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Two 3-D metal-organic frameworks constructed by 2-methyl or 2-ethyl imidazole dicarboxylates

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Two polymeric frameworks, $[\text{Zn}_5(\text{MIDC})_2(\text{HMIDC})_2(\text{phen})_5]_n$ (**1**) (H_3MIDC = 2-methyl-1-*H*-imidazole-4,5-dicarboxylic acid, phen = 1,10-phenanthroline) and $\{[\text{Ca}_2(\text{HEIDC})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**2**) (H_3EIDC = 2-ethyl-1-*H*-imidazole-4,5-dicarboxylic acid), have been solvothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Compound **1** exhibits a 3-D structure constructed from 2-D layer motifs joined by μ_2 -HMIDC²⁻ or μ_3 -MIDC³⁻ ligands. Compound **2** also presents a 3-D framework, generated from 1-D chains linked by HEIDC²⁻ ligands by two different μ_5 -modes. The thermal and solid-state photoluminescence properties of both the complexes have been determined.

Keywords: Coordination polymer; Imidazole dicarboxylate; Crystal structure; Properties

1. Introduction

Metal-organic frameworks (MOFs) have attracted much attention due to their interesting structural features and potential applications such as magnetic, nonlinear optical, and fluorescent materials [1–15]. Multifunctional connector imidazole-4,5-dicarboxylic acid (H_3IDC) has been extensively investigated in coordination chemistry, showing various coordination modes under hydro/solvothermal conditions [16–38]. Several analogue ligands of H_3IDC , 2-methyl-1-*H*-imidazole-4,5-dicarboxylic acid (H_3MIDC) or 2-ethyl-1-*H*-imidazole-4,5-dicarboxylic acid (H_3EIDC) are also used to build up desired complexes. To predict the methyl and ethyl substituent effect in H_3MIDC and H_3EIDC , the optimized geometries and the natural bond orbital (NBO) charge distributions of the free ligands have been calculated [39, 40], revealing that H_3MIDC and H_3EIDC have outstanding coordination properties. However, compared with the well-studied H_3IDC , polymeric frameworks bearing H_3MIDC or H_3EIDC are limited [39–48], encouraging us to construct more MOFs.

Herein, we report the solvothermal synthesis and structural determinations of two coordination polymers, $[\text{Zn}_5(\text{MIDC})_2(\text{HMIDC})_2(\text{phen})_5]_n$ (**1**) and $\{[\text{Ca}_2(\text{HEIDC})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**2**). Single crystal X-ray diffraction reveals that two to three protons

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can be removed from H₃MIDC to coordinate to metal ions in μ_2 - or μ_3 -modes (scheme 1a and 1b), and the doubly deprotonated HEIDC²⁻ assembles with metal ions in two different μ_5 modes (scheme 1c and 1d). The thermal and solid-state photoluminescence properties of **1** and **2** have been determined.

2. Experimental

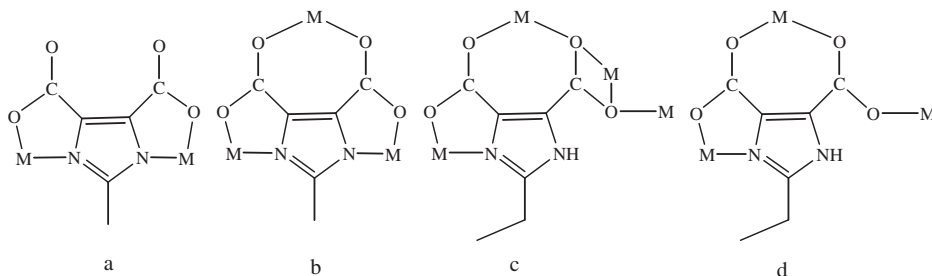
2.1. Materials and physical techniques

All chemicals were of reagent grade, obtained from commercial sources, and used without purification. The organic ligands H₃MIDC and H₃EIDC were prepared according to the literature procedure [49].

IR spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets from 400 to 4000 cm⁻¹. Elemental analyses (C, H, and N) were carried out on a FLASH EA1112 Elemental Analyzer. TG-DSC measurements were performed by heating the crystalline sample from 20°C to 850°C at 10°C min⁻¹ in air on a Netzsch STA 409PC differential thermal analyzer. Fluorescence spectra were obtained at room temperature on an F-4500 fluorescence spectrophotometer (240 nm min⁻¹).

