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Supramolecular isomeric flat and wavy honeycomb networks: additive agent effect on the ligand linkages†

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Two genuine supramolecular isomers of Cd(II) coordination polymers with an identical formula of $[Cd(pptp)(ox)]_n$ (**1a** and **1b**) (pptp = 2-(3-(4-(pyridin-4-yl)phenyl)-1*H*-1,2,4-triazol-5-yl)pyridine, H_2ox = oxalic acid) have been hydrothermally synthesized and characterized. Both compounds possess the rod-like binuclear $[Cd_2(pptp)_2]$ subunit, which are linked by the ox ligand to afford either a flat or wavy two-dimensional (2D) 6^3-**hcb** network, depending upon whether the additive agent is used for the reaction. The photoluminescence behaviour of the compounds was also discussed.

1. Introduction

In a state-of-the-art investigation on supramolecular chemistry and crystal engineering, especially in the field of coordination polymers, a sought-after goal is the supramolecular isomerism, which was firstly coined by Zaworotko.[1] Subsequently, in an extensive review,[2] they classified supramolecular isomers into four types, namely, structural, conformational, catenane (also known as topological) and optical isomerism. Following this pursuit, the Chen group have achieved significant advances and emphasized the significance of genuine supramolecular isomerism in their recent review.[3] Supramolecular isomers have different network structures, but the whole crystals or the coordination networks have the same chemical composition.[4] The occurrence of supramolecular isomerism indicates that the free energy gaps between different crystalline forms are small and the kinetic factors are responsible for the crystal growth, and thus the generation of supramolecular isomers depends on the subtle variation of assembly environments, such as solvent, reaction temperature and concentration effect.[5] Although these factors have been well-recognized in a number of examples,[6] the control of the supramolecular isomers accompanying the change of coordination modes of one or more components by the additive agent is still scarce.[7] For example, Du and coworkers reported one elegant case in which two supramolecular isomers, discrete bimetallocycle and infinite helical chain, were formed under the induction of different organic acids as additive agents.[7a] On the other hand, many so-called supramolecular isomers are based on the coexistence of different guest molecules, which produce different chemical compositions; thus, it would be more suitable to categorize these coordination polymers as pseudo-polymorphs rather than genuine isomers.[8] In contrast, genuine supramolecular isomers have been only sporadically reported.[9]

Our previous work has indicated that the 2-(3-(4-(pyridin-4-yl)phenyl)-1*H*-1,2,4-triazol-5-yl)pyridine (pptp) ligand has multiple coordination sites, such as $N_{pyridine}$ and $N_{triazole}$, and have both bridging and chelating coordination modes to bind metal centers.[10] The diverse binding modes of the oxalate are also quite favorable to the construction of various networks.[11] Based on the above-mentioned points and our previous work, we combined pptp and ox ligands in a Cd(II) coordination polymer system, and two genuine supramolecular isomers $[Cd(pptp)(ox)]_n$ (**1a** and **1b**) (pptp = 2-(3-(4-(pyridin-4-yl)phenyl)-1*H*-1,2,4-triazol-5-yl)pyridine, H_2ox = oxalic acid) were obtained. Both compounds are either a flat or wavy two-dimensional (2D) 6^3-**hcb** networks, depending upon whether the additive agent is used for the reaction (Scheme 1).

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. without further purification. C, N, and H analyses were performed on an EA1110 CHNS-0 CE 65 elemental analyzer. IR (KBr pellet) spectra were recorded on a Nicolet Magna750FT-IR spectrometer. Powder-XRD measurements

