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A Chemically and Electrochemically Switchable [2]Catenane Incorporating a Tetrathiafulvalene Unit[**]

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Highly efficient constructions of mechanically interlocked molecules,[1] such as catenanes and rotaxanes, have followed rapidly in the wake of the development of self-assembly[2] in synthetic supramolecular chemistry.[3] The opportunity now exists to control the relative dispositions of one component with respect to the other(s) in such molecules by either chemical[4] or electrochemical[4a, 5] means. In this context, the tetrathiafulvalene[6] (TTF) unit represents a particularly attractive building block, since it can be oxidized sequentially and reversibly to the monocation ($E_{1/2} = +0.32$ V) and the dication ($E_{1/2} = +0.72$ V). Its redox properties, together with its ability to form[7, 8] a strong green 1:1 complex in both the solution and solid states with cyclobis(paraquat-*p*-phenylene) tetrakis(hexafluorophosphate),[9] have been largely responsible for its incorporation into the thread-like components of pseudorotaxanes,[10] as well as into catenanes[11] and rotaxanes.[8, 12] Here, we describe 1) the self-assembly of a [2]catenane comprising a macrocyclic polyether ring with two π-electron-rich "stations"—namely a 1,5-dioxynaphthalene moiety and a TTF unit—and the π-electron-deficient cyclobis(paraquat-*p*-phenylene),[9] 2) its solid-state structure and superstructure, 3) its spectroscopic characterization in solution, and 4) its ability to be switched both chemically and electrochemically, at the molecular level, between two different "states".

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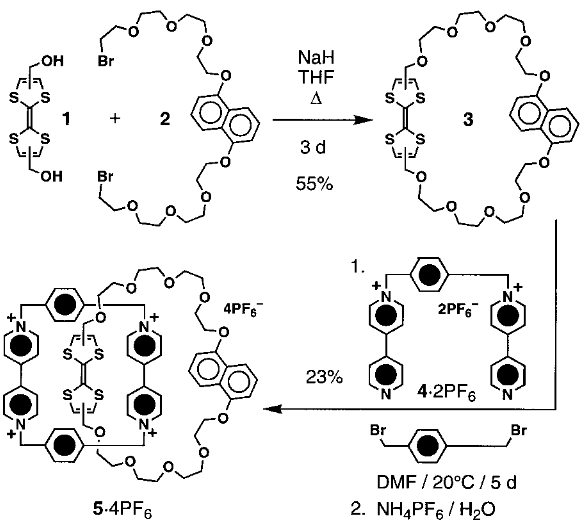
The [2]catenane $\mathbf{5}\cdot 4\,\mathrm{PF}_6$ was self-assembled in 23 % yield, as a pure compound, by employing a "*cis–trans*" isomeric mixture of the crown ether incorporating TTF (**3**) as a template for the formation of catenated cyclobis(paraquat-*p*-phenylene) from $\mathbf{4}\cdot 2\,\mathrm{PF}_6$ and paraxylylene dibromide (Scheme 1). A 55 % yield of **3** was obtained by treatment of the TTF-diol **1**[13] with NaH in THF containing the dibromide **2**.[14] Slow diffusion of *i*Pr$_2$O into a MeCN solution of $\mathbf{5}\cdot 4\,\mathrm{PF}_6$ produced deep bluish-green crystals suitable for X-ray structural analysis.[15] In the solid state the TTF portion of the crown ether is positioned on the "inside" of the tetracationic cyclophane and the 1,5-dioxynaphthalene ring system "alongside" it[16] (Figure 1). The TTF is steeply inclined to the plane of the cyclophane, its central C–C bond subtending an angle of 74° to this plane—a value that is noticeably larger than the 66° observed in the 1:1 complex formed[7,8] between TTF and the cyclobis(paraquat-*p*-phenylene) tetracation.[9] It is important to note that, of the two possible constitutional isomers of the disubstituted TTF, *only* the "*trans*" isomer is observed in the solid state; the [2]catenane structure thus displays a chiral plane.[17] The complex is stabilized by the normal combination of $\pi-\pi$ stacking interactions[18] and [C–H···O] hydrogen bonds[19] from α-bipyridinium hydrogen atoms (the latter, in one instance, to the second oxygen atom from the TTF in one polyether chain and, in the other, to the first oxygen atom from the TTF in the other polyether chain).[20] The catenane molecules pack to form "conventional" polar stacks with a 3.29 Å separation between the 1,5-dioxynaphthalene and bipyridinium ring systems of *C*-face centrally translated molecules.



