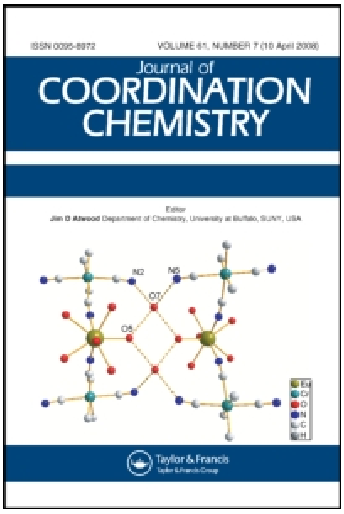

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Syntheses and characterizations of two metal-organic polymers derived from pyridyl substituted terpyridine and 4,5-imidazole dicarboxylate

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Syntheses and characterizations of two metal-organic polymers derived from pyridyl substituted terpyridine and 4,5-imidazole dicarboxylate

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Two metal-organic coordination polymers, [Cd(HIDC)(pytpy)] (**1**) and [Zn(HIDC)(pytpy)]$\cdot$(H_2O) (**2**), have been synthesized by reactions of 4′-(3-pyridyl)-2,2′ : 6′,2″-terpyridine (pytpy), 4,5-imidazoledicarboxylic acid (H_3IDC) with $CdCl_2 \cdot 2.5H_2O$ and $ZnCl_2$, respectively, in the presence of base. Compound **1** is a one-dimensional (1-D) helical chain with the chains extended into a three-dimensional supramolecular network through two different $\pi \cdots \pi$ interactions from pytpy ligands. Compound **2** is also a 1-D helical chain and adjacent chains are packed into a 2-D layer through $\pi \cdots \pi$ interactions between terminal pyridyl and pendant pyridyl rings from pytpy ligands. The photoluminescent properties of the two compounds are also investigated.

Keywords: Coordination polymers; Crystal structures; Terpyridine; Imidazoledicarboxylate

1. Introduction

Metal-organic coordination polymers have been the subject of intensive research because of their intriguing structural motifs and potential applications in catalysis, molecular recognition, separation, and nonlinear optics [1–4]. Success in building such networks relies on judicious selection of metal centers and organic ligands that can bind metal ions in different modes to achieve more robust polymeric structures [5, 6].

4,5-Imidazoledicarboxylic acid (H_3IDC) as a heterocyclic carboxylic acid has attracted intensive interest. Although it is rather simple, it has six potential donor atoms and can be successively deprotonated to generate H_2IDC^-, $HIDC^{2-}$ and IDC^{3-} at different pH's. Therefore, it can coordinate with metal ions in different modes to form a diversity of molecular or supramolecular architectures [7–12]. Many metal complexes containing imidazoledicarboxylate have been explored with multipyridyl ligands as co-ligands [13–17]. Several of these have featured the bidentate ligands 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen). Choice of a suitable co-ligand often

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has a significant effect on formation and structure of metal complexes. We have now included for the first time imidazoledicarboxylate metal complexes with 4′-(3-pyridyl)-2,2′ : 6′,2″-terpyridine (pytpy) as co-ligand.

Compared to the parent terpyridine, pytpy possesses several interesting structural features. First, it contains two distinct coordination domains (monodentate site from pendant pyridyl ring and tridentate site from terpyridyl unit). Therefore, it can be used as either tridentate chelating ligand or mono-tridentate bridging ligand. Second, pytpy can act as both hydrogen-bond acceptor and donor due to the presence of pendant pyridyl nitrogen and hydrogen atoms to construct supramolecular frameworks. Third, the large aromatic rings can generate π–π interactions and extend the structure into higher dimensionality.

We report here the syntheses, structures and luminescent properties of [Cd(HIDC)(pytpy)] (**1**) and [Zn(HIDC)(pytpy) $\cdot$ (H$_2$O)] (**2**).

