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PAPER

Substituted groups-directed assembly of Cd(II) coordination polymers based on 5-R-1,3-benzenedicarboxylate and 4,4'-bis(1-imidazolyl)bibenzene: syntheses, structures and photoluminescent properties†

Hong-Jian Cheng,[a] Hong-Xi Li,[a] Zhi-Gang Ren,[a] Chun-Ning Lü,[a] Jing Shi[a] and Jian-Ping Lang*[ab]

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Hydrothermal reactions of $CdCl_2·2.5H_2O$ with 4,4'-bis(1-imidazolyl)bibenzene (bimb) and 1,3-benzenedicarboxylate (1,3-H_2BDC), 5-methyl-1,3-benzenedicarboxylate (5-Me-1,3-H_2BDC), 5-amino-1,3-benzenedicarboxylate (5-NH_2-1,3-H_2BDC), 5-hydroxy-1,3-benzenedicarboxylate (5-HO-1,3-H_2BDC), 5-nitro-1,3-benzenedicarboxylate (5-NO_2-$H_2$1,3-BDC), or 5-sulfo-1,3-benzenedicarboxylate (5-HSO_3-1,3-H_2BDC) resulted in the formation of six Cd(II) coordination polymers, $[Cd(5\text{-R-}1,3\text{-BDC})(bimb)]_n$ (R = H (**1**), R = Me (**2**), R = NH_2 (**3**), R = OH (**4**)), $\{[Cd_2(H_2O)(5\text{-}NO_2\text{-}1,3\text{-BDC})_2(bimb)]·2H_2O\}_n$ (**5**) and $[Cd(5\text{-}SO_3\text{-}1,3\text{-HBDC})(bimb)]_n$ (**6**). Compounds **1–6** were characterized by elemental analysis, IR, powder X-ray diffraction and single-crystal X-ray diffraction. **1–4** exhibit similar 3D frameworks in which 2D $[Cd_4(5\text{-R-}1,3\text{-BDC})_4]_n$ (R = H, Me, NH_2 and OH) layers are interlinked by bimb ligands. **5** has a two-fold interpenetrating 3D framework in which 1D $[Cd_2(5\text{-}NO_2\text{-}1,3\text{-BDC})_2]_n$ chains are interconnected by bimb ligands. **6** shows a 3D (3,5)-connected framework in which 2D $[Cd_2(5\text{-}SO_3\text{-}1,3\text{-HBDC})_2]_n$ networks are bridged by bimb ligands. The Schläfli symbols for these six 3D nets are $(4·6^2)(4·6^6·8^3)$ (**1–4**), $(4^2·6)(4^2·6·10^2·12)$ (**5**) and $(4·6·8)(4·6^5·8^3·10)$ (**6**). The solid state photoluminescent properties of **1–6** were also investigated.

Introduction

In past decades, much attention has been focused on the rational design and synthesis of functional coordination polymers due to their intriguing architectures[1] and potential applications in absorption,[2] separation,[3] magnetism,[4] luminescence,[5] catalysis,[6] drug delivery[7] and proton conduction,[8] *etc.* Among the numerous strategies for constructing coordination polymers, the employment of the self-assembly of transition metal salts with di- or multi- carboxylic acids and/or multidentate N-donor ligands under solvothermal conditions has become an effective approach.[9] However, many factors, such as metal ions, organic multitopic ligands, pH values, solvents, templates and temperatures, place a great and delicate influence on the structures of the resulting coordination polymers.[10] It is noted that substituent groups of carboxylate ligands also exert great impact on the formation of coordination polymers with different topological structures.[11] For instance, solvothermal reactions of $Co(NO_3)_2$ with 2-R-1,4-benzenedicarboxylic acid (R = H and NH_2) and 4,4′-bipyridine (4,4′-bipy) produced a 2-fold interpenetrating non-porous framework $[Co_2(1,4\text{-BDC})_2(bpy)_2]$ (1,4-BDC = 1,4-benzenedicarboxylate) and a non-interpenetrating porous doubly pillared-layer framework $[Co_2(2\text{-}NH_2\text{-}1,4\text{-BDC})_2(bpy)_2]·8DMF$ (2-NH_2-1,4-BDC = 2-amino-1,4-benzenedicarboxylate).[11d] However, research in this respect is still less explored relative to those related to other factors.

Recently, we have been interested in the syntheses, structures and properties of coordination polymers derived from group IIB and IB metals and polycarboxylates and multidentate N-donor ligands.[12,13] For example, hydrothermal reactions of $Zn(NO_3)_2$ with 5-R-1,3-BDC (R = OH, COOH, NO_2, Me) and 1,4-bis[2-(4-pyridyl)ethenyl]benzene (1,4-bpeb) produced four different coordination polymers $[Zn(H_2O)(5\text{-HO-}1,3\text{-BDC})(1,4\text{-bpeb})]_n$ (1D), $[\{Zn_2(1,3,5\text{-HBTC})_2\}_4]_n$ (2D), $[Zn_4(5\text{-}NO_2\text{-}1,3\text{-BDC})_4(1,4\text{-bpeb})_4]_n$ (2D) and $[Zn_4(5\text{-Me-}1,3\text{-BDC})_4(1,4\text{-bpeb})_4]_n$ (3D).[12d] The results revealed that changes on substituted R groups in the 5-position of 1,3-BDC ligands could lead to big changes in the frameworks or the levels of interpenetration in the resulting supramolecular arrays. As an extension of this work, we selected six 5-R-1,3-benzenedicarboxylic acid derivatives (R = H, Me, NH_2, OH, NO_2, SO_3H) and another N-donor ligand, 4,4′-bis(1-imidazolyl)bibenzene (bimb) (Scheme 1), to react with $CdCl_2$ under the hydrothermal conditions. Six different 3D

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[a] *Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, P. R. China. E-mail: jplang@suda.edu.cn; Fax: 86-512-65880089*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, P. R. China*

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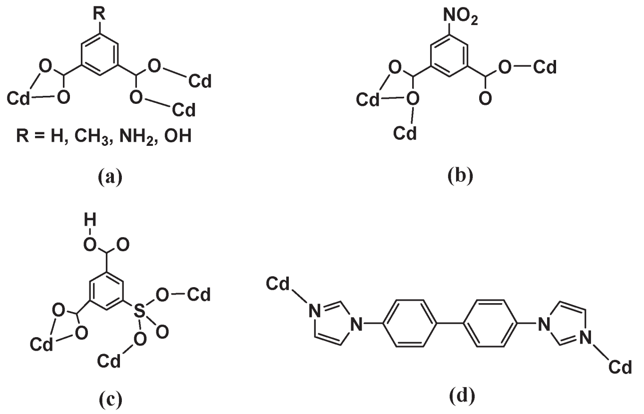

Scheme 1 The coordination modes of 5-R-1,3-BDC in **1–4** (a), 5-NO_2-1,3-BDC in **5** (b), 5-SO_3-1,3-HBDC in **6** (c) and bimb in **1–6**(d).

coordination polymers with three kinds of different topological structures [Cd(5-R-1,3-BDC)(bimb)]$_n$ (R = H (**1**), R = Me (**2**), R = NH_2 (**3**), R = OH (**4**)), {[$Cd_2(H_2O)$(5-NO_2-1,3-BDC)$_2$(bimb)]·$2H_2O$}$_n$ (**5**) and [Cd(5-SO_3-1,3-HBDC)(bimb)]$_n$ (**6**) were isolated. Herein, we report their syntheses, crystal structures and photoluminescent properties.

