Bis(pyrrolo)tetrathiafulvalene – An Efficient π-Donor in Supramolecular Chemistry

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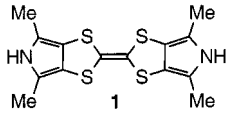
The synthesis of three novel macrocycles **3–5** based on the two electron donors bis(2,5-dimethylpyrrolo)[3,4-*d*]tetrathiafulvalene (**1**) and 1,4-hydroquinone is presented. Their abilities to include the electron acceptor paraquat (**6**) have been investigated by UV/Vis and ^{1}H NMR spectroscopy and an X-ray crystallographic analysis. Also, the complex formation between the cyclic acceptor cyclobis(paraquat-*p*-phenylene) (**7**) and different tetrathiafulvalene derivatives has been studied. A strong association between **1** and **7** facilitates the self-assembly of catenanes from the macrocycles **3–5**. However, the preferred position of the cyclic acceptor **7** in the catenanes around either the pyrrolo-annelated TTF or around the hydroquinone donor relies on a fine balance between all the individual noncovalent forces acting in cooperation.

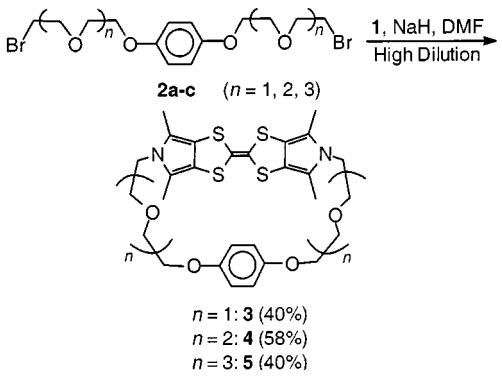
Introduction

The electron donor tetrathiafulvalene (TTF) has been widely used in the field of supramolecular chemistry and is easily incorporated into macrocyclic systems that can interact with for example electron acceptors.[1] Cava et al. have reported an efficient synthesis of the pyrrolo-annelated TTF **1**,[2] which by virtue of its powerful donor properties and lack of *cis*/*trans* isomerism appeared to be a potentially useful entity.[3] Moreover, the presence of only two functionalisable sites in **1** should result in simpler and more symmetric systems than those derived from the nonannelated TTF containing four attachment sites. We therefore decided to prepare macrocyclic systems based on **1** and to investigate their complexation properties, thus allowing a rational design of more elaborate systems.



Results and Discussion

Under high-dilution conditions employing a two-syringe perfusor pump we have incorporated **1** into the macrocycles **3**−**5** by reacting it with the dibromides **2a**−**c**[4][5] in the presence of NaH (Scheme 1). Crystals of **3** and **4** were grown from CH_2Cl_2/cyclohexane. The X-ray crystal structures were solved and are depicted in Figures 1 and 2, respectively. Both macrocycles adopt a conformation in which the two donor moieties are almost perpendicular to each other. As a result of ring strain the pyrrolo-TTF unit in **3** is distorted out of planarity. Thus, the dihedral angle between the least-square planes defined by S1, S2, S3, S4, C1, C2 and N1, C3, C4, C5, C6, C7, C8 is 16.2° and the corresponding angle between the planes S1, S2, S3, S4, C1, C2 and N2, C9, C10, C11, C12, C13, C14 is 15.7°. The larger macrocycle **4** crystallizes in two independent forms, in both of which the distortion is less pronounced, with angles between least-square planes of 6.1 and 14.3° in one macrocycle and 5.4 and 13.1° in the other.



Scheme 1. Synthesis of macrocycles

The ability of these electron-rich macrocycles to act as receptors for the weak electron-acceptor paraquat in solution was investigated by ^{1}H NMR and UV/Vis spectroscopy.[6] A 1:1 mixture of **4** and paraquat hexafluorophosphate (**6**) in chloroform/acetonitrile (1:1) exhibited a broad charge-transfer band centered at 601 nm. Complex formation was also confirmed in the ^{1}H NMR spectrum by significant changes of the chemical shifts for the paraquat protons, most significantly for the β-protons. Macrocycle **4** formed the strongest complex with a chemical shift change

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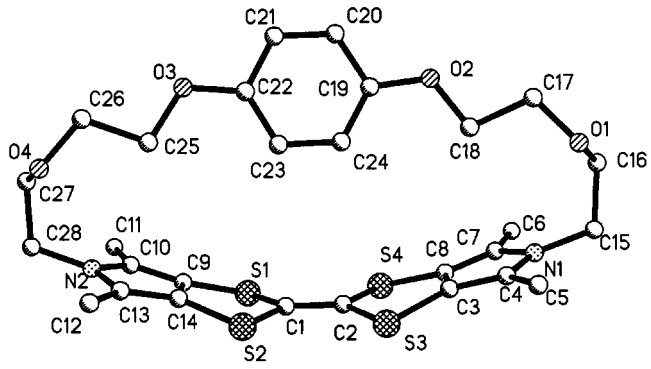


Figure 1. X-ray crystal structure of **3**; one molecule of CH_2Cl_2 has been omitted

