

Two novel 3-D coordination polymers based on isonicotinic acid: Syntheses, crystal structures and fluorescence

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Abstract

The hydrothermal reactions of isonicotinic acid (HIso) and metal salts yielded two novel 3-D coordination polymers $\{[\text{Cu}_4(\text{Iso})_4(\mu_3\text{-O})_2(\text{C}_2\text{H}_5\text{OH})_2] \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot \text{C}_2\text{H}_6\text{N}_4\}_n$ (**1**), $\{[\text{Cd}(\text{Iso})_2(\text{H}_2\text{O})] \cdot \text{OHCCHO}\}_n$ (**2**), in which **1** was constructed from 32-membered rings and 3-D interpenetrating network of **2** from 42-membered rings. The fluorescent characterizations show the emissions at 565 nm for **1** and 440 nm for **2** possibly assigned to LMCT and IL, respectively.

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1. Introduction

Attentions in the search for new porous materials have focused on the design strategies for the synthesis of metal–organic solid with high solvent-accessible volume. Successful approaches to achieve the goal include increasing the spacing between the vertices and long rigid linkers [1], preventing interpenetration with multifunctional bulky organic ligands [2] and using second building blocks (SBUs) as large vertices [3]. A promising approach to the syntheses of open porous materials has obtained the interest in metal–organic framework constructed from metal ions and bridging organic ligands [4]. To choose suitable metal ions and ligands, it is possible to control the sizes and shapes of the pores. Isonicotinic acid (HIso), namely 4-pyridinecarboxylate, a multi-functional chelating and/or bridging ligand, has proved to be very powerful for the construction of multi-dimensional metal–organic coordination networks [5]. Furthermore, the isonicotinic acid complexes have raised interest in fluorescence probing with numerous potential applications for studies of microsecond

diffusion and dynamics of membranes [6]. Considering the versatile coordination abilities of HIso, we have investigated the reactions of HIso with metal ions. Herein, two 3-D coordination polymers based on HIso $\{[\text{Cu}_4(\text{Iso})_4(\mu_3\text{-O})_2(\text{C}_2\text{H}_5\text{OH})_2] \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot \text{C}_2\text{H}_6\text{N}_4\}_n$ (**1**) and $\{[\text{Cd}(\text{Iso})_2(\text{H}_2\text{O})] \cdot \text{OHCCHO}\}_n$ (**2**) were presented in this paper with the determination of crystal structures and character of fluorescence.

2. Experimental

2.1. General

Solvents and starting materials were purchased commercially and used without further purification unless otherwise stated. The IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellet, in the range $4000\text{--}400\text{ cm}^{-1}$. Elemental analyses were carried out on a Vario EL III elemental analyzer. The solid-state fluorescent excitation and emission spectra were performed on a FluoroMax-3 spectrophotometer at room temperature with excitation and emission slits at 5.0 nm, increment 1.0 nm and integration time 0.1 s.

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Table 1
Crystallographic data for compounds **1** and **2**

	1	2
Empirical formula	C ₁₇ H ₂₃ Cu ₂ N ₄ O ₇	C ₁₄ H ₁₀ CdN ₂ O ₇
Color and habit	Blue block	Yellow block
Crystal size (mm)	0.17 × 0.14 × 0.08	0.14 × 0.11 × 0.1
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
<i>a</i> (Å)	12.389(7)	12.181(9)
<i>b</i> (Å)	14.146(9)	15.354(12)
<i>c</i> (Å)	13.259(7)	18.785(15)
β (°)	112.676(10)	90
<i>V</i> (Å ³)	2144(2)	3513(5)
<i>Z</i>	4	8
<i>F</i> _w	522.47	430.64
<i>D</i> _c (mg/m ³)	1.619	1.628
μ (mm ⁻¹)	2.029	1.278
<i>F</i> (0 0 0)	1068	1696
θ (°)	3.33 to 25.02	3.04 to 25.02
Reflections measured	13218	20614
Independent reflections	3760	3086
Observed reflection	2209	1836
(<i>I</i> > 2 σ (<i>I</i>))		
<i>R</i> _{int}	0.1054	0.0766
Goodness-of-fit on <i>F</i> ²	1.007	1.001
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0656, 0.1228	0.0540, 0.1288
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1246, 0.1489	0.0932, 0.1472

