

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

Synthesis, characterization, and luminescence modulation of a rare barium-tetracarboxylate framework with I^2O^1 connectivity

Xiao Chen^a Sha He^a Feiyan Chen^a Yunlong Feng^{*a}

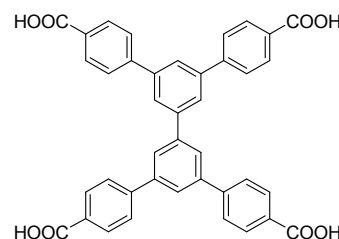
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Solvothermal reaction of a tetracarboxylic acid with $Ba(NO_3)_2$ afforded a barium-organic framework whose single crystal X-ray structure was characterized to have I^2O^1 connectivity and 1D channels of 15.1 Å in diameter. The luminescence intensity of this MOF can be modulated by ion exchange.

Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are crystalline solids consisting of metal ions/clusters connected to multidentate organic ligands via coordination bonds. Ever-increasing interest in the design and synthesis of MOFs stems not only from their aesthetic architectures and topologies,¹ but also from their possible potential applications such as gas storage/separation, catalysis, ion conductivity, drug delivery, and so on.²⁻¹⁷ Most of the current research is mainly focused on MOFs based on the transition metal or rare earth ions. However, using barium ion, one of the alkaline earth metal ions, as the coordination center is less explored but recently received much more research attention. This is because the barium ion has relatively larger radius and is strongly oxophilic, which provides unique opportunities for the formation of diverse inorganic-organic hybrids exhibiting rich structural topologies, good thermal stabilities, and interesting properties. For example, Kitagawa *et al.*¹⁸ have synthesized three barium based MOFs with varied inorganic connectivities, and concluded that barium ion is a structurally malleable metal ion with respect to constructing frameworks.

To target MOFs with desired structures and properties, design and synthesis of organic linkers are also very critical. Among the diverse organic linkers, those containing carboxylate groups, including dicarboxylate, tricarboxylate, tetracarboxylate, hexacarboxylate and octacarboxylate, have been widely employed to synthesize new MOFs because of their preference to stabilize the MOFs through *in situ* formed secondary building units (SBUs).¹⁷ For barium carboxylate frameworks, those based on tetatopic carboxylic acid ligands are still less explored. Therefore, a tetracarboxylic acid, biphenyl-3,3',5,5'-tetra(phenyl-4-carboxylic acid) (H_4L , Scheme 1), was selected specifically as an organic ligand in this work. It is noteworthy that only two MOFs based on this ligand have been reported to date.^{19, 20} Using this ligand, a porous barium tetracarboxylate framework with I^2O^1 connectivity was successfully constructed. Interestingly, the luminescence intensity of the resultant MOF can be modulated by post-synthetic ion exchange.



Scheme 1 The ligand used to construct the barium carboxylate framework.

The ligand H_4L was readily synthesized by Suzuki cross coupling reaction of 3,3',5,5'-tetrabromobiphenyl and (4-methoxycarbonyl)phenyl boronic acid followed by hydrolysis and acidification in good yield. Detailed experimental procedures are presented in the supporting information. The MOF $[Ba_5(L)_3(H_2O)_6] \cdot 25H_2O \cdot 10DMF \cdot 2Me_2NH_2^+$ was obtained as colourless block-shaped crystals via a solvothermal reaction of $Ba(NO_3)_2$ and H_4L in *N,N*-dimethyl formamide (DMF)/ H_2O mixed solvent at 140 °C for 48 h. The formula was established on the basis of single-crystal X-ray diffraction studies, thermogravimetric analysis (TGA, Fig. S1), and microanalysis. The free solvent molecules and counterions have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.²¹ The experimental powder X-ray diffraction (PXRD, Fig. S2) pattern of as-synthesized compound is in good agreement with the one simulated from single-crystal X-ray diffraction data, indicating that the as produced sample is phase pure.

