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Cd(II) MOFs based on cadmium/carboxylate units and 4,4'-bis(benzoimidazol-1-yl)biphenylene: syntheses, structures, and luminescence

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Solvothermal reactions of CdCl₂·2.5H₂O with 4,4'-bis(benzoimidazol-1-yl)biphenylene (bimbb) and 1,4-benzenedicarboxylic acid (1,4-H₂bdc), 4,4'-biphenyldicarboxylic acid (4,4'-H₂bpdb), 5-methyl-1,3-benzenedicarboxylic acid (5-Me-1,3-H₂bdc), or 1,3,5-benzenetricarboxylic acid (H₃btc) afforded four 3-D metal–organic frameworks, {[Cd₂(1,4-bdc)₂(bimbb)₂·H₂O]_n} (1), {[Cd₂(4,4'-bpdb)₂(bimbb)(H₂O)₂]_n} (2), [Cd₂(5-Me-1,3-bdc)₂(bimbb)]_n (3), and {[Cd₃(btc)₂(bimbb)(H₂O)₂·2H₂O]_n} (4). Complexes 1–4 were characterized by elemental analysis, IR spectroscopy, powder X-ray powder diffraction, and single-crystal X-ray diffraction. 1 possesses a 3-D framework with 2-D undulated (8,4) layers which are further connected by bimbb pillars. 2 forms a 3-D pillared-layer framework constructed through 2-D undulated (4,4) layers and bimbb pillars. 3 has 1-D ribbons of [Cd₄(5-Me-1,3-bdc)₄]_n which are linked by bimbb to form a 3-D structure. 4 exhibits a 3-D pillared-bilayer framework consisting of (6,3) double-decker [Cd₉(btc)₆(μ-OH)₆]_n layers and bimbb pillars. The Schläfli symbols for the four frameworks are (4²·6³·8)(4²·6⁵·8³) (1), (4⁴·6⁶) (2), (4⁴·6²)(4⁶·6⁴) (3), and (6³)(6¹⁰) (4). The photoluminescent properties of 1–4 were also investigated.

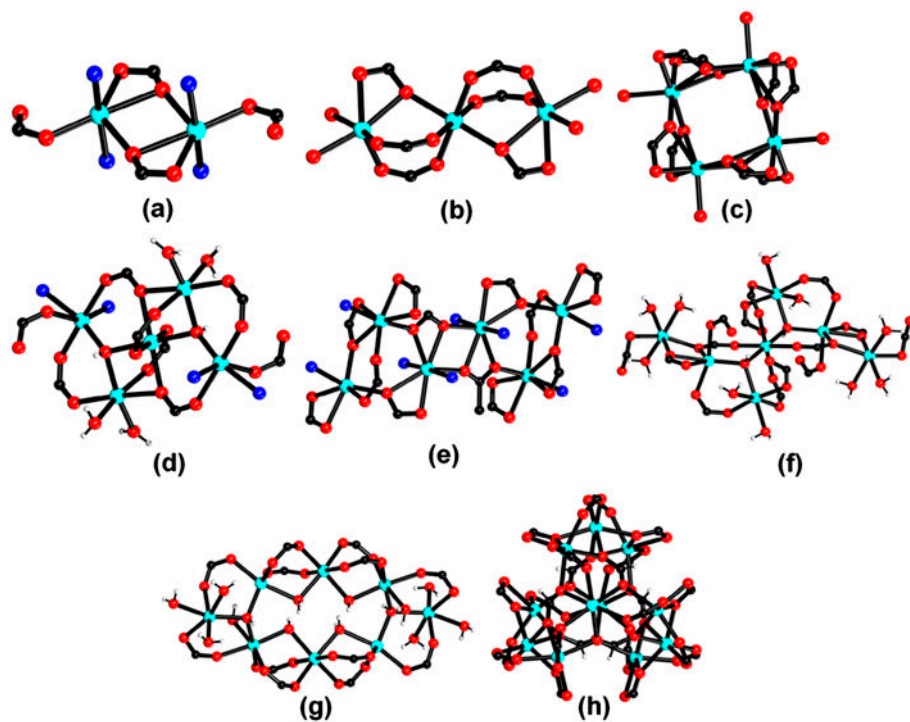
Keywords: Solvothermal reaction; Cadmium; Crystal structure; Coordination polymer; 4,4'-Bis(benzoimidazol-1-yl)biphenylene

1. Introduction

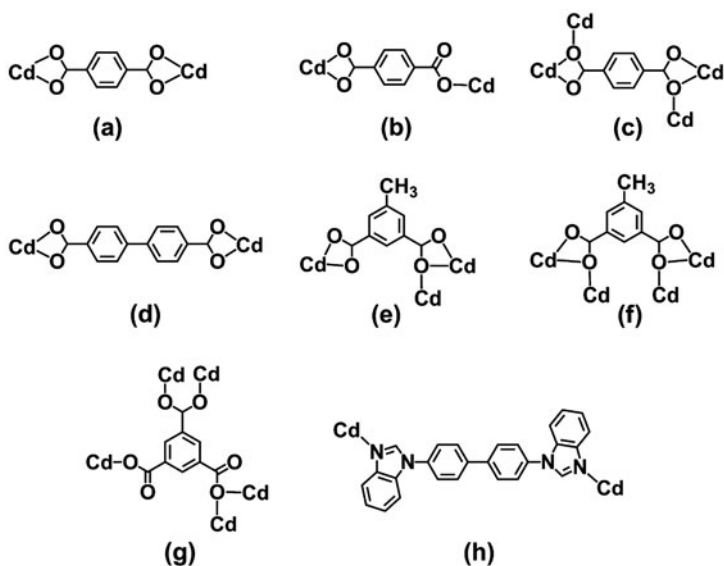
Even after two decades, much interest in metal–organic frameworks (MOFs) continues to be motivated by their intriguing architectures [1] and potential applications in absorption [2], separation [3], magnetism [4], luminescence [5], and catalysis [6]. These extended networks can be self-assembled by metal ions or polynuclear units with organic linkers [7]. By virtue of their well-defined structures and unique properties, some preformed transition-metal clusters can be employed to construct cluster-based MOFs [7j–l, 8]. In addition, polynuclear units generated *in situ* during the reaction of transition metal salts with di- or

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multi-carboxylates and/or multidentate N-donor bridging ligands have become another choice to construct MOFs efficiently [7b, h]. Because cadmium(II) can adopt different coordination geometries when it is assembled with carboxylates [9], various polynuclear Cd/carboxylate (CA) units such as the dinuclear paddlewheel $[\text{Cd}_2(\text{CA})_2]$ unit [9d, f, n], the trinuclear hourglass $[\text{Cd}_3(\text{CA})_6]$ unit [9e, o], the tetranuclear twisted square prism $[\text{Cd}_4(\text{CA})_8]$ unit [9f, p], the pentanuclear cubic $[\text{Cd}_5(\text{CA})_8(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4]$ unit [9g, s], the hexanuclear ribbon-like $[\text{Cd}_6(\text{OAc})_4(\text{CA})_8]$ unit [9h], the heptanuclear central symmetric $[\text{Cd}_7(\text{CA})_8(\mu_3\text{-OH})_2]$ unit [9i], the octanuclear metallacrown $\{[\text{Cd}_8(\text{CA})_{12}(\text{OH})_4(\text{H}_2\text{O})_{10}]\}$ unit [9j], and the undecanuclear C_3 symmetry $[\text{Cd}_{11}(\mu_4\text{-HCOO})_6(\text{CA})_{18}]$ unit [9k] (scheme 1) have been observed. The structures of these units change depending on synthetic conditions such as solvents, reaction temperatures, pH values, etc. [10]. Very recently, we used 1,3-benzenedicarboxylic acid with substituent groups at the 5-positions of the phenyl rings, 5-R-1,3-BDC (R=H, CH₃, NH₂, OH, NO₂), to react with $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and 4,4'-bis(1-imidazolyl)biphenylene (bimb). Four pillared-layer structures $[\text{Cd}(5\text{-R-1,3-BDC})(\text{bimb})]_n$ (R=H, Me, NH₂, OH) based on the dinuclear $[\text{Cd}_2(5\text{-R-1,3-BDC})_4]$ unit and one twofold interpenetrating 3D framework $\{[\text{Cd}_2(\text{H}_2\text{O})_2(5\text{-NO}_{2-1,3\text{-BDC}})_2(\text{bimb})] \cdot 2\text{H}_2\text{O}\}_n$ based on the dinuclear $[\text{Cd}_2(5\text{-NO}_{2-1,3\text{-BDC}})_4(\text{H}_2\text{O})_2]$ unit were isolated [11]. These results showed that the substituents on organic carboxylate ligands could exert great impact on the formation of Cd/carboxylate units and tune the topology of MOFs. If we introduce steric



Scheme 1. Structures of polynuclear Cd/carboxylate units found in the literature: (a) dinuclear paddlewheel unit; (b) trinuclear hourglass unit; (c) tetranuclear twisted square prism unit; (d) pentanuclear cubic unit; (e) hexanuclear ribbon-like unit; (f) heptanuclear central symmetric unit; (g) octanuclear metallacrown unit; (h) undecanuclear C_3 symmetry unit. The red, blue, cyan and gray balls represent O, N, Cd and H atoms, respectively. (see <http://dx.doi.org/10.1080/00958972.2013.804179> for color version)



Scheme 2. The coordination modes of 1,4-bdc in **1** (a–c), 4,4'-bpdb in **2** (d), 5-Me-1,3-bdc in **3** (e–f), btc in **4** (g), and bimbb in **1–4** (h).

hindrance on the imidazolyl groups of bimbb, can the resulting bimbb analogs, when they react with Cd(II) salts and carboxylic acids, produce new Cd(II) MOFs with different Cd/carboxylate units and different topological structures and properties? With this in mind, we prepared one bimbb analog, 4,4'-bis(benzoimidazol-1-yl)biphenyl (bimbb) [12], and carried out its reactions with $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and 1,4-benzenedicarboxylic acid (1,4- H_2bdc), 4,4'-biphenyldicarboxylic acid (4,4'- H_2bpdb), 5-methyl-1,3-benzenedicarboxylic acid (5-Me-1,3- H_2bdc), or 1,3,5-benzenetricarboxylic acid (H_3btc) (scheme 2) under solvothermal conditions. Four different 3-D MOFs, $\{[\text{Cd}_2(1,4\text{-bdc})_2(\text{bimbb})_2] \cdot \text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Cd}_2(4,4'\text{-bpdb})_2(\text{bimbb})(\text{H}_2\text{O})_2]_n$ (**2**), $[\text{Cd}_2(5\text{-Me-1,3-bdc})_2(\text{bimbb})]_n$ (**3**), and $\{[\text{Cd}_3(\text{btc})_2(\text{bimbb})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**4**) were isolated. Herein, we report their syntheses, crystal structures, and photoluminescent properties.

