Versatile Self-Complexing Compounds Based on Covalently Linked Donor–Acceptor Cyclophanes

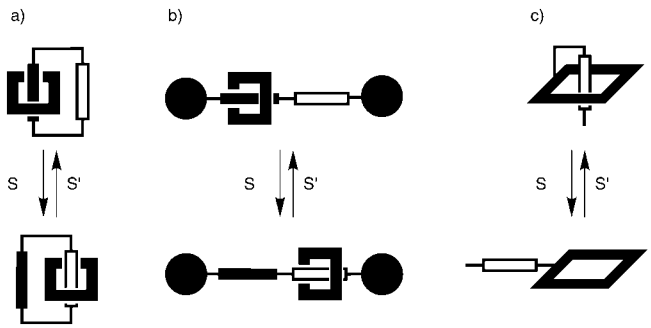
Yi Liu, Amar H. Flood, Ross M. Moskowitz, and J. Fraser Stoddart*[a]

Abstract: A range of covalently linked donor–acceptor compounds which contain 1) a hydroquinone (HQ) unit, 2) a 1,5-dioxynaphthalene (DNP) ring system, or 3) a tetrathiafulvalene (TTF) unit as the π-donor, and 4) cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) as the π-accepting tetracationic cyclophane were prepared and shown to operate as simple molecular machines. The π-donating arms can be included inside the cyclophane in an intramolecular fashion by virtue of stabilizing noncovalent bonding interactions. What amounts to self-complexing/decomplexing equilibria were shown to be highly temperature dependent when the π-donating arm contains either an HQ or DNP moiety. The thermodynamic parameters associated with the equilibria have been unraveled by using variable-temperature ^{1}H NMR spectroscopy. The negative $\Delta H°$ and $\Delta S°$ values account for the fact that the "uncomplexed" conformation becomes the dominant species, since the entropy gain associated with the decomplexation process overcomes the enthalpy loss resulting from the breaking of the donor–acceptor interactions. The arm's in-and-out movements with respect to the linked cyclophanes can be arrested by installing a bulky substituent at the end of the arm. In the case of compounds carrying a DNP ring system in their side arm, two diastereoisomeric, self-complexing conformations are observed below 272 K in hexadeuterioacetone. By contrast, control over the TTF-containing arm's movement is more or less ineffective through the thermally sensitive equilibrium although it can be realized by chemical and electrochemical ways as a result of TTF's excellent redox properties. Such self-complexing compounds could find applications as thermo- and electroswitches. In addition, the thermochromism associated with the arm's movement could lead to some of the compounds finding uses as imaging and sensing materials.

Keywords: donor–acceptor systems · molecular switches · self-complexing · thermochromism · thermodynamics

Introduction

As early as in 1959, Feynman addressed the importance of materials functioning at the molecular level in his lecture entitled "There is Plenty of Room at the Bottom".[1] Since then, the design and synthesis of functional molecules[2] have become one of the most important branches of chemistry. In particular, a molecular machine[3] refers to a molecule that contains multiple movable components, the locations and motions of which can be controlled by external stimuli. An efficient molecular machine requires fast and reversible actions in response to a given stimulus associated with the generation of distinctive signals. Recent examples[4] of such systems (Scheme 1a and b) include bistable switchable [2]catenanes[5,6] and [2]rotaxanes,[7,8] which contain two ring



Scheme 1. Graphical representations of switchable molecular machines, a) a bistable [2]catenane, b) a bistable [2]rotaxane and c) a covalently linked donor–acceptor macrocyle. S and S′ indicate external stimuli.

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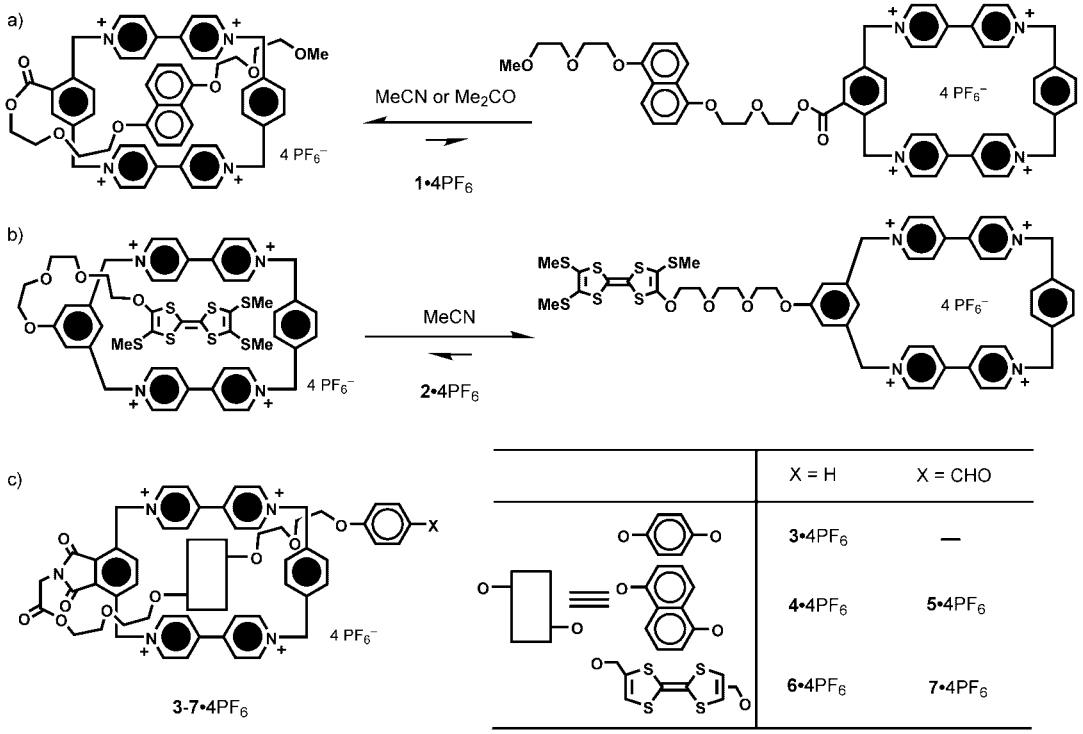
components and one ring and one dumbbell component, respectively, that are interlocked with each other by mechanical bonds. The relative ring-to-ring or ring-to-dumbbell locations are dictated by noncovalent interactions. By switching "off" and "on" these mutual interactions using chemical,[9] electrochemical,[10] or photochemical[11] means, the relative locations of the components can be changed accordingly to generate machinelike molecular motions.

Following an analogous yet different approach, controllable molecular motions can exist in a self-complexing system (Scheme 1c), in which an arm that is covalently linked to a ring component has sufficient flexibility such that the arm can be included inside the ring's cavity by virtue of the preprogrammed, stabilizing, noncovalent bonding interactions. Several self-complexing systems[12–14] have been constructed by the attachment of an arm component to an already preformed ring, for example, a β-cyclodextrin,[12] a crown ether,[13] or a cyclam.[14] Controlling the arm's movement takes advantage in these different systems of 1) hydrophobic interactions,[12] 2) hydrogen bonding,[13a] and 3) ionic[13b,14] interactions.

Self-complexing compounds—such as **1**•4 PF_6 and **2**•4 PF_6 shown in Scheme 2—have also been obtained[15,16] by carrying out macrocyclizations mainly with the aid of donor–acceptor interactions[17] around an aromatic template (usually π-donating) that is covalently linked to one of the ring's precursors. In the case of the cyclophane **1**•4 PF_6, it was found (Scheme 2a) that the self-complexing conformation in which the 1,5-dioxynaphthalene (DNP) ring system resides inside the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$), is strongly favored[15] over the "uncomplexed" conformation in solution. However, in the case of the cyclophane **2**•4 PF_6, the "uncomplexed" conformation in which the substituted tetrathiafulvalene (TTF) unit is present in a dangling arm (Scheme 2b) was observed to be much more favored[16] in a very slow equilibrium process. In the case of both of these examples, temperature is a less than successful handle for controlling the arm's position, thus limiting the usage of these systems as thermoswitches. For the purpose of building more efficient machines that can generate quick and reversible molecular movements, the molecular structures need to be fine-tuned in order to adjust their self-complexing abilities.

In this paper, we demonstrate that the in-and-out movements of the arms can be made highly sensitive to temperature and applied voltages after an all-important structural modification, thus rendering these systems potential thermosensors and electroswitches. In contrast with the benzoyl linkage in **1**•4 PF_6, a π-donor-containing arm is attached[18] by a spacer to a diimide that is fused symmetrically onto the $CBPQT^{4+}$ cyclophane in the molecular structures (Scheme 2c) of compounds **3**–**7**•4 PF_6. The diimide moiety serves to increase the distances between the donors and the acceptors, as well as simplifying the spectroscopic analyses. We describe here 1) the template-directed synthesis of five self-complexing compounds **3**–**7**•4 PF_6, 2) their quick and reversible thermally and electrochemically controllable switching behavior together with 3) a description of switching hysteresis, 4) a novel diastereoisomerism observed in the DNP-containing compounds in addtion to their chromo-

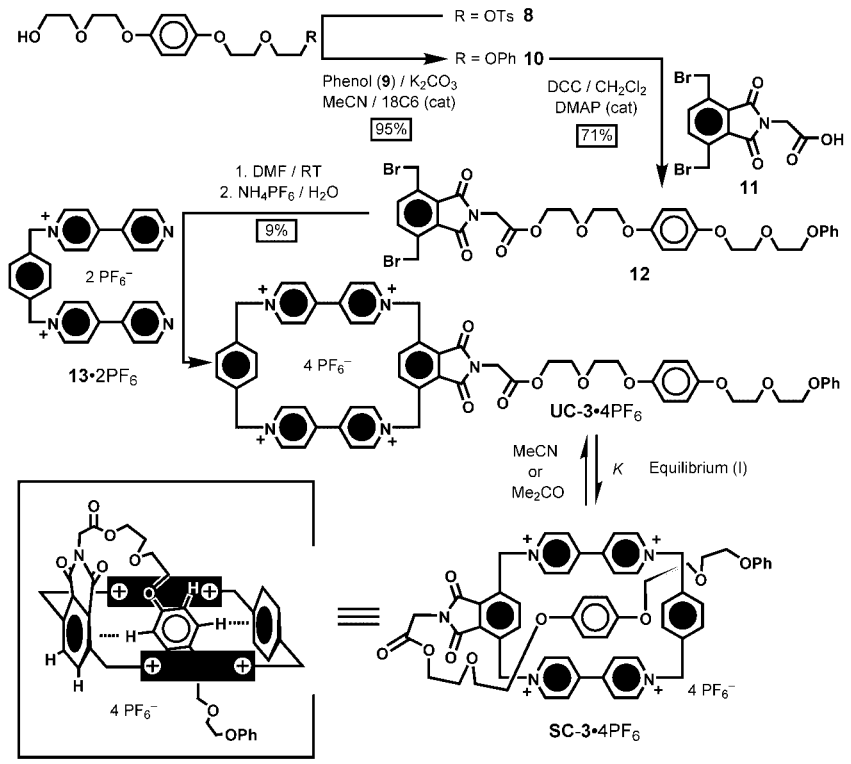


Scheme 2. The complexation/decomplexation equilibria for a) **1**•4 PF_6 and b) **2**•4 PF_6 in solution showing that **1**•4 PF_6 favors a self-complexed conformation, while **2**•4 PF_6 favors an "uncomplexed" one, and c) molecular structures of self-complexing compounds **3**–**7**•4 PF_6.

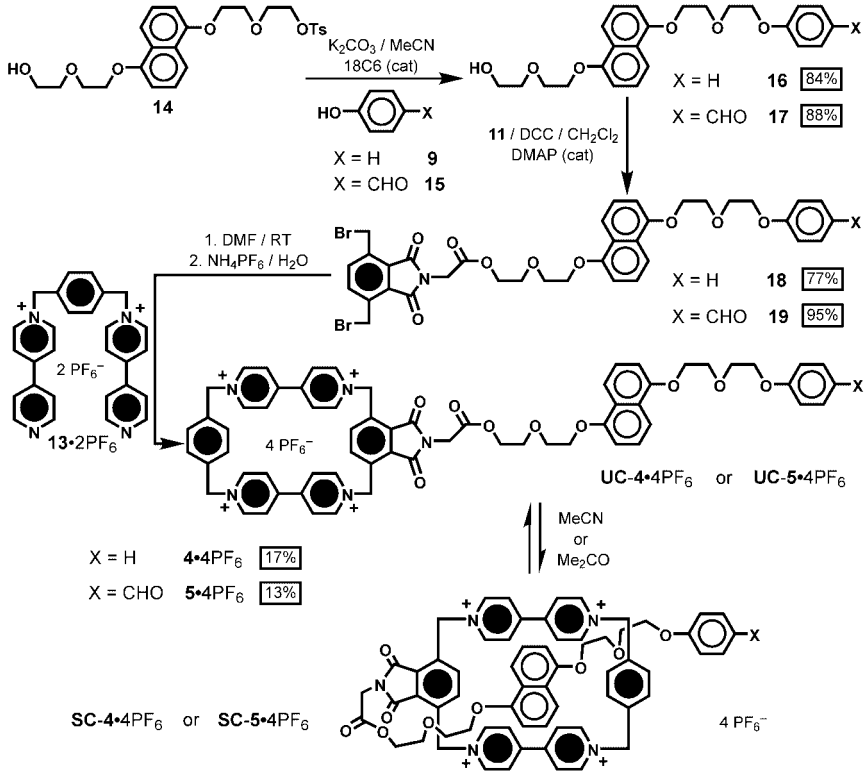
phoric receptor behavior toward TTF, and 5) the fixing of the threading/dethreading motion of the arm in one case by attachment of a bulky stopper to the end of its arm. The potential of the self-complexing molecules to undergo reversible movements of their arm into and out of their ring's cavities in response to a particular stimulus renders them viable candidates for the construction of nanoscale machinery.[19] In addition, interesting properties associated with the thermo-switching behavior could lead to their future applications as imaging and sensing materials.

Results and Discussion

Synthesis: The synthesis of **3**•4 PF_6 is outlined in Scheme 3. The alcohol **10** was obtained by reaction of the tosylate **8**[7b] with phenol (**9**) in the presence of K_2CO_3 in 95% yield. Esterification of **10** with the carboxylic acid derivative **11**[18] with 1,3-dicyclohexyl carbodiimide (DCC) as the coupling agent gave the desired dibromide **12** in 71% yield. The cyclophane **3**•4 PF_6 was isolated in a yield of 9% by reaction of the dibromide **12** with the bis(hexafluorophosphate) salt **13**•2 PF_6,[15] followed by counter-ion exchange and column chromatography, by using a mixture of MeOH/NH_4Cl (2 M)/$MeNO_2$ (7:2:1) as the eluent. The equilibrium between "uncomplexed" (**UC**) and self-complexed (**SC**) conformations in solution are described in Equilibrium (I) (Scheme 3). The equilibrium constant *K* refers to the molar ratio of the **SC** to the **UC** conformation present in the solution. The synthesis of DNP-containing compounds **4**•4 PF_6[18] and **5**•4 PF_6 are outlined in Scheme 4. The alcohols **16** and **17** were obtained by re-

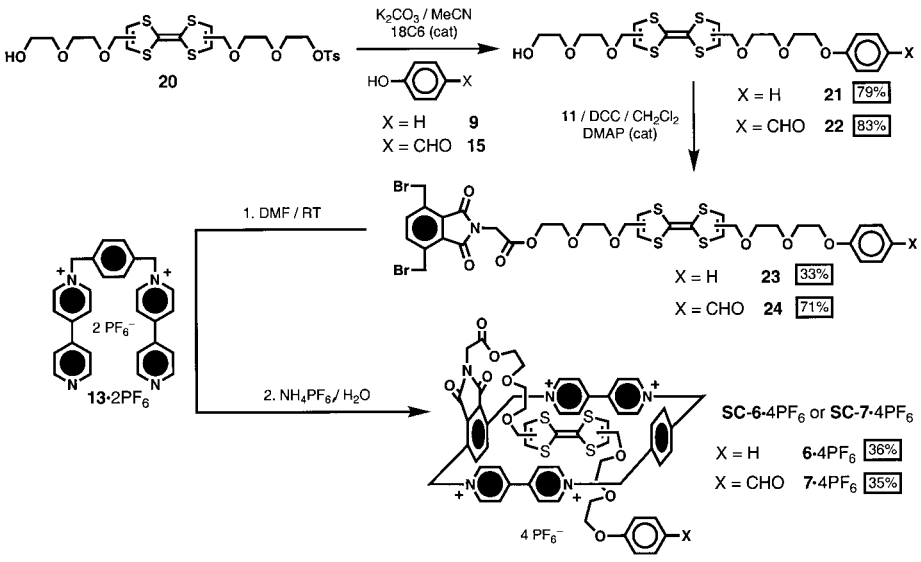


Scheme 3. The synthesis of the HQ-containing compound **3**•4 PF_6 and the equilibrium (I) between the "uncomplexed" and self-complexing conformations **UC-3**•4 PF_6 and **SC-3**•4 PF_6, respectively.



