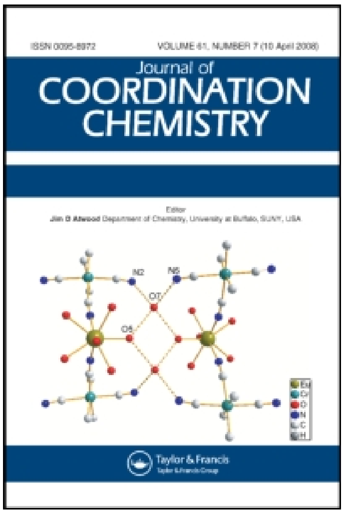

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A zinc(II) coordination polymer, [Zn$_4$(<i>o</i>-bda)$_4$(<i>p</i>-pbim)$_4$]$_{\text{<i>n</i>}}$, with strong blue fluorescence

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A zinc(II) coordination polymer, $[Zn_4(o\text{-bda})_4(p\text{-pbim})_4]_n$, with strong blue fluorescence

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A zinc(II) coordination polymer, $[Zn_4(o\text{-bda})_4(p\text{-pbim})_4]_n$ (**1**) (*p*-pbim = 4-pyridylbenzimidazole, *o*-bda^{2-} = *o*-phenylenediacetic acid dianion), has been synthesized by hydrothermal method and characterized by elemental analysis, IR, TG, photoluminescence and X-ray single crystal diffraction. Complex **1** crystallizes in a monoclinic system and space group $P2_1/n$, with $a = 14.231(3)$ Å, $b = 16.257(4)$ Å, $c = 16.794(4)$ Å, $\beta = 100.262(1)°$, and $Z = 8$; R_1 for 6475 observed reflections $[I > 2\sigma(I)]$ was 0.0420. Complex **1** shows a bi-chain structure fabricated by the tetranuclear zinc unit. Two zinc(II) ions are five coordinate with distorted trigonal-bipyramid geometry; the other two zinc(II) ions are four coordinate with distorted tetrahedral geometry. Complex **1** builds the 1-D bi-chain structure with two different subrings A and B, which are 32-member and 14-member rings, respectively. There exists a 2-D supramolecular network linked by hydrogen-bonding interactions (2.695 and 2.807 Å). A 3-D supramolecular network is further constructed by non-covalent interactions between the 1-D bi-chain structure. The TG/DTG shows that the chain skeleton is thermally stable to 356°C. Blue fluorescent emission of the complex was determined at 404 nm in the solid state with short decay lifetime of 1.67 ns.

Keywords: Zinc(II) complex; Crystal structure; Fluorescent property

1. Introduction

There has been extensive interest in preparing benzimidazole and derivative polymers with potential applications such as photochemical and photophysical properties [1–5]. *o*-Phenylenediacetic acid with double flexible groups is attractive because the flexibility and conformational freedom of the ligands offer various possibilities for construction of frameworks with unique structures and useful properties [6, 7]. *p*-Pyridylbenzimidazole (*p*-pbim) has attracted attention not only due to exhibiting proton-transfer excited state that can be used for proton transfer lasers [8–10], but also its strong coordination as

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multidentate ligand for metal complexes having a broad scope of properties [11–15]. Herein we report a 1-D bi-chain complex, $[Zn_4(o\text{-bda})_4(p\text{-pbim})_4]_n$ (**1**) with both o-H_2bda and p-pbim ligands. At room temperature in the solid state, the free ligand p-pbim has blue luminescence with the maximum at 395 nm and short decay lifetime of 0.932 ns, free o-H_2bda is at 420 nm with a very long decay lifetime of 3.98 ns and blue fluorescent emission of **1** was at 404 nm with short decay lifetime of 1.67 ns.

2. Experimental

All solutions and chemicals were commercial reagents and used without further purification. Elemental analysis was carried out on a PE 1700 CHN auto elemental analyzer. The solid infrared spectra (IR) were obtained from a Bruker IFS66V vacuum-type FT-IR spectrophotometer using KBr pellets. Thermogravimetry (TG) analysis was measured on a Perkin Elmer TG/DTA 6300 thermal analyzer under flowing N_2 at a heating rate of 10°C min^{-1}. Fluorescence measurements were performed on a Model RF-5 spectrofluorimeter. The crystal structure was determined using a Bruker APEX area-detector diffractometer and SHELXL crystallographic software.

2.1. *Synthesis of p-pbim*

The ligand was synthesized by condensation of pyridine-4-carboxylic acid with o-phenylenediamine in 1,2-ethandiol according to the literature [16].

