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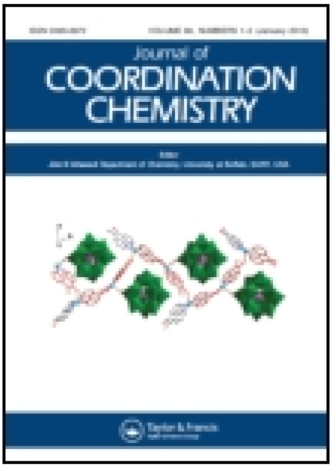

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Two 1-D zinc(II) coordination polymers based on flexible bis(2-methylbenzimidazole) and rigid dicarboxylate co-ligands

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Accepted author version posted online: 28 May 2014.Published online: 19 Jun 2014.

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To cite this article: Jin Ming Hao, Hao Zhang, Guang Yue Li & Guang Hua Cui (2014) Two 1-D zinc(II) coordination polymers based on flexible bis(2-methylbenzimidazole) and rigid dicarboxylate co-ligands, Journal of Coordination Chemistry, 67:11, 1992-2003, DOI: 10.1080/00958972.2014.928288

To link to this article: http://dx.doi.org/10.1080/00958972.2014.928288

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Journal of Coordination Chemistry, 2014
Vol. 67, No. 11, 1992–2003, http://dx.doi.org/10.1080/00958972.2014.928288

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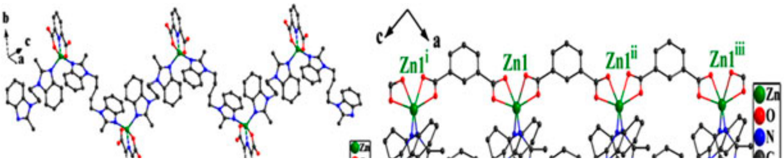
(*Received 30 October 2013; accepted 1 April 2014*)



Two coordination polymers, $\{[Zn(bbi)(pydca)]\cdot 2H_2O\}_n$ (**1**) and $[Zn(bmb)(1,3\text{-}bdc)]_n$ (**2**), where (bbi = 1,1′-(1,4-butanediyl)bis(2-methylbenzimidazole), H_2pydca = pyridine-2,6-dicarboxylic acid, bmb = 1,3-bis(2-methylbenzimidazol-1-ylmethyl)benzene and 1,3-H_2bdc = 1,3-benzenedicarboxylic acid), have been hydrothermally synthesized and characterized by elemental analysis, IR spectroscopy, and powder and single-crystal X-ray diffraction. Structural analysis showed that **1** is a 1-D zigzag chain coordination polymer, which is further linked into a 3-D supramolecular framework via classical O–H···O hydrogen bonding interactions. In **2**, the 1-D loop-like chains are additionally assembled by four C–H···π hydrogen bond interactions to construct a 3-D supramolecular network. The thermal stabilities and fluorescence properties of the complexes were investigated.

Keywords: Bis(benzimidazole); Crystal structure; Fluorescence properties; Zn(II) coordination polymers

1. Introduction

Metal–organic coordination polymers (MOCPs) made from organic ligands and transition metals have become a major focus in supramolecular and materials chemistry for their intriguing structural diversity and potential applications in fluorescence, catalysis, gas adsorption, and magnetic materials [1–4]. Although many efforts have been devoted to the preparation of specific coordination compounds with 1-, 2-, and 3-D structures, the rational preparation of MOCPs is still a challenge [5, 6]. The formation of MOCPs is influenced by the organic ligands, the nature of the metal ions, the counterions and solvents, and non-bonding interactions such as hydrogen bonding and π–π stacking [7, 8]. A great

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*Corresponding author. Email: tscghua@heuu.edu.cn number of organic bridging ligands have been employed to prepare new coordination polymers. Especially flexible bis(benzimidazole) ligands have been used as classic N-containing ligands that can satisfy the coordination requirements of the metal centers and consequently generate robust and intricate networks, such as (6^5.8) **msw/*P*42/*nnm*** and **mok** topologies, interpenetrating networks, and multidimensional frameworks [9, 10]. Furthermore, a methyl substituent at the 2-position of the benzimidazole ring can greatly enhance the electron donor ability of the ligands. Flexible bis(2-methylbenzimidazole) ligands with two N-donor sites have two freely rotating methylene groups that can adopt different conformations to facilitate coordination of the N-donor sites with metal ions, which can be beneficial for construction of extended architectures and may be more likely to afford meso-helices.

