reagents **6**–**8**.



The synthesis of the bromide **6** is summarized in Scheme 1. Firstly, the ester **9**[5f] was reduced with $LiAlH_4$ according to a



Scheme 2. Synthesis of TTF-tetracation.



Scheme 3. Synthesis of TTF-biscrown.

modified literature procedure,[5f] generating the alcohol **10**, which was subsequently treated with PPh_3/CBr_4, yielding **6**.

The bromide **6** was then reacted (Scheme 2) with the tetrathiolate (TTFTT) produced in situ from **4**, by adding 4.5 equiv. of cesium hydroxide to the reaction mixture. From this mixture, the TTF-compound **11**, containing four protected amine functions, was obtained. The Boc groups were removed with trifluoroacetic acid (TFA) in chloroform, affording[7] the tetra-amine **12**. Although protonation of the central fulvene bond upon the acid treatment is very likely to have occurred, as evidenced by the dark red coloration of the solution, when treated with base during the work-up, deprotonation of all the ammonium centers and the TTF occurs.[8] Finally, the tetra-amine was protonated with 3 M HCl(aq), before counterion exchange with saturated aqueous NH_4PF_6 yielded the salt **2**·$4PF_6$.

The synthesis[9] of the biscrown ether compound **3** is outlined in Scheme 3. Firstly, the diiodide **8**, obtained from the ditosylate **7** by a Finkelstein reaction with NaI, was reacted, under high-dilution conditions, with the in situ generated bisthiolate of **5**, affording the macrocycle **13**. This 1,3-dithiole-2-thione was converted into the 1,3-dithiole-2-one **14** by treatment of **13** with $Hg(OAc)_2$. Subsequent coupling of **14** in the presence of $P(OEt)_3$ afforded **3** in good yield.

3. Complexation studies

3.1. ^{1}H NMR spectroscopy

Although the salt **2**·$4PF_6$ is insoluble in dichloromethane, it can be extracted into this solvent containing BPP34C10. According to the ^{1}H NMR spectrum, the crown is able to extract ca. 0.5 equiv. of the ammonium salt. This 1:2 stoichiometry is in accordance with the principle of maximal site occupancy,[10] i.e., all the binding sites in

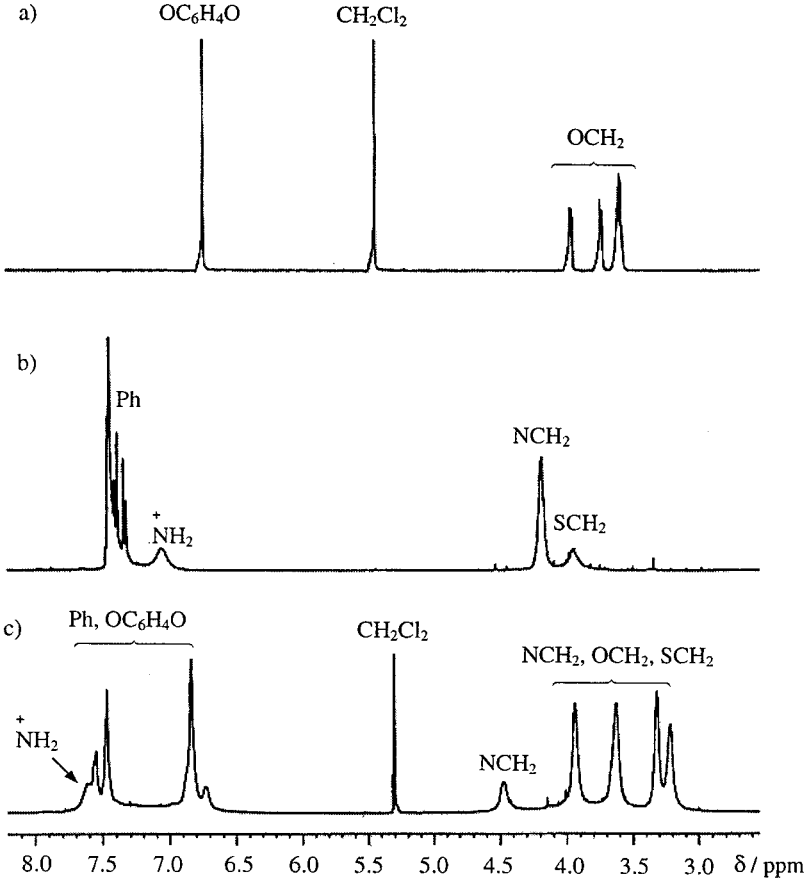


Figure 1. ^{1}H NMR spectra (400 MHz) of (a) BPP34C10 in CD_3CN; (b) **2**·$4PF_6$ in CD_3CN; and (c) **2**·$4PF_6$ in CD_2Cl_2 containing 2 equiv. of BPP34C10.

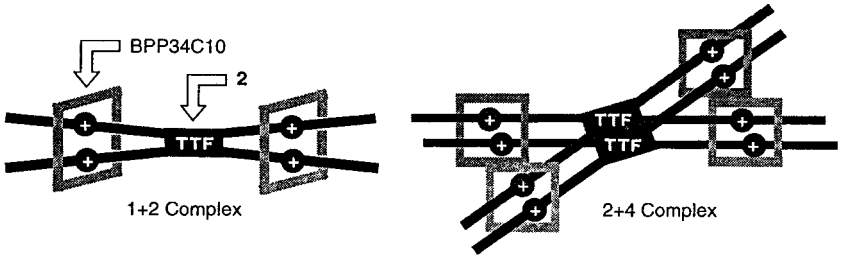


Figure 2. 1:2 and 2:4 complexes of **2**·4PF_6 and BPP34C10.

2·4PF_6 and BPP34C10 are occupied. Indeed, from an inspection of the ^{1}H NMR spectrum (Fig. 1) it would appear that none of the free components are present. The stoichiometry corresponds (Fig. 2) to the formation of either 1:2 or 2:4 complexes. The formation of polymeric arrays seem unlikely in solution on the basis of entropy considerations.

Upon complexation with BPP34C10, a signal centered on δ 4.5 for eight NCH_2 protons in **2**·4PF_6 was observed (Fig. 1c), i.e., it had been shifted downfield from the signal for the other eight NCH_2 protons, which were identified to resonate at ca. 3.7 ppm (in the OCH_2/SCH_2 region) in the ^{1}H–^{1}H COSY spectrum as a result of scalar coupling to the NH_2^+ protons. Complexation to form a supermolecule is supported, not only by the downfield shift of the NCH_2 signal, but also by the broad peaks observed for most of the other signals in the ^{1}H NMR spectrum. The signal for the exchangeable NH_2^+ protons in the ^{1}H NMR spectrum (Fig. 1b) of **2**·4PF_6 disappeared upon addition of D_2O, thus confirming its assignment.

