DALTON
COMMUNICATION

# A three-dimensional porous metal–organic framework $[Fe_2L_3{\cdot}(DMF)_7{\cdot}(C_4H_{10}O)_{0.5}]$ constructed from triple-helices {L = bis[2,4-dihydroxybenzaldehyde]hydrazone}

**Mo Hong, Guo Dong, Duan Chun-ying,* Li Yu-ting and Meng Qing-jin**

*Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing, 210093, P. R. China. E-mail: duancy@nju.edu.cn*

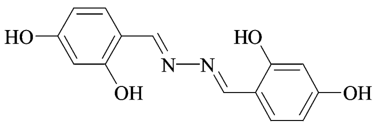
***Received 10th July 2002, Accepted 13th August 2002***
***First published as an Advance Article on the web 23rd August 2002***

**A novel 3-D large porous metal–organic framework was achieved from triple metal helices *via* π–π stacking interactions between the aromatic groups of the helices.**

Recently, intense research activities have been directed towards the development of open porous frameworks including the assembly of inorganic metal clusters, coordination complexes, and organic molecules into extended motifs held together either by strong metal–ligand bonding or by weaker bonding forces such as hydrogen-bonding and π–π interactions.[1–3] The use of discrete molecular units in the assembly of open porous frameworks is an attractive synthetic approach since the structural integrity of the building units can be maintained throughout the reaction, and the desired physical properties can be imparted to solid-state materials.[4,5] While a number of open frameworks with new structural aspects have been assembled by the reactions of metal ions with organic molecules such as di-, tri-, and poly-topic N-bound organic linkers or carboxylate linkers such as 4,4′-bipyridine (BPY)[6] and benzene-1,3,5-tricarboxylate (BTC),[7] large porous open frameworks sustained by π–π interactions are still rare or lacking.[8]

On the other hand, helicity is a fundamental structural feature of great current interest in inorganic and coordination chemistry, and much effort has been devoted to the design of metal complexes exhibiting helical architectures, due to their potential applications in some emerging fields of asymmetric catalysis, non-linear optical materials and aesthetically appealing topology of helical compounds.[9,10] Although the basic features of the design necessary to assemble such a helix are now fairly well established, exerting sufficient control over this aggregation to afford porous open metal–organic frameworks remains challenge.[11,12] To the best of our knowledge the use of helical metal–organic architectures as building blocks for the formation of 3-D networks has not been explored before.

Herein we report a novel metal–organic framework (MOF) with large pores achieved from triple metal helices, and the exploitation of π–π stacking interactions between the aromatic groups of the helices to sustain and generate porosity. The ligand used to assemble the triple helix is one of the simplest imine-based ligands (Scheme 1). The ease of synthesis of these ligand systems has allowed us to systematically probe the effects of modifications to the ligand backbone through which the precise topography or macroarchitecture of the arrays should be controlled. The hydroxyl groups in the ligand helices have the potential to form classical hydrogen bonds with the guest molecules in the pores, which is reported to be important for the inclusion chemistry of such open frameworks.



$H_2L$

**Scheme 1**

Ligand $H_2L$ is readily prepared by mixing 2,4-dihydroxybenzaldehyde and hydrazine hydrate in methanol. The porous complex **1** was obtained by assembling $H_2L$ and $Fe(NO_3)_3$.† Crystallographic study of complex **1**‡ has unequivocally confirmed that the porous networks are constructed from triple helical molecules (Fig. 1). Complex **1** crystallizes in a centrosymmetric space group *C*2/*c*, consequently the molecules occur as a racemic mixture of Λ and Δ configuration enantiomers, whereby the equivalent fragments are inter-related by the $C_2$ axis which runs perpendicular to the N(1) to N(1A) bond. Each iron center is bound to three ON binding units to attain a distorted octahedral coordination geometry with an Fe ··· Fe separation of *ca.* 3.91 Å. Each ligand loses two protons and coordinates to two metal centers as a bis(bidentate) ligand to complete the helical arrangement.

