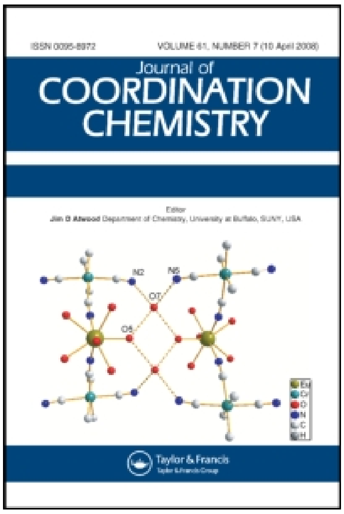

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Polymeric frameworks constructed from Zn with benzenetricarboxylic acid ligands and monodentate 4,4'-bipyridine: hydrothermal synthesis, crystal structures and luminescence

Jikun Li[a]; Chunlin Ma[b]; Guofang He[a]; Linlin Qiu[b]
[a] Department of Materials Science and Chemical Engineering, Taishan University, Taian 271021, P.R. China [b] Taishan University, Taian 271021, P.R. China

To cite this Article Li, Jikun , Ma, Chunlin , He, Guofang and Qiu, Linlin(2008) 'Polymeric frameworks constructed from Zn with benzenetricarboxylic acid ligands and monodentate 4,4'-bipyridine: hydrothermal synthesis, crystal structures and luminescence', Journal of Coordination Chemistry, 61: 2, 251 — 261, First published on: 22 September 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970701324044

URL: http://dx.doi.org/10.1080/00958970701324044

Journal of Coordination Chemistry
Vol. 61, No. 2, 20 January 2008, 251–261

Polymeric frameworks constructed from Zn with benzenetricarboxylic acid ligands and monodentate 4,4′-bipyridine: hydrothermal synthesis, crystal structures and luminescence

JIKUN LI*†, CHUNLIN MA‡, GUOFANG HE† and LINLIN QIU‡

†Department of Materials Science and Chemical Engineering,
Taishan University, Taian 271021, P.R. China
‡Taishan University, Taian 271021, P.R. China

(*Received 21 October 2006; revised 24 December 2006; in final form 29 December 2006*)

Two metal-organic coordination polymers, $[Zn(1,2,4\text{-BTC})(bipy)]_n$ (**1**) (1,2,4-BTC = 1,2,4-benzenetricarboxylic acid, bipy = 4,4′-bipyridine) and $[Zn(1,3,5\text{-BTC})(bipy)(H_2O) \cdot 3H_2O]_n$ (**2**) (1,3,5-BTC = 1,3,5-benzenetricarboxylic acid, bipy = 4,4′-bipyridine), have been synthesized using the principle of crystal engineering. Despite similar reactants and reaction conditions, complex **1** is an infinite 2-D square-grid network while complex **2** is a 1-D zigzag chain. 4,4′-bipyridine is a terminal monodentate ligand towards the Zn centers, which is rare in Zn polymers because 4,4′-bipyridine is a linear molecule and bridges central ions using two nitrogen atoms. Both coordination polymers show blue luminescence in the solid state at room temperature.

Keywords: Zinc coordination polymer; Crystal structure; Benzenetricarboxylic acid; Hydrothermal; Luminescence

1. Introduction

Transition metal-organic coordination polymers attract attention for their fascinating applications in catalysis, co-operative magnetic behavior, non-linear optical activity and electrical conductivity, and also for their interesting topologies [1–11]. To design metal-organic coordination polymers from transition metals and organic ligands with novel architectures and desired functionalities by the principles of crystal engineering has been a challenging subject in coordination chemistry. Selection or design of a ligand containing features such as flexibility, versatile binding modes, and the ability to form hydrogen bonds is crucial to the construction of polymeric complexes [12].

Flexible benzenetricarboxylic acids are good candidates for construction of metal-organic complexes, showing many advantages over other organic ligands: they have

---

*Corresponding author. Email: lijk0212@yahoo.com.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701324044

three carboxyl groups that can be completely or partially deprotonated with rich coordination modes; they can act not only as a hydrogen-bond acceptor but also as a hydrogen-bond donor, depending upon the number of deprotonated carboxyl groups; they may connect metal ions in different directions due to their rigidity and polycarboxylate groups; it is easy to form crystalline complexes of them, and their metal-organic complexes always show high dimensional structures [12–34].

Especially, 1,2,4-benzenetricarboxylate, an unsymmetrical benzene polycarboxylate, can be assembled around metal centers in diverse arrangements owing to the possession of two or more coordination sites with differing donor ability, resulting in structures with novel topologies. However, only a few metal-organic frameworks have been constructed from 1,2,4-BTC [25–34]. So from the standpoint of molecular design, we have attempted to assemble high dimensional metal-organic complexes using 1,2,4-BTC as the bridging ligand.

4,4′-bipyridine is an excellent rigid bridging ligand for construction of metal-organic frameworks, the two terminal nitrogens can link central ions to form 1D, 2D or 3D structures; there have been many reports on various dimensional hybrid complexes assembled by 4,4′-bipy ligands [35–40]. The analysis above provides motivation for design and synthesis of metal-organic interpenetrating frameworks containing 1,2,4-BTC and 4,4′-bipy.