2.2. Syntheses

Synthesis of {[Cu₄(Iso)₄(μ ₃-O)₂(C₂H₅OH)₂] · 2C₂H₅OH · C₂H₆N₄]_{*n*} (**1**): while using method of one pot, the mixture of CuCl₂ · 2H₂O (34 mg, 0.2 mmol), HIso (25 mg, 0.2 mmol), formaldehyde (3 mg, 0.1 mmol) and hydrazine hydrate (2 drops) (to prepare a guest of H₂C = N–N = CH₂) with 10 mL mixed-solvent of water and EtOH (V/V = 1:1) in a Teflon-lined stainless-steel autoclave at 393 K for 72 h resulted blue block crystals. Yield based on Cu: 19 mg, 38%. IR data (KBr, cm⁻¹): 3434(s), 2973(m), 2923(w), 1628(s), 1557(m), 1498(w), 1421(m), 1384(m), 1231(w), 1083(m), 1056(s), 873(w), 778(w), 703(w). Elemental analysis (%) calculated for C₁₇H₂₃Cu₂N₄O₇: C 39.08, H 4.44, N 10.72; found: C 38.18, H 4.51, N 10.68.

Synthesis of {[Cd(Iso)₂(H₂O)] · OHCHO]_{*n*} (**2**): the mixture of CdI₂ (73 mg, 0.2 mmol), HIso (25 mg, 0.2 mmol), biformyl (6 mg, 0.1 mmol) and hydrazine hydrate (2 drops) (to prepare a guest) with 10 mL mixed-solvent of water and EtOH (V/V = 1:1) in a Teflon-lined stainless-steel autoclave at 393 K for 72 h resulted yellow block crystals. Yield based on Cd: 23 mg, 27%. IR data (KBr, cm⁻¹): 3436(s), 2975(m), 2122(w), 1630(s), 1452(w), 1380(w), 1271(w), 1091(w), 1049(m), 878(w), 663(w). Elemental analysis (%) calculated for C₁₄H₁₀CdN₂O₇: C 39.05, H 2.34, N 6.50; found: C 38.14, H 2.41, N 6.45.

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

Cu(1)–O(1)#1	1.956(2)	Cu(2)–N(11)#4	1.991(2)
Cu(1)–O(5)#2	1.963(2)	Cu(2)–O(5)	1.998(2)
Cu(1)–O(6)	1.988(2)	Cu(2)–O(2)	2.256(2)
Cu(1)–N(21)	1.988(3)	Cu(2)–Cu(2)#3	2.9961(14)
Cu(1)–O(3)#1	2.205(2)	N(11)–C(16)	1.310(4)
Cu(2)–O(4)	1.910(2)	N(11)–C(12)	1.359(4)
Cu(2)–O(5)#3	1.9891(17)		
O(1)#1–Cu(1)–O(5)#2	89.17(9)	N(11)#4–Cu(2)–O(2)	95.94(9)
O(1)#1–Cu(1)–O(6)	151.64(10)	O(5)–Cu(2)–O(2)	87.42(8)
O(5)#2–Cu(1)–O(6)	92.72(10)	O(4)–Cu(2)–Cu(2)#3	133.57(6)
O(1)#1–Cu(1)–N(21)	88.83(10)	O(5)#3–Cu(2)–Cu(2)#3	41.41(6)
O(5)#2–Cu(1)–N(21)	175.34(9)	N(11)#4–Cu(2)–Cu(2)#3	132.74(9)
O(6)–Cu(1)–N(21)	87.05(11)	O(5)–Cu(2)–Cu(2)#3	41.17(5)
O(1)#1–Cu(1)–O(3)#1	114.35(8)	O(2)–Cu(2)–Cu(2)#3	92.58(7)
O(5)#2–Cu(1)–O(3)#1	91.46(9)	C(16)–N(11)–Cu(2)#5	123.4(2)
O(6)–Cu(1)–O(3)#1	93.90(10)	C(12)–N(11)–Cu(2)#5	119.06(19)
N(21)–Cu(1)–O(3)#1	93.20(10)	C(17)–O(1)–Cu(1)#6	122.87(18)
O(4)–Cu(2)–O(5)#3	93.08(9)	C(17)–O(2)–Cu(2)	120.62(16)
O(4)–Cu(2)–N(11)#4	88.97(11)	C(22)–N(21)–Cu(1)	120.60(19)
O(5)#3–Cu(2)–N(11)#4	166.53(9)	C(26)–N(21)–Cu(1)	122.4(2)
O(4)–Cu(2)–O(5)	168.46(7)	C(27)–O(3)–Cu(1)#6	129.1(2)
O(5)#3–Cu(2)–O(5)	82.58(9)	C(27)–O(4)–Cu(2)	125.48(18)
N(11)#4–Cu(2)–O(5)	92.84(10)	Cu(1)#7–O(5)–Cu(2)#3	109.80(9)
O(4)–Cu(2)–O(2)	103.74(9)	Cu(1)#7–O(5)–Cu(2)	115.46(9)
O(5)#3–Cu(2)–O(2)	96.50(8)	Cu(2)#3–O(5)–Cu(2)	97.42(9)

Symmetry code: #1 = $-x+1.5, y+0.5, -z-0.5$; #2 = $x+0.5, -y+0.5, z-0.5$; #3 = $-x+1, -y, -z$; #4 = $-x+0.5, y+0.5, -z-0.5$; #5 = $-x+0.5, y-0.5, -z-0.5$; #6 = $-x+0.5, y-0.5, -z-0.5$; #7 = $x-0.5, -y+0.5, z+0.5$; #8 = $-x+1, -y+1, -z-2$.

