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A Novel Coordination Polymer Constructed from Flexible Bis-Methylbenzimidazole Ligand and Aromatic Polycarboxylate[1]

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Abstract—A novel coordination polymer $[Zn(Bmb)_{0.5}(H_2O)_2(Tba)]_n$ (**I**) (Bmb = (1,4-bis(2-methylbenzimidazol-1-yl)butane, H_2Tba = 5-*tert*-butyl-1,3-benzene dicarboxylic acid) has been hydrothermally synthesized and fully characterized by IR, fluorescence spectrum, single crystal and powder X-ray diffraction techniques (CIF file CCDC no. 992083). Crystal structure revealed that the title polymer crystallized in monoclinic, space group $C2/c$, $a = 22.824(5)$, $b = 10.742(2)$, $c = 19.156(4)$ Å, $\beta = 102.37(3)°$, $Z = 8$. A ladder-like chain is found in polymer **I**, which is expended to a 3D supramolecular structure through hydrogen bonding and $\pi\cdots\pi$ interactions.

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INTRODUCTION

The rational design and construction of novel coordination polymers continues to be a productive research area, owing to their aesthetically beautiful structures and potential applications as new materials [1–5]. Of many rational approaches to the design of these materials, the tailored introduction of mixed organic ligands, especially the neutral N-donor ligand and anionic O-donor ligand as building blocks with metal ions or metal clusters as nodes has been proven to be an efficient strategy [6, 7]. As an important member of neutral N-donor ligand, bis-benzimidazol are considered as appropriate building blocks because of their flexibility along with their versatile coordination ability that offer various possibilities for constructing frameworks with unique structures and useful properties [8–10]. So, we chose the N-donor ligand 1,4-bis(2-methylbenzimidazol-1-yl) butane (Bmb) to construction of novel coordination polymers. As Bmb has been used to obtain some interesting coordination polymers with anionic O-donor polycarboxylate ligand, ancillary coligand H_2Tba was introduced to assemble frameworks. Furthermore, the different coordination preference of ancillary coligand H_2Tba is expected to result in structural diversities of coordination polymers based on the Bmb ligand.

In this contribution, we describe our recent research on a novel coordination polymer $[Zn(Bmb)_{0.5}(H_2O)_2(Tba)]_n$ (**I**) with unique ladder-like chain synthesized from Bmb, H_2Tba and transition metal ions Zn(II) as metal center based on hydrothermal synthesis process. In addition, polymer **I** indicates high thermal stabilities and intense photoluminescence emission in the solid state.

EXPERIMENTAL

Materials and physical measurements. All reagents and solvents were commercially available except for Bmb, which was synthesized according to the literature [11]. The FT–IR spectra were recorded from KBr pellets in the range of 400–4000 cm^{-1} on a Bruker Tensor 27 spectrophotometer. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. PXRD Patterns were recorded using Cu$K_{\alpha 1}$ radiation on a PANalytical X'Pert PRO diffractometer. Thermal analyses were performed on a Netzsch STA 449C thermal analyzer from room temperature at a heating rate of 10°C min^{-1} in air. The luminescence spectra for the powdered solid samples were measured at room temperature on a Hitachi F-4500 fluorescence spectrophotometer. The excitation slit, as well as the emission slit were 2.5 nm.

Synthesis of I. A mixture of $Zn(NO_3) \cdot 6H_2O$ (59.5 mg, 0.2 mmol), H_2Tba (73.1 mg, 0.2 mmol), NaOH (8.0 mg, 0.2 mmol) and Bmb (22.2 mg, 0.1 mmol) in 10 mL distilled H_2O was sealed in a 25 mL Teflon-lined stainless steel container and

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[1] The article is published in the original.

