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A porous metal–organic framework (MOF) with unusual 2D→3D polycatenation based on honeycomb layers†

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**A novel mixed-ligand 3D metal–organic framework (MOF), $\{Zn_2(TMTA)(bipy)_{0.5}(H_2O)_2 \cdot NO_3 \cdot 2DMF \cdot H_2O\}_n$ (1) (H_3TMTA = 4,4′,4″-(2,4,6-trimethylbenzene-1,3,5-triyl)tribenzoic acid, bipy = 4,4′-bipyridine, DMF = dimethylformamide), was constructed based on bipy-pillared honeycomb bilayers and showed the unusual 2D→3D polycatenation of bilayers.**

Metal–organic frameworks (MOFs), as potentially functional materials, have been widely studied in recent years due not only to their potential applications such as in separation and gas storage, but also their intriguing variety of topologies and entanglement motifs.[1–4] To construct a high-dimensional MOF with high stability, two main strategies can be employed: (i) utilization of rigid secondary building units (SBUs) and multitopical organic ligands; (ii) polycatenation or interpenetration among low-dimensional networks. According to Ciani, Carlucci and Proserpio, polycatenation and interpenetration are quite different.[5–6] The component motifs in polycatenation normally have lower dimensionality than that of the resulting framework, while the component motifs in interpenetration normally have the same dimensionality with that of the resulting architectures. Hence, polycatenation can increase the dimensionality of the framework, while interpenetration can improve the stability of the architecture.[7] In the past decades, many high-dimensional MOFs have been constructed through polycatenation. Known examples include the polycatenation among 1D ladders giving rise to 2D or 3D architectures, 2D layers resulting in 3D frameworks, and polycatenation among motifs with different dimensionalities.[8–10] Recently, the polycatenation between two different layer motifs has also been disclosed by Yao and coworkers.[11] However, polycatenation between bilayers with a large cavity to generate 3D porous MOF has seldom been reported. In this communication, we report a 3D mixed-

ligand MOF,[12] $\{Zn_2(TMTA)(bipy)_{0.5}(H_2O)_2 \cdot NO_3 \cdot 2DMF \cdot H_2O\}_n$ (1), which is generated from the 2D→3D polycatenation among neighboring bilayers.

In our previous work, we showed a new type of supramolecular isomer with honeycomb layers, $Zn_2(TMTA)(H_2O)_2 \cdot NO_3 \cdot 6H_2O \cdot DEF$ (**α-1**) and $Zn_2(TMTA)(H_2O)_2 \cdot NO_3 \cdot 2H_2O \cdot 0.5DMA$ (**β-1**), based on trigonal SBU and organic linker.[13] In the trigonal SBU, both Zn(II) ions adopt tetrahedral geometry with one coordination site occupied by a coordinated water molecule (Fig. S1, ESI†). From a design perspective, if the coordinated water molecules are replaced by a bridging organic ligand, the 2D layer will be further connected to form two new architectures, bilayer or 3D pillared framework, based on the linking mode of the bridging ligand, as shown in Scheme 1.
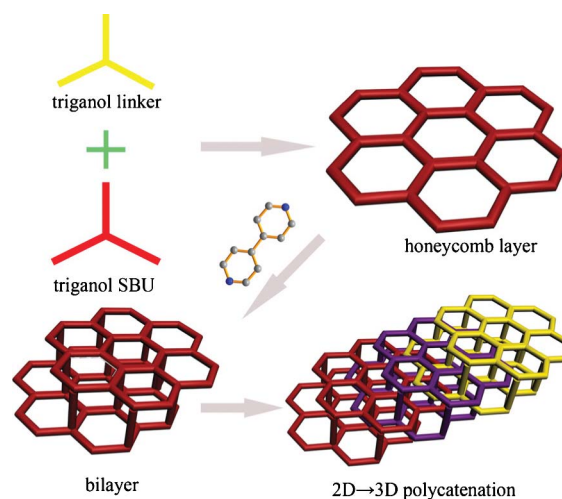
Scheme 1 Schematic representation of the formation of a single honeycomb layer, bipy-pillared bilayer and 3D framework from polycatenation of bilayers.

The solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$, H_3TMTA, and 4,4′-bipyridine in DMF/1,4-dioxane/H_2O (5 : 2 : 1, v/v/v) in the presence of 0.05 mL HBF_4 gave rise to a large amount of colorless prism crystals of **1**. The formula of $\{Zn_2(TMTA)(bipy)_{0.5}(H_2O)_2 \cdot NO_3 \cdot 2DMF \cdot H_2O\}_n$ was further confirmed by elemental analysis and thermogravimetric analysis (ESI†). Powder X-ray diffraction (PXRD) has been used to check

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the phase purity of the bulky samples in the solid state (ESI†). For **1**, full phase-purity could not be achieved and the X-ray powder diffractogram of the as-synthesized sample was obtained by manually picking suitable crystals one by one.

Single crystal X-ray diffraction reveals that complex **1** is a two-dimensional bilayer based on a honeycomb network with the binuclear $[Zn_2(COO)_3]$ as SBU. It should be pointed out that, compared to $[M_2(COO)_4]$, the three-connected $[M_2(COO)_3]$ SBUs are quite rare in the construction of functional MOFs.[14] Furthermore, different from other reported $[Zn_2(COO)_3]$ clusters, although the two zinc ions in **1** adopt a tetrahedral coordination environment, the coordinated water molecule in one of the Zn(II) ion was replaced by a bipy molecule (Fig. S2†). Interestingly, all the coordinated water molecules in the same side of the honeycomb layer were replaced by the bridging bipy ligands. Thus, two such honeycomb layers were connected by bipy ligands to generate a bilayer (Fig. 1) with a distance between the honeycomb layers of 14.2 Å.
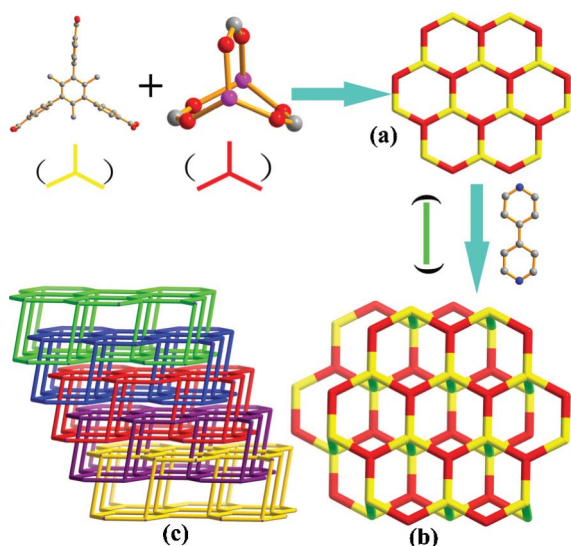

Fig. 1 (a) the 2D (6,3) honeycomb layer; (b) two layers connected by bipy; (c) the 2D→3D polycatenation among different bilayers.

The two honeycomb layers in the bilayer are parallel but do not overlap completely (Fig. 1b). It is interesting to find that the polycatenation among the bilayers further extends the 2D net into a 3D porous framework (Fig. 1c). From a topology view, the binuclear $[Zn_2(COO)_3]$ and the TMTA ligand can be seen as four-connected node and three-connected linker, so the overall 2D net is a 2-nodal (3,4)-connected layer with the point (Schläfli) symbol $\{6^3\}\{6^6\}$ and vertex symbol [6(2).6(2).6(2)] [6.6(2).6.6(2).6.6(2)] calculated by TOPOS software.[15] Each bilayer contains two honeycomb layers belonging to other bilayers with a distance of 4.7 Å. The C–H $\cdots \pi$ interactions (3.605 Å) between the side benzene rings and the central benzene rings in different honeycomb layers further stabilize the parallel polycatenation and link the TMTA ligands in different layers to generate a 1D chain (see Fig. 2), as found in our previous results.[13]

In general, the polycatenation in a single layer and a bilayer is somewhat different: for a single planar layer, the dihedral angle (α) between the layers should fall into the range of $0 < \alpha \leq 90$, and it is a stagger polycatenation; however, for a bilayer, the dihedral angle
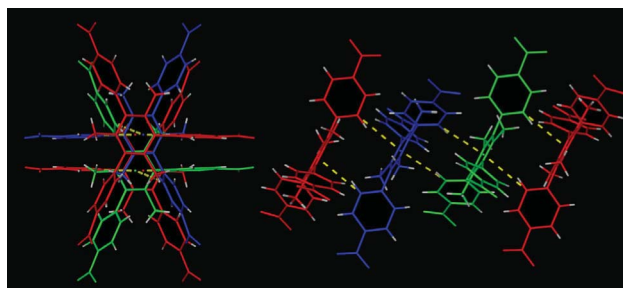