Hydrothermal synthesis has proven to be a powerful method for preparation of metal-organic coordination compounds; in this manuscript used to prepare a zinc complex $[Zn(1,2,4\text{-}BTC)(bipy)]_n$. The structure forms an infinite 2-D square-grid network, crystallizing in the space group *P*2(1)/c. The zinc coordination number is five, unlike the normal four or six. Only one nitrogen atom of 4,4′-bipyridine is coordinated to Zn ion while the other is uncoordinated. As continuing study of the zinc complexes with benzenetricarboxylates and heteroaromatic N-donor ligands, we also prepared the zinc complex with 1,3,5-BTC and 4,4′-bipy, $[Zn(1,3,5\text{-}BTC)(bipy)(H_2O) \cdot 3H_2O]_n$, which forms a zigzag chain structure; 4,4′-bipy also is a monodentate terminal ligand.

2. Experimental

2.1. *Preparation of zinc complexes*

$Zn(CH_3COO)_2 \cdot 2H_2O$, 1,3,5-benzenetricarboxylic acid and 1,2,4-benzenetricarboxylic acid were purchased from Aldrich and used without further purification. All other reagents were commercially available and used as received.

2.2. *[Zn(1,2,4-BTC)(bipy)]*$_n$ *(1)*

$Zn(CH_3COO)_2 \cdot 2H_2O$ (110 mg, 0.5 mmol), 1,2,4-benzenetricarboxylic acid (105.1 mg, 0.5 mmol) and 4,4′-bipyridine (99.1 mg, 0.5 mmol) were mixed in 10 mL deionized water. After stirring 30 min, the mixture was placed in a 25 mL Teflon-lined reactor and heated at 160°C in an oven for 4 d. The resulting solution was cooled slowly to room temperature; well-shaped colorless single crystals of **1** suitable for X-ray four-circle diffraction analysis were obtained. Yield: 76%. Anal. Calcd for

$C_{19}H_{12}N_2O_6Zn$: C, 53.06; H, 2.79; N, 6.52%; Found: C, 52.98; H, 2.85; N, 6.58%. IR (KBr pellet, cm^{-1}): 1411 cm^{-1} (V_{sCOO^-}), 1546 cm^{-1} (V_{asCOO^-}).

2.3. *[Zn(1,3,5-BTC)(bipy)(H_2O) · 3H_2O]$_n$ (2)*

$Zn(CH_3COO)_2 \cdot 2H_2O$ (110 mg, 0.5 mmol), 1,3,5-benzenetricarboxylic acid (105.1 mg, 0.5 mmol) and 4,4′-bipyridine (99.1 mg, 0.5 mmol) were mixed in 10 mL deionized water. After stirring 30 min, the mixture was placed in a 25 mL Teflon-lined reactor and heated at 160°C in an oven for 4d. The resulting solution was cooled slowly to room temperature; well-shaped colorless single crystals of **2** suitable for X-ray four-circle diffraction analysis were obtained. Yield: 62%. Anal. Calcd. for $C_{19}H_{20}N_2O_{10}Zn$: C, 45.44; H, 3.99; N, 5.58%; Found: C, 45.37; H, 4.02; N, 5.48%. IR (KBr pellet, cm^{-1}): 1412 cm^{-1} (V_{sCOO^-}), 1546 cm^{-1} (V_{asCOO^-}).

2.4. *Measurements and apparatus*

Elemental analyses (C, H, N) were determined with an *Elementar Cario EL* elemental analyzer. IR spectra were recorded with a Nexus 912 AO446 FT-IR spectrophotometer (KBr pellet) in the 4000 ~ 400 cm^{-1} region. The luminescence (excitation and emission) spectra for the solid complexes were determined with a Perkin-Elmer LS-55 spectrophotometer, whole excitation and emission slit widths were 10 and 5 nm, respectively.

2.5. *Crystal structure determination*

X-ray single-crystal diffraction data for crystals with dimensions 0.15 × 0.10 × 0.08 mm for **1** and 0.10 × 0.05 × 0.05 mm for **2** were performed with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) on a CCD detector four-circle diffractometer and were collected by the ω–2θ scan technique. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS-97 and SHELXL-97 [41, 42].

3. Results and discussion

3.1. *Crystal structures of zinc complexes*

The structures of [Zn(1,2,4-BTC)(bipy)]$_n$ (**1**) and [Zn(1,3,5-BTC)(bipy)(H_2O) · 3H_2O]$_n$ (**2**) were determined by single crystal X-ray crystallography. The crystallographic and refinement data are in table 1, with selected bond lengths and angles for **1** and **2** listed in table 2.