2. Experimental

2.1. *Reagents and physical measurements*

The ligand pytpy was synthesized according to literature [18]. 4,5-Imidazoledicarboxylic acid was purchased from Aldrich and used without further purification, all the other reagents and solvents were commercially available and used as purchased. Elemental analyses (C, H, N) were determined with a Vario EL III elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bruker EQUINOX-55 spectrometer. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

2.2. *X-ray crystallography*

Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Empirical absorption corrections were applied by using SADABS. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using SHELXTL-97 [19]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. Crystal data and structural refinement parameters for **1** and **2** are summarized in table 1 and selected bond distances and angles are listed in table 2.

2.3. *Syntheses of the complexes*

2.3.1. [Cd(HIDC)(pytpy)] (1). A mixture of CdCl$_2 \cdot 2.5$H$_2$O (0.023 g, 0.10 mmol), H$_3$IDC (0.016 mg, 0.10 mmol), NaOH (0.008 g, 0.20 mmol) and pytpy (31.0 mg, 0.10 mmol) in 10 mL water-methanol (1 : 1) was stirred for 30 min, then sealed in a 15 mL Telfon-lined stainless steel container which was heated to 160°C for 96 h. After cooling to room temperature at a rate of 2°C per hour, yellow crystals were

Table 1. Crystal data and structural refinement parameters for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{25}H_{16}CdN_6O_4$	$C_{25}H_{18}N_6O_5Zn$
Formula weight	576.84	547.82
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	8.761(2)	9.912(3)
b	11.885(3)	10.226(4)
c	21.046(5)	22.864(8)
α	90	90
β	96.702(3)	96.848(6)
γ	90	90
V (Å^3)	2176.4(9)	2301(1)
Z	4	4
ρ_{Calcd} (g cm^{-3})	1.760	1.581
μ (mm^{-1})	1.052	1.119
F(000)	1152	1120
λ (Mo-Kα) (Å)	0.71073	0.71073
Reflections collected	10576	11254
Unique reflections	3855	4043
Parameters	362	340
S on F^2	1.051	0.992
R_1, wR_2 [$I>2\sigma(I)$]	0.0299, 0.0737	0.0560, 0.1044
R_1, wR_2 (all data)	0.0397, 0.0799	0.1289, 0.1373
$\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ (e Å^{-3})	0.589 and −0.458	0.459 and −0.419

Table 2. Selected bond distances and angles (Å, °) for **1** and **2**.

Complex **1**			
Cd1–N1	2.330(3)	Cd1–N2	2.340(2)
Cd1–N3	2.394(3)	Cd1–N5	2.302(3)
Cd1–N6#1	2.204(3)	Cd1–O1	2.749(3)
Cd1–O4#1	2.792(3)		
N6#1–Cd1–N5	135.8(1)	N6#1–Cd1–N1	103.64(9)
N5–Cd1–N1	96.2(1)	N6#1–Cd1–N2	139.38(9)
N5–Cd1–N2	84.51(9)	N1–Cd1–N2	69.67(9)
N6#1–Cd1–N3	104.4(1)	N5–Cd1–N3	84.4(1)
N1–Cd1–N3	138.48(9)	N2–Cd1–N3	69.07(9)
N6#1–Cd1–O1	77.93(9)	N5–Cd1–O1	64.89(9)
N1–Cd1–O1	84.77(9)	N2–Cd1–O1	137.79(9)
N3–Cd1–O1	130.80(8)		
Complex **2**			
Zn1–N1	2.155(5)	Zn1–N2	2.087(4)
Zn1–N3	2.264(5)	Zn1–N5	2.060(4)
Zn1–N6#1	2.003(5)		
N6#1–Zn1–N5	118.8(2)	N6#1–Zn1–N2	138.7(2)
N5–Zn1–N2	99.8(2)	N6#1–Zn1–N1	106.4(2)
N5–Zn1–N1	103.7(2)	N2–Zn1–N1	75.6(2)
N6#1–Zn1–N3	91.4(2)	N5–Zn1–N3	89.4(2)
N2–Zn1–N3	73.9(2)	N1–Zn1–N3	148.5(2)