Experimental

Materials and methods

The ligand bimb was prepared according to the literature method.[14] Other chemicals and reagents were obtained from commercial sources and used as received. Elemental analyses for C, H and N were performed on a Carlo-Erbo CHNO-S microanalyzer. The IR spectra (KBr disc) were recorded on a Nicolet MagNa-IR550 FT-IR spectrometer (4000–400 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 Elipse fluorescence spectrophotometer equipped with a continuous Xenon Lamp.

Preparation of compounds 1–6

Preparation of [Cd(1,3-BDC)(bimb)]$_n$ (1). To a 10 mL Pyrex glass tube was added $CdCl_2·2.5H_2O$ (24 mg, 0.1 mmol), 1,3-H_2BDC (17 mg, 0.1 mmol), bimb (28 mg, 0.1 mmol) and 3 mL of H_2O. The tube was sealed and heated in an oven to 170 °C for 1 d and then cooled to ambient temperature at the rate of 5 °C h^{-1} to form colorless crystals of **1**, which were washed with water–methanol and dried in air. Yield: 30 mg (53% yield based on Cd). Anal. calcd for $C_{26}H_{18}CdN_4O_4$: C, 55.48; H, 3.22; N, 9.95. Found: C 55.40, H 3.18, N 10.02. IR (KBr, cm^{-1}): 1610 (m), 1568 (s), 1551 (s), 1515 (s), 1375 (s), 1264 (s), 1060 (s), 820 (s), 724 (s), 649 (s), 423 (m).

Preparation of [Cd(5-Me-1,3-BDC)(bimb)]$_n$ (2). Compound **2** was prepared as colorless crystals in a similar manner to that described for **1**, using $CdCl_2·2.5H_2O$ (24 mg, 0.1 mmol), 5-Me-1,3-H_2BDC (18 mg, 0.1 mmol), bimb (28 mg, 0.1 mmol) and 3 mL of H_2O. Yield: 26 mg (45% yield based on Cd). Anal. calcd for $C_{27}H_{20}CdN_4O_4$: C 56.21; H 3.49; N 9.71. Found: C 62.63, H 3.59, N 4.88. IR (KBr, cm^{-1}): 2922 (w), 1616 (m), 1572 (s), 1514 (s), 1418 (s), 1363 (m), 1302 (m), 1247 (s), 1060 (s), 820 (s), 647 (s), 422 (m).

Preparation of Cd(5-NH_2-1,3-BDC)(bimb)]$_n$ (3). Compound **3** was prepared as colorless crystals in a similar manner to that described for **1**, using $CdCl_2·2.5H_2O$ (24 mg, 0.1 mmol), 5-NH_2-1,3-H_2BDC (18 mg, 0.1 mmol), bimb (28 mg, 0.1 mmol) and 3 mL of H_2O. Yield: 35 mg (61% yield based on Cd). Anal. calcd for $C_{26}H_{19}CdN_5O_4$: C 54.04; H 3.31; N 12.12. Found: C 53.96, H 3.24, N 12.20. IR (KBr, cm^{-1}): 3462 (w), 3332 (w), 1608 (s), 1549 (s), 1510 (s), 1420 (s), 1368 (s), 1060 (s), 818 (s), 724 (s), 648 (m), 423 (m).

Preparation of [Cd(5-HO-1,3-BDC)(bimb)]$_n$ (4). To a 10 mL Pyrex glass tube was added $CdCl_2·2.5H_2O$ (24 mg, 0.1 mmol), 5-OH-1,3-H_2BDC (18 mg, 0.1 mmol), bimb (28 mg, 0.1 mmol) and 3 mL of H_2O. After the pH value was adjusted to 4.8 by addition of HNO_3 (0.01 M, 10 μL), the tube was sealed and heated in an oven to 170 °C for 1 d and then cooled to ambient temperature at the rate of 5 °C h^{-1} to form colorless crystals of **4**, which were washed with water–methanol and dried in air. Yield: 25 mg (43% yield based on Cd). Anal. calcd for $C_{26}H_{18}CdN_4O_5$: C 53.95; H 3.13; N 9.68. Found: C 54.04, H 3.20, N 9.24. IR (KBr, cm^{-1}): 3272 (w), 1617 (s), 1580 (s), 1520 (s), 1419 (s), 1365 (s), 1272 (s), 1060 (s), 820 (s), 720 (s), 647 (s), 520 (m), 430 (m).

Preparation of {[$Cd_2(H_2O)_2$(5-NO_2-1,3-BDC)$_2$(bimb)$_2$]·$2H_2O$}$_n$ (5). Compound **5** was prepared as colorless crystals in a similar manner to that described for **1**, using $CdCl_2·2.5H_2O$ (24 mg, 0.1 mmol), 5-NO_2-1,3-H_2BDC (22 mg, 0.1 mmol), bimb (28 mg, 0.1 mmol) and 3 mL of H_2O. Yield: 19 mg (37% yield based on Cd). Anal. Calcd. for $C_{34}H_{28}Cd_2N_6O_{16}$: C 40.78; H 2.82; N 8.39. Found: C 40.80, H 2.76 N 8.30. IR (KBr, cm^{-1}): 1617 (s), 1517 (s), 1454 (m), 1344 (s), 1251 (m), 1063 (s), 862 (m), 822 (m), 729 (m), 644 (s), 518 (m).

Preparation of [Cd(5-SO_3-1,3-HBDC)(bimb)]$_n$ (6). Compound **6** was prepared as colorless crystals in a similar manner to that described for **1**, using $CdCl_2·2.5H_2O$ (24 mg, 0.1 mmol), 5-HSO_3-1,3-H_2BDC (25 mg, 0.1 mmol), bimb (28 mg, 0.1 mmol) and 3 mL of H_2O. Yield: 26 mg (41% yield based on Cd). Anal. calcd for $C_{26}H_{18}CdN_4O_7S$: C, 48.57; H, 2.82; N, 8.71. Found: C 48.62, H 2.92, N 8.81. IR (KBr, cm^{-1}): 3163 (m), 1707 (s), 1605 (s), 1516 (m), 1400 (s), 1121 (s), 1101 (s), 1037 (s), 812 (w), 692 (w), 621 (s).

