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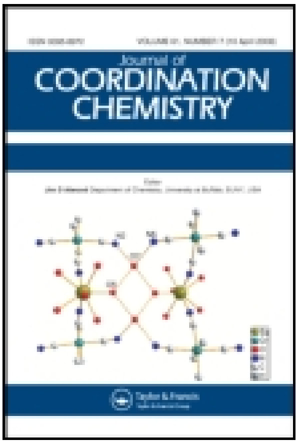

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Crystal engineering of Cd(II) metal-organic frameworks bridged by dicarboxylates and N-donor coligands

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Crystal engineering of Cd(II) metal–organic frameworks bridged by dicarboxylates and N-donor coligands

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Two new metal–organic coordination polymers, $\{[Cd_4(bpea)_4(IP)_8]\cdot 6H_2O\}_n$ (**1**) and $\{[Cd_{1.5}(suc)_{1.5}(IP)_{1.5}]\cdot 4H_2O\}_n$ (**2**) (bpea = biphenylethene-4,4′-dicarboxylate, H_2suc = succinic acid and IP = 1H-imidazo[4,5-f][1,10]-phenanthroline), have been obtained through two types of dicarboxylate linkers. Complex **1** contains a neutral 2-D puckered sheet that is interdigitated by neutral 1-D zigzag chains. Compound **2** shows a 2-D (4,4) net, which is extended into a 3-D supramolecular framework by weak aromatic interactions. The different structures demonstrate the effect of the dicarboxylate ligands on the formation of such coordination architectures. The fluorescence property of the two complexes was also investigated.

Keywords: Cadmium; Supramolecular chemistry; Luminescence

1. Introduction

Design of metal–organic frameworks (MOFs) or coordination polymers by crystal engineering have drawn great interest [1, 2]. Much effort has been devoted to rational construction of 1-D, 2-D, and 3-D MOFs. Construction of molecular architecture depends on metal ions, organic ligands, solvent system, synthetic methods, pH, reaction temperature, etc. [3], especially selection and utilization of building blocks as well as tectonic operation contributing to varieties of MOFs. Carboxylates are attractive metal-binding units in coordination networks because the negative charge enhances their ability to bond strongly to metal centers, contributing to the robust nature of the resulting materials [4–6]. The work by Yaghi *et al.* [7–9] highlights carboxylate-based systems in generation of highly stable, porous, functionalized crystalline materials. Carboxylic acids (such as 1,4-benzenedicarboxylate) are widely used in formation of MOFs [7]. Studies on the effect of different angular conformational aliphatic dicarboxylates and aromatic dicarboxylate on the construction of coordination polymers are sparse.

Control of the packing of low-dimensional structural motifs, which is dependent on weak non-covalent interactions, is still a challenge fraught with difficulties [10]. Therefore, it is important to investigate different packing modes of low-dimensional structures, which may help us to exploit new functional materials in a more

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controlled manner. As an extension of our previous work, another two types of dicarboxylates which possess longer size/flexible systems were used in this article and are good candidates for construction of supramolecular motifs. Herein, we report the syntheses, structures and properties of two Cd(II) polymers, $\{[Cd_4(bpea)_4(IP)_8]\cdot 6H_2O\}_n$ (**1**) and $\{[Cd_{1.5}(suc)_{1.5}(IP)_{1.5}]\cdot 4H_2O\}_n$ (**2**) (bpea = biphenylethene-4,4'-dicarboxylate, H_2suc = succinic acid and IP = 1H-imidazo[4,5-f][1,10]-phenanthroline). Complex **1** contains a neutral 2-D puckered sheet that is interdigitated by neutral 1-D zigzag chains. Compound **2** shows a 2-D (4,4) net, which is extended into a 3-D supramolecular framework by weak interactions.

2. Experimental

2.1. *Materials and general procedures*

All reagents were purchased from commercial sources and used as received. FT-IR spectra (KBr pellets) were taken on a FT-IR 170SX (Nicolet) spectrometer. Elemental analyses were performed on a Perkin Elmer 240C analyzer. The luminescent spectra of the solid samples were acquired at an ambient temperature by using a JOBIN YVON/HORIBA SPEX Fluorolog t3 system (slit: 0.2 nm).

