Organic & Biomolecular Chemistry

A Neutral Redox Switchable [2]Rotaxane

John-Carl Olsen,[a] Albert C. Fahrenbach,[a] Ali Trabolsi,[a] Douglas C. Friedman,[a] Sanjeev K. Dey,[a] Chris M. Gothard,[a] Alexander K. Shveyd,[a] Travis B. Gasa,[a] Jason M. Spruell,[a] Mark A. Olson,[a] Cheng Wang,[a] Henri-Pierre Jacquot de Rouville,[a] Youssry Y. Botros[b,c,d] and J. Fraser Stoddart[a]

[a]*Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA.* [b]*Department of Materials Science and Engineering, Northwestern University 2145 Sheridan Road, Evanston, IL 60208, USA.* [c]*Intel Labs, Building RNB-6-61, 2200 Mission College Blvd., Santa Clara, CA 95054-1549 USA.* [d]*National Center for Nano Technology Research, King Abdulaziz City for Science and Technology (KACST) P.O. Box 6086, Riyadh, 11442 Saudi Arabia.*

SUPPORTING INFORMATION

Correspondence Address

Professor J Fraser Stoddart
Department of Chemistry
Northwestern University
2145 Sheridan Road
Evanston, IL 60208 (USA)
Tel: (+1)-847-491-3793
Fax: (+1)-847-491-1009
Email: stoddart@northwestern.edu

UV/Vis Measurements of Binding

The association constants, K_a, between the macrocycle **2** and the two guests, **6** and **7**, were determined (Figures S1 and S2) from UV/Vis spectroscopic measurements using the program SpecFit and assuming one-to-one binding interactions between the macrocycle and each of the guests. The macrocycle **2** and the guest **6** form a yellow charge-transfer complex in CH_2Cl_2 with λ_{max} = 442 nm. The association constant, K_a, between **2** and **6** was calculated to be 5.8 x 10^2 M^{-1} at 298 K. The macrocycle **2** and the guest **7** form a dark green charge-transfer (CT) complex in CH_2Cl_2 with λ_{max} = 608 nm and K_a = 6.3 x 10^3 M^{-1} at 298 K. In each titration experiment, the concentration of the macrocycle **2** was 2 mM.

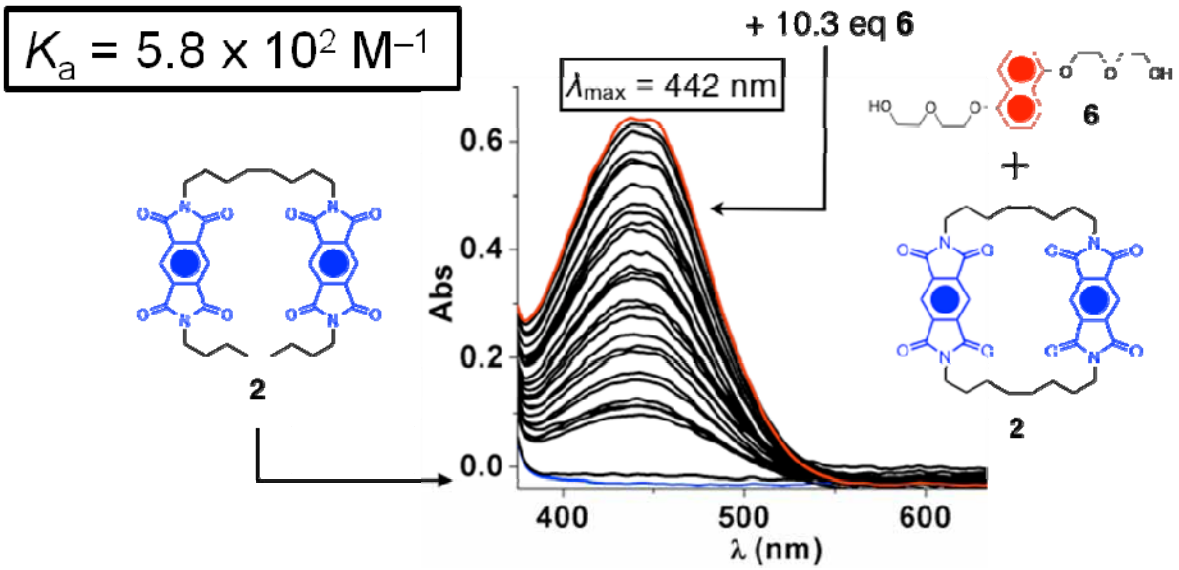

Figure S1. UV/Vis spectra resulting from a titration experiment in CH_2Cl_2 with macrocycle **2** and guest **6**. The increase in absorption centered on 442 nm reflects the charge-transfer interaction between **2** and **6** and results in a yellow-colored solution.