Fig. 2 The CH $\cdots \pi$ interactions between different honeycomb layers.

between the layers fall into the range of $0 \leq \alpha \leq 90$, if $\alpha = 0$, it is a parallel polycatenation. In the past decades, the polycatenation in a single layer was widely reported. However, the polycatenation in a double layer to generate a 3D framework is somewhat rare in the literature. Wu and coworkers reported a 3D framework based on a cadmium bilayer through parallel polycatenation.[16] A homochiral 3D framework constructed from a chiral ligand through parallel polycatenation was also synthesized by the Bu group.[17] Due to polycatenation, the final frameworks are normally nonporous, although the single net possesses large cavities. However, complex **1** is a porous 3D framework with 39.4% solvent-accessible volume calculated from PLATON.[18] In order to check the permanent porosity of complex **1**, the N_2 adsorption behavior of the activated sample, which has been vacuum-dried at 95 °C, has been studied (Fig. 3). Derived from the N_2 adsorption data, complex **1** has a Langmuir surface area of 350 m^2 g^{-1}.
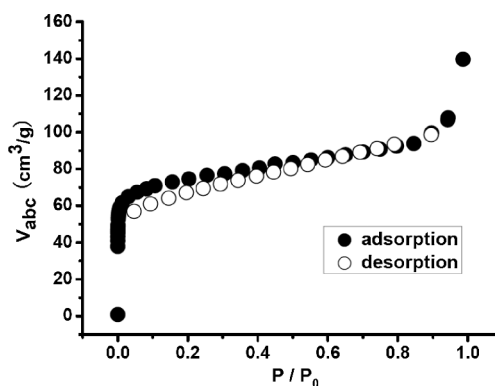

Fig. 3 Gas sorption isotherms of **1**. Symbols: solid, adsorption; open, desorption (N_2 at 77 K).

MOFs with d^{10} metal atoms are promising candidates for luminescent materials.[19] The solid-state luminescent properties of complex **1** and free H_3TMTA ligand were investigated at room temperature. The emission band is observed at 362 nm ($\lambda_{ex} = 260$ nm) for H_3TMTA (Fig. S6, ESI†), which can be assigned to the ligand-centered electronic transition, that is, the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ electronic transition. It was observed that the emission of **1** occurred at 427 nm upon excitation at 330 nm for **1** (Fig. 4). Because the Zn(II) ion is difficult to oxidize or to reduce due to its d^{10} electronic configuration, the emission bands of both complexes are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature.[20] The emissions of them can probably be assigned to the intraligand $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions because of the resemblance of the emission spectrum in comparison with the free ligand.[21]
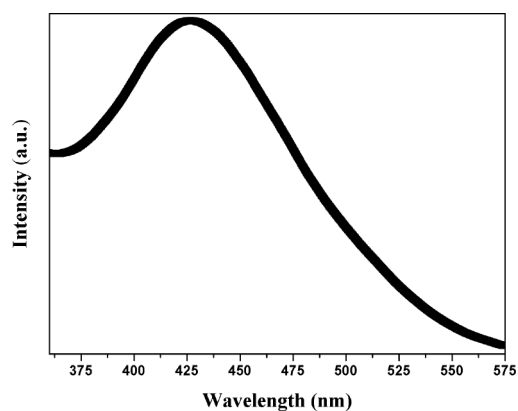
Fig. 4 Solid-state fluorescence spectrum of **1** at room temperature.

In conclusion, a novel 3D MOF based on a honeycomb layer has been synthesized and characterized. Complex **1** exhibits the polycatenation among bilayers and possesses permanent porosity based on nitrogen adsorption measurements. Our results may provide a new strategy for the construction of a new type of MOF through polycatenation based on honeycomb layers.

