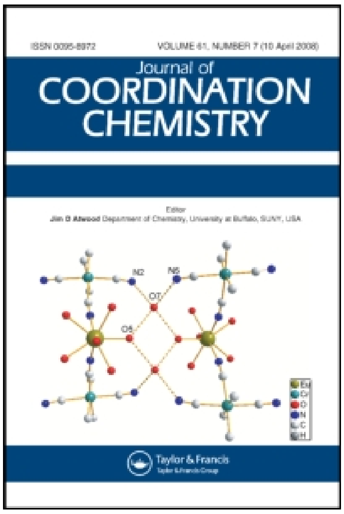


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure, and luminescence of a new zinc(II) coordination polymer based on 2-naphthol-5-carboxylate and 4,4'-bipyridine

Chun-Sen Liu[a]; Min Hu[a]; Qiang Zhang[a]; Li-Ming Zhou[a]; Shao-Ming Fang[a]
[a] Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou University of Light Industry, Zhengzhou, Henan 450002, P.R. China

To cite this Article Liu, Chun-Sen , Hu, Min , Zhang, Qiang , Zhou, Li-Ming and Fang, Shao-Ming(2010) 'Synthesis, crystal structure, and luminescence of a new zinc(II) coordination polymer based on 2-naphthol-5-carboxylate and 4,4'-bipyridine', Journal of Coordination Chemistry, 63: 20, 3541 — 3550

To link to this Article: DOI: 10.1080/00958972.2010.517266

URL: http://dx.doi.org/10.1080/00958972.2010.517266

Journal of Coordination Chemistry
Vol. 63, No. 20, 20 October 2010, 3541–3550

Synthesis, crystal structure, and luminescence of a new zinc(II) coordination polymer based on 2-naphthol-5-carboxylate and 4,4′-bipyridine

CHUN-SEN LIU, MIN HU, QIANG ZHANG, LI-MING ZHOU
and SHAO-MING FANG*

Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou University of Light Industry, Zhengzhou, Henan 450002, P.R. China

(*Received 8 March 2010; in final form 16 July 2010*)

To further explore the coordination possibilities of naphthalene-based carboxylic acids, a Zn^{II} coordination polymer, $[Zn_3(\mathbf{L})_6(bipy)_2]_n$ (**1**), with bulky 2-naphthol-5-carboxylate (**L**) and bridging 4,4′-bipyridine (bipy), was synthesized and characterized. Structural analysis reveals that **1** is a 1-D polymeric chain with trinuclear units as nodes, which are further extended *via* interchain secondary interactions, such as $O–H \cdots O$ hydrogen-bonding and aromatic $\pi \cdots \pi$ stacking interactions, to form an overall 3-D framework. Complex **1** exhibits strong solid-state luminescence emission at room temperature, mainly originating from intraligand $\pi \rightarrow \pi^*$ transition of **L**.

Keywords: Zn^{II} complex; 2-Naphthol-5-carboxylate ligand; Crystal structure; Luminescent property

1. Introduction

Rational design and preparation of metal–organic frameworks (MOFs) or coordination polymers has become an exciting branch in crystal engineering and supramolecular chemistry because of their structural diversities and potential applications in the fields of catalysis, guest–host chemistry, optics, and magnetism [1]. An attractive target of the research in this field is the controllable assembly of coordination polymers with desired structures and properties [2], through appropriate choice of organic ligands as spacers, bridges, or terminal groups with metal ions or metal clusters as nodes. Carboxylic acids exhibit diverse coordination modes, especially for benzene- and naphthalene-based di- or multi-carboxylic acids such as 1,2-, 1,3-, and 1,4-benzenedicarboxylic acid [3–5], 1,3,5-benzenetricarboxylic acid [6], 1,2,4,5-benzenetetracarboxylic acid [7], 1,4- and 2,6-naphthalenedicarboxylate [8, 9] as well as 1,4,5,8-naphthalenetetracarboxylate [10] used in the preparation of various coordination polymers. However, in comparison with the benzene- and naphthalene-based di- and multi-carboxylic acid ligands,

---

*Corresponding author. Email: smfang@zzuli.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.517266

investigation of monocarboxylic acid ligands with naphthalene ring skeleton such as 2-naphthol-5-carboxylic acid (**HL**) used here, have been less common. Introduction of 2,2′-bipyridine bidentate chelating or 4,4′-bipyridine linear bridging molecules into reaction systems involving various carboxylic acids, as auxiliary co-ligands, may generate some interesting coordination architectures [11].

