Unprecedented helix-based microporous metal–organic frameworks constructed from a single ligand†

Rui-Li Sang[ab] and Li Xu*[a]

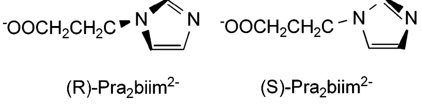
Received (in Cambridge, UK) 21st August 2008, Accepted 19th September 2008
First published as an Advance Article on the web 14th October 2008
DOI: 10.1039/b814524e

Unprecedented helix-based MMOFs with a cylindrical channel constructed from a single, newly designed Na_2Pra_2biim [Na_2Pra_2biim = 1,1′-di(propionic acid)-2,2′-biimidazole disodium salt], $[M(Pra_2biim)(H_2O)]_n \cdot xnH_2O$ (M = Cd, Pb) have been presented, which are built from alternately arranged left- and right-handed helical M-biim tubes interconnected by the carboxyl arms of the ligand, and these findings reveal the promising potential of functionalized helical ligands in the construction of helix-based MMOFs from a single linker.

Microporous metal–organic frameworks (MMOFs) are of great current interest in view of their fascinating structural topologies and potential applications in gas storage, separation, catalysis, *etc.*, as well as their framework dynamics and guest-sensitive properties.[1] These MMOFs are utilizing polyfunctional organic ligands as linkers and the well-defined metal centers as nodes.[2] Their practical applications depend largely on two important factors: high porosity and structural kinetic stability (*i.e.* intact upon removal of the guest molecules). However, these two factors are often contradictory and thus the design and synthesis of MMOFs of high structural kinetic stability offers a great, current challenge in the development of MMOFs-based materials.[3] Several effective strategies such as reticular syntheses and *in situ* formed metal cluster units as secondary building units (SBUs) have been well established.[1a,4] However, the use of helices as SBUs in the construction of MMOFs has been much less developed. The helix-based structures are of fundamental importance for life, which has provided an important impetus for the creation of artificial helical structures in supramolecular chemistry and materials science with potential applications in the fields of asymmetric catalysis, nonlinear optical materials and the aesthetically appealing topologies of helical compounds.[5] A large number of helical coordination polymers have been known, but few further studies of their role in the construction of MMOFs have been carried out.[6] Moreover, although the several helix-based MOFs have been known, they, without exception, contain auxiliary ligands as a second linker.[7] To our knowledge, helix-based MMOFs constructed from a single linker have not been reported.

2,2′-Biimidazole (H_2biim) has been widely used as a biomimetic ligand in bioinorganic chemistry,[8] a bridging ligand in oligometallic chemistry for catalysis,[9] antitumour drugs,[10] and building blocks of supermolecular frameworks.[11] H_2biim is able to form varied helical coordination polymers in either *cis* or *trans* coordinating mode.[12] The coordination chemistry of *N*-substituted biimidazole such as the *N*,*N*′-dimethylated derivative of biimidazole (Me_2biim) behaves quite differently, and is dominated by the larger dihedral angle (67 to 89°) between the two imidazole rings as a consequence of repulsion between the substituents and thus bridging rather than chelating coordination modes.[13] However, like H_2biim, *N*-substituted derivatives such as Me_2biim can also be linked by metal ions into one-dimensional helical structures.[13a] Meanwhile, polycarboxylate groups have proven to be one of the most successful multifunctional ligands in the construction of MOFs because of their strong coordination ability, structural rigidity and chemical stability.[14] With these two concerns in mind, a new multifunctional ligand, Na_2Pra_2biim [Na_2Pra_2biim = 1,1′-di(propionic acid)-2,2′-biimidazole disodium salt], has been designed as illustrated in Scheme 1. One additional advantage of this ligand is that it displays the flexibility usually required in the formation of MMOFs, that is, the two imidazole rings can rotate around the central C–C bond as shown in Scheme 1. The present work will present an unprecedented example of helix-based MMOFs constructed from a single ligand: Na_2Pra_2biim.

Herein we report two helix-based MMOF species, $[M(Pra_2biim)(H_2O)]_n \cdot xnH_2O$ [M = Cd, x = 2 (**1**), M = Pb, x = 1 (**2**)], which were synthesized by the diffusion reaction of $M(NO_3)_2 \cdot 4H_2O$ and Na_2Pra_2biim (see ESI†). The X-ray structural analyses of **1** and **2** show that they are isostructural with each other.‡ As shown in Fig. 1, the Cd(II) ion lying on the crystallographic two-fold rotation axis has a distorted pentagonal bipyramidal coordination geometry with the two apical positions taken up by the free N and equatorial ones occupied by the two carboxyl groups and one water molecule. Pra_2biim^- uses all six coordinating atoms available including



Scheme 1 The configuration of Pra_2biim.

