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Multi-Component Self-assembled Metal-organic [3]Rotaxanes

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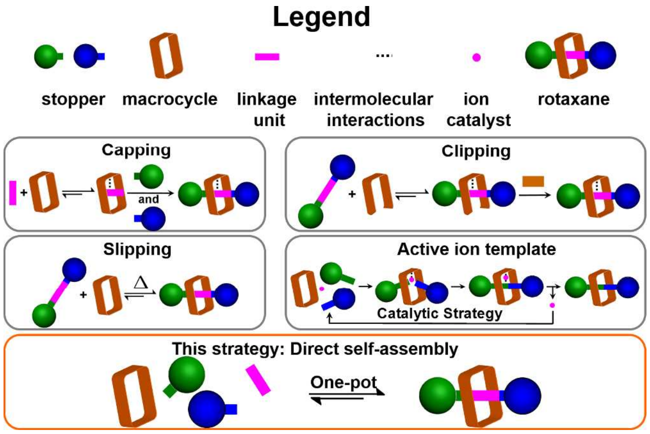
ABSTRACT: A set of environmentally responsive metal-organic [3]rotaxanes is described. These mechanically interlocked macromolecules may be prepared in quantitative yield via a one-pot procedure involving treatment of a flexible tetracationic macrocycle, known as the 'Texas-Sized' molecular box, with tri-1,3,5-benzenetricarboxylate anion and silver cations (Ag^+). The use of this three component mixture gives rise to a metal-organic [3]rotaxane via a self-assembly process that occurs under ambient conditions in DMSO-d_6 solution. The complex is stable in the presence of excess TFA. However, disassembly of the [3]rotaxane to produce anion-box associated species may be triggered by adding a competitive counter anionic species (e.g., I^-). Adding excess Ag^+ serves to reverse this decomplexation process. The nature of the [3]rotaxane complex could be fine-controlled via application of an external stimulus. Increasing the temperature or adding small molecules (e.g., D_2O, methanol-d_4, acetonitrile-d_3, DMF-d_7, acetone-d_6, THF-d_8) to the initial DMSO-d_6 solution induces conformational "flipping" of macrocycle within the overall complex (e.g., from limiting chair- to chair-like forms). Support for the molecular stimuli responsive nature of the various structures came from solution phase one- and two-dimensional (^1H, 1D and 2D NOESY) NMR spectroscopic studies carried out in DMSO-d_6. The core metal-linked rotaxane unit was characterized via single-crystal X-ray diffraction analysis. Initial evidence that the present self-assembly process is not limited to the use of the Ag^+ cation came from studies involving Cd^{2+}; this replacement results in formation of 2D metal-organic rotaxane-containing frameworks (MORFs).

Introduction

Over the last three decades, the field of mechanically interlocked molecules (MIMs) has seen rapid development and intense interest from the chemical community.[1] These complex molecular architectures are often organized or stabilized by weak non-covalent bonding interactions and are of considerable interest for use in a broad range of applications, including molecular electronics,[2] molecular switching,[3] molecular devices,[4] and sensor development.[5] Rotaxanes are well known MIMs and typically consist of a dumbbell-shaped molecule threaded through the center of a macrocyclic unit.[6] Rotaxanes have been used extensively in material and biological sciences, e.g., in the development of molecular machines,[7] gels,[8] drug carriers,[9] and other applications.[10] These applications rely on effective syntheses of the constituent MIMs. Known strategies for generating rotaxanes include capping,[11] clipping,[12] slipping,[13] and ion templatation,[14] as depicted in Scheme 1. However, new approaches could lead to advances in the field.

Recently, the use of anionic precursors in the construction of threaded molecular architectures has garnered attention. In seminal studies, Vögtle et al., demonstrated that organic oxoanions could be used as templates in rotaxane synthesis.[15] Beer et al., expanded the scope of anion templated syntheses of interlocked molecules and demonstrated applications in anion sensing.[16] In more recent work, Flood et al., utilized phosphate anions as a template to create an unprecedented [3]rotaxane.[17]

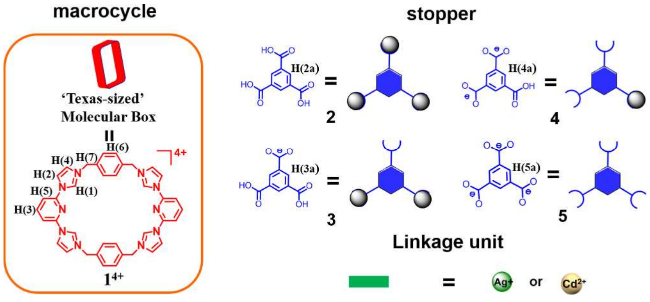
However, to the best of our knowledge all the reported methods for generating rotaxane structures have relied on a precursor, cation, or other template, that is "inserted" in the central cavity of the macrocyclic unit (viz., capping, clipping, and slipping approaches).[18]



Scheme 1. Schematic summary of rotaxane syntheses.

Herein, we report a facile one-pot synthesis of metal-organic rotaxane structures. Specifically, a flexible tetracationic macrocycle (cyclo[2](2,6-di(1H-imidazol-1-yl)pyridine)[2](1,4-dimethylenebenzene)) known as the 'Texas-Sized' molecular box (i.e., **1**$^{4+}$; studied as the PF_6^- salt),[19] was used in combination with benzene-1,3,5-tricarboxylic acid (**2**) and silver cations (Ag^+ as its PF_6^- salt) to generate a metal-organic [3]rotaxane species ($[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(Ag^+)_5]^{4+}$) in DMSO-$d_6$ solution. Interpenetrated species constructed with these three components (i.e., $\mathbf{1}^{4+}$, **5** and Ag^+), specifically a metal-organic [2]rotaxanes $[\mathbf{1}^{4+}\bullet((Ag^+)_2\bullet\mathbf{5}_2\bullet4H_2O)]$, have been characterized in the solid state.

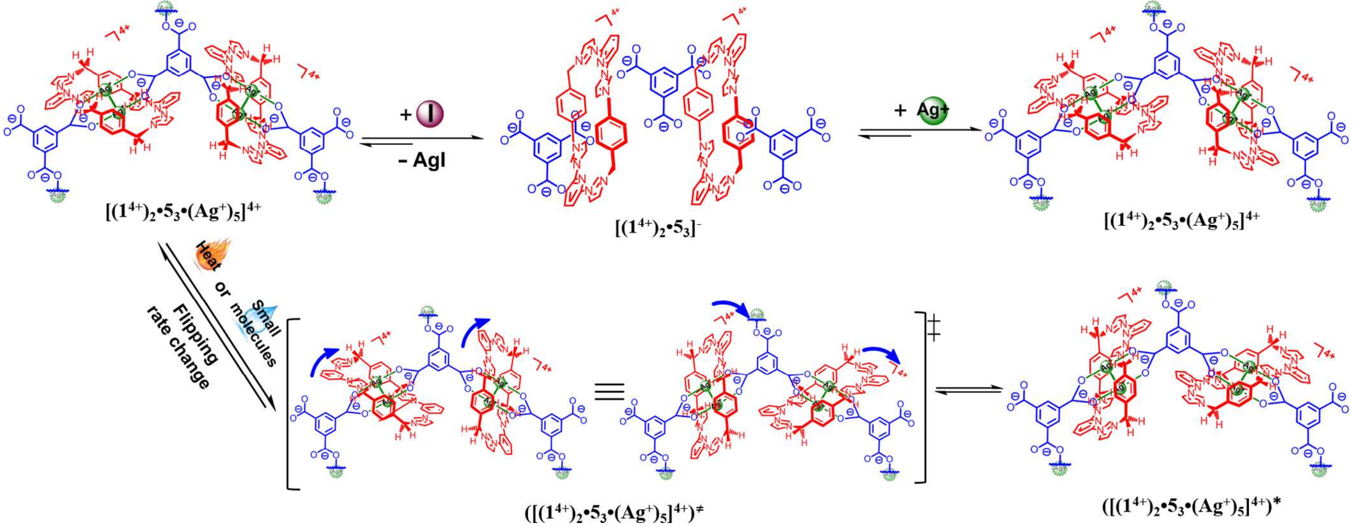
The synthesis proved rather invariant to the relative stoichiometry of the components and the order in which they were mixed. Specifically, the same self-assembled rotaxane structure was obtained under a variety of solution phase reaction conditions. This invariance leads us to postulate that the self-assembled ensemble obtained from the mixing of the box, the trianionic form of **2** (designated as **5**), and silver cation represents the thermodynamic product of the reaction. However, pre-complexation of the cation and preorganization of the anionic species derived from **2** outside of the central cavity of macrocycle $\mathbf{1}^{4+}$ may serve to template the reaction in a kinetic sense. Consistent with this latter supposition is the finding that the rate of formation of the [3]rotaxane structure proved highly dependent on the protonation state of the anionic precursor, with the trianion of **2** (**5**) displaying the highest rate of formation as compared to its various other, more highly protonated conjugate acid forms.



Scheme 2. Schematic representation of the key subunits used to create rotaxane structures according to the direct self-assembly strategy illustrated in Scheme 1. The cationic species were studied as their PF_6^- salts, whereas the anionic forms of **2** were studied as their tetramethylammonium salts unless otherwise indicated.

Rotaxanes have been studied extensively as environmentally responsive species that might have potential utility as smart materials.[20] The present MIMs were also studied in this regard. As detailed below, chemical transformations involving the [3]rotaxane complex, $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(Ag^+)_5]^{4+}$, could be induced via application of appropriate chemical stimuli. For instance, adding iodide anion to the pre-assembled MIM species $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(Ag^+)_5]^{4+}$ led to slow decomposition and generation of associated anionic species, such as $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3]^-$, as inferred from solution phase NMR spectroscopic studies. The subsequent addition of excess Ag^+ cation then induced recovery of the original interpenetrated structure. This process could be repeated several times. The rates of the individual interconversion steps could be fine-tuned by changing the temperature. Finally, we show that either warming the DMSO-d_6 solution or adding small molecules (e.g., D_2O, methanol-d_4, acetonitrile-d_3, DMF-d_7, acetone-d_6, THF-d_8) leads to a change in the rate at which the strut-threaded macrocyclic ring undergoes conformational flipping.

The combination of a relatively simple preparation, in concert with the environmental responsive nature of the metal-organic [3]rotaxane that results from mixing $\mathbf{1}^{4+}$, **5**, and Ag^+, leads us to suggest that the self-assembled approach used to create $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(Ag^+)_5]^{4+}$ could allow access to complex molecular architectures with controllable switching features that might otherwise by inaccessible through conventional synthetic methods. Initial support for this latter postulate comes from the finding that replacing the Ag^+ by Cd^{2+} leads to formation of 2D metal organic rotaxane frameworks (MORFs).



Scheme 3. Chemical transformations involving the metal-organic [3]rotaxane $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(Ag^+)_5]^{4+}$. Also shown are schematic representations of internal molecular motions that occur within the ensemble, specifically the chair-to-chair conformational flipping of the box-like macrocyclic rings.

Results and Discussion

Initially a set of experiments was devised to probe the effect of protonation on the interaction between 1,3,5-benzene tricarboxylic acid (**2**) and its anionic forms (i.e., mono-anion **3**, dianion **4**, and trianion **5**). This particular class of substrates was chosen for its ability to serve potentially as a three-coordinate ligand in molecular assembly.[21] It was also considered likely that, in conjunction with $\mathbf{1}^{4+}$, a flexible macrocycle that has found application in the construction of MIMs,[19] new framework structures might be produced. The present study was undertaken in an effort to test this hypothesis.

