

Electrochemically Induced Molecular Motions in Pseudorotaxanes: A Case of Dual-Mode (Oxidative and Reductive) Dethreading

Masumi Asakawa, Peter R. Ashton, Vincenzo Balzani,* Alberto Credi, Gunter Matternsteig, Owen A. Matthews, Marco Montalti, Neil Spencer, J. Fraser Stoddart,* and Margherita Venturi*

Abstract: The electrochemical and spectroscopic properties of a pseudorotaxane formed in acetonitrile solution by self-assembly of a wire-type electron donor based on the tetrathiafulvalene unit and the cyclobis(paraquat-*p*-phenylene) tetracationic electron acceptor have been investigated. We show that a) reversible dethreading/rethreading cycles of the pseudorotaxane can be performed by *either* oxidation and successive reduction of the electron-donor wire *or* reduction and successive oxidation of the electron-accepting tetracationic cyclophane, and b) because of this special behavior, the input (electrochemical)/output (absorption spectrum) characteristics of this molecular-level system correspond to those of an XNOR logic gate.

Keywords

cyclic voltammetry • logic gates • molecular devices • pseudorotaxanes • spectroelectrochemistry

Introduction

In the last few years, it has been shown that it is possible to construct assemblies of molecular components designed to achieve specific functions (molecular-level devices).^[1] Particular attention has recently been paid to systems based on pseudorotaxanes,^[2] rotaxanes,^[3] and catenanes,^[4] in which the relative positions of the component parts can change as a result of some external stimulus and so behave as molecular machines. Three types of energy can be used to make molecular machines work: chemical energy,^[2b,c,g, 3a, 4d,f] electrical energy,^[2c,f, 3a, 4a,b,e] and light.^[2a,f, 3b, 4c] It has also been shown that suitably designed systems of this kind can perform complex logic operations.^[2g]

Pseudorotaxanes, composed of a macrocyclic ring threaded over a wirelike component, are models of simple molecular machines, since they can undergo threading/dethreading processes that recall the movement of a piston in a cylinder.^[2a] Here, we report the case of a pseudorotaxane (whose components are shown in Scheme 1) in which the dethreading/rethreading

movement can be achieved by either an oxidation–reduction or a reduction–oxidation cycle (Figure 1). We will also show that, because of this special behavior, the input (electrochemical)/output (absorption spectrum) characteristics of this molecular-level system correspond to those of an XNOR logic gate.

Results and Discussion

1. Properties and self-assembly of the molecular components:

The molecular components used in this work are shown in Scheme 1. The tetracationic cyclophane cyclobis(paraquat-*p*-

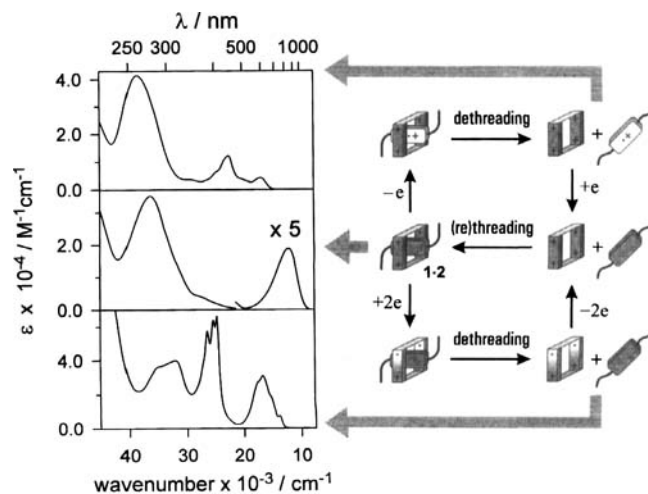
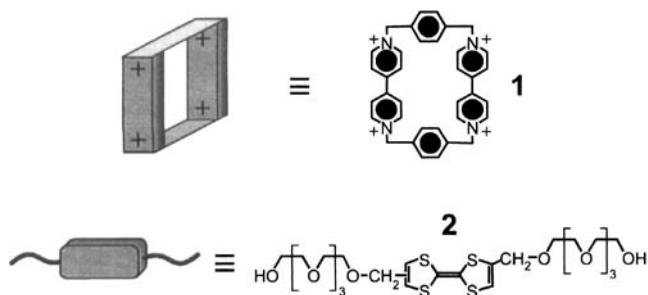


Figure 1. Schematic representation of dethreading/rethreading of pseudorotaxane 1·2 upon electrochemical reduction or oxidation. The absorption spectra before (center) and after reduction (bottom) or oxidation (top) are shown.

