Environmentally Responsive Threading, Dethreading, and Fixation of Anion-Induced Pseudorotaxanes

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S *Supporting Information*

ABSTRACT: The tetracationic macrocycle cyclo[2](2,6-di(1*H*-imidazol-1-yl)pyridine)[2](1,4-dimethylenebenzene) hexafluorophosphate ($1^{4+} \cdot 4PF_6^-$) acts as a large, flexible "molecular box" that supports the formation of environmentally responsive anion-induced pseudorotaxanes, as well as other extended structures, including metal-linked supramolecular polyrotaxanes. Specifically, the combination of the tetracation 1^{4+} and bis-carboxylate guests derived from 4,4′-biphenyldicarboxylic acid and 2,6-naphthalenedicarboxylic acid results in the formation of pseudorotaxanes that respond to changes in environmental stimuli, including pH and temperature. The resulting structures can be "locked into place" via the addition of a metal-linker in the form of Ag(I); this gives rise to an ordered metal-linked polyrotaxane. The interpenetrated constructs described in this article were characterized in solution and in the solid state by one- and two-dimensional (^{1}H and NOESY) NMR spectroscopy, as well as by mass spectrometry (ESI-MS) and single-crystal X-ray diffraction methods.
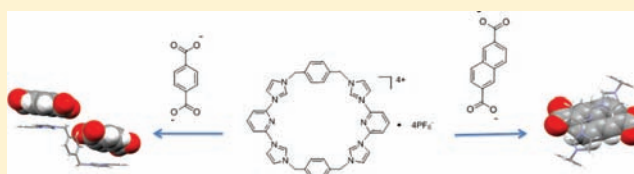
INTRODUCTION

In the past three decades, synthetic and material chemists have made tremendous strides in exploiting non-covalent interactions to create complex molecular architectures.[1−3] Within the context of this general paradigm, one area that has seen explosive growth in recent years involves the production of interpenetrated structures, such as pseudorotaxanes,[4−6] rotaxanes,[7−9] catenanes,[9−15] pseudo[*n*]polyrotaxanes,[16,17] and polyrotaxanes.[18−22] However, the use of anionic precursors as the key components in the construction of interlocked structures has not been extensively explored and may represent an underdeveloped approach that could complement other, better studied threading strategies. In a series of seminal studies, Beer and co-workers used anionic structures as templating agents in the construction of interlocked species, particularly in the formation of various elegant catenated products.[4−6,23−25] Further, combinations of anionic and cationic components have been used to form pseudorotaxanes[26,27] and polyrotaxanes.[28] Recently, we showed that a large "molecular box", the tetracationic macrocyclic receptor cyclo[2](2,6-di(1*H*-imidazol-1-yl)pyridine)[2](1,4-dimethylenebenzene) hexafluorophosphate ($1^{4+} \cdot 4PF_6^-$, cf. Chart 1), could be used to create pseudorotaxanes and poly-pseudorotaxanes from the monoterephthalate anion (i.e., **3**).[29] This initial work led us to explore whether dianionic structures, particularly bis-carboxylate dianions, could be used to construct stabilized threaded structures (i.e., pseudorotaxanes). Bis-carboxylate dianions have received

tremendous attention for their role in the construction of metal−organic frameworks (MOFs),[30] and their incorporation into interlocked structures that exploit the self-assembly features of supramolecular chemistry could lead to a new approach to the preparation of dynamic and mechanically robust materials. Herein we report that the "box-like" macrocycle 1^{4+} acts as a conformationally flexible molecular receptor that is able to incorporate several anionic guests, namely 4,4′-biphenyldicarboxylic acid and 2,6-naphthalenedicarboxylic acid in their various deprotonated forms (cf. Chart 1; structures **5−10**), to produce well-defined pseudorotaxanes, both in DMSO solution and in the solid state. Further, we show that these interpenetrated supramolecular complexes respond to external stimuli, including pH and temperature, with the formation of pseudorotaxane complexes being specifically "turned-off" when the guest species are fully protonated. The decomplexation and formation of the pseudorotaxane complexes is easily controlled with pH switching. Such molecular-scale switching provides a functional core for making many different types of molecular devices, such as the ones created with the blue box of Stoddart and co-workers,[19] as well as with other macrocycles such as cyclodextrins and crown ethers.[31−34] Finally, we detail how the addition of Ag(I) to the starting reaction mixture consisting of 1^{4+} and 2,6-naphthalenedicarboxylate dianion

Chart 1. Structure of the Tetracationic Molecular Box $(1^{4+} \cdot 4PF_6^-)^a$ and Aromatic Guest Molecules Derived from Terephthalic Acid (2–4), 4,4′-Biphenyldicarboxylic Acid (5–7), and 2,6-Naphthalenedicarboxylic Acid (8–10)
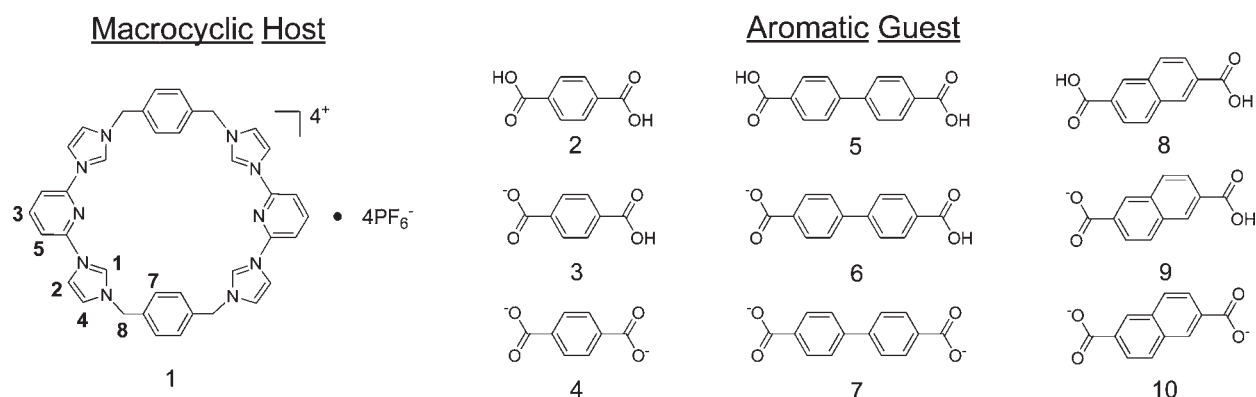
^{a} The protons of **1** have been labeled 1–8 for clarity.

