Unprecedented (3,4)-connected metal–organic frameworks (MOFs) with 3-fold interpenetration and considerable solvent-accessible void space

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***Via* solvothermal synthesis, the self-assembly of $CuCl_2$, 1,3,5-benzenetricarboxylic acid, and *N,N′*-bis(4-pyridylformamide)-1,4-benzene in DMF generated a novel coordination polymer containing an unprecedented (3,4)-connected network; 3-fold interpenetration and considerable solvent-accessible cavities occupied by reversible guest water molecules were also observed.**

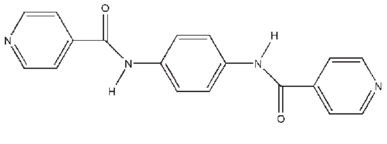
Crystalline metal–organic frameworks (MOFs) exhibiting large surface area and porosity retention upon solvent removal have achieved considerable attention because of their elegant topology and potential applications in separation, catalysis, nonlinear optics, and gas storage.[1–4] The modular construction of MOFs allows their pore size and shape to be systematically tuned by the judicious choice of metal-containing secondary building units (SBUs) and/or bridging organic linkers, and by making use of framework interpenetration or interweaving.[5] Based on the considerations of the thermal robustness, the current metal–organic frameworks are mainly based on rigid polycarboxylate ligands, such as biphenyl, terphenyl, and quaterphenyl tetracarboxylic acids.[6] By varying the length of the organic backbone of these ligands, many desired MOFs are built.[7]

Multipyridylamides have been proven to be very useful in self-assembly processes through hydrogen bonding, and the assembled products are relevant to biological systems. Remarkably, Ghadiri *et al.* first published their delicate work in 1994 regarding the formation of nanotube frameworks with a diameter of 1.3 nm built from polypeptide bonds as basic subunits as well as through inter-ring N–H···O=C hydrogen bonds.[8] These nanotubes represent a new and important class of functional materials. Following this, several outstanding research results were reported, such as the 0D face-driven corner-linked octahedral nanocages,[9] 1D helical chains,[10] a 2D 'two-over/two-under' wave structure,[11] three-fold parallel interpenetrating 2D brick-wall networks,[12] and 3D non-interpenetrating (3,6)-connected frameworks.[13] More detailed examination shows that the exclusive synthetic method for these compounds is the layering of solutions. Furthermore, previous work has focused on the synthesis of such multipyridylamides, the coordination behavior of them towards metal centers (Pd(II), Ag(I), Cu(I), Au(I)), and the construction of supramolecular frameworks. The thermal stability of these compounds has been poor. Thus there remain significant challenges in this area.

In this work, we selectively chose dipyridyl-amide ligands as organic linkers to construction of MOFs, based on the following considerations: (i) so far, only two *N,N′*-bis(4-pyridylformamide)-1,4-benzene (L)-based examples have been reported;[14] (ii) the aforementioned ligand L possesses a flexible backbone containing bifunctional binding sites (both pyridyl groups), as well as a strong capacity for hydrogen bonding of the amide groups, which is anticipated to play a vital role in the assembly of flexible MOFs.[15] Furthermore, in order to increase the thermal stability of the target MOFs, the co-ligand H_3BTC (H_3BTC = 1,3,5-benzenetricarboxylic acid) is introduced. In order to increase the solubility of the reaction reagents but avoid the decomposition of L ligands, we selected a mild solvothermal synthesis (120 °C) in DMF solution.

The ligand L (Scheme 1) was prepared by literature methods,[8–12] and complexed with $CuCl_2$ and H_3BTC in DMF; this mixture was sealed to carry out the solvothermal reactions. Green crystals of **1**, $[Cu_3(BTC)_2(L)_3]\cdot 5H_2O$, were obtained with a yield of 56% based on Cu.† The single-crystal X-ray diffraction data suggested that **1** crystallized in a rhombohedral space group $R\bar{3}$.‡ In **1**, the copper atoms show the four-coordinated CuO_2N_2 square geometry completed by L nitrogen atoms and BTC^{3-} oxygen atoms, together with two weak, Jahn–Teller distorted Cu–O axial bonds (Cu–O1/2.551 Å). The equatorial Cu–O bond lengths (1.931 Å) are comparable with the Cu–N bond lengths (2.032Å). The BTC^{3-} ligands, with C_3 symmetry, adopt the tri(monodentate) coordinated mode. The copper(II) ions are connected by the BTC^{3-} ligands to give neutral (6,3) sheets with edges of *ca.* 9.3 Å, calculated by the metal-to-metal distance. These sheets are then interconnected by the bridging, 2-connecting L *via* the N(L)–Cu bonds.