2.2. *Synthesis of $[Zn_4(o\text{-bda})_4(p\text{-pbim})_4]_n$*

p-Pyridylbenzimidazole (0.195 g, 1 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1 mmol) were dissolved in a hot aqueous solution of o-phenylenediacetic acid (0.194 g, 1 mmol) and the pH of the solution was adjusted to 6.5 with 0.2 mol L^{-1} sodium hydroxide solution. The solution was sealed in a 15 mL Teflon-lined stainless steel bomb and held at 433 K for 5 d. The bomb was then cooled naturally to room temperature. Yellow block crystals were obtained (78% yield based on o-$BDAH_2$). CHN analysis, Calcd (%) for $C_{22}H_{17}ZnN_3O_4$: C, 58.36; H, 3.75; N, 9.28. Found (%): C, 58.28; H, 3.68; N, 9.21. Selected IR data (KBr, cm^{-1}): 3436, 1619, 1571, 1448, 1286, 1026, 723.

The peaks of 1619 and 1448 cm^{-1} are shown in IR spectra of the complex and attributed to $\nu_{asym}(OCO^-)$ and $\nu_{sym}(OCO^-)$, respectively. The value of $\Delta(OCO^-)$ is 171 cm^{-1}, which is less than 200 cm^{-1}, indicating that the dianionic o-bda coordinates to Zn(II) in the bidentate chelate mode [17]. The absorption vibrations of ν_{asym}(C–O–C) and ν_{sym}(C–O–C) are at 1286 and 1026 cm^{-1}, respectively. The broad peak at 3436 cm^{-1} was attributed to hydrogen bonded ν(OH).

2.3. *X-ray crystallography*

Intensity data on **1** were collected at 296(2) K on a Bruker APEX area-detector equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using an

ω-2θ scan mode in the range of $3.05 \le \theta \le 27.46°$. A total of 35361 independent reflections were measured, of which 8572 were unique ($R_{\mathrm{int}} = 0.0361$) and 6475 were observed ($I > 2\theta\,(I)$) and used in the subsequent structure determination and full-matrix least-square refinements. Absorption correction was performed by SADABS [18]. The structure was solved by direct methods and subsequent difference Fourier syntheses, revealing the positions of all non-hydrogen atoms. The hydrogen atoms were located geometrically. All non-hydrogen atoms were refined anisotropically. All calculations were performed using the SHELXTL package [19]. The crystal data and structure analysis parameters of **1** are given in table 1. Selected bond lengths (nm) and bond angles (°) are listed in table 2. The hydrogen bond lengths (nm) and bond angles (°) are listed in table 3. Figures 1 and 2 illustrate the structures of **1**.

3. Results and discussion

As shown in figure 1, two zinc(II) ions are five coordinate with distorted trigonal bipyramid geometry and the other two zinc(II) ions are four coordinate with distorted tetrahedral geometry. The benzimidazole rings and pyridine ring in *p*-pbim ligand are not in the same plane, with the dihedral angles being 49.499(8)°. The C–O bond distances of each carboxyl group are nearly identical (table 2), for the atoms O7B, C44B, O8B and Zn1 being in the same plane, giving the four-membered ring, with

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

Formula	$C_{22}H_{17}ZnN_3O_4$
CCDC deposit no.	671901
Formula weight	452.76
T (K)	296(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$P21/n$
Unit cell dimensions (Å, °)	
a	14.231(3)
b	16.257(4)
c	16.794(4)
β	100.262(1)
Z	8
V (Å^3)	3823(2)
D_{Calcd} (g cm^{-3})	1.573
Absorption coefficient (mm^{-1})	1.321
$F(000)$	1856
Crystal size (mm^3)	0.34 × 0.33 × 0.24
θ_{min}, θ_{max} (°)	3.05, 27.46
Index ranges	$-18 \le h \le 18, -21 \le k \le 21, -21 \le l \le 21$
Total data	35361
Total unique data	8572
Completeness $\theta = 27.46°$	98.0%
Absorption correction	Empirical
Max. and min. transmission	0.7448, 0.6586
Data/restraints/parameters	8572/0/549
Goodness-of-fit on F^2	1.002
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0420$, $wR_2 = 0.11080.0597$
R indices (all data)	$R_1 = 0.0597$, $wR_2 = 0.1204$
Largest diff. peak and hole (e Å^{-3})	0.937, −0.405