In our previous work, 2-naphthol-5-carboxylic acid (**HL**) has been used to construct a 3-D Ag^I as well as two dinuclear Cd^{II} and Eu^{III} coordination complexes which exhibit interesting luminescent properties [12–14]. To further explore the coordination possibilities of naphthalene-based monocarboxylic acid ligands, we chose **HL** by taking advantage of its carboxylate-bridging ability together with the steric bulk of its naphthalene ring to construct new functional d^{10} coordination complexes. Herein, we report the synthesis, structure, and luminescent/thermal properties of $[Zn_3(\mathbf{L})_6(bipy)_2]_n$ ($\mathbf{L}$ = 2-naphthol-5-carboxylate).

2. Experimental

2.1. *General methods*

All reagents and solvents were commercially available and used as received. IR spectra were measured on a TENSOR 27 (Bruker) FT-IR spectrometer with KBr pellets from 4000 to 400 cm^{-1}. Elemental analyses (C, H, and N) were performed on a Vario EL III elemental analyzer. The powder X-ray diffraction (PXRD) was recorded on a Bruker D8 Advance diffractometer (Cu-Kα, $\lambda = 1.54056$ Å) at 40 kV and 30 mA using a Cu-target tube and a graphite monochromator. Intensity data were recorded by continuous scan in a $2\theta/\theta$ mode from 3° to 80° with a step size of 0.02° and a scan speed of 8° min^{-1}. Simulation of the PXRD spectra was carried out from single-crystal data and diffraction-crystal module of the commercially available Cerius2 program [15]. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 800°C under nitrogen at a heating rate of 10°C min^{-1}. The emission/excitation spectra were recorded on an F-7000 (HITACHI) spectrophotometer at room temperature.

2.2. *Synthesis of 1*

A mixed solution of 2-naphthol-5-carboxylic acid (**HL**) (0.05 mmol) and 4,4′-bipyridine (bipy) (0.05 mmol) in CH_3OH (10 mL) in the presence of excess 2,6-dimethylpyridine (*ca* 0.05 mL for adjusting the pH to basic condition) was carefully layered on top of a H_2O solution (15 mL) of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol) in a test tube. Colorless, cubic, single crystals suitable for X-ray analysis appeared at the tube wall after *ca* 3 weeks at room temperature. Yield: ~40% based on **HL**. Anal. Calcd for $C_{86}H_{58}N_4O_{18}Zn_3$ (%): C, 63.31; H, 3.58; N, 3.43. Found (%): C, 63.10; H, 3.49; N, 3.62. IR (KBr pellet, cm^{-1}): 3305(s, br), 2540(w), 1847(w), 1632(m), 1607(vs), 1567(vs), 1513(s), 1465(m), 1417(vs), 1380(s), 1282(m), 1239(m), 1220(m), 1167(m), 1144(w), 1068(w), 1045(w), 1011(w), 977(w), 953(m), 865(w), 839(w), 810(m), 787(w), 767(w), 726(w), 661(w), 638(w), 550(w), 528(w), 499(w), 457(w).

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

Empirical formula	$C_{86}H_{58}N_4O_{18}Zn_3$
Formula weight	1631.53
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.8719(5)
b	11.9062(11)
c	15.5073(14)
α	74.156(8)
β	82.416(6)
γ	76.483(6)
Volume (Å^3), Z	1700.3(2), 1
Calculated density (g cm^{-3})	1.593
Absorption coefficient (mm^{-1})	1.133
F(000)	836
Crystal size (mm^3)	0.28 × 0.21 × 0.15
θ range for data collection (°)	3.24 to 25.00
Reflections collected	11,186
Independent reflection	5822 [R(int) = 0.0420]
Goodness-of-fit on F^2	0.973
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0453$, $wR_2 = 0.0868$
R indices (all data)	$R_1 = 0.0767$, $wR_2 = 0.0946$

$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

2.3. *Crystal structure determination*

A crystal of $0.28 \times 0.21 \times 0.15\,\mathrm{mm}^3$ was examined on a Bruker Smart 1000 CCD area-detector diffractometer at 293(2) K with Mo-Kα radiation ($\lambda = 0.71073$ Å) by ω scan mode. The program SAINT [16] was used for the integration of the diffraction profiles. Semi-empirical absorption corrections were applied using SADABS. The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [17]. The non-hydrogen atoms were refined anisotropically and hydrogens were added according to theoretical models. A summary of crystallographic data and refinement parameters is in table 1, while selected bond lengths and angles and hydrogen-bonding geometries are listed in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Synthesis and general characterization*

