# **One-Dimensional Channels Encapsulated in Supramolecular Networks** Constructed of Zinc(II), Manganese(II), or Nickel(II) Atoms with 3-(Carboxymethyl)-2,7-dimethyl-3H-benzo[d]imidazole-5-carboxylic Acid

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Abstract. Four complexes with supramolecular architectures, namely, MZCA·3H<sub>2</sub>O (1),  $[Zn(H_2O)_6]^{2+} [MZCA]_2 [H_2O]_6$  (2),  $[Mn(MZCA)_2(H_2O)_4]$ ·2H<sub>2</sub>O (3), and  $[Ni(MZCA)_2(H_2O)_4]$ ·2H<sub>2</sub>O (4) [MZCA = 3-(carboxymethyl)-2,7-dimethyl-3H-benzo[d]imidazole-5carboxylic acid], were synthesized and characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. Com-

### Introduction

The rational design of microporous solids based on supramolecular architectures have attracted considerable interest in recent years, mainly due to the potential use of their resulting cavities and channels in nanotechnology, including shape- and size-selective molecular recognition,<sup>[1]</sup> separation,<sup>[2]</sup> ion exchange,<sup>[3]</sup> storage, adsorption,<sup>[4]</sup> catalysis,<sup>[5]</sup> electronic and magnetic properties.<sup>[6]</sup> However, the control of crystal and network structures in a predictable manner still remains an elusive task because of the delicate balance and competition between directional noncovalent interactions such as hydrogen bonds and nondirectional noncovalent interactions such as van der Waals (dispersive) packing forces. The formation of hydrogenbonded and metal coordination networks with large cavities often results in self-interpenetration to fill the voids in the initial host structure.[7]

The understanding of different molecular interactions plays a major role in supramolecular chemistry and crystal engineering.<sup>[8]</sup> Hydrogen bonding and  $\pi$ - $\pi$  stacking interactions are by far the most well-studied interactions.<sup>[9]</sup> They are employed to control the conformational and topological features of the molecular assembly in the solid state.<sup>[10]</sup> Many scientists have been involved in the analysis of weak interactions focusing on benzimidazole derivatives due to their relevance to DNA,

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plexes 1 and 2 display a remarkable 3D network with 1D hydrophilic channels. Complexes 3 and 4 are isostructural and exhibit a 3D structure encapsulating 1D 24-membered ring microporous channels. The UV/Vis and fluorescent spectra were measured to characterize complexes 1-4. The thermal stability of complexes 2-4 were also examined.

proteins, and other biological systems.<sup>[11]</sup> During the last decade, the structure of benzimidazole carboxylate was widely used in the design of therapeutic agents, such as diuretic and natriuretic,<sup>[12]</sup> antiparasitic, serotonin antagonist, antineoplastic and antiflarial,<sup>[13]</sup> herbicidal, and antihypertensive compounds.<sup>[14]</sup> The analysis of various interactions in drugs has attracted considerable interest for their wide-ranging antiviral activity and the possibility of forming supramolecular aggregates with transition metal ions. However, reports on the coordination behavior of benzimidazole carboxylate compounds remain scarce.<sup>[15]</sup> To the best of our knowledge, supramolecular frameworks constructed by 3-(carboxymethyl)-2,7-dimethyl-3H-benzo[d]imidazole-5-carboxylic acid (MZCA) have not yet been reported.

From a structural point of view, MZCA has three interesting characteristics: (i) the nitrogen atom in benzimidazole ring and the oxygen atoms in carboxylate group are both potential sites of hydrogen bonding interactions, given that the presence of solvent molecules, such as water or methanol, might serve as possible hydrogen-bond donors;<sup>[16]</sup> (ii) due to the benzimidazole rings, we can predict that the  $\pi$ - $\pi$  interactions might devote to the formation of crystal structures;[17] (iii) the relatively large  $\pi$ -conjugated system in benzimidazole ring might contribute much to the desirable fluorescence property.

Herein, we report the syntheses and structures of four new compounds MZCA·3H<sub>2</sub>O (1),  $[Zn(H_2O)_6]^{2+}[MZCA]_2\cdot[H_2O]_6$ (2),  $[Mn(MZCA)_2(H_2O)_4]$ ·2H<sub>2</sub>O (3), and  $[Ni(MZCA)_2(H_2O)_4]$ ·  $2H_2O$  (4) [MZCA = 3-(carboxymethyl)-2,7-dimethyl-3Hbenzo[d] imidazole-5-carboxylic acid]. Complexes 1 and 2 both have remarkable hydrogen-bonded 3D networks encapsulating 1D hydrophilic channels. Complexes 3 and 4 are isostructural and both have unusual hydrogen-bonded 3D networks encapsulating 1D 24-membered ring microporous channels.

# **Results and Discussion**

### $MZCA \cdot 3H_2O(1)$

The overall structure of the crystal for **1** with atom labeling is shown in Figure 1. One carboxylic group [O(1), C(1), O(2)]of MZCA is coplanar with the molecular plane: the dihedral angle between the benzimidazole ring and the O(1)/C(1)/O(2)plane is  $3.3(4)^{\circ}$ . The other carboxylic group [O(3), C(12),O(4)] is almost perpendicular to the molecular plane: the dihedral angle between the benzimidazole ring and the O(3)/C(12)/O(4) plane is 72.8(4)°. In the structure of MZCA, one carboxylic acid group is deprotonated and the nitrogen atom is protonated. Therefore, MZCA is in the inner-salt form. A similar feature has been reported in the complex *N*-(2-oxopyrrolidin-1-ylmethyl)-L-valine-2H<sub>2</sub>O.<sup>[18]</sup>

Table 1. Hydrogen bonding parameters /Å,° for compounds 1-4.