X-ray crystallography

Single crystals of **1–6** 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-Kα (λ = 0.71073 Å). Single crystals of **1–6** were mounted with grease at the top of a glass fibre at 293 K (**1** and **3–6**) or 223 K (**2**) in a liquid nitrogen stream. 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 the program *CrystalClear* and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **1–6** were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the *SHELXL*-97 program.[15] In **3**, the C8 and C9 atoms of one bimp ligand are disordered over two sites with an occupancy factor of 0.33/0.67 for C8/C8A and C9/C9A. All of the non-H atoms were refined anisotropically. The H atoms of the water molecule in **5** and the uncoordinated –COOH group in **6** were located from the Fourier map. All other H atoms were placed in geometrically idealized positions (C–H = 0.96 Å for methyl groups, N–H = 0.86 Å for amino groups, O–H = 0.82 Å for hydroxyl groups, or C–H = 0.93 Å for phenyl groups) and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups, $1.2U_{\text{eq}}(\text{N})$ for amino groups, and $1.5U_{\text{eq}}(\text{O})$ for hydroxyl groups. All of the calculations were performed on a Dell workstation using the Crystal Structure crystallographic software package (Rigaku and MSC, ver. 3.60, 2004). A summary of the important crystallographic information for **1–6** are summarized in Table 1.

Results and discussion

Synthetic and spectral aspects

The hydrothermal reaction of $CdCl_2{\cdot}2.5H_2O$ with 1,3-H_2BDC and bimb in a 1 : 1 : 1 molar ratio at 170 °C for 1 day gave rise to colorless crystals of **1** in 53% yield. Analogous reactions with 5-Me-1,3-H_2BDC, 5-NH_2-1,3-H_2BDC, 5-NO_2-1,3-H_2BDC and 5-HSO_3-1,3-H_2BDC afforded colorless crystals of **2** (45% yield), **3** (61% yield), **5** (37% yield) and **6** (41% yield), respectively. However, we could not isolate any Cd/5-HO-1,3-BDC/bimb complexes from similar reactions of these three components with 1 : 1 : 1 and other molar ratios. Thus, the pH value of the solution of a mixture containing $CdCl_2{\cdot}2.5H_2O$, 5-HO-1,3-H_2BDC and bimb (molar ratio = 1 : 1 : 1) was adjusted by 0.01 M HNO_3 up to 4.8. Such a resulting solution was preformed by a hydrothermal treatment at 170 °C to afford colorless crystals of **4** in 43% yield. As discussed later in this paper, complexes **1–4** possess similar 3D structures, while complexes **5** and **6** have two different 3D structures. For **1–4**, one carboxylate group of the 5-R-1,3-BDC ligand takes a chelating bidentate mode, while the other a bridging bidentate one (Scheme 1a). The R (CH_3, NH_2, OH) group was not involved in the binding to Cd centres. For **5**, the 5-NO_2-1,3-BDC ligand adopts monodentate and μ_3-chelating/bridging coordination modes (Scheme 1b). For **6**, one carboxylate group of the 5-HSO_3-1,3-BDC ligand remains intact, while the other takes a chelating bidentate fashion. In addition, the SO_3^- group of this ligand coordinates at Cd atoms through a bridging bidentate coordination mode (Scheme 1c). The bimb ligand in three kinds of topological structures has the same coordination mode, but somewhat different configurations related to two imidazolyl groups. Thus, the substituent groups in the 5-position of 1,3-BDC ligands in **1–6** did affect their coordination modes, which subsequently leads to the formation of the different topological structures of **1–6**.

Complexes **1–6** are air-stable and insoluble in common solvents. The elemental analysis was consistent with their chemical formulas of **1–6**. The IR spectra of **1–6** showed strong peaks in the range of 1550–1618 cm^{-1} and 1314–1465 cm^{-1}, indicating that they all contain coordinated carboxylic groups. The strong peaks at *ca.* 1060 cm^{-1} and 650 cm^{-1} mean the existence of imidazolyl groups in **1–6**. The bands at 2922 cm^{-1}, 3332 cm^{-1}, 3272 cm^{-1}, 1365 cm^{-1} and 1707 cm^{-1} could be assigned to the vibrations of the –Me, –NH_2, –OH, –NO_2 and –COOH groups, respectively.[16] The PXRD showed that the experimental patterns for each compound correlate well with its simulated one generated from single-crystal X-ray diffraction data (Fig. S1, ESI†). The identities of **1–6** were further confirmed by single crystal X-ray diffraction analysis.

Table 1 A summary of crystal data and structure refinement parameters for **1–6**

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{26}H_{18}CdN_4O_4$	$C_{27}H_{20}CdN_4O_4$	$C_{26}H_{19}CdN_5O_4$	$C_{26}H_{18}CdN_4O_5$	$C_{34}H_{28}Cd_2N_6O_{16}$	$C_{26}H_{18}CdN_4O_7S$
Formula mass	562.85	576.88	577.87	578.85	1001.45	642.92
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$
Crystal dimensions (mm^3)	0.4 × 0.1 × 0.1	0.26 × 0.24 × 0.18	0.6 × 0.4 × 0.2	0.4 × 0.3 × 0.3	0.3 × 0.25 × 0.1	0.6 × 0.3 × 0.3
a/Å	9.762(2)	9.857(2)	9.5702(19)	9.6647(19)	9.967(2)	29.425(6)
b/Å	13.486(3)	14.011(3)	14.329(3)	14.032(3)	12.179(2)	9.4342(19)
c/Å	16.804(3)	16.884(3)	16.631(3)	16.543(3)	15.859(2)	20.233(4)
α (°)					96.41(3)	
β (°)	100.04(3)	100.93(3)	98.75(3)	98.79(3)	96.96(3)	123.71
γ (°)					104.19(3)	
V/Å ^{3}	2178.3(8)	2289.5(8)	2254.1(8)	2217.1(8)	1832.5(6)	4672.2(23)
D_c/g cm^{-3}	1.716	1.674	1.703	1.734	1.815	1.828
Z	4	4	4	4	2	8
μ(Mo-Kα)/mm^{-1}	1.046	0.998	1.015	1.034	1.245	1.084
F(000)	1128	1160	1160	1160	996	2576
Total reflections	23 311	20 898	21 176	21 086	17 804	21 883
Unique reflections	4973	5192	4119	4049	6640	4274
No. observations	3712	4442	3735	3708	5269	3749
No. parameters	317	325	344	325	523	356
$R_1{}^a$	0.0608	0.0674	0.0423	0.0361	0.0412	0.0388
w$R_2{}^b$	0.1115	0.1051	0.0926	0.0863	0.0918	0.0858
GOF^c	1.091	1.096	1.074	1.036	1.069	1.103
$\Delta\rho_{\max}/\Delta\rho_{\min}$/e Å^{-3}	1.064, −0.734	0.580, −0.754	0.889, −0.422	0.932, −0.795	0.918, −0.713	0.725, −0.445

[a] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [c] $\text{GOF} = \{\Sigma w((F_o^2 - F_c^2)^2)/(n - p)\}^{1/2}$, where *n* = number of reflections and *p* = total numbers of parameters refined.