Complex **1** was synthesized by using slow diffusion in a test tube under mild conditions (ambient temperature and pressure). The presence of excess 2,6-dimethylpyridine is a key point for the formation of **1**, adjusting the pH to basic. IR spectra of **1** show features attributable to each part of **1** [18]. The strong, broad band, centered at 3305 cm^{-1} for **1** indicates O–H stretching of hydroxyl in **L**. IR absorptions of

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

Zn(1)–N(1)$^{\#1}$	2.126(3)	Zn(2)–O(4)	1.922(2)
Zn(1)–N(1)	2.126(3)	Zn(2)–O(2)	1.923(2)
Zn(1)–O(3)$^{\#1}$	2.152(2)	Zn(2)–N(2)$^{\#2}$	2.073(3)
Zn(1)–O(3)	2.152(2)	Zn(2)–O(5)	2.079(2)
Zn(1)–O(1)$^{\#1}$	2.182(2)	Zn(2)–O(6)	2.358(3)
Zn(1)–O(1)	2.182(2)		
N(1)$^{\#1}$–Zn(1)–N(1)	180.0	O(3)–Zn(1)–O(1)	96.20(9)
N(1)$^{\#1}$–Zn(1)–O(3)$^{\#1}$	93.94(10)	O(1)$^{\#1}$–Zn(1)–O(1)	180.00(9)
N(1)–Zn(1)–O(3)$^{\#1}$	86.06(10)	O(4)–Zn(2)–O(2)	131.89(10)
N(1)$^{\#1}$–Zn(1)–O(3)	86.06(10)	O(4)–Zn(2)–N(2)$^{\#2}$	92.54(11)
N(1)–Zn(1)–O(3)	93.94(10)	O(2)–Zn(2)–N(2)$^{\#2}$	98.35(11)
O(3)$^{\#1}$–Zn(1)–O(3)	180.000(1)	O(4)–Zn(2)–O(5)	113.35(10)
N(1)$^{\#1}$–Zn(1)–O(1)$^{\#1}$	93.66(10)	O(2)–Zn(2)–O(5)	110.51(10)
N(1)–Zn(1)–O(1)$^{\#1}$	86.34(10)	N(2)$^{\#2}$–Zn(2)–O(5)	100.21(10)
O(3)$^{\#1}$–Zn(1)–O(1)$^{\#1}$	96.20(9)	O(4)–Zn(2)–O(6)	89.11(10)
O(3)–Zn(1)–O(1)$^{\#1}$	83.80(9)	O(2)–Zn(2)–O(6)	97.68(10)
N(1)$^{\#1}$–Zn(1)–O(1)	86.34(10)	N(2)$^{\#2}$–Zn(2)–O(6)	156.83(10)
N(1)–Zn(1)–O(1)	93.66(10)	O(5)–Zn(2)–O(6)	58.30(9)
O(3)$^{\#1}$–Zn(1)–O(1)	83.80(9)		

Symmetry codes for **1**: $^{\#1} = -x+1,\ -y,\ -z+1$; $^{\#2} = -x,\ -y+1,\ -z+1$.

Table 3. Hydrogen–bonding geometry (Å, °) for **1**.

