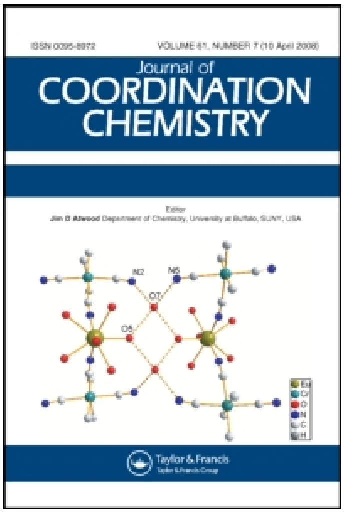


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

[Cd(SDC)(H_2O)]: a 3-D hybrid open framework with an interpenetrated (4,4) topology and double-strand helicates (SDC=4,4'-stilbenedicarboxylate)

Kun-Lin Huang[a]; Yan-Ting He[b]; Mei Huang[a]
[a] College of Chemistry, Chongqing Normal University, Chongqing 400047, China [b] Chinese Academy of Inspection and Quarantine, Institute of Industrial Product Inspection, Beijing 100025, China

To cite this Article Huang, Kun-Lin , He, Yan-Ting and Huang, Mei(2008) '[Cd(SDC)(H_2O)]: a 3-D hybrid open framework with an interpenetrated (4,4) topology and double-strand helicates (SDC=4,4'-stilbenedicarboxylate)', Journal of Coordination Chemistry, 61: 17, 2735 — 2742

To link to this Article: DOI: 10.1080/00958970801968799

URL: http://dx.doi.org/10.1080/00958970801968799

Journal of Coordination Chemistry
Vol. 61, No. 17, 10 September 2008, 2735–2742

[Cd(SDC)(H_2O)]: a 3-D hybrid open framework with an interpenetrated (4,4) topology and double-strand helicates (SDC = 4,4′-stilbenedicarboxylate)

KUN-LIN HUANG*†, YAN-TING HE‡ and MEI HUANG*§

†College of Chemistry, Chongqing Normal University, Chongqing 400047, China
‡Chinese Academy of Inspection and Quarantine, Institute of Industrial Product Inspection, Beijing 100025, China
§Pharmacology Teaching and Studying Office, Changchun Medical College, Changchun 130031, China

(*Received 29 April 2007; in final form 28 August 2007*)

A 3-D, two-fold interpenetrated coordination polymer [Cd(SDC)(H_2O)] has been synthesized using *trans*-4,4′-stilbenedicarboxylic acid (H_2SDC) and $Cd(NO_3)_2 \cdot 6H_2O$ under hydrothermal conditions, and characterized. Single crystal X-ray structural analysis indicates that the title compound crystallizes in a monoclinic lattice, $P2/c$ with $a = 15.158(2)$, $b = 6.4390(15)$, $c = 7.1330(19)$ Å, $\beta = 91.937(2)°$, $Z = 1$, $V = 695.8(3)$ Å^3, $D_c = 1.888$ Mg m^{-3}, $F(000) = 390$, $R_1 = 0.0476$, $wR_2 = 0.0935$. The title compound has an interpenetrated (4,4) topology in which Cd(II) has greatly distorted hexahedral geometry. There are two distinct double-strand helicates, and interpenetrated rhombic nanochannels in the 3-D open framework. Compound **1** exhibits expected strong luminescence at $\lambda_{max} = 460$ nm upon excitation at 392 nm.

Keywords: Cadmium; 4,4′-Stilbenedicarboxylic acid; Coordination polymer; Interpenetration; Luminescence

1. Introduction

Three-dimensional (3-D) hybrid open frameworks [1] attract attention due to their intriguing network topologies [2] such as zeolite-type [3], interpenetrated [4] and diamondoid [5] networks, and potential applications as functional materials in gas storage [6], catalysis [7], and separation [8]. The versatility of multidentate carboxylate anions, which can adopt bridging modes for connecting transition metal centers, has also led to extensive research on the optical properties of carboxylato complexes [5, 9]. From symmetrical carboxylates, for example, 1,4-benzenedicarboxylate, 4,4′-biphenyldicarboxylate, 1,3,5-benzenetricarboxylate and 1,2,4,5-benzenetetracarboxylate, many functional 3-D solid-state materials have been synthesized [10]. However, *trans*-4,4′-stilbenedicarboxylic acid (H_2SDC) [11], a symmetrical organic building unit, has not been well explored in the field of hybrid materials [12]. Herein, we report the synthesis,