(i.e., **10**) results in the spontaneous assembly of an ordered, metal-linked polyrotaxane structure wherein every other dianionic subunit in the 1-D inorganic array is threaded through an individual molecular box (i.e., interpenetrated through a subunit of 1^{4+}). This structure is stable until exposed to highly acidic solutions, thus effectively fixing the constituent pseudorotaxane subunits in a permanently threaded, mechanically locked form.

Environmentally responsive, as well as mechanically locked, threaded systems are of considerable current interest. They have been widely exploited to produce *inter alia* a range of topologically unique chemical entities, as well as complex molecular systems that elicit a particular structural response, such as molecular motion, when subject to appropriate stimuli.[35,36] Quite recently, it was proposed that incorporating mechanically interlocked structures into MOFs could add complexity and impart dynamic features into these already robust systems.[37,38] In first efforts directed toward this goal, Stoddart, Yaghi, and co-workers reported MOFs that bear appended rings that can *inter alia* store guest molecules via formation of pseudorotaxanes.[39–41] In these structures, the critical ring subunits were fused to the dicarboxylate bridges and used to create the extended, metal-linked structure. As a consequence, none of the MOF-defining structural elements were actually threaded through a macrocyclic or catenated ring. However, a variety of metal-linked threaded structures based on cucurbiturils and nitrogen–cation interactions have been described by the Kim group.[42,43] Separately, Liu utilized Cu(II) binding to preorganize a dimeric β-cyclodextrin[44] and also reported polymeric rotaxanes with nickel(II) ions[45] and Ru(bpy)$_2$ centers linked via interpenetrated sp^2-hybridized nitrogen donor groups.[46] Nitrogen coordination was also used by Loeb to develop metal–organic rotaxane frameworks.[47–49] Additionally, Su incorporated polyoxometalates into MOFs.[50,51] Surprisingly, however, simple dicarboxylates, which have proved so effective for MOF construction, have yet to be used to create metal-based interpenetrated structures with long-range order. To the best of our knowledge, the present report describes one of the first examples of a metal-linked polymeric rotaxane structure generated via anion-induced threading. It also constitutes the first report of anion-threaded species that respond to simple changes in the chemical environment.

■ RESULTS AND DISCUSSION

The synthesis of macrocycle 1^{4+} (cf. Chart 1 for structure) was accomplished in two steps as recently reported.[29] Briefly, the key trimeric fragment 2,6-di(1H-imidazol-1-yl)pyridine was prepared via an Ullman-type coupling; it was then cyclized with 1,4-bis(bromomethyl)benzene and finally converted to the tetrahexafluorophosphate salt (via exposure to aqueous ammonium hexafluorophosphate) to give $1^{4+} \cdot 4PF_6^-$.

Previously, we noted that exposing 1^{4+} to terephthalic acid (**2**) resulted in no observable binding, as judged by ^{1}H NMR spectroscopic analysis. On the other hand, the diterephthalate anion (i.e., **4**) was found to bind to the outer periphery of macrocycle 1^{4+} with $K_a = (3.3 \pm 0.1) \times 10^3$ M^{-1}. (This and all other anions were studied as their respective triethylammonium (HTEA$^+$) salts.) Finally, exposure to the monoterephthalate anion (**3**) resulted in formation of a pseudorotaxane structure ($K_a = (2.1 \pm 0.1) \times 10^3$ M^{-1}, corresponding to a 1:1 complex), wherein macrocycle 1^{4+} adopts a chairlike conformation. Under certain conditions, the resulting pseudorotaxane structures were shown to self-assemble into oligomeric species that were characterized both in solution ($K_a = (2.4 \pm 0.2) \times 10^5$ M^{-2}, corresponding to a 2:3 complex, was noted in DMSO-d_6) and in the solid state. In an effort to probe the generality of these findings, expand our understanding of the reversible nature of these systems, and explore whether these building blocks could be used to create 1D metal-linked polyrotaxanes, we have now studied the interactions of 1^{4+} with two other larger aromatic diacids, namely 4,4′-biphenyldicarboxylic acid and 2,6-naphthalenedicarboxylic acid, as well as their anionic forms. The results of these investigations, which have been extended to include a first, Ag(I)-stabilized extended polyrotaxane structure based on 1^{4+} and **10**, are detailed below.