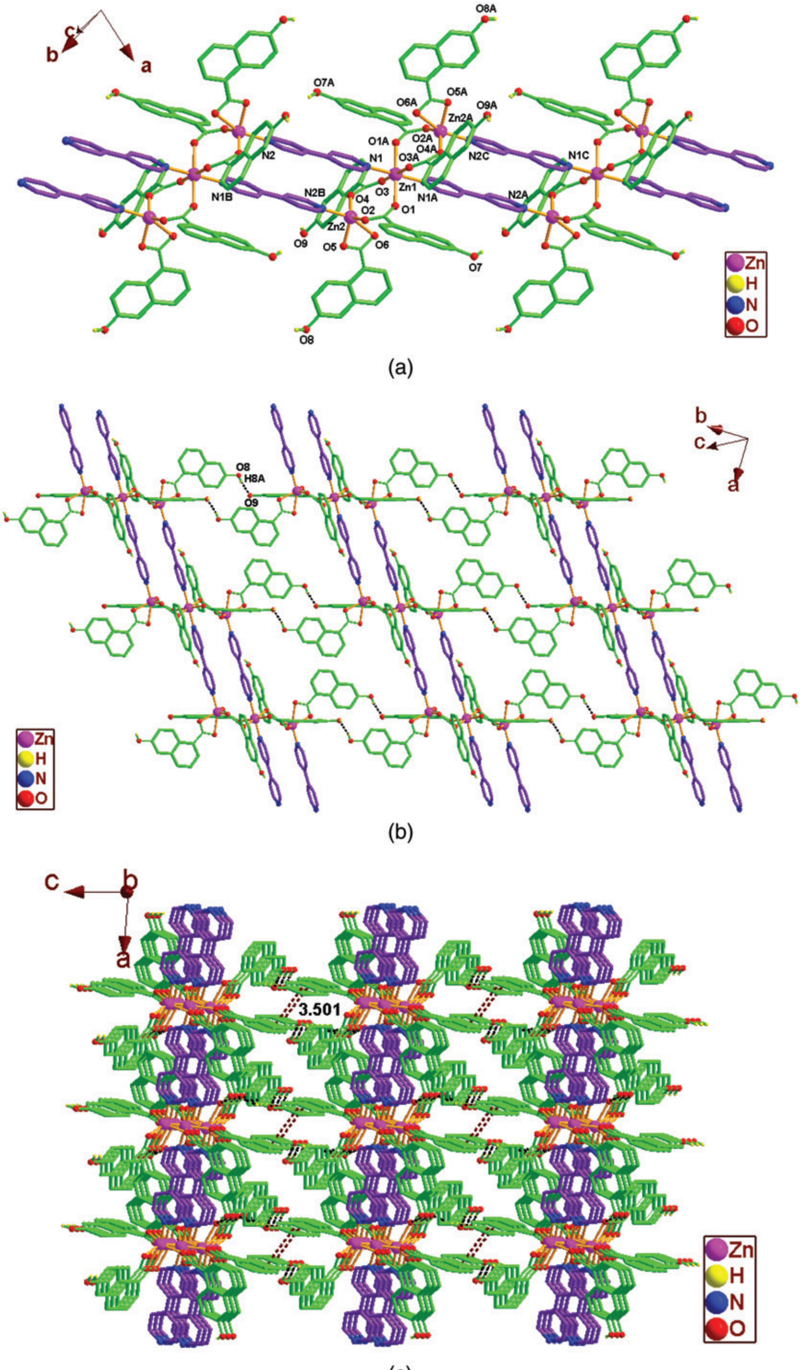
D–H $\cdots$ A	D–H	H $\cdots$ A	D $\cdots$ A	D–H $\cdots$ A
O(7)–H(7B) $\cdots$ O(6)$^{\#1}$	0.820	1.91	2.728(1)	180
O(8)–H(8A) $\cdots$ O(9)$^{\#2}$	0.820	1.93	2.737(1)	168
O(9)–H(9B) $\cdots$ O(7)$^{\#3}$	0.820	1.93	2.751(1)	174

Symmetry codes for **1**: $^{\#1} = -x+2,\ -y,\ -z+1$; $^{\#2} = -x+1,\ -y+1,\ -z+2$; $^{\#3} = x-1,\ y,\ z+1$.

carboxylates are very complicated owing to coordination diversity with metal ions. For **1**, the characteristic bands of carboxylates appear at *ca* 1607–1567 cm^{-1} for the antisymmetric stretching vibrations and at *ca* 1417–1380 cm^{-1} for the symmetric stretching vibrations; the $\Delta\nu$ values [$\Delta\nu = \nu_{as}(COO^-) - \nu_s(COO^-)$] indicating coordination modes of carboxylate in **1** are 190 and 187 cm^{-1}, consistent with structural features observed in the crystal structure [19].

3.2. *Crystal structure of 1*

Single-crystal X-ray diffraction reveals that **1** has a 1-D ribbon-like coordination array containing the centrosymmetric trinuclear [Zn$_3$(**L**)$_6$(bipy)$_2$] as nodes (figure 1a). Each asymmetric unit is composed of one and a half Zn^{II}, three **L**, and one bipy. Zn(1) and Zn(2) have different coordination spheres (figure 1a), Zn(1) is six-coordinate with a N_2O_4 distorted octahedral environment formed by four oxygens from four different **L** and two nitrogens from two distinct bipy. Zn(2) is five-coordinate by four oxygens from three different **L** and one nitrogen donor from one bipy. Two types of coordination of carboxylate were observed for **L**, μ_2-$\eta^1:\eta^1$-bridging, and μ_1-$\eta^1:\eta^1$. In **1**, bipy serves as a linear bridging spacer [N(1)–Zn(1)–N(2) angle: 180°]. Four carboxylates from four distinct **L** interlink Zn^{II} to generate a centrosymmetric trinuclear [Zn$_3$(**L**)$_6$(bipy)$_2$]



