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# A Bistable Pretzelane†

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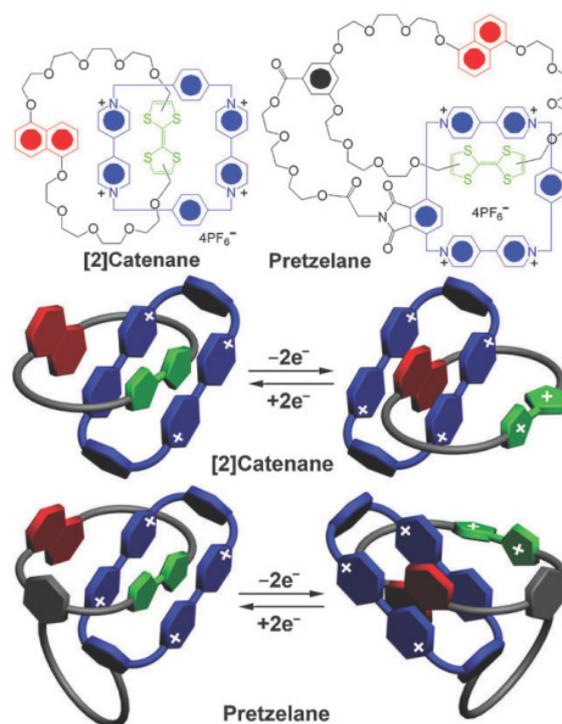
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A switchable donor-acceptor pretzelane composed of a crown ether containing tetrathiafulvalene and 1,5-dihydroxynaphthalene recognition units and covalently tethered cyclobis(paraquat-*p*-phenylene) ring exhibits unidirectional motion on both oxidation (forwards) and reduction (backwards).

The widespread use of controlled molecular-level motion in biological systems<sup>1</sup> suggests to us that artificial molecular machines can carry out specific tasks by relying mainly on physical and chemical stimuli in order to mimic the motion found in the molecular machinery present in living cells. Thus, the preparation and application of artificial molecular machines<sup>2,3</sup> have attracted the attention of chemists, physicists, material scientists and engineers in recent times. In the realm of synthetic molecular machinery, stimuli-responsive molecular switches<sup>2a,2g,3a,3c,3g</sup> are highly desirable prototypes in the fabrication of artificial machines.

Electrochemically-driven molecular mechanical switches, such as bistable donor-acceptor [2]catenanes and [2]rotaxanes<sup>2a,2g,3a,3c</sup> have been the subject of a number of forays into solid-state devices, as well as in solution. We have developed<sup>4</sup> a template-directed protocol (Scheme 1) for the synthesis of a bistable [2]catenane incorporating a crown ether containing  $\pi$ -electron rich tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) recognition units interlocked with a tetracationic cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup>) ring comprised of two  $\pi$ -electron deficient bipyridinium units. The bistability of this switchable [2]catenane relies on the ability of the CBPQT<sup>4+</sup> ring to encircle much more strongly the TTF unit than it does the considerably less  $\pi$ -electron rich DNP unit in the crown ether. Switching is achieved by the reversible oxidation of the TTF unit, firstly to the radical cation (TTF<sup>•+</sup>) and then subsequently to its dication (TTF<sup>2+</sup>), thus producing Coulombic charge-charge repulsion between the oxidized TTF<sup>•+</sup> or TTF<sup>2+</sup> species and the CBPQT<sup>4+</sup> ring, leading to the movement of the CBPQT<sup>4+</sup> ring to the DNP unit. After reduction of the TTF<sup>•+</sup> radical cation or TTF<sup>2+</sup> dication to the neutral form, the CBPQT<sup>4+</sup> ring migrates back to the TTF recognition unit, indicating that the redox-switchable process in the [2]catenane is fully reversible. When the crown ether is tethered covalently to a preformed part of the CBPQT<sup>4+</sup> ring, the resulting macrocyclization<sup>5</sup> from its synthetic precursors occurs intramolecularly to generate a bistable pretzelane. Based on this synthetic protocol, we describe here (Scheme 1) the template-directed synthesis and redox-active switching properties of the bistable pretzelane **1**•4PF<sub>6</sub> containing a CBPQT<sup>4+</sup> ring and TTF/DNP units encircled by a tethered crown ether component. Particular attention has been given to determining the redox-

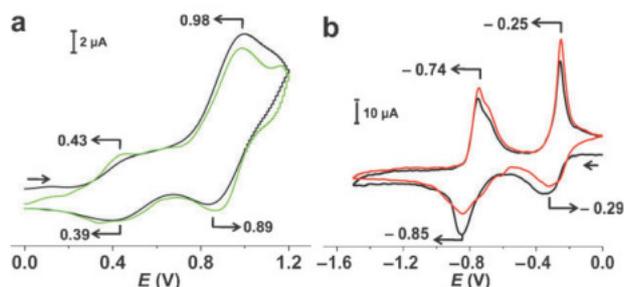
responsive switching behaviour of the CBPQT<sup>4+</sup> ring in **1**•4PF<sub>6</sub> and it is also discussed therein.