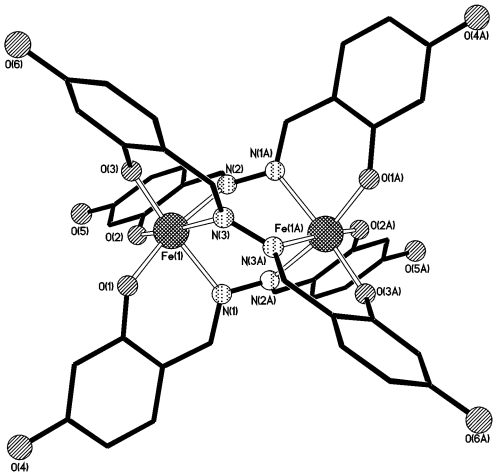


**Fig. 1** Molecular structure of complex **1** showing the triple helical arrangement. Selected bond lengths (Å): Fe(1)–O(3) 1.922(3), Fe(1)–O(2) 1.931(3), Fe(1)–O(1) 1.906(3), Fe(1)–N(1) 2.144(3), Fe(1)–N(3) 2.182(3), Fe(1)–N(2) 2.129(4).

The most intriguing structural feature of the complex in the solid state is that it forms a three-dimensional porous framework into which guest molecules are adsorbed (Fig. 2). The phenyl rings I and II[13] stack to their symmetry-related ones IB and IIC from other helices (symmetry code B: −*x*, 2 − *y*, 1 − *z*; C: −0.5 − *x*, 1.5 − *y*, 1 − *z*), respectively, to form two-dimensional networks. The π–π stacking interactions between aromatic rings are characterized by short inter-planar atom ··· atom separations of 3.35 [C(4) ··· C(6B)] and 3.48 Å [C(12) ··· C(12C)] for the parallel rings in each stack pair, respectively. Those two-dimensional sheets are connected together using the C–H ··· O hydrogen bonds of the types C(18)–H(18A) ··· O(6′D) and C(18′)–H(18B) ··· O(6D) (symmetry code D: −*x*, 1 − *y*, 1 − *z*) to produce a very open

DOI: 10.1039/b206702a

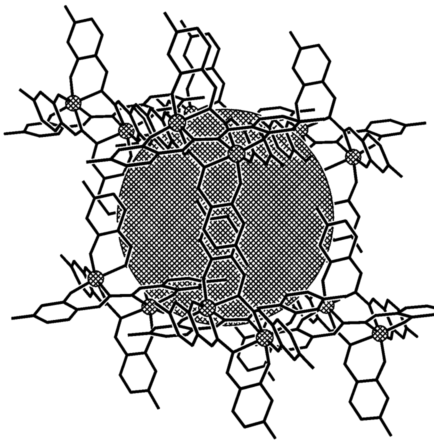


**Fig. 2** Crystal structure of complex **1**, with large apertures and voids achieved by π–π stacking interactions.

porous MOF. The D ··· A separations are 2.62 and 2.50 Å, and D–H ··· A angles are 157 and 176°, for the two kinds of hydrogen bonds, respectively. Seven DMF molecules and half a diethyl ether molecule per formula unit are found to fill the 3-D body. The oxygen atoms of the DMF molecules form hydrogen bonds with the *p*-hydroxy groups stabilizing the inclusion compound. The O ··· O separations range from 2.61 to 2.83 Å and the O–H ··· O angles range from 161 to 175°, respectively. The remarkable openness of the MOF structure is indicated by the presence of a wide square aperture of 7–9 Å, and spherical internal voids of diameter *ca.* 13–15 Å. The volume of a van der Waals sphere that would just fit inside the voids is *ca.* 940 Å$^3$,[14] a value which exceeds that observed for most open zeolites.[15]

To evaluate the mobility of the guests within the framework, we examined the as-synthesized crystals by thermal gravimetric techniques (Fig. 3). In flowing nitrogen, a crystalline sample was heated at a constant rate of 5 °C min$^{-1}$. A rapid weight loss of 35% was observed below 200 °C corresponding to the liberation of all seven DMF and the half molecule of diethyl ether per formula unit (calc. 37%); over the temperature range of 200–250 °C almost no weight loss was observed. Above this temperature, a weight loss step between 250 and 350 °C was observed and is attributed to decomposition of the framework. A powder X-ray diffraction pattern of the sample (complex **2**), which is obtained by heating complex **1** to 200 °C for 2 hours, shows that the positions of the most intense lines remain unchanged relative to the simulated pattern based upon the single-crystal data of complex **1** (Fig. 4).[8] The good agreement between the peaks in both diagrams demonstrates that the porous framework is retained in the absence of guest molecules in the pores.[6]

