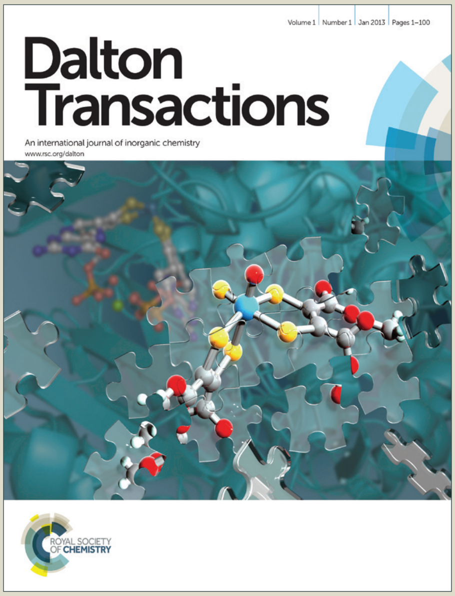
Dalton Transactions

Accepted Manuscript



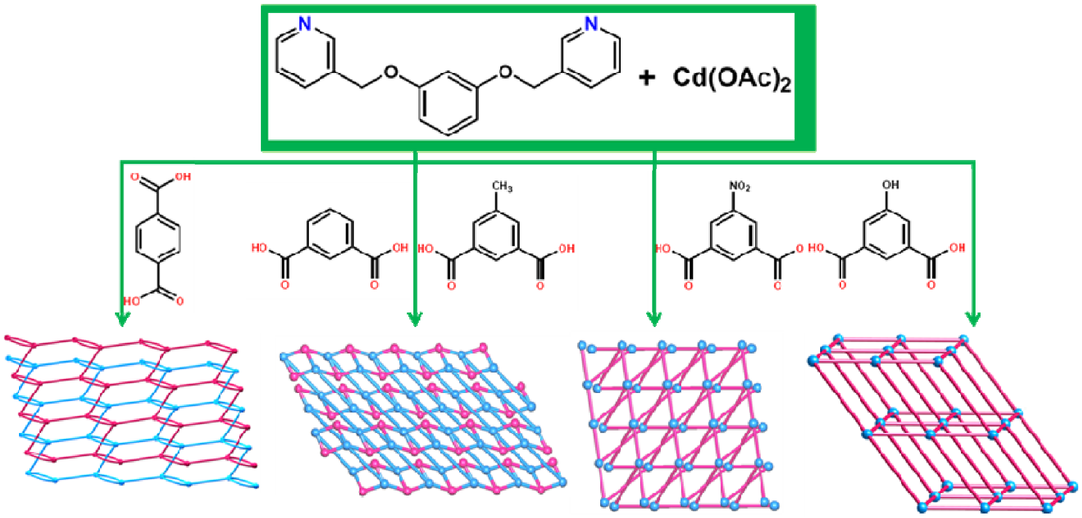
ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Graphic Contents Entry

Hydrothermal reactions of Cd(OAc)$_2$·2H$_2$O with flexible V-shaped bipyridyl benzene and five benzenedicarboxylic acid derivatives gave rise to five new new coordination polymers. Complexes **1–5** are characterized by elemental analysis, IR, powder X-ray diffraction, and single-crystal X-ray diffraction. These compounds exhibited relatively good photocatalytic activity towards the degradation of methylene blue (MB) in aqueous solution under UV irradiation.

Figure for Graphic Contents Entry



Structural diversity and photocatalytic properties of Cd(II) coordination polymers constructed by a flexible V-shaped bipyridyl benzene ligand and dicarboxylate derivatives†

Lei-Lei Liu,*[a] Cai-Xia Yu,[a] Feng-Ji Ma,[a] Ya-Ru Li,[a] Jing-Jing Han,[a] Lu Lin[a] and Lu-Fang Ma*[b]

Received (in XXX, XXX) xxxxx 2014, Accepted xxxxx 2014
First published on the web xxxxx 2014
DOI: 10.1039/c000000x

Hydrothermal reactions of $Cd(OAc)_2 \cdot 2H_2O$ with flexible V-shaped bipyridyl benzene ligand and five benzenedicarboxylic acid derivatives gave rise to five new coordination polymers $[Cd(1,4\text{-}BDC)(bpmb)(H_2O)]_n$ (**1**), $\{[Cd(1,3\text{-}BDC)(bpmb)] \cdot 0.125H_2O\}_n$ (**2**), $[Cd_2(5\text{-}Me\text{-}1,3\text{-}BDC)_2(bpmb)_2]_n$ (**3**), $[Cd(5\text{-}NO_2\text{-}1,3\text{-}BDC)(bpmb)(H_2O)]_n$ (**4**) and $[Cd(5\text{-}OH\text{-}1,3\text{-}BDC)(bpmb)(H_2O)]_n$ (**5**) (bpmb = 1,3-bis(pyridine-3-ylmethoxy)benzene, 1,4-H_2BDC = 1,4-benzenedicarboxylic acid, 1,3-H_2BDC = 1,3-benzenedicarboxylic acid, 5-Me-1,3-H_2BDC = 5-methyl-1,3-benzenedicarboxylic acid, 5-NO_2-1,3-H_2BDC = 5-nitro-1,3-benzenedicarboxylic acid, 5-OH-1,3-H_2BDC = 5-hydroxy-1,3-benzenedicarboxylic acid). Their structures have been determined by single-crystal X-ray diffraction analyses, elemental analyses, IR spectra, powder X-ray diffraction (PXRD) and thermogravimetric analyses (TGA). Compound **1** is a two-fold interpenetrating networks showing the coexistence of polyrotaxane and polycatenane characters. Compounds **2** and **3** exhibit similar 2D (3,5)-connected $(4^2 \cdot 6^7 \cdot 8)(4^2 \cdot 6)$ nets in which the bpmb ligands works as lockers interlocking 1D $[Cd(1,3\text{-}BDC/5\text{-}Me\text{-}1,3\text{-}BDC)]_n$ chains. Compound **4** shows a 2D 4-connected (6^6) sandwich-like structure with differently oriented $[Cd(5\text{-}NO_2\text{-}1,3\text{-}BDC)]_n$ chains. Compound **5** is a 3D supramolecular *pcu* net based on 1D ladder-shaped chain. These results suggest that substituted postions of carboxylate groups and changes in substituted R groups in the 5-position of BDC ligands have significant effect on the final structures. These compounds exhibited relatively good photocatalytic activity towards the degradation of methylene blue (MB) in aqueous solution under UV irradiation. Moreover, solid-state photoluminescence properties of **1**–**5** were also investigated.

Introduction

Current interest in coordination polymers (CPs) is rapidly expanding owing to their intriguing aesthetic structures and topological features as well as their potential applications as functional materials.[1–3] Significant effort has been devoted to producing CPs with desired structures and properties using various approaches, such as retrosynthesis, modular chemistry and supramolecular chemistry.[4] One of the most successful approach is rational selection of metal centers and organic ligands to construct target CPs with specific structural characteristics.[5] Earlier, much studies were devoted to using linear rod-like ligands, such as 4,4′-bipyridine or its analogs for the construction of diverse CPs.[6] Some of these CPs show excellent sorption, catalytic and fluorescence properties. However, less effort has been given towards flexible angular linkers for the preparation of CPs.

Flexible angular linkers with potential functional information may provide greater structural diversity with additional properties.[7] For examples, Gao and co-workers have investigated the coordination chemistry of angular bipyridyl ligands with Zn(II), Ag(I), Hg(II) salts and so on, and obtained several helical compounds as well as cage-like structures.[8] Steel and Mirkin have reported some silver(I) compounds with zigzag chains that were obtained by reacting 1,4-bis(pyridine-2-ylmethoxy)benzene with various Ag(I) salts.[9] Accordingly, such flexible angular ligands could be justified as efficient and versatile organic building units for the construction of coordination architectures.[8–10] With that in mind, we synthesized a flexible V-shaped bipyridyl ligand, 1,3-bis(pyridine-3-ylmethoxy)benzene (bpmb), which contain rigid benzene ring piece and two freely rotating pyridyl arms combined by intervening methoxy groups. The pyridine arms can freely twist around the –O–CH_2– group forming nine possible conformations (Scheme 1) to meet the requirements of the coordination arrangements of metal atoms in the assembly processes, which can easily produce unique structural motifs with beautiful aesthetics and useful functional properties.[11]

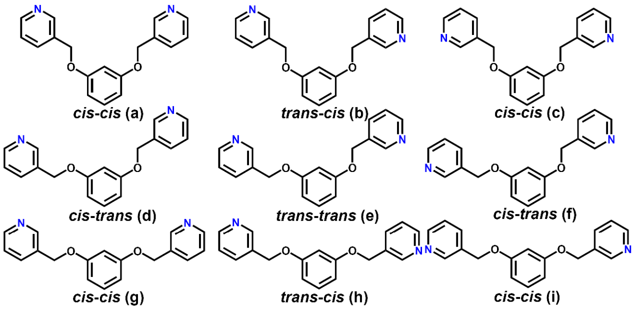
On the other hand, polycarboxylates are often used as bridging ligands to produce CPs due to their versatile coordination modes, high structural stability and the ability to balance the positive charges.[12] Moreover, in view of the previous reports, we found that different substituted groups on the polycarboxylate ligands