(a)

(b)

(c)

Figure 1. View of (a) the 1-D chain running along the [1$\bar{1}$0] direction in **1**, showing the coordination environment of Zn^{II} ions in **1**, (b) the 2-D network, parallel to the (110) plane, formed by inter-chain O–H $\cdots$ O hydrogen-bonds (black dashed lines), and (c) the 3-D framework, viewed along the [010] direction, formed by inter-chain O–H $\cdots$ O hydrogen-bonds (black dashed lines) and inter-chain $\pi \cdots \pi$ stacking (red and black dashed lines) interactions. The symmetry-related atoms labeled with the suffixes A, B, and C are generated by the symmetry operation $(-x+1, -y, -z+1)$, $(-x, -y+1, -z+1)$, and $(x+1, y-1, z)$. Some hydrogens have been omitted for clarity.

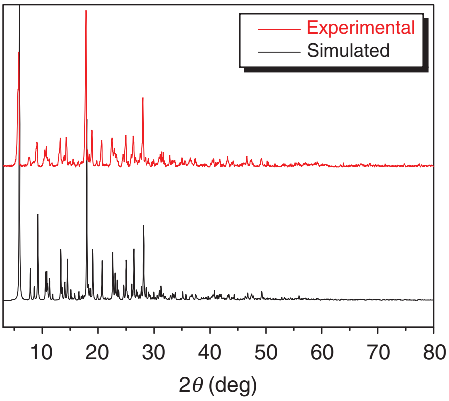


Figure 2. PXRD pattern for **1**.

cluster with non-bonding Zn(1)$\cdots$Zn(2) separation of 4.021(6) Å and Zn(2)$\cdots$Zn(1)$\cdots$Zn(2A) angle of 180° ($A = -x+1, -y, -z+1$). The trinuclear $[Zn_3(\mathbf{L})_6(bipy)_2]$ clusters are further linked by four donors from four different bipy to extend into a 1-D ribbon-like chain running along the $[1\bar{1}0]$ direction (figure 1a).

Adjacent 1-D chains are further interlinked to generate a 2-D sheet, parallel to the (110) plane, and then an overall 3-D framework, formed by the inter-chain O–H$\cdots$O hydrogen bonds between **L** ligands [O(7)–H(7B)$\cdots$O(6)#1, O(8)–H(8A)$\cdots$O(9)#2, and O(9)–H(9B)$\cdots$O(7)#3; $\#1 = -x+2, -y, -z+1$, $\#2 = -x+1, -y+1, -z+2$; $\#3 = x-1, y, z+1$; see table 3] and $\pi\cdots\pi$ stacking interactions between parallel phenyl rings of **L** with a centroid–centroid separation of 3.501 Å (figure 1b and c).

As typical aromatic carboxylates, benzene- and naphthalene-based di- or multi-carboxylic acids have been widely used to construct metal–organic coordination architectures. For instance, incorporating bipy as a bridging co-ligand, a 2-D polymeric network with supertetranuclear Zn_4O cores as building units, $[Zn_4O(ip)_3(bipy)]_n$ (ip = isophthalate) [20], a 2-D Zn^{II}-1,4-naphthalenedicarboxylate, $\{[Zn(bipy)(1,4\text{-}ndc)(H_2O)_2]\cdot(H_2O)\}_n$ (1,4-ndc = 1,4-naphthalenedicarboxylate) [21], and a 1-D double chain complex, $[Zn_4(1,8\text{-}ndc)_4(bipy)_2(en)_{0.5}(H_2O)]_n$ (1,8-ndc = 1,8-naphthalenedicarboxylate and en = 1,2-ethylenediamine) [22], have been reported. In addition, when employing multi-carboxylates instead of dicarboxylates, to react with Zn^{II} and bipy under certain conditions, $[Zn_3(btc)_2(bipy)(H_2O)_2]_n$, $\{[Zn(Hbtc)(bipy)(H_2O)](H_2O)_3\}_n$, and $[Zn(Hbtc)(bipy)(H_2O)]_n$ (btc = 1,3,5-benzenetricarboxylate) [23] as well as a 2-D polymer, $\{[Zn_2(bipy)(4btc)(H_2O)_2](H_2O)_2\}$ (4btc = 1,2,4,5-benzenetetracarboxylate) [24], have also been documented. In this work, however, **1** with **L** and bipy produced a 1-D ribbon-like coordination array. Our result exhibits a new example of the coordination versatility of simple monocarboxylic acid with a bulky naphthalene ring skeleton.