No evidence of interaction was observed when the fully protonated form **2** was combined with $\mathbf{1}^{4+}$ in a 1:1 molar ratio in DMSO-d_6 (the solvent used for all studies unless otherwise noted), as inferred from the lack of spectral shifts associated with $\mathbf{1}^{4+}$ in the associated ^{1}H NMR spectra. To probe whether the deprotonated forms of **2** might interact with $\mathbf{1}^{4+}$ more strongly, tetramethylammonium hydroxide ($\text{TMA}^+\bullet\text{OH}^-$) was used to produce the corresponding mono-, di- and trianions **3**, **4**, and **5**, respectively. Direct titration of these latter preformed species into $\mathbf{1}^{4+}$ gave rise to distinct changes in the ^{1}H NMR spectrum of $\mathbf{1}^{4+}$ (most notably in the imidazole C–H resonance) (cf. Supporting Information). This was taken as initial evidence that hydrogen bonding and/or other weak intermolecular bonding interactions take place between $\mathbf{1}^{4+}$ and the anionic forms of **2** in DMSO-d_6 solution.

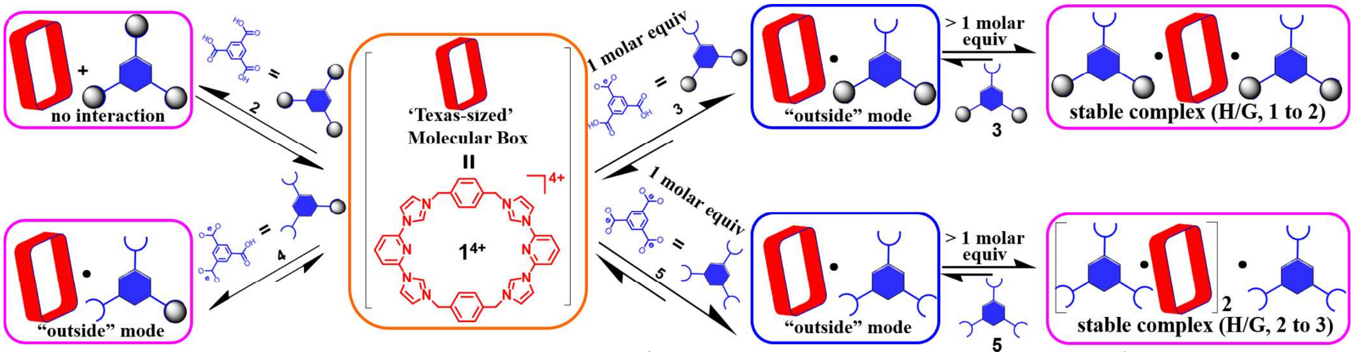
To analyze further the interactions between $\mathbf{1}^{4+}$ and **3**, **4**, or **5** in DMSO-d_6 solution, two-dimensional nuclear Överhauser effect spectroscopic (NOESY) analyses were carried out. No observable cross peaks were seen in these studies, leading us to suggest that in solution the anionic guests (G) **3**, **4**, or **5** are located “outside” of the cationic host (H) $\mathbf{1}^{4+}$ (cf. Scheme 4).

Job plots, constructed from ^{1}H NMR spectral analyses (cf. Supporting Information), revealed maximum values of 0.67, 0.50, and 0.60 ([G]/([H]+[G])) in the case of guest **3**, **4**, or **5**, respectively. These values are consistent with the formation of complexes with net 1:2, 1:1, and 2:3 (H:G) binding stoichiometry between $\mathbf{1}^{4+}$ and guests **3**, **4**, or **5**, respectively. The excess positive charge in these complexes is balanced by the residual PF_6^- anions.

Additional support for the proposed formation of multicomponent supramolecular complexes came from ESI-MS analyses, which revealed peaks corresponding to $[\mathbf{1}^{4+}+(\mathbf{3})_2\text{-}2\text{H}]^{+\bullet}$ (m/z= 1047.3040), $[\mathbf{1}^{4+}+\mathbf{3}\text{-}2\text{H}]^{+\bullet}$ (m/z = 837.2882), $[\mathbf{1}^{4+}+(\mathbf{4})_2]^{+\bullet}$ (m/z = 1047.3067), $[\mathbf{1}^{4+} + \mathbf{4}\text{-H}]^{+\bullet}$ (m/z = 837.2909), and $[\mathbf{1}^{4+}+(\mathbf{5})_2\text{+2H}]^{+\bullet}$ (m/z = 1047.3064), $[\mathbf{1}^{4+} + \mathbf{5}]^{+\bullet}$ (m/z = 837.2899) in the gas phase (cf. Supporting Information).

As a complement to the Job plot analyses, isodesmic titrations were performed in DMSO-d_6. Here, the changes in the chemical shift corresponding to the imidazole C-H signal (e.g., H(1); cf. Scheme 2; Supporting Information) were monitored as the concentration of guests **3**, **4**, or **5** was increased while leaving that of host $\mathbf{1}^{4+}$ unchanged. Based on fits of the titration data, association constants of $K_{a1} = (2.7 \pm 0.1) \times 10^3$ M^{-1} for the 1:1 complex ($[\mathbf{1}^{4+}\bullet\mathbf{3}]^{3+}$) and $K_{a2} = (3.6 \pm 0.2) \times 10^2$ M^{-1}, corresponding to the subsequent conversion to $[\mathbf{1}^{4+}\bullet\mathbf{3}_2]^{2+}$, were calculated. For the formation of $[\mathbf{1}^{4+}\bullet\mathbf{4}]^{2+}$ in solution, a value of $K_a = (1.0 \pm 0.1) \times 10^5$ M^{-1} was obtained. In the case of the trianion **5** and $\mathbf{1}^{4+}$ association constants of $K_{a1} = (3.5 \pm 0.2) \times 10^6$ M^{-1} and $K_{a2} = (1.3 \pm 0.1) \times 10^{15}$ M^{-2} were calculated; based on the Job plot analysis above, these binding constants were considered to reflect formation of strongly-bound 1:1 and 2:3 host-guest complexes, respectively.

Further evidence for the proposed complexes came from single crystal X-ray diffraction analyses. Diffraction grade single crystals were obtained from mixtures of $\mathbf{1}^{4+}$ (5 mM) and 5 molar equiv of the anionic species **3**, **4**, or **5** via slow evaporation from solution using mixtures of water/DMF (v/v = 1:1) (cf. Supporting Information). The structures corresponding to these crystals (i.e., $[\mathbf{1}^{4+}\bullet\mathbf{3}_4\bullet12\text{H}_2\text{O}]$, $[\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet12\text{H}_2\text{O}]$ and $[\mathbf{1}^{4+}\bullet\mathbf{5}\bullet\text{OH}^-\bullet2\text{DMF}\bullet17\text{H}_2\text{O}]$; cf. Figure 1) were solved and used to confirmed the outside binding mode proposed from the NMR solution studies. As seen in previous studies,[18a] the “box” $\mathbf{1}^{4+}$ proved to have a high degree of structural flexibility, and demonstrates the ability to conform its shape and size to accommodate guest binding. In fact, several different conformations, including a “complete-chair”, “partial chair”, and “twist chair”, were seen in the complexes formed with **3**, **4**, or **5**, respectively (cf. Supporting Information)



Scheme 4. Schematic representation of the interactions between $\mathbf{1}^{4+}$ and guest species **3**, **4**, and **5**, as inferred from ^{1}H NMR spectroscopic analyses carried out in DMSO-d_6.

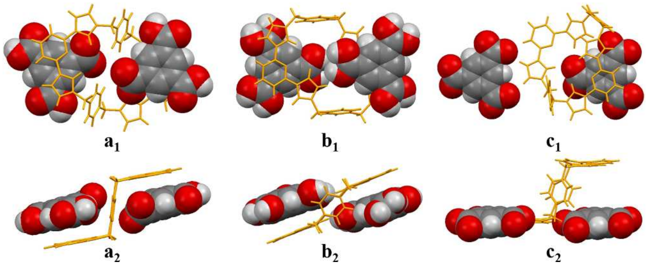


Figure 1. Top (a$_1$, b$_1$, or c$_1$) and side (a$_2$, b$_2$, or c$_2$) views of the 1:2 (H:G) subunits formed from $\mathbf{1}^{4+}$ and various anionic guest species, namely $[\mathbf{1}^{4+}\bullet\mathbf{3}_2]^{2+}$ (a$_{1,2}$), $[\mathbf{1}^{4+}\bullet\mathbf{4}_2]$ (b$_{1,2}$), and $[\mathbf{1}^{4+}\bullet\mathbf{5}_2]^{2-}$ (c$_{1,2}$), as seen within three independent complexes, $[\mathbf{1}^{4+}\bullet\mathbf{3}_4\bullet12\text{H}_2\text{O}]$, $[\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet12\text{H}_2\text{O}]$, and $[\mathbf{1}^{4+}\bullet\mathbf{5}\bullet\text{OH}^-\bullet2\text{DMF}\bullet17\text{H}_2\text{O}]$, respectively, as determined by single crystal X-ray diffraction analysis. Some of the counter ions and solvent molecules have been omitted for clarity. Note the “complete-chair”, “partial chair”, and “twist chair” conformation of $\mathbf{1}^{4+}$ present in these three structures, respectively.

Taken in concert, the solution and solid state studies described above provide evidence that $\mathbf{1}^{4+}$ is capable of interacting with anionic guest **3**, **4**, and **5** via an outside binding mode prior to addition of any metal cationic species. The nature of these interactions led us to consider the possibility of actual threading based on the use of an appropriate metal cation to stabilize the formation of mechanically interlocked structures. To test this hypothesis, Ag^+ (as its PF_6^- salt) was titrated into a DMSO-d_6 mixture containing one molar equiv each of $\mathbf{1}^{4+}$ and **5**. Based on the observation of a new set of proton signals in the ^{1}H NMR spectrum (Figure 2) and integrations of the respective peak intensities, it is concluded that roughly 67% of $\mathbf{1}^{4+}$ is transformed into a new stable product when the Ag^+ cation is added in excess (i.e., 3 - 20 molar equiv relative to $\mathbf{1}^{4+}$). A ^{1}H NMR spectroscopic-based Job plot was carried out while maintaining the total concentration of $\mathbf{1}^{4+}$ and **5** equal to 2 mM in the presence of 24 mM $Ag^+\bullet PF_6^-$ in DMSO-d_6. The maximum complex concentration was seen when the value of $[\mathbf{5}]/([\mathbf{1}^{4+}]+[\mathbf{5}])$ was 0.6. Such a finding is consistent with the formation of a supramolecular complex, with a 2:3 stoichiometry ($\mathbf{1}^{4+}$ relative to **5**), upon mixing the components under these solution phase conditions.

With the ratio between $\mathbf{1}^{4+}$ and **5** set as 2:3, another Job-plot analysis was carried out, wherein the overall concentration of $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3]^-$ and $Ag^+\bullet PF_6^-$ was 0.2 mM. In this case, the peak maximum was seen at a $[Ag^+]/([\mathbf{1}^{4+}]+[Ag^+])$ ratio of 0.71. This observation leads us to suggest that the final product contains 5 Ag^+ centers, 2 equivalents of $\mathbf{1}^{4+}$, and 3 molar equivalents of the anionic precursor **5**.

To obtain further insights into the stoichiometry, a second set of ^{1}H NMR spectral titration studies was carried out wherein the molar ratio of $\mathbf{1}^{4+}$ and **5** was held constant at 2:3 while Ag^+ was titrated into the solution until 4 molar equiv of Ag^+ (relative to $\mathbf{1}^{4+}$) had been added. On the basis of the observed ^{1}H NMR spectral changes, it is concluded that approximately 2.5 molar equiv of Ag^+ (relative to $\mathbf{1}^{4+}$) were needed to effect essentially complete conversion to the product. The spectral features of the resulting complex were identical to those produced above (cf. Figure 2).

In a third experiment, the trianion **5** was titrated into a mixture containing one molar equiv of $\mathbf{1}^{4+}$ and 2.5 molar equiv of Ag^+ (cf. Figure 2). The resulting NMR spectrum showed that again, at a 2:3 molar ratio of $\mathbf{1}^{4+}$ and **5** essentially all of the host and guest (i.e., $\mathbf{1}^{4+}$ and **5**) were co-bound in solution.

