

An Electrochromic Tristable Molecular Switch

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S Supporting Information

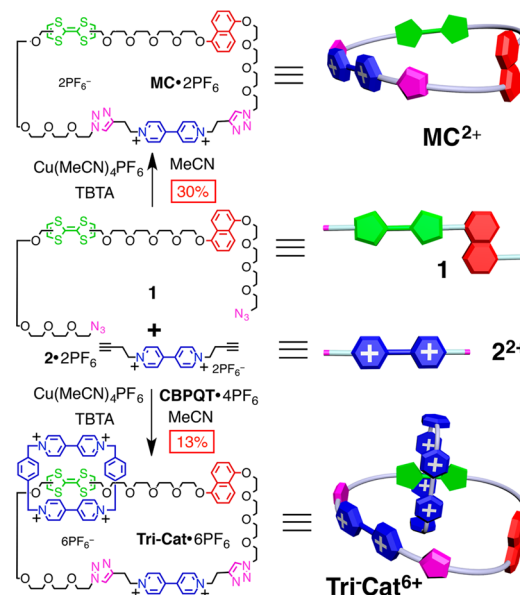
ABSTRACT: A tristable [2]catenane, composed of a macrocyclic polyether incorporating 1,5-dioxynaphthalene (DNP) and tetrathiafulvalene (TTF) units along with a 4,4'-bipyridinium (BIPY^{•+}) radical cation as three very different potential recognition sites, interlocked mechanically with the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺), was synthesized by donor–acceptor templation, employing a “threading-followed-by-cyclization” approach. In this catenane, movement of the CBPQT⁴⁺ ring in its different redox states among these three potential recognition sites, with corresponding color changes, is achieved by tuning external redox potentials. In the starting state, where no external potential is applied, the ring encircles the TTF unit and displays a green color. Upon oxidation of the TTF unit, the CBPQT⁴⁺ ring moves to the DNP unit, producing a red color. Finally, if all the BIPY²⁺ units are reduced to BIPY^{•+} radical cations, the resulting CBPQT^{2(•+)} diradical dication will migrate to the BIPY^{•+} unit, resulting in a purple color. These readily switchable electrochromic properties render the [2]-catenane attractive for use in electro-optical devices.

Rotaxanes and catenanes, representing the two principal types of mechanically interlocked molecules (MIMs),¹ have attracted the attention of the scientific community not only because of their unique structures, but also on account of their exotic chemical and physical properties, in addition to their facile synthesis² by means of highly efficient template-directed protocols. In particular, those catenanes and rotaxanes whose components are capable of undergoing mechanical movements among multiple recognition sites in response to external stimuli show significant promise for diverse applications, e.g., molecular electronics,³ drug delivery,⁴ and catalysis.⁵

During the past two decades, we have been investigating switchable bistable [2]rotaxanes⁶ and [2]catenanes,⁷ which commonly consist of an electron-deficient tetracationic ring, i.e., cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺), and two electron-rich recognition sites, e.g., tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) units. The CBPQT⁴⁺ ring moves between the TTF and DNP recognition sites in response to changes in redox potentials. Each co-conformation is characterized by a distinct color—green for the TTF/CBPQT⁴⁺ co-conformation and red for the DNP/CBPQT⁴⁺ co-conformation—and thus these MIMs have been used⁸ to construct two-state electro-optical devices, taking advantage of their electrochromic properties.

Considerable effort has been devoted to investigating theoretically,⁹ in addition to synthesizing,¹⁰ tristable [2]-catenanes by incorporating a third redox-active recognition site along with the DNP and TTF units, so that they can display a wider range of colors at varying external redox potentials. These potentially tristable [2]catenanes have turned out to exhibit only bistability owing to the mismatch between the redox potentials and the binding affinities of the three recognition sites toward the CBPQT⁴⁺ ring. It occurred to us that the fabrication of electrochromic tristable [2]catenanes requires a precise balance between these two factors. The design and synthesis of truly tristable [2]catenanes (Scheme 1) have now been achieved.¹¹

Scheme 1. Syntheses of the Macrocyclic Polyether MC•2PF₆ and the Tristable [2]Catenane Tri-Cat•6PF₆



