

## Self-assembly of a Mixed Valence Copper Triangular Prism and Transformation to Cage Triggered by an External Stimulus

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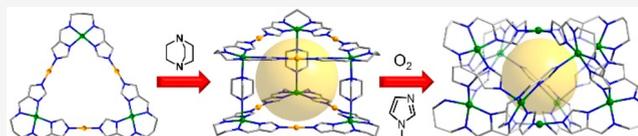


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**ABSTRACT:** A triangular prismatic metal–organic cage based on mixed valence copper ions has been designed and synthesized by using metallocycle panels and pillar ligands. The triangular prism will be quickly transformed to a 10-nuclear cage upon an external chemical stimulus, which features a bicapped square antiprism structure. This prismatic cage can act as a catalyst for oxidation of aromatic alcohols to their corresponding aromatic aldehydes with high yields at room temperature under O<sub>2</sub> atmosphere.



### INTRODUCTION

In a biological system, the implementation of functions depends on the robust signal transductions, which usually involve molecular-scale responses to stimuli and conformation changes. To mimic a biological system, chemists investigate the stimuli-responsive behavior at a molecular scale, which will probably help the design of advanced materials that show functions in response to an external stimulus (e.g., light, pH, or the presence of a chemical species).<sup>1</sup> Metal–organic cages (MOCs) containing well-defined cavities via coordination-driven self-assembly are typical models for mimicking enzymes<sup>2</sup> which have a variety of applications, including in separation,<sup>3</sup> recognition and sensing,<sup>3b,4</sup> catalysis,<sup>2,5</sup> and biomedicine.<sup>6</sup> MOCs based on dynamic coordination bonds will probably undergo structural changes after induction of external stimuli, e.g., light,<sup>7</sup> pH,<sup>8</sup> guest,<sup>9</sup> solvents,<sup>10</sup> and crystallization.<sup>11</sup> For example, Clever et al. found that a series of photoactive Pd<sub>2</sub>L<sub>4</sub> coordination cages based on dithienylene-thene ligands allowed triggering of guest uptake and released by irradiation.<sup>7,12</sup> Nitschke et al. reported that the presence of guest ClO<sub>4</sub><sup>−</sup> anions promoted a structural transformation of the M<sub>4</sub>L<sub>6</sub> tetrahedron into an M<sub>10</sub>L<sub>15</sub> pentagonal prism.<sup>13</sup> Crowley et al. designed and synthesized a heterobimetallic PdPtL<sub>4</sub> cage, which can reversibly transform from opened to closed state selectively at one end upon treatment with different stimuli (*N,N'*-dimethylaminopyridine and *p*-toluenesulfonic acid).<sup>14</sup> To the best of our knowledge, however, there are very few MOCs in which both the oxidation states of metal ions and structure are changed after cage-to-cage transformation upon an external stimulus.<sup>15</sup>

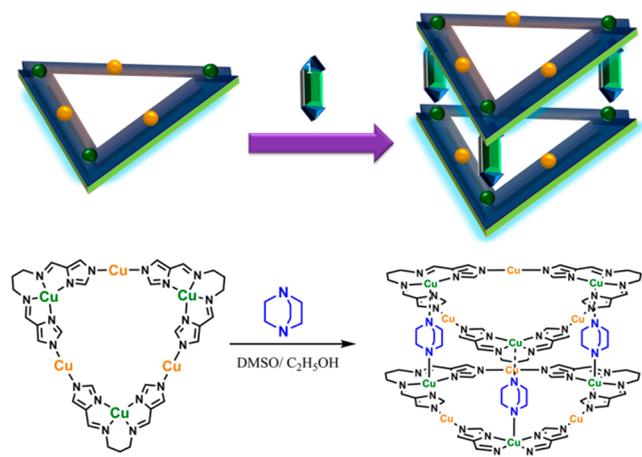
The rational design of coordination cages is available by utilizing the directional feature of coordination bonds and defined coordination geometry of metal ions.<sup>16</sup> Many types of prismatic cages have been successfully designed and synthesized by precisely choosing metal ions and multitopic ligands (e.g., triangular prism,<sup>17</sup> quadrangular prism,<sup>18</sup> pentaprism,<sup>19</sup> and hexagonal prism<sup>20</sup>). The metal–organic triangular prism is