2.2. *X-ray crystallography*

Single crystal X-ray diffraction analyses of the compounds were carried out on a Bruker SMART APEX II CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by using ϕ/ω scan technique at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on multi-scan techniques; all structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXL-97 [11]. Absorption corrections were applied by using multi-scan program SADABS [12]. The hydrogens of organic ligands were placed in calculated positions and refined riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The crystal of **1** scattered weakly, and only low-angle data could be detected because of the presence of heavily disordered solvent molecules in the cavities. Thus, 2203 restraints were applied during refinement of the structure, including distance restraint (dfix) and thermal restraints (flat, isor, and delu) which have been used in some unreasonable atoms. In **1**, solvent molecules in the structure were highly disordered and impossible to refine using conventional discrete atom models. To resolve these issues, the contribution of solvent–electron density was removed using the SQUEEZE routine in PLATON [13], thereby producing a set of solvent-free diffraction intensities. The final formulas were calculated from the SQUEEZE results in combination with those of elemental analyses and thermogravimetric analyses (TGA). The U_{eq} parameters of some waters are relatively larger, mainly due to the low quality of the single-crystal samples; however, their structural modes are believed to be reliable. Table 1 shows crystallographic data of **1** and **2**. Selected bond distances and angles, and H-bonding parameters are listed in tables S1 and S2.

Table 1. Crystallographic data and structure refinement information for **1** and **2**.

Compounds	**1**	**2**
Empirical formula	$C_{168}H_{116}Cd_4N_{32}O_{22}$	$C_{51}H_{53}Cd_3N_{12}O_{20}$
Formula weight	3384.53	1491.25
Temperature (K)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2$	$C2/c$
Unit cell dimensions (Å, °)		
a	35.478(10)	10.8873(9)
b	17.354(5)	25.239(2)
c	26.470(7)	20.0677(16)
α	90	90
β	114.170(3)	99.7130(10)
γ	90	90
Volume (Å^3), Z	14868(7), 4	5435.2(8), 4
$F(000)$	6624	2968
Calculated density (g cm^{-3})	1.464	1.816
Goodness-of-fit	1.084	0.966
Reflections collected	22276	4955
Unique reflections	36698 [R(int) = 0.0424]	13647 [R(int) = 0.0223]
Final R indices [$R^{\alpha}(I > 2\sigma(I))$]	$R_1 = 0.0795$, $wR_2 = 0.2240$	$R_1 = 0.0257$, $wR_2 = 0.0779$
R indices (all data)	$R_1 = 0.0974$, $wR_2 = 0.2429$	$R_1 = 0.0306$, $wR_2 = 0.0825$

2.3. *Synthesis of the complexes*

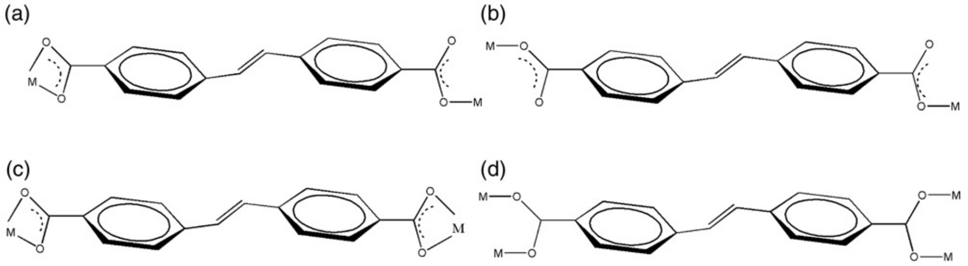
2.3.1. $\{[Cd_4(bpea)_4(IP)_8]\cdot 6H_2O\}_n$ (1). A mixture of $CdSO_4\cdot 7H_2O$ (0.036 g, 0.1 mmol), IP (0.023 g, 0.1 mmol), H_2bpea (0.25 g, 0.1 mmol), CH_3CN (2 mL), NaOH (0.03 mmol) and deionized water (10 mL) was stirred for 20 min in air, then transferred and sealed in a 25 mL Teflon reactor, which was heated at 150°C for 72 h. The solution was then cooled to room temperature at a rate of 5°C h^{-1} to yield a very fine pale yellow crystalline product **1** in 40% yield based on Cd. Calcd: C, 59.61; H, 3.45; and N, 13.24. Found: C, 59.52; H, 3.55; and N, 13.08. IR (KBr, cm^{-1}): 3596(vs), 3163(m), 1521(m), 1488(vs), 1271(m), and 782(m).

