[2]Rotaxanes

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Preparation of Cyclobis(paraquat-*p*-phenylene)-Based [2]Rotaxanes Without Flexible Glycol Chains**

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The emergence of supramolecular chemistry[1] has stimulated contemporary chemists interest in interlocked compounds, such as catenanes and rotaxanes.[2] Special attention[3–9] has been paid to catenanes and rotaxanes incorporating the π-electron accepting cyclophane cyclobis(paraquat-*p*-phenylene)[10] ($CBPQT^{4+}$), which gives rise to strong charge-transfer (CT) interactions[11] with complementary π-donor guest molecules. These CT interactions play an important role in the preparation of rotaxanes because they template the formation of the $CBPQT^{4+}$ cyclophane by a clipping reaction around the dumbbell-shaped component. When the CT interactions are considered by themselves, however, they have always been thought insufficient to allow clipping to occur efficiently. Up until recently,[12] therefore, glycol chains[13] have been incorporated into the backbone of the π-donor precursors to guide the clipping reaction. These chains provide additional C–H···O hydrogen-bonding interactions between some of the glycolic ether oxygen atoms and the benzylic and α-hydrogen atoms in the paraquat moiety,[14] and hence ensure high yields. This supramolecular assistance to molecular synthesis comes at a price, since the glycol chains create an inherently flexible system that can adopt multiple conformations, thus potentially reducing the efficiency of motions in [2]rotaxane-based molecular machines.[6,15–17] Furthermore, the hydrogen-bonding nature of the glycol chains induces strong solvent and temperature effects in bistable [2]rotaxanes.[2a,18] Finally, this flexibility hampers the incorporation of interlocked molecules into functional organic systems with rigid components, such as conducting polymers for electronics,[19] sensors,[20] and scaffolds.[21]

Consequently, we can foresee a large potential for new functional catenanes and rotaxanes based on the $CBPQT^{4+}$ cyclophane, provided that the flexible glycol chains can be omitted. Along these lines, the recent construction[22] of a [2]rotaxane incorporating the monopyrrolotetrathiafulvalene[23] (MPTTF) donor unit, in which one of the glycol chains is omitted, provided the impetus to completely remove the supramolecular assistance provided by the glycol chains. As a first proof of concept, we set out to synthesize two elementary rotaxanes constructed from rigidified backbones incorporating only π donors to determine the efficiency of the clipping reaction that forms the $CBPQT^{4+}$ cyclophane. Subsequently, the structural and electronic properties of the resulting class of locked CT [2]rotaxanes were characterized to reveal the effects of rigid molecular encapsulation.

Two dumbbell-shaped molecules **5** and **7**, neither of which contain glycol arms, were prepared (Scheme 1) in single steps from 3,5-di(*tert*-butyl)-bromomethylbenzene (**4**) and bispyrrolotetrathiafulvalene[23b] (**3**, BPTTF) or 1,5-dihydroxynaphthalene (**6**, DNP), respectively. The strong BPTTF donor unit and the medium-strength DNP donor unit in the two dumbbell-shaped molecules serve as templates for the subsequent clipping reaction, and each dumbbell-shaped compound is stoppered proximal to the donor units by 3,5-di-*tert*-butyl benzylic groups. The corresponding [2]rotaxanes $\mathbf{1}\cdot 4PF_6$ and $\mathbf{2}\cdot 4PF_6$ were obtained in acceptable yields of 22% and 27%, respectively, after employing a standard high-pressure clipping reaction.[24] These yields compare favorably to those of [2]rotaxanes constructed previously from flexible, glycol-containing dumbbell-shaped molecules incorporating tetrathiafulvalene[25] (TTF; 39–57%), MPTTF[26] (21–55%), or BPTTF[18b] (47%) as donors.

