

# CrystEngComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

# Heterometal-organic framework with *pcu* net constructed from mixed linear ligands

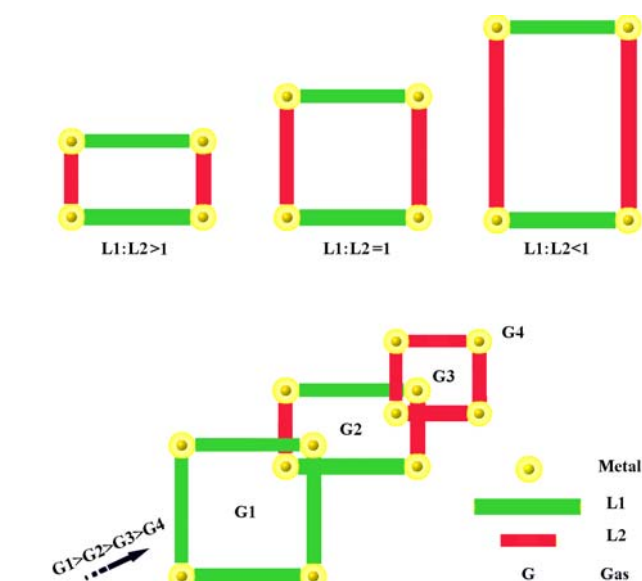
Wei-Hui Fang and Guo-Yu Yang\*

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Under the cooperation of two linear organic ligands, a novel heterometal-organic framework  $[\text{La}_2\text{Cu}_2(\text{ox})_2\text{L}_6]\cdot 4\text{HL}$  (HL = 4-pyridin-4-yl-benzoic acid) with non-interpenetrated 3D *pcu* net was obtained. Notably, the neutral molecular HL species are observed as structure-directing agents, which in turn contribute to the stability of the framework.

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) are unique organic-inorganic hybrids made by organic linkers and inorganic connectors. MOFs have quickly developed into a fruitful research area for their tailorable frameworks and corresponding adsorption and separation properties.<sup>1</sup> They can be identified by three-letter topology symbol like *pcu*,<sup>2</sup> *dia*,<sup>3</sup> *nbo*,<sup>4</sup> *ncb*<sup>5</sup> etc. To some extent, researchers can adjust and modify the structures of MOFs without changing their topology. For example, in an ideal primitive cubic *pcu* net (schläfli symbol,  $4^{12}\cdot 6^3$ , the maximum lattice symmetry is the space group  $Pm\bar{3}m$ ) contains one kind of vertex and one kind of edge. And inorganic single metal ions or cores of  $\text{Cu}_2$ ,  $\text{Zn}_4$  and  $\text{Ln}_4$  incorporating different linear organic ligands with or without side groups have been constructed various octahedral *pcu* net.<sup>6</sup> Besides one kind of linker, two types of linear ligands with different length ratio can also be used to construct *pcu* net.<sup>7</sup> On one hand, the size of the porous can be adjusted by changing the length ratio of the two linkers; On the other hand, similar to the function of the sieve, different shape of the porous will be obtained so as to adsorb and separate multicomponent mixed gases (Scheme 1). In our previous work, linear isonicotinic acid (Hin, length: 4.9 Å) was introduced to construct hydroxyl lanthanide (Ln) cluster organic frameworks.<sup>8</sup> However, the condensed rather than open frameworks are obtained. As continuing exploration to make more open frameworks with potential applications, lengthened Hin, 4-pyridin-4-yl-benzoic acid (HL, length: 9.2 Å) was employed. In addition, we chose the shortest linear bicarboxylate linker, oxalate (length: 2.7 Å), as the second ligands not only for its high coordination capability to the 3d or 4f ions, but also for it may be a good auxiliary candidate benefits the occurrence of *pcu* net.<sup>9</sup> Despite many *pcu* nets have been documented, heterometallic analogues are rarely reported. Fortunately, a heterometallic MOF with *pcu* net based on two types of linear linkers of L and oxalate has been successfully made under hydrothermal condition, formulated as  $[\text{La}_2\text{Cu}_2(\text{ox})_2\text{L}_6]\cdot 4\text{HL}$  (**1**). It is

