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Reactant ratio-modulated entangled Cd(II) coordination polymers based on rigid tripodal imidazole ligand and tetrabromoterephthalic acid: interpenetration, interdigitation and self-penetration†

Lei Wang,* Zhi-Hao Yan, Zhenyu Xiao, Dong Guo, Wenqiang Wang and Yu Yang

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By adjusting the molar ratio of the reactant metal salt and ligands, three new entangled coordination polymers, $[\mathrm{Cd(tib)(tbta)(H_2O)}]_n$ (**1**) and $[\mathrm{Cd(Htib)(tbta)\cdot Htbta\cdot 2CH_3OH}]_n$ (**2**) and $[\mathrm{Cd_2(tib)_2(tbta)_2(H_2O)\cdot 10H_2O}]_n$ (**3**) (tib = 1,3,5-tris(1-imidazolyl)benzene and H_2tbta = tetrabromoterephthalic acid), have been prepared and structurally characterized by X-ray diffraction analyses. Complex **1** is a 2-fold interpenetrated three-dimensional (3D) 8-connected uninodal net with rare **hex** topology. Complex **2** presents a 2D 6^3-**hcb** network, which is interdigitated with each other to form the 3D supramolecular framework stabilized hydrogen bonds and halogen bonds. Interestingly, an unprecedented hydrogen-bonded $[\mathrm{(Htbta)_2(CH_3OH)_4}]$ cluster was unmasked in the void of **2**. Complex **3** is a complicated 3D self-penetrated framework with a point symbol of $\{4\cdot 6\cdot 8\}\{4\cdot 6^5\cdot 8^4\}\{6^6\}$, which can be seen as a pair of 2-fold interpenetrated networks by breaking bidentate-bridging tib ligand. The comparative study revealed that **1–3** are particularly sensitive to the metal–ligand ratio in this system. The thermal stabilities and photoluminescence behaviors of **1** and **2** were also discussed.

Introduction

Recently, remarkable progress has been witnessed in the study of polymeric coordination networks, or named coordination polymers (CPs), not only due to their aesthetic topology and intriguing structures but also owing to their interesting physical and chemical properties, such as photoluminescence, magnetism, ferroelectricity, gas storage, ion exchange, catalysis, *etc.*[1] It is well known that the construction of CPs mainly depends on the nature of organic spacer and metal ion. In order to obtain novel structures and expected functionality, many crystal engineers have studied the design and synthesis of novel organic ligands, such as multidentated pyridyl, imidazolyl and various carboxylate ligands.[2] However, other factors, such as solvent,[3] temperature,[4] counterion[5] and the molar ratio of reactants[6] also can induce the formation of diverse CPs, which are rarely subjected to systematic investigation, although some sporadic reports have appeared. These variable synthetic parameters give us both opportunities and challenges, that is, more and more novel structures may be obtained through changing the synthetic conditions, at the same time, so many parameters also create obstacles to the exploration of the suitable reaction conditions and prediction of resulting structures.

Although many investigations have been devoted to the above-mentioned fields, the influence of molar ratios on the self-assembly process has been subjected to rare attention.[7] Different reactant ratios may perturb the delicate coordination equilibrium preventing the crystal formation or resulting in a different CPs with respect to the original or expected structure.[8] An enhanced understanding about any potential correlations between reactant ratio and resulting structures of CPs is highly desirable because it may be useful in the synthetic design and the functionalization of new crystalline materials.

On the other hand, both 1,3,5-tris(1-imidazolyl)benzene (tib)[9] and tetrabromoterephthalate (tbta)[10] are rigid organic building blocks with triangular and linear geometries, respectively, which have been proved as versatile linkers to connect metal ions into higher dimensional structures through various coordination modes as well as secondary interactions such as hydrogen bond and halogen bond. Although a search in the CSD (Cambridge Structure Database) survey with the help of ConQuest version 1.3[11] shows 48 and 15 hits based on the tib and tbta ligands, respectively, the study of a combination of them in one CP has not been done yet. In order to further study mixed two kinds of

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College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China. E-mail: inorchemwl@126.com; Fax: +86 532-840-22681

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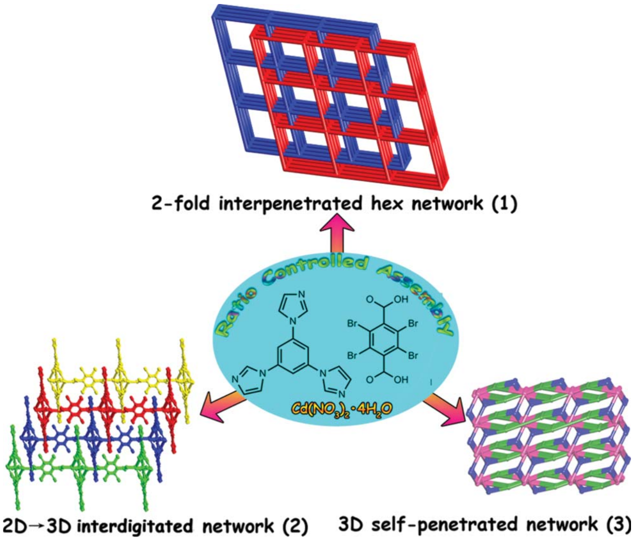

