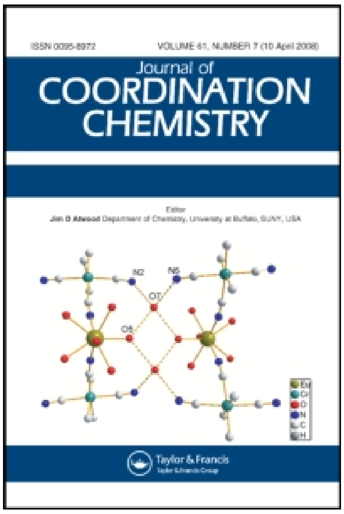

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Syntheses, structures, and characterizations of two coordination polymers assembled from zinc(II) salts with 1,2-bis[3-(1,2,4-triazolyl)-4-amino-5-carboxylmethylthio]ethane

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Syntheses, structures, and characterizations of two coordination polymers assembled from zinc(II) salts with 1,2-bis[3-(1,2,4-triazolyl)-4-amino-5-carboxylmethylthio]ethane

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Two new coordination polymers, $[ZnL]_n$ (**1**) and $\{[Zn(phen)(L)(H_2O)]\cdot 3H_2O\}_n$ (**2**) (H_2L = 1,2-bis[3-(1,2,4-triazolyl)-4-amino-5-carboxylmethylthio]ethane, phen = 1,10-phenanthroline), have been synthesized and characterized by elemental analysis, IR, and X-ray diffraction. Polymer **1** is a 1-D infinite chain (space group $P\bar{1}$) and further forms a 3-D supramolecular structure by $S\cdots S$ interactions and hydrogen bonds. Polymer **2** displays a mononuclear structure (space group $P\bar{1}$) and extends into a 3-D supramolecular structure through hydrogen bonds. In addition, spectra and thermal stability of **1** and **2** are also discussed. Strong luminescence characteristics of both polymers are found, suggesting their potential applications as luminescent materials.

Keywords: Coordination polymer; Zn(II); Crystal structure; Luminescence

1. Introduction

Metal–organic coordination polymers have attracted interest for developing crystalline materials with potential functionality. Essentially, these assemblies are driven by coordinative interactions occurring between organic ligands with specific functional groups and metal ions with different binding preferences [1–4]. Furthermore, weak noncovalent interactions such as hydrogen bonds, aromatic stacking, and van der Waals forces are crucial in the construction of such crystalline materials [5–7], which make supramolecular architectures more diverse [8, 9]. Many hydrogen-bonded, supramolecular architectures based on carboxylates have been reported [10].

Carboxylates are excellent candidates in supramolecular assembly as a result of versatile coordination modes [11–13]. Great efforts have been devoted in constructing polymers with rigid aromatic ligands, such as 1,3,5-benzenetricarboxylate [14, 15], imidazole-4,5-dicarboxylate [16], etc. Efforts have also been made on synthesizing

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coordination polymers of transition metals with flexible ligands, such as $\{[Zn(4,4'\text{-}bpy)(SC_6H_4CH_3\text{-}4)_2]\cdot DMF\}_n$ based on 4-methylbenzenethiolates and ancillary ligand 4,4′-bipyridine (4,4′-bpy) [17], $[Zn(btp)(NCS)_2]_n$, $\{[Zn(btp)_3](BF_4)_2\}_n$, and $\{[Zn(btp)_3]\cdot(ClO_4)_2\}_n$ based on 1,3-bis(1,2,4-triazol-1-yl)propane (btp) [18–20]. Furthermore, another flexible ligand, (1,3,4-thiadiazole-2,5-diyldithio)diacetic acid (H_2tzda), has also been reported [21–23]. Some Zn(II) examples display significant luminescence properties. However, investigation on flexible carboxylate-containing ligands in the construction of zinc-organic frameworks is not as comprehensive as rigid carboxylates [24].

A feasible strategy in building such networks is to employ an appropriate flexible ligand to achieve more conformational and coordination versatility. Herein, two new coordination polymers of zinc(II) salts based on a flexible ligand H_2L $\{H_2L = $ 1,2-bis[3-(1,2,4-triazolyl)-4-amino-5-carboxylmethylthio]ethane$\}$, $[ZnL]_n$ (**1**), and $\{[Zn(phen)(L)(H_2O)]\cdot 3H_2O\}_n$ (**2**), have been synthesized by hydrothermal reaction; the crystal structures and spectral properties of **1** and **2** are investigated.