2.3.2. $\{[Cd_3(suc)_3(IP)_3]\cdot 8H_2O\}_n$ (2). Complex **2** was synthesized by a method similar to that of **1**, using H_2suc (0.1 mmol) instead of H_2bpea, giving pale yellow crystalline product **2** in 45% yield based on Cd. Calcd: C, 41.08; H, 3.58; and N, 11.27. Found: C, 41.01; H, 3.22; and N, 11.28. IR (KBr, cm^{-1}): 3555(s), 1607(m), 1481(s), 1232(m), and 759(m).

3. Results and discussion

3.1. *$\{[Cd_4(bpea)_4(IP)_8]\cdot 6H_2O\}_n$ (1)*

Single-crystal X-ray diffraction analysis reveals that **1** shows a 1-D zigzag chain directed by bpea and IP linkers. The crystal structure of **1** consists of four six-coordinate Cd(II)s, four bpea anions, eight IP ligands and six lattice waters. All Cd(II)s are coordinated by two oxygens of two adjacent bi(monodentate) carboxylates (scheme 1b) and four nitrogens from two chelating IP, showing distorted octahedral geometries (figure 1). All bond distances are in the normal range [14]. Neighboring Cd(II) ions are connected by bpea with two carboxyl ends both bridging *bis*-mondentate to form a 1-D zigzag chain with a period of 63.16 Å (figure 2a), a quite fascinating span in 1-D chain. These same directional chains are extended into 2-D sheets along the *bc* plane *via* π–π stacking of pyridyl and imidazole rings of IP ligands (face-to-face distance of *ca* 3.62 Å). The layers extend in the third direction with significant C–H–π interactions between carbon from IP and phenyl rings of bpea rings ($H \cdots \pi = 2.65(5)$ Å and $C–H \cdots \pi = 162(9)^{\circ}$) to provide a 3-D porous framework (figure 2b). The effective free voids calculated by



Scheme 1. The coordination modes of bpea.

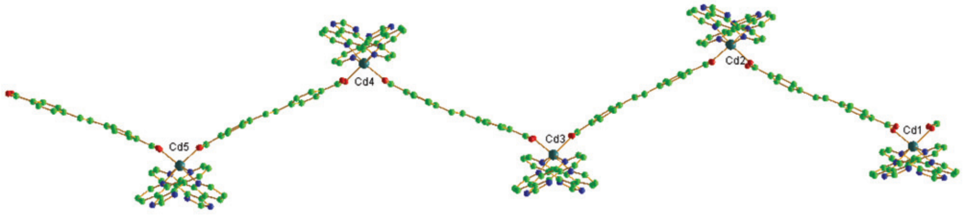


Figure 1. The coordination geometries of the metal centers and the ligand geometry in **1**.

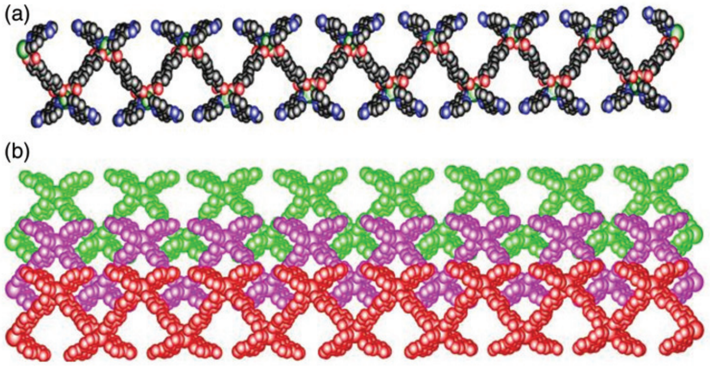


Figure 2. The structure of **1**: (a) a portion of the 1-D zigzag chain; (b) view of aromatic stacking interactions of the interchains.

