CrystEngComm

Dynamic Article Links ▶

COMMUNICATION

A huge diamondoid metal−organic framework with a neo-mode of tenfold interpenetration

Tien-Wen Tseng,*[a] Tzuoo-Tsair Luo,[b] Chen-Chuan Tsai,[ab] Kuang-Lieh Lu*[b]

A huge diamondoid metal−organic framework featuring a tenfold interpenetrating neo-mode, with an extra-framework volume of up to 48.7%, despite its very high degree of inpenetration, is reported. The hydrogen bonding of the
10 **internetwork directs the relative position of frameworks and exhibits a self-catenated net with a Schläfli symbol of $\{(6^2.8^4)(6^4.8.10)_2\}$.**

Many astonished advances in the field of metal−organic framework (MOF) materials have been made owing to their
15 intriguing crystal structures and framework topologies,[1–2] and potential applications.[3] Among a variety of 3D frameworks, the most common and important type of topology is related to diamondoid 4-connected networks (denoted as **dia**), for their potential as porous materials with remarkable structural
20 characteristics and properties.[4–5] Despite the use of the deliberate organic linkers with suitable tectons in preparing such MOFs, their topological features are unpredicted and will evoke considerable interest in crystal engineering.[6] The construction of dia MOFs with variable cavities and different degrees of
25 interpenetration would be achieved using tetrahedral metal ions, such as the $M(COO)_4$ unit, and bulky aromatic bridging linkers.[7–8] Due to the increased degree of interpenetration, pore size should decrease and the interpenetrated MOFs easily become nonporous, but with high stability. Avoiding and/or
30 tuning the interpenetration is a bigger challenge.[9–10] In particular, the preparation of 3D diamondoid MOFs with high degree interpenetration and many cavities is currently unusual.[7]

As part of our ongoing efforts to design and synthesize functional framework materials,[11] herein we report on a huge
35 diamondoid MOF of $[\{[Cd(cip)_2]\cdot 2NH_2Me_2\cdot 6DMF\cdot 12H_2O\}_n]$ (**1**), which was assembled from a bulky and elongated ligand, H_2cip (4,4'-(2,8-di-tert-butyl-4,10-dihydropyreno[4,5-d:9,10-d']diimi-dazole-5,11-diyl)dibenzoic acid). Importantly, compound **1** features: (1) an unprecedented huge and nearly
40 undistorted adamantane cage with a Cd···Cd edge separation of up to 25.9451(2) Å (Fig. 1a); (2) the tenfold interpenetrated diamondoid MOF with a mode of Class Ia net (Fig. 1b−d); (3) an extra-framework volume of up to 48.7%, in spite of its very high degree of inpenetration; (4) the hydrogen bonding of
45 internetwork directs the relative position of frameworks and exhibits a self-catenated net with a Schläfli symbol of
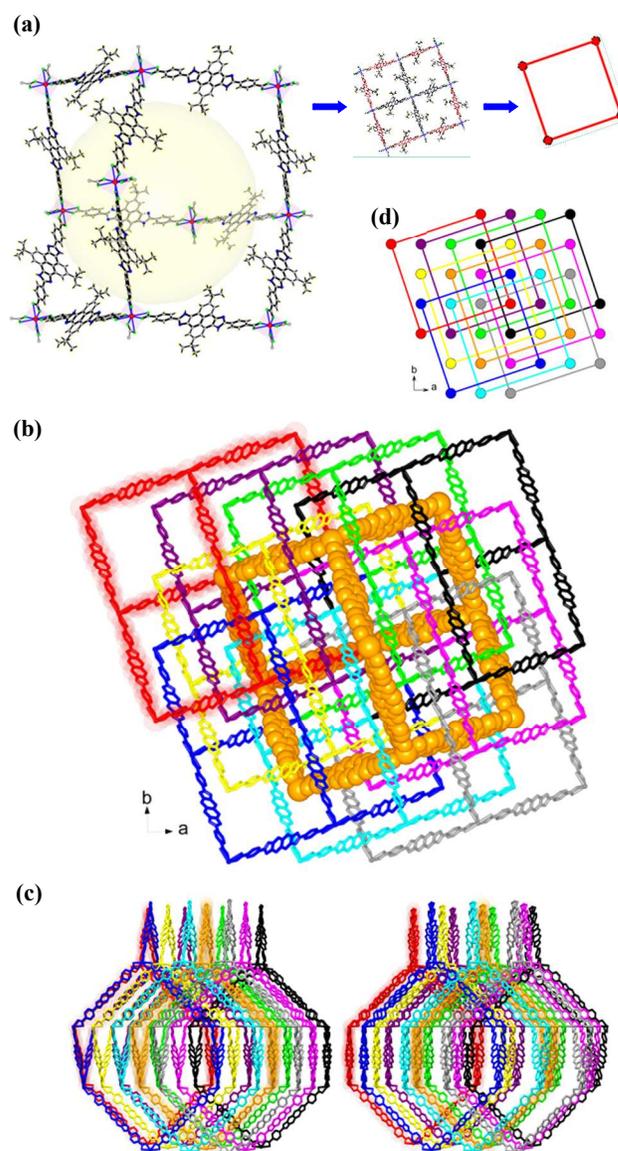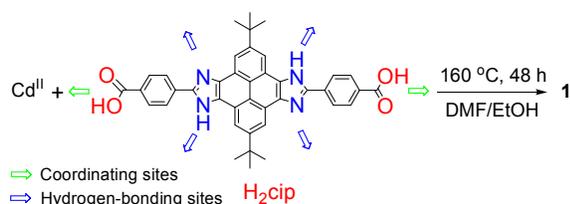

