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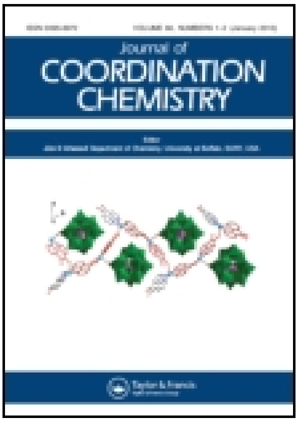

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Syntheses, structures, and properties of three MOFs based on tertbutylphenyl imidazole dicarboxylate

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Syntheses, structures, and properties of three MOFs based on tertbutylphenyl imidazole dicarboxylate

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By hydrothermal reactions of a newly designed ligand, 2-(*p*-tert-butylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid ($H_3BuPhIDC$) with Cd(II) or Zn(II), three metal-organic frameworks, $[Cd(\mu_3\text{-}HBuPhIDC)(H_2O)]\cdot 2H_2O$ (**1**), $[Cd(\mu_3\text{-}HBuPhIDC)(4,4'\text{-}bipy)_{0.5}]$ (4,4′-bipy = 4,4′-bipyridine) (**2**), and $[Zn_2(\mu_3\text{-}HBuPhIDC)_2(CH_3OH)_2]$ (**3**), have been obtained and characterized by elemental analyses, IR spectroscopy, and single-crystal X-ray diffraction. In **1**, small countless diamond grids form a mesh structure and then are bridged through μ_3-$HBuPhIDC^{2-}$ linkers building a 3-D framework. Compared with **1**, 4,4′-bipy participates in the construction of a 3-D structure of **2**. Polymer **3** shows an interesting 3-D open architecture, which contains infinite 1-D octagonal channels built by left- and right-handed helical chains. Thermal and solid-state photoluminescence properties of the polymers have been investigated.

Keywords: Imidazole dicarboxylate; Metal-organic framework; Crystal structure; Properties

1. Introduction

Metal-organic frameworks (MOFs) have attracted intense attention due to their intriguing structures [1–3] and potential applications in molecular magnetism, luminescence, catalysis, gas adsorption, etc. [4–6]. To obtain MOFs, the design and synthesis of promising bridging ligands are extremely important. People found that the geometry of ligating atoms within a ligand, the flexibility of the ligand backbone, and additional functional groups of the ligand all play important roles in construction of the resulting MOFs.

Due to the ability and versatility of carboxylate and imidazole in forming strong coordination bonds and generating abundant structural motifs, a large number of MOFs with imidazole-4,5-dicarboxylic acid (H_3IDC) or its two-position substituted derivatives have been reported [7–22]. Among them, imidazole dicarboxylate ligands bearing two-position phenyl substituted groups have attracted much attention [18–22]. This is not only because of their strong coordination ability but also their various coordination modes under appropriate reaction

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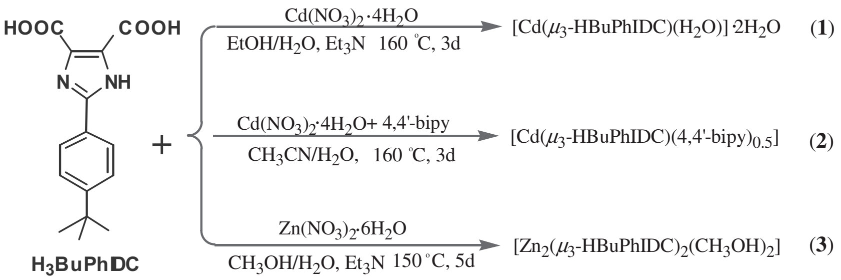


Scheme 1. The syntheses of **1**–**3**.

conditions. Several MOFs have been prepared and characterized. For examples, seven Cd(II), Mn(II), Pb(II), and Sr(II) MOFs based on 2-phenyl-1H-imidazole-4,5-dicarboxylic acid showing 1-D to 3-D structures have been prepared [18, 19]. Recently, we used 2-p-methoxyphenyl-1H-imidazole-4,5-dicarboxylic acid (H_3MOIDC) and 2-(3,4-dimethylphenyl)-1H-imidazole-4,5-dicarboxylic acid (H_3DMIDC) to synthesize four 1-D polymers $[Cu(\mu_2\text{-HMOPhIDC})(H_2O)]_n$, $[Zn(\mu_2\text{-HMOPhIDC})(2,2'\text{-bipy})]_n$ (2,2′-bipy = 2,2′-bipyridine), $[Co(\mu_2\text{-HMOPhIDC})(2,2'\text{-bipy})]_n$, $[Co(\mu_2\text{-HMOPhIDC})(phen)]_n$ (phen = 1,10-phenanthroline), two 2-D polymers $[Cd_{1.5}(\mu_2\text{-}H_2MOPhIDC)(\mu_3\text{-HMOPhIDC})(H_2O)]_n$ and $\{[Co_{1.5}(\mu_2\text{-}H_2MOPhIDC)(\mu_3\text{-HMOPhIDC})(py)]\cdot2H_2O\}_n$ (py = pyridine), and another two interesting polymers $\{[Co_3(\mu_3\text{-DMPhIDC})_2(H_2O)_6]\cdot2H_2O\}_n$ and $\{[Mn_5(\mu_3\text{-DMPhIDC})_2\text{-}(\mu_2\text{-HDMPhIDC})_2(Phen)_5]\cdot2CH_3OH\cdot3H_2O\}_n$ [20, 21]. These interesting findings prompt us to design similar imidazole dicarboxylate ligands and synthesize more MOFs.