---

[a] *College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang 455000, Henan, P. R. China. E-mail: liuleileimail@163.com*
[b] *College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, Henan, P. R. China. E-mail: mazhuxp@126.com*

† Electronic supplementary information (ESI) available: PXRD patterns, TGA curves, emission spectra and additional figures for **1-5**. CCDC reference numbers: 1009548-1009552. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x

may have an influence on the assembling processes, the structures and even the properties of CPs due to their geometric and electronic effects.[13] In addition, nowadays, using the mixed N-donor ligand and polycarboxylate is being a good strategy to construct new metal organic compounds.[14] Taking these into account, in this work we carefully selected 1,4-benzenedicarboxylic acid (1,4-H_2BDC) and four kinds of substituted 1,3-benzenedicarboxylic acid derivatives (5-R-1,3-H_2BDC, R = H, Me, NO_2, OH) to assemble with flexible V-shaped 1,3-bis(pyridine-3-ylmethoxy)benzene (bpmb) and $Cd(OAc)_2\cdot 2H_2O$. The selection of such benzenedicarboxylic acid derivatives was based on the following considerations: (a) The substituted positions of carboxylic groups on the certain ligand may produce isomeric effect, which may cause the formation of different structures. (b) Hydrogen-bonding interactions usually result in multidimensional architectures. The OH group usually works as a hydrogen-bonding donor while the NO_2 group is more prone to act as a hydrogen-bonding acceptor as it has no O–H bond. Hydrothermal reactions of $Cd(OAc)_2\cdot 2H_2O$ with H_2BDC derivatives and bpmb gave rise to five CPs $[Cd(1,4\text{-}BDC)(bpmb)(H_2O)]_n$ (**1**), $\{[Cd(1,3\text{-}BDC)(bpmb)]\cdot 0.125H_2O\}_n$ (**2**), $[Cd_2(5\text{-}Me\text{-}1,3\text{-}BDC)_2(bpmb)_2]_n$ (**3**), $[Cd(5\text{-}NO_2\text{-}1,3\text{-}BDC)(bpmb)(H_2O)]_n$ (**4**) and $[Cd(5\text{-}OH\text{-}1,3\text{-}BDC)(bpmb)(H_2O)]_n$ (**5**). These five CPs were found to be able to photocatalytically degrade methylene blue (MB) in water in a relatively efficient way.



Scheme 1 Possible conformations of the bpmb ligand.

Experimental

Materials and physical measurements

The ligand bpmb was prepared according to the previously reported procedure with significant modification.[15] All other chemicals and reagents were obtained from commercial sources and used as received. IR spectra were recorded with a Varian 800 FT-IR spectrometer as KBr disks (4000-400 cm^{-1}). The elemental analyses for C, H, and N were performed on an EA1110 CHNS elemental analyzer. Powder X-ray diffraction (PXRD) was performed using a PANalytical X'Pert PRO MPD system and Bruker Ultima III X-ray diffractometer. Luminescent spectra were recorded with a JASCO FP-8600 fluorescence spectrophotometer. Thermal analysis were performed with a Netzsch STA-449F3 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} and a flow rate of 20 cm^3 min^{-1} (N_2).

Preparation of compounds 1–5

$[Cd(1,4\text{-}BDC)(bpmb)(H_2O)]_n$ (1). A 10 mL Pyrex glass tube was loaded with $Cd(OAc)_2\cdot 2H_2O$ (11 mg, 0.04 mmol), 1,4-H_2BDC (3 mg, 0.02 mmol), bpmb (6 mg, 0.02 mmol) and 4 mL of H_2O. The tube was then sealed and heated in an oven to 150 °C for four days, and then cooled to ambient temperature at a rate of 5 °C h^{-1}. The colourless blocks of **1** were formed four day later, which were collected and dried in air. Yield: 6 mg (51%, based on bpmb). Anal. Calcd. for $C_{26}H_{22}N_2CdO_7$: C, 53.21; H, 3.78; N, 4.77. Found: C, 53.50; H, 3.38; N, 4.31. IR (KBr disc): 3424 (m), 2913 (w), 1656 (m), 1605 (m), 1562 (s), 1545 (m), 1437 (m), 1378 (m), 1338 (w), 1265 (m), 1154 (m), 1048 (m), 1035 (w), 991 (w), 936 (w), 890 (w), 862 (w), 837 (w), 786 (m), 646 (m) cm^{-1}.

$\{[Cd(1,3\text{-}BDC)(bpmb)]\cdot 0.125H_2O\}_n$ (2). Compound **2** (colourless rods) was prepared in the same way as **1**, except using 1,3-H_2BDC (3 mg, 0.02 mmol) instead of 1,4-H_2BDC as well as the reaction temperature was fixed at 170 °C. Yield: 5 mg (44%, based on bpmb). Anal. Calcd. for $C_{26}H_{20.25}N_2CdO_{6.125}$: C, 54.68; H, 3.57; N, 4.91. Found: C, 54.58; H, 3.99; N, 4.51. IR (KBr disc): 3489 (m), 3055 (w), 1601 (s), 1547 (s), 1493 (m), 1438 (m), 1384 (s), 1295 (m), 1183 (m), 1147 (w), 1082 (w), 1046 (m), 965 (w), 789 (w), 745 (w), 722 (w), 704 (w), 732 (w), 654 (w) cm^{-1}.

$[Cd_2(5\text{-}Me\text{-}1,3\text{-}BDC)_2(bpmb)_2]_n$ (3). Compound **3** (colourless rods) was prepared in the same way as **2**, except using 5-Me-1,3-H_2BDC (4 mg, 0.02 mmol) instead of 1,3-H_2BDC. Yield: 5 mg (43%, based on bpmb). Anal. Calcd. for $C_{54}H_{44}N_4Cd_2O_{12}$: C, 55.64; H, 3.80; N, 4.81. Found: C, 55.92; H, 3.77; N, 4.75. IR (KBr disc): 3450 (m), 3122 (w), 1606 (m), 1570 (m), 1543 (s), 1466 (s), 1398 (m), 1295 (m), 1114 (m), 1019 (w), 992 (w), 770 (w), 687 (m), 665 (w), 609 (w) cm^{-1}.

$[Cd(5\text{-}NO_2\text{-}1,3\text{-}BDC)(bpmb)(H_2O)]_n$ (4). Compound **4** (colourless blocks) was prepared in the same way as **2**, except using 5-NO_2-1,3-H_2BDC (4 mg, 0.02 mmol) instead of 1,3-H_2BDC. Yield: 7 mg (55%, based on bpmb). Anal. Calcd. for $C_{26}H_{21}N_3CdO_9$: C, 49.42; H, 3.35; N, 6.65. Found: C, 49.66; H, 2.97; N, 6.85. IR (KBr disc): 3450 (m), 3098 (w), 1656 (m), 1616 (s), 1563 (m), 1544 (m), 1493 (w), 1459 (w), 1438 (m), 1364 (m), 1344 (m), 1290 (w), 1145 (m), 1180 (w), 1082 (w), 925 (w), 814 (w), 789 (w), 730 (m), 700 (w), 647 (w) cm^{-1}.

$[Cd(5\text{-}OH\text{-}1,3\text{-}BDC)(bpmb)(H_2O)]_n$ (5). Compound **5** (colourless blocks) was prepared in the same way as **2**, except using 5-OH-1,3-H_2BDC (4 mg, 0.02 mmol) instead of 1,3-H_2BDC. Yield: 6 mg (50%, based on bpmb). Anal. Calcd. for $C_{26}H_{22}N_2CdO_8$: C, 51.80; H, 3.68; N, 4.65. Found: C, 51.99; H, 3.82; N, 3.77. IR (KBr disc): 3495 (m), 2902 (w), 1591 (m), 1565 (s), 1486 (m), 1438 (m), 1387 (s), 1290 (w), 1256 (w), 1147 (m), 1003 (w), 894 (w), 834 (m), 755 (m), 701 (m), 684 (w), 649 (w) cm^{-1}.

X-Ray data collection and structure determination

Single crystals of **1**–**5** were obtained directly from the above preparations. All measurements were made on a Bruker Smart Apex-II CCD area detector by using graphite monochromated Mo Kα (λ = 0.071073 nm). These crystals were mounted on glass fibers at 296 K for **1**–**5**. Diffraction data were collected at f and ω modes with a detector distance of 35 mm to the crystals. Cell parameters were refined by using the program

Bruker *SAINT*. The collected data were reduced by using the program Bruker *SAINT* A, and the absorption corrections (multi-scan) were applied. The reflection data were also corrected for Lorentz and polarization effects. The crystal structures of **1**–**5** were solved by direct method refined on F^2 by full-matrix least-squares techniques with the SHELXTL-97 program.[16] A summary of the key crystallographic information for **1**–**5** is tabulated in Table 1 and their selected bond lengths are given in Table 2.