By comparison of ^{1}H NMR spectra (Fig. 3), the biscrown **3** is clearly able to extract 2 equiv. of **1**·PF_6 into CH_2Cl_2 as expected. However, peaks are evident in the spectrum (Fig. 3c) for both complexed and uncomplexed components, confirming that the equilibrium illustrated in Fig. 4 is slow on the ^{1}H NMR timescale. Upon complexation, the singlet observed for the NCH_2 protons is not only shifted downfield (by +0.45 ppm) but also takes on a multiplet character by virtue of coupling to the NH_2^+ protons, a phenomenon which is observed[5b] when they are encircled by DB24C8.

The dibenzylammonium ion $\mathbf{1}^+$ is also in slow exchange on

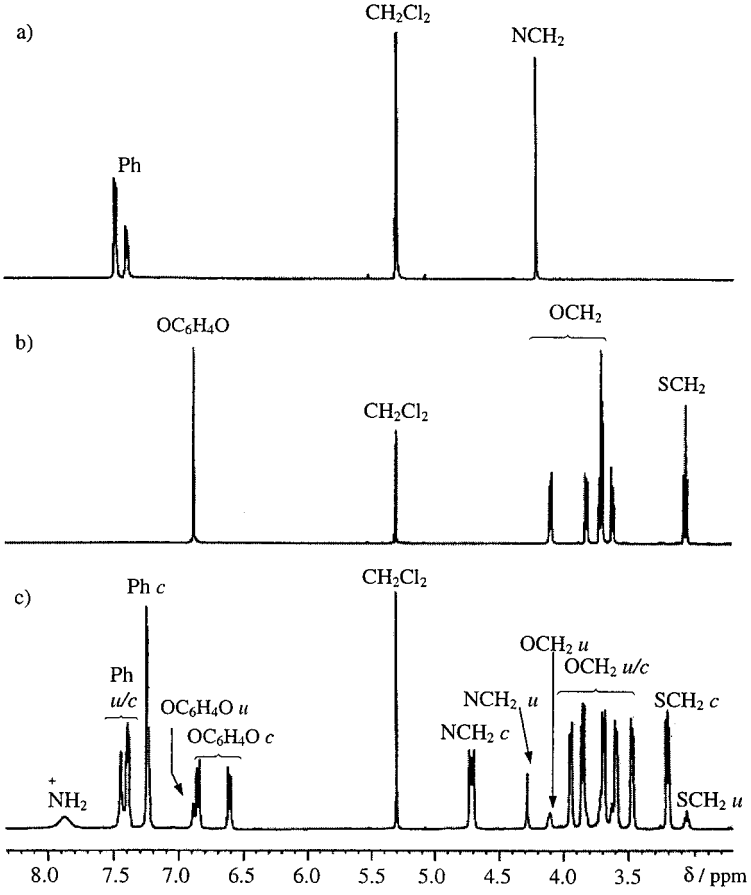


Figure 3. ^{1}H NMR spectra (400 MHz) of (a) **1**·PF_6 in CD_3CN; (b) **3** in CD_2Cl_2; and (c) **3**+**1**·PF_6 (2 equiv.) in CD_2Cl_2. Notation: *c*=complexed, *u*=uncomplexed.

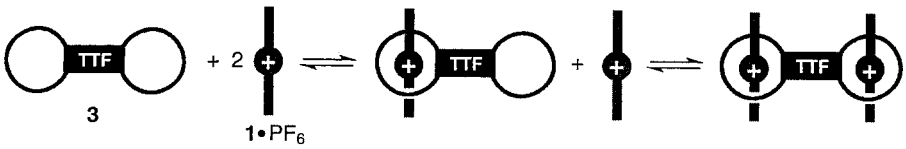


Figure 4. The equilibria between $\mathbf{1}^+$ and **3** in solution (dichloromethane).

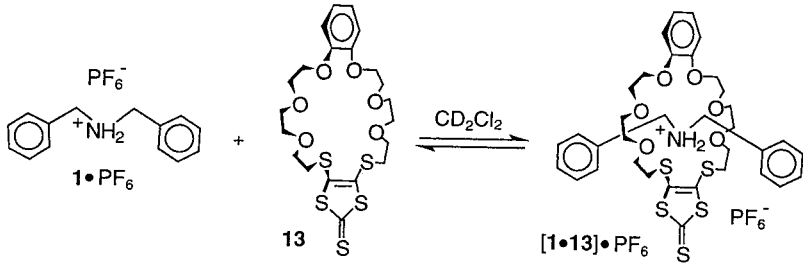


Figure 5. Formation of pseudorotaxane between **13** and **1**·PF_6.

the ^{1}H NMR timescale (400 MHz) with the crown **13** in the formation of their 1:1 complex (Fig. 5). This observation made possible the determination of the association constant (K_a=2750 M^{-1}) for the formation of this complex in CD_2Cl_2 at 300 K. This K_a value can be compared with that[5a] of 27000 M^{-1} when **13** is replaced by DB24C8. Not surprisingly, the replacement of two oxygen atoms in the 24C8 constitution by two sulfur atoms reduces the binding constant by an order of magnitude.

3.2. Electrochemistry

The redox potentials of **2**·4PF_6 and its complexes with BPP34C10 and DB24C8 were determined by differential pulse voltammetry and are listed in Table 1. The first and second potentials of the ammonium salt are significantly shifted relative to tetramethylthiotetrathiafulvalene (TMT–TTF), $\Delta E_{1/2}{}^1$=+0.08 V, $\Delta E_{1/2}{}^2$=+0.13 V (in MeCN). These shifts can be explained by electrostatic repulsion between the charges generated on $\mathbf{2}^{4+}$ upon oxidation and the four positive charges already present in the tetracations. Adding a large excess of DB24C8 to **2**·4PF_6 in MeCN did not alter the potentials to any significant extent. However, in CH_2Cl_2, where the formation of 1:4 complexes with DB24C8 is expected to occur to a higher degree than in MeCN, the redox potentials are comparable to those of TMT–TTF (in CH_2Cl_2). This observation indicates that the four cationic centers are no longer influencing the oxidation of TTF. When **2**·4PF_6 was extracted into a solution of BPP34C10 in CH_2Cl_2, the first and second oxidations occurred at values even lower than those observed for TMT–TTF. Lowering of the first potential may be explained by the favorable formation of a π-dimer between two radical cations in close proximity, hence indicating formation of the 2:4 complex. However, an explanation for the decrease in the second potential is less obvious.

