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The “Texas-Sized” Molecular Box: A Versatile Building Block for the Construction of Anion-Directed Mechanically Interlocked Structures

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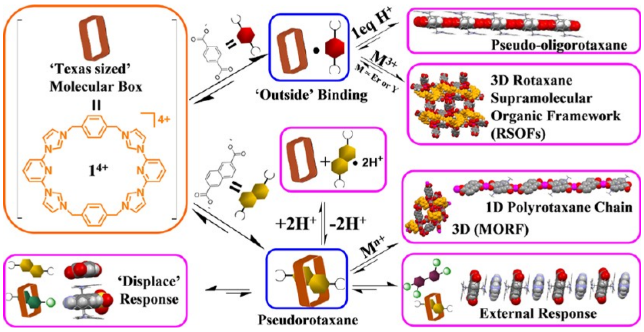
CONSPECTUS



Over the last two decades, researchers have focused on the synthesis and development of mechanically interlocked molecules (MIMs). The intramolecular motion of mechanical bonds and the ability to induce this effect with the choice of the proper external stimuli has prompted the development of macromolecular systems that possess the ability to “perform work” at the molecular level. Currently, researchers are working to incorporate interlocked species into complex structural systems, such as molecular frameworks and nanoparticles, and to create ever more elegant noncovalent architectures. This effort provides an incentive to generate new building blocks for the construction of MIMs. In this Account, we describe progress in the development of a new cationic building block inspired by the “blue box” of Stoddart and collaborators.

The blue box (cylcobis(paraquat-*p*-phenylene) or $CBPQT^{4+}$) is a tetracationic, electron-deficient macrocycle widely recognized for its role in the construction of MIMs. This venerable receptor displays a high affinity for a variety of π-donor guests, and researchers have used them to construct a wide range of molecular and supramolecular structures, including rotaxanes, catenanes, pseudorotaxanes, polypseudorotaxanes, pseudo[*n*]polyrotaxanes, and electrochemically switchable molecules. To date, several synthetic analogues of the basic $CBPQT^{4+}$ structure have been reported, including systems containing biphenylene linkers and chiral tetracationic cyclophanes. However, researchers have not yet fully generalized the promise of the blue box.

In this Account, we chronicle the development of a larger, more flexible tetracationic macrocycle, referred to as the “Texas-sized” molecular box. To highlight its relatively increased size and to distinguish it from $CBPQT^{4+}$, we have chosen to color this new receptor burnt orange. The Texas-sized box (cyclo[2](2,6-di(1*H*-imidazol-1-yl)pyridine)[2](1,4-dimethylenebenzene), $1^{4+}\cdot 4PF_6^{-}$) acts as a dynamic molecular receptor that displays an ability to adjust its shape and conformation to accommodate anionic guests of different size and charge within its central core. The use of different guests can favor different binding modes and promote the formation of different macromolecular aggregates. Furthermore, the proper selection of the guest allows for the “turning on” or “turning off” of molecular threading and can be used to produce new kinds of threaded species. This dynamic behavior is a special feature of the Texas-sized molecular box, as is its ability to stabilize a range of polypseudorotaxanes, rotaxane-containing metal–organic frameworks (MORFs), and rotaxane-based supramolecular organic frameworks (RSOFs).

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Introduction

The field of supramolecular chemistry is noted for its wealth of elegant molecular architectures stabilized via noncovalent binding interactions.[1−3] This field, which continues to draw inspiration from the biological world,[4,5] has expanded to include systems capable of acting as molecular machines.[6−8] The ability to generate complex molecular architectures has been aided by developments in the field of mechanically interlocked molecules (MIMs). Systems, such as catenanes,[9−11] rotaxanes,[12−14] polypseudorotaxanes,[15−17] polyrotaxanes,[18−21] and polycatenanes,[22,23] that rely on so-called mechanical bonds have received attention not only for their aesthetic beauty but also for their potential utility in a variety of applications where molecular-scale motion and switching are of potential benefit.

One of the classic building blocks used to develop interlocked structures is the "blue box" (cyclobis(paraquat-*p*-phenylene) or CBPQT^{4+}) developed by Stoddart and collaborators.[24−26] This electron-deficient molecular receptor has a high affinity for a variety of π-electron donors and has been used to stabilize a wide range of molecular, supramolecular, and interlocked structures. Several variations on the basic CBPQT^{4+} motif have been reported. These include larger systems with biphenylene linkers,[27−29] various constitutional isomers,[30] and chiral analogues.[31] More recently, the diradical dicationic CBPQT$^{2(\bullet+)}$ was shown to form inclusion complexes with the viologen radical cation (V$^{\bullet+}$),[32] as well as the 1,1′-dialkyl-4,4′-bipyridinium radical cation (BIPY$^{\bullet+}$),[33] allowing access to radically based switching motifs. Unfortunately, larger cationic macrocycles can be difficult to prepare or to isolate free of interpenetrated substrates. In this Account, we detail one solution to this problem. Specifically, we summarize recent work with cyclo[2](2,6-di(1*H*-imidazol-1-yl)pyridine)[2](1,4-dimethylenebenzene) hexafluorophosphate (**1**$^{4+}\cdot 4PF_6^-$; Scheme 1) and describe how this "Texas-sized molecular box" is able to support the formation of structures that are not accessible using the classic CBPQT^{4+} motif.[34]

This larger molecular box (Figure 1), colored in burnt orange in schematic representations to contrast it from the original blue box, is conformationally flexible. It displays an ability to alter its shape in order to accommodate guests of different sizes, shapes, and charge. It will even adopt different conformations in the presence of the same guest.

Initially, we investigated the ability of **1**$^{4+}$ to generate threaded structures when combined with bis-carboxylate dianions. Beer and co-workers have published seminal work involving threaded anionic species,[35,36] and have reported various elegantly constructed catenated structures.[37,38] In our initial studies with bis-carboxylate anions, it was found that the Texas-sized box supported the formation of pseudorotaxane structures. It was also observed that the structures in question self-assembled to form a polypseudorotaxane, or "molecular necklace" in the solid state.[34] Subsequent studies revealed that the resulting supramolecular complexes were responsive to external stimuli (e.g., temperature, concentration, and pH).[39] It was also found that the addition of Ag(I) could be used to "lock" the resulting pseudorotaxane structures into place via formation of a metal-linked polyrotaxane.

The preliminary results above led us to consider whether these motifs could be used to generate more complex three-dimensional molecular frameworks. In 2010, it was suggested by Stoddart, Yaghi, and co-workers that an amalgamation of MIMs and metal−organic frameworks (MOFs) could

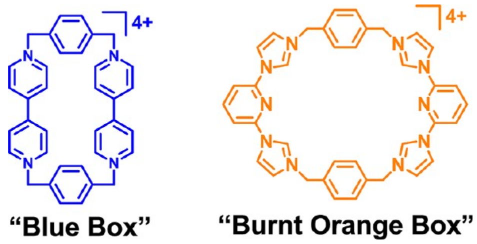
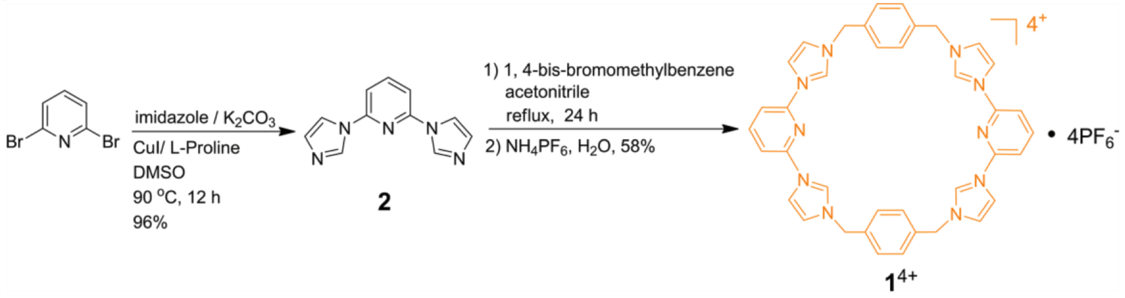


FIGURE 1. Schematic depiction of the "blue box" and the "burnt orange box".