Figure 1. Molecular structure of 1 showing 30% probability displacement ellipsoids and the atom-numbering scheme.

Hydrogen bond lengths and angles are listed in Table 1. As shown in Figure 2a, the hydrogen bonds  $[O(5)-H(5E)\cdots O(3) = 2.690(4) \text{ Å}, O(2)-H(2)\cdots O(5) = 2.548(4) \text{ Å}]$  bridge molecules forming a 1D helical chain along the *b* axis, which is intercon-

	D–H•••A	d(D-H)	<i>d</i> (H••• <i>A</i> )	$d(D \cdot \cdot \cdot A)$	$\angle (D-H\cdots A)$
<b>1</b> a)	O(2)–H(2)•••O(5)	0.82	1.75	2.548(4)	165
	O(5)–H(5D)•••O(6) <sup>i</sup>	0.88	2.04	2.666(4)	127
	O(5)-H(5E)•••O(3) <sup>ii</sup>	0.86	1.84	2.690(4)	171
	O(6)–H(6A)•••O(7) <sup>iii</sup>	0.88	1.93	2.760(5)	155
	O(6)-H(6B)O(4)	0.86	1.87	2.681(5)	157
	O(7)–H(7A)•••O(7) <sup>iv</sup>	0.85	2.27	2.886(10)	129
	$O(7)-H(7B)-O(1)^{v}$	0.89	2.21	2.874(4)	130
	N(2)-H(2A)•••O(4) <sup>vi</sup>	0.86	1.84	2.702(3)	177
<b>2</b> <sup>b)</sup>	OW(1)-HW(1)•••O(1)	0.76	1.93	2.655(3)	159
	OW(2)-HW(2A)···O(2)	0.86	1.87	2.708(4)	164
	OQ(1)-HQ(1A)•••O(3)	0.75	1.99	2.732(4)	174
	OQ(2)–HQ(2B)•••O(3)	0.82	2.02	2.795(4)	158
	OQ(3)–HQ(3C)•••O(2)	0.85	2.07	2.914(4)	177
	$OW(1)$ - $HW(1B)$ ···O $(1)^i$	0.80	1.90	2.685(3)	165
	OW(2)-HW(2B)OQ(3) <sup>ii</sup>	0.85	1.87	2.720(4)	171
	OW(3)-HW(3A)-OQ(2)iii	0.81	2.18	2.947(4)	157
	OW(3)–HW(3B)•••O (4) <sup>iv</sup>	0.84	1.87	2.701(4)	170
	$OQ(1) - HQ(1B) - OW(1)^{v}$	0.82	2.09	2.899(4)	167
	$OQ(2) -HQ(2A) -OQ(1)^{vi}$	0.88	1.80	2.674(4)	170
	OQ(3) –HQ(3B)•••O(4) <sup>vii</sup>	0.85	1.86	2.709(5)	177
	$N(2) -HN(2) -OQ(2)^{viii}$	0.86	1.91	2.768(4)	172
<b>3</b> c)	N(2)–H(2A)•••O(7) <sup>i</sup>	0.89	1.77	2.639(3)	164
	O(5)–H(5D)•••O(4) <sup>i</sup>	0.85	1.90	2.728(3)	163
	O(5)–H(5E)•••O(4) <sup>ii</sup>	0.85	1.86	2.680(3)	161
	O(6)–H(6A)•••O(3) <sup>iii</sup>	0.86	2.01	2.826(3)	159
	O(6)–H(6B)•••O(2)	0.86	1.87	2.723(3)	170
	O(7)–H(7A)•••O(3) <sup>iii</sup>	0.85	1.85	2.673(3)	164
	O(7)–H(7B)•••O(2) <sup>iv</sup>	0.85	1.96	2.793(3)	166
<b>4</b> <sup>d)</sup>	OW(1)-HW(1A)-O(4)i	0.96	1.78	2.737(3)	173
	OW(1)-HW(1B)O(4)ii	0.89	1.80	2.684(3)	170
	OW(2)-HW(2A)•••O(2)	0.86	1.98	2.716(3)	143
	OW(2)-HW(2B)O(3)iii	0.87	1.98	2.846(3)	170
	OW(3)-HW(3A)-O(3)iv	0.90	1.81	2.680(3)	161
	OW(3)-HW(3B)···O(2)v	0.99	1.81	2.787(3)	168
	N(1)–HN(1)•••OW(3)	0.92	1.76	2.630(3)	157
Symmetry	v codes: a) (i), -x+1/2, y-1/2, -z+1/2; (ii), -z+1/2;	x+1/2, y+1/2, -z+1/2; (i	ii), <i>x</i> +1/2, <i>y</i> -1/2, <i>z</i> ;	(iv), - <i>x</i> , <i>y</i> +2, - <i>z</i> -1; (v)	), <i>x</i> , <i>y</i> +1, <i>z</i> ; (vi) <i>x</i> , – <i>y</i> ,