Fig. 1 Structures of **1**: (a) a huge adamantane cage and its simplification, (b) perspective view of the ten individually entangled adamantane cages along the *c* axis (only the main aromatic skeleton is shown for clarity), (c) side stereoview of part (b), (d) the simplified pattern of part (b).

Scheme 1. Self-assembly of 1 from the bulky H_2cip ligand.

$\{(6^2.8^4)(6^4.8.10)_2\}$. Interpenetration is an important and essentially ubiquitous phenomenon in the crystal engineering of huge frameworks.[7] This innovative finding can be used to successfully prepare increasingly large diamondoid frameworks,

5 likely with infinite degrees of interpenetration. To the best of our knowledge, such an entangled **dia** MOF with a 10-fold interpenetration mode is currently rare.[7]

Compound **1** was synthesized by reacting $Cd(ClO_4)_2 \cdot H_2O$ and H_2cip under solvothermal conditions at 160 °C for 48 h through

10 a single-step, self-organization process (Scheme 1). The multifunctional H_2cip ligand was deliberately designed so as to not only contain long heteroaromatic-rigid dicarboxylate scaffold and to be thin at the ends, but also has unusual characteristics in that it poessesses a sterically bulky cross-

15 shaped skeleton around the middle. The use of bulky and elongated organic scaffolds represents a promising strategy for the preparation of new MOF materials. Unlike the flexible aliphatic linear ligands, it could be a source of useful coordinating and specific imidazole hydrogen-bonding sites,

20 since the tendency would be to form giant and porous MOFs, rather than densely packed structures.[12]

A single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the tetragonal space group $P4_2/n$ and is comprised of an extraordinarily large, anionic diamondoid

25 framework. The asymmetric unit consists of one Cd^{II} center, half of the cip^{2-} ligand, and one hydrogen-bonded water molecule; other disordered cations and guest molecules were not crystallographically well-defined. An analysis of the local symmetry of the metal cations showed that the Cd^{II} center

30 resides in a special position containing a fourfold axis of rotation. Each Cd^{II} center is bound to eight carboxylate oxygen atoms from four individual cip^{2-} ligands in a distorted antiprismatic manner. The Cd^{II} atom can be regarded as a four-connecting tetrahedral node. The cip^{2-} ligand functions as an

35 extended linker, bridging two Cd^{II} centers. As shown in Fig. 1a, the presence of a huge adamantane cage is apparent. All of the $Cd\cdots Cd$ edge separations equal 25.9451(2) Å (Table S3, in the SEI†) and the $Cd\cdots Cd\cdots Cd$ angles range from 102.34 to 113.15º, exhibiting maximal dimensions (corresponding to long

40 intracage $Cd\cdots Cd$ distances) of $\sqrt{20}a \times \sqrt{20}b \times 2c$ (i.e., 57.17 × 57.17 × 65.07 Å³), in which could accommodate an imaginary sphere with a diameter of up to 33 Å (Fig. 1a). The ratio of $2c/\sqrt{20}a = 1.1382$ indicates that this huge adamantane cage only has a slight tetragonal elongation.

