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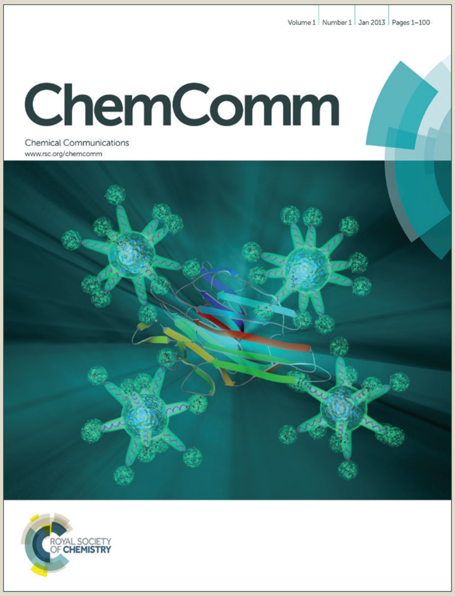

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Aromatic sulfonate anion-induced pseudorotaxanes: Environmentally benign synthesis, selectivity, and structural characterization

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Anion-induced molecular threading is an emerging strategy for generating mechanically interlocked molecular architectures. Herein, we report the preparation of two pseudorotaxane structures generated from aromatic sulfonate anions and a tetraimidazolium-containing macrocycle in organic media, as well as under environmentally benign aqueous conditions.

Over the last three decades, the field of mechanically interlocked molecules (MIMs) has seen rapid development, while attracting increasing interest from the broader chemical community.[1] These complex molecular architectures are often organized and/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] Recently, anion-induced self-assembly has emerged as a viable method for generating MIMs.[6] Work in this area has successfully produced wide range of interlocked structures, including pseudorotaxanes,[7] rotaxanes,[8] psuedopolyrotaxanes,[9] and polyrotaxanes.[10] It has also allowed access to complex molecular architectures, such as metal-organic rotaxanes[11] and materials that respond to external stimuli.[12] A variety of anionic species, including inorganic (*e.g.*, Cl^-, Br^-,[13] and phosphate anions[14]) and organic species (*e.g.,* organic oxoanions[15]), have been used in the development of anion-induced MIMs. Our group in particular has obtained MIMs by inserting aromatic dicarboxylate species into a large, flexible tetraimidazolium macrocycle referred to as a "Texas box" (*i.e.*, cyclo[2](2,6-di(1H-imidazol-1-yl)pyridine)[2] (1,4-dimethylene benzene); $\mathbf{1}^{4+}$).[6c] This success led us to question whether aromatic sulfonate anions, which have more hydrogen bonding sites and which act as weaker Brønsted bases, might have potential advantages when combined with this same box-like receptor (*i.e.*, $\mathbf{1}^{4+}$). There are several reports which describe the use of sulfate anions in the construction of supramolecular organic frameworks (SOFs),[16] metal-organic frameworks (MOFs),[17] and a few reports in which sulfate anions are included in the framework of the macrocyclic unit of MIMs.[16-18] However, to our knowledge the use of sulfonate-containing precursors as the threading entities in the construction of rotaxanes or pseudorotaxanes has not been reported. It is our belief that interlocked molecules containing threaded sulfonate anionic (or dianionic) axels would constitute a new set of mechanically interlocked structures. The preparation of such species might also provide valuable insights into the binding behavior of $\mathbf{1}^{4+}$. Herein, we report the generation of two pseudorotaxane species (*i.e.*, $[\mathbf{1}^{4+}\bullet\mathbf{3}]^{2+}$ and $[\mathbf{1}^{4+}\bullet\mathbf{4}]^{2+}$) *via* the anion-induced self-assembly of aromatic disulfonate precursors (**3** and **4**) and $\mathbf{1}^{4+}$ under conditions of controlled stoichiometric mixing and crystallization. Single crystal analysis of both resulting complexes revealed that in the solid state ordered arrays of 1-dimensional supramolecular species are obtained, which are stabilized by a combination of apparent electrostatic and donor-acceptor-donor (DAD) interactions. These sulfonate-derived pseduorotaxanes, $[\mathbf{1}^{4+}\bullet\mathbf{3}]^{2+}$ and $[\mathbf{1}^{4+}\bullet\mathbf{4}]^{2+}$, may also be obtained via single pot reactions carried out in aqueous solution using sodium hydroxide as the base.