Recently, we discovered¹² that bipyridinium radical cations (BIPY^{•+}) and the CBPQT^{2(•+)} diradical dication can form thermodynamically stable tris-radical inclusion complexes BIPY^{•+}•CBPQT^{2(•+)} via intermolecular radical–radical interactions.¹³ These complexes have been employed as templates¹⁴ to prepare otherwise difficult to obtain MIMs and as the recognition motif¹⁵ to enhance the switching performance in MIMs. More importantly, they have the appropriate absorption

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characteristics to afford the elusive purple color. As a consequence, radical chemistry can be utilized in electrochromic investigations in combination with the TTF and DNP recognition sites. The resulting electrochromic tristable [2]-catenane could potentially be used in electro-optical devices that would out-compete traditional two-state electrochromic devices. Here we feature the synthesis of a tristable [2]catenane and describe the detailed investigation of its electro-switching and corresponding electrochromic properties employing UV-vis-NIR absorption spectroscopy and cyclic voltammetry (CV), as well as ^1H NMR and electron paramagnetic resonance (EPR) spectroscopies.

The syntheses of both the macrocyclic polyether $\text{MC}\cdot 2\text{PF}_6$ and the tristable [2]catenane **Tri-Cat** $\cdot 6\text{PF}_6$ begin with the preparation of the known polyether¹⁶ **1** and the viologen derivative¹⁵ $2\cdot 2\text{PF}_6$ (Scheme 1). Copper(I)-catalyzed azide-alkyne cycloaddition¹⁷ (CuAAC) under dilute conditions affords $\text{MC}\cdot 2\text{PF}_6$ from its acyclic precursor as a brown solid in 35% yield. For **Tri-Cat** $\cdot 6\text{PF}_6$, the “threading-followed-by-catenation” approach was employed,¹⁵ involving first of all the formation of the donor-acceptor complex, 1CCBPQT^{4+} , and then catenation using a CuAAC reaction. Formation of 1CCBPQT^{4+} is supported by both ^1H NMR spectroscopy and isothermal titration calorimetry (ITC) (Figures S9 and S10). The CuAAC reaction between the preformed complex $1\text{CCBPQT}\cdot 4\text{PF}_6$ and $2\cdot 2\text{PF}_6$ gave **Tri-Cat** $\cdot 6\text{PF}_6$ as a green solid in 13% yield.

To gain insight into the switching mechanism, a UV-vis-NIR titration was carried out on a MeCN solution of **Tri-Cat** $\cdot 6\text{PF}_6$. Oxidation of the TTF unit by stepwise addition of $\text{Fe}(\text{ClO}_4)_3$ is illustrated in Figure 1. Before addition, the spectrum exhibits a characteristic broad charge-transfer (CT) absorption band¹⁹ centered on 830 nm (Figure 1a, black trace), indicating that the CBPQT^{4+} ring encircles the TTF unit. Upon addition of $\text{Fe}(\text{ClO}_4)_3$, the CT absorption band gradually decreases in intensity and eventually disappears when a total of 1 equiv has been added. Two new absorption bands centered on 420 and 600 nm, both of which grow in intensity, can be assigned¹⁹ to the $\text{TTF}^{\bullet+}$ radical cation. On addition of a further 1 equiv of $\text{Fe}(\text{ClO}_4)_3$, the absorption bands corresponding to the $\text{TTF}^{\bullet+}$ radical cation disappear (Figure 1b), in keeping with the formation of the TTF^{2+} dication. The simultaneous emergence of an absorption band centered on 530 nm, a characteristic CT band for the inclusion complex DNPCCBPQT^{4+} , implies that the CBPQT^{4+} ring has moved from the oxidized TTF unit to the DNP recognition site. A reductant, cobaltocene (Cp_2Co), was added in a stepwise manner to explore the reverse switching process. In unison with Figure 1a,b, the spectral changes shown in Figure 1c,d are reversed, and the original spectrum is restored when 2 equiv of Cp_2Co has been added, which indicates that the switching of the CBPQT^{4+} ring between the DNP and TTF recognition sites is fully reversible.

