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A high yielding template-directed synthesis of the first fluorenone-containing [2]catenane

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Abstract—A new crownophane containing both 2,7-dioxyfluorenone and 1,5-dioxynaphthalene moieties bridged by triethylene glycol units has been synthesized and used as a highly efficient template for the preparation of the first fluorenone-containing [2]catenane incorporating a cyclobis(paraquat-*p*-phenylene) tetracation as a second macrocyclic component.

The potential opportunity of using noncovalently interlocked molecules such as catenanes and rotaxanes for the design of molecule-level machines and electronic devices[1–4] has attracted significant attention toward the synthesis and chemistry of these supramolecules.[5–7] One of the most fruitful approaches to catenanes is template-directed synthesis based on template assistance of one macrocycle for the formation of the second macrocycle.[8–11] As a powerful recognition tool for the efficient template-directed syntheses of catenanes incorporating bipyridinium-based components mechanically interlocked with dioxyarene-based polyether components, a combination of the stabilizing effects of [C–H···O] hydrogen bonds, [π–π] stacking, and [C–H···π] interactions have been successfully employed.[5–7] The electrostatic component plays a dominant role in these interactions, and in the case of polar subsystems included in the macrocyclic host framework, it is possible to identify recognition efficiency and determine the complexes stabilization energy within the limits of the electrostatic energy term.[12] This immediately suggests that the introduction of aromatic units containing electron-rich polar groups in the framework of one macrocyclic component can reinforce ion–dipole interactions with the positively charged second component and hence enhance the efficiency of the catenation process. Being interested in this simple opportunity of optimizing the template effect of the donor component, we have synthesized fluorenonocrownophane **3** for the first time as a template for the formation of the cyclobis(paraquat-*p*-phenylene) tetracation ($CBPQT^{4+}$) as the second macrocyclic component of the [2]catenane.

Macrocyclization of bistosylate **1**[13] with bisphenol **2**, under high dilution conditions, gave after work-up and chromatographic purification over silica gel, the crownophane **3**.[14] Employing the strategy developed by Raymo and Stoddart[7] the catenation of **3** was carried out with a 2-fold excess of the bis(bipyridinium) derivative **4**·$2PF_6$ and 1,4-bis(bromomethyl)benzene **5** under atmospheric pressure to afford the [2]catenane **6**·$4PF_6$ in a yield of 91%, after counterion exchange[15] (Scheme 1). The yield of **6**·$4PF_6$, one of the highest ever obtained for the catenanes, reflects a very efficient preorganization of the reactants, evidently augmented by electrostatic interaction between the fluorenonocrownophane **3** carbonyl group and the bipyridinium dication **4**·$2PF_6$, or its monoalkylated intermediate, in addition to conventional noncovalent interactions. Thus, the fluorenone unit is superior to other dioxyarene derivatives in this self-assembly process.

Keywords: Catenanes; Cyclophanes; Fluorenonophanes; Self-assembly; Template synthesis.

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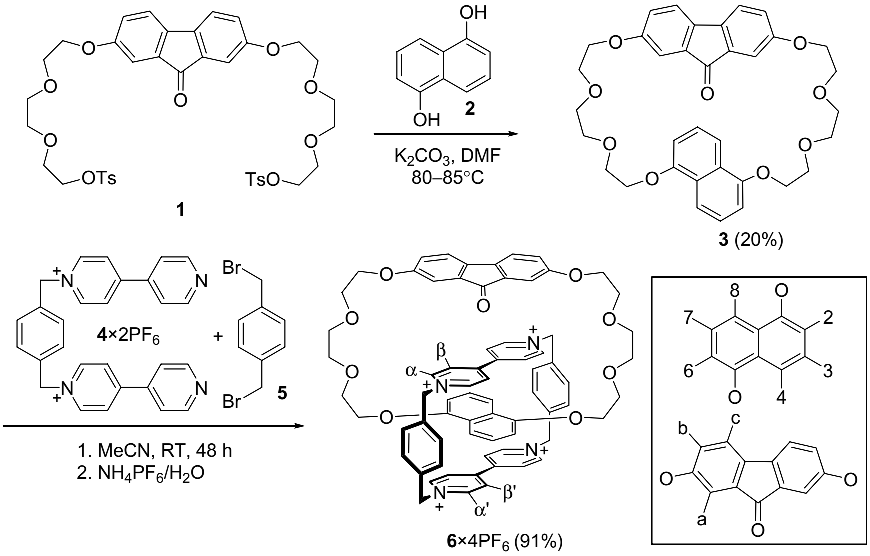

Scheme 1. Synthesis of crownophane **3** and [2]catenane **6**·4PF_6.