The reaction yields demonstrate that the oligoethyleneglycol chains are not, as previously assumed, an essential requirement for directing the formation of the tetracationic cyclophane $CBPQT^{4+}$ around π-electron-rich stations. On the contrary, these results show that the mere presence of a π-electron-rich donor unit in the dumbbell-shaped molecule is sufficient to guide the formation of even sterically crowded [2]rotaxanes, such as $\mathbf{1}\cdot 4PF_6$ and $\mathbf{2}\cdot 4PF_6$. This discovery therefore provides access to a new generation of rigid rotaxanes hitherto believed to be inaccessible or only obtainable in very low yields. Moreover, in the rotaxanes $\mathbf{1}\cdot 4PF_6$ and $\mathbf{2}\cdot 4PF_6$, the $CBPQT^{4+}$ cyclophane is confined to encircle the guest station irrespective of whether the station is

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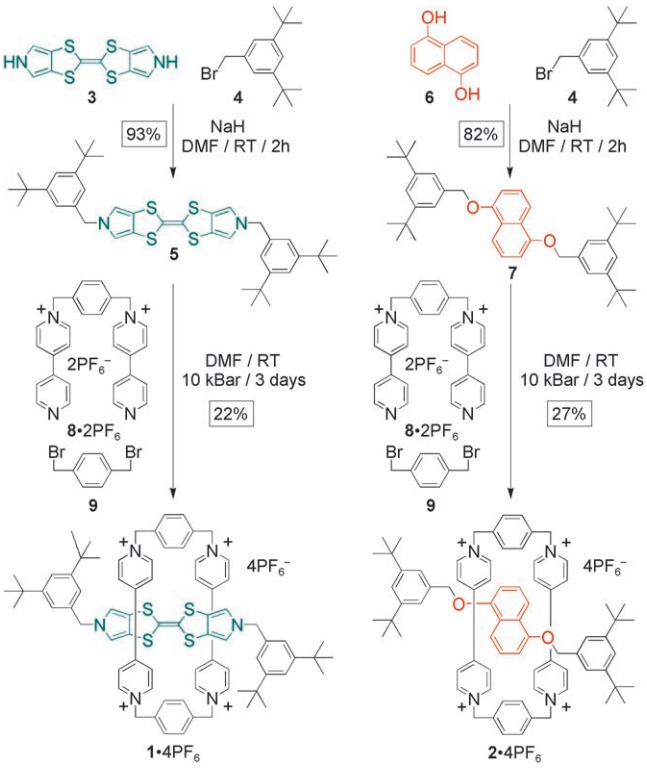

Scheme 1. Synthesis of the BPTTF-containing thread **5** and the DNP-containing thread **7** and the subsequent high-pressure (10 kbar) clipping reaction carried out to prepare the two [2]rotaxanes **1**·4 PF_6 and **2**·4 PF_6.

switched from an attractive to a repulsive state by using redox chemistry. Thus, these locked rotaxanes constitute canonical representations of BPTTF/$CBPQT^{4+}$ and DNP/$CBPQT^{4+}$ rotaxanes, which are free from any significant conformational changes that might result from changes in oxidation state, solvent, or temperature.

The interlocked nature of **1**·4 PF_6 and **2**·4 PF_6 was confirmed unambiguously by electrospray ionization mass spectrometry (ESIMS), ^{1}H NMR spectroscopy, and X-ray crystallography (see the Supporting Information for details). While most [2]rotaxanes rarely yield high-quality crystals, both **1**·4 PF_6 and **2**·4 PF_6 were readily crystallized by slow vapor diffusion of isopropanol into a MeCN solution to give crystals of sufficient quality for single-crystal X-ray structure determination (Figure 1 a).[27] The crystal structure of **1**·4 PF_6 is in itself unique in that it is the first reported structure for a [2]rotaxane containing a TTF-based unit. The structure reveals that the [2]rotaxane lies on a crystallographic center of inversion, with the BPTTF unit slightly tilted (6.2°) and twisted (76.1°) with respect to the paraquat units of the cyclophane ring. The location and orientation of the BPTTF unit within the cavity of $CBPQT^{4+}$ is comparable to the only three reported crystal structures of $CBPQT^{4+}$ cyclophanes containing TTF units, that is, one [2]pseudorotaxane[28] and two [2]catenanes.[29] The [2]rotaxane **2**·4 PF_6 adopts a conformation in the solid state (Figure 1 b) in which the DNP unit displays a small tilt of 6.1° with respect to the $CBPQT^{4+}$ cyclophane. At the same time, the DNP unit (as given by the central C–C bond) is twisted 29.0° with respect to the long axis of paraquat. This twist is generally found in DNP–$CBPQT^{4+}$ host–guest systems, and directs the H4 and H8 protons of the DNP unit towards the center of the *p*-phenylene group of the $CBPQT^{4+}$ cyclophane, and thus is consistent with C–H···π interactions.[30] Comparison of the structures of **1**·4 PF_6 and **2**·4 PF_6 show that the steric confinement of the tetracationic cyclophane $CBPQT^{4+}$ is less pronounced in **1**·4 PF_6 since the BPTTF unit is longer than the DNP unit. Thus, the distance between the two benzylic -CH_2- groups linking the π-donor stations to the stoppers is only 8.516(6) Å for the DNP rotaxane **2**·4 PF_6 while it is 13.384(11) Å for the BPTTF system, **1**·4 PF_6.