Scheme 1 The three reactant ratio-modulated entangled complexes.

ligands based CPs and investigate the influence of reactant molar ratio on the coordination connectivity and related network, we designed the reactions of them with Cd(II) salt in congener but three different reactant ratios. The fine distinctions of ratio led to three entirely different structures. In this paper, we report three entangled mixed-ligand CPs, $[Cd(tib)(tbta)(H_2O)]_n$ (**1**), $[Cd(Htib)(tbta)\cdot Htbta\cdot 2CH_3OH]_n$ (**2**) and $[Cd_2(tib)_2(tbta)_2(H_2O)\cdot 10H_2O]_n$ (**3**) (tib = 1,3,5-tris(1-imidazolyl)benzene and H_2tbta = tetrabromoterephthalic acid), which range from 2-fold interpenetrated **hex** network to 3D self-penetrated framework (Scheme 1).

Experimental section

General materials and methods

Chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were measured on a Nicolet 330 FTIR Spectrometer at the range of 4000–400 cm^{-1}. Elemental analyses were carried out on a CE instruments EA 1110 elemental analyzer. Photoluminescence spectra were measured on a Hitachi F-7000 Fluorescence Spectrophotometer (slit width: 5 nm; sensitivity: high). X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu Kα radiation. Thermogravimetric analyses were performed on a NETZSCH TG 209 F1 Iris® Thermogravimetric Analyser from 30 to 800 °C at a heating rate 10 °C min^{-1} under the N_2 atmosphere (20 mL min^{-1}).

Syntheses of the complexes 1–3

$[Cd(tib)(tbtpa)(H_2O)]_n$ (1). A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (123.4 mg, 0.4 mmol), tib (110.4 mg, 0.4 mmol) and H_2tbtpa (192.7 mg, 0.4 mmol), KOH (1.2 mg, 0.02 mmol) were dissolved in 10 mL methanol–H_2O (v:v = 1 : 1) in a 25 mL Teflon-lined stainless steel vessel. The mixture was sealed and heated at 120 °C for 4300 min. After the mixture was cooled to room temperature at a rate of 9 °C h^{-1}. The resulting pale yellow block crystals were collected in 89% yield. Elemental analysis: anal. calc. for $C_{23}H_{14}Br_4CdN_6O_5$: C 31.16, H 1.59, N 9.48%. Found: C 31.55, H 1.02, N 9.75%. IR (KBr): $\nu(cm^{-1})$ = 3433 (s), 1613 (s), 1504 (m), 1404 (m), 1331 (m), 1240 (w), 1113 (w), 1072 (w), 1013 (w), 649 (w), 562 (w).

$[Cd(Htib)(tbtpa)\cdot Htbtpa\cdot 2CH_3OH]_n$ (2). Synthesis of **2** was similar to that of **1**, but the ratio of $Cd(NO_3)_2\cdot 4H_2O$/tib/H_2tbtpa is 1 : 1 : 2. Pale-yellow crystals of **2** were obtained in 92% yield. Elemental analysis: anal. calc. for $C_{33}H_{22}Br_8CdN_6O_{10}$: C 28.03, H 1.57, N 5.94%. Found: C 28.79, H. 1.21, N 6.28%. Selected IR peaks (cm^{-1}): 3441 (s), 1615 (s), 1585 (s), 1506 (m), 1382 (s), 1334 (w), 1243 (w), 1073 (w), 1012 (w), 819 (w), 562 (w).

$[Cd_2(tib)_2(tbta)_2(H_2O)\cdot 10H_2O]_n$ (3). Synthesis of **3** was similar to that of **1**, but the ratio of $Cd(NO_3)_2\cdot 4H_2O$/tib/H_2tbtpa is 1 : 1 : 3. Few yellow crystals of **3** were picked up from a large quantity of unidentified white precipitates with a very low yield (below 5%). Due to the extremely low yield, only structure determination was carried out for this complex.

X-ray crystallography

Single crystals of the complexes **1–3** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data were collected on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). The crystal was positioned at 60 mm from the CCD. A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 12 frames each, each frame corresponds to a 0.5° scan in 5 s, followed by spot integration and least-squares refinement. For **1–3**, data were measured using ω scans of 0.5° per frame for 10 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.[12] Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[12] In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97[13] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.[14] Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C atoms. Part of tbta ligand in complex **3** is split over two sites with a total occupancy of 1. There are also some solvent accessible void volumes in the crystals of **3** which are occupied by highly disordered water molecules. No satisfactory disorder model could be achieved, and therefore the SQUEEZE program implemented in PLATON[15] was used to remove these electron densities. All structures were examined using the Addsym subroutine of PLATON to assure that no additional symmetry could be applied to the models. Pertinent crystallographic data collection and refinement parameters are collated in Table 1. Selected bond lengths and angles are collated in Table 2.