3.3. *PXRD result*

To confirm that the crystal structure is the representative of the bulk material, PXRD experiment has been carried out for **1**. The PXRD experimental and computer-simulated patterns of the corresponding complexes are shown in figure 2. Although the

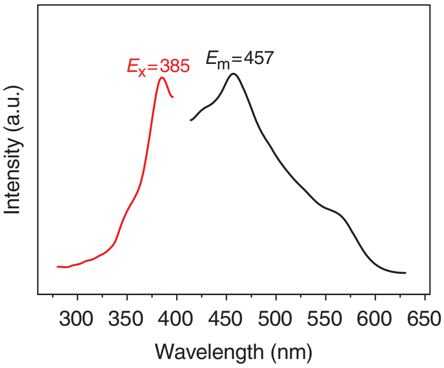


Figure 3. Solid-state excitation/emission spectra of **1** at room temperature.

experimental pattern has a few unindexed diffraction lines and some are slightly broadened in comparison with those simulated from the single-crystal modes, it still can be considered that the bulk synthesized materials and the as-grown crystals are homogeneous for **1**.

3.4. *Luminescence*

The synthesis of luminescent coordination complexes with carefully chosen ligands and d^{10} metal ions can be an efficient method for the construction of luminescence materials [25–27]. The solid-state emission spectra of **1** have been investigated at room temperature (figure 3). Excitation of the microcrystalline sample of **1** at 385 nm produced intense luminescence with peak maximum at 457 nm. Photoluminescent properties of free **HL** and bipy were explored in our previous work [11, 12]. By comparing the locations and profiles of their excitation/emission peaks with **1**, we can presume that the emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT), because Zn^{II} atom with d^{10} configuration is difficult to oxidize or to reduce [25], and should mainly be ascribed to the intraligand $\pi \rightarrow \pi^*$ transitions of **L**, which are similar to those of the reported coordination complexes with a naphthalene skeleton [14, 25]. In addition, compared with the emission peak of **HL** [12], the red shift in **1** may be caused by the bridging of bipy, which effectively changes the rigidity and conjugation upon metal coordination, reducing the loss of energy *via* a radiationless pathway [28].

3.5. *Thermogravimetric analysis*

To examine the stability of **1**, TGA was performed from room temperature to 800°C (figure 4). The weight loss curve indicates that **1** was thermally stable beyond 300°C. Then, the framework of **1** began to decompose quickly in two consecutive steps (at 349°C and 475°C), whose weight loss (obsd: 53.57%) can be attributed to loss of bipy and partial **L** (Calcd: 54.98%). The final residue is not characterized because its weight loss does not stop until heating ends at 800°C.

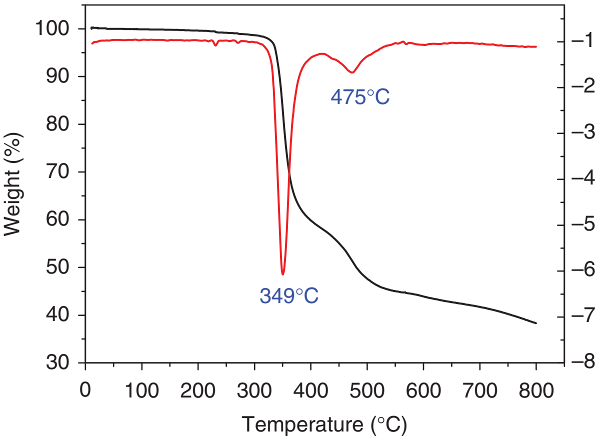


Figure 4. TGA plot of **1**.

4. Conclusions

We have obtained a 1-D Zn^{II} coordination polymer, $[Zn_3(\mathbf{L})_6(bipy)_2]_n$ (**1**), with bulky 2-naphthol-5-carboxylate (**L**) and bridging bipy. Complex **1** can be excited directly and emit intense luminescence at room temperature, closely related to the intrinsic structure arrangement. Isolation of **1** is new proof of the coordination versatility of monocarboxylates bearing a bulky aromatic skeleton, which could be used to react with different 3d transition metal ions such as Cu^{II}, Co^{II}, Ni^{II}, and Mn^{II} for constructing other coordination complexes with potential magnetic properties. Research into this possibility is underway in our laboratory.

