

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa



Synthesis, crystal structures, luminescence and catalytic properties of two d^{10} metal coordination polymers constructed from mixed ligands



Xiao-xiao Wang^a, Ming-xi Zhang^a, Baoyi Yu^b, Kristof Van Hecke^b, Guang-hua Cui^{a,*}

^a College of Chemical Engineering, Hebei United University, 46 West Xinhua Road, Tangshan 063009, Hebei, PR China ^b Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 S3, B-9000 Ghent, Belgium

HIGHLIGHTS

- Two new metal coordination polymers were synthesized.
- IR, XPRD, TGA technique for the polymers.
- X-ray single-crystal structure analyses and discussion for the polymers.
- Luminescence properties of two complexes have been investigated.
- Catalytic properties of two complexes have been presented.

ARTICLE INFO

Article history: Received 17 October 2014 Received in revised form 29 November 2014 Accepted 17 December 2014 Available online 27 December 2014

Keywords: Crystal structure Bis(benzimidazole) ligand Metal–organic framework Luminescence

G R A P H I C A L A B S T R A C T



ABSTRACT

Two new coordination polymers $[Cd(bmb)(hmph)]_n$ (1), $[[Ag(bmb)] \cdot H_2btc]_n$ (2) (bmb = 1,4-bis(2-methylbenzimidazol-1-ylmethyl)benzene, H₂hmph = homophthalic acid, H₃btc = 1,3,5-benzenetetracarboxylic acid) were synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction methods, IR spectroscopy, TGA, XRPD and elemental analysis. Complex 1 features a 3D threefold interpenetrating **dia** array with a 4-connected 6⁶ topology. Complex 2 shows a 1D helix chain structure connected by L1 ligands, which is finally extended into a rarely 2D **4L2** supramolecular network via C-H···O hydrogen bond interactions. In addition, the luminescence and catalytic properties of the two complexes for the degradation of the methyl orange azo dye in a Fenton-like process were presented. The degradation efficiency of the methyl orange azo dye for 1 and 2 are 56% and 96%, respectively.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Crystal engineering of metal-organic coordination polymers (MOCPs) has now reached a stage where intense interest is slowly shifting from design strategies of different structural motifs to exploration their potentials as functional materials in catalysis, fluorescence, magnetism, and biological chemistry [1–6]. Generally, the generation of intriguing and useful MOCPs is greatly influenced by metal ions, organic ligands, solvent system, pH value and

non-covalent interactions such as H-bonding and π - π interactions. Nevertheless, how to reasonably construct the expected architectures with unique properties is still a huge challenge. Selective design of organic ligands is usually crucial for the formation of these novel coordination frameworks. In recent years, the flexible bis(benzimidazole) ligands have been used as classic N-containing ligands coordinating to metal centers to generate more robust and intricate networks [7–9]. Semirigid N-donor ligand 1,4-bis(2-methylbenzimidazol-1-ylmethyl)benzene (bmb) with a spacer of $-(CH_2-Ph-CH_2)$ - and two freely rotating methylbenzimidazol arms have attracted much attention within coordination and supramolecular chemistry by our and other groups, due to their good

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

coordination ability and versatile conformations [10-14]. The 2position substituent methyl of bmb effectively enhances the donated electrons ability of benzimidazole rings and makes it exhibit strong collaborative coordination ability with organic carboxylate ligands, which would be a powerful precursor for the construction of MOCPs with diverse structures and topologies. In addition, aromatic dicarboxylates and tricarboxylates have proven among the most popular choice of O-donor ligands to construct coordination polymers [15,16]. Such as homophthalic acid (H₂₋ hmph), 1,3,5-benzenetricarboxylate (H₃btc) are of particular interest due to their coordination geometry preferences, the disposition of carboxylate groups, and numerous accessible bridging and binding modes leading to diverse structures of the resulting architecture. However, the MOCPs incorporation of semirigid bis(2methylbenzimidazol) mixed with H₃btc (or H₂hmph) coligands have received scant attention [17]. As ongoing our previous work [18,19], two new d^{10} metal coordination polymers with interesting luminescence and catalytic properties were prepared and structurally characterized. $[Cd(bmb)(hmph)]_n$ (1) reveals a 3-fold interpenetrating 3D dia array with 4-connected 6⁶ framework, while $\{[Ag(bmb)] \cdot H_2 btc\}_n$ (2) shows a 1D helix chain structure.

