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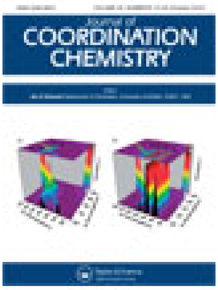

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Three new coordination frameworks based on 2-ethyl-imidazole-4,5-dicarboxylate and 1,10-phenanthroline: syntheses, crystal structures, and luminescence

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Three new coordination frameworks based on 2-ethyl-imidazole-4,5-dicarboxylate and 1,10-phenanthroline: syntheses, crystal structures, and luminescence

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Three new coordination polymers based on 2-ethyl-imidazole-4,5-dicarboxylate with 1,10-phenanthroline as ligands, Pb(HEIDC)(phen)$_2$ (**1**), [Zn(EIDC)(phen)]$_n$ (**2**), and {[Ba(H$_2$EIDC)$_2$(phen)]·(phen)$_2$·[Ba(H$_2$EIDC)(HEIDC)(phen)]}$_n$ (**3**) (H$_3$EIDC = 2-ethyl-1-*H*imidazole-4,5-dicarboxylate; phen = 1,10-phenanthroline), have been synthesized under hydrothermal conditions and characterized by elemental analysis, infrared spectroscopy, thermogravimetric analysis, and single-crystal X-ray diffraction. Complex **1** displays a tetranuclear square constructed of four Pb(II) centers, four HEIDC, and eight phen, resulting in a 3-D network with a 1-D open channel along the *c*-axis *via* C–H···O hydrogen bonds, C–H···π, and π–π stacking interactions. Complex **2** is an infinite zigzag chain resulting in the final 3-D supramolecular framework *via* C–H···O and π–π stacking interactions. Complex **3** is composed of two individual Ba chains, exhibiting a 3-D framework *via* O–H···O, O–H···N hydrogen bonds, and π–π stacking interactions. The photoluminescence spectra of **1** and **2** in the solid state have been investigated, **1** exhibits green photoluminescence in the solid state at room temperature.

Keywords: Hydrothermal synthesis; 2-Ethyl-1*H*-imidazole-4,5-dicarboxylate; 1,10-Phenanthroline; Luminescent properties

1. Introduction

Construction of metal–organic coordination polymers based on supramolecular chemistry and crystal engineering have been an active area of materials research due to varieties of structures and unique properties, such as photoluminescence, magnetism, conductivity, ion exchange, gas adsorption/separation, and catalysis [1–6]. The self-assembly process can be influenced by solvent system, counterions, pH, reaction temperature, metal-to-ligand ratio, the metal ions and the choice of ligands in which the properties of the ligands and coordination modes of metal ions are related to the final

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structures of their complexes. Supramolecular interactions, such as hydrogen-bonding, π–π stacking, and metallophilic interactions, also contribute to constructing the final high-dimensional framework. Thus, selection of multifunctional ligands is important in constructing metal–organic coordination polymers [7].

Ligands containing N and O donors, especially N-heterocyclic carboxylates, are excellent candidates for producing network structures, 4,5-imidazole dicarboxylic acid (H_3IDC), a planar rigid ligand, has attracted interest because it possesses flexible multifunctional coordination sites involving two nitrogen atoms of imidazole and four carboxylate oxygen atoms protonated to varying degrees at different pH values with potential hydrogen-bonding donors and acceptors.

These advantages and syntheses of coordination polymers with IDC [8] prompt us to study a very close analog, H_3EIDC with an ethyl substituent at C2 of the imidazole group to generate new metal–organic coordination polymers due to the constraining effect of the ethyl in the assembly. Wang and co-workers reported one 3-D Cd(II) coordination polymer [8c]; Zhang and co-workers reported four complexes with H_3EIDC, a tetranuclear Ni(II) coordination polymer, two 2-D Mn(II) coordination polymers, and one 3-D Cd(II) coordination polymer [8d]. Very recently, four lanthanide complexes have been synthesized and characterized by Feng *et al.* [8e].

In previous research, we reported the first series of metal–organic compounds with H_3EIDC, as well as the crystal structure of 2-ethyl-1*H*-imidazole-4-carboxylate monohydrate and one Na complex [9]. To continue our research, we report three new complexes based on 2-ethyl-imidazole-4,5-dicarboxylate with 1,10-phenanthroline, Pb(HEIDC)(phen)$_2$ (**1**), $[Zn(EIDC)(phen)]_n$ (**2**), and $\{[Ba(H_2EIDC)_2(phen)]\cdot(phen)_2\cdot[Ba(H_2EIDC)(HEIDC)(phen)]\}_n$ (**3**). Hydrogen-bonding and π–π stacking play vital roles in generating extended high-dimensional supramolecular frameworks in these complexes. The photoluminescence spectra of **1** and **2** are also investigated.