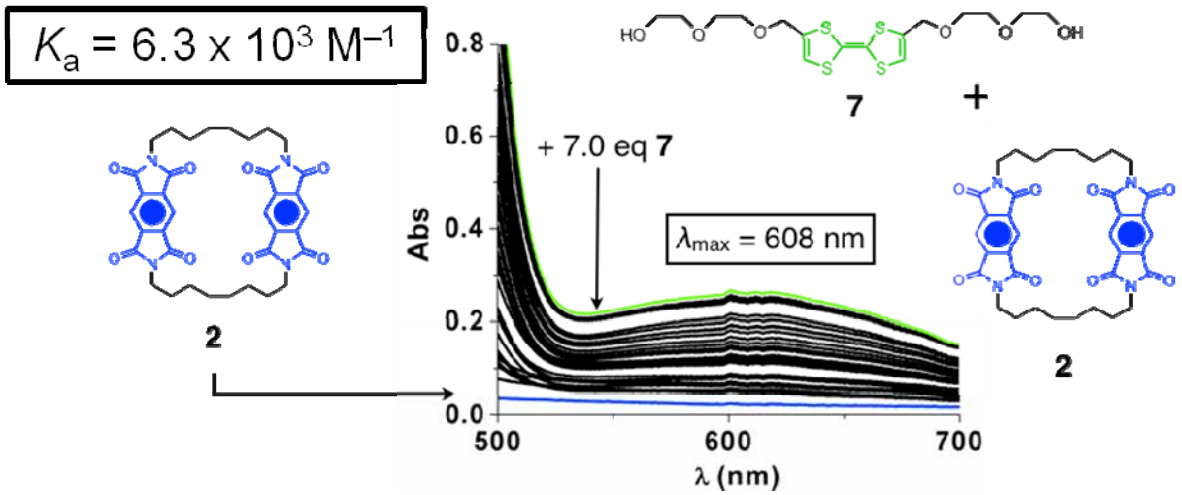

Figure S2. UV/Vis spectra resulting from a titration experiment with macrocycle **2** and guest **7**. The increase in absorption centered at 608 nm reflects the charge-transfer interaction between **2** and **7** and results in a green-colored solution.

^{1}H NMR Spectroscopy

The ^{1}H NMR spectroscopic data of **1** recorded in CD_2Cl_2 at 298 K (Figure S3) were consistent with the structure of the expected interlocked nature of **1**. An ^{1}H-^{1}H COSY spectrum (Figure S4) of **1**, recorded in CD_2Cl_2 at 298 K, aided in the assignment of key resonances annotated in

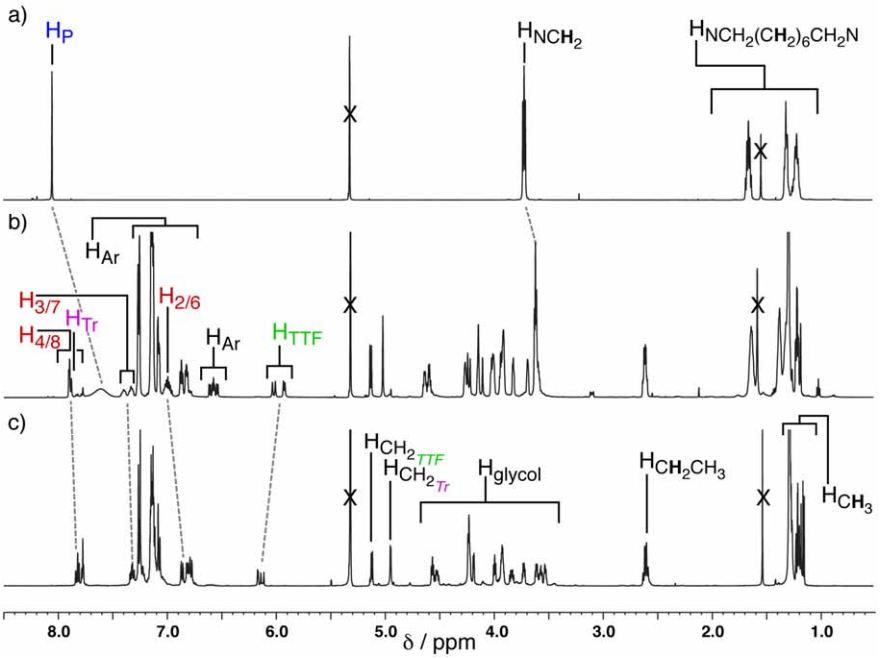

Fig. S3. ^{1}H NMR spectra (600 MHz, CD_2Cl_2, room temperature) of (a) macrocycle **2**, (b) neutral, bistable [2]rotaxane **1**, and (c) the dumbbell component **5**. Gray dashed lines indicate key chemical shift changes observed in the rotaxane in relation to the macrocycle and dumbbell.

Figure S3. Although the cis-trans isomers of the TTF unit, which occur in a roughly 1:1 ratio adds an extra degree of complexity to the spectrum, assignments of resonances arising from the protons of the triazole units, the DNP unit, the TTF unit, as well as the macrocycle could be made.