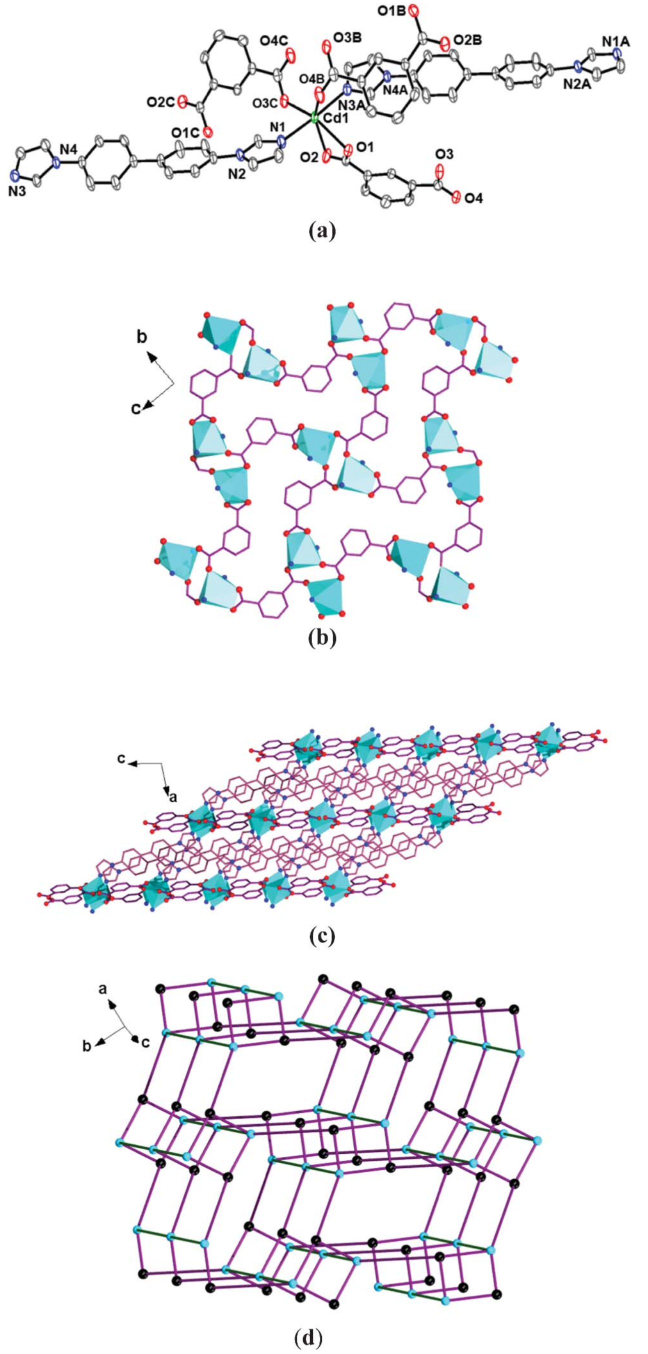

Fig. 1 (a) A view of the coordination environment of Cd(1) in **1** with a labelling scheme and 30% thermal ellipsoids. All H atoms have been omitted for clarity. Symmetry codes: (A) $x + 1, y, z + 1$; (B) $- x + 1, y + 1/2, - z + 1/2$; (C) $x, - y + 1/2, z - 1/2$. (b) A view of a 2D $(4{,}8^2)$ network that is constructed by $Cd_2(1,3\text{-BDC})_4$ units (extending along the *bc* plane). All of the bimb ligands are omitted for clarity. Each cyan tetrahedron represents one Cd atom. The red and blue balls represent O and N, respectively. (c) The 3D net of **1** (looking down the *b* axis). (d) A schematic view of a $(4{\cdot}6^2)(4{\cdot}6^6{\cdot}8^3)$ topological net of **1**. The cyan and black balls represent 5-connecting Cd centres and 3-connecting 1,3-HBDC ligands. Each pink line represents one bimb ligand.

Table 2 Selected bond lengths (Å) and angles (°) for **1–4**[a]

	1	2	3	4
Cd(1)–O(1)	2.339(3)	2.380(3)	2.338(3)	2.298(2)
Cd(1)–O(2)	2.482(4)	2.420(4)	2.530(3)	2.649(3)
Cd(1)–O(3C)	2.245(3)	2.239(3)	2.245(3)	2.243(3)
Cd(1)–O(4B)	2.293(4)	2.288(3)	2.293(3)	2.274(2)
Cd(1)–N(1)	2.314(4)	2.306(4)	2.312(4)	2.301(3)
Cd(1)–N(3A)	2.320(4)	2.318(4)	2.319(4)	2.305(3)
O(1)–Cd(1)–O(2)	54.41(11)	54.88(11)	53.68(9)	52.40(8)
O(1)–Cd(1)–O(4B)	94.42(13)	97.95(12)	98.80(11)	98.41(9)
O(1)–Cd(1)–O(3C)	147.48(13)	144.19(13)	140.72(11)	140.83(9)
O(2)–Cd(1)–O(3C)	93.14(13)	89.31(13)	87.36(10)	88.84(8)
O(2)–Cd(1)–O(4B)	148.63(13)	152.84(12)	151.27(11)	149.48(9)
O(3C)–Cd(1)–O(4B)	118.10(14)	117.85(13)	120.48(11)	120.76(9)
N(1)–Cd(1)–O(1)	100.17(14)	99.73(14)	100.79(12)	98.84(10)
N(1)–Cd(1)–O(2)	98.83(15)	101.23(15)	94.83(12)	91.82(9)
N(1)–Cd(1)–O(3C)	85.62(14)	85.72(14)	85.77(13)	86.39(11)
N(1)–Cd(1)–O(4B)	81.84(14)	81.84(14)	81.41(12)	83.54(10)
N(3A)–Cd(1)–O(1)	81.58(13)	82.16(14)	81.57(12)	81.20(10)
N(3A)–Cd(1)–O(2)	89.11(15)	87.43(15)	91.70(12)	92.23(10)
N(3A)–Cd(1)–O(3C)	97.49(14)	98.17(14)	96.45(13)	96.82(11)
N(3A)–Cd(1)–O(4B)	89.57(15)	88.78(15)	91.94(13)	91.38(11)
N(1)–Cd(1)–N(3A)	171.32(15)	170.59(16)	173.19(13)	174.88(11)

[a] Symmetry codes: (A) $x + 1, y, z + 1$; (B) $-x + 1, y + 1/2, -z + 5/2$; (C) $x, -y + 1/2, z - 1/2$ for **1**. (A) $x - 1, y, z - 1$; (B) $-x + 1, y - 1/2, -z + 1/2$; (C) $x, -y + 1/2, z + 1/2$ for **2**. (A) $x + 1, y, z + 1$; (B) $-x + 1, -y + 1/2, -z + 3/2$; (C) $x, -y + 1/2, z - 1/2$ for **3**. (A) $x + 1, y, z + 1$; (B) $-x + 1, y - 1/2, -z + 3/2$; (C) $x, -y + 3/2, z - 1/2$ for **4**.