Symmetry codes for **1**: #1 ($-x+1/2$, $y+1/2$, $-z+1/2$); for **2**: #1 ($-x+1$, $y+1/2$, $-z+3/2$).

obtained in ca 73% yield based on Cd. Anal. Calcd for $C_{25}H_{16}CdN_6O_4$ (%): C, 52.05; H, 2.80; N, 14.57. Found: C, 52.08; H, 2.77; N, 14.61. FT-IR (KBr, cm^{-1}): 3421(br), 1697(w), 1609(s), 1544(s), 1476(s), 1435(m), 1394(s), 1243(m), 1102(w), 1013(w), 788(m), 657(w), 633(w).

2.3.2. [Zn(HIDC)(pytpy)]·(H$_2$O) (2). Compound **2** was obtained using a procedure similar to that for **1** except that ZnCl$_2$ (0.014 g, 0.10 mmol) was used instead of CdCl$_2$·2.5H$_2$O. Yellow crystals were obtained in ca 59% yield based on Zn. Anal. Calcd for $C_{25}H_{18}N_6O_5Zn$ (%): C, 54.81; H, 3.31; N, 15.34. Found: C, 54.83; H, 3.31; N, 15.38. FT-IR (KBr, cm^{-1}): 3429(br), 1691(m), 1616(s), 1554(s), 1491(s), 1438(m), 1397(m), 1372(m), 1237(m), 1106(m), 1013(m), 789(m), 659(w), 635(w).

3. Results and discussion

3.1. *Structural description*

3.1.1. The structure of [Cd(HIDC)(pytpy)] (1). Single crystal X-ray diffraction analysis reveals that **1** is a 1-D chain. As shown in figure 1, the asymmetric unit of **1** contains one Cd^{II}, one pytpy and one HIDC^{2-}. Each Cd^{II} is coordinated by five nitrogens, three of which belong to pytpy and the other two to two imidazole rings. The Cd–N distances are in the range 2.204(3)–2.394(3) Å. However, the Cd1–O1 and Cd1–O4A distances are 2.749(3) and 2.790(3) Å, respectively, suggesting weak coordination.

H$_3$IDC is partially deprotonated to HIDC^{2-}. Each ligand is stabilized by strong internal hydrogen bonds [O2–H2···O3, 2.475(4) Å, 176.8°]. Similar hydrogen bonds were observed in the literature [15]. HIDC^{2-} ligands adopt a bis-N, O-chelating μ_2 coordination, bridging two cadmium(II) atoms into a 1-D helical chain with a Cd···Cd distance of 6.493 Å (figure 2).

Each pytpy as a tridentate chelating ligand coordinates to Cd^{II} atom and occupies the interchain space. The terpyridyl domain is approximately coplanar, the torsion angle between pyridyl rings containing N1 and N2 is 5.88° and the value between pyridyl rings containing N2 and N3 is 4.73°.

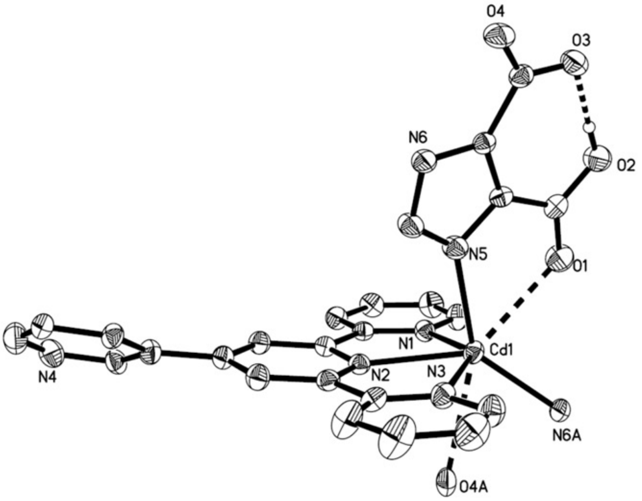

Figure 1. ORTEP diagram showing the coordination environment of Cd^{II} in **1**, drawn with displacement ellipsoids at the 30% probability.