Herein, we design and prepare 2-(*p*-tert-butylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid ($H_3BuPhIDC$) and explore its coordination features. To our excitement, three 3-D MOFs, $[Cd(\mu_3\text{-HBuPhIDC})(H_2O)]\cdot2H_2O$ (**1**), $[Cd(\mu_3\text{-HBuPhIDC})(4,4'\text{-bipy})_{0.5}]$ (4,4′-bipy = 4,4′-bipyridine) (**2**), and $[Zn_2(\mu_3\text{-HBuPhIDC})_2(CH_3OH)_2]$ (**3**), have been isolated (scheme 1). Their crystal architectures and properties are also presented.

2. Experimental

2.1. *Materials and instrumentation*

All chemicals were of reagent grade quality obtained from commercial sources and used without purification. $H_3BuPhIDC$ was prepared according to literature procedure [23].

The C, H, and N microanalyses were carried out on a FLASH EA 1112 analyzer. IR spectra were recorded on a BRUKER TENSOR 27 spectrophotometer as KBr pellets from 400 to 4000 cm^{-1}. TG measurements were performed by heating the crystalline sample from 20 to 700 °C at a rate of 10 °C min^{-1} in air on a Netzsch STA 409PC differential thermal analyzer. Fluorescence spectra were characterized at room temperature by a F-4500 fluorescence spectrophotometer. X-ray powder diffraction measurements were recorded on a PANalytical X’pert PRO X-ray diffractometer.

2.2. *Preparation of $[Cd(\mu_3\text{-HBuPhIDC})(H_2O)]\cdot2H_2O$ (1)*

A mixture of $Cd(NO_3)_2\cdot4H_2O$ (15.6 mg, 0.05 mM), $H_3BuPhIDC$ (14.5 mg, 0.05 mM) CH_3CH_2OH/H_2O (3/4, 7 mL), and Et_3N (0.014 mL, 0.1 mM) was sealed in a 25 mL

Teflon-lined stainless steel autoclave, heated at 160 °C for three days, and then cooled to room temperature. Block-shaped buff crystals of **1** were isolated, washed with distilled water, and dried in air (9.89 mg, 46% yield based on Cd). Anal. Calcd for $C_{60}H_{70}N_8O_{23}Cd_4$: C, 41.88; H, 4.10; N, 6.51%. Found: C, 41.70; H, 3.56; N, 6.34%. IR (cm^{-1}, KBr): 3422 (m), 2963 (m), 1663 (m), 1552 (s), 1461 (s), 1382 (m), 1269 (m), 1123 (m), 996 (w), 836 (w), 525 (w).

2.3. *Preparation of [Cd(μ_3-HBuPhIDC)(4,4′-bipy)$_{0.5}$] (2)*

A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (15.6 mg, 0.05 mM), H_3BuPhIDC (14.5 mg, 0.05 mM) 4,4′-bipy (7.8 mg, 0.05 mM), and CH_3CN/H_2O (5/2, 7 mL) was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 160 °C for three days, and then cooled to room temperature. Block-shaped colorless crystals of **2** were isolated, washed with distilled water, and dried in air (10.97 mg, 46% yield based on Cd). Anal. Calcd for $C_{20}H_{18}N_3O_4Cd$: C, 50.37; H, 3.78; N, 8.82%. Found: C, 50.24; H, 3.66; N, 8.94%. IR (cm^{-1}, KBr): 3430 (m), 2962 (m), 1679 (m), 1564(s), 1460 (s), 1389 (m), 1269 (m), 1121 (s), 1009 (w), 843 (w), 628 (w).

2.4. *Preparation of [Zn$_2$(μ_3-HBuPhIDC)$_2$(CH$_3$OH)$_2$] (3)*

A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (14.9 mg, 0.05 mM), H_3BuPhIDC (14.5 mg, 0.05 mM) CH_3OH/H_2O (5/2, 7 mL), and Et_3N (0.014 mL, 0.1 mM) was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 150 °C for five days, and then cooled to room temperature. Colorless block-shaped crystals of **3** were isolated, washed with distilled water, and dried in air (10.32 mg, 54% yield based on Zn). Anal. Calcd for $C_{32}H_{33}N_4O_{10}Zn_2$: C, 50.23; H, 4.31; N, 7.32%. Found: C, 50.09; H, 4.48; N, 7.04%. IR (cm^{-1}, KBr): 3385 (m), 2963 (m), 2869 (w), 1576 (s), 1464 (s), 1366 (m), 1282 (m), 1128 (m), 1005 (w), 843 (m), 759 (w).

2.5. *X-ray crystallography*

Crystal data and experimental details for **1–3** are contained in table 1. Measurements of **1–3** were made on a Bruker Smart APEXII CCD diffractometer with graphite-monochromated Mo-*Kα* radiation (λ = 0.71073 Å). Single crystals of **1–3** were selected and mounted on a glass fiber. All data were collected at room temperature using $\omega - 2\theta$ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied.

The three structures were solved by direct methods and expanded using the Fourier technique. Nonhydrogen atoms were refined with anisotropic thermal parameters. The final cycle of full-matrix least squares refinement was based on 29,511 observed reflections and 250 variable parameters for **1**, 26,313 observed reflections and 257 variable parameters for **2**, and 18,314 observed reflections and 441 variable parameters for **3**. The t-butyl group in **1** was disordered in two positions with site occupancy factors of 0.546 and 0.454, respectively. The hydrogen in protonated COO in **1** was found at reasonable positions in the difference Fourier map and located there. All hydrogens were included in the final refinement. All calculations were performed using SHELX-97 crystallographic software [24]. Selected bond lengths and angles are listed in table 2.

