

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/259955500>

The photoluminescence and gas sorption properties of three Cd(II) MOFs based on 1,3,5-benzenetribenzoate with -NH₂ or -OH groups

ARTICLE *in* DALTON TRANSACTIONS · JANUARY 2014

Impact Factor: 4.2 · DOI: 10.1039/c3dt52940a · Source: PubMed

CITATIONS

12

READS

39

3 AUTHORS, INCLUDING:



Fei Wang

Chinese Academy of Sciences

72 PUBLICATIONS 1,415 CITATIONS

SEE PROFILE

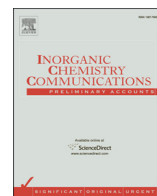


Jian Zhang

Fudan University

690 PUBLICATIONS 12,945 CITATIONS

SEE PROFILE



Synthesis and characterization of homo- and heterometallic metal–organic frameworks based on 1,2,4,5-benzenetetracarboxylate ligand

E. Yang^{a,b,*}, Qing rong Ding^{a,b}, Yao Kang^b, Fei Wang^{b,*}

^a College of Chemistry and Chemistry Engineering, Fujian Normal University, Fuzhou, Fujian 350007, People's Republic of China

^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

ARTICLE INFO

Article history:

Received 18 July 2013

Accepted 29 August 2013

Available online 5 September 2013

Keywords:

MOFs

Zinc

Lithium

Topology

Photoluminescence

Crystal structure

ABSTRACT

Two new three-dimensional metal–organic frameworks, $[\text{H}_2\text{N}(\text{CH}_3)_2]_2[\text{Zn}(\text{btec})]\cdot\text{DMF}$ (**1**, H_4btec = 1,2,4,5-benzenetetracarboxylate acid) and $[\text{H}_2\text{N}(\text{CH}_3)_2][\text{ZnLi}(\text{btec})]\cdot\text{DMF}$ (**2**), have been solvothermally synthesized and structurally characterized by single crystal X-ray diffraction. Compound **1** based on μ_4 -btec features an anionic homometallic framework with 4-connected **pts** topology. Compound **2** is a heterometallic organic framework with rare (4, 4, 8)-connected network topology, which can be considered as constitute of a Li-btec (**pts**) net and a Zn-btec net. Moreover, the luminescent properties of two compounds are investigated in the solid state at room temperature.

© 2013 Elsevier B.V. All rights reserved.

Metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) have attracted much attention not only for their potential applications in gas storage, separation, sensing and heterogeneous catalysis, but also for fascinating architectures and intriguing topologies [1]. The architectures of MOFs are mainly depended on the assembly of metals and linkers. As we know, some famous framework materials such as MOF-5, ZIF-8 and HZIFs, are all based on the assembly of Zn cation [2]. In MOF-5, a cationic oxide-centered Zn_4O tetrahedron is edge-bridged by six carboxylates to give the neutral octahedron-shaped SBU that reticulates into a three-dimensional (3D) cubic porous network with pcu type topology [2a]. Indeed, the design strategy in many ZIFs (zeolitic imidazolate frameworks) uses tetrahedral Zn^{2+} centers linked by different uninegative imidazolate derivatives, forming 4-connected zeolite-like structures [2b,3]. As mentioned above, most of these frameworks are homometallic materials, and the heterometallic framework materials are relatively less reported, especially Zinc–alkali metal heterometallic complexes.

In this work, we reported two new three-dimensional homometallic and heterometallic MOFs $[\text{H}_2\text{N}(\text{CH}_3)_2]_2[\text{Zn}(\text{btec})]\cdot\text{DMF}$ (**1**, H_4btec = 1,2,4,5-benzenetetracarboxylate acid) and $[\text{H}_2\text{N}(\text{CH}_3)_2][\text{ZnLi}(\text{btec})]\cdot\text{DMF}$ (**2**). Compound **1** based on μ_4 -btec and tetrahedral building unit features a three-dimensional (3D) anionic framework with 4-connected **pts** topology. Compound **2** is a heterometallic organic framework with trinodal (4, 4, 8)-connected network topology, which can be simplified as constitute of a Li-btec (**pts**) net and a Zn-btec net. Although the

simple Li-btec or Zn-btec system has been largely explored during the last decade [4], no mixed Zn–btec–Li structures are known to date. In addition, the luminescent properties of these compounds were investigated in the solid state at room temperature.