[*] Prof. V. Balzani, Prof. M. Venturi, Dr. A. Credi, Dr. M. Montalti
Dipartimento di Chimica "G. Ciamician", Università di Bologna
via Selmi 2, I-40126 Bologna (Italy)
Fax: Int. code + (51) 259-456
e-mail: vbalzani@ciamician.unibo.it

Prof. J. F. Stoddart, Dr. M. Asakawa, Dr. G. Matternsteig, Dr. O. A. Matthews, Dr. N. Spencer, P. R. Ashton
School of Chemistry, University of Birmingham
Edgbaston, Birmingham B152TT (UK)

[*] Current address:
Department of Chemistry and Biochemistry
University of California at Los Angeles
405 Hilgard Avenue, Los Angeles, CA 90095 (USA)
Fax: Int. code + (310) 206-1843



Scheme 1. Schematic representations of tetracationic cyclophane **1** and polyether-substituted tetrathiafulvalene **2**.

phenylene) (**1**), extensively used as a macrocyclic ring in pseudorotaxanes, rotaxanes, and catenanes,^[5] exhibits electron-acceptor properties. The first and second reversible reduction processes of the two equivalent and noninteracting paraquat units of **1** occur (bielectronic waves)^[4b,6] at -0.28 and -0.72 V vs. SCE in acetonitrile solution^[7] (Figure 2). The TTF wire-type derivative 4,4'-(5')-bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxymethylene]tetrathiafulvalene (**2**) exhibits electron-donating properties.^[8] In acetonitrile solution, **2** undergoes two successive reversible one-electron oxidation processes (Figure 2). The reduction potentials of the $2^{2+}/2^{+}$ and $2^{+}/2$ couples are $+0.70$ and $+0.35$ V, respectively. We have investigated the adduct **1·3** as a model compound for the pseudorotaxane **1·2**, where the wire-type component **2**, based on a TTF moiety, is replaced by the simple TTF unit **3**. As is the case for **2**, **3** undergoes two successive reversible one-electron oxidation processes ($+0.72$ V for the $3^{2+}/3^{+}$ couple and $+0.32$ V for the $3^{+}/3$ couple, Figure 2).^[9]

Pseudorotaxane **1·2** and adduct **1·3**, represented schematically in Figure 1, result from a self-assembly process based on an electron-donor–acceptor interaction between the TTF moiety and the paraquat units of the macrocyclic ring. Unequivocal evidence that the electron-rich TTF unit is sandwiched between the electron-deficient paraquat units of the ring is given by NMR spectroscopy and, in the case of **1·3**, by X-ray crystallography.^[11] Several proton resonances in the ^1H NMR spectrum of an equimolar mixture of **1** and **2** (recorded in CD_3CN at ambient temperature) undergo significant complexation-induced shifts, which are of a similar magnitude to those reported for the adduct **1·3** and are consistent with the proposed struc-