On the basis of the conversion stoichiometries observed in the above experiments, we suggest that a 2:3 complex between $\mathbf{1}^{4+}$ and **5** represents the dominant species formed in DMSO-d_6 solution in the presence of Ag^+ and that the final thermodynamic product contains two molecules of $\mathbf{1}^{4+}$, three molecules of **5**, and five Ag^+ cations under conditions where none of the components is limiting.

Operating within the context of this assumption, efforts were made to obtain insights into the degree of complexation between the various species involved in the equilibrium. On the basis of independent ^{1}H NMR spectral titrations carried out in DMSO-d_6 (cf. Supporting Information), the binding constants corresponding to the interactions between **5** and Ag^+ were found to be $K_{a1} = (1.4 \pm 0.1) \times 10^5\ M^{-1}$ and $K_{a2} = (6.1 \pm 0.6) \times 10^{15}\ M^{-2}$ for complexes with 1:1 and 2:3 stoichiometry, respectively. For the full conversion to $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(Ag^+)_5]^{4+}$ an association constant $K_a \geq 10^{58}\ M^{-9}$ could be calculated (cf. Supporting Information). However, the various assumptions underlying the derivation of this value, including those associated with speciation, lead us to suggest that this association constant be used only as a qualitative indicator of the strong interactions that occur when $\mathbf{1}^{4+}$, **5**, and Ag^+ are mixed in DMSO-d_6 under conditions where the concentration of no individual components is limiting.

In contrast to what is seen for the ternary mixture, control ^{1}H NMR spectroscopic studies, in which Ag^+ is added directly to a solution of $\mathbf{1}^{4+}$ in DMSO-d_6 in the absence of **5**, revealed no evidence of interaction, as inferred from the lack of discernible shifts in the imidazolium protons peaks of $\mathbf{1}^{4+}$. We thus conclude that no appreciable insertion of Ag^+ into the macrocyclic cavity of $\mathbf{1}^{4+}$ occurs in the absence of trianion **5**. We thus do not believe that the silver cation per se is serving to “gather” and “thread” directly anion **5**, as seen in more traditional, metal-based rotaxane syntheses.

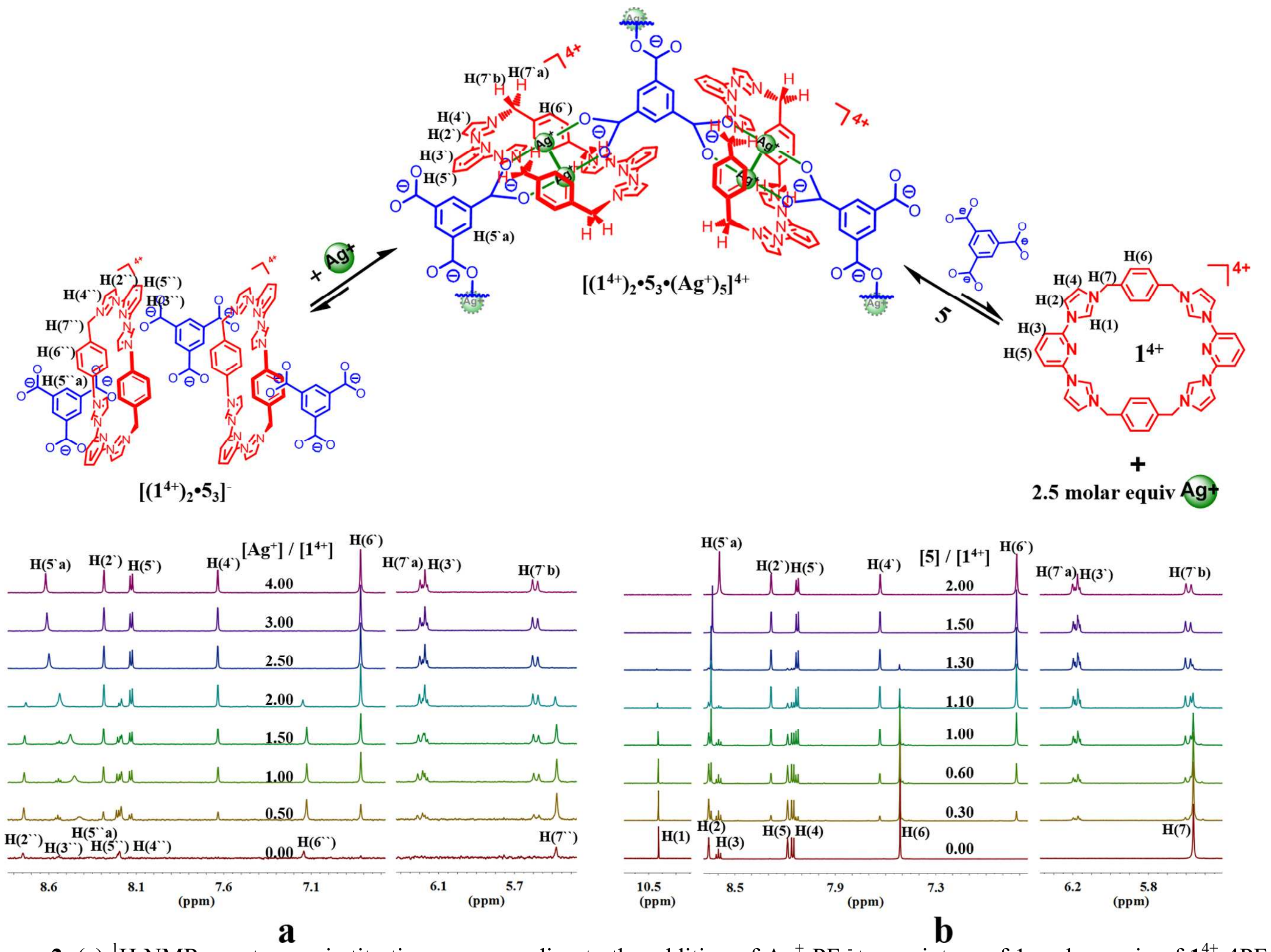


Figure 2. (a) ^{1}H NMR spectroscopic titration corresponding to the addition of $\mathrm{Ag}^+\bullet\mathrm{PF}_6^-$ to a mixture of 1 molar equiv of $\mathbf{1}^{4+}\bullet4\mathrm{PF}_6^-$ (2.00×10^{-4} M) and 1.5 molar equiv of the tri-1,3,5-benzenetricarboxylate anion (**5**) in the form of its TBA^+ salt; (b) ^{1}H NMR spectroscopic titration corresponding to the addition of the tri-1,3,5-benzenetricarboxylate anion (**5**) in the presence of 1 molar equiv of $\mathbf{1}^{4+}\bullet4\mathrm{PF}_6^-$ (1.00×10^{-3} M) and 2.5 molar equiv of $\mathrm{Ag}^+\bullet\mathrm{PF}_6^-$. All spectra were recorded in DMSO-d_6 at 300 K (600 MHz) 1 h after the various components were mixed.

Insights into how $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$ might be forming under conditions where the components are mixed in DMSO-d_6 came from time dependent ^{1}H NMR spectral analyses wherein the mixing order of the three components was changed. When the concentration of receptor $\mathbf{1}^{4+}$ was kept constant at 0.2 mM and the ratio $[\mathbf{1}^{4+}]$:[**5**]:$[\mathrm{Ag}^+]$ was set at 2:3:5, we found that three disparate mixing procedures yielded the associated complex $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$ in near-quantitative yield. The first two of these procedures consisted of 1) mixing $\mathbf{1}^{4+}$ and Ag^+ and then adding the anionic precursor **5**, or 2) adding Ag^+ into the complex of $\mathbf{1}^{4+}$ and **5**, respectively. Both methods gave the [3]rotaxane product at similar rates (54% five minutes after mixing). In contrast, slower formation kinetics were seen when $\mathbf{1}^{4+}$ was added into a mixture of **5** and Ag^+. In this case, only 30% conversion is seen at 5 min after all three components were mixed. In all three cases, complete conversion was seen at longer times. On the basis of these observations, we conclude that the pre-organized "outside" complex formed between $\mathbf{1}^{4+}$ and **5** (vide supra) abets kinetically the self-assembly process leading to the [3]rotaxane $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$, while pre-complexation between **5** and Ag^+, to the extent it occurs, retards complex formation. The present self-assembly process thus differs dramatically from the classic metal-based "gathering" and "threading" approach used to make cation-coordinated MIMs.

The stable product obtained upon mixing $\mathbf{1}^{4+}$, **5**, and Ag^+, ($[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$), was characterized by split (doubled) signals for protons H(7\`a) and H(7\`b) in the ^{1}H NMR spectrum. These two protons are on the same carbon. However, in a locked conformation, one points outside of the cavity, and the other inward. The observed splitting is thus consistent with limited dynamic motion in the complex product, $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$. The other protons (i.e., H(2\`), H(3\`), H(4\`), H(5\`) and H(6\`)) on $\mathbf{1}^{4+}$ are characterized by one set of signals, a finding that is consistent with free rotation of the imidazolium groups occurring around the single-bonds within the complex (cf. Supporting Information).

Diffusion-ordered spectroscopic (DOSY) analyses revealed that in the presence of Ag^+ all the protons on each individual organic species (i.e., $\mathbf{1}^{4+}$ and **5**) showed similar diffusion coefficients in DMSO-d_6 solution (cf. Supporting Information). Although not a proof of either structure or stoichiometry, the DOSY analysis does provide further evidence that a stable complex was constructed from the mixture of host $\mathbf{1}^{4+}$, guest anion **5**, and Ag^+.

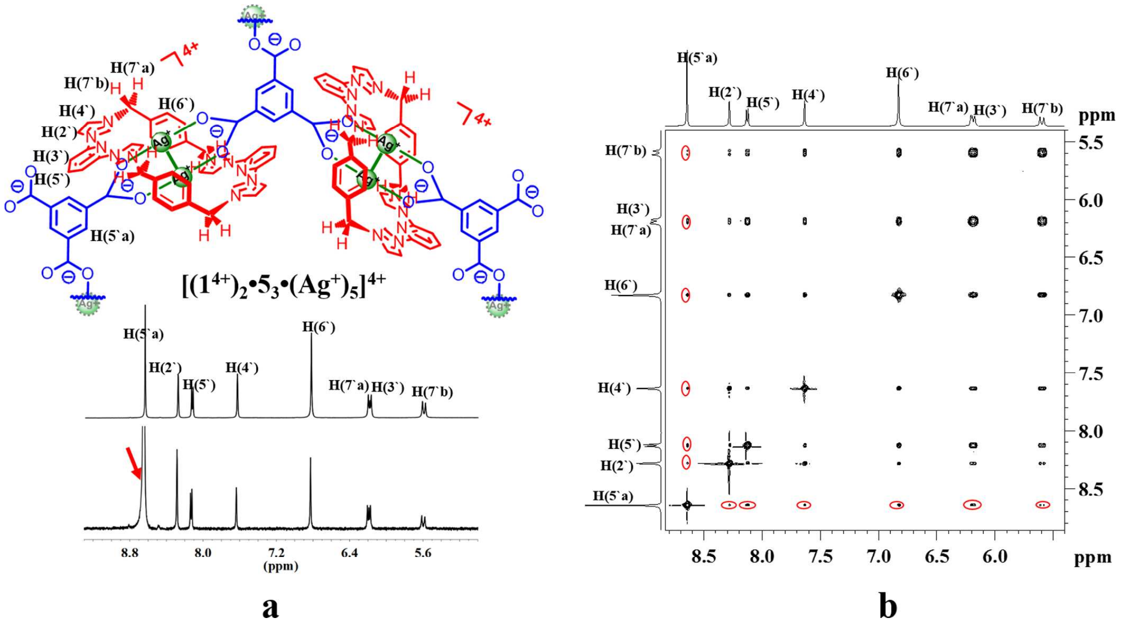


Figure 3. (a) One-dimensional NOE NMR spectral studies and (b) two-dimensional NOESY NMR spectroscopic analysis of complex $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$ recorded in DMSO-d_6 at 300 K (500 MHz). The red arrow in (a) indicates irradiation at the frequency of H(5`a) on anion **5**, while the small red circles in (b) designate the cross signals between H(5`a) on **5** and H(2`), H(3`), H(4`), H(5`), H(6`), H(7a`), and H(7b`) on $\mathbf{1}^{4+}$.

