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Poised on the Brink between a Bistable Complex and a Compound

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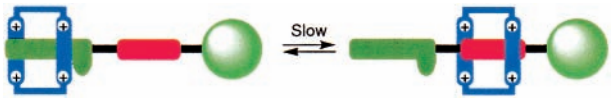
ABSTRACT



An enmeshed supramolecular complex, based on a semi-dumbbell-shaped component containing an asymmetrically substituted tetrathiafulvalene site and a 1,5-dioxynaphthalene site for encirclement by a cyclobis(paraquat-*p*-phenylene) ring component and with a "speed bump" in the form of an thiomethyl group situated between the two recognition sites, has been self-assembled. This complex is a mixture in acetone solution of two slowly interconverting [2]pseudorotaxanes, one of which is on the verge of being a [2]rotaxane at room temperature.

The advent of supramolecular chemistry has aroused the interest of chemists of many different persuasions in compounds such as catenanes and rotaxanes.[1] The synthetic guidance provided by noncovalent bonds has transformed these interlocked molecular compounds from chemical curiosities into a vibrant area of modern-day research. They are now prime candidates for the construction of artificial molecular machines[2] and the fabrication of molecular electronic devices.[2b,3] Much effort has been devoted during the past two decades to trying to understand and control the use of noncovalent interactions in the synthesis of catenanes and rotaxanes.

A [2]rotaxane is a molecule composed of a ring and dumbbell-shaped component.[1] The ring encircles the linear portion of the dumbbell-shaped component and is trapped mechanically around it by two bulky stoppers. By contrast, in a [2]pseudorotaxane,[1] at least one of the stoppers on the dumbbell-shaped component is absent with the consequence that dissociation into its two components can occur spontaneously, i.e., it behaves like a 1:1 complex. Slipping of macrocycles over the bulky stoppers of dumbbell-shaped components has been used sparingly[4] to self-assemble rotaxanes in solution under thermodynamic control. Judicious[4e] choice of the constitutions and the sizes of the slippage stoppers and the macrocycle's cavity is essential in order to reach that fine balance between the system being capable of slippage and not. When such a balance is achieved, the macrocyclic component will possess sufficient thermal energy in solution just above room temperature to permit its slow passage over the slippage stopper. In this regard, it has been concluded[5] that a well-defined cutoff between

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rotaxanes and pseudorotaxanes does not exist.[6] In this Letter, we present a rare example of "piggy-back" supramolecular assistance leading to the formation in solution of two nonidentical [2]pseudorotaxanes, one of which is on the brink of becoming a [2]rotaxane. We have reported previously[7] that slow "internal" passage of the macrocyclic ring component, cyclobis(paraquat-*p*-phenylene) $CBPQT^{4+}$, over an SMe group occurs (Figure 1a) in the amphiphilic bistable [2]rotaxane $\mathbf{1}^{4+}$. Here, we record the results of kinetic and thermodynamic studies between semi-dumbbell-shaped compound **2** and $CBPQT^{4+}$ (Figure 1b). Compound **2** contains two different recognition sites—a tetrathiafulvalene (TTF) unit and a 1,5-dioxynaphthalene (DNP) ring system—for $CBPQT^{4+}$ along with a "speed bump" in the form of an SMe group situated on the rod section between the two recognition sites.

The inclusion of TTF derivatives inside the cavity of $CBPQT^{4+}$ is well documented[8] and leads to the formation of pseudorotaxanes[1] under thermodynamic control upon mixing of their acyclic and cyclic components in solution. The occurrence of the threading process is evidenced by the ^{1}H NMR and absorption spectra.[8,9] As a model system for **2**·$CBPQT{\cdot}4PF_6$, we chose to investigate the complexation (Figure 2) of $CBPQT^{4+}$ with **3** containing only a monopyrrolo-TTF unit on its rod section. Mixing equimolar proportions of the semi-dumbbell-shaped compound[3d,10] **3** and the