The ability to generate interlocked molecular species in aqueous media is of interest in light of recent attention focused on MIM products prepared under so-called green conditions. Recent contributions from Liu, *et al.*, have shown that is possible to generate pseudorotaxanes by grinding.[19] Likewise, there have been several reports describing the synthesis of MIMs from aqueous media including from Tian, *et al.*,[20] who reported a polyrotaxane synthesis and Stoddart, *et al.*,[21] who described the

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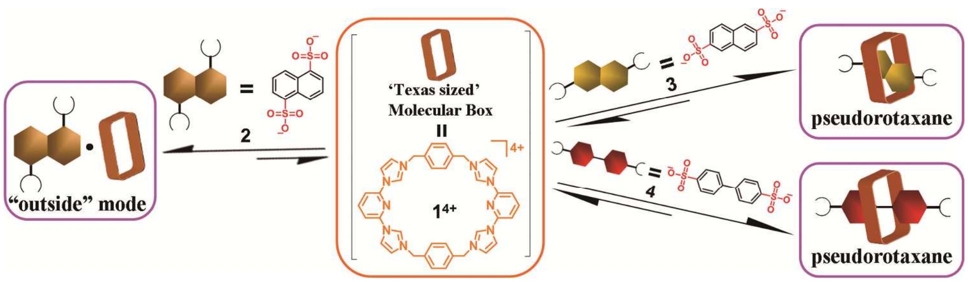

Scheme 1. Aromatic sulfonate anion-induced selective pseudorotaxane construction

preparation of catenanes in aqueous media. Pantoş and co-workers also obtained a series of catenane structures in an aqueous phase.[22] Hydrophobic interactions appear to play a critical role in driving the formation of these MIM systems. In contrast, the pseudorotaxanes formed from **3** or **4** and $\mathbf{1}^{4+}$ were found to be primarily stabilized by electrostatic interactions. Moreover, the self-assembly process leading to their formation is particularly facile, as discussed below. These systems thus represent a new set of readily accessible MIM structures.

We chose to start investigating the interactions between the molecular box $\mathbf{1}^{4+}$ and disulfonate anions by exploring the binding interactions between $\mathbf{1}^{4+}$ and 1,5-naphthalene disulfonate dianion (**2**) in DMSO-d_6 solution. A ^{1}H NMR spectral titration of $\mathbf{1}^{4+}$ with **2** (studied as its tetramethylammonium (TMA^+) salt made *in situ* by mixing $2\mathrm{H}^+\bullet\mathbf{2}$ with 2 molar equiv. of $\mathrm{TMA}^+\bullet\mathrm{OH}^-\bullet 5\mathrm{H_2O}$) in DMSO-$d_6$ solution showed distinct, concentration dependent changes in the chemical shift of the peaks associated with the imidazole C-H resonance. Further, analysis by two-dimensional nuclear Overhauser enhancement spectroscopy (NOESY) revealed no cross peaks between protons on $\mathbf{1}^{4+}$ and guest **2**. Such findings are consistent with the anionic guest **2** being bound to the outside of the central cavity of $\mathbf{1}^{4+}$ (*cf.* Scheme 1), rather than the formation of a pseudorotaxane or other MIM structure. A diffusion ordered spectroscopic (DOSY) study (DMSO-d_6**)** revealed that all proton signals, including those located on $\mathbf{1}^{4+}$ and **2**, showed similar diffusion times in the representative solution state mixtures (*cf.* ESI).

In an effort to characterize the complex formed between $\mathbf{1}^{4+}$ and **2** in solution, a continuous variation analysis (Job plot) was carried out in DMSO-d_6. The resulting plot, obtained by monitoring y (defined as the product of chemical shift change value of H(1) on $\mathbf{1}^{4+}$ and the corresponding host concentration), revealed a maximum value when the ([G]/([H]+[G])) ratio was 0.5. This finding leads us to suggest that a binding stoichiometry of 1:1 (H:G) best describes the interaction between $\mathbf{1}^{4+}$ and anion **2** under these solution phase conditions An isodesmic titration was then performed in DMSO-d_6. Here, the change in the chemical shift corresponding to the imidazole C-H proton (*i.e.*, H(1); *cf.* ESI) was monitored as the concentration of guest **2** was increased. From this study, an association constant (K_a) of $(1.0 \pm 0.1) \times 10^3\ \mathrm{M}^{-1}$ was calculated for the formation of the outside-bound host:guest complex (*i.e.*, $[\mathbf{1}^{4+}\bullet\mathbf{2}]^{2+}$). Separately, a white precipitate was obtained *via* mixing a solution of $\mathbf{1}^{4+}\bullet 4\mathrm{PF_6}^-$ (4.1 mmol in 1 mL acetonitrile) and a mixture consisting of $2\mathrm{H}^+\bullet\mathbf{2}\bullet 4\mathrm{H_2O}$ (20.6 mmol) and $\mathrm{TMA}^+\bullet\mathrm{OH}^-\bullet 5\mathrm{H_2O}$ (41.2 mmol) dissolved in 1 mL of acetonitrile. After washing this solid with a mixture of water/acetonitrile (1:1, v/v), electrospray Ionization mass spectrometry (ESI-MS) analysis revealed a peak corresponding to $[\mathbf{1}^{4+} + \mathbf{2} - \mathrm{H}]^+$ (*m/z* 915.2) in the gas phase. The above results, taken in concert, are considered evidence for formation of a 1:1 molecular complex when $\mathbf{1}^{4+}$ and **2** are mixed in DMSO-d_6 solution.