Table 1. Crystallographic data and refinement parameters for **I**

Parameter	Value
Formula weight	480.87
Crystal system	Monoclinic
Space group	$C2/c$
a, Å	22.824(5)
b, Å	10.742(2)
c, Å	19.156(4)
β, deg	102.37(3)
Volume, Å^3	4587.6(16)
Z	8
ρ_{calcd}, g cm^{-3}	1.381
μ, mm^{-1}	1.109
F(000)	1976
θ Range, deg	2.52–25.00
Measured reflections	13309
Unique reflections, R_{int}	3928 (0.0412)
Observed reflections	3446
Data/restraints/parameters	3928/0/285
Goodness of fit on F^2	1.046
R_1 ($I > 2\sigma(I)$)*	0.0664
wR_2 (all data)*	0.1956
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.960/–0.508

$^*R_1 = \sum|F_0| - |F_c||/\sum|F_0|$; $wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$.

heated at 160°C for 4 days. After the mixture cooled to room temperature at a rate of 5°C/h, colorless block crystals of **I** were obtained with a yield of 25% (based on Zn). The FT–IR main absorption bands are centered mainly at 3440 m, 2924 w, 2853 w, 1562 s, 1509 m, 1475 w, 1456 m, 1382 s, 1290 m, 1258 w, 1223 w, 1159 w, 1015 m, 991 w, 836 s, 751 s, 739 m, 527 m, 474 w, 431 w.

For $C_{22}H_{27}N_2O_6Zn$

anal. calcd., %:	C, 54.95;	H, 5.66;	N, 5.83.
Found, %:	C, 54.87;	H, 5.72;	N, 5.87.

X-ray crystallography. The data of polymer **I** was collected on a Rigaku Saturn 724 CCD diffractomer (MoK_α, λ = 0.71073 Å) at temperature of 20 ± 1°C. Absorption corrections were applied by using multi-scan program. The data was corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined with a full-matrix least-squares technique based on F^2 with the SHELXL-97 crystallographic software package [12]. The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic crystal data and structure processing parameters for **I** is summarized in Table 1. Selected bond lengths and bond angles of **I** is listed in Table 2. Supplementary material for polymer **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 992083; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSIONS

The asymmetry unit of **I** is composed of one Zn^{2+} ion, half Bmb ligand, one Tba^{2-} anion, and two lattice water molecules. As shown in Fig. 1, Zn^{2+} ion is in a twisting octahedral coordination environment and coordinated by five oxygen atoms from three different

Table 2. Selected bond lengths (Å) and angles (deg) for **I***

Bond	d, Å	Bond	d, Å
Zn(1)–O(3)$^{\#1}$	2.259(5)	Zn(1)–N(1)	2.249(5)
Zn(1)–O(2)$^{\#2}$	2.361(5)	Zn(1)–O(1)	2.297(5)
Zn(1)–O(1)$^{\#2}$	2.386(5)	Zn(1)–O(4)$^{\#1}$	2.395(5)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(1)Zn(1)O(3)$^{\#1}$	93.4(2)	O(3)$^{\#1}$Zn(1)O(2)$^{\#2}$	126.68(19)
N(1)Zn(1)O(1)	107.5(2)	O(1)Zn(1)O(2)$^{\#2}$	129.02(17)
O(3)$^{\#1}$Zn(1)O(1)	100.6(2)	N(1)Zn(1)O(1)$^{\#2}$	105.7(2)
N(1)Zn(1)O(2)$^{\#2}$	89.3(2)	O(3)$^{\#1}$Zn(1)O(1)$^{\#2}$	160.9(2)
O(3)$^{\#1}$Zn(1)O(4)$^{\#1}$	56.24(19)	O(1)Zn(1)O(1)$^{\#2}$	75.2(2)
O(1)Zn(1)O(4)$^{\#1}$	99.9(2)	O(2)$^{\#2}$Zn(1)O(1)$^{\#2}$	53.84(16)
O(2)$^{\#2}$Zn(1)O(4)$^{\#1}$	92.84(19)	N(1)Zn(1)O(4)$^{\#1}$	142.62(19)
O(1)$^{\#2}$Zn(1)O(4)$^{\#1}$	105.61(19)		

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x + 1, y, -z + 1/2$; $^{\#2}$ $-x + 1, -y + 1, -z$.