---

*Corresponding authors. Email: kunlin@cqnu.edu.cn; huangmei5511@tom.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970801968799

crystal structure, and photoluminescence of a 3-D two-fold interpenetrated coordination polymer, $[Cd(SDC)(H_2O)]$ (**1**) (SDC = 4,4′-stilbenedicarboxylate) (scheme 1).

2. Experimental

2.1. *General methods*

All chemicals used in these syntheses are reagent grade and used as purchased without further purification. Infrared (IR) spectra are recorded from KBr pellets in the range 400–4000 cm^{-1} on a Nicolet Impact 410 FTIR spectrometer. Elemental analyses are performed on a Perkin-Elmer 2400 elemental analyzer. The thermogravimetric analyses are performed with a Mettler Toledo TGA/SDTA 851e analyzer in N_2 with a heating rate of 5°C min^{-1} from 30 to 800°C. Excitation and emission spectra were obtained on a– RF-5301PC spectrofluorometer equipped with a 450 W xenon lamp as the excitation source; measurements of solid state samples were performed at room temperature.

2.2. *Synthesis*

H_2SDC was prepared by using a previously reported method [11].

$[Cd(SDC)(H_2O)]$ (**1**): A solution of H_2O (10 mL) containing H_2SDC (0.2 mmol), $Cd(NO_3)_2 \cdot 6H_2O$ (0.2 mmol) and Et_3N (0.04 mL) is sealed in a reactor of 23 mL and heated at 160°C for 72 h, then cooled to room temperature. The yellowish crystals are

Table 1. Crystallographic data and structure refinement summary for **1**.

Formula	$C_{32}H_{22}O_{10}Cd_2$
Fw	791.30
Size (mm^3)	0.13 × 0.10 × 0.03
Crystal system	Monoclinic
Space group	$P2/c$
a (Å)	15.158(2)
b (Å)	6.4390(15)
c (Å)	7.1330(19)
α (°)	90
β (°)	91.937(2)
γ (°)	90
V (Å^3)	695.8(3)
Z	1
T (K)	298(2)
Wavelength (Å)	0.71073
D_{calcd} ($mg\,m^{-3}$)	1.888
$F(000)$	390
θ (°)	1.34–25.01
Reflections collected	3302
Independent reflections	1236 [$R(int) = 0.0460$]
Data/parameters	1236/101
Goodness-of-fit	1.078
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0476$, $wR_2 = 0.0935$
R indices (all data)	$R_1 = 0.0637$, $wR_2 = 0.0984$
Largest diff. peak and hole (e Å^{-3})	0.975, −0.878

washed with ethanol (3×3 mL) to give **1** in yield of 70%. Elemental analysis for $C_{32}H_{22}O_{10}Cd_2$ (%), Calcd: C, 48.53; H, 2.78. Found: C, 48.49; H, 2.72. IR (KBr): 3351m, 3236m, 3032w, 1580s, 1535s, 1509m, 1175m, 955m, 863m, 796m, 710w.

2.3. *Crystallographic studies*

A suitable single crystal is glued to a thin glass fiber and mounted on a Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å)) operating at 50 kV and 40 mA. Intensity data are collected at room temperature. Data processing is performed using the SAINT processing program. The structure is solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL97 [13]. All hydrogen atoms of O–H$\cdots$O hydrogen bonds and non-hydrogen atoms are easily found from the difference Fourier maps and refined anisotropically. The crystallographic data and details on refinement for **1** are summarized in table 1. Selected bond distances and angles are listed in table 2. Additional information is given in the supplementary material.

