d^{10}-Metal coordination polymers based on analogue di(pyridyl)imidazole derivatives and 4,4′-oxydibenzoic acid: influence of flexible and angular characters of neutral ligands on structural diversity†

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A series of mixed-ligand coordination complexes, namely $[Zn(L^1)(oba)]$ (**1**), $[Cd(L^1)(oba)]$ (**2**), $[Zn_2(L^2)(oba)_2]\cdot 8H_2O$ (**3**), $[Cd_2(L^2)(oba)_2]\cdot 2H_2O$ (**4**), $[Zn_3(L^3)(oba)_3]$ (**5**), $[Cd_2(L^3)(oba)_2]\cdot(L^3)$ (**6**), $[Cd(L^4)(oba)]\cdot H_2O$ (**7**) and $[Cd(L^5)(oba)]\cdot 3H_2O$ (**8**), where L^1 = 2-(2-pyridyl)imidazole, L^2 = 1,4-bis[2-(2-pyridyl)imidazol-1-yl]butane, L^3 = 1,4-bis[2-(2-pyridyl)imidazol-1-ylmethyl]benzene, L^4 = 1,3-bis[2-(2-pyridyl)imidazol-1-ylmethyl]benzene, L^5 = 1,2-bis[2-(2-pyridyl)imidazol-1-ylmethyl]benzene and H_2oba = 4,4′-oxydibenzoic acid, have been synthesized under hydrothermal conditions. Their structures have been determined by single crystal X-ray diffraction analyses and further characterized by elemental analyses, IR spectra, and thermogravimetric (TG) analyses. In compounds **1** and **2**, oba^{2-}, L^1 ligand and Zn^{II} or Cd^{II} ions assemble to form the parallel chains or parallel sheets which are linked by the weak hydrogen bonding and $\pi\cdots\pi$ stacking interactions to give the 2D supramolecular sheet or 3D supramolecular net, respectively. For **3**, L^2 ligands connect [Zn(oba)] chains to generate a unusual (10,3)-b topological structure which is the first example for eight-fold interpenetrating framework based on the (10,3)-b net. In **4**, L^2 ligands link [Cd(oba)] double-chains to give a 2D sheet which is assembled by $\pi\cdots\pi$ stacking interactions to obtain a 3D supramolecular net. In **5**, L^3 ligands link Zn^{II} ions from α-Po net formed by Zn^{II} ions and oba^{2-} anions to show a novel 3D 8-connected self-penetrating framework with the unreported $(4^{16}\cdot 6^{11}\cdot 8)$ topological structure. In **6**, the double-chains constructed by Cd^{II} and oba^{2-} anions are linked by one kind of L^3 ligand to form a layer-like structure which is assembled by $\pi\cdots\pi$ stacking interactions to show a 3D supramolecular structure. In **7**, oba^{2-} anions coordinate to Cd^{II} cations to form chains which are connected by L^4 to form a four-fold interpenetrating diamond network. In **8**, the weak hydrogen bonding and $\pi\cdots\pi$ stacking interactions connect the $[Cd(L^5)(oba)]$ chains to give a 2D supramolecular sheet. By careful inspections of the structures of **1–8**, we believe that the different flexible and angular neutral ligands, coordination geometries of metal centers and weak interactions (hydrogen bonds and $\pi\cdots\pi$ stacking interactions) are crucial factors for the formation of the different structures. The photoluminescent properties of **1–8** have been studied in the solid state at room temperature.

Introduction

Metal–organic frameworks (MOFs) are rapidly increasing not only because of their tremendous potential applications in functional materials, nanotechnology and biological recognition,[1] but also because of their intriguing variety of architectures and topologies.[2] One of the obvious challenges for construction of novel coordination polymers is the rational and controllable preparation of metal–organic frameworks, which is greatly affected by the ligand nature, anions, template, metal ions and other factors.[3] Among them, multi-carboxylate ligands act as multifunctional organic anionic ligands not only due to their various coordination modes to metal ions, resulting from completely or partially deprotonated sites allowing for the large diversity of topologies,[4] but also because of their abilities to act as H-bond acceptors and donors to assemble various supramolecular structures.[5]

Among aromatic multi-carboxylates, V-shaped aromatic dicarboxylate H_2oba (4,4′-oxydibenzoic acid)[6] is introduced because it has irregular orientations when it coordinates to metals, which may produce various structural topologies, large pores or beautiful helical structures, owing to its bidentate carboxylate arms and its steric bulk. The use of H_2oba as a bridging ligand in constructing high-dimensional structures is relatively mature. Therefore, the resulting topological structures can be predicted and designed.

In addition, a careful selection of the properties of the second ligands, such as shape, functionality, flexibility, angle and symmetry, is a key step for the rational design of structures and specific chemical and physical properties.[7] In previous studies,[8] we focused our attention on the construction of metal

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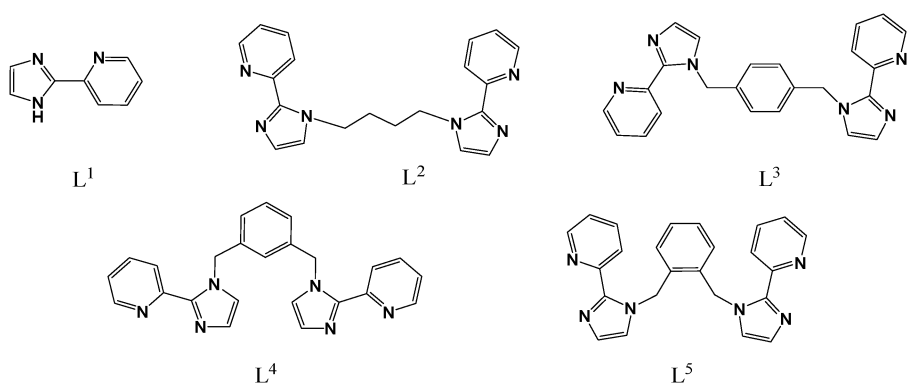


Chart 1 Structures of the ligands L^1–L^5.

organic frameworks with metal salts and flexible bis(imidazol) ligands, for example, 1,4-bis(imidazol-1-yl)butane, 1,2-bis(imidazol-1-ylmethyl)benzene, 1,3-bis(imidazol-1-ylmethyl)benzene and so on. In comparison with the above-mentioned ligands, 2-(2-pyridyl)imidazole (L^1) may tune the frameworks of the coordination polymers through non-covalent interactions such as $\pi\cdots\pi$ stacking and hydrogen bonding interactions. In addition, four different flexible and angular *exo*-bis(bidentate) ligands (L^2–L^5; Chart 1) with various conformations and coordination modes are engaged in this system.

Well-known d^{10} metal ions, such as Zn^{II} and Cd^{II}, have attracted considerable attention not only because of their appealing structures but also because of their good luminescent properties.[9] Here, we will describe a series of luminescent Zn(II) and Cd(II) coordination complexes with diverse network structures. Eight mixed-ligand coordination complexes, namely [Zn(L^1)(oba)] (**1**), [Cd(L^1)(oba)] (**2**), [Zn$_2$(L^2)(oba)$_2$]·8H$_2$O (**3**), [Cd$_2$(L^2)(oba)$_2$]·2H$_2$O (**4**), [Zn$_3$(L^3)(oba)$_3$] (**5**), [Cd$_2$(L^3)(oba)$_2$]·(L^3) (**6**), [Cd(L^4)(oba)]·H$_2$O (**7**) and [Cd(L^5)(oba)]·3H$_2$O (**8**), have been synthesized under hydrothermal conditions. Their structures have been determined by single crystal X-ray diffraction analyses and further characterized by elemental analyses, IR spectra, and thermogravimetric analyses. The effects of neutral ligands, coordination geometries of metal centers and weak interactions (hydrogen bonds and $\pi\cdots\pi$ stacking interactions) for the formation of coordination complexes were elucidated. Thermal and photoluminescent properties for the compounds were also investigated.

Experimental section

General procedures

Chemicals were purchased from commercial sources and used without further purification. Ligands 2-(2-pyridyl)imidazole 1,4-bis[2-(2-pyridyl)imidazol-1-yl]butane, 1,4-bis[2-(2-pyridyl)-imidazol-1-ylmethyl]benzene, 1,3-bis[2-(2-pyridyl)imidazol-1-ylmethyl]benzene, 1,2-bis[2-(2-pyridyl)imidazol-1-ylmethyl]benzene were prepared according to the literature.[10]

Synthesis of [Zn(L^1)(oba)] (1). A mixture of 4,4′-oxydibenzoic acid (0.16 g, 0.50 mmol), L^1 (0.07 g, 0.50 mmol), Zn(OAc)$_2$·2H$_2$O (0.11 g, 0.50 mmol), NaOH (0.04 g, 1.00 mmol) and H$_2$O (10 mL) was stirred for 1 h and then sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 150 °C and held at that temperature for 72 h, then cooled to 100 °C at a rate of 5 °C h^{-1}, and held for 8 h, followed by further cooling to 30 °C at a rate of 3 °C h^{-1}. Colorless crystals of **1** were collected in 80% yield based on Zn(OAc)$_2$·2H$_2$O. Anal. Calcd for C$_{22}$H$_{15}$N$_3$O$_5$Zn (466.74): C, 56.61; H, 3.24; N, 9.00. Found: C, 56.49; H, 3.34; N, 9.01%. IR (cm^{-1}): 3122 (w), 1600 (s), 1546 (s), 1499 (m), 1474 (m), 1409 (s), 1354 (s), 1296 (w), 1235 (s), 1156 (m), 875 (m), 846 (w), 777 (m), 695 (w).

Synthesis of [Cd(L^1)(oba)] (2). A mixture of 4,4′-oxydibenzoic acid (0.16 g, 0.50 mmol), L^1 (0.07 g, 0.50 mmol), Cd(OAc)$_2$·2H$_2$O (0.13 g, 0.50 mmol), NaOH (0.04 g, 1.00 mmol) and H$_2$O (10 mL) was stirred for 1 h and then sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 150 °C and held at that temperature for 72 h, then cooled to 100 °C at a rate of 5 °C h^{-1}, and held for 8 h, followed by further cooling to 30 °C at a rate of 3 °C·h^{-1}. Colorless crystals of **2** were collected in 81% yield based on Cd(OAc)$_2$·2H$_2$O. Anal. Calcd for C$_{22}$H$_{15}$CdN$_3$O$_5$ (513.77): C, 51.43; H, 2.94; N, 8.18. Found: C, 51.51; H, 3.00; N, 8.20%. IR (cm^{-1}): 3070 (w), 1683 (s), 1594 (s), 1500 (m), 1422 (s), 1293 (m), 1245 (s), 1158 (s), 1104 (m), 1009 (w), 936 (w), 859 (m), 770 (m), 695 (w), 648 (w).

Synthesis of [Zn$_2$(L^2)(oba)$_2$]·8H$_2$O (3). A mixture of 4,4′-oxydibenzoic acid (0.16 g, 0.50 mmol), L^2 (0.17 g, 0.50 mmol), Zn(OAc)$_2$·2H$_2$O (0.11 g, 0.50 mmol), NaOH (0.04 g, 1.0 mmol) and H$_2$O (10 mL) was stirred for 1 h and then sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 150 °C and held at that temperature for 72 h, then cooled to 100 °C at a rate of 5 °C h^{-1}, and held for 8 h, followed by further cooling to 30 °C at a rate of 3 °C h^{-1}. Colorless crystals of **3** were collected in 70% yield based on Zn(OAc)$_2$·2H$_2$O. Anal. Calcd for C$_{48}$H$_{52}$N$_6$O$_{18}$Zn$_2$ (1131.70): C, 50.94; H, 4.63; N, 7.42. Found: C, 51.01; H, 4.68; N, 7.39%. IR (cm^{-1}): 3394 (m), 1680 (s), 1597 (s), 1548 (m), 1499 (m), 1414 (m), 1295 (m), 1241 (s), 1159 (s), 1103 (w), 878 (w), 774 (m), 694 (w), 658 (w).