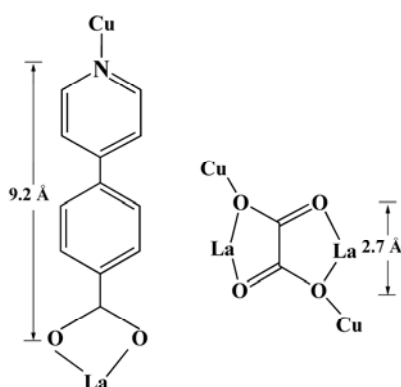


Scheme 1 Scheme representation of the different sizes of the porous supported by two linear linkers.

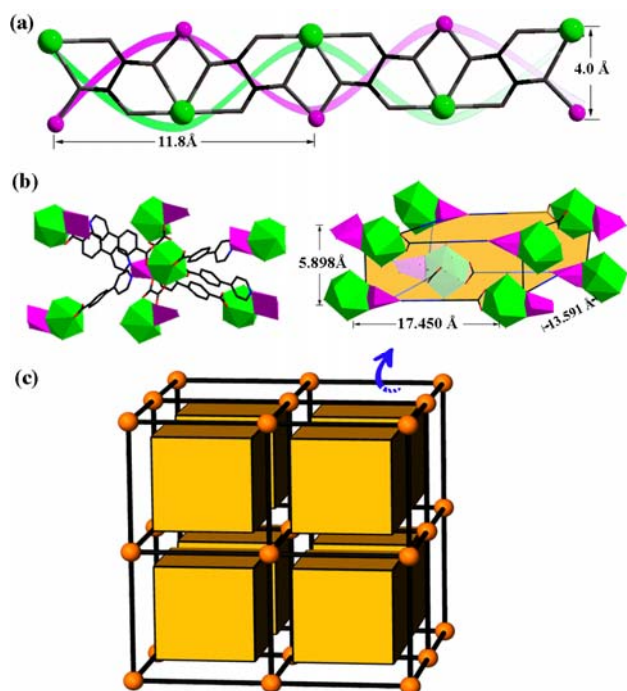
worth noting that latticed HL molecules captured in **1** smartly avoid the interpenetration, which occurs for the available space and stability of the frameworks sometimes in *pcu* net.<sup>6c,7b,9-10</sup>

Blue block crystals of **1** were made by hydrothermal treatment of  $\text{La}_2(\text{ox})_3\cdot 9\text{H}_2\text{O}$ ,  $\text{CuBr}_2$  and HL at 200°C for 6 days in the presence of  $\text{HClO}_4$  (pH = 2).<sup>11</sup> X-ray crystal structure analysis reveals that **1** crystallizes in the monoclinic space group  $P2_1/c$  and features a neutral 3D porous heterometallic framework with non-interpenetrate *pcu* net.<sup>12</sup> In our previous lanthanum oxalate hydrate-copper halide system,<sup>13</sup> the dosage of copper halide is quite a lot, which is beneficial to the formation of copper halide motifs. While in this text,  $\text{Cu}^{2+}$  ions keep their valence state when the amount decreased. The asymmetric unit of **1** contains two  $\text{La}^{3+}$  ions, two  $\text{Cu}^{2+}$  ions, two oxalate, six deprotonated and four free HL ligands (Fig. S1). The metal coordination sphere of  $\text{La}^{3+}$  ions are completed with ten carboxylate oxygen atoms ( $\text{O}_{\text{COO}^-}$ ) from two oxalate and three L anions (Fig. S2). The La-O bond lengths lie between 2.478(8) and 2.753(4) Å (Table S1), which fall into the range of normal values.<sup>14</sup> Attribute to the *pseudo*-Jahn-Teller effect of  $\text{Cu}^{2+}$  ions, the coordination environment of the  $\text{Cu}^{2+}$