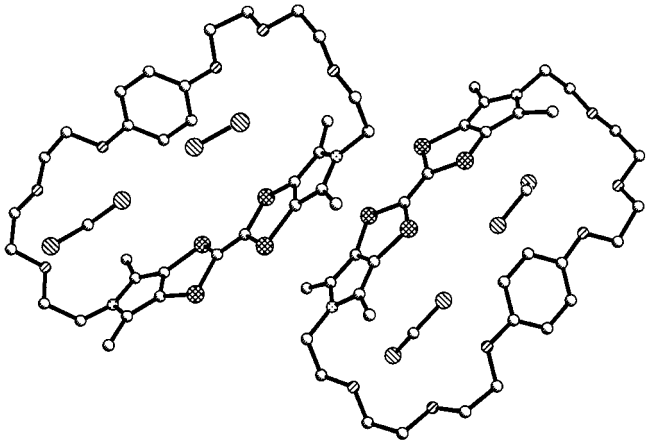
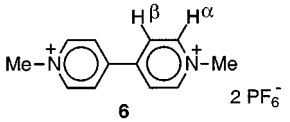


Figure 2. X-ray crystal structure of **4**; CH_2Cl_2 solvent molecules are included

of $\Delta\delta_{\beta\text{-H}} = -0.16$ upon complexation in $CDCl_3/CD_3CN$ (1:1) compared to shift changes of -0.03 and -0.12 for **3** and **5**, respectively, all measured at the same concentration (5 mM). A 1:1 stoichiometry for the **4·6** complex was determined from a Job plot.[7] In the same solvent mixture ($CDCl_3/CD_3CN$ 1:1) we found an association constant of 250 M^{-1} (at 300 K) from an ^1H NMR dilution experiment[8] by observing the paraquat β-protons.



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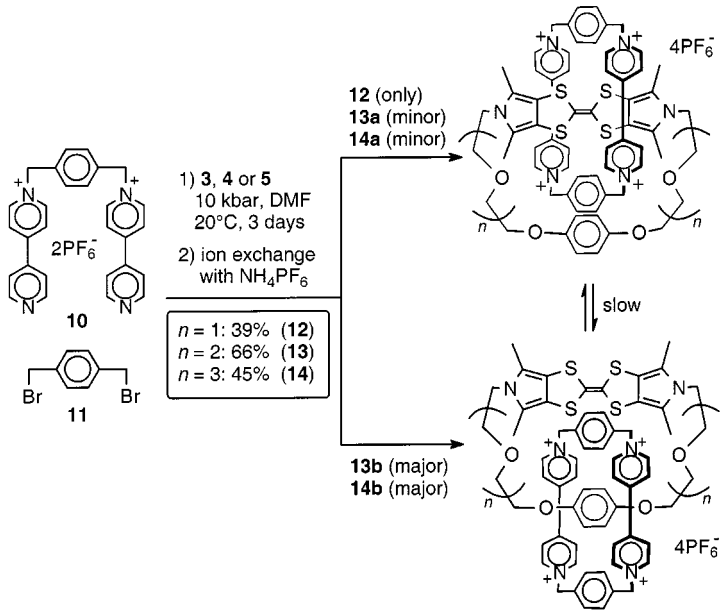
The X-ray crystal structure of the **4·6** complex was solved[9] and in contrast to the solution state behavior it revealed a complex consisting of two molecules of **4** per molecule of **6** (Figure 3). Each macrocycle adopts a conformation in which the angle between the hydroquinone and the tetrathiafulvalene moiety is 70.1° while two of them dimerize to give a box-like structure encapsulating one completely planar paraquat molecule. The distance between the two tetrathiafulvalene moieties is 7.08 Å and thus optimal for charge-transfer and/or π−π interactions to stabilize the inclusion of paraquat,[5] although paraquat is tilted 15.9° away from co-planarity with the TTF′s. The distance between the two hydroquinone moieties is 8.71 Å, and the angle between the hydroquinone unit and paraquat is 54.2°. An interaction between the oxygen atoms in the ethylene glycol chain and the charged paraquat unit, especially its H_α protons, is probably an important factor for the stabilization of the complex.[5][10]

We have previously reported catenanes based on derivatives of the weaker donor tetramethylthiotetrathiafulvalene (**8**) and cyclobis(paraquat-*p*-phenylene) (**7**).[1c–e] The complexation/decomplexation of both **1** and **8** with **7** is slow on the ^1H NMR timescale (250 MHz) resulting in proton resonances assignable to both the complex and the free species. In contrast, the association process between the unsubstituted TTF **9** and **7** has been characterized by a fast exchange kinetic study,[11] in accordance with the smaller



Scheme 2. Synthesis of catenanes

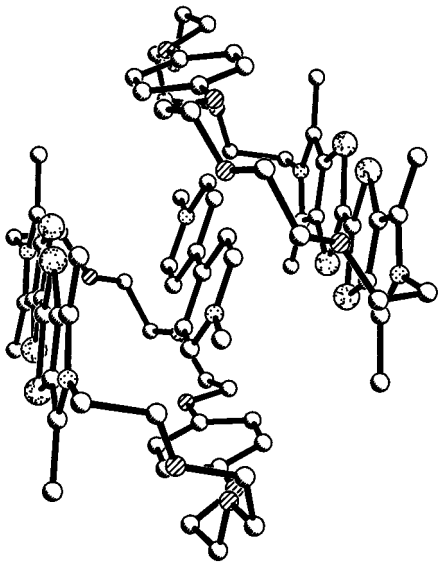


Figure 3a. X-ray crystal structure (centrosymmetric) of the 2:1 complex between **4** and **6**; solvent molecules and counterions are omitted for clarity

