Synthesis, structures and fluorescent properties of cadmium/zinc coordination polymers with 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene and 1,3,5-benzenetricarboxylic acid

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ABSTRACT

The compounds $[Cd_2^{II}(titb)(BTC)Cl]_n$ (**1**), $[Zn_2^{II}(titb)(BTC)Cl]_n$ (**2**) and $[Zn_2^{II}(titb)(BTC)NO_3]_n$ (**3**), were synthesized with mixed ligands of 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titb) and 1,3,5-benzenetricarboxylic acid (H_3BTC) by solvothermal reactions. All of the three compounds feature novel structurally characterized tri-carboxylate bridged bimetallic units. The binuclear units, completed by titb ligands, are linked by BTC^{3-} anions. X-ray single crystal diffraction analysis reveals that **1** and **2** are isomorphs and each metal-organic frameworks (MOFs) has interesting (3, 6)-connected net topology by self-penetration of two sets of (10, 3)-a nets. Fluorescent analyses in the solid state of **1**, **2** and **3** shows that they may be potential photoactive materials.

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1. Introduction

The design and synthesis of novel metal-organic frameworks (MOFs) attracts great attention by chemists not only due to their intriguing structural diversities and novel topologies but also owing to the large majority of useful properties and great potential applications as functional materials [1–4]. One of the reasonable approaches to obtain such kind of MOFs is employing multidentate organic ligands to connect to metal ions with definite coordination geometry to give coordination frameworks [5–8]. Indeed, the structural and property studies of a myriad of reported coordination polymers have been elaborated by controlling the molecular properties of the organic ligands such as size, shape, functionality, flexibility, steric torsion and symmetry [4,9,10]. The use of both known and new metal-organic clusters as secondary building units (SBUs) can be generally applied to understanding, determining, and predicting new structure patterns and topologies of MOF structures [11]. Yaghi and his co-workers developed many SBUs using multidentate carboxylate functionalities, such as MOF-35, MOF-36, MOF-37 and so on [11]. From this strategy most porous MOFs were formed with rigid multidentate organic ligands. How-

ever, to access tailor-made solids with the required structures and properties from so-called default structures is a lasting challenge to chemists [12]. On considering that nonrigid ligands play a pivotal role in fabricating entangled structures due to their diverse conformations when coordinate to metals, Wang and co-workers used 1,4-bis(1,2,4-triazol-1-yl)butane and 4,4′-oxy-bis(benzoate) in their study [13]. The molecular entanglement in terms of catenanes, rotaxanes and knots is very fascinating in view of their aesthetic and often complicated architectures and topologies [14,15]. Furthermore, the overall architectural flexibility of self-penetrating MOFs has potential applications ranging from drug delivery vehicles to sensor devices [15,16]. So, further study of such species might pave a way to the exploitation of function materials. To our knowledge, the reported flexible imidazole-based tridentate ligands are relatively rare to date [17–22]. Hence, we selected 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titb) in our study since it usually has two different conformations (*cis*, *cis*, *cis* and *cis*, *trans*, *trans*) in coordination polymers. As a result, three compounds, namely, $[Cd_2^{II}(titb)(BTC)Cl]_n$ (**1**), $[Zn_2^{II}(titb)(BTC)Cl]_n$ (**2**) and $[Zn_2^{II}(titb)(BTC)NO_3]_n$ (**3**) with novel (3, 6)-connected nets by self-penetration of two sets of (10, 3)-a nets were obtained via the solvothermal reaction of Cd^{2+} (or Zn^{2+}) with mixed ligands of titb and H_3BTC (H_3BTC = 1,3,5-benzenetricarboxylic acid). The photoluminescence properties of these three compounds were also studied here.

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2. Experimental

2.1. Physical measurements

The infrared spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer in KBr matrices. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyser. Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer.

2.2. Preparation of the ligand and the compounds

All reagents except that titb was synthesized according to the reported method [17] were purchased commercially and used without further purification. $CdCl_2$ (0.2 mmol), H_3BTC (0.1 mmol) and titb (0.1 mmol) were placed in a 25 mL of Teflon-lined stainless steel vessel with 8 mL of mixed-solvent of H_2O and ethanol ($V/V = 3:1$). The mixture was heated to 160 °C in 4 h and kept to this temperature for 3 days. After cooling to room temperature at a rate of 2.5 °C/h, pale yellow crystals of **1** were obtained with the yield of about 45%. Compounds **2** and **3** were obtained by used $ZnCl_2$ and $Zn(NO_3)_2$ to substitute $CdCl_2$ with the yield of about 39% and 52%, respectively. Elemental analysis: **1**, $C_{30}H_{27}Cd_2N_6O_6Cl$, Calc.: C, 43.53; H, 3.29; N, 10.15%. Found: C, 43.27; H, 3.63; N, 10.09%. **2**, $C_{30}H_{27}Zn_2N_6O_6Cl$, Calc.: C, 49.11; H, 3.71; N, 11.45%. Found: C, 48.68; H, 3.94; N, 11.29%. **3**, $C_{10}H_9Zn_{0.67}N_{2.33}O_3$, Calc.: C, 47.39; H, 3.58; N, 12.90%. Found: C, 46.78; H, 4.01; N, 12.43%. FT-IR (cm^{-1}) (KBr disk): for **1**: 3120w, 1627vs, 1518w, 1363s, 1229w, 1092m, 763m, 618m for **2**: 3126vw, 1642vs, 1518w 1358s, 1230w, 1090m, 763m for **3**: 3120vw, 1642vs, 1519w, 1360s, 1229w, 1092m, 762m.

