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The synthesis of a pyrrole-functionalized cyclobis(paraquat-*p*-phenylene) derivative and its corresponding [2]rotaxane and [2]catenane and their subsequent deposition onto an electrode surface

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Abstract—We report the convenient synthesis of a pyrrole-functionalized tetracationic cyclophane, [2]rotaxane, and [2]catenane. X-ray crystallography has confirmed the interlocked structure of the catenane. We have investigated the solution properties of these systems using solution electrochemistry, NMR, and UV–vis spectroscopy. We have also demonstrated that it is possible to immobilize these systems onto a platinum working electrode surface. We have shown that films of the cyclophane have the ability to undergo complexation with a dialkyloxynaphthalene derivative.

1. Introduction

Rotaxanes and catenanes incorporating the tetracationic cyclophane cyclobis(paraquat-*p*-phenylene)($CBPQT^{4+}$)[1] have undoubtedly become important supramolecular building blocks for the construction of molecular-scale machines and devices.[2] In attempts to facilitate their future applications, attention has focused upon the transferral of these systems from solution to the solid state, where the resulting surface-confined assemblies have the ability to function coherently.[3] For the most part, the transferal has been achieved by the fabrication of self-assembled monolayers onto a range of solid substrates. As an alternative strategy for depositing components onto surfaces, electropolymerization of systems functionalized with polymerizable units (e.g., thiophene and pyrrole) offers a convenient and versatile method for surface deposition. Furthermore, as the polymerization process provides a conjugated backbone with interesting physical properties, this method not only facilitates communication between the components of the film, but also should facilitate the molecular electronics and device applications of these systems.[4] As part of our continuing exploration of using electropolymerization to immobilize interlocked structures onto surfaces,[4f,5] we now report a convenient synthetic route to introduce electro-active pyrrole moieties into cyclophane **1**[6] and its corresponding [2]rotaxane **2** and [2]catenane **3**. We also report a convenient method of depositing these species onto an electrode surface.

2. Results and discussion

2.1. Synthesis

The synthesis of compounds **1**,[6] **2**, and **3** is given in Scheme 1. Key building block **5** was readily synthesized from 1-*N*-pyrrolepropionic acid[7] and alcohol **4**.[6] Cyclophane **1** was synthesized from compounds **5** and **6** using a template directed clipping methodology using **7**.[8,9] Rotaxane **2** and catenane **3** were also readily synthesized using this methodology by replacing template **7** with axle **8**[9] or macrocycle **9**,[10] respectively. The cyclophane **1** and interlocked