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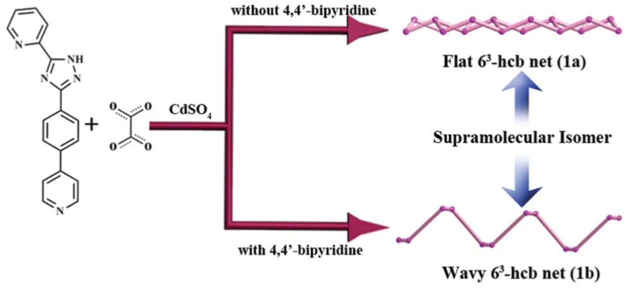
† Electronic supplementary information (ESI) available: The preparation of compounds **1a** and **1b**, Tables S1 and S2, IR, TGA and powder XRD patterns. X-ray crystallographic files in CIF format for the **1a** and **1b**. CCDC 898678 and 898679. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce26386f



Scheme 1 Synthetic procedures of two supramolecular isomers.

were recorded on a D/Max-2500 X-ray diffractometer using Cu Kα radiation. The fluorescent spectra were measured on an F-4500 FL Spectrophotometer. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C thermal analyzer from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

2.2. Syntheses

2.2.1. SYNTHESIS OF 1A. A mixture of Cadmium(II) sulfate octahydrate (51.2 mg, 0.067 mmol), pptp (60 mg, 0.20 mmol), oxalic acid (36 mg, 0.40 mmol), sodium hydroxide (16 mg, 0.40 mmol) and 14 mL of H_2O were sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 170 °C for 3 days, and then slowly cooled to room temperature. Colorless crystals of 1 were obtained in 67% yield. Elemental analysis (%): calcd for $C_{20}H_{13}N_5O_4Cd$ (499.75): C 48.02, H 2.60, N 14.01; found: C 47.68, H 2.71, N 13.92. IR (KBr pellet, cm^{-1}): 1615 (vs), 1453 (m), 1300 (s), 1161 (m), 977 (w), 824 (m), 778 (m).

2.2.3. SYNTHESIS OF 1B. The procedure was similar to the preparation of **1a**, except that 4,4′-bipyridine (35 mg, 0.20 mmol) was used as an additive agent. Pale yellow crystals of **1b** were obtained in 59% yield. Elemental analysis (%): calcd for $C_{20}H_{13}N_5O_4Cd$ (499.75): C 48.02, H 2.60, N 14.01; found: C 47.84, H 2.79, N 13.74. IR (KBr pellet, cm^{-1}): 1599 (vs), 1461 (m), 1400 (m), 1300 (w), 1154 (m), 970 (w), 809 (m), 755 (m).

3. Results and discussion

3.1. X-Ray crystallography

Single crystals of the complexes **1a** and **1b** with appropriate dimensions were chosen under an optical microscope and mounted on a glass fiber for data collection. Single-crystal X-ray diffraction was performed using a Bruker Apex II CCD diffractometer equipped with a fine-focus sealed-tube X-ray source (Mo Kα radiation, graphite monochromated). In both cases, the highest possible space group was chosen. Both structures were solved by direct methods using SHELXS-97[12] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.[13] 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. Both structures were examined using the Addsym subroutine of PLATON[14] 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 for **1a** and **1b** are collated in Table 2.

Table 1 Crystal data for **1a** and **1b**

Empirical formula	$C_{20}H_{13}CdN_5O_4$	$C_{20}H_{13}CdN_5O_4$
Formula weight	499.75	499.75
Temperature/K	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	8.6361(11)	9.955(6)
b/Å	10.8402(15)	19.393(11)
c/Å	19.795(3)	10.077(6)
α (°)	90.00	90.00
β (°)	95.624(3)	108.590(11)
γ (°)	90.00	90.00
Volume/Å^3	1844.3(4)	1843.9(18)
Z	4	4
ρ_{calc}/mg mm^{-3}	1.800	1.800
μ/mm^{-1}	1.225	1.225
F(000)	992.0	992.0
Crystal size/mm^3	0.46 × 0.18 × 0.15	0.36 × 0.25 × 0.21
2θ range for data collection (°)	4.14 to 50	4.2 to 50
Index ranges	$-10 \leqslant h \leqslant 9, -12 \leqslant k \leqslant 12, -19 \leqslant l \leqslant 23$	$-11 \leqslant h \leqslant 10, -23 \leqslant k \leqslant 22, -11 \leqslant l \leqslant 10$
Reflections collected	9116	9213
Independent reflections	3246 [R_{int} = 0.0323]	3221 [R_{int} = 0.0506]
Data/restraints/parameters	3246/0/271	3221/0/271
Goodness-of-fit on F^2	0.989	0.915
Final R indexes [$I > = 2\sigma (I)$]	R_1 = 0.0251, wR_2 = 0.0549	R_1 = 0.0358, wR_2 = 0.0704
Final R indexes [all data]	R_1 = 0.0309, wR_2 = 0.0560	R_1 = 0.0464, wR_2 = 0.0740
Largest diff. peak/hole/e Å^{-3}	0.32/−0.56	0.74/−0.97