Table 1. Differential pulse data for the oxidation of TTF in the presence or absence of ammonium centers (reference electrode: Ag/AgCl; working and counter electrodes: Pt. Supporting electrolyte: *n*-Bu_4NPF_6 (0.1 M))

Compound	Solvent	$E_{1/2}{}^1$/V	$E_{1/2}{}^2$/V
TMT–TTF	CH_2Cl_2	0.56	0.91
TMT–TTF	MeCN	0.50	0.75
2·4PF_6	MeCN	0.58	0.88
2·4PF_6+DB24C10 (excess)	MeCN	0.60	0.89
2·4PF_6+DB24C10 (excess)	CH_2Cl_2	0.58	0.90
2·4PF_6+BPP34C10 (1:2)[a]	CH_2Cl_2	0.51	0.84
3	CH_2Cl_2	0.53	0.76
3	CH_2Cl_2/MeCN 9:1	0.48	0.71
3+**1**·PF_6 (excess)	CH_2Cl_2/MeCN 9:1	0.49	0.69

[a] Extraction of **2**·4PF_6 into a CH_2Cl_2 solution of BPP34C10.

In conclusion, formation of complexes between **2**·4PF_6 and BPP34C10 or DB24C8 cancels the electrostatic repulsion between the mono/dioxidized TTF and the four ammonium centers. Adding **1**·PF_6 (ca. 70 equiv.) to the biscrown **3** (in CH_2Cl_2/MeCN 9:1) does not alter the oxidations of the TTF unit all that much. Thus, inclusion of two ammonium centers in the two crown cavities does not affect the TTF unit. This observation is in agreement with the finding that complexation of **2**·4PF_6 cancels the electrostatic repulsion from the ammonium centers, i.e., when included in the polyether crown, the dispersed positive charge of the ammonium group does not affect the redox behavior of the TTF unit.

3.3. Mass spectrometry

The complexes were also studied in the gas phase employing fast atom bombardment (FAB) and electrospray (ES) mass spectrometry. Although the ES-MS of a mixture between **2**·4PF_6 and BPP34C10 showed peaks which can be assigned (Table 2) to 1:1 and 1:2 complexes, no evidence for a 2:4 complex was obtained. The ES-MS of a mixture of **1**·PF_6 and **3** reveals peaks corresponding to occupation of either one or both crown ether units of **3** by $\mathbf{1}^+$ ions.

3.4. X-Ray crystallography

Although there is evidence of complexation occurring in solution, the crystals produced[11] from crystallizations of both **3** and **13** carried out from solutions containing the

Table 2. Peaks (*m*/*z*) assigned to complexes in the mass spectra

	1:1 Complex $[M-zPF_6]^{z+}$	1:2 Complex $[M-zPF_6]^{z+}$
2·4PF_6·BPP34C10	999 (z=2)[a], 617.7 (z=3)[a]	1267 (z=2)[a], 796.3 (z=3)[a], 561 (z=4)[a]
1·PF_6·**13**	734 (z=1)[a,b]	
1·PF_6·**3**	1206 (z=1)[a,b]	702 (z=2)[a]

[a] ES-MS.
[b] FAB-MS.

salt **1**·PF_6 were found to be free of any complexed cations $\mathbf{1}^+$.

The biscrown ether **3** is centrosymmetric, having a planar TTF core with the dithio-24-crown-8 components adopting twisted self-filling conformations (Fig. 6). The molecules form continuous π–π stacks (Fig. 7) with the dominant intermolecular interactions being between the TTF components (mean planar separation,[12] 3.63 Å) with a significantly weaker interaction between the catechol rings (mean interplanar separation 3.49 Å, but with a ring centroid···ring centroid distance of 4.98 Å).

The crystal structure (Fig. 8) of the crown ether **13** shows the dithia-24-crown-8 portion of the macrocycle to have a similar twisted self-filling conformation to that observed in **3**. The molecules stack along the crystallographic *b* direction with negligible π–π overlap of either the 1,3-dithiole-2-thione or catechol rings; the mean interplanar separations are 3.64 and 3.31 Å, respectively, but with centroid–centroid separations of 5.03 Å in each case.

4. Conclusions

New functionalized TTF derivatives have been synthesized and used for the construction of hydrogen bonded multicomponent pseudorotaxanes, as evidenced by ^{1}H NMR spectroscopy, mass spectrometry and differential pulse voltammetry. However, these supramolecular architectures dissociate on crystallization. The high propensity for TTF units to form π–π stacks in the solid state is presumably the