2. Experimental

2.1. Materials and instruments

The bimbb ligand was prepared according to the literature method [13]. Other chemicals and reagents were obtained from commercial sources and used as received. C, H, N elemental analyses were performed on a Carlo-Erba CHNO-S microanalyzer. The IR spectra (KBr disk) were recorded on a Nicolet MagNa-IR550 FT-IR spectrometer ($4000\text{--}400\text{ cm}^{-1}$). The powder X-ray diffraction (PXRD) measurements were carried out on a PANalytical X'Pert PRO MPD system (PW3040/60). The emission/excitation spectra were measured on a Varian Cary Eclipse fluorescence spectrophotometer equipped with a continuous Xenon Lamp.

2.2. Preparation of 1–4

2.2.1. Preparation of $\{[\text{Cd}_2(1,4\text{-bdc})_2(\text{bimbb})_2]\cdot\text{H}_2\text{O}\}_n$ (1). A 10 mL Pyrex glass tube was charged with $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$ (23 mg, 0.1 mM), 1,4- H_2bdc (17 mg, 0.1 mM), bimbb (39 mg, 0.1 mM), 2 mL of H_2O , and 1 mL of MeCN. The tube was sealed and heated in an oven to 170 °C for 2 d and then cooled to ambient temperature at the rate of 5 °C h⁻¹. Dark brown blocks of **1** (32 mg, 48% yield based on 1,4-bdc) were washed with water–methanol and dried in air. Anal. Calcd for $\text{C}_{68}\text{H}_{46}\text{Cd}_2\text{N}_8\text{O}_9$ (%): C, 60.77; H, 3.45; N, 8.34. Found: C, 61.23; H, 3.35; N, 8.22. IR (KBr, cm⁻¹): 1606(m), 1567(s), 1508(s), 1384(s), 1237(s), 1017(w), 834(s), 747(s), 531(m).

2.2.2. Preparation of $\{[\text{Cd}_2(4,4'\text{-bpdb})_2(\text{bimbb})(\text{H}_2\text{O})_2]\}_n$ (2). Complex **2** was prepared as brown chips (20 mg, 35% yield based on Cd) in a similar manner to that described for **1** using $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$ (23 mg, 0.1 mM), 4,4'-bpdb (24 mg, 0.1 mM), bimbb (39 mg, 0.1 mM), 2 mL of H_2O and 1 mL of MeCN. Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{CdN}_2\text{O}_5$ (%): C, 57.51; H, 3.40; N, 4.97. Found: C, 56.96; H, 3.55; N, 5.03. IR (KBr, cm⁻¹): 3108(w), 1618(m), 1508(s), 1406(s), 1384(m), 1302(m), 1176(s), 1113(s), 770(s), 620(s), 427(m).

2.2.3. Preparation of $[\text{Cd}_2(5\text{-Me-1,3-bdc})_2(\text{bimbb})]_n$ (3). Complex **3** was prepared as brown blocks (18 mg, 37% yield based on Cd) in a similar manner to that described for **1** using $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$ (23 mg, 0.1 mM), 5-Me-1,3-bdc (18 mg, 0.1 mM), bimbb (39 mg, 0.1 mM), 2 mL of H_2O and 1 mL of MeCN. Anal. Calcd for $\text{C}_{44}\text{H}_{30}\text{Cd}_2\text{N}_4\text{O}_8$ (%): C, 54.62; H, 3.13; N, 5.79. Found: C, 54.73; H, 3.02; N, 5.71. IR (KBr, cm⁻¹): 2918(w), 1614(m), 1535(s), 1509(s), 1421(m), 1373(m), 1231(m), 1111(s), 778(s), 733(s), 429(m).

2.2.4. Preparation of $\{[\text{Cd}_3(\text{btc})_2(\text{bimbb})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}\}_n$ (4). Complex **4** was prepared as brown chips (20 mg, 50% yield based on Cd) in a similar manner to that described for **1** using $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$ (23 mg, 0.1 mM), H_3btc (21 mg, 0.1 mM), bimbb (39 mg, 0.1 mM), 2 mL of H_2O and 1 mL MeCN. Anal. Calcd for $\text{C}_{44}\text{H}_{32}\text{Cd}_3\text{N}_4\text{O}_{16}$ (%): C, 43.68; H, 2.67; N, 4.63. Found: C, 43.27; H, 2.38; N, 4.72. IR (KBr, cm⁻¹): 3422(s), 3052(w), 1611(m), 1534(s), 1421(s), 1376(m), 1297(m), 1236(s), 1111(s), 779(s), 733(s), 624(m).

2.3. X-ray diffraction crystallography

Crystals of **1–4** suitable for X-ray analysis were obtained directly from the above preparations. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer using graphite monochromated Mo-K α ($\lambda=0.71073$ Å) at 293 K. Each single crystal of **1–4** was mounted with grease at the top of a glass fiber. Cell parameters were refined on all observed reflections using the program *CrystalClear* (Rigaku and MSc, Ver. 1.3, 2001). The collected data were reduced by *CrystalClear* and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **1–4** were solved by direct methods and refined on F^2 by full-matrix least-squares with the SHELXL-97 program [14]. In **4**, C5, C6, C9, C10, C12, and C13 of the bimbb ligands were found to be disordered over two sites with an occupancy factor of 0.56/0.44 for C5/C5A, C6/C6A, C9/C9A, C10/C10A, C12/C12A, and C13/C13A.

Table 1. Crystallographic data and structure refinement parameters for 1–4.

	1	2	3	4
Empirical formula	C ₆₈ H ₄₆ Cd ₂ N ₈ O ₉	C ₂₇ H ₁₉ CdN ₂ O ₅	C ₄₄ H ₃₀ Cd ₂ N ₄ O ₈	C ₄₄ H ₃₂ Cd ₃ N ₄ O ₉
Formula mass	1343.92	563.84	967.52	1209.94
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.765(2)	13.699(3)	9.958(2)	9.515(19)
<i>b</i> /Å	15.729(3)	5.883(1)	13.999(3)	9.842(2)
<i>c</i> /Å	20.076(4)	29.791(9)	28.165(7)	12.733(3)
α /°	112.19(3)			77.76(3)
β /°	92.51(3)	108.55(3)	105.26(3)	82.39(3)
γ /°	92.39(3)			65.16(3)
<i>V</i> /Å ³	2846.6(10)	2271.5(10)	3787.8(15)	1056.3(4)
<i>D</i> _c /g cm ⁻³	1.568	1.649	1.697	1.902
<i>Z</i>	2	4	4	1
μ (Mo-K α)/mm ⁻¹	0.816	1.004	1.185	1.578
<i>F</i> (000)	1356	1132	1928	596.0
Total reflections	27,353	20,445	11,310	10,176
Unique reflections	10,335	4132	6640	3838
No. observations	9042	3632	5269	3281
No. parameters	784	324	523	359
<i>R</i> ₁ ^a	0.0360	0.0409	0.0445	0.0351
<i>wR</i> ₂ ^b	0.0972	0.0797	0.0907	0.0715
GOF ^c	1.046	1.051	1.124	1.109
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e·Å ⁻³)	1.024, -0.552	1.186, -0.708	1.208, -0.506	1.336, -0.621

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}.$$

$$^c \text{GOF} = \{ \sum w(F_o^2 - F_c^2)^2 / (n - p) \}^{1/2}, \text{ where } n = \text{number of reflections and } p = \text{total numbers of parameters refined.}$$

Table 2. Selected bond lengths (Å) and angles (°) of 1–4.

Complex 1			
Cd(1)–N(1)	2.421(3)	Cd(2)–N(4)	2.262(3)
Cd(1)–N(5)	2.311(2)	Cd(1)–O(1)	2.222(3)
Cd(1)–O(5)	2.464(2)	Cd(1)–O(6)	2.359(2)
Cd(2)–O(7)	2.415(2)	Cd(2)–O(8)	2.280(3)
Cd(1)–O(5A)	2.492(2)	Cd(2)–N(8B)	2.250(3)
Cd(2)–O(3C)	2.322(3)	Cd(2)–O(4C)	2.389(2)
Cd(1)···O(2)	2.743(3)		
O(1)–Cd(1)–N(5)	125.41(10)	O(1)–Cd(1)–O(6)	91.42(10)
N(5)–Cd(1)–O(6)	143.16(8)	O(1)–Cd(1)–N(1)	98.65(10)
N(5)–Cd(1)–N(1)	89.41(9)	O(6)–Cd(1)–N(1)	84.11(9)
O(1)–Cd(1)–O(5)	136.86(9)	N(5)–Cd(1)–O(5)	92.41(8)
O(6)–Cd(1)–O(5)	54.09(8)	N(1)–Cd(1)–O(5)	101.98(8)
O(1)–Cd(1)–O(5A)	87.13(9)	N(5)–Cd(1)–O(5A)	85.95(8)
O(6)–Cd(1)–O(5A)	97.35(8)	N(1)–Cd(1)–O(5A)	174.01(8)
O(5)–Cd(1)–O(5A)	74.47(8)	N(8B)–Cd(2)–N(4)	96.54(10)
N(8B)–Cd(2)–O(8)	156.35(10)	N(4)–Cd(2)–O(8)	87.21(11)
N(8B)–Cd(2)–O(3C)	85.84(10)	N(4)–Cd(2)–O(3C)	148.86(10)
O(8)–Cd(2)–O(3C)	102.94(11)	N(8B)–Cd(2)–O(4C)	112.58(10)
N(4)–Cd(2)–O(4C)	95.32(10)	O(8)–Cd(2)–O(4C)	90.19(10)
O(3C)–Cd(2)–O(4C)	55.89(9)	N(8B)–Cd(2)–O(7)	101.42(10)
N(4)–Cd(2)–O(7)	104.68(10)	O(8)–Cd(2)–O(7)	55.23(9)
O(3C)–Cd(2)–O(7)	105.24(10)	O(4C)–Cd(2)–O(7)	138.09(9)
Complex 2			
Cd(1)–N(1)	2.290(3)	Cd(1)–O(1)	2.312(3)
Cd(1)–O(2)	2.464(3)	Cd(1)–O(5)	2.450(3)