the simplest prismatic structure, which can be obtained by combination of the end-capped metal centers as vertexes, the tritopic planar ligand as roofs and floors, and the bidentate linear ligands as pillars in a 6:2:3 molar ratio.<sup>21</sup> Alternatively, a triangular prism can be obtained by assembly of a two-component approach by using three 0° Pt-based molecular clips to connect two tripodal organic panels.<sup>22</sup> Furthermore, the heteroleptic triangular prism can be synthesized by a three-component reaction of pyridyl and carboxylate ligands with platinum acceptors.<sup>23</sup> Although many metal–organic triangular prisms have been reported,<sup>24</sup> the method of designing a triangular prism by the combination of metal–organic triangular panels and pillar ligands is rarely reported.<sup>25</sup>

In our previous work, we had designed and synthesized a series of hexanuclear mixed valence and heteronuclear triangular metallocycles by using a metalloligand approach.<sup>26</sup> We speculated that we could probably utilize the metallocycles as the triangular panels to construct a triangular prismatic MOC (Scheme 1) based on following reasons. (1) The triangular metallocycle is stable and rigid, and (2) each metallocycle contains three four- or five-coordinated Cu<sup>II</sup> centers with weak coordinated anions, which are possibly coordinated by bidentate pillar ligands to fabricate a triangular prism. In this work, we report the design and assembly of a prismatic MOC formed through coordination of the Cu<sup>II</sup> ions of the metallocycles and bidentate ligands (Scheme 1), formulated as [Cu<sup>I</sup><sub>3</sub>(Cu<sup>II</sup>L1)<sub>3</sub>]<sub>2</sub>L2<sub>3</sub>·8ClO<sub>4</sub>·2H<sub>3</sub>O<sup>+</sup> (denoted as 1, H<sub>2</sub>L1 = *N,N'*-(propane-1,3-diyl)bis(1-(1H-imidazol-4-yl)methanimine) and L2 = triethylenediamine), which features

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**Scheme 1. Schematic Diagram of Self-assembly of the Mixed Valence Metal–Organic Triangular Prism from Triangular Metalloctetrahedra and Pillar Ligands**

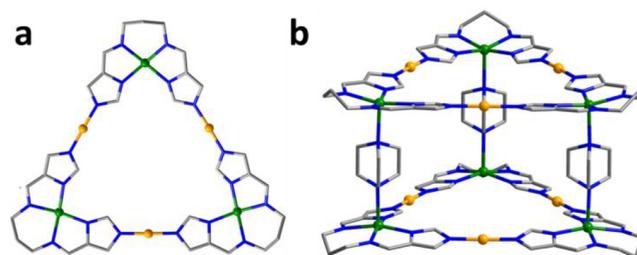


a mixed valence triangular prism structure. The prism **1** is composed of two mixed valence metalocycles and three L2. We found that prism **1** can slowly transform to a metal–organic bicapped square antiprism in organic solvent, which contains ten  $\text{Cu}^{\text{II}}$  and eight L1. Interestingly, the reacting rate can be highly boosted by adding *N*-methylimidazole (NMI) to the reaction mixture, which acts as an organic stimulus for the structure transformation. Furthermore, prism **1** can act as a catalyst for selectively oxidizing the aromatic alcohol to corresponding aldehydes at room temperature.