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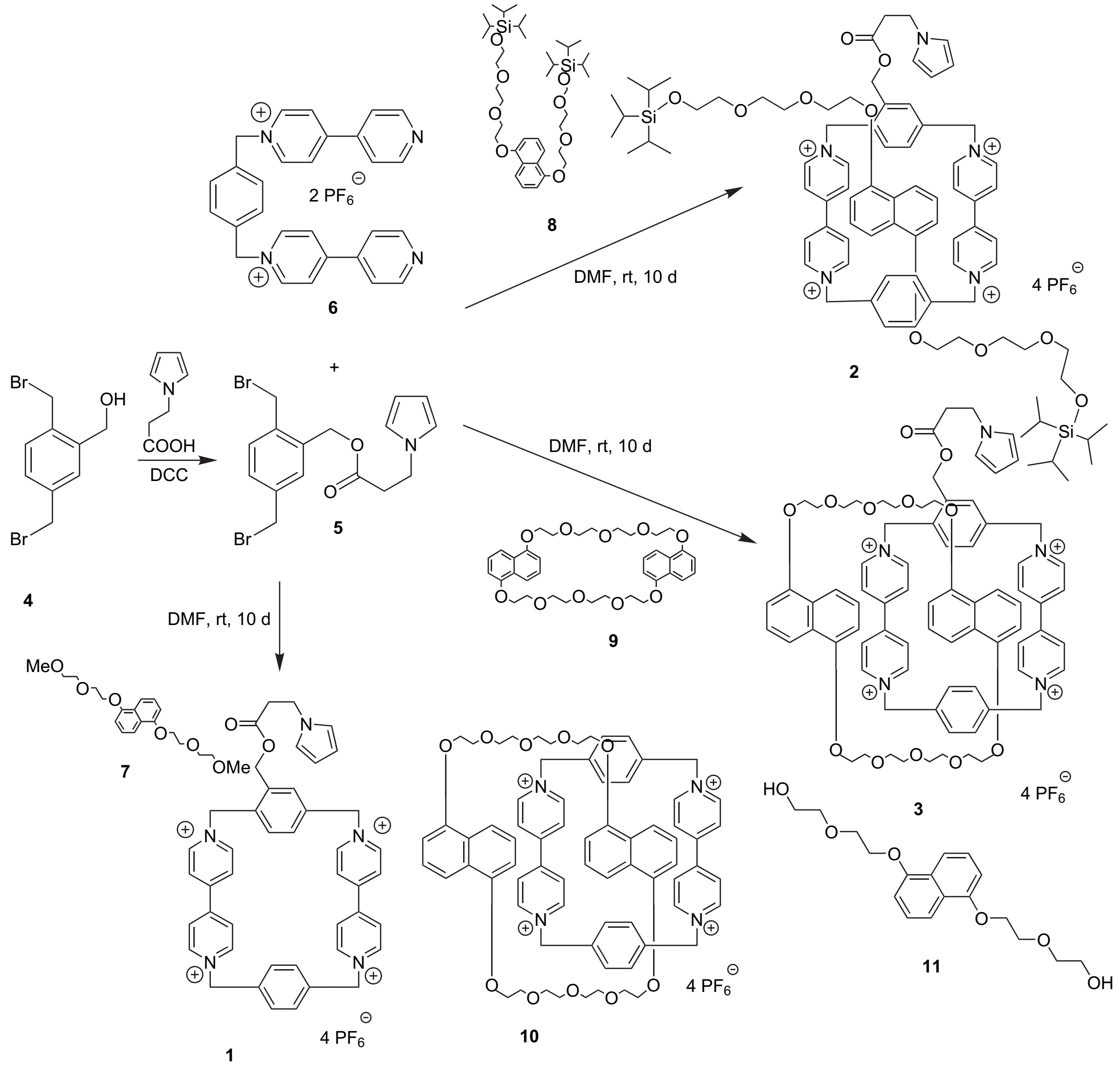

Scheme 1. Synthesis of cyclophane **1**, rotaxane **2**, and catenane **3**.

structures **2** and **3** were purified by column chromatography (SiO_2, $MeOH/NH_4Cl/MeNO_2$). The Cl^- counterions were converted to PF_6^- by exchange reactions with NH_4PF_6 to yield structures **1**–**3**. The analytical data for systems **2** and **3** were consistent with their proposed structures. For example, electrospray mass spectrometry performed on **2** and **3** revealed peaks at m/z=1843 $[M-PF_6]^+$ and 1743 $[M-PF_6]^+$, respectively.

2.2. Solid state structure of 3

Crystals suitable for study by X-ray diffraction were obtained by the slow evaporation of solvent from a concentrated solution of **3** in acetonitrile. Although the crystals were of poor quality, a crystal structure was obtained using a Rigaku R-AXIS RAPID image-plate diffractometer, affording data of sufficient quality to solve and refine the structure from a long data collection in which each image was exposed for a total of 35 min. This type of laboratory image plate set-up is particularly powerful for small, weakly diffracting crystals such as this as it allows for very long exposure times without the dark-current build-up associated with CCD detectors. The crystal structure clearly shows a highly ordered molecular arrangement within the catenane architecture (Fig. 1). One of the 1,5-dinaphtho- residues is sandwiched between the two bipyridinium moieties of the tetracationic cyclophane, whereas the other unit is positioned outside and immediately adjacent to one of the bipyridinium units.[11] It is noteworthy that the naphthalene and bipyridinium aromatic rings adopt a near parallel arrangement, whereas the electron rich pyrrole moiety does not apparently interact significantly with the interlocked structure in the solid state.

2.3. Characterization of 1, 2, and 3 in solution

The solution properties of **1** have been described previously.[6] The absorption spectra recorded in CH_3CN at 298 K, show a broad band in the visible region for both interlocked structures **2** and **3** at 524 and 530 nm, respectively. Inspection of the ^1H NMR spectra of **2** and **3** performed in CD_3CN, showed two characteristic proton resonances at