

# Templation and Concentration Drive Conversion Between a $\text{Fe}^{\text{II}}_{12}\text{L}_{12}$ Pseudo-icosahedron, a $\text{Fe}^{\text{II}}_4\text{L}_4$ Tetrahedron, and a $\text{Fe}^{\text{II}}_2\text{L}_3$ Helicate

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*Supporting Information Placeholder*

**ABSTRACT:** We report the construction of three structurally distinct self-assembled architectures:  $\text{Fe}^{\text{II}}_{12}\text{L}_{12}$  pseudo-icosahedron **1**,  $\text{Fe}^{\text{II}}_2\text{L}_3$  helicate **2**, and  $\text{Fe}^{\text{II}}_4\text{L}_4$  tetrahedron **3**, formed from a single triazatriangulenium subcomponent **A** under different reaction conditions. Pseudo-icosahedral capsule **1** is the largest formed through subcomponent self-assembly to date, with an outer-sphere diameter of 5.4 nm and a cavity volume of 15 nm<sup>3</sup>. The outcome of self-assembly depended upon concentration, where the formation of pseudo-icosahedron **1** was favored at higher concentrations, while helicate **2** exclusively formed at lower concentrations. The conversion of pseudo-icosahedron **1** or helicate **2** into tetrahedron **3** occurred following the addition of a  $\text{CB}_{11}\text{H}_{12}^-$  or  $\text{B}_{12}\text{F}_{12}^{2-}$  template.

Coordination-driven self-assembly is an efficient tool for the construction of polyhedral metal–organic complexes,<sup>1</sup> the cavities of which have proven useful in a range of applications, including molecular recognition,<sup>2</sup> stereochemical sensing,<sup>3</sup> chemical separation,<sup>4</sup> stabilization of reactive species,<sup>5</sup> and catalysis.<sup>6</sup> The strategy of subcomponent self-assembly,<sup>7</sup> involving the formation of structures containing multiple N→Metal and C=N linkages during the same overall process, allows the preparation of a variety of capsules with different shapes and cavity sizes, which bind many different guests.<sup>7a</sup>

An attractive goal is the construction of large self-assembled architectures<sup>8</sup> that resemble the icosahedral structures adopted by some protein cages.<sup>9</sup> As in the cases of icosahedral viral capsids assembled from multiple copies of a single protein subunit, self-assembly can allow the construction of larger architectures from much smaller components. The large internal voids of capsules with a sufficient degree of cavity enclosure may be suitable for binding large substrates,<sup>10</sup> enabling synthetic encapsulants to approach the complex functions exhibited by biological systems.