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

Compound	**1**	**2**	**3**
Formula	$C_{60}H_{70}N_8O_{23}Cd_4$	$C_{20}H_{18}N_3O_4Cd$	$C_{32}H_{33}N_4O_{10}Zn_2$
Fw	1720.84	476.77	764.36
Crystal system	Tetragonal	Tetragonal	Tetragonal
Crystal size (mm^3)	0.20 × 0.20 × 0.20	0.23 × 0.20 × 0.18	0.20 × 0.18 × 0.18
Space group	*I4(1)/a*	*I4(1)/a*	*I-4*
Unit cell dimensions (Å)			
a	21.9367(7)	21.9924(9)	20.611(3)
b	21.9367(7)	21.9924(9)	20.611(3)
c	16.3377(10)	17.6206(15)	16.284(4)
α	90	90	90
β	90	90	90
γ	90	90	90
V (Å^3)	7862.0(6)	8522.5(9)	6918(2)
Dc (Mg m^{-3})	1.450	1.486	1.468
Z	4	16	8
μ (mm^{-1})	1.138	1.053	1.447
Reflns. collected/unique	29,511/3466	26,313/5312	18,314/6556
	R(int) = 0.0388	R(int) = 0.0277	R(int) = 0.0720
Data/restraints/parameters	3466/1317/250	5312/0/257	6556/0/441
R^a	0.0483	0.0310	0.0552
R_w^b	0.1481	0.1002	0.1283
GOF on F^2	1.121	0.0995	0.967
$\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ (e Å^{-3})	−0.730 and 0.762	−0.520 and 1.481	−0.672 and 0.550

3. Results and discussion

3.1. *Synthesis*

Complexes **1–3** were synthesized under hydrothermal conditions at 150–160 °C. In order to optimize phase purities and yields, different solvent systems were used, pure water, water and ethanol mixrure, and water and acetonitrile mixrure. The reactions of metal salt and H_3BuPhIDC all in a molar ratio of 1 : 1 have produced crystals of **1–3**, while other stoichiometries failed to produce suitable crystals or give products with low yields (about 2.6%). For each compound, the pH needs to be about 8 before the solvothermal reaction, otherwise we could not obtain suitable crystals. Furthermore, the nature of anion in metal salt may also influence the formation of crystalline products. If the anions of metal salts used in **1–3** are replaced with Cl^-, SO_4^{2-} and OAc^-, only unidentified powder can be obtained. Complexes **1–3** have been obtained with moderate yield by the solvothermal reactions of metal salts and H_3BuPhIDC in mixed solutions ($EtOH/H_2O$ for **1**, CH_3CN/H_2O for **2**, $MeOH/H_2O$ for **3**). In preparations of **1–3**, change in organic solvent or adoption of hydrothermal synthesis cannot result in crystalline products of **1–3**, but some unidentified powder. The results indicate that forming frameworks of **1–3** is considerably influenced by the nature of the solution.

By controlling synthetic conditions such as solvent, pH, and metal/ligand molar ratio, the reproducibility of our experiments is good.

3.2. *Crystal structure of [Cd(μ$_3$-HBuPhIDC)(H$_2$O)]·2H$_2$O (1)*

Crystal structure data reveal that **1** is a 3-D framework. As shown in figure 1(a), the Cd^{2+} lies in a distorted octahedral coordination geometry with one oxygen from coordinated

Table 2. Selected bond distances (Å) and angles (deg) for **1**–**3**.