Experimental

Materials and measurements

All starting regents are commercially available, analytical grade and used in the experiment without further purification. The ligand bmb was prepared according to the literature method [20]. Elemental analysis (C, H, and N) was performed on a Perkin-Elmer 240C Elemental Analyzer. IR spectra were recorded from KBr pellets in the range of 4000–400 cm⁻¹ on a FT-IR Avatar 360 (Nicolet) spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C with a heating rate of 10 °C/min under N₂ atmosphere. Luminescence spectra for the powdered solid samples were measured at room temperature on a Hitachi F-7000 fluorescence spectrophotometer. X-ray powder diffraction (PXRD) measurements were made on a Rigaku D/Max-2500 diffractometer operated at 40 kV and 100 mA for a Cu-target tube and a graphite monochromator.

Preparation of the complexes 1 and 2

$[Cd(bmb)(hmph)]_n$ (1)

A mixture of CdCl₂ (0.1 mmol, 22.8 mg), bmb (0.1 mmol, 36.6 mg), H₂hmph (0.1 mmol, 18.0 mg) and 10 mL water was heated at 140 °C for 3 days in a 25 mL Teflon-lined vessel container. After, the mixture was cooled to room temperature at a rate of 5 °C/h. The colorless crystals suitable for single-crystal X-ray diffraction were obtained by filtration and washed with distilled water in 63% yield (based on CdCl₂). Anal. Calcd. for C₉₉H₈₄Cd₃N₁₂-O₁₂ (%): C, 60.33, H, 4.30, N, 8.53; Found (%): C, 60.58, H, 4.52, N, 8.79. IR (KBr, cm⁻¹): 3069(w), 2927(m), 1565(s), 1512(s), 1481(m), 1472(s),1460(m), 1393(s), 1292(w), 1151(w), 859(w), 744(s), 685(w).

$\{[Ag(bmb)] \cdot H_2 btc\}_n (\mathbf{2})$

The synthetic procedure of **2** was analogous to the synthesis of **1**, except that AgOAc (0.1 mmol, 16.6 mg), H₃btc (0.1 mmol, 21.0 mg) were used instead of CdCl₂ (0.1 mmol, 22.8 mg) and H₂-hmph (0.1 mmol, 18.0 mg), respectively. Colorless block-shaped crystals of **2** (yield: 43%) could be obtained by filtration and washed with distilled water. Anal. Calcd. for $C_{33}H_{27}AgN_4O_6$ (%): C, 57.99, H, 3.98, N, 8.20; Found (%): C, 57.62, H, 4.06, N, 8.42. IR

443

(KBr, cm^{-1}): 3422(s), 3109(w), 2442(w), 1708(s), 1614(m), 1568(m), 1514(w), 1424(s), 1200(s), 1007(w), 753(s), 653(m), 473(w).

Catalysis experiments

In catalysis experiments, the decomposition of MO (methyl orange) was carried out in a 250 mL round-bottom flask, containing the solid catalysts **1** or **2** (50 mg) azo dye (MO solution 150 mL with 10 mg/L) and Na₂S₂O₈ (30 mg) at 30 °C. The solution was stirred and 5 mL samples were taken at regular time intervals and separated through centrifugation and then subsequently analyzed by UV–visible spectrometer at 506 nm. The degradation efficiency can be expressed as the percentage of discoloration (%*D*), considering the initial and the final absorbance values of the dye solution at a wavelength of 506 nm (A_0 and A_{f_r} , respectively).

$$\% D = [(A_0 - A_f)/A_0] \times 100 \tag{1}$$

X-ray crystallography

Crystallographic data for complexes **1** and **2** were collected on a Bruker Smart CCD diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å) with $\omega - 2\theta$ scan mode at 293 K. Semi-empirical absorption corrections were applied using the SADABS program [21]. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXL-97 program package [22]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bonded to carbon atoms were placed in geometrically calculated positions and refined isotropically. The hydrogen atoms of two carboxyl groups in **2** were located from difference Fourier maps and refined with isotropic displacement parameters. Crystallographic data and structure determination statistics are listed in Table 1, and selected

Table 1Crystal and refinement data for complexes 1 and 2.