Single-crystal X-ray diffraction studies reveal that the compound is a three-dimensional (3D) framework which

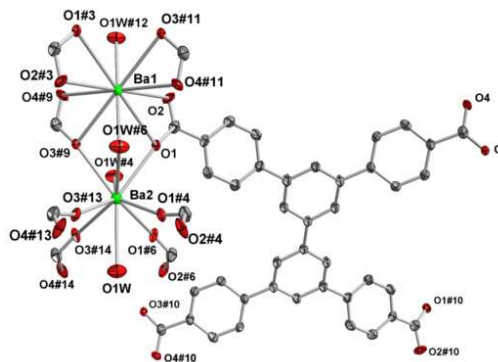


Fig. 1 View of the coordination environments of Ba(II) ions (symmetry codes are the same as Table S2).

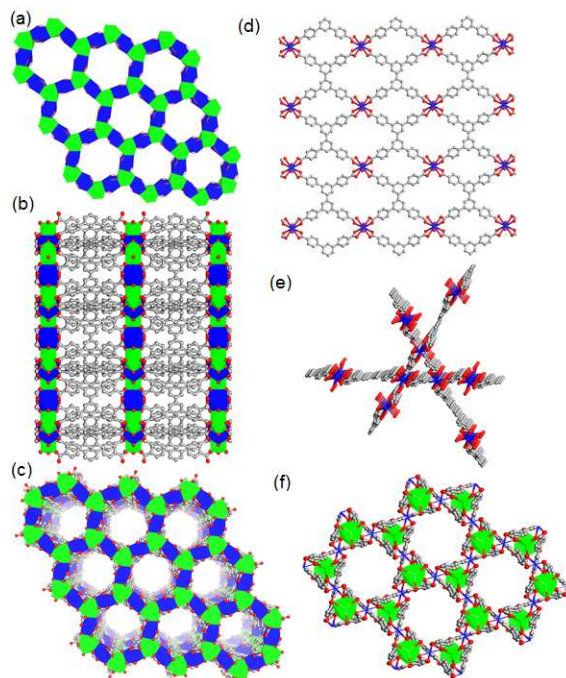


Fig. 2 2D inorganic Ba-O-Ba layers (a) were connected by tetracarboxylates (b) to form 1D honeycomb-like channels along the *c* direction (c). Three sets of 2D layer (d) formed by Ba1 ions and the ligands catenate to each other in a parallel-parallel arrangement to form a 2D + 2D → 3D inclined polycatenation structure (e), which are further joined together *via* Ba2 ions, shown in green polyhedra (f).

crystallizes in a hexagonal centrosymmetric space group *P6/m* with unit cell parameters $a = b = 15.0263 \text{ \AA}$, and $c = 17.6363 \text{ \AA}$.

The asymmetric unit contains five-twelfths of crystallographically independent barium Ba(II) ions, one fourth of fully deprotonated L^4 ligand, a half of the bridging water molecule, one sixth of $(Me_2NH_2^+)_2$ counterions, five-sixths of free DMF solvent molecules, and two and one-twelfth of water molecules. The ligand is almost planar with a dihedral angle of 0.93° between the central benzene rings. All four carboxylate groups of the organic linker adopt the same coordination modes ($\mu_2-\eta^2:\eta^1$), which has been observed in previously reported barium coordination polymer $[Ba_{1.5}(BPTC)(NMF)_2]_n$ (BPTC = biphenyl tricarboxylate; NMF = *N*-methyl formamide).²² As shown in Fig. 1, Ba1 ions are coordinated to ten oxygen atoms from four different carboxylate groups of four different ligands and two bridging water molecules, to afford a distorted $\{BaO_{10}\}$ bicapped square-antiprism geometry; while Ba2 ions are nine-coordinated with the coordination sites occupied by six different carboxylate oxygen atoms from six different ligands and three bridging water molecules, furnishing a distorted $\{BaO_9\}$ tricapped trigonal prismatic geometry. The Ba1-O bond lengths range from 2.815 to 2.888 \AA , and the Ba2-O distances are in the range of 2.775 to 2.971 \AA , which are comparable to those reported for ten- and nine-coordinated Ba(II) ions, respectively.^{18, 22, 23} Each $\{BaO_{10}\}$ polyhedron connects two neighbouring $\{BaO_9\}$ polyhedra, and each $\{BaO_9\}$ polyhedron connects with three neighbouring $\{BaO_{10}\}$ polyhedra *via* face sharing. These connectivities link the polyhedra into a beautiful 2D honeycomb-