Topologically, if the BTC^{3-} units and Cu(II) centers are viewed to be the 3- and 4-connected nodes, respectively, and then this framework becomes a binodal (3,4)-connected net with $(6^3)_2(6^4\cdot 8\cdot 10)_3$ topology built on trigonal organic spacers and square metal centers. Among the known (3,4)-connected nets in coordination polymers,[16] the most symmetrical and important examples are $Cu_{15}Si_4$, boracite, Pt_3O_4 and the twisted boracite net.



Scheme 1 The present L ligand shows antiparallel orientation of amide and C=O groups.

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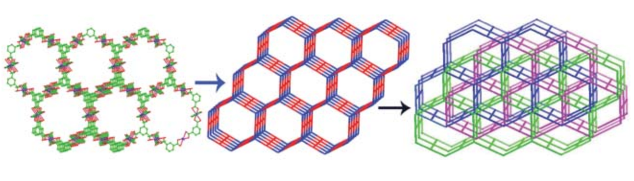

Fig. 1 The unprecedented (3,4)-connected frameworks with the 3-fold interpenetration.

The net displayed by **1** has been assigned the **tfz** notation,[17] but we are not aware of any coordination polymer reported with this topology. Further inspection of the reported (3,4)-connected nets shows that they are constructed by alternately linking the 3- and 4-connecting nodes; by contrast, in **1** there are links *between* the 4-connected nodes, as well as between the 3- and 4-connected nodes. The structure of **1** also shows 3-fold interpenetration of these networks; previous reports of interpenetrating (3,4)-connected nets had only shown 2-fold interpenetration. Thus, the present structure displays a new (3,4)-connected net, and has the highest degree interpenetration for such nets (Fig. 1). Despite the occurrence of interpenetration, however, there remains a considerable void space (*ca.* 1450Å^3, equal to 24.9% of the cell volume),[18] where distorted water molecules locate.

In addition, the structure is stabilised by extensive hydrogen bonding between the interpenetrating nets (N(–H)···O = 3.08Å). The interpenetration also generates two sets of cage-like cavities which contain numerous amine functional groups, as illustrated in Fig. 2.

Thermogravimetric analysis (TG) shows the loss of free water molecules at 30–200 °C (calc. −5.5%, found −5.4%), followed by a plateau from 200 °C to 300 °C; this indicates the high thermal robustness of the guest-free framework (Fig. 3). Surprisingly, the desolvated interpenetrating framework of **1a** retains its single crystal nature up to 300 °C. The single-crystal X-ray diffraction data shows that **1a** shows the same space group of **1**, but with slightly reduced cell parameters and cell volume. The phase purity of the crystal samples for **1** and **1a** is confirmed by XRD (powder X-ray diffraction) studies (Fig. 4). The guest-free phase is also confirmed by elemental analysis (EA) and IR spectroscopy. Soaking such guest-free phases in water for one day regenerated the guest-filled phase of **1**, which was corroborated by single-crystal X-ray diffraction, IR and EA. The host interpenetrating framework expands back to its former volume upon guest inclusion. This reversible cycle can be repeated many times without loss of crystallinity.

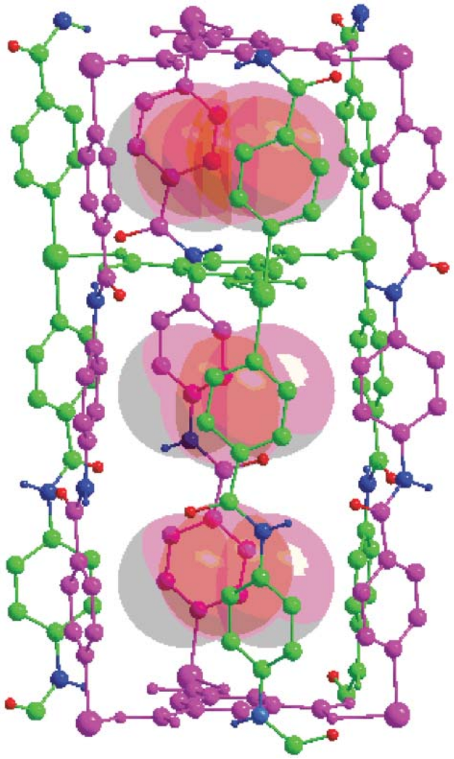

Fig. 2 View of the cage-like cavities with the intercalated guest water molecules, constructed by phenyl and pyridyl groups of L and BTC^{3-} from two interpenetrating (3,4)-connected nets.