2. Experimental

2.1. *Materials and measurements*

All chemicals were of reagent grade quality obtained from commercial sources and used without purification. Elemental analyses (C, H, and N) were performed on a Carlo–Erba 1160 Elemental Analyzer. IR spectra were recorded from 4000 to 400 cm^{-1} on a Nicolet NEXUS 470-FTIR spectrophotometer with pressed KBr pellets. Emission spectra were taken using an F-4500 HITACHI fluorescence spectrophotometer.

2.2. *Synthesis of H_2L*

1,2-bis[3-(1,2,4-Triazolyl)-4-amino-5-mercapto]ethane was prepared according to the reported procedure [25] as follows: (1.89 g, 0.02 mol) chloroacetic acid, (2.58 g, 0.01 mol) 1,2-bis[3-(1,2,4-triazolyl)-4-amino-5-mercapto]ethane, and (3.12 g, 0.02 mol) sodium carbonate were refluxed in 50 mL water for 3 h with stirring. The mixture was then cooled to room temperature and concentrated hydrochloric acid was introduced with stirring until pH = 2. The precipitate was filtered off and washed with water, giving a fine white powder in 64% yield (2.4 g). m.p. 186–187°C. Anal. Calcd for $C_{10}H_{14}N_8O_4S_2$ (%): C, 32.05; H, 3.74; N, 29.91. Found (%): C, 31.98; H, 3.78; N, 29.94. IR (KBr, cm^{-1}): 3354 (w), 3206 (w), 2930 (w), 1707 (s), 1632 (w), 1428 (m), 1374 (s), 1309 (m), 1229 (m), 1186 (m), 912 (w), 674 (w).

2.3. *Synthesis of $[ZnL]_n$ (1)*

Polymer **1** is hydrothermally synthesized by the reaction of $Zn(NO_3)_2\cdot 6H_2O$ (1 mmol, 297.48 mg), H_2L (1 mmol, 374 mg), NaOH (2 mmol, 80 mg), and deionized water (14 mL) in a sealed Teflon-lined stainless-steel vessel (25 mL) at 130°C for 5 days. After being cooled to room temperature, crystals of **1** (colorless, block-like) were collected by filtration. Yield: 45% (based on Zn). Anal. Calcd for $C_{10}H_{12}ZnN_8O_4S_2$ (%): C, 27.41; H, 2.74; N, 25.58. Found (%): C, 28.02; H, 3.02; N, 24.96. IR (KBr, cm^{-1}): 3321 (w), 3163 (w), 1623 (s), 1580 (s), 1432 (s), 1388 (s), 1335 (m), 1241 (m), 1147 (m), 1034 (s), 967 (m), 866 (m), 776 (m).

2.4. *Synthesis of $\{[Zn(phen)(L)(H_2O)]\cdot 3H_2O\}_n$ (2)*

Polymer **2** is hydrothermally synthesized by the reaction of $Zn(NO_3)_2\cdot 6H_2O$ (1 mmol, 297.48 mg), H_2L (1 mmol, 374 mg), NaOH (2 mmol, 80 mg), 1,10-phenanthroline (0.5 mol, 98 mg), and deionized water (14 mL) in a sealed Teflon-lined stainless-steel vessel (25 mL) at 130°C for 3 days. After being cooled to room temperature, crystals of **2** (colorless, block-like) were collected by filtration. Yield: 38% (based on Zn). Anal. Calcd for $C_{22}H_{22}ZnN_{10}O_8S_2$ (%): C, 38.59; H, 3.22; N, 20.47. Found (%): C, 38.72; H, 3.57; N, 20.12. IR (KBr, cm^{-1}): 3320 (w), 1588 (s), 1518 (s), 1425 (s), 1384 (s), 1228 (m), 1145 (w), 1006 (w), 909 (w), 852 (m), 776 (w), 725 (m).

2.5. *Crystallographic data collection and structure determination*

Intensity data for **1** and **2** were collected at 293 K on a Rigaku Saturn 724 CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were assigned with common isotropic displacement factors and included in the final refinement by using geometrical constraints. The final cycle of full-matrix least-squares refinement was based on the observed reflections and variable parameters. All calculations were performed using SHELXL-97 crystallographic software package [26]. Table 1 shows crystallographic data of polymers **1** and **2**. Selected bond distances and angles for H_2L and **1** and **2** are listed in table 2.