Compound **1** was solvothermally synthesized by employing $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and H_4btec ligands in mixed $\text{N,N}'$ -dimethylformamide (DMF) and 1,3-dimethyl-2-imidazolidinone (DMI) solvents [5]. Such mixed solvents provide not only proper templates for the formation of pores, but also the charge-balancing $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ cations which are in situ generated by the decomposition of DMF [7]. X-ray crystallography reveals that compound **1** has a 3D anionic open framework constructed from Zn atoms and μ_4 -btec ligands, which is charge-balanced by $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ cations [8].

The asymmetric unit of **1** includes one half Zn^{2+} center, one half btec ligand and one $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ cation, respectively. As depicted in Fig. 1a, The Zn cation has the distorted tetrahedral coordination geometry and is coordinated by four O atoms from four carboxylate groups of four btec ligands. The Zn–O distances are ranging from 1.950(2) to 1.973(2) Å. In compound **1**, there is one independent btec ligand and adopts the μ_4 -bridging mode with four carboxylate groups being a unidentate fashion (Fig. 1a). The μ_4 -btec ligands link Zn atoms to generate a 3D anionic framework exhibiting 1D channels (Fig. 1b), occupied by the disordered guest molecules as well as $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ cations to balance charge. From the viewpoint of structural topology, each Zn unit and each μ_4 -btec ligand can be viewed as a 4-connected node, respectively (Fig. 1c); thus, the whole framework of **1** can be simplified to a 4-connected **pts** net (Fig. 1d).

When the Li_2CO_3 was added to the synthesis system of **1**, a new 3D heterometallic framework **2** was obtained. The compound **2** crystallizes

* Corresponding authors.

E-mail addresses: yangeli66@yahoo.com.cn (E. Yang), wangfei04@fjirsm.ac.cn (F. Wang).

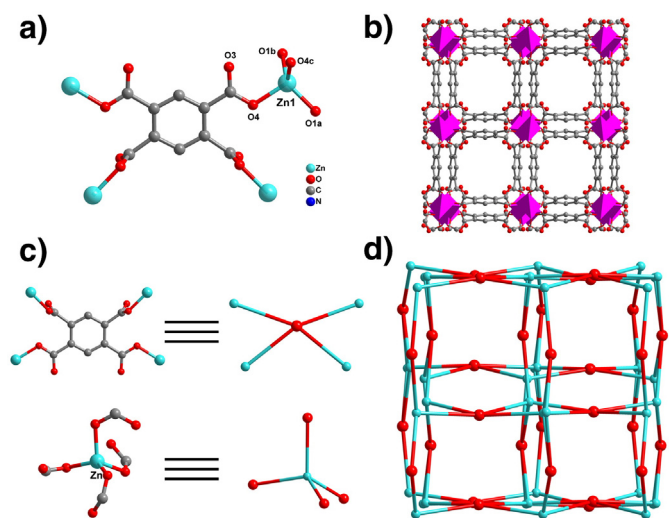


Fig. 1. (a) The coordination environment in **1** (Symmetry codes: a, $x, -y + 1, -z$; b, $y - 1/4, -x + 3/4, z + 1/4$; c, $-y + 3/4, -x + 3/4, -z + 1/4$); (b) the 3D framework of **1**; (c) the defined 4-connected nodes; (d) the 4-connected **pts** net of **1**.

in the orthorhombic space group *Fddd*. The asymmetric unit of **2** contains one crystallographically independent Zn center, one half Li1, one half Li2, one btec ligand and one $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ cation, respectively. As shown in Fig. 2a, The Zn center has the distorted tetrahedral coordination environment with ZnO_4 donor set by four O atoms from four carboxylate groups of four btec ligands. The Zn–O distances are ranging from 1.924(2) to 1.975(2) Å and both Li1 and Li2 cations also have the same distorted tetrahedral coordination environment, which is surrounded by four O atoms from four different carboxylate

groups of btec ligands. The Li–O distances are ranging from 1.926(2) to 2.005(2) Å. In comparison to **1**, the Li^+ cations participate in the assembly of **2**, meanwhile they replace parts of $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ cations to balance charge. Compound **2** also has one independent btec ligand, but it adopts the μ_8 -bridging mode with four carboxylate groups being a bidentate fashion (Fig. 2a), coordinating to four Zn atoms and four Li atoms. The μ_8 -btec ligands link Zn and Li atoms to generate a 3D anionic framework exhibiting 1D channels (Fig. 2c), occupied by the disordered guest molecules as well as $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ cations to balance charge.