Synthesis of [Cd$_2$(L^2)(oba)$_2$]·2H$_2$O (4). A mixture of 4,4′-oxydibenzoic acid (0.16 g, 0.50 mmol), L^2 (0.17 g, 0.50 mmol), Cd(OAc)$_2$·2H$_2$O (0.13 g, 0.50 mmol), NaOH (0.04 g, 1.0 mmol) and H$_2$O (10 mL) was stirred for 1 h and then sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 150 °C and held at that temperature for 72 h, then cooled to 100 °C at a rate of 5 °C h^{-1}, and held for 8 h, followed by further cooling to 30 °C at a rate of 3 °C h^{-1}. Colorless crystals of **4** were collected in 58% yield based on $Cd(OAc)_2 \cdot 2H_2O$. Anal. Calcd for $C_{48}H_{40}Cd_2N_6O_{12}$ (1117.66): C, 51.58; H, 3.61; N, 7.52. Found: C, 51.61; H, 3.69; N, 7.48%. IR (cm^{-1}): 3050 (w), 1682 (m), 1596 (s), 1547 (s), 1497 (s), 1468 (m), 1372 (s), 1228 (s), 1160 (m), 876 (w), 779 (m), 690 (w), 656 (w).

Synthesis of $[Zn_3(L^3)(oba)_3]$ (5). A mixture of 4,4′-oxydibenzoic acid (0.16 g, 0.50 mmol), L^3 (0.20 g, 0.50 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (0.11 g, 0.50 mmol), NaOH (0.04 g, 1.0 mmol) and H_2O (10 mL) was stirred for 1 h and then sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 150 °C and held at that temperature for 72 h, then cooled to 100 °C at a rate of 5 °C h^{-1}, and held for 8 h, followed by further cooling to 30 °C at a rate of 3 °C h^{-1}. Colorless crystals of **5** were collected in 56% yield based on $Zn(OAc)_2 \cdot 2H_2O$. Anal. Calcd for $C_{66}H_{44}N_6O_{15}Zn_3$ (1357.18): C, 58.40; H, 3.27; N, 6.19. Found: C, 58.40; H, 3.29; N, 6.22%. IR (cm^{-1}): 3046 (w), 1683 (s), 1592 (s), 1501 (m), 1423 (m), 1292 (s), 1249 (s), 1158 (s), 1104 (m), 935 (w), 858 (m), 768 (w), 544 (w).

Synthesis of $[Cd_2(L^3)(oba)_2] \cdot (L^3)$ (6). A mixture of 4,4′-oxydibenzoic acid (0.16 g, 0.50 mmol), L^3 (0.20 g, 0.50 mmol), $Cd(OAc)_2 \cdot 2H_2O$ (0.13 g, 0.50 mmol), NaOH (0.04 g, 1.0 mmol) and H_2O (10 mL) was stirred for 1 h and then sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 150 °C and held at that temperature for 72 h, then cooled to 100 °C at a rate of 5 °C h^{-1}, and held for 8 h, followed by further cooling to 30 °C at a rate of 3 °C h^{-1}. Colorless crystals of **6** were collected in 52% yield based on $Cd(OAc)_2 \cdot 2H_2O$. Anal. Calcd for $C_{76}H_{56}Cd_2N_{12}O_{10}$ (1522.13): C, 59.67; H, 3.71; N, 11.04. Found: C, 59.69; H, 3.68; N, 11.00%. IR (cm^{-1}): 3067 (w), 1682 (w), 1596 (s), 1546 (s), 1479 (m), 1401 (s), 1291 (m), 1247 (s), 1156 (s), 1096 (m), 1004 (w), 934 (w), 876 (w), 782 (m), 737 (m), 692 (m), 655 (m).

Synthesis of $[Cd(L^4)(oba)] \cdot H_2O$ (7). A mixture of 4,4′-oxydibenzoic acid (0.16 g, 0.50 mmol), L^4 (0.20 g, 0.50 mmol), $Cd(OAc)_2 \cdot 2H_2O$ (0.13 g, 0.50 mmol), NaOH (0.04 g, 1.0 mmol) and H_2O (10 mL) was stirred for 1 h and then sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 150 °C and held at that temperature for 72 h, then cooled to 100 °C at a rate of 5 °C h^{-1}, and held for 8 h, followed by further cooling to 30 °C at a rate of 3 °C h^{-1}. Colorless crystals of **7** were collected in 43% yield based on $Cd(OAc)_2 \cdot 2H_2O$. Anal. Calcd for $C_{38}H_{30}CdN_6O_6$ (779.08): C, 58.58; H, 3.88; N, 10.79. Found: C, 58.61; H, 3.84; N, 10.82%. IR (cm^{-1}): 3057 (w), 1683 (s), 1594 (s), 1499 (m), 1424 (s), 1292 (s), 1249 (s), 1157 (m), 1103 (m), 935 (w), 859 (m), 768 (m), 692 (w), 543 (w).

Synthesis of $[Cd(L^5)(oba)] \cdot 3H_2O$ (8). A mixture of 4,4′-oxydibenzoic acid (0.16 g, 0.50 mmol), L^5 (0.20 g, 0.50 mmol), $Cd(OAc)_2 \cdot 2H_2O$ (0.13 g, 0.50 mmol), NaOH (0.04 g, 1.0 mmol) and H_2O (10 mL) was stirred for 1 h and then sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 150 °C and held at that temperature for 72 h, then cooled to 100 °C at a rate of 5 °C h^{-1}, and held for 8 h, followed by further cooling to 30 °C at a rate of 3 °C h^{-1}. Colorless crystals of **8** were collected in 73% yield based on $Cd(OAc)_2 \cdot 2H_2O$. Anal. Calcd for $C_{38}H_{34}CdN_6O_8$ (815.11): C, 55.99; H, 4.20; N, 10.31. Found: C, 56.01; H, 4.16; N, 10.31%. IR (cm^{-1}): 3042 (w), 1682 (m), 1595 (m), 1496 (m), 1427 (s), 1310 (s), 1249 (s), 1157 (s), 1102 (w), 932 (m), 858 (w), 765 (s), 700 (m), 544 (w).

Physical measurements. The C, H, and N elemental analysis was conducted on a Perkin–Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. TGA was performed on a Perkin–Elmer TG-7 analyzer heated from 35 to 800°C under nitrogen. The emission/excitation spectra were recorded on a Varian Cary Eclipse spectrometer.

X-Ray crystallography

Single-crystal X-ray diffraction data for compounds **1–8** were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 293K. Absorption corrections were applied using multi-scan technique. All the structures were solved by Direct Method of SHELXS-97[11] and refined by full-matrix least-squares techniques using the SHELXL-97 program[12] within WINGX.[13] Non-hydrogen atoms were refined with anisotropic temperature parameters. The hydrogen atoms of the organic ligands were refined as rigid groups. The hydrogen atoms of the O3w molecule in **8** could not be located, but have been included in the formula. And other H atoms of water molecules were located from difference Fourier maps. The disordered 2-(2-pyridyl)imidazole group in compound **1** was refined using C and N atoms split over two equivalent sites, with a total occupancy of 1. The detailed crystallographic data and structure refinement parameters for **1–8** are summarized in Table 1.

Results

Structures

Structure description of 1. The asymmetric unit consists of one kind of Zn^{II} cation, oba^{2-} anion and L^1 ligand (Fig. 1a). Each Zn^{II} is in a distorted octahedral coordination environment, in which four oxygen atoms (Zn(1)–O(1) = 2.078(3), Zn(1)–O(2) = 2.299(4), Zn(1)–O(4)#1 = 2.103(3) and Zn(1)–O(5)#1 = 2.216(4) Å) from two oba^{2-} anions and two nitrogen atoms (Zn(1)–N(2)= 2.119(4) and Zn(1)–N(3) = 2.114(3) Å) from one L^1 ligand are located at the six vertexes. The Zn–O and Zn–N bond lengths are all within the normal ranges.[14] Each oba^{2-} anion coordinates to two Zn^{II} cations by a bis(bidentate) coordination mode (Chart S1a) to give a sinusoidal chain with a period of 25.228 Å (Fig. 1b). The L^1 chelates to each Zn^{II} cation as a terminal ligand with the dihedral angle of 1.6° between pyridine and imidazole rings in the same ligand (Fig. S1).

Interestingly, there are weak π···π and hydrogen bonding interactions in the structure. The π···π stacking interactions[15] show between pyridine and imidazole rings from adjacent layers, with the plane-to-plane distance of 3.46 Å and the centroid–centroid distance of 4.00 Å. And each L^1 donates one hydrogen bond to the carboxylic oxygen atom with the N–H···O distance of 3.116(7) Å (Table S1). So an interesting 2D supramolecular layer is finally formed by linking the sinusoidal chains through π···π and hydrogen bonding interactions (Fig. 1c).

Table 1 Crystal data and structure refinements for compounds **1–8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{22}H_{15}N_3O_5Zn$	$C_{22}H_{15}CdN_3O_5$	$C_{48}H_{52}N_6O_{18}Zn_2$	$C_{48}H_{40}Cd_2N_6O_{12}$	$C_{66}H_{44}N_6O_{15}Zn_3$	$C_{38}H_{28}CdN_6O_5$	$C_{38}H_{30}CdN_6O_6$	$C_{38}H_{34}CdN_6O_8$
Fw	466.74	513.77	1131.70	1117.66	1357.18	761.06	779.08	815.11
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	7.6100(5)	11.7140(4)	17.309(3)	10.0580(4)	14.3040(4)	9.6950(11)	12.4090(3)	11.4920(4)
b/Å	18.888(1)	16.0590(4)	16.441(2)	10.6750(4)	17.4700(4)	12.4600(13)	20.5790(4)	11.7810(4)
c/Å	14.7840(13)	11.2640(5)	18.128(3)	12.0480(5)	25.636(1)	15.1400(16)	14.6440(6)	14.6520(5)
α/°	90	90	90	85.841(1)	90	111.061(2)	90	71.945(1)
β/°	98.806(1)	96.482(1)	92.439(3)	68.774(1)	94.069(1)	96.603(2)	114.637(1)	73.436(1)
γ/°	90	90	90	66.171(1)	90	101.133(2)	90	80.084(1)
V/Å^3	2100.0(3)	2105.38(13)	5154.1(13)	1098.90(8)	6390.1(3)	1640.3(3)	3399.14(17)	1800.08(11)
Z	4	4	4	1	4	1	4	2
μ/mm^{-1}	1.208	1.076	1.009	1.041	1.188	0.721	0.700	0.668
D_{calcd}/g cm^{-3}	1.476	1.621	1.458	1.689	1.411	1.541	1.522	1.504
F(000)	952	1024	2344	562	2768	772	1584	832
Reflns collected/unique	12 692/5007	12 844/5054	27 392/10240	6902/5038	19 563/7664	10 241/7502	20 887/8188	11 223/8218
R(int)	0.0227	0.0202	0.0454	0.0161	0.0288	0.0436	0.0192	0.0137
GOF on F^2	1.016	1.045	1.017	1.039	1.042	0.957	1.023	1.030
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0420	0.0250	0.0584	0.0345	0.0399	0.0606	0.0308	0.0341
w$R_2{}^b$	0.1141	0.0603	0.1421	0.0728	0.1202	0.1214	0.0695	0.0855
wR_2 for all data	0.1316	0.0639	0.1572	0.0777	0.1272	0.1335	0.0755	0.0907
Largest residuals/e Å^{-3}	0.391/−0.588	0.377/−0.426	1.019/−0.482	0.449/−0.409	1.517/−0.630	0.864/−0.841	0.591/−0.539	0.963/−0.555

[a] $R_1 = \sum \lVert F_o| - |F_c\rVert / \sum |F_o|$. [b] $wR_2 = |\sum w(|F_o|^2 - |F_c|^2)| / \sum |w(F_o{}^2)^2|^{1/2}$.