In order to obtain insights into how the structure of the disulfonate anion might influence the nature of the complex formed from $\mathbf{1}^{4+}$, we studied an isomer of **2**, namely the 2,6-naphthalene disulfonate dianion (**3**). As above, the dianionic guest **3** was obtained by mixing 2 molar equiv. of $\mathrm{TMA}^+\bullet\mathrm{OH}^-\bullet 5\mathrm{H_2O}$ with $2\mathrm{H}^+\bullet\mathbf{3}$ in DMSO-d_6. Again shifts in the ^{1}H NMR resonances were seen. However, in this case, NOESY spectral analyses carried out in DMSO-d_6 provided evidence for a 1:1 host:guest complex in which the disulfonate anion was inserted into $\mathbf{1}^{4+}$ resulting in the formation of a pseudorotaxane complex. Specifically, peaks correlating the proton signals on host $\mathbf{1}^{4+}$ (*i.e.*, H(1-7)) and those on the anionic guest **3** (H(3a-c)) were observed. These cross peaks included those between H(1) and H(3b, 3c), H(5) and H(3a), H(6) and H(3b), as well between H(7) and H(3a, 3b). As in the case of **2**, a Job plot analysis carried out in DMSO-d_6 revealed a maximum in the y value at a molar ratio of 0.5. Again, this was taken as evidence for the formation of a 1:1 (H:G) complex (*i.e.*, $[\mathbf{1}^{4+}\bullet\mathbf{3}]^{2+}$). A separate isodesmic titration allowed an association constant (K_a) of $(1.6 \pm 0.1) \times 10^3\ \mathrm{M}^{-1}$ to be calculated. Again, similar diffusion times were seen for the proton signals of $\mathbf{1}^{4+}$ and **3** in the DOSY spectrum recorded in DMSO-d_6 (*cf.* ESI). ESI-MS analysis involving a sample prepared in a mixture of water and acetonitrile under the same conditions as used in the case of **2** (*vide supra*) revealed a signal corresponding to $[\mathbf{1}^{4+} + \mathbf{3}]^{2+}$ (*m/z* 458.1).

The different binding modes observed in the case of $[\mathbf{1}^{4+}\bullet\mathbf{2}]^{2+}$ and $[\mathbf{1}^{4+}\bullet\ \mathbf{3}]^{2+}$ was taken as initial evidence that the structure of the sulfonate dianion can dictate the nature of the complex formed from macrocycle $\mathbf{1}^{4+}$. While in DMSO-d_6 solution a pseudorotaxane species is formed when the linear disulfonate anion **3** was used, this was not true for **2**. Presumably, the "wider" nature of guest **2** prevents it from threading successfully into the core of $\mathbf{1}^{4+}$ under these solution phase conditions. It thus binds to the outside of $\mathbf{1}^{4+}$ to form a molecular complex.