In the case of 4,4′-biphenyldicarboxylic acid (**5**), ^{1}H NMR spectroscopic titrations with 1^{4+} revealed no spectral response (all titrations were carried out in DMSO-d_6). However, direct titration of 1^{4+} with the monoanion **6** resulted in distinct chemical shifts in the ^{1}H NMR spectral features associated with both the host and the guest (most notably for the imidazole C–H resonance and in the aromatic peaks corresponding to **6**). Two-dimensional NOESY NMR spectroscopic studies revealed cross peaks consistent with **6** being inserted inside macrocycle 1^{4+}, a binding mode that results in the formation of a pseudorotaxane (Figure 1).
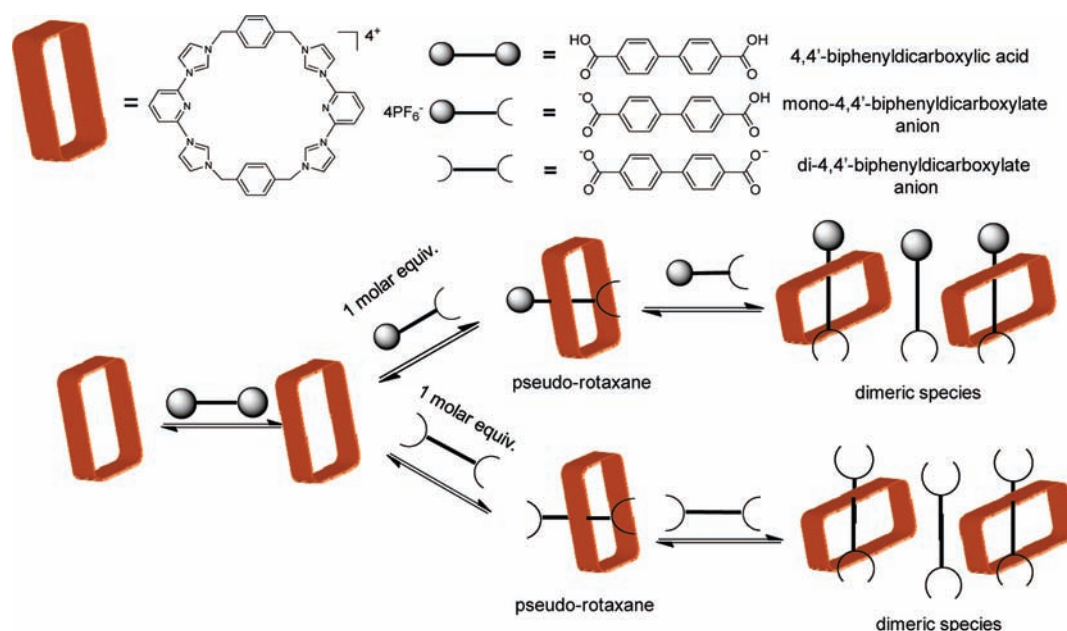
Figure 1. Schematic representation of the observed binding interactions between $\mathbf{1}^{4+}$ and guest species **5**, **6**, and **7**, as inferred from NMR spectroscopic analyses (counteranions have been removed for clarity).

A complementary Job plot analysis revealed a maximum value of 0.4 ($[H]/([H]+[G])$), a result that leads us to suggest that a binding stoichiometry of 2:3 (H:G) best describes the interaction between $\mathbf{1}^{4+}$ and **6** in solution. On the basis of this result and the NOESY NMR analyses noted above, it is proposed that a pseudodimeric species $[(\mathbf{1}^{4+}\cdot\mathbf{6})\cdot\mathbf{6}\cdot(\mathbf{1}^{4+}\cdot\mathbf{6})]^{5+}$ is formed with the excess guest molecular anion **6** "sandwiched" between two sets of individual $[\mathbf{1}^{4+}\cdot\mathbf{6}]^{3+}$ host–guest complexes.[52] Further support for the formation of the proposed pseudodimeric species came from mass spectrometric studies using ESI-MS, which showed a peak corresponding to $[(\mathbf{1}^{4+})_2 + (\mathbf{6})_3 - 3H]^{3+\bullet}$ (m/z = 660.6) in the gas phase.

As a complement to the Job plot analyses, an isodesmic titration was performed, wherein the changes in the chemical shift corresponding to the imidizole C–H (H1; see Supporting Information) were monitored as the overall solution concentration was increased (the molar ratio of host:guest was held constant). Fitting to both 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 $K_{a2} = (1.8 \pm 0.2) \times 10^7$ M^{-2} for 1:1 complexation to give $[\mathbf{1}^{4+}\cdot\mathbf{6}]^{3+}$ and subsequent conversion to $[(\mathbf{1}^{4+}\cdot\mathbf{6})\cdot\mathbf{6}\cdot(\mathbf{1}^{4+}\cdot\mathbf{6})]^{5+}$ to be calculated.

Titrations of $\mathbf{1}^{4+}$ with **7** (the dianion of 4,4′-biphenyldicarboxylic acid) revealed a very similar binding phenomenon. Specifically, Job plot analysis revealed a 2:3 (H:G) binding stoichiometry in solution (cf. Supporting Information, Figure S4); again, this is ascribed to the formation of a sandwich-type, complex dimeric species (e.g., $[(\mathbf{1}^{4+}\cdot\mathbf{7})\cdot\mathbf{7}\cdot(\mathbf{1}^{4+}\cdot\mathbf{7})]^{2+}$; Figure 1), wherein the excess positive charge is balanced by PF$_6^-$ anions. Evidence for the formation of this pseudodimeric species was again found in the gas phase via ESI-MS ($[(\mathbf{1}^{4+})_2 + (\mathbf{7})_3]^{3+\bullet}$; m/z = 660.6).[53]

Two-dimensional NOESY NMR analyses of the complex cation $[(\mathbf{1}^{4+}\cdot\mathbf{7})\cdot\mathbf{7}\cdot(\mathbf{1}^{4+}\cdot\mathbf{7})]^{2+}$ revealed cross-peaks consistent with the formation of a pseudorotaxane complex (cf. Supporting Information, Figure S11). This interpenetrated structure is distinctly different from the previously reported "outside binding"

observed when $\mathbf{1}^{4+}$ is exposed to **4** (terephthalate dianion).[29] Thus, a significant dependence on the choice of the dianion is seen, with the larger of these two dianions (only) forming a pseudorotaxane.

