

Self-Assembly of a [2]Pseudorota[3]catenane in Water

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Supporting Information

ABSTRACT: A donor–acceptor [3]catenane incorporating two cyclobis(paraquat-*p*-phenylene) rings linked together by a dinaphtho[50]crown-14 macrocycle possesses a π -electron-deficient pocket. Contrary to expectation, negligible binding of a hexaethylene glycol chain interrupted in its midriff by a π -electron-rich 1,5-dioxynaphthalene unit was observed in acetonitrile. However, a fortuitous solid-state superstructure of the expected 1:1 complex revealed its inability to embrace any stabilizing [C–H...O] interactions between the clearly unwelcome guest and the host reluctantly accommodating it. By contrast, in aqueous solution, the 1:1 complex becomes very stable thanks to the intervention of hydrophobic bonding.

Since the advent of the field of chemical topology¹ in 1961, chemists have devised² myriad different ways of making mechanically interlocked molecules³ (MIMs). When designing and making molecular expressions of figures-of-eight,⁴ Trefoil knots,⁵ figure-of-eight knots,⁶ pentafoil knots,⁷ Solomon links,⁸ Borromean rings,⁹ and ravels,¹⁰ synthetic chemists more often than not call on their knowledge of host–guest chemistry as a mechanism of introducing topology into MIMs, such as in the case of catenanes that can be self-assembled from a ring (host) and a chain (guest) by a “threading-followed-by-clipping” approach.¹¹ A relatively little explored strategy for preparing topologically complex structures is to utilize MIMs *themselves* as hosts for guests. There are two reported¹² donor (D)–acceptor (A) [2]catenanes having potential electron-deficient recognition sites for electron-rich substrates in the form of chains whose termini can then be capped with bulky stoppers to form MIMs; we have coined¹³ the term “rotacatenane” to describe these structures. Other literature examples of catenanes acting as hosts are rare and have involved the retention of templates implicated in their syntheses.¹⁴ We report herein the template-directed synthesis of a flexible D–A [3]catenane that, through a particular disposition of its three rings in an appropriate medium (water), can act as a host for a chainlike guest, resulting in the formation of a 1:1 complex with a hitherto unknown topology that we have termed a [2]pseudorota[3]catenane. The D–A solid-state superstructure shown in Figure 1a,¹⁵ which consists of a [3]pseudorotaxane formed by electron-deficient cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) rings and an electron-rich threadlike compound composed of

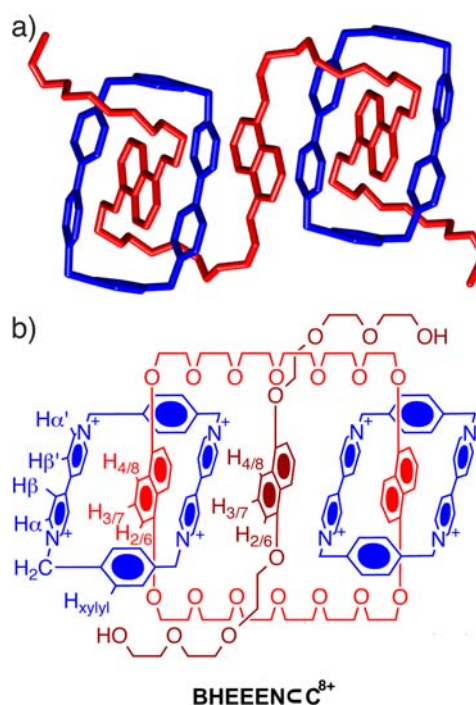


Figure 1. (a) Tubular representation of the solid-state superstructure¹⁵ of a [3]pseudorotaxane exhibiting an ADADADA-stacked arrangement. (b) Structural representation of the [2]pseudorota[3]catenane BHEEENCC⁸⁺ formed when the [3]catenane C⁸⁺ binds BHEEEN. The labeling of protons used later in the ¹H NMR spectroscopic assignments is also shown.

three 1,5-dioxynaphthalene (DNP) units linked together by oligoethylene glycol loops, displays a well-ordered ADADADA stack of seven aromatic rings, leading us to question whether a similar recognition motif could be realized with a completely different connectivity linking the units of the ADADADA stack. The outcome of catenating a sufficiently large crown ether containing two DNP units, both encircled by CBPQT⁴⁺ rings, is the [3]catenane C⁸⁺, which features a binding pocket that is apparently capable, both sterically and electronically, of forming a 1:1 complex with an appropriate guest such as 1,5-bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]naphthalene (BHEEEN) to afford a [2]pseudorota[3]catenane (Figure 1b).¹⁶