2. Experimental

2.1. *Materials and equipment*

All chemicals were commercially available and used without purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. Infrared (IR) spectra were recorded (4000–400 cm^{-1}) as KBr discs on a Bruker 1600 FTIR spectrometer. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TG/DTA6300 system with a heating rate of $10^\circ C\ min^{-1}$ from room temperature to 700°C under nitrogen. Luminescence spectra for crystal solid samples were recorded at room temperature on a Hitachi F-4500 fluorescence spectrophotometer.

2.2. *Syntheses of 1–3*

2.2.1. Pb(HEIDC)(phen)$_2$ (1). A mixture of Pb(AC)$_2$ (0.1 g, 0.5 mmol), 2-ethyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3EIDC) (0.1 g, 0.5 mmol), phen (0.13 g, 1 mmol), and water (15 mL) was stirred for 30 min in air with the pH adjusted to 9 by NaOH, and then sealed in a 20 mL Teflon reactor and kept under autogenous pressure at 150°C for 72 h. The mixture was cooled to room temperature at 5°C h^{-1} and colorless plate crystals were obtained in 39% yield based on the ligand. Anal Calcd for $C_{31}H_{22}N_6O_4Pb$ Found (%): C, 49.57; H, 2.90; N, 11.33. Calcd (%): C, 49.62; H, 2.93; N, 11.20. IR bands (KBr pellets, cm^{-1}): 3071(s), 1524(s), 1247(s), 1119(w), 1034(w), 850(s), 781(w), 723(s), 451(w).

2.2.2. [Zn(EIDC)(phen)]$_n$ (2). The synthetic procedure for **2** was similar to that for **1** except that $Pb(AC)_2$ was replaced by $Zn(NO_3)_2 \cdot 6H_2O$ (0.14 g, 0.5 mmol) and the pH was adjusted to 6 by NaOH. Colorless plate crystals were obtained in 52% yield based on the ligand. Anal Calcd for $C_{19}H_{13}N_4O_4Zn$ Found (%): C, 53.43; H, 3.03; N, 13.23. Calcd (%): C, 53.52; H, 3.04; N, 13.12. IR bands (KBr pellets, cm^{-1}): 3070(s), 2972(s), 1574(s), 1471(s), 1344(s), 1227(w). 1227(w), 1121(w), 1103(w), 1051(w), 866(w), 856(s), 790(w), 728(w), 639(w), 482(w).

2.2.3. {[Ba(H_2EIDC)$_2$(phen)] · (phen)$_2$ · [Ba(H_2EIDC)(HEIDC)(phen)]}$_n$ (3). The synthetic procedure for **3** was similar to that for **1** except that $Pb(AC)_2$ was replaced by $BaCl_2$ (0.10 g, 0.5 mmol) and the pH was adjusted to 7 by NaOH. Colorless plate crystals were obtained in 45% yield based on the ligand. Anal Calcd for $C_{76}H_{65}N_{16}O_{19}Ba_2$ Found (%): C, 51.32; H, 3.51; N, 12.64. Calcd (%): C, 51.21; H, 3.64; N, 12.58. IR bands (KBr pellets, cm^{-1}): 3072(s), 2362(s), 1515(s), 1419(s), 1247(s), 1117(w), 956(w), 844(w), 786(w), 734(w), 490(w).

2.3. *X-ray diffraction determination*

Diffraction data of **1** and **3** were recorded with a Rigaku/MSC Mercury CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K by using an ω scan mode. Intensity data were corrected using the REQAB program [10]. Diffraction data of **2** was obtained with a Bruker SMART CCD 1000 diffractometer operating at 50 kV and 30 mA using Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298 K. Data collection and reduction were performed using SMART and SAINT software [11] and multiscan absorption correction was applied using SADABS [11]. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL program package [12]. Crystallographic data for **1**–**3** are listed in table 1, and selected bond lengths and angles are shown in table 2.

