

Two Stable 3D Metal–Organic Frameworks Constructed by Nanoscale Cages via Sharing the Single-Layer Walls

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In the past decade, the supramolecular assemblies of discrete cages as well as metal–organic frameworks (MOFs) with porous structures have developed rapidly due to their potential uses for gas separation and storage,¹ ion-exchange,² molecular and chiral recognition, and catalysis.³ For example, Yaghi et al. utilized secondary building units (SBUs) to serve as large vertices to construct MOFs with large channels for gas storage.^{1a–d} MOFs with chiral recognition and catalysis properties have also been reported by Lin's group.^{3g–i} On the other hand, Stang^{3a–c} and Fujita^{3d–f} used planar rigid multipyridyl ligands and *cis*-protected square-planar metals to create a series of discrete nanoscale cages and macrocycles for molecular recognition and chiral catalysis. Discrete nanoscale cages can also be prepared by supramolecular assemblies of flexible or semirigid organic ligands with metal ions.⁴ So far, rare effort has been devoted to the combination of these two interesting fields to construct MOFs containing cages resembling the discrete ones.⁵ Herein we present two stable 3D MOFs containing nanoscale cages, which are constructed by a Cd(II) ion and a rigid planar ligand of imidazole-4,5-dicarboxylate (IDC³⁻).

The crystals of {Na₄[Cd₇(IDC)₆]₃bpy·7H₂O}_n (bpy = 4,4'-bipyridyl) (**1**) and {(Bu₄N)K₃Cd₇(IDC)₆·6H₂O}_n (**2**) were obtained⁶ in high yields by the hydrothermal reactions of Cd(NO₃)₂·4H₂O and IDC³⁻ using bpy and Bu₄NBr as templates, respectively. X-ray crystallography⁶ reveals that both **1** and **2** possess the same metal–organic framework, in which the coordination environments of Cd(II) and bridging modes of IDC³⁻ are shown in Figure 1. Among the two crystallographically independent Cd(II) ions, Cd(1) is six-coordinated with four oxygen and two nitrogen atoms from two individual μ₃-IDC³⁻ and one μ₄-IDC³⁻, forming a slightly distorted trigonal prism geometry with N(1vii), O(2), and O(4) atoms composing one triangular plane, and O(1vii), O(1), and N(2) atoms composing the other plane. In contrast, Cd(2) is coordinated to six symmetry related O(3) atoms from three individual μ₃-IDC³⁻ with a perfect trigonal prismatic geometry. Both μ₃-IDC³⁻ and μ₄-IDC³⁻ motifs possess crystallographically imposed C₂ symmetry and are planar with the mean deviations of 0.0221 and 0.0481 Å, respectively. Each μ₃-IDC³⁻ connects one Cd(2) and two Cd(1) atoms, while each μ₄-IDC³⁻ bridges four Cd(1) atoms, giving a planar M₃L triangle and a planar M₄L quadrangle, as depicted in Figure 1.

In both compounds, six μ₃-IDC³⁻ and six μ₄-IDC³⁻ bridge a total of 21 Cd(II) ions to generate a large nanoscale M₂₁L₁₂ cage (Figure 2a) with a diameter of ca. 1.4 nm. As shown in Figure S1a, six M₃L triangles (green) are located in the equatorial positions, and six M₄L quadrangles (blue) wrap around the two polar sites. Theoretically, the M₂₁L₁₂ cage can be considered to consist of eight triangles and fifteen quadrangles, leading to a 3⁸⁴1⁵ cage building unit (CBU), which has not been observed in the known zeolite

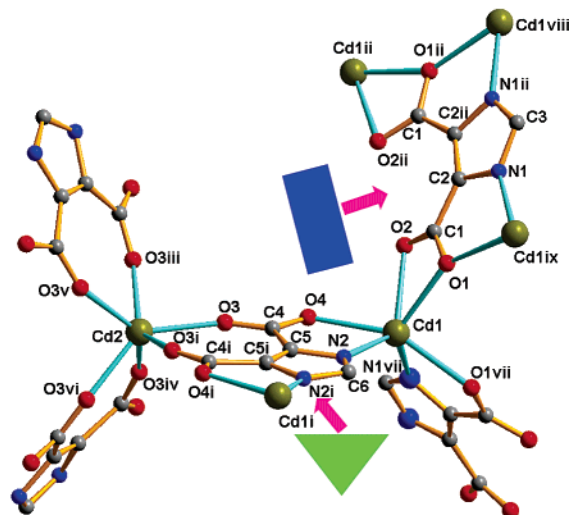


Figure 1. Partial molecular structure of **1** and **2**, showing the coordination environments of Cd(II) and bridging modes of IDC³⁻ ions (represented by blue quadrangle for the μ₄-IDC³⁻ plane and green triangle for the μ₃-IDC³⁻ plane).