Further support for the notion that the choice of sulfonate dianion can affect the nature of species formed from $\mathbf{1}^{4+}$ came from studies with the biphenyl-4,4′-disulfonate dianion **4** (also made in *situ via* mixing $2\mathrm{H}^+\bullet\mathbf{4}$ and 2 molar equiv. of $\mathrm{TMA}^+\bullet\mathrm{OH}^-\bullet 5\mathrm{H_2O}$). This latter dianion has an estimated width of 4.0 Å and, like **3**, was expected to stabilize a MIM structure. As above, evidence for the formation of a 1:1 (H:G) complex with $\mathbf{1}^{4+}$ came from a Job plot analysis carried out in DMSO-d_6. An association constant (K_a) of $(3.0 \pm 0.2) \times 10^3\ \mathrm{M}^{-1}$ was likewise calculated on the basis of an isodesmic titration. In analogy to what was seen for **3**, but in contrast to what was seen with **2**, NOESY spectral studies provided support for the idea that dianion **4** inserts into the central cavity of $\mathbf{1}^{4+}$ to form a pseudorotaxane. Specifically, correlations between H(1, 2, 3, 4, 5, 6 or 7) on $\mathbf{1}^{4+}$ and H(4a or 4b) on **4** were observed (*i.e.,* H(1) and H(4b), H(2) and H(4a, 4b), H(3) and H(4a), H(4) and H(4a, 4b), H(5) and H(4a,4b), H(6) and H(4b), H(7) and H(4b)). Again, similar diffusion times for the proton signals of $\mathbf{1}^{4+}$ and **4** were seen in the DOSY spectrum recorded in DMSO-d_6 under conditions of proposed complex formation (*cf.* ESI). As with **2** and **3**, a peak corresponding to a 1:1 complex ($[\mathbf{1}^{4+}\bullet\mathbf{4}]^{2+}$) was observed in the ESI-MS spectrum (*m/z* = 471.1).

In a separate study, an effort was made to use NaOH as a cost effective alternative to $TMA^{+}\bullet OH^{-}\bullet 5H_2O$ for preparing the requisite 2,6-naphthalene sulfonate dianion. DMSO was also avoided. Instead, analyses were carried out in D_2O using water soluble salts of $\mathbf{1}^{4+}$ (*i.e.*, $\mathbf{1}^{4+}\bullet 4Cl^{-}$) and guests **2**, **3** or **4** (*i.e.*, $2Na^{+}\bullet\mathbf{n}$ (**n** = **2**, **3** or **4**)). Results similar to those observed in DMSO-d_6 were obtained. For instance, Job plots were consistent with the formation of 1:1 complexes. For these latter studies, the change in the chemical shift of H(3) on $\mathbf{1}^{4+}$ was monitored since the more acidic proton, H(1), was found to undergo H/D exchange. Nevertheless, a maximal y value was seen at a molar ratio of 0.5, as would be expected for the formation of a 1:1 (H:G) complex (see ESI). Isodesmic titrations carried out in D_2O while monitoring this same proton signal by ^1H NMR spectroscopy allowed association constants (K_a) of (3.5 ± 0.2) x 10^3 M^{-1}, (3.4 ± 0.2) x 10^5 M^{-1} and (3.5 ± 0.2) x 10^4 M^{-1} to be calculated for the formation of $[\mathbf{1}^{4+}\bullet\mathbf{2}]^{2+}$, $[\mathbf{1}^{4+}\bullet\mathbf{3}]^{2+}$ and $[\mathbf{1}^{4+}\bullet\mathbf{4}]^{2+}$, respectively (*cf.* ESI). 1D NOE and NOESY spectral studies were also carried out and provided support for the formation of pseudorotaxane species, *i.e.*, $[\mathbf{1}^{4+}\bullet\mathbf{3}]^{2+}$ and $[\mathbf{1}^{4+}\bullet\mathbf{4}]^{2+}$, under these purely organic solvent-free conditions (*cf.* ESI). In contrast, but in analogy to what was seen in organic media, no evidence supporting the formation of an interpenetrated structure was obtained in the case of **2**, (*cf.* ESI).

In effort to elucidate further the structural nature of the complexes formed from $\mathbf{1}^{4+}$ and the anionic sulfonates **2-4**, efforts were made to obtain single crystals suitable for X-ray diffraction analysis. Towards this end, the tetramethylammonium (TMA^{+}) salts of dianions **2-4** in water were combined with a solution of $\mathbf{1}^{4+}\bullet 4PF_6^{-}$ in a mixture of acetonitrile/water/DMF (1/1/1, v/v/v), followed by slow evaporation. Using this method, two independent structures were obtained from the combination of $\mathbf{1}^{4+}$ and **2** (*i.e.*, $\mathbf{1}^{4+}\bullet\mathbf{2}_2\bullet 6H_2O$ and $\mathbf{1}^{4+}\bullet\mathbf{2}_2\bullet 14H_2O$). The resulting X-ray diffraction structures revealed the expected "outside" binding mode in the case of both $\mathbf{1}^{4+}\bullet\mathbf{2}_2\bullet 6H_2O$ and $\mathbf{1}^{4+}\bullet\mathbf{2}_2\bullet 14H_2O$ (*cf.* Figure 1). On this basis, we infer that **2** is too wide (6.5 Å) to insert into the center of $\mathbf{1}^{4+}$, which has a maximum cavity size of 5.8 Å (*cf.* ESI). Interestingly, in both structures, macrocycle $\mathbf{1}^{4+}$ was found to adopt a similar "partial chair" conformation. In the case of $\mathbf{1}^{4+}\bullet\mathbf{2}_2\bullet 6H_2O$, the dianion **2** was found to interact with $\mathbf{1}^{4+}$ *via* two different limiting "outside" binding modes, involving intermolecular hydrogen bonding, π-π donor-acceptor, and electrostatic interactions. In contrast, in the structure of $\mathbf{1}^{4+}\bullet\mathbf{2}_2\bullet 14H_2O$, complex stabilization appears to reflect predominantly electrostatic and π-π donor-acceptor interactions (*cf.* ESI).