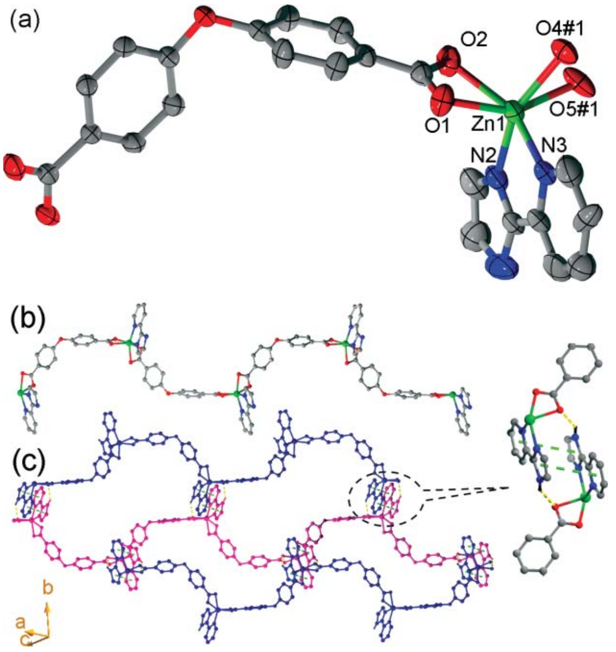


Fig. 1 (a) Coordination environment of Zn^{II} atom in **1** with the ellipsoids drawn at the 30% probability level, all hydrogen atoms were omitted for clarity. (b) The infinite chain-like structure of compound **1** (symmetry transformations used to generate equivalent atoms: #1 $x - 3/2, -y + 1/2, z - 1/2$). (c) View of the 2D supramolecular layer constructed by $\pi\cdots\pi$ stacking (green dashed lines) and H-bonds (yellow dashed lines) interactions connecting the adjacent chains.

Structure description of 2. Compound **2** is a 3D supramolecular structure using Cd^{II} ions instead of Zn^{II} ions. There is one kind of Cd^{II} ion, oba^{2-} anion and L^1 ligand in the asymmetric unit (Fig. 2a). Cd^{II} ion shows a seven-coordinated pentagonal bi-pyramidal coordination geometry which is finished by five carboxylic oxygen atoms (Cd(1)–O(5) = 2.223(4), Cd(1)–O(4) = 2.655(3), Cd(1)–O(1)#1 = 2.255(3) Cd(1)–O(2)#1 = 2.704(3) and Cd(1)–O(1)#2 = 2.462(4) Å) from three oba^{2-} anions and two nitrogen atoms (Cd(1)–N(1) = 2.2892(17) and Cd(1)–N(3) = 2.3973(18) Å) from one L^1 ligand. The Cd–O and Cd–N bond lengths are all within the normal ranges.[16] Each oba^{2-} anion coordinates three Cd^{II} ions (Chart S1b) to give a 2D sheet (Fig. 2b) which contains a [$Cd_2(CO_2)_4$] unit with the Cd$\cdots$Cd distance of 3.72 Å (Fig. S2a). L^1 coordinates chelately to each Cd^{II} cation as a terminal ligand with the dihedral angle of 4.8° between pyridine and imidazole rings in the same ligand (Fig. S2b).

In addition, each L^1 from one sheet donates one hydrogen bond to the adjacent carboxylic oxygen atom with the N–H$\cdots$O distance of 2.767(2) Å. Weak $\pi\cdots\pi$ stacking interactions are exhibited between pyridine and imidazole rings from adjacent layers, with the plane to plane distance of 3.46 Å and the centroid–centroid distance of 3.87 Å. So a 3D supramolecular framework different from **1** is finally formed through $\pi\cdots\pi$ and hydrogen bonding interactions (Fig. 2c).

Comparing the structures of **1** and **2**, they show different 1D and 2D structures, when using Zn^{II} and Cd^{II} ion. The reasons may be that Zn^{II} and Cd^{II} ions have closed d^{10} electronic shell, and there are no crystal field stabilization energies for them when their complexes are formed. The radius of Cd^{II} cation is larger than that of Zn^{II} cation, and the coordination number of Cd^{II} cation in **2** is larger than that of Zn^{II} cation in **1**. So compounds **1** and **2** show different structural types.

Structure description of 3. To evaluate the effects of different bridging spacers within the framework formation of their

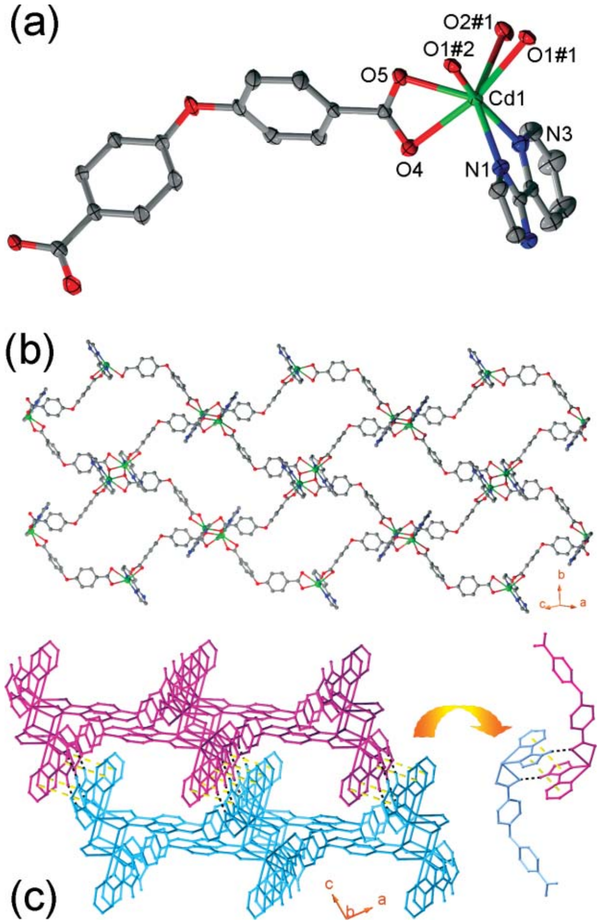


Fig. 2 (a) Coordination environment of Cd^{II} atom in **2** with the ellipsoids drawn at the 30% probability level, all hydrogen atoms were omitted for clarity (symmetry transformations used to generate equivalent atoms: #1 $x+1, -y+1/2, z-1/2$; #2 $-x, y+1/2, -z+1/2$). (b) Ball-and-stick representation of the layer-like structure of **2**. (c) Ball-and-stick representation of the 3D supramolecular structure of **2**.

complexes, four structurally related ligands L^2–L^5 which derive from L^1 have been utilized to synthesize six different frameworks.

When L^1 has been replaced by L^2 and reacted with H_2oba and Zn cations, a particularly fascinating 3D structure of **3** has been obtained. As shown in Fig. 3a, the structure of **3** contains two kinds of unique Zn(II) atoms, two kinds of unique oba^{2-} anions, and one kind of L^2 ligand. Zn1 and Zn2 show six-coordinated octahedral geometries which are surrounded by four oxygen atoms (Zn(1)–O(3)#1 = 2.056(3), Zn(1)–O(1) = 2.061(3), Zn(1)–O(4)#1 = 2.350(4), Zn(1)–O(2) = 2.375(4), Zn(2)–O(7) = 2.087(3), Zn(2)–O(10)#3 = 2.144(3), Zn(2)–O(9)#3 = 2.181(3) and Zn(2)–O(6) = 2.343(3) Å) from two oba^{2-} anions and two nitrogen atoms (Zn(1)–N(1) = 2.036(3), Zn(1)–N(2) = 2.114(3), Zn(2)–N(4) = 2.050(3) and Zn(2)–N(5) = 2.094(3) Å) from the same L^2 ligand, respectively. Two oba^{2-} anions coordinate to two kinds of Zn^{II} cations by bis(bidentate) coordination modes (Chart S1a) to give two kinds of [Zn(oba)] chains, respectively. And the two kinds of chains are arranged by vertical modes (Fig. 3b). L^2 ligand exhibits a TTT (T = *trans*) conformation (Fig. S3a) and coordinates to Zn1 and Zn2 atoms from different chains to generate a 3D framework (Fig. 3c). From the topological view, if each Zn atom is considered as a three-connected node (Fig. S3b) and oba^{2-} and L^2 ligands as linkages, the structure can be classified as an unusual (10,3)-b (or $ThSi_2$) net (Fig. 3d).

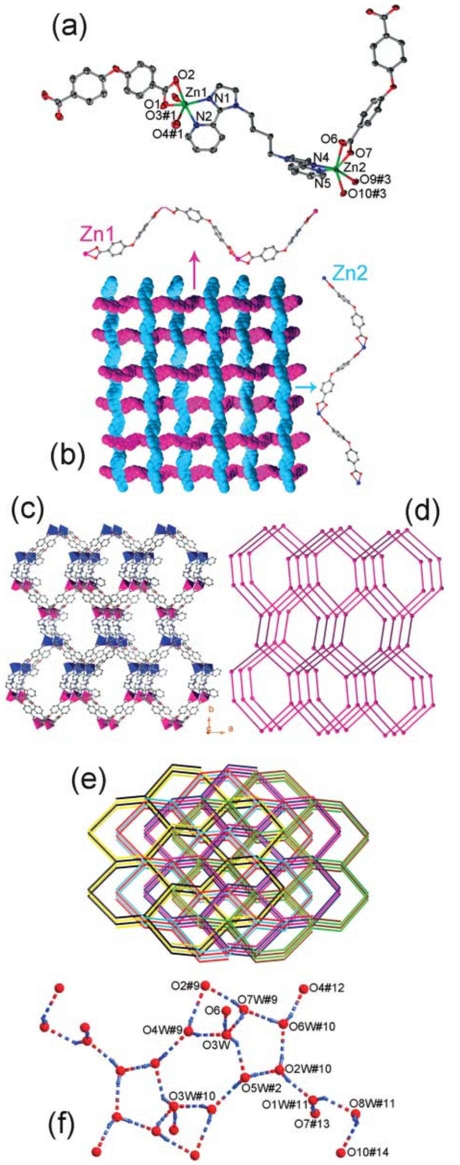


Fig. 3 (a) Coordination environment of Zn^{II} atoms in **3** with the ellipsoids drawn at the 30% probability level, all hydrogen atoms and water molecules were omitted for clarity (symmetry transformations used to generate equivalent atoms: #1 $x-1/2, -y+3/2, z-1/2$; #3 $x-1/2, -y-1/2, z+1/2$). (b) Ball-and-stick and space filling representations two kinds of chains formed by oba^{2-}, Zn1 and Zn2, respectively. (c) and (d) Ball-stick and polyhedral and schematic representations of the 3D structure of **3**. (e) Schematic view of eight-fold interpenetrating topological framework. (f) The water clusters in the structure (symmetry transformations used to generate equivalent atoms: #2 $x, y-1, z-1$; #9 $1/2-x, -1/2+y, 3/2-z$; #10 $1-x, -y, 1-z$; #11 $1/2+x, 1/2-y, 1/2+z$; #12 $x-1/2, 1/2-y, z-1/2$; #13 $x+1/2, -y-1/2, z+1/2$; #14 $1+x, y, z$).

