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Bispyrrolotetrathiafulvalene-Containing [2]Catenanes

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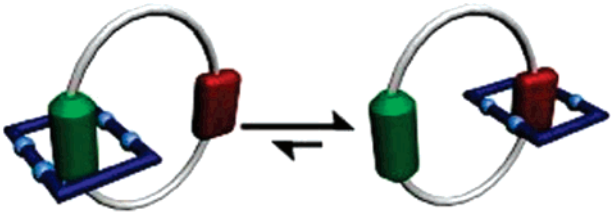

Two [2]catenanes incorporating bispyrrolotetrathiafulvalene (BPTTF) and weaker aryl donors, hydroquinone (HQ) and 1,5-dioxynaphthalene (DNP), respectively, have been prepared and characterized. These [2]catenanes show a predominant amount (>95:5) of the co-conformation in which either the HQ or the DNP unit is encircled by a tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$), contrary to what is observed in systems based on the parent tetrathiafulvalene (TTF). These new [2]catenanes act effectively as molecular switches which are always configured in the "on" state.

A machine is defined[1] as an "apparatus using or applying mechanical power, having several interrelated parts." On the basis of this definition, a molecular machine[2] can be defined[2d] as "an assembly of a discrete number of molecular components designed to perform mechanical-like movements (output) as a consequence of external stimuli (input)." A variety of molecular machines have been prepared over the past decade, including molecular rotary motors,[3a] shuttles,[3b] brakes,[3c] gears,[3d] and muscles.[3e] One class of molecular machine—which has garnered[4] much attention for applications in molecular electronics—has been molecular switches.[4] When either [2]rotaxanes or [2]catenanes (Figure 1), containing two different recognition sites are employed, they become bistable, and switching[2d] can occur through circumrotation of one of the rings via external stimuli.

One ideal recognition site for these systems is tetrathiafulvalene[5] (TTF, **1**). TTF (Figure 2) has proven to be an indispensable building block for materials chemists over the past 25 years. TTF and its derivatives have been incorporated into materials ranging from polymers and organic conductors to ion sensors and molecular switches. The three stable oxidation states of TTF—neutral, radical cation, and dication—make it an ideal recognition site for the construction of molecular switches.[4]

Previously, our group has reported two-station [2]rotaxane-[6] and [2]catenane-based[7] molecular switches composed of a TTF station and a 1,5-dioxynaphthalene (DNP) station. These systems have two possible translational isomers, with the isomer in which the cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) ring encircles the TTF—the GSCC, or "switch-off" state—or the DNP—the

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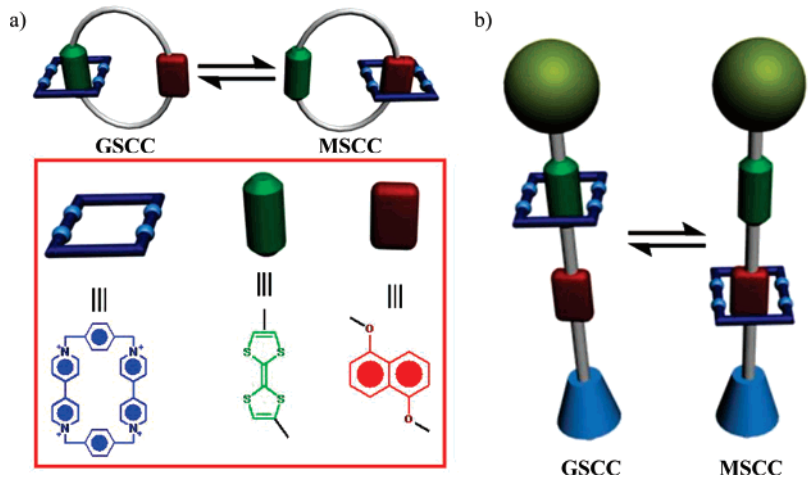

FIGURE 1. Schematic representations of (a) a bistable [2]catenane and (b) a bistable [2]rotaxane showing the equilibrium between the ground state (GSCC) and metastable state (MSCC) co-conformations (translational isomers). The stations represent TTF (green) and 1,5-DNP (red).

MSCC, or "switch-on" state—moiety, respectively. When the parent TTF, **1**, is employed in [2]rotaxanes, the predominant co-conformation was found[8] to be the one where the $CBPQT^{4+}$ encircles the TTF station (~9:1 GSCC/MSCC). However, when TTF is replaced by bispyrrolotetrathiafulvalene (BPTTF, **2**), a shift in this equilibrium occurs. It was found that, for this system, the ratio of isomers was much lower (~4:1 GSCC/MSCC) and additionally was temperature-dependent. We were interested in exploring if similar effects were exhibited in [2]catenane-based systems. Herein, we report the synthesis and characterization of new BPTTF-containing [2]catenanes.