3. Results and discussion

3.1. *Spectra properties and thermal stability*

IR spectra of **1** and **2** show characteristic absorptions of L^{2-}. The absence of bands at 1690–1730 cm^{-1} indicates complete deprotonation of –COOH. The asymmetric and symmetric stretching bands of COO^- appear at 1623, 1580, and 1388 cm^{-1} for **1** and 1588 and 1384 cm^{-1} for **2** [27]. Broad bands at 3000–3420 cm^{-1} and weak bands at 1603–1660 cm^{-1} correspond to O–H stretching and bending vibrations of water. IR bands of benzene are at 1518 cm^{-1} and of 1,10-phenanthroline at 852 and 725 cm^{-1} [28]. IR spectra of **1** and **2** are consistent with the structural results.

The luminescence spectra of **1** and **2** are determined in the solid state at room temperature. The ligand H_2L displays an emission band at 406 nm upon photoexcitation at 354 nm (figure 1), attributable to intraligand π–π^* transition; **1** exhibits intense emission at 414 nm upon excitation at 353 nm with stronger fluorescence intensity than the free ligand. The enhanced fluorescence intensity of **1** is attributed to more rigidity of

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

	1	**2**
Empirical formula	$C_{10}H_{12}ZnN_8O_4S_2$	$C_{22}H_{22}ZnN_{10}O_8S_2$
Formula weight	437.77	684.03
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	7.7215(15)	8.1948(16)
b	9.828(2)	13.296(3)
c	11.208(2)	13.448(3)
α	83.67(3)	88.25(3)
β	86.90(3)	77.78(3)
γ	73.81(3)	77.03(3)
Volume (Å^3)	811.6(3)	1395.3(5)
Z	2	2
Absorption coefficient (mm^{-1})	1.807	1.096
Calculated density (g cm^{-3})	1.791	1.628
$F(000)$	444	700
Goodness-of-fit on F^2	1.078	1.004
R_1 ($I > 2\sigma(I)$)	0.0783	0.0530
wR_2 (all data)	0.2651	0.1179

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

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

Complex **1**			
Zn1–O1B	1.959(5)	Zn1–O3A	1.962(5)
Zn1–N4	2.000(6)	Zn1–N5	2.003(6)
O1B–Zn1–O3A	98.1(2)	O1B–Zn1–N4	109.1(2)
O3A–Zn1–N4	113.4(2)	O1B–Zn1–N5	115.7(2)
O3A–Zn1–N5	113.8(2)	N4–Zn1–N5	106.6(2)
Complex **2**			
Zn1–O5	2.055(2)	Zn1–N1	2.036(2)
Zn1–N5	2.062(2)	Zn1–N9	2.153(2)
Zn1–N10	2.111(2)		
N1–Zn1–O5	103.01(9)	N1–Zn1–N5	100.68(10)
O5–Zn1–N5	90.11(10)	N1–Zn1–N10	99.91(9)
O5–Zn1–N10	88.54(10)	N5–Zn1–N10	159.14(9)
N1–Zn1–N9	104.62(9)	O5–Zn1–N9	150.92(9)
N5–Zn1–N9	93.53(9)	N10–Zn1–N9	77.99(9)

Symmetry code. For **1**: $-x+1$, $-y+1$, $-z$; for **2**: $-x+1$, $-y$, $-z+1$.

the ligand coordinating to Zn(II) than free ligand, effectively reducing the loss of energy [29]. Emission bands at 374 and 391 nm for **2** (figure 2) are obviously different from H_2L, broader than 1,10-phenanthroline, and might be assigned to π–π* transitions of the auxiliary ligands [30–34].

TG analysis suggests that **1** is stable from ambient to 316°C, then shows decomposition of the organic moieties, continuing to 800°C. TG curve of **2** shows two main thermal behaviors. The first-step weight loss starts at 83°C and completes at 224°C, with 8.14% weight loss close to the calculated value (7.89%), corresponding to the release of three lattice water molecules. The second weight loss starts at 265°C and ends at 800°C, corresponding to the loss of coordinated water and decomposition of the organic moieties. The final products are not characterized (figure S1).