## RESULTS AND DISCUSSION

Prism **1** was synthesized by the assembly of the metalocycle and pillar ligand L2 with a mole ratio of 2:3 in a mixed solvent (dimethyl sulfoxide DMSO/ethanol, 4:1, v/v) at 80 °C for 6 h (for details see the Supporting Information), which was protected under nitrogen atmosphere. The green crystalline powder mixed with a few single crystals was obtained with a very high yield (98%). In the reaction, the organic ligand L1 was synthesized from condensation of 4-formylimidazole with 1,3-diaminopropane, while the hexanuclear mixed valence metalocycle,  $\text{Cu}_6\text{L1}_3$ , was obtained by using a stepwise synthesis strategy (Scheme S1).<sup>26</sup> Furthermore, the nitrogen protection is critical for synthesis of prism **1**. When the reaction was not protected by  $\text{N}_2$ , prism **1** cannot be successfully obtained, which is probably caused by oxidation of the  $\text{Cu}^{\text{I}}$  centers in  $\text{Cu}_6\text{L1}_3$ . Moreover, we also tested other typical pillar ligands including pyrazine and 4,4'-bipyridine; however, the prismatic metal–organic cage was not successfully obtained. The possible reason is due to that pyrazine and 4,4'-bipyridine are relatively weaker Lewis bases.

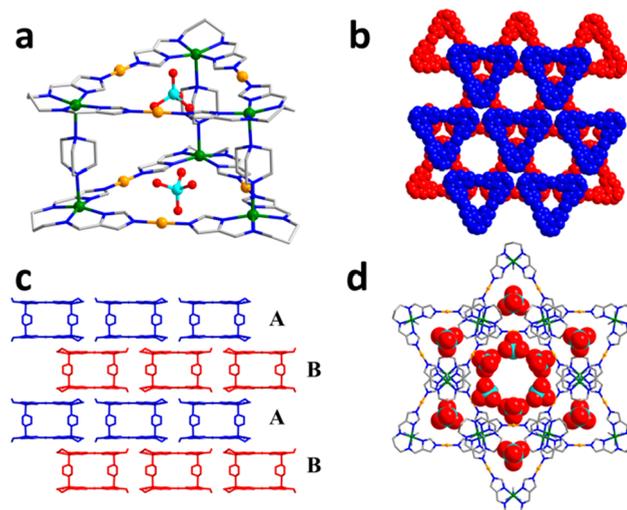
Single-crystal X-ray diffraction (SCXRD) analysis revealed that prism **1** crystallizes in a hexagonal  $P6_3/mmc$  space group, which is obviously different from that of  $\text{Cu}_6\text{L1}_3$  ( $P1$ ). As shown in Figure 1, the hexanuclear triangular metalocycle is similar to  $\text{Cu}_6\text{L1}_3$ , which is further pillared by L2 to form the triangular prism **1**. In prism **1**, there are six  $\text{Cu}^{\text{II}}$  and six  $\text{Cu}^{\text{I}}$  centers, six L1, three L2, and eight  $\text{ClO}_4^-$ . The skeleton of **1** is positive (+6), which is charge-balanced by the  $\text{ClO}_4^-$ . However, there are two excess  $\text{ClO}_4^-$  anions in the crystal lattice, which are probably charge-balanced by two hydroniums ( $\text{H}_3\text{O}^+$ ). The  $\text{Cu}^{\text{II}}$  is five-coordinated and adopts a distorted



**Figure 1.** Metalloctetrahedron structure in prism **1** (a) and the triangular prismatic cage structure of **1** (b). Color codes:  $\text{Cu}^{\text{II}}$ , green;  $\text{Cu}^{\text{I}}$ , orange; C, light gray; N, blue. All hydrogen atoms and anions are omitted for clarity.