Table 2 Selected bond lengths (Å) and angles (°) for **1a** and **1b**

Complex **1a**^{a}

Cd1–O2^{i}	2.325(2)	Cd1–N5^{ii}	2.382(2)
Cd1–O3	2.3546(18)	Cd1–N1	2.422(2)
Cd1–N2	2.358(2)	Cd1–O1	2.4423(19)
Cd1–O4^{i}	2.3718(19)		
O2^{i}–Cd1–O3	71.78(6)	O3–Cd1–N1	84.14(7)
O2^{i}–Cd1–N2	143.77(7)	N2–Cd1–N1	70.07(8)
O3–Cd1–N2	135.15(7)	O4^{i}–Cd1–N1	100.95(7)
O2^{i}–Cd1–O4^{i}	69.99(6)	N5^{ii}–Cd1–N1	168.89(8)
O3–Cd1–O4^{i}	141.71(6)	O2^{i}–Cd1–O1	137.67(7)
N2–Cd1–O4^{i}	80.61(7)	O3–Cd1–O1	68.15(6)
O2^{i}–Cd1–N5^{ii}	96.37(8)	N2–Cd1–O1	77.63(7)
O3–Cd1–N5^{ii}	98.53(7)	O4^{i}–Cd1–O1	147.29(6)
N2–Cd1–N5^{ii}	101.06(8)	N5^{ii}–Cd1–O1	76.92(8)
O4^{i}–Cd1–N5^{ii}	83.69(8)	N1–Cd1–O1	94.27(7)
O2^{i}–Cd1–N1	94.71(8)		

^{a} Symmetry codes: (i) $-x + 2$, $y - 1/2$, $-z + 1/2$; (ii) $-x + 1$, $-y + 1$, $-z$.

Complex **1b**^{b}

Cd1–O1	2.249(3)	Cd1–N5^{ii}	2.342(3)
Cd1–O2^{i}	2.285(3)	Cd1–N2	2.383(3)
Cd1–O4^{i}	2.292(3)	Cd1–N1	2.385(3)
O1–Cd1–O2^{i}	164.49(9)	O4^{i}–Cd1–N2	165.99(10)
O1–Cd1–O4^{i}	93.28(10)	N5^{ii}–Cd1–N2	94.96(11)
O2^{i}–Cd1–O4^{i}	71.71(10)	O1–Cd1–N1	91.38(11)
O1–Cd1–N5^{ii}	85.07(11)	O2^{i}–Cd1–N1	96.09(11)
O2^{i}–Cd1–N5^{ii}	91.14(11)	O4^{i}–Cd1–N1	104.50(11)
O4^{i}–Cd1–N5^{ii}	90.93(11)	N5^{ii}–Cd1–N1	164.36(11)
O1–Cd1–N2	99.87(10)	N2–Cd1–N1	70.60(11)
O2^{i}–Cd1–N2	95.43(10)		

^{b} Symmetry codes: (i) x, $-y + 1/2$, $z + 1/2$; (ii) $-x + 2$, $-y$, $-z + 2$.