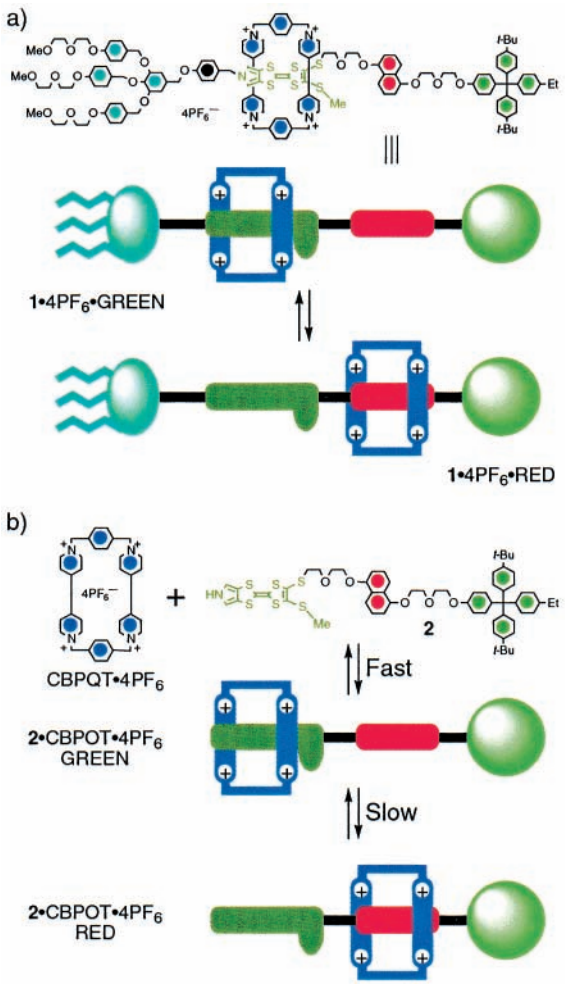

Figure 1. (a) Hindered interconversion in a "slow" bistable amphiphilic [2]rotaxane. (b) Self-assembly of the bistable [2]-pseudorotaxane **2**·$CBPQT{\cdot}4PF_6$·GREEN and its slow interconversion to **2**·$CBPQT{\cdot}4PF_6$·RED.

tetracationic cyclophane[11] $CBPQT^{4+}$ in Me_2CO leads to the formation of the [2]pseudorotaxane **3**·$CBPQT^{4+}$, as shown by the immediate formation of a green-colored solution and the appearance of a broad charge transfer (CT) band centered on 805 nm in the UV−vis spectrum (Me_2CO, 298 K), a situation which is characteristic[8] of superstructures containing

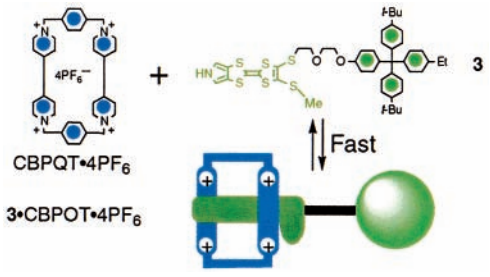

Figure 2. Complexation of **3** by $CBPQT{\cdot}4PF_6$.

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(6) The distinction between rotaxanes and pseudorotaxanes is far from being a straightforward one. When size-complementarity between the stoppers and the macrocyclic component is achieved, certain "rotaxanes" behave as pseudorotaxanes and can dissociate into their constituent components under appropriate conditions. Thus, a species which is a rotaxane at ambient temperature might well be a pseudorotaxane at elevated temperatures. Even a solvent change can turn a rotaxane into a pseudorotaxane at the same temperature. See: (a) Raymo, F. M.; Stoddart, J. F. *Chem. Rev.* **1999**, *99*, 1643−1663. (b) Chiu, S.-H.; Rowan, S. J.; Cantrill, S. J.; Glink, P. T.; Garrell, R. L.; Stoddart, J. F. *Org. Lett.* **2000**, *2*, 3631−3634.

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a TTF unit located inside CBPQT^{4+}. A UV−vis dilution experiment[12] was carried out to determine the binding constant for the 1:1 complexation of CBPQT^{4+} with **3** in Me_2CO at 298 K. The complexation of **3** by CBPQT^{4+} was followed by correlating the maximum absorptions of the CT bands with the absolute concentrations of the components.[8b] The binding constant (K_a), which was calculated to be 1300 ± 200 M^{-1} (ϵ = 1310 L mol^{-1} cm^{-1}) in Me_2CO at 298 K, corresponds to a free energy of complexation[12] ($-\Delta G°$) of 4.2 kcal mol^{-1}. In the case of the 1:1 complex, exchange between the complexed and uncomplexed species occurs rapidly (Figure 3a) on the ^{1}H NMR time scale (CD_3COCD_3, 500 MHz) at 300 K. Thus, the chemical shifts of the observed resonances are the average values between those for the uncomplexed and those for the complexed species. On cooling the CD_3COCD_3 solution down to 170 K, the kinetics enter the regime of slow exchange and both complexed and uncomplexed species can be observed (Figure 3c) in the ^{1}H NMR spectrum. The local asymmetry present in the monopyrrolo-TTF unit is responsible for the desymmetrization of the complexed CBPQT^{4+} ring. It results, for example, in four doublets (J = 6−7 Hz) being observed for the α-bipyridinium protons in **3**·CBPQT^{4+}. At 255 K, fast exchange is reestablished (Figure 3b) between the complexed and uncomplexed species. Figure 3c reveals that the cyclophane protons show significant shifts in their resonances upon complexation, an observation which makes it possible to determine the K_a value at 170 K using the single-point method.[12] A K_a value of 11 500 M^{-1} for the complexation of **3** by CBPQT^{4+} in CD_3COCD_3 at 170 K was obtained. The associated $\Delta G°$ value is −3.2 kcal mol^{-1} at this temperature.