Scheme 1. The self-assembly of the [2]catenane $\mathbf{5}\cdot 4\,\mathrm{PF}_6$ in which the TTF crown ether **3** obtained from diol **1** and dibromide **2** in the presence of a base serves as template for the formation of the cyclobis(paraquat-*p*-phenylene) tetracation.

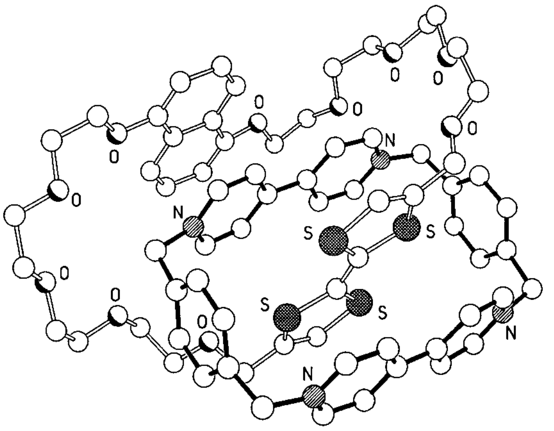


Figure 1. A ball-and-stick representation of the solid-state structure of the [2]catenane $\mathbf{5}^{4+}$.

The UV/Vis spectrum of the [2]catenane $\mathbf{5}\cdot 4\,\mathrm{PF}_6$ (Figure 2, curve a) reveals a charge transfer (CT) absorption band centered on 835 nm ($\varepsilon = 3500\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) characteristic of structures containing a TTF unit "inside" the tetracationic cyclophane.[10] Furthermore, no absorption band is observed in the 500–560 nm region for the CT interaction that would result from the 1,5-dioxynaphthalene moiety's being located "inside" the cyclophane.[5e] Not only does the ^{1}H NMR spectrum (Figure 3a) recorded in CD$_3$CN support this conclusion, it also indicates[21] that only *one* of the two constitutional isomers possible for the arrangement with the TTF unit "inside" the tetracationic cyclophane—almost certainly the "*trans*" isomer, which is the only isomer observed in the solid state (Figure 1)—is present.

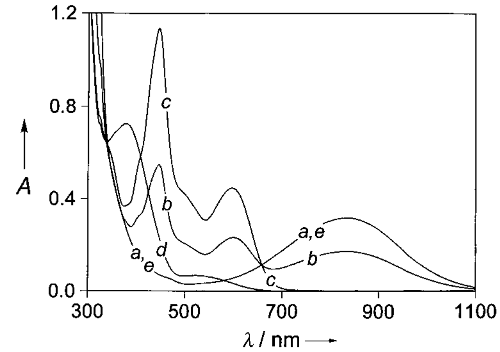


Figure 2. Absorption spectra (MeCN, 298 K) of a $9\times10^{-5}\,\mathrm{M}$ solution of [2]catenane $\mathbf{5}^{4+}$ (curve a) and of the same solution after addition of 0.4, 1.0, and 2.0 equiv of Fe(ClO$_4$)$_3$ (curves b–d). Addition of 2 equiv of ascorbic acid gives back the original spectrum (curve e).

We hypothesized that it should be possible to trigger total and completely reversible redox switching between the two translational "isomers" of the [2]catenane $\mathbf{5}^{4+}$ by either chemical or electrochemical means (Scheme 2). We now demonstrate the truth of this hypothesis in a series of experiments where the redox switching of the [2]catenane between two different "isomeric" states [$\mathbf{5}^{4+}$ and $\mathbf{5}^{5+}$ and/or $\mathbf{5}^{6+}$] is monitored by ^{1}H NMR and UV/Vis spectroscopy (when the switching is driven chemically) and by cyclic voltammetry (when the switching is driven electrochemically).