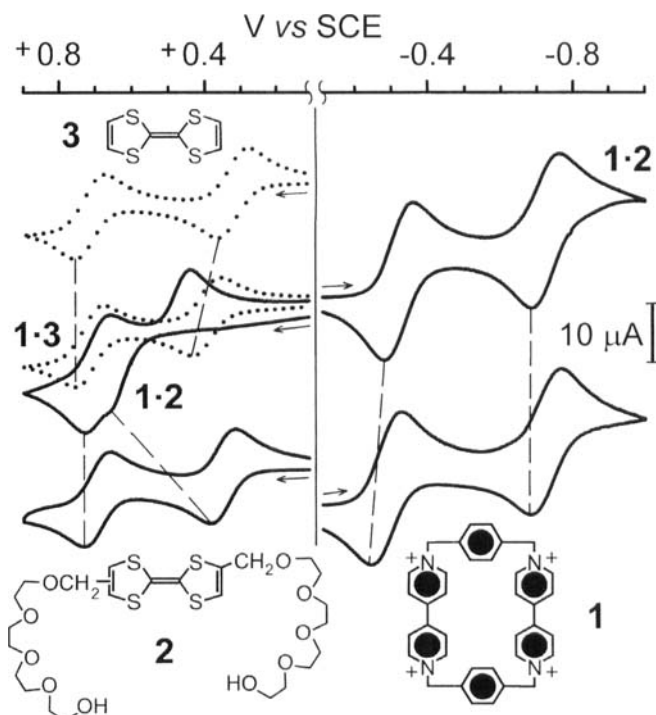


Figure 2. Cyclic voltammetric behavior of the examined compounds (acetonitrile solution, potential values vs. SCE, scan rate 50 mVs^{-1}). The reduction waves for **1·3** practically coincide with those of **1·2**. The current intensity has been corrected to take into account differences in diffusion coefficients.

ture. The presence of two diastereoisomers (*cis* and *trans*) in **1·2** is indicated by two distinct signals for the TTF–CH protons, the methylene protons attached to the TTF core and the β -bipyridinium protons of the tetracationic cyclophane **1**. Intimate association of **1** and **2** in solution is also confirmed by 2D NOESY and 2D ROESY experiments (500 MHz, CD_3CN , 304 K, 400 ms mixing time) which display crosspeaks between the OCH_2 protons of the threadlike component and the CH_2N^+ protons of the tetracationic cyclophane. Because of the electron-donor–acceptor interaction, a low-energy charge-transfer (CT) excited state is present, which is responsible for the weak and broad absorption band with $\lambda_{\text{max}} = 830\text{ nm}$ for **1·2** (Figure 1, central spectrum) and $\lambda_{\text{max}} = 855\text{ nm}$ for **1·3**. The association constants^[12] for **1·2** and **1·3** are $5 \times 10^4\text{ M}^{-1}$ and $1 \times 10^4\text{ M}^{-1}$, respectively, indicating that the presence of the polyether chains strengthens the association by means of hydrogen bonds between the oxygen atoms in the chains and the hydrogen atoms on the methylene groups α to the nitrogen atoms of the paraquat units.^[6]

2. Electrochemical behavior of the pseudorotaxane **1·2 and the adduct **1·3**:** In an acetonitrile solution containing $5.0 \times 10^{-4}\text{ M}$ **1** and **2**, about 95% of the two components are engaged in the **1·2** pseudorotaxane structure. The cyclic voltammetric curves obtained for **1·2** show two reduction and two oxidation waves (Figure 2). The two reduction processes, which are reversible and bielectronic, can be assigned straightforwardly to reduction of the two equivalent paraquat units of the macrocyclic ring **1**. Compared with free **1** (Figure 2, right-hand side), the first process (-0.33 V) is displaced to more negative potentials, whereas the second one (-0.73 V) occurs practically at the same poten-

Abstract in Italian: In acetonitrile, il macrociclo tetracationico ciclobis(paraquat-*p*-fenilene) contenente 2 unità elettron-accettrici ed un filo molecolare basato sull'unità elettron-donatrice tetrathiafulvalene si autoassemblano con notevole efficienza per dare il corrispondente pseudorotassano, del quale sono presentate le proprietà spettroscopiche ed elettrochimiche. I processi di "sfilamento" e "reinfilamento" dello pseudorotassano sono stati ottenuti in modo reversibile mediante ossidazione e successiva riduzione dell'unità tetrathiafulvalene inserita nel filo molecolare, oppure riduzione e successiva ossidazione delle unità elettron-accettrici presenti nel macrociclo. In virtù di tale particolare comportamento, è possibile stabilire un'analogia tra questo sistema supramolecolare ed una porta logica XNOR.

tial. The displacement of the first reduction process is an expected result, because the paraquat units in the pseudorotaxane are engaged in donor–acceptor interactions. The lack of displacement of the second reduction process can be taken as evidence that the pseudorotaxane structure is dethreaded fast (compared to the scan rate used, from 10 to 1000 mVs^{−1}) as a consequence of the first reduction (Figure 1). In the literature^[4b, 6, 13, 14] there is ample evidence that, when dethreading is prevented (e.g., in rotaxane and catenane structures), the potential of the second reduction process is also displaced compared with that of the free component. It should also be noted that, since the dethreading process is very fast compared to the timescale of the electrochemical experiment even at the fastest scan rate used, it is not possible to obtain the potential value for the first reduction of the cyclophane **1** in the pseudorotaxane structure.