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

Cd(1)–O(1W)	2.314(5)	Cd(1)–O(3)#2	2.390(6)
Cd(1)–N(11)#1	2.331(7)	Cd(1)–O(4)#2	2.419(6)
Cd(1)–O(2)	2.324(6)	Cd(1)–O(1)	2.513(6)
Cd(1)–N(21)	2.383(7)		
O(1W)–Cd(1)–N(11)#1	95.3(2)	O(1W)–Cd(1)–O(1)	96.4(2)
O(1W)–Cd(1)–O(2)	88.1(2)	N(11)#1–Cd(1)–O(1)	82.5(2)
N(11)#1–Cd(1)–O(2)	136.4(2)	O(2)–Cd(1)–O(1)	54.00(19)
O(1W)–Cd(1)–N(21)	172.8(2)	N(21)–Cd(1)–O(1)	87.7(2)
N(11)#1–Cd(1)–N(21)	91.1(2)	O(3)#2–Cd(1)–O(1)	139.8(2)
O(2)–Cd(1)–N(21)	89.6(2)	O(4)#2–Cd(1)–O(1)	162.24(19)
O(1W)–Cd(1)–O(3)#2	84.1(2)	C(12)–N(11)–Cd(1)#3	121.1(6)
N(11)#1–Cd(1)–O(3)#2	137.6(2)	C(16)–N(11)–Cd(1)#3	121.6(5)
O(2)–Cd(1)–O(3)#2	85.9(2)	C(26)–N(21)–Cd(1)	121.3(6)
N(21)–Cd(1)–O(3)#2	88.9(2)	C(22)–N(21)–Cd(1)	120.6(6)
O(1W)–Cd(1)–O(4)#2	95.82(19)	C(17)–O(1)–Cd(1)	87.3(5)
N(11)#1–Cd(1)–O(4)#2	83.6(2)	C(17)–O(2)–Cd(1)	95.8(5)
O(2)–Cd(1)–O(4)#2	139.3(2)	C(27)–O(3)–Cd(1)#4	91.2(5)
N(21)–Cd(1)–O(4)#2	81.5(2)	C(27)–O(4)–Cd(1)#4	90.1(5)
O(3)#2–Cd(1)–O(4)#2	54.52(19)		

Symmetry code: #1 = $-x+1, y+0.5, -z+1.5$; #2 = $x-0.5, -y+0.5, -z+2$; #3 = $-x+1, y-0.5, -z+1.5$; #4 = $x+0.5, -y+0.5, -z+2$.

2.3. Structure determinations and refinements of **1** and **2**

Pertinent crystallographic data and other experimental details are summarized in Table 1. The suitable crystals of **1** and **2** were carefully selected and mounted on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated MoK α ($\lambda = 0.7107$ Å). The intensity data were reduced using CrystalClear program [7]. The structures were solved by direct methods using SHELXTLTM package of crystallographic software [8] and refined by full-matrix least-squares technique on F^2 . All non-hydrogen atoms were refined anisotropically for the two structures. Hydrogen atoms were generated in their idealized positions and allowed to ride on their respective parent carbon atoms.

3. Results and discussion

We have successfully employed hydrothermal reactions of HIsO and metal salts to yield the crystals of the present compounds, and X-ray single-crystal studies of **1** and **2**

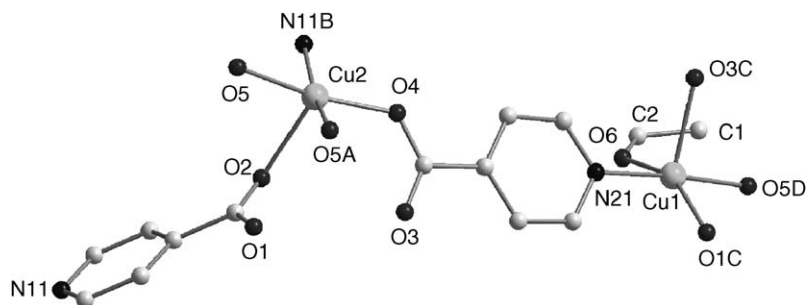


Fig. 1. The coordination spheres of copper(II) atoms of **1**. Symmetry code: A = $1-x, -y, -z$; B = $0.5-x, 0.5+y, -0.5-z$; C = $1.5-x, 0.5+y, -0.5-z$; D = $0.5+x, 0.5-y, -0.5+z$.