3. Results and discussion

3.1. *Description of the crystal structures*

3.1.1. Crystal structure of 1. Single-crystal X-ray diffraction analysis reveals that the molecular structure of **1** can be viewed as a symmetrical tetranuclear molecular square being made up of $[Pb_4(H_2EIDC)_4(phen)_8]$. It crystallizes in tetragonal space group $P4_2/n$ and the asymmetric unit consists of one Pb(II), one double-deprotonated HEIDC, and two phen ligands. Each Pb(II) is six-coordinate in a severely distorted

Table 1. Crystal data and structure refinements for **1–3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{124}H_{88}N_{24}O_{16}Pb4$	$C_{19}H_{13}N_4O_4Zn$	$C_{76}H_{65}N_{16}O_{19}Ba_2$
Formula weight	2998.94	426.70	1781.12
Crystal system	Tetragonal	Monoclinic	Triclinic
Space group	$P4_2/n$	$C2/c$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	17.283(3)	24.811(6)	13.245(3)
b	17.283(3)	9.403(2)	14.343(3)
c	19.408(4)	18.272(5)	20.417(4)
α	90	90	97.23(3)
β	90	124.677(2)	93.30(3)
γ	90	90	100.46(3)
Volume (Å^3), Z	5797.2(19), 2	3505.7(15), 8	3771.0(13), 2
Calculated density (Mg m^{-3})	1.718	1.617	1.569
Absorption coefficient (mm^{-1})	5.867	1.437	1.121
F(000)	2912	1736	1794
Crystal size (mm^3)	0.22 × 0.22 × 0.22	0.30 × 0.25 × 0.21	0.21 × 0.18 × 0.15
θ range for data collection (°)	$3.16 < \theta < 27.47$	$2.28 < \theta < 25.20$	$3.03 < \theta < 26.20$
Limiting indices	$-22 \le h \le 22$; $-22 \le k \le 22$; $-24 \le l \le 25$	$-29 \le h \le 29$; $-10 \le k \le 11$; $-21 \le l \le 21$	$-16 \le h \le 16$; $-17 \le k \le 16$; $-25 \le l \le 24$
Reflections collected/unique	54,002/6627	12,040/3158	33,415/14994
Completeness to $\theta = 25.00$ (%)	99.70	99.90	99.0
Data/restraints/parameters	6627/0/379	3158/0/254	14,994/1526/1104
Goodness-of-fit on F^2	1.001	1.051	1.053
Final R indices [I > $2\sigma(I)$]	$R_1 = 0.0272$, $wR_2 = 0.0534$	$R_1 = 0.0284$, $wR_2 = 0.0722$	$R_1 = 0.0343$, $wR_2 = 0.0783$
R indices (all data)	$R_1 = 0.0464$, $wR_2 = 0.0587$	$R_1 = 0.0362$, $wR_2 = 0.0770$	$R_1 = 0.0528$, $wR_2 = 0.0902$

$R_1 = \sum (|F_o| - |F_c|)/\sum |F_o|$; $wR_2 = [\sum w (|F_o|^2 - |F_c|^2)^2/\sum w (F_o)^2]^{1/2}$.

octahedral geometry, defined by two nitrogen atoms (N1, N2^i) and two oxygen atoms (O1, O4^i) from two HEIDC and two nitrogen atoms (N3, N5) from two different phen molecules (figure 1a). The Pb–O distances are 2.550(2) Å and 2.571(2) Å, respectively. Pb–N distances are 2.580(3)–2.874(3) Å. In the structure, each HEIDC chelates two Pb(II) centers to form two five-membered rings with bis-N,O-chelation (scheme 1a). Thus, Pb(II) centers with terminal phen are angular units and four HEIDC ligands function as rigid linkers, resulting in the tetranuclear molecular square (figure 1b). Pb_4 units are interconnected into a 2-D layer parallel to the *ab*-plane *via* C–H $\cdots \pi$ and π–π stacking interactions, indicated by the short centroid to centroid distance of 3.561(6) Å (figure 1b). Complex **1** assembles into a 3-D network *via* C–H $\cdots$ O hydrogen bonds containing a 1-D open channel along the *c*-axis, which is partially filled with the ethyl groups of HEIDC (figure 1c).

3.1.2. Crystal structure of 2. Single-crystal X-ray diffraction analysis reveals that **2** crystallizes in the monoclinic space group $C2/c$, and the asymmetric unit consists of one Zn^{II}, one fully deprotonated $EIDC^{3-}$, and one phen. The Zn^{II} is six-coordinate in a severely distorted octahedral geometry, defined by two nitrogen atoms (N1, N2) and two oxygen atoms (O1, O3) from two EIDC ligands, and two nitrogen atoms (N3, N4) from two different phen molecules, forming three stable five-membered rings (figure 2a).

Table 2. Selected bond lengths (Å) and angles (°) of **1–3**.