The chemical switching of $\mathbf{5}^{4+}$ was performed by redox reactions. In the ^{1}H NMR experiments, oxidation of the TTF unit of $\mathbf{5}^{4+}$ (concentration: $3.6\times10^{-3}\,\mathrm{M}$) was carried out in

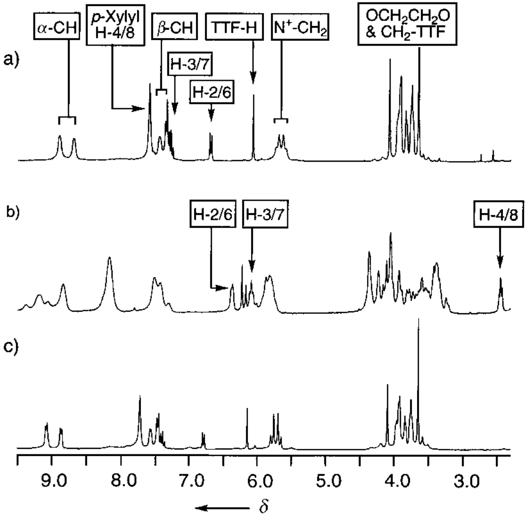
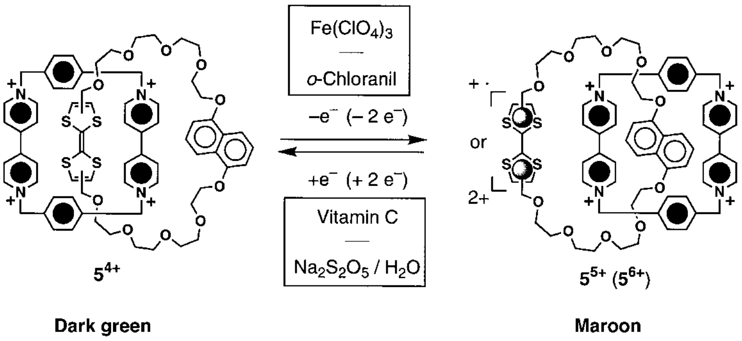


Figure 3. Partial ^{1}H NMR spectra (300 MHz) recorded in CD_3CN of a 3.6×10^{-3} M solution of the [2]catenane $\mathbf{5}^{4+}$ (a), after addition if 2 equiv of *o*-chloranil (b), and after reduction of $\mathbf{5}^{4+}$ with 2.2 equiv of $Na_2S_2O_5$ and isolation of the [2]catenane $\mathbf{5}^{4+}$ as its PF_6^- salt (c).



Scheme 2. The chemically and electrochemically triggered redox switching of [2]catenane.

CD_3CN with two equivalents of *o*-chloranil. After oxidation, the resonance (Figure 3b) for the protons attached to the 4- and 8-positions of the 1,5-dioxynaphthalene moiety is shifted significantly to higher fields and is centered on $\delta = 2.45$: the proton resonances for H-2/6 and H-3/7 appear at $\delta = 6.27$ and $\delta = 5.99$, respectively. The difference between the δ values for H-4/8, H-2/6, and H-3/7 upon oxidation of the TTF unit of the [2]catenane with *o*-chloranil and those of the free, unoxidized macrocycle are -5.33, -0.64, and -1.37, respectively. They are of a similar magnitude to those previously reported[5e, 14, 21] and so support the conclusion that the 1,5-dioxynaphthalene moiety of the macrocycle is encircled by the tetracationic cyclophane after oxidation of the TTF group. Moreover, the integrals for these particular resonances indicate that this mechanical state is the one that is populated exclusively. The ^{1}H NMR spectrum exhibits very little paramagnetic peak broadening, indicating[22] the preferential formation of the oxidized species $\mathbf{5}^{6+}$. Reduction of $\mathbf{5}^{6+}$ with 2.2 equivalents of $Na_2S_2O_5$ in CD_3CN in the presence of a few drops of H_2O and subsequent counterion exchange with NH_4PF_6, followed by evaporation of the solvent, washing of the dark green residue with H_2O, drying, and redissolving it in CD_3CN, yielded an ^{1}H NMR spectrum (Figure 3c) that was virtually identical with the original one (Figure 3a), confirming that the TTF unit is once again residing inside the cavity of the tetracationic cyclophane as shown in $\mathbf{5}^{4+}$ in Scheme 2.

