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A Tuneable Self-Complexing Molecular Switch

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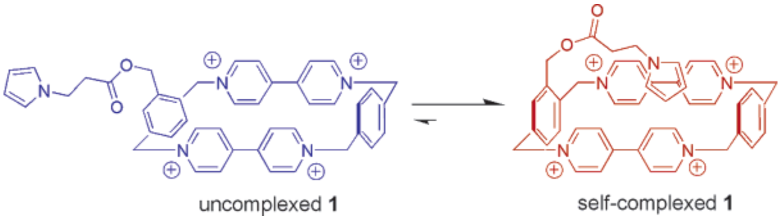
ABSTRACT



A new self-complexing donor–acceptor system has been synthesized that has the propensity to undergo intramolecular decomplexation under thermal and electrochemical perturbation and upon addition of a competitive guest for the cyclophane's cavity.

Self-complexing systems fabricated using complementary donor−acceptor interactions have received considerable attention over the past few years.[1] Supramolecules of this type are of interest due to their intrinsic topology and ability to undergo controllable intramolecular complexation, making them possible candidates for constructing rudimentary molecular machines and devices.[2] Donor-acceptor self-complexing supramolecules have been prepared by attaching an electron-rich arm containing either a 1,5-dioxynaphthalene unit or a tetrathiafulvalene (TTF) unit to the electron-deficient cyclophane cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$). Here, we report a new class of $CBPQT^{4+}$-based self-complexing system whereby the arm contains a pyrrole moiety as the electron-rich unit. Furthermore, we report that the self-complexing properties of this system can be disrupted thermally, electrochemically, and by the addition of a more effective guest for the cyclophane's cavity.

Scheme 1 outlines the synthesis of **1**. Reduction of **2**,[1a] using diisobutylaluminum hydride (DIBAL-H) as reducing agent, afforded the corresponding alcohol **3** in good yield. Subsequent esterification of **3** with acid **4**[3] furnished compound **5**. Formation of the cyclophane was achieved using the clipping methodology, by stirring **5** and salt **6**[4] in the presence of template **7** in DMF at room temperature for 10 days. Compound **1** was separated by column chromatography (SiO_2, $MeOH/NH_4Cl/MeNO_2$) and isolated, after

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(1) For examples, see: (a) Ashton, P. R.; Ballardini, R.; Balzani, V.; Boyd, S. E.; Credi, A.; Gandolfi, M. T.; Gómez-López, M.; Iqbal, S.; Philp, D.; Preece, J. A.; Prodi, L.; Ricketts, H. G.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1997**, *3*, 152−170. (b) Nielsen, M. B.; Nielsen, S. B.; Becher, J. *Chem. Commun.* **1998**, 475−476. (c) Nielsen, M. B.; Hansen, J. G.; Becher, J. *Eur. J. Org. Chem.* **1999**, 2807−2815. (d) Liu, Y.; Flood, A. H.; Stoddart, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 9150−9151. (e) Liu, Y.; Flood, A. H.; Moscowitz, R. M.; Stoddart, J. F. *Chem. Eur. J.* **2005**, *11*, 369−385.

(2) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines: A Journey into the Nano World*; Wiley-VCH: Weinheim, 2003.

(3) Pickett, C. J.; Ryder, K. S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2181−2189.

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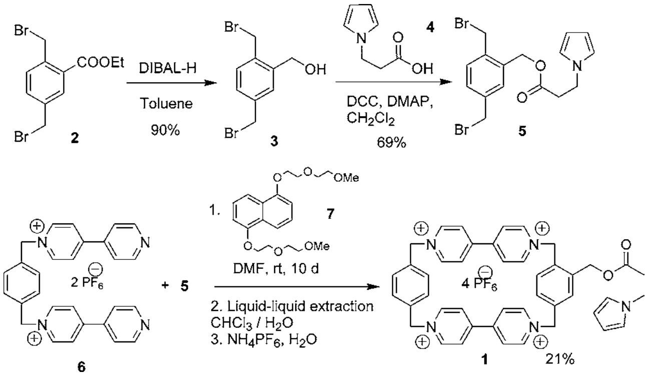
Scheme 1



exchanging the Cl^- counterions of the cyclophane with NH_4PF_6, as an orange-red solid (see the Supporting Information).

The pale orange/red color of **1** in the solid and solution state prompted us to investigate whether the electron-rich pyrrole unit complexes with the $CBPQT^{4+}$ moiety. X-ray quality crystals were obtained by slow evaporation of solvent from a concentrated solution of **1** in acetonitrile/methanol (Figure 1 and the Supporting Information). The structure clearly indicates that the system forms a dimer in the solid-state, with the pyrrole units being located within the electron-deficient cavity of the cyclophane moiety of another molecule of **1**.

