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# Synthesis, structure and photoluminescence of a 2-D cadmium(II) metal-organic framework: $[Cd(\mu_4-NIPH)(\mu_2-OH_2)]_n$ (NIPH = 5-nitroisophthalate)

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### Abstract

A cadmium metal-organic framework  $[Cd(\mu_4-NIPH)(\mu_2-OH_2)]_n$  (1) has been prepared by reaction of H<sub>2</sub>NIPH (H<sub>2</sub>NIPH = 5-nitroisophthalic acid) with Cd (II) under hydrothermal condition and characterized by single-crystal X-ray diffraction and TGA analysis. Single crystal X-ray diffraction analysis indicated that 1 is a 2-D layer structure constructed from polynuclear cadmium chains and bridge NIPH ligands. Furthermore, the layers are connected into 3-D supramolecular network through hydrogen bonds. The framework 1 exhibits photoluminescence at room temperature.

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The rational design and self-assembled construction of novel functional supramolecular coordination polymers or metal-organic frameworks (MOFs) has drawn considerable attention in the field of crystal engineering and material chemistry [1]. This is due to their intriguing network topologies and diverse potential for scientific and technological applications as selective absorption, separation, catalysis, ion exchange, gas storage, optoelectronic and magnetic materials [2–5]. To date, MOFs are usually built up from metal-oxygen or metal-nitrogen molecular building blocks linked to each other through organic bridging ligands [6]. For example, Yaghi and co-workers have reported a series of extended metal-organic open frameworks with rigid spacers and paddle-wheel building blocks  $[M_2(CO_2R)_4]$  which can be considered as square molecular building blocks in polyhedral networks [7]. In an effort of establishing strategies aimed at designing novel metalorganic frameworks, some multidentate carboxylate

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ligands, e.g., terephthalate, 1,3,5-benzenetricarboxylate and 1,2,4,5-benzenetetracarboxylate, are usually chosen to bind metal centers into metal–oxygen clusters, which may act as secondary building units to construct supramolecular architectures [8]. Recent studies have shown that 5nitroisophthalate (NIPH or nip) is a versatile ligand [9]. For example, in coordination polymer  $[Zn(\mu_3-OH)_2(nip)]_n$ , two carboxylate groups form covalent bonds with Zn centers while nitro group acts as hydrogen-bond acceptors [9e]. In the present study, we report the preparation [10], crystal structure [11] and properties of a novel 2-D cadmium (II) metal-organic framework  $[Cd(\mu_4-NIPH)(\mu_2-OH_2)]_n$  (1).

The colorless crystals of the **1** were obtained by using the hydrothermal synthesis method. The X-ray power diffraction pattern (XRD) of **1** was in good agreement with those generated from single-crystal structure analysis result (see Supplementary materials: Fig. S1). X-ray diffraction analysis reveals that **1** is a 2-D layer framework. The asymmetric unit consists of one crystallographically independent Cd atom, one NIPH ligand and one coordinating water mole-

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cule. The local coordination environment around the Cd atom can be described as a slightly distorted pentagonal bipyramidal formed by seven oxygen atoms from four carboxylates of NIPH ligands and two coordination water molecules (Fig. 1a). The Cd–O distances and O–Cd–O angles range from 2.2474(18) to 2.591(2) Å and from  $53.36(6)^{\circ}$  to  $162.06(6)^{\circ}$ , respectively, which are in good agreement with those found in other extended structures constructed from NIPH ligand [9].

Each NIPH ligand in 1 displays a  $\mu_4$ -bridging mode to connect with four Cd atoms and the two carboxylic groups adopt tridentate and bidentate-chelating coordination mode, respectively (Scheme 1). Two cadmium atoms are linked together by two carboxylate groups and two  $\mu_2$ -OH<sub>2</sub> to form a dinuclear [Cd<sub>2</sub>( $\mu_2$ -OH<sub>2</sub>)<sub>2</sub>(CO<sub>2</sub>R)<sub>6</sub>] building block (Cd···Cd 3.46 Å) (Fig. 1b). As a result, polynuclear cadmium chain based on [Cd<sub>2</sub>( $\mu_2$ -OH<sub>2</sub>)<sub>2</sub>(CO<sub>2</sub>)<sub>6</sub>] building blocks is formed through the oxygen atoms (O1 and its equivalent atoms) of the  $\mu_2$ -bridging tridentate carboxylate groups (represented as an edge-sharing polyhedral, with Cd–Cd inter-chain separation 3.649 Å, Fig. S2). The adja-