Complex	1	2
Empirical formula	$C_{99}H_{84}Cd_3N_{12}O_{12}$	C33H27AgN4O6
Formula weight	1970.98	683.46
Temperature	296(2)	296(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	P21
Unit cell dimensions		
a, Å	10.7835(6)	9.4691(9)
<i>b</i> , Å	46.051(3)	11.2247(11)
<i>c</i> , Å	20.4102(9)	13.3695(13)
β, deg	121.094(2)	100.743(10)
<i>V</i> , Å ³	8679.3(8)	1396.1(2)
Ζ	4	2
D_{calc} , g/m ³	1.508	1.626
μ , mm $^{-1}$	0.800	0.778
F(000)	4008	696
Crystal size, nm	$0.24 \times 0.22 \times 0.19$	$0.21\times0.20\times0.19$
Total reflections	52,993	8546
Unique reflections	19,850	5783
R _{int}	0.0538	0.0220
GOF	1.024	1.001
$R_1 (I > 2\sigma(I))^a$	0.0502	0.0314
$wR_2 (I > 2\sigma(I))^{b}$	0.0978	0.0612
Δho max, eÅ $^{-3}$	0.625	0.478
Δho min, eÅ $^{-3}$	-0.563	-0.330

^a $R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$.

^b $wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}.$

Table 2	
Selected bond lengths [Å] and angles [°] for complexes 1 and	2.

Compound 1			
Cd1-01	2.267(3)	Cd1-N3	2.279(3)
Cd1–N1	2.322(3)	Cd1-012A	2.339(3)
Cd1-011A	2.362(3)	Cd1-02	2.536(3)
Cd2-N9	2.283(3)	Cd2-09	2.286(3)
Cd2-07B	2.334(3)	Cd2-N8	2.331(3)
Cd2-08B	2.379(3)	Cd2-010	2.520(3)
Cd3-04	2.208(3)	Cd3-06	2.277(3)
Cd3-N12C	2.280(3)	Cd3-N5	2.297(3)
Cd3-05	2.480(3)	Cd3-03	2.638(3)
01-Cd1-N3	111.38(12)	N9-Cd2-O9	108.46(11)
01-Cd1-N1	91.70(11)	N9-Cd2-07B	98.84(12)
N3-Cd1-N1	102.25(12)	09-Cd2-07B	134.70(11)
01-Cd1-012A	138.62(12)	N9-Cd2-N8	103.78(12)
N3-Cd1-012A	96.09(12)	09-Cd2-N8	93.80(11)
N1-Cd1-012A	112.65(13)	07B-Cd2-N8	114.28(12)
01-Cd1-011A	92.16(11)	N9-Cd2-O8B	153.92(12)
N3-Cd1-O11A	150.81(12)	09-Cd2-08B	92.51(11)
N1-Cd1-011A	93.72(12)	07B-Cd2-08B	55.09(11)
012A-Cd1-011A	54.96(11)	N8-Cd2-O8B	89.70(12)
01-Cd1-02	54.13(10)	N9-Cd2-010	92.07(11)
N3-Cd1-O2	95.19(11)	09-Cd2-010	54.45(10)
N1-Cd1-O2	145.59(13)	07B-Cd2-010	89.99(11)
012A-Cd1-02	94.45(12)	N8-Cd2-010	147.94(11)
011A-Cd1-02	84.60(11)	08B-Cd2-010	87.65(11)
04-Cd3-06	133.45(11)	04-Cd3-N12C	112.48(12)
06-Cd3-N12C	96.88(11)	04-Cd3-N5	97.99(12)
06-Cd3-N5	106.78(11)	N12C-Cd3-N5	107.63(12)
04-Cd3-05	85.97(11)	06-Cd3-05	54.68(10)
N12C-Cd3-O5	149.49(11)	N5Cd3-05	92.74(11)
04-Cd3-03	53.04(11)	06-Cd3-03	93.70(10)
N12C-Cd3-O3	89.95(11)	N5-Cd3-O3	150.72(11)
05-Cd3-03	82.08(11)		
Compound 2			
Ag1–N2	2.177(3)	Ag1–N3A	2.179(3)
N2-Ag1-N3A	164.61(9)		

Symmetry transformations used to generate equivalent atoms in **1**: A: -x + 2, -y, -z + 2; B: x + 1, 0.5 - y, -0.5 + z; C: x + 1, y, z + 1. In **2**: A: x + 1, y - 1, z.

bond lengths and angles for the complexes are listed in Table 2, respectively.