3. Results and discussion

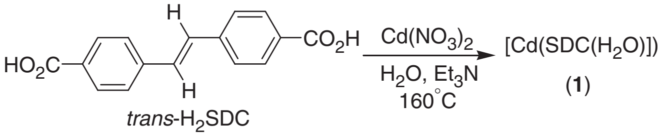
The yellowish crystalline **1** is synthesized by treating $Cd(NO_3)_2$ with H_2SDC in the molar ratio of 1 : 1 in a solution of H_2O and triethylamine at pH 6. The pH of the original mixture is a key experimental condition. The crystal samples are prepared at 150–170°C with large single crystals in 70% yield at 160°C. X-ray diffraction analyses reveal that **1** crystallizes in the space group $P2/c$ (monoclinic and centrosymmetric) (table 1). The crystal structure reveals that **1** consists of neutral $[Cd(SDC)(H_2O)]$. This material is stable in air and is insoluble in common organic solvents such as methanol, ethanol, acetonitrile, acetone, and DMF. The formulation of **1** is supported by FT-IR, microanalysis, and thermogravimetric analysis (TGA). The X-ray power diffraction pattern proves the sample is pure-phase.

In the crystal structure of **1** (figure 1a), the cadmium adopts five-coordinated mode (CdO_5) *via* binding to four oxygen atoms (O1; O1A; O2A; O2AA) originating from

Table 2. Selected interatomic distances (Å) and angles (°) for **1**.

Cd(1)–O(1)#1	2.194(4)
Cd(1)–O(1)	2.194(4)
Cd(1)–O(3)	2.230(8)
Cd(1)–O(2)#2	2.379(5)
Cd(1)–O(2)#3	2.379(5)
O(1)#1–Cd(1)–O(1)	161.6(3)
O(1)–Cd(1)–O(3)	99.20(14)
O(1)#1–Cd(1)–O(2)#2	95.94(17)
O(1)–Cd(1)–O(2)#2	84.72(17)
O(3)–Cd(1)–O(2)#2	87.95(13)
O(2)#2–Cd(1)–O(2)#3	175.9(3)
C(5)#4–C(8)#4–C(8)–C(5)	180.0(0)

Symmetry codes: #1: $-x, y, -z+1/2$; #2: $x, -y+2, z+1/2$; #3: $-x, -y+2, -z$; #4: $-x+1, -y+1, -z$.



Scheme 1. The synthesis of title compound.

separate COO^- carboxylate groups of SDC^{2-} ligands, and one oxygen (O3) of water. The Cd–O bond lengths are in the ranges 2.194–2.379 Å, similar to those observed in [Cd(bpea)(phen)$_2$] [9b] and $\{[Cd(o\text{-}O_2CC_6H_4COFc)_2(bpe)(MeOH)_2]\cdot H_2O\}$ [14]. [CdO_5] is a greatly distorted hexahedron (O2A–Cd1–O2AA 175.91° and O1–Cd1–O1A 161.59°). There are weak Cd1 ··· O2 interactions at 2.823 Å which may stabilize the distorted [CdO_5]. The [CdO_5] hexahedrons pillared by COO^- groups array in a zigzag motif, and a 2-D supramolecular structure is assembled *via* O3A–H3 ··· O2 hydrogen bonds (figure 1c).

Helicates, a helical shape, mostly exist in molecular compounds (molecular level) [15] instead of polymeric frameworks [16]. In this work, although the title compound **1** is an open network, there are two distinct hydrogen-bonded double-strand helicates, namely, the left-handed and the right-handed (figure 1b). With the Cd1 and O3A atoms as sharing nodes, the $Cd(CO_2)_2(H_2O)$ helicate is formed through an O3A–H3 ··· O2 hydrogen bond [O3A(H3) ··· O2 2.674 Å], and may rotate around the Cd ··· Cd axis (the Cd ··· Cd distance of 6.439 Å). The mirror images may be imaged as a pair of dancers oppositely twisting.