CBUs so far.⁷ The polyhedron of 3⁸⁴1⁵ cage contains 21 vertices, 23 faces, and 42 edges, according with the Euler rule of “edge + 2 = vertex + face”. The cage is formed by planar M₃L triangles and M₄L quadrangles, quite similar to that of fullerene (C₆₀) that is constructed by the planar five and six carbon rings and much different from the cages of zeolites, where the void surfaces are composed of bended O–T–O (T = Si, P, Al) connections. There are six large and three small quadrilateral and two small triangular windows on the surface of each cage (Figures 2b and S1a), with the dimensions for the large windows of 3.3 × 3.0 Å². The windows are formed via sharing the vertices of the M₃L triangles and M₄L quadrangles and are open to six neighboring quadrilateral windows and five trigonal prismatic cage-shaped windows around the cage, as shown in Figure 2b. Each cage shares its planar M₃L triangles with six neighboring cages in the equatorial positions (Figure S1b,c) and its planar M₄L quadrangles with three neighboring cages on each polar site (Figure S1d–e). A novel 3D framework is generated through the above cage-to-cage connections (Figure 2c), which exhibits a hexagonal closest packing as A3-type metals if each cage is regarded as one ball (Figure S1f).

Each cage contains three disordered bpy molecules and four Na⁺ ions in **1** (Figure S2a,b) and one disordered Bu₄N⁺ and three K⁺ in **2** (Figure S2c,d), in which the alkali metal ions are located around the large square windows (Figure S2a, d), and are weakly interacted with bpy nitrogen atoms (in **1**), water molecules, and IDC³⁻ oxygen atoms. It is noteworthy that **1** and **2** cannot be obtained without the presence of bpy and Bu₄N⁺ molecules, implying that the bpy

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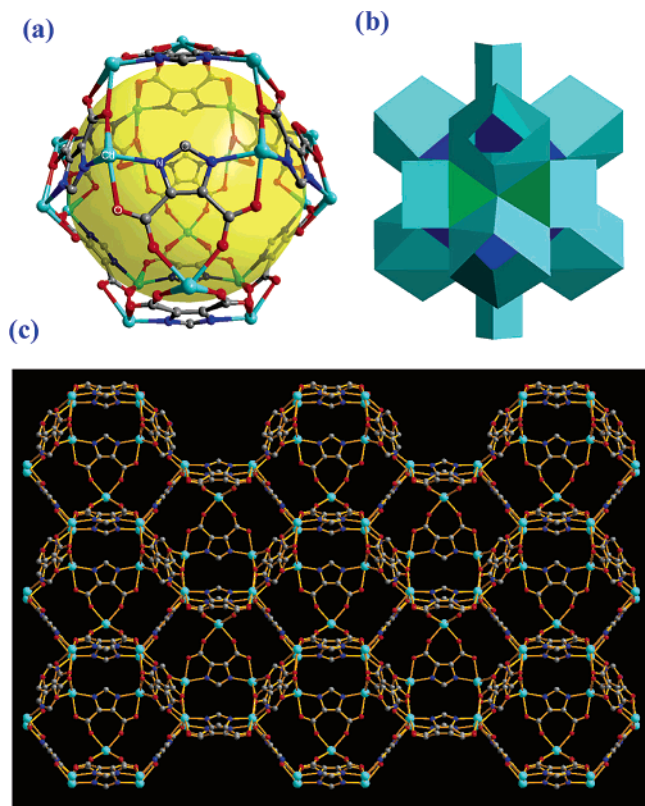


Figure 2. (a) The nanoscale $M_{21}L_{12}$ cage. (b) The windows around the cage. (c) The 3D MOF viewed along the a axis (the guest molecules are omitted for clarity).

and Bu_4N^+ act as the templates during the formation of the cages. Usually, triangular and tetrahedral molecules or ions are used as templates to construct the cage structures,^{3,7} while the formations of cages directed by linear guest molecules are still rare.

