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A tristable [2]pseudo[2]rotaxane

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Electronic Supporting Information

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1. General Methods

Cyclobis(paraquat-*p*-phenylene) tetrakishexafluorophosphate[S1] (**CBPQT**·$4PF_6$), bis-1,5-dioxynaphthalene-38-crown-10[S2] (BDNP38C10), the tristable [2]rotaxane[S3] **1**·$6PF_6$ and its corresponding dumbbell **D1**·$2PF_6$[S3] were prepared according to literature procedures. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 600 and Varian Inova 500 spectrometers, with working frequencies of 600 and 500 MHz for ^{1}H. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvent, CD_3CN: δ 1.94 ppm. Cyclic voltammetry experiments (CV) were carried out at room temperature in argon-purged solutions in MeCN with a Gamry Multipurpose instrument (Reference 600) interfaced to a PC. CV experiments were performed using a glassy carbon working electrode (0.018 cm^2, Cypress system). The electrode surface was polished routinely with 0.05 μm alumina-water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was a Ag/AgCl electrode. The concentration of the sample and supporting electrolyte tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were 1.0×10^{-3} mol L^{-1} and 0.1 mol L^{-1}, respectively. UV-Vis spectra were recorded at room temperature on a Varian 100 Bio-instrument. The spectrophotometric titrations of **1**·$6PF_6$ (2.7×10^{-4} M) with BDNP38C10 macrocycle were carried out in a Hellma quartz optical cell (ℓ = 1 cm) in MeCN. Microvolumes of a concentrated solution of BDNP38C10 (3.99×10^{-3} M) were added to 2 mL of **1**·$6PF_6$ with the help of a microburette (Eppendorf). The $[BDNP38C10]_{tot}/[\mathbf{1}\cdot 6PF_6]_{tot}$ ratios were varied from 0 to 5.5. Special care was taken to ensure that complete equilibration was attained. After each addition, a UV-Vis spectrum was recorded from 350 to 900 nm on a Cary 300 (Varian) spectrophotometer maintained at 25.0 ± 0.2 ºC by the flow of a Haake NB 22 thermostat. The spectrophotometric data were processed using the Specfit program[S4] which adjusts the stability constants and the corresponding extinction coefficients of the species formed at equilibrium. Specfit uses factor analyses to reduce the absorbance matrix and to extract the eigenvalues prior to the multi-wavelength fit of the reduced data set according to the Marquardt algorithm.[S5] Experimental errors: potential values, +/– 10 mV, absorption maxima, +/– 1 nm.

2. ^{1}H NMR Spectroscopy

Confirmation of the Formation of the [2]Pseudo[2]Rotaxane $\mathbf{1}^{6+} \subset$ *BDNP38C10.* The dumbbell $\mathbf{D1}^{2+}$ was characterized by ^{1}H NMR spectroscopy recorded in CD_3CN at room temperature (500 MHz) (Fig. S1a), and the [2]pseudo[2]rotaxane $\mathbf{1}^{6+} \subset$ BDNP38C10 was characterized by ^{1}H-^{1}H gradient selected double quantum filtered phase sensitive COSY (DQF-COSY) recorded in CD_3CN at 243K (600 MHz) (Fig. S1b).

Although the two sets of the alpha and beta protons for $\mathbf{D1}^{2+}$ are not chemically equivalent as a consequence of the asymmetry of the molecule, their resonances nonetheless overlap significantly such that distinction between the two individual alpha and individual beta resonances are not readily made. Therefore, we assign collectively the two alpha protons as H_α and the two beta protons as H_β. The 1D spectrum of $\mathbf{D1}^{2+}$ displays the assignment of the resonances at 8.7 ppm and 8.25 ppm as the alpha and beta protons adjacent to the nitrogens of the bipyrdinium unit, respectively (Fig. S1a). These assignments were corroborated by correlation crosspeaks detected in the 2D DQF-COSY taken under identical conditions.