An outstanding structural feature of **2** is the presence of the integrated topological nets. Topological analysis was performed by using Topos program [9,10]. As shown in Fig. 3a, each Li atom can be reduced to a 4-connected node, each Zn atom is also regarded as a 4-connected node, and each μ_8 -btec ligand can be viewed as an 8-connected node, so the whole framework of **2** can be considered as a rare trinodal (4, 4, 8)-connected network topology (Fig. 3d). The Point (Schläfli) symbol of this net is $(4^5 \cdot 6)_2(4^{10} \cdot 6^6 \cdot 8^{12})$. Considering that the structure of **2** contains two metal centers, to further simplify this complicated topological net, it is easy to divide the whole structure into two parts. Interestingly, if only the connectivity between Li atoms and btec ligands is considered, a 3D Li-btec framework is formed. Such a Li-btec framework can be reduced into a 4-connected **pts** net as well as the topological net of **1** (Fig. 3b). Following the same consideration, the simple connectivity between Zn atoms and btec ligands becomes a binodal (4, 4)-connected net with Point (Schläfli) symbol of $(4^2 \cdot 8^4)(4^2 \cdot 8^3 \cdot 10)$ (Fig. 3c). The final framework of **2** is thus a constitute of a Li-btec net and a Zn-btec net.

Powder X-ray diffraction (PXRD) was measured to confirm the phase purity and to examine the crystallinity of bulk sample (Fig. 4). The simulative (black line) and experimental (red line) X-ray powder diffraction patterns for compound **1** and compound **2** are compared,