Results and discussion

Crystal structures

Crystal structures of $[Cd(bmb)(hmph)]_n$ (1)

Single crystal X-ray diffraction analysis reveals that 1 crystallizes in monoclinic space group $P2_1/c$. The asymmetric unit of **1** contains three crystallographically independent Cd(II) ions, two whole bmb and two half bmb ligands and three hmph^{2–} anions. Cd1 ion possesses six-coordinated octahedral geometry (Fig. 1a), which is completed by four oxygen atoms (01, 02, 03 and 04) from two different hmph²⁻ anions and two nitrogen atoms (N1 and N3) from two bmb ligands. In this octahedral geometry, O2, O3, O4 and N1 lie in the equatorial plane while N3 and O1 are positioned at the axial sites. The coordination configurations of Cd2 and Cd3 ions are the same to that of Cd1. Cd2 formed by three oxygen atoms (09, 010 and 012) and one nitrogen atoms (N10) composing the equatorial plane as well as one oxygen atom (O11) and one nitrogen atom (N11) at the axial sites. Cd3 ion coordinating with three oxygen atoms (05, 07 and 08) and one nitrogen atom (N5) in the equatorial plane and one oxygen atom (O6) as well as one nitrogen atom (N7) form at the axial sites. The Cd-N bond lengths vary from 2.281(4) to 2.334(4) Å, while the Cd-O bond lengths are from 2.207(3) to 2.640(4) Å, which are similar to those in other cadmium coordinated complexes [23].

In **1**, bmb ligands adopt three *trans*-conformation with different $N_{donor} \cdots N-C_{sp3} \cdots C_{sp3}$ torsion angles of 180°, 160° and 158°, respectively. The bmb ligands act in bis-monodentate mode to link adjacent Cd(II) ions to generate two kinds of 1D " Ω "-like chains with Cd1…Cd1 distances of 15.0384(10) Å and 15.2303(9) Å, Cd2…Cd3 lengths of 14.7074(9) Å and 14.9499(10) Å, respectively (Fig. 1b). On the other hand, both carboxyl groups of hmph²⁻ anions adopt chelating bis-bidentate fashion connecting adjacent Cd(II) atoms to generate a helix chain. The interlaced connections from different directions of these chains further give rise to a complicated 3D framework. The Cd…Cd contact distances through hmph²⁻ are 8.659(7) Å, 8.741(7) Å and 8.886(7) Å, respectively.

Notably, the overall framework of **1** is a 3D diamondoid network with large rectangle channels by connecting four linear ligands to the Cd(II) ions (Fig. 1c). The typical diamondoid cage exhibits unusual maximum dimensions of 29.052 × 17.479×15.435 Å corresponding to the longest intracage Cd…Cd distances. From the topological point of view, If Cd1, Cd2 and Cd3 atom are simplified as a 4-connected node, and hmph²⁻ and bmb ligands are considered as linkers. Accordingly, the 3D complex framework of **1** can be simplified to a 4-connected **dia** topology with the topological point symbol of 6^6 , which performed by the TOPOS4.0 software [24]. The potential voids are filled via mutual interpenetration of two other independent equivalent frameworks, generating a 3-fold interpenetrating 3D architecture (Fig. 1d). The three interpenetrated nets are related by a single translational vector (Class Ia) [25], with $Z_t = 3$ and $Z_n = 1$, where Z_t represents the number of interpenetrated nets related by translation and Z_n denotes the number of interpenetrated nets related by crystallographic symmetry [26]. Intriguingly, a void volume of 385 Å³ is also left after interpenetration and the pore volume ratio was calculated to be 4.4% by the PLATON program [27]. It is notable that Hou's group reported the cadmium MOCP based on bmb and 1,4benzenedicarboxylic acid ligands with a 3-fold interpenetrating **dia** framework [14], However, coordination polymer **1** is the first 3D MOF metal-organic framework derived from H₂hmph ligand.