The X-ray crystal structure of the [2]catenane **6**·4PF_6 shows that the 1,5-dioxynaphthalene ring of **3** is located inside the cavity of the tetracationic cyclophane, while the fluorenone unit is positioned outside (Fig. 1).[16] The fluorenone carbonyl group is almost centered with respect to the plane of the internal bipyridinium unit at a distance of 3.74 Å from its centroid. This immediately indicates a considerable dipole–charge interaction between them that undoubtedly is an important stabilization component of the catenane **6**·4PF_6 structure. The mean interplanar separation distances between the 1,5-dioxynaphthalene ring and the internal and external bipyridinium units are 3.29 and 3.31 Å, respectively. The separation between the fluorenone fragment and the internal bipyridinium unit is 3.39 Å. Such distances in the donor–acceptor array, coupled with the near parallel alignments and considerable degree of overlap of all the aromatic moieties of the catenane, indicate their involvement in strong face-to-face π–π stacking interactions. The dioxynaphthalene unit is oriented orthogonally to the planes of the paraxylyl rings and its hydrogen atoms in positions 4 and 8 are located at distances of 2.54 and 2.58 Å, respectively, from the aromatic centre which clearly specifies the presence of [C–H···π] interactions. There are the two bifurcated [C–H···O] hydrogen bonds between diametrically opposite α-CH groups of the internal bipyridinium unit and the central oxygen atoms of the polyether linkages.

Inspection of the packing of the [2]catenane **6**·4PF_6 (Fig. 2) reveals that molecules form centrosymmetric π-stacked dimer pairs involving the partial overlap of fluorenone units. These dimers contain molecules of different planar chirality, (p*R*) and (p*S*), associated with the local C_{2h} symmetry of the 1,5-dioxynaphthalene unit.

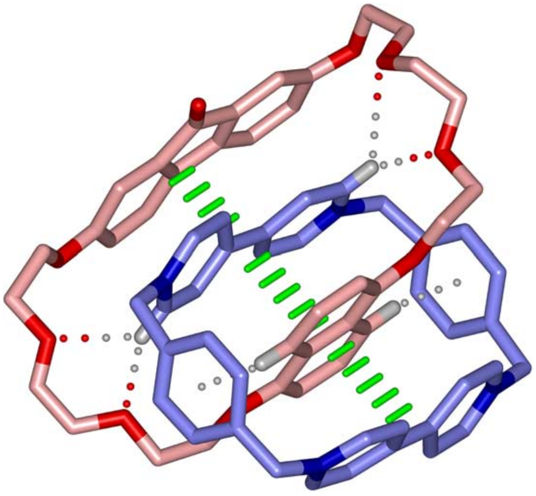

Figure 1. Polytube representation of the solid-state structure of [2]-catenane **6**·4PF_6. For clarity carbon atoms of the crownophane are shown in pink and the carbon atoms of the tetracationic cyclophane in blue; oxygen atoms are depicted in red, nitrogen atoms in dark blue, and selected hydrogen atoms in gray. Water molecules and counterions are not shown. Dots and green bars show hydrogen and π–π stacking interactions, respectively.

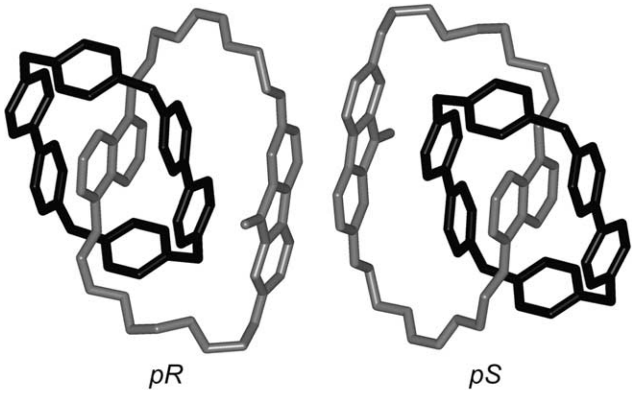

Figure 2. One of the 'enantiomeric pairs' formed by the [2]catenane **6**·4PF_6 in the crystal state.