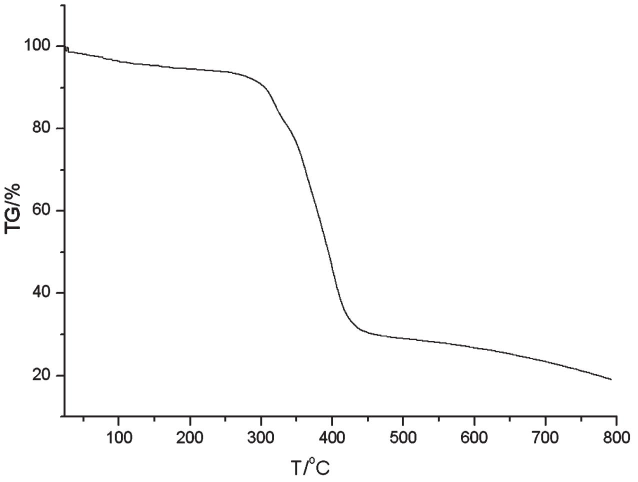

Fig. 3 The TG plot of **1**.

In summary, we report here our initial efforts to construct multipyridylamide-based coordinated polymers with high dimensional framework topologies and high thermal stabilities. By choosing the multicarboxylate ligand H$_3$BTC as a co-ligand and using mild solvothermal synthesis (120 °C) in DMF, we successfully isolated polymer **1**; the structure displays a layered

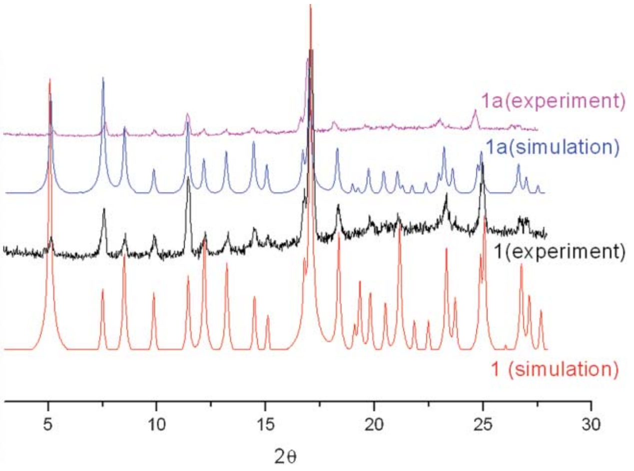

Fig. 4 The simulated XRD patterns from the single crystal data and the experimental XRD patterns of **1** and **1a**.

MOF substructure pillared by long organic spacers (*ca.* 2.0 nm) to generate 3-fold interpenetrating 3D nets and considerable solvent-accessible void space. Significantly, from a topological viewpoint, polymer **1** presents the first example of a new (3,4)-connected net. Furthermore, the highly thermal stability and the reversible uptake and release water cycle without loss of crystallinity in **1** is rare; these guest-free frameworks with largely permanent cavities and highly thermal stability could be utilized as porous materials. In the field of multipyridylamide-based coordinated polymers, the present research is an important milestone as it resolves three important problems: (i) synthesis, (ii) construction of multi-dimensional frameworks, and (iii) the thermal stability of the resulted frameworks. Hence, it is believed that this study will open up a promising way to prepare multipyridylamide-based MOFs.

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Notes and references

† *Synthesis of 1*. $[Cu_3(BTC)_2(L)_3]\cdot 5H_2O$ (**1**): A DMF solution of H_3BTC, $CuCl_2\cdot 2.5H_2O$, and L in a ratio of 1 : 1 : 1 was sealed in a Teflon reactor, and heated at 120 °C for two thousand minutes, and then cooled to room temperature at 3 °C h^{-1}. Subsequently, green hexagonal-prism crystals were obtained in 56% yield based on Cu. Element analysis (%) for **1**: calc: C 52.41, H 3.54, N 10.18; found: C 52.46, H 3.61, N 10.21; **1a**: calc: C 55.44, H 3.10 N 10.77; found: C 55.46, H 3.06, N 10.78. IR(KBr)/cm^{-1}: **1**: 3374(m), 3094(w), 1671(s), 1624(m), 1577(m), 1515(s), 1360(s), 1231(m), 1056(m), 839(s), 760(m), 528(m); **1a**: 3094(w), 1671(s), 1624(m), 1576(m), 1515(s), 1360(s), 1232(m), 1056(m), 839(s), 761(m), 528(m).