45 A topology analysis using the TOPOS software package[13] revealed that compound **1** consists of a 6^6-**dia** tenfold interpenetrated framework belonging to the Class Ia net that
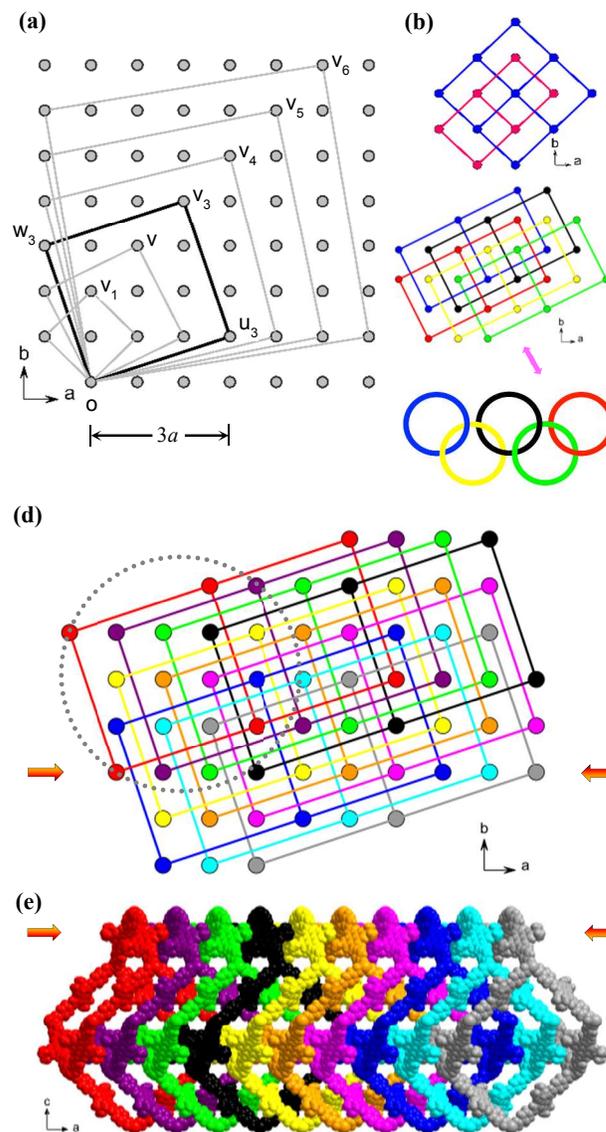

Fig. 2 (a) A systematic diagram of the tenfold interpenetration mode in **dia** nets, viewed along the *c* axis (simplification is the same as that in Fig. 1). (b) The $(1^2 + 1)$-fold interpenetration mode. (c) Ermer's $(2^2 + 1)$-fold interpenetration mode (as shown with the colourful Olympic rings). (d) The tenfold interpenetration mode in compound **1**. (e) Space-filling model of the ten translationally equivalent adamantane cages, generated by the interpenetration vector [1,0,0], showing its available openings along the *b* axis (note the colour sequence is the same as that used in part (d)).

exclusively involves translationally equivalent **dia** nets.[14] It is noteworthy that the bulky cip^{2-} ligand provides net-to-net

50 $NH\cdots N$ hydrogen-bonding interactions ($NH\cdots N = 2.90$ Å, Fig. S8†) to connect all tenfolds into a single binodal four-connected net where the ligand is also four-connected (to two Cd atoms and two other cip^{2-} ligands). As a result, the resulting 3D self-catenated net arising from the formation of the hydrogen bond