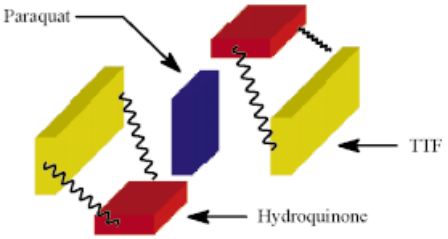


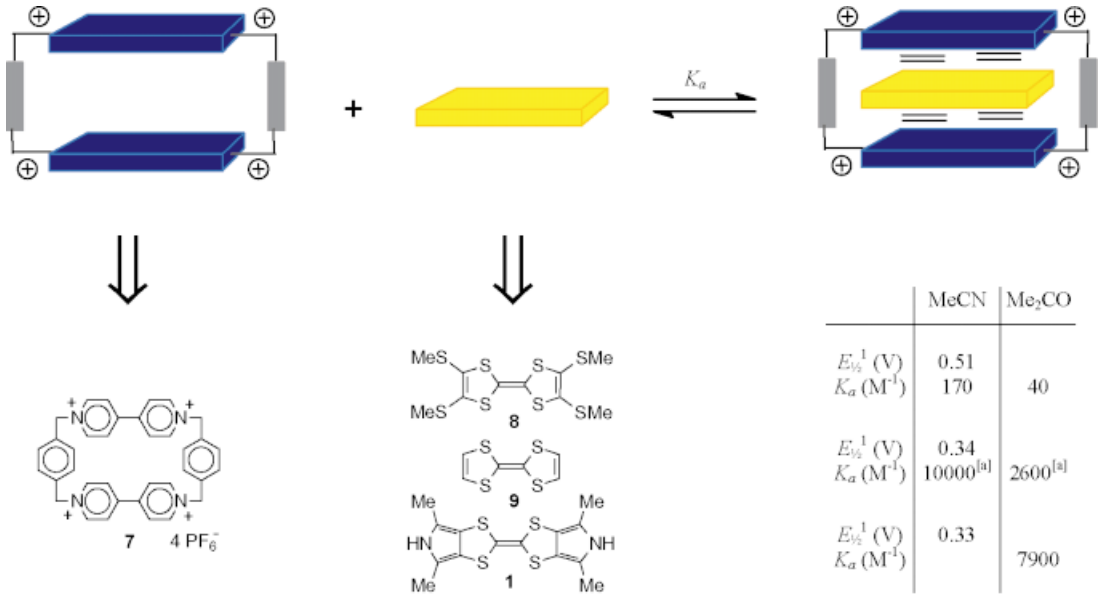
Figure 3b. Schematic drawing of the solid state $(\mathbf{4})_2\cdot\mathbf{6}$ complex

degree of steric hindrance for **9** to enter/leave the host. We have determined the association constants for the guests **1** and **8** employing the single point method[12] (Figure 4). Compound **8** was seen to bind much more weakly than **9**, whereas **1** showed better guest properties, which may be explained by a combination of its extended π-surface and low first oxidation potential, and hence better π-donor properties.

Encouraged by the above results we decided to investigate the ability of **1** to induce the self-assembly of catenanes, employing the strategy developed by Stoddart et al.[5] The catenation of the smallest macrocycle **3** proceeded with an excess of the bis(bipyridinium) derivative **10** and 1,4-bis-(bromomethyl)benzene **(11)** under ultra-high pressure (10 kbar) to afford the [2]catenane **12** in 39% yield. The corresponding larger macrocycles **4** and **5** gave unseparable mixtures of catenanes **13a/b** and **14a/b**, respectively. Compounds **13a/b** could also be prepared under atmospheric pressure in a yield of 66%, reflecting the large template effect in this case.

The room temperature ^{1}H NMR spectrum of **12** in CD_3CN revealed two sets of bipyridinium H_α (δ = 8.99 and 8.68) and H_β (δ = 8.03 and 6.82) protons, a singlet for the *p*-phenylene moieties (δ = 7.78) and two singlets for the NCH_2 protons (δ = 5.84 and 5.74), corresponding to "inside" and "outside" cyclophane protons and implying that rotation of **7** is slow or nonexistent on the ^{1}H NMR timescale (300 MHz). The hydroquinone protons resonate at 5.91 ppm, which is consistent with a hydroquinone unit aligned on the "outside" of **7**, since a large upfield shift would be expected for an "inside" hydroquinone.[5]

The ^{1}H NMR spectra of **13a/b** and **14a/b** in [D_6]DMSO at 30°C showed that the catenanes exist as mixtures of the two translational isomers depicted in Scheme 2. The main



	MeCN	Me_2CO
$E_{1/2}^1$ (V)	0.51	
K_a (M^{-1})	170	40
$E_{1/2}^1$ (V)	0.34	
K_a (M^{-1})	10000[a]	2600[a]
$E_{1/2}^1$ (V)	0.33	
K_a (M^{-1})		7900

