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Self-assembly of three d^{10} metal coordination polymers based on a flexible bis(2-methylbenzimidazole) and dicarboxylate co-ligands

Jin-ming Hao, Ying-na Zhao, Rui Yang, Guang-hua Cui*

College of Chemical Engineering, Hebei United University, 46 West Xinhua Road, Tangshan 063009, Hebei, People's Republic of China

HIGHLIGHTS

- Three *d*¹⁰ metal coordination polymers have been characterized.
- Effect of dicarboxylates on the structure of complexes was discussed.
- TG analysis confirms the stability of the coordination polymers.
- Luminescence properties of complexes have been investigated.

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ABSTRACT

Hydrothermal self-assembly of zinc nitrate with 1,1'-(1,3-propane)bis-(2-methylbenzimidazole) (pbmb) and different dicarboxylic acid ligands gave rise to three new coordination polymers $[Zn(pbmb)(hmph)]_n$ (1), $\{[Zn_2(pbmb)(chdc)_2] \cdot 0.5H_2O\}_n$ (2), $[Zn(pbmb)(mip)]_n$ (3) (H_2 hmph = homophthalic acid, H_2 chdc = 1,4cyclohexanedicarboxylic acid and H_2 mip = 5-methylisophthalic acid). Both complexes 1 and 3 possess 2D $\{6^3\}$ framework and further extend into 3D supramolecular network *via* C–H···O hydrogen bonding or π - π stack interactions. While 2 is a 1D double loop-like chain structure, which arranged into a 2D network through C–H···O hydrogen bonding interactions. Three compounds all exhibit strong photoluminescence at room temperature in solid state and may be good candidates for potential luminescence materials. © 2014 Elsevier B.V. All rights reserved.

Introduction

The rational design and synthesis of metal-organic frameworks (MOFs) have received great considerable attention, not only as their versatile intriguing architectures and topologies, but also as their potential applications in luminescence, magnetism, porosity and biological modeling material [1–4]. Studies in this field have been focused on construction of novel coordination frameworks and the relationships between their structures and properties [5].

http://dx.doi.org/10.1016/j.molstruc.2014.04.037 0022-2860/© 2014 Elsevier B.V. All rights reserved. These MOFs materials result from the reaction between organic and inorganic species could display infinite zero-, one-, two- or three-dimensional structures [6,7]. However, it is still a great challenge to predict the exact structures and compositions of the assembly products built by coordination bonds and/or hydrogen bonds in hydrothermal reactions, owing to the facts that the assembly of such complexes can be easily influenced by the geometrical and electronic properties of metal ions and ligands, temperature, pH value of the solution, etc. [8–14].

Flexible N-containing ligands, which possess rich structural information and free conformation, are highly attractive because their flexibilities allow for greater structural diversity [15,16,13,17,18]. The flexible bis(benzimidazole) derivatives in

^{*} Corresponding author. Tel.: +86 0315 2592169; fax: +86 0315 2592170. *E-mail address:* tscghua@126.com (G.-h. Cui).

which the two benzimidazole rings can freely twist around the flexible $-CH_2$ — spacer to meet the requirements of the coordination geometries of metal atoms in the assembly process. Some complexes with intriguing network topologies and interesting properties based on bis(benzimidazole) ligands have been reported, however, the coordination polymers derived from 1,1'-(1,3-propane)bis-(2-methylbenzimidazole) (pbmb) are relatively rare. As ongoing our previous works [19–21], we report the synthesis and crystal structures of three new zinc(II) coordination polymers: [Zn(pbmb)(hmph)]_n (1), {[Zn₂(pbmb)(chdc)₂]·0.5H₂O₃_n (2), [Zn(pbmb)(mip)]_n (3), where H₂hmph = homophthalic acid, H₂-chdc = 1,4-cyclohexanedicarboxylic acid and H₂mip = 5-methylisophthalic acid. Thermal stabilities and fluorescence properties of these complexes are also discussed.