SCHEME 1. Synthesis of **1**$^{4+}\cdot 4PF_6^-$



provide access to solid-state structures that display mechanical motion.[40] For instance, they described the incorporation of catenated struts into two-[41] and three-dimensional[42] MOF structures. In a separate work, the Kim group demonstrated how cucurbituril could be incorporated into a variety metal-linked polyrotaxane assemblies.[43−45] One-, two-, and three-dimensional metal−organic frameworks (MORFs) have also been reported by Loeb and co-workers.[46−49] As detailed below, we have found that the addition of metal cations to appropriate mixtures of the orange box and dicarboxylate anions allows for the controlled formation of MORFs,[50] as well as supramolecular organic frameworks containing metal-rotaxane subunits (RSOFs).[51]

Synthesis and Structural Characterization

Inspired by recent advances in the area of imidazolium-based anion recognition,[52,53] we considered it possible that new imidazolium tetracationic macrocycles could be developed that would act as larger analogues of the blue box. With this goal in mind, the bis-imidazole precursor **2** was prepared from 2,6-dibromopyridine in high (96%) yield via an Ullmann-type coupling and then cyclized with 1,4-bis-bromomethylbenzene to give the tetrabromide salt ($\mathbf{1}^{4+}\cdot 4\mathrm{Br}^-$). The bromide salt was readily converted to the corresponding tetrahexafluorophoshate salt via exposure to aqueous ammonium hexafluorophosphate. This gave the target receptor $\mathbf{1}^{4+}$ as its tetrakis $\mathrm{PF_6}^-$ salt in 58% yield (over two steps). The relative ease with which $\mathbf{1}^{4+}\cdot 4\mathrm{PF_6}^-$ is prepared has allowed us to explore this system in a variety of ways, as described below.

Macrocycle $\mathbf{1}^{4+}$ contains several aromatic π-surfaces and is characterized by a larger central cavity than that present in CBPQT^{4+}. It also appears to be more flexible, as inferred initially from single-crystal X-ray analyses (Figure 2). For instance, three crystallographically distinct structures for the $\mathbf{1}^{4+}\cdot 4\mathrm{PF_6}^-$ salt were obtained from separate crystallization efforts. As revealed by single-crystal X-ray analyses, in this salt form, the macrocycle can exist in boat-like (Figure 2a), "partial-chair" (Figure 2b), and a more complete chair conformation (Figure 2C). The dynamic nature of $\mathbf{1}^{4+}$ is reminiscent of Alcalde's dicationic imidazolium-based cyclophanes.[54]

Further evidence for the dynamic nature of receptor $\mathbf{1}^{4+}$ came from ^{1}H NMR spectroscopic analyses. In an initial one-dimensional spectroscopic study, only one set of signals was seen, as would be expected from a rapidly interconverting structure. However, the two-dimensional (2D) nuclear Overhauser enhancement spectroscopy (NOESY) NMR spectrum of $\mathbf{1}^{4+}\cdot 4\mathrm{PF_6}^-$ revealed coupling constants that were consistent with the presence of more than one conformer in solution. The flexible nature of this large box (i.e., $\mathbf{1}^{4+}$) and its ability to adopt different conformations to accommodate different electron-rich guest stands in stark contrast to the behavior observed with the blue box and its analogues.

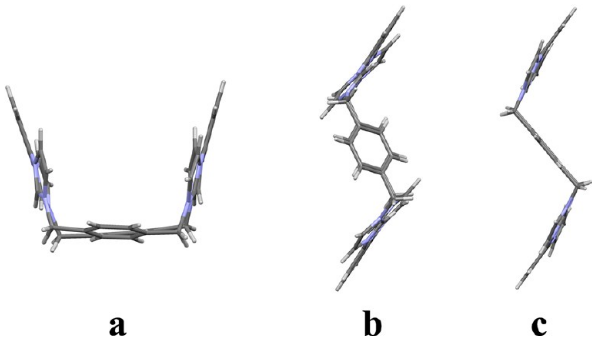


FIGURE 2. Side views of the (a) boat-like, (b) partial-chair, and (c) more complete chair conformations as revealed by three independent single-crystal X-ray analyses of $\mathbf{1}^{4+}\cdot 4\mathrm{PF_6}^-$. The bridged 1,4-phenylenedimethene groups are located on two parallel planes in structure b, the partial-chair conformation. These two bridged fragments are on the same plane in structure c, the more complete chair conformation.

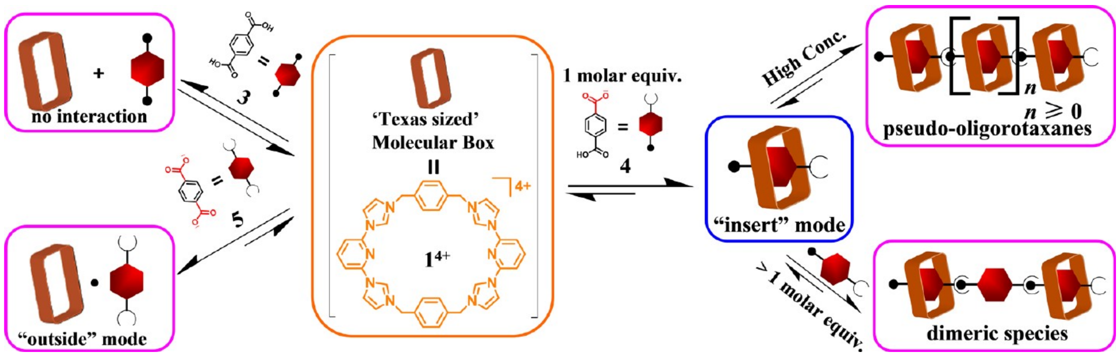


FIGURE 3. Schematic showing the observed binding as determined by ^{1}H NMR spectroscopy between $\mathbf{1}^{4+}$ and terephthalic acid (**3**) or its mono- or dideprotonated anionic forms (**4** or **5**, studied separately). Also shown is the pseudorotaxane complex formed from self-assembly of $(\mathbf{1}^{4+}\cdot\mathbf{4})^{3+}$, as well as the oligomeric aggregates produced at high concentrations.

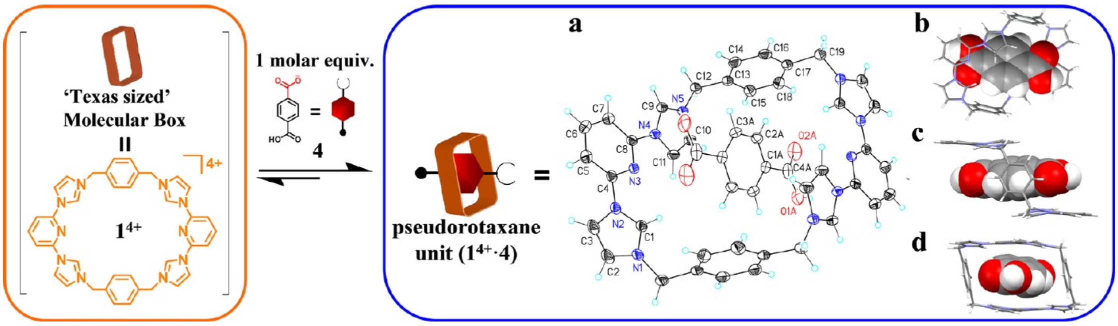


FIGURE 4. Pseudorotaxane complex ($\mathbf{1}^{4+}\cdot\mathbf{4}$) shown in (a) ellipsoid form and (b–d) various views. The excess positive charge is accommodated by PF_6^- anions. These anions and the solvent molecules are omitted for clarity.

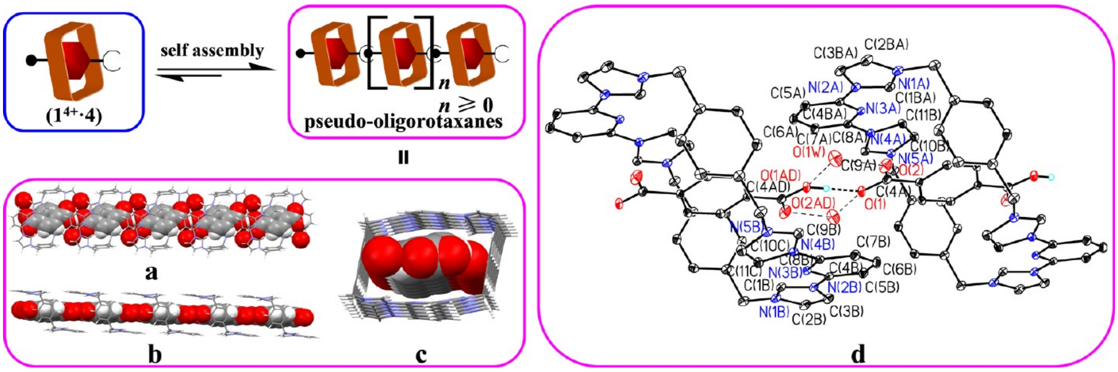


FIGURE 5. Single-crystal X-ray structure of the pseudopolyrotaxane derived from the subunits ($\mathbf{1}^{4+}\cdot\mathbf{4}$) shown as (a) top, (b) side, and (c) front views. (d) The ellipsoid form to show the interactions between two neighbor pseudorotaxane ($\mathbf{1}^{4+}\cdot\mathbf{4}$) units.