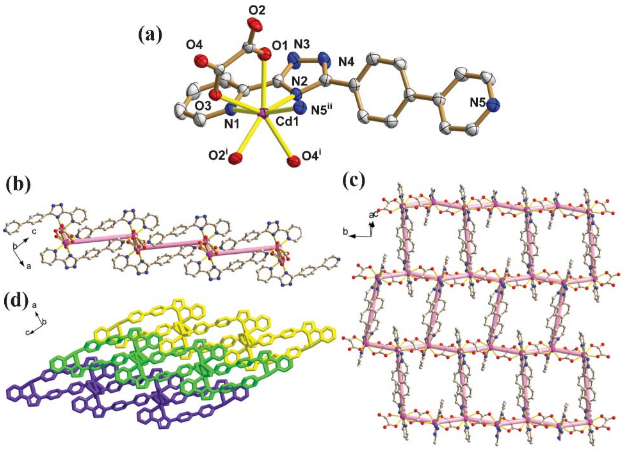


Fig. 1 (a) ORTEP representation of **1a** showing the local coordination environment around the Cd(II) center with 50% thermal ellipsoid probability. (Symmetry codes: (i) $-x + 2$, $y - 1/2$, $-z + 1/2$; (ii) $-x + 1$, $-y + 1$, $-z$.) (b) and (c) Ball-and-Stick representation of the flat 2D 6^3-**hcb** network along different directions. (e) Perspective view of the packing structure of 2D flat networks.

3.2. Synthesis and general characterization

Colorless crystals of **1a** and pale yellow **1b** were synthesized by solvothermal reaction of $CdSO_4 \cdot 6H_2O$, pptp and H_2ox in a similar process, but without and with 4,4′-bipyridine as an additive agent, respectively (see ESI†). Phase purity of **1a** and **1b** is supported by the powder X-ray diffraction patterns (Fig. S1, see ESI†). For **1a** and **1b**, most of the peak positions of simulated and experimental patterns are in good agreement with each other. The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples. The solid FT-IR spectra (Fig. S2, see ESI†) of **1a** and **1b** show characteristic absorption bands for carboxyl groups. Compared to the IR spectra of **1a** and **1b**, the spectra of **1a** and **1b** demonstrate slight but significant differences, due to somewhat different coordination modes of oxalate ligands [bis(bidentate)-chelating *vs.* bidentate + monodentate bridging, respectively].[15]

3.3. Structure description of 1a

The crystal structure of **1a** was determined by single-crystal X-ray diffraction analysis (see ESI†). Complex **1a** crystallizes in the monoclinic space group of $P2_1/c$ with an asymmetric unit that contains one Cd(II) ion, one pptp ligand, and one ox dianion. As shown in Fig. 1a, the Cd1 is seven-coordinated by four O atoms from two ox ligands and three N atoms from two pptp ligands, displaying a distorted pentagon-bipyramidal geometry. Both Cd–N (2.358(2)–2.422(2) Å) and Cd–O (2.325(2)–2.4423(19) Å) bond lengths are well-matched to those observed in similar complexes.[16] The pair of pptp ligands with a μ_3-bridging + chelating mode bind two Cd(II) centers to form a rod-like binuclear $[Cd_2(pptp)_2]$ subunit, which is further extended by $\mu_{1,2,3,4}$-ox ligand to form the resulting 2D network. To better understand the structure of **1a**, the topological analysis approach is employed. If all nodes in one net have identical connectivity, then, according to Wells, it is a *platonic uniform net* and can be represented by the symbol (n, p), where n is the size of the shortest circuit and p is the connectivity of the nodes.[17] In the sheet of **1a**, all Cd(II) ions are 3-connecting and the shortest circuit is a six-membered ring. So this 2D sheet can be simplified to a 6^3-**hcb** net with the window size of *ca.* 15.1 × 17.1 Å (Fig. 1b and 1c). The adjacent nets further interdigitated with each other to form the resulting 3D supramolecular framework (Fig. 1d) through classic N–H···O hydrogen bonds (2.724(3) Å). We previously obtained a 2D → 2D interpenetrated 6^3-**hcb** network with the window dimensions of 21.3 × 25.1.[18] However, no interpenetration was observed in **1a**, which may be caused by the relatively smaller window dimensions in **1a** precluding the insertion of rods of an adjacent window.