To further investigate the influence of carboxylates mixed with bis(2-methylbenzimidazole) ligands on the architectures of zinc(II) coordination polymers, we report in this article the synthesis and characterization of two infinite chain Zn(II) coordination polymers, $\{[Zn(bbi)(pydca)]\cdot 2H_2O\}_n$ (**1**) and $[Zn(bmb)(1,3\text{-bdc})]_n$ (**2**), where bbi = 1,1′-(1,4-butanediyl)bis(2-methylbenzimidazole), H_2pydca = pyridine-2,6-dicarboxylic acid, bmb = 1,3-bis(2-methylbenzimidazol-1-ylmethyl)benzene and 1,3-H_2bdc = 1,3-benzenedicarboxylic acid. Thermogravimetric analyses, X-ray powder diffraction, and fluorescence properties of the two complexes have been investigated.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were of reagent grade, commercially available, and used without purification. The ligands bbi and bmb were prepared according to literature methods [11]. Elemental analyses were made on a Perkin-Elmer automatic analyzer. IR spectra were recorded on a Nicolet FTIR Avatar 360 spectrophotometer from 4000 to 400 cm^{-1} using KBr pellets. Ultraviolet–visible (UV–vis) diffuse reflectance spectra were measured using a UV–vis spectrophotometer (Puxi, UV 1901) equipped with an integrating sphere attachment and on a Thermo Evolution 300 spectrophotometer equipped with a Praying Mantis diffuse reflectance accessory from 230 to 800 nm using $BaSO_4$ as the reflectance standard. The TG measurements were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C under N_2 with a heating rate of 10 °C min^{-1}. X-ray powder diffraction measurements were executed on a D/MAX 2500PC X-ray diffractometer using Cu-Kα radiation ($\lambda = 0.1542$ nm) in the 2θ range of 5°–50° with a step size of 0.02°, and a scanning rate of 10° min^{-1}. The solid fluorescence spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

2.2. *Synthesis of* $\{[Zn(bbi)(pydca)]\cdot 2H_2O\}_n$ *(1)*

A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.1 mM, 29.8 mg), bbi (0.1 mM, 31.9 mg), H_2pydca (0.1 mM, 16.7 mg), NaOH (0.04 g, 1.0 mM), and H_2O (10 mL) was stirred for 1 h in air, and then sealed in a 25 mL Teflon-lined stainless vessel and heated to 140 °C for 72 h under autogenous pressure. The reaction system was cooled to room temperature at 5 °C h^{-1}. Colorless crystals of **1** (24.6 mg, 42% yield based on $Zn(NO_3)_2\cdot 6H_2O$) were obtained.

Calcd for $C_{27}H_{29}N_5O_6Zn$: C, 55.56; H, 5.01; N, 12.01%. Found: C, 55.17; H, 4.86; N, 12.13%. FTIR (KBr pellet, cm^{-1}): 3445 (w), 2928 (w), 1647(s), 1500 (s), 1462 (s), 1427 (w), 1370 (s), 1079 (w), 764 (m), 526 (w), 467 (w).

2.3. *Synthesis of [Zn(bmb)(1,3-bdc)]$_n$ (2)*

This complex was prepared in a manner analogous to that of **1** only bmb (0.1 mM, 36.7 mg) and 1,3-H_2bdc (0.1 mM, 16.6 mg) were used instead of bbi ligand and H_2pydca. Colorless crystals of **2** (30.4 mg, 51% yield based on $Zn(NO_3)_2 \cdot 6H_2O$) were obtained. Calcd for $C_{32}H_{26}N_4O_4Zn$: FTIR (KBr pellet, cm^{-1}): C, 64.49; H, 4.40; N, 9.40%. Found: C, 63.97; H, 4.21; N, 9.14%. FTIR (KBr pellet, cm^{-1}): 3049(w), 2925 (w), 1627 (s), 1566 (s), 1464 (s), 1379 (s), 1076 (w), 756 (s), 683 (w), 537 (w), 473 (w).

2.4. *Single crystal X-ray diffraction experiments*

Suitable single crystals of the complexes were obtained from the reactions described above. X-ray crystallographic data for both complexes were collected using epoxy-coated crystals mounted on glass fibers. All measurements were carried out on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and ω-2θ scan mode at 293(2) K. Absorption corrections were applied using SADABS [12]. The structures of both complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial structures and then refined anisotropically with SHELXTL using