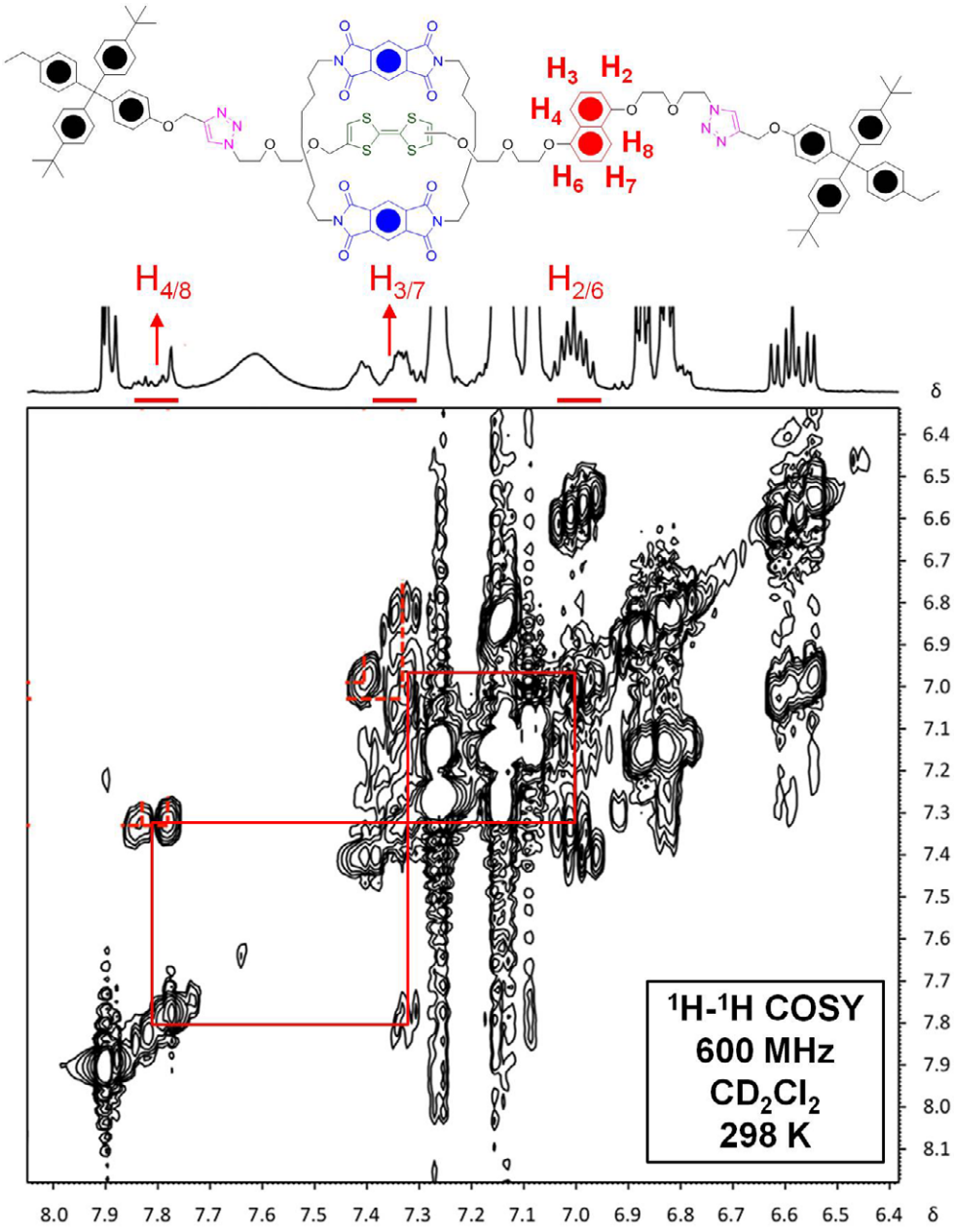

Fig. S4. Partial ^{1}H-^{1}H COSY of the rotaxane **1**, illustrating correlations between resonances hypothesised to arise from protons of the DNP unit.

Electrochemistry

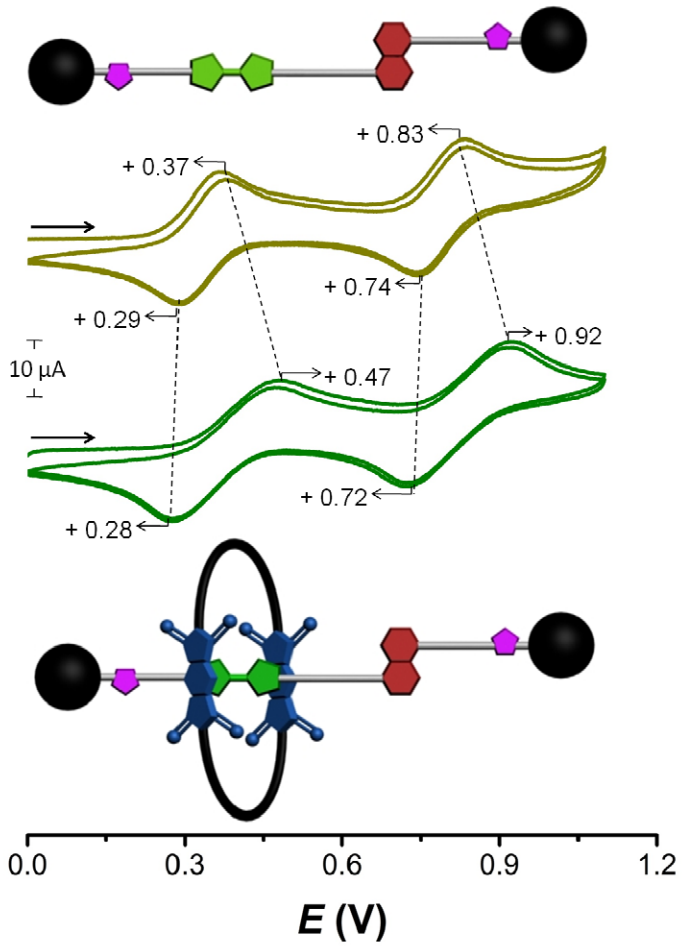

Figure S5. Cylclic voltammograms of the rotaxane **1** and the dumbbell **5** in CH_2Cl_2 with 0.1 M $TBAPF_6$ supporting electrolyte at 298 K. Scan rate = 200 mV s^{-1}; concentrations = 1 mM.

CV experiments were performed initially in CH_2Cl_2, on the rotaxane **1,** but slow electron transfer kinetics in this relatively nonpolar solvent caused shifts in the oxidation peak potentials arising from the TTF unit, which rendered analysis of the switching mechanism more difficult. In particular, the shifts in the oxidation peaks for the case of the rotaxane **1** compared to the dumbbell **5** (Figure S5), were, most likely caused by slow electron transfer kinetics, obscuring the effect of the PmI macrocycle on the redox processes of the TTF station. In order to confirm the hypothesis of slow-electron transfer kinetics, we performed variable scan rate experiments on the rotaxane **1**, which showed clearly shifting and broadening[S1] of the peaks as the scan rate was increased. Peak position and shape were better maintained in Me_2CO. Figure S6 shows CV traces in both CH_2Cl_2 (top) and Me_2CO (bottom).