Crystal structures of 1–4

Being crystallized in the monoclinic space group $P2_1/c$, the asymmetric units for **1–4** consist of one [Cd(1,3-BDC)(bimb)] molecule (**1**), one [Cd(5-Me-1,3-BDC)(bimb)] molecule (**2**), one [Cd(5-NH_2-1,3-BDC)(bimb)] molecule (**3**), or one [5-HO-Cd(1,3-BDC)(bimb)] molecule (**4**). As the structures of **1–4** are very similar, only that of **1** is shown in Fig. 1. The selected bond lengths and angles for **1–4** are compared in Table 2. In **1–4**, each Cd atom has a distorted octahedral coordination geometry, coordinated by four O atoms from three 5-R-1,3-BDC ligands and two N atoms from two different bimb molecules (Fig. 1a). In **1–4**, the carboxylate groups of 5-R-1,3-BDC (R = H, Me, NH_2 and OH) ligands show chelating bidentate and bridging bidentate coordination modes (Scheme 1a). The mean bridging Cd–O bond distances (2.269(3) Å (**1**), 2.233(3) Å (**2**), 2.269(3) Å (**3**) and 2.259(3) Å (**4**)) are shorter than those of the chelating Cd–O bonds (2.410(3) Å (**1**), 2.400(4) Å (**2**), 2.434(3) Å (**3**) and 2.474(3) Å (**4**)). The average Cd–O bond distances (2.340(4) Å (**1**), 2.340(3) Å (**2**), 2.340(3) Å (**3**), and 2.340(3) Å (**4**)) are comparable to those observed in $\{[Cd_3(btc)_2(bimb)_2]{\cdot}2H_2O\}_n$ (btc = 1,3,5-benzenetricarboxylate) (2.339(4) Å).[17] The mean Cd–N bond lengths (2.317(4) Å (**1**), 2.332 Å (**2**), 2.352 Å (**3**), and 2.366 Å (**4**)) are longer than the those of the corresponding ones of $\{[Cd_3(btc)_2(bimb)_2]{\cdot}2H_2O\}_n$ (2.267(3) Å). The dihedral angles of the two imidazolyl groups of bimb in **1–4** are 21.48(2)° (**1**), 12.26(3)° (**2**), 14.94(2)° (**3**) and 23.36(2)° (**4**), respectively. In **1–4**, two Cd atoms are bridged by one pair of 5-R-1,3-BDC ligands to form a $[Cd_2(5\text{-R-}1,3\text{-BDC})_2]$ unit. Four $[Cd_2(5\text{-R-}1,3\text{-BDC})_2]$ units are linked by four 5-R-1,3-BDC ligands in a head-to-tail way to form a $[Cd_2(5\text{-R-}1,3\text{-BDC})_2]_4$ grid with a dimension of 8.81 Å × 10.27 Å (**1**), 8.96 Å × 10.30 Å (**2**), 8.88 Å × 10.33 Å (**3**), or 8.80 Å × 10.30 Å (**4**). Each grid is further connected to its equivalent ones *via* four 1,3-BDC ligands to form a 2D $(4{,}8^2)$ layer extending along the *bc* plane (Fig. 1b). Each bimb ligand acts as a pillar to link the adjacent 2D layers *via* N atoms, thereby forming a 3D net (Fig. 1c). Topologically, if the 1,3-BDC ligands and the Cd centers are considered as 3- and 5-connecting nodes, respectively, **1** may be considered as having a 3D (3,5)-connected topological structure with a $(4{\cdot}6^2)(4{\cdot}6^6{\cdot}8^3)$ Schläfli symbol (Fig. 1d). In **3** and **4**, the NH_2 (or OH) group of 5-NH_2-1,3-BDC (or 5-OH-1,3-BDC) ligand interacts with O(4) of another 5-NH_2-1,3-BDC (or 5-OH-1,3-BDC) ligand to afford an intermolecular H-bonding interaction (O–H···O (or N–H···O)) (Figs. S3 and S4, ESI†).

Crystal structure of 5

Compound **5** crystallizes in the triclinic space group $P\bar{1}$ and its asymmetric unit consists of one $[Cd_2(OH_2)_2(5\text{-}NO_2\text{-}1,3\text{-}BDC)_2(bimb)]$ molecule and two water solvent molecules. Cd(1) and Cd(2) atoms adopt a distorted octahedral coordination geometry, coordinated by one O atom from the coordinated H_2O, four O atoms from three 5-NO_2-1,3-BDC ligands and one N atom from a bimb ligand, though a seventh weak interaction between Cd(1) and O(4D) (2.740(3) Å) or Cd(2) and O(10C) (2.844(3) Å) is observed (Fig. 2a).[17] In **5**, the carboxylate groups of 5-NO_2-1,3-BDC ligand exhibits one monodentate mode and one μ_3 chelating/bridging mode. (Scheme 1b). The mean monodentate Cd–O(COO^-) bond length (2.234(3) Å) (Table 3) are shorter than those of the chelating Cd–O(COO^-) bonds (2.423(3) Å), the bridging Cd–O(COO^-) bonds (2.520(3) Å) and the Cd–O(H_2O) bonds (2.331(3) Å). The average Cd–O length (2.458(3) Å) of the chelating/bridging Cd–O(COO^-) in **5** are longer than that of $Cd_2(HL^1)2(L^3)_4$ (HL^1 = 3-(2-pyridyl)pyrazole, HL^3 = naphthalene–carboxylic acid) (2.395(2) Å).[18] The mean Cd–N bond length of 2.225(4) Å is shorter than those observed in **1–4**. The two imidazolyl groups and the biphenyl groups of bimb in **5** are almost linear. Two Cd(1) and Cd(2) atoms are linked by a couple of 5-NO_2-1,3-BDC ligands to form a four-membered ring [Cd(1)–O(2)–Cd(1)–O(7)] unit with the Cd(1)···Cd(2) separation of 3.908 Å. Such "Cd_2O_2" four-membered rings are interlinked to adjacent ones by one pair of 5-NO_2-1,3-BDC ligands, forming a 1D double chain (extending