Table 1. Crystallographic and structure refinement data for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{27}H_{29}N_5O_6Zn$	$C_{32}H_{26}N_4O_4Zn$
Formula weight	584.92	595.94
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	$P2_1/n$
a (Å)	18.1983(2)	10.8949(9)
b (Å)	10.8779(1)	21.0513(18)
c (Å)	14.653(3)	12.4066(10)
α (°)	90	90
β (°)	116.8240(1)	99.2320(10)
γ (°)	90	90
V (Å^3)	2588.5(6)	2808.6(4)
Z	4	4
D_{Calcd} (g cm^{-3})	1.501	1.409
F (0 0 0)	1216	1232
Reflections collected	7754	17,033
Independent reflections	2943	6404
R_{int}	0.0476	0.0386
Absorption coefficient/mm^{-1}	1.002	0.919
Goodness of fit on F^2	1.015	0.965
Final R indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.0450$, $wR_2 = 0.0926$	$R_1 = 0.0400$, $wR_2 = 0.1053$
R (all data)^{a,b}	$R_1 = 0.0728$, $wR_2 = 0.1038$	$R_1 = 0.0741$, $wR_2 = 0.1296$
$\Delta\rho_{\max}$ (e Å^{-3})	0.577	0.396
$\Delta\rho_{\min}$ (e Å^{-3})	−0.321	−0.391

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma [wF_o{}^2 - F_c{}^{2\ 2}]/\Sigma [wF_o{}^{2\ 2}]\}^{1/2}$.

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

Complex **1**			
Zn(1)–N(3)	1.999(3)	Zn(1)–N(1)	2.007(2)
Zn(1)–O(2)	2.1983(2)	N(3)–Zn(1)–N(1)	124.85(6)
N(3)–Zn(1)–O(2)	76.45(5)	N(1)–Zn(1)–N(1)^i	110.30(1)
N(1)–Zn(1)–O(2)^i	98.11(8)	N(1)–Zn(1)–O(2)	97.28(8)
O(2)–Zn(1)–O(2)^i	152.90(10)		
Complex **2**			
Zn(1)–O(3)	2.020(2)	Zn(1)–O(1)^i	2.065(2)
Zn(1)–N(3)	2.083(2)	Zn(1)–N(1)	2.094(2)
Zn(1)–O(2)^i	2.274(2)	Zn(1)–O(4)	2.470(2)
O(3)–Zn(1)–O(1)^i	144.31(9)	O(3)–Zn(1)–N(3)	98.25(8)
O(1)^i –Zn(1)–N(3)	100.98(8)	O(3)–Zn(1)–N(1)	107.61(8)
O(1)^i–Zn(1)–N(1)	100.17(9)	N(3)–Zn(1)–N(1)	95.47(9)
O(3)–Zn(1)–O(2)^i	96.64(8)	O(1)^i–Zn(1)–O(2)^i	60.25(7)
N(3)–Zn(1)–O(2)^i	160.99(8)	N(1)–Zn(1)–O(2)^i	91.20(9)
O(3)–Zn(1)–O(4)	57.70(7)	O(1)^i–Zn(1)–O(4)	93.51(8)
N(3)–Zn(1)–O(4)	87.08(8)	N(1)–Zn(1)–O(4)	165.31(8)
O(2)^i–Zn(1)–O(4)	90.96(8)		

Note: Symmetry code for **1**: i: $-x+1$, y,$-z+3/2$; for **2**: i: $x-1/2$, $-y+1/2$, $z+1/2$.

a full-matrix least-squares procedure based on F^2 [13]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens of water were located from difference Fourier maps, while other hydrogens were included in calculated positions and refined with isotropic thermal parameters riding on the parent atoms. Crystallographic data and other pertinent information for the coordination polymers are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure of {[Zn(bbi)(pydca)]·2H$_2$O}$_n$ (1)*

Single-crystal X-ray diffraction analysis revealed that **1** crystallized in the monoclinic space group *C2/c*. One half of the Zn(bbi)(pydca) monomer is in the asymmetric unit, and the other half is generated by a crystallographic twofold rotation axis parallel to the *b* axis. As shown in figure 1(a), the Zn is five-coordinate by two N atoms (N1, N1^i) (symmetry code: i $-x+1$, y, $-z+3/2$) from two distinct bbi ligands and N3, and O2 and O2^i from a pydca^{2-}. The constraint imposed by the tridentate, terminal pydca^{2-} in **1** on the Zn(II) center results in a distorted structure which may be described as intermediate between square pyramidal and trigonal bipyramidal. The distortion measured by the τ value index (0.47) [14] suggests that the coordination geometry around the Zn(II) atom is best described as a distorted square pyramid, where N1, N3, O2, and O2^i define the basal plane and N1^i occupies the apical position. The Zn(II) is displaced by 0.5940 Å from the basal plane toward the apical position. The Zn1–O2 bond distance is 2.198(2) Å, and the Zn–N bond lengths are 1.999(3) (Zn1–N3) and 2.007(2) (Zn1–N1) Å. Compared with the similar zinc complexes [Zn (cin)$_2$(bbi)]·H$_2$O (cin = cinnamate anion; Zn–N = 2.033(2) Å; Zn–O = 1.951(2) Å) and [Zn (adi)(bbi)]·H$_2$O (adi = adipate dianion; Zn–O = 1.955(5) and 1.979(5) Å; Zn–N = 2.048(5) and 2.050(5) Å) [11], the Zn–N bond distance in **1** is quite similar, while the Zn–O bond distance in **1** is over 0.2 Å longer. The longer Zn–O bond distance in **1** may be attributed to