Scheme 4. The synthesis of DNP-containing compounds **4**•4 PF_6 and **5**•4 PF_6.

action of the tosylate **14** with phenol (**9**) or 4-hydroxybenzylaldehyde (**15**) in the presence of K_2CO_3. Esterification of **16** or **17** with the carboxylic acid derivative **11**, with DCC as the coupling agent, gave the desired dibromide, either **18** or **19**. The cyclophanes **4**·4 PF_6 and **5**·4 PF_6 were isolated after reaction of either the dibromide **18** or **19** with the bis(hexafluorophosphate) salt **13**·2 PF_6, followed by counterion exchange and column chromatography, by using a mixture of MeOH/NH_4Cl (2 M)/$MeNO_2$ (7:2:1) as the eluent. Following a similar synthetic protocol (Scheme 5), the TTF-containing



Scheme 5. The synthesis of TTF-containing compounds **6**·4 PF_6 and **7**·4 PF_6.

self-complexing compounds **6**·4 PF_6[18] and **7**·4 PF_6 were obtained. The alcohols **21** and **22** were obtained separately by the reactions of the tosylate **20**[20] with either phenol (**9**) or 4-hydroxybenzylaldehyde (**15**) in the presence of K_2CO_3. Esterification of **21** or with the carboxylic acid derivative **11**, with DCC as the coupling agent, gave the desired dibromide, either **23** or **24**. The cyclophanes **6**·4 PF_6 and **7**·4 PF_6 were isolated after the reactions of either the dibromide **23** or **24** with the dicationic salt **13**·2 PF_6, followed by counterion exchange and column chromatography, by using a mixture of MeOH/NH_4Cl (2 M)/$MeNO_2$ (7:2:1) as the eluent.

Establishing the intramolecular self-complexing behavior: The intramolecular self-complexing behavior of **3**–**7**·4 PF_6 was measured by titration experiments by employing ^{1}H NMR and UV-visible spectroscopic methods. For example, the absorption spectrum of **4**·4 PF_6, recorded in MeCN at 25 °C, shows a broad charge-transfer (CT) band in the visible region (λ_{max} = 521 nm, ε_{max} = 900 $M^{-1}cm^{-1}$), which is characteristic of the donor–acceptor interactions between its two bipyridium units and the complementary π-electron-rich DNP ring system.[15] Linear correlations between absorption A and the concentration c_0 over the range 3.6×10^{-3}–2.8×10^{-5} M is observed, suggesting the presence of a unimolecular equilibrium and the absence of any high order equilibria. Moreover, since the ^{1}H NMR spectra of **4**·4 PF_6 recorded at 243 K in CD_3COCD_3 show only marginal concentration dependences in a range 3.11×10^{-2}–0.97×10^{-3} M, it seems unlikely that supramolecular oligomers or polymers are being formed to any significant extent. Similarly, the absorption UV-visible spectra of **6**·4 PF_6, recorded in MeCN at 25 °C, show a strong CT band in the visible region (λ_{max} = 859 nm, ε_{max} = 3342 $M^{-1}cm^{-1}$), which is characteristic for the donor–acceptor interactions between its two bipyridium units and its TTF unit.[9f] A linear correlation between absorption A and concentration c_0 over the range of 1.91×10^{-4} to 5.35×10^{-5} M is also observed, suggesting the absence of high order equilibria. The same conclusions were reached for the other tetracationic cyclophanes **3**·4 PF_6, **5**·4 PF_6, and **7**·4 PF_6.

^{1}H NMR spectroscopy of the HQ- and DNP-containing cyclophanes: Both **SC** and **UC** conformations were observed in CD_3COCD_3 by ^{1}H NMR spectroscopy in the case of **3**·4 PF_6, **4**·4 PF_6, and **5**·4 PF_6. Resonances associated with either the **UC** or **SC** conformation can be differentiated as a result of the following two properties: 1) the complexing/decomplexing equilibria in CD_3COCD_3 are slow on the ^{1}H NMR timescale within a certain temperature range, and 2) the molecular structures of the **SC** conformations possess C_s symmetry, while the **UC** conformations have averaged C_{2v} symmetry on the ^{1}H NMR timescale, as a result of the fast rotation of the bipyridium and xylene units. Consequently, equilibrium constants (K) for the self-complexing equilibria at different temperatures can be obtained by measuring the ratio of these coexisting conformations from ^{1}H NMR integration.

In the ^{1}H NMR spectrum of **3**·4 PF_6 (CD_3COCD_3, 196 K), four resonances were observed (Figure 1) for both the α- and the β-bipyridinium protons, indicating a structure for **SC**-**3**·4 PF_6 with C_s symmetry. The two doublets at very high field (δ = 1.99 and 2.45 ppm), together with two doublets at δ = 5.62 and 5.70 ppm, correspond to the four HQ ring protons, indicating that this ring is located inside the cavity of the cyclophane.[21] Additionally, no resonances were evident for protons from the "uncomplexed" HQ ring. As the temperature was increased in the range between 196 and 260 K,[22] resonances for the **UC**-**3**·4 PF_6 conformation in-

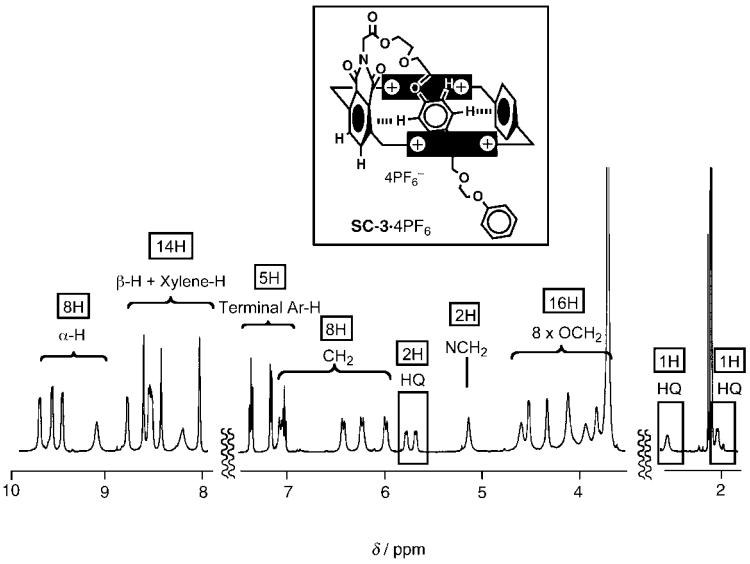


Figure 1. The ^{1}H NMR spectrum of **SC-3**·4PF_6 recorded in CD_3COCD_3 at 196 K corresponding to a self-complexing conformation.

creased in intensity. Equilibrium constants, as well as the derived free energies ($\Delta G°$) at different temperatures were obtained (Table 1). Thermodynamic parameters, such as $\Delta H°$ and $\Delta S°$ values, were deduced by plotting ln$K$ against $1/T$. The van't Hoff plot[23] of Equilibrium (I) (Figure 2) gives $\Delta H°$ and $\Delta S°$ values of -6.95 kcal mol^{-1} and -26.3 cal mol^{-1} K^{-1}, respectively.

Table 1. Thermodynamic data[a] for Equilibrium (I) of **3**·4PF_6 in MeCN at different temperatures.

T [K][b]	K	$\Delta G°$ [kcal mol^{-1}]
207	35.7	-3.6
218	16.8	−2.8
228	9.1	−2.2
237	4.8	−1.6
249	2.1	−0.74
260	1.2	−0.18

[a] Determined by ^{1}H NMR spectroscopy. [b] Calibrated by using a neat MeOH sample.

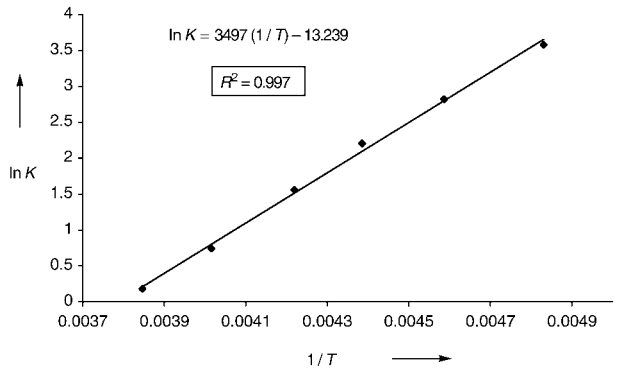
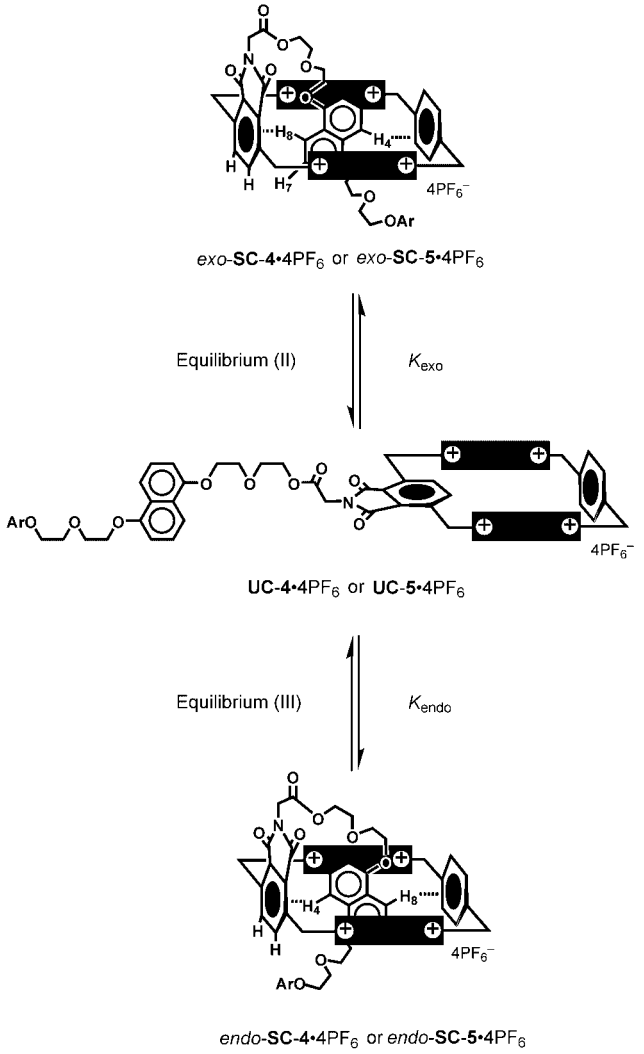


Figure 2. The van't Hoff plot for the equilibrium between the **UC** and **SC** conformations of **3**·4PF_6. The following equation for the equilibrium was obtained: $(\ln K/T) = (-6.95 \text{ kcal mol}^{-1})(1/RT) + (-26.3 \text{ cal mol}^{-1} \text{ K}^{-1})/R$.

Changing the π-electron donor from an HQ ring to a DNP ring system introduces more complexity into ^{1}H NMR spectra, because of the DNP's additional element of planar chirality,[24] a property which gives rise to two self-complexing conformations for each of the DNP-containing cyclophanes **4**·4PF_6 and **5**·4PF_6. One of the two possible self-complexing conformations, in which H-4 on the DNP ring is pointing away from diimidophenylene ring and towards the xylene ring of the tetracationic cyclophane, is denoted as *exo*-**SC** (Scheme 6). The other conformation, in which H-4 on the DNP ring system is pointing towards the diimidophenylene ring of the tetrcationic cyclophane, is denoted as *endo*-**SC**. Both of the **SC** conformations are in equilibrium with a **UC** conformation. The equilibria demonstrated by both **4**·4PF_6 and **5**·4PF_6 in CD_3COCD_3 solutions were char-



Scheme 6. The equilibria between the **UC**-conformation and the *exo*-**SC** conformation and the *endo*-**SC** conformation for the DNP-containing compounds **4**·4PF_6 and **5**·4PF_6. The descriptor *exo* refers to the **SC** conformation in which H-4 on the DNP ring is pointing away from diimidophenylene ring and towards the xylene ring, while the descriptor *endo* refers to the **SC** conformation in which H-4 on the DNP ring is pointing towards the diimidophenylene ring.

acterized by variable-temperature ^{1}H NMR spectroscopy. Although the resonances (Figure 3) from the three conformations overlap each other partially, three species are clearly discernable. In particular, the location of the α-H resonances of the bipyridinium units at low field, and the resonances for H-4 and H-8 on the DNP ring system at high field, are evident for all three conformations. The **UC** conformation of **5**•4PF$_6$, as indicated (Figure 3a) by the two doublets (full circles), was the major one in CD_3COCD_3 solution at 272 K. As the temperature was lowered, however, the equilibria become displaced towards the formation of the **SC** conformations, which are indicated (Figure 3b–e) by the emergence of two sets (empty circles and full squares) of four doublets in the region of $\delta =$ 8.7–9.6 ppm. Formation of the **SC** conformations were also evidenced by the appearance of two sets of doublets with unequal intensities, resonating at very high field between $\delta = 2.5$ and 3.0 ppm and corresponding to the shielded H-4 and H-8 protons on the DNP ring system in the two **SC** conformations.[25]

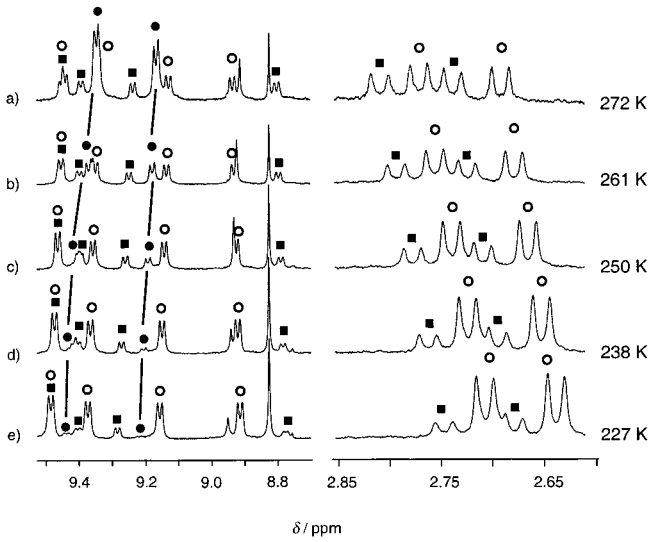


Figure 3. Partial ^{1}H NMR spectra of **5**•4PF$_6$ recorded in CD_3COCD_3 at different temperatures, showing the α-bipyridinium proton region ($\delta =$ 8.7–9.5 ppm) and H-4 and H-8 of DNP ring system ($\delta = 2.6$–2.8 ppm) of the *exo*-**SC** (○), *endo*-**SC** (■) and the **UC**-conformations (●).

On the basis of a 2D TROESY spectrum of **5**•4PF$_6$ recorded at 227 K (Figure 4), the *exo*-**SC** conformation can be assigned as the major self-complexing isomer present in the solution. The ratio of the *exo*-**SC** to the *endo*-**SC** conformation is 3.7:1. A triplet, centered on $\delta = 6.47$ ppm, correlates to a doublet (H-8 of the DNP ring) at $\delta = 2.64$ ppm and thus can be assigned to H-7 of the DNP ring. This triplet, in turn, exhibits through-space correlation to the singlet for the diimidophenylene protons (H-a) at $\delta = 8.82$ ppm (Figure 4). This through-space correlation is the key to the assignment, because it is only in the *exo*-**SC** conformation that such a correlation between DNP protons and diimidophenylene protons could be present. By contrast, in the *endo*-**SC** conformation, no such correlation should be observed, since the DNP and diimidophenylene protons are far apart, as illustrated in Figure 4. Thus, the major isomer is *exo*-**SC**-**5**•4PF$_6$ and the minor one is *endo*-**SC**-**5**•4PF$_6$.