On addition of a further 3 equiv of Cp_2Co (Figure 1e) or an excess of Zn dust (Figure S15), the BIPY^{2+} units in both the MC^{2+} and the CBPQT^{4+} ring are reduced to $\text{BIPY}^{\bullet+}$ radical cations, leading the $\text{CBPQT}^{2(\bullet+)}$ ring to encircle the $\text{BIPY}^{\bullet+}$ unit. This state is characterized¹² by the appearance of two new absorption bands centered on 560 and 1100 nm. As soon as air is allowed to enter the solution, all the $\text{BIPY}^{\bullet+}$ radical cations are oxidized back to BIPY^{2+} dications; hence, the CBPQT^{4+} ring finds itself back encircling the TTF unit following partial circumrotation, evidenced by the disappearance of absorption bands at 560 and 1100 nm and the re-appearance of the absorption band at 830 nm (Figure 1f). In summary, the

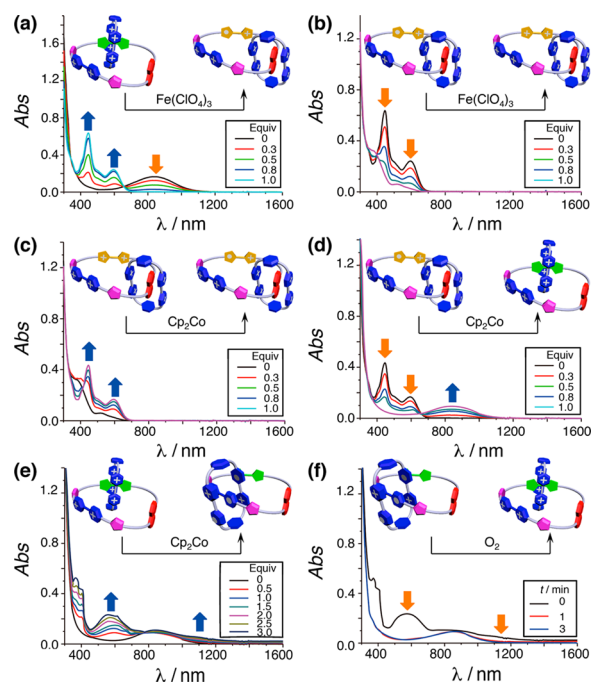


Figure 1. UV-vis-NIR absorption spectroscopy (initial concentration 50 μM , MeCN, 298 K) of the redox-active switching of the tristable [2]catenane. (a,b) Spectra obtained upon adding $\text{Fe}(\text{ClO}_4)_3$ incrementally into a MeCN solution of **Tri-Cat** $\cdot 6\text{PF}_6$. (c,d) Spectra resulting from incremental additions of Cp_2Co to a MeCN solution of **Tri-Cat** $\cdot 6\text{PF}_6/2\text{ClO}_4$, revealing the presence of **Tri-Cat** $^{3(\bullet+)}$ as an intermediate on the way to **Tri-Cat** $^{3+}$. (e) Spectra recorded after addition of 3 equiv of Cp_2Co , showing the presence of **Tri-Cat** $^{3(\bullet+)}$. (f) Spectra obtained upon introducing air into a MeCN solution of **Tri-Cat** $^{3(\bullet+)}$.

CBPQT^{4+} ring can be moved reversibly around these three recognition sites by simply manipulating the redox states of the [2]catenane. The same results were also obtained on carrying out spectroelectrochemical experiments (Figure S17).

Evidence for the switching process was also obtained from electrochemical experiments. The CBPQT^{4+} ring exhibits two typical reversible two-electron reductions with peak potentials at -315 and -758 mV (Figure 2a). The CV profile of MC^{2+} displays two reversible one-electron reductions, $\text{BIPY}^{2+} \rightarrow \text{BIPY}^{(\bullet+)}$ at -452 mV and $\text{BIPY}^{(\bullet+)} \rightarrow \text{BIPY}^0$ at -877 mV, in addition to two reversible one-electron oxidations, assignable to $\text{TTF} \rightarrow \text{TTF}^{(\bullet+)}$ at $+436$ mV and $\text{TTF}^{(\bullet+)} \rightarrow \text{TTF}^{2+}$ at $+817$ mV (Figure 2b). Notably, the reduction potentials of the BIPY^{2+} unit in the MC^{2+} ring are shifted to more negative potentials than those of the CBPQT^{4+} ring. The observed cathodic potential shifts are a consequence of the donor-acceptor interactions between the electron-rich units—i.e., the TTF and DNP units—and the BIPY^{2+} unit within the MC^{2+} ring.