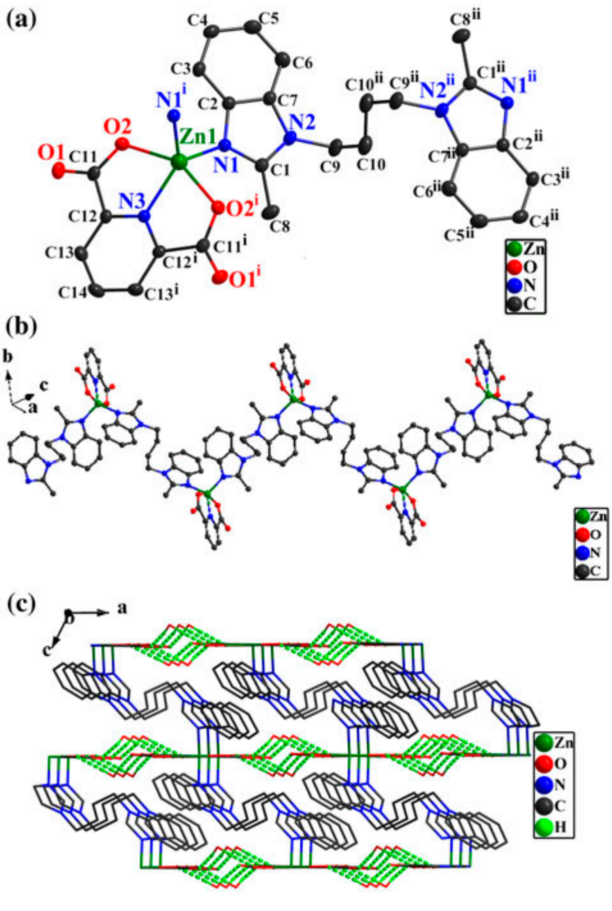

Figure 1. (a) Coordination environment around Zn(II) in **1** with 30% probability thermal ellipsoids; all hydrogens were omitted for clarity (symmetry codes: i: $-x+1$, y, $-z+3/2$, ii: $-x+1/2$, $-y+1/2$, $-z+1$), (b) The 1-D zigzag chain structure of **1**, (c) The 3-D supramolecular network of **1**, constructed by O–H···O hydrogen bonding interactions. The green dashed lines indicate O–H···O bonds (see http://dx.doi.org/10.1080/00958972.2014.928288 for color version).

the tridentate, chelating coordination of $pydca^{2-}$, in contrast to the monodentate coordination mode of the carboxylate groups in the related complexes.

In **1**, each bbi is bis-monodentate bridging neighboring [Zn(pydca)] units into a 1-D zigzag chain [figure 1(b)], with Zn···Zn separation across the bbi ligand of 11.912(9) Å. The bbi adopts an *anti*-conformation, and the mean planes of the two benzimidazole rings are parallel (dihedral angle = 0.00°).

Adjacent 1-D chains are further connected into a 3-D supramolecular architecture via classical O–H···O hydrogen bonding interactions between the lattice water molecules and carboxylate O of $pydca^{2-}$ [figure 1(c)]. The hydrogen bond lengths and angles are listed in table 3.

Ma's group reported a series of related complexes based on bbi and different carboxylate anions [15]. In all complexes, the bbi ligand is bridging and adopts *syn*- or *anti*-conformations. The connectivities of the Zn(II)-containing complexes are strongly

Table 3. Hydrogen bond lengths (Å) and angles (°) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O(1W)–H(1A)···O(1)^{iii}	0.84(4)	1.94(4)	2.771(4)	171(4)
O(1W)–H(1B)···O(2)	0.83(4)	2.16(4)	2.986(4)	174(3)

Note: Symmetry code: iii: $3/2 - x$, $-1/2 + y$, $3/2 - z$.

associated with the accompanying carboxylates. As listed in table 4, each L1, L2, L3, L4, and L5 anion contains one carboxylate, coordinating to only one metal ion as a terminal ligand, and the related complexes show 1-D chain structures. Each L6, L7, and L8 anion contains two carboxylate groups and the corresponding complexes display 2- and 3-D coordination frameworks. While **1** contains pydca^{2-} with two carboxylate groups, the dianion is a terminal, tridentate ligand, and the structure is a 1-D zigzag chain. Thus, we conclude that different organic carboxylate anions with diverse coordination characteristics play important roles in the final structures of their bis(2-methylbenzimidazole)-based zinc(II) coordination polymers.