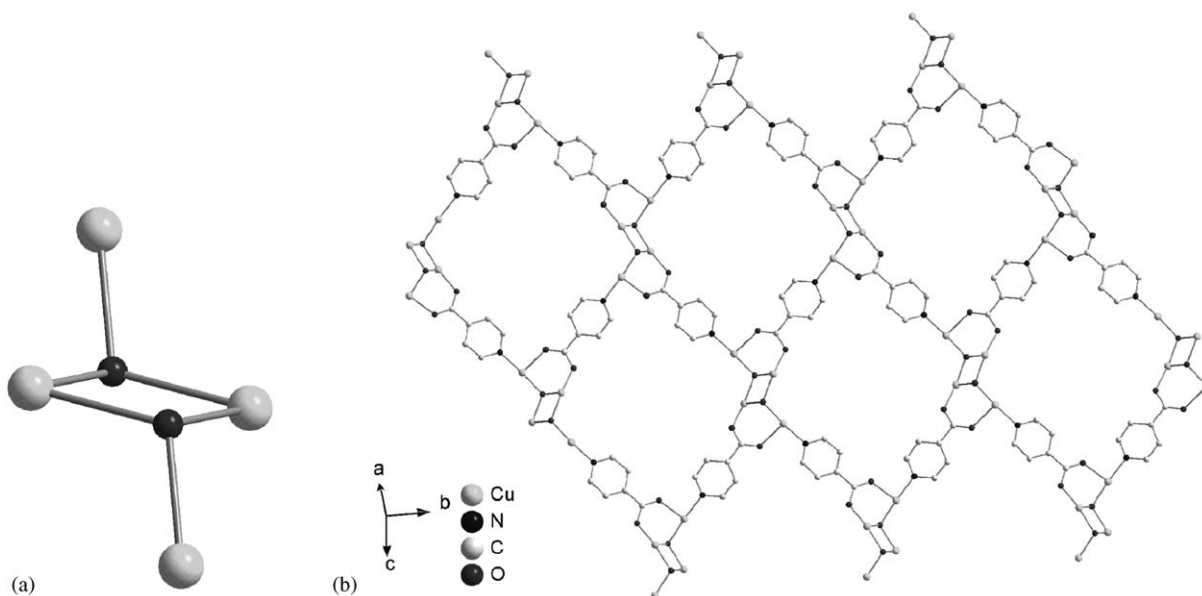


Fig. 2. (a) View of the subunit of $[Cu_4(\mu_3-O)_2]$; (b) the subunits of $[Cu_4(\mu_3-O)_2]$ were linkage by Iso into 2-D layer.