An oxidative CV of **Tri-Cat** $^{6+}$ spanning 0–1.1 V (Figure S16), performed to probe the switching of the CBPQT^{4+} ring between the DNP and TTF recognition sites, exhibits two oxidation waves. The first peak, at $+488$ mV, represents one-electron oxidation of the free TTF unit ($\text{TTF}_f \rightarrow \text{TTF}_f^{(\bullet+)}$), and the second, broad peak, at $+766$ mV, corresponds to one-electron oxidation of both the encircled TTF unit ($\text{TTF}_e \rightarrow \text{TTF}_e^{(\bullet+)}$) and the $\text{TTF}^{\bullet+}$ radical cation ($\text{TTF}^{(\bullet+)} \rightarrow \text{TTF}^{2+}$). It is estimated²⁰ that $\sim 90\%$ of the CBPQT^{4+} ring encircles the TTF unit measured at scan rate of 1 V/s. Following the first scan, the second scan reveals the same peak currents as the first scan, an observation which indicates that, upon reduction of the $\text{TTF}^{\bullet+}$

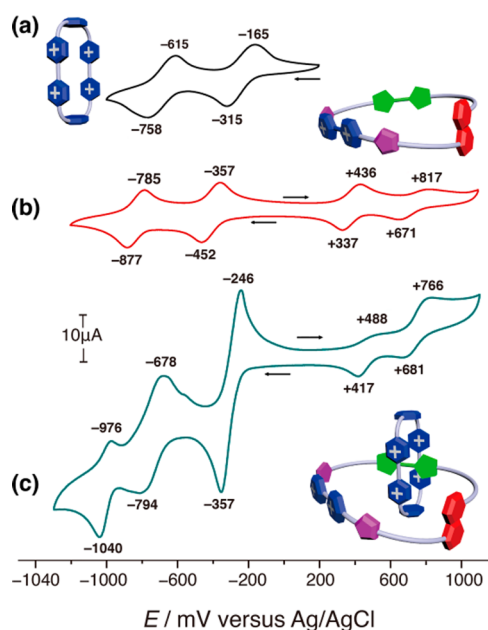


Figure 2. CV traces (MeCN, 0.1 M TBAPF₆, 200 mV/s) of 1 mM solutions of (a) CBPQT·4PF₆, (b) MC·2PF₆, and (c) Tri-Cat·6PF₆.

radical cation, the CPBQT⁴⁺ ring immediately relaxes from the DNP unit back to the TTF unit.

An examination of the full potential range CV of Tri-Cat⁶⁺ (Figure 2c) has unraveled the switching event between the BIPY^(•+) and the TTF recognition sites. Upon reduction, a characteristic three-electron reduction¹² occurs at -357 mV, corresponding to the formation of the BIPY^(•+)CBPQT^{2(•+)} co-conformation. CV reveals ~15% free TTF units by scanning toward +1.3 V, very similar to the ground-state distribution, confirming that switching occurs rapidly.

Switching between the TTF and DNP recognition sites was also investigated by ¹H NMR spectroscopy (Figure 3). In the starting state, the spectrum reveals four proton resonances, at 6.18, 6.09, 6.03, and 5.96 ppm, arising from the encircled TTF

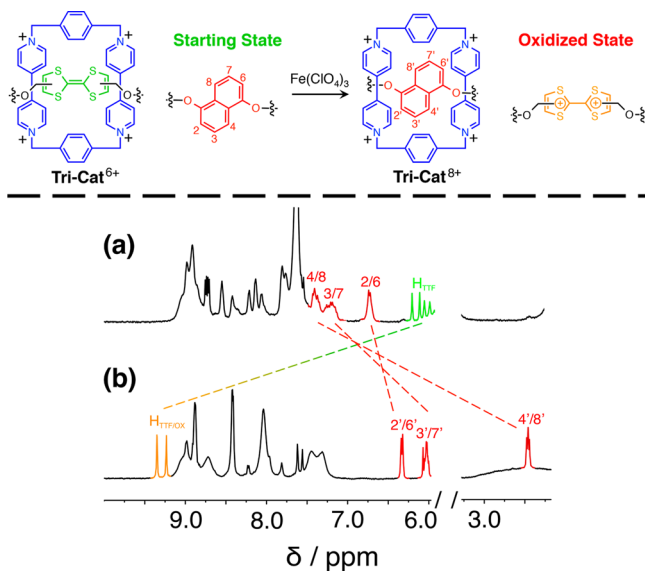


Figure 3. ¹H NMR spectra (400 MHz, CD₃CN, 298 K) of (a) Tri-Cat⁶⁺ and (b) its oxidized form Tri-Cat⁸⁺.