On account of a complicated set of possible exchange pathways for shuttling[S6] of $CBPQT^{4+}$ caused by the *cis-trans* isomerization of the TTF unit and many possible conformations of the tetracationic cyclophane surrounding the TTF subunit, the 2D DQF-COSY of $\mathbf{1}^{6+} \subset$ BDNP38C10 shows the signals from the alpha and beta protons split into two separate regions of broad resonances from 8.2–9.1 and 7.3–8.25 ppm, respectively, the assignment of which can be corroborated by the correlation crosspeaks (Fig. S1b). The 2D DQF-COSY of $\mathbf{1}^{6+} \subset$ BDNP38C10 shows that the beta protons have been shifted upfield relative to the free dumbbell $\mathbf{1}^{6+}$, which is consistent[S7] with the formation of these types of donor/acceptor charge transfer (CT) complexes previously studied.

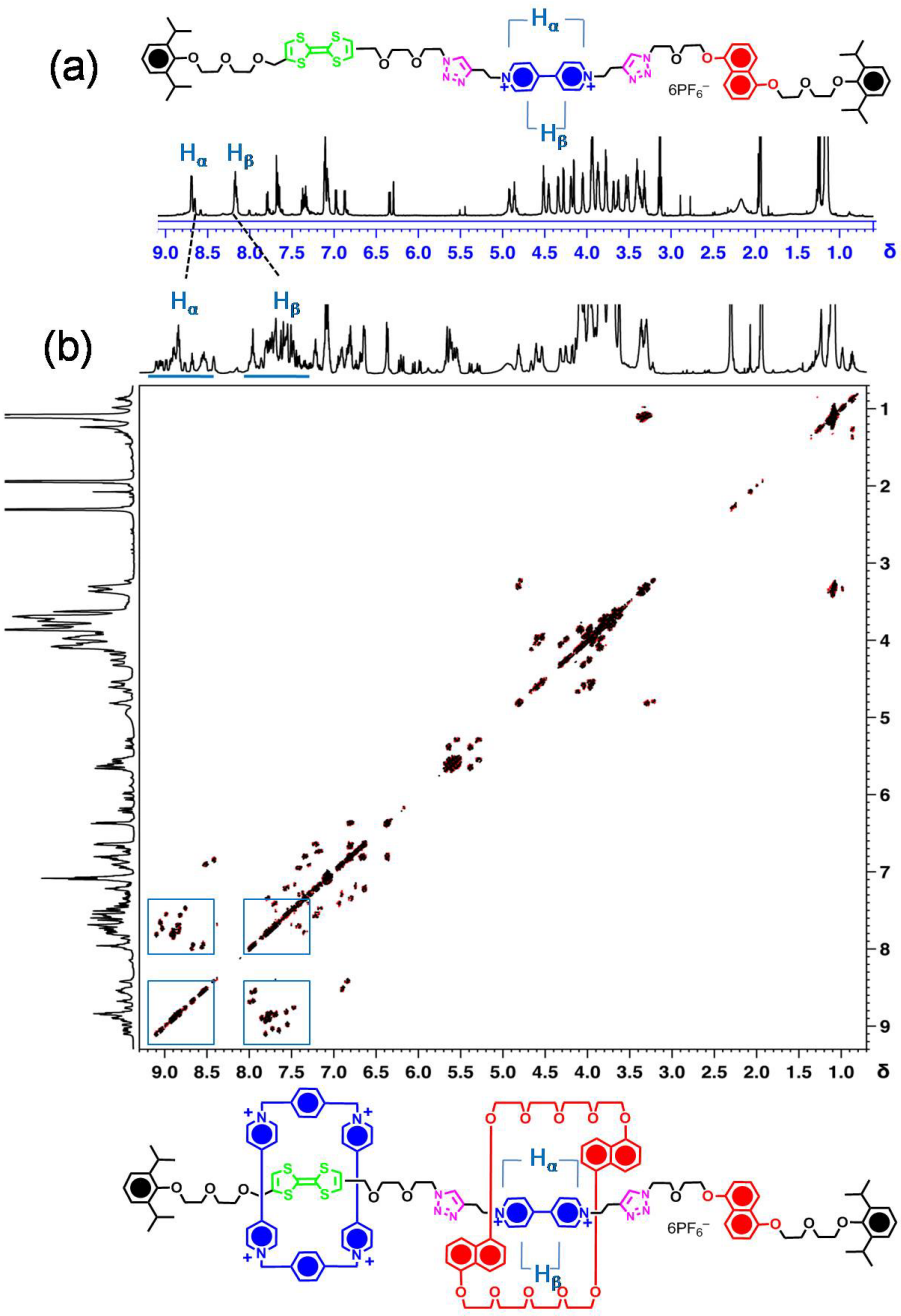

Figure S1. (a) ^{1}H NMR spectrum of the free dumbbell $\mathbf{D1}^{2+}$ recorded at room temperature (500 MHz). The assignments of the resonances for the α- and β-protons of the $BIPY^{2+}$ subunit are shown at 8.70 and 8.25 ppm respectively. (b) ^{1}H-^{1}H DQF-COSY spectrum of the [2]pseudo[2]rotaxane $\mathbf{1}^{6+} \subset$ BDNP38C10 recorded in CD_3CN at 243K (600 MHz). The resonances in the 7.5 to 9.2 ppm region of the spectrum show crosspeak correlations, an observation which indicates these resonances arise from the α- and β-protons. The lack of any resonances at 8.25 ppm provides evidence for the supramolecular binding of BDNP38C10 to the $BIPY^{2+}$ subunit, as binding is known to shift the resonances of the β-protons upfield.

3. Cyclic Voltammetry (CV)