The UV/Vis/NIR absorption spectroscopic data reveal (Figure 2 a) that both **1**·4 PF_6 and **2**·4 PF_6 exhibit very distinct CT absorption bands. In the case of **1**·4 PF_6, a moderately strong CT band ($\varepsilon \approx 2000\,M^{-1}cm^{-1}$) is centered at 865 nm, a situation which is characteristic for an interaction between the $CBPQT^{4+}$ cyclophane and the BPTTF unit.[18a,b] In contrast, for **2**·4 PF_6, a weak CT band ($\varepsilon \approx 550\,M^{-1}cm^{-1}$) is observed at 540 nm, which is well-known to originate from the CT interaction of a DNP unit positioned inside the cavity of the tetracationic cyclophane.[31]

A unique feature of these locked rotaxanes is that the position of the $CBPQT^{4+}$ cyclophane is conformationally restricted, thus leading to a situation where it has virtually no other option than to encircle the donor unit (DNP/BPTTF), independent of the net donor/acceptor properties of the unit that it is encircling. In other words, the $CBPQT^{4+}$ cyclophane

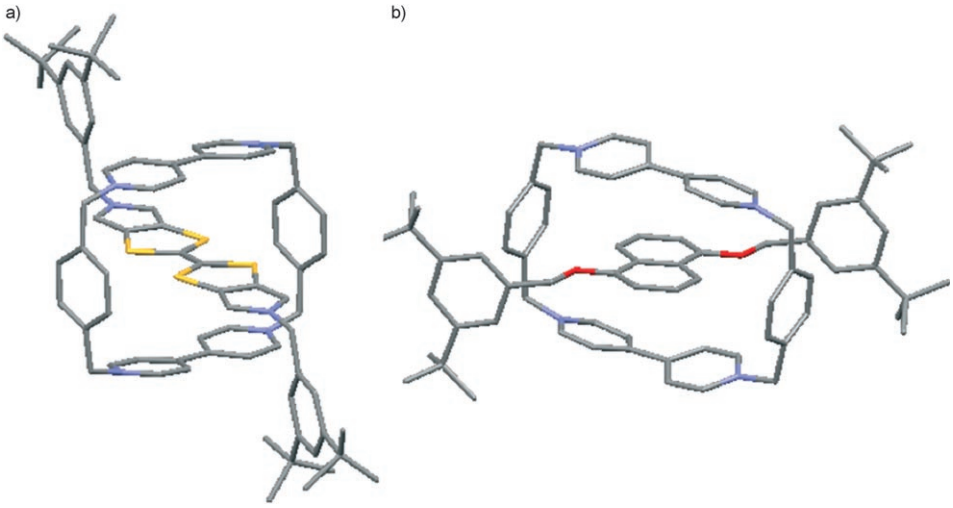

Figure 1. Molecular structure of a) **1**·4 PF_6 and b) **2**·4 PF_6, depicted as capped stick representations, as they are found in the single crystal. H atoms, solvent molecules, and counterions are omitted for clarity.