ions is best described as distorted square pyramid (Fig. S2), in which the basal plane is defined by three pyridine nitrogen atoms ( $N_{PY}$ ) from three L ligand with Cu-N bond lengths of 2.011(8)-2.025(8) Å, as well as one  $O_{COO^-}$  from an oxalate [Cu-O: 2.001(6) and 2.014(5) Å], and the apical position is occupied by one  $O_{COO^-}$  atom [Cu-O: 2.001(6) and 2.014(5) Å]. In the structure, deprotonated L ligands and oxalate adopt  $\mu-\eta^1:\eta^1$  and  $\mu_4-trans-\eta^1:\eta^2:\eta^1:\eta^2$  fashion, respectively (Scheme 2). Such coordination mode of oxalate is rare according to the Cambridge Crystallographic Data Centre (CCDC) updated to May 2013, though as many as eight metal ions can be simultaneously captured by one oxalate.<sup>15</sup> The  $La^{3+}$  and  $Cu^{2+}$  ions are interlinked by oxalate to afford an infinite heterometallic ribbon-like chain with a width of 4.0 Å (Fig. 1a). The ribbon-like chain can be intuitively viewed as the weave of Ln (green)



Scheme 2 Coordination modes of the ligands in compound 1.



**Fig. 1** (a) Ball-stick view of heterometallic chain along the *b* axis. (b-c) The six-connected node and the pcu topology with cuboidal boxes.

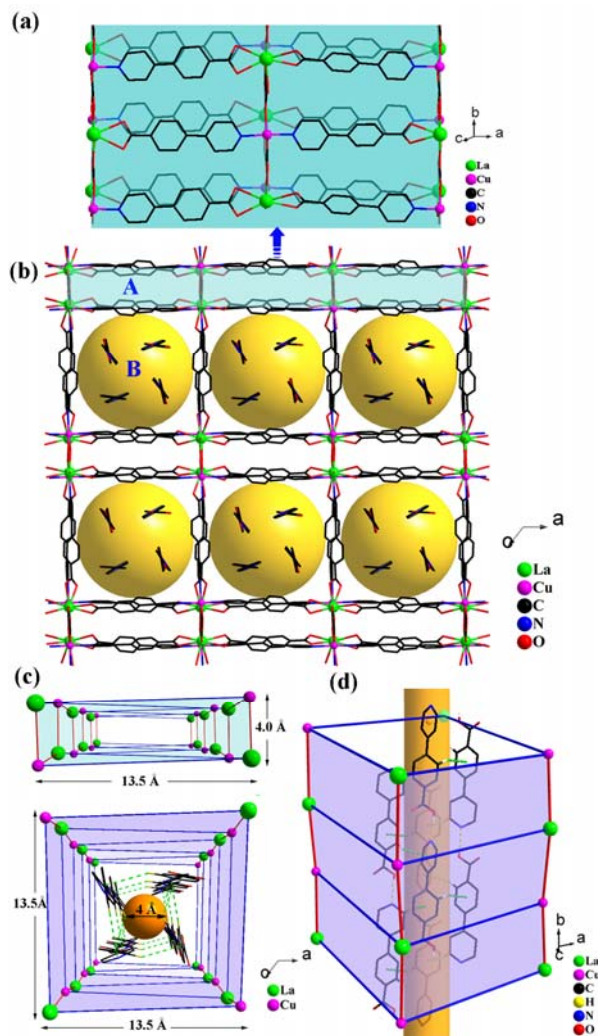
and Cu (pink) chains. And the length of repeated units in this chain is approximately 11.8 Å, which equals to the length of the *b* axis. The rare coordination mode of oxalate makes four

metal ions coplanar to form linear chain rather than zigzag<sup>9,16</sup> or helix<sup>17</sup> chains, which is in favour of the construction of *pcu* net. Then, the weaved ribbon-like chains are double-bridged by L ligands along the *a* axis to form bilayers with a thickness of 4.0 Å (equal to the width of the ribbon-like chain (Fig. 2a, S3). Furthermore, the bilayers are pillared by L ligands to give a 3D open framework (Fig. 2b,S4). From the topology point of view, the overall framework of **1** can be viewed as six-connected *pcu* net (Fig. 1b,c), considering  $La^{3+}$  and  $Cu^{2+}$  ions as nodes, linear oxalate and L ligands as linkers. The distances of the neighbouring nodes are 5.898, 13.591 and 17.450 Å.