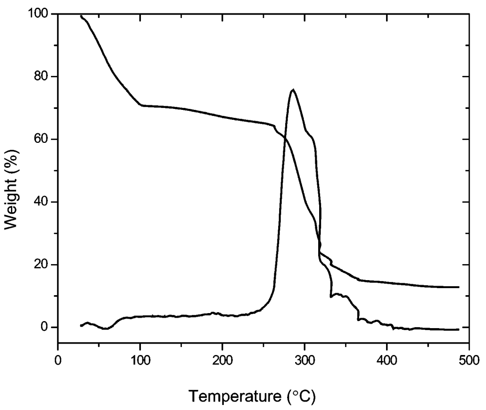


**Fig. 3** EG and TGA for complex **1** from 28.6 to 500 °C.

In conclusion, the present study shows the first example of 3-D porous frameworks assembled from triple helices. The assembly of helical units into a metal–organic porous open framework is interesting both in terms of controlled aggregation of helices and porous materials. The absence of counter ions and the significant large internal void make these and related materials exciting new candidates for examination of their potential utilities in, for example, catalysis or separation processes. It is also noteworthy that although the energy of π–π interactions is only 2–20 kJ mol$^{-1}$, this kind of non-covalent bond has the potential to assemble smaller and simpler fragments into the desired cavities under favorable conditions, which is important in host–guest chemistry and has applications in chemistry, biology and materials science.

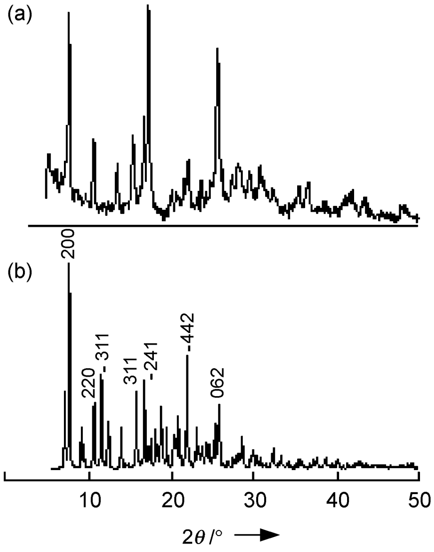


**Fig. 4** Powder X-ray diffraction pattern of complex **2** (a) and the pattern calculated from the single-crystal data for complex **1** (b).

## Acknowledgements

This work was supported by the National Natural Science Foundation of China. We also thank Mr Liu Yong-jiang for collecting the crystal data.

## Notes and references

† Synthesis of H$_2$L. To a 25 mL methanol solution containing 2,4-dihydroxybenzaldehyde (1.38 g, 10 mmol), hydrazine hydroxide (0.31 g, 5 mmol) was added. After refluxing for 4 hours, a yellow solid (H$_2$L) was formed which was isolated by filtration and dried over P$_2$O$_5$ under vacuum. Yield: 84%. Anal. calc. for C$_{14}$H$_{12}$N$_2$O$_4$: C, 61.8; H, 4.4; N, 10.3%. Found: C, 61.8; H, 4.5; N, 10.4%. IR (cm$^{-1}$, KBr disk) 3251 ($\nu_{\text{C–H}}$), 2852, 1619, 1589, 1514, 1465 ($\nu_{\text{C=C}}$, $\nu_{\text{C=N}}$), 1263 ($\nu_{\text{N=N}}$). $\delta_{\text{H}}$ ([$^2$H$_6$]DMSO) 11.33 (2H, s, $^2$H$_{\text{OH}}$), 10.14 (2H, s, $^4$H$_{\text{OH}}$), 8.68 (2H, s, H$_{\text{CH=N}}$), 7.34 (2H, d, $^6$H$_{\text{bz}}$), 6.32 (2H, d, $^5$H$_{\text{bz}}$), 6.25 (2H, s, $^3$H$_{\text{bz}}$).

Synthesis of **1**. To a 25 mL methanol solution containing H$_2$L (0.41 g, 1.5 mmol), Fe(NO$_3$)$_3$·9H$_2$O (0.41 g, 1 mmol) was added. After finishing the addition, the solution was stirred for 1 hour at room temperature. Black solid was isolated by filtration and dried over P$_2$O$_5$ under vacuum. Yield: 62%. Dark-red crystals (complex **1**) suitable for X-ray structural determination were obtained by slow diffusion of diethyl ether into a DMF solution.