**Scheme 1** Bistable [2]catenane and pretzelane **1**•4PF<sub>6</sub> containing the TTF and DNP recognition units and the CBPQT<sup>4+</sup> ring.

The synthesis of **1**•4PF<sub>6</sub> is outlined in Scheme S1 in the Supplementary Information (SI) and the bistable pretzelane was studied by cyclic voltammetry (CV), differential pulse voltammetry (DPV), UV-Vis spectroelectrochemistry (SEC), and <sup>1</sup>H NMR spectroscopy, following initial probing by UV-Vis spectroscopy.

The UV-Vis spectrum of **1**•4PF<sub>6</sub> recorded in MeCN shows a broad charge transfer (CT) absorption band centered on 840 nm which is characteristic<sup>4</sup> of the translational isomer in which the TTF unit is encircled by the CBPQT<sup>4+</sup> ring. No absorption band is observed in the 450–600 nm region for a CT band which would result from the other translational isomer in which the DNP unit is encircled by the CBPQT<sup>4+</sup> ring, a fact which suggests that **1**•4PF<sub>6</sub> exists as a single translational isomer in solution – that is, the one in which the CBPQT<sup>4+</sup> ring encircles the TTF unit. Hence, it was clear that the opportunity presented itself for us to investigate the switching behavior of the CBPQT<sup>4+</sup> ring between the TTF and DNP units in **1**•4PF<sub>6</sub> by addressing the redox states of the TTF unit.

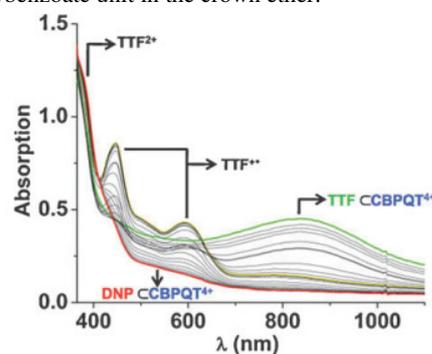


**Fig. 1** Cyclic voltammograms of **1•4PF<sub>6</sub>**. (a) First (black) and second (green) cyclic voltammograms of **1•4PF<sub>6</sub>** displaying the characteristic metastable peak (MSCC, +0.43 V) in the second cycle recorded in Ar-purged MeCN at 298 K with a scan rate of 200 mV s<sup>-1</sup>; (b) First (black) and second (red) cyclic voltammograms of **1•4PF<sub>6</sub>** displaying the reduction region recorded in Ar-purged MeCN at 298 K with a scan rate of 200 mV s<sup>-1</sup>. The concentrations of the sample and supporting electrolyte are 1.0 mM and 0.1 M, respectively.

In the CV experiments (Fig. 1a) of **1•4PF<sub>6</sub>**, the first oxidation peak for the TTF unit which is discernable around +0.43 V for ‘free’ TTF<sup>3c,3h</sup> is hardly detectable at all in the anodic scan. DPV analysis shows (Fig. S1 in the SI) a small peak at +0.48 V. These results indicate the existence of a small presence of ‘free’ TTF in association with a small amount of the minor translational isomer present in **1•4PF<sub>6</sub>** at equilibrium. The first substantial TTF oxidation peak is shifted to higher potential and overlaps with the second oxidation peak at +0.98 V. In the DPV analysis, the first and second TTF oxidation peaks are found around +0.81 V, potentials which correspond to the first oxidation of the TTF unit encircled by the CBPQT<sup>4+</sup> ring and/or the second oxidation of the TTF unit once the ring has migrated from the TTF unit to the DNP unit. In the cathodic scan of **1•4PF<sub>6</sub>**, two CV peaks, corresponding to the reduction of the oxidized TTF<sup>•+</sup> radical cation and the TTF<sup>2+</sup> dication, are observed at +0.39 and +0.89 V, respectively. The cathodic scan of the DPV analysis reveals the related peaks at +0.45 and +0.78 V. The fact that the CBPQT<sup>4+</sup> ring encircles the DNP unit does not affect the reduction potentials of the TTF<sup>•+</sup> radical cation and TTF<sup>2+</sup> dication. In the reducing portion (Fig. 1b) of the CV of **1•4PF<sub>6</sub>**, a typical first two-electron reduction peak and a second two-electron reduction peak of the CBPQT<sup>4+</sup> ring are observed at -0.29 and -0.85 V, respectively.