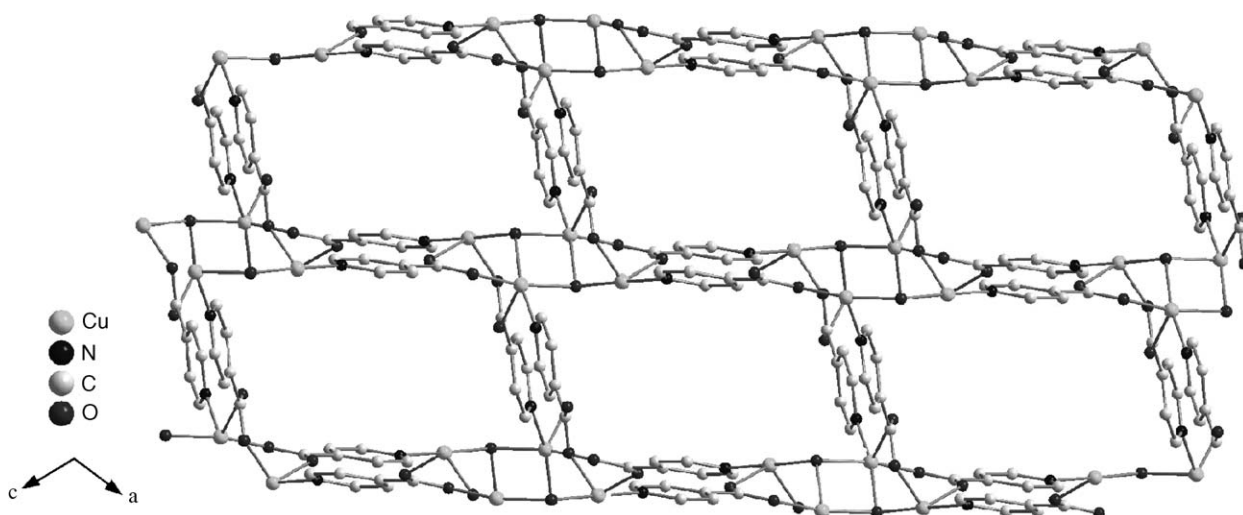
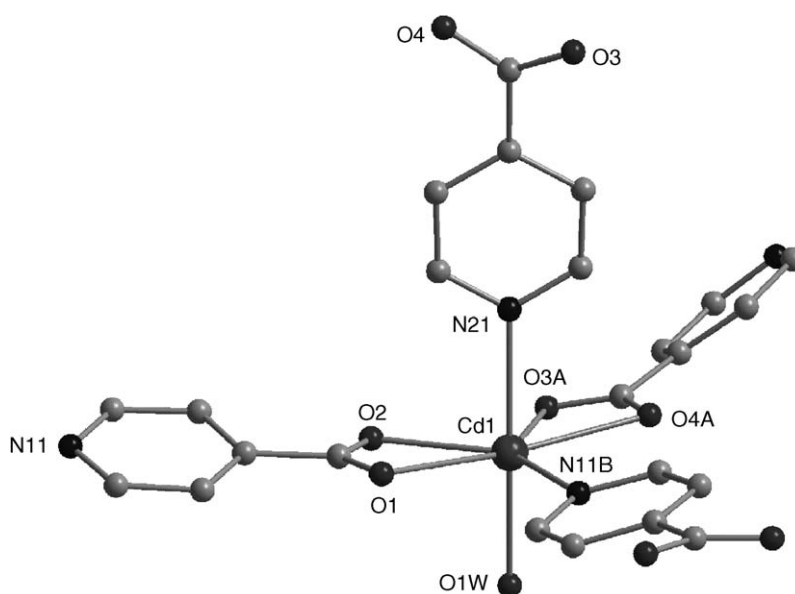


Fig. 3. The 3-D framework of 1.

Fig. 4. The coordination sphere of cadmium(II) atom of 2. Symmetry code: A = $-0.5 + x, 0.5 - y, 2 - z$; B = $1 - x, 0.5 + y, 1.5 - z$.

reveal two 3-D coordination networks. The selected bond distances and bond angles of **1** and **2** are listed in Tables 2 and 3, respectively.

3.1. Structural descriptions of compound 1 and 2

The asymmetry unit of **1** includes two independent copper(II) atoms, two anionic Iso, a coordinated ethanol, one $\mu_3\text{-O}^{2-}$ anion and guest molecules. The neutral skeleton $[\text{Cu}_4(\text{Iso})_4(\mu_3\text{-O})_2(\text{C}_2\text{H}_5\text{OH})_2]$ of the 3-D network contains two independent copper(II) atoms linked by two modes of $\mu_3\text{-O}^{2-}$ bridges and two kinds of Iso with μ_3 coordination mode, whose coordination spheres are shown in Fig. 1. Atom Cu1, in its coordination environment is lighted by

one carboxylic oxygen atom O3C from Iso occupying the axial position, and an oxygen atom O6, a $\mu_3\text{-O}^{2-}$ anion, one carboxylic oxygen atom O1C from Iso and an N atom from pyridyl group lying on the equatorial plane to complete a square pyramidal geometry. Atom Cu2 is surrounded by two $\mu_3\text{-O}^{2-}$ anions, a N atom from pyridyl group and one carboxylic oxygen atom O4 from Iso to form its equatorial plane, one carboxylic oxygen atom O2 from Iso on its axial position. Four copper(II) atoms are bridged by two $\mu_3\text{-O}^{2-}$ anions to form a chair-like subunit $[\text{Cu}_4(\mu_3\text{-O})_2]$ as shown in Fig. 2a. One kind of Iso adopts *exo*-tridentate bridging mode (with coordinating pyridyl group and a μ_2, η^2 -carboxylato bridge) to bridge the four subunits in alternate to form a large 32-membered ring,