Photocatalytic activity measurements

The photocatalytic activities of as-prepared samples were evaluated by the degradation of MB under irradiation of a 350 W Xe lamp. In a typical process, 20 mg of samples as photocatalysts were added into 50 mL of MB solution (4×10^{-5} mol L^{-1}). After the solution was stirred for 30 min in the dark before irradiation to reach adsorption equilibrium between the catalyst and solution and then was exposed to UV irradiation. About 4 mL suspension was continually taken from the reaction cell and collected by centrifugation at 30 or 60 min intervals during the irradiation. The resulting solution was analyzed on a Varian 50 UV/Vis spectrophotometer.

Table 1 Summary of Crystallographic Data for **1**−**5**

Compounds	1	2	3	4	5
Empirical Formula	$C_{26}H_{22}CdN_2O_7$	$C_{52}H_{40.5}Cd_2N_4O_{12.25}$	$C_{54}H_{43}Cd_2N_4O_{12}$	$C_{26}H_{21}CdN_3O_9$	$C_{26}H_{22}CdN_2O_8$
Formula Weight	586.87	1142.20	1164.72	631.86	602.86
Crystal System	triclinic	monoclinic	triclinic	monoclinic	triclinic
Space Group	$P\bar{1}$	$P2/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	6.4235(13)	10.266(2)	10.293(2)	15.109(3)	10.237(2)
b/Å	13.158(3)	13.899(3)	13.662(3)	13.165(3)	10.517(2)
c/Å	14.840(3)	16.102(3)	16.976(3)	25.900(5)	12.560(3)
α/°	87.94(3)	90.00	84.12(3)	90.00	67.40(3)
β/°	78.26(3)	101.31(3)	78.31(3)	102.14(3)	85.63(3)
γ/°	83.90(3)	90.00	84.81(3)	90.00	72.11(3)
V/Å^3	1221.0(5)	2252.9(8)	2319.4(8)	5036.7(17)	1186.7(4)
Z	2	2	2	8	2
Temperature/K	296(2)	296(2)	296(2)	296(2)	296(2)
D_c/g cm^{-3}	1.596	1.684	1.668	1.667	1.687
μ/MoKα, mm^{-1}	0.943	1.017	0.990	0.928	0.976
F(000)	592.0	1149	1174	2544	608
Total reflections	8646	15447	15904	17497	8212
Unique reflections(R_{int})	4284(0.0159)	3981(0.0325)	8108(0.0362)	4424(0.0348)	4169(0.0255)
No. of observations	4014	3302	6272	3770	3703
No. of parameters	333	321	651	352	346
$R_1{}^a$	0.0199	0.0263	0.0519	0.0342	0.0288
$wR_2{}^b$	0.0496	0.0645	0.1499	0.0722	0.0717
GOF^c	1.037	1.055	1.028	1.113	1.051

[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] 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.

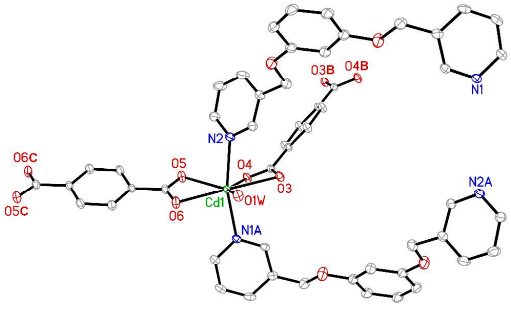
Results and discussion

Synthetic and spectral aspects

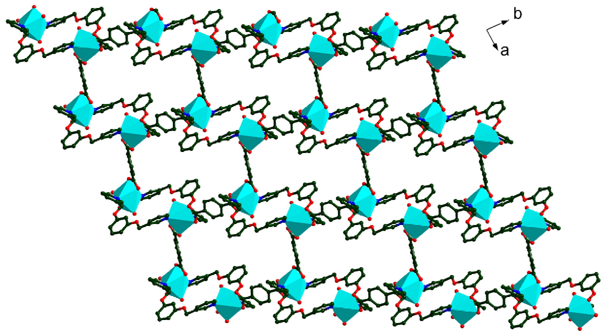
In all solvothermal reactions reported here, the molar ratio of $Cd(OAc)_2 \cdot 2H_2O$ to H_2BDC derivatives and bpmb was kept at 2 : 1 : 1. Reactions of $Cd(OAc)_2 \cdot 2H_2O$ with H_2BDC derivatives and bpmb at 150 °C (**1**) and 170 °C (**2**–**5**) for four days produced colourless crystals of **1** (51% yield), **2** (44% yield), **3** (43% yield), **4** (55% yield) and **5** (50% yield), respectively. When the reaction temperatures were raised up to 170 °C for **1** or lowered to 150 °C for **2**–**5**, no corresponding compounds **1**–**5** formed. Compounds **1**–**5** were stable towards oxygen and moisture, and almost insoluble in common organic solvents. Their elemental analysis was consistent with the chemical formulas of **1**–**5**. In order to check the phase purity of **1**–**5**, the powder X-ray diffraction (PXRD) patterns were measured at room temperature (Fig. S1a-1b, ESI†). The IR spectra of **1**–**5** showed peaks in the range of 1591−1616 cm^{-1} and 1364–1398 cm^{-1}, suggesting they all contain coordinated carboxylate groups. The identities of **1**–**5** were finally confirmed by single-crystal diffraction analysis.

Crystal structure of 1

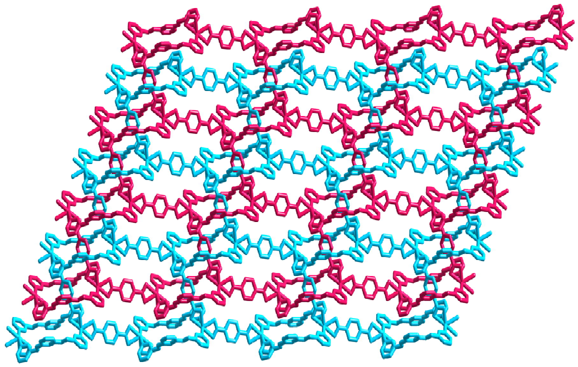
Compound **1** crystallizes in the triclinic space group $P\bar{1}$, and its asymmetric unit contains one Cd atom, one bpmb ligand, two halves of 1,4-BDC ligands and one coordinated H_2O molecule. As shown in Fig. 1a, Cd1 atom adopts a distorted pentagonal bipyramidal coordination geometry and is seven-coordinated by two N atoms of two bpmb ligands, four O atoms of two chelating carboxylate groups from two different 1,4-BDC ligands and one O atom from H_2O molecule. The mean Cd–N, Cd–O and Cd–$O1_{water}$ bond lengths [2.332(2) Å *vs* 2.426(2) Å *vs* 2.340(2) Å] are comparable those of the corresponding one in $\{[Cd(4,4'\text{-}bipy)(H_2O)(egpe)]\cdot(4,4'\text{-}bipy)\cdot 11H_2O\}_n$ [2.299(5) Å *vs* 2.425(4) Å *vs* 2.318(5) Å, 4,4′-bipy = 4,4′-bipyridine, H_2egpe = ethylene glycol bis[4-(carboxyl)phenyl] ether].[17] Cd1 and its symmetry-related Cd1A are linked by N atoms from two bpmb ligands to give a 28-membered dimer ring $[Cd_2(bpmb)_2]$ with the dimensions 9.955 Å × 11.854 Å (Fig. S2a), which is further linked by 1,4-BDC ligand in the chelated modes to form a ringed ribbon-like chain (Fig. S2b), then to a 2D layer (Fig. 1b) with $[Cd_2(bpmb)_2]$ ring approximately perpendicular to the plan of 2D layer. In each 2D layer, four 1,4-BDC and four bpmb ligands join six Cd atoms generating 80-membered dimer ring $[Cd_6(bpmb)_4(1,4\text{-}BDC)_4]$ with the dimensions 10.425 Å × 29.476 Å. From the viewpoint of topology,[18] such a net is described by (6^3) topology, based on the 3-connected Cd atom. The 2D net is spacious enough to contain a second, thus, two identical ones are mutually interpenetrated with each other to form a two-fold parallel interpenetrating networks (Fig. 1c). However, the structure of **1** cannot be simply considered as two-fold interpenetrating networks. The fascinating feature of the structure of **1** is that the $[Cd_2(bpmb)_2]$ rings of each layer are penetrated by one 1,4-BDC ligand of the other layer, and *vice versa*. Meanwhile, the presence of catenated rings by the $[Cd_2(bpmb)_2]$ ring and the $[Cd_6(bpmb)_4(1,4\text{-}BDC)_4]$ ring from adjacent layers makes the nontrivial topology of the entanglement (Fig. 1c, d). So the structure of **1** shows both polyrotaxane and polycatenane characteristics.