Because of the spacious nature of the single network, the potential voids are filled *via* mutual interpenetration of identical 3D frameworks, generating an eight-fold interpenetrating architecture (Fig. 3e). In a previous report, a few (10,3) nets have already been defined by Wells, Koch and Fischer.[17] To our knowledge, only one eight-fold interpenetrating framework based on (10,3) net has been reported[18], in which there are four right- and four left-handed (10,3)-a nets. Of the (10,3)-b type, there are currently only a few known examples.[3e,19] Some of them show two-fold or three-fold interpenetrating frameworks. The framework of **3** is the first example for eight-fold interpenetrating framework based on the (10,3)-b net which is clearly different from other reported network topologies.

Water clusters have been widely studied both theoretically and experimentally.[20] A variety of water clusters, $[(H_2O)_n$, $n =$ 2–18], found in a number of crystal hosts, have been characterized and display different configurations. There exist $(H_2O)_{16}$ polymers which are formed by two crystallographically-related $(H_2O)_8$ octamers in the structure of **3**, and the geometrical parameters of the water polymers and its association with oba^{2-} ligands are provided in Table S1, whereas these distances in regular ice, liquid water, and water vapor are 2.74, 2.85, and 2.98 Å, respectively.[20c] As shown in Fig. 3f, the sixteen lattice water molecules in **3** are assembled into a centrosymmetric polymer by two eight octamers. In each octamer, five water molecules (O3W, O7W#9, O6W#10, O2W#10 and O5W#2) assemble through hydrogen bonds in an approximate pentagon with five water molecules at each corner (O3W $\cdots$ O7W#9 = 2.769(6), O3W $\cdots$ O5W#2 = 2.854(6), O5W#2 $\cdots$ O2W#10 = 2.882(6), O2W#10 $\cdots$ O6W#10 = 2.878(6) and O6W#10 $\cdots$ O7W#9 = 2.722(6) Å). And O3W donates a hydrogen bond to O4W#9 (O3W $\cdots$ O4W#9 = 2.895(7) Å) and O2W donates a hydrogen bond to O1W#11 (O2W $\cdots$ O1W#11 = 2.787(5) Å) which gives hydrogen bonds to one carboxylic oxygen atom (O7#13) and O8W#14 (O1W#11 $\cdots$ O7W#13 = 2.854(5) and O1W#11 $\cdots$ O8W#14 = 2.770(8) Å). As is well known, water molecules often show a three-coordinate mode through hydrogen bond interactions (O1W#11, O2W#9, O4W#9, O5W#2, O6W#10, O7W#9 and O8W#11);[21] however, O3W of this water polymer shows a four-coordinate mode.

Structure description of 4. When using Cd^{II} cations instead of Zn^{II} cations, a 3D supramolecular compound of **4** has been isolated. As shown in Fig. 4a, the structure of **4** contains of one kind of Cd^{II} cation, L^2 ligand and oba^{2-} anion. Cd1 atom is six-coordinated and shows an octahedral coordination geometry, which is completed by four oxygen atoms (Cd(1)–O(3) = 2.216(2), Cd(1)–O(1)#1 = 2.341(2), Cd(1)–O(1)#2 = 2.3600(19) and Cd(1)–O(2)#2 = 2.544(2) Å) from three oba^{2-} anions and two nitrogen atoms (Cd(1)–N(1) = 2.270(2) and Cd(1)–N(3) = 2.369(2) Å) from the same L^2 ligand. The oba^{2-} anion shows a different coordination mode (Chart S1c) from **1–3**. Two oba^{2-} anions link two Cd1 cations to give a double-chain structure (Fig. 4b) in which there is a 26-membered ring (I). And the L^2 ligand with a TTT conformation (Fig. S4a) coordinates to two Cd cations from different double-chains to form a 2D sheet (Fig. 4c). Each water molecule is stabilized in the structure by donating one hydrogen bond to one carboxylate oxygen atom (O(1W) $\cdots$ O(3) = 2.825(5) Å).

In addition, the strong $\pi \cdots \pi$ stacking interactions between two phenyl rings of two oba^{2-} anions from adjacent layers (Fig. 4d), with the plane to plane distance of 3.40 Å and the centroid–centroid distance of 3.59 Å which are in the normal ranges (3.3–3.8 Å),[22] link above-mentioned 2D sheets to give a interesting 3D supramolecular framework (Fig. 4e and S4b).

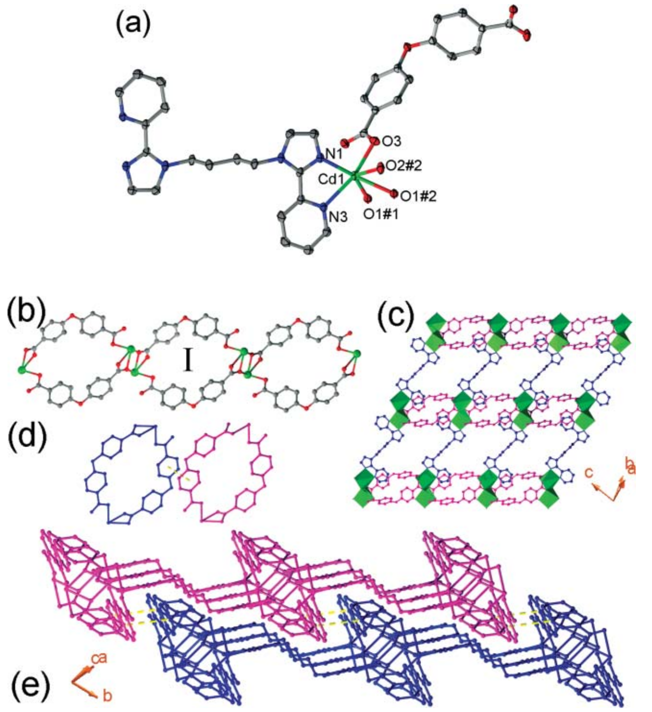


Fig. 4 (a) Coordination environment of Cd^{II} atom in **4** with the ellipsoids drawn at the 30% probability level, all hydrogen atoms and water molecules were omitted for clarity (symmetry transformations used to generate equivalent atoms: #1 $x - 1$, y, $z + 1$; #2 $-x + 2$, $-y + 1$, $-z + 1$). (b) Ball-and-stick representation of the double-chain structure formed by oba^{2-} and Cd1. (c) Ball-stick and polyhedral representation of the 2D structure of **4**. (d) and (e) Ball-and-stick representation of the 3D supramolecular structure of **4**.

Structure description of 5. When using the semi-flexible L^3 ligand instead of the flexible L^2 ligand, compound **5** with a different structural type from others has been obtained. Single crystal X-ray analysis reveals that compound **5** is constructed by two kinds of Zn^{II} cations, two kinds of oba^{2-} anions (oba1 and oba2) and one L^3 ligand (Fig. 5a). Zn1 atom is six-coordinated and exhibits a twisted octahedral geometry which is surrounded by four carboxylic oxygen atoms (Zn(1)–O(6) = 2.001(2), Zn(1)–O(3) = 2.015(2), Zn(1)–O(1)#3 = 2.125(2) and Zn(1)–O(2)#3 = 2.328(2) Å) from three oba^{2-} ligands and two nitrogen atoms (Zn(1)–N(1) = 2.335(3) and Zn(1)–N(2) = 2.068(3) Å) from the same L^3 ligand, while Zn2 lies on an inversion center and is coordinated by six carboxylic oxygen atoms (Zn(2)–O(4) = 2.195(2), Zn(2)–O(5) = 2.280(2), and Zn(2)–O(2)#2 = 2.320(2) Å) from six oba^{2-} ligands and shows a distorted octahedral geometry. The oba1 ligands (Chart S1d) link Zn1 atoms to form a chain which is connected by Zn(2)–O(5) and Zn(2)–O(2)#2 bonds to generate a sheet (Fig. 5b). And then the sheets are pillared by oba2 (Chart S1e) ligands to give a 3D framework (Fig. 5c). In the 3D structure, the Zn2 octahedron is a crystallographic inversion center that connects two crystallographically equivalent Zn1 octahedra in a vertex-sharing mode to form a $[Zn_3(CO_2)_6]$ polyhedral cluster by twelve carboxylic groups from four oba1 and two oba2 ligands with the nonbonding Zn1 $\cdots$ Zn2 distance of 3.66 Å. If each $[Zn_3(CO_2)_6]$ polyhedral cluster is considered as a six-connected node and each oba^{2-} anion as a linkage, the structure formed by oba^{2-} anions and Zn cations shows a α-Po (pcu) net (Fig. 5b).

In addition, each $[Zn_3(CO_2)_6]$ cluster is further linked by two L^3 ligands with an 'S'-shaped conformation (Fig. S5a) to

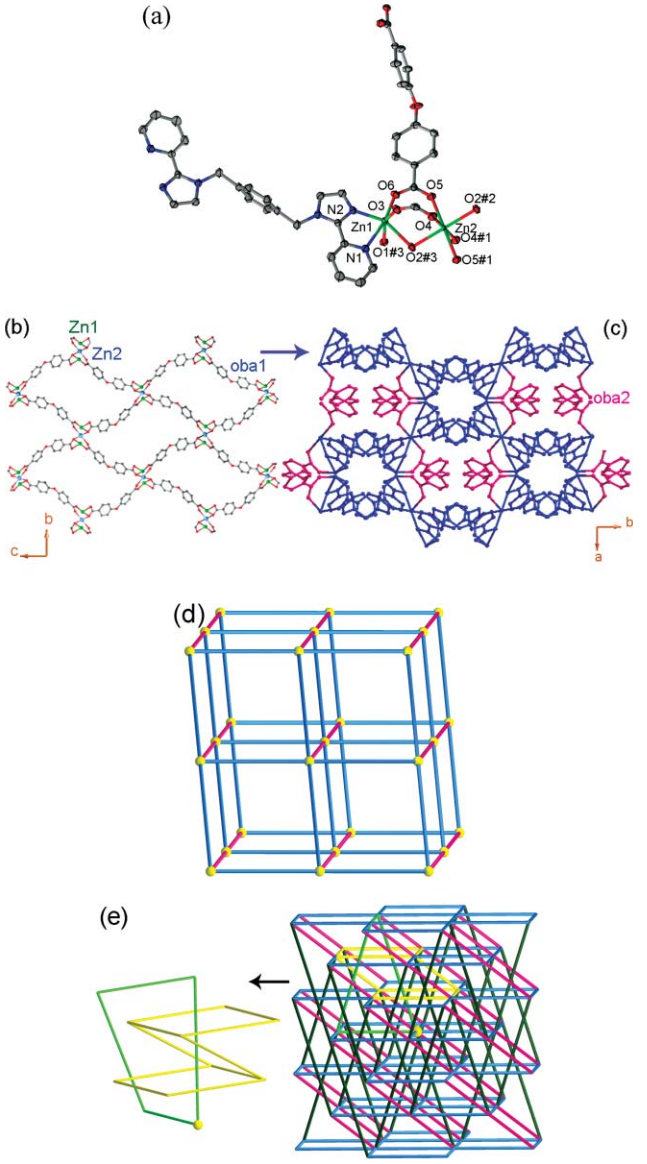


Fig. 5 (a) Coordination environment of Zn^{II} atoms in **5** with the ellipsoids drawn at the 30% probability level (symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, -y + 1/2, -z + 1$; #2 $-x + 1/2, y - 1/2, -z + 1/2$; #3 $x, -y + 1, z + 1/2$). (b) Ball-and stick representation of the layer-like structure formed by one kind of oba^{2-} anion and Zn^{II} cations. (c) and (d) Ball-and stick and schematic representations of the 3D framework by the other kind of oba^{2-} anion pillaring the layers. (e) Schematic representation of the 3D self-penetrating framework of **5**.