like inorganic layer in the crystallographic *ab* plane (Fig. 2a). To the best of our knowledge, such a 2D inorganic connectivity was not observed in the barium based MOFs reported thus far. The interlayer separation is 17.63 \AA , and these layers are further joined by the ligand along the crystallographic *c* axis to form a noninterpenetrated 3D framework (Fig. 2b). There exist 1D honeycomb-like channels running parallel to the crystallographic *c* axis (Fig. 2c), with the pore diameter of *ca.* 15.1 \AA in diameter, which are occupied by free solvents, and the charge-balancing counterions $(Me)_2NH_2^+$ originating from *in situ* decomposition of the DMF solvent during the solvothermal reaction. The guest-accessible void volume, as calculated by PLATON software, is 34% after removal of the free solvent and counterions.

Alternatively, if one does not consider the Ba2 ions, each L^4 ligand connects four Ba1 ions and each Ba1 ion connects four ligands to form a 2D layer (Fig. 2d). There are three sets of layers oriented towards different directions. These three sets of layers catenate to each other in a parallel-parallel arrangement to form a 2D + 2D → 3D inclined polycatenation structure (Fig. 2e). The dihedral angle of the interpenetrated 2D layers is *ca.* 60° . Furthermore, these interpenetrated layers are coordinatively joined together by Ba2 ions to form a noninterpenetrated network (Fig. 2f).

One way of classifying coordination polymers has been proposed by Rao and Cheetham²⁴ by considering their inorganic and organic connectivity, *i.e.*, I^mO^n . I^m is the dimensionality of the inorganic connectivity, and O^n is the dimensionality of the organic connectivity. The sum of $(m + n)$ is the overall connectivity and must be less than or equal to 3. Thus, the compound has I^2O^1 connectivity. From the topological viewpoint, if Ba1 and Ba2 ions are taken as 6-connected and 3-connected nodes, respectively, and the bridging organic linker is considered as having two three-coordinated branch points, the overall 3D framework has a novel (3,3,6)-coordinated net with Schläfli topological symbol of $\{4\cdot6\}_6\{4^2\cdot6^2\cdot7^5\cdot8^6\}_3\{7^3\}_2$ (Fig. 3).

In order to evaluate the thermal stability, TG analysis was performed under flowing N_2 atmosphere with a heating rate of 5 $^\circ\text{C min}^{-1}$ in the temperature range of 30 to 1000 $^\circ\text{C}$ (Fig. S1). The first weight loss of 40.6% occurs in the temperature range of 30-540 $^\circ\text{C}$, approximately corresponding to the release of the solvent molecules. Above this temperature, the compound starts to decompose gradually. The high decomposition temperature is comparable to that of the benchmark MOF UiO-66²⁵ discovered by Cavka *et al.* featuring a decomposition temperature up to 500 $^\circ\text{C}$, which might be mainly attributed to the high inorganic connectivity ($m = 2$). Although the compound possesses a high decomposition temperature as evidenced from the TG analysis above, varied temperature XRD studies showed that the compound lost its integrity above 150 $^\circ\text{C}$ (Fig. S3). Such an inconsistency was also found in some reported literatures.¹⁸

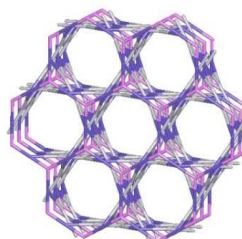


Fig. 3 The (3,3,6)-connected topological net with the Schläfli symbol of $\{4\cdot6^2\}_6\{4^2\cdot6^2\cdot7^5\cdot8^6\}_3\{7^3\}_2$

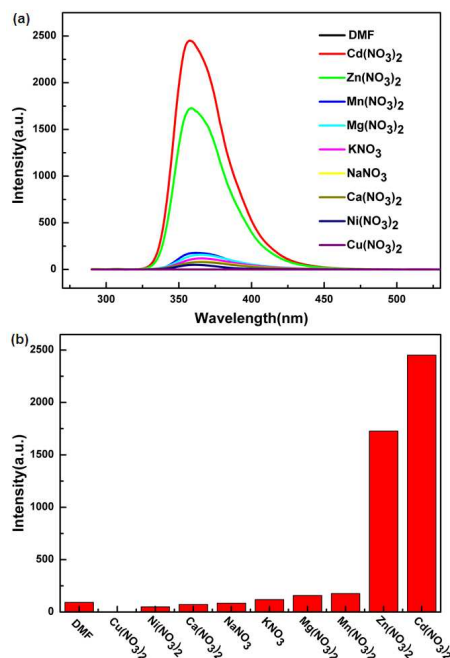


Fig. 4 Comparison of the luminescence intensity of the compound at 363 nm after ion exchange with different metal ions (excited at 281 nm).

