Thermally and Electrochemically Controllable Self-Complexing Molecular Switches

Yi Liu, Amar H. Flood, and J. Fraser Stoddart*

California Nanosystems Institute and Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095-1569

Received March 30, 2004; E-mail: stoddart@chem.ucla.edu

Self-complexing molecules[1] represent an interesting class of compounds in the field of molecular recognition. Their molecular structures often have an arm component covalently linked to a macrocycle with sufficient flexibility such that the arms can be included inside the macrocycle's cavity by virtue of stabilizing noncovalent bonding interactions. Such compounds are attractive not only on account of their topology, but also because of their potential to undergo reversible movement of the arm into and out of the macrocycle's cavity in response to a particular stimulus, rendering them viable candidates for constructing nanoscale molecular machinery.[2]

Several groups have developed[1c−e] self-complexing systems wherein a π-donor in the form of 1,5-dioxynaphthalene (DNP) or tetrathiafulvalene (TTF) units resides in arms that are attached covalently to the π-accepting cyclophane, cyclobis(paraquat-*p*-phenylene) (CBPQT[4+]).[3] The π-donor is self-complexed by the π-accepting cyclophane as a result of a combination of $[\pi\cdots\pi]$ stacking[4] and $[C-H\cdots\pi]$[5] and $[C-H\cdots O]$ interactions.[6] In most of the existing systems, however, these intramolecular interactions are either too strong or too weak, creating a situation where control over the movement of the arm in and out of the cavity is inefficient at best. In this communication we demonstrate that, by fine-tuning the structures of these molecules, their self-complexing abilities can be changed delicately and dramatically. Indeed, these in-and-out movements can be made highly sensitive to temperature and applied voltages, rendering the systems potential thermosensors and electroswitches.

Compounds **1·4PF$_6$** and **2·4PF$_6$** contain (Scheme 1) DNP and TTF units, respectively, in their arms, which are attached by a spacer to a diimide fused symmetrically onto the CBPQT[4+] ring. This

Scheme 1. Equilibria between the "Uncomplexed" (**UC**) and Self-Complexed (**SC**) Conformations of **1·4PF$_6$** and **2·4PF$_6$** in Solution
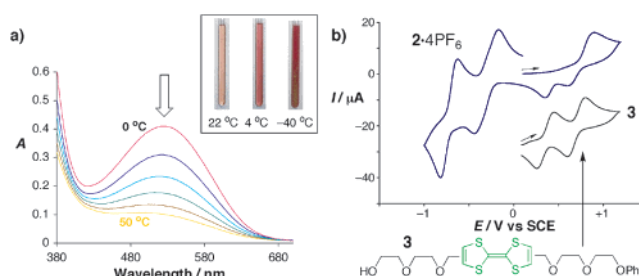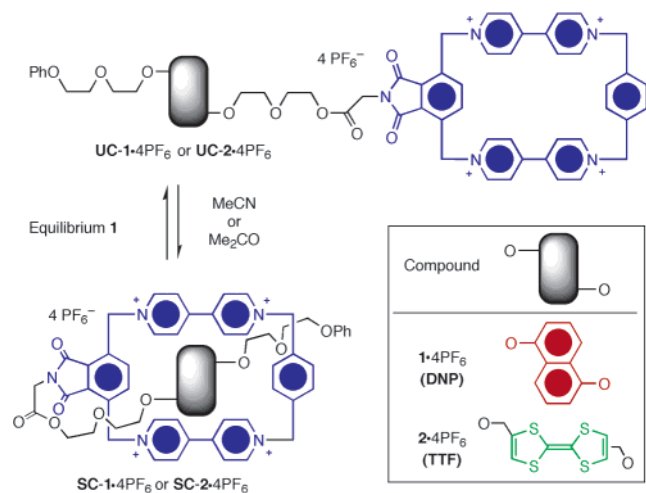
Figure 1. (a) Variable temperature UV/vis absorption spectra of **1·4PF$_6$** recorded in MeCN (1.0×10^{-3} M) from 0 °C (pink) to 50 °C (yellow). The inset illustrates the changes in color of this same solution going from +22 °C down to +4 °C and then down to −40 °C. (b) Cyclic voltammograms of the oxidation and reduction of **2·4PF$_6$** and the oxidation of the control **3** recorded at 1000 mV s^{-1} in a 0.1 M TBAPF$_6$ MeCN solution at room temperature with a glassy carbon electrode.

diimide moiety also serves to increase the distances between the donors and acceptors, as well as simplifying the spectroscopic analyses. As shown in Scheme 1, an equilibrium is rapidly established for each compound in either MeCN or Me$_2$CO solutions. The equilibrium between "uncomplexed" (**UC**) and self-complexed (**SC**) conformations was measured by titration experiments employing UV/vis and ^{1}H NMR spectroscopies. The absorption UV/vis spectrum (Figure 1a) of **1·4PF$_6$** recorded in MeCN shows a broad charge-transfer (CT) band in the visible region ($\lambda_{max} = 521$ nm), a feature which is characteristic of donor−acceptor interactions involving DNP/CBPQT[4+]. Linear correlations (see Supporting Information) between absorption and concentration over the range 3.6×10^{-3} to 2.8×10^{-5} M are observed, suggesting the presence of a unimolecular equilibrium and the absence of higher order equilibria. The ^{1}H NMR spectra of **1·4PF$_6$** recorded in CD$_3$CN (298 K) and CD$_3$COCD$_3$ (243 K) show no concentration dependence from 3.11×10^{-2} down to 9.70×10^{-4} M. It is unlikely, therefore, that supramolecular oligomers are formed to any significant extent under the conditions examined. The same conclusion was reached for **2·4PF$_6$**.