In the solid state, two types of π–π stacking interactions from the lateral pytpy ligands can be observed. The π–π stacking between central and terminal rings (centroid-to-centroid 3.693 Å) connect the chains alternatively extending in the clockwise and anticlockwise directions into a 2-D achiral layer (figure 3). The other π–π interactions between terminal rings (centroid-to-centroid 3.623 Å) link the chains in the same direction into a 2-D supramolecular layer (figure 4). Therefore, the overall structure of **1** can be described as a 3-D achiral supramolecular network.

3.1.2. The structure of [Zn(HIDC)(pytpy)]·(H_2O) (2).

Compound **2** is also a 1-D chain. As shown in figure 5, the asymmetric unit of **2** contains one Zn^{II}, one pytpy, one $HIDC^{2-}$ and one lattice water. Each Zn^{II} is five-coordinate with five nitrogens, three from one chelating pytpy ligand and the other two from two $HIDC^{2-}$ anions. The Zn^{II} is approximately square-pyramidal with N1, N2, N3, N6A in the equatorial plane and N5 in the axial position. The Zn–N distances are in the range 2.003(5)–2.264(5) Å, comparable to those reported for other Zn^{II} complexes with nitrogen ligands.

Each $HIDC^{2-}$ adopts μ_2 coordination bridging two zinc(II)'s with two nitrogens, giving a 1-D helical chain with Zn···Zn distance of 6.037 Å (figure 6). The coordination mode in **2** is different from that in **1**. To the best of our knowledge, seven coordination modes of H_3IDC ligand have been reported [14] however, the coordination mode in **2** has not been reported. Similar to **1**, one of the carboxylate oxygens in $HIDC^{2-}$ forms a very strong internal hydrogen bond [O2–H2···O3, 2.449(6) Å, 176.1°].

The pytpy as a tridentate chelating ligand occupies the interchain space. The terpyridyl domain is approximately coplanar with torsion angle between pyridyl rings

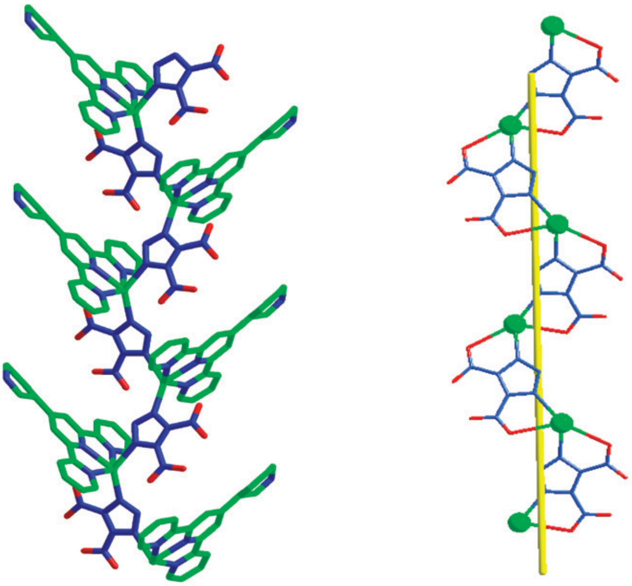

Figure 2. Perspective view of the 1-D helical chain in **1**.