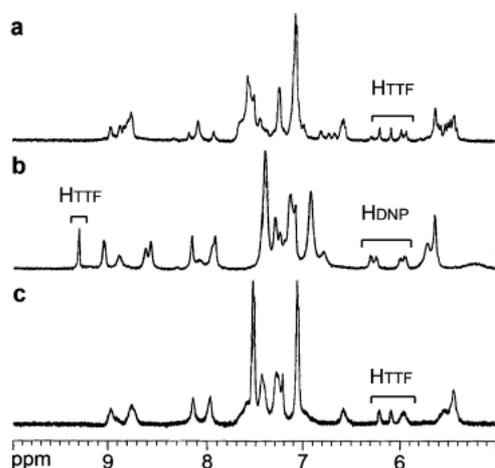
There is an equilibrium<sup>3c,6</sup> established between the CBPQT<sup>4+</sup> ring encircling the TTF unit – called the ground-state co-conformer (GSCC) – and the DNP unit – called the metastable state co-conformer (MSCC). The first oxidation state of the GSCC corresponds to the removal of an electron from the TTF unit, and is accompanied by a rapidly driven swinging of the CBPQT<sup>4+</sup> ring to the DNP unit while the TTF<sup>•+</sup> radical cation is further oxidized to its TTF<sup>2+</sup> dication. Upon reduction of this dication back to its neutral state, the MSCC is formed. The MSCC and GSCC are readily distinguished from each other by CV since the oxidation potential of the ‘free’ TTF unit on the MSCC is approximately 200 mV<sup>3c</sup> less positive than that for the GSCC. The return of the MSCC to the GSCC constitutes a recovery of the equilibrium distribution and is activated thermally. By varying the time between the first and second CV scans, the kinetic parameters for relaxation from the MSCC to the GSCC can be found. Fig. S2 in the SI displays a fitted first-order

decay profile for this relaxation process obtained from the CV data of **1•4PF<sub>6</sub>** in Ar-purged MeCN at 298K with scan rates in the range of 50–700 mV s<sup>-1</sup>. From these experiments, we have calculated<sup>3c,6</sup> the kinetic parameters that describe the recovery of the equilibrium distribution. The values for the decay time ( $\tau_{298}$ ), kinetic constant ( $k_{298}$ ), and free energy of activation ( $\Delta G_{298}^\ddagger$ ) are  $0.65 \pm 0.03$  s,  $1.52 \pm 0.07$  s<sup>-1</sup>, and  $17.0 \pm 0.8$  kcal mol<sup>-1</sup>, respectively. These kinetic parameters are similar to those ( $0.6$  s,  $1.7$  s<sup>-1</sup>, and  $17 \pm 0.4$  kcal mol<sup>-1</sup>)<sup>3c</sup> observed in the case of the [2]rotaxane, indicating the fact that the CBPQT<sup>4+</sup> ring is tethered covalently to the crown ether ring in the pretzelane, does not affect significantly the switching behavior of the CBPQT<sup>4+</sup> ring between the TTF and DNP recognition sites upon redox activation. Unlike the random-directed circling of the CBPQT<sup>4+</sup> ring around the crown ether in the [2]catenane,<sup>3c</sup> a unidirectional reversible circling of the CBPQT<sup>4+</sup> ring between the TTF and DNP recognition sites is preferable in the pretzelane upon redox stimulation the CBPQT<sup>4+</sup> ring cannot pass through the 3,5-dihydroxybenzoate unit in the crown ether.



**Fig. 2** The changes in the UV-Vis spectra during the SEC measurements conducted on **1•4PF<sub>6</sub>**. The applied potential changes from  $E = 0$  (green), 0.6 (yellow) to 1.1 V (red). All data were recorded in Ar-purged MeCN at 298 K. The concentrations of the sample and supporting electrolyte were 1.0 mM and 0.1 M, respectively.