Table 1 Crystal data for **1** and **2**

	1	**2**	**3**
Empirical formula	$C_{23}H_{14}Br_4CdN_6O_5$	$C_{33}H_{22}Br_8CdN_6O_{10}$	$C_{46}H_{46}Br_8Cd_2N_{12}O_{19}$
Formula weight	886.44	1414.25	1934.98
Temperature/K	298(2)	298(2)	298(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	10.7437(14)	12.5908(13)	13.5703(10)
b/Å	11.9023(15)	12.7757(14)	14.4080(11)
c/Å	12.0615(16)	13.7370(15)	19.4879(15)
α/°	90.789(2)	86.559(2)	93.9370(10)
β/°	108.826(2)	80.567(2)	109.8560(10)
γ/°	110.710(2)	72.878(2)	93.5050(10)
Volume/Å^3	1351.2(3)	2083.0(4)	3560.8(5)
Z	2	2	2
ρ_{calc}/mg mm^{-3}	2.179	2.255	1.637
m/mm^{-1}	6.769	8.259	5.136
F(000)	844.0	1340.0	1668.0
Reflections collected	6503	10 148	17 054
Independent reflections	4686	7161	12 129
R_{int}	0.0196	0.0280	0.0380
Data/parameters	4686/353	7161/528	12 129/747
Goodness-of-fit on F^2	1.003	0.995	0.959
R indexes [$I > 2\sigma(I)$]	R_1 = 0.0332, wR_2 = 0.0697	R_1 = 0.0382, wR_2 = 0.0792	R_1 = 0.0597, wR_2 = 0.1568
R indexes [all data]	R_1 = 0.0483, wR_2 = 0.0756	R_1 = 0.0674, wR_2 = 0.0889	R_1 = 0.0920, wR_2 = 0.1715

Result and discussion

Synthesis and general characterization

Complexes **1–3** were synthesized by using a mixture of $Cd(NO_3)_2 \cdot 4H_2O$, tib and H_2tbta but with different reactant ratios. The Cd/tib/H_2tbta ratios are 1 : 1 : 1, 1 : 1 : 2 and 1 : 1 : 3 for **1–3**, respectively. Other molar ratios of Cd/tib/H_2tbta were also attempted and did not give satisfactory single crystals or give the single crystals in such a poor yield that they were hard to isolate. We have changed solvents and ratios to improve the yield of **3**, unfortunately, no improvement could be obtained. The single crystals of **1–3** were grown in Teflon-lined stainless steel vessel with programmed warming and cooling process.

Powder X-ray diffraction (PXRD) has been used to check the phase purity of the bulk samples in the solid state. For complexes **1** and **2**, the measured PXRD patterns closely match the simulated patterns generated from the results of single-crystal diffraction data (Fig. S1, ESI†), indicative of pure products. In the IR spectra (Fig. S2, ESI†) of complexes **1** and **2**, the broad peaks at *ca.* 3400 cm^{-1} indicate the presence of water molecules. The IR spectra also show characteristic absorption bands mainly attributed to the asymmetric (ν_{as}: *ca.* 1600 cm^{-1}) and symmetric (ν_s: *ca.* 1385 cm^{-1}) stretching vibrations of the carboxylic groups. No band in the region 1690–1730 cm^{-1}, indicates complete deprotonation of the carboxylic groups,[20] which is consistent with the result of the X-ray diffraction analysis.

Structure descriptions

[Cd(tib)(tbta)(H_2O)]$_n$ (1). X-ray single-crystal diffraction analysis reveals that **1** is a unique 2-fold interpenetrated **hex** network. It crystallizes in the triclinic crystal system with space group of $P\bar{1}$. The asymmetric unit consists of one Cd(II) ion, one tib ligand, one tbta ligand and one coordinated water molecule. As depicted in Fig. 1a, the Cd1 center is six-coordinated by three N atoms from three distinct tib molecules (Cd–N: 2.274(4)–2.359(4) Å), two carboxyl oxygen atoms from two tbta ligands (Cd–O: 2.296(3) and 2.313(3) Å) and one coordinated water (Cd–O_{water}: 2.402(3) Å) to give a slightly distorted CdN_3O_3 octahedral geometry. Both Cd–N and Cd–O bond lengths are well-matched to those observed in similar complexes.[16] Each tib ligand coordinates to three Cd(II) atoms with a non-planar geometry. The three imidazole rings of tib ligand in **1** are inclined to the central benzene ring at dihedral angles of 39.4°, 63.1° and 23.3°, respectively. Due to the steric hindrance of Br atoms, two carboxyl groups of tbta ligand are approximately perpendicular to the central phenyl ring with two small dihedral angles 85.6° and 81.5°, respectively.