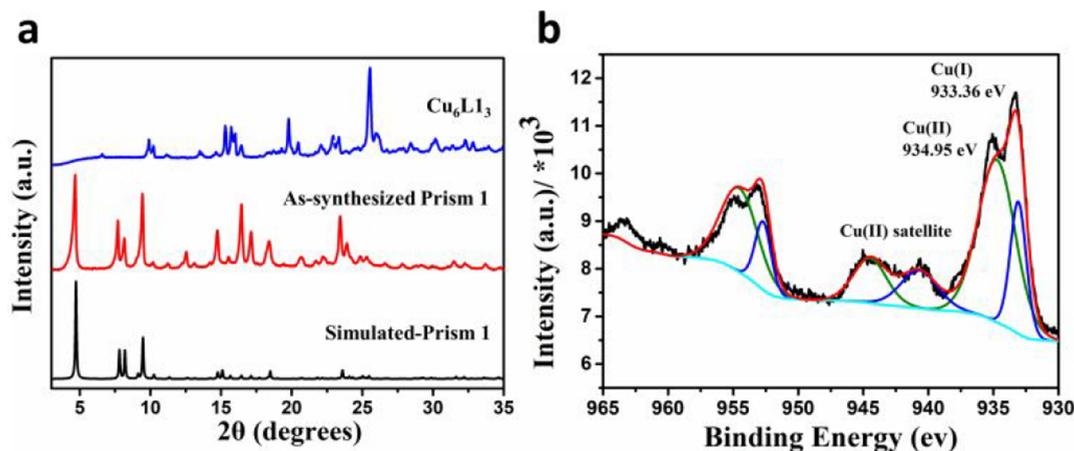
square pyramidal geometry, while the  $\text{Cu}^{\text{I}}$  adopts a linear coordination geometry. The  $\text{Cu}^{\text{II}}\text{--N}$  bond distances are in the range of 1.991–2.297 Å, and the  $\text{Cu}^{\text{I}}\text{--N}$  bond distance is 1.860 Å. The coordination bond distances in prism **1** are in good agreement with those in  $\text{Cu}_6\text{L1}_3$ . The difference between the metalocycle in **1** and  $\text{Cu}_6\text{L1}_3$  is the planarity. The triangular  $\text{Cu}_6\text{L1}_3$  is distorted, while metalocycle of **1** becomes planar after coordination to L2 (Figure S1).

Prism **1** is a regular prism, in which its height is about 7.166 Å and its width of triangle base is about 11.654 Å. Interestingly, similar to  $\text{Cu}_6\text{L1}_3$ , the cavities of the two triangular metalocycles in **1** are occupied by  $\text{ClO}_4^-$  anion as a guest, as shown in Figure 2a. The  $\text{ClO}_4^-$  ions are located in the



**Figure 2.** Encapsulation of  $\text{ClO}_4^-$  anions by the metalocycles of **1** (a); the “ABAB” packing structure of **1** along the  $c$ -axis (b, space-filling mode), the “ABAB” packing structure of **1** along the  $b$ -axis (c); and a hexagonal channel filled with  $\text{ClO}_4^-$  anions (d). Color codes:  $\text{Cu}^{\text{II}}$ , green;  $\text{Cu}^{\text{I}}$ , orange; C, light gray; N, blue; O, red; Cl, light blue. All hydrogen atoms are omitted for clarity.

center of the metalocycle panels. The encapsulation of  $\text{ClO}_4^-$  ions is probably due to the weak  $\text{C}\cdots\text{H}\cdots\text{O}$  interactions ( $\text{H}\cdots\text{O}$  bond distance of 2.602 Å, Figure S2) and electrostatic effect between  $\text{ClO}_4^-$  and positive skeleton of prism **1**. As shown in Figure 2b and 2c, prism **1** can be described as an “ABAB” layer packing where each prism has six nearest neighbors. Regular hexagonal channels are formed by packing these prisms with a diameter about 12.39 Å (defined by  $\text{H}\cdots\text{H}$  distance of diagonal imidazole groups, without consideration of van der Waals force), which are filled with  $\text{ClO}_4^-$  anions (Figure 2d). The



**Figure 3.** PXRD patterns of the as-synthesized metallocycle  $\text{Cu}_6\text{L}_3$  and prism **1** and the calculated pattern from the single-crystal structure of prism **1** (a). XPS spectrum of prism **1** with fitting peaks (b, blue  $\text{Cu}^{\text{I}}$ , green  $\text{Cu}^{\text{II}}$ ).

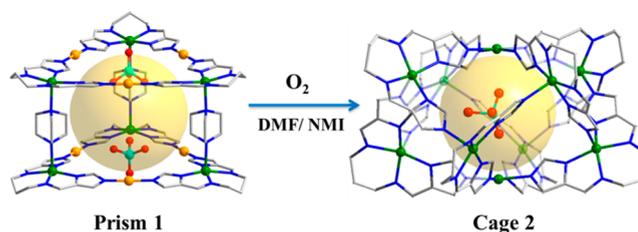
total potential solvent area volume of **1** is  $3977 \text{ \AA}^3$  (43.5%) in a unit cell, which was checked by the PLATON program.