Figure 4. Association constants (K_a; error: ±10%) for the inclusion of **1** and **8** by **7** were determined at 30°C; [a] the K_a value for **9** in Me_2CO (21°C) was taken from ref.[9c] whereas the value in MeCN (25°C) was taken from ref.[9d]; the redox potentials (*vs* Ag/AgCl) were measured by cyclic voltammetry using 0.1 M tetrabutylammonium hexafluorophosphate as counter electrolyte

isomer (**b**) is the one in which **7** is occupying the position around the hydroquinone unit, and this isomer only possesses one set of H_α and H_β protons as a result of fast rotation of **7** about the hydroquinone. The minor isomer **13a** gave rise to a signal for the hydroquinone ring protons at 6.28 ppm consistent with a hydroquinone moiety on the "outside" of **7**, indicating that the TTF was encircled by **7**. Isomer **13a** exhibits two sets of H_α and H_β protons, whereas fast rotation of **7** about the TTF in **14a** resulted in only one set. At room temperature the protons of the "inside" hydroquinone of **13b** and **14b** were hidden under the strong water signal. Upon heating **13a/b** to 60°C the water signal underwent an upfield shift and a sharp signal from the "inside" hydroquinone protons of **13b** was revealed at 3.35 ppm − upfield shifted by virtue of the shielding exerted by **7**. Integration of the signals for the two isomers at room temperature revealed a distribution ratio of roughly 1:10 for **13a/b** and 1:20 for **14a/b**. However, upon heating **13a/b** to 120°C the ratio changed to ca. 1:1.

The small catenane **12** shows a very prominent absorption band at $\lambda_{max} = 699$ nm ($\varepsilon = 2180\ M^{-1}cm^{-1}$) as a result of a charge-transfer interaction between **1** and **7**, confirming that the TTF is indeed encircled by **7**. The larger catenanes **13a/b** and **14a/b** also exhibit charge-transfer interactions with TTF ($\lambda_{max} = 920$ nm, $\varepsilon \approx 900-1500\ M^{-1}cm^{-1}$), but also a significant band arising from interactions with the hydroquinone donor is observed at ca. 410 nm ($\varepsilon \approx 2400-2600\ M^{-1}cm^{-1}$). However, it should be noted that the macrocycles also absorb in this region, but with a much lower extinction coefficient ($\varepsilon \approx 100-400\ M^{-1}cm^{-1}$).

Cyclic voltammetry of **12** in MeCN showed anodic shifts in the first and second redox potentials (vs Ag/AgCl) of the TTF unit [**12**: $E^1_{1/2} = 0.96$V, $E^1_{1/2} = 1.46$V (quasi-reversible)] relative to **1** ($E^1_{1/2} = 0.33$V, $E^2_{1/2} = 0.74$V). The TTF units in catenanes **13** and **14** are less influenced by the cyclic acceptor, but still exhibit significant shifts (**13**: $E^1_{1/2} = 0.54$V, $E^2_{1/2} = 0.94$V; **14**: $E^1_{1/2} = 0.49$V, $E^2_{1/2} = 0.87$V).

The X-ray crystal structure of the catenane **14b** is shown Figure 5. Compound **7** is seen to occupy the position around the hydroquinone moiety in accordance with the conclusions drawn from the spectroscopic studies. The catenane units are arranged in such a way that the pyrrolotetrathiafulvalene moiety takes part in a face-to-face interaction with a paraquat unit from the neighboring catenane, thus generating a donor-acceptor array.

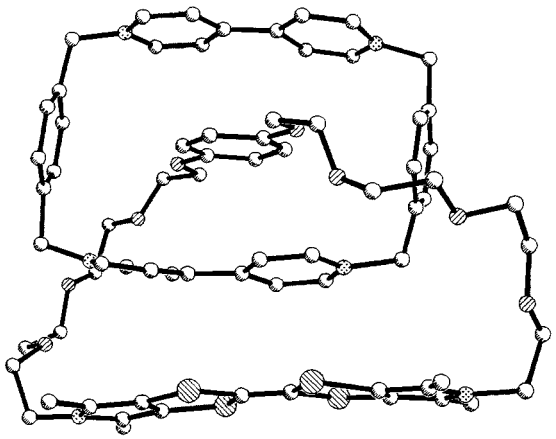


Figure 5. X-ray crystal structure of **14b**; solvent molecules and counterions are omitted for clarity

The high yields obtained for the catenanes reflect a very efficient preorganization of the reactants. Thus, the pyrrolotetrathiafulvalene unit is superior to other nonannelated tetrathiafulvalene derivatives in the self-assembly process.[1c−1f] Moreover, the pyrrolotetrathiafulvalene-based donor-acceptor systems generally give rise to more crystalline products on account of the highly symmetric donor. Nevertheless, a striking difference in the preferred position for **7** in the catenanes was observed. The association contant between 1,4-dimethoxybenzene and **7** has earlier been determined as $K_a = 18\ M^{-1}$ in acetonitrile.[13] However, 1,4-bis[2-(2-hydroxyethoxy)ethoxy]benzene associates in a much stronger complex ($K_a = 2200\ M^{-1}$ in acetonitrile)[5][14] on account of hydrogen bonding. Recent calculations by Houk et al.[10] show that the ethyleneoxy groups are indeed very important in the complexation process. The somewhat surprising result that the hydroquinone moiety is occupied in preference to the pyrrolotetrathiafulvalene unit in **13** and **14** reflects the complicated and subtle balance between all the individual noncovalent forces acting in cooperation. A major factor is the ability of the polyether oxygens to interact with the quaternary nitrogen centers and to form H-bonds to the α-H's. However, occupation of the extended bis(pyrrolo)tetrathiafulvalene moiety by **7** diminishes the possibility for the bipyridiniums to interact with the polyether oxygens compared to a situation where **7** occupies the smaller hydroquinone moiety.