Equilibrium constants [K_{exo} for Equilibrium (II) and K_{endo} for Equilibrium (III); Scheme 6] and the derived free energies $\Delta G°$ (Table 2) for self-complexing in **5**•4PF$_6$ were measured at different temperatures. The van't Hoff plots (Figure 5) give $\Delta H°$ and $\Delta S°$ values of −11.2, −7.45 kcal mol^{-1} and −44.1, −29.6 cal mol^{-1} K^{-1} for the Equilibria (II) and (III), respectively. A similar treatment was applied to **4**•4PF$_6$, from which equilibrium constants [K_{exo} for Equilibrium (II) and K_{endo} for Equilibrium (III)] and derived free energies $\Delta G°$ (Table 2) for its self-complexation at different temperatures were obtained. The van't Hoff plots (Figure 6) give $\Delta H°$ and $\Delta S°$ values as −9.67, −6.72 kcal mol^{-1} and

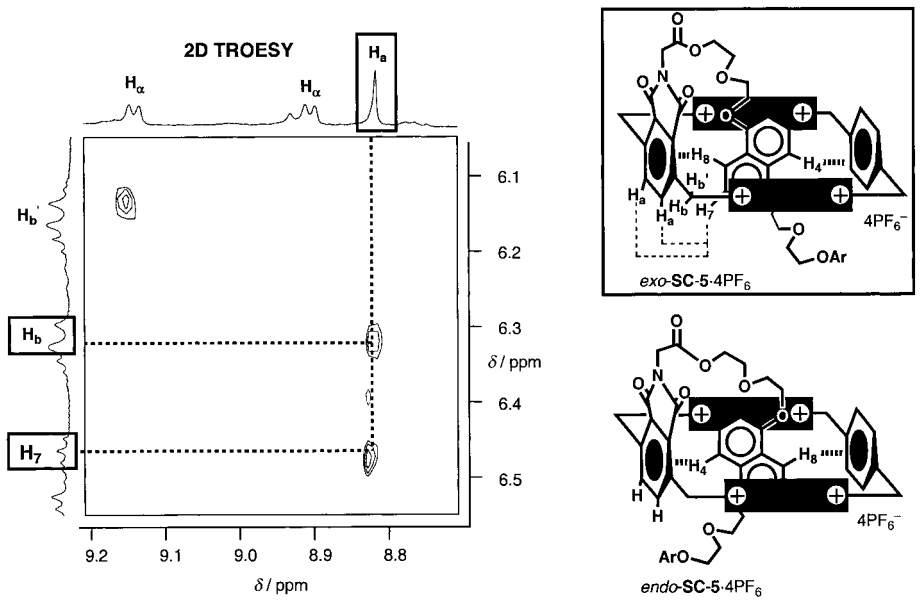


Figure 4. The partial 2D TROESY spectrum of **5**•4PF$_6$ recorded in CD_3COCD_3 at 227 K. The correlation between the DNP proton (H-7) and the diimidophenylene protons (H-a) in the major conformational isomer *exo*-**SC**-**5**•4PF$_6$ is highlighted (Box). The diastereotopic CH_2 protons (H-b and H-b′) can also be assigned as a result of a correlation of H-b (at $\delta = 6.32$ ppm) with H-a.

Table 2. Thermodynamic data[a] for Equilibria (II) and (III) of both **4**·4PF_6 and **5**·4PF_6 in MeCN at different temperatures.

	T [K][b]	K_{exo}	K_{endo}	ΔG^{o}_{exo} [kcal mol^{-1}]	ΔG^{o}_{endo} [kcal mol^{-1}]
4·4PF_6	227	18.2	3.8	−1.3	−0.60
	238	7.0	2.0	−0.92	−0.33
	250	2.5	1.0	−0.46	0.00
	261	1.1	0.59	−0.031	0.28
	272	0.55	0.31	0.32	0.63
5·4PF_6	227	18.2	4.9	−1.3	−0.72
	237	7.7	2.5	−0.96	−0.44
	248	2.9	1.3	−0.53	−0.14
	259	0.95	0.65	0.026	0.22
	271	0.33	0.34	0.60	0.58

[a] Determined by ^{1}H NMR spectroscopy. [b] Calibrated by using a neat MeOH sample.

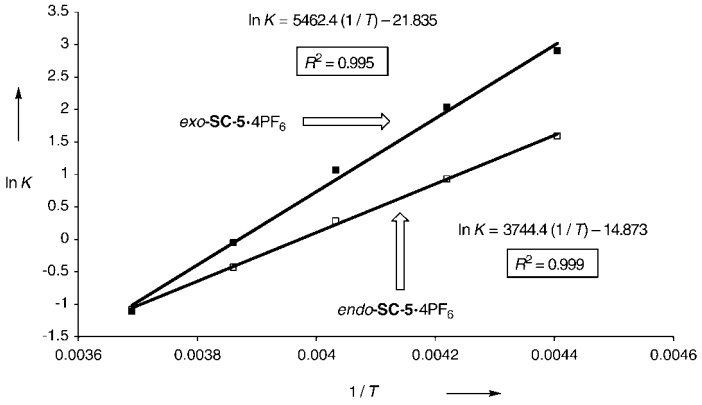


Figure 5. The van't Hoff plots for the equilibria between the **UC** conformation and the *exo*-**SC** or the *endo*-**SC** conformations of **5**·4PF_6. The following equations for the two equilibria were obtained: $(\ln K/T) = (-11.2\ \text{kcal mol}^{-1})(1/RT) + (-44.1\ \text{cal mol}^{-1}\ \text{K}^{-1})/R$ and $(\ln K/T) = (-7.45\ \text{kcal mol}^{-1})(1/RT) + (-29.6\ \text{cal mol}^{-1}\ \text{K}^{-1})/R$.

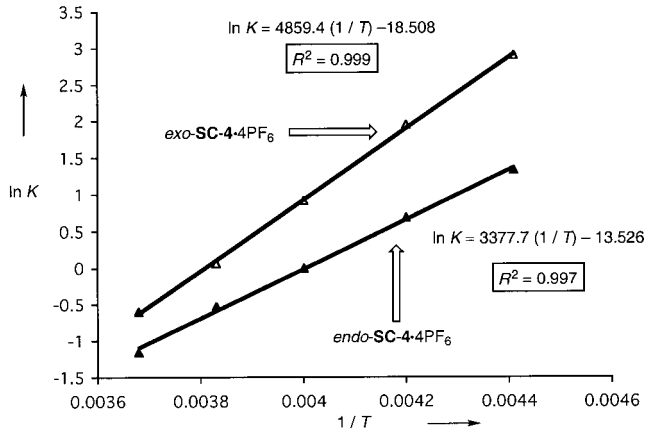


Figure 6. The van't Hoff plots for the equilibria between the **UC** conformation and the *exo*-**SC** or the *endo*-**SC** conformations of **4**·4PF_6. The following equations for the two equilibria were obtained: $(\ln K/T) = (-9.67\ \text{kcal mol}^{-1})(1/RT) + (-36.8\ \text{cal mol}^{-1}\ \text{K}^{-1})/R$ and $(\ln K/T) = (-6.72\ \text{kcal mol}^{-1})(1/RT) + (-26.9\ \text{cal mol}^{-1}\ \text{K}^{-1})/R$.

−36.8, −26.9 cal mol^{-1} K^{-1} for Equilibria (II) and (III), respectively.

The negative $\Delta H°$ values associated with Equilibria (I)–(III) indicate that the formation of **SC** conformations is an enthalpically favored process as a result of favorable donor–acceptor interactions, while the negative $\Delta S°$ values suggest that **SC** conformations have more constrained structures and are less flexible than the **UC** conformations. As temperature increases, the entropy gain associated with the decomplexation processes overcomes the enthalpy loss from diminishing donor–acceptor stabilization, pointing the equilibrium towards the formation of **UC** conformations.

Thermochromism: One interesting property associated with the temperature-dependent complexing/decomplexing behavior is thermochromism. Since the **UC** conformations are colorless, while the **SC** conformations are colored, a thermoreversible color change can be displayed by the heat-induced conformational changes. Typically, variable-temperature UV-visible absorption spectroscopic studies of a solution of **4**·4PF_6 in MeCN (Figure 7) reveal that, as the solution is heated from 0 to 50 °C, the intensity of the CT band around 520 nm decreases accordingly, correlating with the decomplexation of the **SC**-**4**·4PF_6. The temperature-dependent color change is completely reversible and can be recycled many times. This thermochromic behavior occurs as a result of thermally induced molecular motions. By contrast, the TTF-bearing **6**·4PF_6 and **7**·4PF_6 compounds display very small temperature-dependent spectroscopic changes in the temperature range +10 to +50 °C, with an intense green color persisting throughout. The stronger donor–acceptor interactions[9f] between TTF and $CBPQT^{4+}$ is believed to be responsible for the weaker temperature dependence shown by **6**·4PF_6 and **7**·4PF_6.

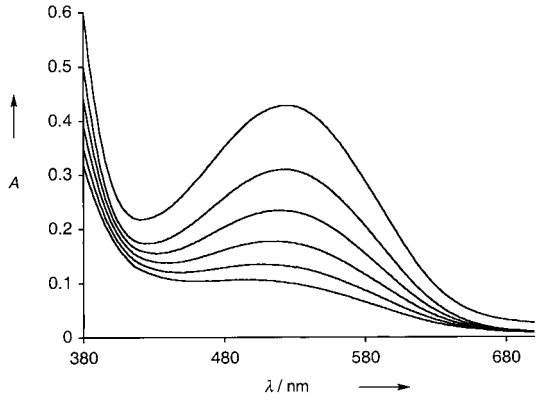


Figure 7. UV-visible spectra of **4**·4PF_6 recorded in MeCN in the temperature range 0–50 °C, showing the intensity decrease of the charge-transfer band at around 520 nm.

^{1}H NMR spectroscopy of the TTF-containing cyclophanes: No **UC** conformation is observed in the ^{1}H NMR spectra of the TTF-containing compounds **6**·4PF_6 and **7**·4PF_6, an observation that is presumably the result of the strong donor–acceptor interactions between the TTF unit and the $CBPQT^{4+}$ cyclophane. In addition, each compound exists as

a mixture of *cis*/*trans*-TTF isomers. These isomers can interconvert between each other under different conditions (vide infra).

The ^{1}H NMR spectra of both **6**·4PF$_6$ and **7**·4PF$_6$ recorded in CD_3COCD_3 show that two species with C_s symmetry are present such that the ratio varies when they experience different conditions, for example, acid,[26] electricity,[27] and light.[28] The interconversion suggests that the two species are indeed the *cis*/*trans*-TTF isomers that can interconvert between each other when conditions favorable to *cis*/*trans* isomerization are established. The ^{1}H NMR spectrum (CD_3COCD_3, 253 K) of **6**·4PF$_6$, recorded immediately after workup, shows that the *cis*/*trans* isomers are present in the ratio of about 2:3. However, when a solid mixture is stored in the dark for two months only one of the isomers is favored (Figure 8a)—probably the *trans* one.[29] Four doublets

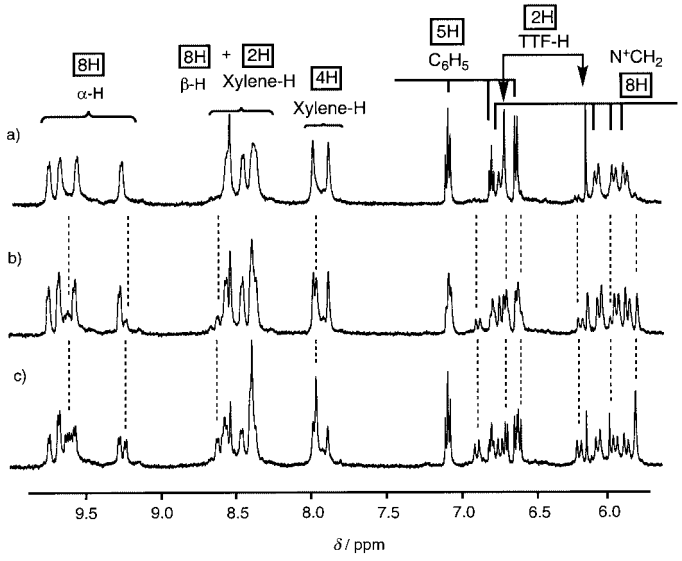
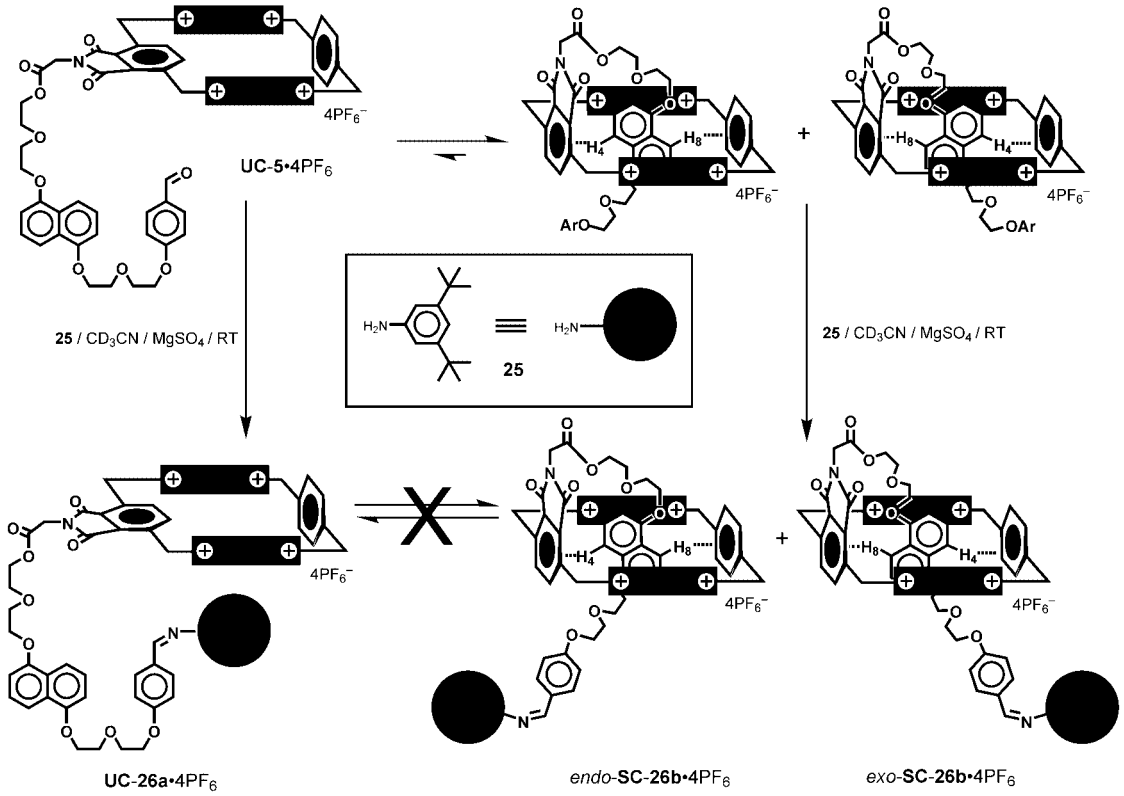


Figure 8. Partial ^{1}H NMR spectra for the self-complexing cyclophane **6**·4PF$_6$ recorded in CD_3COCD_3 after irradiation with visible light (500 W) for a) 0 min, b) 20 min, and c) 50 min, indicating the formation of presumably the *cis*-TTF-containing isomer from the *trans* one.

resonating between $\delta = 10.0$ and 9.0 ppm, together with four doublets resonating between $\delta = 7.0$ and 6.0 ppm, can be assigned to the eight α-protons of the bipyridinium units and the eight methylene protons of the cyclophane, respectively. The occurrence of four sets of signals is consistent with the location of the TTF unit residing inside the cavity of the cyclophane. In addition, the two protons of the disubstituted TTF units experience different shielding effects and are well separated. When a solution of the all-*trans* self-complex, obtained after dark storage, in CD_3COCD_3 is irradiated with broad-band visible light (500 W) at room temperature, the *trans*-to-*cis* isomerization is triggered, as evidenced by the emergence of signals associated with the *cis* self-complex of **6**·4PF$_6$ (Figure 8b and 8c). An equilibrium (photostationary state) is reached after 50 min when the *cis*/*trans* ratio is approximately 2:3. By comparison, such an isomerization is almost imperceptible under ambient light conditions. The *trans*-to-*cis* isomerization can also be triggered by the addition of acid. When a trace amount of trifluoroacetic acid (TFA) is added into a solution of *trans*-**6**·4PF$_6$ in Me_2CO, the same equilibrium state (*cis*/*trans* = 2:3) is attained after two weeks. The all-*cis* self-complex could not be prepared.