Cyclic voltammetry of the rotaxane **1** as well as that of the free macrocycle **2** were performed (Figure S7) under reducing conditions in order to probe the redox properties of the PmI subunits. The free macrocycle **2** was observed to undergo two, two-electron reduction processes with peak potentials occurring at −1.10 and −1.67 V, respectively. These redox processes are assignable[S2] to the PmI units being reduced first to the radical anion $PmI^{\bullet -}$ and then to the dianion PmI^{2-}. In a similar fashion, the CV of the rotaxane **1** in the reductive region shows once again two, two-electron processes, assignable to the first and second reduction of the PmI units of the macrocycle component. In the case of both the free macrocycle **2** and rotaxane **1**, the two redox processes appear to be quasi-reversible, most likely on account of slow electron transfer kinetics that occurs in CH_2Cl_2 solutions.

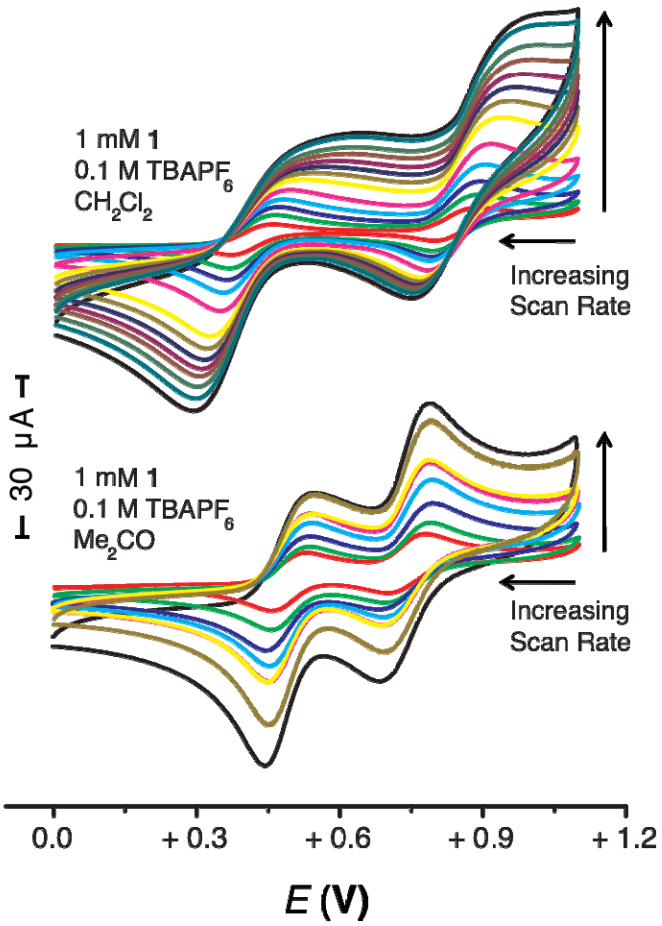

Figure S6. CV Traces of **1** in CH_2Cl_2 (top traces, 25–1000 mV s^{-1}, second scans) and Me_2CO (traces, 50–1000 mV s^{-1}, second scans). In the relatively nonpolar solvent CH_2Cl_2, the broadening and flattening of the voltammograms at higher scan rates is indicative of slow electron transfer kinetics.

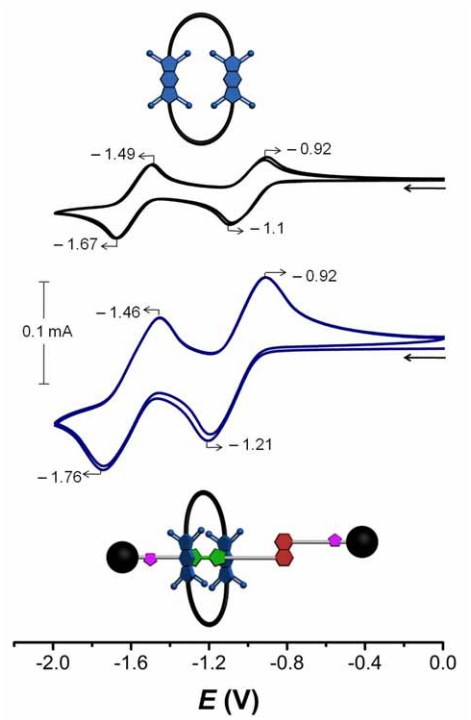

Figure S7. CV traces of the rotaxane **1** and the free macrocycle **2** in CH_2Cl_2 (1 mM, 200 mV s^{-1}, first and second scans) at 298 K with 0.1 M $TBAPF_6$ supporting electrolyte.

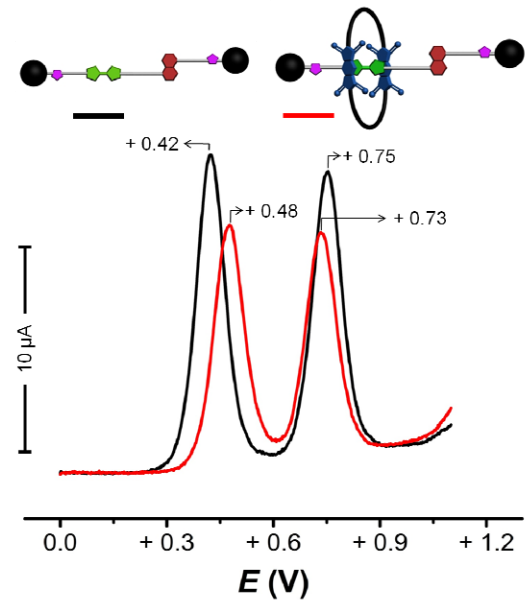

Figure S8. Square-wave differential pulse voltammetry (DPV) of the rotaxane **1** and the dumbbell **5** in Me_2CO (1 mM) at 298 K with 0.1 M $TBAPF_6$ supporting electrolyte.