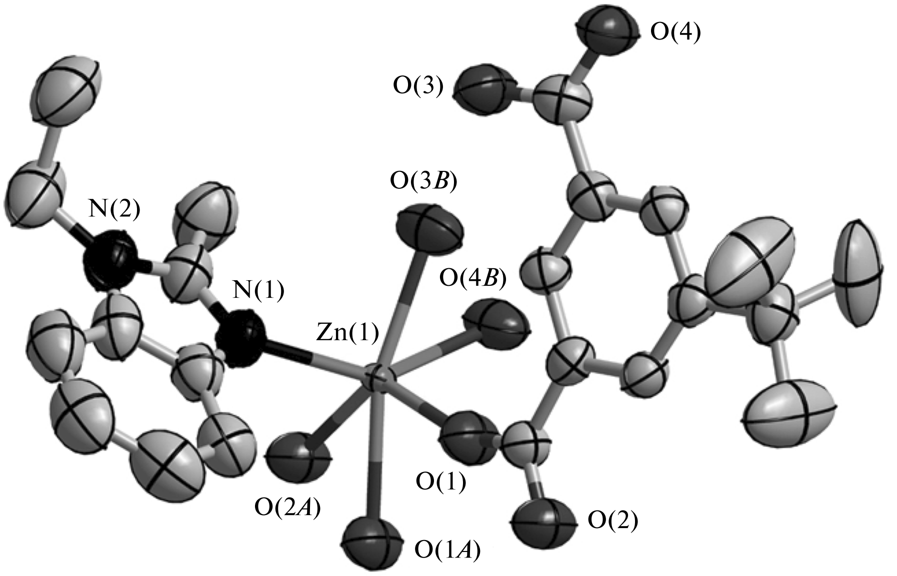

Fig. 1. The asymmetric unit of polymer **I** with thermal ellipsoids at 30% probability level (the lattice water molecules and hydrogen atoms are omitted for clarity). Symmetry codes: (*A*) $1 - x, 1 - y, -z$; (*B*) $1 - x, y, 0.5 - z$.

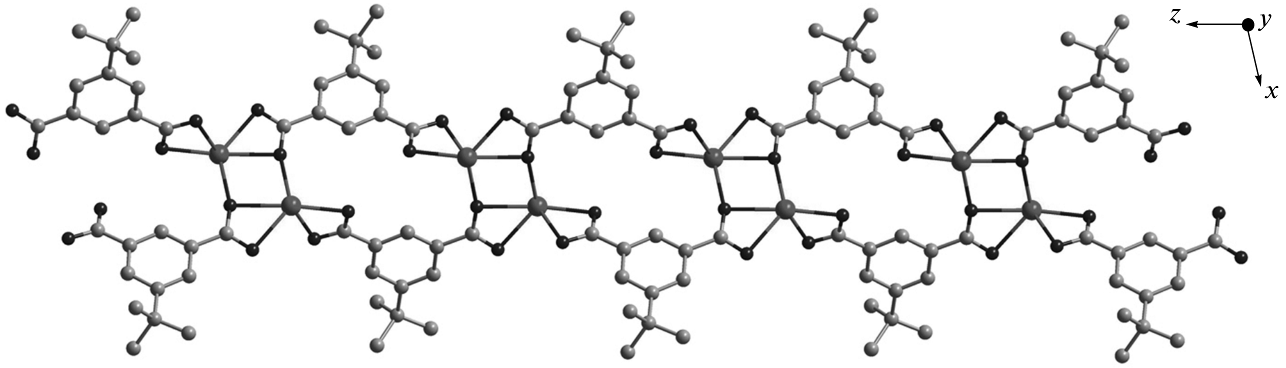

Fig. 2. 1D ladder-like chain constructed from Zn(II) and Tba^{2-}.