Scheme 1. The coordination modes of the carboxylic groups of NIPH ligand in 1.

cent chains are connected through NIPH ligands to form 2-D layer framework (Fig. 2). In addition, there exist strong O–H···O hydrogen bonds between water molecules and NIPH ligands in layers  $[O(7) \cdots O(4) \ 2.633(2) \ \text{Å}]$ . Finally, the whole 3-D supramolecular network (Fig. 3) is then stabilized by inter-layer strong O–H···O and C–H···O hydro-



Fig. 1. Perspective view of coordination environment of Cd(II) (a) and building block  $[Cd_2(\mu_2-OH_2)_2(CO_2R)_6]$  (b) in 1.



Fig. 2. A polyhedral representation of the 2-D layer structure of polynuclear cadmium chains coordinated linking of organic ligands of NIPH.



Fig. 3. The 3-D supramolecular network formed by hydrogen bonds packed along *a*-axis of **1**.

gen bonds in which nitro groups as acceptor (see Supplementary materials: Table S3 and Fig. S3).

The framework 1 is stable in air at ambient temperature and almost insoluble in common solvents, such as water, chloroform, carbon tetrachloride, alcohol, acetone and acetonitrile. The thermal behavior of 1 was examined by thermogravimetric analysis (TGA) under atmosphere with the heating rate of 10 °C min<sup>-1</sup>. The TGA result indicates that 1 does not decompose up to 188 °C. Due to the loss of water molecules, the first weight loss of 5.11% occurs from 188 to 253 °C, which is consistent with the calculated value 5.31%. The second weight loss between 393 and 664 °C is ascribed to the loss of NIPH ligands. The remaining product is cadmium oxides CdO (38.20%), which is in agreement with the calculated value (37.82%). 1 displays strong blue emission with maximum intensity at 431 nm ( $\lambda_{ex} = 308$  nm). The emission spectrum of 1 in the solid state at room temperature is presented in Fig. 4. It may be possible to develop high stable luminescent materials based on 1.

In summary, we have successfully synthesized a novel 2-D cadmium (II) metal-organic framework  $[Cd(\mu_4-NIPH)(\mu_2-OH_2)]_n$  (1) under hydrothermal conditions. In 1, two kinds of coordination mode for NIPH ligand have been demonstrated. The cadmium atoms are linked



Fig. 4. The emission spectrum of 1 at room temperature.

together with carboxylate groups and  $\mu_2$ -OH<sub>2</sub> to form polynuclear cadmium chains. The adjacent chains are connected through NIPH ligands to form 2-D layer structure. Threedimensional supramolecular framework are further formed via inter-layer hydrogen bonding interaction. **1** exhibits strong blue photoluminescence at room temperature.

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#### Appendix A. Supplementary data

Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Center with the deposition number of CCDC 603977. These data can be obtained

free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.04.017.

## References

- [1] (a) K. Kasai, M. Aoyagi, M. Fujita, J. Am. Chem. Soc. 122 (2000) 2140;
  - (b) B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629;
  - (c) C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem., Int. Ed. 43 (2004) 1466;
  - (d) X.Q. Lu, J.J. Jiang, C.L. Chen, B.S. Kang, C.Y. Su, Inorg. Chem. 44 (2005) 4515;
  - (e) B.H. Ye, M.L. Tong, X.M. Chen, Coord. Chem. Rev. 249 (2005) 545.
- [2] (a) H. Byrd, A. Clearfield, D. Poojary, K.P. Reis, M.E. Thompson, Chem. Mater. 8 (1996) 2239;
  (b) J.S. Seo, D.M. Whang, H.Y. Lee, S.I. Jun, J.H. Oh, Y.J. Jeon, K. Kim, Nature 404 (2000) 982;
  - (c) T. Sawaki, Y. Aoyama, J. Am. Chem. Soc. 121 (1999) 4793.
- [3] M. Meyn, K. Beneke, G. Lagaly, Inorg. Chem. 29 (1990) 5201.
- [4] S. Noro, S. Kitagawa, M. Kondo, K. Seki, Angew. Chem., Int. Ed. 39 (2000) 2082, and references therein.
- [5] (a) N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi, Science 300 (2003) 1127;
  (b) R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, Angew. Chem., Int. Ed. 115 (2003) 444;
  (c) H.J. Choi, T.S. Lee, M.P. Suh, Angew. Chem., Int. Ed. 111 (1999) 1490.
- [6] (a) E.Y. Lee, M.P. Suh, Angew. Chem., Int. Ed. 43 (2004) 2798, and references therein;
  (b) X.Q. Lu, J.J. Jiang, L. Zhang, C.L. Chen, C.Y. Su, B.S. Kang,
- Cryst. Growth Des. (2005) 419; (c) X.M. Zhang, X.M. Chen, Eur. J. Inorg. Chem. (2003) 413.
- [7] M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319.