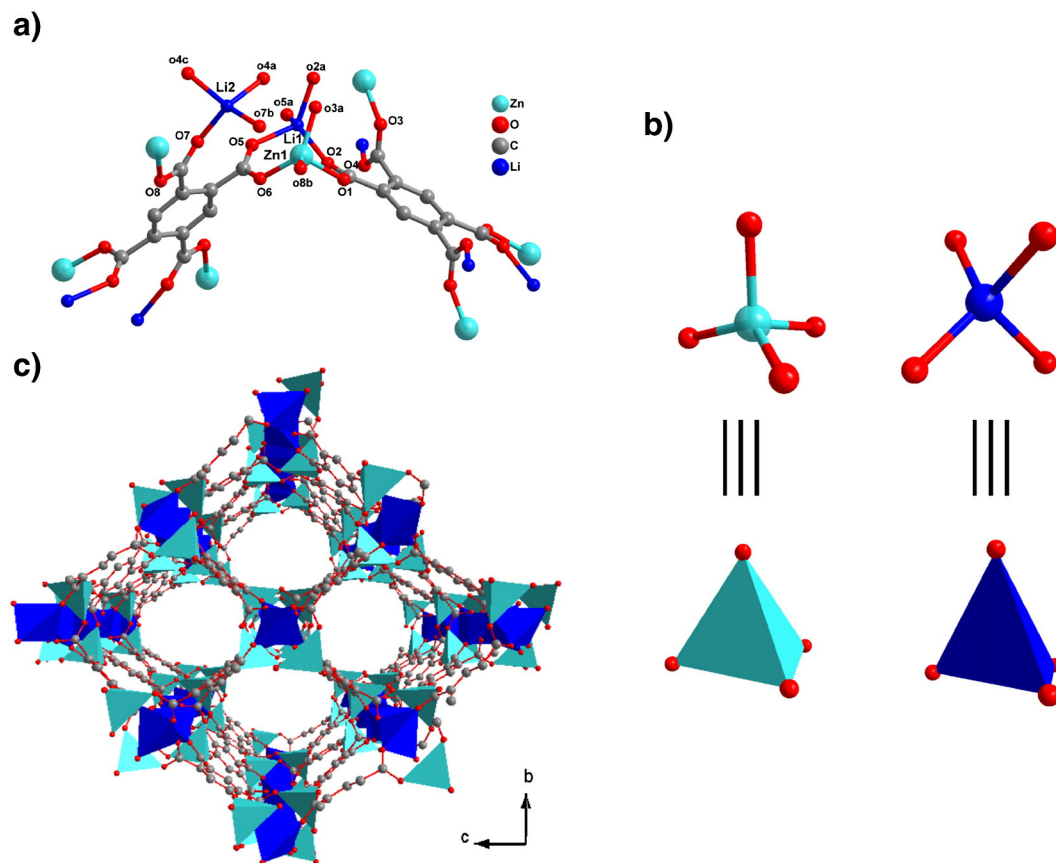


Fig. 2. (a) The coordination environment in **2** (Symmetry codes: a, $-x - 1/4, -y + 3/4, z$; b, $-x + 1/4, y, -z + 1/4$; c, $x + 1/2, -y + 3/4, -z + 1/4$); (b) the distorted tetrahedral coordination mode of Zn and Li cations in **2**; (c) the 3D framework of **2**.

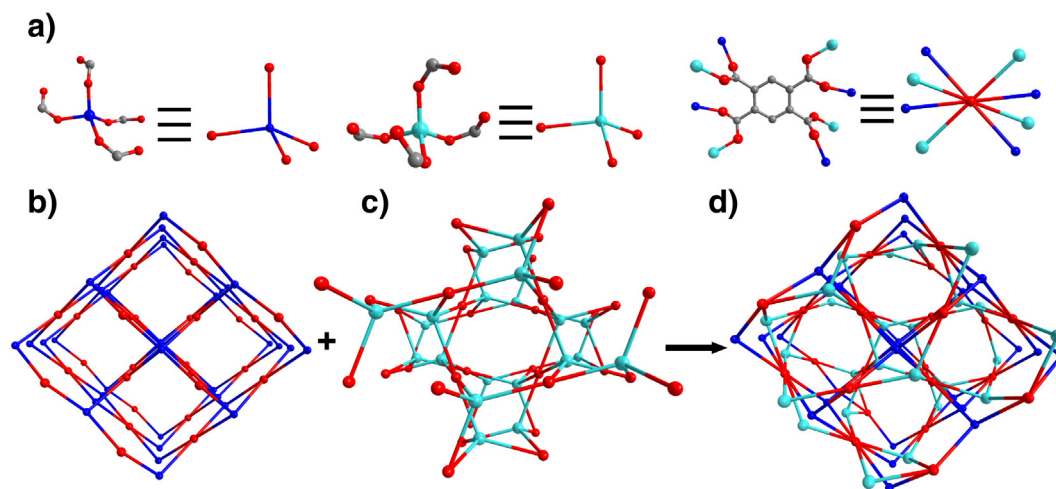


Fig. 3. (a) The defined 4-connected and 8-connected nodes; (b) the 4-connected **pts** net from Li-btec framework; (c) the (4,4)-connected net from Zn-btec framework; (d) the (4,4,8)-connected net of **2**.

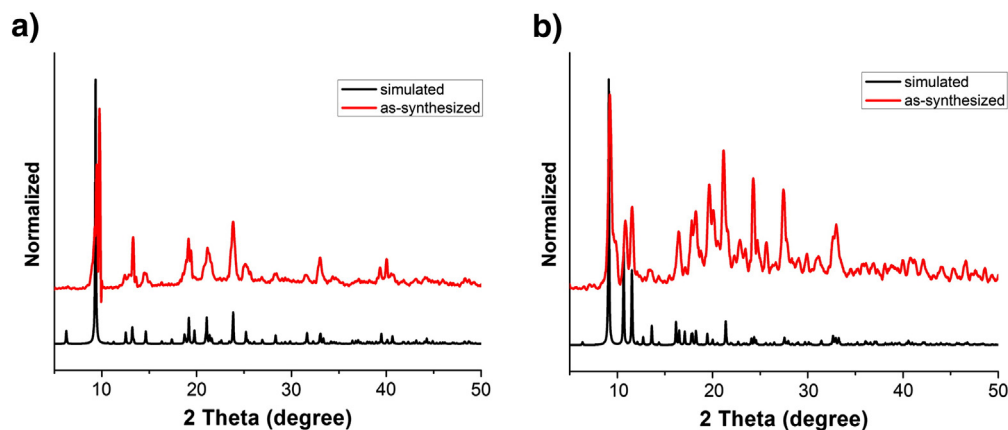


Fig. 4. (a) The powder XRD patterns of **1**; (b) the powder XRD patterns of **2**.

respectively. The diffraction (XRD) peaks are corresponded well in position, indicating the phase purity of the experimental compounds.