2.2. Synthesis of [Zn₅(MIDC)₂(HMIDC)₂(phen)₅]_n (**1**)

A mixture of H₃MIDC (34.0 mg, 0.2 mmol), Zn(OAc)₂ (43.9 mg; 0.2 mmol), phen (39.6 mg, 0.2 mmol), Et₃N (0.056 mL, 0.4 mmol), and EtOH:H₂O (4:3, 7 mL) was sealed in a 25 mL Teflon-lined bomb and heated at 160°C for 96 h. The reaction mixture was then allowed to cool to room temperature at a rate of 10°C h⁻¹. Colorless block-shape crystals of **1** were collected, washed with deionized water, and dried in air. Crystals of **1** are stable in air. Yield: 68% (based on Zn). Anal. Calcd for C₈₄H₅₄N₁₈O₁₆Zn₅: C, 53.10; H, 2.84; N, 13.28. Found: C, 52.82; H, 2.93; N, 13.04. IR (cm⁻¹, KBr): 3416 (m), 3059 (w), 1572 (s), 1544 (s), 1426 (s), 1342 (m), 1287 (w), 1253 (m), 1121 (m), 962 (w), 856 (m), 726 (s), 638 (w), 422 (w).



Scheme 1. Coordination modes of MIDC³⁻, HMIDC²⁻, or HEIDC²⁻ anions.

2.3. Synthesis of $\{[Ca_2(HEIDC)_2(H_2O)] \cdot H_2O\}_n$ (**2**)

A mixture of H_3EIDC (36.8 mg, 0.2 mmol), $Ca(NO_3)_2 \cdot 4H_2O$ (23.6 mg, 0.1 mmol), Et_3N (0.056 mL, 0.4 mmol), and $EtOH : H_2O$ (4 : 3, 7 mL) was sealed in a 25 mL Teflon-lined bomb and heated to $160^\circ C$ for 96 h. After the mixture was cooled to room temperature at a rate of $10^\circ C h^{-1}$, pink plates of **2** were obtained, washed with deionized water, and dried in air. Crystals of **2** are stable in air. Yield: 65% (based on Ca). Anal. Calcd for $C_{14}N_4O_{10}H_{16}Ca_2$: C, 34.99; H, 3.36; N, 11.66%. Found: C, 35.15; H, 3.23; N, 11.98%. IR (cm^{-1} , KBr): 3422 (m), 2988 (w), 1600 (s), 1523 (s), 1384 (s), 1238 (m), 1113 (m), 867 (m), 792 (s), 611 (w), 447 (w).

2.4. X-ray crystallography

Crystal data and experimental details for **1** and **2** are given in table 1. All measurements were made on a Bruker Smart 1000 CCD imaging plate area detector with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Colorless block crystals of **1** ($0.32 \times 0.21 \times 0.20 \text{ mm}^3$) and plates of **2** ($0.31 \times 0.30 \times 0.28 \text{ mm}^3$) were selected and mounted on a glass fiber. All data were collected at 296(2) K using the $\omega - 2\theta$ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied. The structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were included but not refined. The final cycle of full-matrix least squares refinement was based on 7814 observed reflections and 558 variable parameters for **1**, and 3399 observed reflections and 282 variable parameters for **2**.

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

Compound	1	2
Empirical formula	$C_{84}N_{18}O_{16}H_{54}Zn_5$	$C_{14}N_4O_{10}H_{16}Ca_2$
Formula weight	1898.30	480.47
Crystal system	Orthorhombic	Monoclinic
Crystal size (mm^3)	$0.32 \times 0.21 \times 0.20$	$0.31 \times 0.30 \times 0.28$
Space group	<i>Fdd2</i>	<i>P2(1)/n</i>
Unit cell dimensions (\AA , $^\circ$)		
<i>a</i>	11.8787(4)	8.4769(17)
<i>b</i>	68.916(3)	10.892(3)
<i>c</i>	20.5275(7)	19.770(5)
α	90	90
β	90	92.232(11)
γ	90	90
Volume (\AA^3), <i>Z</i>	16804.4(10), 8	1824.0(7), 4
Calculated density ($Mg m^{-3}$)	1.501	1.750
Absorption coefficient (mm^{-1})	1.484	0.692
Reflections collected	59,748	13,696
Independent reflection	7814 [<i>R</i> (int) = 0.0412]	3399 [<i>R</i> (int) = 0.0199]
Data/restraints/parameters	7814/89/558	3399/48/282
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0561, <i>wR</i> ₂ = 0.1531	<i>R</i> ₁ = 0.0436, <i>wR</i> ₂ = 0.1177
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0593, <i>wR</i> ₂ = 0.1554	<i>R</i> ₁ = 0.0470, <i>wR</i> ₂ = 0.1211
Goodness-of-fit on <i>F</i> ²	1.020	1.036
Largest difference peak and hole ($e \text{ \AA}^{-3}$)	−0.472 and 0.691	−1.039 and 1.003