form a complicated 3D framework. It is interesting that each L^3 ligand penetrates two 2D sheets formed by the Zn and oba1. So the $[Zn_3(CO_2)_6N_4]$ is a 8-connected node (Fig. S5b), and the whole structure of **5** is a 3D eight-connected self-penetrating framework with the $(4^{16}6^{11}8)$ topological structure (Fig. 5e). To our best knowledge, only a few examples of eight-connected 3-D self-penetrating MOFs are reported until now,[6b,23] and the structure of **5** is completely different from that of the well-known eight-connected self-penetrating frameworks with $(4^{24}56^3)$, $(4^{20}6^8)$, $(4^{24}6^4)$ and $(4^{12}5^66^77^28)$ topologies.[6b,23] In the reported 3D eight-connected self-penetrating frameworks, the two shortest four-membered cycles are catenated. And in this case, one four-membered cycle catenates the three shortest four-membered cycles. The structure of **5** shows a new type of 3D eight-connected self-penetrating framework, which could help us deeply understand the nature of coordination polymer frameworks and better design functional materials.

Structure description of 6. Compound **6** shows a different structure from **5**, by using Cd^{II} cation instead of Zn^{II} cation in the same reaction conditions. Single crystal X-ray analysis reveals that compound **6** contains one kind of Cd^{II} cation and oba^{2-} anion, and two kinds of L^3 ligands (Fig. 6a). The Cd^{II} ion is coordinated by four oxygen atoms (Cd(1)–O(4)#1 = 2.264(3), Cd(1)–O(2) = 2.343(4), Cd(1)–O(1) = 2.382(4) and Cd(1)–O(4)#2 = 2.455(3) Å) from three distinct oba^{2-} ligands and two nitrogen atoms

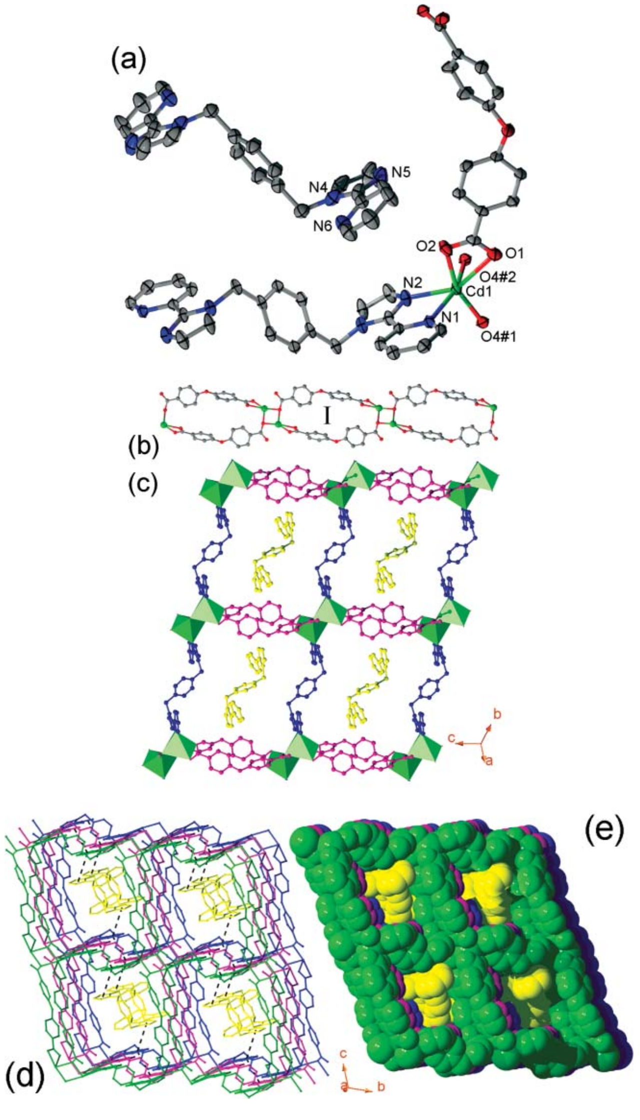


Fig. 6 (a) Coordination environment of Cd^{II} atom in **6** with the ellipsoids drawn at the 30% probability level, all hydrogen atoms were omitted for clarity (symmetry transformations used to generate equivalent atoms: #1 $x, y, z + 1$; #2 $-x + 1, -y, -z$). (b) Ball-and-stick representation of the double-chain structure formed by oba^{2-} and Cd1. (c) Ball-stick and polyhedral representation of the 2D structure of **6**. (d) and (e) Ball-and-stick and space filling representations of the 3D supramolecular structure of **6**.

(Cd(1)–N(1) = 2.387(4) and Cd(1)–N(2) = 2.323(4) Å) from one L^3 ligand, showing distorted octahedral coordination geometry (Fig. 6a). Two oba^{2-} anions link two Cd^{II} cations (Chart S1f) to give a double-chain structure (Fig. 6b) in which there is a 26-membered ring (I). And one kind of L^3 ligand with an 'S'-shaped conformation coordinates two Cd cations from different double-chains to form a 2D sheet (Fig. 6c). And the other kind of L^3 ligand with the same conformation co-crystallizes in the structure (Fig. S6).

In addition, there are $\pi\cdots\pi$ stacking interactions in the structure (Fig. 6d). The weak $\pi\cdots\pi$ stacking interactions between two pyridine rings of two L^3 ligands coordinating to metal centers from adjacent layers, with the plane to plane distance of 3.42 Å and the centroid–centroid distance of 3.93 Å, connect sheets to give a 3D supramolecular structure. And the $\pi\cdots\pi$ stacking interactions between pyridine and imidazole rings of two kinds of L^3 ligands, with the plane to plane distance of 3.47 Å and the centroid–centroid distance of 3.82 Å, stabilize the isolated L^3 ligands in the structure (Fig. 6e).

Structure description of 7. When using the different angular character of L^4 instead of L^3, compound **7** with four-fold interpenetrating diamond topological framework has been obtained. The structure of **7** contains one kind of Cd^{II} ion, oba^{2-} anion and L^4 ligand (Fig. 7a). Each Cd^{II} ion is seven-coordinated by four carboxylic oxygen atoms (Cd(1)–O(2) = 2.3332(16), Cd(1)–O(5)#2 = 2.3507(16), Cd(1)–O(4)#2 = 2.4158(15) and Cd(1)–O(1) = 2.6436(18) Å) from two oba^{2-} anions and three nitrogen atoms (Cd(1)–N(2) = 2.2723(17), Cd(1)–N(5)#1 = 2.2869(18) and Cd(1)–N(3) = 2.6357(19) Å) from two L^4 ligands, showing a pentagonal bi-pyramidal coordination geometry. Each of the oba^{2-} anion with a bis(bidentate) coordination mode (Chart S1a) links two Cd^{II} ions to give a chain (Fig. 7b). Unexpectedly, L^4 ligand coordinates to two Cd^{II} ions (Fig. S7a) from different chains with a mono(bidentate) coordination mode to form a 3D framework (Fig. 7c).

From the topological view, if each Cd^{II} ion is considered as a 4-connected node (Fig. S7b), and each oba^{2-} anion and L^4 ligand as linkages, the structure of **7** is a 3D diamond topological net (Fig. 7d). Because of the spacious nature of the single network, the potential voids are filled *via* mutual interpenetration of identical 3D frameworks, generating a four-fold interpenetrating architecture (Fig. 7e). This kind of four-fold interpenetrating structure has been described in previous reports.[24] Lattice water molecule occupies the residual space and is hydrogen-bonded to the carboxylate groups (O(1W)$\cdots$O(1) = 2.859(3) and O(1W)$\cdots$O(5)#5 = 2.920(3) Å).

Structure description of 8. When the smallest angular L^5 ligand was selected to react with Cd^{II} ion and H_2oba, we obtained compound **8**. There is one kind Cd^{II} ion, oba^{2-} anion and L^5 ligand (Fig. 8a). The Cd^{II} ion exhibits a pentagonal bi-pyramidal coordination geometry which is completed by five carboxylic oxygen atoms (Cd(1)–O(2) = 2.2935(18), Cd(1)–O(4)#1 = 2.4048(19), Cd(1)–O(5)#2 = 2.4049(18), Cd(1)–O(1) = 2.4492(18) and Cd(1)–O(5)#1 = 2.4594(19) Å) from three oba^{2-} anions and two nitrogen atoms (Cd(1)–N(2) = 2.262(2) and Cd(1)–N(3) = 2.401(2) Å) from one L^5 ligand. The oba^{2-} anions (Chart S1b) link Cd ions to give a double-chain structure (Fig. 8b) which contains a $[Cd_2]$ unit with the Cd$\cdots$Cd distance of 3.85 Å. It is unexpected that L^5 acts as a chelate and terminal ligand and coordinates to a Cd ion with a 'V'-shaped conformation (Fig. S8).

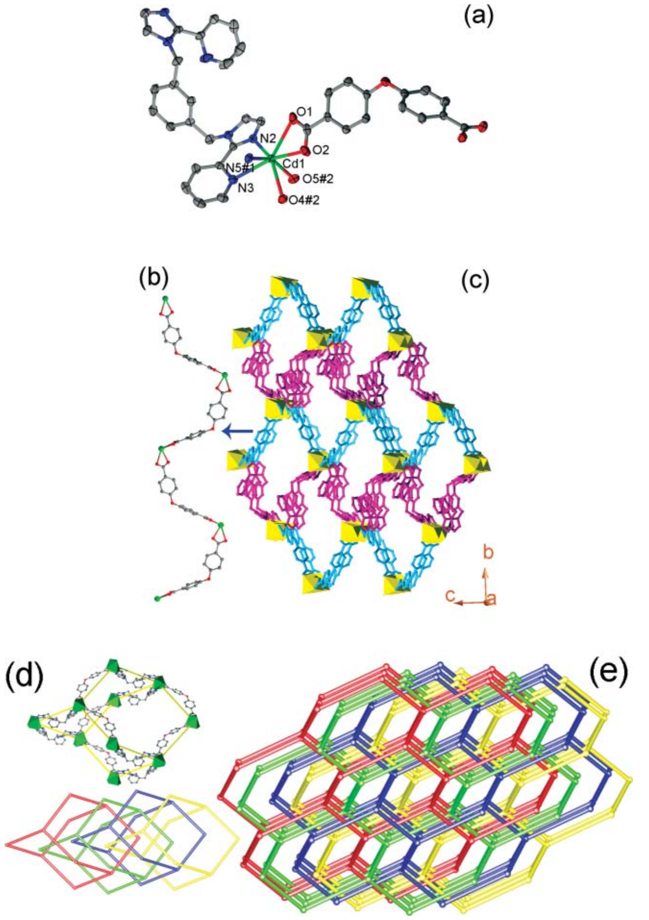


Fig. 7 (a) Coordination environment of Cd^{II} atom in **7** with the ellipsoids drawn at the 30% probability level, all hydrogen atoms and water molecule were omitted for clarity (symmetry transformations used to generate equivalent atoms: #1 $x - 1/2, -y + 1/2, z - 1/2$; #2 $x - 1/2, -y + 3/2, z + 1/2$). (b) Ball-and-stick representation of the chain structure formed by oba^{2-} and Cd1. (c) Ball-stick and polyhedral representation of the 3D structure of **7**. (d) and (e) Schematic view of four-fold interpenetrating topological framework.