In conclusion, both complexation studies and the ability to assist catenane formation have demonstrated that **1** appears as a promising building block for future developments in supramolecular chemistry.

Experimental Section

General Methods: DMF was pre-dried by standing over 4Å molecular sieves for a week before it was transferred to a dry bottle containing new 4Å molecular sieves and used without subsequent distillation. Melting points were determined on a Büchi apparatus and are uncorrected. Microanalyses were performed at The Microanalytical Lab., University of Copenhagen, Denmark, or at Atlantic Microlab. Inc., Georgia, USA. Analytical TLC was performed on Merck DC-Alufolien Kiselgel 60 F_{254} (0.2 mm) precoated TLC plates or on Polygram Alox N/UV_{254} Alumina on precoated plastic sheets (0.2 mm). Column chromatography was performed on Merck Kiselgel 60 (0.040−0.063 mm, 230−400 mesh) or on Merck basic alumina 60 (0.063−0.200 mm, 70−230 mesh). Deactivation of basic alumina was achieved by addition of 2−4 w/w% of water followed by shaking for one hour. Deactivation of silica gel was achieved by stirring the silica gel in DCM containing 2% Et_3N for 10 min. before it was filtered off and washed with DCM and dried. NMR spectra were recorded on a Bruker AC250 (250 MHz), a Varian Gemini 2000 (300 MHz), or a Bruker AC360 (360 MHz) with either the solvent or TMS as the internal standard. Chemical

shifts are given in ppm relative to TMS. Plasma Desorption Mass Spectrometry (PDMS) was performed on a Bio-ion 20R time-of-flight instrument. Electrospray (ES) mass spectra were recorded on a Finnigan MATTSQ 700 triple quadrupole mass spectrometer. Cyclic Voltammograms (CV) were performed on a single-compartment cell using an ECO CHEMIE, PGSTAT10 potentiostat with Ag/AgCl as reference electrode. The working and counter electrodes were made of platinum. The voltammograms were recorded in MeCN with Bu_4NPF_6 as the supporting electrolyte (0.1M) with a scan speed of 100 mV/s.

Macrocycle 3: A solution of bis(2,5-dimethylpyrrolo)[3,4-*d*]tetrathiafulvalene (**1**) (430 mg, 1.26 mmol) and a solution of 1,4-bis[2-(2-bromoethoxy)ethoxy]benzene (**2a**) (490 mg, 1.19 mmol) each in dry degassed DMF (50 mL) were simultaneously added to a slurry of NaH (504 mg of a 60% suspension in mineral oil, 12.6 mmol) in dry degassed DMF (10 mL) over 17 hours (3 mL/hour), with the aid of a medical perfusor pump. After the addition the orange/brown reaction mixture was allowed to stir for another two hours before it was filtered through a plug of Celite.[15] The filtrate was transferred to a separatory funnel and washed with petroleum ether (2 × 50 mL), and concentrated in vacuo. The red residue was subjected to column chromatography (Al_2O_3 − deactivated with 4% H_2O; Eluent: CH_2Cl_2/cyclohexane from 2:1 to 4:1). The yellow band was collected to give **3** (281 mg, 40%). M.p. > 250°C. − ^{1}H NMR ([D$_6$]DMSO): δ = 6.45 (s, 4 H, C_6H_4), 3.90 (t, *J* = 4.2 Hz, 4 H, NCH_2), 3.63 (t, *J* = 4.3 Hz, 4 H, OCH_2), 3.55 (t, *J* = 6.8 Hz, 4 H, OCH_2), 3.18 (t, *J* = 7.1 Hz, 4 H, OCH_2), 2.16 (s, 12 H, CH_3). − MS (PD): *m*/*z* = 588.8 (M^+). − $C_{28}H_{32}N_2O_4S_4$ (588.8): calcd C 57.11, H 5.48, N 4.76; found C 57.19, H 5.40, N 4.70.