All calculations were performed using the SHELX-97 crystallographic software package [50]. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. Synthesis

According to the previous studies [41, 47], $[\text{Zn}(\text{H}_2\text{MIDC})_2(\text{H}_2\text{O})_2]$ (0-D), $\{[\text{Zn}_3(\text{MIDC})_2(\text{H}_2\text{O})_2(\text{DMF})_2] \cdot 0.5\text{H}_2\text{O}\}$ (2-D) and $[\text{Ca}(\text{H}_2\text{O})_2(\text{H}_2\text{EIDC})_2]$ (2-D) have been obtained. By analyzing the adopted methods, we tried to synthesize crystals by solvothermal method using a mixed solvent of ethanol and water. To our surprise, the 3-D polymers **1** and **2** were obtained, suggesting that the mixed solvent is more suitable for the growth of crystals with high-dimensional structures. Factors governing the reaction and formation of the hydrothermal or solvothermal products are complicated. For example, the same imidazole dicarboxylate ligand and metal were used by Song *et al.* [41] and by us in this work in different solvents and with or without phen. Three different Zn(II) products were obtained. The Ca(II)-H₃EIDC reaction system reported by Tian *et al.* [47] and by us here are also complicated. So we could not determine the effect of metal center and auxiliary ligands on final structure, but we can find that H₃MIDC or H₃EIDC show strong coordination abilities and various coordination modes from the structural data of **1** and **2**.

The final pH of the solutions is a crucial factor for the formation of crystalline products. We used Et₃N to neutralize the protons contained in carboxyl groups so that they can coordinate with metal ions easily; pH can be controlled by Et₃N at 7–8, which is suitable for the growth of crystals.

3.2. Crystal structure of $[\text{Zn}_5(\text{MIDC})_2(\text{HMIDC})_2(\text{phen})_5]_n$ (**1**)

Single-crystal X-ray analysis reveals that **1** possesses a 3-D network and crystallizes in the orthorhombic space group *Fdd2*. As shown in figure 1(a), there are three crystallographically unique Zn(II) centers in the asymmetric unit. All Zn(II) ions are six coordinate with slightly distorted octahedral geometries: for Zn(1), three carboxylate oxygens (O1, O2A, O3A), and one nitrogen (N1) are from two μ_3 -MIDC³⁻, other two nitrogens (N3, N4) come from one phen. Oxygens (O1, O2) from μ_3 -MIDC³⁻ link neighboring Zn1(II) ions to form a 1-D zigzag chain composed of fused five-membered rings along the *b*-axis as shown in figure 1(b) and auxiliary phen is arranged regularly in the side chain. The nearest Zn1...Zn1 distance is 5.9402(9) Å in the chain; for Zn(3), two carboxylate oxygens (O4, O5) and two nitrogens (N2, N5) are from μ_3 -MIDC³⁻ and μ_2 -HMIDC²⁻ units, respectively, and other two nitrogens (N8, N9) come from one phen. Zn(9) has the same coordination environment as Zn(3). The Zn–O bond lengths vary from 2.038(6) to 2.226(6) Å and the Zn–N bond lengths from 2.231(2) to 2.269(2) Å. The bond angles around each Zn(II) vary from 74.4(2)° to 177.56(18)°.