In the UV/Vis experiments ($\mathbf{5}^{4+}$ concentration: 9×10^{-5} M), $Fe(ClO_4)_3$ was used as an oxidant in MeCN solution. As shown in Figure 2, addition of the oxidant (up to 1 equiv) caused a continuous decrease in the intensity of the CT band at 835 nm, characteristic of the encircling of the TTF unit by the tetracationic cyclophane. Accompanying this decrease, an increase in the intensity of the absorption bands with $\lambda_{max} = 450$ and 600 nm, characteristic of the mono-oxidized form of the TTF unit,[23] was observed (Figure 2, curve c). As a consequence of these spectral variations, the color of the solution changes from dark green to maroon. The CT band ($\lambda_{max} = 515$ nm) due to the encirclement of the naphthalene moiety by the tetracationic cyclophane,[5b,e] expected on the basis of the ^{1}H NMR results, cannot be seen because it is hidden by the more intense bands of the oxidized TTF unit. Further addition of the oxidant (up to 2 equiv) caused the disappearance of the absorption bands of mono-oxidized TTF and formation of a new band ($\lambda_{max} = 375$ nm), which may be attributed to the bis-oxidized TTF unit.[24] An important observation is that the band due to the encirclement of the naphthalene moiety by the tetracationic cyclophane can now be seen (Figure 2, curve d). On addition of 1 equiv of ascorbic acid (as reductant), the bands of the TTF radical cation were completely restored. Further addition of 1 equiv of ascorbic acid yielded the original absorption spectrum with the characteristic CT band due to the encirclement of the TTF unit by the tetracationic cyclophane (Figure 2, curve e). Identical spectral changes have been obtained with Ag powder as reductant in place of ascorbic acid.

In conclusion, the ^{1}H NMR and UV/Vis experiments show clearly that the oxidation/reduction cycle of the TTF unit causes switching between the two translational "isomers" of $\mathbf{5}^{4+}$ (Scheme 2).

Switching can also be induced electrochemically. On electrochemical oxidation,[25] the two processes involving the TTF unit (+0.28 and +0.70 V vs SCE in crown ether **3**) and, at more positive potentials, the oxidation of the 1,5-dioxynaphthalene moiety (+1.17 V vs SCE in **3**) are expected.[26] Furthermore, since the ^{1}H NMR spectroscopic data show that the only observed "isomer" of $\mathbf{5}^{4+}$ has the TTF unit residing in the "inside" position, in the catenane the first oxidation of the TTF unit should be displaced toward more positive potentials relative to those of the free crown ether **3**. This prediction is confirmed by the experimental results. However, contrary to what happens in the crown ether, the first oxidation process of the TTF unit is characterized by a very large separation between the anodic and cathodic peaks. On increasing the scan rate, the former moves toward more positive potentials, the latter toward less positive potentials. At a scan rate of 50 mV s^{-1}, there is only one anodic peak at +0.80 V vs SCE, whose current intensity indicates the occurrence of a bielectronic process. Therefore, at this potential, the second oxidation of TTF also takes place; this process is reversible (halfwave potential +0.76 V vs SCE) as indicated by the cathodic part of the scan. The oxidation of the 1,5-dioxynaphthalene moiety is strongly displaced toward positive potentials (+1.60 V vs SCE) relative to those of the free crown ether.