(Continued)

Table 2. (Continued)

Cd(1)–O(3A)	2.296(3)	Cd(1)–O(4A)	2.402(3)
Cd(1)–O(5B)	2.451(3)		
N(1)–Cd(1)–O(3A)	97.95(14)	N(1)–Cd(1)–O(1)	82.94(12)
O(3A)–Cd(1)–O(1)	163.03(10)	N(1)–Cd(1)–O(4A)	105.74(12)
O(3A)–Cd(1)–O(4A)	55.36(10)	O(1)–Cd(1)–O(4A)	140.81(10)
N(1)–Cd(1)–O(5)	91.42(12)	O(3A)–Cd(1)–O(5)	80.01(11)
O(1)–Cd(1)–O(5)	83.02(10)	O(4A)–Cd(1)–O(5)	133.52(10)
N(1)–Cd(1)–O(5B)	169.16(12)	O(3A)–Cd(1)–O(5B)	91.00(12)
O(1)–Cd(1)–O(5B)	86.72(11)	O(4A)–Cd(1)–O(5B)	84.36(10)
O(5)–Cd(1)–O(5B)	84.10(6)	N(1)–Cd(1)–O(2)	93.69(12)
O(3A)–Cd(1)–O(2)	141.56(10)	O(1)–Cd(1)–O(2)	54.78(9)
O(4A)–Cd(1)–O(2)	86.23(9)	O(5)–Cd(1)–O(2)	136.34(10)
O(5B)–Cd(1)–O(2)	82.91(10)		
Complex 3			
Cd(1)–N(1)	2.298(3)	Cd(2)–O(1)	2.317(3)
Cd(1)–O(1)	2.640(3)	Cd(1)–O(2)	2.259(3)
Cd(1)–O(5)	2.411(3)	Cd(2)–O(5)	2.644(3)
Cd(2)–O(6)	2.259(3)	Cd(1)–O(3B)	2.431(3)
Cd(1)–O(4B)	2.343(3)	Cd(2)–O(7D)	2.349(4)
Cd(1)–O(4C)	2.439(3)	Cd(2)–O(8D)	2.287(3)
Cd(2)–N(3A)	2.240(4)		
O(2)–Cd(1)–N(1)	132.14(13)	O(2)–Cd(1)–O(4B)	126.00(11)
N(1)–Cd(1)–O(4B)	97.92(12)	O(2)–Cd(1)–O(5)	96.96(12)
N(1)–Cd(1)–O(5)	85.53(12)	O(2)–Cd(1)–O(3B)	85.16(12)
O(2)–Cd(1)–O(3B)	85.16(12)	N(1)–Cd(1)–O(3B)	141.36(12)
O(4B)–Cd(1)–O(3B)	54.66(10)	O(5)–Cd(1)–O(3B)	79.14(12)
O(5)–Cd(1)–O(3B)	79.14(12)	O(2)–Cd(1)–O(4C)	84.70(12)
N(1)–Cd(1)–O(4C)	92.34(12)	O(4B)–Cd(1)–O(4C)	72.72(11)
O(5)–Cd(1)–O(4C)	177.85(10)	O(3B)–Cd(1)–O(4C)	102.41(11)
O(2)–Cd(1)–O(1)	52.80(11)	N(1)–Cd(1)–O(1)	83.87(12)
O(4B)–Cd(1)–O(1)	177.79(10)	O(5)–Cd(1)–O(1)	71.55(10)
O(3B)–Cd(1)–O(1)	123.15(11)	O(4C)–Cd(1)–O(1)	108.57(10)
N(3A)–Cd(2)–O(6)	120.32(12)	N(3A)–Cd(2)–O(8D)	95.73(13)
O(6)–Cd(2)–O(8D)	127.26(13)	N(3A)–Cd(2)–O(1)	93.90(12)
O(6)–Cd(2)–O(1)	105.63(11)	N(3A)–Cd(2)–O(7D)	150.16(13)
O(6)–Cd(2)–O(7D)	85.02(14)	O(8D)–Cd(2)–O(7D)	54.57(13)
O(1)–Cd(2)–O(7D)	93.73(19)	N(3A)–Cd(2)–O(5)	82.80(12)
O(6)–Cd(2)–O(5)	52.62(10)	O(8D)–Cd(2)–O(5)	177.72(12)
O(1)–Cd(2)–O(5)	72.88(10)	O(7D)–Cd(2)–O(5)	126.98(12)
Complex 4			
Cd(1)–N(2)	2.274(4)	Cd(1)–O(2)	2.289(3)
Cd(2)–O(2)	2.315(3)	Cd(1)–O(7)	2.476(3)
Cd(2)–O(7)	2.488(3)	Cd(1)–O(5A)	2.238(3)
Cd(2)–O(4B)	2.142(2)	Cd(1)–O(3B)	2.305(3)
		Cd(1)···O(1)	2.657(4)
Cd(1)···O(6)	2.703(4)		
O(5A)–Cd(1)–N(2)	102.28(14)	O(5A)–Cd(1)–O(2)	121.64(9)
N(2)–Cd(1)–O(2)	109.07(12)	O(5A)–Cd(1)–O(3B)	138.70(11)
N(2)–Cd(1)–O(3B)	83.06(13)	O(2)–Cd(1)–O(3B)	93.71(10)
O(5A)–Cd(1)–O(7)	89.61(11)	N(2)–Cd(1)–O(7)	160.47(12)
O(2)–Cd(1)–O(7)	76.50(10)	O(3B)–Cd(1)–O(7)	77.83(10)
		O(4C)–Cd(2)–O(2)	93.36(10)
O(4B)–Cd(2)–O(2)	86.64(10)		
O(4C)–Cd(2)–O(7)	84.10(10)	O(4B)–Cd(2)–O(7)	95.90(10)
O(2D)–Cd(2)–O(7D)	75.79(10)	O(2D)–Cd(2)–O(7)	104.21(10)
		O(2D)–Cd(2)–O(7D)	75.79(10)

^aSymmetry codes: For **1**: (A) $-x+2, -y, -z+2$; (B) $-x, -y+1, -z+1$; (C) $x, y, z-1$. For **2**: (A) $x, -y+1/2, z-1/2$; (B) $-x+1, y-1/2, -z+1/2$. For **3**: (A) $x+1, -y+3/2, z+1/2$; (B) $x+1, y, z$; (C) $-x, -y+2, -z+2$; (D) $x-1, y, z$. For **4**: (A) $x, y-1, z$; (B) $x-1, y, z$; (C) $-x+2, -y+1, -z+2$; (D) $-x+1, -y+1, -z+2$.

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the water solvate molecules in **1**, **2**, and **4** were located from the Fourier map. The hydrogen atoms of the water molecules in **1** and **4** were constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ for hydroxyl groups. All calculations were performed on a Dell workstation using the CrystalStructure crystallographic software package (Rigaku and MSC, Ver. 3.60, 2004). A summary of crystallographic data and refinement parameters for **1–4** are in table 1 and selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. Preparation and characterization of **1–4**

The solvothermal reaction of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ with 1,4- H_2bdc and bimbb in a 1 : 1 : 1 M ratio at 170 °C for 2 d gave rise to dark brown crystals of **1** in 48% yield. Analogous reactions with 4,4'- H_2bpd , 5-Me-1,3- H_2bdc or H_3btc afforded brown crystals of **2** (35% yield), **3** (37% yield), and **4** (50% yield), respectively. In **1–4**, the four carboxylate ligands display different coordination modes shown in scheme 2. According to the literature [12b, 15], the spacers of biimidazolyl/bibenzoimidazolyl-containing ligands range from flexible alkyl $-(\text{CH}_2)_n-$ to semirigid $-(\text{CH}_2\text{PhCH}_2)-$ to rigid phenylene and biphenyl functionalities and display different geometries, which offers us the opportunity to systematically study the relationship between the geometry of the ligand and the resulting frameworks. As described later in this article, **1–4** also show different 3-D topological structures with different Cd/carboxylate units such as a dinuclear $[\text{Cd}_2(1,4\text{-bdc})_3]$ unit and a centrosymmetric dinuclear $[\text{Cd}_2(1,4\text{-bdc})_4]$ unit (**1**), zigzag chain $[\text{Cd}(4,4'\text{-bpd})_2(\mu\text{-OH}_2)]$ unit (**2**), tetranuclear rod-like $[\text{Cd}_4(5\text{-Me-1,3-bdc})_8]$ unit (**3**), and trinuclear hourglass $[\text{Cd}_3(\text{btc})_6(\mu\text{-OH}_2)_2]$ unit (**4**). All these observations showed that carboxylate ligands with different spacer lengths or substituents significantly affect their coordination modes, the Cd/carboxylate structural units, the conformations of bimbb ligands, and the topological structures of the final products.