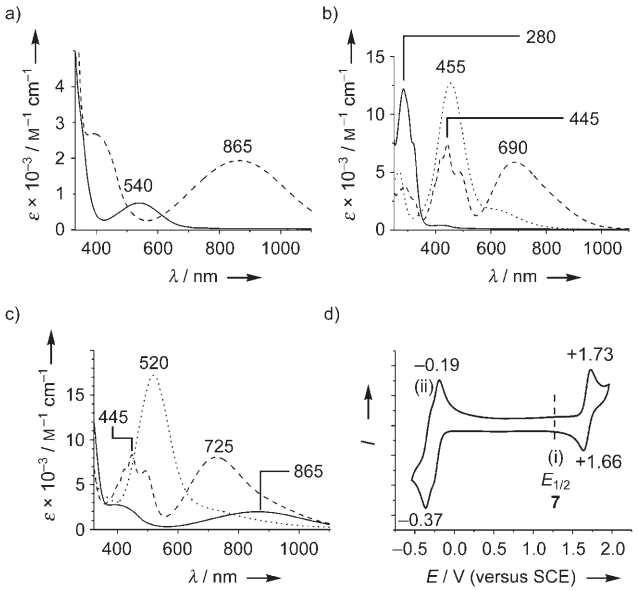

Figure 2. a) UV/Vis/NIR absorption spectra recorded at room temperature in MeCN of the two locked [2]rotaxanes **1**·4 PF_6 (-----) and **2**·4 PF_6 (——); b) UV/Vis/NIR absorption spectra recorded at room temperature in MeCN of the BPTTF-containing **5** (——), the BPTTF radical cation $\mathbf{5}^{\bullet+}$ (-----), and the BPTTF dication $\mathbf{5}^{2+}$ (•••••); c) UV/Vis/NIR absorption spectra recorded at room temperature in MeCN of the locked [2]rotaxanes $\mathbf{1}^{4+}$ (——), the radical BPTTF cation $\mathbf{1}^{5\bullet+}$ (-----), and the BPTTF dication $\mathbf{1}^{6+}$ (•••••); d) electrochemical data showing: i) half-wave potential measured for the DNP-containing **7** marked by a dashed line for simplicity and ii) the cyclic voltammogram of the rotaxane **2**·4 PF_6. (1 mM, 0.1 M $TBAPF_6$, MeCN, 200 mV s^{-1}, glassy carbon).

encapsulates[32] the donor unit and thereby protects it from contact with the chemical environment,[33] irrespective of the redox properties of the guest donor found inside the cavity of the cyclophane. This encapsulation gives rise to a number of interesting redox properties, as revealed by UV/Vis/NIR absorption spectroscopy and electrochemistry.

The addition of a chemical oxidant ($Fe(ClO_4)_3$) by titration to a rotaxane based on MPTTF/BPTTF and $CBPQT^{4+}$ is well-known to lead to the sequential formation of the $MPTTF^{\bullet+}$/$BPTTF^{\bullet+}$ radical cation and the $MPTTF^{2+}$/$BPTTF^{2+}$ dication.[22] The restricted nature of the [2]rotaxane **1**·4 PF_6 prevents the expected Coulombic repulsion induced movement of the tetracationic cyclophane away from the $BPTTF^{2+/\bullet+}$ ions, thereby forcing the two positively charged components to remain close together. This intimate contact results in some significant changes in the spectroscopic properties of the encapsulated $BPTTF^{2+}$ dication relative to those of the free dication. The addition of one equivalent of the chemical oxidant $Fe(ClO_4)_3$ to **5** results in the formation (Figure 2b) of two strong absorptions centered at 445 and 690 nm, characteristic of the BPTTF radical cation, as well as the disappearance of the band at 280 nm originating from the neutral BPTTF transition. The addition of a second equivalent of $Fe(ClO_4)_3$ results in a bleaching of the bands corresponding to the $BPTTF^{\bullet+}$ radical cation and the formation of a single high intensity band at 455 nm, which is indicative of the formation of the $BPTTF^{2+}$ dication. In a similar manner, the $BPTTF^{\bullet+}$ radical cation and the $BPTTF^{2+}$ dication of **1**·4 PF_6 can be generated (Figure 2c) by sequential addition of the chemical oxidant, and concomitant with a bleaching of the CT band at 865 nm. However, when the oxidized BPTTF unit is encapsulated by $CBPQT^{4+}$, the locations of its signature bands change. Specifically, the radical cation band appearing at 690 nm in **5** is red-shifted to 725 nm in **1**·4 PF_6 and the absorption band of the dication is red-shifted more dramatically from 455 nm in **5** to 520 nm in **1**·4 PF_6.