Another remarkable feature in **1** is that each SDC^{2-} links four separate cadmium atoms, that is to say, SDC^{2-} adopts an *exo*-tetradentate coordination mode, to generate a 3-D two-fold interpenetrated architecture (figure 2). In the structure of **1** (figure 2a), the nanosized *trans*-SDC^{2-} ligand (ca. 13.6 Å) is coplanar, in other words, all the atoms of two phenyl rings, CH=CH, and two COO^- groups are almost in the same plane. The coplanar configuration of SDC^{2-} spacers may be possibly due to the large p-π conjugate system (20 centers and 22 electrons) (see supplementary figures S1), stabilizing the structure of **1**. The SDC^{2-} spacers and Cd centers build up a (4,4) topological framework with rhombic nanochannels (ca. 17 Å × 6 Å) (see supplementary figure S2). The open architecture of **1** avoids extremely large void space by forming a two-fold interpenetrated structure (figure 2c), similar to that observed in $[Zn_4(\mu_4\text{-}O)(L1)_3(dmf)_2]\cdot DMF\cdot 3CH_3OH\cdot 2H_2O$ [17]. Despite the large conjugate system of the SDC^{2-}, there are no $\pi\cdots\pi$ interactions in the same covalent networks, but $\pi\cdots\pi$ contacts (ca. 3.4 Å) exist between two adjacent CH=CH vinyl groups in the interpenetrated network (see supplementary figure S3). For interpenetration and short $\pi\cdots\pi$ contacts, the title complex displays very poor porosity (see supplementary figure S4).

The thermogravimetric analysis (TGA) for **1** (figure S6) measured under N_2 displays no weight loss under 330°C, and framework decomposition in the temperature range of 330–800°C. Among the new luminescent cadmium-organic complexes from functional ligands [9b], a remarkable 2-D $\{[Cd(mpdc)(phen)]\cdot H_2O\}$ with $\lambda_{max} = 525$ nm based on carboxylate ligands was reported in our previous work [18]. In this work, the 3-D compound **1** also shows strong photoluminescent emission maximum at $\lambda = 460$ nm at room temperature upon excitation at $\lambda = 392$ nm (figure 3). Because of the emission maximum of H_2SDC at 466 nm with a 439 nm shoulder (upon excitation at $\lambda = 384$ nm), the photoluminescence of **1** could be based on intraligand $\pi^* \rightarrow \pi$ transition [19].