The two processes observed on oxidation of **1·2** (Figure 2, left-hand side) can be assigned to the two successive oxidations of the TTF unit of threaded **2**. The first oxidation process for **1·2** occurs at a much more positive potential than that of free **2**, on account of the donor–acceptor interaction between the two components in the pseudorotaxane structure. Such an oxidation process, however, is affected by the scan rate. On increasing scan rate, the anodic peak moves toward more positive potentials and the cathodic peak moves toward less positive potentials (at a scan rate of 10 mVs^{−1}, $E_{pa} = +0.63$ V and $E_{pc} = +0.46$ V; at a scan rate of 1 Vs^{−1}, $E_{pa} = +0.75$ V and $E_{pc} = +0.38$ V). In principle, the lack of reversibility of the electrode process could be due to restricted access to the inside TTF unit. This possibility, however, can be ruled out considering the fully reversible behavior shown by the enclosed electroactive units of all the previously investigated rotaxanes and catenanes.^[4b, 6, 13, 14] Therefore, the observed behavior indicates that the first oxidation process is followed by a reaction that occurs on the timescale of the electrochemical experiment. At high scan rates, E_{pa} merges into the second oxidation wave, which is almost unaffected by the scan rate and occurs at a potential close to that of free **2** (Figure 2). These results suggest that the reaction taking place after the first oxidation process is the dethreading of the pseudorotaxane. This interpretation is supported by the fact that the cathodic peak of the first oxidation process moves toward less positive potentials (i.e., toward the value of the reduction peak of free **2**⁺) with increasing scan rate.^[15]

In order to elucidate still better the electrochemical behavior of **1·2**, we have investigated the electrochemical properties of adduct **1·3**, which serves as a model for the pseudorotaxane. The adduct has two reduction and two oxidation waves.^[16] The reductive behavior is substantially the same as that observed for **1·2**—reduction processes at -0.32 and -0.72 V; the displacement of the first reduction process, compared with free **1**, indicates once again the presence of donor–acceptor interactions. The lack of displacement of the second reduction process shows that the adduct undergoes fast (compared to the scan rate used, from 10 to 1000 mVs^{−1}) disruption as a consequence of the first reduction.

The two processes observed on oxidation of **1·3** (Figure 2, left-hand side) can be assigned to the two successive oxidations of the TTF unit. Both processes are fully reversible. The first one occurs at a more positive potential ($+0.39$ V) than that of free

3, as expected because of the donor–acceptor interaction between the two components. The second oxidation process ($+0.72$ V) occurs at the same potential as that for free **3**. These results show that one-electron oxidation causes a very fast (compared with the scan rate used, from 10 to 1000 mVs^{−1}) disruption of the adduct, and successive one-electron reduction causes a very fast (compared again with the scan rate) back-formation of the adduct. The much faster disruption and reassociation of **1·3** compared with dethreading and rethreading of **1·2** is not surprising because of the more complex structure of the pseudorotaxane.

3. Dual-mode dethreading/rethreading cycles of the pseudorotaxane **1·2**:

The results obtained show that the dethreading/rethreading of pseudorotaxane **1·2** can be achieved by either a reduction–oxidation cycle of the electron-accepting macrocyclic ring (Figure 1, right, lower cycle) or an oxidation–reduction cycle of the electron-donating wire-type component (Figure 1, right, upper cycle). To our knowledge, this is the first example of such a dual-mode electrochemically driven dethreading/rethreading process. Interestingly, the results obtained at different scan rates show that the dethreading/rethreading processes are faster in the reduction–oxidation than in the oxidation–reduction cycle. This behavior is probably a result of the fact that the reduction of the macrocyclic ring affects both the donor–acceptor and hydrogen-bond interactions, whereas oxidation of the electron-donor wire destroys only the donor–acceptor interaction.