1			
Bond distances (Å)			
Pb(1)–O(4)^{i}	2.550(2)	Pb(1)–N(2)^{i}	2.580(3)
Pb(1)–O(1)	2.571(2)	Pb(1)–N(1)	2.582(3)
Bond angles (°)			
O(4)^{i}–Pb(1)–O(1)	146.06(7)	O(4)^{i}–Pb(1)–N(1)	87.99(7)
O(4)^{i}–Pb(1)–N(2)^{i}	65.94(7)	O(1)–Pb(1)–N(1)	65.79(7)
O(1)–Pb(1)–N(2)^{i}	88.78(7)	N(2)^{i}–Pb(1)–N(1)	83.04(8)
2			
Bond distances (Å)			
Zn(1)–O(1)	2.1275(18)	Zn(1)–N(2)^{i}	2.1353(18)
Zn(1)–N(1)	2.1286(18)	Zn(1)–O(3)^{i}	2.1934(18)
Zn(1)–N(3)	2.136(2)	Zn(1)–N(4)	2.233(2)
Bond angles (°)			
O(1)–Zn(1)–N(1)	79.75(7)	N(3)–Zn(1)–N(2)^{i}	157.39(7)
O(1)–Zn(1)–N(3)	97.51(7)	O(1)–Zn(1)–O(3)^{i}	175.31(6)
N(1)–Zn(1)–N(3)	100.10(7)	N(1)–Zn(1)–O(3)^{i}	97.51(7)
O(1)–Zn(1)–N(2)^{i}	97.88(7)	N(3)–Zn(1)–O(3)^{i}	86.69(7)
N(1)–Zn(1)–N(2)^{i}	98.86(7)	N(2)^{i}–Zn(1)–O(3)^{i}	78.72(6)
N(1)–Zn(1)–N(4)	168.07(7)	O(1)–Zn(1)–N(4)	89.43(7)
N(3)–Zn(1)–N(4)	76.17(7)	O(3)^{i}–Zn(1)–N(4)	93.61(7)
3			
Bond distances (Å)			
Ba(1)–O(8)^{i}	2.701(2)	Ba(2)–O(2W)	2.762(3)
Ba(1)–O(1W)	2.715(3)	Ba(2)–O(11)	2.803(2)
Ba(1)–O(4)	2.749(2)	Ba(2)–O(13)	2.846(3)
Ba(1)–O(5)	2.772(3)	Ba(2)–O(16)^{iii}	2.892(3)
Ba(1)–O(1)^{ii}	2.784(3)	Ba(2)–N(2)	2.902(3)
Ba(2)–O(3W)	2.744(3)	O(16)–Ba(2)^{iii}	2.892(3)
Bond angles (°)			
O(8)^{i}–Ba(1)–O(1W)	77.74(9)	O(1W)–Ba(1)–N(8)	123.15(9)
O(8)^{i}–Ba(1)–O(4)	69.99(7)	O(4)–Ba(1)–N(8)	77.48(9)
O(1W)–Ba(1)–O(4)	133.95(7)	O(5)–Ba(1)–N(8)	146.52(8)
O(8)^{i}–Ba(1)–O(5)	86.78(8)	O(1)^{ii}–Ba(1)–N(8)	139.51(8)
O(1W)–Ba(1)–O(5)	75.74(8)	O(8)^{i}–Ba(1)–N(7)	118.24(8)
O(4)–Ba(1)–O(5)	70.60(8)	O(1W)–Ba(1)–N(7)	99.61(8)
O(8)^{i}–Ba(1)–O(1)^{ii}	147.52(8)	O(4)–Ba(1)–N(7)	124.25(9)
O(1W)–Ba(1)–O(1)^{ii}	78.63(8)	O(5)–Ba(1)–N(7)	153.39(8)
O(1)^{ii}–Ba(1)–N(7)	87.46(9)	O(16)^{iii}–Ba(2)–N(5)	75.52(8)
N(8)–Ba(1)–N(7)	57.47(9)	N(2)–Ba(2)–N(5)	146.94(8)
O(8)^{i}–Ba(1)–N(11)	123.96(8)	N(1)–Ba(2)–N(5)	147.87(8)
O(1W)–Ba(1)–N(11)	156.26(8)	N(3)–Ba(2)–N(5)	126.30(7)

Symmetry codes for **1**: $i = y, -x+1/2, -z+1/2$; for **2**: $i = 0.5-x, 0.5+y, 0.5-z$; for **3**: $i = -x+1, -y, -z+1$; $ii = -x+1, -y+1, -z+1$; $iii = -x+1, -y+1, -z$.