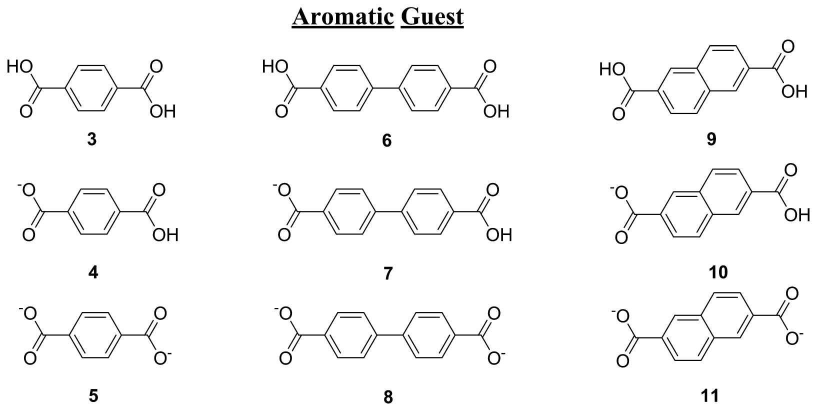


FIGURE 6. Aromatic bis-carboxylates explored as guest species.

Anion Binding and Threaded Species

The tetracationic nature of $\mathbf{1}^{4+}$ led us to postulate that anionic guests with electron-rich aromatic rings might be stabilized within the core of this macrocycle. Thus, $\mathbf{1}^{4+}\cdot 4PF_6^-$ was titrated with neutral terephthalic acid and its corresponding mono- and dianions (this and all titrations were carried out in DMSO-d_6 unless otherwise indicated). The associated spectral changes were then followed via ^{1}H NMR spectroscopy.

When $\mathbf{1}^{4+}$ was titrated with the fully protonated (diacid) form of terephthalic acid (i.e., **3**), no changes in the spectrum of $\mathbf{1}^{4+}$ were observed. However, upon titration of $\mathbf{1}^{4+}$ with the diterephathalate anion (i.e., **5**; studied as the triethylammonium (HTEA$^+$) salt), a strong spectral response was observed. These changes could be fit to a 1:1 binding profile allowing an effective affinity constant, K_a, of $(3.3 \pm 0.1) \times 10^3$ M^{-1} to be calculated. However, further investigations, involving 2D NOESY NMR spectroscopy, provided support for the conclusion that the diterephthlate anion was bound to the "outside" of the macrocyclic cavity, rather than being threaded through the molecular box (Figure 3).

Different binding behavior was seen when the monoterephthalate anion (i.e., **4**, as the $HTEA^+$ salt) was used as the guest species. In this case, ^1H NMR spectroscopic titrations proved consistent with a 1:1 binding profile and allowed a K_a value of $(2.1 \pm 0.1) \times 10^3$ M^{-1} to be calculated. Further, and in contrast to what was true for the dianion, 2D NOESY NMR analysis carried out using 1 mol equiv of **4** revealed that the guest species was threaded through the center of $\mathbf{1}^{4+}$, resulting in the formation of a pseudorotaxane complex (Figure 3). More detailed investigations, involving spectral curve fitting and Job plot analyses, provided evidence that in the presence of more than one molar equiv of **4**, a dimeric species was formed. Presumably, this supramolecular product results from the interactions between one guest and two pseudorotaxane "monomers" (i.e., $[(\mathbf{1}^{4+}\cdot\mathbf{4})\cdot\mathbf{4}\cdot(\mathbf{1}^{4+}\cdot\mathbf{4})]^{5+}$, with the excess positive charge accommodated by PF_6^- anions). Dominant features consistent with a dimeric assembly were also seen in the Fourier transform ion cyclotron resonance mass (FT-ICR-MS) spectrum, as were those ascribable to other aggregated species.

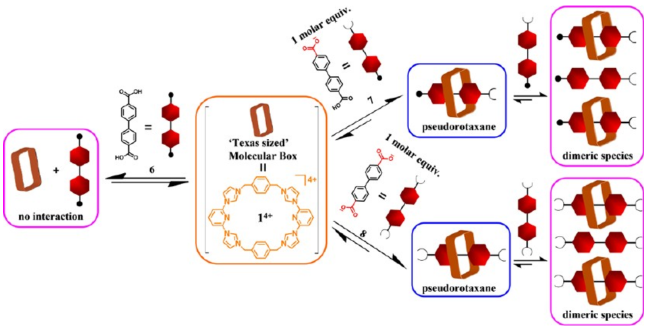


FIGURE 7. Schematic depiction of the binding interactions between $\mathbf{1}^{4+}$ and guest species **6**, **7**, and **8** (counteranions have been removed for clarity), as inferred from ^1H NMR spectroscopic analyses.[39]

Increasing the solution concentration, while holding the molar ratios of both the host and the guest species constant at 1:1, resulted in the formation of various aggregates, including dimeric $((\mathbf{1}^{4+}\cdot\mathbf{4})_2$; $K_a = (1.3 \pm 0.2) \times 10^2$ $M^{-1})$ and trimeric $((\mathbf{1}^{4+}\cdot\mathbf{4})_3$; $K_a = (8.8 \pm 2.1) \times 10^1$ $M^{-1})$ species, where again the excess positive charge is accommodated by PF_6^- anions. At very high concentrations, an insoluble precipitate was obtained, leading us to suggest that polydisperse oligomeric aggregates were formed. The soluble aggregates were characterized by use of vapor pressure osmometry (VPO) (analyses carried out in DMF), which revealed M_n values corresponding to the average formation of a dimeric species, specifically $(\mathbf{1}^{4+}\cdot\mathbf{4})_2$. Taken in concert, these results provide support for the key conclusion that receptor $\mathbf{1}^{4+}$ can stabilize oligomeric, threaded structures in solution, at least in the case of **4**.

Evidence that $\mathbf{1}^{4+}$ is capable of stabilizing anion-induced pseudorotaxane structures came from single-crystal X-ray analysis of the complex formed with **4** (Figure 4). The resulting structural analysis revealed that receptor $\mathbf{1}^{4+}$ folds into a chairlike conformation with **4** inserted through the central cavity. The $(\mathbf{1}^{4+}\cdot\mathbf{4})$ units appeared to be stabilized through a combination of hydrogen bonding and electrostatic interactions, similar to what is observed in the case of the blue box. An inter-ring distance of 3.5 Å, which is consistent with the presence of $CH\cdots\pi$ hydrogen bonding interactions between the aromatic hydrogen atoms of the anion and the perpendicular benzene rings of the macrocycle, was observed.

The individual pseudorotaxane subunits $(\mathbf{1}^{4+}\cdot\mathbf{4})$ were found to assemble through noncovalent linkages into a linear pseudopolyrotaxane structure (Figure 5). Two water molecules are involved in the linkage and provide hydrogen bond bridging interactions; for these, selected interatomic distances of O(1)···O(1AD) 2.465 Å, O(2)···O(1W) 2.676 Å, and O(1W)···O(1AD) 2.773 Å were found. Based on the

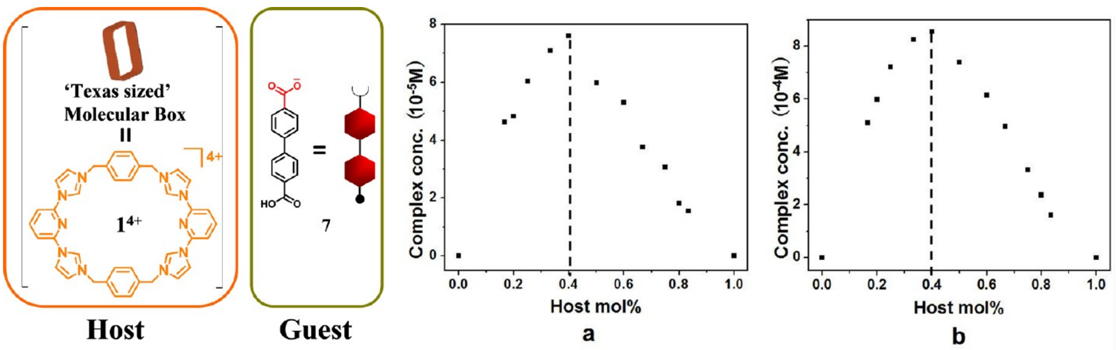


FIGURE 8. Job plots corresponding to the binding between $\mathbf{1}^{4+}\cdot 4PF_6^-$ and monoanion **7** (in DMSO-d_6) where in (a) [host] + [guest] = 5×10^{-4} M and (b) [host] + [guest] = 5×10^{-3} M.[39]

structural parameters, it was concluded that a combination of hydrogen bonding, anion$-\pi$, and electrostatic interactions contribute to the stability of this ensemble, as well as those involving constituent anions, cations, and π-surfaces. The result is a highly organized polymeric structure that is best considered as being a supramolecular necklace.