From ^{1}H NMR spectral titrations, carried out in analogy to those involving $\mathbf{1}^{4+}$ and **6**, K_a values of $(1.8 \pm 0.2) \times 10^3$ and $(1.1 \pm 0.1) \times 10^7$ M^{-2} were derived for formation of the 1:1 complex $[\mathbf{1}^{4+}\cdot\mathbf{7}]^{2+}$ and the sandwich-type pseudodimeric species $[(\mathbf{1}^{4+}\cdot\mathbf{7})\cdot\mathbf{7}\cdot(\mathbf{1}^{4+}\cdot\mathbf{7})]^{2+}$, respectively (cf. Figure 1 and Supporting Information, Figure S6).

Given the disparity in binding behavior observed for the dianions of terephthalic acid and 4,4′-biphenyldicarboxylic acid (i.e., **4** and **7**), we investigated the ability of $\mathbf{1}^{4+}$ to interact with 2,6-naphthalenedicarboxylic acid (**8**) and its mono- (**9**) and dianions (**10**) (cf. Figure 2). As in the case of diacids **2** and **5**, solution-based ^{1}H NMR spectroscopic titration studies involving the addition of fully protonated species **8** (i.e., 2,6-naphthalenedicarboxylic acid) to a DMSO-d_6 solution of $\mathbf{1}^{4+}$ revealed no detectable variations in the NMR spectrum. However, analogous titrations of $\mathbf{1}^{4+}$ with **9** (monoanion) provided evidence for the formation of a 1:1 complex (as revealed by Job plot analysis) with an association constant $K_a = (2.1 \pm 0.1) \times 10^3$ M^{-1}. Further, analysis by NOESY NMR methods provided support for the conclusion that, in this 1:1 complex, the monoanion (**9**) is indeed inserted into the macrocyclic core (Figure 2). However, in stark contrast to what was seen for **3** and **6**, no evidence for the formation of dimeric or trimeric species (either linear or sandwich type) was found in the case of the resulting complex, $[\mathbf{1}^{4+}\cdot\mathbf{9}]^{3+}$ (discussed in more detail below). Therefore, even though the key threading chemistry was seen in the case of all three monoanions, it is important to note that the supramolecular structures (if any) built up from the interaction between the intercalated species differed dramatically. Again, this underscores the subtle differences seen with different anions.

An absence of higher order structures was also found in the case of the dianion (2,6-naphthalenedicarboxylate, **10**). In this case, as with **7**, an ^{1}H NMR-based spectroscopic titration,
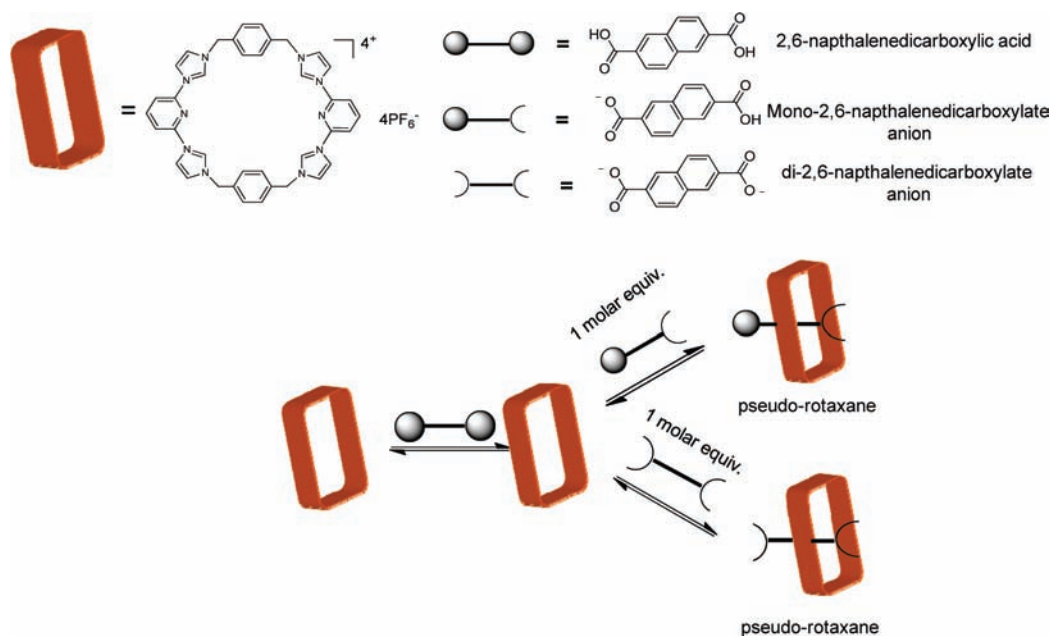
Figure 2. Schematic representation of the observed binding interactions between 1^{4+} and guest species **8**, **9**, and **10**, as inferred from NMR spectroscopic analyses.