The synthesis[9] of BPTTF-containing [2]catenanes and their corresponding macrocycles[10] (Scheme 1) was a simple two-step procedure. The alkylation of BPTTF under high dilution conditions with glycol-appended aryl donors[11] **3** generated macrocycles **4** as an inseparable mixture with higher oligomers. Reactions of this mixture of macrocycles with dication **5**·$2PF_6$ and 1,4-bis(bromomethyl)benzene (**6**) at high pressure afforded[9] the corresponding [2]catenanes **7**·$4PF_6$ in modest yields following purification.

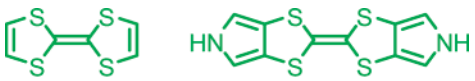

FIGURE 2. Structural formulas for tetrathiafulvalene (TTF, **1**) and bispyrrolotetrathiafulvalene (BPTTF, **2**).

Although the yield of macrocycle DNP-containing **4b** is quite good, the catenation forming **7b**·$4PF_6$ proceeds in low yield. This low yield is recorded even when the reaction mixture is subjected to ultrahigh pressures. We speculate that the enhanced rigidity of BPTTF causes the cavity of **4b** to be smaller, bringing the BPTTF and the DNP moieties closer to one another. The shrinking of the macrocycle does not allow **5**·$2PF_6$ to fit in the cavity and, in turn, causes a much lower yield to be observed.

The predominant translational isomer (GSCC in Figure 1) for [2]catenanes containing the parent TTF has the TTF moiety encircled by $CBPQT^{4+}$, whereas the major translational isomer for both **7a**·$4PF_6$ and **7b**·$4PF_6$ has the weaker aryl donor encircled (MSCC in Figure 1) by $CBPQT^{4+}$. The change in the GSCC is observed by both ^1H NMR and UV−vis spectroscopy[12] and is independent of solvent or temperature (see Supporting Information). This change in the favored translational isomer is in good agreement with previous observations[8] for BPTTF-based [2]rotaxanes. However, the ratio between these translational isomers for both **7a**·$4PF_6$ and **7b**·$4PF_6$ is <5:95 BPTTF/HQ/DNP, in stark contrast to the ~4:1 for a previously reported[8] BPTTF [2]rotaxane. The cyclic voltammetry data (Table 1) provide evidence that the isomer where either HQ or DNP is surrounded by $CBPQT^{4+}$ is not only the favored but also the major co-conformation for both [2]catenanes prepared. For **4a/b** two, well-defined oxidation waves are observed. Two distinct oxidation waves, at similar potential are also observed for **7a/b**·$4PF_6$. Previously, it has been shown[6−8] that, when TTF is

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(12) The UV−vis spectra for **7a/b**·$4PF_6$ show CT bands for $CBPQT^{4+}$ interaction with both the aryl donors (~425 nm) and BPTTF (~850 nm). We attribute the broad absorbances observed at ~850 nm to an alongside interaction between the BPTTF station and the $CBPQT^{4+}$ ring. For a more detailed explanation of alongside interactions between TTF and $CBPQT^{4+}$, see: Nygaard, S.; Hansen, S. W.; Huffman, J. C.; Jensen, F.; Flood, A. H.; Jeppesen, J. O. *J. Am. Chem. Soc.* **2007**, *129*, 7354−7363.

SCHEME 1. Synthesis of BPTTF-Based Macrocycles and [2]Catenanes

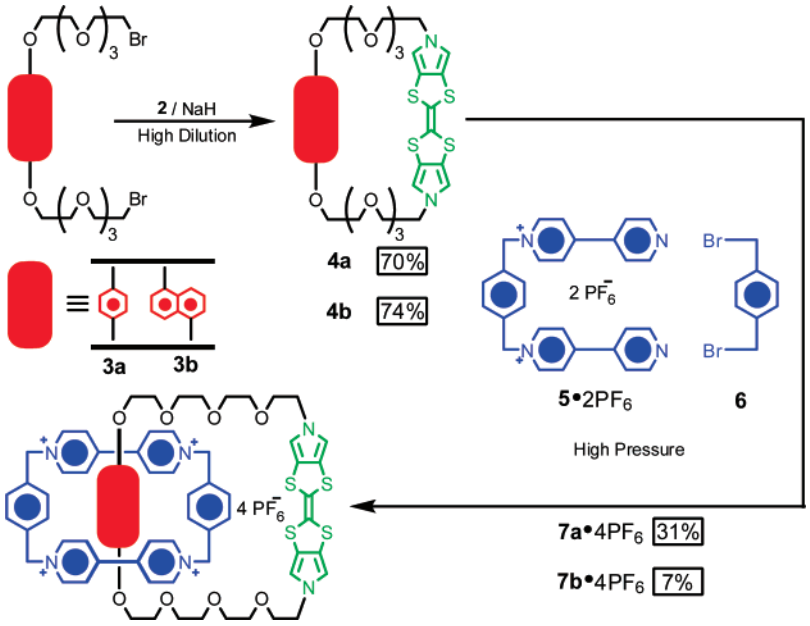

TABLE 1. Oxidation Potentials $E_{1/2}^1$ and $E_{1/2}^2$ and Difference in Potentials $\Delta E_{1/2}$ of Macrocycles 4a and 4b and [2]Catenanes 7a·4PF$_6$, and 7b·4PF$_6$ Determined by Cyclic Voltammetry[a]