55 bridges,[15] and which topology can also be classified as a net with a Schläfli symbol of $\{(6^2.8^4)(6^4.8.10)_2\}$. In spite of the very high degree of interpenetration, compound **1** still contains
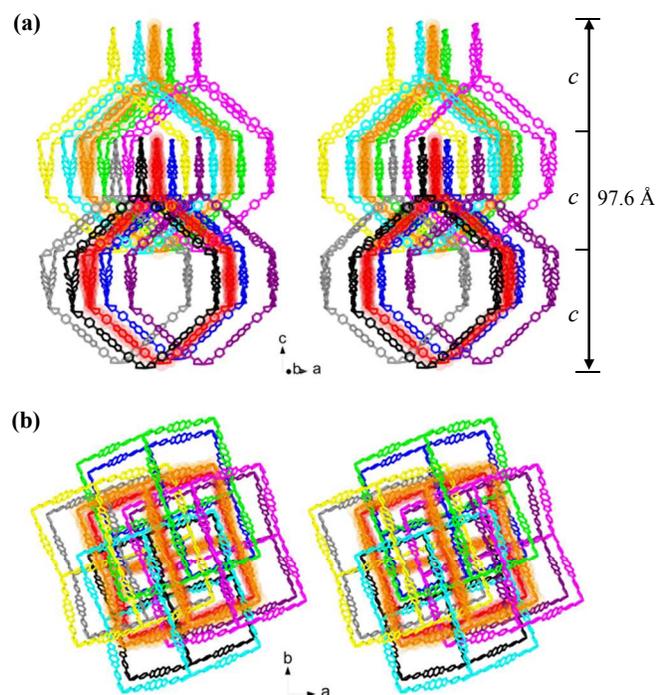
Fig. 3 (a) Perspective stereoview of the five pairs of catenated adamantane cages in compound **1**. (b) Top view of part (a).

numerous small pore openings with dimensions of 4.5×3 Å^2 and 2×1.5 Å^2 along the *a* and *b* axes (Fig. 2e). Analysis using the PLATON[16] software tool indicated that the extra-framework volume per unit cell is up to 48.7% (in the absence of all guests),

5 which corresponds to a low calculated density of 0.91 g cm^{-3}. The results of hydrogen adsorption isotherm of **1** indicated a moderate hydrogen uptake (0.35 wt%) at 77 K and 1 atm (Fig. S14†). In addition, there is no significant nitrogen adsorption that can be attributed to the interpenetrated structure of **1**, which

10 still contains numerous small pore openings with dimensions of 4.5×3 Å^2 and 2×1.5 Å^2 along the *a* or *b* axes (Fig. S10†), but lack appropriate intermolecular interactions at low temperature.[17] Each adamantane cage of **1** was simplified as a square and the ten squares are then arranged in a special manner

15 (Fig. 1). In addition, as shown in Fig. 2a, the translational vectors in the tetragonal system are denoted by **a**, **b**, **c** and with lengths *a*, *b*, *c*. The side lengths of the square "ou$_3$v$_3$w$_3$" are equal and its diagonal length is $\sqrt{20}a$. Of great interest is the fact that the adamantane cage of $\sqrt{20}a \times \sqrt{20}b \times 2c$ in compound **1**

20 is very imilar to that of Ermer's fivefold **dia** structure of $\sqrt{10}a \times \sqrt{10}b \times c$.[18] Ermer's diamond-like net and the compound **1** net, the diagonal of their related squares are similarly defined by the vectors **a** + 3**b** and 2**a** + 4**b**; their diagonal lengths equal $\sqrt{10}a$ and $\sqrt{20}a$, respectively. Their symmetry patterns are completely

25 consistent with the predicted values.

The color drawings shown in Fig. 2b−d provide a vivid and pictorial impression of how the **dia** nets are mutually catenated. Apparently, only specific degrees of interpenetration can be consistent with these geometric limitations in Fig. 2a. The

30 diagonal vectors of these increasing-sized squares ov$_1$, ov$_2$, ov$_3$,

ov$_4$, ov$_5$ are **2b**, **a** + 3**b**, 2**a** + 4**b**, 3**a** + 5**b**, 4**a** + 6**b**, respectively, which correspond to 2-, 5-, 10-, 17-fold interpenetration patterns. Thus, a characteristic ($n^2 + 1$)-fold interpenetration rule could be proposed and may be also applied to similar **dia** frameworks.