The scan-rate dependence of the separation between the anodic and cathodic peaks of the first oxidation process of the TTF unit of $\mathbf{5}^{4+}$ indicates that oxidation is followed by a reaction taking place on the time scale of the electrochemical experiment.[27] The nature of such a reaction is elucidated by the following observations: 1) the second oxidation of the TTF unit is reversible, which shows that the system does not undergo any further reaction after one-electron oxidation; 2) the strongly positive potential value for oxidation of the 1,5-dioxynaphthalene moiety indicates that it is trapped within the tetracationic cyclophane.[28] These features strongly suggest that the action taking place as a consequence of the first oxidation of the TTF unit is the circumrotation of the macrocyclic polyether with respect to the tetracationic cyclophane to yield the translational "isomer" with the 1,5-dioxynaphthalene moiety positioned "inside" the cyclophane (Scheme 2). This observation is consistent with the dethreading observed[10b] upon one-electron oxidation of a pseudorotaxane in which a TTF-containing thread is located "inside" the tetracationic cyclophane. We have also found by fluorescence measurements that a 1,5-dioxynaphthalene-containing thread like **2** replaces the TTF unit "inside" the tetracationic cyclophane when the TTF moiety is mono-oxidized.

We have shown that total and completely reversible switching between the two translational "isomers" of catenane $\mathbf{5}^{4+}$ can be performed by either chemical or electrochemical oxidation/reduction cycles.[29] The process, which is accompanied by a clearly detectable color change, can be followed by ^{1}H NMR spectroscopy, UV/Vis spectroscopy, and cyclic voltammetry. This result represents a further step toward the design of chemical systems whose structures and properties can be controlled by use of external stimuli.

Experimental Section

3: NaH (288 mg, 12.0 mmol) was suspended in dry, degassed THF (280 mL) and a mixture of the diol **1**[13] (925 mg, 3.50 mmol), and the dibromide **2**[14] (2.24 g, 3.50 mmol) in dry, degassed THF (250 mL containing 50 mg of both LiBr and CsOTs) was added with stirring during 20 h while refluxing under Ar. After refluxing and stirring had been continued for a further 72 h, the reaction mixture was cooled down to 10°C, and wet THF (20 mL) was added with care. The solvents were removed under vacuum, and the residue extracted into CH_2Cl_2 (2 × 250 mL). The combined organic layers were washed with saturated aqueous NaCl solution (50 mL) and H_2O (4 × 30 mL), before being dried ($MgSO_4$) and concentrated under reduced pressure to afford a residue which was subjected to column chromatography (SiO_2:CH_2Cl_2/MeOH 30:1). The macrocycle **3** was isolated as a yellow wax (1.61 g, 55%). MS (LSI): $m/z = 740$ [M^+]; ^{1}H NMR (CD_3CN, 300 MHz, 25°C): $\delta = 3.40-3.72$ (m, 26H), 3.84–3.94 (m, 6H), 4.18–4.28 (m, 6H), 6.85–6.95 (m, 2H), 7.31–7.41 (m, 2H), 7.47–7.84 (m, 2H); ^{13}C NMR (CD_3CN, 75.1 MHz, 25°C): $\delta = 51.9$, 62.0, 69.1, 70.2, 70.4, 71.2, 71.6, 72.1, 73.4, 106.9, 115.1, 118.6, 126.5, 127.6, 155.3. Elemental analyses calcd for $C_{34}H_{44}O_{10}S_4$: C 55.11, H 5.99, S 17.31; found C 54.99, H 5.98, S 17.4.