In analogy to the structural changes of biological molecules,<sup>11</sup>

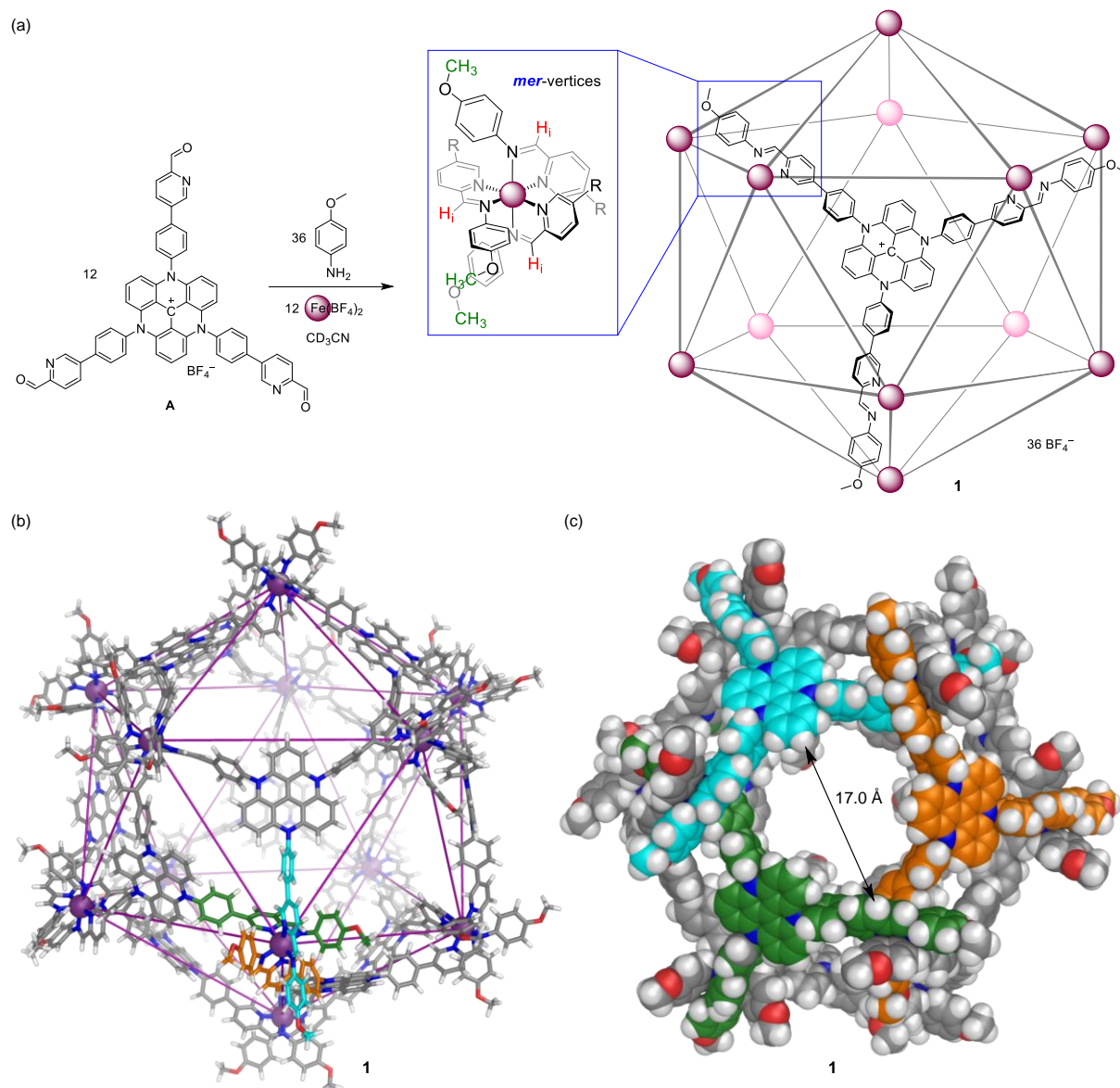
designing stimuli-responsive transformations within systems of discrete self-assembled container molecules is an important challenge in supramolecular chemistry.<sup>12</sup> Such transformations may lead to functions that include guest uptake and release,<sup>13</sup> chemical purification,<sup>14</sup> reagent storage,<sup>15</sup> and drug delivery.<sup>16</sup> Various stimuli, such as light,<sup>13b,17</sup> pH,<sup>18</sup> temperature,<sup>19</sup> solvent,<sup>2c,20</sup> concentration,<sup>21</sup> or additional chemical signals,<sup>22</sup> have been employed to trigger transformation processes that lead to structural conversions. Supramolecular transformations involving multiple different structure types based upon a single ligand and metal ion remain rare,<sup>23</sup> however.

Here we report the preparation of three different architectures, a  $\text{Fe}^{\text{II}}_{12}\text{L}_{12}$  pseudo-icosahedron, a  $\text{Fe}^{\text{II}}_2\text{L}_3$  helicate, and a  $\text{Fe}^{\text{II}}_4\text{L}_4$  tetrahedron, assembled from the same triazatriangulenium (TATA) subcomponent under different reaction conditions. Changes in ligand concentration or the addition of template anions triggered complete conversions between these assemblies.

Subcomponent **A** (Figure 1) was prepared following our previously reported procedure.<sup>24</sup> We first explored its self-assembly at a concentration of 4.4 mM in acetonitrile. The reaction of subcomponents **A** (1 equiv) and *p*-anisidine (3 equiv) with  $\text{Fe}(\text{BF}_4)_2$  (1 equiv) in acetonitrile at 70 °C resulted in the formation of the very large architecture **1**. ESI-MS showed a series of sharp peaks (Figure 2b), corresponding to charge states from 18+ to 11+, all of which were consistent with a  $\text{Fe}^{\text{II}}_{12}\text{L}_{12}$  composition.