Experimental

Materials and measurements

All chemicals were of reagent grade, commercially available and used without further purification. The ligand pbmb (Chart 1) was prepared according to the literature method [22]. Elemental analyses were made on a Perkin–Elmer automatic analyzer. IR spectra were recorded on a Nicolet FT-IR Avatar 360 spectrophotometer in 4000–400 cm⁻¹ region using KBr pellets. Thermal analyses were performed on a Netzsch TG 209 thermal analyzer from room temperature at a heating rate of 10 °C/min. X-ray powder diffraction measurement was executed on a D/MAX 2500PC X-ray diffractometer using Cu K α radiation (λ = 0.1542 nm) in the 2 θ range of 5–50° with a step size of 0.02° and a scanning rate of 10° min⁻¹. The solid fluorescence spectra were performed with a Hitachi F-7000 fluorescence spectrophotometer at room temperature.

Synthesis of complex $[Zn(pbmb)(hmph)]_n$ (1)

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol), pbmb (0.1 mmol), H_2 hmph (0.1 mmol), NaOH (0.2 mmol) and H_2O (10 mL) was placed in a 25 mL Teflon-lined stainless steel vessel. The mixture was sealed and heated at 140 °C for 3 days. After the mixture was cooled to room temperature at a rate of 5 °C/h, colorless blockshaped crystals of **1** were obtained with a yield of 41% (based on Zn). Anal. Calcd. for $C_{28}H_{26}ZnN_4O_4$ (Mr = 547.90): C 61.38, H 4.78, and N 10.23%. Found: C 60.86 H 4.53 and N 9.84%. IR (KBr, cm⁻¹): 2922(w), 1644(s), 1608(s), 1513(w), 1461(m), 1416(s), 1247(w), 1151(m), 1074(m), 937(w), 748(m), 670(w), 451(m).

Synthesis of complex $\{[Zn_2(pbmb)(chdc)_2] \cdot 0.5H_2O\}_n$ (2)

The procedure was similar to that of **1** except H₂chdc were used instead of H₂hmph. The colorless crystals were obtained with a yield of 36% (based on Zn). Anal. Calcd. for $C_{35}H_{41}N_4O_{8.50}Zn_2$ (Mr = 784.46): C 53.59, H 5.27 and N 7.14%. Found: C 53.24, H 5.02 and N 6.92%. IR (KBr, cm⁻¹): 3420(m), 3039(w), 2932(m), 1610(s), 1575(s), 1520(w), 1455(m), 1415(s), 1295(w), 924(w), 749(m), 656(w), 454(w).



Chart 1. The ligand pbmb.

Synthesis of complex $[Zn(pbmb)(mip)]_n$ (3)

The procedure was similar to that of **1** except that H_2mip were used instead of H_2hmph . The colorless crystals were obtained with a yield of 52% (based on Zn). Anal. Calcd. for $C_{28}H_{26}N_4O_4Zn$ (Mr = 547.90): C 61.38, H 4.78 and N 10.23%. Found: C 61.16, H 4.59 and N 10.02%. IR (KBr, cm⁻¹): 2918(w), 1634(s), 1516(m), 1450(m), 1372(s), 1328(m), 1265(m), 1159(w), 1090(w), 935(w), 759(m), 465(w).

X-ray crystallography

All data were collected on a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at room temperature with ω -scan mode. A semi-empirical absorption correction was applied using SADABS program [23]. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL [24]. Hydrogen atoms of water molecules were located on a difference Fourier map, while other hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on the parent atoms. Crystallographic crystal data and structure processing parameters for **1**, **2** and **3** are summarized in Table 1. Selected bond lengths and bond angles of the complexes are listed in Table S1 (Supporting Information).