In addition, there are weak $\pi\cdots\pi$ interactions between two pyridine rings of L^5 ligands from adjacent chains with the plane to plane distance of 3.51 Å and the centroid–centroid distance of 3.99 Å. At the same time, O1W donates two hydrogen bonds to an N atom of L^5 ligand and an O atom (O(1W)$\cdots$N(5)#4 = 2.950(5) and O(1W)$\cdots$O(4)#1 = 2.870(3) Å) of oba^{2-} anion from adjacent chains. And O2W donates two hydrogen bonds to O1W and O3W (O(2W)$\cdots$O(1 W) = 2.804(5) and O(2W)$\cdots$O(3 W) = 2.958(9) Å). So the non-covalent interactions play important roles for linking the chains to generate a 2D supramolecular sheet (Fig. 8c).

Effect of the anion and neutral ligand on the structures

From the above structural descriptions, it can be seen that the anion and neutral ligands have great influences on the frameworks of the complexes.

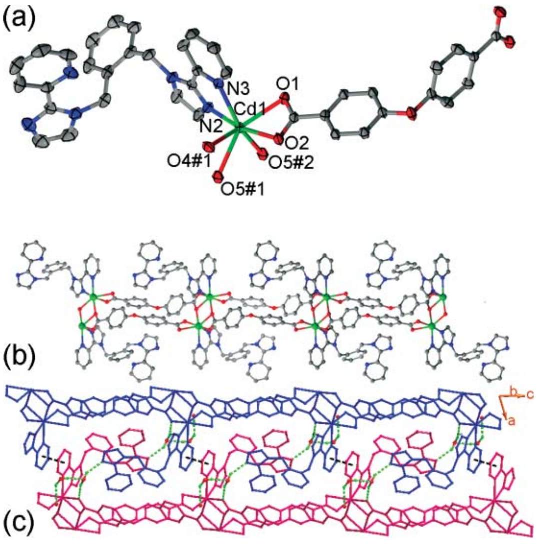


Fig. 8 (a) Coordination environment of $\mathrm{Cd^{II}}$ atom in **8** with the ellipsoids drawn at the 30% probability level, all hydrogen atoms and water molecule were omitted for clarity (symmetry transformations used to generate equivalent atoms: #1 x, y, $z - 1$; #2 $-x$, $-y$, $-z + 2$). (b) Ball-and-stick representation of the chain structure of **8**. (c) View of the 2D supramolecular layer constructed by $\pi\cdots\pi$ (black dashed lines) and H-bonds (green dashed lines) interactions connecting the adjacent chains.

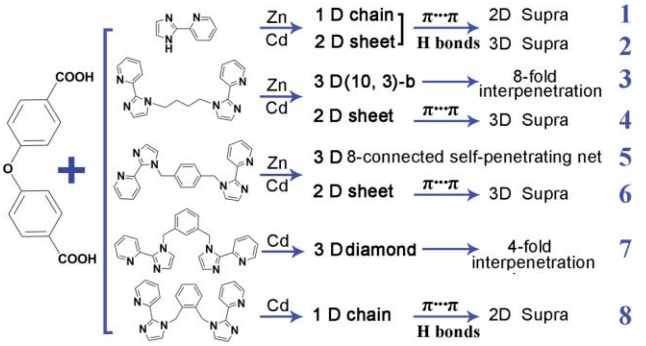
Each of these anions may act as a versatile ligand to construct various $\mathrm{M^{II}}$–oba metal–organic units. In this case, $\mathrm{oba^{2-}}$ anions display a variety of coordination modes (Chart S1a–S1f) and coordinate to 2–4 metal centers to give different $\mathrm{M^{II}}$–oba metal–organic units. In **1**, **3** and **7**, $\mathrm{oba^{2-}}$ anions link $\mathrm{Zn^{II}}$ or $\mathrm{Cd^{II}}$ ions to generate 1D chain-like structures, and they show 1D double chain-like structures in **4** and **6**. While in **2** and **5**, $\mathrm{oba^{2-}}$ anions assemble $\mathrm{Zn^{II}}$ or $\mathrm{Cd^{II}}$ ions to form 2D and 3D nets, respectively. The various $\mathrm{M^{II}}$–oba metal–organic units can be decorated five neutral ligands to form the ultimate compounds. And a variety of coordination modes for $\mathrm{oba^{2-}}$ anions may be expected.

Due to the structural features of five neutral ligands, $\mathrm{L^1}$ ligand tends to act as a terminal ligand coordinating to one metal center with two nitrogen atoms, and $\mathrm{L^2}$–$\mathrm{L^5}$ maybe prefer to adopt bis(bidentate)-cheating bridging modes with four aromatic N atoms coordinating to two metal centers. Because the different coordination behaviors of $\mathrm{L^1}$–$\mathrm{L^5}$, it is anticipated that the structures of **1–8** are various. For **1** and **2**, $\mathrm{L^1}$ ligands decorate with metal centers from 1D and 2D $\mathrm{M^{II}}$–oba units as terminal ligands to show the ultimate 1D and 2D structures, respectively. For **3**, **4**, **6** and **7**, $\mathrm{L^2}$–$\mathrm{L^4}$ ligands link various 1D $\mathrm{M^{II}}$–oba units by coordinating to two metal centers as bridges to give different 2D or 3D frameworks, respectively. In **5**, $\mathrm{L^3}$ ligands link the 3D $\mathrm{M^{II}}$–oba unit to exhibit a 3D self-penetrating topological framework. Unexpectedly, $\mathrm{L^5}$ as terminal ligands connect one metal center to show a 1D chain in **8**.

Comparing the structures of **1** and **3**, the result indicates that the neutral bridging ligand ($\mathrm{L^2}$) can link similar $\mathrm{M^{II}}$–oba units (1D $\mathrm{M^{II}}$–oba unit in **1** and **3**) to form higher dimensional structures (1D in **1** and 3D in **3**) than neutral terminal ligand ($\mathrm{L^1}$). A similar change of dimensionalities also occurs in compounds **4**, **6**, and **7**. In **4** and **6**, the similar $\mathrm{M^{II}}$–oba double-chains are pillared by $\mathrm{L^2}$ and $\mathrm{L^3}$ to generate a sheet with the two $\mathrm{Cd^{II}}$ ions distances ($\mathrm{Cd^{II}}$ ions coordinated by the same neutral ligands) of 14.06 and 14.93 Å. The difference of the distance is from the different flexibilities of $\mathrm{L^2}$ and $\mathrm{L^3}$ ligands, so in **6** the semi-flexible $\mathrm{L^3}$ ligands can link the double-chains to give a bigger pore which can accommodate the other isolated $\mathrm{L^3}$ ligand. While the $\mathrm{L^4}$ ligand with a smaller angle can coordinate to two $\mathrm{Cd^{II}}$ ions with the distance of 13.48 Å, which is benefit to form a different structure for **4** and **6**. So the structural characters and coordination modes of five neutral ligands have significant influences on the ultimate structures.

Effect of the weak interactions on the structures

Interestingly, the $\pi\cdots\pi$ stacking interactions in **1**, **2**, **4**, **6** and **8** can link lower polymeric units (1D or 2D) to from higher supramolecular structures (2D or 3D) (Scheme 1). In addition, $\mathrm{L^1}$ donates one hydrogen bond to the carboxylic oxygen atom in **1** and **2**, so interesting 2D and 3D supramolecular structures are finally formed by combining $\pi\cdots\pi$ and hydrogen bonding interactions. In **8**, the hydrogen bonding interactions play an important role on generating higher dimensional structure. And the hydrogen bonds in **8** are formed by water clusters which are different from **1** and **2**. Although there is a hydrogen bond in **4**, it does not assist to form the higher supramolecular structure. So in **4** and **6**, the higher dimensional supramolecular structures are constructed by $\pi\cdots\pi$ stacking interactions. And those are formed by $\pi\cdots\pi$ and hydrogen bonding interactions in **1**, **2** and **8**.



Scheme 1 Schematic view of eight compounds in this work.

Based on the above discussions, many factors, such as the various coordination modes of $\mathrm{oba^{2-}}$ anions, the coordination modes and conformations of different neutral ligands, the radii of metal cations, the versatilities of the metal coordination geometries and $\pi\cdots\pi$ stacking and hydrogen bonding interactions play fundamental roles in the formation of the final products. These factors work together to affect the structures.

Luminescent properties

Luminescent compounds are of great current interest because of their various applications in chemical sensors, photochemistry and electroluminescent display.[25] The photoluminescent spectra of compounds **1–8** and free neutral ligands $\mathrm{L^1}$–$\mathrm{L^5}$ were measured at room temperature (Fig. 9), and the wavelengths of the emission maximums and excitation are listed in Table 2. In comparison with the free ligands, the emission maximums of compounds **1–8** have changed. This may be caused by the charge-transfer transition between ligands and metal centers,[10c,26] and ligand coordinating

Table 2 The wavelengths of the emission maximums and excitation (nm)

Ligand	L^1	L^2	L^3	L^4	L^5			
λ_{em}	504	532	360, 506	547	356, 500			
λ_{ex}	370	370	320	480	320			
Compound	1	2	3	4	5	6	7	8
λ_{em}	379	411	375	398	388	364	382	376
λ_{ex}	320	320	290	310	310	300	290	330

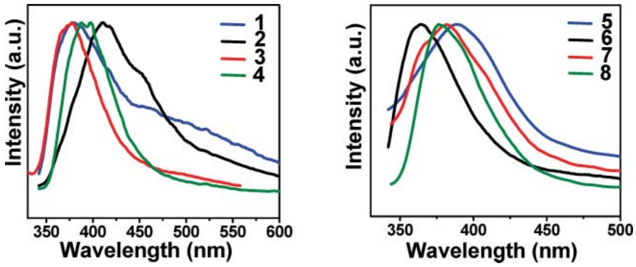


Fig. 9 Solid-state photoluminescent spectra of **1–8** at room temperature.

to the metal center which effectively increases the rigidity of the ligand and reduces the loss of energy by radiation-less decay[27] In all, the emissions of compounds **1–8** may be attributed to a joint contribution of the intra-ligand transitions or charge-transfer transitions between the coordinated ligands and the metal center. These observations indicate that these condensed polymeric materials may be excellent candidates for potential photoactive materials, since they are thermally stable and insoluble in common polar and nonpolar solvents.

Thermal Analysis

In order to characterize the compounds more fully in terms of thermal stability, their thermal behaviors were studied by TGA. The experiments were performed on samples consisting of numerous single crystals of **1–8** under N_2 atmosphere with a heating rate of 10 °C min^{-1}, as shown in Fig. S9 in the ESI.