2.3. X-ray crystallographic data collection and refinement

Single crystals with dimensions of $0.25 \times 0.22 \times 0.22$ mm for **1**, $0.20 \times 0.15 \times 0.15$ mm for **2** and $0.22 \times 0.20 \times 0.20$ mm for **3** were selected and mounted on a glass fiber, respectively. Data collection was performed at 293(2) K on a Mercury CCD diffractometer equipped with a graphite-monochromated $MoK\alpha$ $(\lambda = 0.71073 \text{ Å})$ by using φ and ω scan mode in the ranges of $2.38 < \theta < 27.48°$, $2.41 < \theta < 27.48°$ and $2.77 < \theta < 27.48°$ for **1**, **2** and **3**, respectively.

The structures were solved by direct methods with SHELXS-97 [23]. The H atoms were assigned in the calculated sites and the final refinement in the riding model approximation, with displacement parameters derived from the mother atoms to which they were bonded. In compound **3**, the NO_3 groups were refined with partial occupancies, with N—O distances restrained to 1.24 Å and O—O distances 2.15 Å. Disorder for the atoms N3, O3 and O5 of the NO_3^- group in compound **3** was resolved and successfully modeled in a 1:1:1 ratio. The full-matrix least-squares refinement on F^2 was carried out with SHELXL-97 [24]. The crystallographic data and details of refinements for compounds **1–3** are summarized in Table 1; selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Spectroscopic studies

The IR spectra of compounds **1**, **2** and **3** (Supplementary Figs. S1–S3) show the presence of vibrational bands 1642–1550 cm^{-1}, which are characteristic of the asymmetric stretching of the deprotonated carboxylic groups of BTC^{3-} ligand. And the symmetric vibrations of the complete deprotonated carboxylic groups are the absorptions at 1432–1358 cm^{-1}. The C—H stretching vibration of imidazole group is at 3120–3126 cm^{-1}. The band of C=N is at 1518–1519 cm^{-1} [25]. Other complicated peaks show the characteristic C—H and C—C vibrational frequencies for the mesitylene rings of titb ligands and the C—C vibrational frequencies for the phenyls of BTC^{3-} ligands.

3.2. Crystal structures of $[Cd_2^{II}(titb)(btc)Cl]_n$ (**1**), $[Zn_2^{II}(titb)(btc)Cl]_n$ (**2**) and $[Zn_2^{II}(titb)(btc)NO_3]_n$ (**3**)

Compounds **1** and **2** are isomorphs for they have the same space group and the similar cell parameters (Table 1), compound **3** has a very similar topology structure with compound **1**, so we describe the structure of compound **1** in detail for simplicity. X-ray single-crystal diffraction analysis reveals that the fundamental unit of **1** consists of two cadmium centers, one crystallographical titb ligand, one crystallographical BTC^{3-} ligand and one chlorine atom (Fig. 1). Two cadmium centers (Cd1 and Cd2), which are bridged

Table 1
Crystal data and structure refinement details of compounds **1–3**.

	1	2	3
Formula	$C_{30}H_{27}Cd_2N_6O_6Cl$	$C_{30}H_{27}Zn_2N_6O_6Cl$	$C_{10}H_9Zn_{0.67}N_{2.33}O_3$
fw	827.83	733.77	253.44
Temp (K)	293(2)	293(2)	293(2)
Cryst syst	Orthorhombic	Orthorhombic	Cubic
Space group	P2(1)2(1)2(1)	P2(1)2(1)2(1)	P2(1)3
a (Å)	14.1833(6)	14.1150(8)	14.7046(2)
b (Å)	15.0437(6)	14.7916(7)	14.7046(2)
c (Å)	15.3021(6)	15.1031(8)	14.7046(2)
V (Å³)	3265.0(2)	3153.3(3)	3179.51(7)
Z	4	4	12
ρ (Mg/m³)	1.684	1.546	1.588
μ (mm⁻¹)	1.435	1.658	1.274
F(0 0 0)	1640	1496	1552
Limiting indices	$-17 \leftarrow h \leftarrow 18 - 17 \leftarrow k \leftarrow 19 - 19 \leftarrow l \leftarrow 19$	$-17 \leftarrow h \leftarrow 18 - 19 \leftarrow k \leftarrow 18 - 12 \leftarrow l \leftarrow 19$	$-15 \leftarrow h \leftarrow 19 - 18 \leftarrow k \leftarrow 19 - 18 \leftarrow l \leftarrow 19$
No. of rflns collected	25098	24625	24729
No. of unique rflns	6799 ($R_{int} = 0.0397$)	6484($R_{int} = 0.0386$)	2359($R_{int} = 0.0259$)
No. of data/restraints/params	7475/0/406	7220/0/401	2423/6/147
Goodness of fit on F^2	1.044	1.065	1.057
R values ($I > 2\sigma(I)$)	$R_1 = 0.0335$, $wR_2 = 0.0800$	$R_1 = 0.0407$, $wR_2 = 0.0894$	$R_1 = 0.0332$, $wR_2 = 0.0842$
R values (all data)	0.0374	0.0482	0.0343
Abs structure param	0.00(2)	0.006(12)	0.006(18)
Peak and hole (e Å⁻³)	−0.578 and 1.162	−0.385 and 0.561	−0.710 and 0.433

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