A diffraction grade single crystal of $\mathbf{1}^{4+}\bullet\mathbf{3}_2\bullet 7.5H_2O$ was also obtained *in situ* using a procedure analogous to that used in the case of $\mathbf{1}^{4+}$ and **2** (*cf.* ESI). Analysis of the resulting X-ray structure showed that one molecule of **3** was inserted into the center of host receptor $\mathbf{1}^{4+}$ resulting in the formation of a pseudorotaxane. This solid state structure thus supports the solution spectroscopic analyses described above. In particular, and in contrast to what is seen for **2**, a self-assembled MIM is formed from this relatively narrow dianion. Based on the structural parameters, it was concluded that the pseudorotaxane species seen in this complex is stabilized by a combination of electrostatic, intermolecular hydrogen bonding, and π-π donor-acceptor interactions (*cf.* Figure 1 and Figure S39; ESI). A second molecule of **3** was found sandwiched between two molecules of $[\mathbf{1}^{4+}\bullet\mathbf{3}]^{2+}$ with an interatomic distance of less than 3.5 Å between this dianion and the 2,6-di(1H-imidazol-1-yl)pyridine moieties on both neighboring pseudorotaxane units. The net result is an ordered 1-dimensional supramolecular array that is stabilized by electrostatic and donor-acceptor-donor (DAD) interactions that run along the chain axis (*cf.* Figure S40; ESI).

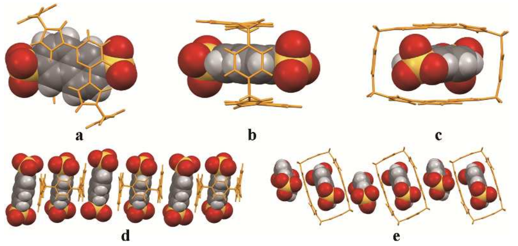

Figure 1. Views of the single-crystal X-ray structure of $\mathbf{1}^{4+}\bullet\mathbf{3}_2\bullet 7.5H_2O$. Top (a), side (b) and front (c) views of the pseudorotaxane unit $[\mathbf{1}^{4+}\bullet\mathbf{3}]^{2+}$ in the structure. Side (d) and front (e) views of the 1D donor-acceptor-donor (DAD) self-assembled coordination polymer present in the solid state. Solvents molecules and some counteranions have been omitted for clarity.

In an effort to obtain structural insights into the molecular complex(es) obtained from the combination of $\mathbf{1}^{4+}$ and **4**, three separate single crystals were analyzed. The first was obtained *via* slow evaporation from the same acetonitrile/water/DMF (1/1/1, v/v/v) mixture used in the case of **2** and **3**. The other set of diffraction grade crystals was obtained by subjecting the products of the organic solvent- and organic base-free "green" synthesis noted above, to recrystallization from a mixture of DMF and water mixture (1:1, v/v) under conditions of slow evaporation (*cf.* ESI)). Analysis of the single crystal obtained under the first set of conditions revealed a structure of net stoichiometry $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet DMF\bullet 5.5H_2O$. In contrast, the single crystal obtained from the DMF/water mixture gave rise to two crystallographically independent structures (*i.e.*, $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet DMF\bullet 6H_2O$ and $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet 9.5H_2O$).