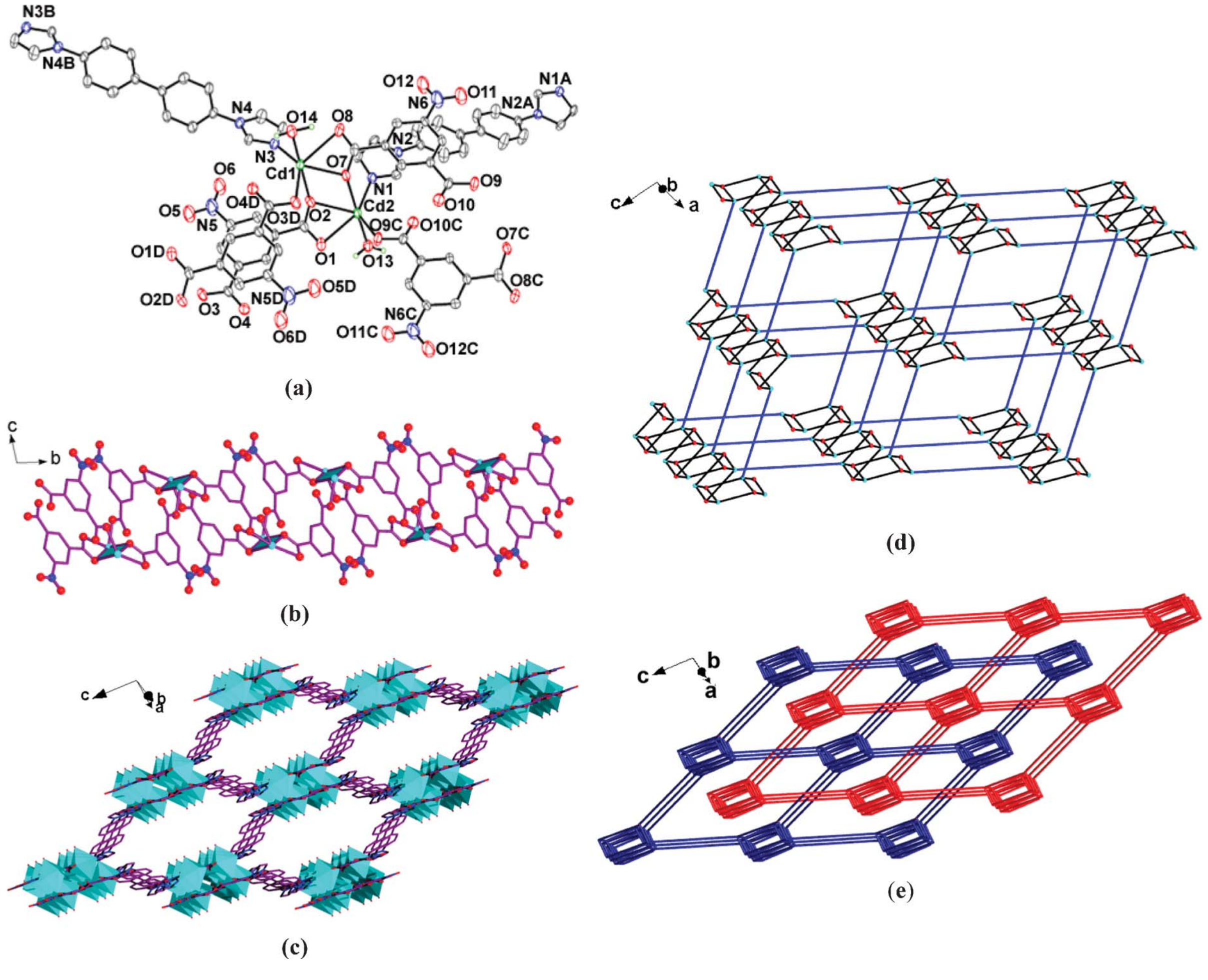

Fig. 2 (a) A view of the coordination environments of Cd1 and Cd2 in **5** with a labelling scheme and 30% thermal ellipsoids. All H atoms except those from coordinated water have been omitted for clarity. Symmetry codes: (A) $-x$, $-y+2$, $-z$.; (B) $-x+3$, $-y+1$, $-z$; (C) $-x+1$, $-y+2$, $-z+1$; (D) $-x+2$, $-y+1$, $-z+1$. (b) A view of a section of the 1D chain (extending along the *a* axis). The red and blue balls represent O and N atoms. Each cyan tetrahedron represents one Cd atom. (c) A view of the 3D net of **5** (looking down the *b* axis). (d) A schematic view of a $(4^2{\cdot}6)(4^2{\cdot}6{\cdot}10^2{\cdot}12)$ topological net of **5**. The cyan and black balls represent 4-connecting Cd centres and 3-connecting 5-NO_2-1,3-HBDC ligands. Each blue line represents one bimb ligand. (e) A view of the 2-fold interpenetrating mode of **5** looking down the *b* axis.

Table 3 Selected bond lengths (Å) and angles (°) for **5** and **6**[a]

Compound **5**			
Cd(2)–N(1)	2.230(4)	Cd(1)–N(3)	2.220(4)
Cd(2)–O(1)	2.358(3)	Cd(2)–O(2)	2.459(3)
Cd(1)–O(2)	2.553(3)	Cd(1)–O(7)	2.305(3)
Cd(2)–O(7)	2.486(3)	Cd(1)–O(8)	2.541(3)
Cd(2)–O(9C)	2.216(3)	Cd(2)–O(13)	2.342(3)
Cd(1)–O(14)	2.320(3)	Cd(1)–O(3D)	2.253(3)
Cd(1)···O(4D)	2.740(3)	Cd(2)···O(10C))	2.844(3)
N(3)–Cd(1)–O(3D)	135.63(14)	N(3)–Cd(1)–O(14)	95.64(14)
O(3D)–Cd(1)–O(14)	90.23(13)	N(3)–Cd(1)–O(7)	137.14(13)
O(3D)–Cd(1)–O(7)	82.69(12)	O(14)–Cd(1)–O(7)	103.81(12)
N(3)–Cd(1)–O(8)	93.91(13)	O(3D)–Cd(1)–O(8)	130.35(12)
O(14)–Cd(1)–O(8)	79.82(12)	O(7)–Cd(1)–O(8)	53.80(11)
N(3)–Cd(1)–O(2)	86.89(13)	O(3D)–Cd(1)–O(2)	87.38(13)
O(14)–Cd(1)–O(2)	177.34(11)	O(7)–Cd(1)–O(2)	74.73(11)
O(8)–Cd(1)–O(2)	100.86(11)	N(1)–Cd(2)–O(13)	91.98(13)
O(9C)–Cd(2)–O(13)	92.40(13)	N(1)–Cd(2)–O(1)	144.97(14)
O(9C)–Cd(2)–O(1)	84.40(13)	O(9C)–Cd(2)–O(2)	130.26(11)
O(13)–Cd(2)–O(1)	82.95(13)	O(13)–Cd(2)–O(2)	106.55(12)
N(1)–Cd(2)–O(2)	95.05(12)	O(9C)–Cd(2)–O(7)	89.20(13)
O(1)–Cd(2)–O(2)	54.22(12)	O(13)–Cd(2)–O(7)	177.93(11)
N(1)–Cd(2)–O(7)	85.98(13)	O(2)–Cd(2)–O(7)	73.32(11)
O(1)–Cd(2)–O(7)	98.52(12)		
Compound **6**			
Cd(1)–N(1)	2.243(4)	N(3A)–Cd(1)	2.245(4)
Cd(1)–O(1B)	2.368(3)	Cd(1)–O(2B)	2.559(3)
Cd(1)–O(5)	2.418(4)	Cd(1)–O(7C)	2.332(3)
O(5)–Cd(1)–N(1)	83.26(15)	O(5)–Cd(1)–N(3A)	90.28(15)
N(1)–Cd(1)–N(3A)	173.44(13)	O(5)–Cd(1)–O(7C)	130.95(13)
N(1)–Cd(1)–O(7C)	86.16(13)	N(3A)–Cd(1)–O(7C)	97.29(13)
O(5)–Cd(1)–O(1A)	91.14(13)	N(1)–Cd(1)–O(1B)	90.44(13)
N((3A)–Cd(1)–O(1B)	90.83(13)	O(7C)–Cd(1)–O(1B)	136.79(11)
O(5)–Cd(1)–O(2B)	138.27(13)	N(1)–Cd(1)–O(2B)	84.47(11)
N(3A)–Cd(1)–O(2B)	108.43(13)	O(7C)–Cd(1)–O(2B)	180.0
O((1B)–Cd(1)–O(2B)	52.91(11)		