Crystal structures of $\{[Ag(bmb)] \cdot H_2 btc\}_n$ (2)

The single-crystal X-ray diffraction analysis reveals that complex **2** crystallizes in the monoclinic space group $P2_1$. The asymmetric unit of **2** is composed of one silver ion, one bmb ligand and one uncoordinated H_2btc^- anion. The coordination environment around the Ag(I) center is illustrated in Fig. 2a. The Ag(I) atom is coordinated by two N-atoms deriving from two different bmb ligands with distances Ag1-N2 = 2.177(3) Å and Ag1-N3A = 2.179(3) Å (A: x + 1, y - 1, z). Bond distances in **2** are within the normal range observed in other N-containing Ag(I) complexes.

The Ag(I) atoms in **2** are bridged by bmb in a bis-monodentate mode to form a 1D helix chain, as shown in Fig. 2b, where the Ag...Ag distances are 14.685 (11) Å and Ag...Ag...Ag angles are 180°. In **2**, the bmb act as *trans*-configuration ligands in which the dihedral angles between two benzimidazole planes of bmb molecule are nearly parallel of 2.57(7)°. In addition, the 1D helix chain is extended into a 2D supramolecular network (Fig. 2c) by two kinds of C-H···O intermolecular hydrogen bonds among the bmb ligands and carboxylate groups, in which the lengths of $H \cdots O$ are 1.95 Å and 1.74 Å, respectively (Table 3). In the 2D network, the dimensions of the intralayer incipient voids are $11.225(11) \times 9.249(9)$ Å, as measured by through-space Ag...Ag distances. In order to better understand the final architecture of the complex, the framework of 2 can be abstracted as a 4-connected **4L2** supramolecular layer with a point symbol of $(6^5 \cdot 8)$. There is no residual solvent accessible void in complex 2, as calculated by the PLATON program. To the best of our knowledge, this 2D supramolecular topology represents the first example of a metal-organic replica of the 4L2 network.



Fig. 1. (a) The coordination environment for Cd(II) ion in complex **1**, showing thermal displacement ellipsoids at the 30% probability level. Symmetry codes: A: -x + 2, -y, -z + 2; B: x + 1, 0.5 - y, -0.5 + z; C: x + 1, y, z + 1; (b) Perspective view of the 1D " Ω "-like chains in **1**. Symmetry codes: D: x - 1, y, z - 1; E: -x - 1, -y, -z; F: -x, -y, -z + 1; (c) Single 3D dia net with large rectangle channels; (d) View of the threefold interpenetrating **dia** network in **1**.

Effect of organic ligands and metal centers on the structures of the complexes

It is well known that the organic ligands and metal centers play an important role in determining the final structures of target complexes. The related complexes, namely $\{[Cd(bmb)(o-phda)]_n (3),$ and $[Zn(pbmb)(hmph)]_n$ (**4**) (pbmb = 1,1'-(1,3-propane)bis-(2methylbenzimidazole), H₂phda = phenylenediacetic acid) were reported previously [14]. In all the four complexes, the flexible bis(2-methylbenzimidazole) derivatives adopt trans-configuration to connect the metal centers (Cd, Ag or Zn), but exhibit different torsional arrangements, leading to a variety of different distances between metal centers and distinct geometries. In 1 and 3, the bmb ligands uniformly behave as bis-monodentate linkers to connect the Cd centers, the hmph²⁻ and o-phda²⁻ ligands take on the same bidentate bridging coordination fashion acting as linkers to form 3-fold interpenetrating dia array in 1 and 3, respectively. When the bmb was replaced by pbmb, hmph²⁻ anions adopt bismonodentate coordination mode acting connectors leading to a 2D butterfly-shaped network for 4. While 2 is a 1D helix chain connected by bmb, which is further extended into a 2D supramolecular network by non-classical hydrogen bonds. The results reveal that the organic ligands with different spacer and the distinct metal centers play a significant role in promoting the diversity of the observed structural motifs.