involving the addition of **10** to a DMSO-d_6 solution of 1^{4+}, gave rise to changes in the spectrum consistent with the formation of a 1:1 pseudorotaxane complex, $[1^{4+} \cdot 10]^{2+}$. A binding constant of $K_a = (3.5 \pm 0.2) \times 10^4 \, M^{-1}$ was calculated, and separate NOESY NMR analyses provided support for the conclusion that, in this 1:1 complex, **10** is inserted into the macrocyclic core (cf. Supporting Information for the relevant spectra). However, in contrast to what was seen with **7**, no features ascribable to higher ordered aggregates were observed (Figure 2). The K_a corresponding to the formation of the pseudorotaxane complex $[1^{4+} \cdot 10]^{2+}$ is slightly larger than that for either $[1^{4+} \cdot 4]^{2+}$ or $[1^{4+} \cdot 7]^{2+}$, a finding that may reflect the relatively enhanced hydrogen bond acceptor and π-donor abilities of **10**. The resulting greater stabilization of the complex could account for the fact that no higher order species are seen. However, steric factors cannot be ruled out; in $[1^{4+} \cdot 10]^{2+}$, the intercalated dianion is less favorably disposed to interact with other entities, threaded or otherwise.

As might be expected given their non-covalent, threaded nature, the pseudorotaxanes in this study were found to be sensitive to changes in the environmental conditions. The reversible nature of pseudorotaxane formation was studied in the case of the pseudorotaxanes $[1^{4+} \cdot 6]^{3+}$, $[1^{4+} \cdot 7]^{2+}$, $[1^{4+} \cdot 9]^{3+}$, and $[1^{4+} \cdot 10]^{2+}$ as they were exposed to changes in temperature and pH. Initially, variable-temperature ^{1}H NMR spectroscopic studies revealed losses in the signals corresponding to the threaded species (specifically, shifts were seen for the imidazole C–H (H1) resonance in the signals ascribed to the non-interpenetrated form) as the temperature was increased (see Supporting Information, Figures S15, S16, S34, and S35). Such a finding is consistent with the formation of complexes stabilized by weak intermolecular hydrogen bonds and donor–acceptor interactions, as opposed to more robust covalent or mechanical bonds.

Further support for the reversible nature of these self-assembly systems came from pH-dependent ^{1}H NMR spectroscopic studies. Here, it was found that, upon addition of triethylamine (TEA) to DMSO-d_6 solutions containing 1^{4+} and either diacid species (**5** and **8**, respectively), the H(1) and H(7) signals of 1^{4+}

shift to higher field. This leads us to suggest that, under these conditions, **5** and **8** are deprotonated and thus converted to the corresponding dianionic species (**7** and **10**, respectively), which leads to pseudorotaxane formation. Increasing the acidity of the resulting solutions (containing $[1^{4+} \cdot 7]^{2+}$ and $[1^{4+} \cdot 10]^{2+}$, respectively) via the addition of deuterated trifluoroacetic acid (CF$_3$CO$_2$D) results in dethreading of the pseudorotaxane complexes. This is evidenced by a change in the H(1) and H(7) signals back to near their original positions. Under these conditions, the dianionic guests are effectively neutralized and converted back to their corresponding carboxylic acid species (i.e., **5** and **8**, respectively), which leads to dethreading and regeneration of free 1^{4+}. This process may be repeated with subsequent additions of base and acid serving to "switch on" and "switch off" pseudorotaxane formation. As expected, the increased salt in solution serves to buffer the effect of each new addition of base or acid. The result is a "dampening" of the effect with each cycle. Nevertheless, it is possible to repeat the threading and dethreading process a number of times, as can be seen from an inspection of Figure 3.

The results described above underscore the key point that these complexes are environmentally responsive and, as is true for many non-interpentrated supramolecular structures, can be made to undergo decomposition by exposure to appropriate external stimuli. What distinguishes the present species from many other supramolecular complexes is their threaded nature and strong proton dependence. In particular, conversion of the dianions to the corresponding dicarboxylic acid forms causes complete decomplexation of the interpenetrated substrate. This cycling of the protonation states of the guest molecules effectively acts as an external chemical "switch" through which formation and break-up of the pseudorotaxane complexes can be controlled. As previously noted, molecular switching effects are of great interest in the design of environmentally responsive materials and molecular machines.