[a] Symmetry codes: (C) $-x + 1$, $-y + 2$, $-z + 1$; (D) $-x + 2$, $-y + 1$, $-z + 1$ for **5**. (A) $x - 1/2$, $y - 1/2$, $z - 1$; (B) x, $-y + 2$, $z + 1/2$; (C) $-x + 1/2$, $y - 1/2$, $-z + 1/2$ for **6**.

along the *b* axis) (Fig. 2b). Such a chain is further connected to its equivalent ones by bimb ligands to give a 3D framework (Fig. 2c). This single framework has 1D channels (its window size being *ca.* 17.37 Å × 24.35 Å) along the *b* axis. If the 5-NO_2-1,3-BDC ligands and the Cd centers are considered as 3- and 4-connecting nodes, respectively, **5** possesses a 3D (3,4)-connected topological structure with a $(4^2{\cdot}6)(4^2{\cdot}6{\cdot}10^2{\cdot}12)$ Schläfli symbol (Fig. 2d). The resulting channels are further filled by interpenetration of one independent equivalent net, generating a two-fold interpenetrating 3D architecture (Fig. 2e). A total of 147.6 $Å^3$ (8.1% of the unit cell volume calculated by the Platon program) void in each unit cell is occupied by the guest water molecules. The coordinated and uncoordinated water molecules in the channels interact with the carboxyl groups and NO_2 groups to form complicated intra- and inter-molecular H-bonding interactions.

Crystal structure of 6

Compound **6** crystallizes in the monoclinic space group *C*2/*c* and its asymmetric unit contains [Cd(5-SO_3-1,3-HBDC)(bimb)] molecule. As shown in Fig. 3a, each Cd atom is octahedrally coordinated by two O atoms from two different SO_3^-groups, two O atoms from one COO^- groups and two N atoms from two different bimb ligands. The average chelating Cd–O(COO^-) length (2.464(3) Å) is between those of **1–3** and that of **4**. The average Cd–O(SO_3^-) length (2.371(4) Å) is shorter than that observed in $[Cd_5(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(5\text{-}SO_3\text{-}1,3\text{-}HBDC)_2(H_2O)_5]_n$ (2.467(2) Å).[19] The mean Cd–N bond length of 2.244(4) Å is shorter than those of **1–4**. The dihedral angles of the two imidazolyl groups of bimb in **6** are 23.61(2)°. For the 5-SO_3-1,3-HBDC ligand in **6**, one COO^- group adopts a chelating mode, while the other remains intact. The SO_3^- group takes a bridging bidentate mode. Two Cd atoms are coordinated by two 5-SO_3-1,3-HBDC ligands to generate a binuclear $[Cd_2(5\text{-}SO_3\text{-}1,3\text{-}HBDC)_2]$ grid with dimensions of 3.51 Å × 7.77 Å. Such a grid is linked to its equivalent ones by a pair of 5-SO_3-1,3-HBDC ligands, forming a 2D 3-connected $(4{\cdot}8^2)$ network extending along the *bc* axis (Fig. 3b). Each bimb ligand links the adjacent 2D layers to afford a 3D framework (Fig. 3c). If the 5-SO_3-1,3-HBDC ligand and the Cd center are considered as 3- and 5-connecting nodes, respectively, **6** has a 3D (3,5)-connected topological structure with a $(4{\cdot}6{\cdot}8)(4{\cdot}6^5{\cdot}8^3{\cdot}10)$ Schläfli symbol (Fig. 3d). Within the $[Cd_2(5\text{-}SO_3\text{-}1,3\text{-}HBDC)_2]$ grid, the centroid–centroid separation between imidazole rings of the two bimb ligands is 3.585 Å, while that between phenyl rings is 3.796 Å from such pairs of bimb ligands, indicating the presence of weak intermolecular π···π interactions. In addition, the O(1) atom of one 5-SO_3-1,3-HBDC ligand acts as an acceptor to interact with the uncoordinated carboxyl group of another 5-SO_3-1,3-HBDC ligand to yield an intermolecular hydrogen bond (O(3)–H(3B)···O(1)).

Thermal and photoluminescent properties

Thermogravimetric (TGA) experiments were carried out to study the thermal stability of **1–6** (Fig. S5, ESI†). The TGA analysis revealed that **1–6** were stable up to 422 °C (**1**), 435 °C (**2**), 460 °C (**3**), 429 °C (**4**) and 423 °C (**6**). For **1–4** and **6**, only one weight loss of 77.62% (**1**), 78.98% (**2**), 77.27% (**3**) 78.53% (**4**) and 79.37% (**6**) in the range of 422–750 °C (**1**), 435–680 °C (**2**), 460–700 °C (**3**), 429–730 °C (**4**) and 423–900 °C (**6**) amounts roughly to the loss of the bimb and 5-R-1,3-BDC (R = H, Me, NH_2, OH, HSO_3) ligands (calculated 77.19% for **1**, 77.74% for **2**, 77.78% for **3**, 77.82% for **4** and 80.02% for **6**). For **5**, the first weight loss of 6.87% in the range of 45–119 °C corresponds roughly to the loss of two uncoordinated and two coordinated water molecules per formula (calculated 7.19%). The second weight loss of 67.63% in the range of 367–780 °C approximately amounts to the loss of the bimb and 5-NO_2-1,3-BDC (calculated 67.17%). In all cases, the remaining substance with a weight of 22.38% (**1**), 21.02% (**2**), 22.73% (**3**), 21.47% (**4**), 25.01% (**5**) and 20.63% (**6**) was assumed to be CdO (calculated 22.81% for **1**, 22.26% for **2**, 22.22% for **3**, 22.18% for **4**, 25.64% for **5** and 19.97% for **6**).

The photoluminescent properties of **1–6** in the solid state were investigated at ambient temperature (Fig. 4). For **1–6**, upon excitation at 327 nm (**1**), 307 nm (**2**), 330 nm (**3**), 312 nm (**4**), 300 nm (**5**) and 333 nm (**6**), they exhibited strong photoluminescence with emission maxima at *ca.* 377 nm (**1**), 349/364 nm (**2**), 394 nm (**3**), 354/366 nm (**4**), 372 nm (**5**) and 397 nm (**6**), respectively. The emission peaks of **2** and **4** were similar to that of the bimb ligand (λ_{em} = 348 nm and 361 nm, λ_{ex} = 300 nm). Their origins may be tentatively assigned to the π–π * intraligand fluorescence.[20] It is noted that the emission maxima of **1**, **3**, **5** and **6** are red-shifted compared to that of bimb. The bands