Square-wave differential pulse voltammetry (DPV) was performed on the rotaxane **1** and the dumbbell **5** under oxidative conditions in Me_2CO in order to confirm the results from the CV experiments which reveal a shift in the redox potential of the first oxidation of the TTF unit in the rotaxane **1** compared to the free dumbbell **5**. The square-wave DPV traces of **1** and **5** are shown in Figure S8. The first redox potential of the TTF unit in **1** was observed to be shifted more positive by 60 mV compared to the dumbbell **5**, while the second redox potential of the TTF unit in the rotaxane was shifted slightly more negative by 20 mV. These results are consistent with the proposed mechanism of switching wherein the macrocycle encircles the TTF unit predominantly in the ground state and undergoes translational movement after the first oxidation of the TTF unit resulting in encirclement of the DNP unit, most likely on account of a loss of affinity between PmI and $TTF^{\bullet+}$ radical cation units.

Spectroelectrochemistry

In order to gain insight into the spectroelectrochemical behaviour of the rotaxane **1**, experiments were performed (Figure S9) on the dumbbell **5** as a control. As expected, after application of a +550 mV potential to a solution of **5** in CH_2Cl_2, absorption bands characteristic[S3] of the $TTF^{\bullet+}$ radical cation were observed, while application of a 1000 mV potential resulted in absorption bands consistent[S3] with the presence of the TTF^{2+} dication. In the case of the rotaxane **1**, the resulting UV/Vis spectra, after generating either the $TTF^{\bullet+}$ radical cation or TTF^{2+} dication, show broader and more intense absorption bands in the 400–700 nm region compared to those of the dumbbell. This difference can be explained as a result of the relatively intense CT band between the PmI units of the macrocycle component and the DNP unit of the dumbbell that results (see Figure S1) from the DNP station encircled by the ring after the first oxidation of TTF.

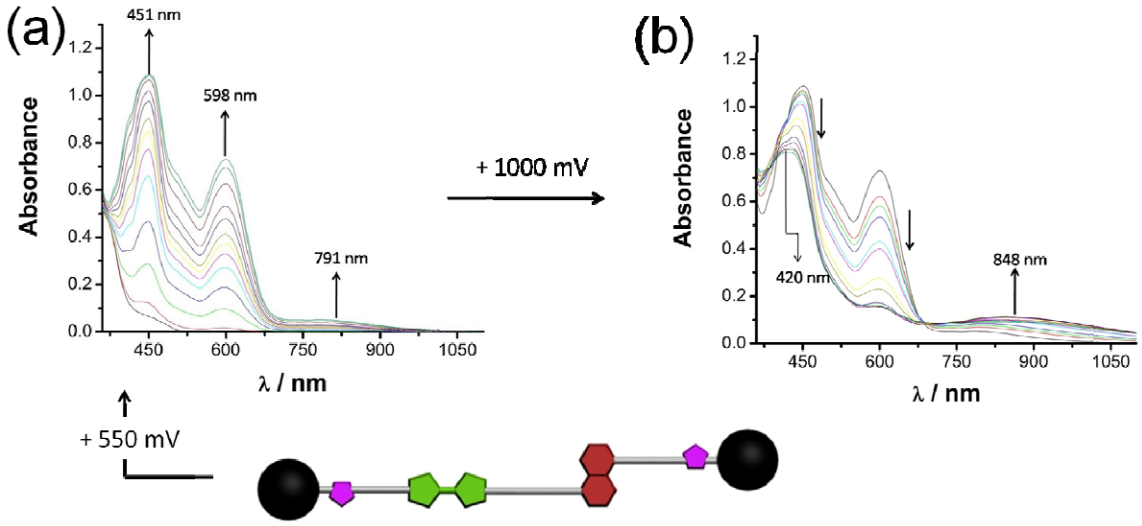

Fig. S9. SEC Experiments of a 1.0 mM solution of dumbbell **5** in argon-purged CH_2Cl_2 containing 0.1 M $TBAPF_6$ taken at different applied oxidation potentials. (a) Resulting spectra of **5** after applying a potential of +550 mV. (b) Resulting spectra of **5** after applying a voltage +1000 mV immediately following the initial +550 mV potential.

^{1}H NMR Monitoring of Switching

In order to gain insight about the ^{1}H NMR spectroscopic behaviour of the rotaxane **1** after oxidation of its TTF unit to its TTF^{2+} dication, an ^{1}H NMR spectrum of the complex formed between the guest **6** and the ring **2** (Figure S10) was recorded in CD_2Cl_2 at room temperature. The results show marked upfield shifts of the resonances arising from the aromatic protons of both the ring **2** and the guest **6**. From this data, we might expect that, after oxidation of the TTF unit in the rotaxane **1**, the resonances arising from the protons of the DNP unit should also undergo upfield shifts, which they do (Fig. S12).