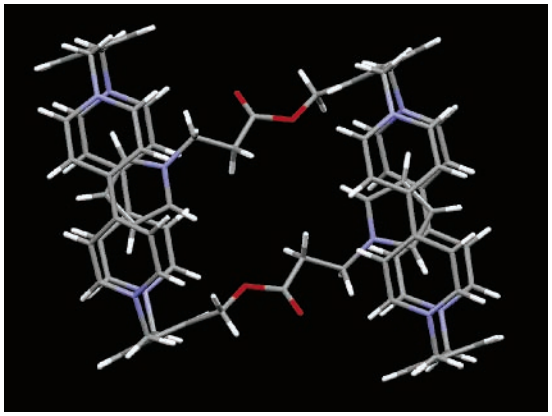


Figure 1. X-ray crystal structure of **1**.

To obtain insight into the structure of **1** in solution, UV−vis spectroscopy, 1D NMR, and 2D NOESY experiments were undertaken. The absorption spectrum of **1** recorded in CH_3CN at 298 K shows a broad band in the visible region ($\lambda_{max} = 433$ nm, $\epsilon = 677$ $M^{-1}cm^{-1}$) resulting from charge-transfer (CT) interactions between the pyrrole moiety and the π-electron-deficient bipyridinium units of the cyclophane (Figure 2). The absorbance of **1** decreased linearly upon dilution (within the concentration range 4×10^{-3} to 5×10^{-5} M, see the Supporting Information), suggesting the presence of a intramolecular equilibrium and the absence of higher order equilibria. Moreover, significant concentration dependence was not observed in the ^1H NMR spectrum of **1** recorded in CD_3CN (10^{-2}−10^{-4}M, $\Delta\delta < 0.1$ ppm), further suggesting the absence of intermolecular complexation in the solution state (see the Supporting Information). Thus, it is unlikely that supramolecular oligomers of **1** are formed in solution to any significant extent under the conditions examined, which is in contrast to its structure in the solid state, where intermolecular complexation is clearly observed.

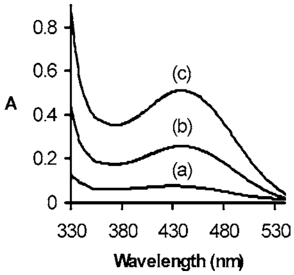


Figure 2. Selected UV−vis spectra of **1** recorded at the following concentrations in CH_3CN at 298 K: (a) 0.1 mmol, (b) 0.4 mmol, (c) 0.8 mmol.

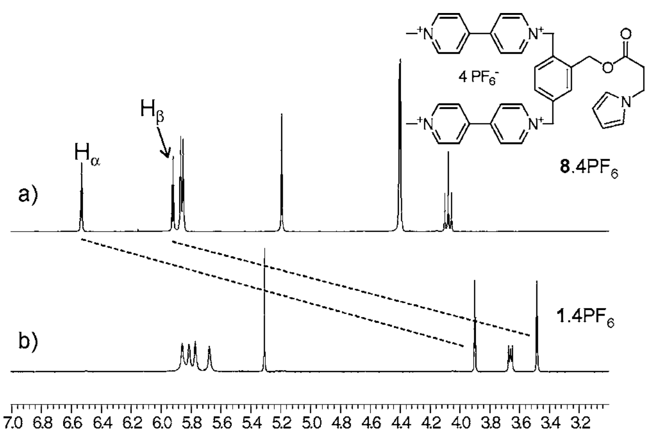


Figure 3. Partial ^1H NMR spectra of (a) **8** and (b) **1** recorded in CD_3CN at 298 K, showing the relative position of protons H_α and H_β of their pyrrole moieties.

The most important features of the ^1H NMR spectra of **1** recorded in CD_3CN at 298 K are summarized in Figure 3. First, the two pyrrole proton resonances (H_α, H_β) are centered at unusually high fields of 3.90 and 3.48 ppm, respectively, compared to those belonging to the "open" model **8** and *N*-methylpyrrole, suggesting that the pyrrole ring is located

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

inside the cavity of the tetracationic cyclophane. Second, the lack of “uncomplexed” pyrrole proton resonances between 6 and 7 ppm indicate a fast equilibrium, at least on ^{1}H NMR time scale, between the “self-complexed” and the “uncomplexed” forms of **1**.

The presence of the pyrrole moiety inside the cavity has been confirmed using 2D NOESY spectroscopy recorded in CD_3COCD_3 at 298 K (Figure 4). The spectrum exhibits several cross-peaks between both the H_α and H_β protons of the pyrrole moiety and either the phenylene protons (H_i, H_q) or those belonging to the viologen moieties (H_e, H_o, H_f, H_g) of **1**, suggesting that the pyrrole moiety probably adopts an average position close to the center of the cavity. This hypothesis is also supported by the strongest dipolar correlation observed between the H_β and the H_f protons. Moreover, the lack of dipolar correlations between the protons H_1 and H_2 of the pendant arm and the protons of the tetracationic macrocycle indicates that the pyrrole part is not deeply included in the cyclophane’s cavity (Figure 4).