The <sup>1</sup>H NMR spectrum of  $\text{Fe}^{\text{II}}_{12}\text{L}_{12}$  **1** displayed a complex pattern of signals, consistent with desymmetrization of the ligand (Figure 2a and Figure S4). Three magnetically-distinct chemical environments for the protons on the initially *C*<sub>3</sub>-symmetric ligand were observed, with the imine and methoxy signals each exhibiting three sharp peaks with a 1:1:1 integration ratio. The <sup>1</sup>H DOSY spectrum confirmed that all <sup>1</sup>H signals belonged to a single species in solution (Figure 2a and Figure S10).

These NMR and MS data were consistent with the formation of a  $\text{Fe}^{\text{II}}_{12}\text{L}_{12}$  pseudo-icosahedral capsule with *meridional* (*mer*)



**Figure 1.** (a) Subcomponent self-assembly of  $\text{Fe}^{\text{II}}_{12}\text{L}_{12}$  pseudo-icosahedron **1**, with cutout showing the *meridional* metal coordination geometry. (b) PM7-optimized molecular model of pseudo-icosahedron **1**. Carbon atoms for the three distinct ligand arms about one of the *mer*-vertices have been colored cyan, green, and orange, respectively. (c) Model of **1** in space-filling mode, to show the porosity. Carbon atoms of the three triazatriangulenium ligands surrounding a large pore of **1** have been colored cyan, green, and orange, respectively.

coordination geometry at all iron(II) vertices (Figure 1a). The  $^1\text{H}$  NMR spectrum of **1** was fully assigned through 2D NMR (Figure S7-S9). This type of assembly has been observed for a smaller  $\text{C}_3$ -symmetric triamine subcomponent, where a mixture of pseudo-icosahedron and tetrahedron was obtained.<sup>25</sup> We infer the formation of the larger capsule, rather than a  $\text{Fe}^{\text{II}}_4\text{L}_4$  tetrahedral cage, to result from the Coulombic repulsions between the cationic triazatriangulenium panels, which would be stronger in a tetrahedron where these panels are spatially closer together.

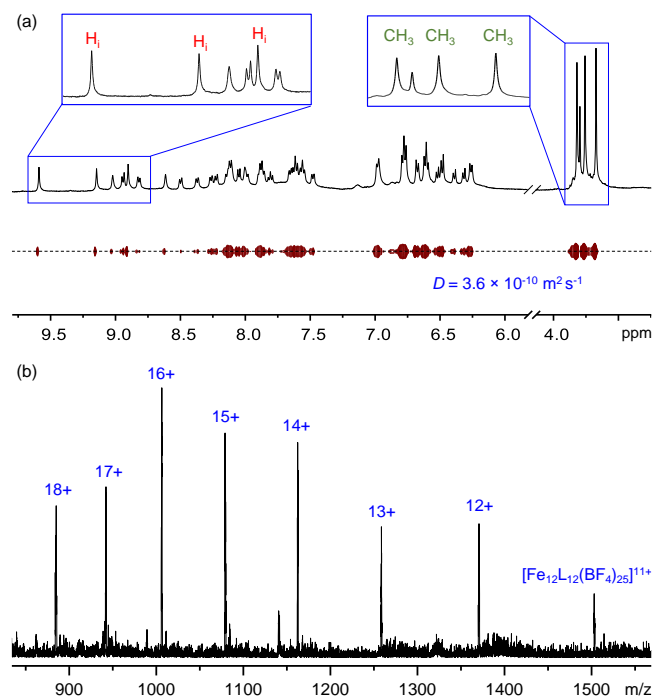
After many unsuccessful attempts at growing crystals of **1** suitable for X-ray diffraction, energy minimization of a pseudo-icosahedral structure for **1** at the PM7 level of theory was carried out (Figure 1b and Table S2). The twelve iron(II) centers describe the vertices of an icosahedron, with the tris(bidentate) ligands capping twelve of the twenty icosahedral faces. All iron(II) centers in **1** display *mer* coordination around the metal centers, where two ligand arms

extend above a triangular face of the ‘icosahedron’ (Figure 1b, cyan and orange) and the third extends from below (Figure 1b, green). The longest  $\text{Fe}\cdots\text{Fe}$  distance between antipodal vertices within this model of **1** is 4.1 nm, and the longest distance between the outermost methoxy groups is approximately 5.4 nm.