Measuring the Lifetime of the MSCC for $\boldsymbol{1}^{6+}$. In the CV experiments, the first oxidation potential (+0.4 V vs Ag/AgCl) of the TTF unit encircled by $CBPQT^{4+}$ is shifted to a higher potential (Fig. S2b) compared to "free" TTF because of the lowering of the HOMO energy level caused by the encapsulation of the $CBPQT^{4+}$ ring. The second oxidation of the TTF unit in $\mathbf{1}^{6+}$ is not influenced by the $CBPQT^{4+}$ ring, indicating that the ring has already moved away from the TTF unit and encircled the DNP recognition site. Starting at a potential of +1.0 V with an equilibration time of 10 seconds, the resulting cathodic scan displays two well-separated reduction peaks observed at +0.65 and +0.34 V, corresponding to the reduction of the oxidized TTF^{2+} dication and the $TTF^{\bullet+}$ radical cation, respectively. The positions of these peaks are consistent with those for "free" TTF units, an observation that indicates that the $CBPQT^{4+}$ ring remains on the DNP unit during the reductive process of TTF. After regeneration of neutral TTF corresponding to the reduction peak observed at +0.34 V (Fig. S2b), the $CBPQT^{4+}$ ring regains recognition of this once-again electron-rich moiety, leading to the formation of the MSCC (Fig. S2a). Quantification of the amount of "free" TTF – corresponding to the relative population of $\mathbf{1}^{6+}$ in the MSCC compared to the GSCC – is accomplished through integration of the relative intensities on the return anodic scan of the first oxidation peak observed at +0.40 V compared to the second subsequent oxidation peak observed at +0.75 V. The time allotted for relaxation to the GSCC to occur is controlled through variation of the scan rates used in the experiment.