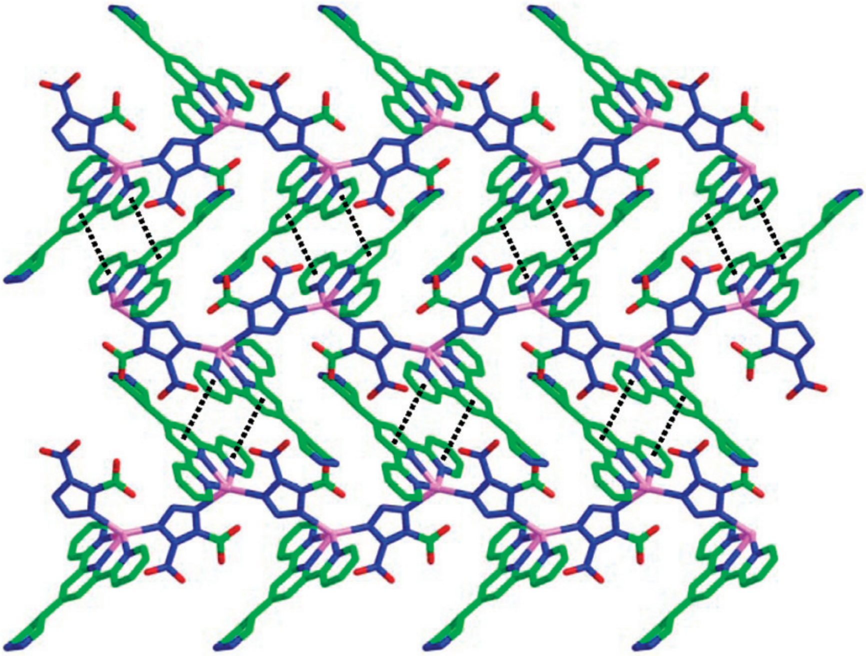

Figure 3. View of the 2-D achiral layer extended in the *bc* plane formed by $\pi\cdots\pi$ stackings.

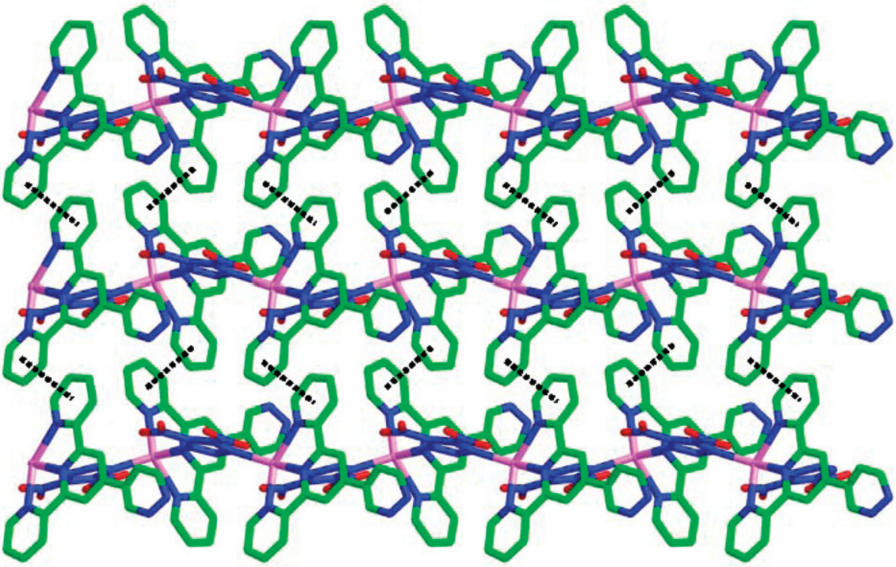

Figure 4. View of the 2-D layer extended in the *ac* plane formed by $\pi\cdots\pi$ stackings.

containing N1 and N2 is 6.30° and the value between pyridyl rings containing N2 and N3 is 5.35°. These values are a little bit larger than in **1**.