The dual-mode electrochemically driven dethreading/rethreading process of **1·2** is fully reversible, as evidenced by spectroelectrochemical experiments. As shown by the spectra displayed in Figure 1, exhaustive electrolysis at -0.3 V of an acetonitrile solution of **1·2** caused the disappearance of the charge-transfer band of the pseudorotaxane and the formation of the characteristic bands^[2a] of the reduced cyclophane. This process resulted in a distinct color change from green to blue. Exhaustive reoxidation at 0 V led back quantitatively to the original spectrum. Subsequent exhaustive electrolysis of the same solution at $+0.5$ V once again caused the disappearance of the charge-transfer band of the pseudorotaxane with formation of the characteristic bands of the oxidized TTF moiety (color change from green to brown).^[10] Exhaustive back reduction at 0 V restored the original spectrum.

It should also be noted that the dethreading/rethreading cycles of pseudorotaxane **1·2** driven by electrochemical techniques could be effected, in principle, by any other redox-type input such as direct addition of redox reactants or photochemical generation of the reduced or oxidized forms of **1·2**.

4. Pseudorotaxane **1·2 as an XNOR logic gate:** The design and construction of molecular-level systems capable of performing logic functions is a topic of great scientific interest.^[11, g, 17, 18] Molecular systems that can perform YES and NOT operations are very common.^[11, g, 19] A molecule that fluoresces (output) only in acid media (i.e., in the presence of a proton input) acts as a YES gate. Conversely, a fluorescent molecule whose emission (output) disappears under a proton input, can be regarded as a NOT logic device. In order to perform more complex logic operations, however, carefully designed multicomponent chem-

ical systems are needed. Examples of chemical systems capable of performing the AND and OR logic operations have been reported by de Silva and co-workers,^[17] and a pseudorotaxane in which the input (chemical)/output (fluorescence) characteristics correspond to those of an XOR (eXclusive OR) logic gate has recently been described.^[26] The input/output characteristics of the **1·2** pseudorotaxane studied in this paper correspond to those of an XNOR (eXclusive NOR) logic gate.^[20, 21] The truth table of the XNOR logic operation is shown in Table 1.

Table 1. Truth table of the XNOR logic operation. For more details, see text.

INPUTS		OUTPUT
<i>a</i>	<i>b</i>	<i>c</i>
0	0	1
1	0	0
0	1	0
1	1	1

In the present system, the inputs *a* and *b* are the reduction and oxidation of **1·2**, respectively, and the output *c* is the charge-transfer absorption band of **1·2** with $\lambda_{\text{max}} = 830$ nm. Before receiving any redox input, the system exhibits such an absorption band (Figure 1, central spectrum). In logic language, this system can be read as $a \equiv 0$, $b \equiv 0$, $c \equiv 1$ (Table 1, first row). After the reduction process, the absorption band with $\lambda_{\text{max}} = 830$ nm is no longer present (Figure 1, bottom spectrum) because the two components are dethreaded ($a \equiv 1$, $b \equiv 0$, $c \equiv 0$, second row in Table 1). After the oxidation process, the absorption band with $\lambda_{\text{max}} = 830$ nm has once again disappeared (Figure 1, top spectrum) because the two components are dethreaded ($a \equiv 0$, $b \equiv 1$, $c \equiv 0$, third row in Table 1). In the presence of both inputs (which can be seen as the simultaneous addition of a reductant and an oxidant in stoichiometric amounts), the band with $\lambda_{\text{max}} = 830$ nm is present ($a \equiv 1$, $b \equiv 1$, $c \equiv 1$, fourth row in Table 1).

Although the described system behaves as an XNOR logic gate like an electric circuit that obeys the truth table shown in Table 1, it should be pointed out that a comparison between the characteristics of two XNOR gates as different as a chemical system and an electric circuit should be made with great care. Under some aspects (e.g., extrapolation to real applications of the chemical systems), such a comparison could be inappropriate or misleading.