Stimuli Response and Fixation of Pseudorotaxanes

The noncovalent interactions observed in the solid state, led us to postulate that the exact structures formed from $\mathbf{1}^{4+}$ might depend on the nature of the anionic guest. To explore this possibility, we expanded the scope of the substrates under investigation to include larger aromatic diacids and their deprotonated forms (Figure 6).

Various protonated forms of two aromatic diacids, namely, 4,4′-biphenyldicarboxylic acid (i.e., **6**−**8**) and 2,6-napthalenedicarboxylic acid (i.e., **9**−**11**), were used in these studies. Initial ^{1}H NMR spectroscopic titrations with $\mathbf{1}^{4+}$ and **6** (the fully protonated form of biphenyldicarboxylic acid) revealed no spectral response. This result was consistent with the previously studied diacid system (i.e., **3**). In contrast, ^{1}H NMR spectral titrations and accompanying NOESY NMR spectroscopic studies involving $\mathbf{1}^{4+}$ and the monoanion **7** provided support for the conclusion that **7** threads into macrocycle $\mathbf{1}^{4+}$ to give a pseudorotaxane (Figure 7).

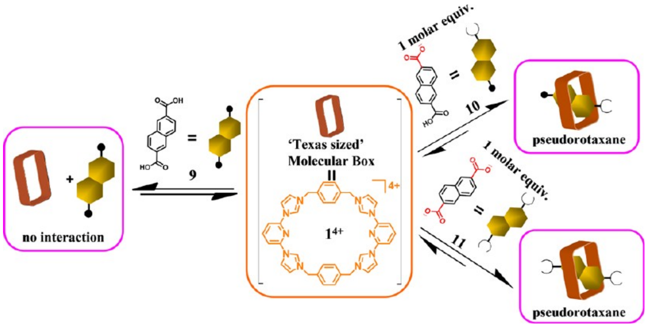


FIGURE 9. Schematic depiction of the binding interactions observed between $\mathbf{1}^{4+}$ and guest species **9**, **10**, and **11** as inferred from ^{1}H NMR spectroscopic analyses.[39]

To investigate further the behavior of $\mathbf{1}^{4+}$ and the monoanion **7** in solution, a Job plot analysis (Figure 8) was carried out. It revealed a maximum value of 0.4 ([H]/([H]+[G]) when evaluated over the 0.5−12.5 mM concentration range. This finding is consistent with a binding stoichiometry of 2:3 (H/G) and, in combination with the 2D NOESY NMR spectroscopic analyses, led us to propose that a pseudodimeric species is formed in solution (i.e., $[(\mathbf{1}^{4+}\cdot\mathbf{7})\cdot\mathbf{7}\cdot(\mathbf{1}^{4+}\cdot\mathbf{7})]^{5+}$ where the excess positive charge is balanced by PF_6^- anions). Further evidence for the existence of this proposed pseudodimeric species came from ESI mass spectrometric analyses, which revealed a peak corresponding to $[(\mathbf{1}^{4+})_2+(\mathbf{7})_3-3H]^{3+}$ (m/z= 660.6) in the gas phase.

Separately, we investigated the interactions between $\mathbf{1}^{4+}$ and **8** (the dianion of 4,4′-biphenyldicarboxylic acid). As above, a combination of Job plot and ^{1}H NMR spectroscopic analyses led to the conclusion that a pseudodimeric species exists in solution in the form of a sandwich-type complex (i.e., $[(\mathbf{1}^{4+}\cdot\mathbf{8})\cdot\mathbf{8}\cdot(\mathbf{1}^{4+}\cdot\mathbf{8})]^{2+}$). The pseudorotaxane complex formed upon exposure to dianion **8** stands in stark contrast to what is seen with **5**, where an "outside" binding mode is observed. This difference underscores how the choice of guest can influence the complexation behavior of $\mathbf{1}^{4+}$.

In the case of the wider, naphthalene-derived substrates, it was again found that the fully protonated form (**9**) did not

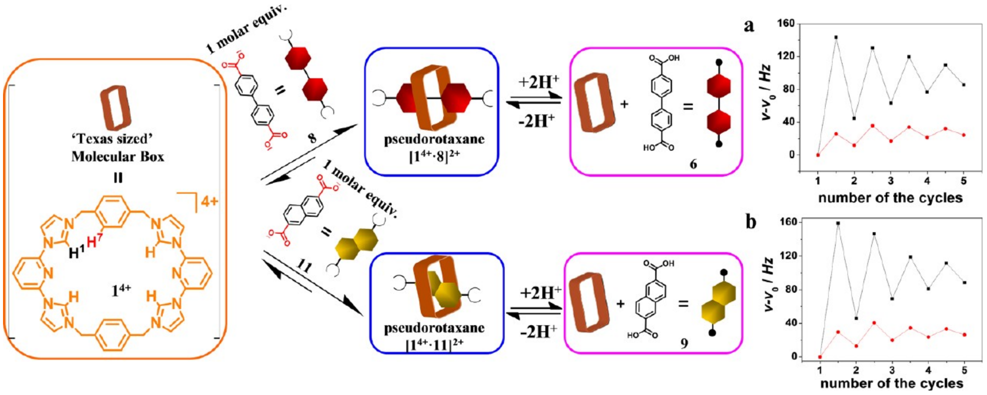


FIGURE 10. Schematic of the threading and dethreading of pseudorotaxane complexes $[\mathbf{1}^{4+}\cdot\mathbf{8}]^{2+}$ and $[\mathbf{1}^{4+}\cdot\mathbf{11}]^{2+}$, as well as graphs the cycling of this event in both complex (a) $[\mathbf{1}^{4+}\cdot\mathbf{8}]^{2+}$ and (b) $[\mathbf{1}^{4+}\cdot\mathbf{11}]^{2+}$ as inferred from pH-dependent ^{1}H NMR spectroscopic studies. Changes in chemical shift of protons H(1) (represented by "■") and H(7) (represented by "red circles") on $\mathbf{1}^{4+}$ at 300 K in DMSO-d_6 were used to monitor the switching "on" and "off" of the supramolecular complexes.[39]

interact appreciably with $\mathbf{1}^{4+}$. However, ^{1}H NMR spectroscopic titration of $\mathbf{1}^{4+}$ with **10** provided evidence for the formation of a 1:1 complex, as determined by Job plot analysis, with a experimentally determined association constant $K_a = (2.1 \pm 0.1) \times 10^3$ M^{-1}. Two-dimensional NOESY NMR analyses revealed the presence of a pseudorotaxane complex ($\mathbf{1}^{4+}\cdot\mathbf{10}$) (Figure 8). In this case, no evidence for the formation of higher ordered solution aggregates was found. When analogous studies were carried out with dianion **11**, ^{1}H NMR spectroscopic titrations revealed changes in the corresponding spectra consistent with the formation of a 1:1 pseudorotaxane complex, ($\mathbf{1}^{4+}\cdot\mathbf{11}$) ($K_a = (3.5 \pm 0.2) \times 10^4$ M^{-1}) (cf. Figure 9). Thus, as above, the choice of substrates clearly plays a critical role in dictating the self-assembly features of $\mathbf{1}^{4+}$ and its complexes.

Given the fact that these assemblies are generated from noncovalent interactions, we decided to investigate how the resulting systems responded to external stimuli. The first step in these studies was to determine the changes, if any, that occurred when the concentration of the constituent monomers was increased. In the case of $\mathbf{1}^{4+}$ and **7**, it was observed that as the solution concentration of both monomers increased, changes associated with the imidazole C$-$H signals were observed in the ^{1}H NMR spectrum. Fitting the corresponding plots of chemical shift vs concentration to a 1:1 and a 2:3 binding profile allowed association constants of $K_a = (1.5 \pm 0.1) \times 10^3$ M^{-1} and $K_{a_2} = (1.8 \pm 0.2) \times 10^7$ M^{-2} to be derived for formation of the 1:1 complex and its subsequent conversion to the more complex aggregate $[(\mathbf{1}^{4+}\cdot\mathbf{7})\cdot\mathbf{7}\cdot(\mathbf{1}^{4+}\cdot\mathbf{7})]^{5+}$, respectively. In the case of $\mathbf{1}^{4+}$ and **8**, K_a values of $(1.8 \pm 0.2) \times 10^3$ M^{-1} and $(1.1 \pm 0.1) \times 10^7$ M^{-2} were derived for formation of the 1:1 complex $[\mathbf{1}^{4+}\cdot\mathbf{8}]^{2+}$ and the more complex sandwich-type pseudodimeric species $[(\mathbf{1}^{4+}\cdot\mathbf{8})\cdot\mathbf{8}\cdot(\mathbf{1}^{4+}\cdot\mathbf{8})]^{2+}$, respectively.