Acknowledgements

Notes and references

1 (a) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127; (b) S. Q. Ma, D. F. Sun, J. M. Simmons, C. D. Collier, D. Q. Yuan and H. C. Zhou, *J. Am. Chem. Soc.*, 2008, **130**, 1012; (c) L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (d) J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670; (e) H. Wu, W. Zhou and T. Yildirim, *J. Am. Chem. Soc.*, 2009, **131**, 4995; (f) S. Q. Ma and H. C. Zhou, *Chem. Commun.*, 2010, **46**, 44; (g) R. E. Morris and P. S. Wheatley, *Angew. Chem., Int. Ed.*, 2008, **47**, 4966.
2 (a) J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; (b) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe and Y. Mita, *Nature*, 2005, **436**, 238; (c) B. Chen, C. Liang, J. Yang, D. S. Contreras, Y. L. Clancy, E. B. Lobkovsky, O. M. Yaghi and S. Dai, *Angew. Chem., Int. Ed.*, 2006, **45**, 1390; (d) S. Ma, D. Sun, X.-S. Wang and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2007, **46**, 2458; (e) H. L. Guo, G. S. Zhu and S. L. Qiu, *J. Am. Chem. Soc.*, 2009, **131**, 1646.
3 (a) S. Wang, T. T. Zhao, G. H. Li, L. Wojtas, Q. S. Huo, M. Eddaoudi and Y. L. Liu, *J. Am. Chem. Soc.*, 2010, **132**, 18038; (b) M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782.
4 (a) S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (b) G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191; (c) M. P. Suh, Y. E. Cheon and E. Y. Lee, *Coord. Chem. Rev.*, 2008, **252**, 1007; (d) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705.
5 L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.
6 (a) L. Carlucci, G. Ciani, S. Maggini and D. M. Proserpio, *Cryst. Growth Des.*, 2008, **8**, 162; (b) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 4562.
7 (a) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (b) S. R. Batten, *CrystEngComm*, 2001, **18**, 1; (c) J. J. Zhang, L. Wojtas, R. W. Larsen, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2009, **131**, 17040; (d) L. Q. Li and W. B. Lin, *J. Am. Chem. Soc.*, 2008, **130**, 13834.
8 (a) A. M. L. Fuller, D. A. Leigh, P. J. Lusby, A. M. Z. Slawin and D. B. Walker, *J. Am. Chem. Soc.*, 2005, **127**, 12612; (b) T. S. M. Abedin, L. K. Thompson and D. O. Miller, *Chem. Commun.*, 2005, 5512; (c) L. Carlucci, G. Ciani and D. M. Proserpio, *J. Chem. Soc., Dalton Trans.*, 1999, 1799.
9 (a) M. R. Sambrook, P. D. Beer, J. A. Wisner, R. L. Paul and A. R. Cowley, *J. Am. Chem. Soc.*, 2004, **126**, 15364; (b) C. M. Jin, L. Y. Wu, H. Lu and Y. Xu, *Cryst. Growth Des.*, 2008, **8**, 215; (c) M. Fujita, O. Sasaki, K. Watanabe, K. Ogura and K. Yamaguchi, *New J. Chem.*, 1998, **22**, 189; (d) D. Sun, Q.-J. Xu, C.-Y. Ma, N. Zhang, R.-B. Huang and L.-S. Zheng, *CrystEngComm*, 2010, **12**, 4161.
10 (a) C. Qin, X. L. Wang, E. N. Wang and Z. M. Su, *Inorg. Chem.*, 2008, **47**, 5555; (b) B. L. Li, Y. F. Peng, B. Z. Li and Y. Zhang, *Chem. Commun.*, 2005, 2333.