35 Conceptually, it is currently difficult to predict and fully realize the degree and topology of interpenetration in MOF materials, possibly because the known networks are not sufficiently large.[7]

As shown in Fig. 3, there are five paired sets of twofold mutually interpenetrated **dia** nets, which are related by the

40 partial interpenetration vector [0,0,1] and the crystallographic translation *c* (32.53 Å). Each five individual nets can be merged into each other by shifting them by half of the *c* translation. Therefore, the topology is a unique 10-fold, [2 + 2 + 2 + 2 + 2] mode.[7d] As noted above, compound **1** contains an

45 interpenetrated **dia** network with a Class Ia mode and multi-dimensional displacement translations.[19]

In conclusion, we report on a rational synthetic strategy for successfully preparing a diamondoid network with a tenfold interpenetration neo-mode. This huge framework, which is

50 comprised of bulky heterocyclic organic scaffolds, has the potential to be very useful in the field of materials science and many mysteries associated with them are currently unexplored. Our innovative findings not only highlight an important research topic, but also open interesting perspectives in the study of these

55 supramolecular entangled networks.

Notes and references

60 *ᵃDepartment of Chemical engineering, National Taipei University of Technology, Taipei 106, Taiwan. Fax: +886-2-2776-2383; Tel: +886-2-2771-2171 ext 2538; E-mail: f10403@ntut.edu.tw*
ᵇInstitute of Chemistry, Academia Sinica, Taipei 115, Taiwan

1   (*a*) L. Carlucci, G. Ciani and D. M. Poserpio, *Coord. Chem. Rev.*,
80   2003, **246**, 247−289; (*b*) G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191−214; (*c*) W. B. Lin, W. J. Rieter and K. M. L. Taylor, *Angew. Chem., Int. Ed.*, 2009, **48**, 650−658; (*d*) H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**,
85   424−428; (*e*) W. L. Leong and J. J. Vittal, *Chem. Rev.*, 2011, **111**, 688−764.

2   (*a*) M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, **23**, 283−288; (*b*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460−1494; (*c*) A. J. Blake, N. R. Champness, P. Hubbersrey, W. S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117−138; (*d*) O. Delgado- Friedrichs, M. D. Foster, M. O'Keeffe, D. M. Proserpio, M. M. J. Treacy and O. M. Yaghi, *J. Solid State Chem.*, 2005, **178**, 2533−2554; (*e*) T. T. Luo, H. L. Tsai, S. L. Yang, Y. H. Liu, R. D. Yadav, C. C. Su, C. H. Ueng, L. G. Lin, K. L. Lu, *Angew. Chem., Int. Ed.*, 2005, **44**, 6063−6067.

3   (*a*) P. Thanasekaran, T. T. Luo, C. H. Lee and K. L. Lu, *J. Mater. Chem.*, 2011, **21**, 13140−13149; (*b*) X. L. Ni, X. Xiao, H. Cong, L. L. Liang, K. Cheng, X. J. Cheng, N. N. Ji, Q. J. Zhu, S. F. Xue and Z. Tao, *Chem. Soc. Rev.*, 2013, **42**, 9480−9508; (*c*) W. Lu, Z. Wei, Z. Y. Gu, T. F. Liu, J. H. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch and H. C. Zhou, *Chem. Soc. Rev.*, 2014, **43**, 5561−5593; (*d*) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C. Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011−6061.

4   (*a*) M. Jansen and J. C. Schön, *Angew. Chem., Int. Ed.*, 2006, **45**, 3406−3412; (*b*) J. J. Perry, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38** 1400−1417.

5   (*a*) S. T. Zheng, J. Zhang, X. X. Li, W. H. Fang and G. Y. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 15102−15103; (*b*) Y. L. Liu, V. C. Kravtsov, D. A. Beauchamp, J. F. Eubank and M. Eddaoudi, *J. Am. Chem. Soc.*, 2005, **127**, 7266−7267; (*c*) X. L. Wang, C. Qin, E. B. Wang, L. Xu, Z. M. Su and C. W. Hu, *Angew. Chem., Int. Ed.*, 2004, **43**, 5036−5040.

6   (*a*) S. R. Batten, *CrystEngComm*, 2001, **18**, 1−7; (*b*) H. L. Jiang, T. A. Makal and H. C. Zhou, *Coord. Chem. Rev.*, 2013, **257**, 2232−2249.