Complexes **1–4** are air-stable and insoluble in common solvents. The elemental analyses were consistent with the chemical formulas of **1–4**. The IR spectra of **1–4** showed strong peaks in the range of 1550–1618 and 1314–1465 cm^{-1} , indicating that they all contain coordinated carboxylic groups. The strong peaks at *ca.* 1060 and 650 cm^{-1} in **1–4** were consistent with the presence of imidazolyl groups. PXRD was employed to confirm the bulk-phase homogeneity of the four complexes. For **1–4**, the measured PXRD patterns closely match the simulated patterns generated from the results of single crystal X-ray diffraction data (ESI, figure S1). The identities of **1–4** were further confirmed by single crystal X-ray diffraction analysis.

3.2. Descriptions of structures of **1–4**

3.2.1. $\{[\text{Cd}_2(1,4\text{-bdc})_2(\text{bimbb})_2] \cdot \text{H}_2\text{O}\}_n$ (1**).** Complex **1** crystallizes in the triclinic space group $P\bar{1}$ and the asymmetric unit contains a $[\text{Cd}_2(1,4\text{-bdc})_2(\text{bimbb})_2]$ moiety and one water solvent molecule. As shown in figure 1(a), Cd1 is octahedrally coordinated by two N atoms from different bimbb ligands and four O atoms from three 1,4-bdc ligands, though a weak interaction between Cd1 and O2 (2.743(3) Å) is observed. Cd2 is also octahedrally surrounded by four O atoms from two 1,4-bdc ligands and two N atoms from

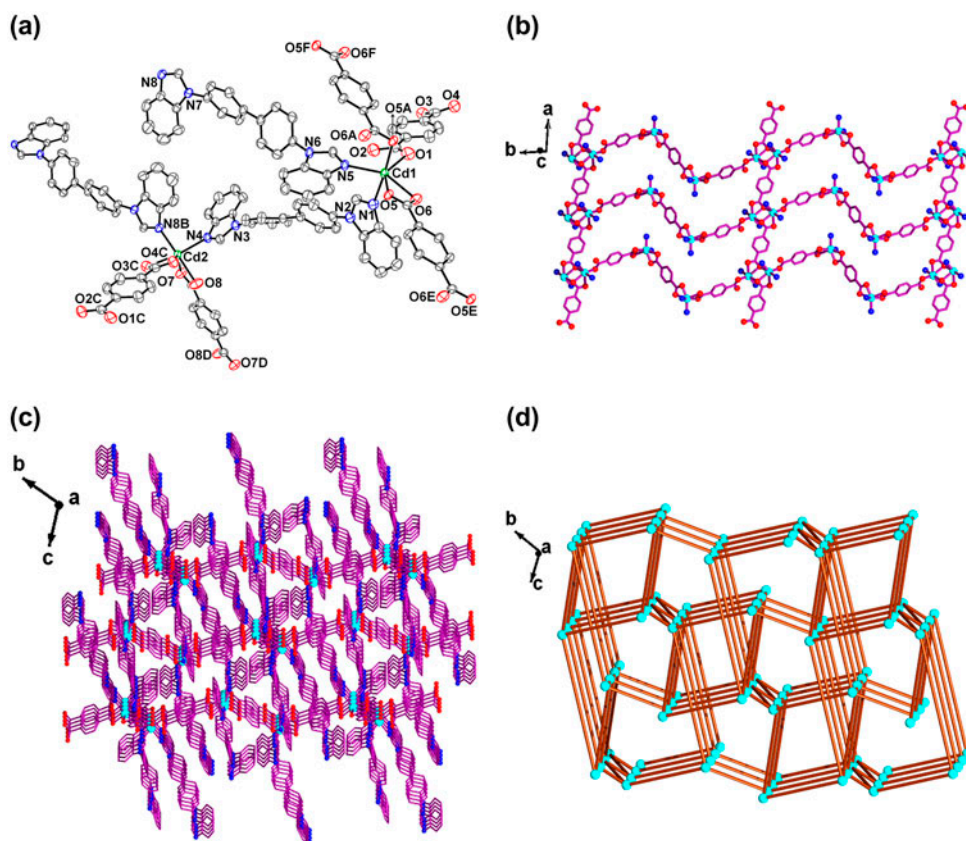


Figure 1. (a) View of the coordination environments of Cd1 and Cd2 in **1** with labeling scheme and 40% thermal ellipsoids. All hydrogens have been omitted for clarity. Symmetry codes: (A) $-x+2, -y, -z+2$; (B) $-x, -y+1, -z+1$; (C) $x, y, z-1$; (D) $-x+2, -y+2, -z+1$; (E) $-x+3, -y, -z+2$; (F) $x-1, y, z$. (b) View of the 2-D (8,4) network extending along the *ab* plane. (c) View of the 3-D net of **2** looking down the *a* axis. (d) Schematic view of a $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6^3 \cdot 8^3)$ topological net of **1**. The red, blue, and cyan balls represent O, N, and Cd, respectively. Each brown line represents one bimbb or one 1,4-bdc. (see <http://dx.doi.org/10.1080/00958972.2013.804179> for color version)

two bimbb ligands. The 1,4-bdc ligands in **1** display three coordination modes; both carboxylate groups of a 1,4-bdc are chelating bidentate (O7, O8) (scheme 2(a)), or one is semi-chelating (O1, O2) [16a] and the other is chelating bidentate (O3, O4) (scheme 2(b)), or both groups are μ_3 -chelating/bridging tridentate (μ -O5, O6) (scheme 2(c)). The bimbb ligands show two conformations. One has a N–N distance of 14.086 Å (N1/N4 pair) and a dihedral angle of 57.67° between the benzoimidazolyl groups and a dihedral angle of 32.32° between the two benzene groups, while the other has a N–N distance of 14.182 Å (N5/N8 pair) and the corresponding dihedral angles of 73.66° and 47.36°, respectively. The Cd1–O1 bond length (2.222(3) Å) is shorter than those of the average chelating Cd2–O (O3C/O4C/O7/O8) bond length (2.352(3) Å) and the average μ_3 -chelating/bridging Cd1–O (O5/O6/O5A) bond length (2.438(2) Å) (table 2). The average Cd–O length (2.368 (2) Å) in **1** is slightly shorter than that in $\{[\text{Cd}_2(1,4\text{-bdc})_2\text{L}_2](1,4\text{-H}_2\text{bdc})_{3/2}(\text{H}_2\text{O})\}_n$ (L = 3-(2-pyridyl)pyrazole) (2.391(2) Å) [16b]. The average Cd–N bond length (2.311(3) Å) is shorter than that of $\{[\text{Cd}(\text{bimbb})_3](\text{ClO}_4)\}_n$ (2.386(6) Å) [11]. As shown in figure 1(b), two Cd1 atoms are bridged by two μ_3 -chelating/bridging carboxylate groups to give a

centrosymmetric dinuclear $[\text{Cd}_2(1,4\text{-bdc})_2]$ unit. In this unit, the $\text{Cd}\cdots\text{Cd}$ distance (3.946 (1) Å) is longer than that found in $\{[\text{Cd}(\text{pnta})_2]\cdot 3.8\text{DMF}\}_n$ (3.837(1) Å, pnta = 6-(pyridin-4-yl)nicotinic acid) [9d]. Two Cd2 centers are also linked by one chelating bidentate 1,4-bdc to form a dinuclear $[\text{Cd}_2(1,4\text{-bdc})]$ unit. These two units are interconnected through shared semi-chelating/chelating bidentate 1,4-bdc to form a $[\text{Cd}_4(\mu_3\text{-}1,4\text{-bdc})_2(1,4\text{-bdc})_3]$ chain extending along the *b* axis. This chain is further linked to its equivalent ones by the two μ_3 -chelating/bridging 1,4-bdc to afford a 2-D undulated (8,4) layer with dimensions of 9.77 Å \times 26.98 Å for a $[\text{Cd}_8(1,4\text{-bdc})_8]$ grid. The bimbb ligands connect this 2-D layer to its two neighboring layers, thereby forming a 3-D framework with triangular, rectangular, and pentagonal channels along the *a* axis (figure 1(c)). The effective solvent accessible volume of 89.0 Å³ per unit cell (3.1% of the total cell volume calculated by the Platon program [16c]) is filled with water solvate molecules. These water molecules interact with the carboxylate groups to form intermolecular H-bonding interactions (O(9)–H \cdots O(7)) (ESI, table S1). If the Cd1 centers and the Cd2 centers are considered as five- and four-connecting nodes, respectively, the whole net of **1** has a 3-D (4,5)-connected topological structure with a $(4^2\cdot 6^3\cdot 8)(4^2\cdot 6^5\cdot 8^3)$ Schläfli symbol (figure 1(d)).