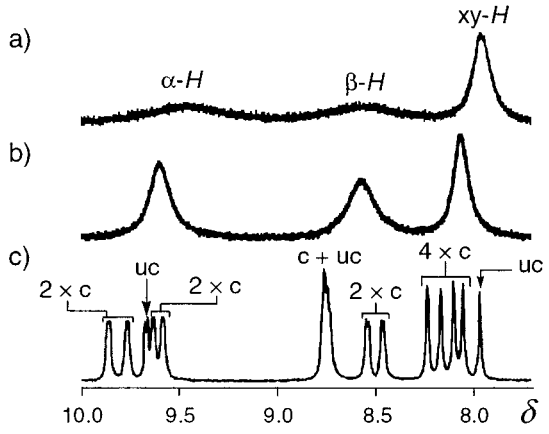

Figure 3. Partial (cyclophane region) ^{1}H NMR spectra (500 MHz) of the complex formed between CBPQT^{4+} and the semi-dumbbell **3** in CD_3COCD_3 at (a) 300 K, (b) 255 K, and (c) 170 K. The descriptions c and uc refer to complexed and uncomplexed CBPQT^{4+} components, respectively. Spectra were recorded on a 1.73×10^{-3} M solution of CBPQT^{4+} (equal to that of **3**). The ratio between the integrals of complexed CBPQT^{4+} and uncomplexed CBPQT^{4+} was 4:1 in favor of the complexed CBPQT^{4+} at 170 K.

Mixing equimolar amounts of the semi-dumbbell-shaped compound[7] **2** and CBPQT^{4+} in Me_2CO leads to the formation (Figure 1b) of **2**·CBPQT·4PF_6·GREEN, as evidenced by the spontaneous production of a green-colored solution. The UV−vis spectrum (Figure 4a) recorded at 296 K in Me_2CO of this solution showed, immediately after its preparation, a broad band centered on 805 nm as a result of the CT interactions that occur when CBPQT^{4+} encircles[8] the TTF unit. Allowing the green solution to stand for 24 h at room temperature produced a brown solution. The UV−vis spectrum recorded (Figure 4c) on this solution revealed a CT band centered on 805 nm, together wth the appearance of a shoulder at 540 nm, a feature which results from the DNP ring system being located inside the cyclophane.[13] It indicates that a partial interconversion of **2**·CBPQT·4PF_6·GREEN into **2**·CBPQT·4PF_6·RED has taken place. The kinetics of the movement of CBPQT^{4+} from the TTF to the DNP recognition site were investigated using UV−vis spectroscopy. Immediately after mixing equimolar amounts of CBPQT^{4+} and **2**, a UV−vis spectrum was recorded (Figure 4a) and the movement of CBPQT^{4+} from the TTF to the DNP recognition site was followed at 296 K using the TTF−CBPQT^{4+} CT band (805 nm) as the probe. After 24 h, the system had reached equilibrium and no perceptible changes were observed in UV−vis spectra recorded subsequently. The experimental data were subject to a first-order analysis[12] and a rate constant (k = 2.4 × 10^{-5} s^{-1}) was obtained for the passage of CBPQT^{4+} over the SMe group in the direction from **2**·CBPQT·4PF_6·GREEN to **2**·CBPQT·

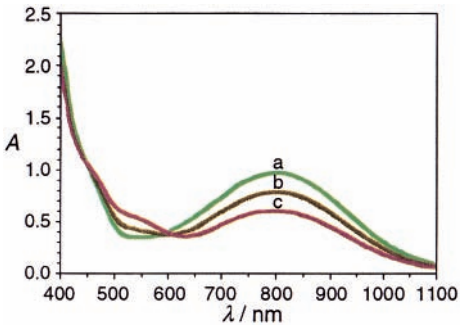

Figure 4. Absorption spectra recorded in Me_2CO at 296 K on a 1:1 mixture of **2** and CBPQT·4PF_6 immediately after their mixture (trace a), after 2.5 h (trace b), and after 24 h (trace c).