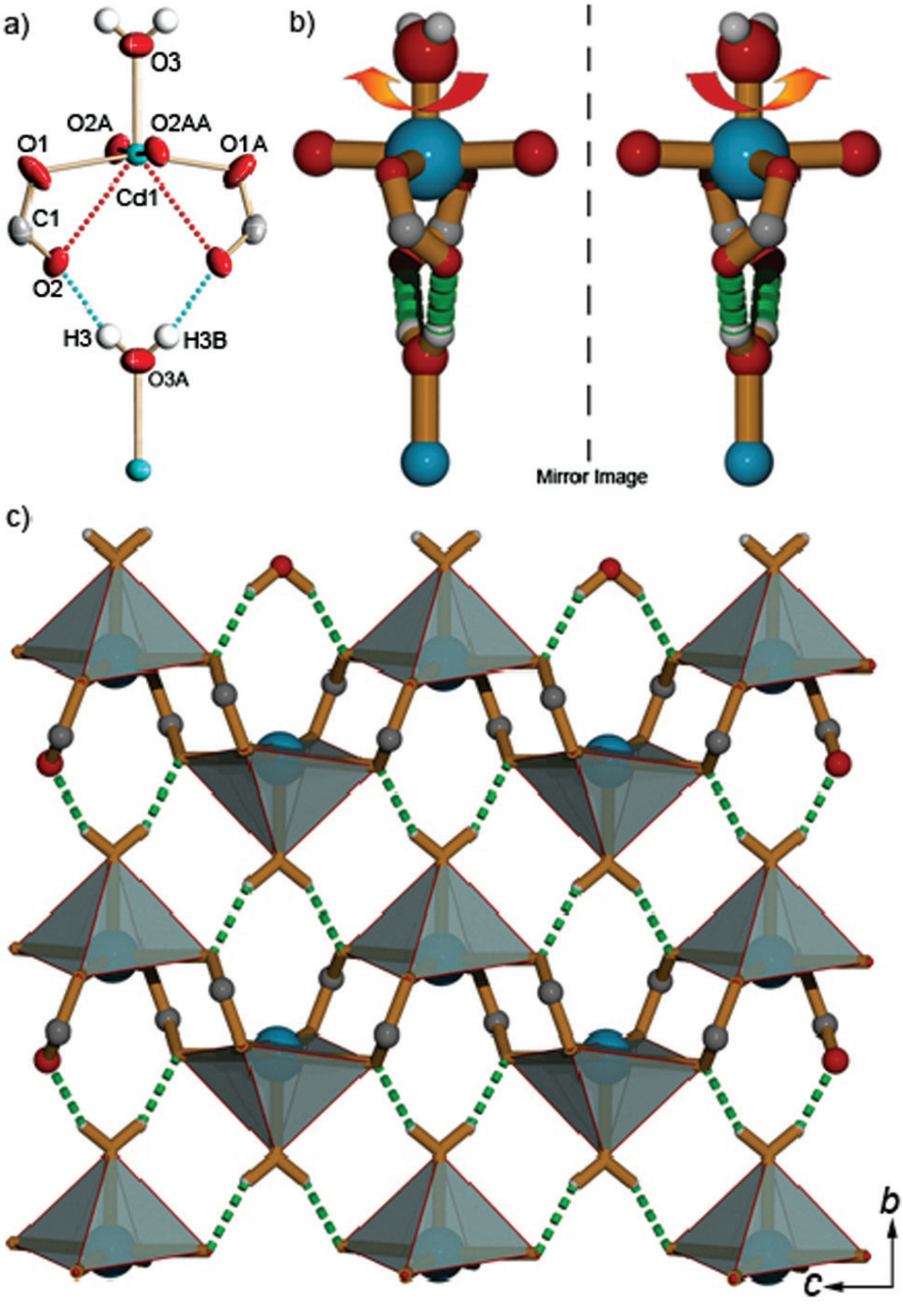


Figure 1. (a) The coordination environment of Cd^{2+}: (selected bond length and angles) O1–Cd1 2.194 Å, O2AA–Cd1 2.378 Å, O3–Cd1 2.230 Å, O2 $\cdots$ Cd1 2.823 Å, O3A(H3) $\cdots$ O2 2.674 Å, O2A–Cd1–O2AA 175.91° (upward) and O1–Cd1–O1A 161.59° (downward); (b) Mirror images of the twisted left-handed (L^{-}) and right-handed (R^{-}) helical sheets, namely, hydrogen-bonded double-strand helicates. Atoms labeled with the letter A are related by symmetry to those without such designation; (c) View of the zigzag array of [CdO5] clusters pillared by CO_2-groups, and the 2-D supramolecular sheet. The CdO5 is highlighted as the extremely distorted hexahedron, and the dashed represent O3 $\cdots$ O2 hydrogen bonds. Gray ball C, red O, and white H.