1					
Cd(1)–N(1)	2.206(4)	Cd(1)–N(2)#1	2.260(4)	Cd(1)–O(5)	2.273(5)
Cd(1)–O(4)#2	2.323(3)	Cd(1)–O(4)#1	2.371(4)	Cd(1)–O(1)	2.456(4)
N(1)–Cd(1)–N(2)#1	116.57(14)	N(1)–Cd(1)–O(5)	120.43(17)	N(2)#1–Cd(1)–O(5)	96.61(17)
N(1)–Cd(1)–O(4)#2	94.59(13)	N(2)#1–Cd(1)–O(4)#2	144.39(13)	O(5)–Cd(1)–O(4)#2	80.37(17)
N(1)–Cd(1)–O(4)#1	148.35(15)	N(2)#1–Cd(1)–O(4)#1	72.46(13)	O(5)–Cd(1)–O(4)#1	86.25(17)
O(4)#2–Cd(1)–O(4)#1	71.93(13)	N(1)–Cd(1)–O(1)	72.59(13)	N(2)#1–Cd(1)–O(1)	93.00(15)
O(5)–Cd(1)–O(1)	157.00(16)	O(4)#2–Cd(1)–O(1)	79.67(15)	O(4)#1–Cd(1)–O(1)	76.80(13)
2					
Cd(1)–N(1)	2.271(2)	Cd(1)–N(2)#1	2.310(2)	Cd(1)–N(3)	2.333(3)
N(2)–Cd(1)#3	2.310(2)	Cd(1)–O(1)	2.387(2)	Cd(1)–O(4)#2	2.442(2)
Cd(1)–O(4)	2.333(2)	O(4)–Cd(1)#2	2.442(2)		
N(1)–Cd(1)–N(2)#1	117.22(8)	N(1)–Cd(1)–N(3)	114.36(10)	N(2)#1–Cd(1)–N(3)	89.22(9)
N(1)–Cd(1)–O(4)	100.52(8)	N(2)#1–Cd(1)–O(4)	138.01(8)	N(3)–Cd(1)–O(4)	91.51(9)
N(1)–Cd(1)–O(1)	72.54(8)	N(2)#1–Cd(1)–O(1)	84.48(9)	N(3)–Cd(1)–O(1)	172.36(9)
O(4)–Cd(1)–O(1)	90.30(9)	N(1)–Cd(1)–O(4)#2	150.71(8)	N(2)#1–Cd(1)–O(4)#2	71.01(8)
N(3)–Cd(1)–O(4)#2	93.03(9)	O(4)–Cd(1)–O(4)#2	67.02(8)	O(1)–Cd(1)–O(4)#2	80.86(8)
3					
Zn(1)–N(4)#1	2.040(5)	Zn(1)–N(15)	2.083(5)	Zn(1)–O(9)	2.090(5)
Zn(1)–O(4)	2.186(4)	Zn(1)–O(1)	2.199(4)	Zn(1)–O(8)	2.271(4)
Zn(2)–N(3)	2.018(5)	Zn(2)–N(1)	2.087(5)	Zn(2)–O(10)	2.126(5)
Zn(2)–O(4)	2.170(5)	Zn(2)–O(1)	2.246(4)	Zn(2)–O(6)	2.294(5)
N(4)–Zn(1)#2	2.040(5)				
N(4)#1–Zn(1)–N(15)	110.5(2)	N(4)#1–Zn(1)–O(9)	110.3(2)	N(15)–Zn(1)–O(9)	100.6(2)
N(4)#1–Zn(1)–O(4)	95.63(18)	N(15)–Zn(1)–O(4)	150.99(18)	O(9)–Zn(1)–O(4)	81.04(19)
N(4)#1–Zn(1)–O(1)	157.13(19)	N(15)–Zn(1)–O(1)	78.61(18)	O(9)–Zn(1)–O(1)	87.62(19)
O(4)–Zn(1)–O(1)	72.50(15)	N(4)#1–Zn(1)–O(8)	78.79(18)	N(15)–Zn(1)–O(8)	92.39(18)
O(9)–Zn(1)–O(8)	159.89(17)	O(4)–Zn(1)–O(8)	80.19(17)	O(1)–Zn(1)–O(8)	79.93(16)
N(3)–Zn(2)–N(1)	118.2(2)	N(3)–Zn(2)–O(10)	111.6(2)	N(1)–Zn(2)–O(10)	96.0(2)
N(3)–Zn(2)–O(4)	151.81(19)	N(1)–Zn(2)–O(4)	79.64(18)	O(10)–Zn(2)–O(4)	86.08(19)
N(3)–Zn(2)–O(1)	89.11(18)	N(1)–Zn(2)–O(1)	151.44(18)	O(10)–Zn(2)–O(1)	80.09(18)
O(4)–Zn(2)–O(1)	71.90(15)	N(3)–Zn(2)–O(6)	78.93(18)	N(1)–Zn(2)–O(6)	95.28(19)
O(10)–Zn(2)–O(6)	158.25(17)	O(4)–Zn(2)–O(6)	77.71(17)	O(1)–Zn(2)–O(6)	81.13(17)

Symmetry transformations used to generate equivalent atoms for **1**: #1: *y* − 1/4, −*x* + 3/4, *z* − 1/4. #2: −*y* + 1/4, *x* + 1/4, −*z* + 1/4. #3: *y* − 1/4, −*x* + 1/4, −*z* + 1/4. #4: −*y* + 3/4, *x* + 1/4, *z* + 1/4. For **2**: #1: *y* − 1/4, −*x* + 3/4, *z* − 1/4. #2: −*x*, −*y* + 1, −*z*. #3: −*y* + 3/4, *x* + 1/4, *z* + 1/4. #4: −*y* + 1/4, *x* + 1/4, −*z* + 1/4. #5: *y* − 1/4, −*x* + 1/4, −*z* + 1/4. #6: −*x*, −*y* + 3/2, *z*. For **3**: #1: −*y* + 2, *x*, −*z* + 2. #2: *y*, −*x* + 2, −*z* + 2. #3: *y* + 1/2, −*x* + 3/2, −*z* + 3/2. #4: −*y* + 3/2, *x* − 1/2, −*z* + 3/2.

water, two nitrogens, and three oxygens from three different HBuPhIDC^{2-} ligands. Two μ_3-HBuPhIDC^{2-} coordinate to Cd^{2+} with O, N chelating donors (N1, O1, N2a and O4a) to form two five-membered chelating rings and the other independent μ_3-HBuPhIDC^{2-} provides O4b to also coordinate to cadmium. The Cd-O$_{\text{carboxyl}}$ bond distances are 2.273(5)–2.455(4) Å and Cd-N$_{\text{imidazole}}$ distances are 2.206(4) and 2.260(4) Å, respectively, all of which are comparable to those reported for other imidazole-based dicarboxyate Cd(II) complexes [18]. H_3BuPhIDC are doubly deprotonated and imidazole-based dicarboxyates serve as bridges to connect Cd^{2+} ions via monodentate and bidentate modes (scheme 2).