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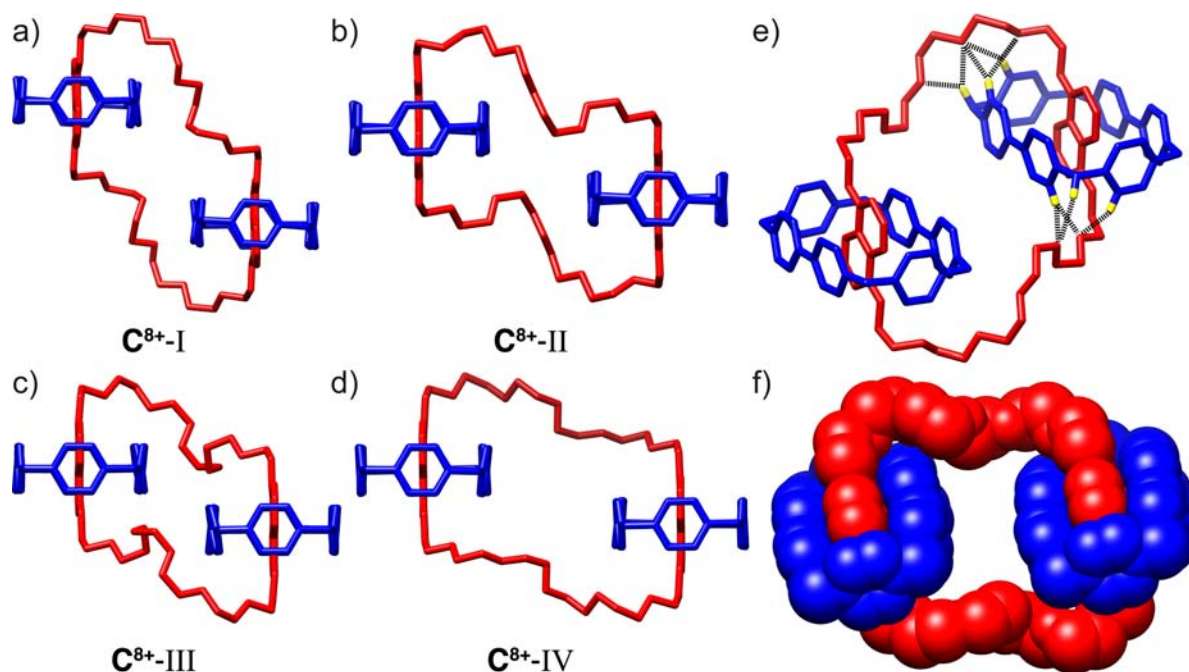


Figure 2. Solid-state structures of the four polymorphs of C^{8+} solved by X-ray crystallography. (a–d) Tubular representations of (a) C^{8+} -I, (b) C^{8+} -II, (c) C^{8+} -III, and (d) C^{8+} -IV rendered with DN50C14 in red and the CBPQT $^{4+}$ rings in blue, illustrating the different coconformations that C^{8+} adopts in the various structures. (e) View of C^{8+} -II from a different angle, showing in yellow the H atoms of the CBPQT $^{4+}$ ring involved in [C–H...O] contacts, which are shown as dashed black lines. A center of inversion repeats these interactions in both halves of the [3]catenane. (f) Space-filling representation of C^{8+} -IV showing the ca. 7 Å binding pocket for guests in its interior. All counterions (PF_6^-), H atoms not involved in [C–H...O] contacts, and solvent molecules have been removed for clarity. CCDC depositions 898082–898085 contain all of the crystallographic data for these structures (see section S5).

Guided by some preliminary molecular modeling, we identified 1,5-dinaphtho[50]crown-14 (DN50C14)¹⁷ as the crown ether of choice because we expected that, when two CBPQT $^{4+}$ cyclophanes were clipped around its DNP units, its long polyether loops would endow the resulting [3]catenane C^{8+} with the flexibility to accommodate guests within a potential binding pocket in its interior (Figure 1b). The synthesis of $C \cdot 8PF_6$ was achieved in 35% yield by employing DN50C14 as a template; the precursors (5 equiv each) were combined routinely¹⁸ with 1 equiv of the crown ether in order to clip CBPQT $^{4+}$ rings around DNP units in DMF under ultrahigh pressure (15 kbar) for 5 days at room temperature, followed by counterion exchange [see section S2 in the Supporting Information (SI)]. Significant amounts of the intermediate [2]catenane¹⁹ were also obtained (see section S3).