$\mathbf{5}\cdot 4PF_6$: A solution of **3** (1.39 g, 1.88 mmol), $\mathbf{4}\cdot 2PF_6$ (1.33 g, 1.88 mmol) and *p*-xylylene dibromide (496 mg, 1.88 mmol) in dry, degassed DMF (125 mL) was stirred under Ar for 5 days, and then the solvent was removed under vacuum. After the residue had been extracted with CH_2Cl_2, MeCN was added. Undissolved polymeric material was filtered off, and the MeCN solution concentrated to a residue, which was subjected to column chromatography (SiO_2, MeOH:2 N NH_4Cl:$MeNO_2$ 4:1.5:1.5). The darkish green fraction was collected, the solvent evaporated off, the residue dissolved in H_2O (100 mL), and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation occurred. The precipitate was filtered off, washed with H_2O (2 × 10 mL), and dried under vacuum. The pure [2]catenane $\mathbf{5}\cdot 4PF_6$ was obtained as a bluish-green solid (808 mg, 23%). M.p. 300°C; MS (LSI): $m/z = 1840$ [M^+], 1695 [$M - PF_6$]$^+$, 1551 [M+H − 2PF_6]$^+$, 1406 [M+H − 3PF_6]$^+$; ^{1}H NMR (CD_3CN, 300 MHz, 25°C): $\delta = 3.50-4.00$ (m, 32H), 4.08 (br s, 4H), 5.55–5.78 (m, 8H), 6.08 (br s, 2H), 6.68–6.73 (m, 2H), 7.24-7.31 (m, 2H), 7.32–7.37 (m, 4H), 7.40–7.60 (m, 4H), 7.60–7.70 (m, 10H), 8.65–8.75 (m, 4H), 8.85–9.00 (m, 4H); ^{13}C NMR (CD_3CN, 75.1 MHz, 25°C): $\delta = 65.2$, 68.5, 68.6, 70.4, 70.5, 70.7, 71.1, 71.3, 71.6, 72.0, 106.6, 114.6, 119.8, 125.0, 125.3, 126.9, 133.5, 136.7, 143.9, 144.3, 145.5, 146.4, 154.6. Elemental analysis calcd for $C_{70}H_{76}F_{24}N_4O_{10}S_4P_4$: C 45.66, H 4.16, N 3.04, S 6.96; found C 45.55, H 4.28, N 3.18, S 7.1.

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[15] Crystal data for **5** $\cdot 4\,PF_6 \cdot 6\,MeCN$: monoclinic, space group *Cc* (no. 9), $a = 21.780(1)$, $b = 16.294(1)$, $c = 27.436(2)$ Å, $\beta = 93.94(1)^\circ$, $V = 9713.9(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.428\ g\,cm^{-3}$, $\mu(Cu_{K\alpha}) = 24.5\ cm^{-1}$, $T = 203$ K, 6549 independent reflections measured, 5555 observed with $|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 114^\circ$, refined on F^2 to $R_1 = 0.072$, $wR_2 = 0.183$ for 1023 parameters. The polarity of the structure was determined from the Flack parameter. The data were collected on a Siemens P4/RA diffractometer with ω scans and graphite monochromated $Cu_{K\alpha}$ radiation. The structure was solved by direct methods. The non-hydrogen atoms of the crown, the PF_6^- anions, and the included MeCN molecules were refined anisotropically; due to a shortage of observed data, the non-hydrogen atoms of the tetracation were refined isotropically. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100460. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: int. code + (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

[16] The $OC_6H_{10}O$ vector of the "alongside" 1,5-dioxynaphthalene moiety is inclined by 18° to the mean plane of the tetracation.

[17] The [2]catenane molecules crystallize in a noncentrosymmetric space group, which contains a glide plane. Hence there are equal numbers of enantiomeric molecules present in the crystal.

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[20] The mean interplanar separations between the "inside" disubstituted TTF ring system and the "inside" and "alongside" bipyridinium units are 3.43 and 3.37 Å, respectively; the separation between the "alongside" 1,5-dioxynaphthalene moiety and the "inside" bipyridinium unit is 3.31 Å. Hydrogen bonds between α-bipyridinium hydrogen atoms on the "inside" bipyridinium unit and the two polyether oxygen atoms have the following geometries: $[C \cdots O]$ 3.39 and 3.12 Å, $[H \cdots O]$ 2.43 and 2.40 Å; $C{-}H \cdots O$ angles 174° and 132°. The diametrically opposite sulfur atoms adjacent to the "*trans*"-substituted carbon atoms lie about 3.6 Å from the centroids of their proximal para-xylylene rings.

[21] When a 1,5-dioxynaphthalene moiety is located "inside" the tetracationic cyclophane, the H-4,8 protons resonate (M. Asakawa, P. R. Ashton, S. E. Boyd, C. L. Brown, R. E. Gillard, O. Kocian, F. M. Raymo, J. F. Stoddart, M. S. Tolley, A. J. P. White, D. J. Williams, *J. Org. Chem.* **1997**, *62*, 26–37) at very high field ($\delta = 2.1-2.6$). The fact that these naphthalene ring protons in the [2]catenane give rise to a masked signal (identified by a COSY experiment) in the region $\delta = 7.60-7.70$ confirms unequivocally that the 1,5-dioxynaphthalene moiety of the macrocycle is not located inside the tetracationic cyclophane. Intimate encirclement of the TTF unit by the tetracationic cyclophane was confirmed by 2D ROESY experiments (400 MHz, CD_3CN, 31°C, 200 ms mixing time), which display cross-peaks between the OCH_2 protons attached to the TTF core, and both the α-bipyridinium and the *p*-xylyl protons of the tetracationic cyclophane. No cross-peaks could be observed indicating that none of the 1,5-dioxynaphthalene moiety is located inside!