Chromophoric receptor behavior of self-complexing cyclophanes toward TTF: The self-complexing cyclophanes **3**·4PF$_6$, **4**·4PF$_6$, and **5**·4PF$_6$ also behave as chromophoric probes for the receptor binding of TTF. For instance, addition of one molar equivalent of TTF to the solution of **5**·4PF$_6$ in MeCN results in a dramatic color change of the solution from purple to green, consistent with the inclusion of TTF inside its cavity with the concomitant exclusion of the DNP ring system. The color change reflects a shift in the absorbance maximum, corresponding to the CT band[30] associated with donor–acceptor interactions, from $\lambda_{max} =$ 521 nm (when the DNP ring system is the donor) to $\lambda_{max} =$ 850 nm (when the TTF unit is the donor). The ^{1}H NMR spectrum of this complex, recorded in CD_3CN, displays signals at $\delta = 6.84$ (1H), 7.11 (1H), 7.34 (2H), and 7.79 ppm (2H) for the unbound DNP ring protons, indicating that the DNP ring system is indeed expelled from the cavity. By contrast, the TTF ring protons resonate in the spectrum as a singlet at $\delta = 5.69$ ppm, reflecting the fact that they are shielded within the cavity of the tetracationic cyclophane.[30] A UV-visible dilution method was employed to determine the binding constant (K_a) between TTF and **5**·4PF$_6$ in MeCN, and a K_a value of 3250 M^{-1} was obtained. Such a chemosensitive color change, based on a supramolecular switching action, is characterized by its efficiency and simplicity.

Stoppering the arm movement of a DNP-containing cyclophane: The in-and-out movement of the arm with respect to the linked cyclophane can be arrested by installing a bulky substituent at the end of the arm (Scheme 7). 3,5-Di-*tert*-butylaniline (**25**) was chosen for 1) its bulk and 2) its reactivity towards the formyl group in **5**·4PF$_6$. Both the **SC** conformations and the **UC** conformation of **5**·4PF$_6$ should react with **25** to generate stoppered version of all three conformations. While the self-complexing equilibrium of **5**·4PF$_6$ is temperature sensitive, such behavior is expected to be prohibited after the condensation reaction, since the bulky stopper will prevent the arm from passing through the linked cyclophane. A mixture of **25**, **5**·4PF$_6$, and $MgSO_4$ in CD_3CN were kept in an NMR tube at room temperature and the condensation reaction was monitored by ^{1}H NMR spectroscopy. The completion of the reaction was verified by the disappearance of the resonance at $\delta = 9.95$ ppm, corresponding to the aldehyde proton in **5**·4PF$_6$. The electrospray ionization mass spectrometry (ESI-MS) of the reaction mixture showed a singly charged peak at *m/z* value 1691.6 ($[M-PF_6]^+$), together with doubly and triply charged peaks at *m/z* values 773.3 ($[M-2PF_6]^{2+}$) and 467.2 ($[M-3PF_6]^{3+}$), an observation which corresponds to the consecutive loss of one, two, and three hexafluorophosphate ions (mol. wt. =



Scheme 7. The "in" and "out" motion of the DNP-containing arm of **5**•4 PF_6 is prevented when it is treated with a sterically hindered amine **25**, which undergoes a condensation reaction with **5**•4 PF_6 to give **26**•4 PF_6.

145 Da each) from the mixture of products which we will refer to as **26**•4 PF_6.

The ^{1}H NMR spectrum of a solution recorded at 298 K indicates (Figure 9a) the presence of a major species corresponding to **UC-26a**•4 PF_6, together with small amount of another species, which is presumably a mixture of *exo*-**SC-26b**•4 PF_6 and *endo*-**SC-26b**•4 PF_6. All these forms of **26**•4 PF_6 are the stoppered versions of the three different conformations of **5**•4 PF_6. By comparison, the spectrum of **5**•4 PF_6, taken under the same condition (Figure 9b) is similar except that 1) it is broader and 2) the signals of **SC** conformations are barely evident, suggesting that the complexation/decomplexation equilibrium is fast on the ^{1}H NMR timescale at this temperature. As the temperature is lowered to 233 K, **UC-26a**•4 PF_6 remains the major species in solution (Figure 9c), while the resonances for **SC-26b**•4 PF_6 become sharper. By contrast, lowering the temperature of a solution of **5**•4 PF_6 to

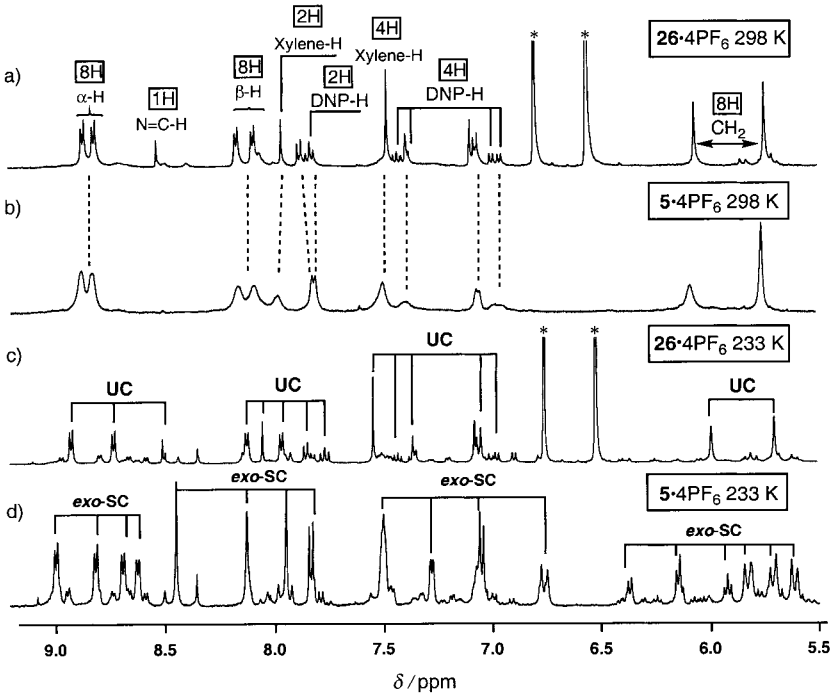


Figure 9. Partial ^{1}H NMR spectra of a) **26**•4 PF_6 at 298 K, b) **5**•4 PF_6 at 298 K, c) **26**•4 PF_6 at 233 K, and d) **5**•4 PF_6 at 233 K. The peaks with asterisks in a) and c) represent an excess of 3,5-di-*tert*-butylanaline (**25**).

233 K displaces the equilibria towards the formation of **SC** conformations (Figure 9d). Concurrently, there is no visual color change when the solution of **26**·4PF_6 is cooled down from room temperature to −40 °C, in sharp contrast to the behavior of unstoppered **5**·4PF_6. All these observations suggest that, by attaching a bulky stopper to the end of the self-complexing system, the threading action of the side-arm is passivated to generate an approximate "snapshot" of the fixed equilibrium state. This stoppering strategy provides a delicate way of controlling molecular motions through dynamic covalent-bond formation.[31]

Chemical switching behavior of a TTF-containing cyclophane: Although temperature is more or less ineffective in controlling the movement of the TTF arm in **SC**-6^{4+} and **SC**-7^{4+}, both chemical and electrochemical methods work well. The reason is that the molecular recognition between a TTF donor and a $CBPQT^{4+}$ acceptor can be turned "off" by the oxidation of the TTF unit to a charged species—either $TTF^{\bullet+}$ or TTF^{2+}—and "on" by their reduction back to the neutral form. The chemical redox cycle of **6**·4PF_6 has been monitored by ^{1}H NMR spectroscopy at 253 K in CD_3COCD_3 (Figure 10). Prior to its oxidation, the TTF unit in **SC**-**6**·4PF_6 is observed to be a 2:3 mixture ($\delta = 6.0$–7.0 ppm) of *cis/trans*-isomers (Figure 10a). Upon addition of two equivalents of the chemical oxidant, tris(*p*-bromophenyl)aminium hexachloroantimonate,[9f] into the solution of **6**·4PF_6 in CD_3COCD_3, a much simpler spectrum (Figure 10b) is observed, indicating that, upon oxidation, the TTF^{2+} dication no longer resides inside the $CBPQT^{4+}$ cavity: its protons resonate at $\delta = 9.83$ ppm. The remainder of the spectrum of the hexacationic species is commensurate with the **UC**-6^{6+} conformation with averaged C_{2v} symmetry. When Zn dust is added to the NMR tube, the original spectrum (Figure 10c) is regenerated, indicating a return to the **SC**-6^{4+} conformation with the neutral TTF unit back inside the cavity of the $CBPQT^{4+}$ cyclophane.

Electrochemical switching behavior of a TTF-containing cyclophane: The cyclic voltammograms (CVs) of the self-complexing macrocycle **6**·4PF_6, and of the dumbbell analogue **21**, were recorded in order to reveal its electrochemical switching behavior. In addition, the dynamic processes responsible for the oxidatively initiated switching between the self-complexing and uncomplexed forms were investigated. The decomplexation/complexation and oxidative electrochemical processes can be considered with reference to a reaction scheme involving five species (Scheme 8). In the starting state, an excess of **SC**-6^{4+} exists relative to **UC**-6^{4+}, with the relative amounts of each controlled by a dynamic equilibrium process, reaction A (K_a). The singly oxidized $TTF^{\bullet+}$ states of the two forms of **6**·4PF_6 can be generated by applying positive potentials. Oxidation of the **SC** conformation by reaction B results in the generation of a single positive charge on the TTF unit residing within the tetracationic cyclophane and consequently its oxidation potential, E'(**SC**-**6**)$^{5+/4+}$ is expected to lie at more positive potentials than that for the

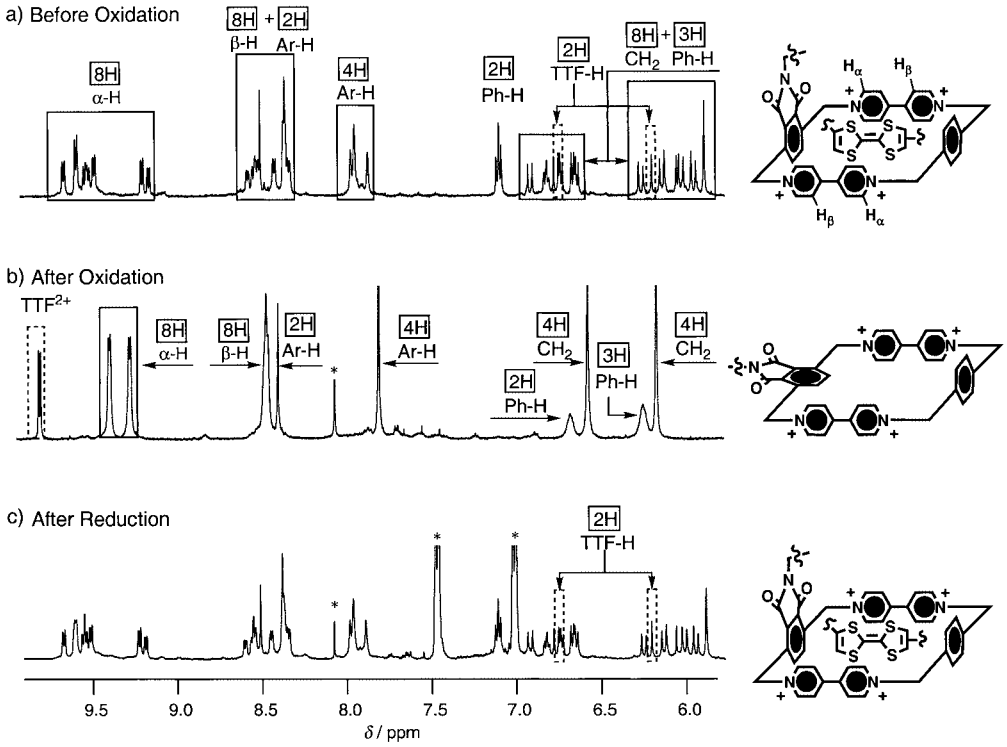
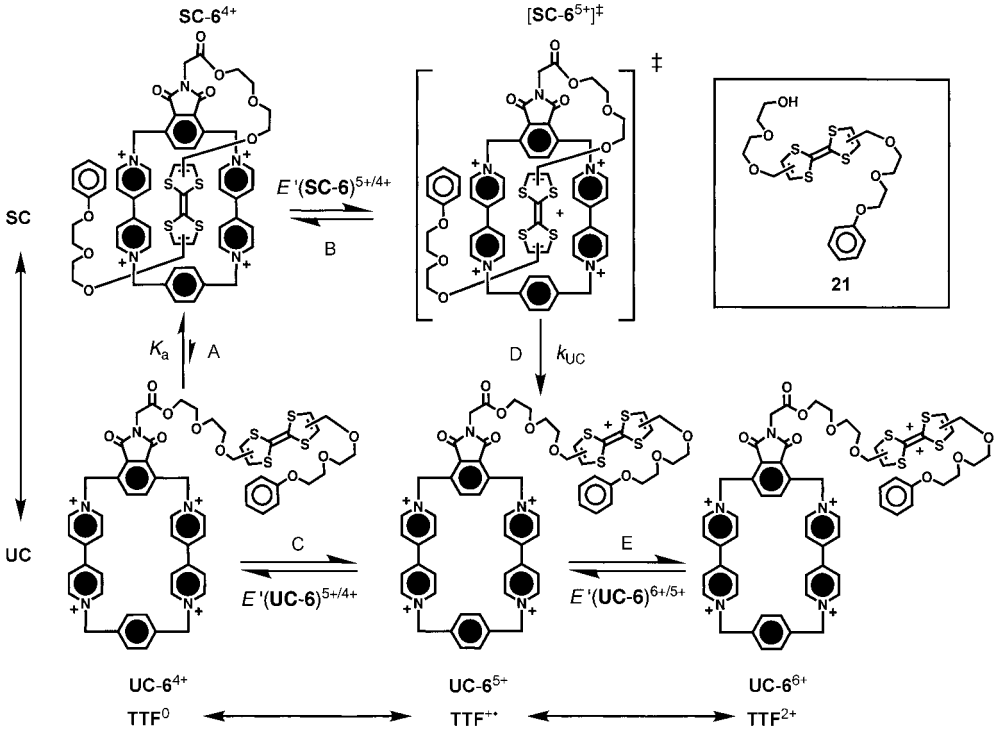


Figure 10. Partial ^{1}H NMR spectra of **6**·4PF_6 recorded in CD_3COCD_3 at 253 K a) before oxidation, b) after addition of two eqeuivalents of tris(*p*-bromophenyl)aminium hexachloroantimonate, and c) after addition of Zn dust as a reductant. The resonances indicated by the asterisk arise from the oxidant.



Scheme 8. Parametric reaction scheme illustrating how **6**·4PF$_6$ interconverts between **SC** and **UC** conformations (parameter 1) as a function of the TTF oxidation state (parameter 2). Process A is a reversible thermodynamic equilibrium; processes B, C, and E are reversible electrochemical equilibria; and D is an irreversible reaction.

dumbbell **21**. The monocationic state, initially in the **SC** conformation, is electrostatically unfavored—equivalent to a transition state (‡)—and so, rapidly decomplexes by reaction D (k_{UC}) to the thermodynamically favored **UC** conformation. The small amount of **UC**-**6**·4PF$_6$, which will also be present in the starting state on account of equilibrium A, resembles the free dumbbell and has a formal reduction potential, associated with reaction C (E'(**UC**-**6**)$^{5+/4+}$), which is predicted to lie at a similar potential as that for the dumbbell **21**. The **UC** conformation is the only stable form of the monocation. It displays one further single-electron oxidation process, reaction E (E'(**UC**-**6**)$^{6+/5+}$), which is predicted to lie at the same potential as that for the dumbbell. The **SC** conformation of the dication TTF^{2+} (not shown in Scheme 8) is predicted to be highly unfavored and thus, is not considered an important species when considering the switching behavior of **6**·4PF$_6$.