The tridentate tib and bidentate tbta link the Cd centers to form a regular 3D porous framework as illustrated in Fig. 1c. It is noteworthy that there are open channels with dimension of *ca.* 11.9 × 10.7 Å in the single 3D net of **1** along the *c* direction, which allows another identical net to penetrate, namely, the entire structure of **2** is a 2-fold interpenetrated 3D framework (Fig. 1e and 1f). A better insight into the nature of this 3D framework can be obtained using the program package TOPOS.[17] Each Cd center connects other eight neighboring Cd centers through three tib and two tbta ligands; hence, each Cd can be regarded as a 8-connected node (Fig. 1b). According to this simplification principle, this 3D network could be simplified to a 8-connected uninodal network with **hex** topology (Fig. 1d) and the short Schläfli symbol for this net is $\{3^6 \cdot 4^{18} \cdot 5^3 \cdot 6\}$. An analysis of the topology of the interpenetration according to a recent classification[18] reveals that **1** belongs to class **IIa**, that is, two interpenetrated nets are generated only by symmetry element (here is inversion center) from the single net. As we know, the 8-connected networks are still in their infancy because the construction of such networks

Table 2 Selected bond lengths (Å) and angles (°) for **1–3**

Complex **1**			
Cd1–N4^{i}	2.274(4)	Cd1–N6^{iii}	2.326(4)
Cd1–O3^{ii}	2.296(3)	Cd1–N1	2.359(4)
Cd1–O2	2.313(3)	Cd1–O1W	2.402(3)
N4^{i}–Cd1–O3^{ii}	91.52(13)	O2–Cd1–N1	78.09(12)
N4^{i}–Cd1–O2	90.15(13)	N6^{iii}–Cd1–N1	90.87(13)
O3^{ii}–Cd1–O2	177.22(12)	N4^{i}–Cd1–O1W	84.82(14)
N4^{i}–Cd1–N6^{iii}	167.22(13)	O3^{ii}–Cd1–O1W	91.06(11)
O3^{ii}–Cd1–N6^{iii}	86.85(12)	O2–Cd1–O1W	86.88(11)
O2–Cd1–N6^{iii}	91.03(13)	N6^{iii}–Cd1–O1W	82.55(13)
N4^{i}–Cd1–N1	101.82(14)	N1–Cd1–O1W	163.50(12)
O3^{ii}–Cd1–N1	103.73(12)		
Symmetry codes: (i) $x, y, z - 1$; (ii) $x, y + 1, z$; (iii) $x + 1, y, z$.			
Complex **2**			
Cd1–O3	2.153(4)	Cd1–N1	2.220(5)
Cd1–N5^{i}	2.198(5)	Cd1–O1	2.239(4)
O3–Cd1–N5^{i}	111.28(17)	O3–Cd1–O1	125.60(16)
O3–Cd1–N1	108.50(18)	N5^{i}–Cd1–O1	100.52(18)
N5^{i}–Cd1–N1	107.23(19)	N1–Cd1–O1	102.23(17)
Symmetry code: (i) $-x + 1, -y, -z + 2$.			
Complex **3**			
Cd1–N1	2.314(6)	Cd2–N12	2.292(7)
Cd1–N10^{i}	2.328(6)	Cd2–O7^{ii}	2.306(6)
Cd1–O1	2.365(5)	Cd2–O5	2.318(6)
Cd1–N7	2.403(7)	Cd2–N6^{iii}	2.320(6)
Cd1–O3	2.407(8)	Cd2–O8B^{iv}	2.383(13)
Cd1–O1W	2.531(7)		
N1–Cd1–N10^{i}	173.0(2)	N7–Cd1–O1W	76.8(2)
N1–Cd1–O1	88.5(2)	O3–Cd1–O1W	159.1(3)
N10^{i}–Cd1–O1	87.1(2)	N12–Cd2–O7^{ii}	95.6(3)
N1–Cd1–N7	90.2(2)	N12–Cd2–O5	174.3(2)
N10^{i}–Cd1–N7	92.0(2)	O7^{ii}–Cd2–O5	87.2(2)
O1–Cd1–N7	159.7(2)	N12–Cd2–N6^{iii}	92.2(2)
N1–Cd1–O3	101.7(3)	O7^{ii}–Cd2–N6^{iii}	106.2(2)
N10^{i}–Cd1–O3	85.2(2)	O5–Cd2–N6^{iii}	91.7(2)
O1–Cd1–O3	116.4(3)	N12–Cd2–O8B^{iv}	84.8(3)
N7–Cd1–O3	83.7(3)	O7^{ii}–Cd2–O8B^{iv}	92.9(3)
N1–Cd1–O1W	85.9(3)	O5–Cd2–O8B^{iv}	90.1(3)
N10^{i}–Cd1–O1W	88.1(2)	N6^{iii}–Cd2–O8B^{iv}	160.9(3)
O1–Cd1–O1W	82.9(2)		
Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $x, y + 1, z$.			