The kinetics associated with the free-energy barrier ($\Delta G^{\ddagger}$) for relaxation of the $CBQPT^{4+}$ ring from the MSCC to the GSCC for $\mathbf{1}^{6+}$ were also analyzed (MeCN at 298 K). The oxidation of the TTF→TTF^{2+} will induce the translation of the $CBPQT^{4+}$ ring to DNP site (Fig. S2a). Returning the system to zero bias will reduce the TTF^{2+} dication back to its neutral state (TTF), forming the MSCC, which re-equilibrates to the equilibrium mixture of the GSCC and MSCC. The MSCC can be measured as the relative amount of free TTF observed in the anodic scan after first oxidizing the system and then returning it back to the neutral state. The kinetics of the relaxation of the MSCC back to the GSCC were quantified by variable scan rate CV (50 – 800 mVs^{-1}) (Fig. S2b) and fitting a first order decay model to the population ratios of the MSCC state and the

relaxation times (Fig. S2c). The free-energy barrier ($\Delta G^{\ddagger}$) for relaxation from the MSCC to the GSCC in MeCN for $\mathbf{1}^{6+}$ was calculated to be 19 ± 1 kcal mol^{-1}, which is significantly more than the 16.2 ± 0.3 kcal mol^{-1} for the previously reported bistable rotaxane.[S8]