The CV of **6**·4PF$_6$ reveals a typical profile[5b] for a complexed TTF unit and is assigned to two reversible TTF-based oxidations concomitant with molecular motion and a scan-rate-dependent behavior. At the faster scan rate of 1000 mV s^{-1}, the CV displays only one two-electron oxidation peak at +0.91 V versus SCE, together with two single-electron reduction peaks on the return sweep (Figure 11a). At 10 mV s^{-1}, two separate one-electron oxidation processes are observed at +0.53 and +0.73 V versus SCE with their corresponding reduction processes along the return sweep (Figure 11b). This scan-rate-dependent observation differs from that of the dumbbell, which displays two reversible and well-separated, one-electron oxidation processes, $E_{1/2}$(**21**)$^{+/0}$ = +0.36 and $E_{1/2}$(**21**)$^{2+/+}$ = +0.70 V versus SCE, both of which are independent of the scan rate. Furthermore, CV resolution of the *cis* and *trans* isomer forms in the 2:3 mixture was not observed by comparison with the CVs of the all-*trans*-**SC**-**6**·4PF$_6$ compound.

The scan-rate dependence of the CV can be rationalized from Scheme 8. At 10 mV s^{-1} the starting state will contain both **UC** and **SC** conformations. The initially small concen-

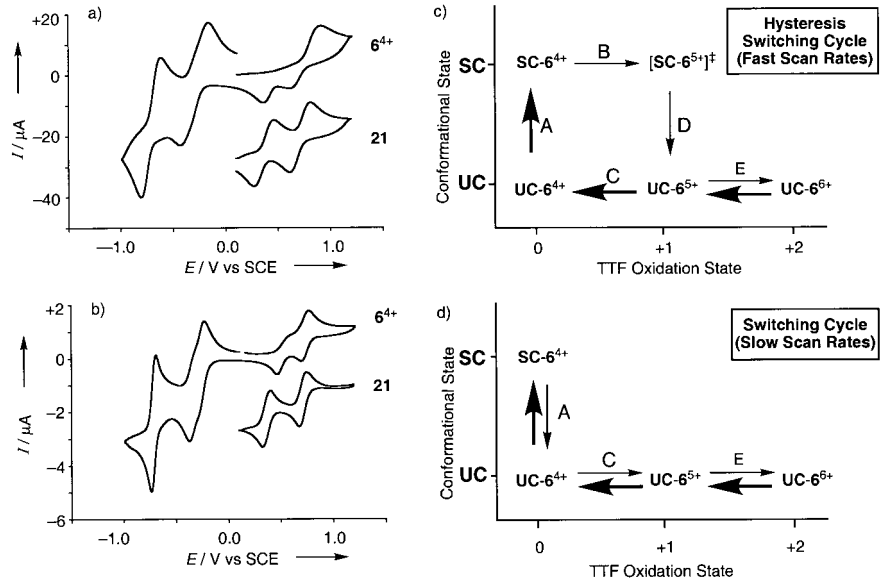


Figure 11. Cyclic voltammograms of 1×10^{-3} M solutions of **6**·4PF$_6$ and **21** in MeCN at a) 1000 mV s^{-1} and b) 10 mV s^{-1}, and the proposed mechanistic pathways along which the oxidation process (thin arrows) and reduction process (bold arrows) occurs at the c) fast and d) slow scan rates, respectively.

tration of the **UC** starting state will continually decrease by electrochemical oxidation (reaction C). However, it will also be continually replenished by the decomplexation equilibrium A. The rate of replenishment by equilibrium A is sufficiently fast to convert all of the **SC** conformation in the starting state into the **UC** conformation, ready for subsequent oxidation at applied potentials that are greater than $+0.53$ V, that is, all of the starting state becomes oxidized along the reaction pathway C before it can be oxidized by reaction B. Subsequently, the oxidative process E, which is responsible for interconverting between the mono- and dicationic states, is dominated by the **UC** conformation, as evidenced by the redox couple's reversibility ($\Delta E = 70$ mV) and its similarity to the dumbbell. Returning the monocationic state of the **UC** conformation to the **SC** starting state is, again, along a pathway that is dominated by coupling between the electrochemical reaction C and the dynamic equilibrium A. The coupling of these two reactions generates the appearance of a quasi-reversible ($\Delta E = 120$ mV) oxidation process at $+0.53$ V that is anodically shifted by 170 mV (Figure 11a) relative to the dumbbell. Anodic shifts of 140 mV have been reported for TTF-based macrocyclic hosts in the presence of the ionic Pb^{2+} guests,[32] and a similar rationalization for the observed shift was proposed. In contrast, at 1000 mV s^{-1}, the rate of the decomplexation equilibrium A is slow by comparison with the sweep rate of the applied potential. Therefore, the singly-oxidized state of the **SC** conformation is produced by reaction B at or near the same potential ($\approx +0.9$ V) as reaction E, which produces the dicationic state of the decomplexed form. Consequently, $E_{1/2}(\mathbf{SC\text{-}6})^{5+/4+} = E_{1/2}(\mathbf{UC\text{-}6})^{6+/5+}$ and the two peaks coalesce to give the *appearance* of a $2e^-$ process in the CV. Therefore, the **UC** conformation of the dication is produced along a different pathway at a faster scan rate than at a slower scan rate. However, the starting state of the **SC** conformation is regenerated along the same pathway at both slow and fast scan rates, because the $TTF^{\bullet+}$-based **UC** conformation is not in dynamic equilibrium with any other species.

The scan-rate dependent behavior distinguishes between two different mechanisms that are available for electrochemically switching the self-complexed **6**·4 PF_6 between two states. At fast scan rates, the switching is *oxidatively driven* and results in a hysteresis cycle; that is, when the monocationic state of the **SC** conformation is generated by oxidation B, it rapidly proceeds by the irreversible decomplexation reaction D at potentials that are sufficient to produce simultaneously the dicationic state by oxidation process E. At slower scan rates, the **UC** conformation of the starting state is *oxidatively trapped*. In this case, the interconversion between **SC**-$\mathbf{6}^{4+}$ and **UC**-$\mathbf{6}^{5+}$ is along the same pathway. Consequently, the applied potential needs only to sit at intermediary voltages for oxidation reaction C to be initiated in order to drive decomplexation reaction A to completion. In summary, when the switching reaction is driven quickly, the dicationic form TTF^{2+} is generated; however, when it is driven slowly, it is the monocationic $TTF^{\bullet+}$ form that is produced.

It is informative to consider how the two mechanisms of switching can be rationalized in terms of two explanatory models[33] for biomolecular machinery.[34] The *oxidatively driven* process is akin to the "power-stroke" mechanism,[33] postulated to account for the rotary motions in ATPase. In this instance, chemical oxidation of the TTF unit, rather than binding and hydrolysis of ATP, generates an instantaneous high-energy conformational state that relaxes by molecular mechanical movements. Furthermore, given that the cycle of switching at fast scan rates can be considered as a hysteresis (Figure 11c) in two parameters—TTF oxidation state and conformational state—then these molecular machines display a parametric trajectory that has been postulated[35] to produce unidirectional motion at these nanoscopic length scales. Alternatively, the *oxidatively trapped* process reflects the utilization of the TTF's oxidation, rather than ATP's hydrolysis, as a switch[36] that captures the molecule in its "uncomplexed" conformation that is itself generated by stochastic Brownian motions. Although a thorough analysis of the self-complexing systems, together with other molecular switches is the objective of future work, this brief discussion suggests that technological applications with artificial molecular machinery may continue to profit[36b,37] by the transfer of concepts from the life sciences to materials science.

In addition to its oxidative activity, **6**·4 PF_6 displays reversible reduction electrochemistry. The first two-electron reduction is split into two closely spaced one-electron processes at -0.25 and -0.35 V versus SCE. This splitting can be assigned to the presence of chemical inequivalence between the two paraquat units.[5b,38] The second two-electron reduction process, observed at -0.71 V versus SCE, occurs at the same position as the free cyclophane[5b,38] and is therefore consistent with the formation of the "uncomplexed" form following the first two single-electron reduction processes.

The UV-visible spectroelectrochemistry of the oxidation cycle of **6**·4 PF_6 (Figure 12), obtained by using a controlled-electrolysis protocol in an optically-transparent thin-layer electrochemical (OTTLE) cell, was investigated in order to confirm the site of redox activity and the slow-scan-rate electrochemically driven decomplexation and complexation reactions. Two oxidation and two reduction processes are observed; this is consistent with the CV recorded at 10 mV s^{-1}, included as insets in Figure 12. The first oxidation process C is initiated at $+0.4$ V and continues as the applied potential is increased in 50 mV steps up to $+0.65$ V. The $TTF \rightarrow CBPQT^{4+}$ band at 853 mm is bleached concomitant with the formation of the TTF^{+}-based chromophore in the visible region.[39] The second oxidation process E displays a bleach of the TTF^{+} chromophore as the TTF^{2+}-based band at 388 nm is observed to emerge. These changes are initiated directly after the completion of the first series of changes at $+0.65$ V in a manner that is consistent with the two closely spaced oxidation waves observed in the CV (10 mV s^{-1}). The reduction processes display the reverse spectroscopic changes over a range of applied voltages that are less positive than those required for the oxidation, an observation

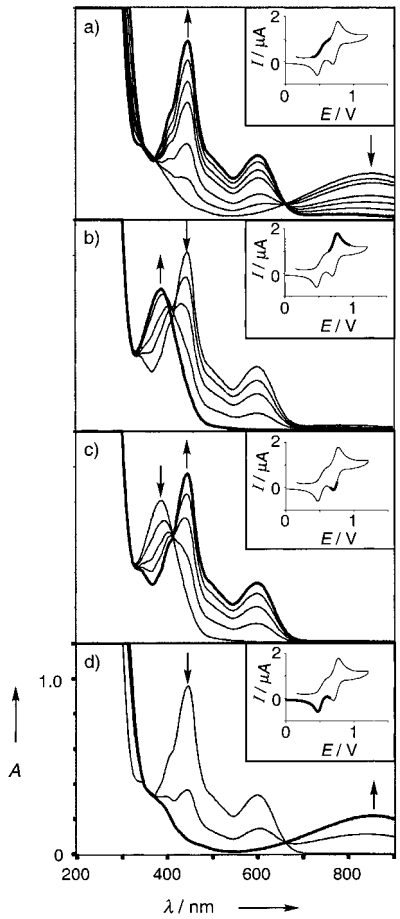


Figure 12. UV-visible spectroelectrochemistry of a 1×10^{-3} M MeCN (0.1 M $TBAPF_6$) solution of **6**·4PF_6 at a) 0.40–0.65, b) 0.65–0.95, c) 0.75–0.65, and d) 0.65–0.00 V. Insets: 10 mV s^{-1} CV, with the potential ranges that correspond to each redox process highlighted in bold.

that is consistent with the CV. The charge transfer band at 853 nm of the self-complexed neutral TTF state grows back with the bleaching of the monocation's spectrum. The presence of $TTF^{\bullet+}$ and TTF^{2+} chromophores in the spectroelectrochemistry is consistent with oxidation processes centered on the TTF unit. The reformation of the spectrum of the ground state is consistent with a switch that can be reversibly operated under electrochemical control.

Conclusion

A series of molecular switches in the form of covalently linked donor–acceptor cyclophanes have been prepared by fine-tuning the molecular structures so that they display reversible thermally or redox-activated molecular motions. The donor-bearing arms in the former class, containing either hydroquinone or 1,5-dioxynaphthalene ring systems, are capable of rapidly complexing and decomplexing into and out of the cyclophane's cavity, respectively, under thermal control over a range of ambient temperatures from −40 up to +50 °C. Furthermore, the cyclophanes bearing the 1,5-dioxynaphthalene ring system are purple in their self-complexed form and consequently display thermochromism. On the other hand, the compounds containing tetrathiafulvalene can be switched using chemical or electrochemical means. In this manner, the initial self-complexed state can be converted completely and almost instantaneously to the "uncomplexed" conformation by electrochemical oxidation of the tetrathiafulvalene unit to its dication or more slowly via its monocation. Of the systems studied, the thermochromic self-complexing compound is the most promising switch for imaging and sensing materials.

Experimental Section

General methods: Reagents were purchased from Aldrich or synthesized as described. The tosylates **8**,[7b] **14**,[18] and **20**,[20] the carboxylic acid derivative **11**,[18] and the bis(hexafluorophosphate) **13**·2PF_6[15] were all prepared according to literature procedures. Solvents were purified according to literature procedures.[40] Thin-layer chromatography (TLC) was carried out by using aluminum sheets, precoated with silica gel 60F (Merck 5554). The plates were inspected by UV-light prior to development with iodine vapor. Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. UV-visible spectra were obtained using a Varian Cary 100 Bio spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500, Avance 600, or ARX500 spectrometers, using the deuterated solvent as lock and the residual protiated solvent as internal standard. All chemical shifts are quoted using the δ scale, and all coupling constants (J) are expressed in Hertz (Hz). Electrospray mass spectra (ESI-MS) were measured on a VG ProSpec triple focusing mass spectrometer. Elemental analyses were performed by Quantitative Technologies Inc.

General procedure for the preparation of the alcohols 10, 16, 17, 21, and 22: A mixture of the appropriate monotosylate (1.0 mmol), the phenol **9** or **15** (1.2 mmol), K_2CO_3 (2.0 mmol), LiBr (catalytic amount), and [18]crown-6 (catalytic amount) in MeCN (30 mL) was heated under reflux for 24 h. The resulting suspension was filtered and the solid was washed with Me_2CO until the filtrate was colorless. The combined organic solution was evaporated and subjected to column chromatography (SiO_2: hexanes/EtOAc 1:4) to give the product.

Alcohol 10: This alcohol was obtained as a white solid (0.34 g, 95 %). M.p. 67.0–68.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 2.94 (br s, 1H), 3.65 (t, J = 4.2 Hz, 2H), 3.75 (m, 2H), 3.82 (t, J = 4.2 Hz, 2H), 3.91 (m, 4H), 4.07 (t, J = 4.2 Hz, 2H), 4.11 (t, J = 4.2 Hz, 2H), 4.15 (m, 2H), 6.87 (s, 4H), 6.95 (m, 3H), 7.30 ppm (m, 2H); ^{13}C NMR (CD_3COCD_3, 125 MHz, 298 K): δ = 61.5, 67.2, 67.9, 68.0, 69.6, 69.8, 69.9, 72.6, 114.5, 115.5, 115.6, 120.8, 129.3, 152.9, 153.1, 158.6 ppm; HRMS (MALDI): m/z calcd for $C_{20}H_{26}O_6Na^+$ $[M+Na]^+$: 385.1622; found: 385.1605; elemental analysis calcd (%) for $C_{20}H_{26}O_6$: C 66.28, H 7.23; found: C 66.12, H 7.23.

Alcohol 16: This alcohol was obtained as a white solid (0.35 g, 84 %). ^{1}H NMR (CD_3OD, 500 MHz, 298 K): δ = 7.88, 7.85 (2d, J = 3.7 Hz, 2H), 7.42–7.24 (m, 4H), 6.96–6.92 (m, 5H), 4.33 (m, 4H), 4.18 (t, J = 4.5 Hz, 2H), 4.06 (t, J = 4.5 Hz, 2H), 4.00 (m, 4H), 3.76 ppm (m, 4H); ^{13}C NMR (CD_3OD, 125 MHz, 298 K): δ = 159.0, 154.2, 154.2, 128.9, 126.6, 126.6, 124.6, 124.6, 120.3, 114.1, 114.0, 114.0, 105.3, 105.2, 72.4, 69.6, 69.5, 69.3, 67.6, 67.0, 60.8, 60.8 ppm; MS (EI): m/z (%): 412.2 (90) $[M]^+$.

Alcohol 17: This alcohol was obtained as a white solid (0.39 g, 88 %). M.p. 81.0–82.5 °C; ^{1}H NMR (CD_3COCD_3, 500 MHz, 298 K): δ = 9.86 (s, 1H), 7.82 (m, 4H), 7.34 (m, 4H), 7.10 (d, J = 7.6 Hz, 2H), 6.95 (t, J = 7.6 Hz, 2H), 4.30 (m, 6H), 4.04 (t, J = 4.5 Hz, 2H), 3.99 (t, J = 4.5 Hz, 2H), 3.95 (t, J = 4.5 Hz, 2H), 3.65 ppm (m, 4H); ^{13}C NMR (CD_3COCD_3, 125 MHz, 298 K): δ = 163.8, 154.3, 154.3, 131.5, 130.2, 126.6, 125.0, 114.8, 114.1, 114.1, 105.6, 105.5, 72.8, 72.8, 69.5, 69.3, 67.9, 67.8, 61.0. 60.9 ppm; HRMS (MALDI): m/z calcd for $C_{25}H_{28}O_7Na^+$ $[M+Na]^+$: 463.1727;

found: 463.1754; elemental analysis calcd (%) for $C_{25}H_{28}O_7$: C 68.17, H 6.41; found: C 68.22, H 6.38.