Results and discussion

Crystal structures of 1

Single crystal X-ray diffraction analysis shows that complex **1** crystallizes in the monoclinic space group $P2_1/n$ and is a 2D network. In the asymmetric unit of **1**, there is one Zn center, one pbmb and one hmph²⁻ ligands. As shown in Fig. 1a, each Zn(II) atom sits in a

Table 1

Crystal and refinement data for complexes 1, 2 and 3.

	1	2	3
Empirical formula	$C_{28}H_{26}N_4O_4Zn$	$C_{35}H_{41}N_4O_{8.50}Zn_2$	$C_{28}H_{26}N_4O_4Zn$
Formula weight	547.90	784.46	547.90
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	ΡĪ	$P2_1/n$
a (Å)	11.368(2)	10.3024(10)	12.090(2)
b (Å)	17.489(3)	11.9362(11)	17.439(3)
c (Å)	13.533(2)	13.6767(13)	12.629(2)
α (deg)		84.1570(10)	
β (deg)	109.706(2)	85.3840(9)	108.314(3)
γ (deg)		83.8400(10)	
$V(Å^3)$	2533.0(8)	1659.3(3)	2527.9(8)
Ζ	4	2	4
D_{calc} (g/m ³)	1.437	1.570	1.440
μ (mm $^{-1}$)	1.012	1.507	1.014
F(000)	1136	814	1136
Crystal size (mm)	$0.25\times0.22\times0.21$	$\textbf{0.26} \times \textbf{0.23} \times \textbf{0.22}$	$0.26\times0.23\times0.23$
Total reflections	15,079	8507	15,369
Unique reflections	5768	5779	5848
R _{int}	0.0727	0.0251	0.0466
GOF	0.968	1.024	1.008
$R_1 (I > 2\sigma(I))$	0.0499	0.0406	0.0460
$wR_2 (I > 2\sigma(I))$	0.0949	0.1024	0.1198
Δho max (eÅ $^{-3}$)	0.369	0.434	0.421
$\Delta ho { m min}$ (eÅ ⁻³)	-0.271	-0.401	-0.343

 $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|; \ wR_2 = \Sigma [wF_0^2 - F_c^{2/2}] / \Sigma [wF_0^{2/2}]^{1/2}.$



Fig. 1. (a) The coordination environment of Zn(II) ions in complex 1 with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity (symmetry code: #1 x + 1/2, -y + 1/2, z + 1/2; #2 - x + 1, -y + 1, -z + 1); (b) 1D zig-zag chain constructed by hmph2⁻ anions; (c) view of the 2D butterfly-shaped layer structure of 1; (d) view of the 2D 63 network of 1; (e) simplified view of the 3D binodal (4,4)-connected net of {3.4.5.6.7²}²{3.6.7².8²} topology in complex **1**.

four-coordinate tetrahedral geometry with the value of the τ_4 factor being 0.84 [25], defined by two nitrogen atoms N3 and N1#2 from two different pbmb ligands and two oxygen atoms (O1 and O3#1)

from two independent hmph^{2–} anions (symmetry code #1: x + 1/2, -y + 1/2, z + 1/2; #2: -x + 1, -y + 1, -z + 1). The Zn–N bond distances are 2.031(3) Å (Zn1–N3) and 2.084(3) Å (Zn1–N1#2) and

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Zn—O lengths are 1.931(2) (Zn1—O3#1) and 1.955(2) Å (Zn1—O1), which are comparable to those of the similar zinc complexes [26].