- [8] (a) J. Kim, B.L. Chen, T.M. Reineke, H.L. Li, M. Eddaoudi, D.B. Moler, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 123 (2001) 8239;
  (b) J.C. Dai, X.T. Wu, Z.Y. Fu, S.M. Hu, W.X. Du, C.P. Cui, L.M. Wu, H.H. Zhang, R.Q. Sun, Chem. Comm. (2002) 12.
- [9] (a) J. Tao, X. Yin, Z.B. Wei, R.B. Huang, L.S. Zheng, Eur. J. Inorg. Chem. (2004) 125;
  (b) J.H. Luo, M.C. Hong, R.H. Wang, R. Cao, L. Han, D.Q. Yuan, Z.Z. Lin, Y.F. Zhou, Inorg. Chem. 42 (2003) 4486;
  (c) J.H. Luo, M.C. Hong, R.H. Wang, R. Cao, L. Han, Z.Z. Lin, Eur. J. Inorg. Chem. (2003) 2705;
  (d) H. Abourahma, B. Moulton, V. Kravtsov, M.J. Zaworotko, J. Am. Chem. Soc. 124 (2002) 9990;
  (e) J. Tao, X. Yin, Y.B. Jiang, L.F. Yang, R.B. Huang, L.S. Zheng,
  - (e) J. 1ao, A. Yin, Y.B. Jiang, L.F. Yang, K.B. Huang, L.S. Zheng, Eur. J. Inorg. Chem. (2003) 2678.
- [10] Synthesis of 1: A mixture of  $3CdSO_4 \cdot 8H_2O$  (0.385 g, 0.5 mmol),  $H_2NIPH$  (0.105 g, 0.5 mmol) and piperazine (0.08 g, 1 mmol) was dissolved in water (10 ml), stirred for 40 min, followed by heating for 72 h at 140 °C under autogenous pressure in a Teflon-lined stainless steel autoclave (25 ml). Final products were crystallized as colorless blocks at room temperature, then were washed with water (yield about 72% based on Cd). Element analysis calcd (%) for C<sub>8</sub>H<sub>5</sub>NO<sub>7</sub>Cd: C 28.30%, H 1.48%, N 4.13%; Found: C 28.42%, H 1.31%, N 4.27%. FT-IR (KBr, cm<sup>-1</sup>) data: 3403(m), 3090(m), 1609(vs), 1551(s), 1456(s), 1410(s), 1351(vs), 1196(w), 1086(m), 931(w), 787(w), 734(m), 603(w), 554(w), 516(w).
- [11] Crystal date of 1: crystal dimensions:  $0.35 \times 0.30 \times 0.22$  mm<sup>3</sup>, Formula: C<sub>8</sub>H<sub>5</sub>NO<sub>7</sub>Cd,  $M_r = 339.53$ , triclinic system, space group P1, a = 5.5701(4) Å, b = 8.7252(6) Å, c = 10.1198(9) Å,  $\alpha = 108.643(3)^{\circ}$ ,  $\beta = 91.893(3)^{\circ}$ ,  $\gamma = 95.713(4)^{\circ}$ ,  $V = 462.60(6) \text{ Å}^3$ , Z = 4, $D_{\rm c} = 2.438 \text{ g/cm}^3$ ,  $\mu = 2.387 \text{ mm}^{-1}$ , F(000) = 328,  $R_1 = 0.0186$ ,  $wR_2 = 0.0521$ . The intensity data were collected on a Rigaku R-AXIS RAPID diffractometer with Mo/ka radiation ( $\lambda = 0.71073$  Å, graphite monochromator) at 293(2) K using  $\omega$ -scan mode. The structure was solved by direct methods and refined by full-matrix least squares on  $F^2$  using SHELXTL97 software [12]. Empirical adsorption correction was applied for all date. The heaviest atoms were first found. Atoms O, N, C and H were subsequently located in difference Fourier maps. All non-hydrogen atoms were refined anisotropically.
- [12] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, 1997.