Doubly deprotonated HMIDC²⁻ and triply deprotonated MIDC³⁻ coexist in **1** with two types of coordination modes (schemes 1a and 1b), μ_2 -*k*N, O: *k*N', O', and μ_3 -*k*N, O: *k*O: *k*N', O'. Each MIDC³⁻ bridges three Zn(II) ions in *N,O*-, *O,O'*- and *N',O'*-chelating modes. Every HMIDC²⁻ bridges two Zn(II) ions in *N,O*- and *N',O'*-chelating

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

1			
Zn(1)–N(1)	2.043(6)	Zn(1)–O(3)#1	2.073(5)
Zn(1)–O(1)	2.161(4)	Zn(1)–N(3)	2.196(6)
Zn(3)–N(2)	2.038(6)	Zn(3)–N(5)	2.072(5)
Zn(3)–O(4)	2.167(5)	Zn(3)–N(8)	2.170(6)
Zn(9)–N(6)	2.082(6)	Zn(9)–N(6)#2	2.082(6)
Zn(9)–N(7)#2	2.189(7)	Zn(9)–O(8)#2	2.203(6)
Zn(1)–O(2)#1	2.075(4)	Zn(3)–O(5)	2.372(5)
Zn(1)–N(4)	2.226(6)	Zn(9)–N(7)	2.189(7)
Zn(3)–N(9)	2.162(5)	Zn(9)–O(8)	2.203(6)
N(1)–Zn(1)–O(3)#1	96.3(2)	N(1)–Zn(1)–O(2)#1	100.3(2)
O(2)#1–Zn(1)–O(1)	177.56(18)	O(3)#1–Zn(1)–O(2)#1	91.8(2)
N(1)–Zn(1)–O(1)	77.8(2)	O(3)#1–Zn(1)–O(1)	89.9(2)
O(2)#1–Zn(1)–N(3)	93.3(2)	O(3)#1–Zn(1)–N(4)	169.6(2)
N(1)–Zn(1)–N(3)	161.8(2)	O(3)#1–Zn(1)–N(3)	95.4(2)
N(3)–Zn(1)–N(4)	74.4(2)	N(1)–Zn(1)–N(4)	94.2(3)
O(1)–Zn(1)–N(3)	88.3(2)	O(1)–Zn(1)–N(4)	92.0(2)
O(2)#1–Zn(1)–N(4)	86.6(2)	N(5)–Zn(3)–N(9)	91.9(2)
N(2)–Zn(3)–N(5)	102.5(2)	N(2)–Zn(3)–N(9)	165.0(2)
N(9)–Zn(3)–O(4)	87.7(2)	N(9)–Zn(3)–N(8)	77.5(2)
N(5)–Zn(3)–O(5)	76.0(2)	N(8)–Zn(3)–O(5)	167.42(19)
N(2)–Zn(3)–O(4)	77.4(2)	N(5)–Zn(3)–O(4)	160.6(2)
N(2)–Zn(3)–N(8)	101.3(2)	N(5)–Zn(3)–N(8)	108.1(2)
O(4)–Zn(3)–N(8)	90.7(2)	N(2)–Zn(3)–O(5)	89.0(2)
N(9)–Zn(3)–O(5)	90.63(19)	O(4)–Zn(3)–O(5)	84.61(18)
N(6)–Zn(9)–N(6)#2	96.5(3)	N(6)–Zn(9)–N(7)	94.7(3)
N(6)#2–Zn(9)–N(7)	165.5(3)	N(7)–Zn(9)–N(7)#2	75.9(4)
N(6)–Zn(9)–N(7)#2	165.5(3)	N(6)#2–Zn(9)–N(7)#2	94.7(3)