3.4. Structure description of 1b

The supramolecular isomeric 2D network of **1b** was obtained under similar reaction conditions but with 4,4′-bipyridine as an additive agent. Single-crystal X-ray analysis revealed that it crystallized in the same space group to that of **1a** and the asymmetric unit of **1b** consists of completely identical components to those in **1a**. In contrast to **1a**, the coordination geometry of Cd(II) in **1b** is a six-coordinated octahedron, completed by three O atoms and three N atoms (Fig. 2a). The similar rod-like binuclear $[Cd_2(pptp)_2]$ subunits also exist in **1b**, which were connected by $\mu_{1,2,3}$-ox ligands to form the resulting 2D 6^3-**hcb** net (Fig. 2c). The different arrangement of

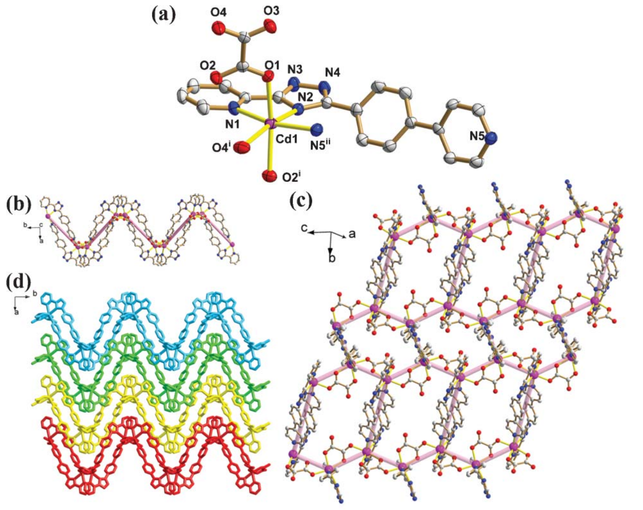


Fig. 2 (a) ORTEP representation of **1b** showing the local coordination environment around the Cd(II) center with 50% thermal ellipsoid probability. (Symmetry codes: (i) x, $-y + 1/2$, $z + 1/2$; (ii) $-x + 2$, $-y$, $-z + 2$.) (b) and (c) Ball-and-Stick representation of the wavy 2D 6^3-**hcb** network along different directions. (e) Perspective view of the packing structure of 2D wavy networks.

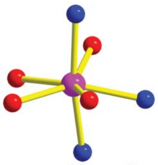
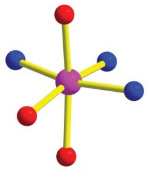
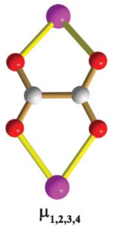
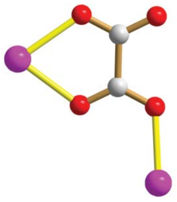
the two ox ligands around one Cd(II) center in **1a** and **1b** made the resultant 6^3-**hcb** nets different in their geometries. The 2D net in **1b** is more corrugated than that in **1a**, reflecting a large dihedral angle of 86.99° between adjacent hexagons (Fig. 2b). The 2D nets in **1b** pack into a 3D supramolecular framework with a 'peak-and-valley' mode (Fig. 2d). Another noteworthy point is the unusual $\mu_{1,2,3}$ coordination mode of the ox ligand. As we know, the more frequently encountered coordination modes of ox are $\mu_{1,2,3,4}$, $\mu_{1,2}$, $\mu_{1,1,2}$ and $\mu_{1,1,2,3}$, however, the ox ligand acting as a $\mu_{1,2,3}$-tridentate bridging ligand is scarce.[19] As indicated by a CSD (Cambridge Structure Database) survey with the help of ConQuest version 1.3,[20] only 45 hits among 2440 ox-based coordination compounds show the $\mu_{1,2,3}$-mode.