In complex **1**, the carboxylate groups of hmph²⁻ ligands adopt bis-monodentate coordination mode bridge adjacent Zn atoms giving rise to a 1D zig-zag chain [Zn(hmph)] (Fig. 1b), in which the Zn···Zn separation is 7.703(8) Å. The pbmb ligands exhibit anticonformation with the dihedral angle between the two benzimidazole planes of $83.870(8)^\circ$ and the Zn···Zn distance across a pbmb ligand is 10.648(1) Å. The chains are connected by pbmb ligands to form a 2D butterfly-shaped network (Fig. 1c). From a topological perspective, if Zn(II) ion is simplified as a 3-connected node and the ligands all are considered as linkers, the 2D structure can be described as a 6³ topology (Fig. 1d). In addition, the adjacent 2D layers are further stacked into a 3D supermolecule framework by three kinds of H-bonding interactions in which the C8-H8A...O3#3, C9-H9B...O4#2 and C11-H11A...O4#2 (svmmetry code #3: 1/2 - x, 1/2 + y, 1/2 - z) bond distances are 3.190(6), 3.191(5) and 3.076(4) Å and the bond angles are 150°, 146° and 118°. To better understand the supermolecule framework of 1, the topological analysis approach is employed. All Zn(II) centers acting as four-connecting nodes, connecting two pbmb ligands and two hmph²⁻ anions. And the pbmb ligands implified to be 4-connected nodes bridging two hmph²⁻ anions and two Zn(II) centers and then the hmph²⁻ are simplified as 4-connected nodes. As a result, the 3D supermolecule network can be reduced as a new binodal (4,4)-connected net by TOPOS 4.0 program [27], with a point symbol of $\{3.4.5.6.7^2\}^2\{3.6.7^2.8^2\}$ (Fig. 1e).

Crystal structures of 2

Complex 2 crystallizes in the triclinic system with Pi space group. As shown in Fig. 2a, the fundamental structural unit of 2 contains two crystallographic independent Zn(II) centers (Zn1 and Zn2), one bridging pbmb, two $chdc^{2-}$ anions and half a lattice water molecule. Each Zn1 is five-coordinated by one N1 atom and four oxygen atoms (03#1, 04, 05#1 and 06) (symmetry code #1: -x + 1, -y + 1, -z + 1) from four chdc²⁻ anions in a monodentate mode to conform the square pyramid coordination geometry. which is pointed out by a τ_5 value of 0.009. A pair of Zn1 centers with a separation of 3.021(6) Å are bridged by four carboxylate groups from four chdc^{2–} anions lying about 90° apart about each other to form a paddle wheel-like unit of [Zn₂(chdc)₄], leaving the apical sites at both terminals of the $Zn \cdots Zn$ axis occupied by the nitrogen atoms. The Zn1-N bond distance is 2.037(3) and the Zn1–O bond lengths are in the range of 2.027(3)–2.085(2) Å, which are comparable to those of the similar zinc complexes [26]. While Zn2 centers are also five-coordinated to one chelating and two monodentate carboxylate groups (O1#3, O2#3, O7#2 and O8) (symmetry code #2: -x, -y + 1, -z + 2; #3: x - 1, y, z + 1) belonging to three chdc²⁻ anions and one nitrogen atom (N4), which have different coordination configuration with Zn1 units, the value of the τ_5 factor being 0.516 demonstrating a distort trigonal bipyramidal structure. Two Zn2 atoms linked by four $chdc^{2-}$ anions to form a dinuclear unit $Zn_2(COO)_6$ with a 8-member ring and the non-bonding Zn2···Zn2 distance is 3.798(7) Å. And then, two kinds of dinuclear units $[Zn_2(chdc)_4]$ and $Zn_2(COO)_6$ arranged alternately to generate a 1D loop-like chain (Fig. 2b). Interestingly, the dinuclear units are further bridged by the pbmb ligands with *anti*-conformations to form a double loop-like chain (Fig. 2c), where the $Zn1 \cdots Zn2$ distance across pbmb ligand is 7.936(9) Å and the dihedral angles between the mean planes of the two benzimidazole rings are 77.053(7)°. Furthermore, the adjacent 1D chains are constructed to a 2D supermolecule framework via intermolecular C-H···O hydrogen-bonding interactions between the lattice water molecules and pbmb ligands $(C(19)-H(19C)\cdots O(1W) = 2.91(2) \text{ Å, } 123^{\circ})$ and carboxyl groups