Symmetry codes: a) (i), -x+1/2, y-1/2, -z+1/2; (ii), -x+1/2, y+1/2, -z+1/2; (iii), x+1/2, y-1/2, z; (iv), -x, y+2, -z-1; (v), x, y+1, z; (vi) x, -y, z+1/2. b) (i), -x+1, -y, -z; (ii), -x, -y-1, -z; (iii), -x, -y-1, -z; (iii), -x, -y-1, -z-1; (vii), -x, -y-1, -z-1; (vii), x, y-1, z. C) (i), -x+3/2, y+1/2, -z+3/2; (ii), x+1/2, -y+1/2, z+1/2; (iii), -x+3/2, -y+1/2, -z+3/2; (iii), x+1/2, -y+1/2, z+1/2; (iii), -x+1/2, -y-1/2. d) (i), -x+1/2, y-1/2, -z+1/2; (ii), x-1/2, -y+1/2, -z-1/2; (iii), -x+1/2, -y+1/2, -z+1/2; (iii), -x+1/2, -x+1/2; (iii), -x+1/2; (i

nected by the hydrogen bonds  $[N(2)-H(2A)\cdots O(4) =$ 2.702(3) Å] and  $\pi$ - $\pi$  stacking interactions, giving rise to a 2D helical architecture. Furthermore, the 2D structure is extended through the water molecules into a 3D network with 1D hydrophilic channels (Figure 2b), in which water chains containing acyclic water hexamers are observed. Each water chain consists of acyclic water hexamers, interlinked by hydrogen bonds  $[O(5)-H(5D)\cdotsO(6) = 2.666(4) \text{ Å}, O(6)-H(6A)\cdotsO(7) =$ 2.760(5) Å, and O(7)–H(7A)···O(7') = 2.886(10) Å] and short contacts  $[O(6) \cdot O(6') = 2.590(5) \text{ Å}]$ . In the water hexamer, the average O···O distance is 2.771 Å. This distance is slightly longer than the corresponding values in ice  $I_{\rm h}$  (2.759 Å)<sup>[19]</sup> and the calculated value of 2.718 Å for cyclic water hexamer and comparable to that in water trapped in organic compound of DMNY  $\cdot 2.5 H_2 O$  (2.776 Å, DMNY = 2,4-bimethyl-5aminobenzo[b]-1,8-naphthyridine).<sup>[20]</sup> However, it is shorter than that observed in the metal-organic framework of  $[Pr(pdc)-(Hpdc)(H_2O)_2]$ ·4H<sub>2</sub>O (2.783 Å, pdc = pyridine-2,6dicarboxylic acid)<sup>[21]</sup> and in liquid water (2.854 Å) and the ring water hexamer with a planar arrangement (2.905 Å).<sup>[22]</sup> The water molecules O(6) and O(7) in the cluster are in a tetrahedral arrangement with three water-water interactions and one water-carboxylate interaction. Meanwhile, the water molecule O(5) involves one water-water interaction and two water-carboxylate interactions. Therefore, the water molecule O(5) acts as single-hydrogen-bond donor, the water molecule O(6) acts as single-hydrogen-bond donor and single-hydrogenbond acceptor, and the water molecule O(7) functions as single-hydrogen-bond donor and double-hydrogen-bond acceptors in the water hexamer (Figure 2c).

# $[Zn(H_2O)_6]^{2+} \cdot [MZCA^-]_2 \cdot [H_2O]_6 (2)$

The asymmetric unit of complex **2** contains one MZCA molecule, half a  $Zn^{II}$ , three coordinated water molecules, and three lattice water molecules (Figure 3). The central zinc atom is hexacoordinated by six oxygen atoms from water molecules with bond length of 2.067(2)–2.129(2) Å, MZCA molecules connect zinc atoms by the hydrogen bonds between the carboxylic oxygen atoms from MZCA molecules and oxygen atoms from water molecules. Each MZCA molecule loses two protons from the carboxylic acid group and one of the two protons transfers to the nitrogen atom. Therefore, each MZCA molecule provides one negative charge. The dihedral angles between the benzimidazole ring and the carboxylic groups are 9.9(4)° for O(3)/C(11)/O(4) and 82.0(4)° for O(1)/C(10)/O(2), respectively, these values are larger than those observed in **1**.

As shown in Figure 4a, one  $[Zn(H_2O)_6]^{2+}$  cation is attached to the other  $[Zn(H_2O)_6]^{2+}$  cation by hydrogen bonds with the water molecules as bridges  $[OW(3)-HW(3A)\cdots OQ(2) =$ 2.947(4) Å,  $OQ(2)-HQ(2A)\cdots OQ(1) =$  2.674(4) Å, OQ(1)- $HQ(1B)\cdots OW(1) =$  2.899(4) Å], forming a 1D linear metalwater chain along the *a* axis with the intermolecular Zn···Zn distance is 7.566 Å. Interestingly, the metal–water chain consists of the acyclic  $(H_2O)_4$  cluster and the  $[Zn(H_2O)_4]^{2+}$ cation. This conformation contrasts with that in the  $\{[Cd(dpp)(sip)(H_2O)_3]\cdot 0.5Cd(H_2O)_6\cdot 5H_2O\}_n$  complex [dpp =



Figure 2. (a) Projection of the 2D structure of 1. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity and hydrogen bonds are shown as dashed lines. (b) Space-filling diagram shows the hydrogen-bonded 3D network of 1 viewed along the c axis, with water molecules and all hydrogen atoms are omitted for clarity. (c) Projection of the 1D water chain and its coordination environment of 1. Dashed lines indicate hydrogen bonds.



Figure 3. Asymmetric unit of complex 2 showing 30% probability displacement ellipsoids and the atom-numbering scheme.

1,3-bis(4-pyridyl)propane and NaH<sub>2</sub>sip = 5-sulfoisophthalic acid monosodium salt], in which the infinite chain consists of the water decamer and  $[Cd(H_2O)_4]^{2+}$ .<sup>[23]</sup>

(a)



**Figure 4.** (a) Projection of the 1D linear metal-water chain formed by  $[Zn (H_2O)_6]^{2+}$  cations in **2** viewed along the *a* axis. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity and hydrogen bonds are shown as dashed lines. (b) Projection of the 2D network formed by MZCA molecules in **2**. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity and hydrogen bonds are shown as dashed lines. (c) Space-filling diagram shows the hydrogen-bonded 3D network of **2** viewed along the *b* axis, with  $[Zn(H_2O)_6]^{2+}$  cations, water molecules and all hydrogen atoms are omitted for clarity.