To probe in greater detail the molecular complex formed in solution between $\mathbf{1}^{4+}$, **5**, and Ag^+, two-dimensional nuclear Överhauser effect spectroscopic (NOESY) studies were carried out. In these studies, cross signals between H(5`a) on guest anion **5** and H(2`) , H(3`), H(4`), H(5`), H(6`), H(7a`), and H(7b`) on $\mathbf{1}^{4+}$ were observed. Such findings are consistent with guest **5** being inserted inside macrocycle $\mathbf{1}^{4+}$, as would be expected for a metal-organic [3]rotaxane (cf. Figure 3). One-dimensional nuclear Överhauser effect (NOE) NMR spectroscopic analyses, which are more sensitive than two-dimensional NOESY, showed correlations between the signals on **5** and $\mathbf{1}^{4+}$. This latter analysis thus supports the conclusions drawn from the 2D-NOESY spectral analysis (cf. Supporting Information).

The effect of adding Ag^+ to $\mathbf{1}^{4+}$ in the presence of either **3** or **4** (the mono and dianion of **2**, respectively) was also studied. In DMSO-d_6, similar ^{1}H NMR spectral shifts were obtained (cf. Supporting Information). However, it was found that the rate of conversion to the final complex was highly dependent on the protonation state of **2**. For instance, in the presence of **3**, **4**, or **5** equilibrium times of roughly 10, 3, or 1 h, respectively, were required before a reproducible set of ^{1}H NMR spectra were obtained following mixing of the components (cf. Supporting Information). It was also found that the protonation state of **2** directly impacted the yield of the resulting host-guest Ag^+-containing complexes. It was found that when the same amount of Ag^+ (i.e., 2.5 molar equiv relative to $\mathbf{1}^{4+}$) was added to a mixture of $\mathbf{1}^{4+}$ and 1.5 molar equiv of **3**, **4**, or **5**, the yield of the products (all of which gave rise to identical proton signals for $\mathbf{1}^{4+}$ in the ^{1}H NMR spectra) was found to be 27, 65, and 100%, respectively. Increasing the anionic character of the trifunctionalized carboxylic acid substrate appears to increase the rate of the reaction as well as improving the yield.

We rationalize these findings in terms of two limiting explanations: (1) Increased protonation reduces the number of stabilizing hydrogen bonding interactions between $\mathbf{1}^{4+}$ and the anionic guest and (2) labile protons serve to compete directly with cation Ag^+ for the Lewis basic binding sites in $\mathbf{1}^{4+}$.

The multicomponent nature of complex $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$ led us to consider that it might display environmentally responsive behavior in solution. In an effort to understand the relative importance of the individual components play in stabilizing the three-component complex of $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$, I^- (in the form of its tetrabutylammonium (TBA^+) salt) was added to a solution of the [3]rotaxane species in DMSO-d_6. It was found that the addition of 2 molar equiv of I^- (relative to Ag^+) to a 1 mM solution of $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$, followed by storage under ambient conditions for 168 h, resulted in only about 20% of the complex undergoing decomposition, as inferred from ^{1}H NMR spectroscopic analyses (cf. Supporting Information). In contrast, the addition of 1 molar equiv of I^- (relative to Ag^+) served to effect full and immediate decomposition of the complex formed from **5** (0.3 mM) and Ag^+ (0.45 mM). Taken in concert, these two results provide evidence that the presence of $\mathbf{1}^{4+}$ in the [3]rotaxane $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$ serves to "protect" the Ag^+ cation from precipitating out as AgI ($K_{sp} = 8.52 \times 10^{-17}\ \mathrm{M}^{-1}$ in water[22,23]).

To explore the above chemistry in greater detail, an additional molar equiv of Ag^+ was added to the solution of $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$ that had been subject to partial, iodide-induced dissociation. On the basis of ^{1}H NMR spectroscopic monitoring, it was concluded that the original [3]-rotaxane structure was fully reformed in 48 hours.

The rate of the stimulus-induced decomplexation and reformation sequence proved temperature dependent. Carrying out the sequential addition procedure at 343 K rather than 298K, the overall cycle time decreased from 96 h to 3 h. The kinetics could be further fine-tuned by carrying out the decomplexation step at 298K and reassembly at 343K, the first part of the switching cycle required roughly 48, whereas the reformation step required only 1.5 h. The decomposition-reconstruction cycles could be repeated a number of times without appreciable degradation (cf. Figure 4).

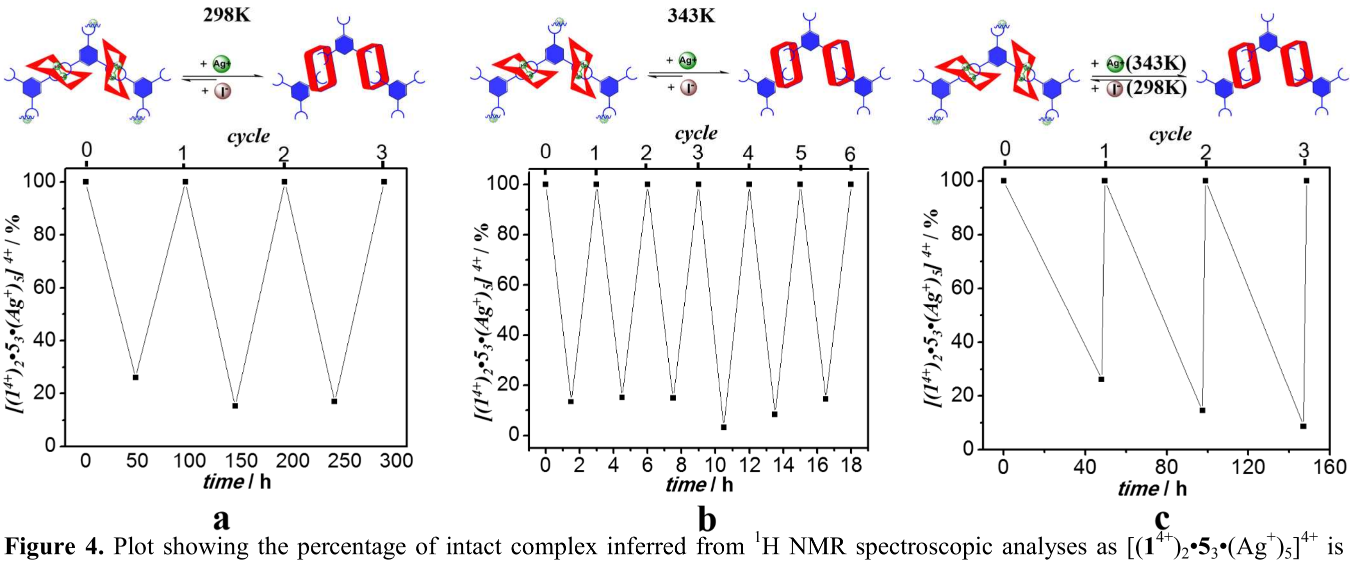


Figure 4. Plot showing the percentage of intact complex inferred from ^{1}H NMR spectroscopic analyses as $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$ is subject to cycles of iodide anion-induced decomposition and silver cation-promoted reassembly in DMSO-d_6 at 298K (a), 343K (b) or decomposition at 298K and reassembly at 343K (c).

Further support for the proposed responsive nature of $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$ was provided by a series of temperature dependent ^{1}H NMR spectroscopic measurements. It was found that upon increasing the temperature, the signal of H(3`) on $\mathbf{1}^{4+}$ shifted to lower field. Warming the solution was also found to result in splitting of the H(7`) signal. These findings lead us to suggest that the complex $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$ becomes less tightly bound as the temperature is raised and that macrocycle $\mathbf{1}^{4+}$ becomes more conformationally mobile as thermal energy is added to the original DMSO-d_6 solution.

The presumed conformational changes involving macrocycle $\mathbf{1}^{4+}$ within the complex $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$ were evaluated from 298K to 388K in DMSO-d_6 using a two-site exchange model. The kinetic parameters for the inferred molecular motion of $\mathbf{1}^{4+}$, derived from ^{1}H NMR spectroscopy, were then calculated using methods reported in the literature.[24] These analyses gave values of -2.1 ± 0.1 kJ•M^{-1} for $\Delta H^{\neq}$ and -195.2 ± 0.2 J•K^{-1}•M^{-1} for $\Delta S^{\neq}$. The activation energy at 298 K was calculated to be 56.0 ± 0.2 kJ•M^{-1}. Based on these values, a potential energy profile for the underlying processes could be constructed; it is shown in Figure 5.

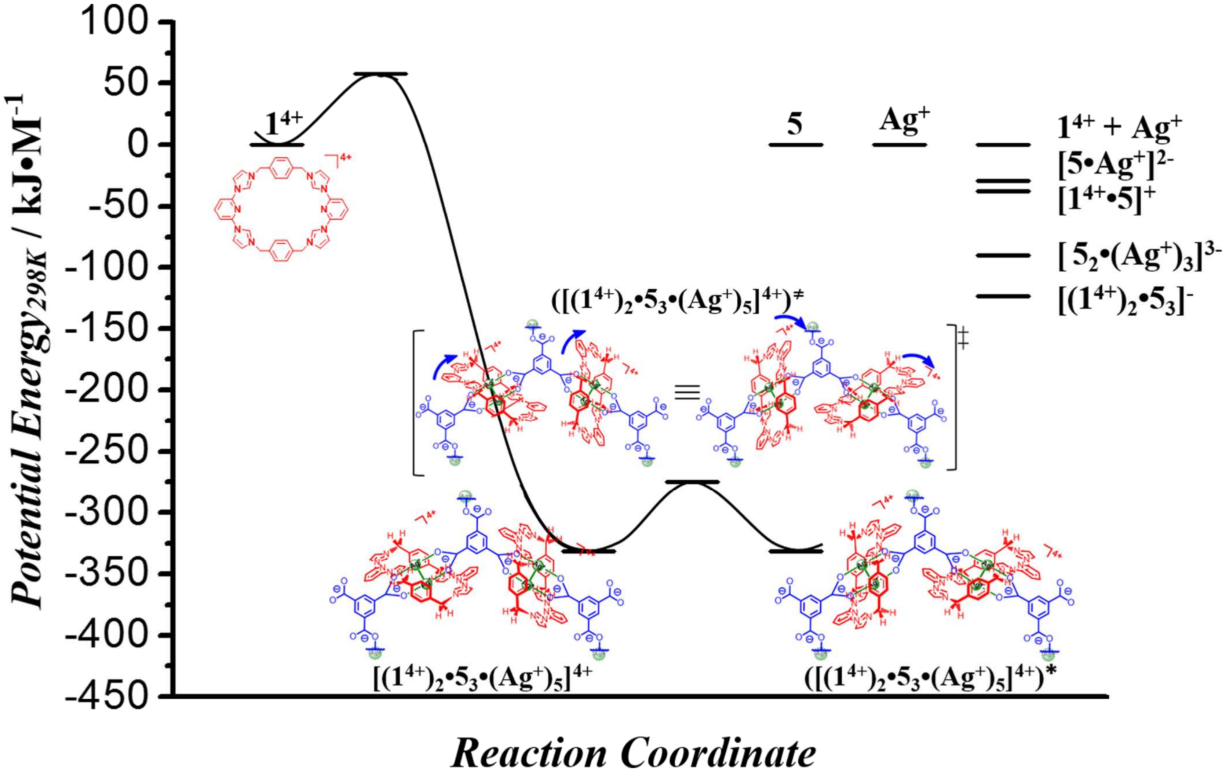


Figure 5. Potential energy diagram for the formation of different species relative to $\mathbf{1}^{4+}$, $\mathbf{5}$, and Ag$^+$ at 298 K and the inferred conformational motions involving $\mathbf{1}^{4+}$ within the [3]rotaxane complex $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_2]^{4+}$.