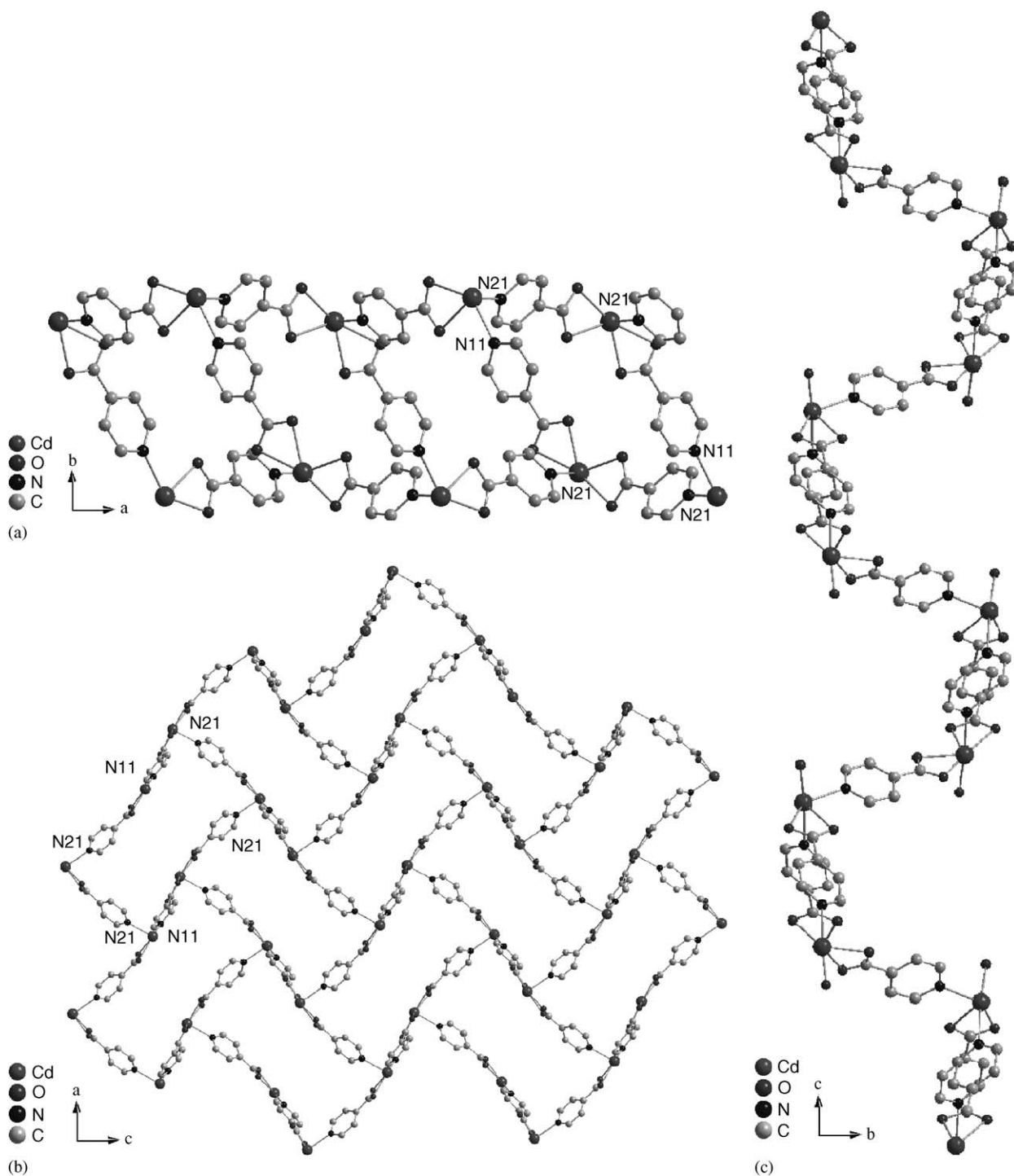


Fig. 5. (a) The 2-D layer of **2** viewed along the *b*-axis. (b) The 2-D layer of **2** viewed along the *c*-axis. (c) The 2-D layer of **2** viewed along the *a*-axis.

whose growth results in a 2-D layer (Fig. 2b). The other kind of *exo*-tridentate Iso groups along (010) plane act as pillars to link the adjacent 2-D layers into an extended 3-D coordination network (Fig. 3) containing 1-D parallelogram-like channels along the *b*-axis with $8.961 \times 11.851 \text{ \AA}^2$ cross-section (Fig. S1). The total solvent-accessible volume of the channels in the unit is 773.2 \AA^3 accounting for 36.1% calculated by PLATON [9]. However, the guest molecules

effectively fill in the channels with the left solvent-accessible volume only being 4.3%. The shortest centroid-to-centroid distance between pyridyl groups of Iso pillars or linkers in 2-D sheet is 5.626 \AA , indicating no π - π stacks in the structure.