As shown in Figure 4b, one MZCA molecule is attached to the other molecule via hydrogen bonds with the water molecules OQ(2) as bridges  $[OQ(2)-HQ(2B)\cdots O(3) =$ 2.795(4) Å, N(2)-HN(2)\cdots OQ(2) = 2.768(4) Å], forming a 1D chain along the *b* axis, which is further interlinked through water molecules OQ(1) by hydrogen bonds [OQ(1)-HQ(1A)···O(3) = 2.732(4) Å, OQ(2)-HQ(2A)···OQ(1) = 2.674(4) Å] and form a graph-set motif of R<sub>6</sub><sup>4</sup>(12). These chains are interconnected by water molecules OQ(3) via hydrogen bonds  $[OQ(3)-HQ(3A)\cdots O(2) = 2.914(4) \text{ Å}, OQ(3)-HQ(3B)\cdots O(4) = 2.709(5) \text{ Å}]$  and  $\pi-\pi$  stacking interactions, giving rise to a 2D structure, which are further interlinked to the  $[Zn(H_2O)_6]^{2+}$  cations by hydrogen bonds  $[OW(3)-HW(3B) \cdots O(4) = 2.701(4) \text{ Å}, OQ(1)-HQ(1B)\cdots OW(1) = 2.899(4) \text{ Å}, OW(2)-HW(2A)\cdots O(2) = 2.708(4) \text{ Å}]$  into a 3D network (Figure 4c). Interestingly, a hydrophilic channel is observed, being enclosed by the MZCA molecules. The  $[Zn(H_2O)_6]^{2+}$  cations and water molecules OQ(3) are accommodated in each channel.

# $[Mn(MZCA)_2(H_2O)_4] \cdot 2H_2O$ (3) and $[Ni(MZCA)_2(H_2O)_4] \cdot 2H_2O$ (4)

X-ray diffraction revealed that complexes 3 and 4 are isostructural. Both structures contain two MZCA molecules, one metal atom, four coordinated water molecules, and two lattice water molecules. Two MZCA molecules are almost perpendicular to each other; the dihedral angles between two benzimidazole rings are 69.43(8) and 68.87(8)° for 3 and 4, respectively. The coordination arrangement around the metal ion, comprising of two oxygen atoms belonging to two monodentate carboxylate groups from two MZCA located at the axial positions, and four oxygen atoms from water molecules located at the equatorial plane, can be described as a distorted octahedral. The average M-O bond lengths are 2.179 and 2.068 Å for **3** and 4, respectively. The overall structure of the crystal for 3 is shown in Figure 5. Similar to 2, each MZCA provides one negative charge. One carboxylic group [O(1), C(1), O(2)] of MZCA is coplanar with the benzimidazole ring: the dihedral angles between the benzimidazole ring and the O(1)/C(1)/O(2)plane are  $3.4(4)^{\circ}$  for **3** and  $1.8(3)^{\circ}$  for **4**, these values are similar to those observed in 1, and smaller than those observed in 2. The other carboxylic group [O(3), C(12), O(4)] is almost perpendicular to the benzimidazole ring: the dihedral angles between the benzimidazole ring and the O(3)/C(12)/O(4) plane are  $87.9(4)^{\circ}$  for **3** and  $88.1(4)^{\circ}$  for **4**, these values are larger than those observed in 1 and 2.



**Figure 5.** Molecular structure of **3** showing 30% probability displacement ellipsoids and the atom-numbering scheme. Symmetry code (A): -x, y, -z+1/2.

As shown in Figure 6a, the molecules are connected to each other by hydrogen bonds with distances of  $O(5)-H(5D)\cdots O(4) = 2.728(3)$  Å and  $O(6)-H(6A)\cdots O(3) = 2.826(3)$  Å, resulting in 1D ribbons along the *b* axis and forming a graph-set motif

of  $R_2^{2}(8)$ . On the other hand, there exist  $\pi$ - $\pi$  stacking interactions in complexes **3** and **4** with distances of 3.497 and 3.482 Å, respectively (Figure S1, Supporting Information). Hydrogen bonds [O(7)–H(7B)···O(2) = 2.793(3) Å, N(2)–H(2A)···O(7) = 2.639 (3) Å] and  $\pi$ - $\pi$  stacking interactions bridge molecules forming 1D chains along the *a* axis, and further interconnect the ribbons into 2D layer structures (Figure 6b), in which the grid-like 22-membered ring (22-MR) cavities is observed.

As shown in Figure 6c, hydrogen bonds  $[O(7)-H(7A)\cdots O(3) = 2.673(3) \text{ Å}, O(7)-H(7B)\cdots O(2) = 2.793(3) \text{ Å}, O(5)-H(5D)\cdots O(4) = 2.728(3) \text{ Å}]$  bridge molecules forming a 2D architecture, and form a graph-set motif of  $R_8^{-6}(24)$  which shares the C–O and *M*–O bond. The 2D structure is further extended into a 3D supramolecular network by hydrogen bonds  $[N(2)-H(2A)\cdots O(7) = 2.639(3) \text{ Å}, O(6)-H(6A)\cdots O(3) = 2.826(3) \text{ Å}, O(5)-H(5E)\cdots O(4) = 2.680(3) \text{ Å}]$ . The interesting feature, a 24-MR microporous channel running along the *c* axis, is observed in the 3D network (Figure 6d).

#### UV/Vis and Fluorescence Spectroscopy

The UV/Vis spectra of MZCA and complexes 2–4 in CH<sub>3</sub>OH were measured at room temperature (Figure S2, Supporting Information). MZCA shows a broad absorption at 270 nm. Because the absorption bands of complexes 2–4 are similar to that of the free MZCA ligand with a slight bathochromic shift, it should be assigned to the  $\pi \rightarrow \pi^*$  transition of the MZCA ligand.