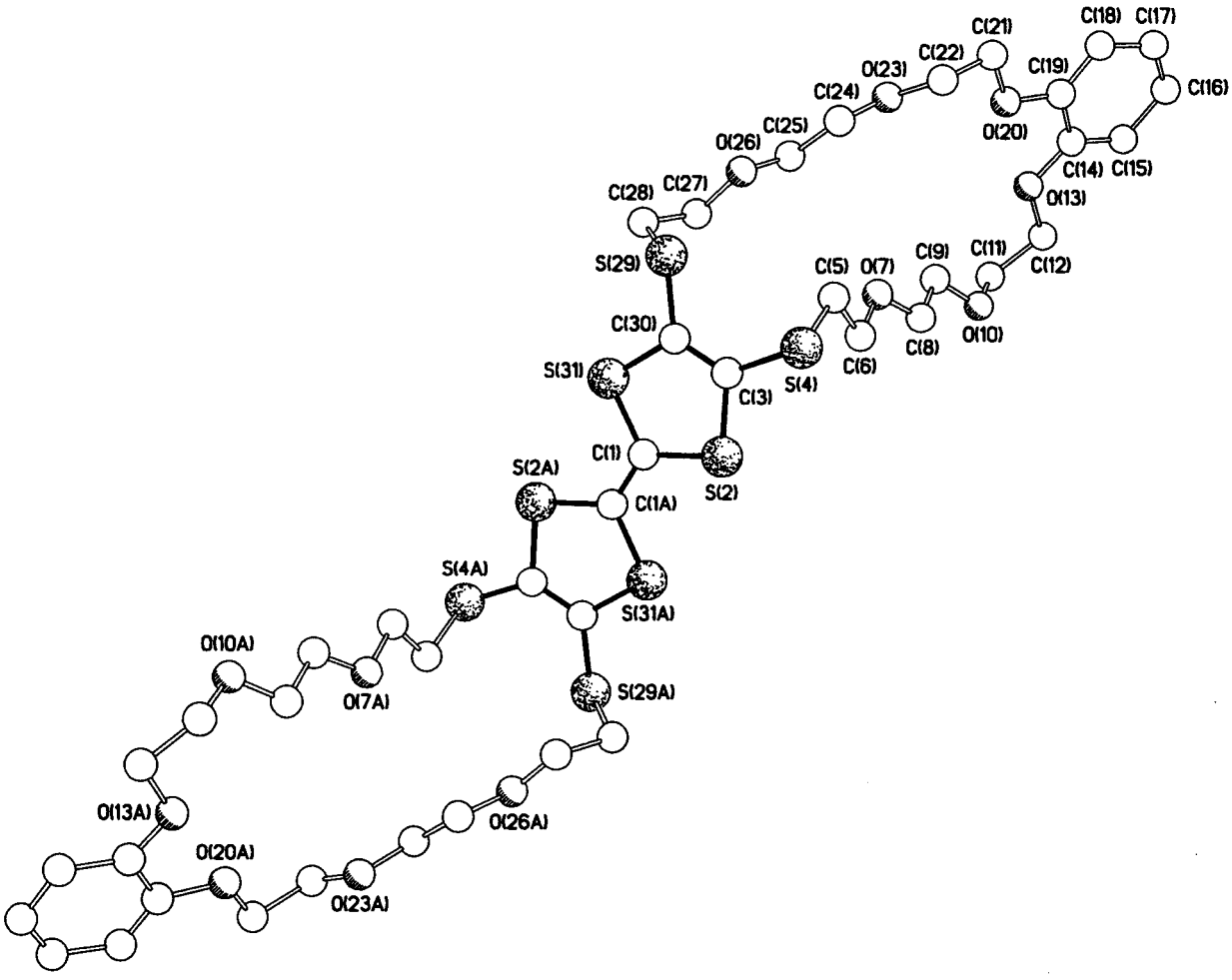


Figure 6. The solid state structure of **3**.

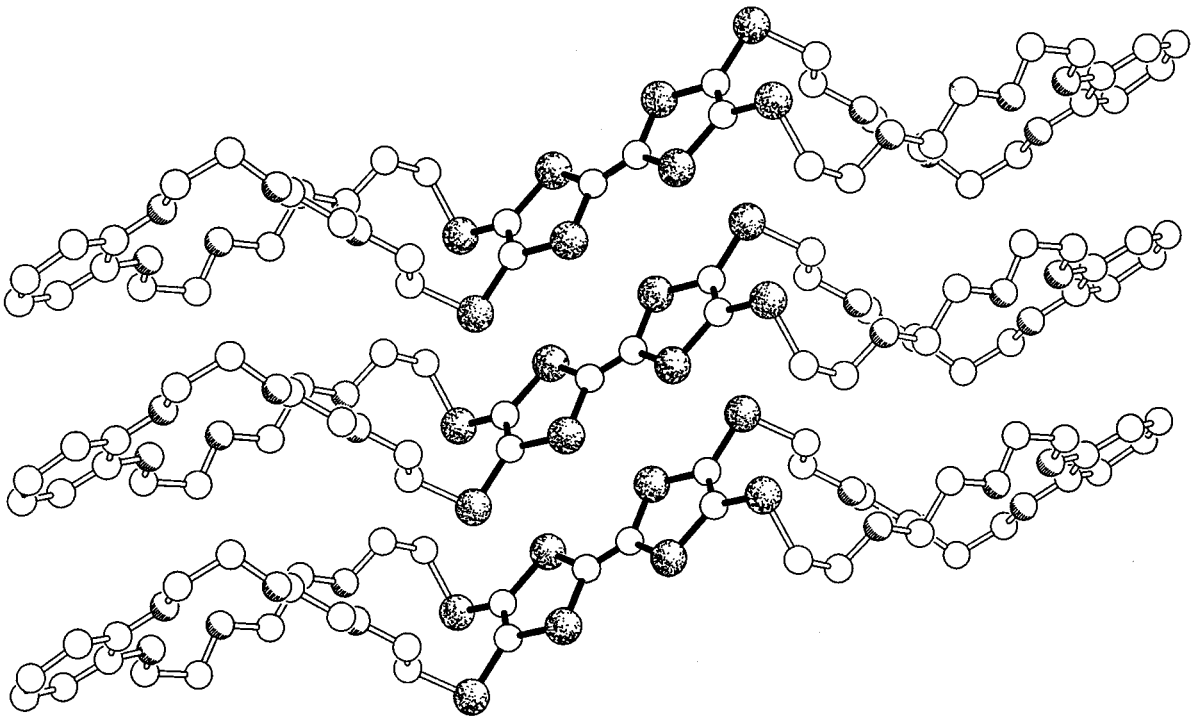


Figure 7. The π–π stacking of the TTF units in the structure of **3**.

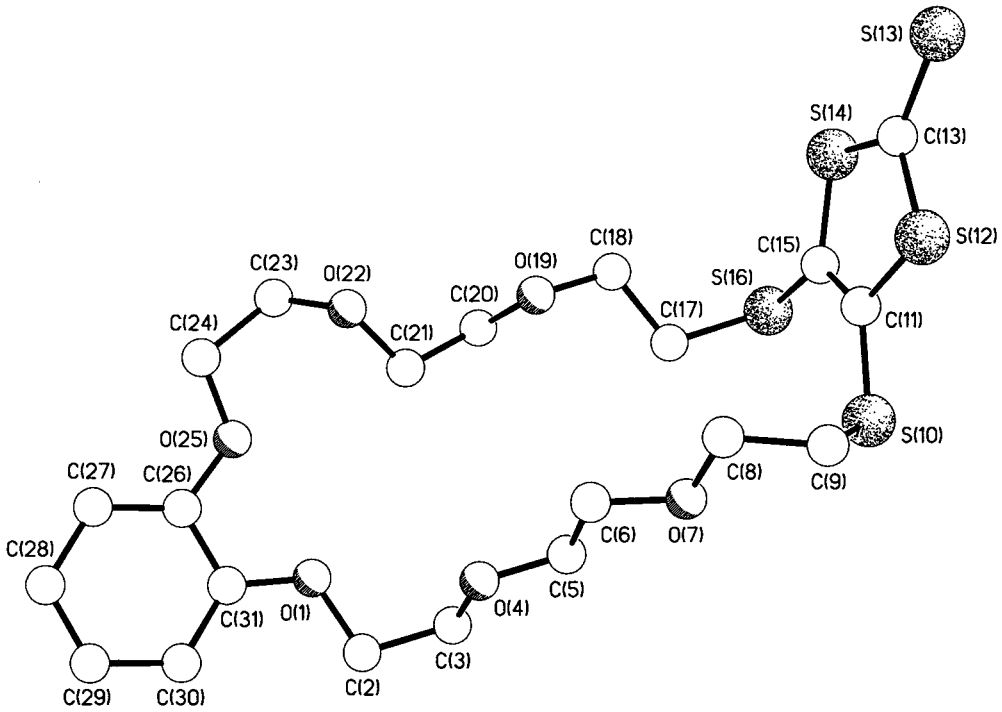


Figure 8. The solid state structure of **13**.

driving force for the decomplexation of the 1:2 complex formed in solution between the bis-crown ether **3** and the dibenzylammonium ion $\mathbf{1}^{+}$. Supramolecular arrays, which combine (1) the recognition of substituted NH_2^{+} centers with macrocycles based on 24-crown-8 constitutions with (2) the ability of TTF units to form donor–acceptor complexes with electron-deficient species, represent a worthwhile goal for crystal engineers to pursue in the future.