The enforced encapsulation of the donor units by the tetracationic cyclophane in both [2]rotaxanes is most strongly manifested in their redox properties. The BPTTF unit in **5** can be oxidized in two discrete and reversible one-electron processes at potentials below +1 V versus the saturated calomel electrode (SCE), and the presence of the positively charged cyclophane significantly affects the potential that needs to be applied to oxidize this unit.[22] The DNP unit, on the other hand, is normally oxidized in a chemically irreversible manner at potentials higher than +1.2 V versus SCE.[34] The DNP radical cation is short-lived (lifetime <0.2 ms for 1,4-dimethoxynaphthalene) and trace amounts of H_2O prove detrimental to its stability.

The cyclic voltammogram of **1**·4 PF_6 (see the Supporting Information) shows two reversible one-electron oxidation processes at +0.69 and +1.24 V, which are shifted a remarkable +330 and +410 mV, respectively, towards higher potentials relative to the oxidation processes in the **5** on account of the close presence of the tetracationic cyclophane $CBPQT^{4+}$. The reversible reduction of the paraquat units of the tetracationic cyclophane is observed at negative potentials for both locked rotaxanes **1**·4 PF_6 and **2**·4 PF_6. In each case, the first reduction process of the $CBPQT^{4+}$ cyclophane is observed as two well-separated one-electron reductions occurring at −0.26 and −0.33 V in **1**·4 PF_6 and at −0.28 and −0.37 V in **2**·4 PF_6. In both cases, the first of these peaks is located at less-negative potentials than the corresponding single two-electron reduction observed at −0.31 V in free $CBPQT^{4+}$. This behavior can be assigned[22b] to a mixing of the highest occupied molecular orbital (HOMO; located on BPTTF) and the lowest unoccupied molecular orbital (LUMO; located on $CBPQT^{4+}$). What is even more remarkable is that the DNP-containing [2]rotaxane **2**·4 PF_6 displays (Figure 2d) a single and now reversible one-electron process at +1.70 V. This position corresponds to a dramatic +430 mV shift of the DNP oxidation process relative to the irreversible oxidation process observed in **7** (see the Supporting Information). The oxidation of **2**·4 PF_6 is stable on the timescale of the cyclic voltammetry (CV) experiments down to 20 mV s^{-1}, as evidenced by the coincidence of the CV data recorded in two consecutive cycles. This enhanced stability enabled the UV/Vis/NIR spectra of the oxidation product to be recorded. A structured band grows (Figure 3) at longer wavelengths with maxima at 870 and 1000 nm and with the concomitant loss of intensity of the CT band when the voltage is stepped from +1.4 to +2.0 V. Although the oxidation product was not stable over the time period of the electrolysis (ca. 10 min), the spectrum obtained is representative of the monooxidized $DNP^{\bullet+}$ radical cation.[34] By comparison with

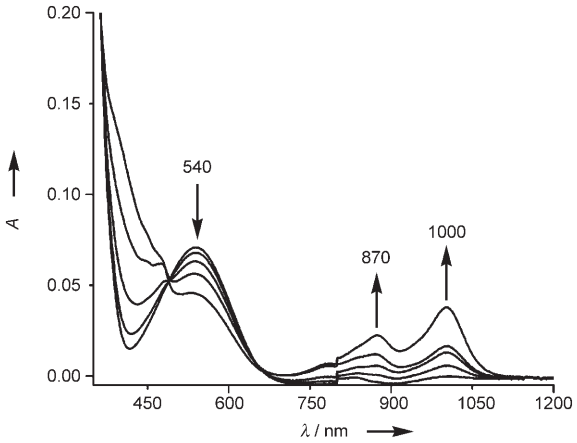

Figure 3. UV/Vis/NIR spectroelectrochemistry of the DNP-containing [2]rotaxane **2**·4 PF_6 (1.0 mM of **2**·4 PF_6 in 0.1 M $TBAPF_6$/MeCN) recorded at applied voltages of +1.4, +1.7, +1.8, +1.9, and +2.0 V.