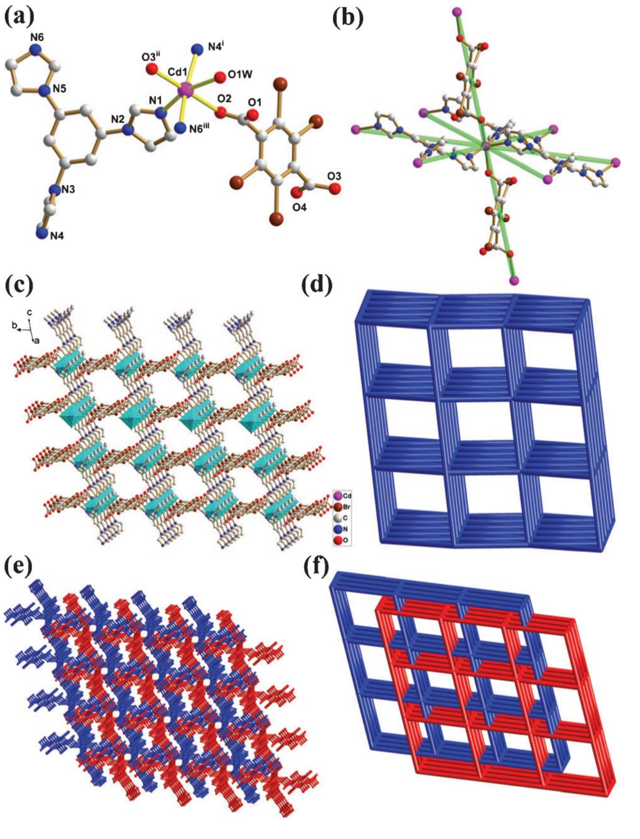

Fig. 1 (a) The coordination environment of Cd(II) ion in **1**. (b) The linking of the 8-connected Cd(II) center in **1**. (c) Ball-and-stick presentation of single 3D framework. (d) Schematic representation of the 8-connected single 3D network with **hex** topology. (e) 2-Fold interpenetrated 3D framework. (f) 2-Fold interpenetrated **hex** network. (Symmetry codes: (i) $x, y, z - 1$; (ii) $x, y + 1, z$; (iii) $x + 1, y, z$.)

is rigorously hampered both by the number of available coordination sites and by the sterically demanding nature of the rigid ligands.[19] For 8-connected networks, the 8-connected nodes often are highly coordinated rare earth ions[20] or polynuclear metal building blocks,[21] however, using single metal center as node to construct the 8-connected network is still rare. Moreover, the most commonly encountered 8-connected network is **bcu**-type (CsCl) net,[22] but the **hex** network, especially the interpenetrated example is relatively scarce.[23] Recently, Ma and Batten reported a pair of interesting supramolecular isomers, and one of them is the first 3-fold interpenetrated **hex** network based on dinuclear Co(II) building blocks.[24]

[Cd(Htib)(tbta)·Htbta·2CH$_3$OH]$_n$ (2). Structural analysis of complex **2** indicates an interesting 2D → 3D interdigitated network based on 2D 6^3-**hcb** net. Complex **2** also crystallizes in the triclinic $P\bar{1}$ space group. The asymmetric unit of **2** is composed of one crystallographically independent Cd(II) ion, one Htib ligand, two half coordinated tbta ligands lying about inversion centres, one whole guest Htbta molecule and two lattice methanol molecules. As shown in Fig. 2a, the Cd1 is located in a rare tetrahedral geometry, completed by two N atoms belonging to two different Htib ligands and two O atoms of two tbta ligands. The average Cd–O and Cd–N distances are 2.196(4) and 2.209(5) Å. The bond angles around Cd1 range from 100.52(18) to 125.60(16)°. The distortion of the tetrahedron can be indicated by the calculated value of the τ_4 parameter introduced by Houser[25] to describe the geometry of a four-coordinate metal system, which is 0.87 (for ideal tetrahedron τ_4 = 1). As we know, the most encountered coordination geometry for Cd(II) is six-coordinated octahedron, while the four-coordinated tetrahedral geometry is very rare.[26] The search in the CSD survey shows 4992 hits for six-coordinated Cd(II) complexes, but only 1256 hits (25%) for four-coordinated Cd(II) complexes. It is noteworthy that the Htib ligand coordinates with two, rather than three like in **1**, Cd(II) atoms using two of its three imidazole groups, and the third one with N4 was protonated and did not participate in the coordination, which has been observed previously.[27] The average dihedral angle formed between central phenyl ring and three terminal imidazole groups is 29.1°.