One prominent structural feature of the neutral framework is the presence of the two types of regular 4-ring channels, rectangular A and square B, viewing down along the *b* axis (Fig. 2b). Attribute to the size of the lengthened ligands (9.2 Å) and the width of the heterometallic chains (4.0 Å), channel A possess a window size of 4.0 × 13.5 Å (including metal van der Waals radius), and the channel B counterparts is 13.5 × 13.5 Å (Fig. 2c). Besides the deprotonated L ligands in the framework, there are protonated HL neutral molecules served as guest molecules filling in the larger channel B, which is suggested by location of H atoms in the X-ray structure refinement and charge balance. The HL molecules are slightly twisted with a torsion angle between the adjacent phenyl and pyridyl rings. These guest molecules linked each other to define tubular motifs (Fig. 2d), which are further adhesive to the framework *via* weak interaction of hydrogen bonding (Table S2) and  $\pi-\pi$  interaction. The disposition and arrangement of HL found in the channels B may be markedly effected as a result of the confined channel region. The removal of all guest molecular moieties would create an accessible free volume of 5246 Å<sup>3</sup>, or 47.4% of the volume of the unit cell estimated by PLATON software.<sup>18</sup> Similarly, these neutral HL molecules can also be found in our previous report Ln-cluster organic frameworks.<sup>19</sup> In comparison, they are arranged into a pure organic layer, which further linked alternately by Ln layers to generate a 3D supramolecular structure. In fact, considerable uncoordinated natural guest molecules captured *via* weak interactions can also be observed in some MOFs, such as MIL-47,<sup>20</sup> GWMOF-3,<sup>21</sup> [Er<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(hma)(cba)<sub>5</sub>]-Hcba (Hcba = 4-chlorobenzoic acid, H<sub>3</sub>hma = hemimellitic acid),<sup>22</sup> and [Tb(Pidc)(H<sub>2</sub>O)<sub>4</sub>]-H<sub>3</sub>Pidc-4H<sub>2</sub>O (H<sub>3</sub>Pidc = 2-pyridin-4-yl-4,5-imidazole-dicarboxylic acid).<sup>23</sup> It seems that the presences of these organic guests play important roles in the formation of the porous frameworks. “Templating” in zeolites has been well defined by Davis and Lobo early in 1992. They pointed out that the organic guest molecules may act as space-filling species, structure-directing agents, or true templates. Similarly, it can also be extended to templates in MOF systems. Since the true templates are hard to define as they must create unique topologies that are irreproducible when similar molecules are used. So HL molecules in our work can be considered as space-filling species and structure-directing agents.

The good accordance between the experimental and simulated powder X-ray diffraction (PXRD) patterns indicates phase purity of the sample of **1** (Fig. S5). The characteristic feature





**Fig. 2** (a) The top view of the bilayer. (b) The overall framework of **1** with two types of channels. (c) Perspective drawing of channels A and B viewing along the [010] direction. The oxalate and L ligands are represented in red and blue lines for clarity. (d) Schematic representation of the neutral HL in channels B.

of carboxyl dominates the IR spectrum (Fig. S6). The strong vibrations from  $1593\text{ cm}^{-1}$  to  $1313\text{ cm}^{-1}$  are corresponding to the asymmetric and symmetric stretching vibrations of the deprotonated carboxylates, respectively. The vibrations from  $1638$  to  $1711$  and  $3415\text{ cm}^{-1}$  suggest the presence of protonated carboxyls. To investigate the thermal stability of **1**, thermogravimetric analysis (TGA) and temperature-dependent PXRD measurements are carried out. The TGA shows the weight loss from  $30$  to  $500^\circ\text{C}$  corresponding to the release of organic ligands (Fig. S7). Assuming that the residue corresponds to  $\text{La}_2\text{O}_3$  and  $\text{CuO}$ , the observed weight is in good agreement with the calculated value (calcd/found:  $18.9/19.7\%$ ). PXRD patterns of **1** as a function of temperature show that the experimental PXRD heating from room temperature to  $250^\circ\text{C}$  correspond well to the simulated patterns in position, indicating the frameworks of **1** can be stabilized up to  $250^\circ\text{C}$  (Fig. S8). The 3D framework of **1** with large porosity and its thermal stability prompt us to study gas-adsorption properties. Unfortunately, these guest moieties can