For compounds **1** and **2**, the weight losses in the range of 33–276 °C for **1** and 37–331 °C for **2** correspond to the removal of the organic components, and the remaining weight corresponds to the formation of ZnO in **1** (obsd 17.9%, calcd 17.4%) and CdO in **2** (obsd 25.4%, calcd 25.0%). The TGA curve of **3** shows that it loses the water molecules from room temperature to 102 °C (obsd 12.4%, calcd 12.7%), and then the anhydrous compound begins to decompose, leading to the formation of zinc oxide as the residue (obsd 15.2%, calcd 14.4%). The TG curve of compound **4** shows a weight loss of 3.7% from room temperature to 96 °C, corresponding to the release of one water molecule (calcd 3.2%). The anhydrous composition begins to decompose at 190 °C and ends above 422 °C. The remaining weight of 22.5% corresponds to the percentage (23.0%) of CdO. For **5**, the decomposition weight loss begins at 262 °C and ends above 517 °C. The remaining weight of 18.4% corresponds to the percentage (18.0%) of ZnO. The TGA curve of **6** shows that it loses the dissociative L^3 ligand from room temperature to 183 °C (obsd 25.8%, calcd 25.8%), and then the remaining composition begins to decompose and lead to the formation of CdO as the residue (obsd 18.1%, calcd 16.9%). For **7** and **8**, the weight loss attributed to the gradual release of water molecules is observed in the range 20–103 °C for **7** and 18–146 °C for **8**, and the decomposition of the residual composition occurs from 194 °C to 492 °C for **7** and 248 °C to 502 °C for **8**, leading to the formation of CdO as the residue (obsd 16.8%, calcd 16.5%) for **7** and (obsd 16.2%, calcd 15.8%) for **8**.

Conclusion

In conclusion, we have been designed and synthesized eight coordination polymers based on analogue bis(pyridyl)imidazole derivatives and 4,4′-oxydibenzoic acid. By careful inspections of the structures of **1–8**, we believe that various bis(pyridyl)imidazole derivatives with different conformation and coordination modes, metal centers with different coordination numbers, 4,4′-oxydibenzoic acid showing various coordination modes and weak interactions (hydrogen bonds and $\pi \cdots \pi$ stacking interactions) have influences on the structures. It is a feasible method to introduce ancillary ligands with different characters to construct coordination polymers with different structural types. It is expected that the integration of novel neutral ligands and multi-carboxylate anion may offer new opportunities to construct new types of MOFs. Investigations in this direction are currently under way.

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References

1 (*a*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*b*) S. Masaoka, S. Furukawa, H.-C. Chang, T. Mizutani and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2001, **40**, 3817; (*c*) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; (*d*) R. S. Rarig, R. Lam, P. Y. Zavalij, J. K. Ngala, R. L. LaDuca, J. E. Greedan and J. Zubieta, *Inorg. Chem.*, 2002, **41**, 2124; (*e*) R. Kitaura, K. Fujimoto, S.-I. Noro, M. Kondo and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2002, **41**, 133; (*f*) M. Kondo, T. Okubo, A. Asami, S.-I. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka and K. Seki, *Angew. Chem., Int. Ed.*, 1999, **38**, 140; (*g*) G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe and J. A. Ripmeester, *Chem. Commun.*, 1999, 461; (*h*) O. R. Evans and W. Lin, *Inorg. Chem.*, 2000, **39**, 2189; (*i*) L. Pan, B. S. Finkel, X. Huang and J. Li, *Chem. Commun.*, 2001, 105; (*j*) V. A. Russell, C. C. Evans, W. Li and M. D. Ward, *Science*, 1997, **276**, 575; (*k*) J. A. Swift, A. M. Privovar, A. M. Reynolds and M. D. Ward, *J. Am. Chem. Soc.*, 1998, **120**, 5887.

2 (*a*) C. Janiak, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1431; (*b*) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (*c*) N. Guillou, Q. Gao, P. M. Forster, P. M. Forster, J.-S. Chang, M. Noguès, S.-E. Park, G. Férey and A. K. Cheetham, *Angew. Chem., Int. Ed.*, 2001, **40**, 2831; (*d*) C.-D. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940; (*e*) G. B. Garder, Y.-H. Kiang, S. Lee, A. Asgaonkar and D. Venkatarman, *J. Am. Chem. Soc.*, 1996, **118**, 6946; (*f*) C.-Y. Su, A. M. Goforth, M. D. Smith, P. J. Pellechia and H.-C. zur Loye, *J. Am. Chem. Soc.*, 2004, **126**, 3576; (*g*) C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158; (*h*) T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 1651; (*i*) M. Dincă, A. F. Yu and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 8904; (*j*) B. D. Chandler, D. T. Cramb and G. K. H. Shimizu, *J. Am. Chem. Soc.*, 2006, **128**, 10403;

(*k*) L. G. Beauvais, M. P. Shores and J. R. Long, *J. Am. Chem. Soc.*, 2000, **122**, 2763; (*l*) A. Rujiwatra, C. J. Kepert, J. B. Claridge, M. J. Rosseinsky, H. Kumagai and M. Kurmoo, *J. Am. Chem. Soc.*, 2001, **123**, 10584; (*m*) L. G. Beauvais and J. R. Long, *J. Am. Chem. Soc.*, 2002, **124**, 12096; (*n*) S. Xiang, X. Wu, J. Zhang, R. Fu, S. Hu and X. Zhang, *J. Am. Chem. Soc.*, 2005, **127**, 16352; (*o*) S. Triki, J. S. Pala, M. Decoster, P. Molinié and L. Toupet, *Angew. Chem., Int. Ed.*, 1999, **38**, 113.

3 (*a*) S. Banfi, L. Carlucci, E. Caruso, G. Ciani and D. M. Proserpio, *J. Chem. Soc., Dalton Trans.*, 2002, 2714; (*b*) H. L. Zhu, Y. X. Tong and X. M. Chen, *J. Chem. Soc., Dalton Trans.*, 2000, 4182; (*c*) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (*d*) M. L. Tong, X. M. Chen, B. H. Ye and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645; (*e*) H. Gudbjarlson, K. M. Poirier and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1999, **121**, 2599; (*f*) C. Y. Su, Y. P. Cai, C. L. Chen, F. Lissner, B. S. Kang and W. Kaim, *Angew. Chem., Int. Ed.*, 2002, **41**, 3371; (*g*) S. Banfi, L. Carlucci, E. Caruso, G. Ciani and D. M. Proserpio, *J. Chem. Soc., Dalton Trans.*, 2002, 2714; (*h*) H. L. Zhu, Y. X. Tong and X. M. Chen, *J. Chem. Soc., Dalton Trans.*, 2000, 4182; (*i*) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (*j*) M. L. Tong, X. M. Chen, B. H. Ye and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645; (*k*) H. Gudbjarlson, K. M. Poirier and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1999, **121**, 2599; (*l*) C. Y. Su, Y. P. Cai, C. L. Chen, F. Lissner, B. S. Kang and W. Kaim, *Angew. Chem., Int. Ed.*, 2002, **41**, 3371; (*m*) Y. Q. Lan, S. L. Li, X. L. Wang, Z. M. Su, K. Z. Shao and E. B. Wang, *Chem. Commun.*, 2007, 4863.

4 (*a*) C. Janiak, *Dalton Trans.*, 2003, 2781; (*b*) O. R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; (*c*) S. R. Batten, *CrystEngComm*, 2001, **18**, 1; (*d*) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176; (*e*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*f*) C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466; (*g*) S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*h*) V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2004, **6**, 377.

5 (*a*) B. Moulton and M. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*b*) M. Du, X.-J. Jiang and X.-J. Zhao, *Inorg. Chem.*, 2006, **45**, 3998; (*c*) F. A. A. Paz and J. Klinowski, *Inorg. Chem.*, 2004, **43**, 3882; (*d*) H. Abourahma, B. Moulton, V. Kravtsov and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2002, **124**, 9990; (*e*) R. Wang, M. Hong, J. Luo, R. Cao, Q. Shi and J. Weng, *Eur. J. Inorg. Chem.*, 2002, 2904; (*f*) K. Biradha, *CrystEngComm*, 2003, **5**, 374; (*g*) S. Varughese and V. R. Pedireddi, *Chem.–Eur. J.*, 2006, **12**, 1597.

6 (*a*) X.-L. Wang, C. Qin, E.-B. Wang, Y.-G. Li, Z.-M. Su, L. Xu and L. Carlucci, *Angew. Chem., Int. Ed.*, 2005, **117**, 5974; (*b*) X.-L. Wang, C. Qin, E.-B. Wang and Z.-M. Su, *Chem.–Eur. J.*, 2006, **12**, 2680; (*c*) M. Kondo, Y. Irie, M. Miyazawa, H. Kawaguchi, S. Yasue, K. Maeda and F. Uchida, *J. Organomet. Chem.*, 2007, **692**, 136; (*d*) K.-S. Burger, P. Chaudhuri, K. Wieghardt and B. Nuber, *Chem.–Eur. J.*, 1995, **1**, 583; (*e*) J.-Q. Liu, Y.-Y. Wang, L.-F. Ma, F. Zhong, X.-R. Zeng, W.-P. Wu and Q.-Z. Shi, *Inorg. Chem. Commun.*, 2007, **10**, 979; (*f*) C.-Y. Sun, S. Gao and L.-P. Jin, *Eur. J. Inorg. Chem.*, 2006, 2411; (*g*) J.-P. Zhang, Y.-Y. Lin, X.-C. Huang and X.-M. Chen, *Eur. J. Inorg. Chem.*, 2006, 3407; (*h*) X.-M. Chen and G.-F. Liu, *Chem.–Eur. J.*, 2002, **8**, 4811; (*i*) G.-F. Liu, Z.-P. Qiao, H.-Z. Wang, X.-M. Chen and G. Yang, *New J. Chem.*, 2002, **26**, 791; (*j*) Z.-B. Han, X.-N. Cheng and X.-M. Chen, *Cryst. Growth Des.*, 2005, **5**, 695; (*k*) J. Tao, J.-X. Shi, M.-L. Tong, X.-X. Zhang and X.-M. Chen, *Inorg. Chem.*, 2001, **40**, 6328; (*l*) M. Kondo, Y. Irie, Y. Shimizu, M. Miyazawa, H. Kawaguchi, A. Nakamura, T. Naito, K. Maeda and F. Uchida, *Inorg. Chem.*, 2004, **43**, 6139.

7 (*a*) L. Beitone, C. Huguenard, A. Gansmuller, M. Henry, F. Taulelle, T. Loiseau and G. Férey, *J. Am. Chem. Soc.*, 2003, **125**, 9102; (*b*) H. W. Roesky and M. Andruh, *Coord. Chem. Rev.*, 2003, **236**, 91; (*c*) S. A. Barnett and N. R. Champness, *Coord. Chem. Rev.*, 2003, **246**, 145; (*d*) L. Pan, D. H. Olson, L. R. Ciemnolonski, R. Heddy and J. Li, *Angew. Chem., Int. Ed.*, 2006, **45**, 616; (*e*) X.-L. Wang, C. Qin, E.-B. Wang, L. Xu, Z.-M. Su and C.-W. Hu, *Angew. Chem., Int. Ed.*, 2004, **43**, 5036; (*f*) Z.-H. Zhang, T.-A. Okamura, Y. Hasegawa, H. Kawaguchi, L.-Y. Kong, W.-Y. Sun and N. Ueyama, *Inorg. Chem.*, 2005, **44**, 6219; (*g*) M. Oh, G. B. Carpenter and D. A. Sweigart, *Acc. Chem. Res.*, 2004, **37**, 1; (*h*) Q.-R. Fang, G.-S. Zhu, Z. Jin, M. Xue, X. Wei, D.-J. Wang and S.-L. Qiu, *Angew. Chem., Int. Ed.*, 2006, **45**, 6126; (*i*) H. Kim, H. Chun, G.-H. Kim, H.-S. Lee and K. Kim, *Chem. Commun.*, 2006, 2759.