Powder X-ray diffraction (PXRD) analysis showed that the PXRD pattern of prism **1** closely matched with its simulated patterns from SCXRD data, indicating that the pure phase of prism **1** was obtained (Figure 3a). The PXRD pattern of prism **1** was obviously different to the pattern of  $\text{Cu}_6\text{L}_3$ , indicating the successful assembly of prism **1** from metallocycle and L2. X-ray photoelectron spectroscopy (XPS) is an important tool used to characterize the type and valence state of metal ions. To confirm the oxidation of the copper centers in the prism **1**, the XPS spectrum of prism **1** was measured. As shown in Figure 3b, the spectrum of prism **1** showed a strong asymmetric Cu  $2p_{3/2}$  photoelectron peak with satellite peaks, indicating the mixed valence characteristic of the copper center in prism **1**.<sup>27</sup> The Cu  $2p_{3/2}$  peaks can be deconvoluted into two contributions, which are located at 933.36 and 934.95 eV, respectively (Figure 3b), which is in good agreement with that of metallocycle  $\text{Cu}_6\text{L}_3$ . Bond valence sum (BVS) also has been utilized to determine the oxidation state of copper ions in prism **1**.<sup>28</sup> The calculations of the BVS value for the five-coordinated Cu center gives 2.071, while that for the linear coordination Cu center gives 0.949. The BVS results of prism **1** are consistent with that of metallocycle  $\text{Cu}_6\text{L}_3$ . Both XPS and BVS calculations indicate the mixed valence states of copper centers in prism **1**, which is similar to  $\text{Cu}_6\text{L}_3$ .

Thermogravimetric analysis (TGA) revealed that prism **1** was thermally stable up to approximately  $262 \text{ }^\circ\text{C}$  (Figure S3). To study its porous property,  $\text{N}_2$  adsorption measurement was carried out. The activated **1** could adsorb approximately about  $30 \text{ cm}^3 \text{ g}^{-1} \text{ N}_2$  (77 K,  $P/P_0 = 0.3$ , Figure S4). The Brunauer–Emmett–Teller (BET) and Langmuir surface areas are calculated to be 50 and  $74 \text{ m}^2/\text{g}$ , respectively. The lower  $\text{N}_2$  adsorption for **1** is probably due to the pores of **1** being blocked by the partial decomposition of its packing structure.

The  $\text{Cu}^{\text{I}}$  centers are presented in the prism **1**, which will probably be oxidized to  $\text{Cu}^{\text{II}}$  and induce the structure change. This hypothesis encourages us to study the cage-to-cage transformation property of prism **1**. The solubility of prism **1** is poor in common organic solvents, e.g., DMSO, DMF, and acetonitrile. However, we found that the prism **1** will slowly dissolve in DMF in 3 days, and a green solution was obtained. Slow vapor diffusion of ethyl acetate into this green solution of **1** provided green rod-like crystals suitable for SCXRD analysis.

SCXRD analysis revealed that the new green crystal crystallizes in a  $C2/c$  space group, which features a bicapped square antiprism cage structure. This cage, formulated as  $\text{Cu}_{10}\text{L}_8 \cdot 4\text{ClO}_4$  (denoted **2**), is identical to our previously reported structure (Figure 4), whose conformation depends on the size