Macrocycle 4: A solution of **1** (0.68 g, 2.00 mmol) and a solution of 1,4-bis{2-[2-(2-bromoethoxy)ethoxy]ethoxy}benzene (**2b**) (1.10 g, 2.20 mmol) each in dry degassed DMF (100 mL) were simultaneously added to a slurry of NaH (0.80 g of a 60% suspension in mineral oil, 20.0 mmol) in dry degassed DMF (20 mL) over 17 hours (6 mL/hour), with the aid of a medical perfusor pump. After addition the orange/brown reaction mixture was allowed to stir for another two hours before it was filtered through a plug of Celite.[15] The filtrate was transferred to a separatory funnel and washed with petroleum ether (3 × 50 mL) and concentrated in vacuo. The red residue was subjected to column chromatography [Al_2O_3 − deactivated with 2% H_2O; Eluent: CH_2Cl_2/EtOAc (100:1)]. Collection of the broad yellow band afforded pure **4** (0.79 g, 58%) as a yellow powder. M.p. 222°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 6.69 (s, 4 H, C_6H_4), 3.94 (t, *J* = 4.8 Hz, 4 H, NCH_2), 3.75−3.80 (m, 4 H, OCH_2), 3.57 (t, *J* = 4.8 Hz, 4 H, OCH_2), 3.45−3.55 (m, 12 H, OCH_2), 2.15 (s, 12 H, CH_3). − ^{13}C NMR ([D$_6$]DMSO): δ = 152.47, 119.21, 116.95, 115.05, 113.13, 70.48, 69.86, 69.69, 69.16, 67.34, 44.32, 11.76. − MS (PD): *m*/*z* = 676.7 (M^+). − $C_{32}H_{40}N_2O_6S_4$ (676.9): calcd C 56.78, H 5.96, N 4.14; found C 56.81, H 6.06, N 4.12.

Macrocycle 5: A solution of **1** (0.50 g, 1.48 mmol) and a solution of 1,4-bis(2-{2-[2-(2-bromoethoxy)ethoxy]ethoxy}ethoxy)benzene (**2c**) (0.87 g, 1.48 mmol) each in dry degassed DMF (50 mL) were simultaneously added to a slurry of NaH (0.59 g of a 60% suspension in mineral oil, 14.8 mmol) in dry degassed DMF (20 mL) over 12.5 hours (4 mL/hour), with the aid of a medical perfusor pump. After addition the orange/brown reaction mixture was allowed to stir for another two hours before it was filtered through a plug of Celite.[15] The filtrate was transferred to a separatory funnel and washed with petroleum ether (2 × 100 mL), and concentrated in vacuo. The red residue was subjected to column chromatography [Al_2O_3 deactivated with 2% H_2O; Eluent: CH_2Cl_2/MeOH (100:1)]. The yellow band was collected to give **5** (0.45 g, 40%) as a yellow glass. The product is not stable for longer periods of time as it gradually becomes red upon standing. − ^{1}H NMR ([D$_6$]DMSO): δ = 6.80 (s, 4 H, C_6H_4), 3.85 (m, 8 H, NCH_2, OCH_2), 3.66 (t, *J* = 4.7 Hz, 4 H, OCH_2), 3.40−3.60 (m, 20 H, OCH_2), 2.11 (s, 12 H, CH_3). − ^{13}C NMR ([D$_6$]DMSO): δ = 152.63, 119.22, 118.34, 115.25, 113.03, 70.23, 70.14, 70.11, 70.07, 69.96, 69.03, 67.51, 44.32, 11.70. − MS (PD): *m*/*z* = 764.5 (M^+). − $C_{36}H_{48}N_2O_8S_4$ (765.0): calcd C 56.52, H 6.32, N 3.66; found C 56.37, H 6.34, N 3.51.

Catenane 12: A solution of **3** (100 mg, 0.17 mmol), dication **10** (360 mg, 0.50 mmol) and 1,4-bis(bromomethyl)benzene (**11**) (148 mg, 0.56 mmol) in dry degassed DMF (6 mL) was subjected to high pressure (10 kbar) for 3 days. The solvent was removed in vacuo to give a green residue. After concentration in vacuo the green residue was subjected to column chromatography [SiO_2; Eluent: MeOH/NH_4Cl (2M)/$MeNO_2$/MeCN (14:4:2:5); applied on the column in a 1:1 mixture of $MeNO_2$ and the eluent (10 mL)]. The bluish-green band (R_f = 0.3) was collected and the solvent was removed in vacuo. Ion exchange with NH_4PF_6, followed by careful washing with H_2O gave the [2]-catenane **12** (112 mg, 39%). M.p.: dec. over a wide temperature range. The product was recrystallized by vapor diffusion of diisopropyl ether into a solution of the catenane in MeCN to give small brown crystals. − ^{1}H NMR (CD_3CN): δ = 8.99 (d, *J* = 7.3 Hz, 4 H, BIPY H_α), 8.68 (d, *J* = 7.0 Hz, 4 H, BIPY H_α), 8.03 (d, *J* = 6.9 Hz, 4 H, BIPY H_β), 7.78 (s, 8 H, C_6H_4), 6.82 (d, *J* = 7.0 Hz, 4 H, BIPY H_β), 5.91 (s, 4 H, OC_6H_4O), 5.84 (s, 4 H, BIPY NCH_2), 5.74 (s, 4 H, BIPY NCH_2), 4.17 (t, *J* = 5.0 Hz, 4 H, pyrrole NCH_2), 3.95−3.80 (m, 12 H, OCH_2), 2.35 (s, 12 H, CH_3). − MS (ES): *m*/*z* = 1543.5 (M − $PF_6)^+$, 699.3 (M − $2PF_6)^{2+}$, 417.8 (M − $3PF_6)^{3+}$. − $C_{64}H_{64}F_{24}N_6O_4P_4S_4$ (1689.3): calcd. C 45.50, H 3.82, N 4.97; found C 45.26, H 3.91, N 5.04.