Tba^{2-} anions and one nitrogen atom from Bmb molecule. As shown in Table 2, the Zn–O, Zn–N bond lengths and OZnO, OZnN bond angles range from 2.249(5) to 2.395(5) Å and 56.24(19) to 160.9(2)°, respectively, which are in the normal range [8]. In polymer **I**, each Tba^{2-} anion links two Zn^{2+} ions with two carboxylate groups in different coordination mode: one of the carboxylate groups adopts μ_2-η^2:η^1-chelating-bridging coordination mode and the other one behaves μ_2-η^1:η^1-chelating mode. Pairs of symmetry-related Tba^{2-} anions act as bridges joining adjacent Zn(II) bimetal pairs to give birth to a $[Zn_2(Tba)_2]_n$ 1D ladder-like chain (Fig. 2) along the *z* axis, and Bmb ligands are joined in the 1D ladder-like chain in a winding fashion (Fig. 3). As shown in Fig. 4, with the help of π···π interactions, the adjacent 1D ladder-like chains turns into 2D layer. The adjacent 2D layers are extended into 3D supramolecular structure by O–H···O hydrogen bonding interactions (Fig. 5).

The powder X-ray diffraction pattern of polymer **I** and the pattern simulated on the basis of single crystal structure is shown that the positions of the diffraction peaks in both patterns correspond well, which indicate the phase purity of polymer **I**. The slight differences in reflection intensities between the simulated and the experimental patterns are due to the variation in the crystal orientation of the powder sample.

The TGA study of polymer **I** shows a weight loss of 7.45% (calcd. 7.49%) from 50 to 120°C, suggesting that the two lattice H_2O molecules are released. The sharp weight loss (75.36%) attributes to the combustion of Tba^{2-} and Bmb (calcd. 75.58%) accompanied

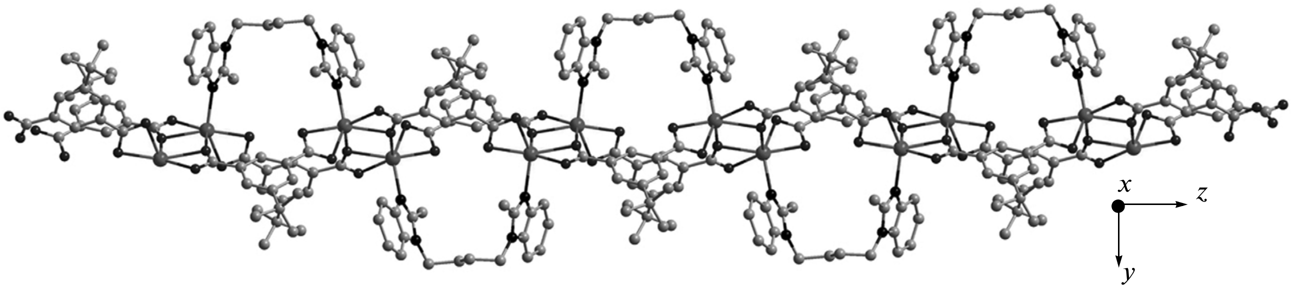

Fig. 3. Bmb ligands are joined in the 1D ladder-like chain in a winding fashion.

by the initial breakdown of the organic moieties ranging from 407 to 520°C. The final products ZnO (17.19%, calcd. 16.93%) are obtained.

The photoluminescence properties of polymer **I**, together with the free Bmb ligand and H_2Tba in the solid state are investigated at room temperature. The fluorescent emission spectra are shown in Fig. 6. Emissions were observed at 395 nm (λ_{ex} = 355 nm) for the free H_2Tba and 340 nm (λ_{ex} = 310 nm) for Bmb. The main emission peaks of polymer **I** is observed at 441 nm (λ_{ex} = 336 nm). It is clear that the red-shifted emissions in **I** is caused by coordination of organic ligands to the metal centers [13, 14]. It has been reported that the ligand conformational rigidity may be increased due to their coordination to the metal centers resulting in a decrease in the nonradiative decay of intraligand excited states. Obviously, such broad band of **I** may be tentatively assigned to ligand(Tba)-to-metal charge transfer (LMCT) as reported for other d^{10} metal polymers [15, 16].