[Zn(1,2,4-BTC)(bipy)]$_n$ crystallizes in the monoclinic system, with space group *P*2(1)/c. As shown in figure 1, the fundamental units of **1** contain one Zn center, one 1,2,4-BTC and one 4,4′-bipy. The Zn center is penta coordinate by four carboxylate oxygens and one pyridyl nitrogen; the coordination geometry can be described in terms of a slightly distorted tetragonal pyramidal configuration. The four oxygen

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Formula	$C_{19}H_{12}N_2O_6Zn$	$C_{19}H_{20}N_2O_{10}Zn$
Relative molecular weight M	429.68	501.74
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Radiation	Mo-Kα	Mo-Kα
Crystal system	*P*2(1)/c	*C*2/c
Space group	Monoclinic	Monoclinic
Unit dimensions (Å, °)		
a	9.910(5)	7.874(3)
b	16.796(8)	17.312(6)
c	11.333(5)	32.429(11)
β	99.994(7)	92.308(6)
V (Å^3)	1857.7(16)	4417(3)
Z	4	8
D_c (Mg m^{-3})	1.536	1.509
F(000)	872	2064
Crystal size (mm^3)	$0.15 \times 0.10 \times 0.08$	$0.10 \times 0.05 \times 0.05$
θ range for data collection (°)	2.19 to 25.01	1.26 to 25.01
Reflections/collected/unique	6452/3252 [R(int) = 0.0305]	9173/3908 [R(int) = 0.0827]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3252/0/253	3908/0/289
Goodness-of-fit on F^2	1.043	1.078
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0484$, $wR_2 = 0.1149$	$R_1 = 0.0742$, $wR_2 = 0.1910$
Largest diff. peak and hole (e Å^{-3})	0.891 and −0.568	1.445 and −0.499

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

1		**2**	
Zn(1)–O(5)	2.017(4)	Zn(1)–O(2)	1.924(5)
Zn(1)–O(2)	2.020(4)	Zn(1)–O(3)	1.939(5)
Zn(1)–N(1)	2.025(4)	Zn(1)–N(1)	2.026(6)
Zn(1)–O(1)	2.038(4)	Zn(1)–O(7)	2.072(6)
Zn(1)–O(6)	2.048(4)		
O(5)^a–Zn(1)–O(2)^b	87.47(18)	O(2)–Zn(1)–O(3)^a	119.2(2)
O(5)^a–Zn(1)–N(1)	105.09(17)	O(2)–Zn(1)–N(1)	127.9(2)
O(2)^b–Zn(1)–N(1)	103.28(16)	O(3)^a–Zn(1)–N(1)	104.1(2)
O(5)^a–Zn(1)–O(1)	90.03(18)	O(2)–Zn(1)–O(7)	103.8(2)
O(2)^b–Zn(1)–O(1)	158.13(16)	O(3)^a–Zn(1)–O(7)	99.3(2)
N(1)–Zn(1)–O(1)	98.36(16)	N(1)–Zn(1)–O(7)	95.6(2)
O(5)^a–Zn(1)–O(6)^c	157.64(17)		
O(2)^b–Zn(1)–O(6)^c	86.96(18)		
N(1)–Zn(1)–O(6)^c	97.26(17)		
O(1)–Zn(1)–O(6)^c	87.16(17)		

Symmetry transformations used to generate equivalent atoms:
For complex **1**: $^a-x+3/2,\ y+1/2,\ -z+3/2$. $^bx+1,\ -y+2,\ -z+1$. $^cx-1/2,\ -y+3/2,\ z-1/2$. $^d-x+3/2,\ y-1/2,\ -z+3/2$. $^ex+1/2,\ -y+3/2,\ z+1/2$.
For complex **2**: $^ax-1/2,\ y-1/2,\ z$. $^bx+1/2,\ y+1/2,\ z$.

atoms O(1), O(2), O(5) and O(6) are from four different carboxylate groups, binding Zn in a symmetrical fashion from Zn(1)–O(1) distance of 2.038(4) Å, Zn(1)–O(2) distance of 2.020(4) Å, Zn(1)–O(5) distance of 2.017(4) Å and a Zn(1)–O(6) distance of 2.048(4) Å.

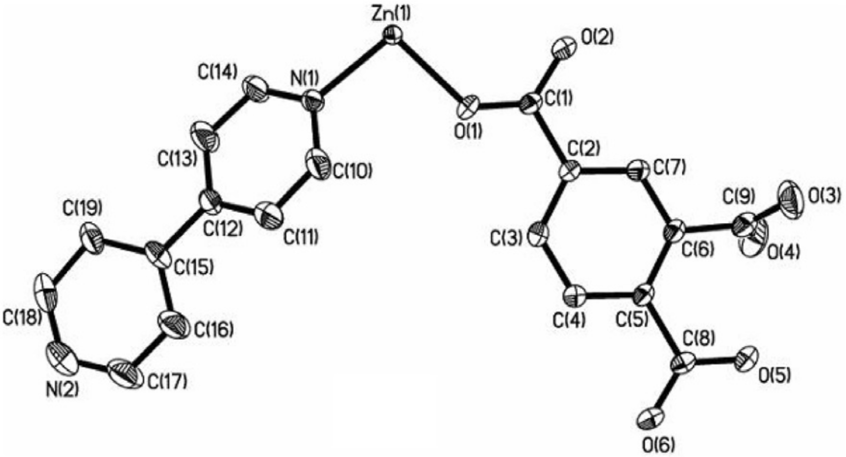

Figure 1. The ORTEP drawing for **1** with atom labeling scheme.