In **1**, HBuPhIDC^{2-} shows only one coordination mode, μ_3-kN,O: kO: kN′,O′. The μ_3-HBuPhIDC^{2-} in **1** link Cd(II) ions to propagate octahedra into a serrated polymeric chain (figure 1(b)). These chains are connected into a fascinating 2-D structure (figure 1(c)) through O, N chelating μ_3-HBuPhIDC^{2-}. The 2-D grid sheet contains infinite repeating subunits which are comprised of four Cd(II) cations and nine μ_3-HBuPhIDC^{2-} anions (figure 1(d)). Figure 1(b) shows that Cd–O–Cd–O forms a small diamond. In this structure, there are infinite dimeric [Cd_2O_2] cores which are constructued by two Cd(II) cations and two carboxylate oxygens from two μ_3-HBuPhIDC^{2-}. Consequently, these dimeric cores are

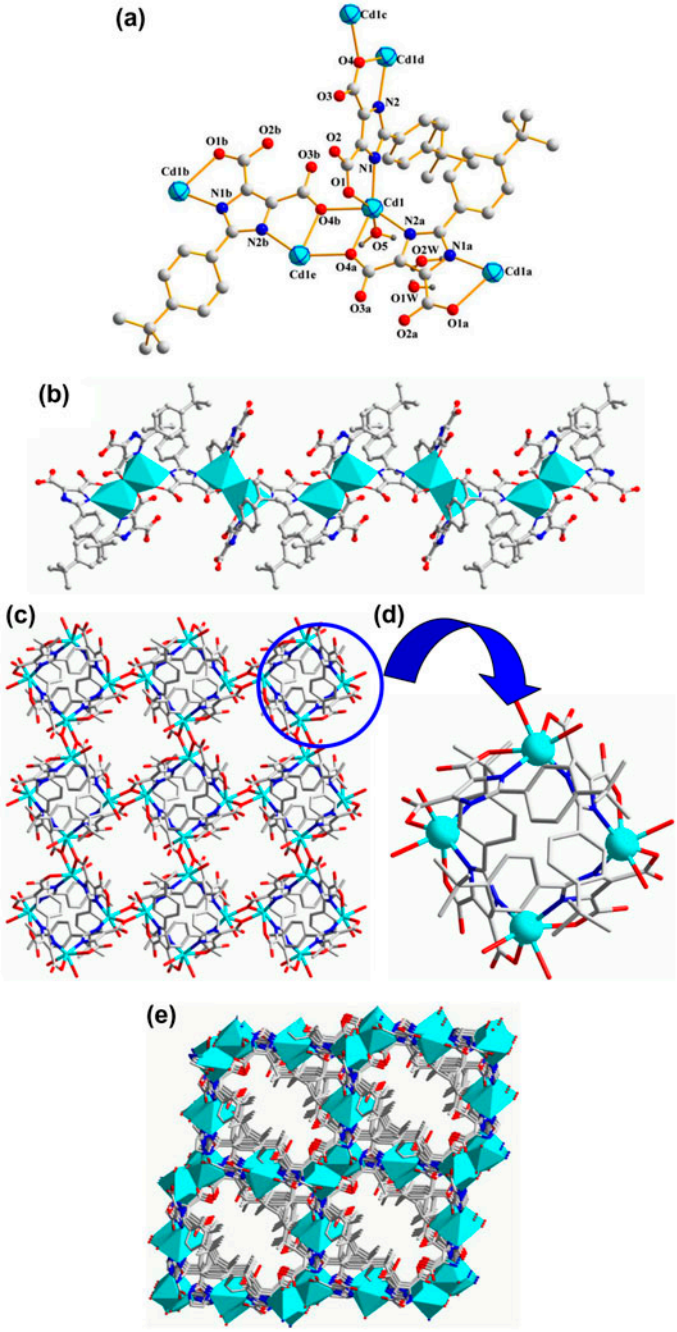
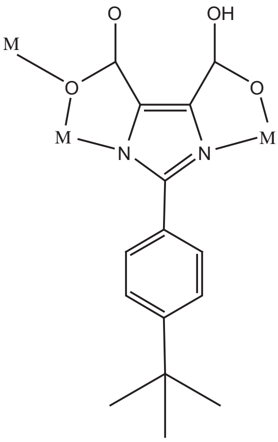


Figure 1. (a) Coordination environment of Cd(II) with atom labels in **1** (hydrogens and solvent are omitted for clarity; 50% thermal ellipsoids). (b) The chain of **1** is supported by Cd(II) and μ_3-HBuPhIDC^{2-} (hydrogens are omitted for clarity). (c) The grid sheet contains infinite repeating subunits which are comprised of four Cd(II) cations and nine μ_3-HBuPhIDC^{2-} anions (hydrogens are omitted for clarity). (d) The subunit of the sheet in **1** (hydrogens are omitted for clarity). (e) The 3-D framework of **1** (hydrogens are omitted for clarity; color code: Cd: turquiose; O: red; N: blue; C: gray) (see http://dx.doi.org/10.1080/00958972.2013.830288 for color version).



Scheme 2. Coordination mode of HBuPhIDC^{2-} anion.

linked by the organic ligands to form a 2-D grid which contains countless 4Cd and 8Cd rings (figure 1(c)). The 2-D grids are conjoined by the organic ligands to build up a 3-D architecture (figure 1(e)).

3.3. *Crystal structure of [Cd(μ$_3$-HBuPhIDC)(4,4′-bipy)$_{0.5}$] (2)*

Single-crystal X-ray analysis reveals that **2** is in the tetragonal *I*4(1)/a space group, as is **1**. It is assembled in a 3-D framework with one Cd(II), one HBuPhIDC^{2-}, and a half 4,4′-bipy in each asymmetric unit. Similar to **1**, the coordination geometry around Cd1 can be described as a distorted octahedron and dimeric cores of [Cd_2O_2] can be formed. As shown in figure 2(a), Cd1 is coordinated with three oxygens (O1, O4, O4b) and two nitrogens (N1, N2a) from three individual μ$_3$-HBuPhIDC^{2-} in μ$_3$-kN,O: kO: kN′,O′ mode (scheme 2) and one nitrogen (N3) from a 4,4′-bipy. The coordination environment of **2** is similar to **1** except that N3 from 4,4′-bipy in **2** replaces O5 from coordinated water in **1**. The Cd–N distances are 2.271(2) and 2.333(3) Å and Cd–O lengths vary from 2.333(2) to 2.442(2) Å, comparable to previously reported values [25]. The bond angles around each Cd(II) vary from 67.02(8) to 172.36(9).