In order to shed further light on the mechanical movement of the CBPQT<sup>4+</sup> ring between the TTF and DNP units, the switching of the bistable pretzelane **1•4PF<sub>6</sub>** was investigated (Fig. 2) in solution by SEC. The ground state ( $E = 0$  V) UV-Vis spectrum of **1•4PF<sub>6</sub>** displays the characteristic CT band at 840 nm, corresponding to the CT interaction between the TTF unit and the CBPQT<sup>4+</sup> ring. The absorption spectrum starts to change on applying a potential of +0.6 V, and the ground state bands bleach and are replaced by bands in the visible region at 445 and 595 nm associated with absorptions of the TTF<sup>•+</sup> radical cation. These observations indicate that the CBPQT<sup>4+</sup> ring migrates away from the TTF<sup>•+</sup> radical cation to the DNP unit during this process. When the applied potential is increased above +1.1 V, the TTF<sup>•+</sup> radical cation is oxidized to the TTF<sup>2+</sup> dication. The absorption bands for the TTF<sup>•+</sup> radical cation are bleached and a small absorption peak at 525 nm associated with the CT band between the DNP unit and the CBPQT<sup>4+</sup> ring can be detected. The spectrum gradually reverts back to its original format when the applied potential is switched off ( $E = 0$  V) and the sample is allowed to stand at room temperature for 12 h, indicating that all the electrochemical redox processes undergone by **1•4PF<sub>6</sub>** are fully reversible.



**Fig. 3** Partial  $^1\text{H}$  NMR spectra of  $1\cdot 4\text{PF}_6$  (1.0 mM) recorded in  $\text{CD}_3\text{CN}$ . (a)  $1\cdot 4\text{PF}_6$  at 298 K, (b) oxidized  $1\cdot 4\text{PF}_6$  at 243 K, and (c) reduced  $1\cdot 4\text{PF}_6$  at 298 K.

A series of  $^1\text{H}$  NMR spectra were recorded in order to investigate the redox-controllable switching of the  $\text{CBPQT}^{4+}$  ring in the bistable pretzelane  $1\cdot 4\text{PF}_6$ . In the  $^1\text{H}$  NMR spectrum (Fig. 3a) of  $1\cdot 4\text{PF}_6$  recorded in  $\text{CD}_3\text{CN}$  at 298K, the signals for the heterotopic protons on the TTF unit were observed at 5.92, 5.98, 6.19, and 6.20 ppm, indicating that the TTF unit in  $1\cdot 4\text{PF}_6$  exists in *cis* and *trans* isomeric forms, even when it is encircled by the  $\text{CBPQT}^{4+}$  ring. After addition of 2 equiv of the oxidant, tris(*p*-bromophenyl)aminium hexachloroantimonate,<sup>7</sup> to the NMR tube, the  $^1\text{H}$  NMR spectrum was recorded again (Fig. 3b) at 243K in order to ensure the stability of the oxidised pretzelane. The signals for the TTF unit move downfield to 9.28 ppm, the chemical shift characteristic of the free  $\text{TTF}^{2+}$  dication in the oxidized version of the pretzelane. Further evidence for the movement of the  $\text{CBPQT}^{4+}$  ring from the oxidized TTF unit to the DNP unit can be found in the dramatic changes in the chemical shifts for the DNP protons. The resonances of the DNP protons around 7–8 ppm experience large up-field shifts to 2.29 and 2.31 (H-4/8), 5.94 and 5.97 (H-3/7), and 6.24 and 6.27 (H-2/6) ppm, respectively, on account of the shielding effect of the encircling  $\text{CBPQT}^{4+}$  ring. Addition of zinc powder to the NMR tube led to the reduction of the  $\text{TTF}^{2+}$  dication to its neutral form, resulting in the movement of the  $\text{CBPQT}^{4+}$  ring away from the DNP and back to the TTF unit and the restoration (Fig. 3c) of the original  $^1\text{H}$  NMR spectrum.

One additional feature of the redox switching in the bistable pretzelane is worthy of note. Since the  $\text{CBPQT}^{4+}$  ring is tethered covalently to the crown ether ring in the pretzelane, it exhibits, of necessity, unidirectional reversible switching behavior between its TTF and DNP recognition sites. In this respect, it displays a fundamental characteristic exhibited by very few mechanically interlocked molecules investigated to date<sup>3b</sup> with different recognition sites.

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† Electronic Supplementary Information (ESI) available: synthesis and characterization. See DOI: 10.1039/b000000x/its

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