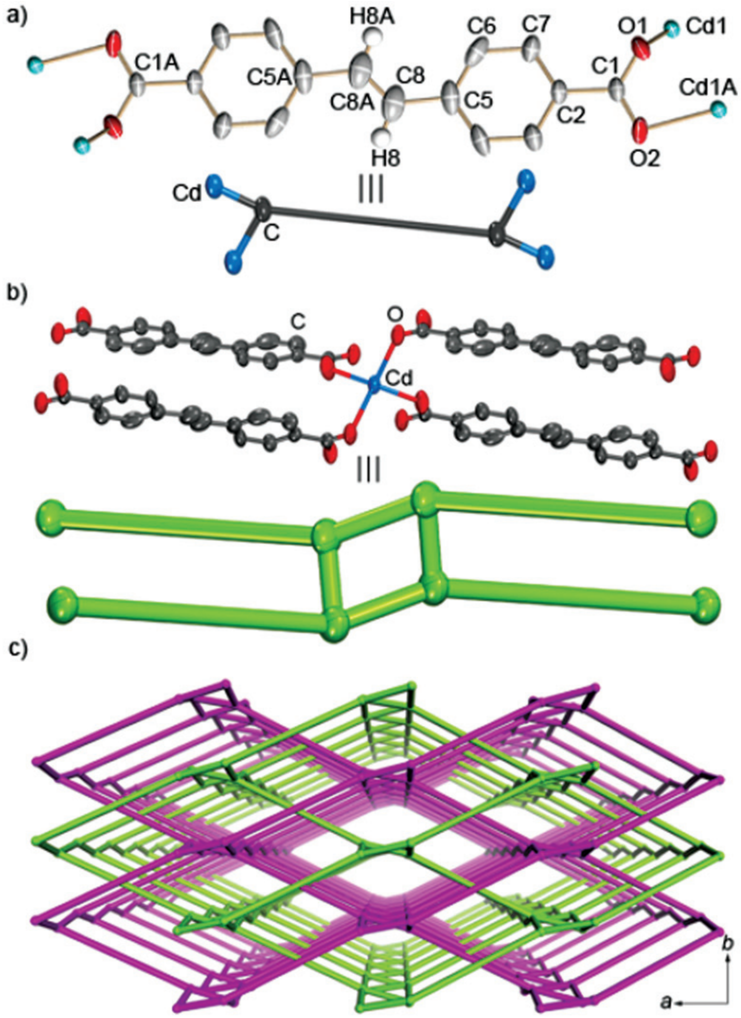


Figure 2. (a) The *trans*-structure, coordination of the nano-sized SDC ligand (ca. 13.6 Å) and simplified coordination in **1**; (b) The secondary building unit (SBU) for **1** and its simplified form. (c) View of the simplified 3-D framework with a (4, 4) topology assembled from SBUs with interpenetrated rhombic nanochannels (ca. 17Å × 6Å). Double-color networks exhibit the two-fold interpenetration.

The enhancement (relative to that of free ligand) may be attributed to ligand chelation to the metal center, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay. The strong fluorescence emission may make **1a** potentially useful photoactive solid-state material.

4. Conclusion

[Cd(SDC)(H_2O)] has an interpenetrated (4,4) topology in which Cd(II) has greatly distorted hexahedral geometry. There are two distinct double-strand helicates in the

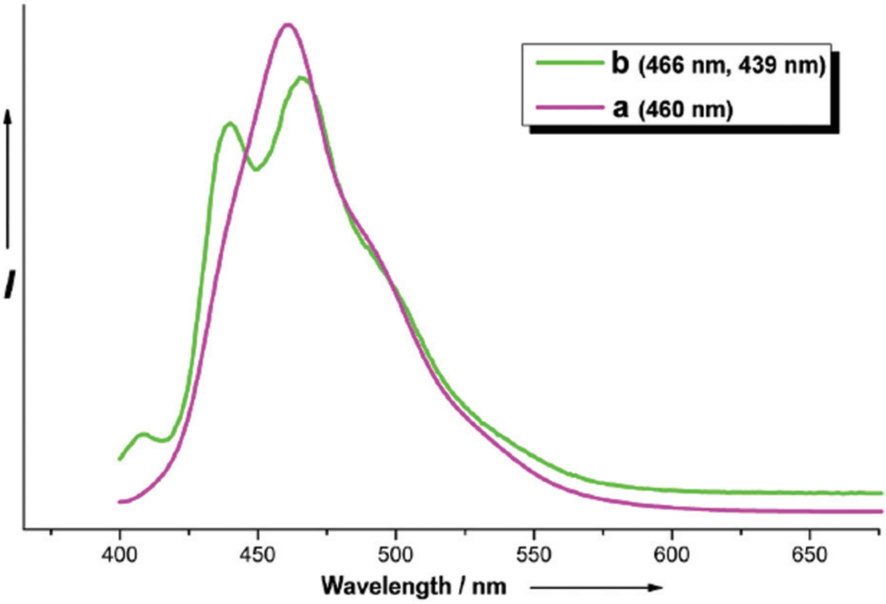


Figure 3. Emission spectra of **1** and H_2SDC: (a) **1**, $\lambda_{max,Em} = 460$ nm upon excitation at 392 nm, and (b) H_2SDC, $\lambda_{max, Em} = 466$ nm with the shoulder peak of 439 nm, upon excitation at 384 nm (Em = emission).