The bidentate Htib and tbta ligands link the tetrahedral Cd(II) centers to form an infinite 2D network with typical 6^3-

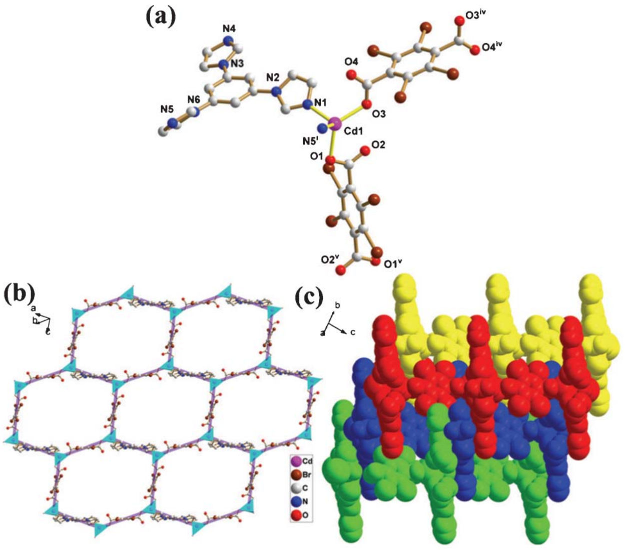

Fig. 2 (a) The coordination environment of Cd(II) ion in **2**. (b) Ball-and-stick presentation of the 2D 6^3-**hcb** net. (c) Space-filling view of the 2D → 3D interdigitated motif of **2**. (Symmetry codes: (i) *x*, *y*, *z* − 1; (ii) *x*, *y* + 1, *z*; (iii) *x* + 1, *y*, *z*.)

hcb net which contains large windows with the pore size of 22.2 × 24.5 Å (Fig. 2b). The phenyl and one of three imidazole groups are out of the plane defined by the 6^3-**hcb** net, causing the large aperture, which allowed the protuberant groups to embed, forming the resulting 2D → 3D interdigitated network (Fig. 2c). There are still large voids in spite of interdigitation. Interestingly, an unprecedented hydrogen-bonded $[(Htbta)_2(CH_3OH)_4]$ cluster (Fig. 3a) was unmasked in the remaining voids and consolidated through type-I C–O⋯Br halogen bond[28] with Br2⋯O7, Br6⋯O1 and Br7⋯O4 contacts of 2.980(5), 2.864(5) and 2.967(5) Å, respectively, which are *ca.* 12% shorter than the sum of Br and O van der Waals radii (3.37 Å) (Fig. 3b).[29]

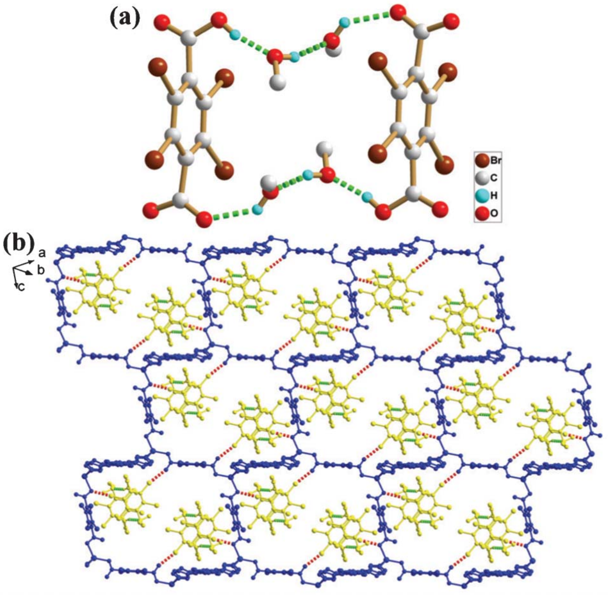

Fig. 3 (a) The hydrogen-bonded $[(Htbta)_2(CH_3OH)_4]$ cluster in **2**. (b) The halogen bonding between 2D network and $[(Htbta)_2(CH_3OH)_4]$ cluster. (Halogen bond and hydrogen bond are highlighted by red and green dashed lines.)