Two nitrogens from each μ$_3$-HBuPhIDC^{2-} bridge a four-membered ring, Cd1-O4-Cd1-O4, to form a 1-D zigzag chain. In the four-membered ring, the distance from Cd(II) and Cd(II) is 3.9818(3) Å. 1-D infinite chains are linked to a 2-D layer by bridging 4,4′-bipy (figure 2(c)). The Cd-4,4′-bipy-Cd has a slight curvature with dihedral angles between the two pyridine rings within a 4,4′-bipy and between Cd-$N_{4,4'\text{-bipy}}$ bond the neighboring pyridine ring of 33.8 and 109.8°, respectively, indicating a large twist. This can be found in the related 4,4′-bipy-based coordination polymers [26–28]. The structure looks like an intersection of four rings in which each ring contains eight Cd(II) ions. Adjacent parallel 2-D layers are further linked to construct a 3-D framework by bridging μ$_3$-HBuPhIDC^{2-} (figure 2(d)).

3.4. *Crystal structures of [Zn$_2$(μ$_3$-HBuPhIDC)$_2$(CH$_3$OH)$_2$] (3)*

Single-crystal X-ray analyses reveal that **3** shows an open 3-D architecture. The asymmetrical unit of **3** consists of two Zn^{2+} ions, two discrete HBuPhIDC^{2-}, and two coordinated

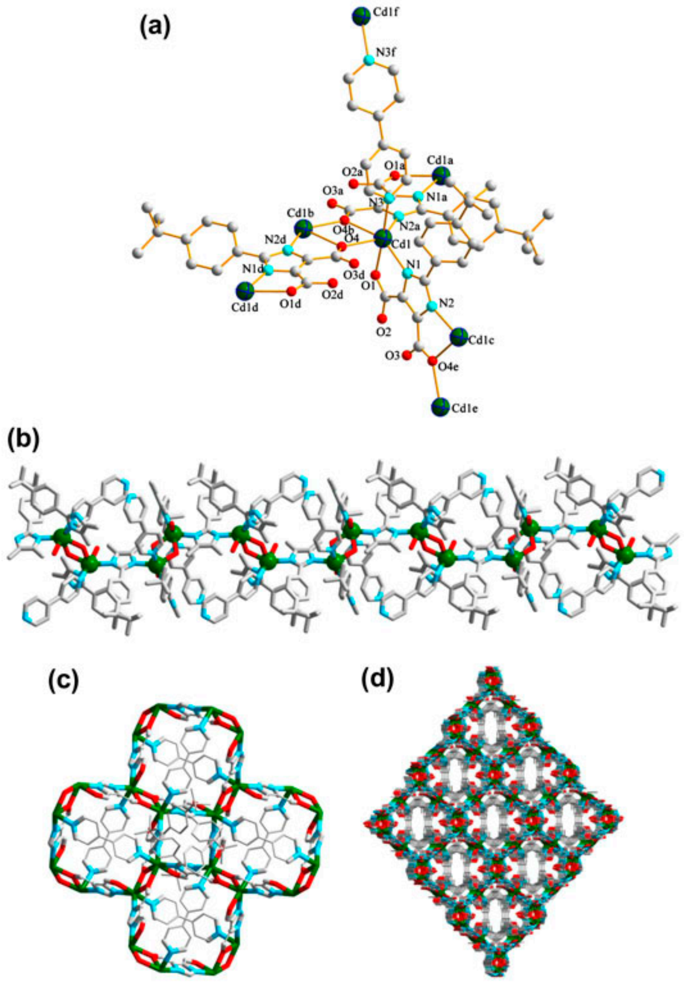


Figure 2. (a) Coordination environment of Cd(II) with atom labels in **2** (hydrogens are omitted for clarity; 50% thermal ellipsoids). (b) The chain of **2** supported by Cd(II) and μ_3-HBuPhIDC^{2-} (hydrogens are omitted for clarity). (c) Schematic representation of the 2-D layer structure of **2** (hydrogens are omitted for clarity). (d) The 3-D framework of **2** (some atoms omitted for clarity; color code: Cd: green O: red; N: sky blue; C: gray) (see http://dx.doi.org/10.1080/00958972.2013.830288 for color version).

methanols. Two Zn ions are bridged by two imidazole dicarboxylates forming a dimeric core. Each Zn(II) is in a slightly distorted octahedral geometry [ZnN_2O_4] with two imidazole nitrogens (N5 and N4a) and two carboxylate oxygens (O8 and O1) from two individual HBuPhIDC^{2-} anions, one carboxylate oxygen (O4) from another μ-bridging HBuPhIDC^{2-}, and one oxygen (O9) from coordinated methanol (figure 3(a)). Zn-N bond lengths are 2.018 (5) and 2.087(5) Å, while the Zn-O distances are 2.090(5) to 2.294(5) Å with no significant difference from those reported [29]. Each HBuPhIDC^{2-} in **3** adopts the same coordination as that in **1** linking three Zn ions by μ_3-kN, O: kO: kN′, O′ mode (scheme 2). The distance between two dinuclear Zn^{2+} ions is 3.5545(10) Å. As viewed from the *bc*-plane (figure 3 (b)), the 2-D grid can be observed, constructed by conjoining the 1-D left- and right-handed helical chains. These helical chains are from N$_{imidazole}$ of HBuPhIDC^{2-} bridging neighboring metal centers. Individual ring structures as secondary building units present clearly in the grid, while the ring structure looks like a rhombus window of approximate dimensions 10.893 × 10.893 Å. Neighboring 2-D layers are further connected via μ-bridging carboxylate, giving a 3-D framework with 1-D channels (figure 3(c)). In order to better understand the 3-D network, we simplified this through topological considerations (figure 3(d)).