Fig. 2. (a) The coordination environment of Zn(II) ions in complex **2**. Hydrogen atoms and the free water molecule are omitted for clarity (symmetry code: #1: -x + 1, -y + 1, -z + 1; #2: -x, -y + 1, -z + 2; #3: x - 1, y, z + 1); (b) 1D loop-like chain generate by two kinds of dinuclear units; (c) the 1D double loop-like chain of **2**; (d) simplified view of the trinodal (3,4,6)-connected network topology of **2**.

of chdc^{2–} and pbmb ligands (C(11)–H(11B)···O(2) = 3.189(5) Å, 169°), respectively. In order to more fully understand the architecture of complex **2**, the topological method was used to simplify and analyze the 2D supramolecular framework. The first kind of dinuclear units implified to be a 6-connected node bridging four pbmb ligands and two dinuclear units, the second dinuclear units bound by two pbmb ligands and two dinuclear units acting as a 4-connected node and then the pbmb ligands are simplified as topologically equivalent 3-connected nodes. The succeeding topology analysis by TOPOS 4.0 program suggests the 2D coordination framework can be simplified as a trinodal (3,4,6)-connected network with a point symbol of $\{3.4.5\}^2\{3^2.4^2.5^2.6^2.7^4.8^2.9\}\{3^2.6^2.7^2\}$ (Fig. 2d).

Crystal structures of 3

Single-crystal X-ray analysis shows that complex **3** is a 2D lamella structure and it crystallizes in monoclinic space group $P2_1/n$. The asymmetric unit contains a crystallographically distinct Zn(II) cation, one completely deprotonated mip^{2–} anion and one

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Fig. 3. (a) The coordination environment of Zn(II) ions in complex 3. Hydrogen atoms are omitted for clarity (symmetry code: #1: x + 1/2, -y + 1/2, z + 1/2; #2: -x + 2, -y, -z); (b) 1D *zig-zag*-shaped chain bridged by mip2⁻ anions along the c axis; (c) 2D {6³} undulated layer in complex **3**; (d) view of the 3D supramolecular framework by π - π interactions.

pbmb molecule, as shown in Fig. 3a. Each Zn(II) ion is four-coordinated by two carboxylate oxygen atoms from two different mip^{2–} anions (Zn1–O1#1 1.925(2) Å, Zn1–O3 1.928(2) Å) (symmetry code #1: x + 1/2, -y + 1/2, z + 1/2) and two nitrogen atoms from two pbmb ligands (Zn1–N1 2.018(2) Å, Zn1–N3 2.074(2) Å), showing a trigonal pyramidal geometry with the τ_4 value of 0.834. In **3**, each mip^{2–} anion acts as a bridging ligand to link two neighboring Zn(II) centers, a *zig–zag*-shaped chain can be formed (Fig. 3b). The neighboring Zn…Zn separation across one mip^{2–} is 7.967(9) Å. These 1D chains are further linked by flexible pbmb ligands to produce a 2D {6³} undulated layer (Fig. 3c). The

flexible pbmb adopts *anti* conformation with the dihedral angles between two benzimidazole rings being 84.033(8)°. Furthermore, the adjacent 2D layers are extended into 3D supramolecular framework by the π - π stacking interactions with the center-to-center separations of 3.502 Å between neighboring imidazole rings and benzene rings (Fig. 3d).