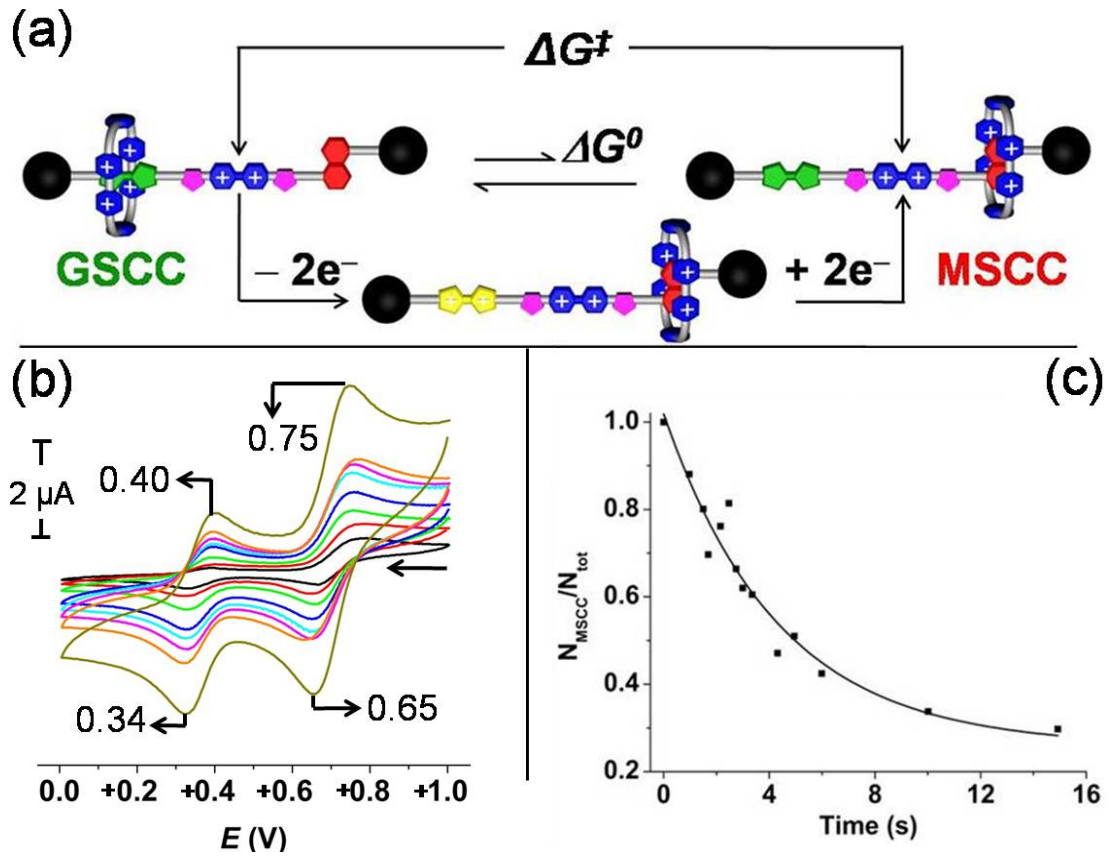

Figure S2. (a) Measuring the lifetime of the metastable state co-conformation (MSCC). The oxidation at +0.40 V can be assigned to the first oxidation of "free" TTF, which on the return anodic scan corresponds to the MSCC. (b) Variable scan rate CV in a 1 mM MeCN solution at 298 K, first scans: black trace (10 mV s^{-1}), red trace (30 mV s^{-1}), green trace (50 mV s^{-1}), blue trace (100 mV s^{-1}), light blue trace (150 mV s^{-1}), pink trace (200 mV s^{-1}) orange trace (300 mV s^{-1}), gold trace (500 mV s^{-1}). (c) A first-order plot derived from the relative integration of the peak observed at +0.40 V as a function of time (scan rate) reveals the lifetime of the metastable state, and hence, the free energy barrier to relaxation. The barrier was determined to be 19 ± 1 kcal mol^{-1}.

Tristabilty of $\mathbf{1}^{6+}$ *and* $\mathbf{1}^{6+} \subset$ *BDNP38C10.* A typical cyclic voltammogram of $\mathbf{1}^{6+}$ is shown in Figure S3a. When measured separately as their individual components, the CBPQT^{4+} ring component of the [2]rotaxane undergoes two consecutive reversible two-electron processes corresponding to the redox couples CBPQT^{4+} / CBPQT$^{2(\bullet+)}$ and CBPQT$^{2(\bullet+)}$ / CBPQT^{0}, while the

bipyridinium unit ($BIPY^{2+}$) in the dumbbell undergoes two consecutive reversible one-electron processes. However, in the case of the rotaxane $\mathbf{1}^{6+}$, the second reduction of $BIPY^{2+}$ from the dumbbell as well as one of the bipyridinium subunits of the $CBPQT^{4+}$ ring exhibit a large negative shift in potential corresponding the reduction peak observed at –1.00 V. As a consequence, the second reduction of $CBPQT^{4+}$ separates into a set of two one-electron processes. These observations are in a good agreement with the encirclement of the $CBPQT^{2(\bullet+)}$ diradical dication around the $BIPY^{\bullet+}$ radical cation of the dumbbell ($BIPY^{\bullet+} \subset CBPQT^{2(\bullet+)}$).[S3] The first reduction peaks of $BIPY^{2+}$ of the dumbbell and $CBPQT^{4+}$ appear as one three-electron

process with an oxidation peak observed at –0.32 V. The second reduction peak of $CBPQT^{4+}$ is observed to split into a set of two one-electron reduction peaks (–0.80 V and –1.00 V) in addition to a large negative overall shift (~ –200 mV). Additionally, the second reduction peak of the $BIPY^{2+}$ component, shifts to a more negative value (~ –150 mV). These large negative shifts signify the stabilizing radical cation "pymerization" between $CBPQT^{2(\bullet+)}$ and $BIPY^{\bullet+}$ consistent with previously published viologen-based systems. The peak at –0.80 V, which integrates for a one electron process, corresponds to the reduction ($BIPY^{\bullet+} \subset CBPQT^{2(\bullet+)} \rightarrow BIPY^{\bullet+} \subset CBPQT^{\bullet+}$) of a single bipyridinium radical cation in the encircling $CBPQT^{2(\bullet+)}$. The CV of the