The PM7 model also indicates the capsule to be porous, with  $\text{C}_3$ -symmetric openings, having diameters of as large as 17 Å, each surrounded by three triazatriangulenium ligands (one type of openings is shown in Figure 1c). Pseudo-icosahedron **1** encloses a cavity volume of 15095 Å<sup>3</sup>, as determined by VOIDOO calculations (Table S1).<sup>26</sup> Capsule **1** thus represents the largest architecture prepared to date, to the best of our knowledge, using subcomponent self-assembly.<sup>7i,25,27</sup>

As the cavity of pseudo-icosahedron **1** is large and positively charged, we tested the binding of a series of large anionic and

neutral prospective guests. None of these prospective guests, listed in Scheme S3, gave any evidence of guest encapsulation. We infer that they are not large enough to provide a good fit for the cavity, as most have been reported to be encapsulated within smaller capsules.<sup>28</sup>



**Figure 2.** (a)  $^1\text{H}$  DOSY NMR spectrum (500 MHz, 298 K,  $\text{CD}_3\text{CN}$ ) of pseudo-icosahedron **1**. The labelled peaks correspond to the imine and methoxy groups are highlighted in Figure 1a. (b) ESI-mass spectrum of **1**.

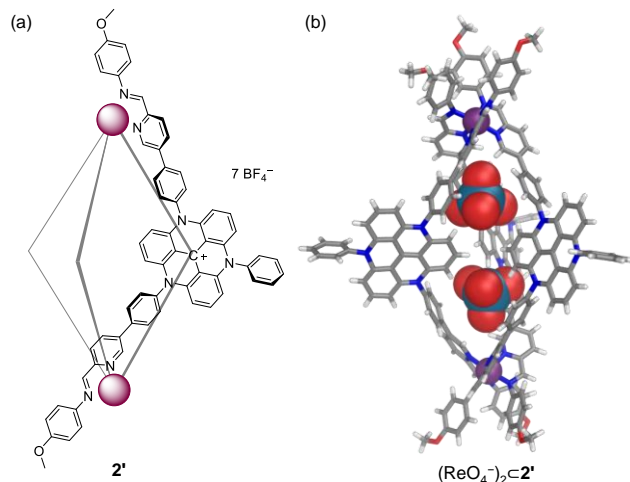
In contrast, when **A** (1 equiv) reacted with *p*-anisidine (3 equiv) and  $\text{Fe}(\text{BF}_4)_2$  (either 0.67 or 1 equiv gave the same result) in acetonitrile at the lower **A** concentration of 2.2 mM, helicate **2** was formed instead of **1** (Scheme S4 and Figures S11-S16). An overall 7+ charge for **2** was confirmed by ESI-MS (Figure S17). The  $^1\text{H}$  NMR spectrum of **2** displayed signals corresponding to a  $C_2$ -symmetric bis-bidentate ligand, with one pyridyl-imine arm remaining uncoordinated (Figure S11). Both the imine and methoxy  $^1\text{H}$  NMR signals of **2** exhibited a 2:1 integral ratio, consistent with the formation of a helicate with  $D_3$  symmetry, in which both iron(II) centers adopted the same  $\Lambda$  or  $\Delta$  handedness.<sup>22,29</sup>

The formation of smaller assembly **2** at a lower concentration is expected on the basis of Le Chatelier's principle.<sup>30</sup> The electrostatic interactions between the small  $\text{BF}_4^-$  anion and the small cavities of the cationic assembly may also render  $\text{BF}_4^-$  a suitable template for helicate formation.

The anion binding ability of helicate **2** was confirmed by carrying out  $^1\text{H}$  NMR titrations. The progressive addition of tetrabutylammonium perchlorate to a solution of **2** in  $\text{CD}_3\text{CN}$  resulted in displacement of  $\text{BF}_4^-$  by  $\text{ClO}_4^-$ , as indicated by shifts in the helicate  $^1\text{H}$  signals, consistent with binding in fast exchange on the NMR chemical shift timescale (Figure S18). The addition of excess  $\text{ReO}_4^-$ ,  $\text{PF}_6^-$ , or  $\text{I}^-$  led to similar NMR observations, but  $\text{Tf}_2\text{N}^-$  did not (Figure S19). The lack of shifts in the  $^1\text{H}$  signals of **2** ( $< 0.02$  ppm at most) after adding excess  $\text{Tf}_2\text{N}^-$  indicated negligible interactions of this anion with helicate **2** relative to  $\text{BF}_4^-$ .