compound	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)	$\Delta E_{1/2}$ (V)
4a	+0.46	+0.80	0.34
4b[b]	+0.44	+0.88	0.44
7a·4PF$_6$	+0.45	+0.80	0.35
7b·4PF$_6$	+0.45	+0.83	0.38

[a] Conditions: Reference electrode: SCE; working electrode: glassy carbon; counter electrode: Pt wire; solvent: MeCN; supporting electrolyte: TBAPF$_6$ 0.1 M. [b] Solvent: CH_2Cl_2.

encircled by a CBPQT^{4+} ring, the first oxidation wave is shifted to higher potentials. With no appreciable shift in the first oxidation potentials observed, we speculate that the CBPQT^{4+} moiety resides around the weaker aryl donor.

We reason that there are three factors why the favored translational isomer in both **7a**·4PF$_6$, and **7b**·4PF$_6$ has the CBPQT^{4+} ring residing on the aryl moiety. First, enthalpic contributions[8] from the glycol chains favor complex formation between the aryl donor unit and CBPQT^{4+} ring. Second, the aromatic nitrogen of the BPTTF donor cannot participate in hydrogen bonding with the tetracationic cyclophane. The [C−H···O] interactions between the macrocycle glycol chain oxygen atoms and the bipyridinium hydrogen atoms in the CBPQT^{4+} ring impart[13] stability on the CBPQT^{4+}−aryl donor complex formed. Last, the extended nature of BPTTF[10a] makes it less likely for the glycol oxygens to partake in [C−H···O] interactions with the CBPQT^{4+} ring. For these systems, the competition between hydrogen bonding and donor strength shows the subtle balance of noncovalent forces at work.

In this note, we have described the preparation of two [2]-catenanes, incorporating bispyrrolotetrathiafulvalene (BPTTF) units. These compounds provide further evidence that, for certain mechanically interlocked systems, where the BPTTF unit acts as a station, as opposed to the parent TTF unit, the replacement of TTF with BPTTF imparts a drastic change upon the equilibrium between translational isomers. For the case of these [2]catenanes, the equilibrium lies almost exclusively toward the translational isomer where the aryl donor resides within the cavity of CBPQT^{4+}, effectively providing a molecular switch which is always turned on!

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Experimental Section

BPTTF-HQ Macrocycle (4a). Solutions of **2** (238 mg, 0.844 mmol) in DMF (50 mL) and of **3a** (524 mg, 0.891 mmol) in DMF (50 mL) were added simultaneously to a slurry of 60% NaH (411 mg, 17.1 mmol) in DMF (20 mL), under Ar, over 12 h by means of a syringe pump. The mixture was then filtered over Celite with DMF. The filtrate was washed with light petroleum (3 × 50 mL), and the solvent was removed. The residue was subjected to chromatography over Al_2O_3 with 98:2 CH_2Cl_2/MeOH as the eluent. The orange-colored fraction was collected and the solvent removed under reduced pressure to give **4a** as an orange glass (417 mg, 70%): ^{1}H NMR (500 MHz, CD_3SOCD_3) δ = 3.47−3.53 (m, 12H), 3.63−3.68 (m, 12H), 3.91−3.99 (m, 8H), 6.77 (s, 4H), 6.79 (2, 4H); ^{13}C NMR (125 MHz, CD_3SOCD_3) δ = 50.3, 67.9, 69.4, 69.5, 70.1, 70.4, 70.5, 70.7, 114.1, 115.7, 117.2, 119.2, 152.9; HR-MALDI calcd for $C_{32}H_{40}N_2O_8S_4$ 708.1667, found *m*/*z* 708.1650 $[M]^+$.