The pendant pyridyl ring is twisted to the central pyridyl ring with a dihedral angle of 20.96°. The packing in **2** is different from that in **1**. Face-to-face $\pi\cdots\pi$

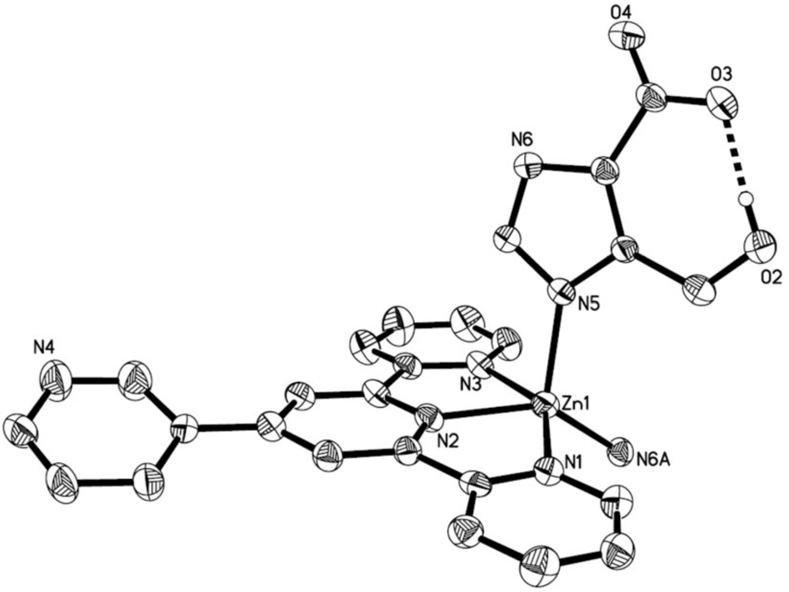

Figure 5. ORTEP diagram showing the coordination of Zn^{II} in **2**, drawn with displacement ellipsoids at the 30% probability. Solvent molecule has been omitted for clarity.

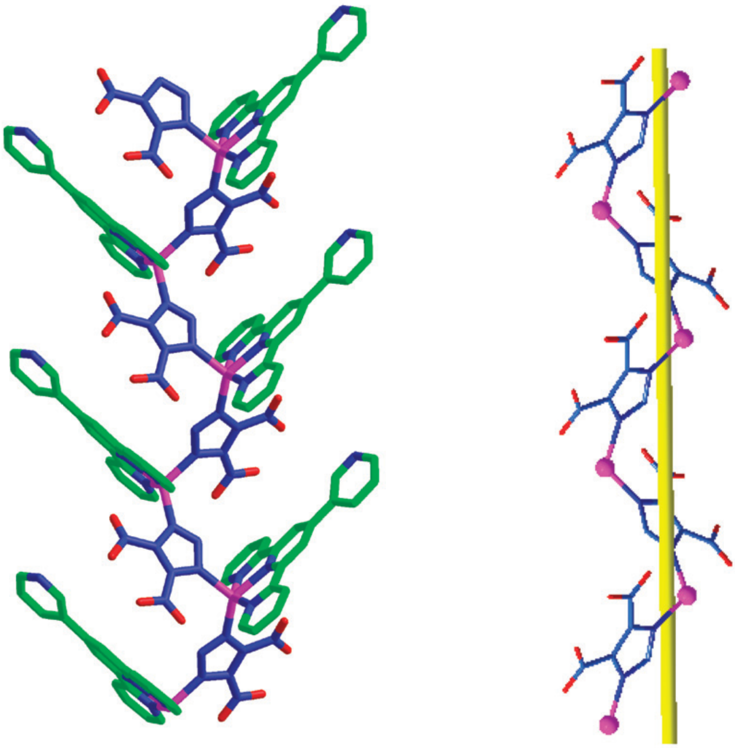

Figure 6. Perspective view of the 1-D helical chain in **2**.