PLATON correspond to *ca* 10.2% of the cell volume [13]. Similar 1-D chain is observed in Cd–bpea system in the presence of chelating organic ligands. Unlike most chiral polymeric frameworks, which usually contain chiral bridging molecules, the present compound is constructed by Cd(II) and two rigid ligands that complete the spontaneous resolution. In most cases, such nonchiral components result in formation of nonchiral or racemic materials. We suggest that steric selectivity of bpea associated with IP may be responsible for this spontaneous resolution.

3.2. $\{[Cd_{1.5}(suc)_{1.5}(IP)_{1.5}]\cdot 4H_2O\}_n$ (2)

The structure of **2** consists of a layer of $\{[Cd_3(IP)_3(suc)_3]\}_n$, in which there are two crystallographically independent Cd(II) with similar coordination geometries. The first Cd(II) (Cd1) is coordinated by four oxygens from one $(k^1-\mu_2)-\mu_2$, bidentate-chelating and one monodentate carboxylate from three suc ligands and two nitrogens of one chelating IP to form a distorted octahedral geometry; the second Cd(II) (Cd2) is also six-coordinate to four oxygens from one $(k^1-\mu_2)-\mu_2$ and one bidentate-chelating carboxylate of two adjacent suc ligands and two nitrogens of one chelating ligand, as shown in figure 3. Based on this connection, suc links metal centers into a 2-D sheet along the *ac* plane (figure 4a). This sheet is very similar to that of $\{[Cd_3(IP)_3(fum)_3]\cdot 8H_2O\}$ (H_2fum = fumaric acid) [15]. The IP entities on both sides of the coordination layers show weak interlayer π–π stacking interactions (figure 4b) with centroid-to-centroid distances of 3.57(2) and 3.86(6) Å. Moreover, there are two symmetry equivalent waters located within the pore space. Hydrogen bonding interactions exist between free molecules and water and between uncoordinated oxygens from carboxylate groups and free water, as shown in figure 4(b). O8 is H-bonded to two waters (O7 and O9), forming a trimeric water cluster. In addition, two

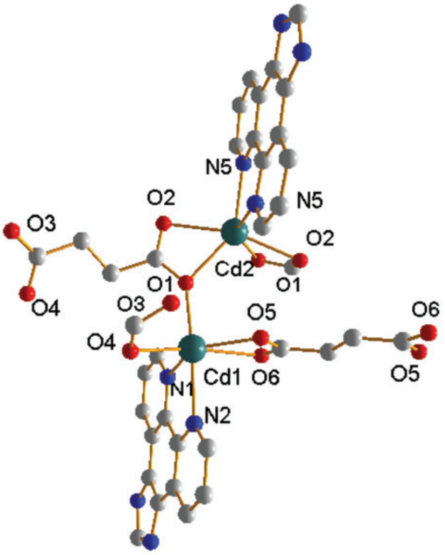


Figure 3. Coordination environment of Cd(II) in **2**.

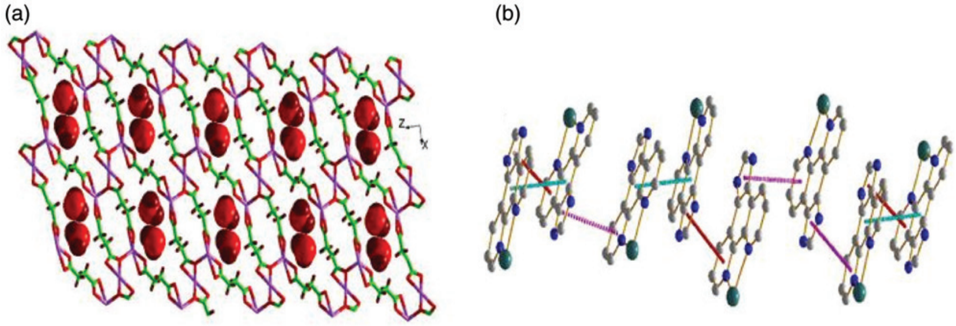


Figure 4. The structure of **2**: (a) water is located in the pores; (b) view of stacking interaction between rings from IP molecules.