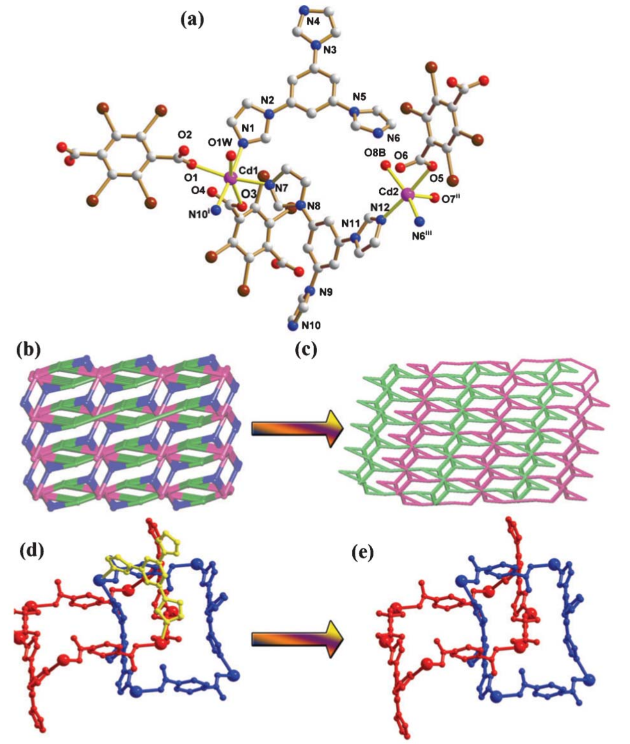

Fig. 4 (a) The coordination environment of Cd(II) ion in **3**. (b) View of 3D framework with 3-nodal 3,4,5-connected topology (purple: 5-connected Cd node; green: 4-connected Cd node; blue: 3-connected tib node). (c) The 2-fold interpenetrated 3,3,4-connected network by breaking bidentate-bridging tib ligand. (d) View of the details of self-interpenetration by the bidentate tib ligand highlighted by yellow. (e) Formation of the interpenetration by omitting the bidentate tib ligand. (Symmetry codes: (i) −*x* + 2, −*y* + 1, −*z* + 1; (ii) −*x* + 1, −*y* + 1, −*z* + 1; (iii) −*x* + 1, −*y* + 2, −*z* + 1; (iv) *x*, *y* + 1, *z*.)

$[Cd_2(tib)_2(tbta)_2(H_2O)\cdot 10H_2O]_n$ (3). Complex **3** is an intricate 3D self-penetrated network. As shown in Fig. 4a, the asymmetric unit of **3** contains two crystallographically unique Cd(II) ion, two tib ligands, one whole tbta ligand and two half tbta ligands lying about inversion centres, one coordinated water molecules and lattice water molecules in a severely disordered fashion. Two Cd(II) centers are in different coordination geometries. The Cd1 locates in a distorted octahedral geometry, completed by three imidazole N atoms, two carboxyl O atoms and one water molecule. The Cd2 is coordinated by two tib and three tbta ligands, giving a distorted square-pyramidal geometry. The distortion of the CdO_5 square-pyramid is indicated by the calculated value of the τ_5 factor,[30] which is 0.22 for Cd2 (for ideal square-pyramidal geometry, τ_5 = 0). Both Cd–N and Cd–O bond lengths are in the normal ranges. The imidazole ring planes deviate from the benzene ring planes with dihedral angles ranging from 9.1 to 36.8°. Two crystallographically unique tib ligands show bidentate and tridentate coordination modes, respectively.

The Cd(II) ions are bridged by tib and tatb ligands to form a complicated 3D framework. The most striking structural feature of **3** is a self-penetrating net. The topology may be described in terms of two kinds of mononuclear Cd(II) centers as 4- and 5-connected nodes and the tridentate tib ligand as a 3-connected node. Notably, the 2-connected tib and tbta ligands are not ascribed to any node. So the overall 3D framework belongs to a new 3-nodal 3,4,5-connected network with short Schläfli symbol being $\{4{\cdot}6{\cdot}8\}\{4{\cdot}6^5{\cdot}8^4\}\{6^6\}$ (Fig. 4b). To further understand this complicated structure of **3**, we deleted the bidentate tib ligand which bridges a pair of adjacent networks, generating a 2-fold interpenetrated network (Fig. 4c). Due to the reduction of the coordination number of the Cd(II) center, the topology of the 2-fold interpenetrated network becomes a 3-nodal 3,3,4-connected network with short Schläfli symbol of $\{4{\cdot}6{\cdot}8^3{\cdot}10\}\{4{\cdot}6{\cdot}8\}\{6{\cdot}8^2\}$. Therefore, the framework of **3** is clearly a self-penetrating net and can be considered as derived from cross-linking of 2-fold interpenetrated nets *via* bidentate tib ligand (Fig. 4d and 4e). An analysis of the interpenetrated topology with the TOPOS program suggests that this network belongs to class **Ia**, that is, both the interpenetrated nets are generated only by translation and the translating vector is the crystallographic *b* axis (14.4080(11) Å).