Alcohol 21: This alcohol was obtained as a yellow wax (0.41 g, 79%). ^{1}H NMR (CD_3COCD_3, 500 MHz, 298 K): δ = 7.29 (m, 2H), 6.96 (m, 3H), 6.57 (s, 1H), 6.55 (s, 1H), 4.36 (s, 4H), 4.15 (t, J = 4.5 Hz, 2H), 3.85 (t, J = 4.5 Hz, 2H), 3.70–3.56 (m, 10H), 3.54 ppm (t, J = 4.5 Hz, 2H); ^{13}C NMR (CD_3COCD_3, 125 MHz, 298 K): δ = 158.9, 134.7, 129.2, 120.4, 116.6 (2), 116.5 (2), 114.4, 109.9, 72.6, 70, 3, 70.0, 69.4, 69.1 (2), 67.6, 67.5, 67.1, 61.0 ppm; MS (FAB): m/z (%): 516.05 (75) $[M]^+$.

Alcohol 22: This alcohol was obtained as a yellow wax (0.45 g, 83%). ^{1}H NMR (CD_3COCD_3, 500 MHz, 298 K): δ = 9.92 (S, 1H), 7.90 (dd, J^1 = 8.8 Hz, J^2 = 1.7 Hz, 2H), 7.16 (dd, J^1 = 8.8 Hz, J^2 = 1.7 Hz, 2H), 6.57 (s, 1H), 6.55 (s, 1H), 4.36 (s, 4H), 4.30 (t, J = 4.5 Hz, 2H), 3.90 (t, J = 4.5 Hz, 2H), 3.73 (m, 2H), 3.67–3.59 (m, 8H), 3.55 ppm (t, J = 4.5 Hz, 2H); ^{13}C NMR (CD_3COCD_3, 125 MHz, 298 K): δ = 190.2, 163.8, 134.8, 134.7, 134.7, 131.5, 130.2, 116.6, 116.5, 116.5 114.8, 72.6, 70, 3, 70.1, 69.2, 69.2 69.1, 67.8, 67.6, 67.5, 61.0 ppm; HRMS (MALDI): m/z calcd for $C_{23}H_{28}O_7S_4^+$ $[M]^+$: 544.0712; found: 544.0695.

Synthesis of the carboxylic acid derivative 11:[18] A mixture of 3,6-dimethylphthalimide (1.57 g, 8.97 mmol), *tert*-butyl 2-bromoacetate (1.92 g, 9.90 mmol), and K_2CO_3 (2.48 g, 17.90 mmol) in MeCN (50 mL) was heated under reflux for 3 h. The resulting suspension was filtered and the filtrate was evaporated to give a pale yellow solid, which was recrystallized from EtOAc and hexanes (1:1) as colorless crystals (2.48 g, 95%). Subsequently, a mixture of the obtained cyrstal (1.90 g, 6.57 mmol), NBS (2.34 g, 13.15 mmol), and AIBN (20 mg, cat. amount) in CH_2Cl_2 (20 mL) was heated under reflux for 4 h. The resulting suspension was filtered, and the filtrate was evaporated and subjected to column chromatography (SiO_2: hexanes/EtOAc, 8:1) to give a white solid (1.40 g). The solid was dissolved in CH_2Cl_2 (10 mL) and placed in an ice/water bath, and HNO_3 (1.5 mL, 90%) was added dropwise into the solution. The mixture was then stirred at room temperature for three more hours. The solvent was evaporated under reduced pressure and the remaining solid was washed with hexanes to give **11** as a white solid (1.09 g, 41% for three steps). M.p. 228.0–230.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 7.90 (s, 2H), 5.07 (s, 4H), 4.44 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ = 167.7, 166.3, 137.3, 136.7, 128.5, 38.2, 25.8 ppm; MS (EI): m/z (%): 389.0 (25) $[M]^+$, 309.0 (100) $[M-Br]^+$; elemental analysis calcd (%) for $C_{12}H_9Br_2NO_4$: C 36.86, H 2.32, N 3.58; found: C 37.07, H 2.21, N 3.58.

General procedure for the preparation of the dibromides 12, 18, 19, 23, and 24: A mixture of the appropriate alcohol (0.50 mmol), the carboxylic acid derivative **11** (0.55 mmol), 1,3-dicyclohexylcarbodiimide (1.0 mmol), and 4-dimethylaminopyridine (catalytic amount) in CH_2Cl_2 (20 mL) was stirred overnight at room temperature. The resulting suspension was filtered, and the filtrate was evaporated and subjected to column chromatography (SiO_2: hexanes/EtOAc 1:1) to give the dibomide.

Dibromide 12: This dibromide was obtained as a white wax (0.26 g, 71%). ^{1}H NMR (CD_3COCD_3, 500 MHz, 298 K): δ = 7.92 (s, 2H), 7.30 (t, J = 8.5 Hz,, 2H), 6.96 (m, 3H), 6.90 (s, 4H), 5.09 (s, 4H), 4.51 (s, 2H), 4.37 (t, J = 4.5 Hz, 2H), 4.17 (t, J = 4.5 Hz, 2H), 4.12 (t, J = 4.5 Hz, 2H), 4.07 (t, J = 4.5 Hz, 2H), 3.90, (m, 4H), 3.81 ppm (m, 4H); ^{13}C NMR (CD_3COCD_3, 125 MHz, 298 K): δ = 167.1, 166.2, 158.9, 153.1, 137.3, 136.7, 129.2, 128.4, 120.4, 115.4, 115.3, 114.3, 69.6, 69.5, 69.4, 68.5, 67.8, 67.2, 64.7, 38.4, 25.8 ppm; HRMS (MALDI): m/z calcd for $C_{32}H_{33}Br_2NO_9$·Na^+ $[M+Na]^+$: 756.0414; found: 756.0411.

Dibromide 18: This dibromide was obtained as a yellow semisolid (0.30 g, 77%). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 7.91, 7.88 (2d, J = 8.5 Hz, 2H), 7.64 (s, 2H), 7.40–7.29 (m, 4H), 7.00–6.97 (m, 3H), 6.87 6.86 (2d, J = 7.5 Hz, 2H), 4.94 (s, 4H), 4.49 (s, 2H), 4.44 (t, J = 4.5 Hz, 2H), 4.33 (t, J = 4.5 Hz, 2H), 4.30 (t, J = 4.5 Hz, 2H), 4.21 (t, J = 4.5 Hz, 2H), 4.10 (t, J = 4.5 Hz, 2H), 4.04 (t, J = 4.5 Hz, 2H), 4.00 (t, J = 4.5 Hz, 2H), 3.90 ppm (t, J = 4.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ = 167.0, 166.3, 158.7, 154.2, 154.1, 137.0, 136.4, 129.3, 128.2, 126.6, 125.1, 125.0, 120.8, 114.6, 114.6, 114.5, 105.7, 69.9, 69.9, 69.7, 69.0, 67.9, 67.8, 67.4, 64.9, 38.7, 25.7 ppm; MS (EI): m/z (%): 785.1 (10) $[M]^+$; HRMS (MALDI): m/z calcd for $C_{36}H_{35}Br_2NO_9$ $[M]^+$: 783.0679; found: 783.0685.

Dibromide 19: This dibromide was obtained as a yellow solid (0.39 g, 95%). M.p. 65.0–67.0 °C; ^{1}H NMR (CD_3COCD_3, 600 MHz, 298 K): δ = 9.89 (s, 1H), 7.83 (m, 4H), 7.75 (s, 2H), 7.36 (t, J = 8.2 Hz, 1H), 7.33 (t, J = 8.2 Hz, 1H), 7.11 (d, J = 8.2 Hz, 2H), 6.92 (dd, J = 7.7 Hz, 2.7 Hz, 2H), 4.98 (s, 4H), 4.49 (s, 2H), 4.40 (t, J = 4.5 Hz, 2H), 4.30 (m, 4H), 4.26 (t, J = 4.5 Hz, 2H), 4.05 (t, J = 4.5 Hz, 2H), 4.01 (t, J = 4.5 Hz, 2H), 3.97 (t, J = 4.5 Hz, 2H), 3.87 ppm (t, J = 4.5 Hz, 2H); HRMS (MALDI): m/z calcd for $C_{37}H_{35}Br_2NO_{10}Na^+$ $[M+Na]^+$: 834.0520; found: 834.0568.

Dibromide 23: This dibromide was obtained as a yellow wax (0.15 g, 33%). ^{1}H NMR (CD_3COCD_3, 500 MHz, 298 K): δ = 7.95 (s, 2H), 7.29 (m, 2H), 6.96 (m, 3H), 6.57 (s, 1H), 6.55 (s, 1H), 5.12 (s, 4H), 4.52 (s, 2H), 4.36 (s, 4H), 4.18 (t, J = 4.5 Hz, 2H), 3.85 (t, J = 4.5 Hz, 2H), 3.74–3.62 ppm (m, 12H); ^{13}C NMR (CD_3COCD_3, 125 MHz, 298 K): δ = 167.1, 166.3, 158.9, 137.3, 136.8, 134.7, 129.3, 128.4, 120.4, 116.6, 114.3, 70.3 (2), 69.4, 69.1, 69.0, 68.5, 67.2, 64.7, 38.5, 25.9 ppm; MS (FAB): m/z (%): 886.96 (20) $[M]^+$.

Dibromide 24: This dibromide was obtained as a yellow wax (0.32 g, 71%). ^{1}H NMR (CD_3COCD_3, 500 MHz, 298 K): δ = 9.91 (s, 2H), 7.92 (s, 2H), 7.88 (t, J = 8.8 Hz, 2H), 7.15 (t, J = 8.8 Hz, 2H), 6.56 (s, 1H), 6.54 (s, 1H), 5.10 (s, 4H), 4.52 (s, 4H), 4.35 (m, 2H), 4.30 (t, J = 4.5 Hz, 2H), 3.90 (t, J = 4.5 Hz, 2H), 3.76–3.61 ppm (m, 10H); ^{13}C NMR (CD_3COCD_3, 125 MHz, 298 K): δ = 190.2, 167.1, 166.3, 163.8, 137.3, 136.7, 134.7, 134.7, 130.5, 130.1, 128.4, 116.6, 116.5, 114.8, 70.3, 70.3, 69.2, 69.1, 69.1, 69.1, 68.5, 67.9, 64.7, 38.5, 25.9 ppm; MS (FAB): m/z (%): 914.95 (25) $[M]^+$.

General procedure for the preparation of the self-complexing compounds 3–7·4 PF_6: A solution of the appropriate dibromide (0.36 mmol) and the bipyridium salt **13**·2 PF_6 (0.36 mmol) in DMF (5 mL) was stirred at room temperature for eight days. In order to ensure full precipitation of the purple salt, Et_2O (50 mL) was added to the reaction mixture. The precipitate was filtered off under reduced pressure and subjected to column chromatography (SiO_2: MeOH/NH_4Cl (2M)/$MeNO_2$ 7:2:1). The fractions containing the product were combined and concentrated. NH_4PF_6 was added to precipitate the product as a solid.

Cyclophane 3·4 PF_6: This compound was obtained as a red solid (47 mg, 9%). M.p. 190 °C (decomp); ^{1}H NMR of the **SC**-conformer (CD_3COCD_3, 500 MHz, 196 K): δ = 9.65 (d, J = 5.4 Hz, 2H), 9.52 (d, J = 5.4 Hz, 2H), 9.42 (d, J = 5.4 Hz, 2H), 9.06 (brs, 2H), 8.75 (d, J = 5.4, 2H), 8.58 (s, 2H), 8.52 (d, J = 5.4, 2H), 8.50 (d, J = 5.4, 2H), 8.50 (s, 2H), 8.18 (brs, 2H), 8.01 (s, 2H), 7.35 (t, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 12.8 Hz, 2H), 7.01 (t, J = 8.4 Hz, 1H), 6.41 (d, J = 12.8 Hz, 2H), 6.22 (d, J = 12.8 Hz, 2H), 5.97 (d, J = 12.8 Hz, 2H), 5.77 (d, J = 7.4 Hz, 1H), 5.67 (d, J = 7.4 Hz, 1H), 5.12 (brs, 2H), 4.59 (br, 2H), 4.51 (br, 2H), 4.32 (br, 2H), 4.11 (br, 2H), 3.92 (br, 4H), 3.82 (br, 4H), 2.53 (br, 1H), 2.02 ppm (d, J = 7.4 Hz, 1H); HRMS (ESI): m/z calcd for $C_{60}H_{57}F_{24}N_5O_9P_4S_4$ $[M-PF_6]^+$: 1554.1606; found: 1554.1638.

Cyclophane 4·4 PF_6: This compound was obtained as a purple solid (96 mg, 17%). M.p. 220 °C (decomp); ^{1}H NMR of the major isomer (CD_3COCD_3, 500 MHz, 253 K): δ = 9.69 (d, J = 5.4 Hz, 2H), 9.63 (d, J = 5.4 Hz, 2H), 9.52 (d, J = 5.4 Hz, 2H), 9.23 (d, J = 5.4 Hz, 2H), 8.65 (brd, 2H), 8.54 (s, 2H), 8.45 (brd, 2H), 8.36 (m, 4H), 7.98 (s, 2H), 7.88 (s, 2H), 7.10 (t, J = 8.4 Hz, 2H), 6.82 (t, J = 8.4 Hz, 1H), 6.75 (d, J = 12.8 Hz, 2H), 6.74 (s, 1H), 6.61 (d, J = 8.4 Hz, 2H), 6.20 (s, 1H), 6.13 (d, J = 12.8 Hz, 2H), 6.02 (d, J = 12.8 Hz, 2H), 5.94 (d, J = 12.8 Hz, 2H), 4.72 (s, 2H), 4.62 (brd, 2H), 4.30 (m, 4H), 4.23 (s, 2H), 4.15 (brt, 2H), 4.05 (br. t, 2H), 3.97 (brt, 2H), 3.75 (brt, 2H), 3.68 (brt, 2H), 3.59 (brt, 2H), 2.77 (d, J = 8.4 Hz, 1H), 2.67 ppm (d, J = 8.4 Hz, 1H); HRMS (ESI): m/z calcd for $C_{64}H_{59}F_{24}N_5O_9P_4$ $[M-PF_6]^+$: 1476.2869; found: 1476.3189; HRMS (ESI): m/z calcd for $C_{64}H_{59}F_{24}N_5O_9P_4$ $[M-2PF_6]^{2+}$: 665.6793; found: 665.6796.

Cyclophane 5·4 PF_6: This compound was obtained as a purple solid (77 mg, 13%). M.p. 214 °C (decomp); ^{1}H NMR of the major isomer (CD_3COCD_3, 500 MHz, 227 K): δ = 9.82 (s, 1H), 9.46 (d, J = 6.2 Hz, 2H), 9.37 (d, J = 6.2 Hz, 2H), 9.15 (d, J = 6.2 Hz, 2H), 8.92 (d, J = 6.2 Hz, 2H), 8.83 (s, 2H), 8.47 (s, 2H), 8.22 (s, 2H), 8.00 (d, J = 6.2 Hz, 2H)), 7.93 (d, J = 6.2 Hz, 2H), 7.88 (d, J = 6.2 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.60 (br, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 12.8 Hz, 2H), 6.54 (d, J = 8.4 Hz, 2H), 6.47 (t, J = 8.4 Hz, 1H), 6.35 (d, J = 8.4 Hz, 1H), 6.31 (d, J = 12.8 Hz, 2H), 6.19 (t, J = 8.4 Hz, 1H), 6.16 (d, J = 12.8 Hz, 2H), 6.00 (d, J = 12.8 Hz, 2H), 5.28 (s, 2H), 4.65–4.38 (m, 12H), 4.19 (br, 2H), 4.03 (br, 2H), 2.71 (d, J = 8.4 Hz, 1H), 2.64 ppm (d, J = 8.4 Hz, 1H); HRMS

(ESI): m/z calcd for $C_{65}H_{59}F_{24}N_5O_{10}P_4$ $[M-PF_6]^+$: 1504.3182; found: 1504.3624; HRMS (ESI): m/z calcd for $C_{65}H_{59}F_{24}N_5O_{10}P_4$ $[M-2PF_6]^{2+}$: 679.6767; found: 679.6905.