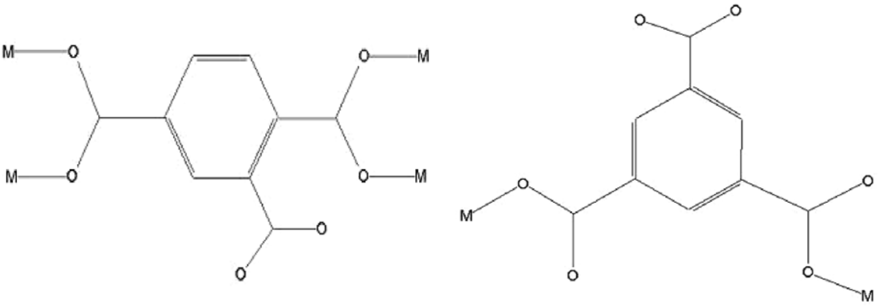

Figure 2. The coordination modes of 1,3,5-BTC and 1,2,4-BTC in **1** and **2**.

All 1,2,4-BTC ligands are doubly deprotonated, acting as tetradentate-bridging ligands towards Zn. For one 1,2,4-BTC anion, four oxygen atoms from the two opposite carboxylates are coordinated to four Zn centers, as shown in figure 2(a). Two Zn centers are connected into a centrosymmetric binuclear unit $[Zn(1,2,4\text{-}BTC)(bipy)]_2$; the 1,2,4-BTC bridges are symmetric with eight-membered rings $[Zn(1)–O(1)–C(1)–O(2)]_2$ or $[Zn(1)–O(5)–C(1)–O(6)]_2$, giving the distance between two Zn centers of 2.9907(14) Å. The binuclear unit leads to a chain along both the *a* and *b* axes and two equivalent chains intersect to result in a neutral two-dimensional square grid, with a void space of about 11.101 Å, as shown in figure 3. The pyridine rings alternately parallel each other on both sides of the grid planar construction, intruding into the square cavities to result in an interdigitation framework. The interdigitated pyridyl rings form π–π stacks and interdigitation of pyridyl rings from adjacent square grids efficiently fills the void space. Additionally, there are O–H $\cdots$ N intermolecular hydrogen bonds between oxygens of the uncoordinated carboxyls and the nitrogen atoms of the pyridine rings with bond angles of 167.0° $(O(3)–H(3B)\cdots N(2)^{f})$. The interlayer hydrogen bonds are a novel alternate fashion and consolidate the stacked arrangement leading to a 3D supramolecular architecture. Figure 4 shows the packing

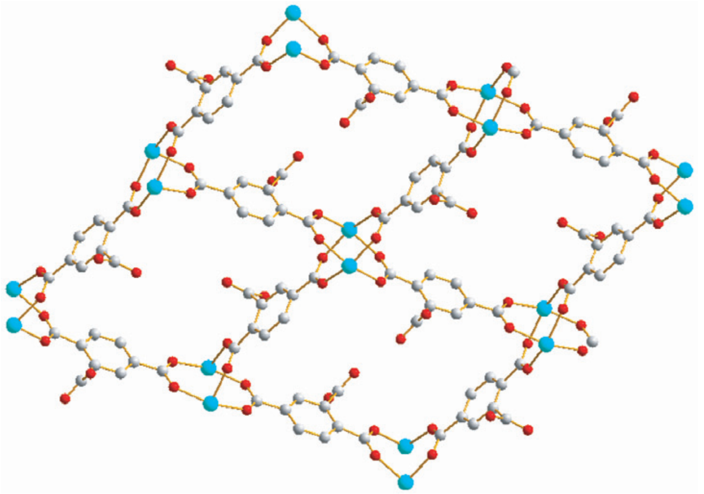

Figure 3. The square grid drawing for **1**.

view of a unit cell for **1**. The detailed hydrogen bonding data for **1** and **2** are shown in table 3.

Complex **2** $[Zn(1,3,5\text{-BTC})(bipy)(H_2O) \cdot 3H_2O]_n$ crystallizes in the monoclinic system, with space group $C2/c$. Figure 5 shows the coordination geometry and atom labeling in the crystal structure of **2**, consisting of one Zn, one 1,3,5-BTC, one bipy, one coordinated water and three lattice water molecules. The crystal structure of **2** consists of a 1-D zigzag chain built from connections of Zn ions and 1,3,5-BTC ligands alternately along the *b* axis. The 1,3,5-BTC benzene rings lie on one side of the zigzag chain in the same plane, and two carboxyl groups are *trans*, which has less steric hindrance and favors crystal growth. Simultaneously, bipy planes are coordinated with Zn(II) centers monodentate on the other side of the zigzag chain alternately paralleling each other. Each Zn center is tetra coordinate by one nitrogen and three oxygens in a distorted tetrahedron. Bond distances between the Zn center and nitrogen from bipy is 2.026(6) Å (Zn(1)–N(1)), similar to **1**; two oxygen atoms are from two bridging carboxylate groups with bond distances of 1.924(5) Å (Zn(1)–O(2)) and 1.939(5) Å (Zn(1)–O(3)); another oxygen atom is from one coordinated water molecule with longer bond distance, 2.072(6) Å (Zn(1)–O(7)).