11 X. Y. Cao, Q. P. Lin, J. Zhang, Z. J. Li, J. K. Cheng and Y. G. Yao, *Cryst. Growth Des.*, 2009, **9**, 20.
12 (a) C. B. Aakeröy, N. R. Champness and C. Janiak, *CrystEngComm*, 2010, **12**, 22; (b) H. A. Habib, J. Sanchiz and C. Janiak, *Inorg. Chim. Acta*, 2009, **362**, 2452; (c) H. A. Habib, A. Hoffmann, H. A. Höppe and C. Janiak, *Dalton Trans.*, 2009, 1742; (d) H. A. Habib, J. Sanchiz and C. Janiak, *Dalton Trans.*, 2008, 1734; (e) B. Wisser, Y. Lu and C. Janiak, *Z. Anorg. Allg. Chem.*, 2007, **633**, 1189.
13 X. L. Zhao, H. Y. He, F. N. Dai, D. F. Sun and Y. X. Ke, *Inorg. Chem.*, 2010, **49**, 8650.
14 (a) M. Y. Wu, F. L. Jiang, W. Wei, Q. Gao, Y. G. Huang, L. Chen and M. C. Hong, *Cryst. Growth Des.*, 2009, **9**, 2559; (b) J. A. Rood, W. C. Boggess, B. C. Noll and K. W. Henderson, *J. Am. Chem. Soc.*, 2007, **129**, 13675.
15 V. A. Blatov, *TOPOS, A Multipurpose Crystallochemical Analysis with the Package*, Samara State University, Russia, 2004.
16 Z. Y. Fu, X. T. Wu, J. C. Dai, L. M. Wu, C. P. Cui and S. M. Hu, *Chem. Commun.*, 2001, 1856.
17 J. Zhang, E. Chew, S. Chen, J. Pham and X. H. Bu, *Inorg. Chem.*, 2008, **47**, 3495.
18 A. L. Spek, *Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool* Utrecht University, Utrecht, The Netherlands, 1998.
19 (a) H. A. Habib, A. Hoffmann, H. A. Höppe and C. Janiak, *Dalton Trans.*, 2009, 1742; (b) H. A. Habib, J. Sanchiz and C. Janiak, *Dalton Trans.*, 2008, 1734; (c) D. Sun, F. J. Liu, R. B. Huang and L. S. Zheng, *Inorg. Chem.*, 2011, **50**, 12393, DOI: 10.1021/ic201746q; (d) D. Sun, D.-F. Wang, X.-G. Han, N. Zhang, R.-B. Huang and L.-S. Zheng, *Chem. Commun.*, 2011, **47**, 746; (e) D. Sun, C.-F. Yang, H.-R. Xu, H.-X. Zhao, Z.-H. Wei, N. Zhang, L.-J. Yu, R.-B. Huang and L.-S. Zheng, *Chem. Commun.*, 2010, **46**, 8168; (f) D. Sun, N. Zhang, R.-B. Huang and L.-S. Zheng, *Cryst. Growth Des.*, 2010, **10**, 3699; (g) D. Sun, D. F. Wang, F. J. Liu, H. J. Hao, N. Zhang, R. B. Huang and L. S. Zheng, *CrystEngComm*, 2011, **13**, 2833; (h) P. Ren, M. L. Liu, J. Zhang, W. Shi, P. Cheng, D. Z. Liao and S. P. Yan, *Dalton Trans.*, 2008, 4711; (i) W. L. Liu, L. H. Ye, X. F. Liu, L. M. Yuan, J. X. Jiang and C. G. Yan, *CrystEngComm*, 2008, **10**, 1395; (j) S. L. Zheng and X. M. Chen, *Aust. J. Chem.*, 2004, **57**, 703; (k) S. Q. Zang, Y. Su, Y. Z. Li, J. G. Lin, X. Y. Duan, Q. J. Meng and S. Gao, *CrystEngComm*, 2009, **11**, 122.
20 (a) L. Wen, Z. Lu, J. Lin, Z. Tian, H. Zhu and Q. Meng, *Cryst. Growth Des.*, 2007, **7**, 93; (b) J.-G. Lin, S.-Q. Zang, Z.-F. Tian, Y.-Z. Li, Y.-Y. Xu, H.-Z. Zhu and Q.-J. Meng, *CrystEngComm*, 2007, **9**, 915; (c) L. Wen, Y. Li, Z. Lu, J. Lin, C. Duan and Q. Meng, *Cryst. Growth Des.*, 2006, **6**, 530.
21 (a) N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenon, E. A. Plummer, K. Rissanen and P. Saarenketo, *J. Chem. Soc., Dalton Trans.*, 2000, 1447; (b) J. P. Collin, I. M. Dixon, J. P. Sauvage, J. A. G. Williams, F. Barigelletti and L. Flamigni, *J. Am. Chem. Soc.*, 1999, **121**, 5009.