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$4PF_6$·RED in Me_2CO at 296 K. The corresponding free energy of activation[12] ($\Delta G^{\ddagger}$) for this co-conformational change is 24 kcal mol^{-1}.

Thin-layer chromatography (TLC) of the equilibrated brown solution containing **2**·CBPQT·$4PF_6$·GREEN and **2**·CBPQT·$4PF_6$·RED showed—besides a yellow and a colorless spot arising from **2** and $CBPQT^{4+}$, respectively—only a red spot, thus indicating that **2**·CBPQT·$4PF_6$·RED may be isolated as a rotaxane-like complex, while **2**·CBPQT·$4PF_6$·GREEN dissociates into its components (i.e., **2** and $CBPQT^{4+}$) on the time scale of the TLC experiment performed on silica gel. By employing flash column chromatography, it was possible to isolate the red co-conformation **2**·CBPQT·$4PF_6$·RED. The UV−vis spectrum (Figure 5a) of **2**·CBPQT·$4PF_6$·RED reveals a CT band in the form of a shoulder at 540 nm. It results from the DNP ring system being located inside[13] $CBPQT^{4+}$. Furthermore, no absorption band is observed in the region 750−850 nm for a CT interaction that would result from the TTF unit being located inside the cyclophane,[8] supporting the conclusion that the DNP ring system in the semi-dumbbell-shaped component is encircled exclusively by $CBPQT^{4+}$. Allowing the red solution of **2**·CBPQT·$4PF_6$·RED to stand for 24 h at 296 K results in a return to the "original" spectrum (Figure 5c) as a consequence of the passage of $CBPQT^{4+}$ from the DNP to the TTF recognition site. The first-order kinetics of this passage wherein $CBPQT^{4+}$ moves from the DNP to the TTF recognition site of **2**·CBPQT·$4PF_6$ were investigated using UV−vis spectroscopy. Immediately after isolation of **2**·CBPQT·$4PF_6$·RED, a UV−vis spectrum was recorded and the passage of $CBPQT^{4+}$ from the DNP to the TTF recognition site was followed (Figure 5a−c) at 296 K using the DNP−$CBPQT^{4+}$ CT band (540 nm) as probe. After 24 h, the system reached equilibrium and no perceptible changes were observed in UV−vis spectra recorded subsequently. As a consequence of the spectroscopic behavior, the color of the solution goes from red to brown. On carrying out a first-order kinetic analysis,[12] a rate constant ($k = 2.5 \times 10^{-5}$ s^{-1}) for the passage of $CBPQT^{4+}$ over the SMe group in the direction from **2**·CBPQT·$4PF_6$·RED to **2**·CBPQT·$4PF_6$·GREEN can be obtained. The $\Delta G^{\ddagger}$ value[12] for this co-conformational change is 24 kcal mol^{-1}.

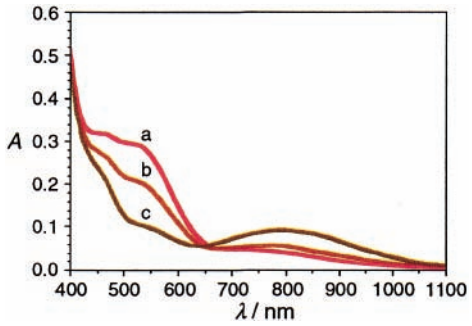

Figure 5. Absorption spectra recorded in Me_2CO at 296 K on **2**·CBPQT·$4PF_6$·RED immediately after its isolation (trace a), after 4 h (trace b), and after 24 h (trace c).

In summary, a bistable supramolecular complex, based on a ring component which threads onto a semi-dumbbell-shaped component containing two different recognition sites in a fast step to form initially a kinetically labile [2]-pseudorotaxane, before progressing more slowly onto forming a second more kinetically stable [2]pseudorotaxane, has been characterized. A "speed bump" in the shape of a thiomethyl group has made it possible to isolate the second of the two [2]pseudorotaxanes, establishing that it has some [2]rotaxane character to it. The unique properties of this bistable complex make it an attractive candidate for incorporation into redox-controllable, piston-like, motor molecules, as well as other kinds of artificial molecular machinery.[2,14]

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Supporting Information Available: Experimental procedures for the syntheses of **2**·CBPQT·$4PF_6$ and **3**·CBPQT·$4PF_6$ and details on the calculations of binding constants and kinetic and thermodynamic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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