N(6)–Zn(9)–O(8)#2	101.8(2)	N(6)#2–Zn(9)–O(8)#2	80.4(2)
N(7)#2–Zn(9)–O(8)#2	89.1(3)	N(6)–Zn(9)–O(8)	80.4(2)
N(7)–Zn(9)–O(8)	89.1(3)	N(7)#2–Zn(9)–O(8)	88.3(2)
N(7)–Zn(9)–O(8)#2	88.3(2)	N(6)#2–Zn(9)–O(8)	101.8(2)
2			
Ca(1)–O(2)#1	2.293(2)	Ca(1)–O(3)#1	2.3486(19)
Ca(1)–O(8)#2	2.4643(17)	Ca(1)–O(1)	2.4686(18)
Ca(1)–O(5)	2.3619(17)	Ca(1)–N(4)#2	2.5017(19)
Ca(1)–N(1)	2.513(2)	Ca(2)–O(4)#3	2.3285(19)
Ca(2)–O(7)#4	2.3287(17)	Ca(2)–O(8)#2	2.3970(16)
Ca(2)–O(9)	2.374(2)	Ca(2)–O(6)#4	2.3955(17)
Ca(2)–O(6)	2.4569(17)	Ca(2)–O(5)	2.5988(17)
O(2)#1–Ca(1)–O(3)#1	77.45(7)	O(2)#1–Ca(1)–O(5)	84.26(7)
O(3)#1–Ca(1)–O(5)	142.42(6)	O(5)–Ca(1)–O(8)#2	73.49(6)
O(2)#1–Ca(1)–O(8)#2	79.15(6)	O(3)#1–Ca(1)–O(8)#2	132.86(6)
O(5)–Ca(1)–O(1)	85.01(6)	O(3)#1–Ca(1)–N(4)#2	79.32(6)
O(2)#1–Ca(1)–O(1)	111.51(7)	O(3)#1–Ca(1)–O(1)	71.99(6)
O(1)–Ca(1)–N(4)#2	129.39(6)	O(5)–Ca(1)–N(1)	85.48(7)
O(8)#2–Ca(1)–O(1)	155.15(6)	O(2)#1–Ca(1)–N(4)#2	101.41(7)
O(5)–Ca(1)–N(4)#2	136.99(6)	O(8)#2–Ca(1)–N(4)#2	66.05(6)
O(2)#1–Ca(1)–N(1)	169.56(8)	O(3)#1–Ca(1)–N(1)	109.94(7)
N(4)#2–Ca(1)–N(1)	87.46(7)	O(1)–Ca(1)–N(1)	65.53(7)
O(8)#2–Ca(1)–N(1)	99.79(7)	O(7)#4–Ca(2)–O(9)	89.59(8)
O(4)#3–Ca(2)–O(7)#4	89.55(7)	O(4)#3–Ca(2)–O(9)	154.53(8)
O(4)#3–Ca(2)–O(6)#4	78.85(7)	O(7)#4–Ca(2)–O(6)#4	75.15(6)
O(9)–Ca(2)–O(6)#4	76.33(8)	O(9)–Ca(2)–O(8)#2	86.18(8)
O(4)#3–Ca(2)–O(8)#2	119.26(7)	O(7)#4–Ca(2)–O(8)#2	94.79(6)
O(7)#4–Ca(2)–O(6)	146.84(6)	O(8)#2–Ca(2)–O(6)	115.61(6)
O(9)–Ca(2)–O(5)	99.69(8)	O(6)–Ca(2)–O(5)	51.04(5)
O(6)#4–Ca(2)–O(8)#2	159.70(6)	O(4)#3–Ca(2)–O(6)	86.86(7)
O(9)–Ca(2)–O(6)	80.08(8)	O(6)#4–Ca(2)–O(6)	71.81(7)
O(4)#3–Ca(2)–O(5)	88.64(6)	O(7)#4–Ca(2)–O(5)	161.83(6)
O(6)#4–Ca(2)–O(5)	122.10(6)	O(8)#2–Ca(2)–O(5)	70.52(5)