It was also found that upon increasing the molar fraction of D_2O in the original DMSO-d_6 solution, the chemical shift difference between H(7`a) and H(7`b) became increasingly small. Such a finding is consistent with a conformational motion that involves chair-to-chair "flipping" of $\mathbf{1}^{4+}$ within $[(\mathbf{1}^{4+})_2•\mathbf{5}_3•(Ag^+)_5]^{4+}$, rather than "ring around axis" rotation (cf. Figure 6). This motion becomes increasingly fast in the presence of D_2O (cf. Figure 7). Specifically, increasing the molar percentage of added D_2O from 0% to 80% serves to increase the rate constant, k_c, from 943 ± 10 Hz to 1043 ± 10 Hz at 298K. One possible explanation for this inferred increase in rate is that the faster exchange of the waters molecules bound to the Ag^+ cation in the presence of D_2O allows for a more facile "flipping" of macrocycle $\mathbf{1}^{4+}$. Support for the proposed interaction between the bound Ag^+ cation and water molecules came from a single crystal diffraction study discussed below.

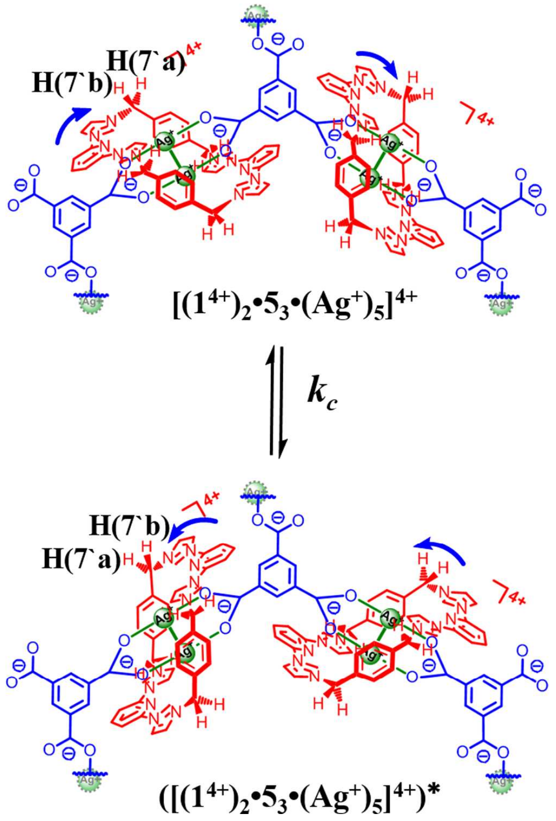
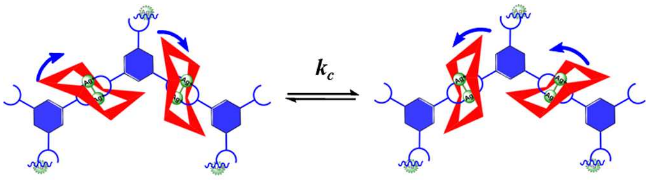


Figure 6. Proposed flipping motion involving $\mathbf{1}^{4+}$ that occurs within the overall complex $[(\mathbf{1}^{4+})_2•\mathbf{5}_3•(Ag^+)_5]^{4+}$.

The effect of other solvents on the rate of macrocycle flipping within $[(\mathbf{1}^{4+})_2•\mathbf{5}_3•(Ag^+)_5]^{4+}$ was probed by adding other small molecules to an initial solution of this [3]rotaxane in DMSO-d_6. Based on ^1H NMR spectroscopic analyses, the addition of methanol-d_4 or acetonitrile-d_3 mirrors what is found upon adding D_2O and serves to increase the rate of conformational motion. In contrast, adding DMF-d_7 did not change the rate of this flipping process appreciably, while adding acetone-d_6 and THF-d_8 served to retard the process (cf. Figure 7). The differential response of $[(\mathbf{1}^{4+})_2•\mathbf{5}_3•(Ag^+)_2]^{4+}$ to different added small molecules highlights an interesting environmental response that does not involve either translational motion along the threading strut or disassembly of the underlying MIM.



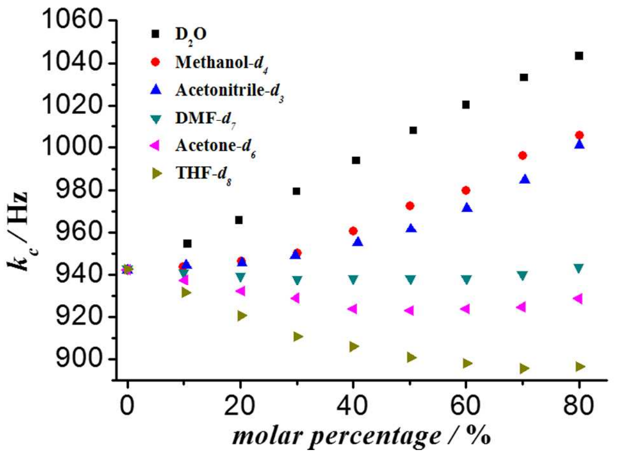


Figure 7. Plot of k_c versus molar percentage of added small molecules (D_2O, methanol-d_4, acetonitrile-d_3, DMF-d_7, acetone-d_6, THF-d_8) into an original DMSO-d_6 solution of $[(\mathbf{1}^{4+})_2•\mathbf{5}_3•(Ag^+)_5]^{4+}$. These additions are thought to modulate the rate of the chair-to-chair conformational "flipping" of $\mathbf{1}^{4+}$ within the [3]rotaxane $[(\mathbf{1}^{4+})_2•\mathbf{5}_3•(Ag^+)_5]^{4+}$. A schematic representation of this flipping process is shown in Figure 6.

Evidence that a metal-organic interpenetrated structure is formed in the solid state came from a single crystal X-ray diffraction analysis of single crystals of $[\mathbf{1}^{4+}•(Ag^+•\mathbf{4}•\mathbf{5})]•[\mathbf{1}^{4+}•((Ag^+)_2{}^+•\mathbf{5}_2•4H_2O)]•29H_2O$. The crystals used in the data analysis were prepared by slow diffusion using a three-layer solution setup. Specifically, 2.0 molar equiv of $Ag^+•PF_6^-$ (based on $\mathbf{1}^{4+}•4PF_6^-$) were dissolved in an aqueous solution and placed in a small vial. A mixture of DMF and water (1:1, v/v) was added as the second layer, and a mixture consisting of $\mathbf{1}^{4+}•4PF_6^-$ (1.0 molar equiv.), 2.0 molar equiv. of **2**, and 6.0 molar equiv of $TMA^+•OH^-$ dissolved in DMF and water (1:1, v/v) was subsequently added as the third layer. Single crystals suitable for X-ray diffraction analyses were obtained within seven days (cf. Supporting Information).

Structural analysis of the above crystals revealed the presence of two independent [2]rotaxane structures. The first of these proved to be a neutral rotaxane unit, $[\mathbf{1}^{4+}•(Ag^+)_2•\mathbf{5}_2•4H_2O)]$, formed from one molecule of $\mathbf{1}^{4+}$, two molecules of **5**, and two Ag^+ cations with two coordinated water ligands per cation. Of particular interest in this structure is the fact that the "rod" or "strut" is composed of an Ag-Ag dimer, which is stabilized via coordination to one of the carboxylate groups on each molecule of **5**, as well as two complexed water molecules. This coordination mode results in a stabilized metal-organic strut threaded through the center of $\mathbf{1}^{4+}$. Based on the geometric parameters, it is inferred that intermolecular hydrogen bonding interactions between the water ligands bound to the Ag^+ cations and to $\mathbf{1}^{4+}$, as well as π-π donor-acceptor interactions between the anion **5** and cation $\mathbf{1}^{4+}$, contribute to the stability of the overall structure (cf. Figure 8).

The second core rotaxane subunit ($[\mathbf{1}^{4+}\bullet(\mathrm{Ag}^+\bullet\mathbf{4}\bullet\mathbf{5})]$ within the overall co-complex with an overall formula $[\mathbf{1}^{4+}\bullet(\mathrm{Ag}^+\bullet\mathbf{4}\bullet\mathbf{5})]\bullet[\mathbf{1}^{4+}\bullet((\mathrm{Ag}^+)_2\bullet\mathbf{5}_2\bullet4\mathrm{H_2O})]\bullet29\mathrm{H_2O}$) is characterized by the presence of threading subunits in two different protonation states. The existence of these two protonated forms is ascribed to Ag^+ acting as a Lewis acid and promoting a hydrolysis process that is presumed to occur under the conditions of crystallization. In contrast to what was seen in the first structure, this particular [2]rotaxane contains only one Ag^+ cation in the rotaxane-defining "rod" that serves to link the anionic species **4** and **5** through the cavity of macrocycle $\mathbf{1}^{4+}$ (cf. Figure 9). The absence of coordinating water ligands on the Ag^+ center leads us to suggest that weak hydrogen bonds along with π-π donor-acceptor interactions between the anionic subunit (either **4** or **5**) and $\mathbf{1}^{4+}$ serve to stabilize the overall rotaxane structure.

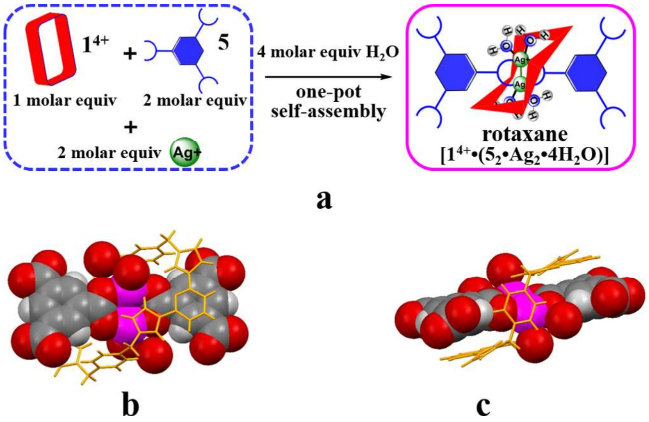


Figure 8. (a) Schematic representation showing the proposed formation of the metal-organic [2]rotaxane unit consisting of $[\mathbf{1}^{4+}\bullet((\mathrm{Ag}^+)_2\bullet\mathbf{5}_2\bullet4\mathrm{H_2O})]$. Top (b) and side (c) views of the $[\mathbf{1}^{4+}\bullet((\mathrm{Ag}^+)_2\bullet\mathbf{5}_2\bullet4\mathrm{H_2O})]$ complex present in $[\mathbf{1}^{4+}\bullet(\mathrm{Ag}^+\bullet\mathbf{4}\bullet\mathbf{5})]\bullet[\mathbf{1}^{4+}\bullet((\mathrm{Ag}^+)_2\bullet\mathbf{5}_2\bullet4\mathrm{H_2O})]\bullet29\mathrm{H_2O}$, as derived from a single crystal X-ray diffraction analysis. Some of the solvent molecules and counter anions have been omitted for clarity.