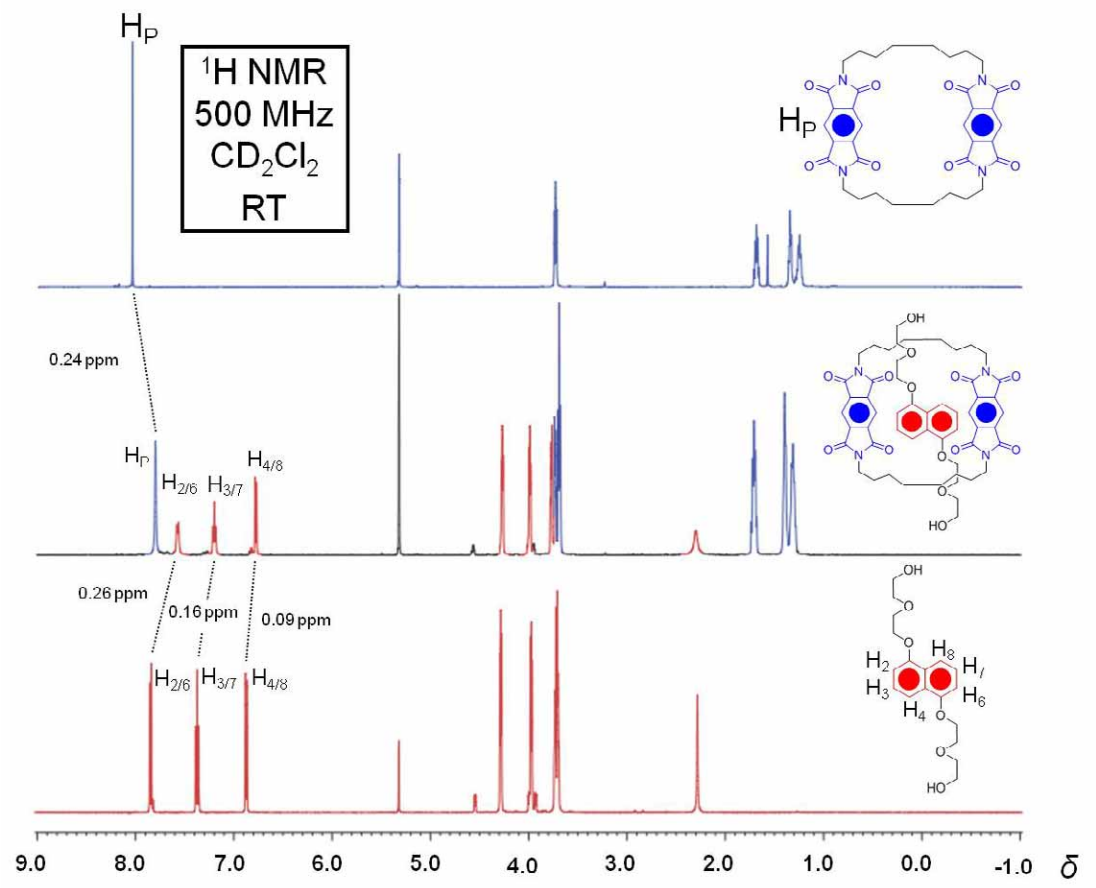

Fig. S10. ^{1}H NMR spectra of (top) the free macrocycle **2**, (bottom) the 1,5-dioxynaphthalene derivative **6**, and (middle) a 1:1 mixture of **2** and **6**, leading to the formation of a [2]pseudorotaxane.

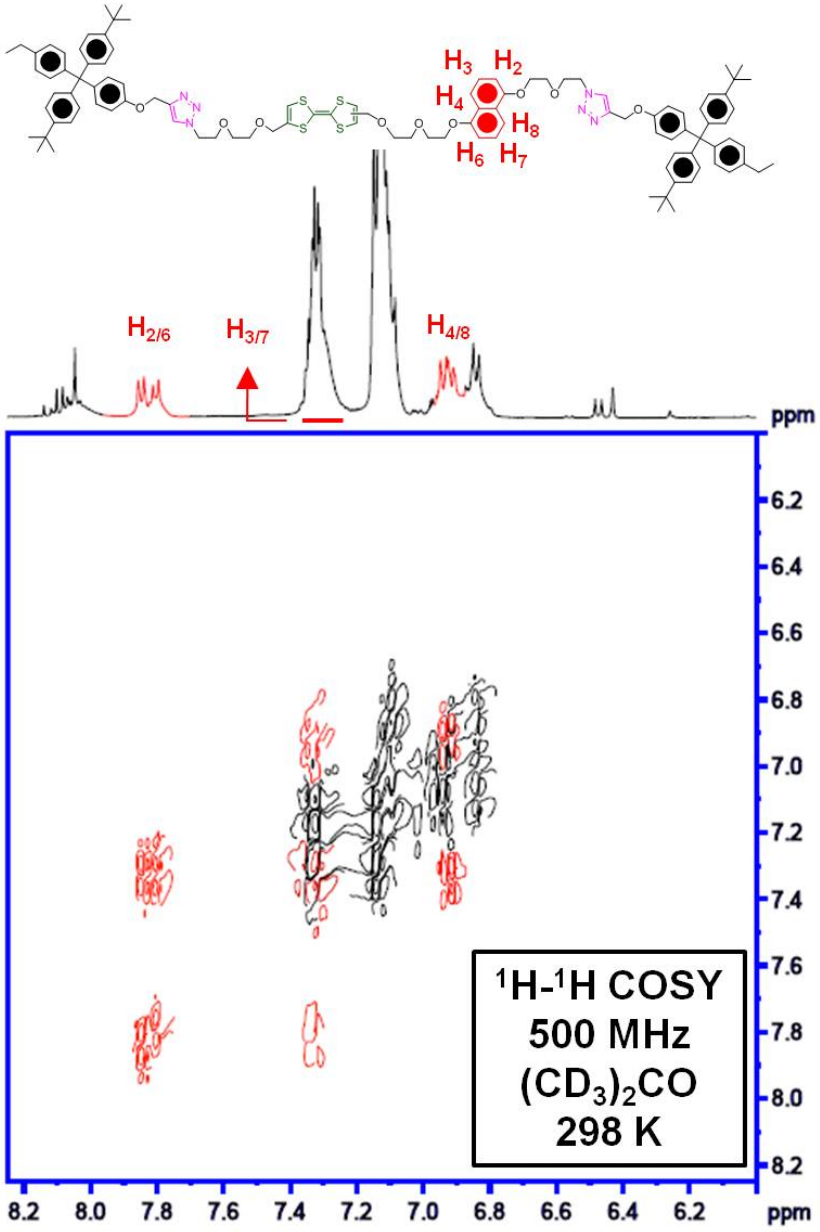

Fig. S11. Partial ^{1}H-^{1}H COSY spectrum of the free dumbbell **5**, illustrating assignments of resonances hypothesized to arise from protons of the DNP unit.