Symmetry transformations used to generate equivalent atoms for **1**: #1: $x+1/4, -y+1/4, z+1/4$; #2: $-x+2, -y, z$. For **2**: #1: $-x+3/2, y+1/2, -z+1/2$; #2: $x+1, y, z$; #3: $x, y+1, z$; #4: $-x+1, -y+2, -z$.

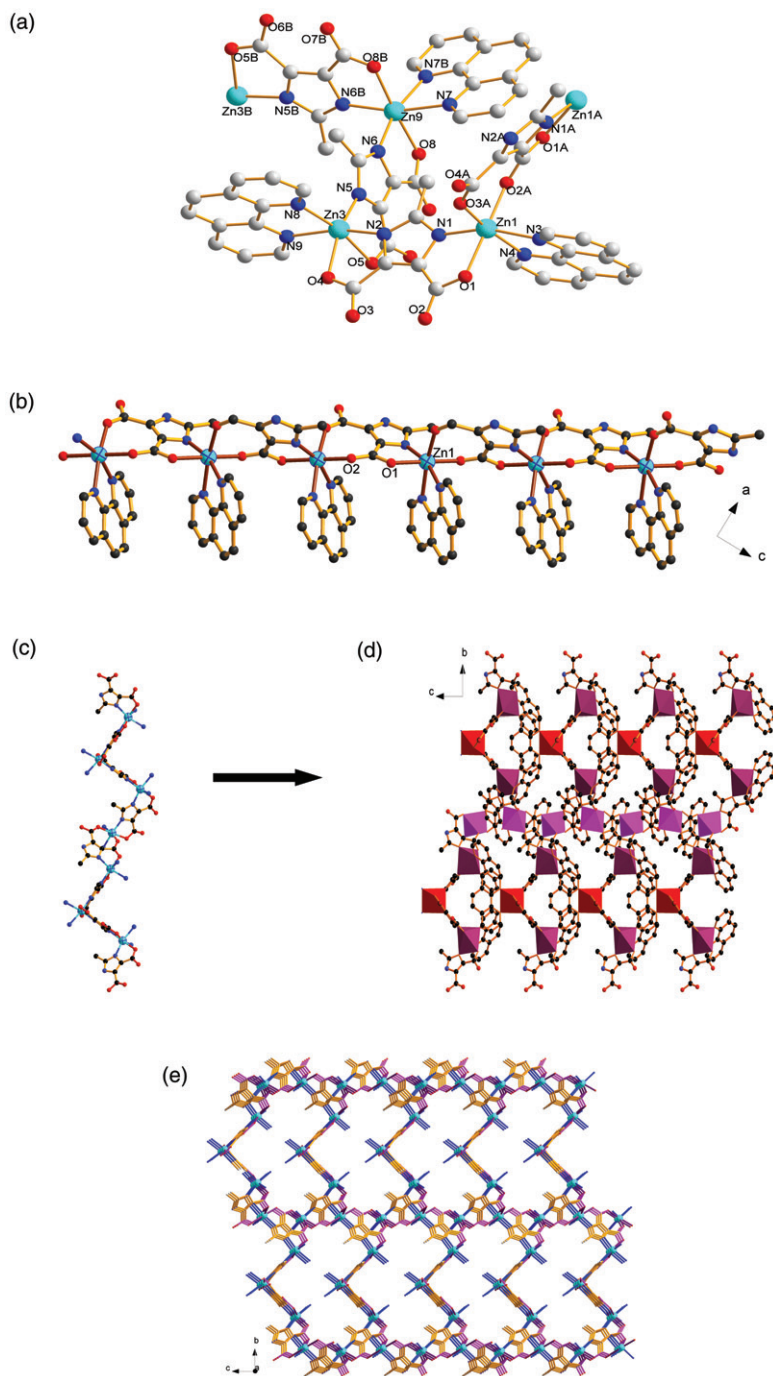


Figure 1. (a) Coordination arrangements of Zn(II) in **1** (hydrogens omitted for clarity). (b) View of the 1-D chain supported by Zn1(II) ions and O1 and O2. (c) View of the 1-D chain structure along the *a*-axis. (d) View of the 2D layer in **1**. (e) View of the 3D framework of **1**.