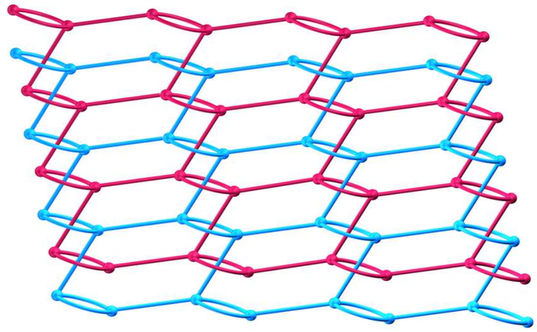
(a)



(b)



(c)



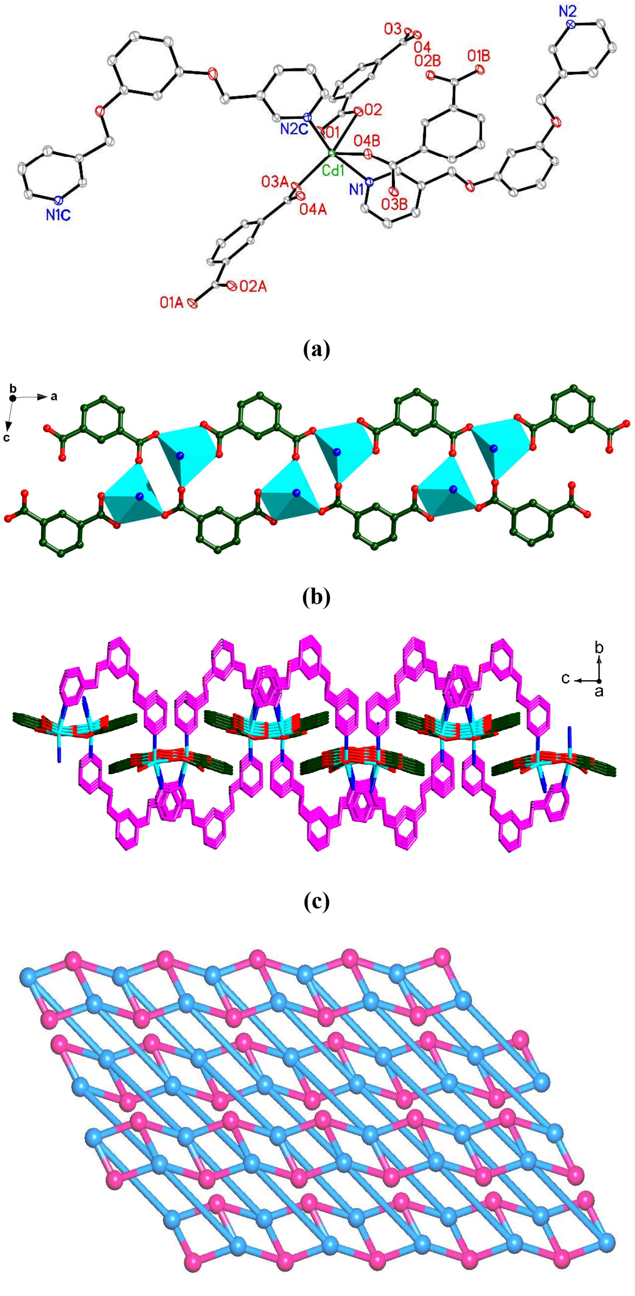
(d)

Fig. 1 (a) View of the coordination environments of Cd center in **1** with labeling schemes. Symmetry codes: (A) $2-x, 1-y, 1-z$; (B) $-x, 1-y, 1-z$; (C) $1-x, -y, -z$. (b) View of the 2D network in **1** extending along the *ab* plane. (c) Stick representation of interlocked nets. (d) Schematic description of the entanglement structure. Atom color codes: Cd, cyan polyhedrons; O, red; N, blue; C, dark green. All H atoms are omitted for clarity.

Crystal structures of 2 and 3

Compound **2** crystallizes in the monoclinic space group *P*2/*c*, and compound **3** crystallizes in the triclinic space group $P\bar{1}$. For **2**, its asymmetric unit contains one [Cd(1,3-BDC)(bpmb)] unit as well as one quarter of H_2O solvent molecule. While for **3**, its asymmetric unit only contains one [Cd(5-Me-1,3-BDC)(bpmb)] unit. The coordination geometries of whole Cd atoms in **2** and **3** are similar. Each Cd atom is coordinated by two N atoms from two different bpmb ligands, two O atoms of chelating carboxylate groups from one 1,3-BDC/5-Me-1,3-BDC ligand and two O atoms of bridging carboxylate groups from two 1,3-BDC/5-Me-1,3-BDC ligands to complete the octahedral geometries (Fig. 2a and Fig. S3a-S3b). The average Cd–N and Cd–O bond lengths (2.346(3) Å *vs* 2.342(2) Å) in **2** are comparable those of in **3** (2.350(5) Å *vs* 2.333(4) Å).

In both of compounds **2** and **3**, as shown in Fig. 2b (**2** for example), each adjoining pair of Cd atoms is connected by 1,3-BDC ligands chelated and bidentate modes to form a 1D $[Cd(1,3\text{-}BDC)]_n$ ribbon-like chain extending along the *a* axis. Interestingly, the bpmb ligands bond to Cd atoms as the up and down fashions in the 1D $[Cd(1,3\text{-}BDC)]_n$ chain producing a 2D layer extending along the *bc* plane (Fig. 2c). Within the 2D layer of **2**, the Cd$\cdots$Cd separations across the bpmb and 1,3-BDC ligands are 11.974, 7.777 and 10.092 Å, respectively, which are shorter than those in **3** (12.157, 7.853 and 10.293 Å, respectively). This may be due to the steric hindrance of methyl in 5-Me-1,3-BDC ligand. From the topological view, if each Cd atom and 1,3-BDC/5-Me-1,3-BDC is considered as a 5- and 3-connected node, respectively, both of the structures of **2** and **3** exhibits a (3,5)-connected $(4^2\cdot6^7\cdot8)(4^2\cdot6)$ topology (Fig. 2d).



(a)

(b)

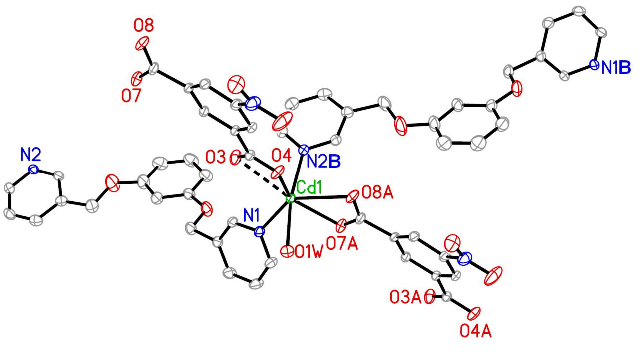
(c)

(d)

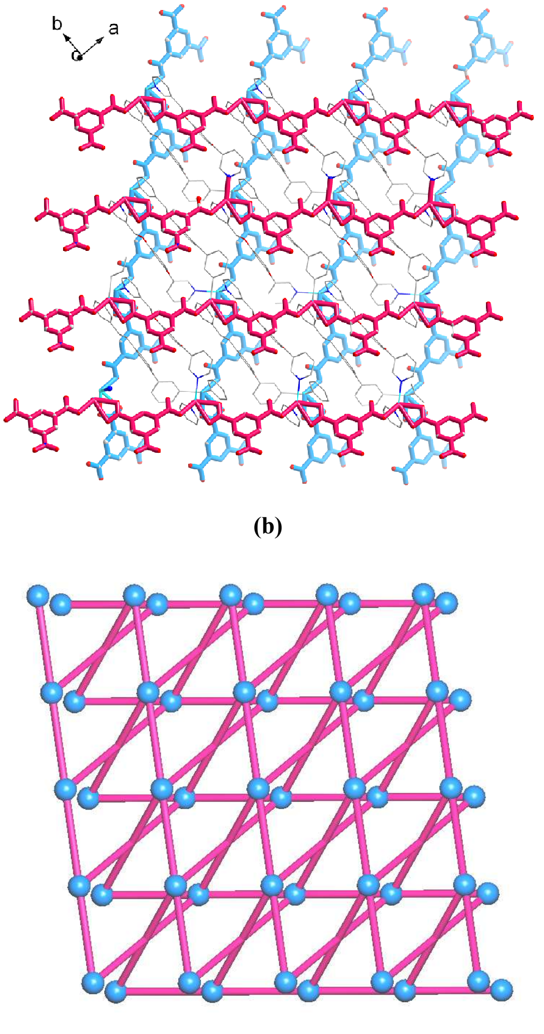
Fig. 2 (a) View of the coordination environments of Cd center in **2** with labeling schemes. Symmetry codes: (A) $-1+x, y, z$; (B) $1-x, y, 1/2-z$; (C) $-1+x, 1-y, -1/2+z$. (b) View of the 1D $[Cd(1,3\text{-}BDC)]_n$ ribbon-like chain in **2** extending along the *a* axis. (c) View of the 2D structure in **2** looking down *a* axis. (d) Schematic view of the (3,5)-connected $(4^2\cdot6^7\cdot8)(4^2\cdot6)$ topology. Atom color codes: Cd, cyan polyhedrons; O, red; N, blue; C, dark green and pink. All hydrogen atoms are omitted for clarity.