IR and XPRD

There is no absorption peak around 1700 cm^{-1} for complex **1**, indicating that all carboxyl groups of the organic moieties are deprotonated, while a characteristic absorption band at 1708 cm^{-1} and 3422 cm^{-1} for **2** suggests incomplete deprotonation of the carboxylic acid [28]. The absorption peaks at 1565 cm^{-1} and 1481 cm^{-1} for **1**, and 1614 cm^{-1} and 1424 cm^{-1} for **2** may be attributed to the asymmetric and symmetric vibra-

tions of carboxylate groups. In complex **2**, all of the carboxylate groups are uncoordinated, but $\Delta v[v_{as}(COO) - v_s(COO)]$ is 84 cm⁻¹ for complex **1**, indicating bidentate coordination of the carboxylate group to the metal center, which is consistent with X-ray structural analysis [29]. Characteristic bands at 1512 cm⁻¹ for **1** and 1514 cm⁻¹ for **2** are assigned to the $v_{C=N}$ stretching vibration of the benzimidazole rings. Some weak bands at 2400–3100 cm⁻¹ are consistent with the v_{C-H} stretching vibration of the benzimidazole rings.

Complexes **1** and **2** were also characterized by X-ray Powder diffraction (XRPD) to confirm the phase purity of the bulk materials are shown in Fig. 3a and b. The XRPD patterns of all as-synthesized products closely match the simulated ones from the single-crystal data, indicating that products are in a pure phase.

Thermal and photoluminescent properties

To evaluate the stability of the coordination architectures, thermogravimetric analyses (TGA) of complexes **1** and **2** were performed (Fig. 4). The results show that both of the complexes are very stable in air at ambient temperature. Polymer **1** displays a high thermal stability, which is stable up to 356 °C and then keeps losing weight until to 684 °C corresponding to the losses of bmb and the decomposition of H₂hmph. Finally, the white CdO residue of 20.16% (calcd: 19.54%) is observed. There is only one weight loss stage in **2** and the weight loss corresponding to the release of the organic components occurs at 297 °C. At 615 °C, a Ag₂O residue of 32.45% (calcd: 33.82%) is obtained.

Coordination polymers with d^{10} metal centers and conjugated organic linkers are promising candidates for photoactive materials with potential applications such as chemical sensors and photochemistry [30]. Hence, the photoluminescent properties of complexes **1** and **2** as well as the free bmb ligand have been investigated in the solid state at room temperature (Fig. 5). The





Fig. 2. (a) Local coordination geometry of the central Ag(1) cation in the complex 2, showing thermal displacement ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Symmetry code: A: x + 1, y - 1, z; (b) View of 1D helix chain in 2; (c) 2D supramolecular network with 4-connected 4L2 topology in 2.

Table 3 The hydrogen bond dis				
d(D-H)	<i>d</i> (D–H)	<i>d</i> (HA)	<i>d</i> (DA)	∠DHA
C15-H15···O5B	0.82	1.95	2.745(4)	162
C16-H16O2C	0.91	1.74	2.639(5)	169

Symmetry transformations used to generate equivalent atoms: B: x - 1, y, z; C: -x + 1, y + 1/2, -z + 2.

free bmb ligand shows intense emissions bands at 307 nm when excited at 250 nm, which can probably be assigned to the $\pi \rightarrow \pi^*$ transitions [31]. The emission with maxima at 390 nm for 1 (λ_{ex} = 240 nm), 400 nm for **2** (λ_{ex} = 260 nm), respectively. The emission band of 1 and 2 are similar to the free bmb ligand, which is neither metal-to-ligand charge transfer (MLCT) nor ligand-tometal charge transfer (LMCT) in nature [32]. Thus, the emission may be assigned to the transitions of N-donor ligand. It is noteworthy that complex **1** showed an intense emission compared with **2**



Fig. 3. (a and b) The powder X-ray diffraction patterns calculated from the singlecrystal data and that obtained from the experiments for polymer 1 and 2, respectively.



Fig. 4. The TGA curves of polymers 1–2 were measured in N₂ atmosphere.

at room temperature, which may be attributed to the effective increase of the rigidity of the complex and reduces the loss of energy by radiationless decay. This result indicates that 1 may be



Fig. 5. Emission spectra of complex 1-2 and the free bmb ligand.



Fig. 6. The experiment results of the catalytic degradation of methyl orange.

a good candidate for potential hybrid inorganic–organic photoactive materials.