Supplementary material

Crystallographic data (excluding structure factors) for the crystal structure reported in this article have been deposited with the Cambridge Crystallographic Data Center and allocated the deposition number CCDC 768607. This material 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; Email: deposit@ccdc.cam.ac.uk).

Acknowledgments

This work was supported by the National Natural Science Funds of China (Grant Nos. 20801049 and 20771095), the Startup Fund for PhDs of Natural Scientific Research of Zhengzhou University of Light Industry

(Grant No. 2007BSJJ001 to Chun-Sen Liu), and the Basic and Frontier Technology Research Program of Henna Province (No. 092300410127 to Li-Ming Zhou).

References

[1] (a) R.J. Kuppler, D.J. Timmons, Q.-R. Fang, J.-R. Li, T.A. Makal, M.D. Young, D. Yuan, D. Zhao, W. Zhuang, H.-C. Zhou. *Coord. Chem. Rev.*, **253**, 3042 (2009); (b) A.M. Ako, V. Mereacre, Y. Lan, W. Wernsdorfer, R. Clérac, C.E. Anson, A.K. Powell. *Inorg. Chem.*, **49**, 1 (2010); (c) H. Zeng, T. Li, Z. Yan, S. Luo, F. Li. *Cryst. Growth Des.*, **10**, 475 (2010); (d) C.S.B. Gomes, P.T. Gomes, M.T. Duarte, R.E. Di Paolo, A.L. Maçanita, M.J. Calhorda. *Inorg. Chem.*, **48**, 11176 (2009); (e) A. Bartyzel, Z. Rzączyńska, A. Danczowska-Burdon. *J. Coord. Chem.*, **63**, 46 (2010).

[2] S. Kitagawa, R. Matsuda. *Coord. Chem. Rev.*, **251**, 2490 (2007).

[3] For examples: (a) J.-C. Yao, W. Huang, B. Li, S. Gou, Y. Xu. *Inorg. Chem. Commun.*, **5**, 711 (2002); (b) S.G. Baca, Y. Simonov, M. Gdaniec, N. Gerbeleu, I.G. Filippova, G.A. Timco. *Inorg. Chem. Commun.*, **6**, 685 (2003); (c) J. Zhang, Z.-J. Li, X.-Y. Cao, Y.-G. Yao. *J. Mol. Struct.*, **750**, 39 (2005).

[4] For examples: (a) M. Du, X.-J. Jiang, X.-J. Zhao. *Inorg. Chem.*, **46**, 3984 (2007); (b) L. Zhang, Y.-Y. Qin, Z.-J. Li, Q.-P. Lin, J.-K. Cheng, J. Zhang, Y.-G. Yao. *Inorg. Chem.*, **47**, 8286 (2008); (c) H. Chun, H. Jung, J. Seo. *Inorg. Chem.*, **48**, 2043 (2009).

[5] For examples: (a) J. Hafizovic, M. Bjorgen, U. Olsbye, P.D.C. Dietzel, S. Bordiga, C. Prestipino, C. Lamberti, K.P. Lillerud. *J. Am. Chem. Soc.*, **129**, 3612 (2007); (b) F.-K. Wang, S.-Y. Yang, R.-B. Huang, L.-S. Zheng, S.R. Batten. *CrystEngComm*, **10**, 1211 (2008); (c) R. Prajapati, L. Mishra, K. Kimura, P. Raghavaiah. *Polyhedron*, **28**, 600 (2009).

[6] For examples: (a) J. Zhang, Y.-B. Chen, S.-M. Chen, Z.-J. Li, J.-K. Cheng, Y.-G. Yao. *Inorg. Chem.*, **45**, 3161 (2006); (b) E.-C. Yang, Z.-Y. Liu, X.-G. Wang, S.R. Batten, X.-J. Zhao. *CrystEngComm*, **10**, 1140 (2008); (c) J. Li, C. Ma, G. He, L. Qiu. *J. Coord. Chem.*, **61**, 251 (2008).

[7] For examples: (a) M.A. Braverman, R.L. LaDuca. *CrystEngComm*, **10**, 117 (2008); (b) M.-X. Li, Z.-X. Miao, M. Shao, S.-W. Liang, S.-R. Zhu. *Inorg. Chem.*, **47**, 4481 (2008); (c) X.-G. Liu, L.-Y. Wang, X. Zhu, B.-L. Li, Y. Zhang. *Cryst. Growth Des.*, **9**, 3997 (2009).