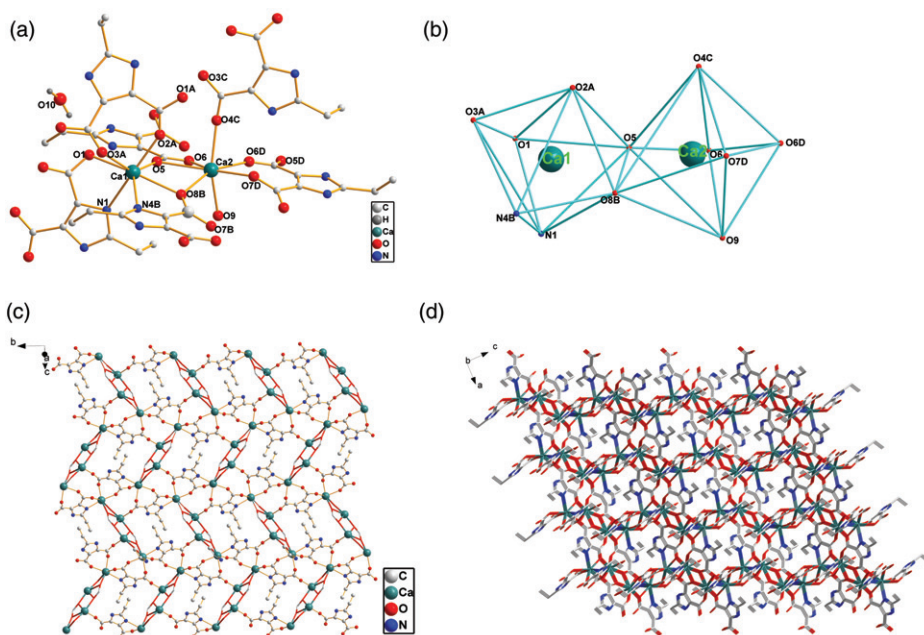


Figure 2. (a) Coordination arrangements of Ca(II) in **2** (hydrogens omitted for clarity). (b) View of the coordination geometries around Ca1 and Ca2. (c) The 2D sheet comprising infinite zigzag chains bridged by μ_5 -HEIDC $^{2-}$ viewed along the a -axis (part of organic ligand omitted for clarity). (d) Perspective view of the 3-D framework for **2** along the b -axis (hydrogens and water omitted for clarity).

coordination to form a 1-D infinite chain (figure 1c) with Zn1...Zn3 and Zn3...Zn9 distances of 6.2796(10) and 6.3716(11) Å along the a -axis. All Zn(II) ions alternately appear as Zn1–Zn3–Zn9–Zn3–Zn1 (figure 1c) and the Zn3–Zn9–Zn3 angle is 95.484(9)°. The 1-D infinite chains are linked to a 2-D layer by μ_3 -MIDC $^{3-}$ bridges (figure 1d). Adjacent layers are pillared by μ_2 -HMIDC $^-$ ligands in N,O - and N',O' -chelating coordination. Finally, a 3-D framework was formed through μ_2 -HMIDC $^-$ ligands (figure 1e).

3.3. Crystal structure of $\{[Ca_2(HEIDC)_2(H_2O)] \cdot H_2O\}_n$ (**2**)

Polymer **2** was also synthesized under solvothermal condition, crystallizing in the monoclinic space group $P2(1)/n$ and assembled in a 3-D MOF made up of $[Ca_2(HEIDC)_2(H_2O)]$ and one noncoordinated water molecules. In the asymmetrical unit (figure 2a), there are two crystallographically independent Ca $^{2+}$ ions, both in a highly distorted pentagonal bipyramid; the two decahedrons share two oxygens (O5 and O8B) from two individual μ_5 -HEIDC $^{2-}$ ligands (figure 2b). HEIDC $^{2-}$ adopts two distinctly different coordination modes (scheme 1c and 1d). As depicted in figure 2(a), Ca1 is surrounded by two chelating N,O -bidentate μ_5 -HEIDC $^{2-}$, and three carboxylate oxygens from two μ_5 -HEIDC $^{2-}$ ligands. Ca2 is also seven-coordinate by four carboxylate oxygens from two individual μ_5 -HEIDC $^{2-}$ ligands, by other two oxygens from two μ_5 -HEIDC $^{2-}$, and by one water molecule. The Ca1...Ca2 distance

is 3.8868(9) Å. The Ca1–N1 and Ca1–N4B bond lengths are 2.513 Å and 2.5017 Å, respectively, and the Ca–O bond lengths range from 2.293 Å to 2.5988 Å, somewhat different than the previously reported values [47].

In **2**, the doubly deprotonated HEIDC²⁻ utilizes four carboxylate oxygens to link Ca1 and Ca2 to form a 1-D zigzag chain, which has an infinite wall-like structure (figure 2c). Adjacent 1-D chains are further linked by μ_5 -HEIDC²⁻ ligands adopting a μ_5 -*k*N, O: *k*O', O'': *k*O''' coordination mode (scheme 1c) in two directions to make up a 2-D layer structure (figure 2c). The 2D sheets are connected by μ_5 -HEIDC²⁻ ligands adopting a μ_5 -*k*N, O: *k*O: *k*O', O'': *k*O''' coordination mode (scheme 1d) to generate the 3-D framework (figure 2d).