The symmetry and flexibility of C^{8+} in solution was confirmed by the simplicity of its 1H NMR spectrum (recorded for the $8PF_6^-$ salt in CD_3CN at 253 K), which exhibits only three resonances for its DNP protons and eight signals for its CBPQT $^{4+}$ protons as a consequence of the local C_2 symmetry of the DNP units commuting with the CBPQT $^{4+}$ rings (see section S4). The two halves of the [3]catenane are related by averaged D_{2h} symmetry. An even simpler 1H NMR spectrum commensurate with rapid realignment²⁰ of the DNP units in the cavities of the CBPQT $^{4+}$ rings was recorded²¹ when a CD_3SOCD_3 solution of $C \cdot 8PF_6$ was used at 363 K (see section S5).

The flexibility of C^{8+} was further confirmed by the fact that no fewer than four individual solid-state structures of their $8PF_6^-$ salts were characterized (C^{8+} -I, C^{8+} -II, C^{8+} -III, and C^{8+} -IV; Figure 2a–d), in which the [3]catenane adopts different coconformations. Displaying these coconformations alongside

one another illustrates the range of relative geometries that C^{8+} is able to visit. The differences can be enumerated by considering the relative spatial arrangements of the CBPQT $^{4+}$ ring in C^{8+} -I–IV (see section S5), where a common feature is the propensity for short [C–H...O] contacts to form between the oxygen atoms of the polyether loops of the DN50C14 ring and the protons of the CBPQT $^{4+}$ rings (as illustrated for C^{8+} -II in Figure 2e). These noncovalent bonding interactions are known to be significant contributors to the stability^{16,22} of related MIMs and supramolecular analogues and are the most likely coconformationally directing forces in C^{8+} -I–IV. The relative disposition of the CBPQT $^{4+}$ rings in C^{8+} -IV, where the inner bipyridinium (bipy $^{2+}$) units are separated by ca. 7 Å (Figure 2d,f), illustrates only too well the potential binding pocket available for the complexation of guests containing aromatic groups.

Next, we employed 1H NMR spectroscopy to assess the extent of binding of an aromatic guest with polyether loops to aid and abet its complexation by the [3]catenane. BHEEEN (Figure 1b) was chosen on account of its constitutional similarities to compounds employed in the efficient self-assembly of D–A oligorotaxanes.¹⁵ Initial experiments carried out with $C \cdot 8PF_6$ in CD_3CN solutions, however, showed little evidence for the formation of a strong 1:1 complex. The differences between the chemical shifts of the DNP protons in BHEEEN (ca. 0.05 ppm) and the bipy $^{2+}$ protons in C^{8+} (ca. 0.1 ppm) in the absence and presence of up to 5 equiv of the potential guest were close to being inconsequential. UV/vis spectroscopic titrations (see section S7) revealed a binding constant of only $33 \pm 12 M^{-1}$ in MeCN, that is, the [3]catenane hardly binds BHEEEN at all in MeCN. Despite the weakness of this 1:1 complex in MeCN, we were able to

obtain, quite fortuitously, single crystals of **BHEEEN**C·8PF₆ by vapor diffusion with Et₂O.²³ X-ray crystallographic analysis of the superstructure (see section S8) showed that the polyether loops in C⁸⁺ prevent the triethylene glycol chains in **BHEEEN** from garnering any significant [C–H···O] interactions with the [3]catenane, thus denying the 1:1 complex the very interactions that have been shown^{16,22} to provide substantial stabilization of D–A assemblies in MeCN. A detailed analysis of the solid-state superstructure (Figure 3a) revealed the expected ADADADA stacking, wherein **BHEEEN** is nestled between the two CBPQT⁴⁺ rings of C⁸⁺ with interplanar distances of 3.22–3.30 Å between the aromatic rings; this is similar to the stacking previously observed^{15,24} in pseudorotaxanes except for one crucial difference (Figure 3b): the DNP unit of **BHEEEN** is not aligned in register with the bipyridinium units in C⁸⁺ but rather is offset by 2 Å, while still being engaged in [π···π] interactions with one of the pyridinium rings on one side of each of the sandwiching CBPQT⁴⁺ rings. The location of the guest at one side of the potential binding pocket (Figure 3c) results in a pinching together of the CBPQT⁴⁺ rings and their enforced deviation from coplanarity by ca. 7.9 Å (Figure 3d). The superstructure does show that the pocket is sufficiently large to accommodate **BHEEEN** as a guest.