8 (*a*) J.-F. Ma, J.-F. Liu, Y. Xing, H.-Q. Jia and Y.-H. Lin, *J. Chem. Soc., Dalton Trans.*, 2000, 2403; (*b*) J.-F. Ma, J.-F. Liu, Y.-C. Liu, Y. Xing, H.-Q. Jia and Y.-H. Lin, *New J. Chem.*, 2000, **24**, 759; (*c*) J.-F. Ma, J. Yang, G.-L. Zheng, L. Li and J.-F. Liu, *Inorg. Chem.*, 2003, **42**, 7531; (*d*) J. Yang, J.-F. Ma, Y.-Y. Liu, S.-L. Li and G.-L. Zheng, *Eur. J. Inorg. Chem.*, 2005, 2174; (*e*) Y. Q. Lan, S. L. Li, X. L. Wang, K. Z. Shao, Z. M. Su and E. B. Wang, *Inorg. Chem.*, 2008, **47**, 529; (*f*) Y. Q. Lan, S. L. Li, Z. M. Su, K. Z. Shao, J. F. Ma, X. L. Wang and E. B. Wang, *Chem. Commun.*, 2008, 58.

9 (*a*) R. F. Ziolo, S. Lipton and Z. Dori, *J. Chem. Soc. D*, 1971, 1124; (*b*) H. D. De Ahna and H. D. Hardt, *Z. Anorg. Allg. Chem.*, 1972, **387**, 61; (*c*) V. W.-W. Yam and K. K.-W. Lo, *Chem. Soc. Rev.*, 1999, **28**, 323.

10 (*a*) B. Chiswell, F. Lions and B. S. Morris, *Inorg. Chem.*, 1964, **3**, 110; (*b*) K. A. Reeder, E. V. Dose and L. J. Wilson, *Inorg. Chem.*, 1978, **17**, 1071; (*c*) S.-L. Li, Y.-Q. Lan, J.-F. Ma, J. Yang, G.-H. Wei, L.-P. Zhang and Z.-M. Su, *Cryst. Growth Des.*, 2008, **8**, 675; (*d*) Y.-Q. Lan, Y.-M. Fu, K.-Z. Shao and Z.-M. Su, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, m2586; (*e*) S.-L. Li, Y.-Q. Lan, J.-F. Ma, J. Fu, Y.-M. Yang, G.-J. Ping, J. Liu and Z.-M Su, *Cryst. Growth Des.*, 2008, **8**, 1610.

11 G. M. Sheldrick, *SHELXS-97, Programs for X-ray Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1997.

12 G. M. Sheldrick, *SHELXL-97, Programs for X-ray Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.

13 L. J. Farrugia, *WINGX, A Windows Program for Crystal Structure Analysis*University of Glasgow, Glasgow, UK, 1988.

14 (*a*) A. Majumder, S. Shit, C. R. Choudhury, S. R. Batten, G. Pilet, D. Luneau, N. Daro, J.-P. Sutter, N. Chattopadhyay and S. Mitra, *Inorg. Chim. Acta*, 2005, **358**, 3855; (*b*) W. Chen, H.-M. Yuan, J.-Y. Wang, Z.-Y. Liu, J.-J. Xu, M. Yang and J.-S. Chen, *J. Am. Chem. Soc.*, 2003, **125**, 9266; (*c*) S. V. Ganesan and S. Natarajan, *Inorg. Chem.*, 2004, **43**, 198; (*d*) S. A. Bourne, J. Lu, B. Moulton and M. J. Zaworotko, *Chem. Commun.*, 2001, 861; (*e*) D. Sun, R. Cao, Y. Liang, Q. Shi, W. Su and M. Hong, *J. Chem. Soc., Dalton Trans.*, 2001, 2335.

15 (*a*) C. J. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885; (*b*) C.-Y. Su, A. M. Goforth, M. D. Smith and H.-C. zur Loye, *Inorg. Chem.*, 2003, **42**, 5685.

16 (*a*) A. J. Carty and N. J. Taylor, *Inorg. Chem.*, 1977, **16**, 177; (*b*) J.-C. Dai, X.-T. Wu, Z.-Y. Fu, C.-P. Cui, S.-M. Hu, W.-X. Du, L.-M. Wu, H.-H. Zhang and R.-Q. Sun, *Inorg. Chem.*, 2002, **41**, 1391; (*c*) R. Wang, M. Hong, J. Luo, R. Cao and J. Weng, *Chem. Commun.*, 2003, 1018; (*d*) X.-J. Luan, X.-H. Cai, Y.-Y. Wang, D.-S. Li, C.-J. Wang, P. Liu, H.-M. Hu, Q.-Z. Shi and S.-M. Peng, *Chem.–Eur. J.*, 2006, **12**, 6281; (*e*) F. A. A. Paz and J. Klinowski, *Inorg. Chem.*, 2004, **43**, 3948; (*f*) R.-Q. Zou, X.-H. Bu and R.-H. Zhang, *Inorg. Chem.*, 2004, **43**, 5382; (*g*) E. Suresh, K. Boopalan, R. V. Jasra and M. M. Bhadbhade, *Inorg. Chem.*, 2001, **40**, 4078.

17 (*a*) A. F. Wells, *Structural Inorganic Chemistry*Clarendon Press, Oxford, 1984; (*b*) A. F. Wells, *Three-Dimensional Nets and Polyhedra* Wiley-Interscience, New York, 1977; (*c*) J. V. Smith, *Chem. Rev.*, 1988, 88, 149; (*d*) J. V. Smith, *Tetrahedral Frameworks of Zeolites, Clathrates and Related Materials*, Landolt-Börnstein New Series IV/14 Subvolume A, Springer, Berlin, 2000; (*e*) M. O'Keeffe, and B. G. Hyde, *Crystal Structures*, I. Patterns, and Symmetry, Mineralogical Society of America, Washington, DC, 1996; (*f*) S. R. Batten, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 820; (*g*) S. R. Batten, B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1995, **117**, 5385; (*h*) B. F. Abrahams, S. R. Batten, M. J. Grannas, H. Hamit, B. F. Hoskins, and R. Robson, *Angew. Chem., Int. Ed.*, 1999, 38, 1475; (*i*) E. Koch and W. Z. Fischer, *Kristallogr*, 1995, **210**, 407.

18 B. F. Abrahams, S. R. Batten, H. Hamit, F. Hoskins and R. Rosbon, *Chem. Commun.*, 1996, 1313.

19 (*a*) K. Biradha and M. Fujita, *Angew. Chem., Int. Ed.*, 2002, **41**, 3392; (*b*) F. Robinson and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1995, 2413; (*c*) O. M. Yaghi and H. L. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295; (*d*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401.

20 (*a*) K. Liu, J. D. Cruzan and R. J. Saykally, *Science*, 1996, **271**, 929; (*b*) J. M. Ugald, I. Alkorta and J. Elguero, *Angew. Chem., Int. Ed.*, 2000, **39**, 717; (*c*) R. Ludwig, *Angew. Chem., Int. Ed.*, 2001, **40**, 1808; (*d*) R. Carballo, B. Covelo, C. Lodeiro and E. M. Vazquez-Lopez, *CrystEngComm*, 2005, **7**, 294; (*e*) D. Li, Y. Wang, X. Luan, P. Liu, C. Zhou, H. Ma and Q. Shi, *Eur. J. Inorg. Chem.*, 2005, 2678; (*f*) U. Mukhopadhyay and I. Bernal, *Cryst. Growth Des.*, 2005, **5**, 1687; (*g*) F. N. Keutsch, J. D. Cruzan and R. J. Saykally, *Chem. Rev.*, 2003, **103**, 2533; (*h*) S. Pal, N. B. Sankaran and A. Samanta, *Angew. Chem.*,

Int. Ed., 2003, **42**, 1741; (*i*) B.-H. Ye, B.-B. Ding, Y.-Q. Weng and X.-M. Chen, *Inorg. Chem.*, 2004, **43**, 6866.

21 G. A. Jeffrey and H. Maluszynska, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1990, **46**, 546.

22 (*a*) C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885; (*b*) C.-Y. Su, A. M. Goforth, M. D. Smith and H.-C. zur Loye, *Inorg. Chem.*, 2003, **42**, 5685.

23 (*a*) X.-L. Wang, C. Qin, E.-B. Wang, Z.-M. Su, X. Lin and S. R. Batten, *Chem. Commun.*, 2005, 4789; (*b*) X. Qu, L. Xu, G. Gao, F. Li and Y. Yang, *Inorg. Chem.*, 2007, **46**, 4775; (*c*) E.-C. Yang, H.-K. Zhao, B. Ding, X.-G. Wang and X.-J. Zhao, *Cryst. Growth Des.*, 2007, **7**, 2009; (*d*) Z. G. Li, G. H. Wang, H. Q. Jia, N. H. Hu, J. W. Xu and S. R. Batten, *CrystEngComm*, 2008, DOI: 10.1039/b807195k.

24 (*a*) V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2004, **6**, 378; (*b*) K. Liang, H. Zheng, Y. Song, M. F. Lappert, Y. Li, X. Xin, Z. Huang, J. Chen and S. Lu, *Angew. Chem., Int. Ed.*, 2004, **43**, 5776; (*c*) K. M. E. Jones, A. H. Mahmoudkhani, B. D. Chandler and G. K. H. Shimizu, *CrystEngComm*, 2006, **8**, 303; (*d*) R.-Q. Zou, Y. Yamada and Q. Xu, *Microporous Mesoporous Mater.*, 2006, **91**, 233; (*e*) M. A. Withersby, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey, A. L. Realf, S. J. Teat and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 2000, 3261; (*f*) X.-J. Li, R. Cao, W.-H. Bi, Y.- Q. Wang, Y.-L. Wang and X. Li, *Polyhedron*, 2005, **24**, 2955; (*g*) Y.-H. Liu, H.-C. Wu, H.-M. Lin, W.-H. Hou and K.-L. Lu, *Chem. Commun.*, 2003, 60; (*h*) J.-P. Zhang, S. Horike and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2007, **46**, 889.

25 (*a*) J. E. McGarrah, Y.-J. Kim, M. Hissler and R. Eisenberg, *Inorg. Chem.*, 2001, **40**, 4510; (*b*) Q. Wu, M. Esteghamatian, N.-X. Hu, Z. Popovic, G. Enright, Y. Tao, M. D'Iorio and S. Wang, *Chem. Mater.*, 2000, **12**, 79; (*c*) G. D. Santis, L. Fabbrizzi, M. Licchelli, A. Poggi and A. Taglietti, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 202.

26 S. L. Li, Y. Q. Lan, J. F. Ma, Y. M. Fu, J. Yang, G. J. Ping, J. Liu and Z. M. Su, *Cryst. Growth Des.*, 2008, **8**, 1610.

27 (*a*) S. L. Zheng, J. H. Yang, X. L. Yu, X. M. Chen and W. T. Wong, *Inorg. Chem.*, 2004, **43**, 830; (*b*) B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, 2002; (*c*) A. W. Adamson, and P. D. Fleischauer, *Concepts of Inorganic Photochemistry*, John Wiley, New York, 1975; (*d*) H. Yersin, and A. Vogler, *Photochemistry and Photophysics of Coordination Compounds*, Springer, Berlin, 1987.