Considering that the MOFs are very promising luminescent materials because both the inorganic and organic components constituting MOFs can provide platforms to generate luminescence, the luminescence properties of the compound and the free ligand in the solid state were investigated at room temperature (Fig. S4). The ligand exhibits a broad luminescence peak centered at 391 nm when excited at 357 nm, which is probably assigned to π or n to π^* transitions, while two emission peaks were observed for the compound under the same excitation, which are located at 373 nm and 441 nm, respectively. The first emission band is similar to that of the free ligand, which can probably be attributed to the interligand fluorescence emission. A new secondary peak observed at 441 nm could be due to emission from barium as reported for [Ba(BDCD)(H₂O)₂].²²

Most remarkably, the luminescence intensity of the compound can be modulated by ion exchange. The as-synthesized sample was impregnated in 0.1 M DMF solution of various metal salts such as NaNO₃, KNO₃, Mg(NO₃)₂, Ca(NO₃)₂, Mn(NO₃)₂, Ni(NO₃)₂, Cu(NO₃)₂, Zn(NO₃)₂, and Cd(NO₃)₂ for 24 h, filtered and washed with fresh DMF to obtain the ion exchanged samples. The PXRD patterns collected for each ion exchanged samples show that the crystalline structure remains almost unaltered and is consistent with that of the parent material. Before luminescence measurement, the samples were prepared as emulsions by sonication treatment of 3 mg of as-synthesized compound in 25 mL of 0.1 M of different metal salts in DMF. Their luminescent spectra were recorded under the same conditions. Luminescence quenching was found for Cu²⁺-exchanged samples. However, notably, the luminescent intensities were significantly enhanced for Zn²⁺ and Cd²⁺-exchanged samples. The origin for the luminescence enhancement is still unclear. We speculated that Zn²⁺/Cd²⁺ ions

significantly reduced the conformational flexibility of the compound *via* complexation with oxygen atoms of the ligands or the bridging water molecules within the compound, and slowed down the non-radiative decay of the intraligand excited state. These results are different with the behaviour observed for the most reported MOF materials where the luminescence intensity was quenched by transition ions. However, such luminescence enhancement has been also observed with respect to organic small molecules or organic polymers based sensors, upon complexation with d¹⁰ metal ions.²⁶⁻²⁸

Although there exists a large channel, repeated attempts to establish the permanent porosity *via* the conventional solvent exchange followed by evacuation were not successful (Fig. S5). We are taking advantage of the mild activation methods such as supercritical CO₂ drying or freeze drying to activate the compound.

In summary, we synthesized a new tetracarboxylic acid ligand and used it as ligand to construct a rare barium carboxylate framework with I²O¹ connectivity. The luminescence of the compound can be modulated by post-synthetic ion exchange. It is expected that the compound can be used as a promising luminescent sensing material in the near future.

This work is financially supported by the National Nature Science Foundation of China (No.21173197)

Notes and references

^a Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, China.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Synthesis of [Ba₃(L)₃(H₂O)₆]-25H₂O-10DMF-2Me₂NH₂⁺. In a 20 mL vial containing Ba(NO₃)₂ (30.0 mg, 44.5 μmol) and H₄L (10.0 mg, 15.7 μmol), 4 mL of 1:1 DMF/H₂O solution was added to yield a white suspension. The vial was then sealed with a Teflon-lined cap and heated at 140 °C for 48 h. The colorless block-shaped crystals were collected and washed with DMF and dried in air to give the product; 26.1 % yield (based on H₄L). Elemental analysis (percentage calculated/found): for C₁₅₄H₂₁₄Ba₃N₁₂O₆₅ (C 46.7/47.1, H 5.40/5.44, N 4.24/4.30).