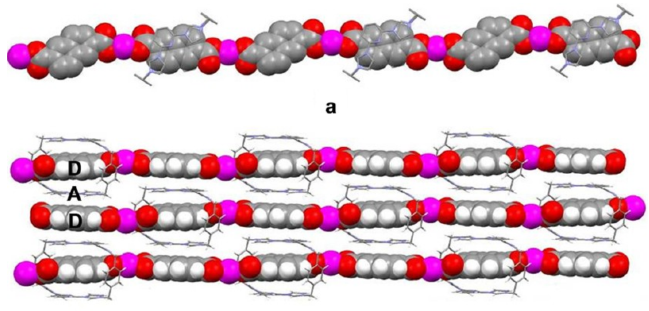


FIGURE 11. Single-crystal X-ray structure of (a) the polyrotaxane generated from monomer $[\mathbf{1}^{4+}\cdot(\mathbf{11})_2\cdot Ag_2]^{2+}$ and (b) the organization of these chains into an ordered donor$-$acceptor$-$donor (DAD) two-dimensional array. This figure originally appeared in ref 39 and is reproduced with permission. Copyright 2011 American Chemical Society.

The use of variable temperature ^{1}H NMR spectroscopy, carried out using DMSO-d_6 solutions, confirmed that the signals corresponding to the threaded species disappeared as the temperature was increased. Further, ^{1}H NMR spectroscopic studies involving the two diacid species in question (i.e., **6** and **9**) revealed resonances for $\mathbf{1}^{4+}$ that shifted to higher field upon addition of TEA. A detailed analysis of the spectral changes occurring as a function of protonation state led to the conclusion that threaded pseudorotaxane species involving the dianionic species (**8** and **11**, respectively) were being produced in the presence of TEA. On the other hand, addition of deuterated trifluoroacetic acid (CF_3CO_2D) to solutions containing $[\mathbf{1}^{4+}\cdot\mathbf{8}]^{2+}$ and $[\mathbf{1}^{4+}\cdot\mathbf{11}]^{2+}$ was found to cause dethreading of the pseudorotaxane complexes. This process of threading and dethreading could be repeated; thereby allowing pseudorotaxane formation to be "switched on" and "switched off" at will (Figure 10).

Further, we found that pseudorotaxanes derived from the naphthalene dicarboxylate anion (i.e., $[\mathbf{1}^{4+}\cdot\mathbf{11}]^{2+}$) could be

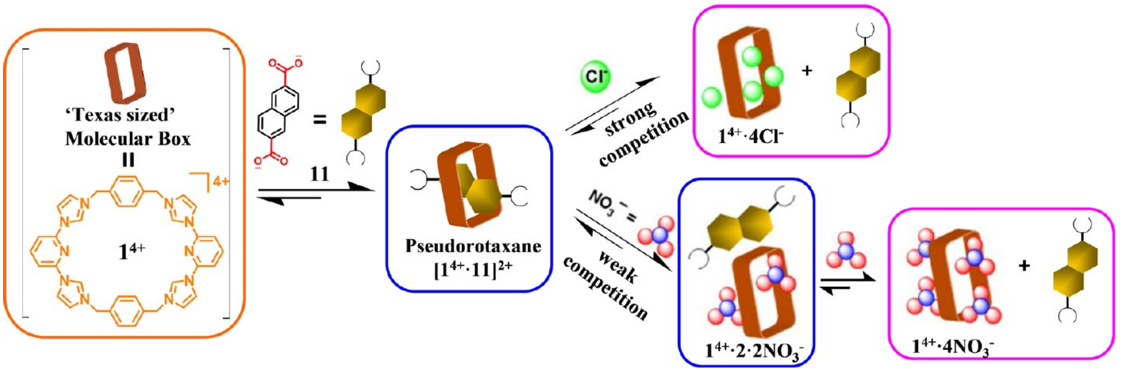


FIGURE 12. Schematic representation based on ^{1}H NMR spectroscopic studies and single-crystal X-ray diffraction analysis depicting the competitive effect of the chloride and nitrate anion on the pseudorotaxane complex $[\mathbf{1}^{4+}\cdot\mathbf{11}]^{2+}$.[55]

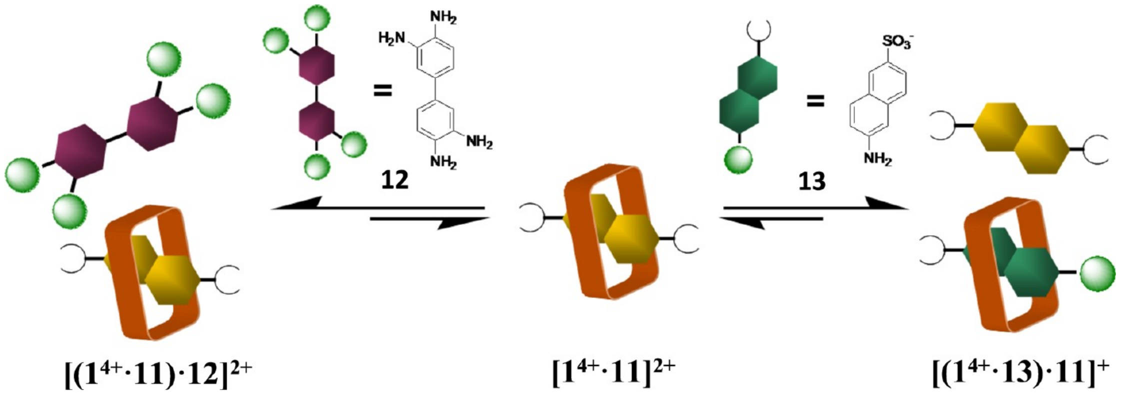


FIGURE 13. Schematic representation of competitive guest binding observed using guests **12** and **13**. This figure was modified from ref 55 (copyright 2012 John Wiley & Sons).

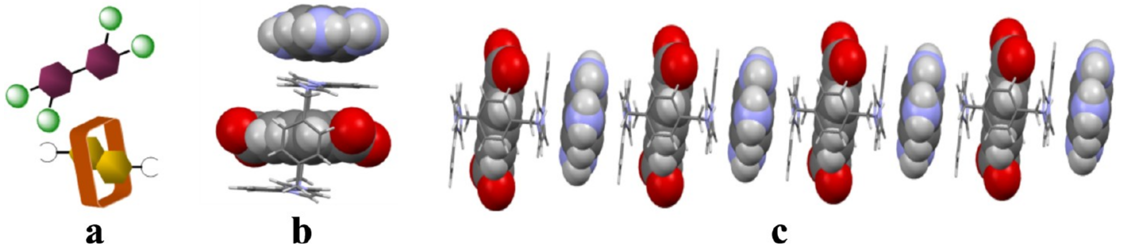


FIGURE 14. Single-crystal X-ray structure of the supramolecular complex $[\mathbf{1}^{4+}\cdot\mathbf{11}_2\cdot\mathbf{12}\cdot 17H_2O]$ shown (a) in schematic form and (b) as side views. Also shown in panel c is the extended structure of the resulting 1D DAD aggregated supramolecular polymer (i.e., $[(\mathbf{1}^{4+}\cdot\mathbf{11})\cdot\mathbf{12}]_n^{2n+}$).

organized into higher order structures via addition of metal salts. Initially, it was found that addition Ag(I) (PF_6^- or NO_3^- salt) to a solution mixture consisting of $[\mathbf{1}^{4+}\cdot PF_6^-]$, 1 molar equiv of **9** (i.e., $2H^+\cdot\mathbf{11}$), and 5 molar equiv of TEA led to the formation of an insoluble precipitate. The structure of this precipitate was confirmed via a single crystal X-ray analysis to be a 1D supramolecular polymer (i.e., a polyrotaxane). In this structure, individual pseudorotaxane units (i.e., $[\mathbf{1}^{4+}\cdot(\mathbf{11})_2\cdot Ag_2]^{2+}$) serve as monomeric species within an overall metal-linked polymeric structure that resembles a "supramolecular necklace" (Figure 11). In the solid state, the polymeric chains are further organized into an ordered two-dimensional array that is apparently stabilized by vertical donor–acceptor–donor (DAD interactions). The resulting metal-linked polymeric assembly served to "lock" the pseudorotaxane substructures into place.