3.2.2. $\{[\text{Cd}_2(4,4'\text{-bpdb})_2(\text{bimbb})(\text{H}_2\text{O})_2]\}_n$ (2**).** Complex **2** crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit consists of half a $[\text{Cd}_2(4,4'\text{-bpdb})_2(\text{bimbb})(\text{H}_2\text{O})_2]$ molecule. As shown in figure 2(a), each Cd center adopts a pentagonal bipyramidal geometry, coordinated by two O atoms from different bridging H_2O molecules, four O atoms from two 4,4'-bpdb ligands, and one N atom from a bimbb ligand. In **2**, the carboxylate groups of each 4,4'-bpdb display only a chelating bidentate mode (O1/O2 and O3/O4) (scheme 2(d)). Each bimbb has a N–N distance of 14.094 Å (N1/N3 pair) and a dihedral angle of *ca.* 0° between the two benzoimidazolyl groups and between the benzene groups. The average chelating Cd–O (Cd1–O1, Cd1–O2, Cd2–O3A, Cd2–O4A) and the Cd1–N1 bond lengths, 2.369(3) and 2.290(3) Å, respectively (table 2), in **2** are slightly shorter than the corresponding values for complexes with pentagonal bipyramidally coordinated Cd atoms, such as $\{[\text{Cd}(\text{pmmid})(\text{pma})_{0.5}(\text{H}_2\text{O})]\cdot 5\text{H}_2\text{O}\}_n$ (pmmid = 1-(4-pyridylmethyl)-2-methylimidazole, H_4pma = pyromellitic acid) (C–O, 2.427(5) and C–N, 2.309(7) Å) [17a]. The Cd–O(μ -OH₂) bond distances in **2** are equivalent and longer than that in $\{[\text{Cd}(\text{pmmid})(\text{pma})_{0.5}(\text{H}_2\text{O})]\cdot 5\text{H}_2\text{O}\}_n$ (2.317(6) Å). Each Cd atom is bridged by μ -H₂O molecules to form a 1-D zigzag chain $[\text{Cd}(\mu\text{-H}_2\text{O})]_n$ (Cd–O–Cd = 127.2(2)°, Cd \cdots Cd = 4.395(7) Å) along the *b* axis (figure 2(b)). This chain is interlinked via 4,4'-bpdb extending along the *bc* plane to give a 2-D (4,4) undulated layer $[\text{Cd}(4,4\text{-bpdb})_2(\mu_2\text{-OH}_2)_2]_n$ with rectangular grids (4.39 Å \times 15.46 Å) (figure 2(b)). Each bimbb acts as a pillar to link the adjacent 2-D layers via N atoms to form a 3-D pillared-layer framework containing two types of rectangular channels (4.39 Å \times 15.46 Å and 7.56 \times 12.49 Å) extending along the *a* axis (figure 2(c)). If the Cd centers are considered as five-connecting nodes, the whole net of **2** has a 3-D five-connected topological structure with a $(4^4\cdot 6^6)$ Schläfli symbol (figure 2(d)). Within the $[\text{Cd}(4,4\text{-bpdb})_2(\mu\text{-OH}_2)_2]_n$ unit, there are many weak intermolecular $\pi\cdots\pi$ interactions between the phenyl groups of two adjacent 4,4'-bpdb ligands (3.669 Å), and between the phenyl group of one bimbb and the benzoimidazolyl rings of an adjacent bimbb (3.477 and 3.789 Å).

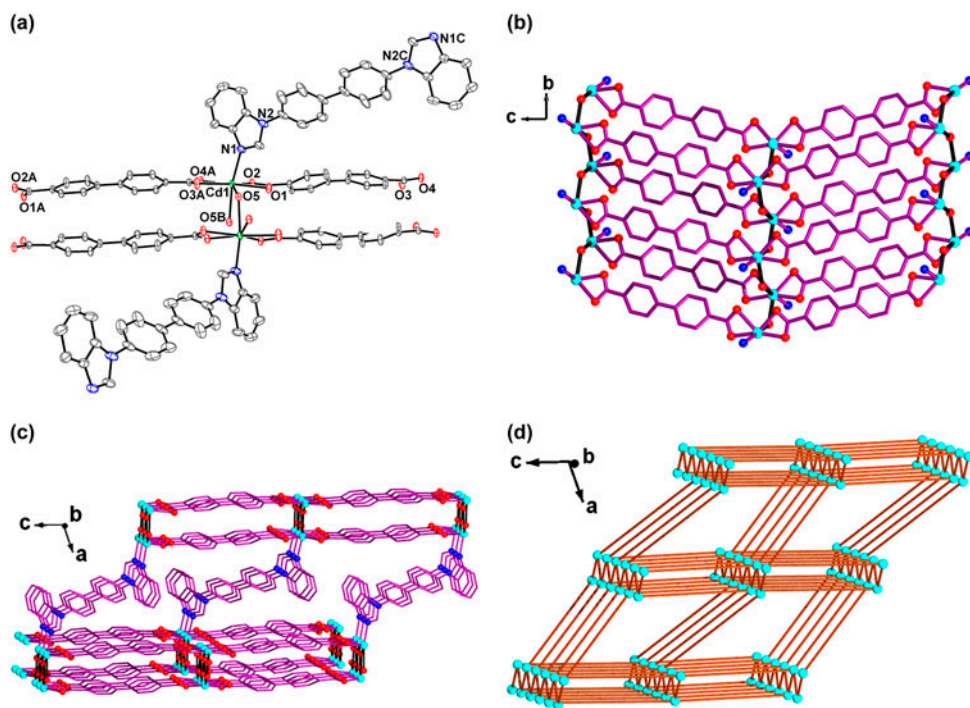


Figure 2. (a) View of the coordination environment of Cd1 in **2** with labeling scheme and 40% thermal ellipsoids. All hydrogens have been omitted for clarity. Symmetry codes: (A) $x, -y+1/2, z-1/2$; (B) $-x+1, y-1/2, -z+1/2$; (C) $-x+2, -y+3, -z+1$. (b) View of the 2-D (6,3) layer of **2** extending along the bc plane. (c) View of the 3-D net of **2** looking down the b axis. (d) Schematic view of a (4⁴.6⁶) topological net of **2**. The red, blue, and cyan balls represent O, N, and Cd, respectively. Each brown line represents one bimbb, one 4,4'-bpdb, or one water. (see <http://dx.doi.org/10.1080/00958972.2013.804179> for color version)

3.2.3. [Cd₂(5-Me-1,3-bdc)₂(bimbb)]_n (3**).** Complex **3** crystallizes in the monoclinic space group $P2_1/c$ and its asymmetric unit contains one [Cd₂(5-Me-1,3-bdc)₂(bimbb)] molecule. As shown in figure 3(a), the Cd centers in **3** have two different coordination geometries. Cd1 has a pentagonal bipyramidal geometry, coordinated by six O atoms from four btc ligands and one N atom from a bimbb ligand. The Cd2 atom is octahedrally coordinated by five O atoms from three btc ligands and one N atom from a bimbb ligand. The 5-Me-1,3-bdc ligand adopts two different coordination modes. In one mode, the carboxylate groups are chelating bidentate (O7, O8) and μ_3 -chelating/bridging (μ -O5, O6) (scheme 2(e)), while in the other mode, both carboxylate groups are μ_3 -chelating/bridging (μ -O1/O2 or O3/ μ -O4) (scheme 2(f)). Each bimbb has a N–N distance of 14.096 Å (N1/N3 pair) and a dihedral angle of 54.73° between the benzoimidazolyl groups and a dihedral angle of 33.73° between the benzene groups. In **3**, the average Cd1–O (O1/O2/O3B/O4B/O4C/O5) bond length (2.421(3) Å) (table 2) is almost the same as those found in **2** and {[Cd(1,4-pda)(biim)]·H₂O}_n (1,4-pda = 1,4-phenylenediacetate acid, biim = 1,1'-(1,6-hexanedidyl)bis(imidazole)) (2.400(4) Å) [17b]. The Cd1–N1 bond length (2.298(3) Å) is also equivalent to those in **2** and {[Cd(1,4-pda)(biim)]·H₂O}_n (2.273(3) Å). The average Cd2–O (O1/O5/O6/O7D/O8D) bond length (2.371(2) Å) is comparable to the corresponding distances in complexes containing octahedrally coordinated Cd atoms such as **1** and [Cd(5-OH-1,3-

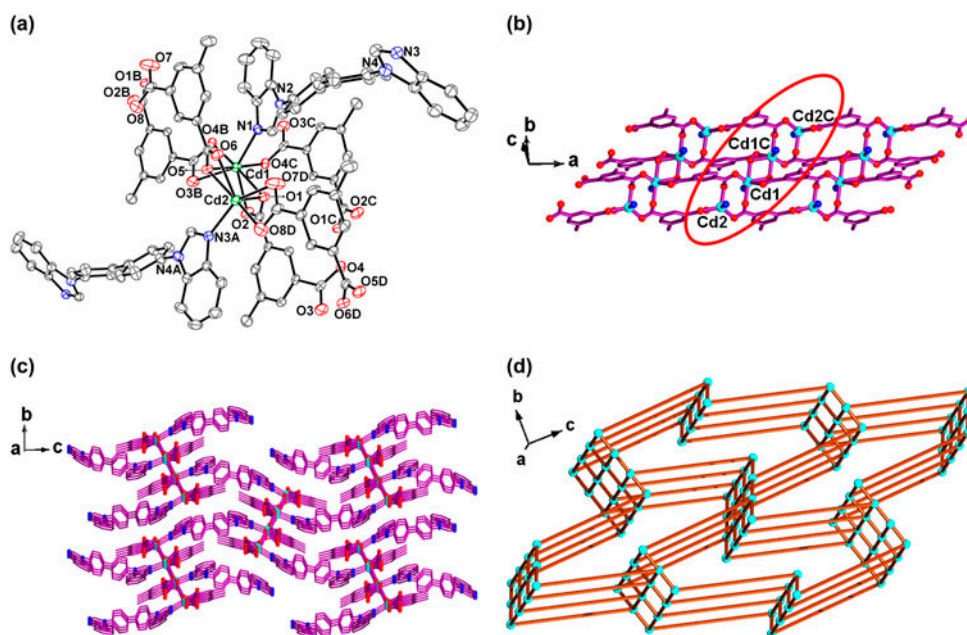


Figure 3. (a) View of the coordination environments of Cd1 and Cd2 in **3** with labeling scheme and 40% thermal ellipsoids. All hydrogens have been omitted for clarity. Symmetry codes: (A) $x+1, -y+3/2, z+1/2$; (B) $x+1, y, z$; (C) $-x, -y+2, -z+2$; (D) $x-1, y, z$. (b) View of a section of the 1-D $[\text{Cd}_4(5\text{-Me-1,3-bdc})_4]_n$ ribbon (extending along the a axis). (c) View of the 3-D net of **3** looking down the a axis. (d) Schematic view of a $(4^4 \cdot 6^2)(4^6 \cdot 6^4)$ topological net of **3**. The red, blue, and cyan balls represent O, N, and Cd, respectively. Each brown line represents one bimbb or 5-Me-1,3-bdc. (see <http://dx.doi.org/10.1080/00958972.2013.804179> for color version)