It should also be noted that besides the absorption band with $\lambda_{\text{max}} = 830$ nm, whose presence or absence is related to the logic behavior already explained above, the reductive–oxidative and oxidative–reductive dethreading/rethreading cycles are characterized by other, distinct spectroscopic features (compare the spectra shown in Figure 1) that carry additional pieces of information useful for other purposes.^[22]

Experimental Section

Chemicals: Acetonitrile (MeCN) used as solvent was Romil High-Dry[®]. Cyclobis(paraquat-*p*-phenylene) hexafluorophosphate salt (**1**) was prepared according to a previously described procedure.^[6a] Tetrathiafulvalene (TTF; **3**) was a Fluka product and was used as received.

1-(4-Toluenesulfonyl)-13-(tetrahydropyran-2-yl)-1,4,7,10,13-pentaoxatridecane (4): 3,4-Dihydro-2*H*-pyran (4.2 g, 50 mmol) and tetraethyleneglycol monotosylate (11.5 g, 33 mmol) were dissolved in dry CH_2Cl_2 (300 mL). To this solution was added pyridinium *p*-toluene sulfonate (PPTS) (50 mg, 0.2 mmol) as a catalyst. The mixture was refluxed for 1 h under N_2 and then stirred at room temperature under N_2 for 16 h. After a second refluxing for 1 h and subsequent cooling the mixture was poured into an aqueous ammonia solution (0.33%, 150 mL). The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (4×100 mL). The combined organic extracts were washed with water (4×100 mL), dried (MgSO_4) and evaporated under reduced pressure. Prolonged drying on a vacuum line afforded the product as a yellow-orange oil (12.8 g, 90%). ¹H NMR (300 MHz, CDCl_3 , 298 K): $\delta = 7.75$ (d, $J = 8.5$ Hz, 2H), 7.32 (d, $J = 8.5$ Hz, 2H), 4.57 (1H, AA'BB'), 4.10 (2H, AA'BB'), 3.85–3.75 (2H, m), 3.65–3.40 (14H, m), 2.40 (3H, s), 1.82–1.42 (6H, m); ¹³C NMR (75 MHz, CDCl_3 , 298 K): $\delta = 144.8$, 133.0, 129.8, 128.0, 99.0, 72.5, 70.7, 70.5, 70.3, 69.3, 68.7, 66.7, 62.3, 61.7, 30.6, 25.4, 21.6, 19.5; FABMS: $m/z = 455$ [$M + \text{Na}$]⁺; HRMS (LSIMS): $\text{C}_{20}\text{H}_{32}\text{O}_8\text{NaS}$: [$M + \text{Na}$]⁺, calcd 455.1716, found 455.1725.

4,4'-(5')-Bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy] ethoxymethylene[tetrathiafulvalene (2): NaH (96 mg, 4.0 mmol) was added to a solution of 4,4'-(5')-bis(hydroxymethylene)tetrathiafulvalene (433 mg, 1.64 mmol) in 50 mL of dry, degassed (argon) THF. The mixture was refluxed for 1 h under argon. Subsequently, a dry, degassed (argon) solution of the monotosylate **4** (1728 mg, 4.0 mmol) in 25 mL of THF was added dropwise over 1 h to the stirred solution while this was refluxed under argon. After refluxing and stirring had been continued for a further 36 h, the reaction mixture was cooled to 10 °C, and wet THF (50 mL) was added with care. The solvents were removed under vacuum and the residue extracted into CH_2Cl_2 (100 mL). The organic layer was washed with saturated aqueous NaCl solution (20 mL) and H_2O (4×20 mL), and dried (MgSO_4). After evaporation of the solvent in vacuo, the resulting oil was subjected to column chromatography (short column, SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$, 98:2) to afford a crude product (yellow-brown oil), which was used for the next step without further purification. For deprotection it was dissolved in ethanol (90%, 30 mL), and a catalytic amount (50 mg) of *p*-TsOH was added. The reaction mixture was refluxed for 38 h under an argon atmosphere. The solution was cooled to room temperature and the solvent removed under reduced pressure. The residue was treated with CH_2Cl_2 (100 mL), washed with 10% aqueous HCl (10 mL), 10% aqueous NaOH, and finally with water (5×30 mL), and dried (MgSO_4). The solvent was removed under vacuum and the residue subjected to column chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$, 96:4) to afford the polyether-elongated TTF **2** as a yellow-brown oil (542 mg, 54%). ¹H NMR (300 MHz, CD_3CN , 298 K): $\delta = 6.39$ (s, 2H), 4.26 (s, 4H), 3.60–3.40 (m, 32H), 2.82 (m, 2H); ¹³C NMR (75.1 MHz, CDCl_3 , 298 K): $\delta = 134.4$, 134.3, 116.3, 116.2, 110.4, 72.4, 70.5, 70.37, 70.2, 69.1, 68.0, 61.5, 56.0; FABMS: $m/z = 616$ [M]⁺; HRMS (LSIMS): $\text{C}_{24}\text{H}_{40}\text{O}_{10}\text{S}_4$: [M]⁺, calcd 616.1504, found 616.1513; $\text{C}_{24}\text{H}_{40}\text{O}_{10}\text{S}_4$: calcd C 46.73, H 6.54, S 20.79; found C 46.65, H 6.47, S 21.0.