---

[a] *State Key Laboratory of Structural Chemistry, Fujian Institution of Research on the Structural Chemistry, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China. E-mail: xli@fjirsm.ac.cn; Fax: (+86)591-8370-5045*

[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100039, China*

† Electronic supplementary information (ESI) available: Detailed experimental procedures, crystallographic data, structural description and figures, TGA, and VT-PXRD patterns. CCDC reference numbers 696180 (**1**) and 696181 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814524e

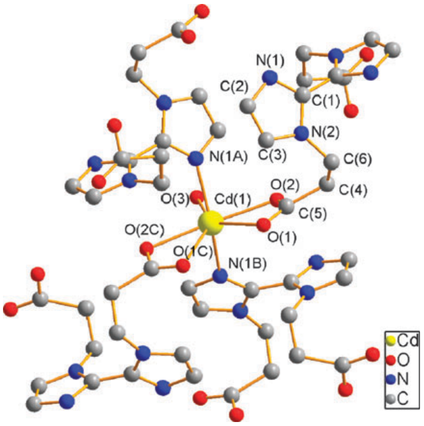


Fig. 1 The coordination environments of Cd1 atoms in **1**. Atoms with 'A', 'B' or 'C' in their labels are symmetry-generated. Symmetry code: (A) 2/3 − *x*, 1/3 − *y*, 1/3 − *z*; (B) 1/3 − *y*, 2/3 − *x*, 1/6 + *z*; (C) *y*, *x*, 1/2 − *z*.

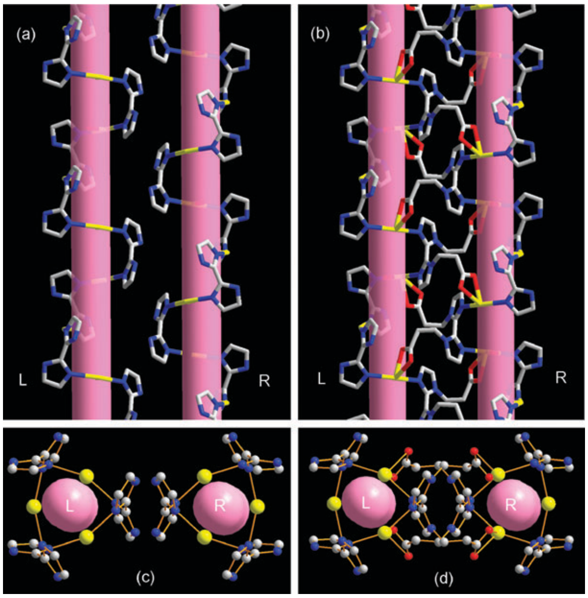


Fig. 3 (a) View of the helical chains along *b*-axis. (b) View along the *c*-axis. (c and d) Neighboring helical chains are interconnected by the carboxyl arms of Pra$_2$biim.

four chelating carboxylate O and two N in a coordination mode (ESI, Fig. 3S†). The Cd–O_{H2O} is 2.27(5) Å, significantly shorter than Cd–$O_{carboxylate}$ [2.409(7), 2.543(11) Å], probably caused by the fact that the location of this water is limited by the H-bonding interactions with two the surrounding carboxylate O atoms (ESI, Fig. 5S†) to be described below. A similar case has also been seen in the Pb analogue **2** [Pb–O_{H_2O}, 2.371(3); Pb–$O_{carboxylate}$, 2.575(2), 2.845(3) Å]. The Cd–N distance is 2.358(5) Å, significantly stronger than Pb–N [2.629(3) Å]. The two imidazole rings of Pra$_2$biim are not coplanar as expected with the dihedral angle of 62.7° in **1** and 56.4° in **2**.