[22] The reduction potential of *o*-chloranil (+0.83 V: L. Horner, E. Geyer, *Chem. Ber.* **1965**, *98*, 2016–2045) substantiates the formation of the dicationic TTF species $\mathbf{5}^{6+}$. The UV/Vis spectrum (concentration: 9×10^{-5} M) recorded in MeCN shows no absorbance at $\lambda_{max} = 600$ nm, which is characteristic of $\mathbf{5}^{5+}$. The other typical band for the monooxidized TTF species at $\lambda_{max} = 450$ nm is hidden by the more intense band of *o*-chloranil ($\lambda_{max} = 435$ nm). Clear evidence for the presence of the bisoxidized TTF unit is provided by mass spectrometry. When examined with electrospray ionization (VG ProSpec mass spectrometer) in MeCN as solvent, the predominant ions observed for a 3:1 mixture of $\mathbf{5}^{4+}$ and *o*-chloranil are $m/z = 775$ and 468. They correspond to the loss of two and three PF_6^- counterions. On observation of the isotopic abundances for these species, the ion corresponding to loss of two counterions at $m/z = 775$ is doubly charged, as evidenced by the 0.5 u separation between the isotopes. The ion at $m/z = 468$ is shown to be triply charged with an isotopic separation of 0.3 u. A freshly prepared sample obtained after mixing *o*-chloranil and $\mathbf{5}^{4+}$ in a 2:1 ratio shows a peak at $m/z = 898$ as the most abundant in the spectrum. This peak corresponds to the incorporation of one counterion derived from *o*-chloranil into the [2]catenane. Once again, this species was found to be doubly charged by examination of isotopic abundances. Additionally, the spectrum shows peaks at $m/z = 775$ and 468. These peaks are the major ones for a sample recorded after standing for one week. The isotopic separations of these ions confirm that they are doubly ($m/z = 775$) and triply ($m/z = 468$) charged species. None of the spectra obtained show evidence for the presence of a monocationic species. As expected with reference to the second oxidation potential of the crown ether **3**, oxidation with *o*-chloranil yields preferentially $\mathbf{5}^{6+}$. We would like to thank one of the referees for asking us to comment on the nature of the oxidation state of the TTF unit.

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[25] The electrochemical experiments were carried out in argon-purged MeCN solutions with a Princeton Applied Research 273 multipurpose instrument interfaced to a personal computer, with cyclic voltammetry and differential pulse voltammetry techniques. The exact configuration and procedures for these measurements have been reported in Ref. [5e].

[26] A detailed study of the interesting electrochemical behavior of crown ether **3** will be reported elsewhere.

[27] The alternative explanation, based on lack of reversibility of the electrode process due to restricted access to the inside TTF unit, can be ruled out on consideration of the behavior observed for all the catenanes and rotaxanes previously investigated. See, for example: a) Ref. [5b]; b) P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi, D. J. Williams, *J. Am. Chem. Soc.* **1996**, *118*, 4931–4951.

[28] We have found that oxidation of a 1,5-dioxynaphthalene moiety in "alongside" and "inside" positions occurs at +1.30 and +1.55 V vs SCE, respectively, in a catenane made of the cyclobis(paraquat-*p*-phenylene) tetracation and a crown ether (1/5DN38C10) containing two 1,5-dioxynaphthalene moieties.

[29] Since, strictly speaking, $\mathbf{5}^{4+}$ and $\mathbf{5}^{5+}(\mathbf{5}^{6+})$, with their different oxidation states, are *not* isomers, we have introduced quotation marks round the term *isomer(s)* in our discussion of these two catenated species.