The fluorescence properties of MZCA and complexes 2–4 in CH<sub>3</sub>OH were measured at room temperature (Figure S3, Supporting Information). It can be observed that the free MZCA has an emission at 335 nm when excited at 278 nm. In contrast, complexes 2–4 exhibit an intense broad emission peak at 341 nm when excited at 277, 280, and 281nm, respectively. Generally, the intraligand fluorescence emission wavelength is determined by the energy gap between the  $\pi$  and  $\pi^*$ molecular orbitals of the free ligand, which is simply related to the extent of conjugation in the system. As for the metal complexes, the bathochromic shift of the band in contrast to that of ancillary ligand should be attributed to the intraligand ( $\pi$ – $\pi^*$ ) fluorescent emission.

#### **PXRD** and Thermogravimetric Analysis

To confirm the phase purity of the complexes, the original samples are characterized by X-ray powder diffraction (PXRD) at room temperature. The peak positions simulated from the single-crystal X-ray data of complexes are in good agreement with those observed (Figure S4–S7, Supporting Information).

In order to examine the thermal stability of the complexes, thermal gravimetric (TG) analyses are carried out for 2–4 (Figure S8, Supporting Information). The TG curve of complex 2 exhibits two weight loss stages. The first weight loss of 27.2% (calcd. 27.8%) from 30 to 165 °C corresponds to the loss of six lattice water molecules and six coordinated water mole-



Figure 6. (a) Projection of the 1D ribbon of 3 viewed along the b axis. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity and hydrogen bonds are shown as dashed lines. (b) Projection of the 2D layer structure of 3 viewed along the b axis. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity and hydrogen bonds are shown as dashed lines. (c) Projection of the 2D network of 3 viewed along the c axis, with all hydrogen atoms are omitted for clarity. Dashed lines indicate hydrogen bonds. (d) View of 3D network of 3 with 1D channel down the c axis.

cules. The residue remains stable up to 298  $^{\circ}$ C and then upon further heating decomposes to unidentified products. The TG curve of complex **3** exhibits two main weight loss steps. The

# ARTICLE

first with a value of 16.2% (calcd. 16.4%) from 30 to 86 °C corresponds to the loss of two lattice water molecules and four coordinated water molecules. The dehydrated compound remains stable up to 313 °C and then upon further heating decomposes to unidentified products. The thermogravimetric studies of complex **4** indicate two main steps of weight losses. The first step starts at approximately 100 °C and completes at approximately 210 °C. The observed weight loss of 16% is corresponding to the loss of two lattice water molecules and four coordinated water molecules (calcd. 16.3%). The dehydrated compound remains stable up to 300 °C and then upon further heating decomposes to unidentified products.

# Conclusions

In this work, the ligand 3-(carboxymethyl)-2,7-dimethyl-3H-benzo[d]imidazole-5-carboxylic acid (MZCA) was employed to construct coordination polymers with Zn<sup>II</sup>, Mn<sup>II</sup>, and Ni<sup>II</sup> in solutions. The MZCA molecules in 1 form 1D helical chains through hydrogen bonds. These chains are further extended through the water molecules and  $\pi - \pi$  stacking interactions into 3D networks with 1D hydrophilic channels. The MZCA anions in 2 form interesting 2D network by hydrogen bonds and  $\pi$ - $\pi$  stacking interactions, which are further interlinked to the  $[Zn(H_2O)_6]^{2+}$  cations by hydrogen bonds into three dimensions with 1D hydrophilic channels. Complexes 3 and 4 are isostructural. The  $M(MZCA)_2(H_2O)_4$  (M = Mn, Ni) molecules in complexes 3 and 4 form 1D ribbons, which are further extended through hydrogen bonds and  $\pi-\pi$  stacking interactions into a 3D network containing a 24-membered ring microporous channel.

# **Experimental Section**

**Materials and General Methods:** The ligand 3-(carboxymethyl)-2,7dimethyl-3H-benzo[d]imidazole-5-carboxylic acid (MZCA) was prepared according to the pathway shown in Scheme 1. Other commercially available chemicals were of analytical grade and were used without further purification. Powder X-ray diffraction measurements were carried out with a Bruker D8 Focus X-ray diffractometer to check phase purity. Elemental analyses (C, H, N) were determined with an Elementar vario EL elemental analyzer. UV/Vis spectra were measured with a GBC Cintra 10e UV/Vis spectrophotometer in MeOH solution. Photoluminescence analyses were performed with a RF-5301PC fluorescence spectrometer in MeOH solution. Thermogravimetric analyses were conducted on a ZRY-2P Thermal Analyses using a heating rate of 20 K·min<sup>-1</sup> from room temperature to 800 °C under nitrogen. The IR spectra were recorded with a Nicolet-AVATAR 360 FT-IR spectrometer using KBr pellets in the 4000–400 cm<sup>-1</sup> regions. <sup>1</sup>H NMR



Scheme 1. Synthetic pathway for MZCA.

spectra were recorded with a Varian 500 Bruker spectrometer in  $[D_6]DMSO$  or  $CDCl_3$ .

Synthesis of MZCA: To a solution of 1a (70 g, 0.386 mol) in CH<sub>3</sub>OH (200 mL) was slowly added concentrated H<sub>2</sub>SO<sub>4</sub> (20 mL). The solution was heated to reflux for 24 h and cooled to room temperature, to yield a yellow precipitate. Intermediate 2a was obtained by filtration and crystallization from methanol (54.7 g, 72.6%). M.p: 78–79 °C. IR (KBr):  $\tilde{v} = 3005$  (br), 1740 (m), 1620 (m), 1590 (m), 1520 (m), 1350 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta = 8.03$ (br., 1 H, Ar–H), 7.9(m, 2 H, Ar–H), 3.97(s, 3 H, CH<sub>3</sub>O), 2.63(s, 3 H, PhCH<sub>3</sub>).