5. Experimental

5.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen. THF was distilled from sodium/benzophenone; methanol was distilled from Mg and I_2; DMF was allowed to stand over molecular sieves (4 Å) for at least 3 days

before use; acetonitrile was distilled from CaH_2. Melting points were determined on a Thomas Hoover Melting Point Apparatus and are uncorrected. Elemental analyses were performed by Quantitative Technologies Inc. NMR spectra were recorded on a Bruker ARX400 (400 MHz) spectrometer using the deuterated solvent as the lock and the residual solvent as internal reference. Fast atom bombardment mass spectra (FAB) were obtained from a ZAB-SE instrument. Electrospray mass spectra were obtained from a VG ProSpec mass spectrometer fitted with an electrospray source and using acetonitrile as the mobile phase at a flow rate of 20 $\mu L\ min^{-1}$. Differential pulse voltammetry was measured on an Autolab, PGSTAT10 potentiostat (ECO CHEMIE BV); Bu_4NPF_6 was used as supporting electrolyte; counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. Notation: *u*=uncomplexed, *c*=complexed; cat.=catechol.

5.1.1. 2,3,6,7-Tetrakis{[4-(*N*-benzylammoniummethyl)-phenyl]methylthio}tetrathiafulvalene tetrakis(hexafluorophosphate) (2·4PF$_6$). A solution of **11** (0.260 g, 0.17 mmol) in $CHCl_3$ (13 mL) was stirred with trifluoroacetic acid (TFA) (0.7 mL) for 2 days (dark red solution). Then the solution was diluted with $CHCl_3$ (100 mL) and washed with 1 M NaOH (2×50 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo to afford **12** (0.177 g, 91%) as an orange oil, which was used without further purification. ^{1}H NMR ($CDCl_3$): δ=2.25 (br, 4H, NH), 3.75 (s, 16H, NCH_2), 3.87 (s, 8H, SCH_2), 7.09–7.32 (m, 36H, Ph); FABMS: *m*/*z*=1168 [M^+]. **12** (0.158 g, 0.14 mmol) was dissolved in THF (3 mL) and MeOH (20 mL), whereupon 3 M HCl was added with stirring to alter the pH to ca. 1. After 2 1/2 h the resulting suspension was concentrated in vacuo. The residue was dissolved in $MeNO_2$ (100 mL) and sat. aqueous NH_4PF_6 (25 mL). The phases were partitioned and the organic phase washed with sat. aqueous NH_4PF_6 (25 mL) and water (5×100 mL). Then it was concentrated in vacuo to afford the tetrakisammonium salt **2**·4PF$_6$ as an orange solid (0.232 g, 98%). ^{1}H NMR (CD_3CN): δ=3.99 (br s, 8H, SCH_2), 4.18 (s, 8H, NCH_2), 4.20 (s, 8H, NCH_2), 7.08 (br, 8H, NH_2), 7.32–7.47 (m, Ph, 36H); FABMS: *m*/*z*=1169 [$M-PF_6-3HPF_6]^+$, 1314 [$M-3HPF_6]^+$, 1462 [$M-2PF_6]^+$, 1607 [$M-PF_6]^+$; ESMS: *m*/*z*=1169 [$M-PF_6-3HPF_6]^+$, 1315 [$M-2HPF_6-PF_6]^+$, 1461 [$M-HPF_6-PF_6]^+$, 1607 [$M-PF_6]^+$. Anal. calcd for $C_{66}H_{68}F_{24}P_4S_8$: C 45.20, H 3.91, N 3.19; found: C 45.40, H 4.00, N 3.27.

5.1.2. 2,3,6,7-Bis[benzene-1,2-diyldioxybis(ethane-1,2-diyl)-dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]-tetrathiafulvalene (3). A solution of **14** (0.200 g, 0.38 mmol) in toluene (4 mL) and triethyl phosphite (8 mL) was heated at 120°C for 4 h. The orange product precipitated upon cooling the solution on ice, but to obtain total precipitation, methanol (50 mL) was added. The solid was filtered and washed with methanol (50 mL). Recrystallization from acetonitrile afforded **3** (0.142, 73%) as an orange solid. Mp 152.5–154°C. ^{1}H NMR ($CDCl_3$): δ=3.02 (t, *J*=5.8 Hz, 8H, SCH_2), 3.66–3.71 (m, 16H, OCH_2), 3.79–3.81 (m, 8H, OCH_2), 3.90 (t, *J*=4.5 Hz, 8H, OCH_2), 4.15 (t, *J*=4.5 Hz, 8H, OCH_2), 6.89 (2×s, 8H, cat.); ^{1}H NMR (CD_2Cl_2): δ=2.99 (t, *J*=6.2 Hz, 8H, SCH_2), 3.60–3.66 (m, 16H, OCH_2), 3.70–3.72 (m, 8H, OCH_2), 3.82 (t, *J*=4.5 Hz, 8H, OCH_2), 4.09 (t, *J*=4.5 Hz, 8H, OCH_2), 6.87 (s, 8H, cat.); FABMS: *m*/*z*=1009 [$M+H^+$]. Anal. calcd for $C_{42}H_{56}O_{12}S_8$: C 49.98, H 5.59; found: C 49.97, H 5.55.

5.1.3. *N*-(*tert*-Butoxycarbonyl)-*N*-benzyl-4-(bromomethyl)-benzylamine (6). To a solution of **10** (2.92 g, 8.9 mmol) in dry THF (250 mL) was added CBr_4 (6.19 g, 18.7 mmol. Then PPh_3 (6.07 g, 23.1 mmol) was added in small portions during 1 h. The reaction mixture was left overnight with stirring, whereupon it was concentrated in vacuo. The residue was subjected to column chromatography [hexanes/EtOAc 5:1], affording **6** (2.97 g, 86%) as a colourless oil. ^{1}H NMR ($CDCl_3$): δ=1.49 (s, 9H, CH_3), 4.33 and 4.41 (two br, both 2H, NCH_2), 4.50 (s, 2H, $BrCH_2$), 7.12–7.37 (m, 9H, Ph); FABMS: *m*/*z*=390 [$M+H]^+$; HR-FABMS: $C_{20}H_{24}NO_2Br$ requires *m*/*z*=390.1069 [$M+H]^+$; found 390.1065. Anal. calcd for $C_{20}H_{24}NO_2Br$: C 61.54, H 6.20, N 3.59; found: C 61.57, H 6.22, N 3.54.