3.5. *Infrared spectra, XRD patterns, thermal analyses and luminescent properties*

Compounds **1–3** have strong and broad absorption bands at 3400–3500 cm^{-1} which indicate the presence of ν_{N-H} or ν_{O-H} from imidazole or water, respectively. The polymers exhibit strong absorptions at 1540–1660 cm^{-1} ($\nu_{as}COO^-$) and 1400–1475 cm^{-1} ($\nu_{s}COO^-$). The vibration of phenyl ring is observed at 1461 cm^{-1} for **1**, 1460 cm^{-1} for **2**, and 1464 cm^{-1} for **3**. The IR band of the tertbutyl due to $\delta_{=C-H}$ can be found at 1382 cm^{-1}, 1389 cm^{-1}, and 1366 cm^{-1} for **1**, **2,** and **3**, respectively.

To confirm the phase purity of these polymers, XRPD patterns were recorded for **1–3** and most of the peak positions of the simulated and experimental patterns are in agreement with each other. Dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples (Supplementary material).

In order to estimate thermal stabilities of the MOFs, thermal gravimetric analyses of **1–3** were carried out in air (Supplementary material). For **1**, weight loss from 58.2 to 301.3 °C corresponds to release of two free and one coordinated water (observed 5.27%, Calcd 6.29%). It keeps losing weight from 301.3 to 356.2 °C, attributed to loss of carboxyl groups of $HBuPhIDC^{2-}$ (observed 16.65%, Calcd 17.24%). The major weight loss occurs above 356.2 °C from decomposition of the remaining $HBuPhIDC^{2-}$ (observed 46.16%, Calcd 46.27%). A plateau is observed from 479.9 to 650 °C; a white amorphous residue is 4CdO (observed 31.92%, calculated 29.91%).

For **2**, a plateau from 29.9 to 391.8 °C proves that **2** has good thermal stability. Weight loss of 72.92% (Calcd 73.10%) from 391.8 to 456.1 °C corresponds to the release of the organic fragments. Finally, the curve shows another plateau from 456.1–700 °C. The remaining weight of 27.08% corresponds to the percentage (Calcd 26.89%) of the Cd and O components, indicating that the final product is CdO.

For **3**, there is no obvious weight loss before 100.5 °C. Weight loss from 100.5 to 198.7 °C (observed 8.51%, Calcd 8.35%) corresponds to the release of two coordinated methanols. A slow weight loss of 10.90% covering 340.5–387.9 °C corresponds to partial destruction of $HBuPhIDC^{2-}$. When the temperature is higher than 387.9 °C, the remaining $HBuPhIDC^{2-}$ is removed (observed 58.89%, Calcd 59.00%). The final residue is 2ZnO (observed 21.79%, Calcd 21.14%).

Because Zn(II) and Cd(II) MOFs usually exhibit good optical properties, the solid-state photoluminescent properties of **1–3** and the corresponding free ligand $H_3BuPhIDC$ have been investigated at room temperature (figure 4). Free $H_3BuPhIDC$ displays luminescence with the emission at maximum 385 and 342 nm, respectively, attributed to $\pi^* \rightarrow n$ transition. Compound **1** shows a broad emission at 370 nm when excited at 323 nm, **2** exhibits a broad emission at 480 nm when excited at 316 nm, and **3** exhibits a broad emission at 369 nm when excited at 332 nm. Since Cd^{2+} and Zn^{2+} are difficult to oxidize or reduce, emissions are neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer [30]. Compared with free $H_3BuPhIDC$, **1** has blue shift of 25 nm, **2** red shift of 83 nm, and **3**