Pseudorotaxane 1·2·4PF₆: An equimolar (25 mM) mixture of the wire-type compound **2** and the tetracationic cyclophane **1** in CD_3CN formed an intensely green solution. ¹H NMR (300 MHz, CD_3CN , 298 K): $\delta = 9.05$ (br, 8H, α -bipyridinium CH), 7.90 (br, 4H, β -bipyridinium CH), 7.79 (br, 4H, β -bipyridinium CH), 7.66 (s, 8H, C_6H_4), 6.23 (s, 1H, TTF CH), 6.07 (s, 1H, TTF CH), 5.73 (br, 8H, CH_2N^+), 4.20 (s, 2H, TTF CH_2), 4.15 (s, 2H, TTF CH_2), 3.90–3.30 (m, 16H, OCH_2), 2.98–2.88 (m, 2H, OH); FABMS: $m/z = 1717$ [$M + \text{H}$]⁺, 1571 [$M - \text{PF}_6$]⁺, 1426 [$M - 2\text{PF}_6$]⁺; $\text{C}_{60}\text{H}_{72}\text{F}_{24}\text{N}_4\text{O}_{10}\text{S}_4\text{P}_4$: calcd C 41.97, H 4.23, N 3.26, S 7.47; found C 42.09, H 4.04, N 3.14, S 7.6.

Apparatus and procedures: Absorption spectra were recorded with a Varian Cary 5 UV/Vis/NIR spectrophotometer. All the experiments took place at room temperature. Electrochemical experiments were carried out in argon-purged acetonitrile solution with a Princeton Applied Research 273 multipurpose instrument interfaced to a personal computer; cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques were used. The working electrode was a glassy carbon electrode (0.08 cm², Amel); its surface was polished with a 0.05 mm alumina–water slurry on a felt surface immediately prior to each use. The counterelectrode was a Pt wire and the reference electrode was a saturated calomel electrode (SCE) separated with a fine glass frit. Tetraethylammonium hexafluorophosphate (0.05 M) was added as sup-

porting electrolyte. Cyclic voltammograms were obtained at scan rates of 10, 20, 50, 200, 500, and 1000 mVs^{-1} . DPV experiments were performed with a scan rate of 20 mVs^{-1} , a pulse height of 75 mV, and a duration of 40 ms. For reversible processes, the same halfwave potential values are obtained from the DPV peaks and from an average of the cathodic and anodic cyclic voltammetric peaks. Both CV and DPV techniques were used to measure the number of exchanged electrons in each redox process by applying the necessary corrections for the diffusion coefficients.^[25] To establish the reversibility of a process, we used the criteria of a) separation of 60 mV between cathodic and anodic peaks, b) ratio close to unity of the intensities of the cathodic and anodic currents, and c) constancy of the peak potential on changing sweep rate in the cyclic voltammograms. Spectroelectrochemical measurements were made in a spectrophotometric cell with optical path 1 cm, using a Pt grid as working electrode, a Pt wire separated with a fine glass frit as counterelectrode, and an Ag/AgCl (Amel) reference electrode. Experimental errors: potential values, ± 10 mV; absorption maxima, ± 2 nm; binding constants, 30%.

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