The luminescent properties of compounds **1** and **2** were investigated in the solid state at room temperature. The emission peaks of the compounds are shown in Fig. 5. Both compounds **1** and **2** display an intense

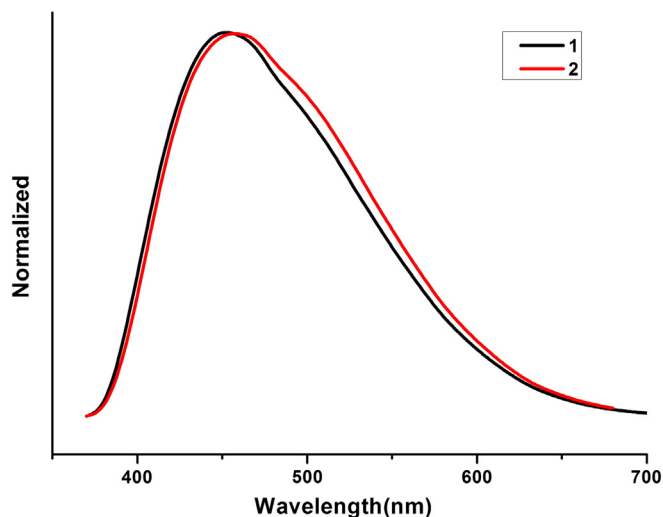


Fig. 5. Solid-state emission spectra of **1** and **2** at room temperature.

emission band at about 450 nm ($\lambda_{\text{ex}} = 350$ nm). Obviously, the emissions of the two compounds are not involved with contributions from the Li^+ cations. In comparison to the free 1,2,4,5-btec ligand which shows the emission band at 397 nm ($\lambda_{\text{ex}} = 270$ nm) [11], the emission peaks of compounds **1–2** show obvious red shifts, and we speculate that the 1,2,4,5-btec ligand makes a significant contribution to the fluorescent emission of **1–2** and the red shifts maybe due to the ligand-to-metal charge transfer (LMCT) since the formation of Zn–O coordination bonds [12].

In summary, two new three-dimensional metal–organic frameworks have been synthesized and structurally characterized. Compound **1** based on μ_4 -btec features an anionic homometallic framework with 4-connected **pts** topology. The Li^+ cation introduced in the reaction system of **1**, results in the Zn–Li cooperative assembly, which generates a new compound **2**. So compound **2** is a heterometallic organic framework with rare (4, 4, 8)-connected network topology, which can be considered as constitute of a Li-btec (**pts**) net and a Zn-btec net. Furthermore, the luminescent properties of two compounds are investigated in the solid state at room temperature.

Acknowledgments

The authors are grateful for the financial support from the National Natural Science Foundation of China (60976019), Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP 20093223110002), Cultivating Fund for Excellent Young Scholar of Fujian Normal University

(FJSDJK2012063), and Program for Innovative Research Team in Science and Technology in Fujian Province University (IRTSTFJ).

Appendix A. Supplementary material

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2013.08.031>.