Effect of dicarboxylate coligands on the structures of 1-3

As it is shown in the descriptions above, three d^{10} coordination polymers 1–3 with the pbmb ligand and different dicarboxylates were successfully synthesized and characterized. Based on the Xray analysis results, the pbmb ligand uniformly behave as the bismonodentate linkers to connect the metal centers in 1-3, but exhibit different bending and rotating ability, which lead to generating different non-bonding $Zn \cdots Zn$ distances (10.648(1) Å for **1**, 7.936(9) Å for **2**, 10,155 Å for **3**) and the different dihedral angles (83,870(8)° in 1,77.053(7)° in 2,84.033(8)° in 3) between two benzimidazole rings with one pbmb ligand. The coordination behavior of dicarboxylate anions also has essential influence on the structures of complexes. In complex **1**, hmph^{2–} anions adopt bis-monodentate coordination mode bridge adjacent Zn atoms giving rise to a 1D zig-zag chain, which is extended by pbmb ligands resulting in a 2D (6, 3) network. While in **2**, $chdc^{2-}$ anions show two kinds of coordination mode fashions. In one fashion, the ligand contains one chelating and one bridging bidentate carboxylate groups; in the other, the ligand contains two bidentate carboxylate groups. The Zn centers are coordinated by chdc²⁻ anions in two fashions mentioned above to form 1D loop-like chain with paddlewheel-like building blocks [Zn₂($chdc)_4$ and dinuclear units $Zn_2(COO)_6$ arranged alternately. The loop-like chain is further bridged by the pbmb ligands to form a double loop-like chain. For **3**, mip^{2–} anions only act as bridging ligand to link two neighboring Zn(II) centers to form a 1D zig-zag-shaped chain, which are linked by flexible pbmb ligands to produce a 2D {6³} undulated layer. These results demonstrate that the coordination behavior of dicarboxylate co-ligands have significant contributions to the conformation of complexes and provide the potential for directing the coordination of flexible ligands with metal ions during the two-ligand assembly system.

IR spectra

In IR spectra of 1, 2 and 3, no band in the region 1690-1730 cm⁻¹, indicates complete deprotonation of the carboxyl groups. The broad band center at around 3420 cm⁻¹ for **2**, relates to the O–H stretching vibration modes of water molecule. The absorption bands observed at 2922 cm^{-1} for polymer **1**, 2932 cm^{-1} for polymer **2** and 2918 cm^{-1} for polymer **3** could be associated with the stretching vibrations of $-CH_2$ -. The bands at 1513 cm⁻¹ for **1**, 1520 cm⁻¹ for **2** and 1516 cm⁻¹ for **3** can be assigned to the $v_{C=N}$ absorption of benzimidazole rings of the ligand pbmb. The asymmetric and symmetric stretching vibrations of carboxyl groups are observed at 1644, 1461 and 1416 cm⁻¹ for **1**, 1610, 1575, 1455 and 1415 cm⁻¹ for **2** and 1634 and 1372 cm⁻¹ for **3**, respectively. The separations $(\Delta v[v_{as}(COO)-v_{s}(COO)])$ between these bands indicate the presence of monodentate (228 cm^{-1} for **1** and 262 cm^{-1} for **3**), chelating $(183 \text{ cm}^{-1} \text{ for } 1 \text{ and } 120 \text{ cm}^{-1} \text{ for } 2)$ and bridging $(195 \text{ cm}^{-1} \text{ for } 2)$ coordination modes of carboxyl groups [28].

X-ray powder diffraction (XRPD) and thermogravimetric analysis (TGA)

Complexes **1**, **2** and **3** were also characterized by X-ray powder diffraction (XRPD) at room temperature (Fig. S1 in the Supporting Information). It is clear that the peak positions in the experimental patterns are well matched to the corresponding simulated patterns

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Fig. 4. TGA curves of the three complexes.



Fig. 5. The solid-state photoluminescent spectra of free pbmb ligands and the three complexes.

calculated from the single-crystal X-ray diffraction data, confirming the phase purities of **1**, **2** and **3**. The differences in peak intensive for the simulations may be due to the preferred orientation of the powder samples.

The thermal stability of the three complexes was also estimated. (Fig. 4) The TGA curve of complex **1** exhibits that it is stable up to 248 °C and then loses weight from 248 to 505 °C, corresponding to the total decomposition of pbmb and hmph^{2–}. The remaining weight corresponds to the formation of ZnO (obsd, 14.96%; calcd., 14.85%). For complex **2**, the weight loss attributed to the release of lattice water molecule is observed from 73 °C to 145 °C (obsd 1.12%, calcd. 1.15%). The sharp weight loss is observed in the range 227–528 °C, corresponding to the decomposition of organic components, finally ZnO residue of 20.82% (calcd. 20.75%) is obtained. Complex **3** is thermally stable to 198 °C, where the weight loss occurs and ends at 496 °C. The remaining weight corresponds to the formation of ZnO (obsd, 14.85%).