Crystal data for [Ba₃(L)₃(H₂O)₆]-25H₂O-10DMF-2Me₂NH₂⁺: hexagonal, P6/m, *a* = *b* = 15.0263(3) Å, *c* = 17.6363(6) Å, *V* = 3448.59(15) Å³, *M_r* = 3960.07, *Z* = 1, *D_c* = 1.907 g·cm⁻³, μ (mm⁻¹) = 1.522, *F*(000) = 2022, *R*(*wR*) = 0.0504 (0.1651) for 1973 observed reflections with *I* > 2σ(*I*), *R*(*wR*) = 0.0772(0.1785) for all data. CCDC 1001306.

- M. Li, D. Li, M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2014, **114**, 1343-1370.
- Y. He, W. Zhou, G. Qian and B. Chen, *Chem. Soc. Rev.*, 2014, **43**, 10.1039/c1034cs00032c.
- Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126-1162.
- M. Zhao, S. Ou and C.-D. Wu, *Acc. Chem. Res.*, 2014, 10.1021/ar400265x.
- P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232-1268.
- J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869-932.
- J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450-1459.
- J.-P. Zhang, Y.-B. Zhang, J.-B. Lin and X.-M. Chen, *Chem. Rev.*, 2012, **112**, 1001-1033.
- H. Wu, Q. Gong, D. H. Olson and J. Li, *Chem. Rev.*, 2012, **112**, 836-868.

10. S. Horike, S. Shimomura and S. Kitagawa, *Nature Chem.*, 2009, **1**, 695-704.
11. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724-781.
- 5 12. Y. Yan, S. Yang, A. J. Blake and M. Schröder, *Acc. Chem. Res.*, 2013, 10.1021/ar400049h.
13. P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80-84.
- 10 14. M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2012, **112**, 782-835.
- 15 15. H.-L. Jiang and Q. Xu, *Chem. Commun.*, 2011, **47**, 3351-3370.
16. C. Hou, Q. Liu, T.-a. Okamura, P. Wang and W.-Y. Sun, *CrystEngComm*, 2012, **14**, 8569-8576.
17. Y. He, B. Li, M. O'Keeffe and B. Chen, *Chem. Soc. Rev.*, 2014, **43**, 10.1039/c1034cs00041b.
18. M. L. Foo, S. Horike, J. Duan, W. Chen and S. Kitagawa, *Cryst. Growth Des.*, 2013, **13**, 2965-2972.
- 20 19. J. Cai, J. Yu, H. Xu, Y. He, X. Duan, Y. Cui, C. Wu, B. Chen and G. Qian, *Cryst. Growth Des.*, 2013, **13**, 2094-2097.
20. S. Yang, L. Liu, J. Sun, K. M. Thomas, A. J. Davies, M. W. George, A. J. Blake, A. H. Hill, A. N. Fitch, C. C. Tang and M. Schröder, *J. Am. Chem. Soc.*, 2013, **135**, 4954-4957.
- 25 21. A. L. Spek, *Acta Cryst.*, 2009, D65, 148-155.
22. X. Zhang, Y.-Y. Huang, M.-J. Zhang, J. Zhang and Y.-G. Yao, *Cryst. Growth Des.*, 2012, **12**, 3231-3238.
23. R. Murugavel, V. V. Karambelkar, G. Anantharaman and M. G. Walawalkar, *Inorg. Chem.*, 2000, **39**, 1381-1390.
- 30 24. Anthony K. Cheetham, C. N. R. Rao and R. K. Feller, *Chem. Commun.*, 2006, 4780-4795.
25. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850-13851.
- 35 26. F. Song, X. Ma, J. Hou, X. Huang, Y. Cheng and C. Zhu, *Polymer*, 2011, **52**, 6029-6036.
27. C.-H. Hung, G.-F. Chang, A. Kumar, G.-F. Lin, L.-Y. Luo, W.-M. Ching and E. W.-G. Diau, *Chem. Commun.*, 2008, 878-980.
28. N. C. Lim and C. Brückner, *Chem. Commun.*, 2004, 1094-1095.

40

CrystEngComm Accepted Manuscript

Abstract

Solvothermal reaction of a tetracarboxylic acid with $\text{Ba}(\text{NO}_3)_2$ afforded a barium-organic framework whose single crystal X-ray structure was characterized to have I^2O^1 connectivity and 1 D channels of 15.1 Å in diameter. This MOF has high thermal stability up to 540 °C, and its luminescence intensity can be modulated by ion exchange.