Reference

- [1] (a) O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Reticular synthesis and the design of new materials, *Nature* 423 (2003) 705–714; (b) G. Férey, C. M.-D., C. Serre, F. Millange, Crystallized Frameworks with Giant Pores: Are There Limits to the Possible? *Acc. Chem. Res.* 38 (2005) 217–225; (c) J.R. Long, O.M. Yaghi, The pervasive chemistry of metal–organic frameworks, *Chem. Soc. Rev.* 38 (2009) 1213–1214; (d) B.L. Chen, S.C. Xiang, G.D. Qian, Metal–organic frameworks with functional pores for recognition of small molecules, *Acc. Chem. Res.* 43 (2010) 1115–1124; (e) Y.J. Cui, Y.F. Yue, G.D. Qian, B.L. Chen, Luminescent functional metal–organic frameworks, *Chem. Rev.* 112 (2011) 1126–1162.
- [2] (a) H.-L. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Design and synthesis of an exceptionally stable and highly porous metal–organic framework, *Nature* 402 (1999) 276–279; (b) X.-C. Huang, Y.-Y. Lin, J.-P. Zhang, X.-M. Chen, Ligand-directed strategy for zeolite-type metal–organic frameworks: zinc(II) imidazoles with unusual zeolitic topologies, *Angew. Chem. Int. Ed.* 45 (2006) 1557–1559; (c) F. Wang, Z.-S. Liu, H. Yang, Y.-X. Tan, J. Zhang, *Angew. Chem. Int. Ed.* 50 (2011) 450–453.
- [3] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O.M. Yaghi, High-throughput synthesis of zeolitic imidazolate frameworks and application to CO₂ capture, *Science* 319 (2008) 939–943.
- [4] (a) S.M. Jessen, H. Kupperts, The structure of dilithium dihydrogen 1,2,4,5-benzenetetracarboxylate tetrahydrate (dilithium dihydrogen pyromellitate tetrahydrate), *Acta Crystallogr.* 46 (1990) 2351–2354; (b) Y.B. Chen, Y. Kang, J. Zhang, New mimic of zeolite: heterometallic organic host framework accommodating inorganic cations, *Chem. Commun.* 46 (2010) 3182–3184; (c) W.-J. Ji, Q.-G. Zhai, S.-N. Li, Y.-C. Jiang, M.-C. Hu, The first ionothermal synthesis of a 3D ferroelectric metal–organic framework with colossal dielectric constant, *Chem. Commun.* 47 (2011) 3834–3836; (d) M.-X. Li, Z.-X. Miao, M. Shao, S.-W. Liang, S.-R. Zhu, Metal–organic frameworks constructed from 2,4,6-Tris(4-pyridyl)-1,3,5-triazine, *Inorg. Chem.* 47 (2008) 4481–4489; (e) J.-D. Lin, J.-W. Cheng, S.-W. Du, Five d¹⁰ 3D metal–organic frameworks constructed from aromatic polycarboxylic acids and flexible imidazole-based ligands, *Cryst. Growth Des.* 8 (2008) 3345–3353.
- [5] Synthesis of 1: Zn(NO₃)₂·6H₂O (0.071 g, 0.24 mmol), 1,2,4,5-benzenetetracarboxylic acid (H₄btec, 0.06 g, 0.24 mmol), 5,5'-(1,4-phenylene)bis(1H-tetrazole) [6] (H₂pbtz, 0.05 g, 0.2 mmol), 2 mL N, N'-dimethylformamide (DMF), 1 mL 1,3-Dimethyl-2-imidazolidinone (DMI) in a 20 mL vial was heated at 100 °C for 4 days, and then cooled to room temperature, colorless block crystals of 1 were obtained (0.104 g; yield: 90% based on H₄btec). Elemental analysis (EA) for 1, C₁₇H₂₅N₃O₉Zn (480.78): Calcd. C 42.47, H 5.20, N 8.73. Found. C 42.58, H 5.46, N 8.54. IR (KBr pellet, cm⁻¹) for 1: 627(w) 764(w) 860(w) 1013(w) 1141(w) 1364(s) 1433(w) 1630(s) 2796(w) 3781(w). Synthesis of 2: compound 2 was obtained by the same solvothermal procedure as that for compound 1 only adding Li₂CO₃ (0.018 g, 0.24 mmol). Colorless block crystals of 2 were obtained (0.086 g; yield: 80% based on H₄btec). Elemental analysis (EA) for 2, C₁₅H₁₇N₂O₉ZnLi (441.63): Calcd. C 40.79, H 3.85, N 6.34. Found. C 41.02, H 3.92, N 6.13. IR (KBr pellet, cm⁻¹) for 2: 507(w) 636(w) 808(w) 1090(w) 116(w) 1364(s) 1425(w) 1493(w) 1630(s) 2796(w) 3781(w).