Pd/C (0.4 g, 5%) was added to a methanol solution (150 mL) of **2a** (7 g, 35.9 mmol) under hydrogen. The mixture was stirred at room temperature for 6 h and afterwards passed through Celite. The filtrate was concentrated to give a brown solid of **3a** (5.286g, 89.1%). M.p:188–121 °C. **IR** (KBr):  $\tilde{v} = 3452$  (br), 3370 (m), 1686 (m), 1597 (m) cm<sup>-1</sup>. <sup>1</sup>H **NMR** (CDCl<sub>3</sub>, 500 MHz):  $\delta = 7.76(s, 1 \text{ H}, \text{ Ar-H}), 7.74(d, {}^{3}J_{\text{H,H}} = 8.21\text{Hz}, 1 \text{ H}, \text{ Ar-H}), 6.64 (d, {}^{3}J_{\text{H,H}} = 8.20\text{Hz}, 1 \text{ H}, \text{ Ar-H}), 4.15(\text{br.}, 2 \text{ H}, \text{NH}_2), 3.85(s, 3 \text{ H}, \text{CH}_3O), 2.17(s, 3 \text{ H}, \text{PhCH}_3).$ 

Acetyl chloride (12 mL) was added dropwise to a solution of **3a** (10 g, 60.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and Et<sub>3</sub>N (22 mL). The solution was allowed to cool to 0–8 °C during the addition, and stirred at r t for 5 h. After filtration, the mixture was washed with water, NaHCO<sub>3</sub> aqueous solution, water, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was removed in vacuo to afford the crude product, which was recrystallized from EtOAc to give a white solid of **4a** (9.804 g, 78.2%). M.p:130–133 °C. **IR** (KBr):  $\bar{\nu} = 3289$  (br), 2941 (m), 1719 (m), 1656 (m), 1527 (m), 891 (m) cm<sup>-1</sup>. <sup>1</sup>H **NMR** ([D<sub>6</sub>]DMSO, 500 MHz):  $\delta = 9.31$ (s, 1 H, NH), 7.80(s, 1 H, Ar–H), 7.77 (d, 2 H, <sup>3</sup>J<sub>H,H</sub> = 9.60Hz, Ar–H), 3.83 (s, 3 H, –COOCH<sub>3</sub>), 2.28(s, 3 H, –COCH<sub>3</sub>), 2.12 (s, 3 H, Ar–CH<sub>3</sub>).

To a solution of fuming HNO<sub>3</sub> (10.2 mL) at -15 °C was slowly added **4a** (3 g, 14.5 mmol). After stirring for 1 h, the mixture was poured into ice water to yield a white precipitate, which was filtered and washed with ice water, NaHCO<sub>3</sub> aqueous solution, and water, and dried to afford the crude product. This was recrystallized from EtOAc to give a white solid of **5a** (2.29 g, 62.6%). m.p:174–176 °C. **IR** (KBr):  $\tilde{v} = 3259$  (br), 2953 (m), 1723 (s), 1667 (m), 1579 (m), 1534 (m), 1512 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 500 MHz):  $\delta = 10.13$  (s, 1 H, NH), 8.17(s, 1 H, Ar–H), 8.15(s, 1 H, Ar–H), 3.89(s, 3 H, –COOCH<sub>3</sub>), 2.38(s, 3 H, –NHCOCH<sub>3</sub>), 2.09(s, 3 H, Ar–CH<sub>3</sub>).

Pd/C (0.1 g, 5%) was added to the methanol solution (20 mL) of **5a** (1.35 g, 5.4 mmol) under hydrogen. The mixture was stirred at room temperature for 7 h. The solution was passed through Celite. The filtrate was concentrated to give a white solid of **6a** (0.85 g, 71.5%). **IR** (KBr):  $\tilde{v} = 3415$  (br), 3244 (m), 2948 (m), 1704 (m), 1649 (m), 1512 (m) cm<sup>-1</sup>.

To a solution of glacial AcOH (30 mL) was added **6a** (3 g, 13.5 mmol), the mixture was heated to reflux for 2 h and afterwards cooled to room temperature. The solvent was removed under reduced pressure to yield a yellow oil, which was dissolved in water (10 mL). Ammonia was added until a pH of about 9 to yield a white precipitate, which was filtered and dried to afford the product of **7a** (1.7 g, 61.6%). M.p:174–176 °C. Elemental analysis for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>: calcd. C 64.69; H 5.92; N 13.72%; found: C 64.71; H 5.89; N 14.73%. **IR** (KBr):  $\tilde{v} = 3422$  (br), 3282 (br), 1727 (m), 1682 (m), 1616 (m) cm<sup>-1</sup>. <sup>1</sup>H **NMR** ([D<sub>6</sub>]DMSO, 500 MHz):  $\delta = :7.96(s, 1 H, Ar-H), 8.10(s, 1 H, Ar-H), 3.96(s, 1 H, -COOCH<sub>3</sub>), 2.70(s, 3 H, -NHCOCH<sub>3</sub>), 2.63(s, 3 H, -Ar-CH<sub>3</sub>).$ 