Like 1,2,4-BTC in **1**, 1,3,5-BTC is doubly deprotonated, however, they are bidentate-bridging towards Zn. For one 1,3,5-BTC anion, two oxygen atoms from two different carboxyls coordinate to two Zn centers, as shown in figure 2(b). The Zn centers are interconnected by bridging 1,3,5-BTC ligands to form an infinite chain (figure 6); the chains are further linked by interchain hydrogen bonds O–H $\cdots$ N between the oxygen of uncoordinated carboxyls and the nitrogen of pyridine with bond angle of 173.8° (O(5)–H(5A) $\cdots$ N(2)^c). Figure 7 shows the packing view of a unit cell for **2**.

3.2. *Comparison with Zn analogs*

Previously, the three-dimensional coordination polymer $[Zn_6(1,2,4\text{-BTC})_4(4,4'\text{-bipy})_5]_n$ had been synthesized, which crystallizes in the triclinic system [26]. In this structure,

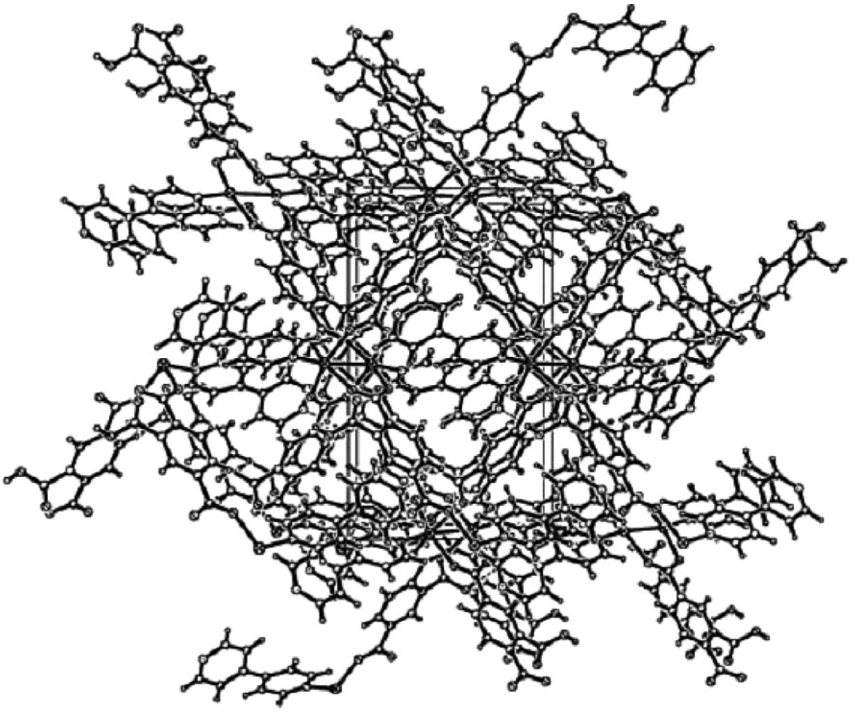

Figure 4. The packing unit cell diagram for **1**.

Table 3. Hydrogen bonds (Å) for **1** and **2**.

D–H ··· A	∠(D–H)	∠(H ··· A)	∠(D ··· A)	∠(DHA)
(1) O(3)–H(3B) ··· N(2)^{f}	0.82	1.87	2.672(7)	167.0
(2) O(5)–H(5A) ··· N(2)^{c}	0.82	1.76	2.581(9)	173.8

Symmetry transformations used to generate equivalent atoms:
For complex **1**: $^{a}-x+3/2,\ y+1/2,\ -z+3/2$. $^{b}x+1,\ -y+2,\ -z+1$. $^{c}x-1/2,\ -y+3/2,\ z-1/2$. $^{d}-x+3/2,\ y-1/2,\ -z+3/2$. $^{e}x+1/2,\ -y+3/2,\ z+1/2$. $^{f}x+3/2,\ -y+3/2,\ z-1/2$.
For complex **2**: $^{a}x-1/2,\ y-1/2,\ z$. $^{b}x+1/2,\ y+1/2,\ z$. $^{c}x-1/2,\ -y+3/2,\ z+1/2$.

both Zn(1) and Zn(2) are tetrahedrally coordinated, whereas Zn(3) is hexa coordinate in a distorted octahedral geometry, unlike the penta coordinate zinc in [Zn(1,2,4-BTC)(bipy)]$_n$. The three zinc centers are bridged by the 1,2,4-BTC ligands to form a trinuclear subunit, which is connected through 4,4′-bipy and 1,2,4-BTC ligands to construct a three-dimensional architecture. The 4,4′-bipy ligands are bidentate-bridging. In addition, 1,2,4-BTC ligands are completely deprotonated at the pH of the reaction (about 7) and a complex with 3 : 2 metal/ligand molar ratio was obtained, differing from 1 : 1 complex, [Zn(1,2,4-BTC)(bipy)]$_n$.