Catalytic properties

Wastewaters from the textile, cosmetics, printing, dying, food coloring, and papermaking industries are polluted by dyes such as methyl orange. Methyl orange, a well-known acidic/anionic dye, is potentially harmful to the environment [33,34]. Therefore, the degradation of methyl orange dye has attracted much attention. In recent years, an advanced oxidation technology based on strongly oxidizing sulfate radicals (SO_4^-) has been developed to degrade organic pollutants [35]. Fenton oxidation technologies utilize $Na_2S_2O_8$, which generates sulfate radicals that are very effective in degrading organic pollutants, but the uncatalyzed reaction rates are generally slow at ambient temperature. Hence, complexes 1 and 2 were used as heterogeneous Fenton catalysts to oxidize such contaminants and they are may be highly effective for the removal of dyes and pigments.

The degradation of the methyl orange dye by $Na_2S_2O_8$, activated with the complexes **1** and **2** was investigated, and the results are shown in Fig. 6. In the absence of the catalyst, when a solution of methyl orange is mixed with $Na_2S_2O_8$, the mixture is stable for a

period of time without any noticeable change in the absorbance of dye, even for a reaction time up to 130 min, and the degradation efficiency of methyl orange was only 18%, which indicates that there is almost no reaction going on between the methyl orange and Na₂S₂O₈. The degradation efficiency of the methyl orange degradation within 40 min reaction was about 30% in the presence of **1**, and reached to approximately 56% after 130 min. Complex **2** performed better than **1**, after 130 min, the final degradation efficiency amounted up to even 96%, which is more higher than that of {Ag₂(bbbi)₂(ntp)(H₂O)·4H₂O}_n (bbbi = 1,1-(1,4-butanediyl)bis-1H-benzimidazole, H₂ntp = 2-nitroterephthalic acid) previously reported by our group [36]. It is obvious that complex **2** shows higher activity for degrading the methyl orange azo dye in a Fenton-like process.

Conclusion

In summary, two new d^{10} coordination polymers have been successfully isolated under hydrothermal conditions by reactions of two aromatic carboxylates, bmb and metal salts. Complex **1** features a 3D threefold interpenetrating **dia** array with 4-connected 6⁶ framework. Complex **2** exhibits a 1D helix chain, which ultimately is extended into a 2D supramolecular network. The results demonstrate that the difference between Cd(II)/Ag(I) in electronic structures and sizes and the coordination geometry of carboxylate anions play an important role in construction of coordination polymers with diverse structural features and charming topologies. Both of the complexes exhibit interesting photoluminescent properties, which may be good candidates for potential photoactive materials. Furthermore, both compounds show good catalytic activity for degradation of methyl orange in a Fenton-like process.

Acknowledgments

The project was supported by the National Natural Science Foundation of China (51474086) and the Hercules Foundation (Project AUGE/11/029"3D-SPACE: 3D Structural Platform Aiming for Chemical Excellence") for funding.

Appendix A. Supplementary data

CCDC 1028732 and 1028733 contain the supplementary crystallographic data for the complexes **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.12.058.

References

- [1] J.W. Liu, L.F. Chen, H. Cui, J.Y. Zhang, L. Zhang, C.Y. Su, Chem. Soc. Rev. 43 (2014) 6011–6061.
- [2] L.B. Sun, J.R. Li, W. Lu, Z.Y. Gu, Z. Luo, H.C. Zhou, J. Am. Chem. Soc. 134 (2012) 15923–15928.
- [3] L. Wang, R. Zhao, L.Y. Xu, T. Liu, J.P. Zhao, S.M. Wang, F.C. Liu, CrystEngComm 16 (2014) 2070–2077.
- [4] C.L. Ming, L.N. Wang, V.H. Kristof, G.H. Cui, Spectrochim. Acta Part A 129 (2014) 125–130.
- [5] J.R. Li, J. Yu, W. Lu, L.B. Sun, J. Sculley, P.B. Balbuena, H.C. Zhou, Nat. Commun. 4 (2013) 1538.
- [6] J.C. Geng, C.J. Wang, F. Wang, H.R. Luo, C.C. Yang, G.H. Cui, Chin. J. Inorg. Chem. 28 (2012) 1060–1064.
- [7] L. Qin, L.N. Wang, P.J. Ma, G.H. Cui, J. Mol. Struct. 1059 (2014) 202–207.
- [8] X.L. Wang, L.L. Hou, J.W. Zhang, G.C. Liu, H.Y. Lin, Polyhedron 61 (61) (2013) 65-72.
- [9] H. Jiang, Y.Y. Liu, J.F. Ma, W.L. Zhang, J. Yang, Polyhedron 27 (2008) 2595–2602.