5.1.4. 1,2-Bis(2-(2-(2-iodoethoxy)ethoxy)ethoxy)benzene (8). A solution of **7** (4.97 g, 7.27 mmol) and NaI (4.36 g, 29.1 mmol) in acetone (150 mL) was refluxed overnight. Then the solution was filtered and concentrated in vacuo. CH_2Cl_2 (200 mL) was added, and the solution was washed with water (2×100 mL) and dried ($MgSO_4$). After removing the solvent in vacuo the residue was subjected to column chromatography [CH_2Cl_2/EtOAc 10:1], affording **8** (3.69 g, 85%) as a yellow oil. ^{1}H NMR ($CDCl_3$): δ=3.26 (t, *J*=6.9 Hz, 4H, ICH_2), 3.67–3.70 (m, 4H, OCH_2), 3.73–3.78 (m, 8H, OCH_2), 3.87 (t, *J*=5.0 Hz, 4H, OCH_2), 4.18 (t, *J*=5.0 Hz, 4H, OCH_2), 6.92 (2×s, 4H, cat.); ^{13}C NMR ($CDCl_3$): δ=2.96 (ICH_2), 68.87 (OCH_2), 69.88 (OCH_2), 70.29 (OCH_2), 70.81 (OCH_2), 71.97 (OCH_2), 114.93 (cat.), 121.66 (cat.), 148.96 (cat.); FABMS: *m*/*z*=594 [M^+]; HR-FABMS: $C_{18}H_{28}I_2O_6$ requires *m*/*z*=593.9975 [M^+]; found: 593.9974.

5.1.5. *N*-(*tert*-Butoxycarbonyl)-*N*-benzyl-4-hydroxymethyl-benzylamine (10). A solution of *N*-(*tert*-butoxycarbonyl)-*N*-benzyl-4-carbomethoxybenzylamine **9** (8.98 g, 25.2 mmol) in anhydrous THF (115 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (1.81 g, 47.6 mmol) in anhydrous THF (85 mL) over a period of 15 min. The reaction mixture was stirred for 21 h at 20°C, before being treated with H_2O (1.8 mL), followed successively by 5 M NaOH (1.8 mL) and more H_2O (5.2 mL). The resulting suspension was stirred for an additional 5 min., before being filtered through a thin pad of Celite. The solution was concentrated under reduced pressure, and the residue partitioned between CH_2Cl_2 (200 mL) and H_2O (200 mL), with the aqueous phase being extracted further with CH_2Cl_2 (2×200 mL). The combined organic extract was washed with H_2O (200 mL), before being dried (Na_2SO_4). The solution was filtered, and the solvent evaporated in vacuo to yield a clear oil (8.09 g, 98%), which was used without further purification. A small portion of this oil was purified by column chromatography [*n*-C_6H_{14}/EtOAc 3:2] to provide the pure title compound **10**. Spectroscopic data in agreement with Ref. 5f.

5.1.6. 2,3,6,7-Tetrakis{[4-(*N*-(*tert*-butoxycarbonyl)-*N*-benzylaminomethyl)-phenyl]-methylthio}tetrathia-fulva-

lene (11). To a solution of **4** (0.75 g, 1.4 mmol) in DMF (120 mL) was added a solution of $CsOH{\cdot}H_2O$ (1.03 g, 6.1 mmol) in MeOH (15 mL) during 10 min. The mixture was stirred for 1 h, whereupon **6** (2.40 g, 6.1 mmol) in DMF (20 mL) was added. After stirring for 3 h, the mixture was concentrated in vacuo. The product was dissolved in CH_2Cl_2 (200 mL), washed with water (2×200 mL), and dried ($MgSO_4$). After filtration, the solution was boiled with active charcoal for 5 min, filtered and concentrated in vacuo. The product was subjected to column chromatography [(i) CH_2Cl_2 elutes excess **7**, (ii) CH_2Cl_2/EtOAc 10:1], affording **11** (1.69 g, 78%) as an orange semicrystalline oil. ^{1}H NMR ($CDCl_3$): δ=1.49 (s, 36H, CH_3), 3.89 (s, 8H, SCH_2), 4.39 and 4.42 (two br, both 8H, NCH_2), 7.09–7.35 (m, 36H, Ph); FABMS: *m*/*z*=1570 $[M+2H]^+$. Anal. calcd for $C_{86}H_{96}N_4O_8S_8$: C 65.78, H 6.16, N 3.57; found: C 65.33, H 6.18, N, 3.44.

5.1.7. 4,5-[Benzene-1,2-dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]-1,3-dithiole-2-thione (13). To a solution of **5** (0.777 g, 2.55 mmol) in MeCN (40 mL) and DMF (10 mL) was dropwise added a solution of $CsOH{\cdot}H_2O$ (0.900 g, 5.36 mmol) in methanol (15 mL) over 10 min. After stirring for 1 h, this solution and a solution of **8** (1.516 g, 2.55 mmol) in MeCN (65 mL) were added simultaneously to a solution of MeCN (100 mL) during 11 h under high dilution conditions by means of a two-syringe perfusor pump. Stirring was continued for an additional 2 h, whereupon the reaction mixture was concentrated in vacuo. Then CH_2Cl_2 (200 mL) was added, and the solution was washed with water (200 mL), dried ($MgSO_4$), and concentrated in vacuo. Column chromatography [CH_2Cl_2/EtOAc 5:1] afforded **13** (0.657 g, 48%) as a yellow solid. Mp. 99–100°C. ^{1}H NMR ($CDCl_3$): δ=3.08 (t, *J*=5.9 Hz, 4H, SCH_2), 3.66–3.68 (m, 4H, OCH_2), 3.75 (t, *J*=5.9 Hz, 4H, OCH_2), 3.78–3.80 (m, 4H, OCH_2), 3.90 (t, *J*=4.5 Hz, 4H, OCH_2), 4.16 (t, *J*=4.5 Hz, 4H, OCH_2), 6.90 (2×s, 4H, cat.); ^{1}H NMR (CD_2Cl_2): δ=3.06 (t, *J*=6.0 Hz, 4H, SCH_2), 3.61–3.63 (m, 4H, OCH_2), 3.71–3.73 (m, 8H, OCH_2), 3.83 (t, *J*=4.5 Hz, 4H, OCH_2), 4.10 (t, *J*=4.5 Hz, 4H, OCH_2), 6.88 (s, 4H, cat.); ^{13}C NMR ($CDCl_3$): δ=36.39 (SCH_2), 69.24 (OCH_2), 69.71 (OCH_2), 69.93 (OCH_2), 70.79 (OCH_2), 70.93 (OCH_2), 114.35 (cat.), 121.53 (cat.), 136.77 (C=C), 148.91 (cat.), 211.20 (C=S); FABMS: *m*/*z*=538 $[M+2H]^+$; HR-FABMS: $C_{21}H_{28}O_6S_5$ requires *m*/*z*=536.04895 $[M+H^+]$; found: 536.0493. Anal. calcd for $C_{21}H_{28}O_6S_5$: C 46.99, H 5.26; found: C 46.94, H 5.18.