The solution studies described above provide initial evidence that 1^{4+} is capable of stabilizing pseudorotaxane structures in the
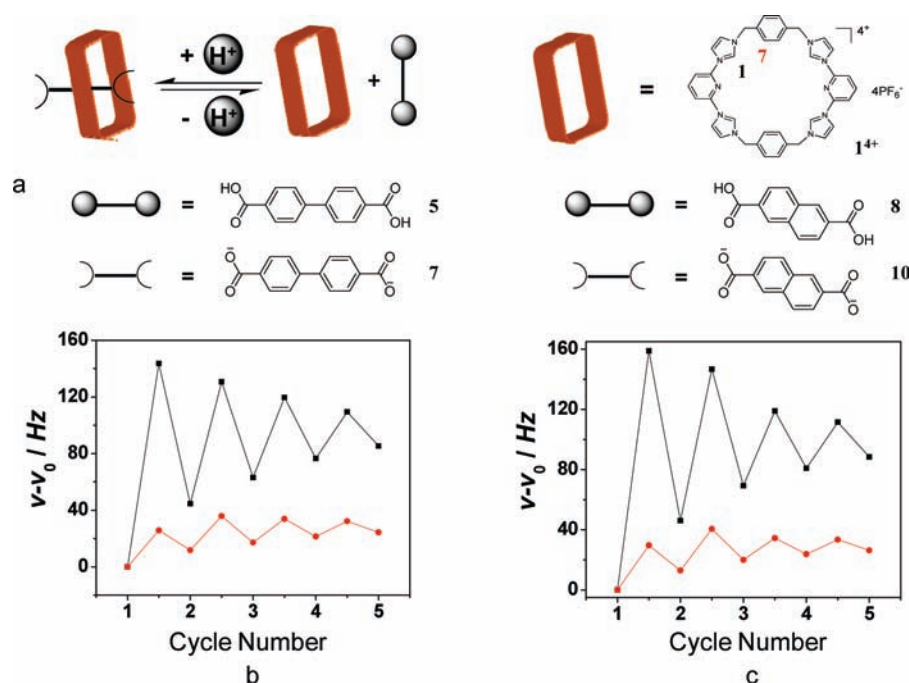
Figure 3. Schematic (a) and graphical representations (b,c) of the threading and dethreading of pseudorotaxane complexes $[\mathbf{1}^{4+}\cdot\mathbf{7}]^{2+}$ (b) and $[\mathbf{1}^{4+}\cdot\mathbf{10}]^{2+}$ (c), as inferred from pH-dependent ^{1}H NMR spectroscopic studies. Here, changes in the chemical shifts of the signals associated with protons H(1) (represented as ■) and H(7) (represented as red ●) of $\mathbf{1}^{4+}$ at 300 K in DMSO-d_6 were used to monitor the switching "on" and "off" of the molecular complexes. The concentrations of $\mathbf{1}^{4+}$ and the corresponding guest moiety (1 molar equiv of $\mathbf{5}$ (left) and $\mathbf{8}$ (right)) were held constant at 2 mM (overall solution concentration) during alternating cycles. The first step in each cycle was the addition of 5 molar equiv of TEA, and the second was the addition of 5 molar equiv CF_3CO_2D.

presence of several anionic species and that the formation of interpenetrated complexes and more complex supramolecular aggregates from these initial structures is highly dependent on several variables, including the choice of guest, the temperature, and the protonation state of the guest moiety. Additional evidence for formation of pseudorotaxane complexes, as well as the inherent structural flexibility of $\mathbf{1}^{4+}$, came from single-crystal X-ray diffraction analyses of $[\mathbf{1}^{4+}\cdot(\mathbf{7})_2\cdot2DMF\cdot7.5H_2O]$ and $[\mathbf{1}^{4+}\cdot(\mathbf{10})_2\cdot10H_2O]$. The structures in question are shown in Figure 4, along with those of $[\mathbf{1}^{4+}\cdot\mathbf{3}\cdot3PF_6{}^-\cdot4H_2O]$ and $[\mathbf{1}^{4+}\cdot(\mathbf{4})_2\cdot16H_2O]$, which are provided for comparison, and discussed in further detail below (note that some solvent molecules and counteranions have been omitted for clarity). Unfortunately, efforts to obtain analogous diffraction-grade single crystals in the case of the putative intercalated complexes formed from monoanionic species, $[\mathbf{1}^{4+}\cdot\mathbf{6}]^{3+}$ and $[\mathbf{1}^{4+}\cdot\mathbf{9}]^{3+}$, proved unsuccessful.

The single-crystal X-ray structure of complex $[\mathbf{1}^{4+}\cdot\mathbf{7}]^{2+}$ (Figure 4c) reveals that, as inferred from the solution-state NMR spectroscopic analyses discussed above, the dianionic guest species is inserted into and bound within the center of macrocycle $\mathbf{1}^{4+}$. This is in stark contrast to the outside binding association observed in $[\mathbf{1}^{4+}\cdot\mathbf{4}]^{2+}$ (Figure 4b). However, in the case of $[\mathbf{1}^{4+}\cdot\mathbf{7}]^{2+}$, the macrocycle adopts a slightly different structural conformation than it does in the case of the previously reported pseudorotaxane $[\mathbf{1}^{4+}\cdot\mathbf{3}]^{3+}$ (Figure 4a). In the case of pseudorotaxane $[\mathbf{1}^{4+}\cdot\mathbf{7}]^{2+}$, the macrocyclic core adopts a "complete chair" conformation as opposed to the "partial chair" conformation seen in the case of $[\mathbf{1}^{4+}\cdot\mathbf{3}]^{3+}$ (see Supporting Information for further details). The "complete chair" conformation seen in $[\mathbf{1}^{4+}\cdot\mathbf{7}]^{2+}$ results in a "molecular box" that is

significantly longer (9.8 vs 5.9 Å across the longest dimension for $[\mathbf{1}^{4+}\cdot\mathbf{7}]^{2+}$ and $[\mathbf{1}^{4+}\cdot\mathbf{3}]^{3+}$, respectively).

The use of a species that is "wider" than dianion $\mathbf{7}$ (i.e., 2,6-naphthalenedicarboxylate dianion), as in the case of the pseudorotaxane $[\mathbf{1}^{4+}\cdot\mathbf{10}]^{2+}$ (Figure 4d), results in the stabilization of a "box-like" conformation for macrocycle $\mathbf{1}^{4+}$. The result is a receptor with a greater width (11.6 Å across) than in the case of $[\mathbf{1}^{4+}\cdot\mathbf{3}]^{3+}$ and $[\mathbf{1}^{4+}\cdot\mathbf{7}]^{2+}$ (9.4 and 10.2 Å, respectively). The length (6.9 Å) of the molecular box present in structure $[\mathbf{1}^{4+}\cdot\mathbf{10}]^{2+}$ was found to be intermediate between what was seen in the case of $[\mathbf{1}^{4+}\cdot\mathbf{3}]^{3+}$ and $[\mathbf{1}^{4+}\cdot\mathbf{7}]^{2+}$ (5.9 and 9.8 Å; see above).