Competitive Guest Binding

To expand on the results outlined in the previous section, we introduced competitive guest species to pseudorotaxane complex $[\mathbf{1}^{4+}\cdot\mathbf{11}]^{2+}$.[55] In the first of these studies, small inorganic anions, specifically chloride and nitrate (as their respective tetrabutylammonium salts (TBA^+) salts), were titrated into a mixture of $[\mathbf{1}^{4+}\cdot PF_6^-]$, $2H^+\cdot\mathbf{11}$ (1 molar equiv of each), and 5 molar equiv of TEA in DMSO-d_6. From these solution state ^1H NMR spectroscopic studies, as well as parallel NOESY NMR studies, it was found that the Cl^- anion binds to macrocycle $\mathbf{1}^{4+}$ with a high affinity ($K_1 = (4.2 \pm 0.2) \times 10^3\ M^{-1}$ and $K_2 = (6.2 \pm 0.3) \times 10^2\ M^{-1}$ for the 1:1 and subsequent 1:2 complexes, respectively). It thus dislodges **11** effectively from its threaded position in the cavity of $\mathbf{1}^{4+}$ (Figure 12). It was also found that the interaction between the nitrate anion and macrocycle $\mathbf{1}^{4+}$ was significantly weaker, resulting in calculated association constants of $K_1 = (2.0 \pm 0.1) \times 10^2\ M^{-1}$ and $K_2 = 6.3 \pm 0.4\ M^{-1}$. Thus, the nitrate anion

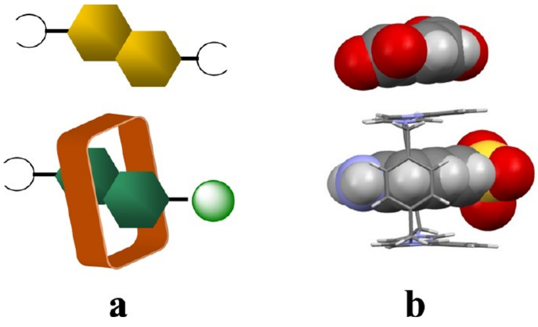


FIGURE 15. Single X-ray crystal structures of the complex of $[(\mathbf{1}^{4+}\cdot\mathbf{13})\cdot\mathbf{11}\cdot OH^-\cdot 25H_2O]$ shown (a) in schematic form and (b) as viewed from the side.

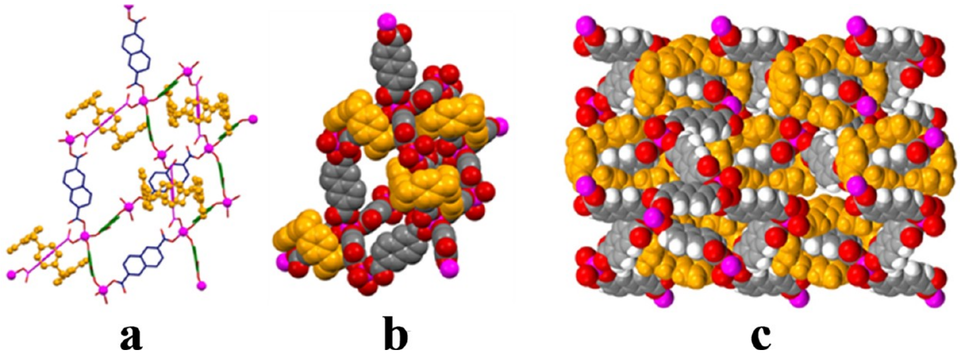


FIGURE 16. Single-crystal X-ray structure showing the (a) stick and (b) space-filling forms of the rotaxanated framework present in $\mathbf{1}^{4+}\cdot(\mathbf{11})_4\cdot Zn_2\cdot 6H_2O$, as well as (c) the packing diagram in space-filling form viewed along the crystallographic *a* axis.

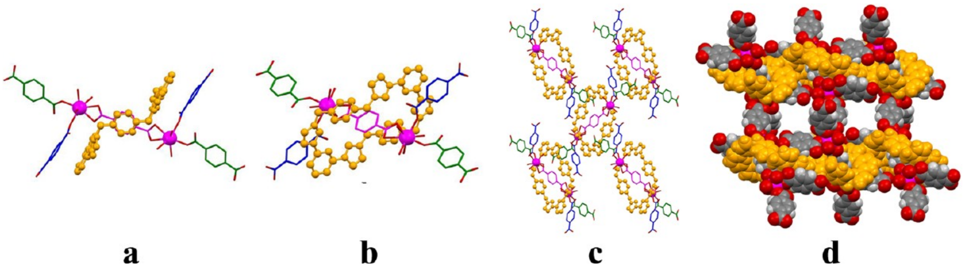


FIGURE 17. Single-crystal X-ray structure of RSOF-Er, showing (a, b) the rotaxane subunits, as well in the representative (c) stick and (d) space-filling forms of $[\mathbf{1}^{4+}\cdot(\mathbf{5})_5\cdot Er_2\cdot 8H_2O]\cdot 19H_2O$.

was only capable of displacing **11** when used in large excess. Support for these solution state studies came from single-crystal X-ray analyses of the chloride and nitrate anion salts of $\mathbf{1}^{4+}$.

As a complement to the studies described above, the addition of larger aromatic substrates containing different pendant moieties (i.e., functionalized with amino and sulfate groups) was explored (Figure 13). Specifically, we investigated the competitive effects of neutral aromatic guest biphenyl-3,4,3′,4′-tetraamine (**12**) on pseudorotaxane formation. As before, initial studies were carried out using competitive ^{1}H NMR spectroscopic titrations in conjunction with 2D NOESY NMR analyses. From these studies, it was concluded that tetraamine **12** binds to the outer periphery of $[\mathbf{1}^{4+}\cdot\mathbf{11}]^{2+}$ and is stabilized via $\pi-\pi$ donor–acceptor interactions. Further support for this postulate was provided by single-crystal X-ray diffraction analysis, which revealed supramolecular aggregates containing this binding motif in the solid state (Figure 14). The multicomponent complex $[\mathbf{1}^{4+}\cdot\mathbf{11}_2\cdot\mathbf{12}\cdot 17H_2O]$ was isolated and analyzed. In this structure, it was found that **12** is aligned parallel between the aromatic π-faces (i.e., the 2,6-di(1*H*-imidazolium-1-yl)-pyridine fragments) of two neighboring $[\mathbf{1}^{4+}\cdot\mathbf{11}]^{2+}$ units. Stacking of these discrete species was found to result in the formation of a 1D DAD supramolecular polymer (i.e., $[(\mathbf{1}^{4+}\cdot\mathbf{11})\cdot\mathbf{12}]_n^{2n+}$) in the solid state.

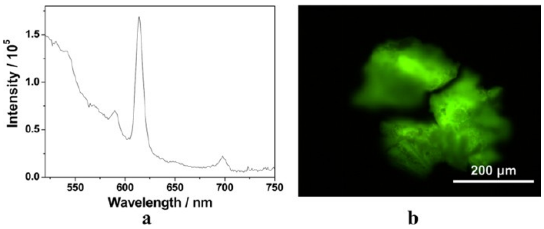


FIGURE 18. Analysis of single crystal of $[\mathbf{1}^{4+}\cdot(\mathbf{5})_5\cdot Lu_2\cdot 8H_2O]\cdot 22H_2O$ via (a) photoluminescence spectra and (b) luminescence microscopy. This figure was modified from ref 51 (copyright 2012 Royal Society of Chemistry) and is used with permission.

In a separate study, the 6-aminonapthalne-2-sulfonate anion (**13**) was investigated as a competitive guest. From ^{1}H NMR and NOESY NMR spectroscopic studies, it was concluded that addition of **13** to $[\mathbf{1}^{4+}\cdot\mathbf{11}]^{2+}$ led not only to displacement of **11** from the center of macrocycle $\mathbf{1}^{4+}$, but also to insertion of **13** into the macrocyclic core, thus forming a new pseudorotaxane structure. Support for this conclusion came from a single-crystal analysis of the supramolecular complex $[(\mathbf{1}^{4+}\cdot\mathbf{13})\cdot\mathbf{11}\cdot OH^-\cdot 25H_2O]$ (Figure 15). In the resulting structure, a pseudorotaxane (i.e., $[\mathbf{1}^{4+}\cdot\mathbf{13}]^{3+}$), involving the cocomplexation of $\mathbf{1}^{4+}$, **13**, and one molecule of **11**, was found bound to the outer face of the pseudorotaxane subunit. These results provide further support for the notion that competitive substrate binding can be used to control the basic recognition chemistry of $\mathbf{1}^{4+}$, as well as the structure of the resulting supramolecular aggregates.