**Figure 4.** Transformation from triangular prism **1** to the bicapped square antiprism **2**.

of anions.<sup>29</sup> Unambiguously, after the transformation, the  $\text{Cu}^{\text{I}}$  center was oxidized to  $\text{Cu}^{\text{II}}$  by  $\text{O}_2$  in the air, and the triangular prism **1** was transformed into **2**. Furthermore, electrospray ionization mass (ESI-MS) spectrometry was employed to study the green solution. As shown in Figure S5, the ESI-MS spectrum showed that the green solution contained **2** and that no **1** was detected, which indicates that the transformation was successful. PXRD analysis showed that the pattern of cage **2** closely matches with its simulated pattern calculated from SCXRD data (Figure S6), suggesting that the product was pure and that prism **1** was completely transformed to cage **2**. We speculated that  $\text{ClO}_4^-$  may play an important role (e.g., as a template) in the transformation process. As shown in Figure 4, after the transformation, one  $\text{ClO}_4^-$  anion was encapsulated in the cavity of cage **2**, which indicates that the  $\text{ClO}_4^-$  anions located in the triangular panels of prism **1** probably templated the formation of cage **2** after the oxidation of  $\text{Cu}^{\text{I}}$  to  $\text{Cu}^{\text{II}}$ .

Although the transformation from prism **1** to cage **2** is successful, the transformation rate is very slow. In biological systems, the conformation change is quick in response to a stimulus. Thus, to mimic a biological system, an accelerated transformation rate is required. In literature, NMI can significantly improve the catalytic effect of lipase<sup>30</sup> and is an important co-catalyst for alcohol oxidation when the copper complexes as the catalyst.<sup>31</sup> Thus, we tried to add NMI into the reaction system to improve the reacting rate for the

transformation. Interestingly, with the addition of NMI (5 equiv of **1**) to the DMF solution, the solid prism **1** dissolved in DMF within about 1 min to give a green solution. The ESI-MS study documented that prism **1** was transformed to cage **2** successfully (Figure S7). The possible reason for NMI accelerating the transformation is due to its strong coordination ability to Cu<sup>I</sup> centers. The binding of NMI on Cu<sup>I</sup> will change its coordination geometry, which probably helps the O<sub>2</sub> oxidation of the Cu<sup>I</sup> centers to Cu<sup>II</sup> and then boosts the transformation process.

In our previous studies, the mixed valence Cu<sup>II</sup>/Cu<sup>I</sup> metallocycle has been a good catalyst for oxidation of (hetero)aromatic alcohols to corresponding (hetero)aromatic aldehydes.<sup>26</sup> Prism **1** also contains the catalytic active Cu<sup>I</sup> sites and has potentially catalytic ability for oxidation of alcohols by employing (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) as a co-catalyst and NMI as the base. As shown in Figure S8, prism **1** can catalyze oxidation of 16 (hetero)aromatic alcohols to their corresponding (hetero)aromatic aldehydes with quantitative yields (except 1-naphthalenemethanol 73%) at room temperature under O<sub>2</sub> atmosphere, when the catalyst system consists of 5 mol % **1**, 10 mol % TEMPO, and 50 mol % NMI in acetonitrile. The catalyst system is optimized by following our previous work.<sup>26</sup> Without prism **1** or TEMPO, trace benzyl aldehyde was detected, suggesting that both the prism **1** and TEMPO are indispensable to the oxidation reaction. The scope of this oxidation reaction was found to be very broad, suggesting that prism **1** is a good catalyst. However, the catalytic activity of prism **1** is not good as the metallocycle, which can achieve the same catalytic efficiency under an air condition.<sup>26</sup> Furthermore, prism **1** can also catalyze the sequential alcohol oxidation/Knoevenagel condensation reaction to yield benzylidenemalononitrile (yield 90%) by using benzyl alcohol and malononitrile as starting materials (Scheme S2).

## CONCLUSION

In summary, we have successfully designed and synthesized a mixed valence copper–organic triangular prism by using triangular metallocycle panels and pillar ligands. The copper–organic triangular prism can be transformed to a bicapped square antiprism cage by oxidation of the cuprous ions to cupric ions by air. The NMI molecules can act as a stimulus to accelerate this transformation process. This work provides a new strategy for constructing a metal–organic triangular prism by using a triangular panel and pillar ligand. The NMI boosting the transformation rate provides a unique example for understanding the cage-to-cage transformation.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02682>.

Experimental characterizations, additional structural presentations, and FT-IR, PXRD, and ESI-MS analyses (PDF)

### Accession Codes

CCDC 2011494 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cam-

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### Notes

The authors declare no competing financial interest.

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