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

Zn(1)–O(1)	0.1961(2)	Zn(2)–O(3)	0.2034(2)
Zn(1)–N(1)	0.2031(2)	Zn(2)–N(4)	0.2054(2)
Zn(1)–N(3)[a]	0.2076(2)	Zn(2)–N(6)[c]	0.2064(2)
Zn(1)–O(7)[b]	0.2092(2)	O(7)–C(44)	0.1254(4)
Zn(1)–O(8)[b]	0.2444(1)	O(8)–C(44)	0.1233(4)
Zn(2)–O(5)	0.1948(2)		
O(1)–Zn(1)–N(1)	107.9(1)	N(3)[a]–Zn(1)–O(8)[b]	91.7(1)
O(1)–Zn(1)–N(3)[a]	112.9(1)	O(7)[b]–Zn(1)–O(8)[b]	56.3(1)
N(1)–Zn(1)–N(3)[a]	116.2(1)	O(5)–Zn(2)–O(3)	128.1(1)
O(1)–Zn(1)–O(7)[b]	93.5(1)	O(5)–Zn(2)–N(4)	106.7(1)
N(1)–Zn(1)–O(7)[b]	124.2(1)	O(3)–Zn(2)–N(4)	91.4(1)
N(3)[a]–Zn(1)–O(7)[b]	100.1(1)	O(5)–Zn(2)–N(6)[c]	114.3(1)
O(1)–Zn(1)–O(8)[b]	144.8(1)	O(3)–Zn(2)–N(6)[c]	98.9(1)
N(1)–Zn(1)–O(8)[b]	80.5(1)	N(4)–Zn(2)–N(6)[c]	116.2(1)

Symmetry codes: a: $-x+1$, $-y+1$, $-z$; b: x, y, $z-1$; c: $-x+1$, $-y+1$, $-z+1$.

Table 3. Hydrogen-bond geometry (Å, °) for **1**.

D—H···A	D—H	H···A	D···A	DHA
N(2)–H(2N)···O(4)[e]	0.821(1)	1.874(1)	2.695(1)	176.8(1)
N(5)–H(5N)···O(7)[f]	1.071(1)	1.753(1)	2.807(1)	168.2(1)

Symmetry codes: e: $-x+1/2$, $y+1/2$, $-z+1/2$; f: $-x+1/2$, $y+1/2$, $-z+3/2$.

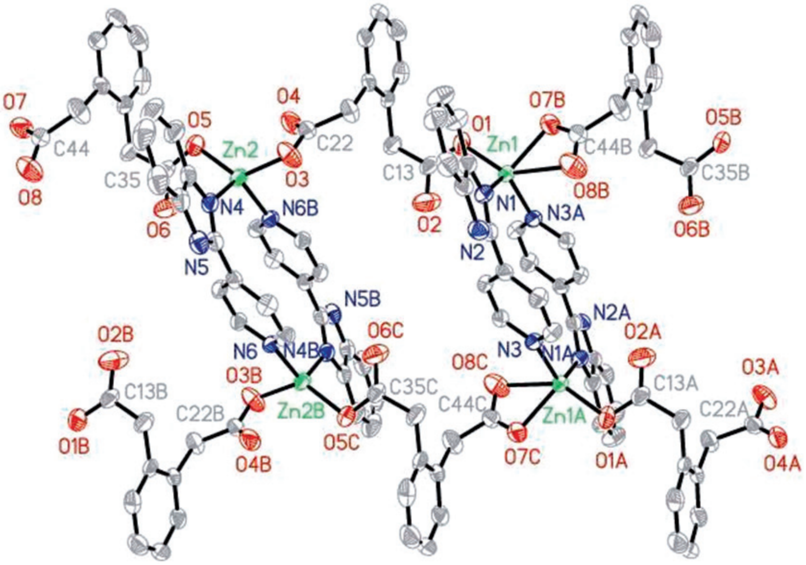

Figure 1. Structure of **1** with atom numbering.

delocalization of the electrons throughout. However, all Zn···O distances lie within the range of the corresponding bond distances reported for Zn-carboxylate complexes [20, 21]. The C35C, C44C, C13 and C22 carboxylate group are approximately perpendicular to the benzene plane, with dihedral angles being 86.282(2)°, 100.584(8)°,

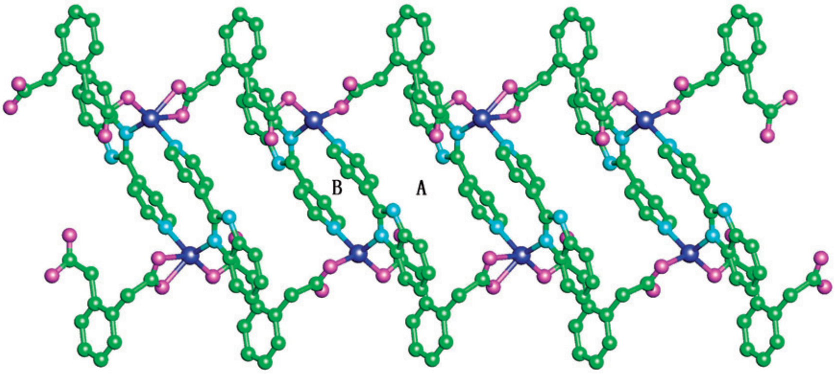

Figure 2. 1-D bi-chain structure of **1**.