To a solution of **7a** (0.78 g, 3.819 mmol) in THF (50 mL) at 0 °C was added NaH (0.6 g, 25 mmol). The mixture was stirred at room temperature for 1 h, afterwards BrCH<sub>2</sub>COOEt (0.8 mL) was added and stirring was continued for 2 h. The solvent was removed under reduced pressure to give a white solid, which was purified by column chromatography (silica; petroleum ether/ethyl acetate; 20:1) to afford **8a** (0.77 g, 69.4%). M.p: 104–107 °C. **IR** (KBr):  $\tilde{v} = 3392$  (br), 1734 (s), 1701 (s), 1520 (m), 1424 (m), 1350 (m), 1279 (m), 1217 (m), 1021 (m), 766 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 500 MHz):  $\delta = 7.84$ (s, 1 H, Ar–H), 7.81(s, 1 H, Ar–H), 4.88(s, 2 H, –CH<sub>2</sub>–COOC<sub>2</sub>H<sub>5</sub>), 4.27 (q, 2 H, <sup>3</sup>J<sub>H,H</sub> = 7.10Hz, –COOCH<sub>2</sub>CH<sub>3</sub>), 3.96 (s, 3 H, –COOCH<sub>3</sub>), 2.69 (s, 3 H, imidazole–CH<sub>3</sub>), 2.65(s, 3 H, Ar–CH<sub>3</sub>), 1.31(t, 3 H, <sup>3</sup>J<sub>H,H</sub> = 7.10Hz, –COOCH<sub>2</sub>CH<sub>3</sub>).

To a solution of **8a** (0.72 g, 2.48 mmol) in CH<sub>3</sub>OH (20 mL) was added 10% NaOH (20 mL). The mixture was heated to reflux for 3 h and next cooled to room temperature. Water (10 mL) was added followed by HCl (0.5 M) until the solution reached pH 7–8 to yield a white precipitate, which was filtered and dried to afford the product of MZCA (0.527 g, 85.6%). Elemental analysis for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: calcd. C 58.06; H 4.87; N 11.28%; found: C 58.03; H 4.89; N 11.31%. **IR** (KBr):  $\tilde{v} = 3407$  (br), 1738 (m), 1686 (s), 1557 (m), 1516 (m), 1427 (s), 1346 (m), 1276 (m), 1209 (s) and 769 (m) cm<sup>-1</sup>. <sup>1</sup>H **NMR** ([D<sub>6</sub>]DMSO, 500 MHz):  $\delta = 13.32$ (br., 1 H, Ar–COOH), 11.67 (br., 1 H, –CH<sub>2</sub>–COOH), 7.93 (s, 2 H, Ar–H), 7.62 (s, 1 H, Ar–H), 5.17 (s, 2 H, –CH<sub>2</sub>–COOH), 2.52 (s, 3 H, Ar–CH<sub>3</sub>).

**Synthesis of MZCA·3H<sub>2</sub>O** (1): A water solution (3 mL) of  $Zn(NO_3)_2$ · 6H<sub>2</sub>O (0.0297 g, 0.1 mmol) was added dropwise to CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH (1:4) solution (5 mL) of MZCA (0.0248 g, 0.1 mmol). The resulting mixture was filtered and colorless block-shaped crystals of **1** were obtained from the filtrate at room temperature after a few days in 73 % Yield (based on MZCA). Elemental analysis for C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>O<sub>7</sub>: calcd. C 47.68; H 6.00; N 9.27%; found: C 47.66; H 5.97; N 9.31%. **IR** (KBr):  $\tilde{v} = 3420$  (w), 2925 (w), 2533 (br), 1707 (s), 1649 (s), 1625 (s), 1363 (m), 1268 (s), 1220 (m), 1174 (s), 771 (m) cm<sup>-1</sup>.

Synthesis of  $[Zn(H_2O)_6]^{2+} \cdot [MZCA]_2 \cdot [H_2O]_6$  (2): A solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0297 g, 0.1 mmol) in CH<sub>3</sub>OH–H<sub>2</sub>O (1:1, 2 mL) was added dropwise to a CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH (1:1, 8 mL) solution of MZCA (0.0248 g, 0.1 mmol). The pH of the resulting mixture was adjusted to 4.5 with a CH<sub>3</sub>OH solution (2 mL) of pyridine (8 µL). The reaction mixture was filtered and the colorless block-shaped crystals of **2** were obtained from the filtrate at room temperature after a few days in 35% Yield (based on MZCA). Elemental analysis for C<sub>24</sub>H<sub>46</sub>N<sub>4</sub>O<sub>20</sub>Zn: calcd. C 37.15; H 5.97; N 7.22%; found: C 37.11; H 5.94; N 7.26%. **IR** (KBr):  $\tilde{v} = 3448$  (br), 1637 (m), 1569 (w), 1384 (vs), 1323 (w), 792 (v) cm<sup>-1</sup>.

**Synthesis of [Mn(MZCA)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O (3):** To a CH<sub>3</sub>CH<sub>2</sub>OH solution (8 mL) of MZCA (0.0248 g, 0.10 mmol), CH<sub>3</sub>OH–H<sub>2</sub>O (1:1) solutions (10 mL) of MnSO<sub>4</sub> (0.0151 g, 0.10 mmol) and Mg(ClO<sub>4</sub>)<sub>2</sub> (0.0446 g, 0.20 mmol) were added dropwise with constant stirring. The pH of the mixture was adjusted to 5 with a 0.1 M NaOH solution, the resulting mixture was filtered and the colorless block-shaped crystals of **3** were obtained from the filtrate at room temperature after a few days in 65% Yield (based on MZCA). Elemental analysis for C<sub>24</sub>H<sub>34</sub>MnN<sub>4</sub>O<sub>14</sub>: calcd. C 43.84; H 5.21; N 8.52%; found: C 43.81; H 5.19; N 8.56%. **IR** (KBr):  $\tilde{v} = 3335$  (br), 1622 (s), 1567 (m), 1396 (s), 1313 (m), 794 (m) cm<sup>-1</sup>.