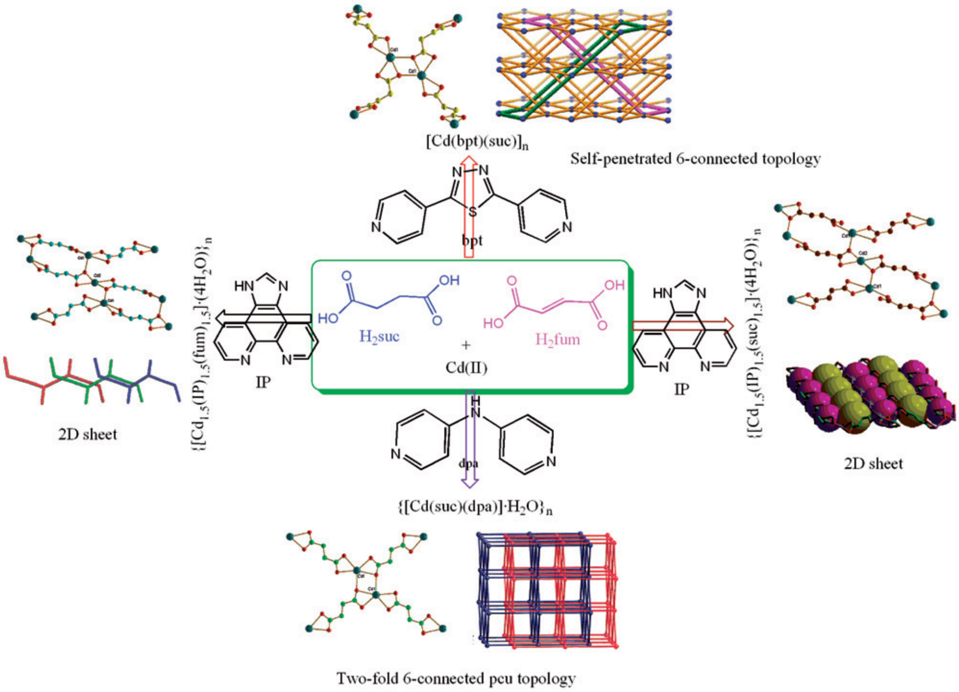
related symmetric O10 waters form a dimer, which is also H-bonded to the uncoordinated oxygen (O3).

With respect to the Cd-suc system, a 3-D polymer of $[Cd(bpt)(suc)]_n$ (bpt = 2,5-*bis*(4-pyridyl)-1,3,4-thiadiazole) with six-connected, self-penetrated topological network and a 3-D compound of $\{[Cd(suc)(dpa)]\cdot H_2O\}_n$ (dpa = 4,4′-dipyridylamine) containing doubly interpenetrated 6-connected Pcu motif [16, 17] have been reported. The suc in the above-mentioned polymers is μ_2-bridging, linking the metal centers into 2-D layers; the N-donor ligands are pillars and extend those structures into 3-D nets. From the above comparison, we conclude that variation of the N-donor ligands reduces the structural changes and plays a dominant factor determining the structure of coordination polymers.

3.3. *Comparison of structures*

$[Cd(bpea)(phen)]_n$ displays a remarkable assembly of nine-fold interlocked homochiral helices that are built from achiral components in all directions, while in **1**, all chains span only one direction (figure 2b). Each pair of IP or phen ligands are nearly perpendicular to each other and point away from the chains. Such difference of the two structures may originate from solvated water and the effect of chelating ligands. Especially, the bigger π-conjugated of IP molecule may reduce the bent orientation of bpea and restrain the independent chains spanning all directions.

The structures of **2**, $[Cd(bpt)(suc)]_n$ and $\{[Cd(suc)(dpa)]\cdot H_2O\}_n$ (bpt = 2,5-*bis*(4-pyridyl)-1,3,4-thiadiazole and dpa = 4,4′-dipyridylamine) have different topological features. $[Cd(bpt)(suc)]_n$ and $\{[Cd(suc)(dpa)]\cdot H_2O\}_n$ exhibit 3-D six-connected, self-penetrated topological networks and 3-D doubly interpenetrated 6-connected Pcu motifs, respectively. In the three compounds, suc connects Cd centers into 2-D sheets. However, a trinuclear metal core is observed in **2** and binuclear cores are formed in $[Cd(bpt)(suc)]_n$ and $\{[Cd(suc)(dpa)]\cdot H_2O\}_n$. $\{[Cd_3(IP)_3(fum)_3]\cdot 8H_2O\}$ (H_2fum = fumaric acid) and **2** have similar structures [15]. The different structural information is concluded in scheme 2. In contrast to the carboxylate and imidazole organic tectons, Cd(II) is used to assemble coordination polymers [18]. Both the composition and