Although numerous attempts to obtain the crystal structure of a host-guest complex of **2** were unsuccessful, we were able to obtain the crystal structure of a host-guest complex of its structural

analogue **2'**, which assembled from a similar subcomponent (**B**) bearing only two pyridine-aldehyde functionalities (Figures 3a and S20-S26). Helicate **2'** bound anions in solution in similar fashion to **2** (Figure S27).

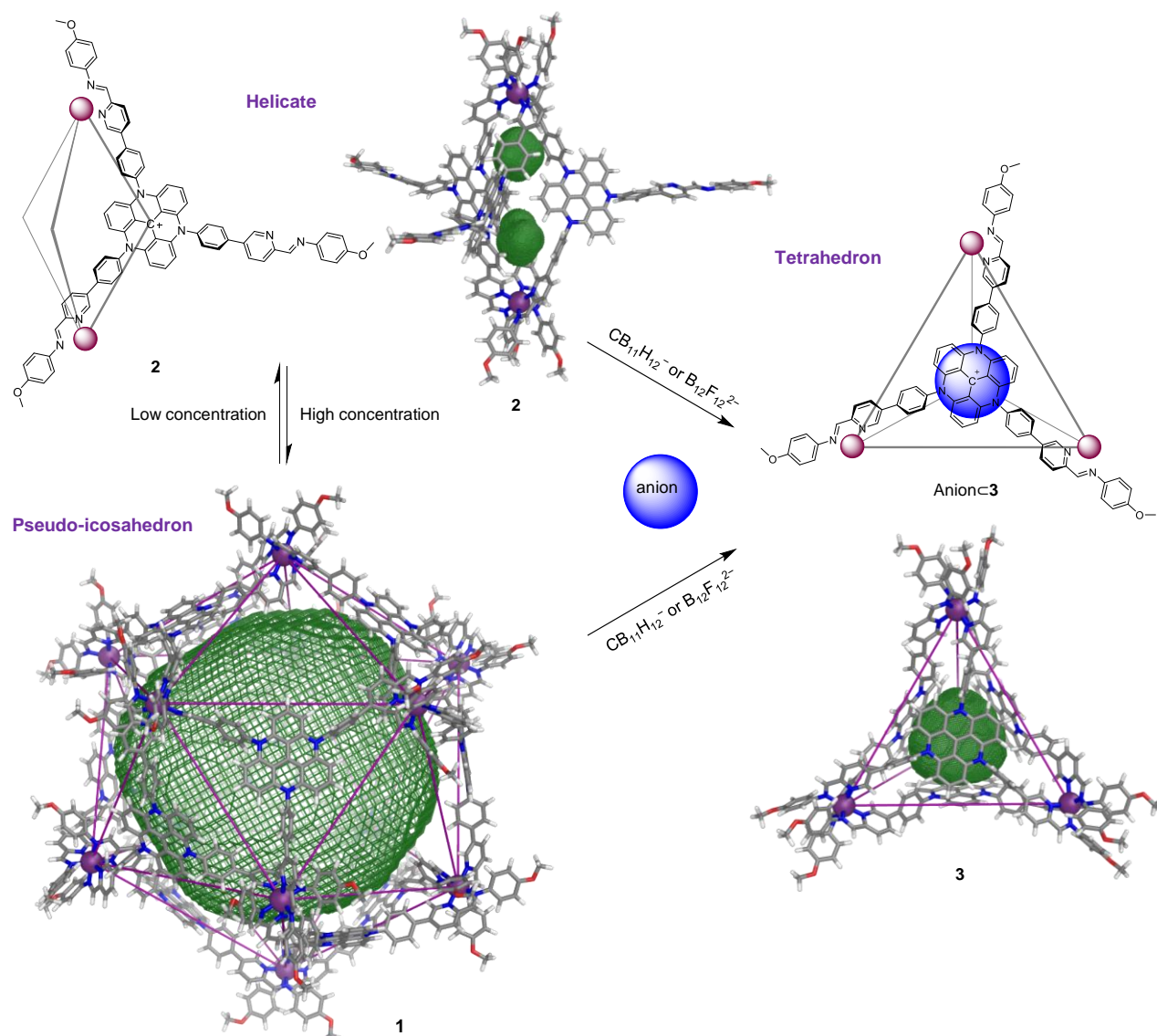


**Figure 3.** Schematic drawing of **2'** (a) and X-ray crystal structure of  $(\text{ReO}_4^-)_2\text{C}2'$  (b). Disorder, non-centrally bound counterions, and solvent of crystallization are omitted for clarity.