To the best of our knowledge, most of the supramolecular isomers reported so far usually show networks with completely different geometries or topologies.[21] One representative example is isomeric binary silver(I)–imidazolates with a stoichiometry of 1 : 1 metal : ligand molar ratio based on 2D 6^3-**hcb** and 4^4-**sql** networks.[22] Recently, silver(I)–2-methylimidazolates including isomeric zigzag chains, helical chain, and S-shaped chain were also unmasked by the same group.[7b] The Zaworotko group also showed two supramolecular isomers based on the identical paddlewheel secondary building units (SBUs) but with Kagomé and NbO topologies, induced by different solvents.[23] However, only a few examples of supramolecular isomers based on networks with the same topology have been reported.[24] The Chen group reported a pair of supramolecular isomers showing 3D frameworks with the same eight-connected **bcg** topology but different magnetic behaviour due to the slightly different linear trinuclear $Co_3(RCOO)_8$ SBU.[24a] Hence, **1a** and **1b** presented here are an unprecedented example showing supramolecular isomerism based on networks with the same 6^3-**hcb** topology.

3.5. Structural comparison of 1a and 1b

1a and **1b** are genuine supramolecular isomers having identical chemical compositions for not only the coordination network but also the whole crystal. Although, topologically, both **1a** and **1b** are 2D 6^3-**hcb** nets, there are three different characters for **1a** and **1b**: (i) coordination geometry of the central Cd(II) ion, pentagon-bipyramid *vs.* octahedron; (ii) ox linkage fashion, $\mu_{1,2,3,4}$ *vs.* $\mu_{1,2,3}$; (iii) flat *vs.* wavy network (Table 3). As described above, both the conformation and coordination mode of the pptp are very similar in **1a** and **1b**, resulting in the same rod-like binuclear $[Cd_2(pptp)_2]$ subunit, within slight differences due to the rotation of C–C single bonds, hence, such negligible geometric differences are not

Table 3 Comparison of coordination geometry of Cd(II) ion and coordination modes of ox ligand in **1a** and **1b**[a]

	1a	1b
Cd(II)	 pentagon-bipyramid	 octahedron
ox	 $\mu_{1,2,3,4}$	 $\mu_{1,2,3}$

[a] purple: Cd; red: O; blue: N.

sufficient in determining the formation of supramolecular isomers. In contrast, different coordination modes of the ox ligand can cause rather drastic differences in the coordination geometry of the metal centers as well as the bonding direction of it, which should be the key factor in the formation of a flat or wavy 2D net. So, the formation of supramolecular isomers in this system is dominated by the ox ligand linkages, which is influenced by whether the 4,4′-bipyridine is used as an additive agent in the reaction. In fact, the isomerism arising from the 4,4′-bipyridine is fortuitously observed since the additive is not incorporated in the final crystalline product of **1b**. This fact intensively indicates that 4,4′-bipyridine molecules may ingeniously influence the micro-environment of the reaction system, generating different superstructures from those crystallized in the absence of 4,4′-bipyridine molecules.[22] On consideration of the potential interconversion between the **1a** and **1b**, we conceived of an idea that may realize the interconversion between **1a** and **1b**. **1a** was obtained in the absence of 4,4′-bipyridine, so we mixed it with 4,4′-bipyridine. This mixture was treated under the same condition as the synthesis of **1b**. The resulting sample (white precipitation) was washed with water and methanol several times. We have carried out a series of trials, but these efforts were proved to have failed through the comparison of XRPD patterns (Fig. S3, see ESI†), which demonstrated that interconversion from **1a** to **1b** was unsuccessful and the resulting white precipitation was neither **1a** nor **1b**.