Fluorescence properties

The solid state photoluminescence properties of the free pbmb ligand and the complexes **1**, **2** and **3** were investigated at room temperature as depicted in Fig. 5. The free pbmb ligand displays an intense emission band at 349 nm upon excitation at 310 nm, which may be attributed to $\pi^* - \pi$ transitions [29]. It can be seen that **1** exhibits a band emission at $\lambda_{em} = 357$ nm ($\lambda_{ex} = 315$ nm) and the emission probably can be assigned to the intraligand fluorescent

emission since very similar emission is also observed for free pbmb ligand. The red shift of emission occurs in complex **1**, compared with free H₂hmph (λ_{em} = 325 nm and λ_{ex} = 274 nm), which is because of the fact that the ligands are not allowed to relax along the torsional mode on photoexcitation [30]. Complex **2** exhibits a strong emission with 369 nm (λ_{ex} = 330 nm) and the observed red shift of ca. 46 nm between **2** and the 1,4-H₂chdc (λ_{em} = 323 nm and λ_{ex} = 264 nm) ligand can be assigned to may be tentatively assigned to ligand-to-metal charge transfer (LMCT) as reported for other Zn^{II} complexes with N-donor ligands [31]. As to **3**, the weak emission of 365 nm (λ_{ex} = 310 nm) with a small red shift as compared with the free pbmb and H₂mip (λ_{em} = 357 nm and λ_{ex} = 315 nm) ligands may be tentatively attribute to the $\pi \rightarrow \pi^*$ transition of the coordinated ligands since the Zn²⁺ ion is difficult to oxidize or to reduce due to its *d*¹⁰ configuration [32–34].

In addition, further investigation indicates that the fluorescent intensities of the three complexes increase as compared with the free pbmb ligand. The varying degrees of red shift may be attributed to different coordination environments of N-containing ligand and the different structures caused by different organic dicarboxylates in this work.

Conclusion

In summary, three new d^{10} coordination polymers based on bis(2-methylbenzimidazole) ligand have been successfully obtained under hydrothermal conditions. The structural analysis demonstrates that the configuration of ligand, carboxylate anions and supramolecular interantions play an important role in leading to the different structures of resulting coordination and supramolecular architectures. Furthermore, the three complexes are stable and have particular fluorescence properties, and they may have promising application in photophysical chemistry.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014. 04.037.