[8] For examples: (a) H. Chun, D.N. Dybtsev, H. Kim, K. Kim. *Chem. Eur. J.*, **11**, 3521 (2005); (b) J.Y. Lu, V. Schauss. *CrystEngComm*, **4**, 623 (2002); (c) T.K. Maji, M. Ohba, S. Kitagawa. *Inorg. Chem.*, **44**, 9225 (2005).

[9] For examples: (a) H.R. Moon, N. Kobayashi, M.P. Suh. *Inorg. Chem.*, **45**, 8672 (2006); (b) R.E. Marsh. *Acta Crystallogr., Sect. B*, **60**, 252 (2004); (c) H.-F. Zhu, J. Fan, T. Okamura, W.-Y. Sun, N. Ueyama. *Cryst. Growth Des.*, **5**, 289 (2005).

[10] For examples: (a) L.-F. Chen, J. Zhang, L.-J. Song, Z.-F. Ju. *Inorg. Chem. Commun.*, **8**, 555 (2005); (b) P. Wang, C.N. Moorefield, M. Panzer, G.R. Newkome. *Chem. Commun.*, 4405 (2005); (c) N. Kerbellec, C. Daiguebonne, K. Bernot, O. Guillou, X. Le Guillou. *J. Alloys Compd.*, **451**, 377 (2008).

[11] J.-J. Wang, C.-S. Liu, T.-L. Hu, Z. Chang, C.-Y. Li, L.-F. Yan, P.-Q. Chen, X.-H. Bu, Q. Wu, L.-J. Zhao, Z. Wang, X.-Z. Zhang. *CrystEngComm*, **10**, 681 (2008).

[12] S.-M. Fang, S.-T. Ma, L.-Q. Guo, Q. Zhang, M. Hu, L.-M. Zhou, L.-J. Gao, C.-S. Liu. *Inorg. Chem. Commun.*, **13**, 139 (2010).

[13] C.-S. Liu, M. Hu, L.-Q. Guo. *Acta Cryst.*, **E65**, m1432 (2009).

[14] C.-S. Liu, M. Hu, Q. Zhang. *Acta Cryst.*, **E65**, m1572 (2009).

[15] Cerius2. *Molecular Simulation Incorporated*, San Diego, CA (2001).

[16] Bruker AXS. *SAINT Software Reference Manual*, Bruker AXS Inc, Madison, WI (1998).

[17] G.M. Sheldrick. *SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany (1997).

[18] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York (1986).

[19] G.B. Deacon, R.J. Phillips. *Coord. Chem. Rev.*, **33**, 227 (1980).

[20] J. Tao, M.-L. Tong, J.-X. Shi, X.-M. Chen, S.W. Ng. *Chem. Commun.*, 2043 (2000).

[21] H.-P. Xiao, S. Aghabeygi, W.-B. Zhang, Y.-Q. Cheng, W.-Y. Chen, J. Wang, A. Morsalic. *J. Coord. Chem.*, **61**, 3679 (2008).

[22] Y.-H. He, X. Feng, Y.-L. Feng, H. Sun, Y.-H. Wen. *Wuji Huaxue Xuebao (Chin.) (Chin. J. Inorg. Chem.)*, **23**, 1805 (2007).

[23] Y.-F. Zhou, B.-Y. Lou, D.-Q. Yuan, Y.-Q. Xu, F.-L. Jiang, M.-C. Hong. *Inorg. Chim. Acta*, **358**, 3057 (2005).

[24] C.-D. Wu, C.-Z. Lu, D.-M. Wu, H.-H. Zhuang, J.-S. Huang. *Inorg. Chem. Commun.*, **4**, 561 (2001).

[25] Z. Chang, A.-S. Zhang, T.-L. Hu, X.-H. Bu. *Cryst. Growth Des.*, **9**, 4840 (2009).

[26] C.-S. Liu, X.-S. Shi, J.-R. Li, J.-J. Wang, X.-H. Bu. *Cryst. Growth Des.*, **6**, 656 (2006).

[27] A.O. Eseola, W. Li, R. Gao, M. Zhang, X. Hao, T. Liang, N.O. Obi-Egbedi, W.-H. Sun. *Inorg. Chem.*, **48**, 9133 (2009).

[28] (a) H. Yersin, A. Vogler. *Photochemistry and Photophysics of Coordination Compounds*, Springer, Berlin (1987); (b) B. Valeur. *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, Germany (2002).