3-D open framework. Compound **1** exhibits luminescence at $\lambda_{max, Em} = 460$ nm upon excitation at 392 nm.

Supplementary materials

CCDC-645464 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Acknowledgements

This work was supported by the Science Foundation of Chongqing Municipal Education Commission (No. KJ060802) and the Doctor Foundation of Chongqing Normal University (No. 956201).

References

[1] (a) O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaodi, J. Kim. *Nature*, **423**, 705 (2003); (b) S.-H. Feng, R.-R. Xu. *Acc. Chem. Res.*, **34**, 239 (2001).
[2] (a) N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keffe, O.M. Yaghi. *Acc. Chem. Res.*, **38**, 176 (2005); (b) X.-L. Wang, C. Qin, E.-B. Wang, Z.-M. Su. *Chem. Eur. J.*, **12**, 2680 (2006).

[3] X.-C. Huang, Y.-Y. Lin, J.-P. Zhang, X.-M. Chen. *Angew. Chem. Int. Ed.*, **45**, 1557 (2006).
[4] S.R. Batten. *Cryst. Eng. Comm.*, **3**, 67 (2001).
[5] O.R. Evans, R.G. Xiong, Z.K. Wang, G.K. Wong, W. Lin. *Angew. Chem. Int. Ed.*, **38**, 536 (1999).
[6] J.L.C. Rowsell, O.M. Yaghi. *Angew. Chem. Int. Ed.*, **44**, 4670 (2005).
[7] C.-D. Wu, W.-B. Lin. *Angew. Chem. Int. Ed.*, **46**, 1075 (2007).
[8] Bradshaw, T.J. Prior, E.J. Cussen, J.B. Claridge, M.J.J. Rosseinsky. *Am. Chem. Soc.*, **126**, 6106 (2004).
[9] (a) O.R. Evans, W.-B. Lin. *Acc. Chem. Res.*, **35**, 511 (2002); (b) X.-L. Wang, C. Qin, E.-B. Wang, L. Xu, Z.-M. Su, C.-W. Hu. *Angew. Chem. Int. Ed.*, **43**, 5036 (2004).
[10] (a) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange. *Acc. Chem. Res.*, **38**, 217 (2005); (b) S. Kitagawa, R. Kitaura, S.-I. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).
[11] W.G. Toland, J. Wilkes, F.J. Brutschy. *J. Am. Chem. Soc.*, **75**, 2263 (1953).
[12] G. Park, H. Kim, G. Ho Lee, S.-K. Park, K. Kim. *Bull. Korean Chem. Soc.*, **27**, 443 (2006).
[13] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Refinement*, Göttingen University, Germany (1997).
[14] J. Zhang, Y. Xie, Q. Ye, R. Xiong, Z. Xue, X. You. *Eur. J. Inorg. Chem.*, 2572 (2003).
[15] (a) M. Albrecht. *Chem. Rev.*, **101**, 3457 (2001); (b) C.S. Purohit, S. Verma. *J. Am. Chem. Soc.*, **129**, 3488 (2007).
[16] (a) E.V. Anokhina, Y.B. Go, Y. Lee, T. Vogt, A.J. Jacobson. *J. Am. Chem. Soc.*, **128**, 9957 (2006); (b) T. Sugimoto, T. Suzuki, S. Shinkai, K. Sada. *J. Am. Chem. Soc.*, **129**, 270 (2007); (c) L. Han, M.-C. Hong. *Inorg. Chem. Commun.*, **8**, 406 (2005).
[17] B. Kesanli, Y. Cui, M.R. Smith, E.W. Bittner, B.C. Bockrath, W.-B. Lin. *Angew. Chem. Int. Ed.*, **44**, 72 (2005).
[18] K.-L. Huang, Y.-T. He, X.-L. Niu, X.-Y. Chen, Y.-N. Chi, Y. Gong, C.-W. Hu. *Inorg. Chem. Commun.*, **9**, 1243 (2006).
[19] Y.-N. Chi, K.-L. Huang, F.-Y. Cui, Y.-Q. Xu, C.-W. Hu. *Inorg. Chem.*, **45**, 10605 (2006).