Crystal structure of 4

Compound **4** crystallizes in the monoclinic space group *C*2/*c*, and its asymmetric unit contains an independent $[Cd(5\text{-}NO_2\text{-}1,3\text{-}BDC)(bpmb)(H_2O)]$ molecule. Similar to **2** and **3**, Cd1 atom in **4** is also six-coordinated by two N atoms (N1 and N2B) from two different bpmb ligands, two O atoms (O7A and O8A) of one chelating carboxylate groups from 5-NO_2-1,3-BDC ligand, one O atom (O4) of one bridging carboxylate groups from second 5-NO_2-1,3-BDC ligand and one O atom (O1W) from water molecule (Fig. 3a). A weak interaction [2.717 (3) Å] exists between atoms Cd1 and O3 (Fig. 3a). The mean Cd–N bond length (2.307(3) Å) is little shorter in comparison with a related structure of $\{[Cd_2(L)_2(BIPH)_2(H_2O)_2]\cdot H_2O\}_n$ (2.314 (5) Å, L = bis(4-imidazol-1-ylphenyl)diazene, H_2BIPH = biphenyl-4,4′-dicarboxylic acid), whereas the mean Cd–O bond length (2.402(3) Å) is longer than that of in $\{[Cd_2(L)_2(BIPH)_2(H_2O)_2]\cdot H_2O\}_n$ (2.338 (5) Å).[19] Different from **2** and **3**, each Cd^{II} ion in **4** is interlinked by bridging 5-NO_2-1,3-BDC ligands to form a 1D $[Cd(5\text{-}NO_2\text{-}1,3\text{-}BDC)]_n$ single chain extending along different direction. Each chain is connected to its adjacent ones *via* bpmb ligands to form a 2D sandwich-like layer extending along the *ab* plane (Fig. 3b). From the viewpoint of topological, such a net is described by a 4-connected net (Fig. 3c) with the Schläfli symbol of (6^6), in which Cd^{II} atoms act as four-connected nodes, 5-NO_2-1,3-BDC and bpmb ligands as linkers. Further investigation of the crystal packing of compound **4** suggests that each sandwich-like layer structure is interconnected with adjacent ones through three intermolecular H-bonding interactions among the O atoms of the carboxylate as well as nitro groups of 5-NO_2-1,3-BDC ligand and the H atoms of the water molecules as well as pyridine rings [O1W–H1WA$\cdots$O8, $(-x+1/2, -y+1/2, -z+1)$, 2.711(3) Å; O1W–H1WB$\cdots$O4, $(-x+1, -y+1, -z+1)$, 2.799(4) Å; C5–H5$\cdots$O5, $(-x+1/2, -y+1/2, -z+1)$, 3.269(5) Å], which leads to the formation of a 3D supramolecular network (Fig. S4).



(a)



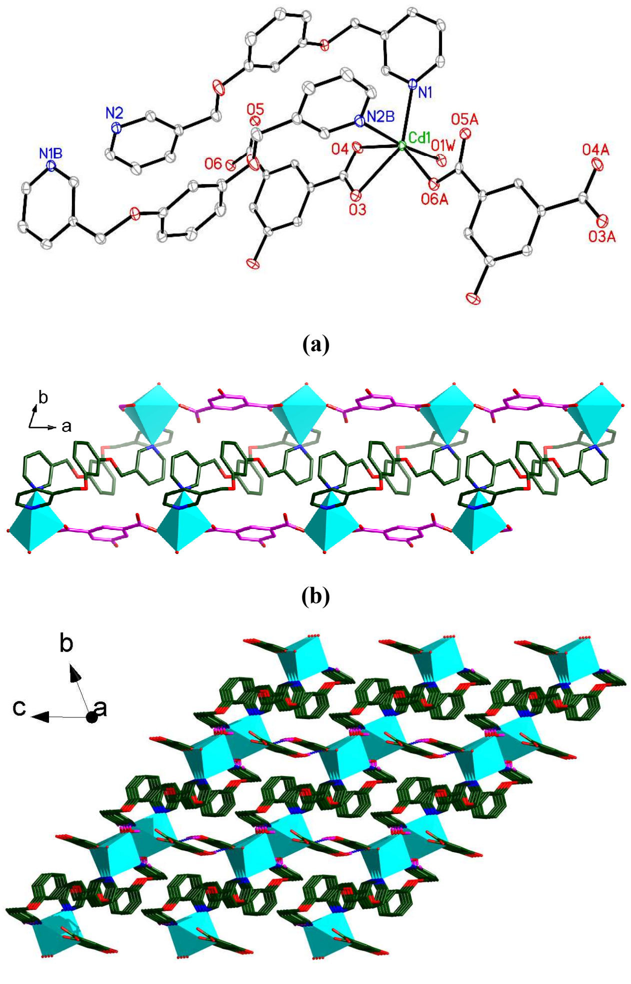
(b)

(c)

Fig. 3 (a) View of the coordination environments of Cd center in **4** with labeling schemes. Symmetry codes: (A) $1/2 + x$, $1/2 + y$, z; (B) $1 - x$, $1 + y$, $1/2 - z$. (b) View of the differently oriented $[Cd(5\text{-}NO_2\text{-}1,3\text{-}BDC)]_n$ chains joined by bpmb ligands giving rise to the 2D sandwich-like structure along *ab* plane. (c) Schematic view of the 4-connected (6^6) net of **4**. All H atoms are omitted for clarity.

Crystal structure of 5

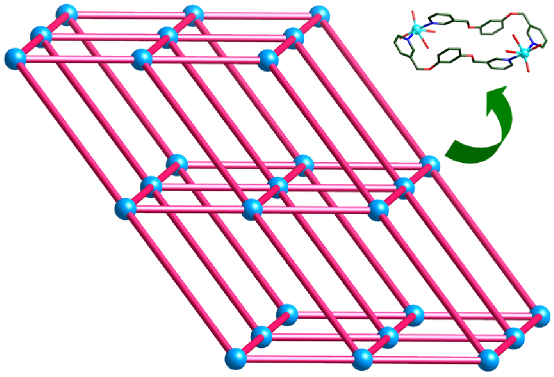
Compound **5** crystallizes in the triclinic space group $P\bar{1}$, and its asymmetric unit contains one [Cd(5-OH-1,3-BDC)(bpmb)(H_2O)] unit. Similar to **2**–**4**, Cd1 atom in **5** is also octahedrally coordinated by two N atoms (N1 and N2B) from two different bpmb ligands, two O atoms (O3 and O4) of one chelating carboxylate group from 5-OH-1,3-BDC ligand, one O atom (O6A) of one bridging carboxylate group from second 5-OH-1,3-BDC ligand and one O atom (O1W) from water molecule (Fig. 4a). The mean Cd–N bond length (2.355(3) Å) is longer than that of in **4** (2.307 (3) Å), whereas the mean Cd–O bond length (2.346(2) Å) is shorter than that of in **4** (2.402 (3) Å). Similar that of in **1**, Cd1 atom and its own symmetry-related atoms are linked by four N atoms from two bpmb ligands to afford a 28-membered dimer ring $[Cd_2(bpmb)_2]$, which can be used as secondary building units. Interestingly, all building units $[Cd_2(bpmb)_2]$ are connected by 5-OH-1,3-BDC ligands, forming a ladder-shaped chain extending along the *a* axis (Fig. 4b). The Cd···Cd separations across the bpmb and 5-OH-1,3-BDC ligands are 12.229 and 10.237 Å, respectively. Further investigation of the crystal packing of compound **1** suggests that there are three kinds of O–H···O hydrogen bonding between adjust the 1D coordination chains, which origin from the oxygen atoms of the coordinated H_2O molecule, uncoordinated hydroxy groups as well as carboxylate group of 5-OH-1,3-BDC ligand [O1W–H1WA···O5, $(-x+1, -y+1, -z+1)$, 2.680(3) Å; O1W–H1WB···O1, $(-x+1, -y+1, -z+1)$, 2.870(3) Å; O7–H7···O3, $(-x+1, -y+1, -z)$ 2.744(3) Å], thereby producing to a 3D supramolecular structure (Fig. 4c). A better insight into the nature of **5** can be achieved by the application of topological approach, that is, reducing multidimensional structures to simple node-and-linker nets. From a viewpoint of network topology, if these further hydrogen bonding interactions are taken into account, 28-membered dimer ring $[Cd_2(bpmb)_2]$ can be cnsidered as 6-connected nodes, which connect two ones through coordination bonds and four ones through hydrogen bonding, and thus, the overall 3D network of **5** is 6-connected *pcu* net (Fig. 4d).



(a)

(b)

(c)



(d)

Fig. 4 (a) View of the coordination environment of Cd center in **5** with labeling schemes. Symmetry codes: (A) $-1+x, y, z$; (B) $1-x, 2-y, -z$. (b) View of a 1D ladder-shaped chain extending along *a* axis. (c) View of the 3D supramolecular structure along *a* axis. The dashed blue lines represent H–bonding interactions. (d) Schematic view of the 6-connected *pcu* net when [$Cd_2(bpmb)_2$] ring is considered as node. Atom color codes: Cd, cyan polyhedrons; O, red; N, blue; C, dark green and pink. All H atoms except those related to H-bonding interactions are omitted for clarity.