not be removed though many efforts of activation have carried out. The UV-vis-IR absorption spectrum is calculated from the data of diffuse reflectance using the Kubelka-Munk function.<sup>24</sup> Besides the local band of the L ligands at  $279\text{ nm}$ , a broad band corresponds to the d-d transition of the  $\text{Cu}^{\text{II}}$  ions is observed at  $700\text{ nm}$ . In their  $F(R)$  and  $E(\text{eV})$  plots, the band gaps are  $3.8\text{ eV}$  (Fig. S9).

In summary, a heterometallic MOF with *pcu* net has been made by two types of linear ligands under hydrothermal conditions. The lengthened ligands are not only served as linkers, but also as structure-directing agents. It can be deduced that mixed linear linkers with different ratio will change the size of the porous, and the more long linkers, the more open framework may be received when effectively to avoid needless interpenetration. Studies on the construction of *pcu* net in the presence of HL ligands with other linear supporting ligands are underway.

## Acknowledgements

This work was supported by the NNSF of China (nos. 91122028, 21221001, and 50872133), the 973 Program (nos. 2014CB932-101 and 2011CB932504), the NNSF for Distinguished Young Scholars of China (no. 20725101).

## Notes and references

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China. Fax: +86-591-83710051; E-mail: ygy@fjirsm.ac.cn.

†Electronic Supplementary Information (ESI) available: X-ray crystallographic file for **1** in CIF format, Table S1,S2, Fig. S1-S9. CCDC reference numbers 967253 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

- (a) H. L. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; (b) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469; (c) J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2011, **112**, 869.
- O. D. Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acta Cryst.*, 2003, **A59**, 22.
- D. Liu, J. P. Lang and B. F. Abrahams, *J. Am. Chem. Soc.*, 2011, **133**, 11042.
- B. L. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4745.
- Y. B. Zhang, H. L. Zhou, R. B. Lin, C. Zhang, J. B. Lin, J. P. Zhang and X. M. Chen, *Nat. Commun.*, 2012, **3**, 1.
- (a) S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2081; (b) X. M. Zhang, Y. Q. Wang, Y. Song and E. Q. Gao, *Inorg. Chem.*, 2011, **50**, 7284; (c) B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath and W. B. Lin, *Angew. Chem., Int. Ed.*, 2005, **44**, 72; (d) J. Xu, W. P. Su and M. C. Hong, *Cryst. Growth Des.*, 2011, **11**, 337.
- (a) L. Sun, L. Ma, J. B. Cai, L. Liang and H. Deng, *CrystEngComm*, 2012, **14**, 890; (b) Y. Gong, J. Li, J. B. Qin, T. Wu, R. Cao and J. H. Li, *Cryst. Growth Des.*, 2011, **11**, 1662; (c) Z. Z. Li, L. Du, J. Zhou, L. Li, Y. Hu, Y. F. Qiao, M. J. Xie and Q. H. Zhao, *New J. Chem.*, 2013, **37**, 2473; (d) F. H. Zhao, Y. X. Che and J. M. Zheng, *Inorg. Chem. Commun.*, 2012, **16**, 55.
- (a) M. B. Zhang, J. Zhang, S. T. Zheng and G. Y. Yang, *Angew. Chem., Int. Ed.*, 2005, **44**, 1385; (b) J. W. Cheng, J. Zhang, S. T. Zheng, M. B. Zhang and G. Y. Yang, *Angew. Chem., Int. Ed.*, 2006, **45**, 73; (c) J. W. Cheng, J. Zhang, S. T. Zheng and G. Y. Yang, *Chem.-Eur. J.*, 2008, **14**, 88.
- Z. Y. Li, J. W. Dai, N. Wang, H. H. Qiu, S. T. Yue and Y. L. Liu, *Cryst. Growth Des.*, 2010, **10**, 2746.