7   **dia** MOFs with high degrees of interpenetration, 25-fold: (*a*) Y. P. He, Y. X. Tan and J. Zhang, *CrystEngComm*, 2012, **14**, 6359−6361; 18-fold: (*b*) Y. B. Men, J. Sun, Z. T. Huang and Q. Y. Zheng, *CrystEngComm*, 2009, **11**, 978−979; 12-fold: (*c*) Y. F. Hsu, C. H. Lin, J. D. Chen and J. C. Wang, *Cryst. Growth Des.*, 2008, **8**, 1094−1096; 10-fold: (*d*) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *Chem. Eur.−J.*, 2002, **8**, 1519−1526; 9-fold: (*e*) K. A. Hirsch, D. Venkataraman, S. R. Wilson, J. S. Moore and S. Lee, *J. Chem. Soc. Chem. Commun.*, 1995, 2199−2200; (*f*) K. A. Hirsch, S. R. Wilson and J. S. Moore, *Chem.−Eur. J.*, 1997, **3**, 765−771; (*g*) H. X. Zhang, Q. X. Yao, X. H. Jin, Z. F. Ju and J. Zhang, *CrystEngComm*, 2009, **11**, 1807−1810.

8   **dia** MOFs: (*a*) X. S. Wang, H. Zhao, Z. R. Qu, Q. Ye, J. Zhang, R. G. Xiong, X. Z. You and H. K. Fun, *Inorg. Chem.*, 2003, **42**, 5786−5788; (*b*) H. Kim and M. P. Suh, *Inorg. Chem.*, 2005, **44**, 810−812; (*c*) J. J. Cheng, Y. T. Chang, C. J. Wu, Y. F. Hsu, C. H. Lin, D. M. Proserpio and J. D. Chen, *CrystEngComm*, 2012, **14**, 537−543; (*d*) J. Zhang, S. Chen, T. Wu, P. Feng and X. Bu, *J. Am. Chem. Soc.*, 2008, **130**, 12882−12883; (*e*) J. Zhang, S. Chen and X. Bu, *Angew. Chem., Int. Ed.*, 2008, **47**, 5434−5437.

9   (*a*) D. J. Collins and H. C. Zhou, *J. Mater. Chem.*, 2007, **17**, 3154−3160; (*b*) S. Ma, D. Sun, M. Ambrogio, J. A. Fillinger, S. Parkin and H. C. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 1858−1859; (*c*) P. Pachfule, Y. Chen, J. Jiang and R. Banerjee, *J. Mater. Chem.*, 2011, **21**, 17737−17745; (*d*) R. Haldar, N. Sihdar and T. K. Maji, *Mater.   Today*,   2014, http://dx.doi.org/10.1016/j.mattod.2014.10.038.

10 (*a*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460−1494; (*b*) S. Furukawa, Y. Sakata and S. Kitagawa, *Chem. Lett.*, 2013, **42**, 570−576.

11 (*a*) T. T. Luo, H. C. Wu, Y. C. Jao, S. M. Huang, T. W. Tseng, Y. S. Wen, G. H. Lee, S. M. Peng and K. L. Lu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9461−9464; (*b*) J. Y. Wu, S. L. Yang, T. T. Luo, Y. H. Liu, Y. W. Cheng, Y. F. Chen, Y. S. Wen, L. G. Lin and K. L. Lu, *Chem. Eur. J.*, 2008, **14**, 7136−7139; (*c*) W. Tseng, T. T. Luo, S. Y. Chen, C. C. Su, K. M. Chi and K. L. Lu, *Cryst. Growth Des.*, 2013, **13**, 510−517; (*d*) T. W. Tseng, T. T. Luo, C. C. Su, H. H. Hsu, C. I. Yang and K. L. Lu, *CrystEngComm*, 2014, **16**, 2626−2633; (*e*) T. W. Tseng, T. T. Luo and K. H. Lu, *CrystEngComm*, 2014, **16**, 5516−5519.