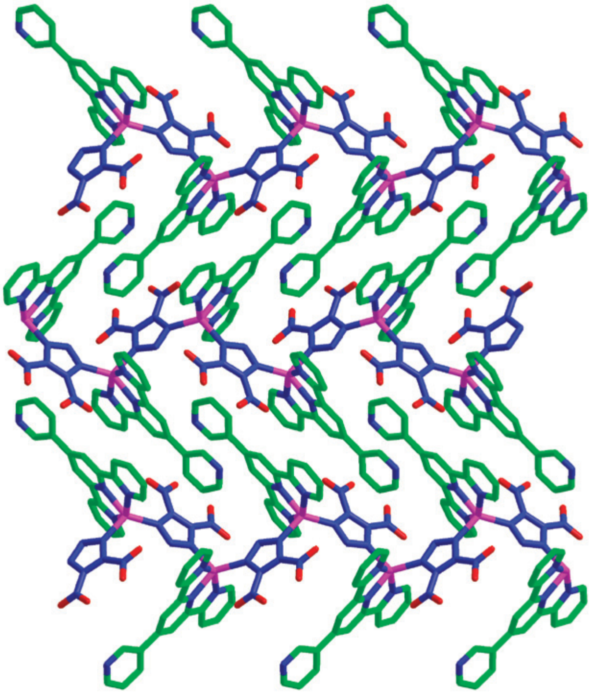

Figure 7. View of the 2-D achiral layer in the *bc* plane formed by $\pi \cdots \pi$ stacking interactions.

stackings between adjacent terminal and pendant pyridyl rings with plane-plane distance of 3.313 Å connect the adjacent chains into a 2-D layer (figure 7). The water molecules locate in the lattice and form strong hydrogen bonds with oxygen atoms from $HIDC^{2-}$ anions and nitrogen atoms from pendant pyridyl rings of pytpy ligands, [O5–H5A $\cdots$ O3, 2.825(6) Å, 155°; O5–H5B $\cdots$ $N4^{i}$, 2.823(8) Å, 164°, symmetry operation (i): $(x+1, y+1/2, -z+3/2)$].

3.2. *Luminescence properties*

Coordination polymers containing cadmium(II) and zinc(II) exhibit photoluminescent properties [21–25]. We investigated the photoluminescent properties of **1** and **2** (figure 8). In the solid state, **1** and **2** exhibit similar violet blue photoluminescent emission with maxima at 394 nm (ex = 245 nm). Since the free H_3IDC ligand shows very weak luminescence in the solid state at ambient temperature upon photoexcitation with 225 nm ultraviolet light [13, 26], the peak at 394 nm observed for **1** and **2** can be assigned to intraligand emission from the pytpy ligand.

4. Conclusion

We have synthesized two Cd^{II}/Zn^{II} coordination polymers based on the use of doubly deprotonated $HIDC^{2-}$ and pytpy as ligands. The $HIDC^{2-}$ as a bridging ligand connects

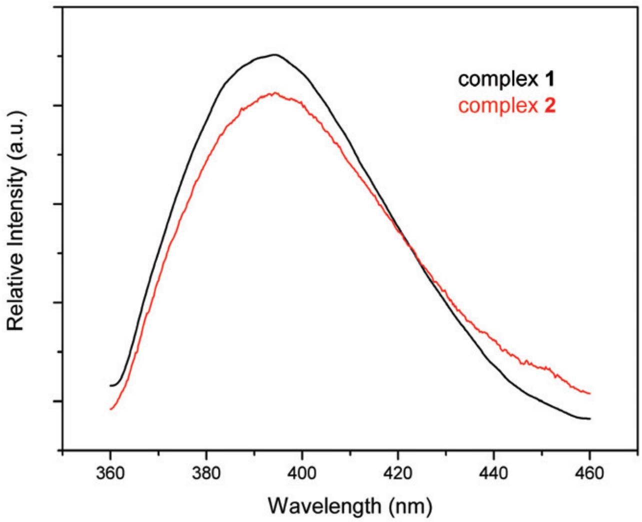

Figure 8. The emission spectra of **1** and **2** in the solid state at room temperature.

metal atoms into a helical chain, while the pytpy as a tridentate chelating ligand occupies the interchain space. The most significant feature in the two compounds is the pytpy ligands form different $\pi \cdots \pi$ interactions and connect the chains into 3-D and 2-D superamolecular structures, respectively.