3.2. *Crystal structure of [Zn(bmb)(1,3-bdc)]$_n$ (2)*

Complex **2** crystallized in the monoclinic space group *P2$_1$/n*. The asymmetric unit contains one Zn(II), one 1,3-bdc^{2-}, and one bmb. The structure of **2** [figure 2(a)] shows each Zn surrounded by four oxygens (O1, O2, O3, and O4) from two different 1,3-bdc^{2-} anions, and N1 and N3 from two distinct bmb ligands in a distorted octahedral geometry. N1 and O4 are located at axial positions, with a N1–Zn1–O4 bond angle of 165.314(8)°, and O1, O2, O3, and N3 are in the equatorial plane. The Zn–O bond lengths for the two carboxylates are 2.065(2) Å (Zn1–O1^{i}) and 2.274(2) Å (Zn1–O2^{i}), and 2.020(2) Å (Zn–O3) and 2.470(2)

Table 4. Comparison of literature complexes with **1** and **2**.

Literature complexes	Metal coordination number	Conformation	Crystal structure	Zn···Zn(Cd···Cd) separation (Å)
{[Zn(bbi)(pydca)]·2H$_2$O}$_n$^{a}	5	*Anti*	1-D zigzag chain	11.912
[Zn(L1)$_2$(bbi)]$_n$^{b}	6	*Anti*	1-D zigzag chain	14.551
[Zn(L2)$_2$(bbi)]$_n$^{b}	6	*Anti*	1-D zigzag chain	14.456
[Zn$_{0.5}$(L3)(bbi)$_{0.5}$]$_n$^{b}	4	*Syn*	1-D "Ω" shaped-chain	12.786
[Zn$_{0.5}$(L4)(bbi)$_{0.5}$(H$_2$O)]$_n$^{b}	6	*Anti*	1-D "S" shaped-chain	12.857
[Zn(L5)$_2$(bbi)]$_n$^{b}	6	*Anti*	1-D zigzag and "S" chain	14.452 and 12.497
[Zn(L6)(bbi)]$_n$^{b}	6	*Anti*	3-D diamond network	6.405 and 14.171
[Zn(L7)(bbi)$_{0.5}$(H$_2$O)]$_n$^{b}	5	*anti*	2-D network	4.340
[Zn(L8)(bbi)$_{0.5}$(H$_2$O)]$_n$^{b}	5	*Anti*	2-D square-grid with rhombic windows	3.784
[Cd$_2$I$_2$(bmb)]^{c}	4	*Syn*	Centrosymmetric dinuclear complex	13.373
[Zn(bmb)(1,3-bdc)]$_n$^{a}	6	*Syn*	A loop-like chain	8.899

Note: HL1 = benzoic acid, HL2 = salicylic acid, HL3 = *p*-nitrobenzoic acid, HL4 = nicotinic acid, HL5 = 3,5-dinitrobenzoic acid, H$_2$L6 = o-phthalic acid, H$_2$L7 = *m*-phthalic acid, H$_2$L8 = fumaric acid.
[a] This work.
[b] Ref. [15].
[c] Ref. [16].