When considered in conjunction with the solution-phase NMR spectroscopic data presented above, the results obtained from the single-crystal X-ray analysis of the two pseudorotaxane complexes $[\mathbf{1}^{4+}\cdot\mathbf{7}]^{2+}$ and $[\mathbf{1}^{4+}\cdot\mathbf{10}]^{2+}$ provide support for the conclusion that the molecular box, $\mathbf{1}^{4+}$, acts as a flexible receptor that, within relatively broad limits, can adapt its conformation to accommodate anionic guests of different sizes and shapes. In all cases, however, the underlying pseudorotaxane structures appear to be stabilized by similar non-covalent interactions that, on the basis of the structural parameters and the solution-phase decomplexation studies, are considered to include, but not be limited to, CH⋯π hydrogen-bonding and π–π interactions.

The finding that $\mathbf{10}$ (naphthalene dianion) could interpenetrate into box $\mathbf{1}^{4+}$ led us to consider that the resulting purely organic complex could be used to support a higher order, metal-linked structure (cf. Figure 5). Initial support for this notion came from the finding that adding Ag(I) ($PF_6{}^-$ or $NO_3{}^-$ salt) to a mixture of $\mathbf{1}^{4+}\cdot4PF_6{}^-$, 1 molar equiv of $\mathbf{8}$ (the acid form of $\mathbf{10}$), and 5 molar equiv of TEA led to the formation of an insoluble
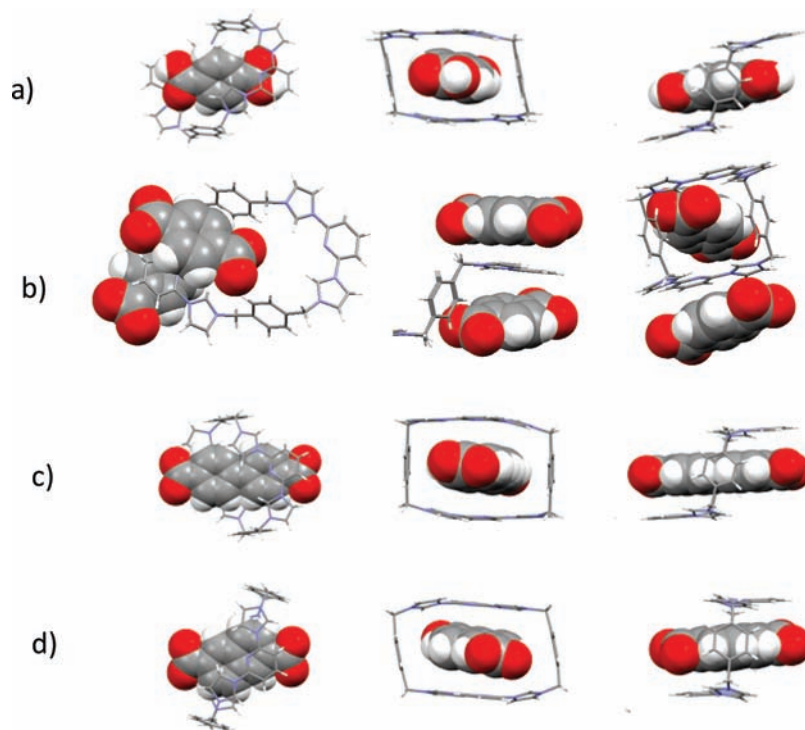
Figure 4. Single-crystal X-ray structures of pseudorotaxane complexes formed from 1^{4+} and various anionic guest species: (a) $[1^{4+} \cdot 3]^{3+}$, (b) $[1^{4+} \cdot 4]^{2+}$, (c) $[1^{4+} \cdot 7]^{2+}$, and (d) $[1^{4+} \cdot 10]^{2+}$. All of the solvent molecules and counteranions have been omitted for clarity. Top, side, and front views are displayed from left to right.
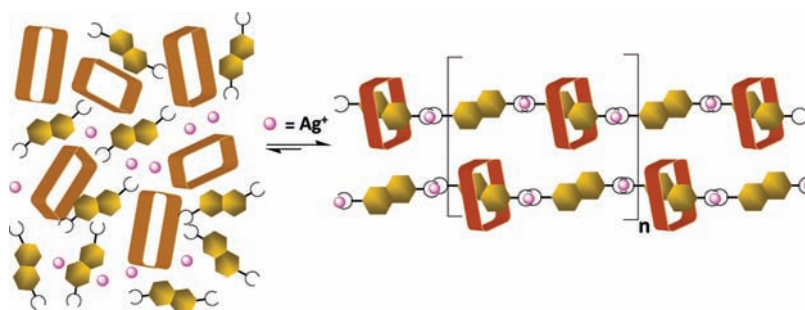