3.6. TGA curves of 1a and 1b

The thermogravimetric (TG) measurements were performed in N_2 atmosphere on polycrystalline samples of **1a** and **1b** and the TG curves are shown in Fig. 3. The TGA curves of **1a** and **1b** suggested that they were stable up to ~350 and ~250 °C, respectively. Above these temperatures, the samples suffered an abrupt weight loss, indicating the collapse of the networks.

3.7. Photoluminescence properties of 1a and 1b

The emission spectra of **1a** and **1b** were examined in the solid state at room temperature, shown in Fig. 4. The free pptp ligand is nearly emission silent in the range 350–550 nm under the excitation at 300 nm at room temperature. The emission spectra for **1a** and **1b** exhibit emission peaks at 412 and 440 nm for **1a** and **1b**, respectively. Both emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since the Cd(II) ion is difficult to oxidize or reduce due to its d^{10} configuration.[25] Thus, they may be assigned to intraligand ($\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$) emission. The enhancement of luminescence in d^{10} complexes may be attributed to ligand chelation to the metal center, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay.[26] The difference of the emission behavior for **1a** and **1b** probably derives from the differences in the rigidity of solid-state crystal packing.

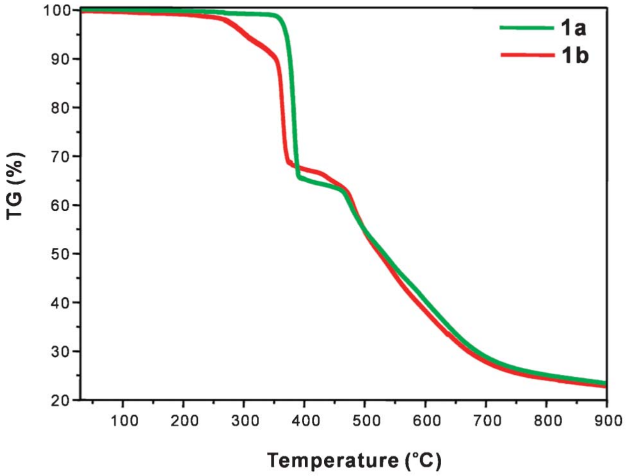


Fig. 3 The TGA curves of **1a** and **1b**.

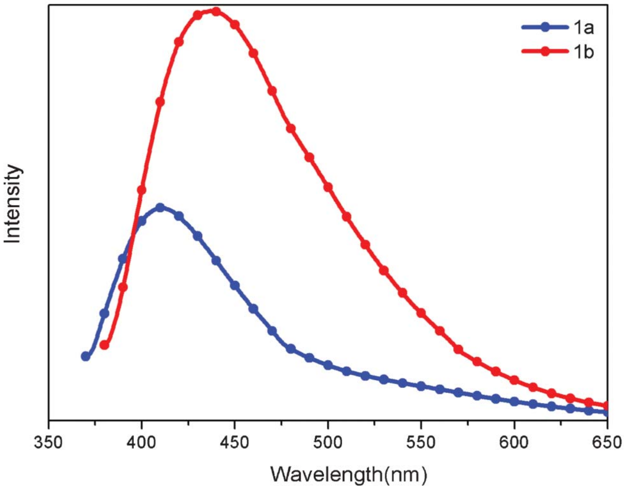


Fig. 4 The photoluminescence of **1a** and **1b** in solid state.

4. Conclusions

In summary, a pair of genuine supramolecular isomers, a flat and a wavy 2D 6^3-**hcb** net, have been synthesized and characterized for the first time. Our analysis based on the structural data suggests that the additive agent exerts a profound influence on the coordination environment of Cd(II) and linking modes of the ox ligand, resulting in the isomerization of the 6^3-**hcb** net from a flat one to a wavy one. Moreover, the photoluminescence behavior of the compounds was also discussed.

Acknowledgements

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