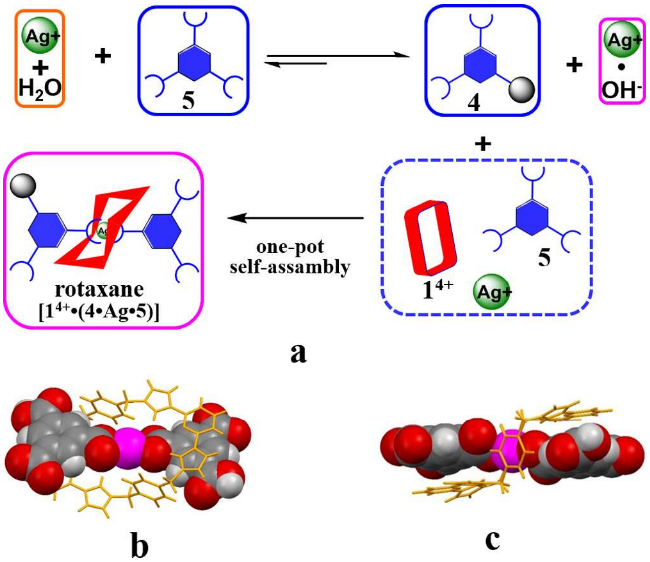


Figure 9. (a) Schematic representation of the proposed formation of the metal-organic [2]rotaxane unit $[\mathbf{1}^{4+}\bullet(\mathrm{Ag}^+\bullet\mathbf{4}\bullet\mathbf{5})]$. Top (b) and side views (c) of the core rotaxane unit $[\mathbf{1}^{4+}\bullet(\mathrm{Ag}^+\bullet\mathbf{4}\bullet\mathbf{5})]$ seen in the single X-ray crystal structure of $[\mathbf{1}^{4+}\bullet(\mathrm{Ag}^+\bullet\mathbf{4}\bullet\mathbf{5})]\bullet[\mathbf{1}^{4+}\bullet((\mathrm{Ag}^+)_2\bullet\mathbf{5}_2\bullet4\mathrm{H_2O})]\bullet29\mathrm{H_2O}$. Some of the solvent molecules and counter anions have been omitted for clarity.

The observation of two distinctly different rotaxane structures (cf. Figures 8 and 9) within the same datum crystal leads us suggest that the nature of the metal-organic [2]rotaxanes stabilized by the imidazolium box $\mathbf{1}^{4+}$ is influenced by the specific protonation states of **2** involved in the threading process. This inference is fully consistent with the solid state and solution phase ^1H NMR studies carried out in the absence of Ag^+, wherein very different outside binding modes are observed, as discussed above.

Conclusions

This study serves to underscore the notion that metal-organic rotaxane structures can be prepared directly via the simple mixing of appropriately chosen components without the need for metal-based "gathering" followed by "threading". In the present case, this paradigm is expressed in the context of a one-pot method that allows for the generation of interlocked species in nearly quantitative yield. Three components are used, namely a flexible tetraimidazolium molecular box ($\mathbf{1}^{4+}$), a trianion, and a source of Ag^+ cations. Their use gives rise to rotaxane species that are stable in solution and in the solid state. In spite of this stability, the nature of the system can be controlled. For instance, sequential treatment with I^- followed by Ag^+ ion in DMSO-d_6 solution allows the sequential partial decomposition and subsequent reconstruction of the core [3]rotaxane entity (complex $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_3\bullet(\mathrm{Ag}^+)_5]^{4+}$). Increasing the temperature or adding certain small molecular species (e.g., D_2O, methanol-d_4, acetonitrile-d_3) serves to increase the rate of internal motion within the overall complex. Other additives, namely acetone-d_6 and THF-d_8 serve to retard the conformational flipping process.

The versatility and simplicity of the current approach leads us to propose that the use of multi-component assembly involving anionic guests, cationic hosts, and appropriately chosen metal centers may allow for the facile synthesis of complex metal-organic MIMs that are not easily accessed *via* other, more classic synthetic methods.

In preliminary work designed to test the above proposition, an effort was made to replace the Ag^+ cation by Cd^{2+} (as the nitrate salt). In this case, when a one-pot preparation analogous to that used to obtain crystals of $[\mathbf{1}^{4+}\bullet(\mathrm{Ag}^+\bullet\mathbf{4}\bullet\mathbf{5})]\bullet[\mathbf{1}^{4+}\bullet((\mathrm{Ag}^+)_2\bullet\mathbf{5}_2\bullet4\mathrm{H_2O})]\bullet29\mathrm{H_2O}$ was employed, single crystals of a complex, $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_4\bullet(\mathrm{Cd}^{2+})_4\bullet(\mathrm{HO}^-)_4\bullet4\mathrm{H_2O}]\bullet19\mathrm{H_2O}$ were obtained. X-ray diffraction analysis revealed a metal organic rotaxane framework (MORF) structure, wherein the Cd^{2+} cations act as bridging units for the anionic components (**5**), which are organized as 2D networks (c.f. Figure 10). The macrocyclic component, $\mathbf{1}^{4+}$, acts as edges about **5** within the overall polyrotaxane structure. The interactions between $\mathbf{1}^{4+}$ and the threading polyanionic guest **5** are characterized by CH-π, anion-π, and intermolecular hydrogen bonding interactions, as inferred from an atomic distance between C(52) and C(101) that is less than 3.8 Å, an atomic distance between O(9) and C(47) $\leq$ 3.4 Å, and atomic distance between O(2) and C(20) that is less than 3.0 Å, respectively. On this basis we think it should be possible to use a variety of anions and cations in conjunction with box $\mathbf{1}^{4+}$ to create new interpenetrated structures. Studies along these lines are currently in progress.

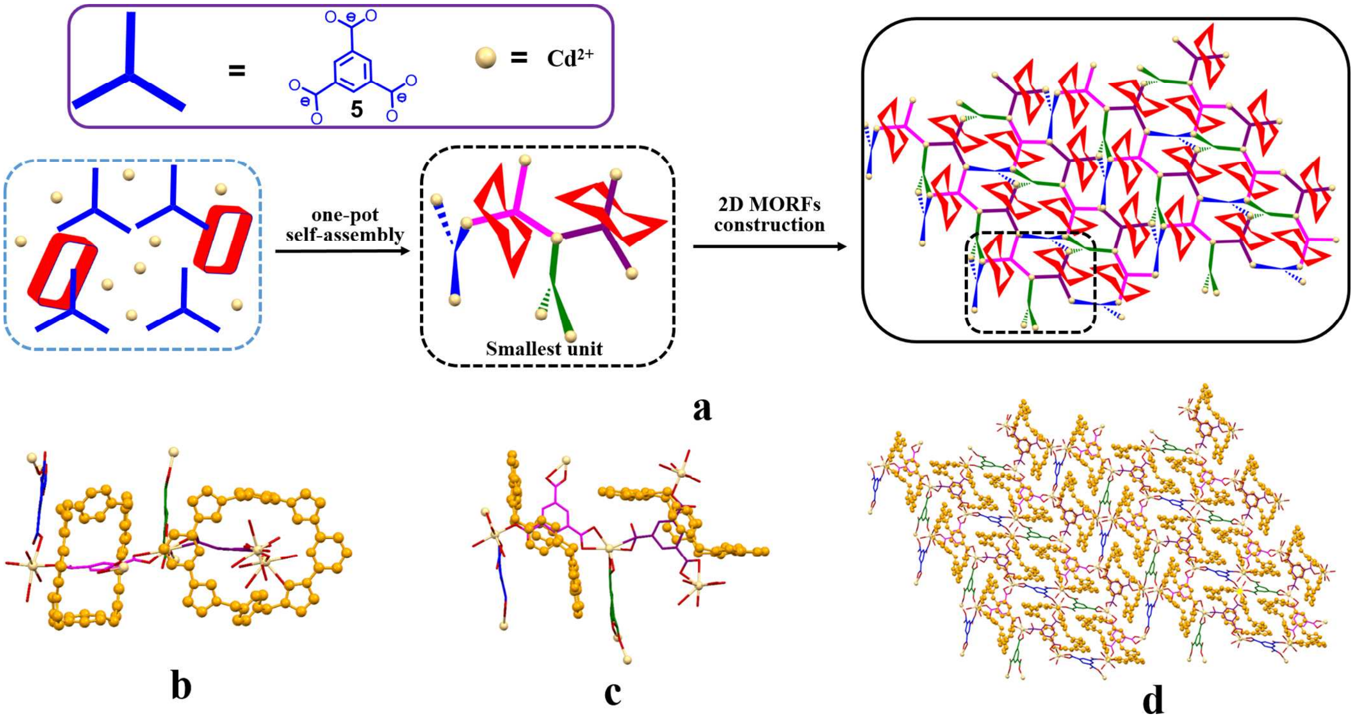


Figure 10. (a) Schematic representation of the proposed formation of the the 2D metal organic rotaxane framework (MORF) consisting of $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_4\bullet(\mathrm{Cd}^{2+})_4\bullet(\mathrm{HO}^-)_4\bullet4\mathrm{H_2O}]_n$. (b) Front and (c) side views of the core rotaxane unit $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_4\bullet(\mathrm{Cd}^{2+})_4\bullet(\mathrm{HO}^-)_4\bullet4\mathrm{H_2O}]$. (d) The 2D metal organic rotaxane structure found within the single X-ray crystal structure of $[(\mathbf{1}^{4+})_2\bullet\mathbf{5}_4\bullet(\mathrm{Cd}^{2+})_4\bullet(\mathrm{HO}^-)_4\bullet4\mathrm{H_2O}]\bullet19\mathrm{H_2O}$. Some of the solvent molecules and counter anions have been omitted for clarity.

ASSOCIATED CONTENT

Supporting Information

Supporting information is provided that includes experimental details, NMR spectroscopic analysis, ESI-MS results and single crystal X-ray diffraction studies. 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 interests.

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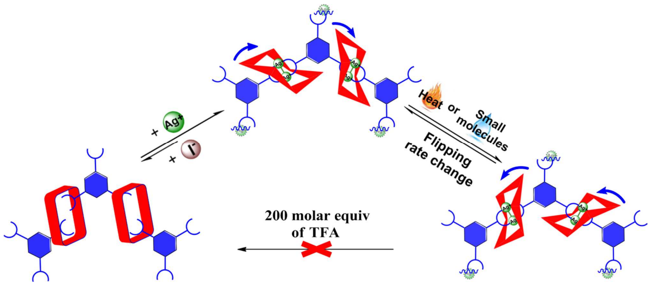
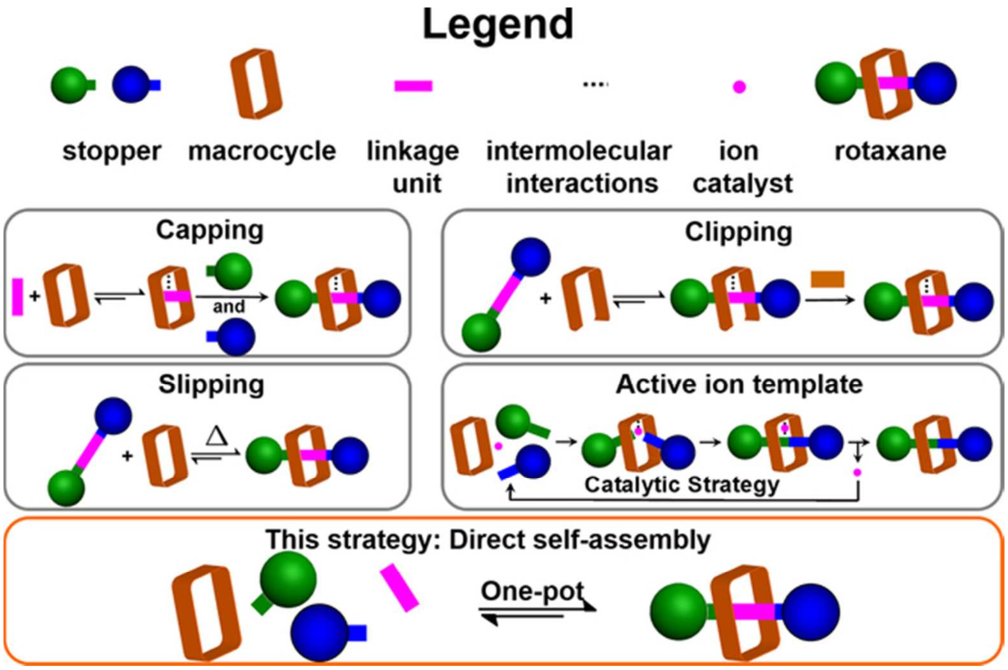