The structures of **1**–**5** are different in the following aspects. Firstly, Cd atoms in **1** are seven-coordinated and adopt the distorted pentagonal bipyramidal coordination geometry while these in **2**–**5** are six-coordinated and show the distorted octahedral coordination geometry. Secondly, for the V-shaped bipyridyl ligands in compounds **1** and **5**, the bpmb exhibit the *cis-trans* conformation (Scheme 1d) with a 108.25° of "V" in **1** and *trans-trans* conformation (Scheme 1e) with a 134.26° of "V" in **5**, respectively. It is noted that the bpmb ligands in **1** and **5** link two Cd atoms both affording the [$Cd_2(bpmb)_2$] units with different architectures. In compounds **2**–**4**, the bpmb ligands display two different *cis-cis* conformations (Schemes 1a and 1c) with 98.53° (**2**), 99.06° (**3**) as well as 138.21° (**4**) of "V", which are bridged by Cd atoms to produce the 1D [$Cd(bpmb)]_n$ chains. Thirdly, the carboxylate groups of the BDC derivatives display μ_1-η^1:η^1 coordination mode in **1**, μ_1-η^1:η^1 and μ_2-η^1:η^1 in **2**–**3**, μ_1-η^1:η^1 and μ_1-η^1:η^0 in **4**–**5**. The BDC ligands in **1**–**4** are employed as linkers to connected Cd atoms all forming 1D chains with different motifs, which may be due to the different types of BDC ligands. Fourthly, in **4**, the NO_2 groups at the 5-position of 1,3-BDC ligands act as hydrogen-bonding acceptors expand the 2D sandwich-like layers into the 3D hydrogen-bonded framework. In **5**, the OH groups work as hydrogen-bonding donors and these are linked by carboxylate groups, which form the 1D chains into the 3D supramolecular structure. While in **2**–**3**, as the H or Me group act neither as a hydrogen-bonding donor nor as a hydrogen-bonding acceptor, it could not induce any hydrogen-bonding interactions. Therefore, the substituted groups in 1,3-BDC play important roles in determining the structures of **2**–**5**. From the above-mentioned comparison, it is noted that the species of BDC derivatives in this study greatly affected the formation of different coordination geometries of Cd(II) atoms, the conformations of the bpmb ligands and the whole structures of these compounds.

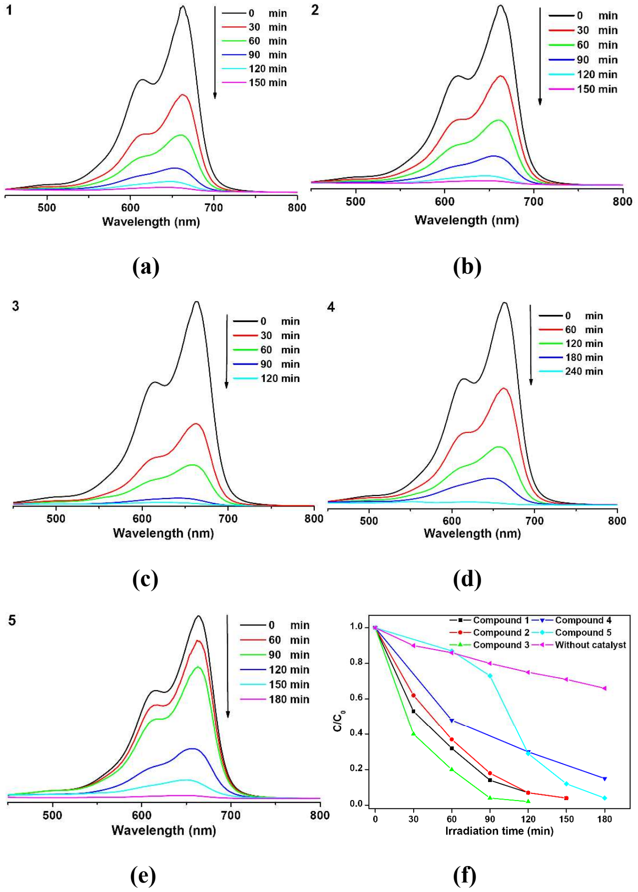
Thermal and photoluminescent properties

Thermogravimetric (TGA) experiments were carried out to study the thermal stability of **1**–**5**. As shown in Fig. S5, the TGA curves of **1**, **4** and **5** show similar profiles. In **1**, **4** and **5**, the first weight losses of 3.22%, 3.45% and 3.03% (calculated 3.07% for **1**, 2.85% for **4**, 2.99% for **5**) from 35 °C to 200 °C correspond to the loss of the coordinated water solvent molecules. The second large weight losses suggested the loss of the bpmb and BDC ligands ligand in **1**, **4** and **5**. For **2** and **3**, because there are no solvent molecules in the frameworks, there is a plateau region ranging from 35 °C to 275 °C in **2** and 298 °C in **3**, followed by a sudden decrease in the weight, suggesting the onset of the decomposition temperature of the compounds. The final residue of 24.21%, 24.59%, 21.87%, 21.92% and 22.90% for **1**–**5**, respectively, is in agreement with the percentage of CdO (calculated 21.88%, 22.40%, 22.03%, 20.32% and 21.30%), indicating that this is the final product.[7c]

Meanwhile, we also investigated the photoluminescence properties of compounds **1**–**5** in solid state at room temperature because of the excellent luminescent properties of d^{10} metal coordination compounds (Fig. S6). The weak fluorescence emission band at λ_{max} = 449 nm under 375 nm excitation of the bpmb ligand can be ascribed to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions.[20] Upon excitation at 332 nm leads to intense blue fluorescent emission bands at 433 nm for **1** and 444 nm for **2**, while weaker fluorescence emissions occur at 466 nm for **3**, 435 nm for **4**, as well as 424 nm for **5**, respectively. As these emission peaks are similar to that of the bpmb ligand, the emission of **1**–**5** may be assigned to the intraligand charge transfer transitions.[21] A slightly different emission peak arises from the different coordination environments of Cd(II) centers.[22]

Photocatalytic Activity

As to know, organic dyes such as MO, MB and RhB are extensively used in the textile industry and resistant to biodegradation. Decomposition of such dye molecules into some simple molecules can reduce the environment pollution caused by them. Recently, much effort has been devoted to developing new photocatalytic materials based on metal-organic frameworks.[23] Particularly, Cd-based CPs exhibited efficient photocatalytic activities to the organic dyes.[23c–d,24] Hence, in this work, the photocatalytic activities of the compounds **1**–**5** were evaluated by the degradation of MB under irradiation at room temperature as the test pollutant. To evaluate the band gaps, the UV–vis absorption spectrum of **1**–**5** is measured at room temperature (Fig. S7). The results give E_g (band-gap energy) values of 2.57, 2.69, 2.72, 3.03 and 3.11 eV for **1**–**5**, respectively (Fig. S8). As illustrated in Fig. 5a-5e, the absorption peaks of MB decreased patently following the reaction time in the presence of **1**–**5**. The degradation efficiencies are defined as C/C_0, where C and C_0 represent the remnant and initial concentration of MB, respectively (Fig. 5f). By contrast, the simple photolysis experiment was also completed under the same conditions without any catalyst. The organic dye concentrations were estimated by the absorbance at 665 nm (MB). Compounds **2**–**3** feature similar photocatalytic effects, and the degradation ratio of MB reached 96.0% exposed to UV light for 150 min. Interestingly, compound **1** display the 98.0% degradation ratio of MB for 120 min. Compared to compounds **1**–**3**, compound **4**–**5** shows a slightly slower photocatalytic effect at the initial reaction, but they also completely degrade MB after 240 min (**4**) and 180 min (**5**) (Fig. 5c-5e). The catalyst was filtered and obtained a colorless solution, which was analyzed by mass spectra. No corresponding species of MB was observed, and thus we assumed that the dyes might be degradation of CO_2 and H_2O.[24a,25] And the photocatalytic efficiencies of these compounds are comparable to those of other Cd-based CP materials. Such as, using the known CPs $\{[Cd(tpcb)_{0.75}(OH)(H_2O)_2](NO_3)\}_n$ (tpcb = tetrakis(4-pyridyl)cyclobutane),[24a] $\{[Cd(btbb)_{0.5}(btec)_{0.5}(H_2O)]\cdot 2H_2O\}_n$ (btbb = 1,4-bis(2-(4-thiazolyl)benzimidazole-1-ylmethyl)benzene, H_4btec = 1,2,4,5-benzenetetracarboxylate)[23d] and $\{[Cd_3(bcb)_2(H_2O)_5]\cdot H_2O\}_n$ (H_3bcb = 3,4-bi(4-carboxyphenyl)-benzoic acid)[23c] as catalysts, *ca.* 82.0%, 92.7% and 88.7% of MB was degraded in 120, 140 and 180 min, respectively. In addition, the PXRD patterns of each powder for **1**–**5** were basically identical to those of the parent compounds, indicating that these compounds are stable during photocatalysis.



(a) (b)

(c) (d)

(e) (f)

Fig. 5 (a-e) Absorption spectra of the MB solution (4 × 10^{-5} mol L^{-1}, 50 mL) during the decomposition reaction under UV light irradiation with the presence of compounds **1**–**5** (20 mg). (f) Concentration changes of MB at different time intervals under Xe lamp irradiation with **1**–**5** as catalysts and without catalyst.