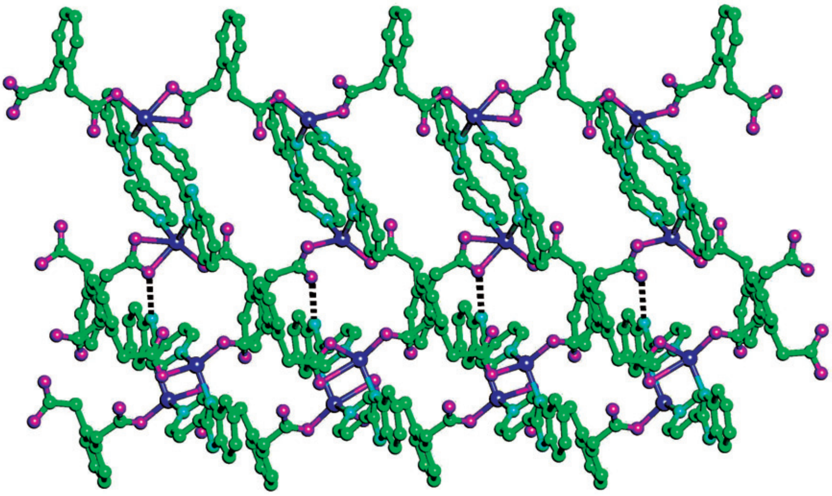

Figure 3. 2-D structure resulting from hydrogen bonds between neighboring chains.

83.226(2)° and 103.802(8)°, respectively, suggesting that the *o*-bda ligand has remarkable flexibility compared to a rigid aromatic carboxylic acid ligand such as terephthalate. In $[Cd(bipy)(terephthalate)(H_2O)]_n$, the dihedral angles of the two carboxyl groups to the phenyl are 5.63° and 12.58°, respectively [22].

The most interesting feature for **1** is that the *o*-bda and *p*-pbim ligands link zinc centers in different ways to produce the 1-D bi-chain structure (figure 2) with two different subrings A and B, which are 32-member and 14-member rings with Zn1 ⋯ Zn2, Zn1A ⋯ Zn2B, Zn1 ⋯ Zn1A, Zn2 ⋯ Zn2B, Zn1 ⋯ Zn2B and Zn2 ⋯ Zn1A distances of 8.4726(2), 8.3287(2), 7.0019(1), 6.9570(1), 9.4269(2) and 12.2134(2) Å, respectively. Adjacent bi-chain structures are alternately packed through hydrogen bonds involving *p*-pbim and *o*-bda ligands (table 3) into a 2-D network parallel to the *bc* plane, as depicted in figure 3. A 3-D supramolecular network is further constructed by non-covalent interactions between the 1-D bi-chain structure (figure 4).

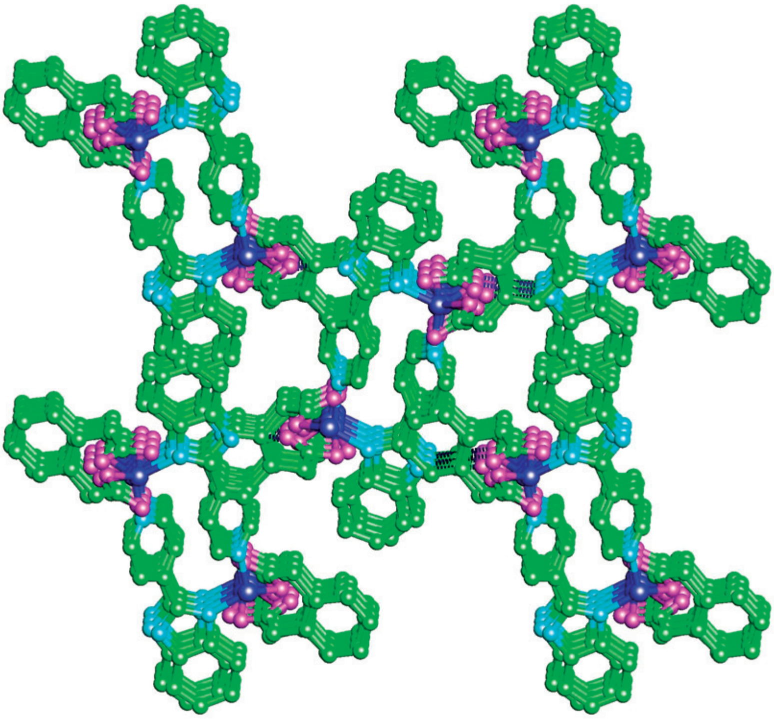

Figure 4. 3-D network of **1**.