The Zn–X bond lengths and X–Zn–X (X = N/O) angles vary from 2.1275(18) Å to 2.233(2) Å and 76.17(7)° to 175.31(6)°, respectively, similar to those observed for other Zn complexes with H_3IDC derivatives [13]. Differing from $[Zn(H_2MIDC)_2(H_2O)_2]$ [14a] and $[Zn_5(MIDC)_2(HMIDC)_2(phen)_5]_n$ [14b], whose ligands exhibit one mono-N,O-chelating mode and two different coordination modes, respectively, each $EIDC^{3-}$ is bis-N,O-chelating (scheme 1b) adjacent to Zn(II) centers *via* N1, O1, and N2, O3, generating an infinite zigzag chain along the *c*-axis (figure 2b). There are two kinds of non-classic hydrogen bonds C–H $\cdots$ O and π–π stacking interactions between parallel chains, linking adjacent chains into a supramolecular framework (figure 2c).

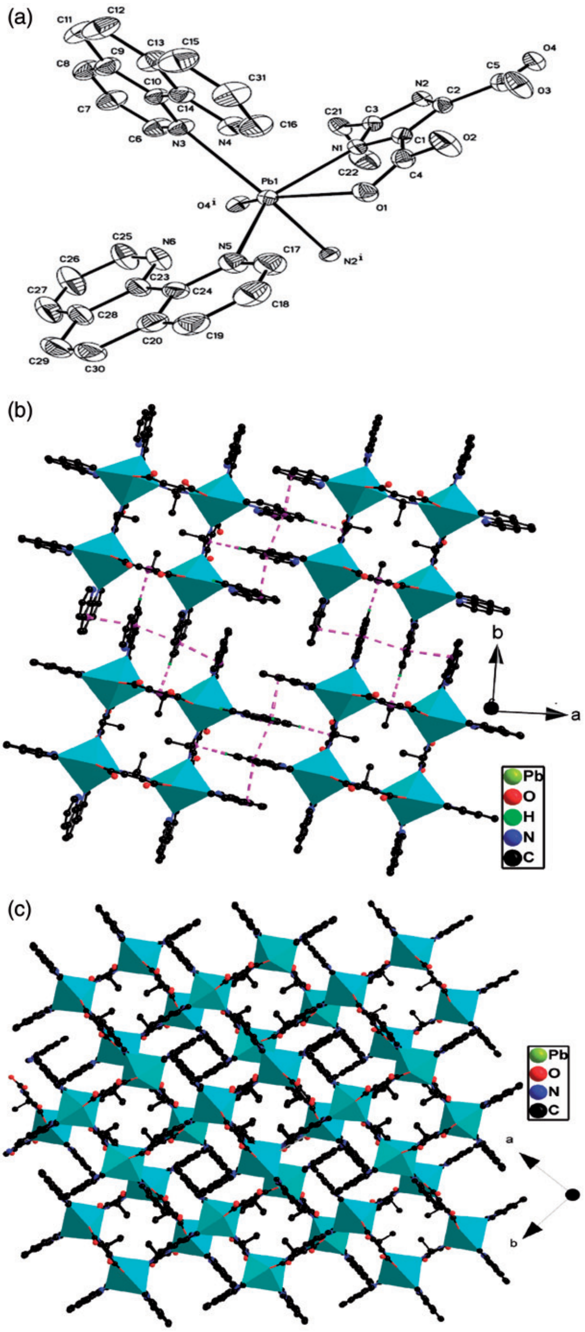
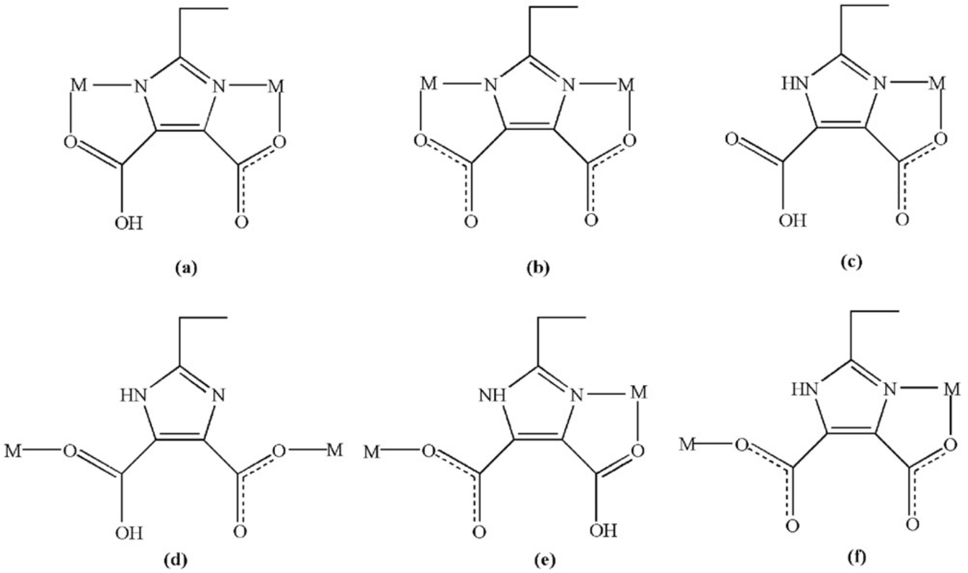