3.4. IR spectroscopy

IR spectra display characteristic absorption bands for water, carboxylate, imidazolyl, and pyridyl units. Polymers **1** and **2** show strong and broad absorptions at 3400–3500 cm⁻¹, indicating the presence of hydrogen bonds. The coordination of carboxylate can be seen from the absorption bands at 1340–1610 cm⁻¹ in **1** and **2** due to $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ vibrations, respectively. Strong bands at 1610–1570 cm⁻¹ in **1** and **2** imply the C=N and C=C stretching bands of imidazole in H₃MIDC and H₃EIDC.

3.5. Thermogravimetric analysis

The TG and DSC curves for **1** and **2** are shown in the “Supplementary material”. TG data show that **1** is stable to 89.5°C, losing weight from 89.5°C to 406.2°C (observed 3.56%). Subsequently, it keeps losing weight from 406.2°C to 471.3°C and then from 471.3°C to 659.4°C. The three steps correspond to the decomposition of the organic units of MIDC³⁻, HMIDC²⁻, and phen (observed 78.93%, calculated 78.63%). Finally, a plateau is observed from 701.2°C to 775°C. The final brown residue is ZnO (observed 21.07%, Calcd 21.44%). There is one very weak exothermic peak at 434.7°C and a very strong exothermic peak at 587.0°C on the DSC curve of **1**.

For **2**, three very weak endothermic peaks at 191.5°C, 289.0°C, and 758.2°C and one very strong exothermic peak at 550.6°C can be observed. It first loses the crystallization water at 80–241°C (observed 8.9%, calculated 7.5%), and the second complicated weight loss from 258 to 762°C corresponding to decomposition of HEIDC²⁻ (observed 68.0%). Finally, a plateau is observed from 762°C to 850°C. The final residue is CaO (observed 23.1%, calculated 23.3%). The thermal data of **1** and **2** are in reasonable agreement with the crystal structure analyses.

3.6. Photoluminescent properties

Metal–organic coordination polymers with d¹⁰ configuration exhibit photoluminescent properties and have potential applications [51–56]. Previous studies have shown that coordination polymers containing Zn and Ca exhibit photoluminescence [36, 41, 57–60]. Hence, we have investigated the solid-state photoluminescence of **1** and **2** and the corresponding free ligands at room temperature. The emission spectra of polymers **1** and **2** and H₃EIDC are illustrated in the “Supplementary material”.

The free H₃MIDC shows luminescence with emission maximum at 430 nm by selective excitation at 300 nm, which is attributed to the $\pi^* \rightarrow n$ transition [39]. Compound **1** has a broad emission band from 465 to 495 nm with a maximum at 475 nm upon excitation at 380 nm. Compared with the emission spectrum of H₃MIDC, a red shift of 45 nm has been observed in **1**. Obviously, the fluorescence intensity of **1** is enhanced due to ligand-to-metal charge transfer (LMCT) [11, 36, 51–56], rather than the $\pi^* \rightarrow n$ transition of the organic ligand.

Free H₃EIDC displays luminescence, with emission maximum at 476 nm upon excitation at 380 nm, attributed to the $\pi^* \rightarrow n$ transition. For **2**, strong emission bands are observed at 412 nm when excited at 340 nm, which also may be due to LMCT.

4. Conclusions

By reactions of imidazole-based dicarboxylates, H₃MIDC, and H₃EIDC with metal ions under hydro(solvo)thermal condition, two 3-D crystalline polymeric products have been prepared. Both ligands display two kinds of coordination modes in constructing the two 3-D frameworks.

There is only one example of Zn(II) H₃MIDC-containing polymer $\{[\text{Zn}_3(\text{MIDC})_2(\text{H}_2\text{O})_2(\text{DMF})_2] \cdot 0.5\text{H}_2\text{O}\}$ [41] which shows a 2-D puckered structure composed of MIDC³⁻ and Zn²⁺. The novelty of **1** is that it contains both H₃MIDC and phen, and shows a 3-D structure.

Imidazole dicarboxylate-based Ca(II) coordination polymers are also very limited [61, 62], especially for Ca(II) with H₃EIDC [47]. The only reported Ca(II) polymer bearing H₂EIDC⁻ ligands is a 2-D layer structure [47]. Our polymer **2** is the second example of coordination polymer built by H₃EIDC, and gives a 3-D structure.

Supplementary material

Crystallographic data for the structures reported in this article in the form of CIF files have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 739527 and 772336 for **1** and **2**, respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk).

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