bdc)(bie)] (5-OH-1,3-bdc = 5-hydroxy-1,3-benzenedicarboxylate, bie = 2,2'-bis(1*H*-imidazolyl)ether) (2.338(2) Å) [16c]. The Cd2–N3A bond length (2.269(4) Å) is shorter than the corresponding distance in **1**. Two Cd1 atoms and two Cd2 atoms are linked by three pairs of μ_3 -chelating/bridging 5-Me-1,3-bdc to form a linear tetranuclear $[\text{Cd}_4(\mu_3\text{-5-Me-1,3-bdc})_6(5\text{-Me-1,3-bdc})_2]$ unit (circled part in figure 3(b)) (Cd1...Cd2 = 4.047(1) Å and Cd1...Cd1C = 3.850(1) Å). This unit is interlinked to neighboring ones to produce a 1-D $[\text{Cd}_4(5\text{-Me-1,3-bdc})_4]_n$ ribbon extending along the a axis (figure 3(b)). Each ribbon is further connected to four others by bimbb to give a 3-D framework with octagonal channels extending along the a axis (figure 3(c)). The effective solvent accessible volume of 99.1 Å³ per unit cell (2.6% of the total cell volume calculated by the Platon program) is too small to be filled with solvent molecules. If the Cd1 centers and the Cd2 centers are considered as five- and four-connecting nodes, respectively, the overall net of **3** can be considered as a 3-D (4,5)-connected structure with a $(4^4 \cdot 6^2)(4^6 \cdot 6^4)$ Schläfli symbol (figure 3(d)).

3.2.4. $\{[\text{Cd}_3(\text{btc})_2(\text{bimbb})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$ (4**).** Complex **4** crystallizes in the triclinic space group $P\bar{1}$ and the asymmetric unit contains half of a $[\text{Cd}_3(\text{btc})_2(\text{bimbb})(\text{H}_2\text{O})_2]$ molecule and one water solvate molecule. There is a crystallographic inversion center located at the Cd2 atom. As shown in figure 4(a), Cd1 is in a square pyramidal environment, coordinated by three O atoms from three btc ligands, one N atom from a bimbb ligand, and one O atom from the bridging water molecule, while Cd2 is octahedrally coordinated by four O atoms from four btc ligands and two O atoms from different bridging water

molecules. Weak interactions between Cd(1) and O(1) (2.657(4) Å), and Cd(1) and O(6) (2.703(4) Å) are observed. In **4**, the three carboxylate groups of each btc are bound to five Cd atoms with three different coordination modes: semi-chelating (O5, O6), μ -bridging bidentate (O3, O4), and semi- μ_2 -chelating/bridging bidentate (μ -O2, O1) (scheme 2(g)). The average Cd1–O (O2B/O3B/O5A) bond length (2.277(3) Å) is comparable to those in **1** and **3**, but longer than that in [Cd(bmb)_{0.5}(oba)]_n (bmb = 1,4-bis(2-methylbenzimidazol-1-ylmethyl)benzene, H₂oba = 4,4'-oxybis(benzoic acid), 2.229(3) Å [16d]. The Cd1–N2 bond length (2.274(4) Å) is shorter than that in **1** but longer than those in [Cd(bmb)_{0.5}(oba)]_n (2.225(3) Å) and **3**. The Cd1–O7 (OH₂) bond length (2.476(3) Å) is longer than that in {[Cd₃(OABDC)₂(4,4'-bipy)₄(H₂O)₄·2H₂O}_n (2.340(16) Å, H₃OABDC = 5-oxyacetate isophthalic acid, bipy = 4,4'-bipyridine) [17e]. The average Cd2–O (O2/O4B) bond length,

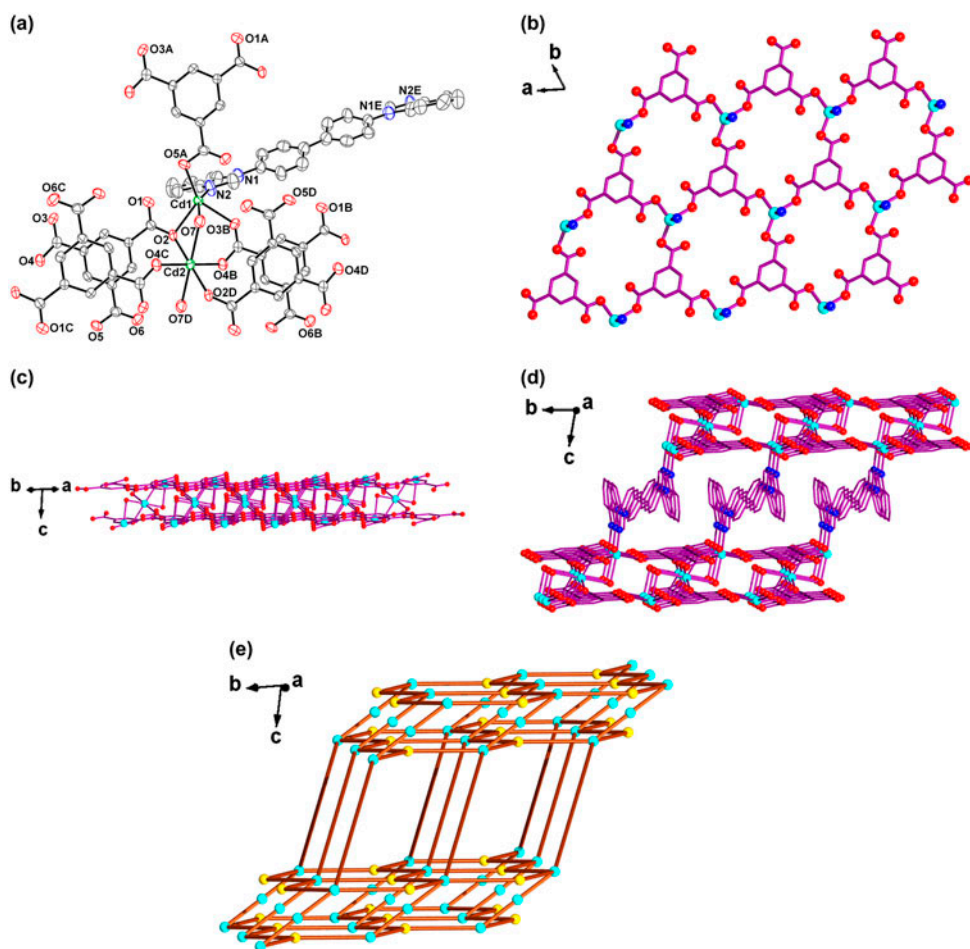


Figure 4. (a) View of the coordination environments of Cd1 and Cd2 in **4** with labeling scheme and 50% thermal ellipsoids. All hydrogens have been omitted for clarity. Symmetry codes: (A) $x, y-1, z$; (B) $x-1, y, z$; (C) $-x+2, -y+1, -z+2$; (D) $-x+1, -y+1, -z+2$; (E) $-x, -y, -z+1$. (b) View of the 2-D (6,3) network extending along the *ab* plane. (c) View of the 2-D double-decked layer structure of **4** extending along the *ab* plane. (d) View of the 3-D net of **4** looking down the *a* axis. (e) Schematic view of a (6³)(6¹⁰) topological net of **4**. The red, blue, cyan, and yellow balls represent O, N, Cd, and 3-connecting btc ligands, respectively. Each brown line represents one bimbb or one water. (see <http://dx.doi.org/10.1080/00958972.2013.804179> for color version)

2.229(3) Å, is shorter than that in $[\text{Cd}_3(\text{bta})_2(\text{H}_2\text{O})_2]$ (2.297(4) Å, bta = benzene-1,3,5-triacetate), but the Cd2–O7(OH₂) bond length, 2.448(3) Å, is longer than the corresponding distance of 2.202(3) Å in $[\text{Cd}_3(\text{bta})_2(\text{H}_2\text{O})_2]$ [17f]. Each bimbb exhibits a N–N distance of 14.096 Å (N2/N2E) and a dihedral angle of *ca.* 0° between the benzimidazolyl groups and between the benzene groups. The three Cd1 centers are linked by three btc bridges to form a trinuclear $[\text{Cd}_3(\text{btc})_3]$ unit, which is further interconnected to form a 2-D (3,6) $[\text{Cd}_3(\text{btc})_3]_n$ sheet containing triangular grids (9.52 Å × 9.84 Å × 10.43 Å) extending along the *ab* plane (figure 4(b)). This sheet is linked to an adjacent 2-D sheet via Cd2, forming a 2-D double-deckered layer $[\text{Cd}_9(\text{btc})_6(\mu\text{-OH}_2)_6]_n$ with the Cd(1)··Cd(2) separation of 3.572 Å (figure 4(c)), which is shorter than that found in $\{[\text{Cd}_3(\text{TMBTC})_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}\}_n$ (3.681(1) Å, TMBTC = 2,4,6-trimethylbenzene-1,3,5-tricarboxylic acid) [9e]. Meanwhile, each bimbb acts as pillar to connect two adjacent 2-D bilayers to afford a pillared-bilayer framework containing two types of rhombic channels (7.14 Å × 9.84 Å and 17.49 Å × 9.84 Å) extending along the *a* axis (figure 4(d)). The effective solvent accessible volume of 63.8 Å³ per unit cell (6.0% of the total cell volume calculated by the Platon program) is filled with water solvate molecules. These water molecules interact with the coordinated water molecules and the carboxylate groups to form intermolecular H-bonding interactions (ESI, table S1). If the btc ligands, the Cd1 centers, and the Cd2 centers are considered as three-, five-, and two-connecting nodes, respectively, the overall net of **4** has a 3-D (3,5)-connected topological structure with a (6³)(6¹⁰) Schläfli symbol (figure 4(e)). Within the double-deckered layer $[\text{Cd}_9(\text{btc})_6(\mu\text{-OH}_2)_6]_n$, the centroid-to-centroid separation between phenyl rings of the two btc ligands is 3.886 Å, indicating the presence of weak intermolecular $\pi \cdots \pi$ interactions.