- [10] R. Pandey, M. Yadav, M. Shahid, A. Misra, D.S. Pandey, Tetrahedron Lett. 53 (2012) 3550–3555.
- [11] P. Rajakannu, B. Shankar, A. Yadav, R. Shanmugam, D. Gupta, F. Hussain, C.H. Chang, M. Sathiyendiran, K.L. Lu, Organometallics 30 (2011) 3168–3176.
- [12] Y.Q. Wang, J. Yang, W.Q. Kan, Y. Yang, J. Guo, J.F. Ma, Eur. J. Inorg. Chem. 2 (2013) 280–292.
- [13] C.M. Qi, D. Zhang, S. Guo, H. Ma, Y. He, S.L. Ma, Y.F. Chen, X.J. Yang, J. Mol. Struct. 891 (2008) 357–362.
- [14] C.Y. Xu, L.K. Li, Y.P. Wang, Q.Q. Guo, X.J. Wang, H.W. Hou, Y.T. Fan, Cryst. Growth Des. 11 (2011) 4667–4675.
- [15] Y. Liu, N. Li, L. Li, H.L. Guo, X.F. Wang, Z.X. Li, CrystEngComm 14 (2012) 2080– 2086.
- [16] Y.W. Li, H. Ma, Y.Q. Chen, K.H. He, Z.X. Li, X.H. Bu, Cryst. Growth Des. 12 (2012) 189–196.
- [17] C.Y. Xu, Q.Q. Guo, X.J. Wang, H.W. Hou, Y.T. Fan, Cryst. Growth Des. 11 (2011) 1869–1879.
- [18] X.X. Wang, B.Y. Yu, K.V. Hecke, G.H. Cui, RSC Adv. 4 (2014) 61281-61289.
- [19] J.M. Hao, L.N. Wang, K. Van Hecke, G.H. Cui, Inorg. Chem. Commun. 41 (2014) 43–46.
- [20] C.B. Aakeroy, J. Desper, E. Elisabeth, B.A. Helfrich, B. Levin, J.F. Urbina, Z. Kristallogr. 220 (2005) 325–332.

- [21] G.M. Sheldrick, SADABS, University of Göttingen, Germany, 1996.
- [22] G.M. Sheldrick, Acta Cryst. A64 (2008) 112–122.
 [23] C.H. He, C.H. Jiao, G.H. Cui, J. Struct. Chem. 54 (2013) 168–172.
- [24] V.A. Blatov, Struct. Chem. 23 (2012) 955–963.
- [25] I.A. Baburin, V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio, J. Solid State Chem. 178 (2005) 2452–2474.
- [26] V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio, CrystEngComm 6 (2004) 378– 395.
- [27] J.R. Li, H.C. Zhou, Angew. Chem. Int. Ed. 48 (2009) 8465-8468.
- [28] J.M. Hao, Y.N. Zhao, R. Yang, G.H. Cui, J. Mol. Struct. 1070 (2014) 58-64.
- [29] B. Tao, W. Lei, F.R. Cheng, H. Xia, Bull. Korean Chem. Soc. 33 (2012) 1929–1933.
- [30] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227-250.
- [31] F.H. Zhao, Y.X. Che, J.M. Zheng, Inorg. Chem. Commun. 24 (2012) 200-204.
- [32] S.L. Xiao, L. Qin, C.H. He, X. Du, G.H. Cui, J. Inorg. Organomet. Polym. Mater. 23 (2013) 771–778.
- [33] L.F. Ma, Q.L. Meng, C.P. Li, B. Li, L.Y. Wang, M. Du, F.P. Liang, Cryst. Growth Des. 10 (2010) 3036–3043.
- [34] M.K. Purkait, S.S. Vijay, S. DasGupta, S. De, Dyes Pigm. 13 (2004) 151-159.
- [35] V.S. Mane, P.V. Vijay Babu, J. Taiwan Inst. Chem. Eng. 44 (2013) 81–88.
- [36] L. Qin, S.L. Xiao, P.J. Ma, G.H. Cui, Transit. Met. Chem. 38 (2013) 627-633.