‡ *Crystal data*. Data collections were performed with MoKα radiation (0.71073Å) on a Rigaku R-axis rapid IP area detector, and the structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full matrix least-squares on F^2 using the SHELXTL program. Crystal data for **1**: rhombohedral, space group $R\bar{3}$, $a = 18.604(3)$Å, $c = 19.756(4)$Å, $V = 5921.7(17)$Å^3, Z = 3, GOF = 1.085, final $R1 = 0.0554$, w$R2 = 0.1605$; Crystal data for **1a**: rhombohedral, space group $R\bar{3}$, $a = 18.5943(16)$Å, $c = 19.761(3)$Å, $V = 5916.9(12)$ Å^3, $Z = 9$, GOF = 1.109, final $R1 = 0.0618$, w$R2 = 0.1718$. The position and composition of the lattice water molecules could not be accurately determined because of their high structural disorder, but were confirmed by EA and TG analysis. CCDC 641708. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706177c

1 O. M. Yaghi, C. E. Davis, G. M. Li and H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861.

2 M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2000, **39**, 3052.

3 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.

4 J. S. Seo, D. Wang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982.

5 (*a*) B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 11559; (*b*) B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021; (*c*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.

6 (*a*) C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1446; (*b*) L. J. Barbour, *Chem. Commun.*, 2006, 1163; (*c*) C. J. Kepert, *Chem. Commun.*, 2006, 695; (*d*) M. J. Rosseinsky, *Microporous Mesoporous Mater.*, 2004, **73**, 15.

7 (*a*) R. Kitaura, K. Fujimoto, S. I. Noro, M. Kondo and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2002, **41**, 133; (*b*) R. Kitaura, K. Seki, G. Akiyama and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2003, **42**, 4; (*c*) S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109; (*d*) J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 4.

8 (*a*) J. D. Hartgerink, T. D. Clark and M. R. Ghadiri, *Chem.–Eur. J.*, 1998, **4**, 1367; (*b*) M. R. Ghadiri, K. Kobayashi, J. R Granja, R. K. Chadha and D. E. McRee, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 93.

9 D. Moon, S. Kang, J. Park, K. Lee, R. P. John, H. Won, G. H. Seong, Y. S. Kim, G. H. Kim, H. Rhee and M. S. Lah, *J. Am. Chem. Soc.*, 2006, **128**, 3530.

10 Z. Qin, M. C. Jennings and R. J. Puddephatt, *Chem.–Eur. J.*, 2002, **8**, 3.

11 Y. H. Li, C. Y. Su, A. M. Goforth, K. D. Shimizu, K. D. Gray, M. D. Smith and H. C. zur Loye, *Chem. Commun.*, 2003, 1630.

12 X. O. Lü, M. Pan, J. R. He, Y. P. Cai, B. S. Kang and C. Y. Su, *CrystEngComm*, 2006, **8**, 827.

13 B. C. Tzeng, B. S. Chen, H. T. Yeh, G. H. Lee and S. M. Peng, *New J. Chem.*, 2006, **30**, 1087.

14 (*a*) J. Pansanel, A. Jouaiti, S. Ferlay, M. W. Hosseini, J. M. Planeix and N. Kyritsakas, *New J. Chem.*, 2006, **30**, 71; (*b*) Y. Y. Niu, Y. L. Song, J. Wu, H. W. Hou, Y. Zhu and X. Wang, *Inorg. Chem. Commun.*, 2004, **7**, 471.

15 K. Uemura, S. Kitagawa, M. Kondo, K. Fukui, R. Kitaura, H. C. Chang and T. Mizutani, *Chem.–Eur. J.*, 2002, **8**, 3587.

16 (*a*) D. N. Dybtsev, H. Chun and K. Kim, *Chem. Commun.*, 2004, 1594; (*b*) J. J. Lu, A. Mondal, B. Moulton and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2001, **40**, 2113; (*c*) M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3; (*d*) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. Gay Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; (*e*) B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021.

17 For the three-letter net codes, see N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176 and the associated website, http://rcsr.anu.edu.au/home.

18 A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, C34; A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, 2001.