Threaded Molecular Frameworks

The use of metal linkers in the organization of threaded arrangements represents an ever-evolving field of study.[56] We therefore explored the use of metals with different favored coordination numbers to control self-assembly. Initial studies in this area led to development of a facile, one-step, self-assembly-based approach to the construction of metal–organic rotaxane frameworks (MORFs) based on the Texas-sized molecular box. Specifically, combining $\mathbf{1}^{4+}$, **11**, and a source of the Zn(II) cation resulted in the formation of an ordered interlocked 3D structure, $[\mathbf{1}^{4+}\cdot(\mathbf{11})_4\cdot Zn_2\cdot 6H_2O]$, as determined via single-crystal X-ray analysis. This structurally complex material contains tetrahedron-like subunits made up of $[\mathbf{1}^{4+}\cdot\mathbf{11}]^{2+}$ pseudorotaxanes. It also contains a closed bicyclic adamantine-like arrangement of zinc cations comprised of three coordination-stabilized rotaxane motifs, as shown in Figure 16.

As an extension of the above work, the trivalent cations, namely, Y(III), Gd(III), Er(III), Tm(III), and Lu(III), were combined (separately) with $\mathbf{1}^{4+}$ and **5**. This led to the characterization of a new class of interpenetrated structure, wherein metal cation coordination in conjunction with hydrogen bonding interactions acts to stabilize complex 3D assemblies consisting of RSOFs. These materials differ from those obtained with zinc(II) in that full [2]rotaxane-containing structures were stabilized as opposed to those based on pseudorotaxanes. Single-crystal X-ray analysis was used to confirm the presence of the inferred rotaxane subunits and the presence of interlocked struts in the resulting RSOF structures. A representative example, (RSOF-Er), is shown in Figure 17.

The RSOF structures described above all contain rare-earth metals. It was thus postulated that they might display species-specific optical features. This hypothesis was tested by analyzing RSOF-Y, RSOF-Er, and RSOF-Lu by single-crystal luminescence spectroscopy. These studies revealed that all samples displayed green luminescence. Weak peaks ascribable to the rare-earth cations were seen in the photoluminescence spectra of RSOF-Y and RSOF-Lu upon excitation at 310 nm. In these samples, as well as RSOF-Er, the spectra were dominated by a broad band that tailed off from 450 to 750 nm, which was ascribed to the interaction between $\mathbf{1}^{4+}$ and **5** as inferred from control studies involving crystals of $\mathbf{1}^{4+}\cdot(\mathbf{5})_2\cdot 10H_2O$ (Figure 18).

Conclusion and Perspectives

Herein we have detailed the development and application of a novel tetraimidazolium macrocycle. This macrocycle is generated through a facile synthetic process in high yield and has proven effective in stabilizing threaded self-assembled molecular structures. Several pseudorotaxane and rotaxane structures have been produced using this molecular receptor in conjunction with aromatic anionic species. The addition of metal cations allows the further stabilization of complex, higher-order molecular assemblies. These include 1D polyrotaxanes stabilized by Ag(I) complexation, metal–organic rotaxanated frameworks based on Zn(II), and rotaxane-based supramolecular organic frameworks derived from trivalent rare earth metal cations.

We believe that this versatile molecular receptor will continue to find application in the field of molecular recognition and self-assembly permitting ultimately the construction of molecular switches and externally triggered supramolecular arrays. To date, the Texas-sized molecular box has allowed for the generation of complex molecular frameworks with threaded struts. Given the facile synthesis of this material and the variety of molecular structures it has been used to produce since being introduced late in 2010, we predict that it and related cyclic imidazolium macrocycles will continue to attract attention within the self-assembly, anion recognition, cation coordination, and MIM communities.

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FOOTNOTES

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The authors declare no competing financial interest.

REFERENCES

1 Lehn, J.-M. From supramolecular chemistry towards consitutional dynamic chemistry and adaptive chemistry. *Chem. Soc. Rev.* **2007**, *36*, 151–160.

2 Champin, B.; Mobian, P.; Sauvage, J.-P. Transition metal complexes as molecular machine prototypes. *Chem. Soc. Rev.* **2007**, *36*, 358–366.

3 Fyfe, M. C. T.; Stoddart, J. F. Synthetic supramolecular chemistry. *Acc. Chem. Res.* **1997**, *30*, 393–401.

4 Lehn, J. M. Toward self-organization and complex matter. *Science* **2002**, *295*, 2400–2403.

5 Lehn, J. M. Supramolecular chemistry. *Science* **1993**, *260*, 1762–1763.

6 Harada, A. Cyclodextrin-based molecular machines. *Acc. Chem. Res.* **2001**, *34*, 456–464.

7 Stoddart, J. F. Molecular machines. *Acc. Chem. Res.* **2001**, *34*, 410–411.

8 Sauvage, J.-P. Transition metal-containing rotaxanes and catenanes in motion: Toward molecular machines and motors. *Acc. Chem. Res.* **1998**, *31*, 611–619.

9 Raymo, F. M.; Stoddart, J. F. Interlocked macromolecules. *Chem. Rev.* **1999**, *99*, 1643–1663.

10 Mohr, B.; Weck, M.; Sauvage, J.-P.; Grubbs, R. H. High-yield synthesis of [2]catenanes by intramolecular ring-closing metathesis. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1308–1310.

11 Faiz, J. A.; Heitz, V.; Sauvage, J.-P. Design and synthesis of porphyrin-containing catenanes and rotaxanes. *Chem. Soc. Rev.* **2009**, *38*, 422–442.

12 Voegtle, F.; Duennwald, T.; Schmidt, T. Catenanes and rotaxanes of the amide type. *Acc. Chem. Res.* **1996**, *29*, 451–460.

13 Stoddart, J. F. The chemistry of the mechanical bond. *Chem. Soc. Rev.* **2009**, *38*, 1802–1820.

14 Ma, X.; Tian, H. Bright functional rotaxanes. *Chem. Soc. Rev.* **2010**, *39*, 70–80.

15 Huang, F.; Gibson, H. W. Polypseudorotaxanes and polyrotaxanes. *Prog. Polym. Sci.* **2002**, *43*, 611–612.

16 Gong, C.; Balanda, P. B.; Gibson, H. W. Supramolecular chemistry with macromolecules: New self-assembly based main chain poly pseudorotaxanes and their properties. *Macromolecules* **1998**, *31*, 5278–5289.

17 Kang, S.; Berkshire, B. M.; Xue, Z.; Gupta, M.; Layode, C.; May, P. A.; Mayer, M. F. Polypseudorotaxanes via ring-opening metathesis polymerizations of [2]catenanes. *J. Am. Chem. Soc.* **2008**, *130*, 15246–15247.

18 Gibson, H. W.; Bryant, W. S.; Lee, S.-H. Polyrotaxanes by free-radical polymerization of acrylate and methacrylate monomers in the presence of a crown ether. *J. Poly. Sci., Part A: Polym. Chem.* **2001**, *39*, 1978–1993.

19 Gong, C.; Gibson, H. W. Polyrotaxanes and related structures: Synthesis and properties. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 647–652.

20 Harada, A.; Takashima, Y.; Yamaguchi, H. Cyclodextrin-based supramolecular polymers. *Chem. Soc. Rev.* **2009**, *38*, 875–882.

21 Terao, J.; Tsuda, S.; Tanaka, Y.; Okoshi, K.; Fujihara, T.; Tsuji, Y.; Kambe, N. Synthesis of organic-soluble conjugated polyrotaxanes by polymerization of linked rotaxanes. *J. Am. Chem. Soc.* **2009**, *131*, 16004–16005.

22 Niu, Z.; Gibson, H. W. Polycatenanes. *Chem. Rev.* **2009**, *109*, 6024–6046.

23 Takata, T.; Kihara, N.; Furusho, Y. Polyrotaxanes and polycatenanes: Recent advances in syntheses and applications of polymers comprising interlocked structures. *Adv. Polym. Sci.* **2004**, *171*, 1–75.

24 Odell, B.; Reddington, M. V.; Slawin, A. M.; Spencer, N.; Stoddart, J. F.; Williams, D. J. Cyclo(paraquat-p-phenylene). A tetracationic Multipurpose Receptor. *Angew. Chem., Int. Ed.* **1988**, *27*, 1547–1550.