Comparison of the structures of 1–3: reactant molar ratio effect

A comparison of three CPs demonstrates that the reactant molar ratio remarkably affects the resulting motifs in this system. When the Cd/tib/H_2tbta ratios are changed from 1 : 1 : 1 to 1 : 1 : 3, we obtained three different infinite motifs varying from 2-fold interpenetrated **hex** network, 2D → 3D interdigitated 6^3-**hcb** network to 3D self-penetrated framework. Although the tbta ligand shows the identical μ_2-η^1:η^1 coordination fashion in **1–3**, but the coordination modes of tib ligand have important variations, these are tridentate, bidentate, and tridentate + bidentate modes for **1–3**, respectively. Due to the different bridging effects of tib ligand, three different infinite motifs ranging from 2-fold interpenetrated **hex** network, 2D → 3D interdigitated network, to 3D self-penetrated framework were observed. Therefore, the diversity of coordination modes of tib plays a central role in the final structures of **1–3**, when changing metal–ligand ratios.

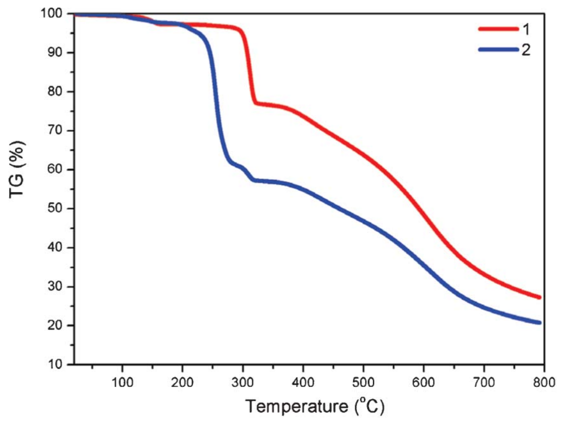

Fig. 5 TGA curves for CPs **1** and **2**.

Thermal analysis

The thermogravimetric (TG) measurements were performed in N_2 atmosphere on polycrystalline samples of complexes **1** and **2** and the TG curves are shown in Fig. 5. The TGA curve of **1** displays a weight loss of 2.87% (calcd: 2.04%) at 110–161 °C, corresponding to the loss of coordinated water molecules. The framework is stable up to 286 °C. Then, the framework starts to collapse, accompanying the release of ligands. Complex **2** shows a first weight loss of 3.61% at 93–155 °C, corresponding to the loss of lattice methanol molecules (calcd: 4.53%). The second weight loss of 35.12% corresponds to the decomposition of uncoordinated Htbta molecule (calcd: 33.99%). And then the framework begins to collapse, accompanying the release of organic ligands.

Photoluminescence properties

The photoluminescence spectra of complexes **1** and **2** are shown in Fig. 6. The free ligand tib displays photoluminescence with emission maxima at 405 nm (λ_{ex} = 360 nm).[31] It can be presumed that this peak originate from the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions. Upon complexation of these ligands with Cd(II) ion, intense emissions are observed at 410 and 423 nm (λ_{ex} = 330 nm) for **1** and **2**, respectively. The resemblance between the emissions of **1** and **2** and those of the free tib indicates that the emissions of **1** and **2** are probably due to the intraligand (IL) $\pi \rightarrow \pi^*$ transitions modified by metal coordination.[32] And the observed small red shift of the emission maximum between the complexes and the ligand was attributed the influence of the coordination of the ligand to the metal atom.

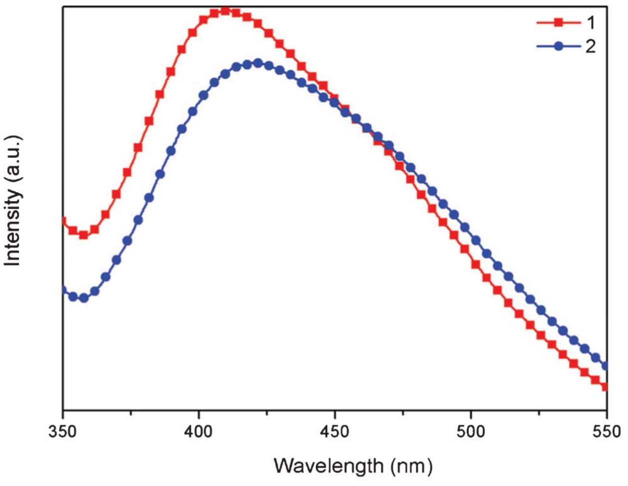

Fig. 6 Photoluminescence spectra of complexes **1** and **2**.

Conclusions

In conclusion, we have fabricated three new entangled Cd(II) CPs using a mixed-ligand strategy. By adjusting the molar ratio of the reactants metal salt and ligands from 1 : 1 : 1 to 1 : 1 : 3, the entangled CPs evolved from a rare 2-fold interpenetrated **hex** framework, 2D → 3D interdigitated 6^3-**hcb** network to 3D self-penetrated framework. Furthermore, the thermal stabilities and photoluminescence behaviors of **1** and **2** were also discussed.

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