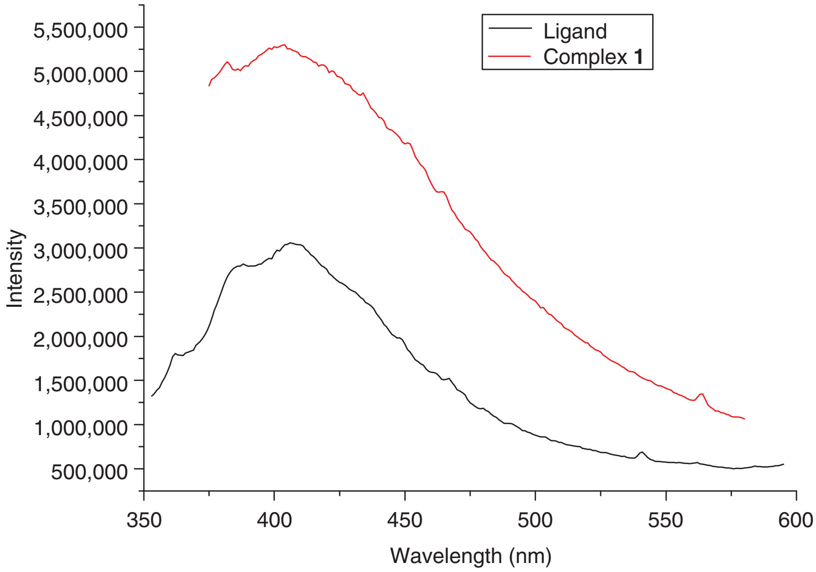

Figure 1. Solid-state photoluminescence spectra of H_2L and **1**.

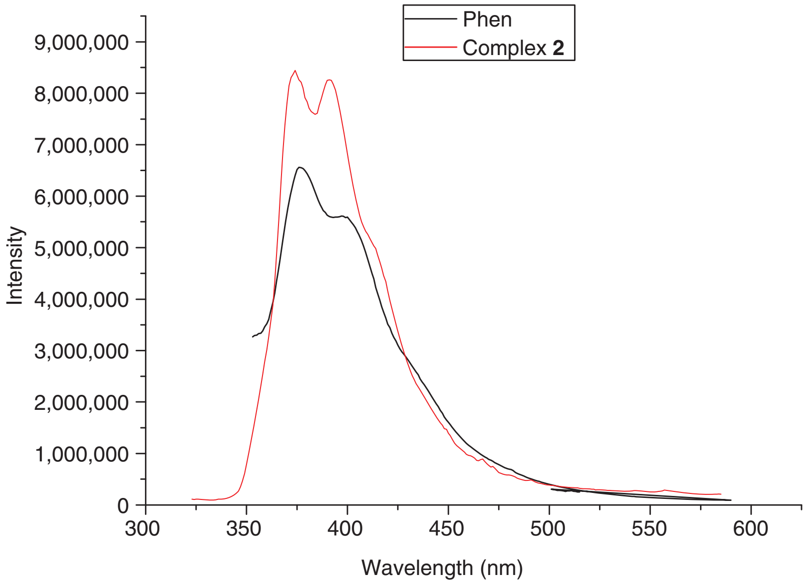

Figure 2. Solid-state photoluminescence spectra of **2** and phen.

3.2. *Crystal structures*

Crystallographic analysis reveals that **1** crystallizes in the triclinic system, space group $P\bar{1}$, and the asymmetric unit consists of one Zn and one L^{2-}. Each Zn is four-coordinate, surrounded by two oxygens from two L^{2-} (O1A, O3A) and two nitrogens (N4, N5) to form a tetrahedron (figure 3). The Zn–O distances range from 1.959(5)