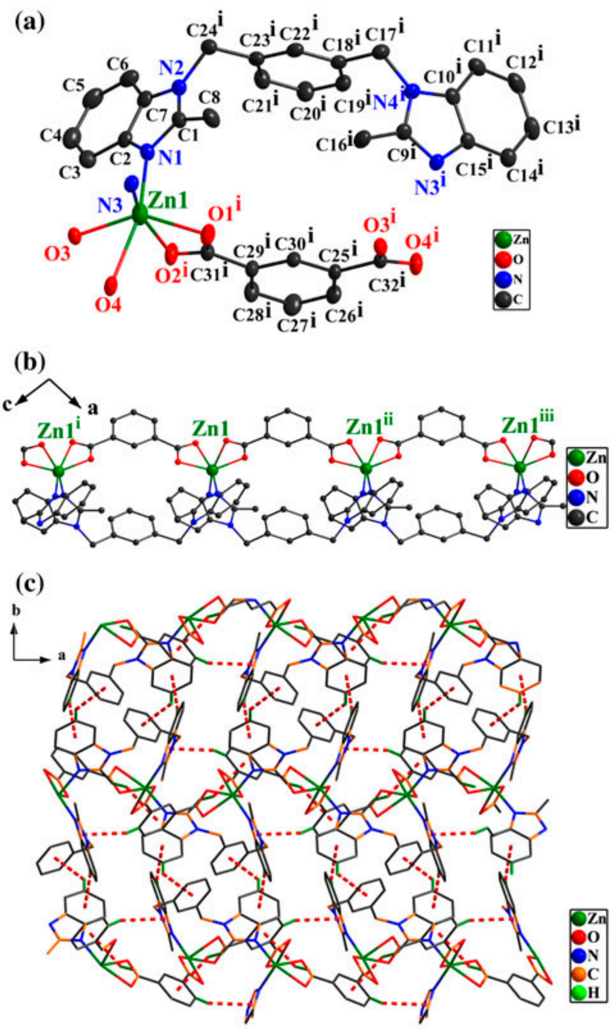

Figure 2. (a) Coordination environment around Zn(II) in **2** with 30% probability thermal ellipsoids; all hydrogens were omitted for clarity (symmetry codes: i: $x-1/2$, $-y+1/2$, $z+1/2$), (b) The 1-D loop-like chain structure of **2** (symmetry codes: i: $x-1/2$, $-y+1/2$, $z+1/2$, ii: $x+1/2$, $-y+1/2$, $z-1/2$, iii: $x+1$, y, $z-1$). (c) The 3-D supramolecular network of **2**, constructed by C–H···π hydrogen bonds. The red dashed lines indicate C–H···π bonds (see http://dx.doi.org/10.1080/00958972.2014.928288 for color version).

Å (Zn1–O4), and the Zn–N bond distances are 2.083(2) (Zn1–N3) and 2.094(2) (Zn1–N1) Å. The Zn–N and Zn–O distances are both shorter than the corresponding distances in the related [Zn(L6)(bbi)] (H_2L6=o-phthalic acid) [15], in which Zn(II) is six-coordinate by four carboxylate oxygens from two L6 anions (Zn–O 2.247(6)–2.525(5) Å) and two N from two bbi ligands (Zn–N 2.306(6)–2.322(7) Å).

In **2**, each 1,3-bdc^{2-} anion bridges two Zn(II) centers, coordinating to each Zn via a carboxylate in an asymmetric, chelating mode, and each bmb ligand links two {Zn(1,3-bdc)} moieties in a *syn*-conformation to form a dinuclear, 20-membered metallomacrocycle, with a Zn1···Zn1^{i} separation of 8.899(7) Å. The dihedral angle between the mean planes of the two benzimidazole rings within one bmb is at 74.46(6)°. These rings repeat and display a loop-like chain structure as illustrated in figure 2(b). Only one complex based on bmb, $[Cd_2I_2(bmb)]$, has been reported [16]. In this complex, the bmb ligand bridges two CdI_2 units, forming a centrosymmetric dinuclear complex with Cd···Cd distance of 13.373(4) Å, which is longer than Zn···Zn separation of 8.899(7) Å in **2**. The Cd(II) adopts a distorted tetrahedral coordination geometry.

The remarkable feature of **2** is that there are four C–H···π hydrogen bond interactions between bmb and 1,3-bdc^{2-} ligands in neighboring 1-D loop-like chains, to generate a 3-D supramolecular network [figure 2(c)]. The C–H···π bonding parameters (C–Cg distance and C–H–Cg angle) are, for C4–H4···Cg4 (Cg4: C10–C11–C12–C13–C14–C15), 3.515(4) Å and 147°; for C12–H12···Cg5 (Cg5: C18–C19–C20–C21–C22–C23), 3.583(3) Å and 140°; for C16–H16···Cg6 (Cg6: C25–C26–C27–C28–C29–C30), 3.713(4) Å and 147°; and for C26–H26···Cg1 (Cg1: N1–C1–N2–C7–C2), 3.585(3) Å and 148°. These weak interactions also play an important role in determining the crystal packing in metal–organic frameworks [17].