Figure 1. (a) Thermal ellipsoid plot of the asymmetric unit of **1** (30% probability ellipsoids), (b) view of 2-D layer parallel to the *ab*-plane constructed by C–H $\cdots\pi$ and π–π stacking interactions, and (c) view of a stable 3-D supramolecular structure constructed by C–H $\cdots$ O hydrogen bonds containing 1-D open channels along the *c*-axis. Symmetry codes for **1**: $\mathrm{i} = y, -x+1/2, -z+1/2$.



Scheme 1. The coordination modes of H_3EIDC in **1** (a), **2** (b), and **3** (c–f).

3.1.3. Crystal structure of 3. Single-crystal X-ray diffraction analysis reveals that **3** crystallizes in the triclinic space group $P\bar{1}$, with the asymmetric unit consisting of two independent Ba^{II} ions with different coordination geometries, four deprotonated ligands (three mono-deprotonated H_2EIDC and one doubly deprotonated HEIDC), two coordinated phen ligands, two solvate phen, and three water ligands. Ba1 is eight-coordinate in a distorted square antiprismatic geometry, defined by one nitrogen and four carboxylate oxygen atoms from three H_2EIDC, two nitrogen atoms from two different phen molecules and one oxygen from one water molecule (figure 3a). The nine-coordinate Ba2 shows slightly distorted tricapped trigonal prismatic coordination geometry, chelated by one mono-deprotonated H_2EIDC and one doubly deprotonated HEIDC in the N,O-mode, the additional five coordination sites are occupied by one carboxylate oxygen atom, two nitrogen atoms from phen, and two oxygen atoms from two terminal water molecules to complete the nine-coordination (figure 3a). Ba–X bond lengths and X–Ba–X (X = N/O) angles vary from 2.701(2) Å to 3.023(3) Å and 56.81(7)° to 156.26(8)°, respectively. Differing from Ba(II) complexes with H_3IDC or its derivatives [9a, 15], in which the ligand only exhibits one or two coordination modes, H_3EIDC in **3** exhibits four coordination modes: the first adopts μ_2-kN,O mode chelating a Ba^{II} (scheme 1c); the second adopts μ_2-kO : O′ mode bridging two Ba^{II} (scheme 1d); the third adopts μ_2-kN,O : O′ mode connecting two Ba^{II} in N,O-chelating and O-bridging fashions (scheme 1e); and the fourth adopts μ_2-kN,O : O′ mode connecting two Ba^{II}, similar to the third coordination mode except that two carboxylates are both deprotonated (scheme 1f). Ba1 centers are interconnected by μ_2-H_2EIDC to generate a chain along the *b*-axis (figure 3b). Two adjacent Ba2 ions are bridged equivalently by two μ_2-HEIDC ligands, forming a dinuclear $[Ba(\mu_2\text{-HEIDC})_2]$ unit, which is further connected into a chain along the *b*-axis *via* O–H $\cdots$ O hydrogen bonds and π–π stacking interactions (figure 3c). Furthermore, the Ba1 chains, Ba2