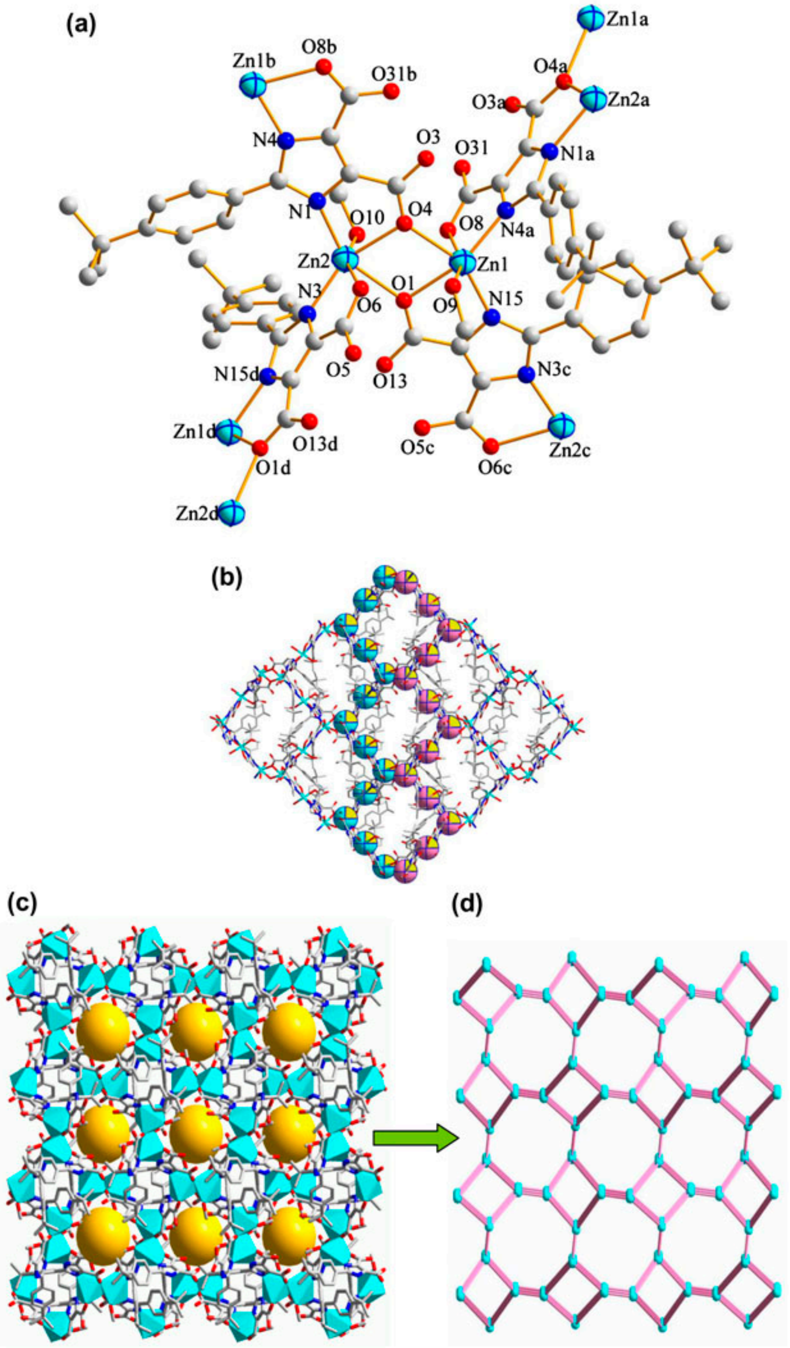


Figure 3. (a) Coordination environments of Zn(II) in **3** (hydrogens and solvent are omitted for clarity; 50% thermal ellipsoids). (b) The layer of **3** viewed along the *a*-axis (hydrogens and solvent are omitted for clarity; to label the left- and right-handed helical chains we magnify the two lines of Zn(II) in the middle). (c) Crystal packing diagram of **3** along the *a*-axis showing the *π*-*π* stacking between the zigzag chains (hydrogens are omitted for clarity; color code: Zn: turquiose; O: red; N: blue; C: gray). (d) The simplified topological consideration of the 3-D network of **3** (the organic ligands are presented by pink lines, Zn by point symbol) (see http://dx.doi.org/10.1080/00958972.2013.830288 for color version).

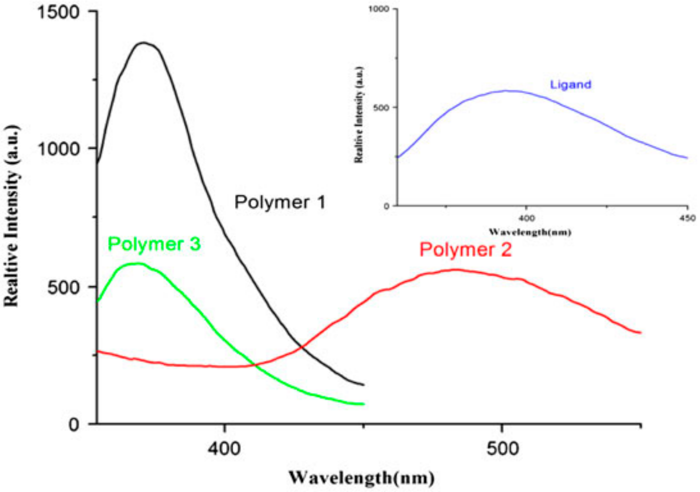


Figure 4. The solid-state photoluminescent spectra of free H_3BuPhIDC (blue), **1** (dark), **2** (red), and **3** (green) at room temperature (see http://dx.doi.org/10.1080/00958972.2013.830288 for color version).

blue shift of 31 nm. The different emission bands of the three polymers may be due to the coordination diversities of the metal centers and the rigidity differences of coordination modes [31].

4. Conclusion

Three transition-metal-organic architectures have been prepared by using H_3BuPhIDC. Their molecular structures have been characterized by single-crystal X-ray diffraction, elemental analyses, thermal analyses, and IR spectra. Modification of organic ligands is an effective way to get different complexes. Obviously, more new MOFs need to be explored using this ligand.

There are a number of reported two-position substituted imidazole dicarboxylate-based Cd(II) [9, 15, 17] and Zn(II) [14–16] coordination polymers which are mainly built by 2-position aliphatic hydrocarbons substituted derivatives. However, Cd(II) [7, 11, 12, 18–20] and Zn(II) [20] polymers constructed from two-position aromatic groups substituted are limited, especially from H_3BuPhIDC.

Supplementary material

Crystallographic data for the structure reported in this article in the form of CIF file has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. 895527, 919806 and 895528 for **1–3**, respectively. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

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