Compound **2** crystallizes in orthorhombic space group *Pbca*. The coordination sphere of cadmium(II) atom of **2** is shown in Fig. 4, whose seven-coordination geometry of

pentagonal bipyramid is formed by four carboxylic oxygen atoms from two Iso with μ_1, η^2 mode and one nitrogen atom from pyridyl group in its equatorial plane, and one nitrogen atom from pyridyl group and a water molecule occupying the axial positions. It is noteworthy that the seven-coordination geometry of pentagonal bipyramidal cadmium(II) atoms is not common, the examples of seven-coordination cadmium(II) complexes with Iso being in very limited number [10]. The two kinds of independent Iso in compound **2** act as two-connecting tridentate bridging ligand (with coordinating pyridyl group and a μ_1, η^2 -carboxylato bridge), different from those in **1**. The ligands of Iso with N21 (Iso^{N21}) link the Cd(II) atom into 1-D chain along the *a*-axis (Fig. 5a), then further connected by Iso with N11 (Iso^{N11}) as pillars into a wave-like 2-D layer. The wave-like 2-D layer can also be viewed as the result of the growth of 42-membered rings constructed from the two subunits of [Cd(Iso^{N21})₂] interconnected with two [Cd(Iso^{N11})] in alternate (Fig. 5b). The neighboring layers are linked with each other by the moieties of Iso^{N21} along the *b*-axis into 3-D network (Fig. S2). It is noteworthy that there exist 3-D interpenetrating networks (Fig. 6). To our surprise, although the structure is interpenetrating, the framework of **2** still offers modestly sized micropores containing ellipse-like channels with $13.383 \times 17.016 \text{ \AA}^2$ cross-section (Fig. S3). The total solvent-accessible volume of the channels in the unit is 1204.3 \AA^3 accounting for 34.3%.

3.2. Optical properties

In contrast to the rich structural chemistry of HIso coordination complexes, to our knowledge, the luminescence data were quite limited, but there are the related rare-earth complexes with nicotinic and HIso N-oxides that included data for erbium and europium site distortions from the changes of the photoluminescence and absorption of the rare-earth line spectra [11]. Herein, solid state emission spectra of the two coordination polymers of **1**, **2** and free HIso show interesting fluorescence features at room temperature, as given in Fig. 7. Excitation of the solid sample of **1** at $\lambda_{\text{ex}} = 370 \text{ nm}$ produces green fluorescence; a broad band at approximately 565 nm. The polymer **2** with $\lambda_{\text{ex}} = 326 \text{ nm}$ produced blue fluorescence with an emission at 440 nm. Compared with that of free ligand HIso (broad peak at about 455 nm, $\lambda_{\text{ex}} = 362 \text{ nm}$), the emissions of **1** and **2** may be assigned to LMCT (Iso \rightarrow Cu) and IL ($\pi-\pi^*$), respectively.

In the IR spectra of the two compounds, specifically, absorption for the asymmetric stretching vibrations $\nu_{\text{as}}(\text{COO}^-)$ were observed at 1628 cm^{-1} for **1** and 1630 cm^{-1} for **2**. Symmetric stretching vibrations $\nu_{\text{s}}(\text{COO}^-)$ were shown at 1384 cm^{-1} for **1** and 1380 cm^{-1} for **2**. The above stretches were shifted to lower values, compared to the carbonyl frequencies of free HIso ligand. The difference $\Delta(\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-))$ were around 150 cm^{-1} , indicating the carboxylate groups in the compounds in the status of coordination to the metal ions [12].