Conclusions

In summary, we demonstrated that treatment of $Cd(OAc)_2\cdot 2H_2O$ with bpmb and 1,4-H_2BDC as well as four 1,3-H_2BDC derivatives with different sized substituted R groups (H, Me, NO_2, OH) at the 5-position formed five different CPs **1**–**5**. These compounds exhibit various structural motifs. The photocatalytic activities of **1**–**5** were evaluated by the decomposition of organic dyes in aqueous solutions under UV irradiation. These compounds show good catalytic performance for the degradation of MB, which were excellent candidates for decomposing other organic dyes.

Table 2 Selected bond lengths (Å) for **1**–**5**[a]

Compound **1**			
Cd(1)–N(1A)	2.3008(19)	Cd(1)–O(1W)	2.3398(16)
Cd(1)–N(2)	2.363(2)	Cd(1)–O(6)	2.3669(17)
Cd(1)–O(4)	2.4294(16)	Cd(1)–O(5)	2.4362(17)
Cd(1)–O(3)	2.4672(16)		
Compound **2**			
Cd(1)–O(3A)	2.239(2)	Cd(1)–N(2B)	2.310(2)
Cd(1)–O(4C)	2.342(2)	Cd(1)–O(1)	2.375(2)
Cd(1)–N(1)	2.380(3)	Cd(1)–O(2)	2.412(2)
Compound **3**			
Cd(1)–O(9A)	2.242(4)	Cd(1)–N(1)	2.316(5)
Cd(1)–O(3)	2.345(4)	Cd(1)–O(7)	2.361(4)
Cd(1)–N(4B)	2.369(5)	Cd(1)–O(8)	2.403(4)
Cd(2)–O(4C)	2.230(4)	Cd(2)–O(10)	2.320(4)
Cd(2)–N(3)	2.328(5)	Cd(2)–O(6)	2.351(4)
Cd(2)–N(2D)	2.387(5)	Cd(2)–O(5)	2.411(4)
Compound **4**			
Cd(1)–O(4)	2.230(3)	Cd(1)–N(1)	2.292(3)
Cd(1)–N(2A)	2.322(3)	Cd(1)–O(7B)	2.358(2)
Cd(1)–O(1W)	2.403(2)	Cd(1)–O(8B)	2.616(3)
Compound **5**			
Cd(1)–O(6A)	2.178(2)	Cd(1)–O(4)	2.315(2)
Cd(1)–N(1)	2.327(3)	Cd(1)–O(1W)	2.361(3)
Cd(1)–N(2B)	2.383(3)	Cd(1)–O(3)	2.530(2)

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

Acknowledgments

This work was supported by the National Natural Science Foundation of China (U1304210, 21401006 and 21371089) and Natural Science Projects of Department of Education of Henan Province (13A150013).

References

1 (*a*) X. Zhao, B. Xiao, A. Fletcher, K. M. Thomas, D. Bradshaw and M. J. Rosseinsky, *Science*, 2004, **306**, 1012; (*b*) M. P. Suh, H. J. Park, T. K. Prasad and D. W. Lim, *Chem. Rev.*, 2012, **112**, 782; (*c*) Y. Yan, S. H. Yang, A. J. Blake and M. Schröder, *Acc. Chem. Res.*, 2014, **47**, 296; (*d*) L. J. Murray, M. Dincá and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (*e*) H. Sato, W. Kosaka, R. Matsuda, A. Hori, Y. Hijikata, R. V. Belosludov, S. Sakaki, M. Takata and S. Kitagawa, *Science*, 2014, **343**, 167; (*f*) D. J. Tranchemontagne, L. J. Mendoza-Cortés, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257; (*g*) R. E. Morris and P. S. Wheatley, *Angew. Chem. Int. Ed.*, 2008, **47**, 4966; (*h*) W. Zhang and R. G. Xiong, *Chem. Rev.*, 2012, **112**, 1163; (*i*) G. P. Yang, L. Hou, X. J. Luan, B. Wu and Y. Y. Wang, *Chem. Soc. Rev.*, 2012, **41**, 6992; (*j*) S. L. Huang, Y. J. Lin, T. S. Andy Hor and G. X. Jin, *J. Am. Chem. Soc.*, 2013, **135**, 8125.

2 (*a*) L. Ma, J. M. Falkowski, C. Abney and W. Lin, *Nat. Chem.*, 2010, **2**, 838; (*b*) O. K. Farha, A. M. Shultz, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2011, **133**, 5652; (*c*) P. Y. Wu, C. He, J. Wang, X. J. Peng, X. Z. Li, Y. L. An and C. Y. Duan, *J. Am. Chem. Soc.*, 2012, **134**, 14991; (*d*) Z. Q. Xu, Q. Wang, H. J. Li, W. Meng, Y. Han, H. W. Hou and Y. T. Fan, *Chem. Commun.*, 2012, **48**, 5736; (*e*) Y. Zhao, D. S. Deng, L. F. Ma, B. M. Ji and L. Y. Wang, *Chem. Commun.*, 2013, **49**, 10299; (*f*) J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; (*g*) H. X. Li, W. Zhao, H. Y. Li, Z. L. Xu, W. X. Wang and J. P. Lang, *Chem. Commun.*, 2013, **49**, 4259; (*h*) Y. Y. Zhang, Y. J. Lin and G. X. Jin, *Chem. Commun.*, 2014, **50**, 2327.

3 (*a*) M. Maes, F. Vermoortele, L. Alaerts, S. Couck, C. E. A. Kirschhock, J. F. M. Denayer and D. E. De Vos, *J. Am. Chem. Soc.*, 2010, **132**, 15277; (*b*) Z. H. Wei, C. Y. Ni, H. X. Li, Z. G. Ren, Z. R. Sun and J. P. Lang, *Chem. Commun.*, 2013, **49**, 4836; (*c*) P. Horcajada, C. Serre, G. Maurin, N. A. Ramsahye, F. Balas, M. Vallet-Regí, M. Sebban, F. Taulelle and G. Férey, *J. Am. Chem. Soc.*, 2008, **130**, 6774; (*d*) M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330; (*e*) Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.*, 2012, **112**, 1126; (*f*) J. Heine and K. Müller-Buschbaum, *Chem. Soc. Rev.*, 2013, **49**, 9232; (*g*) Y. Kang, F. Wang, J. Zhang and X. H. Bu, *J. Am. Chem. Soc.*, 2012, **134**, 17881; (*h*) Z. M. Zhang, L. Y. Pan, W. Q. Lin, J. D. Leng, F. S. Guo, Y. C. Chen, J. L. Liu and M. L. Tong, *Chem. Commun.*, 2013, **49**, 8081; (*i*) H. Li, Y. F. Han, Y. J. Lin, Z. W. Guo and G. X. Jin, *J. Am. Chem. Soc.*, 2014, **136**, 2982.

4 (*a*) L. Brammer, *Chem. Soc. Rev.*, 2004, **33**, 476; (*b*) M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 675; (*c*) Y. F. Han, W. G. Jia, W. B. Yu and G. X. Jin, *Chem. Soc. Rev.*, 2009, **38**, 3419; (*d*) Y. F. Han, W. G. Jia, Y. J. Lin, and Guo-Xin Jin, *Angew. Chem. Int. Ed.*, 2009, **48**, 6243.

5 (*a*) S. Sengupta, S. Ganguly, A. Goswami, P. K. Sukul and R. Mondal, *CrystEngComm*, 2013, **15**, 8353; (*b*) S. Sen, S. Neogi, A. Aijaz, Q. Xu and P. K. Bharadwaj, *Dalton Trans.*, 2014, **43**, 6100; (*c*) Y. F. Hsu, H. L. Hu, C. J. Wu, C. W. Yeh, D. M. Proserpioc and J. D. Chen, *CrystEngComm*, 2009, **11**, 168; (*d*) G. J. Xu, Y .H. Zhao, K. Z. Shao, Y. Q. Lan, X. L. Wang, Z. M. Su and L. K. Yan, *CrystEngComm*, 2009, **11**, 1842; (*e*) M. L. Han, Y. P. Duan, D. S. Li, G. W. Xu, Y. P. Wu and J. Zhao, *Dalton Trans.*, 2014, **43**, 17519; (*f*) S. L. Huang, Y. J. Lin, Z. H. Li and G. X. Jin, *Angew. Chem. Int. Ed.*, 2014, **53**, 11218.

6 (*a*) K. Biradha, M. Sarkar and L. Rajput, *Chem. Commun.*, 2006, 4169; (*b*) S. A. Barnett and N. R. Champness, *Coord. Chem. Rev.*, 2003, **246**, 145.