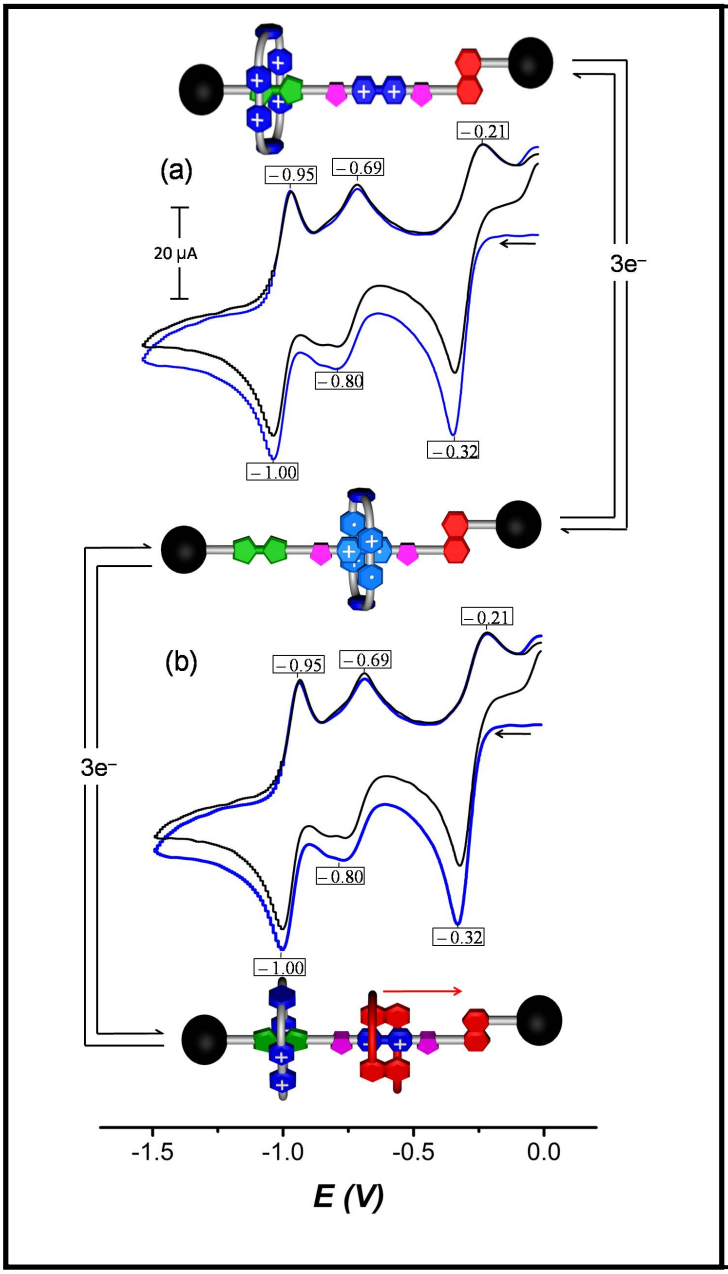

Figure S3. First (blue) and second (black) reduction CV of $\mathbf{1}^{6+}$ (a) and $\mathbf{1}^{6+} \subset$ BDNP38C10 (b). All the CVs were recorded under the same conditions of temperature (298 K), solvent (MeCN), concentrations (1 mM) and electrolyte (0.1 M $TBAPF_6$). The scan rate was set at 200 mV s^{-1}. CV Experiments were performed by using a glassy carbon working electrode (0.018 cm^2, Cypress system). The electrode surface was polished routinely with 0.05 μm alumina-water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was a Ag/AgCl electrode. Both CVs from (a) and (b) are virtually identical, indicating that the encirclement of the $CBPQT^{2(\bullet+)}$ around the $BIPY^{\bullet+}$ unit can still occur even in the presence of BDNP38C10.

[2]pseudo[2]rotaxane $\mathbf{1}^{6+} \subset$ BDNP38C10 is shown in Figure S3b. The CV is virtually identical to the CV of the [2]rotaxane $\mathbf{1}^{6+}$, indicating that the reduction-induced encirclement of the $CBPQT^{2(\bullet+)}$ ring component around the $BIPY^{\bullet+}$ unit in the dumbbell is still able to occur even in the presence of excess BDNP38C10 macrocycle.

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