3.3. *IR and UV–vis spectra*

In the IR spectra of **1** and **2** [figure 3(a) and (b)], bands at 1500 cm^{-1} for **1** and 1506 cm^{-1} for **2** can be assigned to $\nu_{C=N}$ of benzimidazole rings of bbi and bmb. The band at 756 cm^{-1} for **2** can be regarded as arising from the C–H bending motions in the 1,3-disubstituted phenyl rings of bmb and 1,3-bdc^{2-}. There is a broad band at 3445 cm^{-1} for **1** that can be attributed to stretch two lattice waters, and the broad shape of this band suggests the existence of hydrogen bonds. Strong bands at 1647 and 1370 cm^{-1} for **1**, and 1627 and 1464 cm^{-1} for **2**, may be attributed to the asymmetric and symmetric vibrations of the carboxyl groups. The separations ($\Delta\nu$ = [ν_{as}(COO)–ν_s(COO)]) between these bands indicate the presence of monodentate (277 cm^{-1} for **1**) and chelating (163 cm^{-1} for **2**) coordination modes of carboxyl groups [18].

The solid UV–vis diffuse reflectance spectra of **1** and **2** are shown in figure 4. The strong absorption bands of the two complexes are at 260 and 265 nm, respectively. These absorptions correspond to π–π* transitions of the N-donor ligands [19].

3.4. *Thermal properties*

Thermogravimetric experiments were carried out to study the thermal stability of **1** and **2** (figure 5). **1** had two weight loss steps and **2** had only one. For **1**, the first weight loss is about 7.0%, starting at 53 °C and ending at 143 °C, consistent with the removal of two lattice waters (Calcd: 6.2%). The second step between 240 and 465 °C corresponds to loss of bbi and pydca^{2-} (Calcd: 79.9%; found: 79.2%). After 660 °C, no further weight loss was observed, indicating complete decomposition of the complex. The residual weight of 14.1% corresponds to formation of ZnO (Calcd: 13.9%). Complex **2** remained stable up to 290 °C, then the removal of the bmb and 1,3-bdc ligands occurred from 290 to 575 °C (Calcd: 86.3%; found: 86.3%). The remaining weight corresponds to the formation of ZnO (Calcd: 13.7%; found: 13.7%).

3.5. *Powder X-ray diffraction results*

To confirm that the crystal structures are truly representative of the bulk materials, powder X-ray diffraction (PXRD) experiments were also carried out for both complexes.

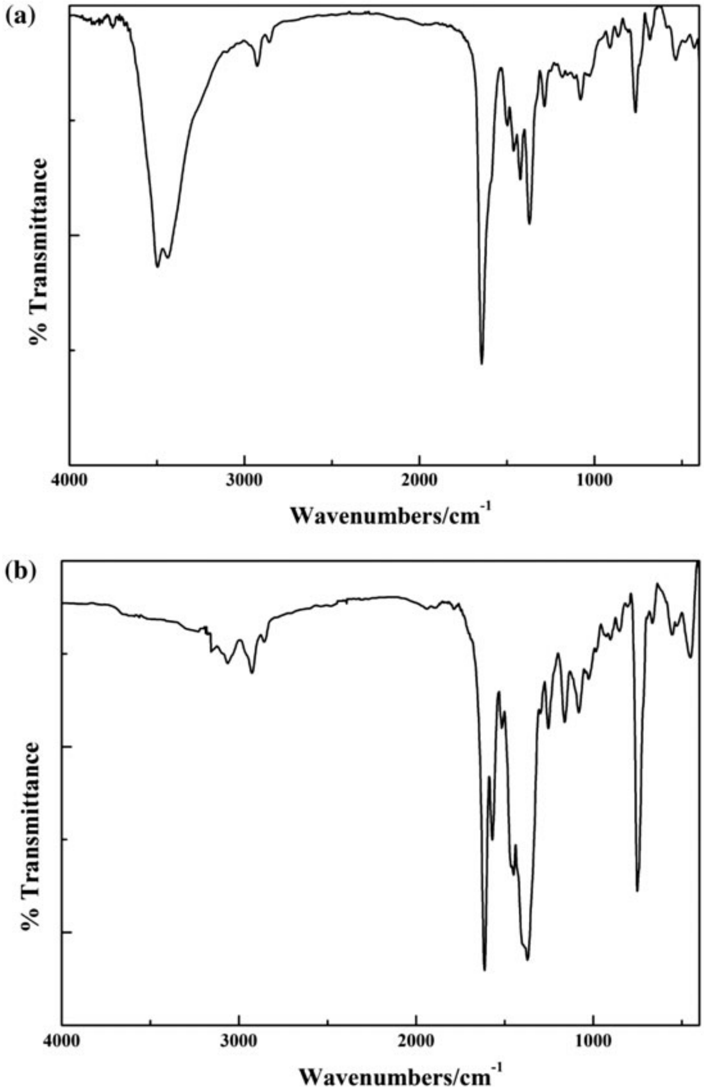

Figure 3. (a) The IR spectrum of **1.** (b) The IR spectrum of **2.**

The experimental and computer-simulated PXRD patterns of **1** and **2** are shown in Supplementary material (see online at http://dx.doi.org/10.1080/00958972.2014.928288). It is obvious that both experimental PXRD patterns are in good agreement with the simulated patterns based on the single-crystal X-ray data, indicating the phase purity of the bulk samples.