The most striking feature of **1** is the microporous structure featuring hexagonal channels constructed from left-and right-handed helical chains (Fig. 2 and 3). The metal centers are singly bridged by the biim moieties into helical structures of crystallographically imposed C_3 symmetry running along *c* with a pitch the length of the *c*-axis [12.0736(6) Å] (Fig. 3). Unlike the cases in the Ag-H$_2$biim helixes[12] with dihedral angles of 26° (*cis* mode) and 150° (*trans* mode), respectively, the dihedral angle of 62.7° in the present Cd-pra$_2$biim helix ($\angle$N–Cd–N, 180°) results in the formation of an interesting triangular helical tube (Fig. 3), so that the central positions can accommodate the coordination water molecules, differing markedly from those in the tetrahedral $[CdX_2(\mu\text{-}Me_2biim)]_n$ (X = Cl, Br, I) (80.5–89.9°, N–Cd–N, $\angle$95–103°)[13a] because of the higher coordination numbers of the Cd atoms in the present case. There are strong hydrogen bonds between the coordinated water molecules and the carboxyl groups with O···O distances of 2.691 Å (ESI, Fig. 5S†) as mentioned above. The centered space group yields the two types (*R* and *L*) of helical tubes alternately arranged around the hexagonal channels. As can be seen from Fig. 3c and d, the two carboxyl arms of Pra$_2$biim$^-$ are both chelating the two metal centers, respectively, to interconnect the helical tubes into a unique open framework (Fig. 2). The framework can be simplified by using 4-connected nodes instead of metal and ligands centers, which produces a network topology of ($4^2 \cdot 6^2 \cdot 12^2$) as shown in Fig. 6S† with space filling from the lattice water molecules.[15]

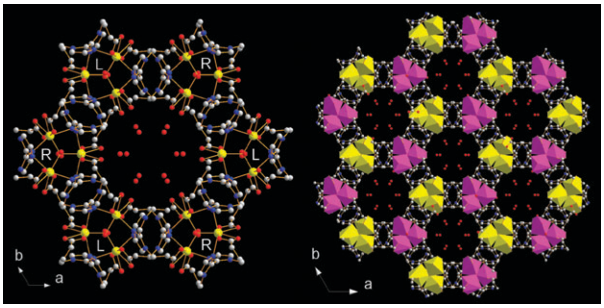


Fig. 2 Cylindrical channels formed by the six interconnected neighboring *R*(*L*) helical tubes with the center occupied by a planar benzene-like $(H_2O)_6$ cluster (left). Polyhedral representation of the open framework (right).

The cylindrical channel has a diameter of *ca.* 10.5015(4) Å[16] wherein a water hexamer is located, comprising 21.4% of the crystal volume of **1**.[17] Interestingly, the planar water hexamer has a benzene-like structure with a doubly enlarged size (O1w-H···O2w = 2.733 Å) (ESI, Fig. 5S†). Each planar water hexamer acting as a donors is H-bonded to the surrounding carboxyl groups (O2w-H···O1 = 2.978 Å) (ESI, Fig. 5S†).

Compound **2** has a similar structure to that of **1** but some differences are noteworthy. The dihedral angle in **2** (56.4°) is significantly smaller than that in **1** (62.7°) presumably as a consequence of the larger atomic size, which leads to the slightly smaller channel [10.1812(6) Å]. However, the channels constitute 24.7% of the crystal volume,[17] larger than that in **1** (21.4%).

Thermal gravimetric analysis (TGA), differential thermal analysis (DTA) and powder XRD measurements at different temperatures were performed to examine the permanent porosity of the MMOFs **1** and **2**. The combined TGA-DTG experiments (ESI, Fig. 7S†) revealed that the loss of the water hexamer (7.8%, calculated 8.1%) occurred in the temperature range 30–135 °C. The release of the coordination water molecules (4.3%, expected 4.1%) took place between 135 to 185 °C. The ligand began to decompose at *ca.* 265 °C. VT-XRPD as shown in Fig. 8S† indicated that the structural integrity of **1** is maintained after the removal of the water molecules, revealing the permanent porosity. The framework structure begins to change at *ca.* 200 °C. Surprisingly, it is recovered after the sample is rehydrated, as indicated by the similar XRPD pattern (e) to that of the fresh one (b).

The photoluminescent properties of the free ligand and compounds **1** and **2** are also investigated in the solid state (ESI, Fig. 11S†). Free Na_2Pra_2biim exhibits an emission maximum at 337 nm when excited at 280 nm. A violet-fluorescent emission band at 366 nm was observed for **1** upon photoexcitation at 290 nm, attributable to the ligand-centered emission. A blue-fluorescent emission band at 480 nm was observed for the lead(II) compound **2** upon photoexcitation at 290 nm, attributable to the ligand-centered emission. Such remarkable bathochromic shift has also been found in several other Pb species.[18]

In summary, the unprecedented helix-based MMOFs with cylindrical channels constructed from single, newly designed Pra_2biim^-, have been presented. They are built from alternately arranged left- and right-handed helical M-biim tubes interconnected by the carboxylate arms of the ligand. The Cd compound **1** exhibits high structural stability and permanent porosity. These findings reveal the promising potential of functionalized helical ligands in the construction of helix-based MMOFs from a single linker. Both compounds display photoluminescent properties with an obvious bathochromic shift observed for the Pb compound **2**.