10. I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2008, **10**, 1822.
11. Synthesis of **1**: A mixture of  $\text{La}_2(\text{Ox})_3 \cdot 9\text{H}_2\text{O}$  (0.2 mmol, 0.141 g),  $\text{CuBr}_2$  (0.2 mmol, 0.045 g), HL (2 mmol, 0.398 g),  $\text{H}_2\text{O}$  (10.0 mL, 0.22 mmol) and three drops of  $\text{HClO}_4$  with the pH value of about 2.0 was sealed in a 30 mL Teflon-lined bomb at 200°C for 6 days, and then cooled to room temperature. Blue block crystals of **1** were recovered by filtration, washed with distilled water and dried at ambient temperature (Yield 27% based on  $\text{La}(\text{ox})_3 \cdot 9\text{H}_2\text{O}$ ). Anal. Calcd. for  $\text{C}_{124}\text{H}_{84}\text{Cu}_2\text{La}_2\text{N}_{10}\text{O}_{28}$ : C 58.02, H 3.30, N 5.46 Found: C 57.53, H 3.46, N 5.79.
12. Crystal data for **1**:  $\text{C}_{124}\text{H}_{84}\text{Cu}_2\text{La}_2\text{N}_{10}\text{O}_{28}$ ,  $M_r = 2566.93$ , monoclinic,  $P2_1/c$ ,  $a = 27.130(5)$  Å,  $b = 11.761(2)$  Å,  $c = 43.999(1)$  Å,  $\beta = 128.01(2)^\circ$ ,  $V = 11061(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.541$  g cm<sup>-3</sup>,  $\mu = 1.220$  mm<sup>-1</sup>,  $F(000) = 5175$ , GOF = 1.028. Of total 70548 reflections collected, 24874 are unique ( $R_{\text{int}} = 0.0629$ ).  $R_1/wR_2 = 0.0879/0.2419$  for 19645 reflections and 1494 parameters ( $I > 2\sigma(I)$ ).
13. W. H. Fang, J. W. Cheng and G. Y. Yang, *Chem.-Eur. J.*, 2014, **20**, doi: 10.1002/chem.201304165.
14. (a) J. W. Cheng, S. T. Zheng and G. Y. Yang, *Dalton Trans.*, 2007, 4059; (b) J. W. Cheng, S. T. Zheng, W. Liu and G. Y. Yang, *CrystEngComm*, 2008, **10**, 765.
15. Q. Chen, S. C. Liu and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1724.
16. H. Y. Zhao, J. W. Zhao, B. F. Yang, H. He and G. Y. Yang, *CrystEngComm*, 2013, **15**, 5209.
17. R. S. Vilela, T. L. Oliveira, F. T. Martins, J. A. Ellena, F. Lloret, M. Julve and D. Cangussu, *C. R. Chim.*, 2012, **15**, 856.
18. A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, 2001.
19. W. H. Fang, L. Cheng, L. Huang and G. Y. Yang, *Inorg. Chem.*, 2013, **52**, 6.
20. K. Barthelet, J. Marrot, D. Riou and G. Ferey, *Angew. Chem., Int. Ed.*, 2002, **41**, 281.
21. D. T. de Lill, N. S. Gunning and C. L. Cahill, *Inorg. Chem.*, 2005, **44**, 258.
22. X. Li, Y. Huang and R. Cao, *CrystEngComm*, 2012, **14**, 6045.
23. L. Sun, G. Z. Li, M. H. Xu, X. J. Li, J. R. Li and H. Deng, *Eur. J. Inorg. Chem.*, 2012, 1764.
24. (a) P. Kubelka and F. Z. Munk, *Tech. Phys.*, 1931, **12**, 593; (b) W. W. Wendlandt and H. G. Hecht, *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966.

Entry for the Table of Contents:

Cooperation of two linear organic ligands under hydrothermal conditions results in the formation of a porous heterometal-organic framework with two types of channels.