+ Ag⁺
+ I⁻
Heat or Small molecules
Flipping rate change
200 molar equiv of TFA



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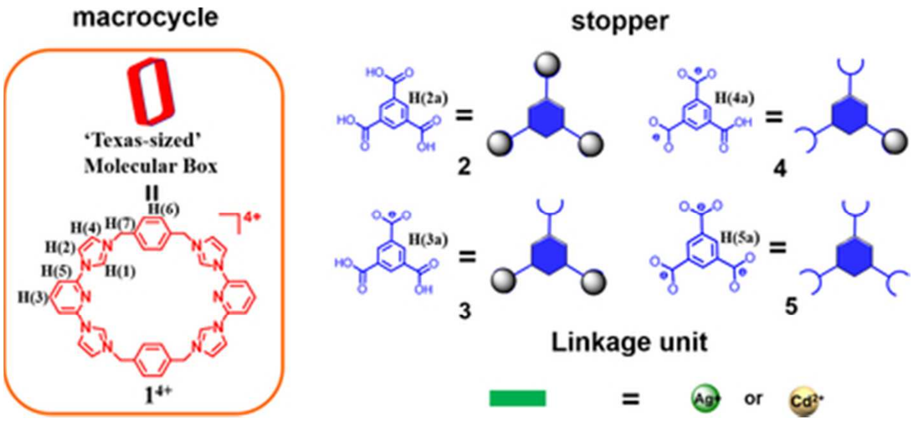

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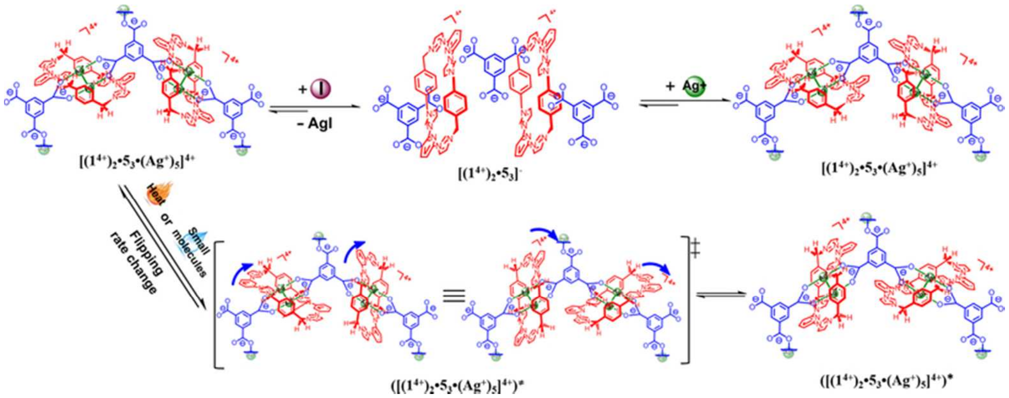

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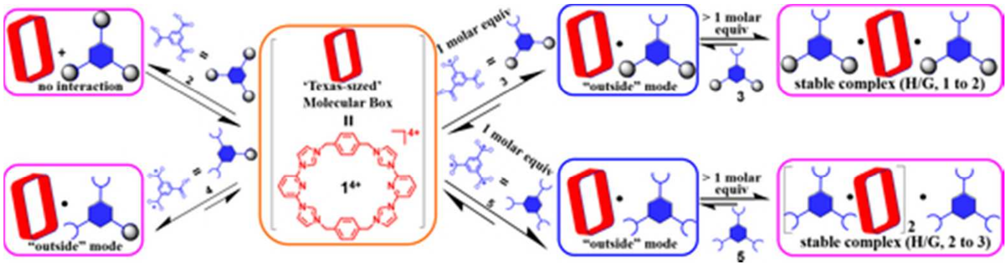

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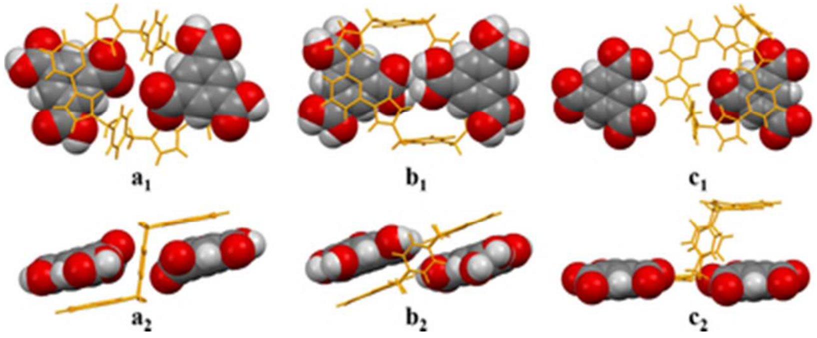

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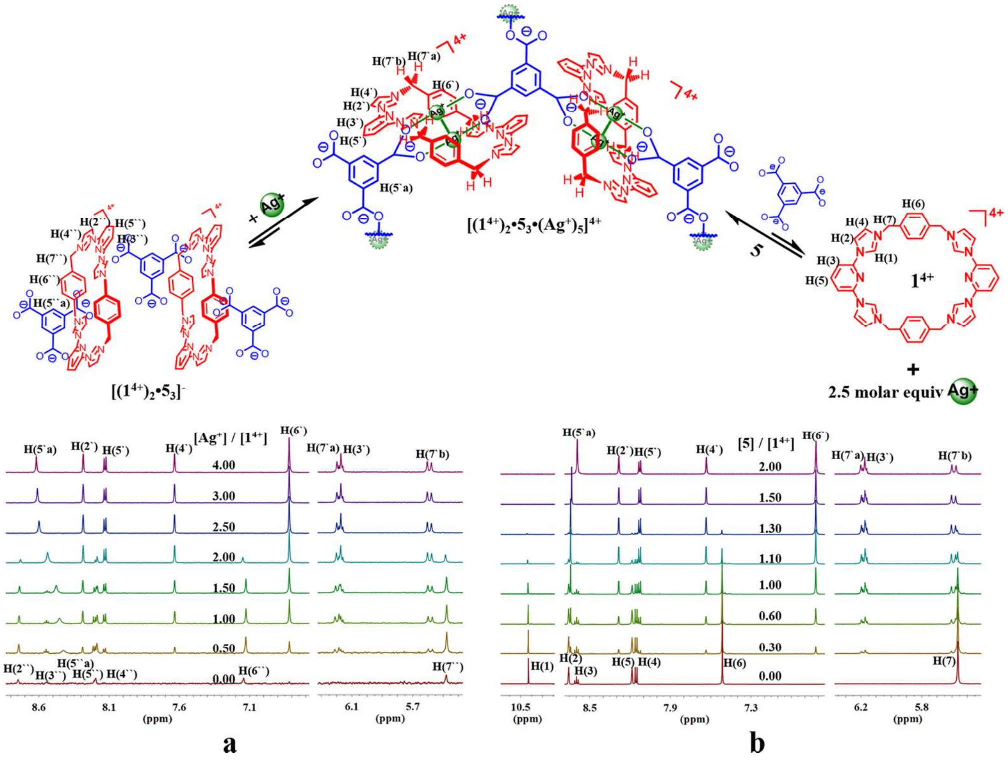

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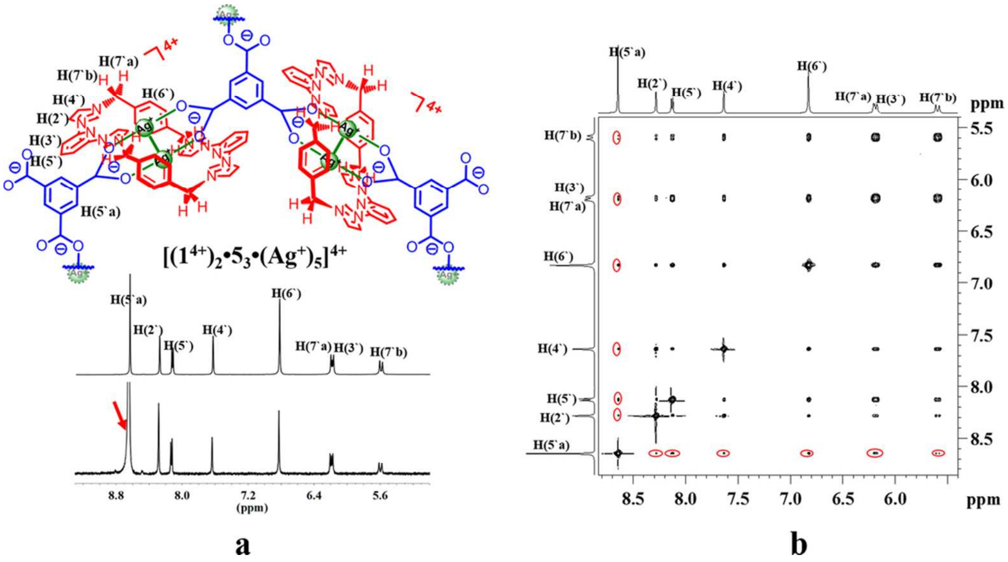

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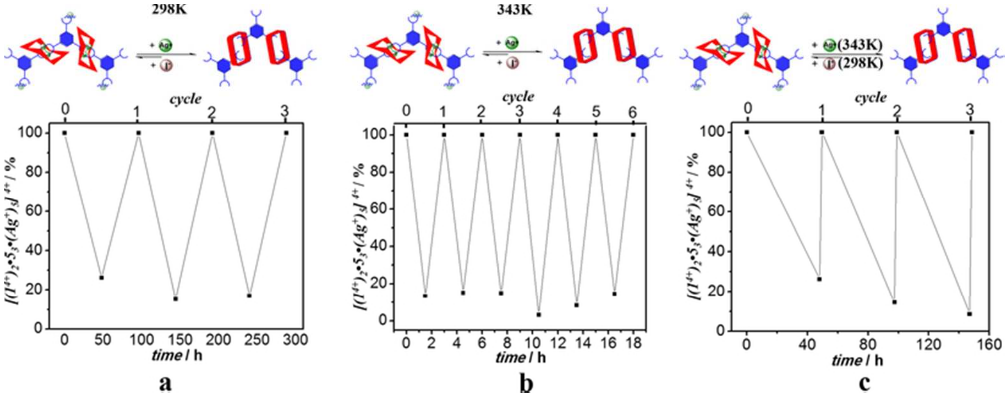

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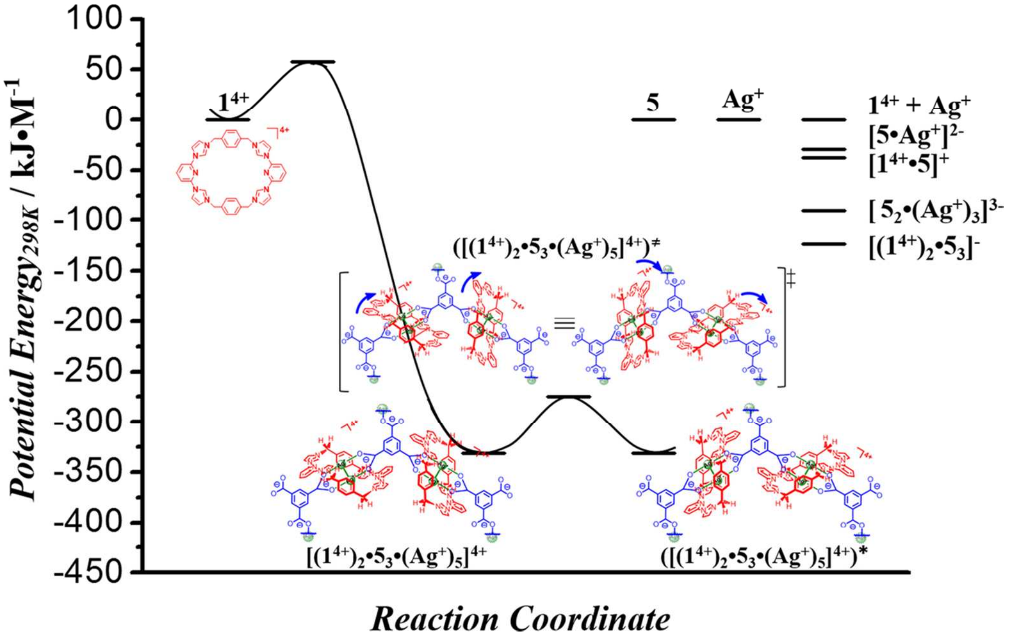