3.1. *Thermal and spectroscopic properties*

The TG-DTG analysis of **1** exhibited two weight-loss steps. One strikingly clean weight loss occurred in the range 356–434°C corresponding to removal of the phenylenediethyl radical (found 28.2, Calcd 28.3%). The final residual weight may be assigned to ZnO (Calcd 17.9%). The result shows that the coordination polymer is thermally stable to 356°C.

Fluorescent emission spectra of the complex and ligands were measured in the solid state at room temperature (figure 5). The time/decay curves of the complex and the ligands were determined (figure 6). The free ligand *p*-pbim exhibited an intense and narrow emission band with a maximum at 395 nm ($\lambda_{ex} = 361$ nm), and the blue luminescence was predominantly $\pi \rightarrow \pi^*$ fluorescence [23], further supported by very short decay lifetime of 0.932 ns. Free *o*-bda presented a broad emission band at 420 nm ($\lambda_{ex} = 365$ nm) with a decay lifetime of 3.98 ns. Upon photoexcitation at 296 and 356 nm, **1** exhibited a blue fluorescent emission band at 404 nm with short decay lifetime (1.67 ns), which was 9 nm red-shifted compared to free *p*-pbim and may be ascribed to an intraligand $\pi \rightarrow \pi^*$ transition [24]. Fluorescent intensities of the complex were weaker than those of the free ligands *p*-pbim and *o*-bda, probably due to negative synergistic effect of the free ligand *p*-pbim [25].

In conclusion, a zinc(II) coordination polymer based on *o*-bda and *p*-pbim was hydrothermally synthesized and exhibits intense blue photoluminescent emission. The TG/DTG shows that its chain skeleton is stable to 356°C. The complex is

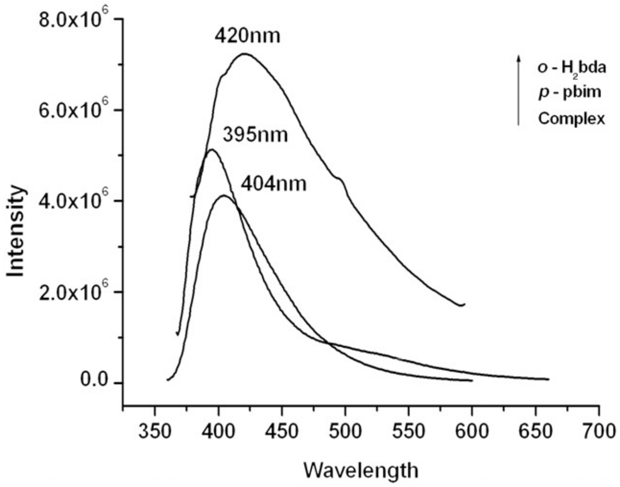

Figure 5. Emission spectra of **1** and the ligands in the solid state at room temperature.

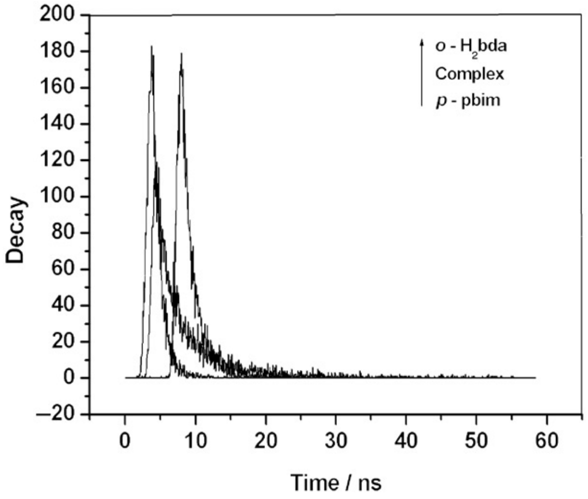

Figure 6. The time/decay curves of **1** and ligands.

promising as a blue-light emitting material for its high thermal stability and the insolubility in common solvents.

Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 671901 for **1**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: 44 1223 336033, Email: deposit@ccdc.cam.ac.uk].

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