Cyclophane 6·4PF$_6$: This self-complexing compound was obtained as a green solid (0.23 g, 36%). M.p. 250°C (decomp); ^{1}H NMR spectroscopy of the major isomer (CD_3COCD_3, 500 MHz, 253 K): $\delta=9.69$ (d, $J=5.4$ Hz, 2H), 9.63 (d, $J=5.4$ Hz, 2H), 9.52 (d, $J=5.4$ Hz, 2H), 9.23 (d, $J=5.4$ Hz, 2H), 8.65 (brd, 2H), 8.54 (s, 2H), 8.45 (brd, 2H), 8.36 (m, 4H), 7.98 (s, 2H), 7.88 (s, 2H), 7.10 (t, $J=8.4$ Hz, 2H), 6.82 (t, $J=8.4$ Hz, 1H), 6.75 (d, $J=12.8$ Hz, 2H), 6.74 (s, 1H), 6.61 (d, $J=8.4$ Hz, 2H), 6.20 (s, 1H), 6.13 (d, $J=12.8$ Hz, 2H), 6.02 (d, $J=12.8$ Hz, 2H), 5.94 (d, $J=12.8$ Hz, 2H), 4.72 (s, 2H), 4.62 (brd, 2H), 4.30 (m, 4H), 4.23 (s, 2H), 4.15 (brt, 2H), 4.05 (brt, 2H), 3.97 (brt, 2H), 3.75 (brt, 2H), 3.68 (brt, 2H), 3.59 ppm (brt, 2H); HRMS (ESI): m/z calcd for $C_{62}H_{59}F_{24}N_5O_9P_4S_4$ $[M-PF_6]^+$: 1580.2121; found: 1580.2232.

Cyclophane 7·4PF$_6$: This self-complexing compound was obtained as a green solid (0.22 g, 35%). M.p. 245°C (decomp); ^{1}H NMR spectroscopy of the major isomer (CD_3COCD_3, 500 MHz, 253 K): $\delta=9.77$ (s, 1H), 9.67 (d, $J=5.4$ Hz, 2H), 9.61 (d, $J=5.4$ Hz, 2H), 9.52 (d, $J=5.4$ Hz, 2H), 9.25 (d, $J=5.4$ Hz, 2H), 8.58–8.52 (m, 4H), 8.45 (d, $J=5.4$ Hz, 2H), 8.40–8.35 (m, 4H), 7.98 (s, 2H), 7.88 (s, 2H), 7.68 (d, $J=5.6$ Hz, 2H), 6.89 (d, $J=5.6$ Hz, 2H), 6.80 (d, $J=13.7$ Hz, 2H), 6.73 (s, 1H), 6.22 (s, 1H), 6.13 (d, $J=13.7$ Hz, 2H), 6.02 (d, $J=13.7$ Hz, 2H), 5.92 (d, $J=13.7$ Hz, 2H), 4.72 (s, 2H), 4.46 (brs, 4H), 4.30 (s, 4H), 4.23 (s, 2H), 4.07 (brt, 2H), 3.97 (brt, 2H), 3.75 (brt, 2H), 3.66 (brt, 2H), 3.61 ppm (brt, 2H); HRMS (ESI): m/z calcd for $C_{63}H_{59}F_{24}N_5O_{10}P_4S_4$ $[M-PF_6]^+$: 1608.2065; found: 1608.2435; HRMS (ESI): m/z calcd for $C_{63}H_{59}F_{24}N_5O_{10}P_4S_4$ $[M-2PF_6]^{2+}$: 731.6209; found: 731.6221.

Electrochemistry and spectroelectrochemistry: Electrochemical and spectroelectrochemical experiments were carried out at room temperature in argon-purged solutions of the compounds in MeCN, with a Princeton Applied Research 263A Multipurpose instrument interfaced to a PC. Cyclic voltammetric experiments were performed by using a glassy carbon working electrode (0.018 cm^2, Cypress Systems); its surface was polished routinely with a 0.05 μm alumina–water slurry on a felt surface immediately before use. The counter electrode was a Pt wire and the reference electrode was a Ag/AgCl electrode ("No Leak" Ag/AgCl Reference Electrode, Cypress Systems). Tetrabutylammonium hexafluorophosphate (0.1 M) was added as supporting electrolyte. Cyclic voltammograms were obtained at scan rates of 10, 100, 500 and 1000 mV s^{-1}. For reversible processes, $E_{1/2}$ was calculated from an average of the cathodic and anodic cyclic voltammetric peaks. To establish the reversibility of a process, we used the critieria of 1) 60 mV between cathodic and anodic peaks, and 2) close to unity ratio of the intensities of the cathodic and anodic currents. $[Ru(bpy)_3]^{2+}$ [$E_{1/2}(Ru^{3+}/Ru^{2+})=+1.290$ V][41] was present in the solution as an internal reference. Spectroelectrochemical experiments were made in a custom built optically-transparent thin layer electrochemical (OTTLE) cell[42] with an optical path of 1 mm, using a Pt grid as working electrode, a Pt wire as counter electrode, and a Ag wire pseudo-reference electrode. Experimental errors: potential values, ±10 mV; absorption maxima, ±2 nm.

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[1] R. P. Feynman, *Eng. Sci.* **1960**, *23*, 22–36.

[2] a) D. H. Busch, N. A. Stephenson, *Coord. Chem. Rev.* **1990**, *100*, 119–154; b) D. Philp, J. F. Stoddart, *Synlett* **1991**, 445–458; c) J. S. Lindsey, *New J. Chem.* **1991**, *15*, 153–180; d) G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312–1319; e) C. A. Hunter, *J. Am. Chem. Soc.* **1992**, *114*, 5303–5311; f) S. Anderson, H. L. Anderson, J. K. M. Sanders, *Acc. Chem. Res.* **1993**, *26*, 469–475; g) A. P. Bisson, F. J. Carver, C. A. Hunter, J. P. Waltho, *J. Am. Chem. Soc.* **1994**, *116*, 10292–10293; h) C. A. Hunter, *Angew. Chem.* **1995**, *107*, 1181–1183; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1079–1081; i) J. P. Schneider, J. W. Kelly, *Chem. Rev.* **1995**, *95*, 2169–2187; j) F. M. Raymo, J. F. Stoddart, *Pure Appl. Chem.* **1996**, *68*, 313–322; k) A. G. Kolchinski, N. W. Alcock, R. A. Roesner, D. H. Busch, *Chem. Commun.* **1998**, 1437–1438; l) M. Fujita, *Acc. Chem. Res.* **1999**, *32*, 53–61; m) J. Rebek, Jr., *Acc. Chem. Res.* **1999**, *32*, 278–286; n) *Templated Organic Synthesis* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1999**; o) M. Nakash, Z. C. Watson, N. Feeder, S. J. Teat, J. K. M. Sanders, *Chem. Eur. J.* **2000**, *6*, 2112–2119; p) J. K. M. Sanders, *Pure Appl. Chem.* **2000**, *72*, 2265–2274; q) D. T. Bong, T. D. Clark, J. R. Granja, M. R. Ghadiri, *Angew. Chem.* **2001**, *113*, 1016–1041; *Angew. Chem. Int. Ed.* **2001**, *40*, 988–1011; r) L. J. Prins, D. N. Reinhoudt, P. Timmerman, *Angew. Chem.* **2001**, *113*, 2446–2492; *Angew. Chem. Int. Ed.* **2001**, *40*, 2382–2426; s) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983; t) J. F. Stoddart, H.-R. Tseng, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4797–4800; u) R. L. E. Furlan, S. Otto, J. K. M. Sanders, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4801–4804; v) D. Joester, E. Walter, M. Losson, R. Pugin, H. P. Merkle, F. Diederich, *Angew. Chem.* **2003**, *115*, 1524–1528; *Angew. Chem. Int. Ed.* **2003**, *42*, 1486–1490; w) L. Hogg, D. A. Leigh, P. J. Lusby, A. Morelli, S. Parsons, J. K. Y. Wong, *Angew. Chem.* **2004**, *116*, 1238–1241; *Angew. Chem. Int. Ed.* **2004**, *43*, 1218–1221; x) X. Zheng, M. E. Mulcahy, D. Horinek, F. Galeotti, T. F. Magnera, J. Michl, *J. Am. Chem. Soc.* **2004**, *126*, 4540–4542.

[3] a) J. F. Stoddart, *Chem. Aust.* **1992**, *59*, 576–577 and 581; b) M. Gómez-López, J. A. Preece, J. F. Stoddart, *Nanotechnology* **1996**, *7*, 183–192; c) V. Balzani, M. Gómez-López, J. F. Stoddart, *Acc. Chem. Res.* **1998**, *31*, 405–414; d) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484–3530; *Angew. Chem. Int. Ed.* **2000**, *39*, 3348–3391; e) A. Harada, *Acc. Chem. Res.* **2001**, *34*, 456–464; f) C. A. Schalley, K. Beizai, F. Vögtle, *Acc. Chem. Res.* **2001**, *34*, 465–476; g) J.-P. Collin, C. Dietrich-Buchecker, P. Gaviña, M. C. Jiménez-Molero, J.-P. Sauvage, *Acc. Chem. Res.* **2001**, *34*, 477–487; h) R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, M. Venturi, *Struct. Bonding* **2001**, *99*, 163–188; i) L. Raehm, J.-P. Sauvage, *Struct. Bonding* **2001**, *99*, 55–78; j) C. A. Stainer, S. J. Alderman, T. D. W. Claridge, H. L. Anderson, *Angew. Chem.* **2002**, *114*, 1847–1850; *Angew. Chem. Int. Ed.* **2002**, *41*, 1769–1772; k) V. Balzani, A. Credi, M. Venturi, *Chem. Eur. J.* **2002**, *8*, 5524–5532; l) H.-R. Tseng, J. F. Stoddart in *Modern Arene Chemistry* (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2002**, pp. 574–599; m) Y. Chen, G.-Y. Jung, D. A. A. Ohlberg, X. Li, D. R. Stewart, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart, R. S. Williams, *Nanotechnology* **2003**, *14*, 462–468; n) J. R. Heath, M. A. Ratner, *Physics Today* **2003**, *May*, 43–49; o) V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines—A Journey into the Nano World*, Wiley-VCH, Weinheim, **2003**; p) A. H. Flood, R. J. A. Ramirez, W.-Q. Deng, R. P. Muller, W. A. Goddard III, J. F. Stoddart, *Aust. J. Chem.* **2004**, *57*, 301–322.

[4] a) T. R. Kelly, H. De Silva, R. A. Silva, *Nature* **1999**, *401*, 150–152; b) N. Koumura, R. W. Zijlstra, R. A. van Delden, H. Harada, B. L. Feringa, *Nature* **1999**, *401*, 152–155; c) Y. Yokoyama, *Chem. Rev.* **2000**, *100*, 1717–1740; d) G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev.* **2000**, *100*, 1741–1754; e) B. L. Feringa, R. A. van Delden, N. Koumura, E. M. Geertsema, *Chem. Rev.* **2000**, *100*, 1789–1816; f) T. R. Kelly, *Acc. Chem. Res.* **2001**, *34*, 514–522; g) S. Shinkai, M. Ikeda, A. Sugasaki, M. Takeuchi, *Acc. Chem. Res.* **2001**, *34*, 494–503; h) K. Oh, K.-S. Jeong, J. S. Moore, *Nature* **2001**, *414*, 889–893; i) N. Koumura, E. M. Geertsema, M. B. van Gelder, A. Meetsma, B. L. Feringa, *J. Am. Chem. Soc.* **2002**, *124*, 5037–5051; j) F. Hawthorne, J. I. Zink, J. M. Skelton, M. J. Bayer, C. Liu, E. Livshits, R. Baer, D. Neuhauser, *Science* **2004**, *303*, 1849–1851; k) J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch, B. L. Feringa, *Science* **2004**, *304*, 278–281.

[5] a) M. Asakawa, P. R. Ashton, V. Balzani, A. Credi, C. Hamers, G. Mattersteig, M. Montalti, A. N. Shipway, N. Spencer, J. F. Stoddart,

M. S. Tolley, M. Venturi, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 357–361; *Angew. Chem. Int. Ed.* **1998**, *37*, 333–337; b) V. Balzani, A. Credi, G. Mattersteig, O. A. Matthews, F. M. Raymo, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Org. Chem.* **2000**, *65*, 1924–1936; c) M. Asakawa, M. Higuchi, G. Mattersteig, T. Nakamura, A. R. Pease, F. M. Raymo, T. Shimizu, J. F. Stoddart, *Adv. Mater.* **2000**, *12*, 1099–1102; d) C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, J. R. Heath, *Science* **2000**, *289*, 1172–1175; e) A. R. Pease, J. O. Jeppesen, J. F. Stoddart, Y. Luo, C. P. Collier, J. R. Heath, *Acc. Chem. Res.* **2001**, *34*, 433–444; f) A. R. Pease, J. F. Stoddart, *Struct. Bonding* **2001**, *99*, 189–236; g) M. R. Diehl, D. W. Steuerman, H.-R. Tseng, S. A. Vignon, A. Star, P. C. Celestre, J. F. Stoddart, J. R. Heath, *ChemPhysChem* **2003**, *4*, 1335–1339.

[6] a) A. Livoreil, C. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1994**, *116*, 9399–9400; b) D. J. Cárdenas, A. Livoreil, J.-P. Sauvage, *J. Am. Chem. Soc.* **1996**, *118*, 11980–11981; c) F. Baumann, A. Livoreil, W. Kaim, J.-P. Sauvage, *Chem. Commun.* **1997**, 35–36; d) A. Livoreil, J.-P. Sauvage, N. Armaroli, V. Balzani, L. Flamigni, B. Ventura, *J. Am. Chem. Soc.* **1997**, *119*, 12114–12124; e) D. G. Hamilton, M. Montalti, L. Prodi, M. Fontani, P. Zanello, J. K. M. Sanders, *Chem. Eur. J.* **2000**, *6*, 608–617.

[7] a) R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, *369*, 133–137; b) J. O. Jeppersen, J. Perkins, J. Becher, J. F. Stoddart, *Angew. Chem.* **2001**, *113*, 1251–1261; *Angew. Chem. Int. Ed.* **2001**, *40*, 1216–1221; c) Y. Luo, C. P. Collier, J. O. Jeppesen, K. A. Nielsen, E. Delonno, G. Ho, J. Perkins, H.-R. Tseng, T. Yamamoto, J. F. Stoddart, J. R. Heath, *ChemPhysChem* **2002**, *3*, 519–525; d) C. P. Collier, J. O. Jeppesen, Y. Luo, J. Perkins, E. W. Wong, J. R. Heath, J. F. Stoddart, *J. Am. Chem. Soc.* **2001**, *123*, 12632–12641; e) J. O. Jeppesen, K. A. Nielsen, J. Perkins, S. A. Vignon, A. Di Fabio, R. Ballardini, M. T. Gandolfi, M. Venturi, V. Balzani, J. Becher, J. F. Stoddart, *Chem. Eur. J.* **2003**, *9*, 2982–3007; f) T. Yamamoto, H.-R. Tseng, J. F. Stoddart, V. Balzani, A. Credi, F. Marchioni, M. Venturi, *Collect. Czech. Chem. Commun.* **2003**, *68*, 1488–1514; g) H.-R. Tseng, S. A. Vignon, P. C. Celestre, J. Perkins, J. O. Jeppesen, A. Di Fabio, R. Ballardini, M. T. Gandolfi, M. Venturi, V. Balzani, J. F. Stoddart, *Chem. Eur. J.* **2004**, *10*, 155–172; h) S. Kang, S. A. Vignon, H.-R. Tseng, J. F. Stoddart, *Chem. Eur. J.* **2004**, *10*, 2555–2564.