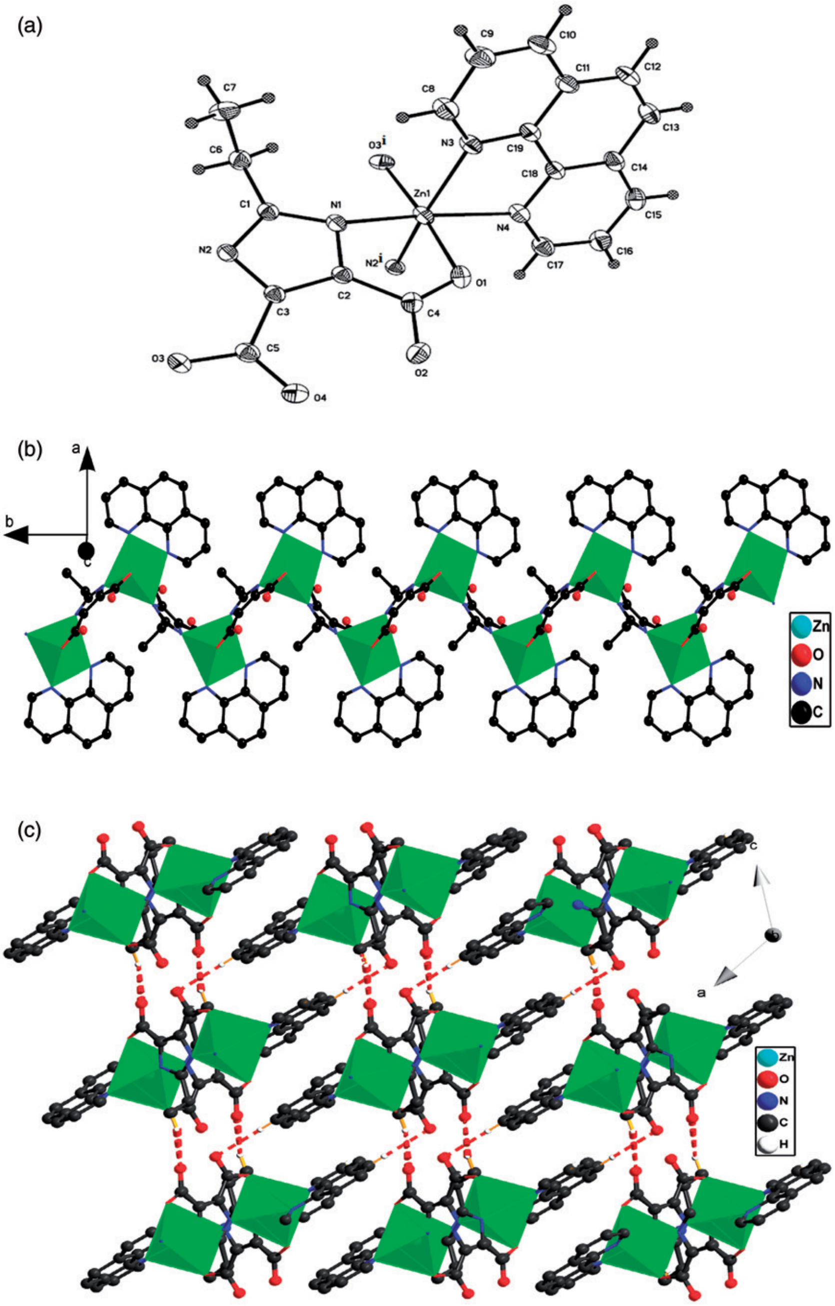


Figure 2. (a) Thermal ellipsoid plot of the asymmetric unit of **2** (30% probability ellipsoids), (b) view of an infinite zig-zag chain along the *c*-axis in **2**, and (c) view of 3-D network along the *b*-axis in **2**. Symmetry codes for **2**: $\mathrm{i} = 0.5 - x,\ 0.5 + y,\ 0.5 - z$.