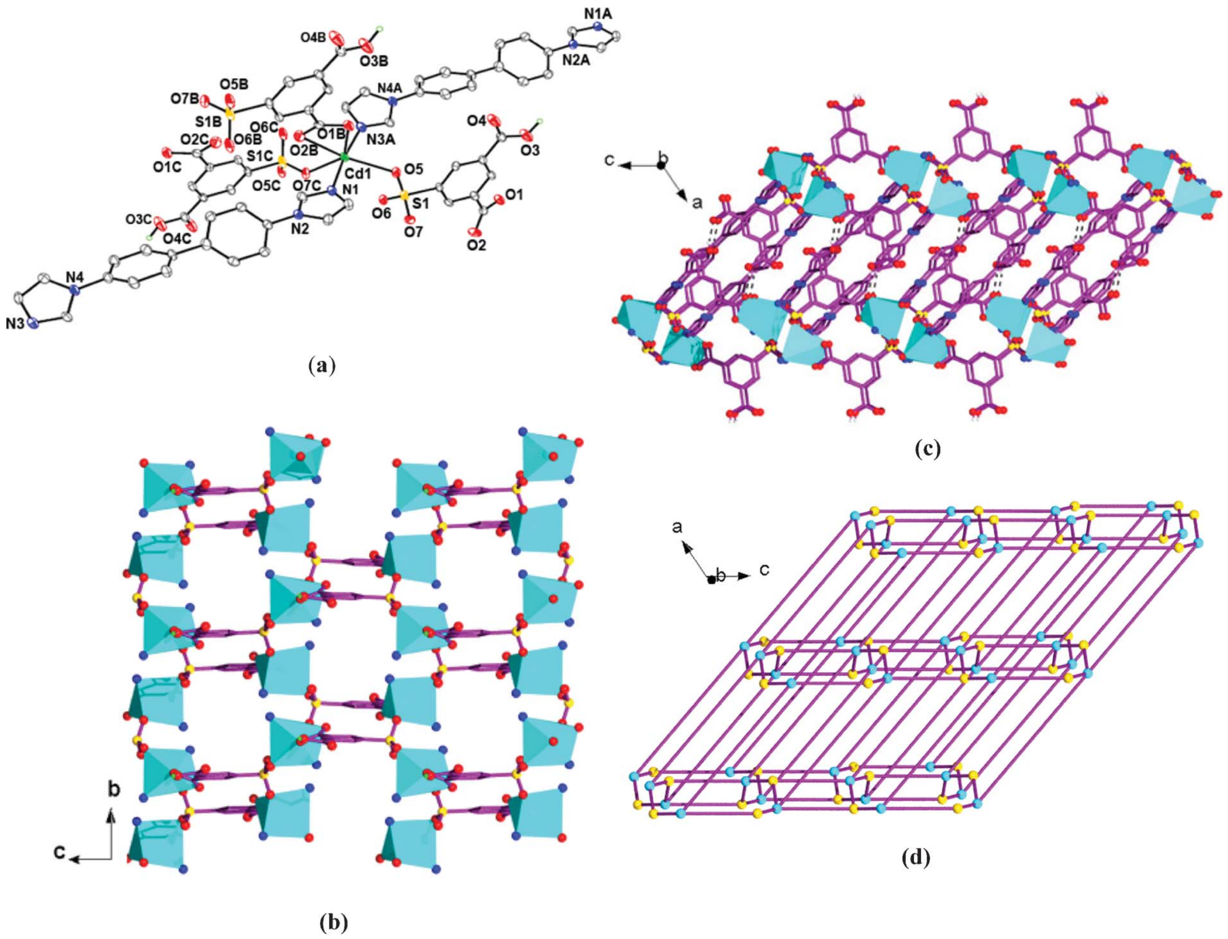

Fig. 3 (a) A view of the coordination environment of Cd1 in **6** with a labelling scheme and 30% thermal ellipsoids. All H atoms except the carboxylic H atoms have been omitted for clarity. Symmetry codes: (A) $x - 1/2$, $y - 1/2$, $z - 1$; (B) x, $-y + 2$, $z + 1/2$; (C) $-x + 1/2$, $y - 1/2$, $-z + 1/2$. (b) A view of the 2D network (extending along the *bc* plane). Each cyan tetrahedron represents one Cd atom. The red, blue and yellow balls represent O, N and S atoms, respectively. (c) A view of the 3D net of **6** (looking down the *b* axis). (d) A schematic view of a $(4{\cdot}6{\cdot}8)(4{\cdot}6^5{\cdot}8^3{\cdot}10)$ topological net of **6**. The cyan and yellow balls represent 5-connecting Cd centers and 3-connecting 5-SO_3-1,3-HBDC ligands. Each pink line represents one bimb ligand.

might be assigned as the metal-to-ligand charge transfer (MLCT) with electrons being transferred from the Cd(II) centres to the unoccupied *p** orbitals of the imidazolyl groups of bimb, according to the literature.[21]

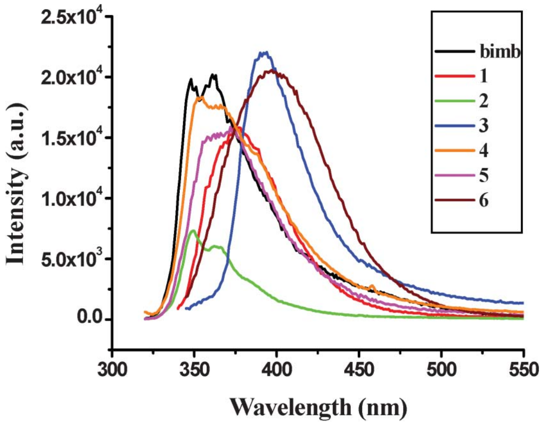

Fig. 4 The solid state emission spectra of **1–6** along with bimb at ambient temperature.

Conclusions

In the work reported here, we demonstrated construction of six Cd(II) coordination polymers **1–6** from hydrothermal reactions of $CdCl_2{\cdot}2.5H_2O$ with bimb and six 5-R-1,3-BDC derivatives with differently sized substituted R (H, Me, NH_2, OH, NO_2, SO_3H) groups at the 5-position. Compounds **1–4** consist of similar 3D frameworks with the Schläfli symbol $(4{\cdot}6^2)(4{\cdot}6^6{\cdot}8^3)$. Compound **5** exhibits a two-fold interpenetrating 3D framework with a Schläfli symbol of $(4^2{\cdot}6)(4^2{\cdot}6{\cdot}10^2{\cdot}12)$. Compound **6** has a 3D framework with a Schläfli symbol of $(4{\cdot}6{\cdot}8)(4{\cdot}6^5{\cdot}8^3{\cdot}10)$. For each dicarboxylate in **1–4**, one carboxyl group takes a chelating mode, while the other works as a bridging one. For **5**, the two carboxyl groups of 5-NO_2-1,3-BDC serve as a monodentate mode and a μ_3-chelating/bridging mode. For **6**, one carboxyl group of the 5-HSO_3-1,3-BDC ligand is kept intact, while the other exhibited a chelating bidentate coordination mode and its SO_3^- group adopted a bridging bidentate coordination mode. The structural diversities of **1–6** were greatly affected by different coordination modes of dicarboxylates, though the role of the bimb ligands showing different conformations in **1–6** may not be ruled out. These results may provide us an interesting insight into how the assembly of Cd(II) coordination polymers is affected by the substituted groups of the ligands.

Acknowledgements

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