25 Ashton, P. R.; Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. Isostructural, alternately-charge receptor stacks. The inclusion complexes of hydroquinone and catechol dimethyl ethers with cyclobis(paraquat-p-phenylene). *Angew. Chem., Int. Ed.* **1988**, *27*, 1550–1553.

26 Amabilino, D. B.; Stoddart, J. F. Self-assembly and macromolecular design. *Pure Appl. Chem.* **1993**, *65*, 2351–2359.

27 Asakawa, M.; Aston, P. R.; Menzer, S.; Raymo, F. M.; Stoddart, J. F. Cyclobis(paraquat-4,4′biphenylene)-an organic molecular square. *Chem. Eur. J.* **1996**, *2*, 877–893.

28 Amabilino, D. B.; Ashton, P. R.; Brown, C. L.; Córdova, E.; Godínez, L. A.; Goodnow, T. T.; Kaifer, A. E.; Newton, S. P.; Rutland, M. T.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. Molecular meccano. 2. Self-assembly of [n]catenanes. *J. Am. Chem. Soc.* **1995**, *117*, 1271–1293.

29 Ashton, P. R.; Menzer, S.; Raymo, F. M.; Shimizu, G. K. H.; Stoddart, J. F.; Williams, D. J. The template-directed synthesis of cyclobis(paraquat-4,4′-biphenylene). *Chem. Commun.* **1996**, 487–490.

30 Amabilino, D. B.; Ashton, P. R.; Tolley, M. S.; Stoddart, J. F.; Williams, D. J. Isomeric self-assembling [2]catenanes. *Angew. Chem., Int. Ed.* **1999**, *32*, 1297–1303.

31 Aston, P. R.; Heiss, A. M.; Pasini, D.; Raymo, F. M.; Shipway, A. N.; Stoddart, J. F.; Spencer, N. Diasteroselective self-assembly of [2]Catenanes. *Eur. J. Org. Chem.* **1999**, *5*, 995–1004.

32 Trabolsi, A.; Khashab, N.; Fahrenbach, A. C.; Friedman, D. C.; Colvin, M. T.; Cotí, K. K.; Benitez, D.; Tkatchouk, E.; Olsen, J.-C.; Belowich, M. E.; Carmielli, R.; Khatib, H. A.; Goddard, W. A., III; Wasielewski, M. R.; Stoddart, J. F. Radically enhanced molecular recognition. *Nat. Chem.* **2010**, *2*, 42–49.

33 Fahrenbach, A. C.; Barnes, J. C.; Lanfranchi, D. A.; Li, H.; Coskun, A.; Gassensmith, J. J.; Liu, Z.; Benítez, D.; Trabolsi, A.; Goddard, W. A.; Elhabiri, M.; Stoddart, J. F. Solution–phase mechanistic study and solid–state structure of a tris(bipyridinium radical cation) inclusion complex. *J. Am. Chem. Soc.* **2012**, *134*, 3061–3072.

34 Gong, H. -Y.; Rambo, B. M.; Karnas, E.; Lynch, V. M.; Sessler, J. L. A `Texas-sized' molecular box that forms an anion-induced supramolecular necklace. *Nat. Chem.* **2010**, *2*, 406–409.

35 Lankshear, M. D.; Beer, P. D. Interweaving anion templation. *Acc. Chem. Res.* **2007**, *40*, 657–668.

36 Beer, P. D.; Sambrook, M. R.; Curiel, D. Anion-templated assembly of interpenetrated and interlocked structures. *Chem. Commun.* **2006**, 2105–2117.

37 Vickers, M. S.; Beer, P. D. Anion template assembly of mechanically interlocked structures. *Chem. Soc. Rev.* **2007**, *36*, 211–225.

38 Vickers, M. S.; Beer, P. D. Sulfate anion templation of macrocycles, capsules, interpenetrated and interlocked structures. *Chem. Soc. Rev.* **2009**, *38*, 1701–1713.

39 Gong, H.-Y.; Rambo, B. M.; Karnas, E.; Lynch, V. M.; Keller, K. M.; Sessler, J. L. Environmentally responsive threading, dethreading, and fixation of anion-induced pseudorotaxanes. *J. Am. Chem. Soc.* **2011**, *133*, 1526–1533.

40 Deng, H.; Olson, M. A.; Stoddart, J. F.; Yaghi, O. M. Robust dynamics. *Nat. Chem.* **2010**, *2*, 439–443.

41 Li, Q.; Zhang, W.; Milajanic, O. S.; Knobler, C. B.; Stoddart, J. F.; Yaghi, O. M. A metal-organic framework replete with ordered donor-acceptor catenanes. *Chem. Commun.* **2010**, *46*, 380–382.

42 Li, Q.; Sue, C.-H.; Basu, S.; Shveyd, A. K.; Zhang, W.; Barin, G.; Fang., L.; Sarjeant, A. A.; Stoddart, J. F.; Yaghi, O. M. A catenated strut in a metal-organic framework. *Angew. Chem., Int. Ed.* **2010**, *49*, 6751–6755.

43 Whang, D.; Kim, K. Polycatenated two-dimensional polyrotaxane net. *J. Am. Chem. Soc.* **1997**, *119*, 451–452.

44 Lee, E.; Heo, J.; Kim, K. A three-dimensional polyrotaxane network. *Angew. Chem., Intl Ed.* **2000**, *39*, 2699–2701.

45 Kim, K. Mechanically interlocked molecules incorporating cucurbituril and their supramolecular assemblies. *Chem. Soc. Rev.* **2002**, *31*, 96–107.

46 Loeb, S. J. Rotaxanes as ligands: From molecules to materials. *Chem. Soc. Rev.* **2007**, *36*, 226–235.

47 Hoffart, D. J.; Loeb, S. J. Metal-organic rotaxane frameworks: Three-dimensional polyrotaxanes from lanthanide-ion nodes, pyridinium n-oxide axles, and crown-ether wheels. *Angew. Chem., Int. Ed.* **2005**, *44*, 901–904.

48 Vukotic, V. N.; Loeb, S. J. One-, two- and three-periodic metal—organic rotaxane frameworks (MORFs): Linking cationic transition-metal nodes with an anionic rotaxane ligand. *Chem. Eur. J.* **2010**, *16*, 13630–13637.

49 Mercer, D. J.; Vukotic, V. N.; Loeb, S. J. Linking [2]rotaxane wheels to create a new type of metal organic rotaxane framework. *Chem. Commun.* **2011**, *47*, 896–898.

50 Gong, H.-Y.; Rambo, B. M.; Cho, W.; Lynch, V. M.; Oh, M.; Sessler, J. L. Anion-directed assembly of a three dimensional metal-organic rotaxane framework. *Chem. Commun.* **2011**, *47*, 5973–5975.

51 Gong, H.-Y.; Rambo, B. M.; Nelson, C. A.; Cho, W.; Lynch, V. M.; Zhu, X.; Oh, M.; Sessler, J. L. Multi component self-assembly: Supramolecular organic frameworks containing metal-rotaxane subunits (RSOFs). *Dalton Trans.* **2012**, *41*, 1134–1137.

52 Yoon, J.; Kim, S. K.; Singh, N. J.; Kim, K. S. Imidazolium receptors for the recognition of anions. *Chem. Soc. Rev.* **2006**, *35*, 355–360.

53 Caltagirone, C.; Gale, P. A. Anion receptor chemistry: Highlights from 2007. *Chem. Soc. Rev.* **2009**, *38*, 520–563.

54 Alcalde, E.; Mesquida, N.; Vilaseca, M.; Alvarez-Rúa, C.; Garcia-Granda, S. Imidazolium-based dicationic cyclophanes. Solid-state aggregates with unconventional $(C\text{-}H)^{+}\cdots Cl^{-}$ hydrogen bonding revealed by X-ray diffraction. *Supramol. Chem.* **2007**, *19*, 501–509.

55 Gong, H. -Y.; Rambo, B. M.; Lynch, V. M.; Keller, K. M.; Sessler, J. L.; Neutral and anionic guest and their effect on the formation of pseudorotaxanes using a flexible tetracationic imidazolium macrocycle. *Chem. Eur. J.* **2012**, Early View 10.1002/chem.201200304.

56 Beves, J. E.; Blight, B. A.; Campbell, C. J.; Leigh, D. A. Strategies and tactics for the metal-directed synthesis of rotaxanes, knots, catenanes, and higher order links. *Angew. Chem., Int. Ed.* **2011**, *50*, 9260–9327.