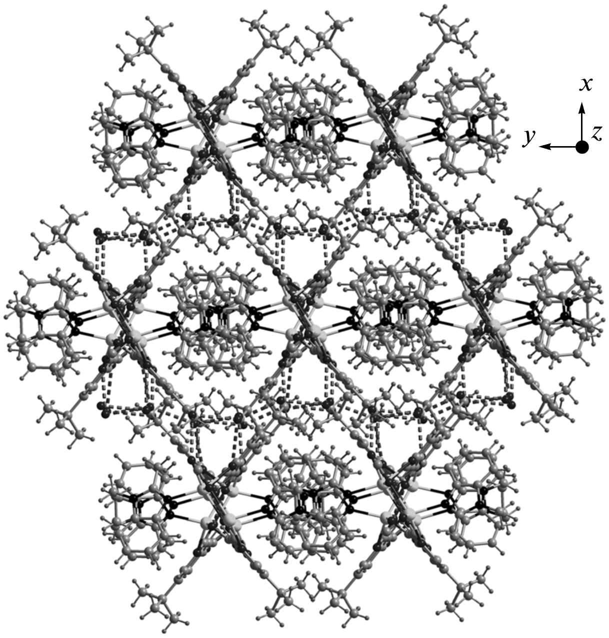

Fig. 5. The adjacent 2D layers are extended into 3D supramolecular structure by O–H···O hydrogen bonding interactions.

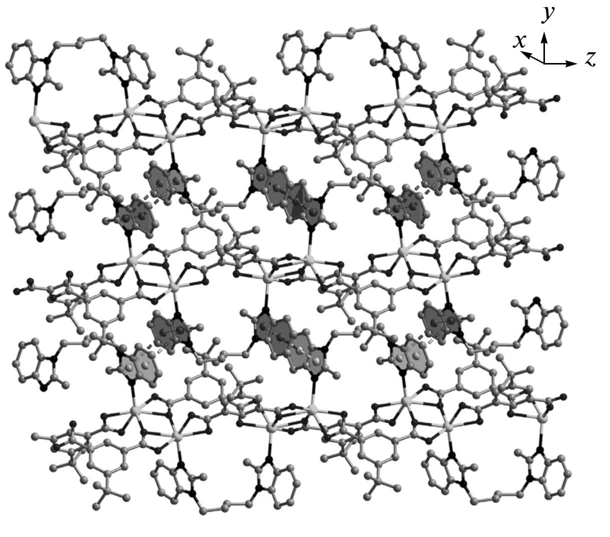

Fig. 4. The adjacent 1D ladder-like chains turns into 2D layer by π···π interactions.

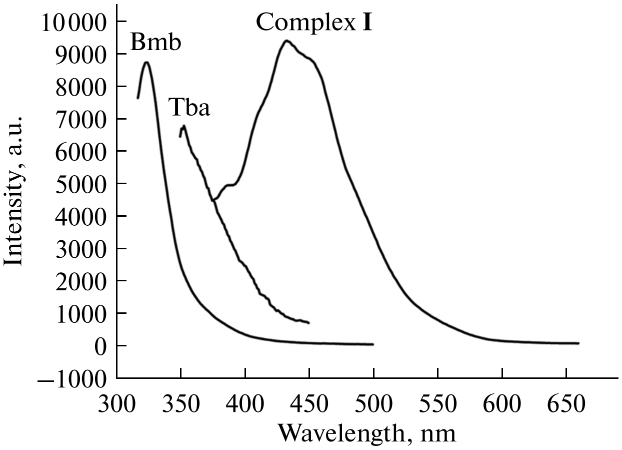

Fig. 6. Photoluminescences of free ligand and polymer **I**.

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