BPTTF-DNP Macrocycle (4b). Solutions of **2** (250 mg, 0.887 mmol) in DMF (50 mL) and of **3b** (575 mg, 0.901 mmol) in DMF (50 mL) were added simultaneously to a slurry of 60% NaH (360 mg, 15.0 mmol) in DMF (35 mL), under Ar, over 12 h by means of a syringe pump. The mixture was filtered over Celite with DMF and subsequently washed with light petroleum (3 × 50 mL), after which time the solvent was removed. The residue was subjected to chromatography over Al_2O_3 with 99:1 CH_2Cl_2/MeOH as the eluent. The orange-colored fraction was collected and the solvent removed under reduced pressure to give **4b** as a red-orange glass (498 mg, 74%): ^{1}H NMR (500 MHz, CD_3SOCD_3) δ = 3.46−3.65 (m, 20H), 3.84 (t, J = 3.6 Hz, 4H), 3.97 (t, J = 4.8 Hz, 4H), 4.18 (t, J = 3.6 Hz, 4H), 6.76 (s, 4H), 6.90 (d, J = 7.2 Hz, 2H), 7.22 (t, J = 9.0 Hz, 2H), 7.68 (d, J = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, CD_3SOCD_3) δ = 54.8, 67.6, 69.0, 69.6, 69.8, 69.9, 70.0, 70.2, 105.8, 113.4, 113.7, 116.7, 118.5, 125.3, 126.0, 153.9; HR-MALDI calcd for $C_{36}H_{42}N_2O_8S_4$ 758.1824, found *m*/*z* 758.1780 $[M]^+$.

BPTTF-HQ [2]Catenane (7a·4PF$_6$). A solution of **4a** (232 mg, 0.327 mmol), **5**·2PF$_6$ (694 mg, 0.982 mmol), and 1,4-bis(bromomethyl)benzene (291 mg, 1.10 mmol) in DMF (13 mL) was subjected to reaction at 11 kbar and 22 °C for 4 days, after which time the solvent was removed in vacuo. The residue was subjected to column chromatography over silica gel using 14:5:4:2 MeOH/MeCN/2 M NH_4Cl/$MeNO_2$ as the eluent. The broad brown-green band was collected and the solvent removed. The solids were dissolved in a minimal amount of H_2O, and the brown solid was filtered off. The solid was then dissolved in MeOH (20 mL), and anion exchange was performed by addition of a saturated MeOH solution of NH_4PF_6. The resulting solid was filtered off and washed with several portions of H_2O to afford **7a**·4PF$_6$ as a green-brown solid (181 mg, 31%): ^{1}H NMR (500 MHz, CD_3SOCD_3) δ = 3.39−4.12 (m, 36H), 5.55 (s, 8H), 6.61 (s, 4H), 7.85 (s, 8H), 8.11 (br s, 8H), 9.02 (br s, 8H); HR-ESI calcd for $C_{68}H_{72}F_{18}N_6O_8P_3S_4$ 1663.3214 [M − PF_6]$^+$, found *m*/*z* 1664.3517 (100) [M − PF_6]$^+$, calcd for $C_{68}H_{72}F_{12}N_6O_8P_2S_4$ 759.1784 [M − 2PF$_6$]$^{2+}$, found *m*/*z* 759.1784 (39) [M − 2PF$_6$]$^{2+}$.

BPTTF-DNP [2]Catenane (7b·4PF$_6$). A solution of **4b** (498 mg, 0.657 mmol), **5**·2PF$_6$ (1.02 mg, 1.44 mmol), and 1,4-bis(bromomethyl)benzene (591 mg, 1.97 mmol) in DMF (12 mL) was subjected to reaction at 15 kbar for 4 days, after which time the solvent was removed in vacuo. The residue was subjected to column chromatography over silica gel using 14:5:4:2 MeOH/MeCN/2 M NH_4Cl/$MeNO_2$ as the eluent. The broad brown-green band was collected and the solvent removed. The solids were dissolved in a minimal amount of H_2O, and the remaining brown solid was filtered off. The solid was then dissolved in MeOH (20 mL), and anion exchange was performed by addition of a saturated MeOH solution of NH_4PF_6. The resulting solid was filtered off and washed with several portions of H_2O to afford **7b**·4PF$_6$ as a green-brown solid (85 mg, 7%): ^{1}H NMR (500 MHz, CD_3CN) δ = 2.37 (d, J = 8.2 Hz, 2H), 3.50−4.25 (m, 32H), 5.42−5.63 (m, 8H), 5.88 (t, J = 8.0 Hz, 2H), 6.15 (d, J = 7.8 Hz, 2H), 6.46 (s, 4H), 7.11 (d, J = 6.3 Hz, 4H), 7.25 (d, J = 5.3 Hz, 4H), 7.85 (s, 4H), 8.07 (s, 4H), 8.44 (d, J = 6.2 Hz, 4H), 8.71 (d, J = 6.3 Hz, 4H); HR-ESI calcd for $C_{72}H_{74}F_{12}N_6O_8P_2S_4$ 784.1862 [M − 2PF$_6$]$^{2+}$, found *m*/*z* 784.1888 [M − 2PF$_6$]$^{2+}$.

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Supporting Information Available: Spectroscopic characterization for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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