References

- H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, Science 341 (2013). 1230444-1-1230444-12.
- [2] R.J. Kuppler, D.J. Timmons, Q.R. Fang, J.R. Li, T.A. Makal, M.D. Young, D.Q Yuan, D. Zhao, W.J. Zhuang, H.C. Zhou, Coord. Chem. Rev. 253 (2009) 3042–3066.
- [3] F. Wang, Z.S. Liu, H. Yang, Y.X. Tan, J. Zhang, Angew. Chem. Int. Ed. 50 (2011) 450–452.
- [4] N.C. Jeong, B. Samanta, C.Y. Lee, O.K. Farha, J.T. Hupp, J. Am. Chem. Soc. 134 (2012) 51–54.
- [5] M. O'Keeffe, O.M. Yaghi, Chem. Rev. 112 (2012) 675–702.
- [6] G.H. Cui, J.R. Li, J.L. Tian, X.H. Bu, S.R. Batten, Cryst. Growth Des. 5 (2005) 1775– 1780.
- [7] W.H. Wang, P.H. Xi, X.Y. Su, J.B. Lan, Z.H. Mao, J.S. You, R.G. Xie, Cryst. Growth Des. 7 (2007) 741–746.
- 8] M. Kawano, M. Fujita, Coord. Chem. Rev. 251 (2007) 2592–2605.
- [9] X.L. Wang, J.X. Zhang, L.L. Hou, J.W. Zhang, J.C. Liu, H.Y. Lin, J. Chem. Crystallogr. 41 (2011) 1579–1585.
- [10] R. Vilar, Angew. Chem. Int. Ed. 42 (2003) 1460-1477.
- [11] D. Guo, K.L. Pang, C.Y. Duan, C. He, Q.J. Meng, Inorg. Chem. 41 (2002) 5978– 5985.
- [12] C.H. Jiao, C.H. He, J.C. Geng, G.H. Cui, J. Coord. Chem. 65 (2012) 2852-2861.
- [13] J.C. Geng, C.H. Jiao, J.M. Hao, G.H. Cui, Z. Naturforsch. 67b (2012) 791-798.
- [14] M. Yoshizawa, M. Nagao, K. Umemoto, K. Biradha, M. Fujita, S. Sakamoto, K. Yamaguchi, Chem. Commun. (2003) 1808–1809.
- [15] J.C. Kim, H. Jo, A.J. Lough, J. Cho, U. Lee, S.Y. Pyun, Inorg. Chem. Commun. 6 (2003) 474–477.
- [16] Y.J. Mu, J.H. Fu, Y.J. Song, Z. Li, H.W. Hou, Y.T. Fan, Cryst. Growth Des. 11 (2011) 2183–2193.
- [17] K. Tan, N. Nijem, P. Canepa, Q. Gong, J. Li, T. Thonhauser, Y.J. Chabal, Chem. Mater. 24 (2012) 3153–3167.
- [18] S. Suman, K. Biradha, CrystEngCommun. 11 (2009) 482-492.

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- [19] L. Qin, G.Y. Li, J. Zheng, S.L. Xiao, G.H. Cui, J. Inorg. Organomet. Polym. 23 (2013) 1266-1273.
- [20] S.L. Xiao, L. Qin, C.H. He, X. Du, G.H. Cui, J. Inorg. Organomet. Polym. 23 (2013) 771-778.
- [21] L. Qin, Y.H. Li, P.J. Ma, G.H. Cui, J. Mol. Struct. 1051 (2013) 215-220.
- [22] R. Bronisz, Inorg. Chem. 44 (2005) 4463–4465.
 [23] G.M. Sheldrick, SADABS (version 2.03), Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 1996.
- [24] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112-122.
- [25] L. Yang, D.R. Powell, R.P. Houser, Dalton Trans. 9 (2007) 955-964.
- [26] L. Liu, X. Li, C. Xu, G. Han, Y. Zhao, H. Hou, Y. Fan, Inorg. Chim. Acta 391 (2012) 66-74.
- [27] V.A. Blatov, Struct. Chem. 23 (2012) 955-963.

- [28] K. Nakamoto, Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1986.
- [29] W.L. Liu, L.H. Ye, X.F. Liu, L.M. Yuan, J.X. Jiang, C.G. Yan, Cryst. Eng. Commun. 10 (2008) 1395-1403.
- [30] J.H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K.P. Lillerud, J. Am. Chem. Soc. 130 (2008) 13850-13851.
- [31] H.Y. Liu, H. Wu, J.F. Ma, Y.Y. Liu, B. Liu, J. Yang, Cryst. Growth Des. 11 (2010) 4795-4805.
- [32] Y.B. Dong, H.Y. Wang, J.P. Ma, D.Z. Shen, R.Q. Huang, Inorg. Chem. 44 (2005) 4679-4692.
- [33] J.L. Yin, Y.L. Feng, Y.Z. Lan, Inorg. Chim. Acta 362 (2009) 3769-3776.
- [34] S. Geranmayeh, A. Abbasi, M.Y. Skripkin, A. Badiei, Polyhedron 45 (2012) 204-212.