Solid sample of **1** displayed a strong blue photoluminescence emission band at 442 nm (Figure S3) at room temperature. The XRPD patterns (Figure S5) at different temperatures indicate that the framework of **1** is stable up to 300 °C. The TGA curves (Figure S6) showed that the weight losses of the crystalline and powder samples of **1** at 300 °C are 6.1 and 14.2%, respectively, indicating that the guest molecules escape much faster when the crystals were crushed to powder, so more guest molecules escape from the cages. However, the crystalline and powder samples of **2** showed similar TGA curves, indicating that the escape of water molecules was not affected by the size of the particles. The above different thermal behaviors may attribute to their structural features. Before crushing, the water and bpy guest molecules in **1** escape very slowly from the inner cages to the limited windows on the surface of the crystals through the long Na^+ and bpy guest-blocked labyrinth-like channels. When the crystals of **1** were crushed to powder, the number of surface windows was much increased, and the pathway from the inner cages to the surface windows became shorter, so the water and bpy guest molecules can escape much faster. However, though the crystals of **2** were crushed to powder, the water molecules still escape slowly from the cages since the channels are still blocked

by larger K^+ and Bu_4N^+ cations. This indicates that the escape rate of the guest molecules can be influenced by the particle sizes of **1** and may be potential use for control release of the absorbed guest molecules.

In conclusion, we demonstrate here that a new type of stable 3D MOFs can be constructed by nanoscale cages via sharing the rigid planar ligands, which display fullerene-like surface and zeolite-like windows. The MOFs show the following unusual features. First, the fullerene-like cages are connected via sharing the single-layer walls. Second, the large nanoscale $M_{21}L_{12}$ cage shows a new type of 3^84^{15} CBU. Third, the escape rate of the guest molecules can be influenced by the particle sizes of **1**. More interestingly, such MOFs combine the common features of traditional zeolites, MOFs, and fullerene and may generate a new kind of materials that combine the useful properties of zeolites, MOFs, and fullerene.

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Supporting Information Available: Synthesis, crystallographic data, structural figures, photoluminescent spectrum, XRPD patterns, and TGA curves (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Sudik, A. C.; Millward, A. R.; Ockwig, N. W.; Cote, A. P.; Kim, J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 7110. (b) Rowsell, J. L. C.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666. (c) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127. (d) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (e) Kesanli, B.; Cui, Y.; Smith, M. R.; Bittner, E. W.; Bockrath, B. C.; Lin, W. B. *Angew. Chem., Int. Ed.* **2005**, *44*, 72. (f) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238. (g) Kubota, Y.; Takata, M.; Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kato, K.; Sakata, M.; Kobayashi, T. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 920. (h) Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109.
- (2) (a) Manos, M. J.; Iyer, R. G.; Quarez, E.; Liao, J. H.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 3552. (b) Trikalitis, P. N.; Rangan, K. K.; Bakas, T.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2002**, *124*, 12255.
- (3) (a) Schweiger, M.; Yamamoto, T.; Stang, P. J.; Blaser, D.; Boese, R. J. *Org. Chem.* **2005**, *70*, 4861. (b) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 224. (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (d) Yoshizawa, M.; Kusukawa, T.; Kawano, M.; Ohhara, T.; Tanaka, I.; Kurihara, K.; Niimura, N.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 2798. (e) Yoshizawa, M.; Tamura, M.; Fujita, M. *J. Am. Chem. Soc.* **2004**, *126*, 6846. (f) Fujita, M.; Umamoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Kawano, M. *Chem. Commun.* **2001**, 509. (g) Wu, C. D.; Hu, A.; Zhang, L.; Lin, W. B. *J. Am. Chem. Soc.* **2005**, *127*, 8940. (h) Hu, A. G.; Ngo, H. L.; Lin, W. B. *Angew. Chem., Int. Ed.* **2004**, *43*, 2501. (i) Kesanli, B.; Lin, W. B. *Coord. Chem. Rev.* **2003**, *246*, 305.
- (4) (a) Su, C.-Y.; Cai, Y.-P.; Chen, C.-L.; Smith, M. D.; Kaim, W.; zur Loye, H.-C. *J. Am. Chem. Soc.* **2003**, *125*, 8589. (b) Hong, M. C.; Zhao, Y. J.; Su, W. P.; Cao, R.; Fujita, M.; Zhou, Z. Y.; Chan, A. S. C. *J. Am. Chem. Soc.* **2000**, *122*, 4819.
- (5) (a) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surlblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040. (b) Fang, Q. R.; Zhu, G. S.; Xue, M.; Sun, J. Y.; Wei, Y.; Qiu, S. L.; Xu, R. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3845. (c) Férey, G.; Serre, C.; Mellot-Draznieks, C.; Millange, F.; Surlblé, S.; Dutour, J.; Margiolaki, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 6296. (d) Abrahams, B. F.; Batten, S. R.; Hamit, H.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1690. (e) Batten, S. R.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1995**, *117*, 5385.
- (6) See Supporting Information.
- (7) Xu, R. R.; Pang, W. Q.; Yu, J. H.; Huo, Q. S.; Chen, J. S. *Chemistry-Zeolites and Porous Materials* (Chinese); Science Press: Beijing, 2004.

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