This work was supported by National Science Foundation of China (#20773129), 973 Program (#2006CB932900) and the Knowledge Innovation Program of the Chinese Academy of Sciences.

Notes and references

‡ Crystal data for **1**: ($C_{12}H_{18}CdN_4O_7$): M = 442.71, trigonal, space group $R\bar{3}c$, a = 27.1286(11), c = 12.0736(6) Å, V = 7695.2(6) Å^3, Z = 18, ρ = 1.720 g cm^{-3}, μ = 1.318 mm^{-1}, F(000) = 3995, GOF = 1.306. Of 18 224 total reflections collected, 1960 were unique (R_{int} = 0.0221). $R1(wR2)$ = 0.0548 (0.1468) for 131 parameters and 1960 reflections [$I > 2\sigma(I)$], 40 restraints. For **2** ($C_{12}H_{16}PbN_4O_6$): M = 519.48, trigonal, space group $R\bar{3}c$, a = 27.4599(8), c = 12.5722(6) Å, V = 8209.9(5) Å^3, Z = 18, ρ = 1.891 g cm^{-3}, μ = 9.279 mm^{-1}, F(000) = 4428, GOF = 1.192. Of 20 059 total reflections collected, 2005 were unique (R_{int} = 0.0385). $R1(wR2)$ = 0.0293 (0.0616) for 126 parameters and 2005 reflections [$I > 2\sigma(I)$], 6 restraints.

1 (*a*) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; (*b*) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*c*) J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670; (*d*) C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466; (*e*) M. O'Keeffe and O. M. Yaghi (Editors), Special Issue on Reticular Chemistry, *J. Solid State Chem.*, 2005, **178**, 2409; (*f*) H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.

2 J. Y. Sun, L. H. Weng, Y. M. Zhou, J. X. Chen, Z. X. Chen, Z. C. Liu and D. Y. Zhao, *Angew. Chem., Int. Ed.*, 2002, **41**, 4471.

3 J.-C. Dai, X.-T. Wu, Z.-Y. Fu, S.-M. Hu, W.-X. Dai, C.-P. Cui, L.-M. Wu, H.-H. Zhang and R.-Q. Sun, *Chem. Commun.*, 2002, 12.

4 (*a*) G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 197; (*b*) L. L. Zheng, H. X. Li, J. D. Leng, J. Wang and M. L. Tong, *Eur. J. Inorg. Chem.*, 2008, 213.

5 (*a*) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; (*b*) Q. Z. Sun, M. L. Wei, Y. Bai, C. He, Q. J. Meng and C. Y. Duan, *Dalton Trans.*, 2007, 4089; (*c*) S. P. Anthony, M. J. Prakash and T. P. Radhakrishnan, *Mol. Cryst. Liq. Cryst.*, 2007, **473**, 67; (*d*) S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276; (*e*) T. Nakano and Y. Okamoto, *Chem. Rev.*, 2001, **101**, 4013; (*f*) L. Han and M. Hong, *Inorg. Chem. Commun.*, 2005, **8**, 406.

6 (*a*) E. V. Anokhina, Y. B. Go, Y. Lee, T. Vogt and A. J. Jacobson, *J. Am. Chem. Soc.*, 2006, **128**, 9957; (*b*) X.-D. Chen, M. Du and T. C. W. Mak, *Chem. Commun.*, 2005, 4417; (*c*) S. N. Semenov, A. Y. Rogachev, S. V. Eliseeva, C. Pettinari, F. Marchetti, A. A. Drozdov and S. I. Troyanov, *Chem. Commun.*, 2008, 1992; (*d*) C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton and A. H. White, *Angew. Chem., Int. Ed.*, 1998, **37**, 920; (*e*) Y.-Q. Sun, J. Zhang, Y.-M. Chen and G.-Y. Yang, *Angew. Chem., Int. Ed.*, 2005, **44**, 5814.