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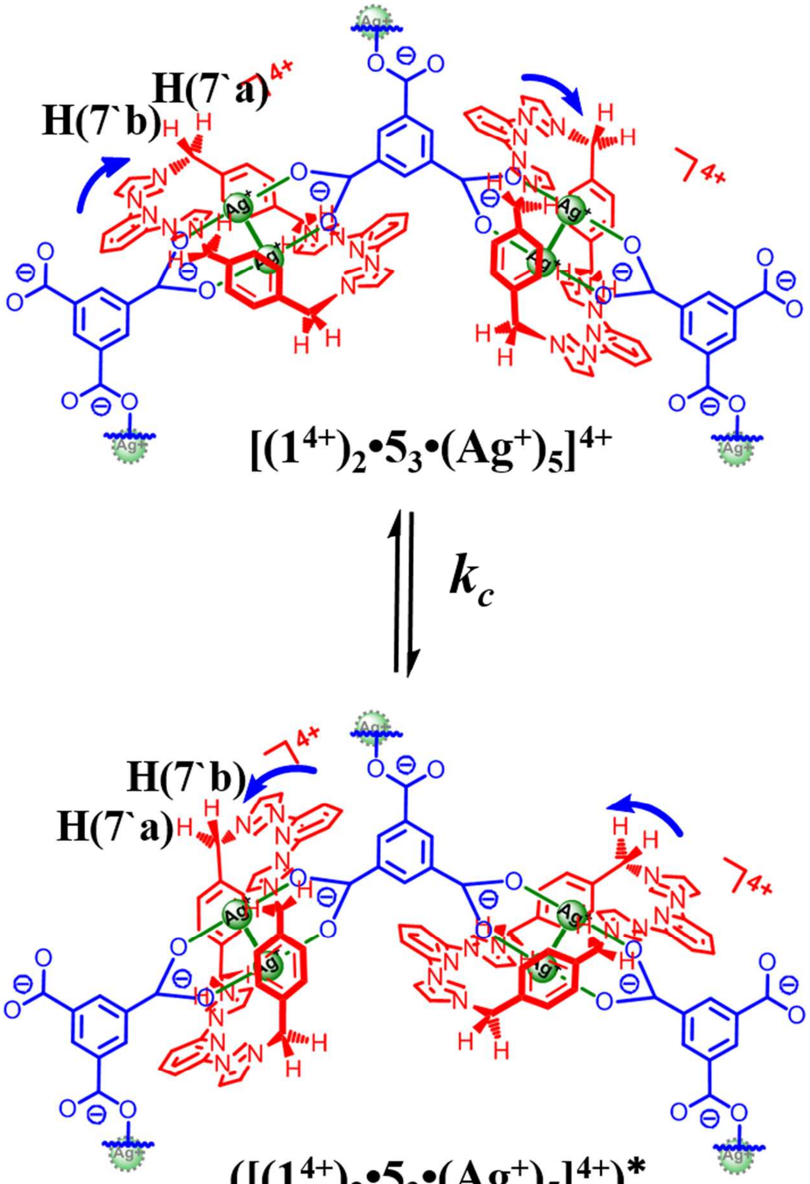

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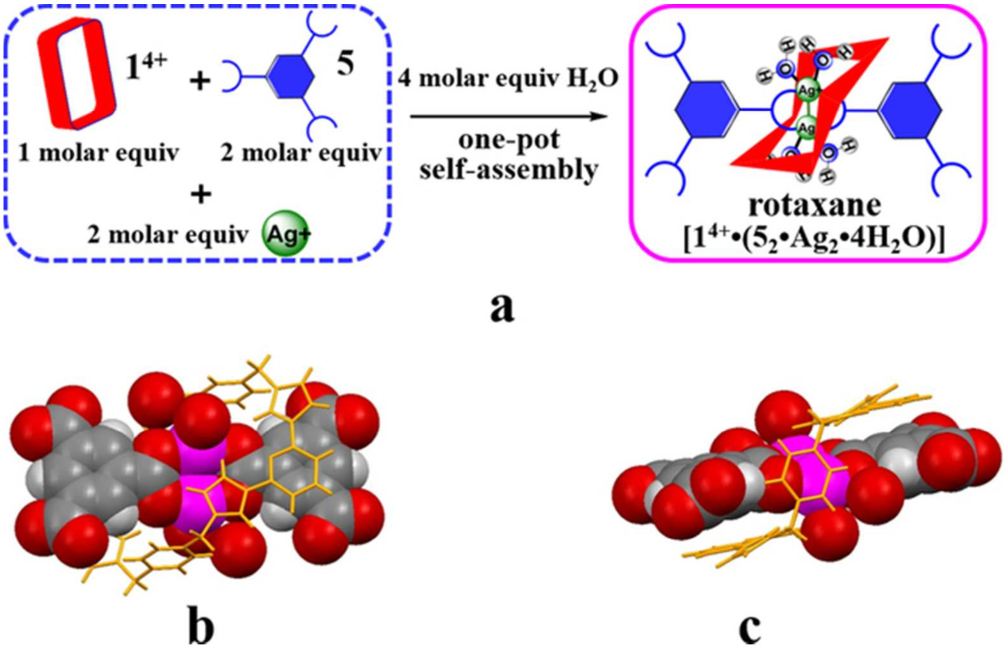

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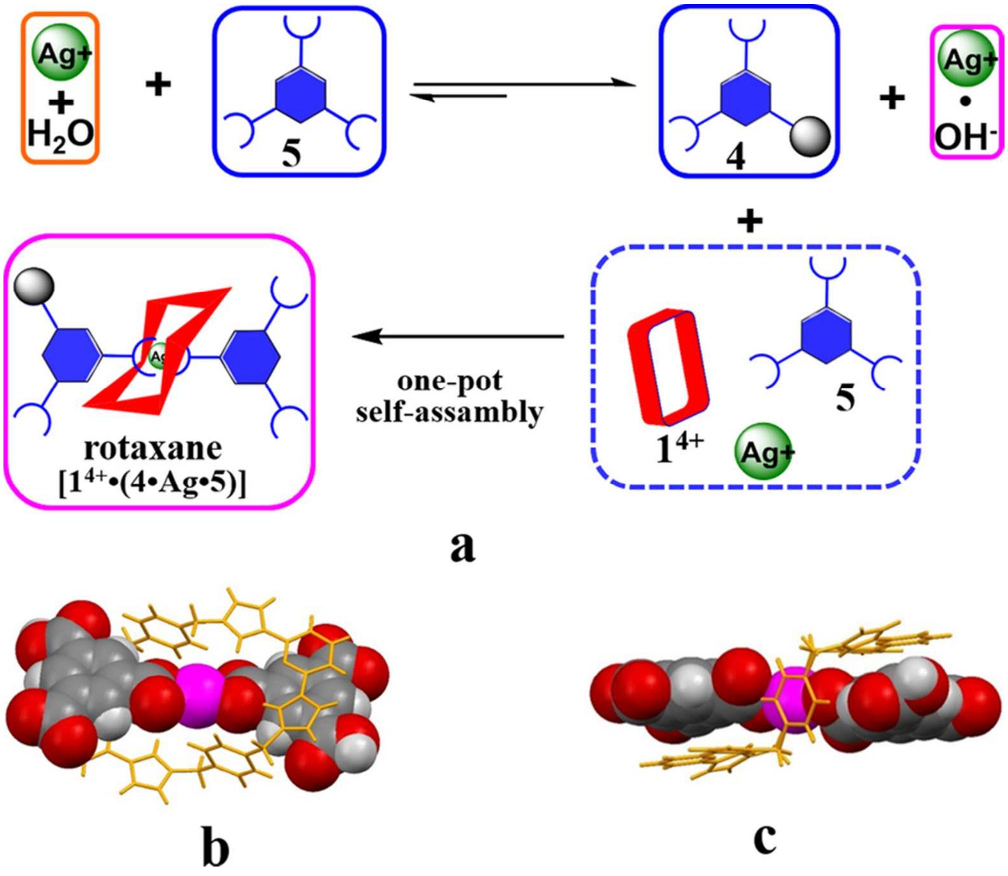

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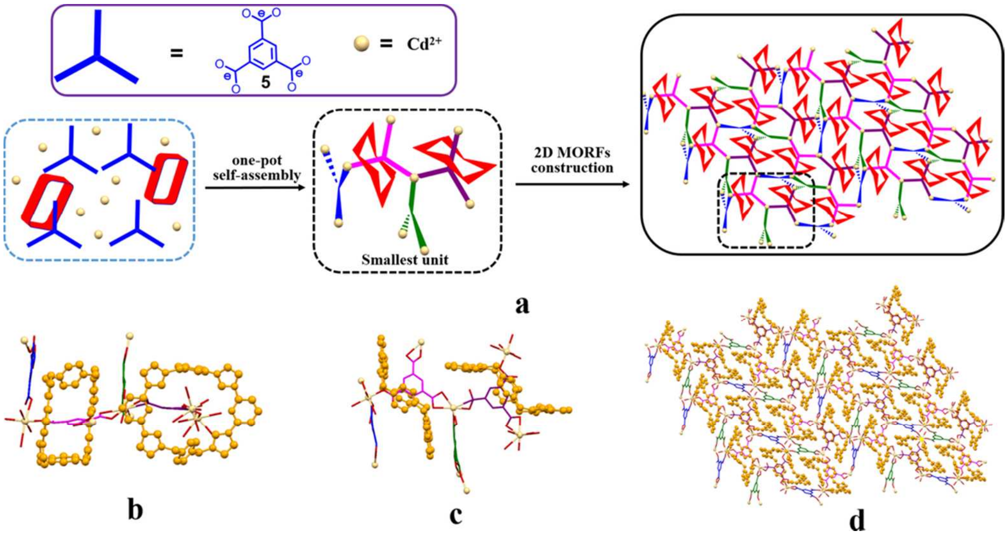

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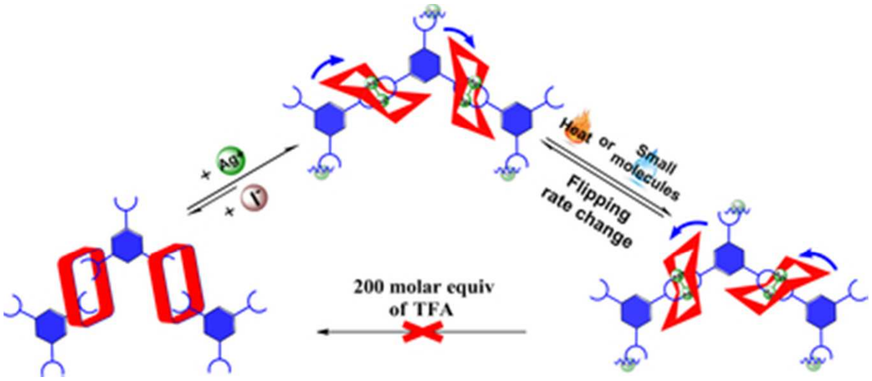

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