As evidenced by variable temperature UV/vis spectroscopy, equilibrium 1 (see Scheme 1) between **UC-1·4PF$_6$** and **SC-1·4PF$_6$** in MeCN solution is highly sensitive to changes in temperature. Since the **UC** conformation is colorless and the **SC** one is purple, a thermoreversible color change is observed as a result of these thermally induced conformational changes in **1[4+]**. Figure 1a shows that, as the temperature is increased from 0 to +50 °C, the intensity of the CT band centered on $\lambda_{max} = 521$ nm decreases, in keeping with equilibrium 1 shifting more toward **UC-1·4PF$_6$**. The inset illustrates visually the color changes; namely, the purple color becomes more intense as the temperature of the MeCN solution is lowered from +22 through +4 to −40 °C. The temperature-dependent color change is completely reversible and can be recycled many times. In contrast, the TTF-bearing **2·4PF$_6$** displays very small

temperature-dependent spectroscopic change in the temperature range +10 to +50 °C with an intense green color[7] persisting throughout.[8]

Although temperature is more or less ineffective in controlling the movement of the TTF arm in SC-2[4+], both chemical and electrochemical methods work well. The reason is that 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[•+] or TTF[2+]—and "on" by their reduction back to the neutral form. The chemical redox cycle has been monitored (Figure 2) by ^{1}H NMR spectroscopy at 253 K in CD_3COCD_3 solution. The TTF unit in SC-2·4PF$_6$ is observed (Figure 2a) to be a 2:3 mixture ($\delta = 6.0-7.0$ ppm) of cis/trans-isomers. The ^{1}H NMR spectrum is characteristic of a conformation for SC-2[4+] with average C_s symmetry. No resonances are detected for UC-2·4PF$_6$. Upon addition of 2 equiv of tris(p-bromophenyl)aminium hexachloroantimonate[9] into the CD_3COCD_3 solution of 2·4PF$_6$, a much simpler spectrum (Figure 2b) is observed, indicating that, upon oxidation, the TTF[2+] dication no longer resides inside the CBPQT[4+] cavity and its protons resonate at $\delta = 9.83$ ppm. The remainder of the spectrum is commensurate with the UC-2[6+] conformation having average C_{2v} symmetry. When Zn dust is added to the NMR tube, the original spectrum is regenerated (Figure 2c), indicating a return to the SC-2[4+] conformation with the neutral TTF unit back inside the cavity of the CBPQT[4+] ring.
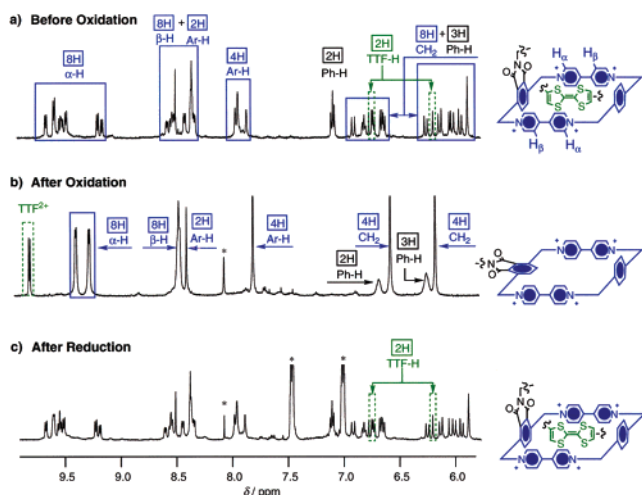
Figure 2. Partial ^{1}H NMR spectra of 2·4PF$_6$ recorded in CD_3COCD_3 at 253 K (a) before oxidation, (b) after addition of 2 equiv of tris(p-bromophenyl)aminium hexachloroantimonate, and (c) after addition of Zn dust as a reductant. The resonances indicated by an asterisk arise from the oxidant.

Cyclic voltammetry (CV) of 2·4PF$_6$ in MeCN reveals its electrochemical switching behavior associated with the TTF-based oxidations.[10] At a scan rate of 1000 mV s^{-1}, the CV displays (Figure 1b) only one two-electron anodic peak at +0.91 V vs SCE, together with the two single-electron cathodic peaks on the return sweep. The behavior differs from that of the control 3 (Figure 1b), which displays two reversible, well-separated one-electron oxidation processes at +0.36 and +0.70 V vs SCE. The CV indicates that the TTF arm in SC-2[4+] undergoes oxidative dethreading in concert with the direct production of the TTF[2+] dicationic form and that it rethreads following formation of the charge-neutral TTF unit.

In conclusion, we have demonstrated the operation of simple molecular switches, based on self-complexing donor−acceptor pairs. The switching can be effected thermally (1[4+]) as an equilibrium event and electrically (2[4+]) as a reaction process. In addition to the obvious applications 1[4+] and 2[4+] could find as thermo- and electroswitches, the thermochromism associated with equilibrium 1 could lead to compounds such as 1·4PF$_6$ having futures as imaging and sensing materials.

Supporting Information Available: Experimental details and spectroscopic data of 1·4PF$_6$ and 2·4PF$_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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