Figure 5. Schematic representation of one-step self-assembly of a silver-linked polyrotaxane built up from the "molecular box" 1^{4+}, Ag(I), and dianion **10**.
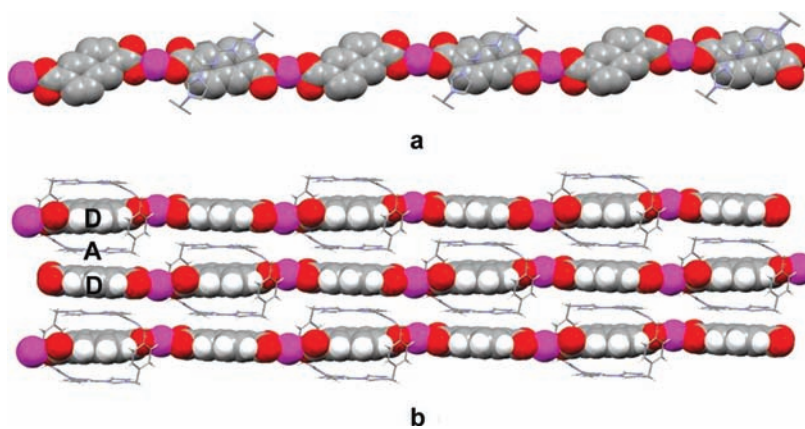

Figure 6. Single-crystal structure of $1^{4+} \cdot (10)_3 \cdot Ag_2 \cdot 16\, H_2O$: (a) top and (b) side views of the silver-linked polyrotaxane chain. Here, A and D refer to acceptor and donor, respectively.

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precipitate. This same precipitation took place when the three components, namely $\mathbf{1}^{4+}$, **8**, and Ag(I), were premixed and then treated with TEA. In this latter case, single crystals suitable for X-ray diffraction analysis could be obtained (cf. Figure 6). In similar studies utilizing dianion **7**, the formation of an insoluble precipitate was observed; unfortunately, efforts to obtain diffraction-grade crystals from this mixture proved unsuccessful.

In the solid state, individual $\left[\mathbf{1}^{4+}\cdot(\mathbf{10})_2\cdot Ag_2\right]^{2+}$ pseudorotaxane units act as monomers within an overall 1D supramolecular polymer (i.e., a polyrotaxane). The monomeric units are characterized by strong donor—acceptor interactions, as evidenced by the short distance (less than 3.5 Å) between the 2,6-di(1*H*-imidazol-1-yl)pyridyl plane in $\mathbf{1}^{4+}$ and the π surface of the inserted dianion. The "tips" of the interpenetrated dianions protrude from the macrocyclic rings and are linked to other interpenetrated dicarboxylate anions via Ag(I) cation bridges; selected interatomic distances for these contacts are $O(2)\cdots Ag(1) = 2.216$ Å and $O(4)\cdots Ag(1) = 2.138$ Å.[54]

The 2,6-naphthalene dicarboxylate dianion present in the metal-linked, oligomeric structure built up from $\left[\mathbf{1}^{4+}\cdot(\mathbf{10})_2\cdot Ag_2\right]^{2+}$ repeat units is characterized by strong donor—acceptor interactions between neighboring chains. Here, an interpenetrated arrangement is seen, wherein rotaxane fragments in one chain stack in proximity to a subunit on a second chain that is not threaded through a tetraimidazolium box. The net result is an ordered two-dimensional array of one-dimensional supramolecular necklaces stabilized by vertical donor—acceptor—donor (DAD) interactions (cf. Figure 6).

CONCLUSIONS

In summary, we have demonstrated that the large molecular box that is the subject of this report, $\mathbf{1}^{4+}$, acts as a dynamic receptor for aromatic bis-carboxylate guests. The flexible nature of this receptor allows the macrocycle to alter its structure in order to accommodate, and thus stabilize, electron-rich anionic guest molecules of different shapes, sizes, and protonation states. The resulting pseudorotaxane structures are responsive to changes in pH and temperature. The formation of the pseudorotaxanes can be effectively "turned off" by lowering the pH. However, as detailed here, the use of monocarboxylate anions, such as **6**, **7**, and **9**, that are "too long" to fit fully within the cavity provided by $\mathbf{1}^{4+}$ precludes aggregation of the initial pseudorotaxanes into linear pseudopolyrotaxanes, in contrast to what was seen previously in the case of **3**.[19] On the other hand, the addition of Ag$^+$ cations to the complex $\left[\mathbf{1}^{4+}\cdot\mathbf{10}\right]^{2+}$ allows for formation of an extended metal-linked pseudorotaxane structure, at least in the solid state. More broadly, the guest-dependent nature of the structures formed from $\mathbf{1}^{4+}$, along with the ability to support the formation of interpenetrated structures that are responsive to external stimuli, such as temperature and pH, leads us to propose that this easy-to-synthesize receptor could have a role to play in the development of "molecular level switches" or other generalized "smart" materials.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed experimental conditions and procedures, NMR spectroscopic analyses, computational calculations, and single-crystal X-ray structures, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data for this paper have also been deposited as CCDC nos. 775822, 775824, 784454, and 775820, which can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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(52) It is presumed that the positive charges on the $[(1^{4+}\cdot 6)\cdot 6\cdot (1^{4+}\cdot 6)]^{5+}$ and $[(1^{4+}\cdot 7)\cdot 7\cdot (1^{4+}\cdot 7)]^{2+}$ complexes are balanced, and perhaps in part stabilized, by coordinating PF_6^- counteranions.

(53) It is observed that the supramolecular dimeric species have different charges in solution than they do in the gas phase; this is thought to reflect the formation of various cation radicals under the conditions of mass spectrometric analysis as the result of proton-transfer processes.

(54) Interestingly, the 2:1 carboxylate-to-Ag(I) coordination mode differs from the 2:2 complexation generally seen in simple (i.e., non-interpenetrated) polymers built up from dicarboxylate dianions and Ag(I) cations; cf., e.g.: Sun, D.; Zhang, N.; Xu, Q.-J.; Huang, R.-B.; Zheng, L.-S. *J. Organomet. Chem.* **2010**, *695*, 1598–1602.

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