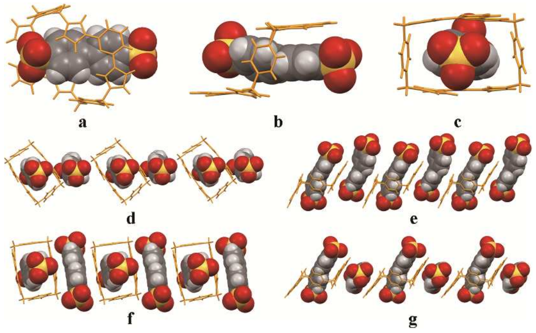

Figure 2. Top (a), side (b) and front (c) views of the pseudorotaxane unit $[\mathbf{1}^{4+}\bullet\mathbf{4}]^{2+}$ present in the single crystal X-ray structures of $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet DMF\bullet 5.5H_2O$, $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet DMF\bullet 6H_2O$, and $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet 9.5H_2O$. Top (d) and side (e) views of the 1D DAD structure present in $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet DMF\bullet 6H_2O$; although not shown, similar extended structures were observed in the case of $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet DMF\bullet 6H_2O$. Top (f) and side (g) views of the 1D DAD structure present in $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet 9.5H_2O$. Solvent molecules and some counteranions have been omitted for clarity.

All three structures were characterized by similar structural features in that the biphenyl-4,4′-disulfonate dianion unit (**4**) is inserted into the central cavity of macrocycle $\mathbf{1}^{4+}$. As inferred from the structural parameters, the resulting pseudorotaxane complexes are stabilized by a combination of electrostatic, intermolecular hydrogen bonding, and π-π donor-acceptor interactions (*cf.* Figure 2 and ESI). As in the case of $[\mathbf{1}^{4+}\bullet\mathbf{3}]^{2+}$, these interactions result in the formation of one-dimensional DAD self-assembled coordination polymers. While similar extended structures were seen in the case of $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet\mathrm{DMF}\bullet5.5H_2O$ and $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet\mathrm{DMF}\bullet6H_2O$, a different arrangement was seen with $\mathbf{1}^{4+}\bullet\mathbf{4}_2\bullet9.5H_2O$, as can be seen from an inspection of Figure 2. The distance between the set of dianions **4** located outside of $\mathbf{1}^{4+}$ and the (1H-imidazol-1-yl)pyridine fragments on neighboring pseudorotaxanes (*cf.* ESI) is notably short (3.4 Å), leading us to suggest that a combination of electrostatic and donor-acceptor interactions play a role in stabilizing the extended structures in the solid state.

The observation that three crystallographically distinct structures have been characterized in the solid state for analogous complexes containing the basic MIM $[\mathbf{1}^{4+}\bullet\mathbf{4}]^{2+}$ core is of interest. It provides support for the notion that many possible arrangements involving residual anions, solvent molecules, and the basic pseudorotaxane units $[\mathbf{1}^{4+}\bullet\mathbf{4}]^{2+}$ and $[\mathbf{1}^{4+}\bullet\mathbf{3}]^{2+}$ could be stabilized by varying further the experimental conditions used in the case of these two anions. Presumably, this reflects the fact that the "box" receptor $\mathbf{1}^{4+}$ is inherently flexible and that the match between it and the dianionic substrates **3** and **4**, while good, is not quite perfect in terms of the idealized concepts of preorganization. Such considerations, to the extent they are true, makes the combination of various sulfonate anions and cationic receptors such as $\mathbf{1}^{4+}$ and its analogues particularly rich in terms of future potential studies.

In summary, pseudorotaxane species may be obtained easily from the combination of $\mathbf{1}^{4+}$ and the sulfonate dianions **3** and **4**. The formation of these interlocked molecular species is supported by a combination of solution phase and solid state analyses. Based on studies with the disulfonate anion **2**, the formation of pseudorotaxane species from $\mathbf{1}^{4+}$ appears to be dependent on the size and shape of the sulfonate dianion guest. An appealing feature of the interlocked pseudorotaxane species formed from a combination of $\mathbf{1}^{4+}$ and **3** and **4** is that they may be effectively prepared under environmentally benign aqueous conditions.

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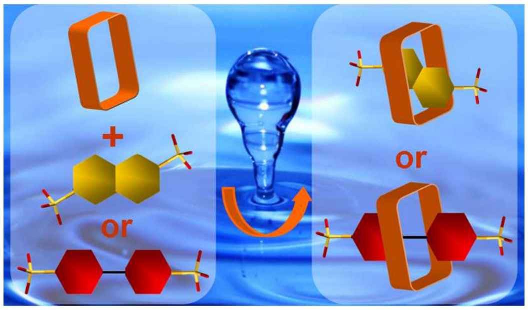

Aromatic sulfonates allow the effective construction of anion-containing pseudorotaxanes from a tetracationic macrocycle known as the "Texas box" in organic media and under organic-free aqueous conditions.