Another three-dimensional coordination polymer [Zn_2(OH)(1,3,5-BTC)]$_2$(4,4′-bipy) crystallizes in the tetragonal system [43]. In this structure, each pair of Zn atoms is bridged by hydroxyl and a carboxylate in a dimonodentate fashion to form a [$Zn_2(OH)(O_2C–)$] unit. Four [$Zn_2(OH)(O_2C–)$] units are further linked by eight carboxylates in a dimonodentate fashion to produce a $Zn_8(OH)_4(O_2C–)_{12}$ secondary

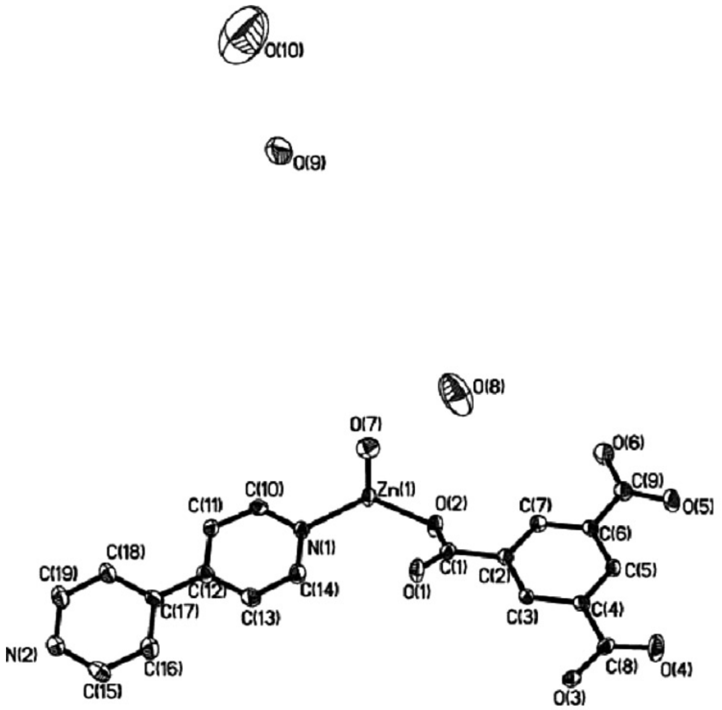

Figure 5. The ORTEP drawing for **2** with atom labeling scheme.

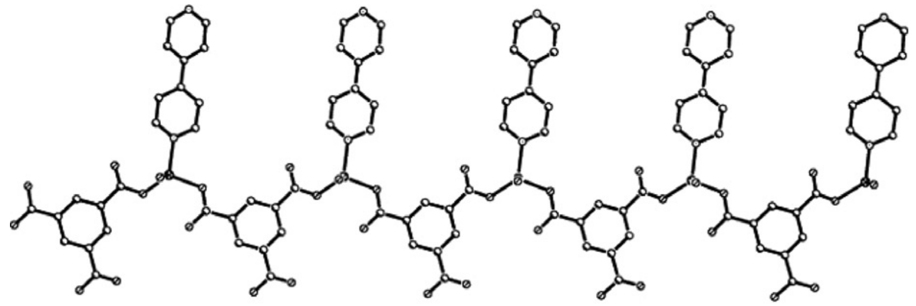

Figure 6. The 1-D chain drawing for **2**.

building unit. 4,4′-bipy molecules exist as templates in the pore formed by Zn and 1,3,5-BTC and aren't coordinated; 1,3,5-BTC ligands are completely deprotonated. Unlike this structure, both coordinated and lattice water molecules exist in $[Zn(1,3,5\text{-}BTC)(bipy)(H_2O) \cdot 3H_2O]_n$.

3.3. *Luminescent properties of zinc complexes*

Complexes **1** and **2** (crystalline state) exhibit an intense blue photoluminescence upon radiation with UV light at room temperature. Using 440 nm as the emission wavelength, the excitation band of **1** has a main peak at 320 nm; under excitation wavelength

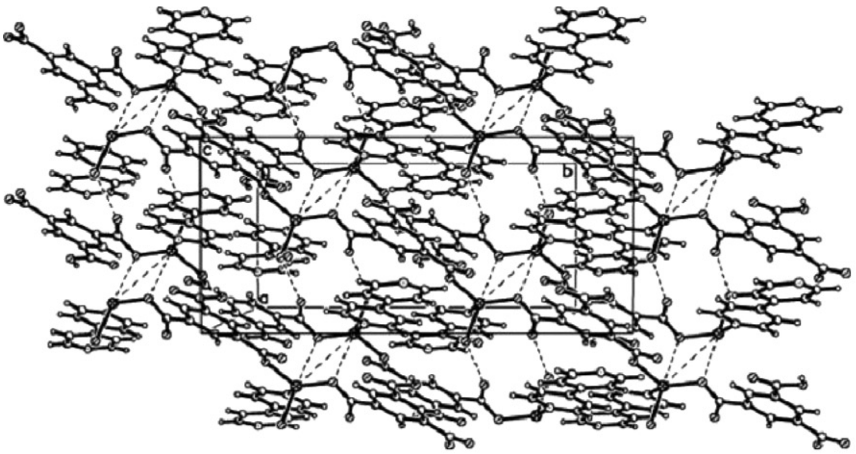

Figure 7. The packing unit cell diagram for **2**.