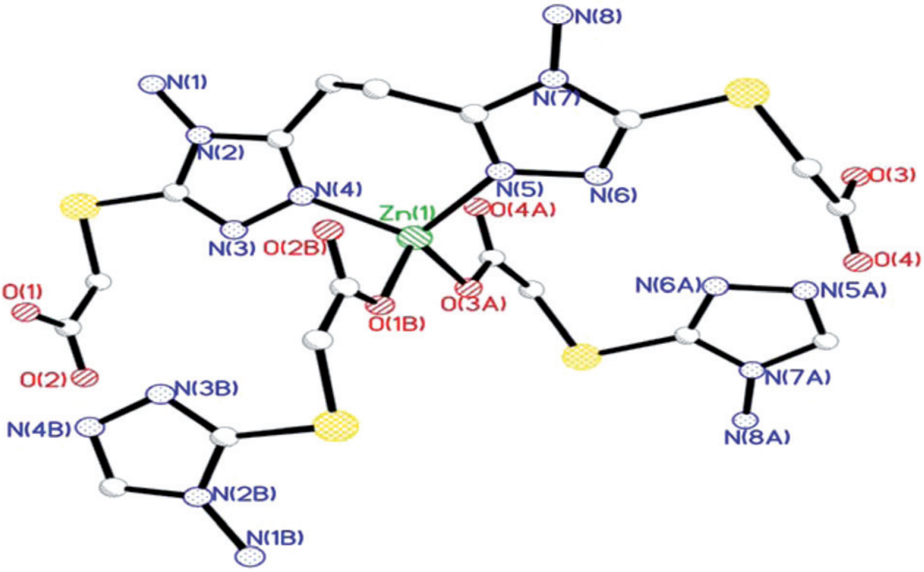

Figure 3. The coordination environment of Zn(II) in **1** (hydrogens are omitted for clarity).

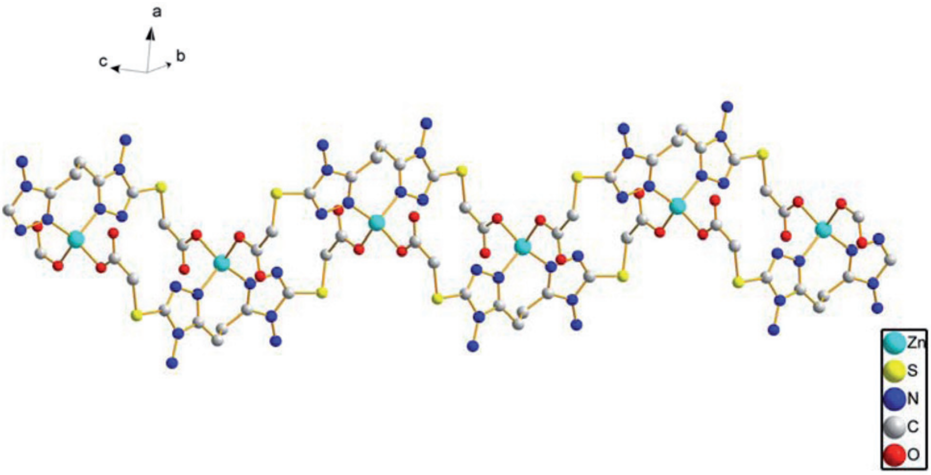

Figure 4. The 1-D chain showing the 16-member macroring enclosed by Zn1 and Zn#1 in **1** (hydrogens are omitted for clarity).

to 1.962(5) Å and the coordination angles vary from 98.1° to 115.7°. In **1**, all carboxyl groups of H_2L are deprotonated, monodentate bridging to link Zn centers, leading to infinite chains. A 16-membered ring containing two Zn ions (Zn1 and Zn#1) is shown in figure 4. The length between Zn1 and Zn1A is 6.966 Å. Weak S···S interactions between S2 and S2A (3.202 Å) further link the adjacent chains into 2-D layers in the *bc* plane (figure S2). In addition, hydrogen bonds between $-NH_2$ and carboxylate

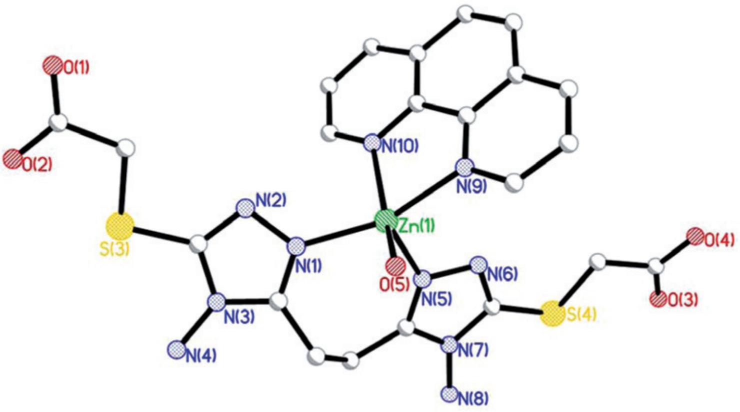

Figure 5. The local geometry around the Zn(II) in **2** (hydrogens are omitted for clarity).