Supplementary data

Crystallographic data (excluding structure factors) reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC numbers are 676334 and 676335 for **1** and **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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References

[1] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keefe, O.M. Yaghi. *Science*, **271**, 49 (1996).
[2] S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).
[3] C.N.R. Rao, S. Natarajan, R. Vaidhyanthan. *Angew. Chem. Int. Ed.*, **43**, 1466 (2004).

[4] J.L.C. Rowsell, O.M. Yaghi. *Angew. Chem. Int. Ed.*, **44**, 4670 (2005).
[5] I.M. Müller, R. Robson. *Angew. Chem. Int. Ed.*, **39**, 4357 (2000).
[6] B.F. Abrahams, P.A. Jackson, R. Robson. *Angew. Chem. Int. Ed.*, **37**, 2656 (1998).
[7] A.L. Cheng, N. Liu, J.Y. Zhang, E.Q. Gao. *Inorg. Chem.*, **46**, 1034 (2007).
[8] Y.Q. Sun, G.Y. Yang. *Dalton Trans.*, 3371 (2007).
[9] B. Zhao, X.Q. Zhao, W. Shi, P.J. Cheng. *J. Mol. Struct.*, **830**, 143 (2007).
[10] J.Z. Gu, W.G. Lu, L. Jiang, H.C. Zhou, T.B. Lu. *Inorg. Chem.*, **46**, 5835 (2007).
[11] R.Q. Zhong, R.Q. Zuo, Q. Xu. *Microporous Mesoporous Mater.*, **102**, 122 (2007).
[12] W.-G. Lu, L. Jiang, X.-L. Feng, T.-B. Lu. *Cryst. Growth Des.*, DOI. 10.1021/cg700979r.
[13] P. Mahata, S. Natarajan. *Eur. J. Inorg. Chem.*, 2156 (2005).
[14] C.-F. Wang, E.-Q. Gao, Z. Hea, C.-H. Yan. *Chem. Commun.*, 720 (2004).
[15] J.Y. Lu, Z. Ge. *Inorg. Chim. Acta*, **358**, 828 (2005).
[16] W.-G. Lu, L. Jiang, X.-L. Feng, T.-B. Lu. *Cryst. Growth Des.*, **6**, 564 (2006).
[17] Y.-L. Wang, D.-Q. Yuan, W.-H. Bi, X. Li, X.-J. Li, F. Li, R. Cao. *Cryst. Growth Des.*, **5**, 1849 (2005).
[18] F. Kröhnke. *Synthesis*, 1 (1976).
[19] G.M. Sheldrick. *SHELXS-97 and SHELXL-97, Program for X-ray Crystal Structure Solution and Refinement*, Göttingen University, Germany (1997).
[20] R.-Q. Fang, X.-M. Zhang. *Inorg. Chem.*, **45**, 4801 (2006).
[21] S.-L. Zheng, X.-M. Chen. *Aust. J. Chem.*, **57**, 703 (2004).
[22] S.-L. Zheng, J.-H. Yang, X.-L. Yu, X.-M. Chen, W.T. Wong. *Inorg. Chem.*, **43**, 830 (2004).
[23] W. Chen, J.Y. Wang, C. Chen, Q. Yue, H.M. Yuan, J.S. Chen, S.N. Wang. *Inorg. Chem.*, **42**, 944 (2003).
[24] J.H. Luo, M.C. Hong, R.H. Wang, R. Cao, L. Han, Z.Z. Lin. *Eur. J. Inorg. Chem.*, 2705 (2003).
[25] J. Tao, X. Yin, Z.B. Wei, R.B. Huang, L.S. Zheng. *Eur. J. Inorg. Chem.*, 125 (2004).
[26] X.L. Wang, C. Qin, E.B. Wang, L. Xu. *J. Mol. Struct.*, **45**, 749 (2005).