Scheme 2. A diagram of frameworks with suc and fum ligands [15, 17, 20].

structures in the present complexes are different than those in reported Cd(II) complexes with carboxylates and imidazoles. For example, $\{[\mathrm{Cd_3(bim)_4(H_2O)_6(btc)_2}]\cdot 2\mathrm{H_2O}\}_n$ (bim = benzimidazole, $\mathrm{H_3btc}$ = 1,3,5-benzenetricarboxylic acid) was prepared from reaction of rigid coligands and is a ladder-liker 1-D polymer [18a]. A polynuclear $\{[\mathrm{Cd_9(IDC)_2(HIDC)_6(bipy)_4}]\cdot 2\,\mathrm{N(CH_3)(CH_2CH_3)_2}\cdot 2\mathrm{DMF}\}_n$ ($\mathrm{H_2IDC}$ = imidazole-4,5-dicarboxylic acid) has a 3-D structure with channels along the *c*-axis, in which free solvent molecules are located [18b]. $[\mathrm{Cd(L_{-H})_2}]_n$ and $\mathrm{Cd(L_{-H})(NO_3)}]_n$ ($\mathrm{L = C_{10}H_8N_2O_2}$) were synthesized by hydrothermal reactions of 4-(imidazole-1-yl)-benzoic acid and $\mathrm{CdX_2}$, and feature an infinite rhombic grid and zigzag chain, respectively [18c]. The $\{[\mathrm{Cd}(_2\text{-mBIM})_3](\mathrm{ClO_4})_2\}_n$ was obtained by *bis*(imidazol-1-yl) (BIM) with $\mathrm{Cd(NO_3)_2}$ in ethanol and water, and features a 16-membered $\mathrm{M_2L_2}$ macrometallacycle [18d]. Those structural discrepancies can be attributed to different ligands and different synthetic methods.

3.4. *Thermogravimetric analyses*

TGA of **1** and **2** were performed (figure S1); **1** shows two weight loss steps. The first corresponding to release of water is observed from 30°C to 280°C (obsd 3%, calcd 3.3%). The anhydrous compound begins to decompose at 356°C. Compound **2** has three weight loss steps; the first of 10.1% corresponds to loss of crystallization water (calcd 9.7%). Removal of organic components occurs in the range 280–805°C. The remaining weight corresponds to the formation of CdO.

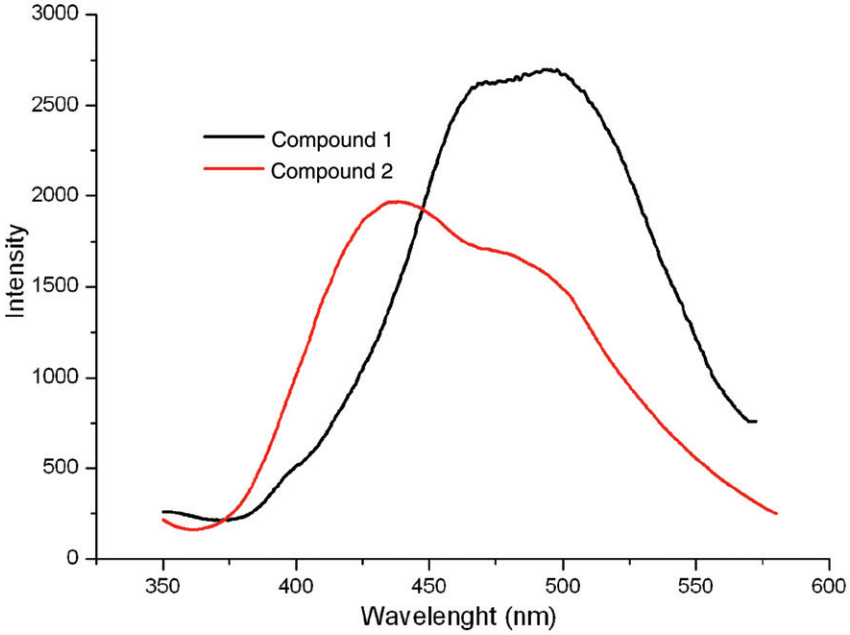


Figure 5. Solid-state emission spectra of **1** and **2** at room temperature.