3.6. *Luminescent properties*

Luminescent compounds constructed by d^{10} metal centers and organic ligands are of interest because of their potential applications in chemical sensors and photochemistry [20]. The photoluminescent spectra of **1**, **2**, and the free ligands were examined in the solid state at

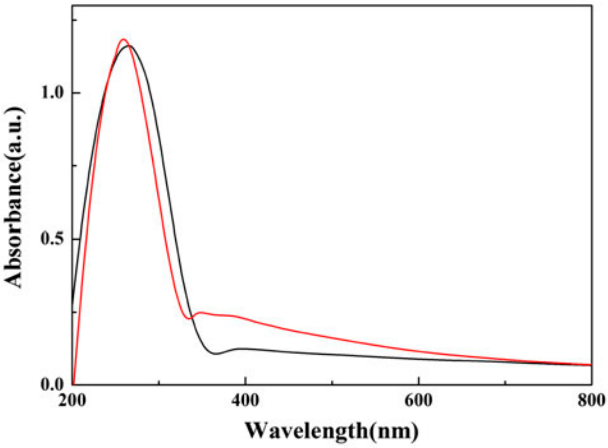

Figure 4. The solid UV–vis absorption spectra of **1** and **2**.

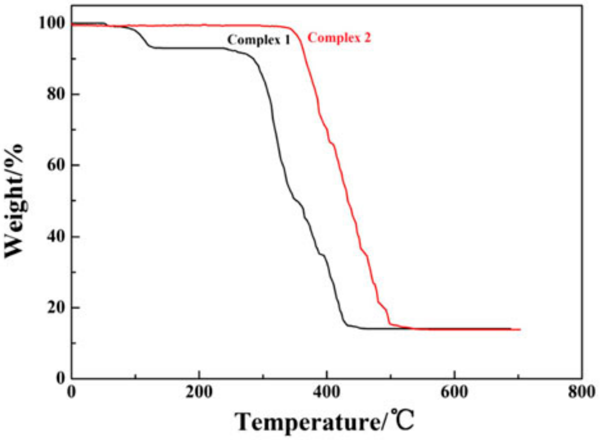

Figure 5. TGA curves of **1** and **2**.

room temperature (Supplementary material). The free bbi, bmb, and 1,3-H_2bdc [3c] displayed luminescence with emission maxima at 363 nm ($\lambda_{ex} = 300$ nm), 306 nm ($\lambda_{ex} = 290$ nm), and 360 nm ($\lambda_{ex} = 310$ nm), respectively, which are attributed to $\pi \rightarrow \pi^*$ transitions. Under the same experimental conditions, the emission intensity of H_2pydca [3c] is much weaker than that of bbi, so the former is considered to have no significant contribution to the fluorescent emission of **1**. Luminescence peaks at 364 nm for **1** and 360 nm for **2** were found in the emission spectra when the complexes were excited at 300 nm. Since the spectrum of **1** is similar to that of bbi, the emission can probably be assigned to the intraligand charge transitions of the ligated bbi. For **2**, there is an obvious red-shifted (54 nm) emission band compared with that for the free bmb ligand, and this band may be tentatively attributed to the $\pi \rightarrow \pi^*$ transition of the coordinated ligands since Zn^{2+} is difficult to oxidize or reduce due to its d^{10} configuration [21].

4. Conclusion

$\{[Zn(bbi)(pydca)]\cdot 2H_2O\}_n$ and $[Zn(bmb)(1,3\text{-bdc})]_n$ have been obtained by hydrothermal reactions under similar conditions. In **1**, the Zn(II) centers are five-coordinate and the structure exhibits a 1-D zigzag chain, while in **2**, the Zn(II) centers are six-coordinate and the structure displays a 1-D loop-like chain. This work illustrates that the organic carboxylate co-ligands have an important influence on the formation of structures and supramolecular architectures. In addition, **1** and **2** show distinct, strong solid-state fluorescence properties at room temperature and could be potential candidates for optical materials.

Supplementary material

PXRD data of **1–2** (Figures S1a and S1b); Fluorescence spectral data of **1–2** and L1, L2 in solid state (Figures S2a and S2b); Crystallographic data in CIF format (CCDC of 967938 and 967937).

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