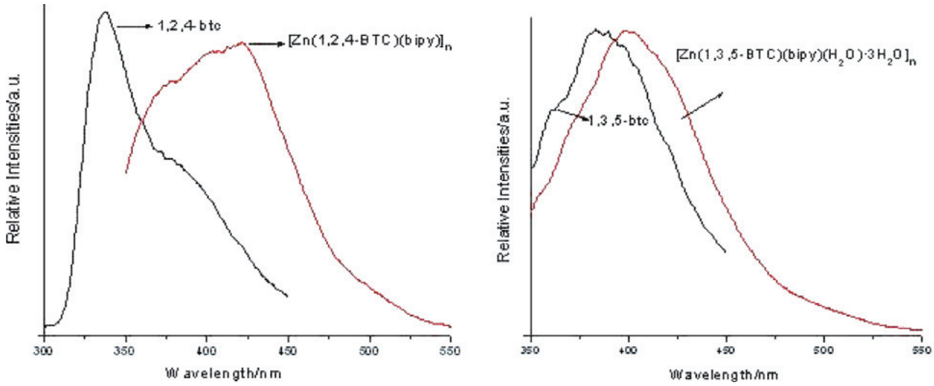

Figure 8. Luminescent emission spectra of Zn complexes.

320 nm, the broad emission band of **1** ranges from 350 to 550 nm with maximum emission at 420 nm. We further measured the emission spectrum of the free 1,2,4-BTC molecule, which shows one emission at 337 nm, indicating that free 1,2,4-BTC has no emission in the visible region, but when it is bound to a zinc center, blue luminescence is observed, as shown in figure 8. The lower energy band would be assigned to the ligand-to-metal charge transfer (LMCT), and the observed luminescence of **1** is attributed to the 1,2,4-BTC ligand [44, 45].

Similarly, excitation bands for **2** under 440 nm show one main peak at 323 nm; the emission band of **2** ranges from 350 to 550 nm with a maximum emission peak at 398 nm; the emission spectrum of free 1,3,5-BTC shows one emission at 385 nm. The observed luminescence of **2** is attributed to the coordinated 1,3,5-BTC ligand.

Since hydrothermal products are usually stable and insoluble in common solvents arising from their polymeric structures, the two complexes may be candidates for photoactive materials.

4. Conclusions

Two polymeric Zn compounds of benzenetricarboxylate and 4,4′-bipydirine have been synthesized by the hydrothermal method. X-ray diffraction crystal structure analysis reveals that **1** is an infinite 2-D square-grid network while **2** is a 1-D zigzag chain, in spite of the similar reactants and reaction conditions. Unusually, 4,4′-bipyridine is a terminal monodentate ligand towards the Zn centers. The fluorescence excitation and emission spectra reveal that both **1** and **2** exhibit a strong blue emission in the solid state at room temperature and may be potential candidates for photoactive materials.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited into the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-259950 for **1** and CCDC-259951 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (20301013).

References

[1] O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto. *Science*, **49**, 271 (1996).
[2] O. Kahn, C. Martinez. *Science*, **44**, 279 (1998).
[3] S.R. Batten, R. Robson. *Angew. Chem., Int. Ed.*, **37**, 1460 (1998).
[4] O.R. Evans, R. Xiong, Z. Wang, G.K. Wong, W. Lin. *Angew. Chem., Int. Ed.*, **38**, 536 (1999).
[5] O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy. *Acc. Chem. Res.*, **31**, 474 (1998).
[6] M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura. *J. Am. Chem. Soc.*, **116**, 1151 (1994).
[7] S.S. Zhu, P.J. Carroll, T.M. Swager. *J. Am. Chem. Soc.*, **118**, 8713 (1996).
[8] L.S. Long, X.M. Chen, M.L. Tong, Z.G. Sun, Y.P. Ren, R.B. Huang, L.S. Zheng. *J. Chem. Soc., Dalton Trans.*, 2888 (2001).
[9] Z.F. Chen, R.G. Xiong, B.F. Abrahams, X.Z. You, C.M. Che. *J. Chem. Soc., Dalton Trans.*, 2453 (2001).
[10] J.Y. Lu, K.A. Runnels, C. Norman. *Inorg. Chem.*, **40**, 4516 (2001).
[11] P. Kapoor, A. Pathak, R. Kapoor, P. Venugopalan. *Inorg. Chem.*, **23**, 6153 (2002).
[12] R. Cao, D.F. Sun, Y.C. Liang, M.C. Hong, K. Tatsumi, Q. Shi. *Inorg. Chem.*, **41**, 2087 (2002).
[13] C.J. Kepert, M.J. Rosseinsky. *Chem. Commun.*, 31 (1998).
[14] T.J. Prior, M.J. Rosseinsky. *Chem. Commun.*, 1222 (2001).
[15] Z.Z. Lin, J.H. Luo, M.C. Hong, R.H. Wang, L. Han, R. Cao. *J. Solid State Chem.*, **177**, 2494 (2004).
[16] K.Y. Choi, K.M. Chun, H. Suh. *Polyhedron*, **20**, 57 (2001).
[17] J. Zhu, X.H. Bu, P.Y. Feng, G.D. Stucky. *J. Am. Chem. Soc.*, **122**, 11563 (2000).
[18] D.P. Cheng, M.A. Khan, R.P. Houser. *Inorg. Chem.*, **40**, 6858 (2001).
[19] F.A.A. Paz, J. Klinowski. *Inorg. Chem.*, **43**, 3882 (2004).
[20] S.M. Ying, J.G. Mao. *Eur. J. Inorg. Chem.*, 1270 (2004).
[21] J.L. Song, J.G. Mao, Y.Q. Sun, A. Clearfield. *Eur. J. Inorg. Chem.*, 4218 (2003).
[22] M.R.S.J. Foreman, T. Gelbrich, M.B. Hursthouse, M.J. Plater. *Inorg. Chem. Commun.*, **3**, 234 (2000).