12 C. C. Tsai, T. T. Luo, J. F. Yin, H. C. Lin and K. L. Lu, *Inorg. Chem.*, 2009, **48**, 8650−8652.

13 V. A. Blatov, *IUCr Compcomm Newsl.*, 2006, **7**, 4−38; or see: http://www. topos.ssu.samara.ru.

14 (*a*) V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2004, **6**, 377−395; (*b*) I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *J. Solid State Chem.*, 2005, **178**, 2452−2474.

15 (*a*) I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2008, **10**, 1822−1838; (*b*) I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *Cryst. Growth Des.*, 2008, **8**, 519−539; (*c*) C. B. Aakeroy, N. R. Champness and C. Janiak, *CrystEngComm*, 2010, **12**, 22−43; (*d*) D. M. Proserpio, *Nature Chem.*, 2010, **2**, 435−436.

16 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7−13.

17 (*a*) J. B. Lin, J. P. Zhang and X. M. Chen, *J. Am. Chem. Soc.*, 2010, **132**, 6654−6656; (*b*) B. Zheng, J. Bai, J. Duan, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, **133**, 748−751; (*c*) C. H. Lee, H. Y. Huang, Y. H. Liu, T. T. Luo, G. H. Lee, S. M. Peng, J. C. Jiang, I. Chao and K. L. Lu, *Inorg. Chem.*, 2013, **52**, 3962−3968; (*d*) Y. Xiong, Y. Z. Fan, R. Yang, S. Chen, M. Pan, J. J. Jiang and C. Y. Su, *Chem. Commun.*, 2014, **50**, 14631−14634.

18 O. Ermer, *J. Am. Chem. Soc.*, 1988, **110**, 3747−3754.

19 (*a*) L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio and S. Rizzato, *Chem.−Eur. J.*, 1999, **5**, 237−243; (*b*) D. S. Reddy, T. Dewa, K. Endo and Y. Aoyama, *Angew. Chem., Int. Ed.*, 2000, **39**, 4266−4268; (*c*) X. L. Wang, C. Qin, S. X. Wu, K. Z. Shao, Y. Q. Lan, S. Wang, D. X. Zhu, Z. M. Su and E. B. Wang, *Angew. Chem., Int. Ed.*, 2009, **48**, 5291−5295; (*d*) Y. Gong, J. Li, J. Qin, T. Wu, R. Cao and J. Li, *Cryst. Growth Des.*, 2011, **11**, 1662−1674; (*e*) Y. F. Peng, L. Y. Zheng, S. Han, B. L. Li and H. Y. Li, *Inorg. Chem. Commun.*, 2014, **44**, 41−45.

CrystEngComm Accepted Manuscript

A huge diamondoid metal−organic framework with a neo-mode of tenfold interpenetration

Tien-Wen Tseng, Tzuoo-Tsair Luo, Chen-Chuan Tsai, Kai-Hsiang Lu
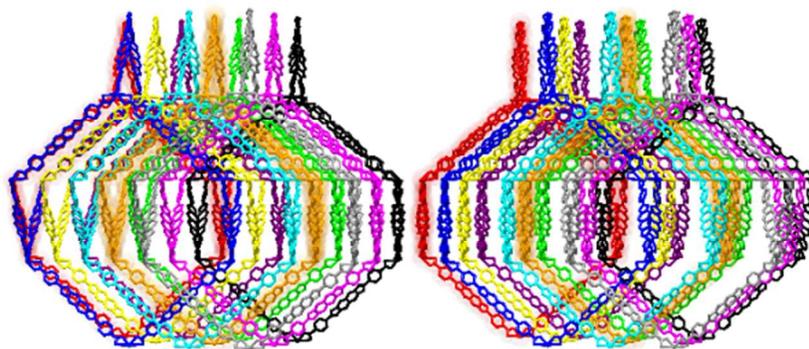
A huge diamondoid framework with the edge distances of the adamantane cages up to 25.95 Å is reported. This MOF displays a neo-mode of tenfold interpenetration, which is constructed from a bulky and elongated aromatic-rigid dicarboxylate scaffolds. Interestingly, the hydrogen bonding of internetworks directs the relative position of frameworks and exhibits a self-catenated net with a Schläfli symbol of $\{(6^2.8^4)(6^4.8.10)_2\}$. In spite of the tenfold interpenetration, it still has an extra-framework volume of up to 48.7%.