the CV data for **7**, these data verify the enhanced stability of the DNP oxidation product in the locked rotaxane format over the course of many seconds under normal solution conditions. Previous reversible oxidations of a substituted 1,4-dimethoxynaphthalene have been reported,[34] but only after exhaustive exclusion of trace amounts of H_2O. The $DNP^{\bullet+}$ radical cation in **2**·4 PF_6 is found to be stable on the timescale of the CV experiment, clearly indicating that encapsulation inside the cavity of the $CBPQT^{4+}$ cyclophane efficiently shields[35] the reactive $DNP^{\bullet+}$ species from the surrounding environment.

In summary, two sterically confined [2]rotaxanes have been constructed from either BPTTF- or DNP-containing π-electron-rich dumbbell-shaped molecules without attached glycol arms by employing the template-directed high-pressure clipping strategy to form the tetracationic cyclophane $CBPQT^{4+}$ around the π-electron-rich station. This design represents a significant deviation from previous strategies and argues against the hypothesis that glycol side chains are essential to guide the efficient formation of interlocked molecules comprising π-electron-rich donor units and the π-electron-poor cyclophane $CBPQT^{4+}$. In this first proof of concept, the locked and rigid nature of the two constructed [2]rotaxanes creates a situation where the tetracationic cyclophane is forced to encapsulate the initially π-electron-rich station, regardless of its oxidation state. The encapsulation of the oxidized donor unit significantly alters the optical and redox properties of the BPTTF-based [2]rotaxane. Moreover, encapsulation provides a means to protect the very unstable $DNP^{\bullet+}$ radical cation from contact with the surrounding environment. These findings may potentially lead to new classes of functionally rigid interlocked molecules where flexible glycol chains can either be omitted entirely or introduced into the molecular design only when the flexibility is needed.

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[27] Crystallographic data for **1**·4 PF_6·4 CH_3CN: $C_{84}H_{94}F_{24}N_{10}P_4S_4$, $M_r = 1951.81$, monoclinic, space group $P2_1/c$, $a = 15.6293(12)$, $b = 17.1943(12)$, $c = 16.7948(10)$ Å, $b = 94.455(3)°$, $V = 4499.7(5)$ Å^3, $T = 180(2)$ K, $m(Mo_{Ka}) = 0.277$ mm^{-1}, $2\theta_{max} = 23.26°$, 31273 reflections measured, 6446 unique reflections ($R_{int} = 0.086$), 3914 observed reflections, $R1(I>2\sigma(I)) = 0.073$, $wR2$(all data) = 0.203, $S = 1.06$. Crystallographic data for **2**·4 PF_6·2 CH_3CN: $C_{80}H_{90}F_{24}N_6O_2P_4$, $M_r = 1747.46$, triclinic, space group $P\bar{1}$, $a = 11.5883(9)$, $b = 12.0788(11)$, $c = 16.9092(15)$ Å, $a = 78.511(3)$, $b = 71.152(3)$, $g = 68.338(3)°$, $V = 2073.1(3)$ Å^3, $T = 180(2)$ K, $\mu(Mo_{Ka}) = 0.195$ mm^{-1}, $2\theta_{max} = 25.11°$, 27954 reflections measured, 7318 unique reflections ($R_{int} = 0.066$), 4215 observed reflections, $R1(I>2\sigma(I)) = 0.057$, $wR2$(all data) = 0.154, $S = 1.06$. CCDC-643792 and CCDC-643793 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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[35] Alternatively, encapsulation may also raise the activation barriers for intramolecular decomposition. The noted complexity of the product distribution (see Ref. [34a]) precludes a complete analysis of which degradation pathway dominates.