5.1.8. 4,5-[Benzene-1,2-dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)dioxybis(ethane-1,2-diyl)bisthio]-1,3-dithiole-2-one (14). To a solution of **13** (0.524 g, 0.98 mmol) in $CHCl_3$ (75 mL) and glacial acetic acid (30 mL) was added $Hg(OAc)_2$ (0.778 g, 2.44 mmol), whereupon the solution was stirred for 3 h. Then it was filtered on Celite, and the Celite layer was rinsed with $CHCl_3$ (100 mL). The filtrate was washed with $NaHCO_3$ (aq) until no more CO_2-evolution was observed, and then finally with water (200 mL). The organic phase was dried ($MgSO_4$), and concentrated in vacuo. Column chromatography [CH_2Cl_2/EtOAc 5:1] afforded **14** (0.373 g, 73%) as a white solid. Mp 101.5–102.5°C. ^{1}H NMR ($CDCl_3$): δ=3.05 (t, *J*=6.1 Hz, 4H, SCH_2), 3.66–3.68 (m, 4H, OCH_2), 3.74 (t, *J*=6.1 Hz, 4H, OCH_2), 3.79–3.81 (m, 4H, OCH_2), 3.90 (t, *J*=4.5 Hz, 4H, OCH_2), 4.16 (t, *J*=4.5 Hz, 4H, OCH_2), 6.90 (2×s, 4H, cat.); ^{13}C NMR ($CDCl_3$): δ=36.21 (SCH_2), 69.25 (OCH_2), 69.71 (OCH_2), 69.90 (OCH_2), 70.77 (OCH_2), 70.91 (OCH_2), 114.32 (cat.), 121.53 (cat.), 127.64 (C=C), 148.91 (cat.), 189.66 (C=O); FABMS: *m*/*z*=520 $[M^+]$; HR-FABMS: $C_{21}H_{28}O_7S_4$ requires *m*/*z*=520.0718 $[M^+]$; found: 520.0711. Anal. calcd for $C_{21}H_{28}O_7S_4$: C 48.44, H 5.42; found: C 48.35, H 5.30.

5.2. Complex formed between 2·4PF$_6$ and BPP34C10

The salt **2**·4PF_6 was extracted into a solution of BPP34C10 (ca. 20 mg) in CD_2Cl_2 (ca. 1 mL), until no more could be dissolved. The solution was filtered and subjected to ^{1}H NMR spectral measurement, and the ratio between **2**·4PF_6 and BPP34C10 was determined from the integrals (1:1.8~1:2). ^{1}H NMR (CD_2Cl_2): δ=3.23 (br s), 3.33 (br s), 3.64 (br s), ~3.7 (very br, position determined by COSY, NCH_2), 3.94 (br s) [3.23–3.94 (80H, SCH_2, OCH_2, NCH_2)], 4.47 (br s, 8H, NCH_2), 6.74 (br s), 6.84 (br s), 6.84–7.47 (br), 7.47 (m), 7.55 (s), 7.56 (s), 7.60 (br s, NH_2) [6.74–7.60 (60H, Ph, OPhO, NH_2)]; ESMS: *m*/*z*=561 [1:2 complex−4PF_6]$^{4+}$, 617.7 [1:1 complex−3PF_6]$^{3+}$, 796.3 [1:2 complex−3PF_6]$^{3+}$, 999 [1:1 complex−2PF_6]$^{2+}$, 1267 [1:2 complex−2PF_6]$^{2+}$.

5.3. Complex formed between 3 and 1·PF$_6$

The salt **1**·PF_6 was extracted into a solution of **3** in CD_2Cl_2 until no more could be dissolved. The solution was filtered and subjected to ^{1}H NMR, and the ratio between **3** and **1**·PF_6 was determined from the integrals (1:2.1~1:2). ^{1}H NMR (CD_2Cl_2): δ=2.98 (br, ca. 1H, SCH_2 *u*), 3.15 (t, *J*=4.8 Hz, ca. 7H, SCH_2 *c*), 3.42–3.43 (m), 3.58 (t, *J*=2.8 Hz), 3.64–3.66 (m), 3.81 (t, *J*=4.8 Hz) [3.42–3.81 (32H, OCH_2 *u*/*c*)], 3.93 (t, *J*=2.8 Hz, 7H, OCH_2 *c*), 4.11 (br, ca. 1H, OCH_2 *u*), 4.26 (s, ca. 1H, NCH_2 *u*), 4.71 (t, *J*=6.7 Hz, ca. 7H, NCH_2 *c*), 6.61 (dd, *J*=3.6 and 6.0 Hz, ca. 3.5H, cat. *c*), 6.84 (dd, *J*=3.5 and 6.0 Hz, ca. 3.5H, cat. *c*), 6.89 (br, ca. 1H, cat. *u*), 7.22 (t, *J*=3.1 Hz, ca. 10H, Ph *c*), 7.37–7.43 (m, ca. 10H, Ph *u*/*c*), 7.80 (br, 4H, NH_2); FABMS: *m*/*z*=1206 [1:1 complex-PF_6]$^+$; ESMS: *m*/*z*=702 [1:2 complex−2PF_6]$^{2+}$, 1206 [1:1 complex−PF_6]$^+$.

5.4. Complex formed between 13 and 1·PF$_6$

Concentrations in CD_2Cl_2: [**13**]=[**1**·PF_6]=0.0097 M. ^{1}H NMR (CD_2Cl_2): δ=3.06 (t, *J*=5.7 Hz, ca. 0.7H, SCH_2 *u*), 3.20 (t, *J*=5.1 Hz, ca. 3.3H, SCH_2 *c*), 3.46–3.48 (m), 3.58–3.62 (m), 3.68–3.71 (m), 3.83–3.86 (m) [3.46–3.86 (16H, OCH_2 *c*/*u*)], 3.94 (t, *J*=3.8 Hz, ca. 3.3H, OCH_2 *c*), 4.11 (br t, ca. 0.7H, OCH_2 *u*), 4.28 (s, ca. 0.7H, NCH_2 *u*), 4.71 (t, *J*=6.9 Hz, ca. 3.3H, NCH_2 *c*), 6.61 (dd, *J*=3.5 and 6.0 Hz, ca. 1.65H, cat. *c*), 6.85 (dd, *J*=3.5 and 6.0 Hz, ca. 1.65H, cat. *c*), 6.89 (br s, ca. 0.7H, cat. *u*), 7.23–7.25 (m, ca. 4.8H, Ph *c*), 7.38–7.41 (m), 7.45 (br s) [7.38–7.45 (ca. 5.2H, Ph *c*/*u*)], 7.88 (br, 2H, NH_2); FABMS: *m*/*z*=734 $[M-PF_6]^+$; ESMS: *m*/*z*=734 $[M-PF_6]^+$.