Catenanes 13a/b: A solution of **4** (200 mg, 0.295 mmol), dication **10** (622 mg, 0.885 mmol) and 1,4-bis(bromomethyl)benzene (**11**) (256 mg, 0.970 mmol) in dry degassed DMF (12 mL) was subjected to high pressure (10 kbar) for 3 days. The solvent was removed in vacuo to give a brown residue. The crude product was subjected to column chromatography [SiO_2; Eluent: MeOH/NH_4Cl (2M)/$MeNO_2$/MeCN (14:4:2:5); applied on the column as a suspension in MeCN]. The broad brown band (R_f = 0.3) was collected, and the solvent was removed in vacuo. The residue was suspended in H_2O (50 mL) and the brown solid was filtered off and washed with H_2O (50 mL). The product was dissolved in MeOH (100 mL) and a saturated solution of NH_4PF_6 in MeOH was added until precipitation was complete. The precipitate was filtered off, washed with H_2O (4 × 50 mL) and dried, affording **13a/b** (347 mg, 66%) as a brown solid. The product was recrystallized for microanalysis by vapor diffusion of diisopropyl ether into a solution of the catenane in MeCN to give small brown crystals. M.p.: dec. over a broad temperature range. − ^{1}H NMR ([D$_6$]DMSO): δ = 9.45 [d, *J* = 6.6 Hz, 0.4 H, BIPY H_α (**a**)], 9.33 [d, *J* = 6.5 Hz, 0.4 H, BIPY H_α (**a**)], 9.04 [br s, 8 H, BIPY H_α (**b**)], 8.31 [d, *J* = 6.7 Hz, 0.4 H, BIPY H_β (**a**)], 8.04 [d, *J* = 4.4 Hz, 8 H, BIPY H_β (**b**)], 7.90 [s, 0.8 H, C_6H_4 (**a**)], 7.85 [s, 8 H, C_6H_4 (**b**)], 7.04 [d, *J* = 6.5 Hz, 0.4 H, BIPY H_β (**a**)], 6.28 [s, 0.4 H, OC_6H_4O (**a**)], 5.87 [s, 0.4 H, NCH_2 (**a**)], 5.74 [s, 0.4 H, NCH_2 (**a**)], 5.65 [s, 8 H, NCH_2 (**b**)], 4.10−3.65 (m), 3.63 (s), 3.58 (br s) [4.10−3.58, 24 H (**b**) + 2.4 H (**a**), NCH_2, OCH_2], 3.35 [4 H, OC_6H_4O (**b**)], 2.18 [s, 1.2 H, CH_3 (**a**)], 2.14 [s, 12 H, CH_3 (**b**)]. − ^{13}C NMR ([D$_6$]DMSO): **13b**: δ = 149.49, 145.53, 143.84, 136.85, 130.50, 125.08, 119.28, 117.73, 112.93, 112.15, 70.18, 69.84, 69.56, 69.42, 43.45, 11.86. − MS (ES): *m*/*z* = 1632.9 (M − $PF_6)^+$, 743 (M − $2PF_6)^{2+}$, 447 (M − $3PF_6)^{3+}$, 299.4 (M − $4PF_6)^{4+}$. −

Table 1. Crystal data, data collection, and refinement parameters for **3**, **4**, (**4**)2·**6** and **14b**

Data	**3**·CH_2Cl_2	**4**·$(CH_2Cl_2)_2$	(**4**)$_2$·**6**·$(C_7H_5N)_4$	**14b**·$(C_2H_3N)_2$ [a]
Formula	$C_{29}H_{34}Cl_2N_2O_4S_4$	$C_{34}H_{44}Cl_4N_2O_6S_4$	$C_{104}H_{114}F_{12}N_{10}O_{12}P_2S_8$	$C_{76}H_{86}F_{24}N_8O_8P_4S_4$
M	673.72	846.75	2242.48	1947.65
Crystal size [mm]	0.30 × 0.30 × 0.10	0.33 × 0.18 × 0.13	0.28 × 0.13 × 0.05	0.38 × 0.05 × 0.04
Crystal system	orthorhombic	triclinic	triclinic	monoclinic
Space group	*Pbca*	$P\bar{1}$	$P\bar{1}$	*C*2/*c*
Temperature [K]	120(2)	293(2)	120(2)	120(2)
a [Å]	17.520(4)	15.2565(2)	11.048(2)	25.3155(5)
b [Å]	15.810(3)	15.88810(10)	13.474(3)	11.939(3)
c [Å]	22.880(5)	17.3212(2)	18.667(4)	59.7877(10)
α [°]	90	90.1680(10)	108.21(3)	90
β [°]	90	94.9910(10)	94.12(3)	93.1840(10)
γ [°]	90	91.2500(10)	91.72(3)	90
V [Å^3]	6338(2)	4181.64(8)	2628.9(9)	18042(5)
Z	8	4	1	8
D_c [g cm^{-3}]	1.412	1.345	1.416	1.434
F(000)	2816	1768	1170	8016
μ [mm^{-1}]	0.506	0.525	0.287	0.281
2θ range [°]	1.78 to 26.38	1.18 to 26.32	1.59 to 26.38	2.96 to 23.26
Reflections collected/unique	63142/6477	43843/16797	25973/10586	60305/12952
R_{int}	0.0804	0.0789	0.0605	0.0704
Completeness of unique refl.	99.9%	98.8%	98.4%	99.8%
Max./min. transmission	0.9511/0.8630	0.9348/0.8457	0.9858/0.9239	0.9888/0.9006
Data/restraints/parameters	6477/18/387	16797/0/901	10586/0/667	12952/86/1013
Goodness-of-fit (S)	1.059	0.948	1.017	2.126
R [F, $I > 2\sigma(I)$]	0.0837	0.0596	0.0629	0.1847
wR (F^2, all)	0.2227	0.1695	0.1501	0.5160
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	1.283/−1.202	0.311/−0.289	0.548/−0.594	3.396/−1.564