[23] T.B. Lu, H. Xiang, R.L. Luck, L. Jiang, Z.W. Mao, L.N. Ji. *New J. Chem.*, **26**, 969 (2002).
[24] W.J. Zheng, X. Liu, J.H. Guo, L.Y. Wu, D.Z. Liao. *Inorg. Chim. Acta*, **357**, 1571 (2004).
[25] Y.Y. Yang, Z.Q. Huang, L. Szeto, W.T. Wong. *Appl. Organomet. Chem.*, **18**, 97 (2004).
[26] P.Q. Zheng, L.S. Long, R.B. Huang, L.S. Zheng. *Appl. Organomet. Chem.*, **17**, 739 (2003).
[27] L. Wang, Z. Shi, G.H. Li, Y. Fan, W.S. Fu, S.H. Feng. *Sol. St. Sci.*, **6**, 85 (2004).
[28] N. Hao, E.H. Shen, Y.G. Li, E.B. Wang, C.W. Hu, L. Xu. *Inorg. Chem. Commun.*, **7**, 131 (2004).
[29] C. Qin, X.L. Wang, E.B. Wang, C.W. Hu, L. Xu. *Inorg. Chim. Acta*, **357**, 3683 (2004).
[30] Y. Yan, C.D. Wu, C.Z. Lu. *Z. Anorg. Allg. Chem.*, **629**, 1991 (2003).
[31] P.Q. Zheng, L.S. Long, R.B. Huang, L.S. Zheng. *Appl. Organomet. Chem.*, **17**, 739 (2003).
[32] P.Q. Zheng, L.S. Long, R.B. Huang, L.S. Zheng. *Appl. Organomet. Chem.*, **17**, 647 (2003).
[33] Z.L. Lu, W. Chen, J.Q. Xu, L.J. Zhang, C.L. Pan, T.G. Wang. *Inorg. Chem. Commun.*, **6**, 244 (2003).
[34] M.J. Plater, M.R.S.J. Foreman, R.A. Howie, J.M.S. Shakle, A.M.Z. Slawin. *Inorg. Chim. Acta*, **315**, 126 (2001).
[35] J. Tao, X. Yin, Y.B. Jiang, L.F. Yang, R.B. Huang, L.S. Zheng. *Eur. J. Inorg. Chem.*, 2678 (2003).
[36] R.W. Gable, B.F. Hoskins, R.J. Robson. *J. Chem. Soc., Chem. Commun.*, 1677 (1990).
[37] O.M. Yaghi, H. Li. *J. Am. Chem. Soc.*, **118**, 295 (1996).
[38] O.M. Yaghi, H. Li, T.L. Groy. *Inorg. Chem.*, **36**, 4292 (1997).
[39] N. Hao, E.H. Shen, Y.G. Li, E.B. Wang, C.E. Hu, L. Xu. *J. Mol. Struct.*, **691**, 273 (2004).
[40] K.J. Nordell, K.N. Schultz, K.A. Higgins, M.D. Smith. *Polyhedron*, **23**, 2161 (2004).
[41] G.M. Sheldrick. *Acta Cryst.*, **A46**, 467 (1990).
[42] G.M. Sheldrick. *SHELXS-97, a Program for X-Ray Crystal Structure Solution, and SHELXL-97, a Program for X-ray Structure Refinement*, Göttingen University, Germany (1997).
[43] Z. Shi, G.H. Li, L. Wang, L. Gao, X.B. Chen, J. Hua, S.H. Feng. *Cryst. Growth Des.*, **4**, 25 (2004).
[44] W.Y. Yang, H. Schmider, Q.G. Wu, Y.S. Zhang, S.N. Wang. *Inorg. Chem.*, **39**, 2397 (2000).
[45] Y.F. Zhou, R.H. Wang, B.L. Wu, R. Cao, M.C. Hong. *J. Mol. Struct.*, **697**, 73 (2004).