7 (*a*) L. Cui, G. P. Yang, W. P. Wu, H. H. Miao, Q. Z. Shi and Y. Y. Wang, *Dalton Trans.*, 2014, **43**, 5823; (*b*) N. Singh and G. Anantharaman, *CrystEngComm*, 2014, **16**, 6203; (*c*) L. L. Liu, C. X. Yu, J. Sun, P. P. Meng, F. J. Ma, J. M. Du, L. F. Ma, *Dalton Trans.*, 2014, **43**, 2915; (*d*) F. L. Hu, W. Wu, P. Liang, Y. Q. Gu, L. G. Zhu, H. Wei and J. P. Lang, *Cryst. Growth Des.*, 2013, **13**, 5050; (*e*) L. Liu, L. Liu and J. J. Wang, *Inorg. Chim. Acta*, 2013, **397**, 75; (*f*) K. K. Bisht and E. Suresh, *Cryst. Growth Des.*, 2013, **13**, 664.

8 (*a*) Y. Liu, P. F. Yan, Y. H. Yu, G. F. Hou, J. S. Gao and J. Y. Lu, *Cryst. Growth Des.*, 2010, **10**, 1559; (*b*) Y. Liu, Y. H. Yu, Y. F. Liu, G. F. Hou, X. D. Wang, B. Wen and J. S. Gao, *Z. Anorg. Allg. Chem.*, 2013, **639**, 193.

9 (*a*) M. Oh, C. L. Stern and Mirkin, C. A. *Inorg. Chem.*, 2005, **44**, 2647; (*b*) C. M. Hartshorn and P. J. Steel, *J. Chem. Soc. Dalton Trans.*, 1998, 3927; (*c*) P. J. Steel and C. M. Fitchett, *Aust. J. Chem.* 2013, **66**, 443.

10 (*a*) H. W. Hou, Y. T. Fan, L. P. Zhang, C. X. Du and Y. Zhu, *Inorg. Chem. Commun.*, 2001, **4**, 168; (*b*) X. Li, W. J. Zhao, Y. Zhang, Y. Zhang, J. T. Tan, Y. L. Lu, X. Feng and X. W. Yang, *Z. Anorg. Allg. Chem.*, 2012, **638**, 785.

11 L. J. Li, C. Qin, X. L.Wang, S. Wang, L. Zhao, G. S. Yang, H. N. Wang, G. Yuan, K. Z. Shao and Z. M. Su, *CrystEngComm*, 2012, **14**, 124.

12 (*a*) C. L. Zhang, M. D. Zhang, L. Qin and H. G. Zheng, *Cryst. Growth Des.*, 2014, **14**, 491; (*b*) L. L. Han, X. Y. Zhang, J. S. Chen, Z. H. Li, D. F. Sun, X. P. Wang and D. Sun, *Cryst. Growth Des.*, 2014, **14**, 2230; (*c*) Y. F. Han, X. Y. Li, L. Q. Li, C. L. Ma, Z. Shen, Y. Song and X. Z. You, *Inorg. Chem.*, 2010, **49**, 10781; (*d*) L. N. Jin, Q. Liu and W. Y. Sun, *CrystEngComm*, 2014, **16**, 3816; (*e*) L. L. Liu, J. M. Du, Y. Y. Liu, F. Zhao and F. J. Ma, *J. Coord. Chem.*, 2014, **67**, 136; (*f*) M. L. Han, Y. P. Duan, D. S. Li, H. B. Wang, J. Zhao and Y. Y. Wang, *Dalton Trans.*, 2014, **43**, 15450.

13 (*a*) T. Liu, S. N. Wang, J. Lu, J. M. Dou, M. J. Niu, D. H. Lia and J. F. Bai, *CrystEngComm*, 2013, **15**, 5467; (*b*) Y. P. Li, Y. Chai, G. P. Yang, H. H. Miao, L. Cui, Y. Y. Wang and Q. Z. Shi, *Dalton Trans.*, 2014, **43**, 10947; (*c*) X. H. Chang, L. F. Ma, H. Guo and L. Y. Wang, *Cryst. Growth Des.*, 2012, **12**, 3638; (*d*) X. L. Sun, Z. J. Wang, S. Q. Zang, W. C. Song and C. X. Du, *Cryst. Growth Des.*, 2012, **12**, 4431; (*e*) Y. Yang, P. Du, Y. Y. Liu and J. F. Ma, *Cryst. Growth Des.*, 2013, **13**, 4781; (*f*) L. L. Liu, C. X. Yu, Y. Zhou, J. Sun, P. P. Meng, D. Liu and R. J. Sa, *Inorg. Chem. Commun.*, 2014, **40**, 194.

14 (*a*) J. X. Yang, Y. Y. Qin, J. K. Cheng and Y. G. Yao, *Cryst. Growth Des.*, 2014, **14**, 1047; (*b*) B. Xu, Z. J. Lin, L. W. Han and R. Cao, *CrystEngComm*, 2011, **13**, 440; (*c*) C. Li, D. S. Li, J. Zhao, Y. Q. Mou, K. Zou, S. Z. Xiao and M. Du, *CrystEngComm*, 2011, **13**, 6601; (*d*) F. J. Liu, D. Sun, H. J. Hao, R. B. Huang and L. S. Zheng, *CrystEngComm.*, 2012, **14**, 379; (*e*) D. Liu, H. X. Li, L. L. Liu, H. M. Wang, N. Y. Li, Z. G. Ren and J. P. Lang, *CrystEngComm.*, 2010, **12**, 3708; (*f*) D. S. Li, J. Zhao, Y. P. Wu, B. Liu, L. Bai, K. Zou and M. Du, *Inorg. Chem.*, 2013, **52**, 8091.

15 J. Xiao, C. X. Chen, Q. K. Liu, J. P. Ma and Y. B. Dong, *Cryst. Growth Des.*, 2011, **11**, 5696.

16 G. M. Sheldrick, *SHELXS-97 and SHELXL-97, Program for X-ray Crystal Structure Solution;* University of Göettingen: Germany, 1997.

17 Y. A. Li, S. K. Ren, Q. K. Liu, J. P. Ma, X. Y. Chen, H. M. Zhu and Y. B. Dong, *Inorg. Chem.*, 2012, **51**, 9629.

18 A. F. Wells, *Three-Dimensional Nets and Polyhedra*; Wiley-Interscience: New York, 1977.

19 R. Singh and P. K. Bharadwaj, *Cryst. Growth Des.*, 2013, **13**, 3722.

20 H. Li, J. Zhou, W. Shi, X. Zhang, Z. Zhang, M. Zhang and P. Cheng, *CrystEngComm*, 2014, **16**, 834.

21 J. Pan, F. L. Jiang, D. Q. Yuan, X. C. Shan, M. Y. Wu, K. Zhou, Y. L. Gai, X. J. Li and M. C. Hong, *CrystEngComm*, 2013, **15**, 5673.

22 J. Tao, M. L. Tong, J. X. Shi, X. M. Chen and S. W. Ng, *Chem. Commun.*, 2000, 2043.

23 (*a*) H. R. Fu, Y. Kang and J. Zhang, *Inorg.Chem.*, 2014, **53**, 4209; (*b*) Y. L. Hou, R. W. Y. Sun, X. P. Zhou, J. H. Wang and Dan Li, *Chem. Commun.*, 2014, **50**, 2295; (*c*) L. Liu, J. Ding, C. Huang, M. Li, H. W. Hou, and Y. T. Fan, *Cryst. Growth Des.*, 2014, **14**, 3035; (*d*) L. Liu, J. Ding, M. Li, X. F. Lv, J. Wu, H. W. Hou and Y. T. Fan, *Dalton Trans.*, 2014, **43**, 12790; (*e*) T. Wen, D. X. Zhang, J. Liu, R. Lin and J. Zhang, *Chem. Commun.*, 2013, **49**, 5660; (*f*) L. L. Wen, F. Wang, J. Feng, K. L. Lv, C. G. Wang and D. F. Li, *Cryst. Growth Des.*, 2009, **9**, 3581; (*g*) Y. Q. Chen, G. R. Li, Y. K. Qu, Y. H. Zhang, K. H. He, Q. Gao and X. H. Bu, *Cryst. Growth Des.*, 2013, **13**, 901; (*h*) T. Wen, D. X. Zhang and J. Zhang, *Inorg. Chem.*, 2013, **52**, 12; (*i*) H. Yang, X. W. He, F. Wang and J. Zhang, *J.*

Mater. Chem., 2012, **22**, 21849; (*j*) F. Wang, Z. S. Liu, H. Yang, Y. X. Tan and J. Zhang, *Angew. Chem. Int. Ed.,* 2011, **50**, 450.

24 (*a*) D. X. Li, C. Y. Ni, M. M. Chen, M. Dai, W. H. Zhang, W. Y. Yan, H. X. Qi, Z. G. Ren and J. P. Lang, *CrystEngComm*, 2014, **16**, 2158; (*b*) W. Meng, Z. Q. Xu, J. Ding, D. Q. Wu, X. Han, H. W. Hou and Y. T. Fan, *Cryst. Growth Des.*, 2014, **14**, 730; (*c*) L. L. Wen, J. B. Zhao, K. L. Lv, Y. H. Wu, K. J. Deng, X. K. Leng and D. F. Li, *Cryst. Growth Des.*, 2012, **12**, 1603.

25 A. G. Ostrofft and R. T. Sanderson, *J. Inorg. Nucl. Chem.*, 1959, **9**, 45.