- [6] J. Tao, Z.-J. Ma, R.-B. Huang, L.-S. Zheng, Synthesis and characterization of a tetrazolate-bridged coordination framework encapsulating D_{2h}-symmetric cyclic (H₂O)₄ cluster arrays, *Inorg. Chem.* 43 (2004) 6133–6135.
- [7] (a) H. Yang, F. Wang, Y. Kang, T.-H. Li, J. Zhang, Chiral assembly of dodecahedral cavities into porous metal–organic frameworks, *Chem. Commun.* 48 (2012) 9424–9426; (b) J.-B. Lin, W. Xue, J.-P. Zhang, X.-M. Chen, An ionic porous coordination framework exhibiting high CO₂ affinity and CO₂/CH₄ selectivity, *Chem. Commun.* 47 (2011) 926–928; (c) S.-T. Zheng, F. Zuo, T. Wu, B. Irfanoglu, C. Chou, R.A. Nieto, P.Y. Feng, X.H. Bu, Cooperative Assembly of three-ring-based zeolite-type metal–organic frameworks and Johnson-type dodecahedra, *Angew. Chem. Int. Ed.* 50 (2011) 1849–1852.
- [8] Crystal data for 1: C₁₇H₂₅N₃O₉Zn, M = 480.78, Tetragonal, a = 18.9381(3) Å, b = 18.9381(3) Å, c = 21.2008(7) Å, α = β = γ = 90° V = 7603.7(3) Å³, T = 296 K, space group I4(1)/amd, Z = 16, 7103 reflections measured, 1929 independent reflections (R_{int} = 0.0288). The final R₁ value was 0.0605 (I > 2σ(I)). The final wR(F₂) value was 0.1987 (I > 2σ(I)). The final R₁ value was 0.0670 (all data). The final wR(F₂) value was 0.2085 (all data). The goodness of fit on F₂ was 1.028. Crystal data for 2: C₁₅H₁₇N₂O₉ZnLi, M = 441.63, Orthorhombic, a = 19.9292(5) Å, b = 25.9815(8) Å, c = 29.2054(10) Å, α = β = γ = 90° V = 15122.3(8) Å³, T = 100 K, space group Fddd, Z = 32, 9122 reflections measured, 3753 independent reflections (R_{int} = 0.0207). The final R₁ value was 0.0360 (I > 2σ(I)). The final wR(F₂) value was 0.1113 (I > 2σ(I)). The final R₁ value was 0.0424 (all data). The final wR(F₂) value was 0.1170 (all data). The goodness of fit on F₂ was 1.071. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 948129, 948128. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).
- [9] (a) V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio, Interpenetrating metal–organic and inorganic 3D networks: a computer-aided systematic investigation. Part I. Analysis of the Cambridge Structural Database, *CrystEngComm* 6 (2004) 377–395; (b) V.A. Blatov, D.M. Proserpio, Topological relations between three-periodic nets. II. Binodal nets, *Acta Crystallogr.* A65 (2009) 202.
- [10] O. Delgado-Friedrichs, M. O'Keeffe, Identification of and symmetry computation for crystal nets, *Acta Crystallogr.* A59 (2003) 351–360.
- [11] W.-J. Ji, Q.-G. Zhai, S.-N. Li, Y.-C. Jiang, M.-C. Hu, The ionothermal synthesis of a 3D indium metal–organic framework: crystal structure, photoluminescence property and photocatalytic activity, *Inorg. Chem. Commun.* 24 (2012) 209–211.
- [12] (a) Z.-Z. Lin, F.-L. Jiang, L. Chen, D.-Q. Yuan, Y.-F. Zhou, M.-C. Hong, Two novel inorganic–organic hybrid frameworks based on In^{III}-BTC and In^{III}-BTEC, *Eur. J. Inorg. Chem.* 436 (2005) 77–81; (b) W.-J. Ji, Q.-G. Zhai, S.-N. Li, Y.-C. Jiang, M.-C. Hu, An anionic metal–organic framework based on infinite [In₃(μ₃-OH)₂]_n inorganic chains synthesized in ionic liquid, *Inorg. Chem. Commun.* 28 (2013) 16–19.