3.5. *Photoluminescence properties*

Organic–inorganic coordination polymers, especially those with d^{10} metal centers, have been investigated for their fluorescent properties and potential applications as fluorescent-emitting materials, such as light-emitting diodes [19]. Therefore, **1** and **2** were studied in the solid state at room temperature. Excitation of the microcrystalline samples at 335 nm leads to generation of fluorescent emissions (figure 5) with the peak maxima occurring at 494 nm for **1** and 483 nm for **2**. IP has a relatively broad band at 460 nm ($\lambda_{ex} = 315$ nm) [15]. The emission bands of these carboxylates can be assigned to $\pi^* \rightarrow n$ transition as previously reported. Fluorescent emission of carboxylate ligands from $\pi^* \rightarrow n$ transition is weaker than those of the $\pi^* \rightarrow \pi$ transitions of IP; thus, the carboxylate ligands have almost no contribution to the fluorescent emission of the complexes. Emission bands of **1** and **2** are red-shifted, assigned to $\pi^* \rightarrow \pi$ transitions; the significant redshifts of these bands in comparison to that of IP would be attributed to the metal–ligand coordination and their different structures.

4. Conclusion

Two interesting supramolecular frameworks were constructed by packing of the polymeric chains and sheets. Structural features show that the backbones of dicarboxylate ligands regulate the resulting dimensions and physical properties. More efforts will focus on the construction of new coordination polymers by selecting different backbones of carboxylate linkers and different metal ions.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; CCDC references numbers are 775012–775013 for **1** and **2**. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). The additional figures can be obtained from the web free of cost.

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References

[1] (a) M.J. Zaworotko. *Cryst. Growth Des.*, **7**, 4 (2007); (b) F.M. Tabellion, S.R. Seidel, A.M. Arif, P.J. Stang. *Angew. Chem.*, **113**, 1577 (2001); *Angew. Chem. Int. Ed.*, **40**, 152 (2001).

[2] (a) T. Nebeshima. *Coord. Chem. Rev.*, **148**, 151 (1996); (b) B.F. Hoskins, R. Robson, D.A. Slizys. *Angew. Chem.*, **109**, 2430 (1997); *Angew. Chem., Int. Ed. Engl.*, **36**, 2336 (1997).

[3] (a) S.N. Wang, J.F. Bai, Y.Z. Li, Y. Pan, M. Scheer, X.Z. You. *CrystEngComm.*, **9**, 1084 (2007); (b) Y. Wei, H.W. Hou, L.K. Li, Y.T. Fan, Y. Zhu. *Cryst. Growth Des.*, **5**, 1405 (2005); (c) A.S. Rao, A. Pal, R. Ghosh, S.K. Das. *Inorg. Chem.*, **48**, 1802 (2009); (d) G.C. Ou, L. Jiang, X.L. Feng, T.B. Lu. *Inorg. Chem.*, **47**, 2710 (2008); (e) L. Liu, S.P. Huang, G.D. Yang, H. Zhang, X.L. Wang, Z.Y. Fu, J.G. Dai. *Cryst. Growth Des.*, **10**, 930 (2010).

[4] (a) M. Du, X.J. Jiang, X.J. Zhao. *Inorg. Chem. Commun.*, **9**, 1199 (2006); (b) C.D. Wu, W.B. Lin. *Dalton Trans.*, 4563 (2006); (c) J. Yang, G.D. Li, J.J. Guo, Q. Yue, G.H. Li, J.S. Chen. *Chem. Eur. J.*, **13**, 3248 (2007).

[5] (a) T.L. Hu, R.Q. Zou, J.R. Li, X.H. Bu. *Dalton Trans.*, 1302 (2008); (b) G.B. Che, C.B. Liu, B. Liu, Q.W. Wang, Z.L. Xu. *Cryst. Eng. Comm.*, **10**, 184 (2008).