(N1 $\cdots$ O1 $[-x, -y+1, -z] = 3.035$ Å, N1 $\cdots$ O3 $[-x, -y, -z+1] = 3.048$ Å) further connect adjacent 2-D layers into a 3-D supramolecular network, as depicted in figure S3.

Different from $[\mathrm{ZnL}]_n$, the reported $[\mathrm{M(tzda)(H_2O)_4}]$ ($\mathrm{H_2tzda}$ = 1,3,4-thiadiazole-2,5-diyldithio)diacetic acid) by Wang *et al.* [22] consists of one Zn, one tzda^{2-}, and four water molecules. Each Zn is six-coordinate by two oxygens provided by two tzda^{2-} anions and four water molecules to form an octahedron. The carboxylates are monodentate bridging Zn centers, leading to an infinite chain. The structural differences between two Zn polymers can be attributed to the different coordination environment of Zn(II).

Polymer **2** crystallizes in the triclinic system, space group $P\bar{1}$, and the asymmetric unit consists of one Zn, one L^{2-}, and one 1,10-phenanthroline. Each Zn is five-coordinate by four nitrogens provided by one L^{2-} (N1, N5) and one 1,10-phenanthroline (N9, N10) and one water molecule (O5) to form a tetragonal pyramid (figure 5). The Zn–N distances range from 2.036(2) to 2.153(2) Å and the coordination angles vary from 77.99° to 159.14°. All carboxyl groups of $\mathrm{H_2L}$ are deprotonated, but are not coordinated and only act as counter anions. Hydrogen bonds formed between the O2 or O3 and coordinated water (O5 $[-x, -y+1, -z+1] \cdots$ O2 $= 2.636$ Å, O5 $[-x+1, -y, -z+2] \cdots$ O3 $= 2.599$ Å) link the [Zn(L)(phen)] units into infinite double chains along the *c*-axis (figure S4). Hydrogen bonds between $-\mathrm{NH_2}$ and carboxylates (N4 $\cdots$ O2 $[-x-1, -y+1, -z+1] = 3.028$ Å) further link adjacent chains into 2-D layers in the *ab* plane, as shown in figure S5.

Other hydrogen bonds formed between $-\mathrm{NH_2}$ and uncoordinated water molecule (N4–H4B $\cdots$ O7 $[-x, -y+1, -z+1] = 3.306$ Å, (N8–H8A $\cdots$ O6 $[x, y, z+1] = 3.104$ Å, (N8–H8B $\cdots$ O7 $[x, y, z+1] = 3.123$ Å) link adjacent 2-D layers into a 3-D supramolecular network, as depicted in figure S6.

4. Conclusion

Two new coordination polymers of zinc(II) have been synthesized by self-assembling 1,2-bis[3-(1,2,4-triazolyl)-4-amino-5-carboxylmethylthio]ethane, Zn(II), and auxiliary ligand 1,10-phenanthroline. In **1** and **2**, the carboxylates are counter anions and also form hydrogen bonds resulting in two 3-D supramolecular architectures. Fluorescence of solid **1** and **2** suggest that they could be utilized as luminescent materials.