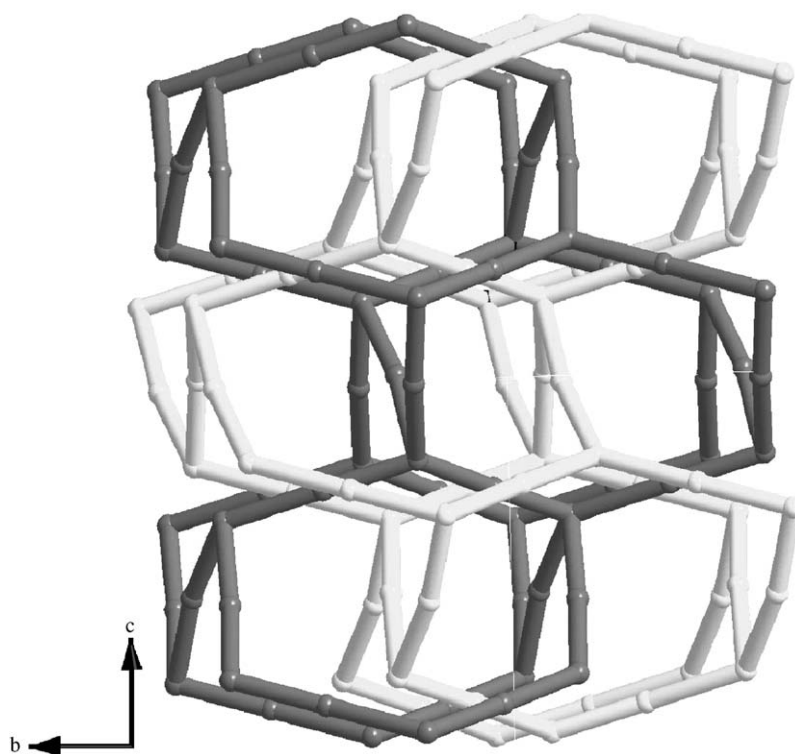


Fig. 6. View of the interpenetrating 3-D networks in **2**. Iso is predigested as a two-connecting node.

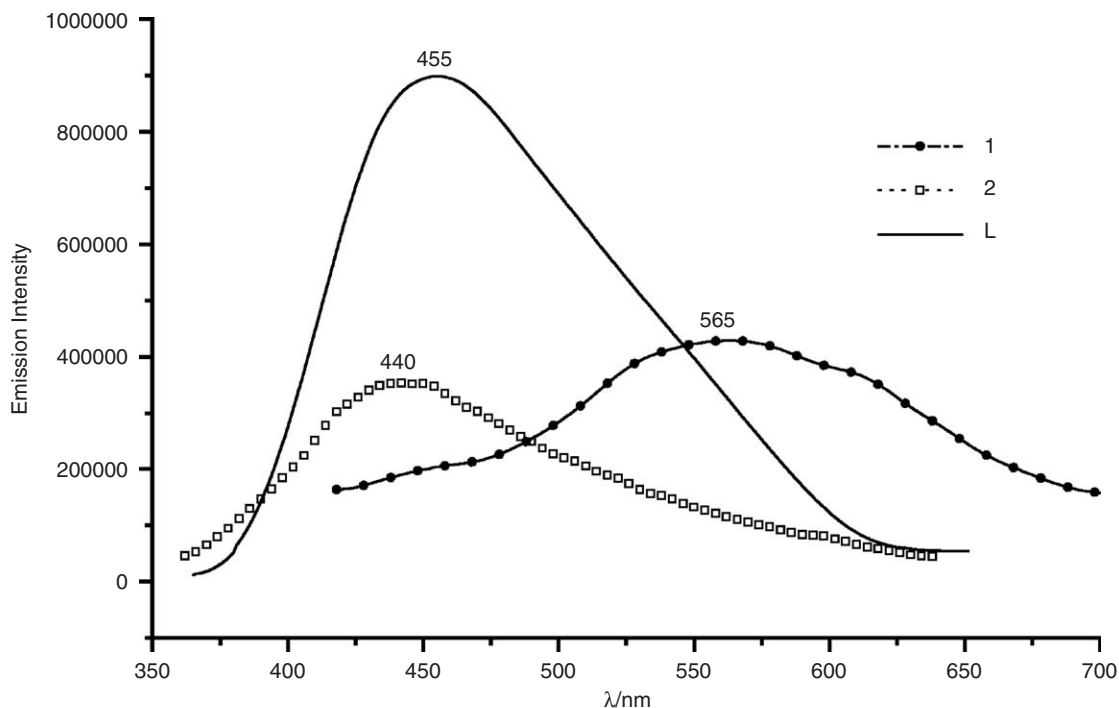


Fig. 7. Solid state emission spectra of **1** ($\lambda_{\text{ex}} = 370$ nm), **2** ($\lambda_{\text{ex}} = 326$ nm) and HIsO ($\lambda_{\text{ex}} = 362$ nm).

4. Conclusion

In summary, two 3-D metal–organic polymers containing different coordination modes of Iso were obtained from the hydrothermal reactions of HIsO and metal salts. Both the linkers of Iso and the metal centers take important roles in the formation of the 3-D frameworks. The ligands of *exo*-tridentate Iso in **1** act as pillars to form a 3-D framework containing 1-D parallelogram-like channels. While in **2**, the coordination number of Cd(II) is larger than that of Cu(II) in **1**; furthermore the carboxylate groups of Iso adopt μ_1 , η^2 -mode, which means the coordination sphere of Cd(II) can admit more Iso to form more complicated framework, 3-D interpenetrating networks in **2**. The fluorescent characterizations of **1** and **2** show different features, green fluorescence for **1** and blue fluorescence for **2**, indicating the title compounds may be good candidates for photoactive materials.

5. Supplementary material

Crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC-283720 (**1**) and -277469 (**2**)). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

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Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2005.12.012.

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