[6] (a) Y. Qi, Y. Che, F. Luo, S.R. Batten, Y. Liu, J. Zheng. *Cryst. Growth Des.*, **8**, 1654 (2008); (b) B. Zhao, P. Cheng, X.Y. Chen, C. Cheng, W. Shi, D.Z. Liao, S.P. Yan, Z.H. Jiang. *J. Am. Chem. Soc.*, **126**, 3012 (2004); (c) S.A. Barnett, N.R. Champness. *Coord. Chem. Rev.*, **246**, 1459 (2003); (d) X.L. Wang, Y.Q. Chen, G.C. Liu, H.Y. Lin, W.Y. Zheng, J.X. Zhang. *J. Org. Chem.*, **694**, 2263 (2009); (e) X.L. Wang, Y.H. Chen, G.C. Liu, H.Y. Lin, J.X. Zhang. *Solid State Sci.*, **11**, 1567 (2009); (f) Y. Ma, A.L. Cheng, J.Y. Zhang, Q. Yue, E.Q. Gao. *Cryst. Growth Des.*, **9**, 867 (2009).

[7] O.M. Yaghi, J.L.C. Rowsell. *J. Am. Chem. Soc.*, **128**, 1304 (2006).

[8] N.W. Ockwig, O.D. Friedrichs, M. O'Keeffe, O.M. Yaghi. *Acc. Chem. Res.*, **38**, 176 (2005).

[9] N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi. *Science*, **300**, 1127 (2003).

[10] (a) A.L. Cheng, Y. Ma, J.Y. Zhang, E.Q. Gao. *Dalton Trans.*, 1993 (2008); (b) B.H. Ye, M.L. Tong, X.M. Chen. *Coord. Chem. Rev.*, **249**, 545 (2005); (c) C. Janiak. *J. Chem. Soc., Dalton Trans.*, 3885 (2000); (d) H.W. Roesky, M. Andruh. *Coord. Chem. Rev.*, **236**, 91 (2003); (e) J.Q. Liu, Y.Y. Wang, Y.N. Zhang, P. Liu, Q.Z. Shi, S.R. Batten. *Eur. J. Inorg. Chem.*, 147 (2009).

[11] G.M. Sheldrick. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Germany (1997).

[12] G.M. Sheldrick. *SADABS 2.05, Program for Area Detector Absorption Correction*, University of Göttingen, Germany (2002).

[13] A.L. Spek. *J. Appl. Crystallogr.*, **36**, 7 (2003).

[14] X.L. Wang, C. Qin, E.B. Wang, L. Xu. *Cryst. Growth Des.*, **6**, 2061 (2006).

[15] J.Q. Liu, Y.N. Zhang, Y.Y. Wang, J.C. Jin, E.L. Lermontova, Q.Z. Shi. *Dalton Trans.*, 5365 (2009).

[16] G.L. Wen, Y.Y. Wang, W.H. Zhang, C. Ren, R.T. Liu, Q.Z. Shi. *CrystEngComm.*, **12**, 1238 (2010).

[17] M.R. Moutney, S.M. Krishnan, N.M. Patel, R.M. Supkowski, R.L. LaDuca. *Cryst. Growth Des.*, **7**, 1145 (2006).

[18] (a) H. Chang, M. Fu, X.J. Zhao, E.C. Yang. *J. Coord. Chem.*, **63**, 3551 (2010); (b) K. Yang, Z.Z. Wang, Z.H. Liu. *J. Coord. Chem.*, **63**, 2286 (2010); (c) J. Cao, K.J. Wei, J. Ni, J.Z. Zhang. *J. Coord. Chem.*, **62**, 257 (2009); (d) C.M. Jin, Z.F. Chen, C.Y. Chen, J.H. Dong. *J. Coord. Chem.*, **62**, 390 (2009).

[19] (a) U.H.F. Buna. *Chem. Rev.*, **100**, 1605 (2000); (b) X. Shi, G.S. Zhu, Q. Zhu, G. Wu, G. Tian, R. Wang, D. Zhang, M. Xue, S.L. Qiu. *Eur. J. Chem.*, 185 (2004); (c) M. Friend, C.L. Cahill. *Dalton Trans.*, **8**, 1518 (2005).

[20] X.L. Wang, C. Qin, E.B. Wang, L. Xu, Z.M. Su, C.W. Hu. *Angew. Chem. Int. Ed.*, **116**, 5146 (2004).