Figure S11 shows a ^{1}H-^{1}H COSY spectrum of the free dumbbell **5** recorded in $(CD_3)_2CO$ at 298 K. These correlations allowed us to make assignments of the resonances associated with the protons on the DNP unit, which serve as a control for making similar assignments in the case of the rotaxane **1**, in its ground state.

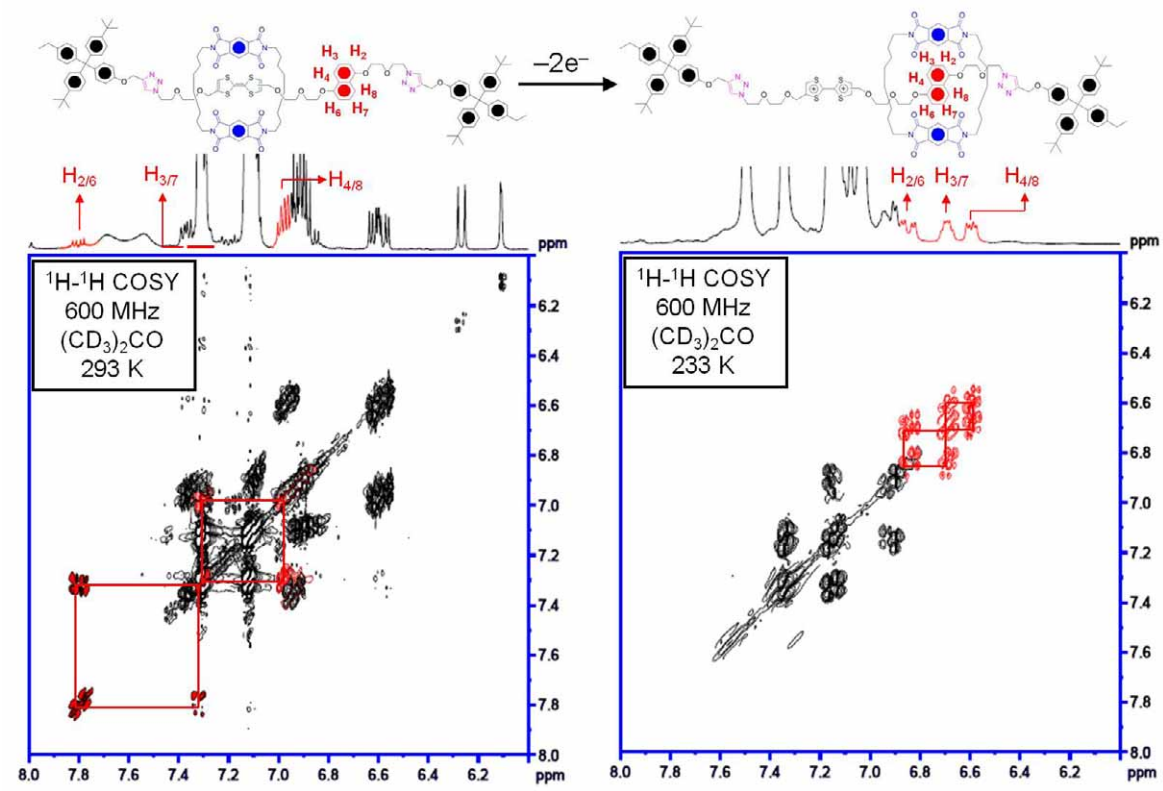

Fig. S12. Partial ^{1}H-^{1}H COSY spectra of the rotaxane **1** before (left) and after oxidation (right) of the TTF unit to its TTF^{2+} dication using tris-(4-bromophenyl)-imminium hexchloroantimonate as the chemical oxidising agent.

In order to probe the bistable nature of the [2]rotaxane **1**, switching was performed in CD_3COCD_3 using tris-(4-bromophenyl)-imminium hexachloroantimonate as the chemical oxidant.[S4] An ^{1}H-^{1}H COSY spectrum of **1** in its neutral state, recorded in CD_3COCD_3 at 293 K, shows correlations (Figure S12, left) resulting from an ABC system. Using assignments of ^{1}H NMR resonances performed on the dumbbell **5** as a control, we have made assignments for the location of the resonances hypothesised to be arising from the protons of the DNP unit. Upon addition of 3.0 equiv of the oxidant, the dark green solution of **1** became a translucent yellow, an observation which indicates formation of the TTF^{2+} dication. An ^{1}H-^{1}H COSY spectrum recorded on this yellow-colored solution shows sets of correlations belonging to ABC systems,

the resonances of one we hypothesise are arising from the protons of the DNP unit encircled by the PmI macrocycle component. Based on these assignments of the resonances of the protons arising from the DNP units before and after oxidation of the TTF to its TTF^{2+} dication, it is clear that all the DNP resonances undergo upfield shifts, an observation which is consistent with encirclement of the PmI macrocycle around the DNP unit.