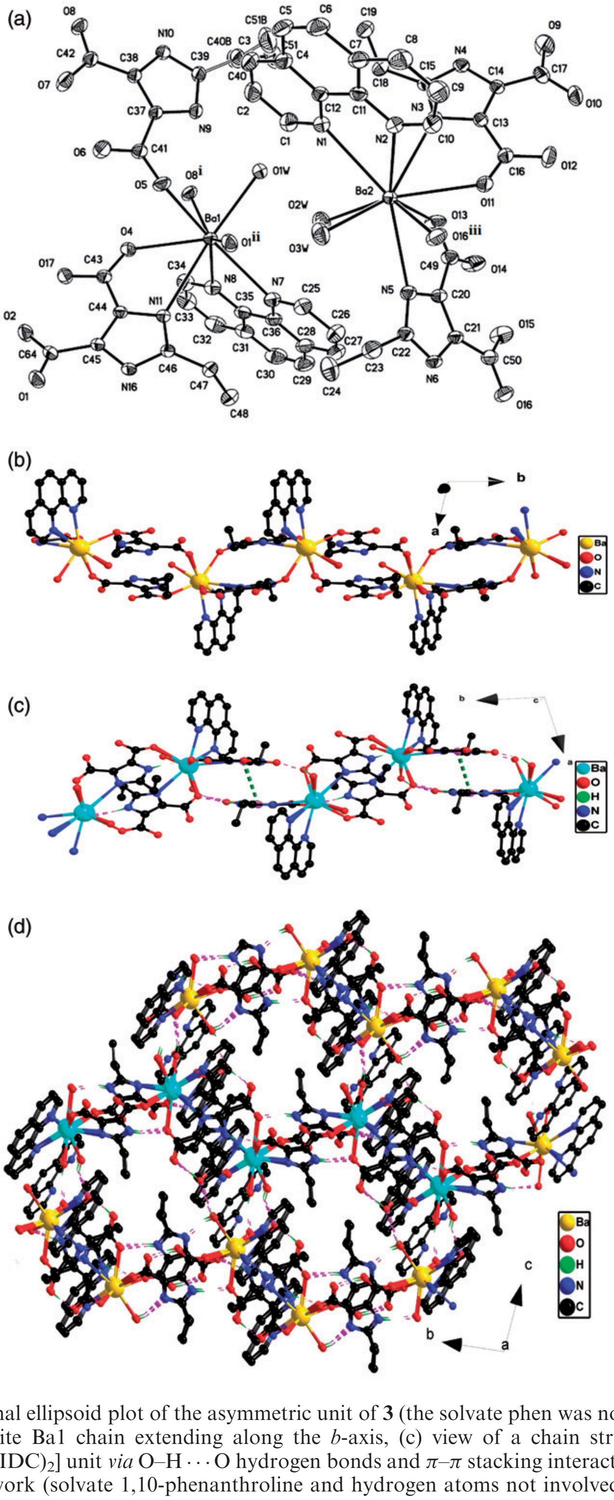


Figure 3. (a) Thermal ellipsoid plot of the asymmetric unit of **3** (the solvate phen was not shown for clarity), (b) view of an infinite Ba1 chain extending along the *b*-axis, (c) view of a chain structure composed of dinuclear [Ba(μ_2-HEIDC)$_2$] unit *via* O–H $\cdots$ O hydrogen bonds and π–π stacking interactions, and (d) view of the final 3-D framework (solvate 1,10-phenanthroline and hydrogen atoms not involved in hydrogen bonds are omitted for clarity). Symmetry codes for **3**: and $\mathrm{i} = -x+1,\ -y,\ -z+1$; $\mathrm{ii} = -x+1,\ -y+1,\ -z+1$; $\mathrm{iii} = -x+1,\ -y+1, -z$.

chains, and the solvate phen interact *via* O–H · · · O, O–H · · · N hydrogen-bonding and π–π stacking interactions, forming a 3-D framework (figure 3d).

3.2. *TGA of 1–3*

TGA of **1**–**3** were performed under N_2 to 700°C at a constant rate of $10^\circ C\,min^{-1}$. The TG curves are depicted in figure S1, **1** is thermally stable with no clean weight loss below 290°C. Weight loss above 296°C corresponds to decomposition of the framework. For **2**, the compound began to decompose above 260°C and the residue accounts for 18.4%, in agreement with the calculated value of 18.9%, by assuming the final product is ZnO. Complex **3** exhibits an initial mass loss of 21.8% between 89°C and 206°C, corresponding to removal of coordinated water and two solvate phen molecules (Calcd 22.0%), followed by a plateau (206–278°C), the next weight loss above 278°C corresponds to partial decomposition of the framework structure.

3.3. *Fluorescent properties*

Coordination polymers adjust the emission wavelength of organic ligands *via* incorporation of metals, important in applications as light-emitting diodes [14]. The photoluminescence spectra of **1**, **2**, and H_3EIDC were investigated in the solid state at room temperature. As indicated in figure S2, emission spectra of free H_3EIDC, **1**, and **2** show strong emission. Emission maxima (λ_{em}) are 385 nm (H_3EIDC), 536 nm (**1**), and 395 nm (**2**) ($\lambda_{ex} = 306$ nm for H_3EIDC, 452 nm for **1**, 285 nm for **2**), respectively. Compared with the free H_3EIDC, **1** exhibits a remarkable red-shift, caused by a metal-centered transition involving the s and p metal orbitals as proposed by Vogler [16]. Complex **1** exhibits green photoluminescence in the solid state at room temperature compared to other Pb complexes emitting blue photoluminescence [11a, 17]. Thus, **1** can be a good candidate for green light-emitting luminescent materials. Complex **2** shows a similar emission with the free ligand [11a], which can be attributed to the intraligand transition of H_3EIDC.

4. Conclusion

We have synthesized and structurally characterized three new supramolecular complexes based on 2-ethyl-imidazole-4,5-dicarboxylate with 1,10-phenanthroline, all of which exhibit 3-D supramolecular networks, weak intermolecular forces, such as the hydrogen-bonding interactions, π–π stacking interactions, and C–H · · · π interactions, play vital roles in constructing 3-D supramolecular networks. Complexes **1** and **2** display intense green and blue photoluminescence spectra in the solid state at room temperature and could be candidates of light-emitting luminescent materials. Further work on the design and synthesis of metal–organic frameworks with intriguing architectures and properties based on this ligand and bridging ligands is ongoing in our laboratory.

Supplementary material

CCDC 840629, 840630, and 866699 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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