[a] The poor quality of the structure determination is related to conformational disorder of three atoms in one of the polyether linkers, disorderd PF_6^- ions, as well as likely presence of unidentified disordered solvent.

$C_{68}H_{72}F_{24}N_6O_6P_4S_4$ (1777.5): calcd C 45.95, H 4.08, N 4.73; found: C 45.53, H 4.30, N 4.99.

Catenanes 14a/b: A solution of **5** (200 mg, 0.261 mmol), dication **10** (550 mg, 0.784 mmol) and 1,4-bis(bromomethyl)benzene (**11**) (228 mg, 0.862 mmol) in dry degassed DMF (12 mL) was subjected to high pressure (10 kbar) for 3 days. The solvent was removed in vacuo to give a brown residue. The crude product was subjected to column chromatography [SiO_2, Eluent: MeOH − NH_4Cl (2M) − $MeNO_2$ − MeCN (14:4:2:5); applied as a suspension in MeCN]. The broad brown band ($R_f = 0.3$) was collected, and the solvent was removed in vacuo. The residue was suspended in H_2O (50 mL) and the brown solid was filtered off and washed with H_2O (50 mL). The product was dissolved in MeOH (100 mL) and a saturated solution of NH_4PF_6 in MeOH was added until precipitation was complete. H_2O (50 mL) was added, and the precipitate was filtered off, washed with H_2O (4 × 50 mL) and dried, affording **14a/b** (220 mg, 45%). The product was recrystallized for microanalysis and X-ray structure determination by vapor diffusion of diisopropyl ether into a solution of the catenane in MeCN to give dark crystals. M.p.: dec. over a wide temperature range. − ^{1}H NMR ([D$_6$]DMSO): **14b**: δ = 9.06 (d, J = 6.5 Hz,, 8 H BIPY H$_\alpha$), 8.23 (d, J = 6.6 Hz, 8 H, BIPY H$_\beta$), 7.88 (s, 8 H, C_6H_4), 5.52 (s, 8 H, BIPY NCH_2), 4.00−3.45 (m, 36 H, NCH_2, OCH_2, OC_6H_4O), 2.08 (s, 12 H, CH_3). − MS (ES): m/z = 787.34 (M − 2PF$_6$)$^{2+}$, 476.56 (M − 3PF$_6$)$^{3+}$, 321.12 (M − 4PF$_6$)$^{4+}$. − $C_{72}H_{80}F_{24}N_6O_8P_4S_4$·$CH_3CN$·2$H_2O$ (1942.6): calcd C 45.75, H 4.51, N 5.05; found: C 45.51, H 4.61, N 5.02.

X-ray Crystallography: The data for **3**, **4**, (**4**)$_2$·**6** and **14b** are collected in Table 1. A Siemens/Bruker SMART CCD diffractometer was employed. Data collection, integration of frame data and conversion into intensities corrected for Lorenz, polarization and absorption effects were performed using the programs *SMART* and *SAINT* [*SMART and SAINT. Area Detector Control and Integration Software. Version 4.05*. Siemens Analytical X-Ray Instruments Inc., Madison, Wisconsin, USA, **1995**] and SADABS [G.M. Sheldrick, *SADABS. Program for Empirical Correction of Area Detector Data*. University of Göttingen, Germany **1996**]. Structure solution, refinement, structure analysis and production of crystallographic illustrations was carried out with the programs *SHELXS97* [G.M. Sheldrick, *Acta Crystallogr.* **1990,** *A46,* 467−473], *SHELXL97* [G.M. Sheldrick, *SHELXL97*. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany, **1997**], *PLATON* [A.L. Spek, *Acta Crystallogr.* **1990** *A46*, C-34], and *SHELXTL* [G.M. Sheldrick, *SHELXTL. Structure Determination Programs. Version 5.10*. Siemens Analytical X-Ray Instruments Inc., Madison, Wisconsin, USA, **1997**]. H atoms were included in calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-133868 (**3**), CCDC-133869 (**4**), CCDC-121722 [(**4**)$_2$·**6**] and CCDC-121723 (**14b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44-1223/336-033; email: deposit@ccdc.cam.ac.uk].

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[8] $\Delta\delta_{\beta-H}$ was measured for a 1:1 mixture of **4** and **6** at different concentrations *c*, and the association constant K_a was determined by nonlinear curve-fitting of these data points (19 data points were collected in total) employing the following expression:

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

where Δδ(sat) denotes the saturated chemical shift change.
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