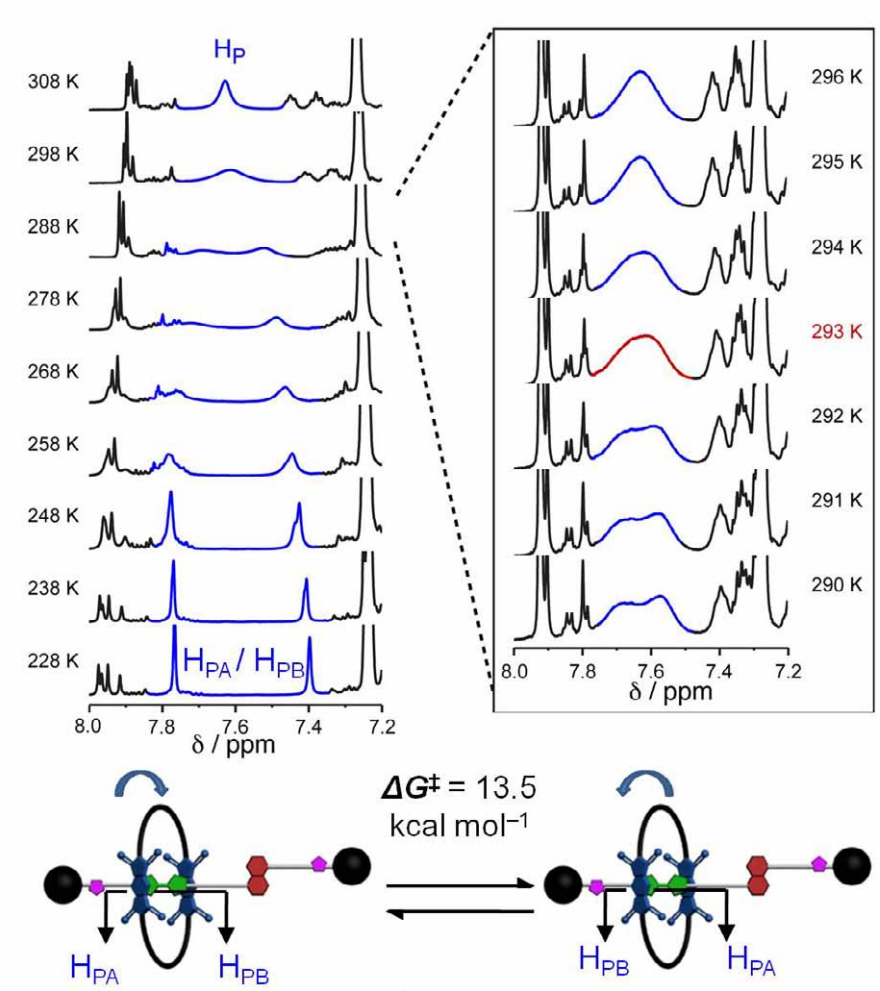

Figure S13. Partial variable temperature ^{1}H NMR spectra (600 MHz, CD_2Cl_2) of [2]rotaxane **1** recorded at temperatures ranging from 228 K–308 K. The resonances associated with the aromatic PmI protons (H_P) are highlighted in blue with the coalescence temperature and spectrum highlighted in red. The coalescence temperature for the two signals that correspond to the PmI protons was found to be 293 K. The rate constant and activation energy for the rotation of the PmI moieties at 293 K were calculated from the chemical shift difference of 222 Hz at 228 K to be k_c = 491 s^{-1} and $\Delta G^{\ddagger}$ = 13.5 kcal mol^{-1}, respectively.

Variable temperature ^{1}H NMR spectroscopic analysis of **1** in CD_2Cl_2 revealed a dynamic process associated with the PmI protons of the ring component. Figure S12 shows ^{1}H NMR spectra recorded in CD_2Cl_2 at temperatures ranging from 228 K to 308 K. While the free ring exhibits a single aryl resonance corresponding to the PmI protons, signal separation occurs in the spectrum of the rotaxane at lower temperatures because of desymmetrisation. At 228 K the PmI protons reside in the slow exchange regime and give rise to two sharp singlets at 7.40 and 7.77 ppm. The presence of two signals for the PmI protons is also consistent with molecular modeling of **1**, an activity which suggests that rotation of the PmI units are hindered when the ring encircles either of the two station, at least at low temperatures. At increasing temperatures, the PmI signals begin to converge, ultimately coalescing to form one broad signal at 7.61 ppm which narrows up to 308 K. This behaviour most likely reflects the following process – (i) movement of the ring off of the TTF station, (ii) rotation of the PmI subunits about their long axis, and (iii) return of the ring to the TTF unit. Such a motion would allow the PmI protons to exchange between two heterotopic positions, one closer to the stopper next to the TTF unit and the other closer to the stopper next to the DNP unit. The kinetics of this dynamic process were determined by identifying the temperature of signal coalescence (T_c = 293 K) and calculating[S5] the rate constant of the proton exchange (k_c = 491 s^{-1}), from whence an energetic barrier of $\Delta G^{\ddagger}$ = 13.5 kcal mol^{-1} was found.

References

S1 A. J. Bard and L. R. Faulkner, "Electrochemical Methods. Fundamentals and Applications." John Wiley & Sons, New York, 1980, pp. 230–231.
S2 T. Iijima, S. A. Vignon, H.-R. Tseng, T. Jarrosson, J. K. M. Sanders, F. Marchioni, M. Venturi, E. Apostoli, V. Balzani and J. F. Stoddart, *Chem. Eur. J.* 2004, **10**, 6375–6392.
S3 V. Balzani, A. Credi, G. Mattersteig, O. A. Matthews, F. M. Raymo, J. F. Stoddart, M. Venturi, A. J. P. White, and D. J. Williams, *J. Org. Chem.* 2000, **65**, 1924–1936.
S4 Oxidation could not be performed in CD_2Cl_2 because of the decomposition of the [2]rotaxane.
S5 I. O. Sutherland, *Annu. Rep. NMR Spectrosc.* 1972, **4**, 71–235.