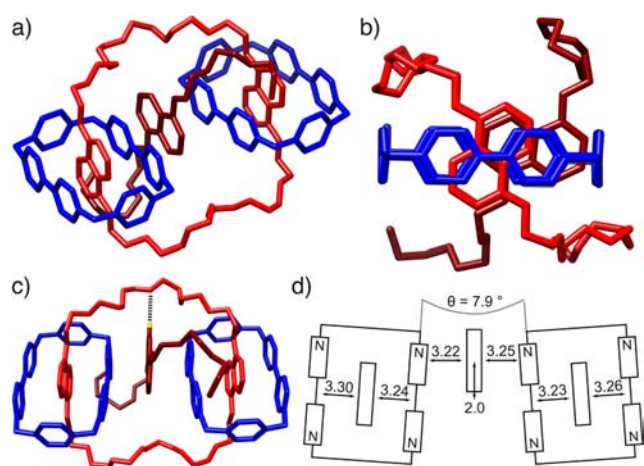


Figure 3. Solid-state superstructure of the complex **BHEEEN**C⁸⁺. (a–c) Tubular representations of the superstructure, with the tetracationic cyclophanes rendered in blue, the crown ether in red, and **BHEEEN** in dark red, showing (a) the ADADADA stack from above and (b, c) the offset nature of the DNP moiety of **BHEEEN** in the center of the stack (b) from the side and (c) from above. All of the PF₆[−] ions, H atoms not involved in [C–H···O] contacts, and solvent molecules have been removed for clarity. CCDC deposition 898081 contains all of the crystallographic data (see the SI). (d) Schematic diagram illustrating pertinent distances (in Å) and angles between the components of the [2]pseudorota[3]catenane.

While the absence of [C–H···O] interactions precludes the formation of a stable 1:1 complex in MeCN, it is well-known^{25,26} that hydrophobic forces operate quite independently of [C–H···O] interactions in water. Hence, the [3]catenane was rendered water-soluble by exchanging its eight PF₆[−] counterions for eight Cl[−] anions. Although **BHEEEN** is only sparingly soluble in water, dissolving C·8Cl in an equimolar suspension of **BHEEEN** in D₂O afforded a clear solution²⁷ of the [3]catenane, indicating the formation of a 1:1 complex, a fact that was confirmed by the significant

movements of resonances associated with the aromatic protons in the partial ¹H NMR spectrum recorded at 293 K (Figure 4). While H_{4/8}, H_{3/7}, and H_{2/6} in **BHEEEN** experienced upfield shifts of −0.56, −0.33, and −0.34 ppm, respectively, all of the signals of the aromatic protons in C⁸⁺ were also shifted upfield by quite substantial margins, suggesting the formation of a tight yet dynamic 1:1 complex.²⁸

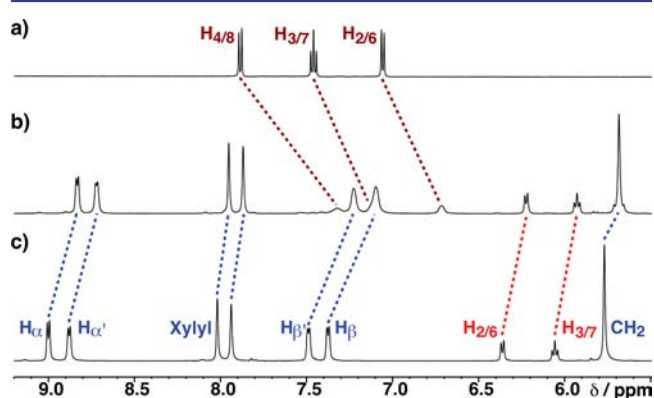


Figure 4. Stacked partial ¹H NMR spectra (600 MHz, 293 K, D₂O), with structural assignments annotated, of (a) the guest **BHEEEN**, (b) a 1:1 mixture of **BHEEEN** and C·8Cl, and (c) C·8Cl alone.

The hydrophobic bonding of an aromatic guest within the binding pocket of an octacationic [3]catenane that is rendered soluble in water by its eight accompanying chloride anions constitutes a rare example of a mechanically interlocked molecule that itself acts as an aromatic-rich host. We are currently exploring the potential of this water-soluble supramolecular synthon in the template-directed synthesis of compounds containing multiple mechanical bonds in aqueous solutions.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthesis and characterization of all compounds and comprehensive spectroscopic and crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (28) While the realignment of the DNP units is slow on the ¹H NMR time scale in the [2]pseudoro[3]catenane in D₂O at 293 K, the super-rotation process involving the two CBPQT⁴⁺ rings is fast, since only two α -bipy²⁺ proton (*H* _{α} and *H* _{α'}) resonances and two β -bipy²⁺ proton (*H* _{β} and *H* _{β'}) resonances are observed.