3.3. Luminescent properties of 1–4

The photoluminescent properties of **1–4** in the solid state were investigated at ambient temperature (figure 5). Upon excitation at 333 nm (**1**), 325 nm (**2**), 330 nm (**3**), and 329 nm (**4**), **1–4** exhibited strong photoluminescence with emission maxima at 396 nm (**1**), 381 nm (**2**), 398 nm (**3**), and 390 nm (**4**), respectively. The emission peaks of **1**, **3**, and **4** were similar to that of the bimbb ligand ($\lambda_{\text{em}} = 394$ nm, $\lambda_{\text{ex}} = 330$ nm), but were broader.

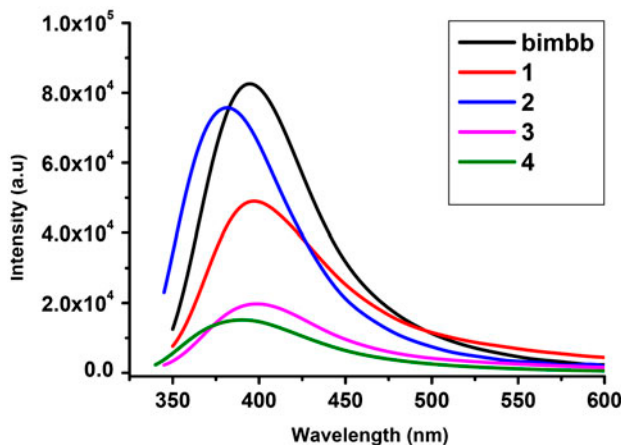


Figure 5. The solid state emission spectra of bimbb and **1–4** at ambient temperature.

emission origins may be tentatively assigned to be the $\pi-\pi^*$ intraligand fluorescence and ligand-to-ligand charge transfer [18]. It is noted that the emission maxima of **2** are blue-shifted compared to that of bimbb. This band might be assigned to a ligand-to-metal charge transfer with electrons being transferred from the unoccupied p^* orbitals of the imidazolyl groups of bimbb to the Cd(II) centers [19]. The emission maxima of bimbb and $[\text{Cd}_2(5\text{-Me-1,3-bdc})_2(\text{bimbb})]_n$ (**3**) are red-shifted compared to that of bimbb (bimbb = 4,4'-bis(1-imidazolyl)bibenzene) ($\lambda_{\text{ex}} = 300$ nm, $\lambda_{\text{em}} = 348$ nm and 361 nm) and $[\text{Cd}(5\text{-Me-1,3-BDC})(\text{bimbb})]_n$ ($\lambda_{\text{ex}} = 307$ nm, $\lambda_{\text{em}} = 349$ nm and 364 nm) [11] due to the different degrees of conjugation in the two ligands [13].

4. Conclusion

We constructed four new Cd(II) MOFs with different topological structures through solvothermal reactions of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ with bimbb and four different benzenecarboxylic acids 1,4- H_2bdc , 4,4'- H_2bpdb , 5-Me-1,3- H_2bdc , and H_3btc . The four carboxylic acids have different structures and exert significant influence on their coordination modes, the Cd/carboxylate motifs, and the conformations of auxiliary N-donor bimbb ligand. The 1,4-bdc ligand with a short spacer between its two carboxylate groups exhibited more complicated coordination modes with both carboxylates chelating bidentate, one each as semi-chelating and chelating bidentate or both μ_3 -chelating/bridging tridentate. 4,4'-bpdb with a longer spacer demonstrated only a chelating bidentate coordination. For 5-Me-1,3-bdc and btc, the former has C_{2v} symmetry while the latter has C_{3v} symmetry. The ligand with lower symmetry, 5-Me-1,3-bdc, adopted more complicated coordination modes, where the two carboxylate groups can be chelating bidentate and μ_3 -chelating/bridging, or both μ_3 -chelating/bridging. The ligand with higher symmetry, btc, took only one coordination mode. These different coordination modes of the four carboxylates in **1–4** resulted in formation of different Cd/carboxylate units in their structures: dinuclear $[\text{Cd}_2(1,4\text{-bdc})_3]$ and centrosymmetric dinuclear $[\text{Cd}_2(1,4\text{-bdc})_4]$ in **1**, zigzag chain $[\text{Cd}(4,4'\text{-bpdb})_2(\mu\text{-OH}_2)]$ in **2**, tetranuclear rod-like $[\text{Cd}_4(5\text{-Me-1,3-bdc})_8]$ in **3**, and trinuclear hourglass $[\text{Cd}_3(\text{btc})_6(\mu\text{-OH}_2)_2]$ in **4**. These Cd/carboxylate units are extended into an undulated 2-D (8,4) $[\text{Cd}_8(1,4\text{-bdc})_8]_n$ layer (**1**), a 2-D undulated (4,4) $[\text{Cd}(4,4'\text{-bpdb})_2(\mu\text{-OH}_2)_2]_n$ layer (**2**), a 1-D $[\text{Cd}_4(5\text{-Me-1,3-bdc})_4]_n$ ribbon (**3**), and a double-deckered $[\text{Cd}_9(\text{btc})_6(\mu\text{-OH}_2)_3]_n$ layer (**4**). For **1**, each 2-D layer is linked to its neighboring and the third layers through bimbb, affording a 3-D framework. For **2** and **4**, bimbb acts as pillars and further links the 2-D layers resulting in two different 3-D pillared-layer frameworks. For **3**, bimbb is a linker to connect the 1-D ribbons, thereby forming a 3-D structure. Each bimbb in **1–4** adopts different conformations due to the different coordination environments. Its two benzene groups or the two benzoimidazole rings in **2** and **4** are approximately coplanar, while those in **1** and **3** are not coplanar. These results provide insight into how the assembly of Cd(II) MOFs is affected by these carboxylate ligands with different spacer lengths or substituent groups.

Supplementary material

CCDC No. 887630 (**1**), 887631 (**2**), 887632 (**3**), and 887633 (**4**) contain the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam>.

ac.uk/conts/retrieving.html, or the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1E2, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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References

- [1] (a) P. Maniam, N. Stock. *Inorg. Chem.*, **50**, 5085 (2011); (b) M. Kim, J.A. Boissonnault, P.V. Dau, S.M. Cohen. *Angew. Chem. Int. Ed.*, **50**, 12193 (2011); (c) Y.Q. Lan, X.L. Wang, S.L. Li, Z.M. Su, K.Z. Shao, E. B. Wang. *Chem. Commun.*, 4863 (2007); (d) L. Luo, P. Wang, G.C. Xu, Q. Liu, K. Chen, Y. Lu, Y. Zhao, W.Y. Sun. *Cryst. Growth Des.*, **12**, 2634 (2012); (e) B. Li, S.Q. Zang, C. Ji, C.X. Du, H.W. Hou, T.C.W. Mak. *Dalton Trans.*, **40**, 788 (2011); (f) Y.J. Mu, G. Han, Z. Li, X.T. Liu, H.W. Hou, Y.T. Fan. *Cryst. Growth Des.*, **12**, 1193 (2012); (g) K. Hirai, S. Furukawa, M. Kondo, M. Meilikhov, Y. Sakata, O. Sakatad, S. Kitagawa. *Chem. Commun.*, **48**, 6472 (2012); (h) J.Q. Wang, C.X. Ren, G.X. Jin. *Organometallics*, **25**, 74 (2006).
- [2] (a) I.M. Hauptvogel, R. Biedermann, N. Klein, I. Senkovska, A. Cadiau, D. Wallacher, R. Feyerherm, S. Kaskel. *Inorg. Chem.*, **50**, 8367 (2011); (b) N. Klein, C. Herzog, M. Sabo, I. Senkovska, J. Getzschmann, S. Paasch, M.R. Lohe, E. Brunner, S. Kaskel. *Phys. Chem. Chem. Phys.*, **12**, 11778 (2010); (c) L. Pan, H.M. Liu, S.P. Kelly, X.Y. Huang, D.H. Olson, J. Li. *Chem. Commun.*, 854 (2003); (d) H. Wu, Q. Gong, D.H. Olson, J. Li. *Chem. Rev.*, **112**, 836 (2012).
- [3] (a) B. Chen, S. Ma, E.J. Hurtado, E.B. Lobkovsky, C. Liang, H. Zhu, S. Dai. *Inorg. Chem.*, **46**, 8705 (2007); (b) M. Maes, S. Schouteden, K. Hirai, S. Furukawa, S. Kitagawa, D.E. De Vos. *Langmuir*, **27**, 9083 (2011); (c) J.R. Li, J. Sculley, H.C. Zhou. *Chem. Rev.*, **112**, 869 (2012).
- [4] (a) W.T. Liu, J.Y. Li, Z.P. Ni, X. Bao, Y.C. Ou, J.D. Leng, J.L. Liu, M.L. Tong. *Cryst. Growth Des.*, **12**, 1482 (2012); (b) Z. Chen, D.L. Gao, C.H. Diao, Y. Liu, J. Ren, J. Chen, B. Zhao, W. Shi, P. Cheng. *Cryst. Growth Des.*, **12**, 1201 (2012); (c) J. Ferrando-Soria, R. Ruiz-García, J. Cano, S.E. Stiriba, J. Vallejo, I. Castro, M. Julve, F. Lloret, P. Amorós, J. Pasán, C. Ruiz-Pérez, Y. Journaux, E. Pardo. *Chem. Eur. J.*, **18**, 1608 (2012); (d) Y.G. Huang, F.L. Jiang, M. C. Hong. *Coord. Chem. Rev.*, **253**, 2814 (2009). (e) X.Y. Wang, Z.M. Wang, S. Gao. *Chem. Commun.*, 1127 (2007).
- [5] (a) Y. Takashima, V.M. Martínez, S. Furukawa, M. Kondo, S. Shimomura, H. Uehara, M. Nakahama, K. Sugimoto, S. Kitagawa. *Nat. Commun.*, **2**, 1170 (2011); (b) Y.J. Cui, Y.F. Yue, G.D. Qian, B.L. Chen. *Chem. Rev.*, **112**, 1126 (2012).
- [6] (a) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. Belosludov, T. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita. *Nature*, **436**, 238 (2005); (b) D. Farrusseng, S. Aguado, C. Pinel. *Angew. Chem. Int. Ed.*, **48**, 7502 (2009).
- [7] (a) D.J. Tranchemontagne, J.L. Mendoza-Cortés, M. O’Keeffe, O.M. Yaghi. *Chem. Soc. Rev.*, **38**, 1257 (2009); (b) M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O’Keeffe, O.M. Yaghi. *Acc. Chem. Res.*, **34**, 319 (2001); (c) O.M. Yaghi, M. O’Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **423**, 6941 (2003); (d) C. Janiak. *Dalton Trans.*, **14**, 2781 (2003); (e) G. Férey. *Chem. Soc. Rev.*, **37**, 191 (2008); (f) S.L. James. *Chem. Soc. Res.*, **44**, 123 (2011); (g) N. Ockwig, O.D. Friedrichs, M. O’Keeffe, O.M. Yaghi. *Acc. Chem. Res.*, **38**, 176 (2005); (h) D. Zhao, D.J. Timmons, D.Q. Yuan, H.C. Zhou. *Acc. Chem. Res.*, **44**, 123 (2011); (i) U. Schubert. *Chem. Soc. Rev.*, **40**, 575 (2011); (j) C. Serre, F. Millange, S. Surbl, G. Férey. *Angew. Chem. Int. Ed.*, **43**, 6285 (2004); (k) X.L. Wang, C. Qin, S.X. Wu, K.Z. Shao, Y.Q. Lan, S. Wang, D.X. Zhu, Z.M. Su, E.B. Wang. *Angew. Chem. Int. Ed.*, **48**, 5291 (2009); (l) Y.L. Bai, J. Tao, R.B. Huang, L.S. Zheng. *Angew. Chem. Int. Ed.*, **47**, 5344 (2008).