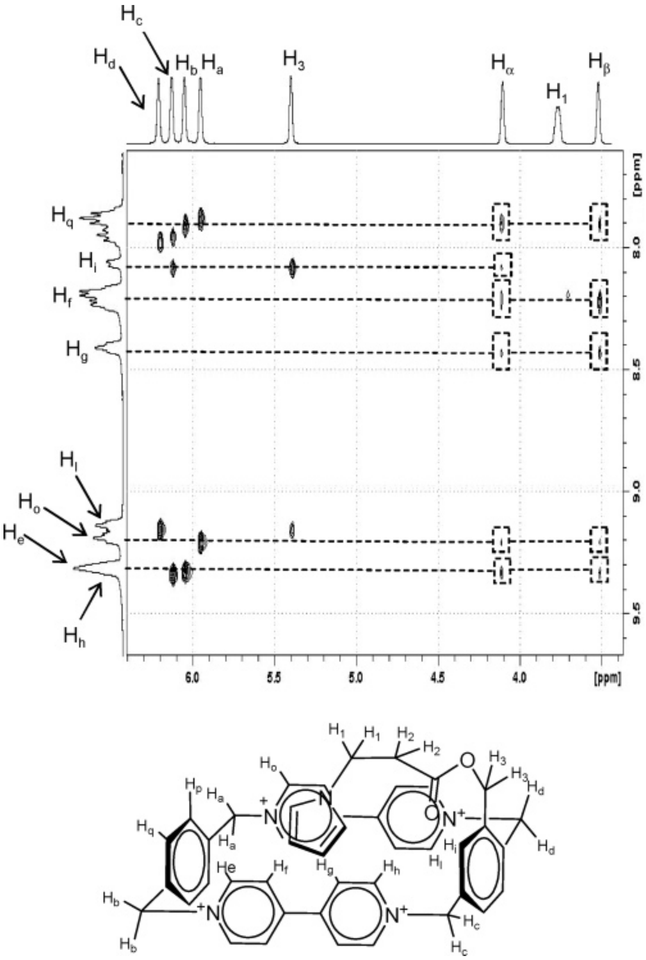

Figure 4. Partial 2D NOESY NMR spectra of **1** recorded in CD_3-$COCD_3$ at 298 K and a representation of the possible geometry of **1** in its self-complexed form.

With self-complexation confirmed for **1**, we next turned our attention to whether complex formation could be controlled using an external stimulus. The fast in−out isomerism of the pyrrole arm has been characterized by variable-temperature ^{1}H NMR spectroscopy (see the Supporting Information). Indeed, by comparison of spectra recorded at 298 K, lowering the temperature of **1** to 203 K causes a significant upfield shift in the chemical shift of the pyrrole protons, indicating the displacement of the equilibria toward the formation of the self-complexed conformation. In contrast, increasing the temperature results in a downfield shift of the pyrrole protons indicating decomplexation occurs. This process could also be monitored spectrophotometrically by recording the UV−vis spectra at different temperatures, which showed that a gradual loss of the charge-transfer absorption occurred as the temperature is increased from ambient temperature. Thus, the data are consistent with decomplexation occurring upon heating **1** above room temperature.

As an alternative strategy for disrupting self-complexation of **1**, we have exploited the well-documented ability of reducing the $CBPQT^{4+}$ unit to its diradical dicationic state to induce pseudorotaxane dethreading.[4] To investigate this, we have compared the cyclic and square wave voltammograms of separate solutions of model compound **9** and **1** in acetonitrile (0.1 M Bu_4NPF_6). These studies indicated that the first reduction wave of **1** occurred at a 32 mV more negative potential than that of **9** (which lacks a pyrrole moiety), presumably due to donor−acceptor interactions between the pyrrole and cyclophane moieties stabilizing the