Slow vapor diffusion of diethyl ether into an acetonitrile solution of **2'** in the presence of  $\text{ReO}_4^-$  yielded crystals of  $(\text{ReO}_4^-)_2\text{C}2'$  suitable for X-ray diffraction. Two  $\text{ReO}_4^-$  anions were found within two distinct cavities of helicate **2'**, separated by the three converging TATA moieties (Figure 3b). Each of the two cavities is surrounded by three phenyl rings, giving cavity volumes of 76 and  $77 \text{ \AA}^3$  (Table S1). The two iron(II) centers of **2'**, separated by 20.0  $\text{\AA}$ , have the same handedness, generating a structure with  $D_3$  symmetry, consistent with solution NMR spectra.

When larger anions were added to helicate **2** in solution, such as carba-*closo*-dodecaborate ( $\text{CB}_{11}\text{H}_{12}^-$ ) or dodecafluoro-*closo*-dodecaborate ( $\text{B}_{12}\text{F}_{12}^{2-}$ ), full conversion into tetrahedron **3** was observed after 12 h, resulting in a set of ligand  $^1\text{H}$  NMR signals consistent with a  $T$ -symmetric tetrahedral cage (Figures 4 and S28-S37). The  $\text{Fe}^{\text{II}}_4\text{L}_4$  composition of **3** was confirmed by ESI-MS (Figures S30 and S35). These results suggested that  $\text{CB}_{11}\text{H}_{12}^-$  and  $\text{B}_{12}\text{F}_{12}^{2-}$  could serve as templates to bring four cationic ligands together into the tetrahedral framework of **3**, overcoming inter-ligand Coulombic repulsions.<sup>31</sup> A cavity volume of  $371 \text{ \AA}^3$  was calculated based on a PM7 model of **3** (Table S4), substantially smaller than that of pseudo-icosahedron **1** ( $15095 \text{ \AA}^3$ ) and larger than the twin cavities of **2** ( $55 \text{ \AA}^3$  each when calculated from a PM7 model of **2** in the absence of bound anions, see Table S3) (Table S1). Conversion of pseudo-icosahedron **1** into tetrahedron **3** also occurred following the addition of either of the template anions  $\text{CB}_{11}\text{H}_{12}^-$  or  $\text{B}_{12}\text{F}_{12}^{2-}$  (Figure 4).

In summary, we have demonstrated the construction of a series of capsules under different reaction conditions from TATA-containing subcomponent **A**, from large pseudo-icosahedron **1**, to medium-sized tetrahedron **3** and smaller helicate **2**. These structures have drastically different cavity volumes, shapes, and sizes. Pseudo-icosahedron **1** encloses a cavity volume that may allow the encapsulation of guests with diameters in the range of 3–4 nm.<sup>10</sup> Prior studies of smaller TATA-based metal-organic assemblies have shown binding to small biological anions in water,<sup>24</sup> suggesting that water-soluble versions<sup>32</sup> of pseudo-icosahedron **1** may prove useful for binding larger and more complex biomolecules, such as proteins and nucleic acids.



**Figure 4.** Interconversion between pseudo-icosahedron **1**, helicate **2**, and tetrahedron **3**, showing PM7-optimized molecular models of each with the cavity volumes outlined in green mesh. Pseudo-icosahedron **1** and helicate **2** interconverted following a change in ligand concentration. Addition of  $\text{CB}_{11}\text{H}_{12}^-$  or  $\text{B}_{12}\text{F}_{12}^{2-}$  to assembly **1** or **2** drove the formation of tetrahedron **3**, with the template anion bound inside the cavity.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Complete experimental details (PDF)

X-ray data for  $(\text{ReO}_4^-)_2\text{C}2'$  (CCDC 2071272)

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### Notes

The authors declare no competing financial interest.

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