Supplementary material

Crystallographic data for the structural analyses have been deposited in the Cambridge Crystallographic Data Center, CCDC Nos 776328 and 776329. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] D. Braga, F. Grepioni, G.R. Desiraju. *Chem. Rev.*, **98**, 1375 (1998).
[2] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).
[3] C. Janiak. *Dalton Trans.*, **14**, 2781 (2003).
[4] P.J. Steel. *Acc. Chem. Res.*, **38**, 243 (2005).
[5] M.W. Hosseini. *Acc. Chem. Res.*, **38**, 313 (2005).
[6] C. Janiak. *J. Chem. Soc., Dalton Trans.*, **21**, 3885 (2000).
[7] M. Nishio. *CrystEngComm.*, **6**, 130 (2004).
[8] G.R. Desiraju. *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam (1989).
[9] W. Jones, C.N.R. Rao. *Supramolecular Organization and Materials Design*, Cambridge University Press, Cambridge (2002).
[10] B.H. Ye, M.L. Tong, X.M. Chen. *Coord. Chem. Rev.*, **249**, 545 (2005).
[11] A. Distler, S.C. Sevov. *Chem. Commun.*, **8**, 959 (1998).
[12] N. Barooah, R.J. Sarma, A.S. Batsanov, J.B. Baruah. *Polyhedron*, **25**, 17 (2006).
[13] C.A. Schalley, A. Lützen, M. Albrecht. *Chem. Eur. J.*, **10**, 1072 (2004).
[14] S.S.Y. Chui, S.M.F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams. *Science*, **283**, 1148 (1999).
[15] N.L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe, O.M. Yaghi. *Angew. Chem., Int. Ed.*, **41**, 284 (2002).
[16] W.G. Lu, C.Y. Su, T.B. Lu, L. Jiang, X.M. Chen. *J. Am. Chem. Soc.*, **128**, 34 (2006).
[17] X.L. Yang, S.B. Ren, J. Zhang, Y.Z. Li, H.B. Du, X.Z. You. *J. Coord. Chem.*, **62**, 3782 (2009).
[18] X. Zhu, K. Liu, Y. Yang, B.L. Li, Y. Zhang. *J. Coord. Chem.*, **62**, 2358 (2009).
[19] F. Wen, R.N. Chang, J.Y. Wang, E.C. Yang, X.H. Zhao. *J. Coord. Chem.*, **63**, 250 (2010).
[20] Y. Xu, C.L. Ran, L.M. Zhu, Y.T. Fan. *J. Coord. Chem.*, **62**, 410 (2009).
[21] Y.T. Wang, L.P. Zhang, Y.T. Fan, H.W. Hou, X.Q. Shen. *Inorg. Chim. Acta*, **360**, 2958 (2007).
[22] Y.T. Wang, X.Q. Shen, Y.T. Fan, H.C. Yao, H.W. Hou. *Supramol. Chem.*, **20**, 501 (2008).
[23] Y.T. Wang, Y.H. Li, Y.L. Wang, Y.T. Fan, H.W. Hou, H.Y. Zhang. *Synth. React. Inorg. Met-Org. Chem.*, **37**, 7 (2007).
[24] H.F. Zhu, Z.H. Zhang, T.A. Okamura, W.Y. Sun, N. Ueyama. *Cryst. Growth Des.*, **5**, 177 (2005).
[25] P.F. Xu, X.W. Sun, L.M. Zhang, Z.Y. Zhang. *J. Chem. Res. (s)*, **2**, 170 (1999).
[26] G.M. Sheldrick. *SHELXL-97, Program for the Solution and Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany (1997).
[27] G.B. Deacon, R.J. Phillips. *Coord. Chem. Rev.*, **33**, 227 (1980).
[28] L.F. Wang, J.G. Wu. *Chem. J. Chin. Univ.*, **9**, 535 (1988).

[29] (a) L.Z. Cai, W.T. Chen, M.S. Wang, G.C. Guo, J.S. Huang. *Inorg. Chem. Commun.*, **7**, 611 (2004); (b) L. Xu, B. Liu, F.K. Zheng, G.C. Guo, J.S. Huang. *J. Solid State Chem.*, **178**, 3396 (2005).
[30] L.Y. Zhang, G.F. Liu, S.L. Zheng, B.H. He, X.M. Zhang, X.M. Chen. *Eur. J. Inorg. Chem.*, 2965 (2003).
[31] J. Tao, J.X. Shi, M.L. Tong, X.X. Zhang, X.M. Chen. *Inorg. Chem.*, **40**, 6328 (2001).
[32] X.L. Wang, C. Qin, E.B. Wang, Y.G. Li, N. Hao, C.W. Hu, L. Xu. *Inorg. Chem.*, **43**, 1850 (2004).
[33] Z. Wang, H.H. Zhang, Y.P. Chen, C.C. Huang, R.Q. Sun, Y.N. Cao, X.H. Yu. *J. Solid State Chem.*, **179**, 1536 (2006).
[34] J.C. Dai, X.T. Wu, Z.Y. Fu, C.P. Cui, S.M. Wu, W.X. Du, L.M. Wu, H.H. Zhang, Q.Q. Sun. *Inorg. Chem.*, **41**, 1391 (2002).