[8] a) A. C. Benniston, *Chem. Soc. Rev.* **1996**, *25*, 427–435; b) C. Gong, H. W. Gibson, *Angew. Chem.* **1997**, *109*, 2426–2428; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2331–2333; c) J.-P. Collin, P. Gaviña, J.-P. Sauvage, *New J. Chem.* **1997**, *21*, 525–528; d) H. Murakami, A. Kawabuchi, K. Kotoo, M. Kunitake, N. Nakashima, *J. Am. Chem. Soc.* **1997**, *119*, 7605–7606; e) J.-P. Collin, P. Gaviña, V. Heitz, J.-P. Sauvage, *Eur. J. Inorg. Chem.* **1998**, 1–14; f) N. Armaroli, V. Balzani, J.-P. Collin, P. Gaviña, J.-P. Sauvage, B. Ventura, *J. Am. Chem. Soc.* **1999**, *121*, 4397–4408; g) M.-J. Blanco, M. C. Jimenez, J.-C. Chambron, V. Heitz, M. Linke, J.-P. Sauvage, *Chem. Soc. Rev.* **1999**, *28*, 293–305; h) M. C. Jimenez-Molero, C. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Eur. J.* **2002**, *8*, 1456–1466; i) T. Da Ross, D. M. Guldi, A. F. Morales, D. A. Leigh, M. Prato, R. Turco, *Org. Lett.* **2003**, *5*, 689–691.

[9] a) A. S. Lane, D. A. Leigh, A. Murphy, *J. Am. Chem. Soc.* **1997**, *119*, 11092–11093; b) P. R. Ashton, R. Ballardini, V. Balzani, I. Baxter, A. Credi, M. C. T. Fyfe, M. T. Gandolfi, M. Gómez-López, M.-V. Martínez-Díaz, A. Piersanti, N. Spencer, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1998**, *120*, 11932–11942; c) M. C. Jiménez, C. Dietrich-Buchecker, J.-P Sauvage, *Angew. Chem.* **2000**, *112*, 3422–3425; *Angew. Chem. Int. Ed.* **2000**, *39*, 3284–3287; d) J. W. Lee, K. Kim, K. Kim, *Chem. Commun.* **2001**, 1042–1043; e) A. M. Elizarov, H.-S. Chiu, J. F. Stoddart, *J. Org. Chem.* **2002**, *67*, 9175–9181; f) H.-R. Tseng, S. A. Vignon, J. F. Stoddart, *Angew. Chem.* **2003**, *115*, 1529–1533; *Angew. Chem. Int. Ed.* **2003**, *42*, 1491–1495; g) J. D. Badjic, V. Balzani, A. Credi, S. Silvi, J. F. Stoddart, *Science* **2004**, *303*, 1845–1849; h) G. Kaiser, T. Jarrosson, S. Otto, Y.-F. Ng, A. D. Bond, J. K. M. Sanders, *Angew. Chem.* **2004**, *116*, 1993–1996; *Angew. Chem. Int. Ed.* **2004**, *43*, 1959–1962.

[10] a) L. Raehm, J.-M. Kern, J.-P. Sauvage, *Chem. Eur. J.* **1999**, *5*, 3310–3317; b) V Bermudez, N. Capron, T. Gase, F. G. Gatti, F. Kajzar, D. A. Leigh, F. Zerbetto, S. Zhang, *Nature* **2000**, *406*, 608–611; c) J.-M. Kern, L. Raehm, J.-P. Sauvage, B. Divisia-Blohorn, P.-L. Vidal, *Inorg. Chem.* **2000**, *39*, 1555–1560; d) R. Ballardini, V. Balzani, W. Dehaen, A. E. Dell'Erba, F. M. Raymo, J. F. Stoddart, M. Venturi, *Eur. J. Org. Chem.* **2000**, 591–602; e) J.-P. Collin, J.-M. Kern, L. Raehm, J.-P. Sauvage in *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2000**, pp. 249–280; f) B. X. Colasson, C. Dietrich-Buchecker, M. C. Jimenez-Molero, J.-P. Sauvage, *J. Phys. Org. Chem.* **2002**, *15*, 476–483; g) A. Altieri, F. G. Gatti, E. R. Kay, D. A. Leigh, F. Paolucci, A. M. Z. Slawin, J. K. Y. Wong, *J. Am. Chem. Soc.* **2003**, *125*, 8644–8654; h) I. Poleschak, J.-M. Kern, J.-P. Sauvage, *Chem. Commun.* **2004**, 474–476.

[11] a) R. Ballardini, V. Balzani, M. T. Gandolfi, L. Prodi, M. Venturi, D. Philp, H. G. Ricketts, J. F. Stoddart, *Angew. Chem.* **1993**, *105*, 1362–1364; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1301–1303; b) P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, R. Dress, E. Ishow, O. Kocian, J. A. Preece, N. Spencer, J. F. Stoddart, M. Venturi, S. Wenger, *Chem. Eur. J.* **2000**, *6*, 3558–3574; c) A. M. Brouwer, C. Frochot, F. G. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia, G. W. H. Wurpel, *Science* **2001**, *291*, 2124–2128; d) J.-P. Collin, A.-C. Laemmel, J.-P. Sauvage, *New J. Chem.* **2001**, *25*, 22–24; e) D. A. Leigh, J. K. Y. Wong, F. Dehez, F. Zerbetto, *Nature* **2003**, *424*, 174–179; f) G. Bottari, D. A. Leigh, E. M. Pérez, *J. Am. Chem. Soc.* **2003**, *125*, 13360–13361; g) F. G. Gatti, S. Len, J. K. Y. Wong, G. Bottari, A. Altieri, M. A. F. Morales, S. J. Teat, C. Frochot, D. A. Leigh, A. M. Brouwer, F. Zerbetto, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 10–14; h) A. Altieri, G. Bottari, F. Dehez, D. A. Leigh, J. K. Y. Wong, F. Zerbetto, *Angew. Chem.* **2003**, *115*, 2398–2402; *Angew. Chem. Int. Ed.* **2003**, *42*, 2296–2300; i) A. M. Brouwer, S. M. Fazio, C. Frochot, F. G. Gatti, D. A. Leigh, J. K. Y. Wong, G. W. H. Wurpel, *Pure Appl. Chem.* **2003**, *75*, 1055–1060.

[12] a) A. Ueno, I. Suzuki, T. Osa, *J. Am. Chem. Soc.* **1989**, *111*, 6391–6397; b) A. Ueno, I. Suzuki, M. Fukushima, M. Okhubo, T. Osa, F. Hamada, K. Murai, *Chem. Lett.* **1990**, 605–608; c) S. Minato, T. Osa, A. Ueno, *J. Chem. Soc. Chem. Commun.* **1991**, 107–108; d) M. Nakamura, A. Ikeda, N. Ise, T. Ikeda, H. Ikeda, F. Toda, A. Ueno, *J. Chem. Soc. Chem. Commun.* **1995**, 721–722; e) R. Corradini, A. Dossena, R. Marchelli, A. Panagia, G. Sartor, M. Saviago, A. Lombardi, V. Pavone, *Chem. Eur. J.* **1996**, *2*, 373–381; f) Y. Takenaka, M. Higashi, N. Yoshida, *J. Chem. Soc. Perkin Trans. 2* **2002**, 615–620.

[13] a) S. Shinkai, M. Ishihara, K. Ueda, O. Manabe, *J. Chem. Soc. Perkin Trans. 2* **1985**, 511–518; b) I. K. Lednev, M. V. Alfimov, *Supramol. Sci.* **1994**, *1*, 55–61.

[14] a) P. Pallavicini, A. Perotti, B. Seghi, L. Fabbrizzi, *J. Am. Chem. Soc.* **1987**, *109*, 5139–5144; b) L. Fabbrizzi, M. Licchelli, P. Pallavicini, L. Parodi, *Angew. Chem.* **1998**, *110*, 838–841; *Angew. Chem. Int. Ed.* **1998**, *37*, 800–802; c) L. Fabbrizzi, F. Foti, M. Licchelli, P. M. Maccarini, D. Sacchi, M. Zema, *Chem. Eur. J.* **2002**, *8*, 4965–4972.

[15] P. R. Ashton, R. Ballardini, V. Balzani, S. E. Boyd, A. Credi, M. T. Gandolfi, M. Gómez-López, S. Iqbal, D. Philp, J. A. Preece, L. Prodi, H. G. Ricketts, J. F. Stoddart, M. S. Tolley, M. Venturi, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1997**, *3*, 152–169.

[16] a) M. B. Nielsen, S. B. Nielsen, J. Becher, *Chem. Commun.* **1998**, 475–476; b) M. B. Nielsen, J. G. Hansen, J. Becher, *Eur. J. Org. Chem.* **1999**, 2807–2815.

[17] a) D. B. Amabilino, J. F. Stoddart, *Pure Appl. Chem.* **1993**, *65*, 2351–2359; b) D. Pasini, F. M. Raymo, J. F. Stoddart, *Gazz. Chim. Ital.* **1995**, *125*, 431–435; c) D. B. Amabilino, F. M. Raymo, J. F. Stoddart, *Compr. Supramol. Chem.* **1996**, *9*, 85–130; d) S. J. Langford, J. F. Stoddart, *Pure Appl. Chem.* **1996**, *68*, 1255–1260; e) D. G. Hamilton, J. E. Davies, L. Prodi, J. K. M. Sanders, *Chem. Eur. J.* **1998**, *4*, 608–620; f) F. M. Raymo, J. F. Stoddart, *Chemtracts* **1998**, *11*, 491–511; g) A. C. Try, M. M. Harding, D. G. Hamilton, J. K. M. Sanders, *Chem. Commun.* **1998**, 723–724; h) D. G. Hamilton, L. Prodi, N. Feeder, J. K. M. Sanders, *J. Chem. Soc. Perkin Trans. 1* **1999**, 1057–1065; i) J. Carver, C. A. Hunter, D. J. Livingstone, J. F. McCabe, E. M. Seward, *Chem. Eur. J.* **2002**, *8*, 2848–2859; j) G. Chessari,

C. A. Hunter, C. R. M. Low, M. J. Packer, J. G. Vinter, C. Zonta, *Chem. Eur. J.* **2002**, *8*, 2860–2867.

[18] Y. Liu, A. H. Flood, J. F. Stoddart, *J. Am. Chem. Soc.* **2004**, *126*, 9150–9151.

[19] a) S. Chia, J. Cao, J. F. Stoddart, J. I. Zink, *Angew. Chem.* **2001**, *113*, 2513–2517; *Angew. Chem. Int. Ed.* **2001**, *40*, 2447–2451; b) L. Raehm, J.-M. Kern, J.-P. Sauvage, C. Hamann, S. Palacin, J.-P. Bourgoin, *Chem. Eur. J.* **2002**, *8*, 2153–2162; c) N. Weber, C. Hamann, J.-M. Kern, J.-P. Sauvage, *Inorg. Chem.* **2003**, *42*, 6780–6792; d) E. Coronado, A. Forment-Aliaga, P. Gaviña, F. M. Romero, *Inorg. Chem.* **2003**, *42*, 6959–6961; e) A. L. Vance, T. M. Willey, T. van Buuren, A. J. Nelson, C. Bostedt, G. A. Fox, L. J. Terminello, *Nano Lett.* **2003**, *3*, 81–84; f) H. Azehara, W. Mizutani, Y. Suzuki, T. Ishida, Y. Nagawa, H. Tokumoto, K. Hiratani, *Langmuir* **2003**, *19*, 2115–2123; g) K. Kim, W. S. Jeon, J.-K. Kang, J. W. Lee, S. Y. Jon, T. Kim, K. Kim, *Angew. Chem.* **2003**, *115*, 2395–2398; *Angew. Chem. Int. Ed.* **2003**, *42*, 2293–2296; h) B. Long, K. Nikitin, D. Fitzmaurice, *J. Am. Chem. Soc.* **2003**, *125*, 15490–15498; i) M. Cavallini, F. Biscarini, S. León, F. Zerbetto, G. Bottari, D. A. Leigh, *Science* **2003**, *299*, 531; j) R. Hernandez, H.-R Tseng, J. W. Wong, J. F. Stoddart, J. I. Zink, *J. Am. Chem. Soc.* **2004**, *126*, 3370–3371; k) H.-R. Tseng, D. Wu, N. Fang, X. Zhang, J. F. Stoddart, *ChemPhysChem* **2004**, *5*, 111–116; l) T. J. Huang, H.-R. Tseng, L. Sha, W. Lu, B. Brough, A. H. Flood, B.-D. Yu, P. C. Celestre, J. P. Chang, J. F. Stoddart, C.-M. Ho, *Nano Lett.* **2004**, *4*, 2065–2071.

[20] H. Yu, Y. Luo, K. Beverly, H.-R. Tseng, J. F. Stoddart, J. R. Heath, *Angew. Chem*, **2003**, *115*, 5884–5889; *Angew. Chem. Int. Ed.* **2003**, *42*, 5706–5711.

[21] a) P. R. Ashton, B. Odell, M. V. Reddington, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1988**, *100*, 1608–1611; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1550–1553; b) M. Asakawa, W. Dehaen, G. L'abbé, S. Menzer, J. Nouwen, F. M. Raymo, J. F. Stoddart, D. J. Williams, *J. Org. Chem.* **1996**, *61*, 9591–9595.

[22] At higher temperatures, the ^{1}H NMR signals become too broad to be able to recognize different conformations.

[23] W. J. Moore, *Physical Chemistry*, 4th ed., Prentice–Hall, London, **1980**.

[24] H.-R. Tseng, S. A. Vignon, P. C. Celestre, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **2003**, *9*, 543–556.

[25] P. R. Ashton, E. J. T. Chrystal, T. T. Goodnow, A. E. Kaifer, K. P. Parry, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, D. J. Williams, *J. Chem. Soc. Chem. Commun.* **1991**, 634–639.

[26] For an example of acid-induced *cis/trans* isomerization of a TTF derivative, see: A. Souizi, A. Robert, *J. Org. Chem.* **1987**, *52*, 1610–1611.

[27] For examples of *cis/trans* isomerizations of TTF derivatives induced electrochemically, see: a) K. Boubekeur, C. Lenoir, P. Batail, R. Carlier, A. Tallec, M.-P. Le Paillard, D. Lorcy, A. Robert, *Angew. Chem.* **1994**, *106*, 1448–1450; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1379–1381; b) J. Lau, P. Blanchard, A. Riou, M. Jubault, M. P. Cava, J. Becher, *J. Org. Chem.* **1997**, *62*, 4936–4942.

[28] For examples of light-induced *cis/trans* isomerizations of a TTF derivative, see a) Y. N. Kreitsberga, E. E. Liepinsh, I. B. Mazheika, O. Y. Neilands, *Zh. Org. Khim.* **1986**, *22*, 416–420; b) R. Ballardini, V. Balzani, J. Becher, A. Di Fabio, M. T. Gandolfi, M. Gunter, M. B. Nielsen, F. M. Raymo, S. J. Rowan, J. F. Stoddart, A. J. W. White, D. J. Williams, *J. Org. Chem.* **2000**, *65*, 4120–4126.

[29] Surprisingly, no conceivable change is observed when a solution of the same sample in CD_3COCD_3 is kept in the dark for two months.

[30] R. Wolf, M. Asakawa, P. R. Ashton, M. Gómez-López, C. Hamers, S. Menzer, I. W. Parsons, N. Spencer, J. F. Stoddart, M. S. Tolley, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1018–1022; *Angew. Chem. Int. Ed.* **1998**, *37*, 975–979.

[31] S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem.* **2002**, *114*, 938–993; *Angew. Chem. Int. Ed.* **2002**, *41*, 898–952.

[32] G. Trippe, E. Levillain, F. Le Derf, A. Gorgues, M. Salle, J. O. Jeppesen, K. Nielsen, J. Becher, *Org. Lett.* **2002**, *4*, 2461–2464.

[33] C. Bustamante, D. Keller, G. Oster, *Acc. Chem. Res.* **2001**, *34*, 412–420.

[34] D. S. Goodsell, *Our Molecular Nature: The Body's Motors, Machines, and Messages*, Copernicus, New York, **1996**.

[35] E. M. Purcell, *Am. J. Phys.* **1977**, *45*, 3–11.

[36] a) R. D. Astumian, *Phil. Trans. R. Soc. Lond.* B **2000**, *355*, 511–522; b) R. D. Astumian, *Sci. Am.* **2001**, *285*, 56–64.

[37] P. T. Glink, J. F. Stoddart, *Pure Appl. Chem.* **1998**, *70*, 419–424.

[38] P.-L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 193–218.

[39] W. Devonport, M. A. Blower, M. R. Bryce, L. M. Goldenberg, *J. Org. Chem.* **1997**, *62*, 885–887.

[40] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, New York, **1998**.

[41] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85–277.

[42] A. Babaei, P. A. Connor, A. J. McQuillan, S. Umapathy, *J. Chem. Educ.* **1997**, *74*, 1200–1204.

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