unit and three broad proton resonances, spanning 7.43–6.61 ppm, associated with the free DNP unit (Figure S4). Upon oxidation of the TTF unit with Fe(ClO₄)₃, proton resonances for the resulting TTF²⁺ dication are shifted dramatically downfield to 9.33 and 9.21 ppm (Figure S6). Meanwhile, all proton resonances of the DNP unit become well resolved and are shifted upfield. Particularly, resonances of protons H_{4/8} are shifted substantially to 2.44 ppm, which indicates very strongly that the CBPQT⁴⁺ ring encircles the DNP unit. Although a co-conformation in which the CBPQT⁴⁺ ring is trapped kinetically between two positively charged TTF²⁺ and BIPY²⁺ units could possibly exist, proton resonances of the free DNP unit, which would be expected in the case of this kinetic co-conformation, are not observed in ¹H NMR spectra (Figures 3b and S6), suggesting that the kinetic co-conformation is not formed.

Each oxidation state of the tristable [2]catenane Tri-Cat⁶⁺ displays a distinct color (Figure 4a), consistent with spectro-

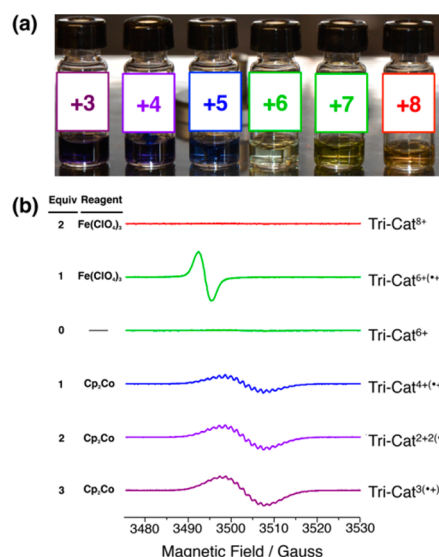


Figure 4. (a) Colors of different redox states of the tristable [2]catenane Tri-Cat·6PF₆ in MeCN (0.2 mM). Left to right, oxidation states are +3 through +8. (b) EPR spectra (0.2 mM, MeCN, 298 K) of the different redox states of the tristable [2]catenane.

scopic observations. In the starting state, the solution is pale green, due to the donor–acceptor TTF⁺CBPQT⁴⁺ co-conformation. In sharp contrast, in the doubly oxidized state, the solution develops a red color due to the DNP⁺CBPQT⁴⁺ co-conformation. A purple color, originating from the tris-radical co-conformation BIPY^{•+}CBPQT^{2(•+)}, is observed for the triply reduced state. For the singly and doubly reduced states, a blue color, arising from the BIPY^{•+} radical cation, is observed.

Finally, EPR spectroscopy was used to investigate the oxidation states involving the radical species. Solutions of the [2]catenane in different oxidation states were prepared by adding varying amounts of either Cp₂Co or Fe(ClO₄)₃ in deaerated MeCN. While both the starting state and the doubly oxidized state of the [2]catenane are EPR silent because of the absence of radicals, the EPR spectrum of the singly oxidized state, as well as those of the singly, doubly, and triply reduced states, shows characteristic signals (Figure 4b) corresponding to the presence of either TTF^{•+} or BIPY^{•+} radicals with distinct g-factors.

In summary, we have synthesized and characterized a tristable [2]catenane, Tri-Cat⁶⁺, composed of a CBPQT⁴⁺ ring interlocked mechanically with a macrocycle containing TTF, DNP,

and BIPY²⁺ units. The CBPQT⁴⁺ ring can be easily switched reversibly among these three units, acting separately as recognition sites, in response to different external redox potentials. Remarkably, this single compound allows us to display a wide range of colors—green for Tri-Cat⁶⁺, red for Tri-Cat⁸⁺, and purple for Tri-Cat^{3(•+)}, as well as blue for Tri-Cat^{4+(•+)} and Tri-Cat^{2+2(•+)}. The electrochromic properties of this tristable [2]catenane render it a potentially useful compound for use in electro-optical devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b09274.

Detailed procedures; spectroscopy and spectroelectrochemical analysis of Tri-Cat-6PF₆ (PDF)

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Notes

The authors declare no competing financial interest.

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