7 (*a*) R. Wang, Y. Zhou, Y. Sun, D. Yuang, L. Han, B. Lou, B. Wu and M. Hong, *Cryst. Growth Des.*, 2005, **5**, 251; (*b*) D.-R. Xiao, E.-B. Wang, H.-Y. An, Y.-G. Li, Z.-M. Su and C.-Y. Sun, *Chem.–Eur. J.*, 2006, **12**, 6528.

8 (*a*) C. Kirchner and B. Krebs, *Inorg. Chem.*, 1987, **26**, 3569; (*b*) C. A. Hester, H. L. Collier and R. G. Baughman, *Polyhedron*, 1996, **15**, 4255; (*c*) J. Cancela, M. J. Gonzalez Garmendia and M. Qurios, *Inorg. Chim. Acta*, 2001, **313**, 156; (*d*) M. A. M. Lorente, F. Dahan, Y. Sanakis, V. Petrouleas, A. Boussedsou and J.-P. Tuchagues, *Inorg. Chem.*, 1995, **34**, 5346; (*e*) S. Fortin and A. L. Beauchamp, *Inorg. Chem.*, 2000, **39**, 4886; (*f*) Y. Cui, H.-J. Mo, J.-C. Chen, Y.-L. Niu, Y.-R. Zhang, K.-C. Zheng and B.-H. Ye, *Inorg. Chem.*, 2007, **46**, 6427.

9 (*a*) S. W. Kaiser, R. B. Saillant and P. G. Rasmussen, *J. Am. Chem. Soc.*, 1975, **97**, 425; (*b*) M. S. Haddad and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 2622; (*c*) A. Maiboroda, G. Rheinwald and H. Lang, *Inorg. Chem. Commun.*, 2001, **4**, 381; (*d*) P. Majumdar, S.-M. Peng and S. Goswami, *J. Chem. Soc., Dalton Trans.*, 1998, 1569; (*e*) M. P. Garcia, A. M. López, M. A. Esteruelas, F. J. Lahoz and L. A. Oro, *Chem. Commun.*, 1988, 793.

10 (*a*) J.-S. Casas, A. Castineiras, Y. Parajo, M.-L. Perez-Paralle, A. Sanchez, A. Sanchez-Gonzalez and J. Sordo, *Polyhedron*, 2003, **22**, 1113; (*b*) B. J. Holliday and Ch. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2023; (*c*) P. A. Zoo, J. S. Casas, M. D. Couse, E. Freijanes, A. Furlani, V. Scarcial, J. Sordo, U. Russo and M. Varela, *Appl. Organomet. Chem.*, 1997, **11**, 963.

11 (*a*) M. Tadokoro, K. Isober, H. Uekusa, Y. Ohashi, J. Toyoda, K. Tashiro and K. Nakasuji, *Angew. Chem., Int. Ed.*, 1999, **38**, 95; (*b*) M. Tadocomo, T. Shiomi, K. Isobe and K. Nakasuji, *Inorg. Chem.*, 2001, **40**, 5476; (*c*) M. Tadomoro and K. Nakasuji, *Coord. Chem. Rev.*, 2000, **198**, 205; (*d*) R. Atencio, M. Chacon, T. Gonzalez, A. Briceno, G. Agrifoglio and A. Sierraalta, *Dalton Trans.*, 2004, 505; (*e*) L. Ohrstrom, K. Larsson, S. Borg and S. T. Norberg, *Chem.–Eur. J.*, 2001, **7**, 4805.

12 (*a*) R.-L. Sang and L. Xu, *Eur. J. Inorg. Chem.*, 2006, 1260; (*b*) C. A. Hester, R. G. Baughman and H. L. Collier, *Polyhedron*, 1997, **16**, 2893.

13 (*a*) R.-L. Sang and L. Xu, *Inorg. Chem.*, 2005, **44**, 3731; (*b*) R.-L. Sang and L. Xu, *Inorg. Chim. Acta*, 2006, **359**, 2337.

14 (*a*) R. C. Mehrotra and R. Bohra, *Metal Carboxylates*, Academic Press, London, 1983; (*b*) F. A. Cotton and R. H. Walton, *Multiple Bonds Between Metal Atoms*, Oxford University Press, Oxford, 1993.

15 M. O'Keeffe, H. Li, M. Eddaoudi, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3.

16 This value is the distance across the channel from the oxygen atom O1 of the carboxylate anions of Pra_2biim^- to the oxygen atom O1 of the carboxylate anions of Pra_2biim^-.

17 A. L. Spek, *PLATON-A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, 2000.

18 Q.-Y. Liu and L. Xu, *Eur. J. Inorg. Chem.*, 2006, 1620.