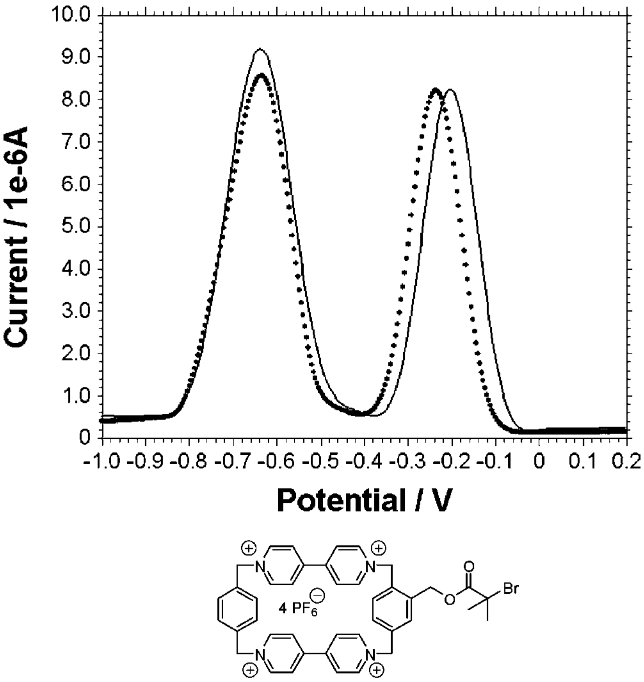

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Figure 5. Square wave voltammograms of **9** (−) and **1** (···). Step potential = 0.004 V; pulse amplitude = 0.025 V; quiet time = 2 s.

diradical dication state of the latter (Figure 5).[5] The half-wave potential of the second reduction wave is largely unaffected, indicating the pyrrole unit dethreads when the cyclophane is first reduced.

Finally, we have explored the addition of TTF to disrupt self-complexation, as it is well established that TTF is an effective guest for $CBPQT^{4+}$-based cyclophanes.[6] Addition of aliquots of TTF to a cuvette containing **1** immediately resulted in the appearance of an emerald-green solution characteristic of TTF−$CBPQT^{4+}$ complexes, resulting from a charge-transfer band centered around 870 nm (Figure 6).

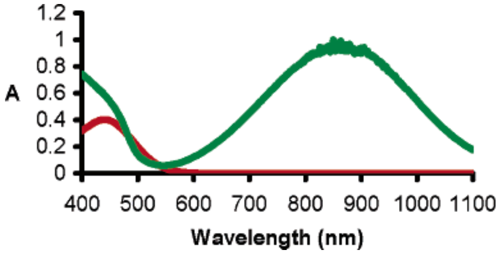

Figure 6. UV−vis spectra of **1** (−) (6.5×10^{-4} M) in CH_3CN and upon the addition of 1 equiv of TTF (−).

This process was also monitored using ^1H NMR spectroscopy and revealed a downfield shift for the H_α and H_β pyrrole protons and a concomitant upfield shift for the TTF protons (compared to the NMR spectra of TTF recorded in CD_3CN) upon addition of aliquots of the latter (see the Supporting Information). Thus, the UV−vis and NMR data are consistent with the TTF unit disrupting self-complexation by forming a pseudorotaxane with the $CBPQT^{4+}$ moiety of **1**.

In conclusion, we have shown that compound **1** self-complexes in solution. Furthermore, by applying an external stimuli in the form of heat, electrochemical reduction or the addition of a completing guest for the cyclophane's cavity, we have shown that self-complexation can be disrupted. Further work in our laboratory will investigate the complex formation between $CBPQT^{4+}$ and noncovalently linked pyrrole units (and their oligomers) and the electropolymerization of the pyrrole moiety of **1** to furnish surface-confined electrochemically tuneable $CBPQT^{4+}$ host units.

Acknowledgment. We thank the EPSRC for funding this work.

Supporting Information Available: Full synthetic details pertaining to the preparation of **1**. Characterization of **1** using single-crystal X-ray diffraction, UV−vis, and NMR spectroscopies and electrochemistry. This material is available free of charge via the Internet at http://pubs.acs.org.

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[5] All electrochemical experiments were performed using a CH Instruments 620A electrochemical workstation. The electrolyte solution (0.1 M) was prepared from recrystallized Bu_4NPF_6 using spectroscopic grade CH_3CN. A three-electrode configuration was used with a 2 mm diameter Pt disc working electrode, a Ag/AgCl reference electrode, and a platinum wire as the counter electrode. The solution was vigorously purged with nitrogen prior to recording the electrochemical data. All voltammetry measurements were recorded under a nitrogen atmosphere.

[6] For examples, see: (a) Devonport, W.; Blower, M. A.; Bryce, M. R.; Goldenberg, L. M. *J. Org. Chem.* **1997**, *62*, 885−887. (b) Ashton, P. R.; Balzani, V.; Becher, J.; Credi, A.; Fyfe, M. C. T.; Mattersteig, G.; Menzer, S.; Nielsen, M. B.;. Raymo, F. M.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 3951−3957. (c) Nielsen, M. B.; Jeppesen, J. O.; Lau, J.; Lomholt, C.; Damgaard, D.; Jacobsen, J. P.; Becher, J.; Stoddart, J. F. *J. Org. Chem.* **2001**, *66*, 3559−3563.