- [8] A. Schoedel, L. Wojtas, S.P. Kelley, M. Eddaoudi, R.D. Rogers, M.J. Zaworotko. *Angew. Chem. Int. Ed.*, **50**, 11421 (2011).
- [9] (a) L. Yi, B. Ding, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang. *Inorg. Chem.*, **43**, 33 (2004); (b) Y.L. Yao, L. Xue, Y.X. Che, J.M. Zheng. *Cryst. Growth Des.*, **9**, 606 (2009); (c) G.X. Liu, Y.Q. Huang, Q. Chu, T. Okamura, W.Y. Sun, H. Liang, N. Ueyama. *Cryst. Growth Des.*, **8**, 3233 (2008). (d) S.Q. Su, W. Chen, X.Z. Song, M. Zhu, C. Qin, S.Y. Song, Z.Y. Guo, S. Wang, Z.M. Hao. *CrystEngComm*, **14**, 1681 (2012); (e) H.Y. He, H.D. Yin, D.Q. Wang, H.Q. Ma, G.Q. Zhang, D.F. Sun. *CrystEngComm*, **14**, 1681 (2012); (f) H. Chun, D. Kim, D.N. Dybtsev, K. Kim. *Angew. Chem. Int. Ed.*, **43**, 971 (2004); (g) R.T. Liu, L. Hou, B. Liu, Y.N. Zhang, Y.Y. Wang, Q.Z. Shi. *Inorg. Chim. Acta*, **366**, 53 (2011); (h) L.Y. Zhang, J.P. Zhang, Y.Y. Lin, X.M. Chen. *Cryst. Growth Des.*, **6**, 1684 (2006); (i) S.Q. Zang, Y. Su, Y.Z. Li, J.G. Lin, X.Y. Duan, Q.J. Meng, S. Gao. *CrystEngComm*, **11**, 122 (2009); (j) S.L. Zheng, J.H. Yang, X.L. Yu, X.M. Chen, W.T. Wong. *Inorg. Chem.*, **43**, 830 (2004); (k) Q.R. Fang, G.S. Zhu, Z. Jin, M. Xue, X. Wei, D.J. Wang, S.L. Qiu. *Angew. Chem. Int. Ed.*, **45**, 6126 (2006); (l) W.B. Lin, O.R. Evans, Y. Cui. *Cryst. Growth Des.*, **2**, 409 (2002); (m) S.N. Wang, H. Xing, Y.Z. Li, J.F. Bai, Y. Pan, M. Scheer, X.Z. You. *Eur. J. Inorg. Chem.*, 3041 (2006); (n) X.J. Wang, Y.H. Liu, C.Y. Xu, Q.Q. Guo, H.W. Hou, Y.T. Fan. *Cryst. Growth Des.*, **12**, 2435 (2012). (o) Z. J. Zhang, L.P. Zhang, L. Wojtas, P. Nugent, M. Eddaoudi, M.J. Zaworotko. *J. Am. Chem. Soc.*, **134**, 924 (2012). (p) R.H. Wang, D.Q. Yuan, F.L. Jiang, L. Han, Y.Q. Gong, M.C. Hong. *Cryst. Growth Des.*, **6**, 1351 (2006). (q) J. Zhang, X.H. Bu. *Chem. Commun.*, 444 (2008). (r) S.P. Argent, A. Greenaway, M. Gimenez-Lopez, W. Lewis, H. Nowell, A.N. Khlobystov, A.J. Blake, N.R. Champness, M. Schröder. *J. Am. Chem. Soc.*, **134**, 55 (2012). (s) X.L. Wang, C. Qin, Y.Q. Lan, K.Z. Shao, Z.M. Su, E.B. Wang. *Chem. Commun.*, 410 (2009).
- [10] (a) P. Mahata, S. Natarajan, P. Panissod, M. Drillon. *J. Am. Chem. Soc.*, **131**, 10140 (2009). (b) K. Gedrich, I. Senkovska, I.A. Baburin, U. Mueller, O. Trapp, S. Kaskel. *Inorg. Chem.*, **49**, 4440 (2010). (c) L.A. Gerrard, P.T. Wood. *Chem. Commun.*, 2107 (2000). (d) M. Kondo, M. Miyazawa, Y. Irie, R. Shinagawa, T. Hori-ba, A. Nakamura, T. Naito, K. Maeda, S. Utsuno, F. Uchida. *Chem. Commun.*, 2156 (2002).
- [11] H.J. Cheng, H.X. Li, Z.G. Ren, C.N. Lü, J. Shi, J.P. Lang. *CrystEngComm*, **14**, 6064 (2012).
- [12] (a) Q.H. Pan, H. Ma, Z.X. Li, T.L. Hu. *J. Mol. Struct.*, **1011**, 134 (2012). (b) Z.X. Li, T.L. Hu, H. Ma, Y.F. Zeng, C.J. Li, M.L. Tong, X.H. Bu. *Cryst. Growth Des.*, **10**, 1138 (2010).
- [13] W. White, Z.M. Hudson, X.D. Feng, S.J. Han, Z.H. Lu, S.N. Wang. *Dalton Trans.*, 892 (2010).
- [14] G.M. Sheldrick, *SHELXS-97 and SHELXL-97, Program for X-ray Crystal Structure Solution*, University of Göttingen, Germany (1997).
- [15] (a) C.H. He, C.H. Jiao, J.C. Geng, G.H. Cui. *J. Coord. Chem.*, **65**, 2294 (2012); (b) C.H. Jiao, C.H. He, J.C. Geng, G.H. Cui. *J. Coord. Chem.*, **65**, 2852 (2012); (c) F. Guo. *J. Coord. Chem.*, **65**, 4005 (2012); (d) B.F. Huang, H. Huang, H.P. Xiao, J.G. Wang, X.H. Li, A. Morsali. *J. Coord. Chem.*, **65**, 3605 (2012).
- [16] (a) G. Guilera, J.W. Steed. *Chem. Commun.*, 563 (1999); (b) R.Q. Zou, X.H. Bu, R.H. Zhang. *Inorg. Chem.*, **43**, 5382 (2004); (c) A.L. Spek. *J. Appl. Crystallogr.*, **36**, 7 (2003).
- [17] (a) F.J. Liu, H.J. Hao, C.J. Sun, X.H. Lin, H.P. Chen, R.B. Huang, L.S. Zheng. *Cryst. Growth Des.*, **12**, 2004 (2012); (b) Y.P. Wu, D.S. Li, J. Zhao, Z.F. Fang, W.W. Dong, G.P. Yang, Y.Y. Wang. *CrystEngComm*, **14**, 4745 (2012); (c) G.H. Wei, J. Yang, J.F. Ma, Y.Y. Liu, S.L. Li, L.P. Zhang. *Dalton Trans.*, 3080 (2008); (d) C.Y. Xu, L.K. Li, Y.P. Wang, Q.Q. Guo, X. J. Wang, H.W. Hou, Y.T. Fan. *Cryst. Growth Des.*, **11**, 4667 (2011); (e) X.Y. Cao, J. Zhang, Z.J. Li, J.K. Cheng, Y.G. Yao. *CrystEngComm*, **9**, 806 (2007); (f) G.X. Liu, Y.Q. Huang, Q. Chu, T.A. Okamura, W.Y. Sun, H. Liang, N. Ueyama. *Cryst. Growth Des.*, **8**, 2009 (2008).
- [18] Y. Wang, F.H. Zhao, Y.X. Che, J.M. Zheng. *Inorg. Chem. Commun.*, **17**, 180 (2012).
- [19] (a) A. Horváth, C.E. Wood, K.L. Stevenson. *Inorg. Chem.*, **33**, 5351 (1994); (b) V.V.W. Yam, K.K.W. Lo. *Chem. Soc. Rev.*, **28**, 323 (1999).