References

1. For a review on TTF macrocycles, see: Nielsen, M. B.; Becher, J. *Liebigs Ann./Recueil* **1997**, 2177.
2. For reviews on TTF in supramolecular chemistry, see: (a) Jørgensen, T.; Hansen, T. K.; Becher, J. *Chem. Soc. Rev.* **1994**, *23*, 41. (b) Bryce, M. R. *Adv. Mater.* **1999**, *11*, 11. (c) Nielsen, M. B.; Lomholt, C.; Becher *J. Chem. Soc. Rev.* **2000**, *29*, 153.
3. (a) Blanchard, P.; Sallé, M.; Duguay, G.; Jubault, M.; Gorgues, A. *Tetrahedron Lett.* **1992**, *33*, 2685. (b) Batsanov, A. S.; Bryce, M. R.; Cooke, G.; Heaton, J. N.; Howard, J. A. K. *J. Chem. Soc., Chem. Commun.* **1993**, 1701. (c) Neilands, O.; Belyakov, S.; Tilika, V.; Edzina, A. *J. Chem. Soc., Chem. Commun.* **1995**, 325. (d) Batsanov, A. S.; Svenstrup, N.; Lau, J.; Becher, J.; Bryce, M. R.; Howard, J. A. K. *J. Chem. Soc., Chem. Commun.* **1995**, 1201. (e) Moore, A. J.; Bryce, M. R.; Batsanov, A. S.; Heaton, J. N.; Lehmann, C. W.; Howard, J. A. K.; Robertson, N.; Underhill, A. E.; Perepichka, I. F. *J. Mater. Chem.* **1998**, *8*, 1541. (f) Ono, G.; Izuoka, A.; Sugawara, T.; Sugawara, Y. *J. Mater. Chem.* **1998**, *8*, 1703. (g) Llacay, J.; Mata, I.; Molins, E.; Veciana, J.; Rovira, C. *Adv. Mater.* **1998**, *10*, 330. (h) Heuzé, K.; Fourmigué, M.; Batail, P.; Canadell, E.; Auban-Senzier, P. *Chem. Eur. J.* **1999**, *5*, 2971.
4. Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1865.
5. (a) Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1869. (b) Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 709. (c) Ashton, P. R.; Glink, P. T.; Martínez-Díaz, M.-V.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1930. (d) Ashton, P. R.; Glink, P. T.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 729. (e) Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2068. (f) Ashton, P. R.; Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 12514. (g) Ashton, P. R.; Collins, A. N.; Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 59. (h) Feiters, M. C.; Fyfe, M. C. T.; Martínez-Díaz, M.-V.; Menzer, S.; Nolte, R. J. M.; Stoddart, J. F.; van Kan, P. J. M.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 8119. (i) Ashton, P. R.; Fyfe, M. C. T.; Martínez-Díaz, M.-V.; Menzer, S.; Schiavo, C.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1998**, *4*, 1523.
6. Simonsen, K. B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mørk, P.; Kristensen, G. J.; Becher, J. *Synthesis* **1996**, *3*, 407.
7. For alternative procedures for preparing amino-functionalized tetrathiafulvalene derivatives, see: (a) Bertho, F.; Robert, A.; Batail, P.; Robin, P. *Tetrahedron* **1990**, *46*, 433. (b) Fabre, J.-M.; Garín, J.; Uriel, S. *Tetrahedron* **1992**, *48*, 3983. (c) Parg, R. P.; Kilburn, J. D.; Petty, M. C.; Pearson, C.; Ryan, T. G. *Synthesis* **1994**, 613. (d) Le Hoerff, T.; Lorcy, D.; Floner, D.; Moinet, C.; Bittner, S.; Mingotaud, C.; Delhaes, P.; Robert, A. *J. Mater. Chem.* **1995**, *5*, 1589. (e) Binet, L.; Fabre, J.-M. *Synthesis* **1997**, 1179.
8. The acidity constant for TTF has been determined to be intermediate between that of Et_2OH^+ and H_3O^+. See: Giffard, M.; Alonso, P.; Garin, J.; Gorgues, A.; Nguyen, T. P.; Richomme, P.; Robert, A.; Roncali, J.; Uriel, S. *Adv. Mater.* **1996**, *6*, 298.
9. (a) For related TTF annelated crown ethers, see: (a) Otsubo, T.; Ogura, F. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1343. (b) Hansen, T. K.; Jørgensen, T.; Becher, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1550. (c) Hansen, T. K.; Jørgensen, T.; Stein, P. C.; Becher, J. *J. Org. Chem.* **1992**, *57*, 6403. (d) Jørgensen, T.; Girmay, B.; Hansen, T. K.; Becher, J.; Underhill, A.; Hursthouse, M. B.; Harman, M. E.; Kilburn, J. D. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2907.
10. Krämer, R.; Lehn, J.-M.; Marquis-Rigault, A. *Proc. Natl. Acad. Sci. USA* **1993**, *34*, 1865.
11. Crystals of **13** were grown from a mixture of **1**·PF_6 and **13** in CH_2Cl_2/MeCN layered with mixed hexanes. Crystals of **3** were grown from of a mixture of **1**·PF_6 and **3** in CH_2Cl_2/MeCN layered with $^iPr_2O$. Crystal data for **3**: $C_{42}H_{56}O_{12}S_8$, M=1009.4, monoclinic, $C2/c$ (no. 15), a=32.635(7), b=4.975(2), c=32.408(6) Å, β=116.01(1)°, V=4728(3) Å^3, Z=4 (the complex has crystallographic C_i symmetry), D_c=1.418 g cm^{-3}, μ(Cu-$K\alpha$)=40.0 cm^{-1}, F(000)=2128, T=293 K; orange needles, 0.70×0.05×0.03 mm, refined based on F^2 to give R_1=0.091, wR_2=0.167 for 1455 independent observed absorption corrected reflections [$|F_o|>4\sigma(|F_o|)$, $2\theta\leqslant120°$] and 280 parameters. CCDC 148827. Crystal data for **13**: $C_{21}H_{28}O_6S_5$, M=536.7, monoclinic, $P21/n$ (no. 14), a=19.633(1), b=5.026(1), c=25.918(2) Å, β=104.66(1)°, V=2474.0(2) Å^3, Z=4, D_c=1.441 g cm^{-3}, μ(Cu-$K\alpha$)=46.2 cm^{-1}, F(000)=1128, T=293 K; yellow needles, 0.77×0.23×0.08 mm, refined based on F^2 to give R_1=0.036, wR_2=0.089 for 3418 independent observed absorption corrected reflections [$|F_o|>4\sigma(|F_o|)$, $2\theta\leqslant126°$] and 290 parameters. CCDC 148826.
12. Compare with the separation of 3.62 Å observed for TTF. See: Phillips, T. E.; Kistenmacher, T. J.; Ferraris, J. P.; Cowan, D. O. *J. Chem. Soc., Chem. Commun.* **1973**, 471.