‡ Crystal data: (C$_{42}$H$_{30}$N$_6$O$_{12}$Fe$_2$)(C$_3$H$_7$NO)$_7$(C$_4$H$_{10}$O)$_{0.5}$, monoclinic, space group, *C*2/*c*, $a$ = 23.682(3), $b$ = 23.465(3), $c$ = 14.912(2) Å, $\beta$ = 112.501(2)°, $T$ = 293(2) K, $V$ = 7656.0(18) Å$^3$, $Z$ = 4, $D_c$ = 1.276 g cm$^{-3}$, $F$(000) = 3092, $\mu$ = 0.453 mm$^{-1}$, 18224 measured reflections, 6590 independent reflections ($R_{\text{int}}$ = 0.0975). Final refinement converged at $R_1$ = 0.074, $wR_2$ = 0.127, respectively. CCDC reference number 186191. See http://www.rsc.org/suppdata/dt/b2/b206702a/ for crystallographic data in CIF or other electronic format.

1 (*a*) O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; (*b*) H. Li, A. Laine, M. O'Keefe and O. M. Yaghi, *Science*, 1999, **283**, 1145; (*c*) H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; (*d*) B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021.

2 (*a*) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; (*b*) V. A. Ruswll, C. C. Evans, W. Li and M. D. Ward, *Science*, 1997, **276**, 575.

3 (*a*) G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature*, 1995, **374**, 792; (*b*) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. A. Kim, *Nature*, 2000, **404**, 982; (*c*) L. J. Barbour, G. W. Orr and J. L. Atwood, *Nature*, 1998, **393**, 671.

4 (*a*) M. J. Zaworotko, *Nature*, 1997, **386**, 220; (*b*) T. E. Mallouk, *Nature*, 1997, **387**, 350; (*c*) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.

5 (*a*) J. B. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. McEnaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartuli and O. M. Yaghi, *Chem. Mater.*, 1999, **11**, 2633; (*b*) T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 1651; (*c*) T. M. Reineke, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 1999, **38**, 2590.

6 (*a*) For example: K. Biradha, Yoshito, H. Hongo and M. Fujita, *Angew. Chem., Int. Ed.*, 2000, **39**, 3843; (*b*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401; (*c*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295; (*d*) S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2081.

7 (*a*) For example: O. M. Yaghi, C. E. Davis, G. Li and H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861; (*b*) C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158; (*c*) C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1998, 31; (*d*) J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239.

8 S. Lai, C. Cheng and K. Lin, *Chem. Commun.*, 2001, 1082.

9 (*a*) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; (*b*) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; (*c*) E. C. Constable, *Polynuclear Transition Metal Helicates* in *Comprehensive Supramolecular Chemistry*, ed. J. P. Sauvage, Elsevier, Oxford, 1996, vol. 9, p. 213.

10 (*a*) C. J. Fang, C. Y. Duan, D. Guo, C. He, Q. J. Meng, Z. M. Wang and C. H. Yan, *Chem. Commun.*, 2001, 2540; (*b*) C. J. Fang, C. Y. Duan, C. He and Q. J. Meng, *Chem. Commun.*, 2000, 1187; (*c*) C. J. Fang, C. Y. Duan, H. Mo, C. He, Q. J. Meng, Y. J. Liu, Y. H. Mei and Z. M. Wang, *Organometallics*, 2001, **20**, 2525; (*d*) C. He, C. Y. Duan, C. J. Fang and Q. J. Meng, *J. Chem. Soc., Dalton Trans.*, 2000, 2419.

11 (*a*) C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton and A. H. White, *Angew. Chem., Int. Ed.*, 1998, **37**, 920; (*b*) T. Ezuhara, K. Endo and Y. Aoyama, *J. Am. Chem. Soc.*, 1999, **121**, 3279; (*c*) L. J. Childs, N. W. Alcock and M. J. Hannon, *Angew. Chem., Int. Ed.*, 2001, **40**, 1079.

12 (*a*) J. M. Lehn and A. Rigault, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1095; (*b*) B. Hasenknopf, J. M. Lehn, N. Boumediene, A. D. Gervais, A. V. Dorsselaer, B. Knesiel and D. Fenske, *J. Am. Chem. Soc*, 1997, **119**, 10956.

13 The phenyl rings I and II are defined by the the carbon atoms C(1) to C(6) and C(8) to C(13), respectively.

14 The van der Waals radius of C (1.70 Å) was employed in the determination of distance parameters, A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

15 J. M. Bennett and J. V. Smith, *Mater. Res. Bull.*, 1968, **3**, 633.