**Synthesis of [Ni(MZCA)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O (4):** A solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.0238 g, 0.1 mmol) in CH<sub>3</sub>CH<sub>2</sub>OH–H<sub>2</sub>O (2:1, 6 mL)

was added dropwise with constant stirring to a CH<sub>3</sub>CH<sub>2</sub>OH–H<sub>2</sub>O (2:1, 6 mL) solution of MZCA (0.0248 g, 0.1 mmol). The pH of the mixture was adjusted to 5–6 with a CH<sub>3</sub>OH solution (2 mL) of pyridine (16 µL), The resulting mixture was heated at reflux for 1 h, cooled to room temperature, and stirred at room temperature for 4 h. Afterwards the reaction mixture was filtered and the green block-shaped crystals of **4** were obtained from the filtrate at room temperature after a few days in 62% Yield (based on MZCA). Elemental analysis for  $C_{24}H_{34}N_4NiO_{14}$ : calcd. C 43.59; H 5.18; N 8.47%; found: C 43.56; H 5.16; N 8.51%. **IR** (KBr):  $\tilde{v} = 3424$  (br), 1630 (m), 1568 (m), 1396 (m), 1313 (w), 793 (m) cm<sup>-1</sup>.

X-ray Crystallography: Crystal diffraction intensities for complexes 1 and 3 were collected with a Bruker SMART 1000 CCD diffractometer with graphite monochromatized Mo- $K_{\alpha}$  radiation ( $\lambda$  = 0.71073 Å) at 294(2) K. Semi-empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXS-97 and SHELXL-97 programs.<sup>[24]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were placed in calculated positions and allowed to ride at distances of 0.93 Å (C–H aromatic), 0.96 Å (CH<sub>3</sub>) and 0.97 Å (CH<sub>2</sub>); whereas those of the aqua molecules were first located in difference Fourier maps, and then fixed at the calculated positions and included in the final refinement. Crystal diffraction intensities for complexes 2 and 4 were collected with a Rapid-AUTO diffractometer with graphite monochromatized Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K. Abscor-Empirical Absorption Corrections were based on Fourier Series Approximation. The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXS-97 and SHELXL-97 programs. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were placed in calculated positions and allowed to ride at distances of 0.93 Å (C-H aromatic), 0.96 Å (CH<sub>3</sub>) and 0.97 Å (CH<sub>2</sub>); whereas those of the aqua molecules were first located in difference Fourier maps, and then fixed at the calculated positions and included in the final refinement. The crystallography details for complexes 1-4 are presented in Table 2. Selected bond lengths and angles are listed in Tables S1-S4 (Supporting Information).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-288684, -284063, -602559and -290069. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http:// www.ccdc.cam.ac.uk)

**Supporting Information** (see footnote on the first page of this article): Diagram of  $\pi$ -··· $\pi$  stacking interactions in complexes **3** and **4** (Figure S1), UV/Vis spectra for **1–4** (Figure S2), fluorescence spectra for **1–4** (Figure S3), PXRD patterns for **1–4** (Figures S4–7), thermogravimetric analyses (TGA) for **2–4** (Figure S8), and selected bond lengths and angles for compounds **1–4** (Tables S1–S4).

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# ARTICLE

	1	2	3	4
Empirical formula	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O <sub>7</sub>	C <sub>24</sub> H <sub>46</sub> N <sub>4</sub> O <sub>20</sub> Zn	C <sub>24</sub> H <sub>34</sub> MnN <sub>4</sub> O <sub>14</sub>	C <sub>24</sub> H <sub>34</sub> N <sub>4</sub> NiO <sub>14</sub>
Formula weight	302.28	776.02	657.49	661.26
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	C2/c	$P\bar{1}$	C2/c	C2/c
Crystal size /mm	$0.22 \times 0.18 \times 0.10$	$0.50 \times 0.15 \times 0.10$	$0.26 \times 0.22 \times 0.16$	$0.50 \times 0.20 \times 0.08$
a /Å	24.678(4)	7.5659(15)	22.391(4)	22.223(4)
b /Å	7.3698(19)	9.757(2)	11.369(2)	11.413(2)
c /Å	16.045(4)	11.634(2)	11.821(2)	11.731(2)
a /°	90	95.82(3)	90	90
β /°	100.367(4)	98.05(3)	102.535(3)	103.43(3)
γ /°	90	94.63(3)	90	90
V/Å <sup>3</sup>	2870.5(12)	842.1(3)	2937.5(9)	2894.0(10)
Z	8	1	4	4
$Dc /g \cdot cm^{-3}$	1.399	1.530	1.487	1.518
$\mu / \text{mm}^{-1}$	0.116	0.819	0.524	0.746
$\theta$ range /°	2.58-26.43	1.78-27.48	1.86-26.37	2.55-27.48
Reflns collected /unique	7821/2937	6392/3653	8093/2995	11390/3308
GOF on $F^2$	1.022	1.005	0.930	0.966
R <sub>int</sub>	0.0369	0.0564	0.0318	0.0594
$R_1^{(a)}, w R_2^{(b)} [I > 2\sigma(I)]$	0.0618, 0.1718	0.0488, 0.1093	0.0469, 0.1318	0.0441, 0.0945
$R_1$ , $wR_2$ (all data)	0.1079, 0.2079	0.0813, 0.1170	0.0723, 0.1552	0.0786, 0.1002
Largest diff. peak, hole /e·Å <sup>-3</sup>	0.436, -0.391	0.336, -0.378	0.376, -0.573	0.354, -0.400

Table 2. Crystal data and details of structure determination of compounds 1-4.

a)  $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ . b)  $wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2] \}^{1/2}$ .

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