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# Syntheses, crystal structures, substituents steric effect, luminescent and moisture-stability studies of three two-dimensional zinc-organic frameworks

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### ABSTRACT

Three new 2D zinc-organic frameworks,  $[Zn_3(L1)_3(DMF)_2]_n$  (1),  $[Zn(L2)(BPP)]_n$  (2) and  $[Zn_2(L3)_2(BPP)]_n \cdot nDMF$  (3), (L1 = 2,5-dimethylterephthalate, L2 = 2-aminoterephthalate, L3 = terephthalate, BPP = 1,3-bis(4-pyridyl)propane, DMF = *N*,*N*-dimethylformamide), have been prepared and characterized. Complex 1 consists of trinuclear zinc clusters connected to six L1 ligands, in which the trinuclear clusters act as pseudo-planar hexagonal nodes to give a 2D network. In complex 2, two 4<sup>4</sup>-sql nets interlock in parallel and give rise to a polycatenated layer (2D  $\rightarrow$  2D). Complex 3 features a 2D (4,4) net when the dinuclear [ $Zn_2(COO)_2N_2O_2$ ] unit is regarded as a quadruply-connected node. These results indicate that the steric effect of 1,4-benzenedicarboxylates substituents has an important effect on the structural topologies of such Zn(II) complexes. All of 1–3 emit the intense indigotin photoluminescence at room temperature, with lifetimes of 28.04, 3.08 and 2.43 ns, respectively. The moisture-stability analyses of 1–3 have also been investigated.

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# 1. Introduction

The design and synthesis of Metal–Organic Frameworks (MOFs) have received widespread attention in recent years due to their potential applications in gas separation, catalysis, magnetism, optics and so on [1]. Studies in these fields have been focused on the design and preparation, as well as on structure-property relationships. Significant progress has been achieved [2]. However, it is still a great challenge to rationally prepare and predict their exact structures, as many factors can affect the overall structure formation. In addition to the choice of ligands and metal ions, reaction conditions such as solvent, pH and temperature can also affect the final structure [3]. Rational design of ligands is usually a useful and important way of studying the controllable synthesis of the resulting MOF structures [4]. Based on this understanding, we have selected three aromatic dicarboxylic anions with different substituents: 2,5-dimethylterephthalic acid (L1), 2-aminoterephthalic acid (L2), and terephthalic acid (L3), chosen according to the following considerations: (1) these phenyl dicarboxylates contain two para-carboxyl groups and different substituents, which can engender spatial effects and thus influence the structural assembly in several different ways [5]; (2) a systemic study of the substituent effects on the generation of such carboxylate coordination frameworks is surprisingly scarce, and much work is still necessary to understand the coordination chemistry [6]. Furthermore, in recent decades, a variety of fascinating coordination polymers have been constructed by carboxylate ligands and N-containing ligands as the auxiliary ligands [7]. It is widely recognized that the flexible 1,3-bis(4-pyridyl)propane ligand (BPP) is an excellent candidate for constructing novel structures as the auxiliary ligands and may act as a bidentate bridge with different conformations or in a monodentate terminal mode, leading to the formation of a variety of 1D chain, 2D layer and 3D network motifs [8].

Extending our previous work on self-assembly of coordination networks as a function of pH [3a], we are studying the substituents steric effects of the 1,4-benzenedicarboxylate ligands on framework formation of the coordination complexes. Three different Zn(II) complexes:  $[Zn_3(L1)_3(DMF)_2]_n$  (1),  $[Zn(L2)(BPP)]_n$  (2) and  $[Zn_2(L3)_2(BPP)]_n \cdot nDMF$  (3), have been successfully isolated by solvothermal conditions and characterized by elemental analysis, IR, TGA, powder X-ray diffraction and single-crystal X-ray diffraction. The photoluminescent properties and moisture-stability of 1–3 are also reported in this paper.

# 2. Experimental

#### 2.1. Materials and physical measurements

All chemicals were commercially available and used as received without further purification. Elemental analyses for C, H, and N

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| Table 1   |
|---|
| Crystal data and structure refinement details of 1-3. |

| Compounds   | 1                           | 2                      | 3   |
|---|-----------------------------|------------------------|---|
| Formula   | $C_{36}H_{38}N_2O_{14}Zn_3$ | $C_{21}H_{19}N_3O_4Zn$ | C <sub>32</sub> H <sub>29</sub> N <sub>3</sub> O <sub>9</sub> Zn <sub>2</sub> |
| Formula weight  | 918.79                      | 442.76                 | 730.32  |
| Crystal system  | monoclinic                  | orthorhombic           | monoclinic  |
| Space group   | C2/c                        | Pbca                   | $P2_1/m$  |
| a (Å)   | 23.719(2)                   | 11.8253(18)            | 8.4580(7)   |
| b (Å)   | 10.7570(9)                  | 17.268(3)              | 21.6474(18)   |
| c (Å)   | 16.0846(13)                 | 19.299(3)              | 9.4309(8)   |
| α (°)   | 90.00                       | 90.00                  | 90.00   |
| β (°)   | 105.226(2)                  | 90.00                  | 109.884(2)  |
| γ (°)   | 90.00                       | 90.00                  | 90.00   |
| $V(Å^3)$  | 3959.9(6)                   | 3940.9(10)             | 1623.8(2)   |
| Ζ   | 4                           | 8                      | 2   |
| $D_{\text{calc}}(g/\text{cm}^3)$                                    | 1.541                       | 1.493                  | 1.494   |
| $\mu ({\rm mm^{-1}})$   | 1.870                       | 1.279                  | 1.534   |
| F(000)  | 1880                        | 1824                   | 748   |
| Reflections collected   | 10793                       | 15311                  | 9316  |
| Independent reflections (R <sub>int</sub> )                         | 3534 (0.0322)               | 3511 (0.0690)          | 2991 (0.0251)   |
| Parameters  | 255                         | 262                    | 232   |
| Goodness-of-fit (GOF) on $F^2$                                      | 1.039                       | 1.015                  | 1.086   |
| $R_1 \left[ I > 2\sigma(I) \right]^a$                               | 0.0348                      | 0.0641                 | 0.0352  |
| $wR_2$ (all data) <sup>b</sup>                                      | 0.0885                      | 0.1718                 | 0.0976  |
| $\Delta  ho_{ m maximum}$ and $_{ m mininimum}$ (e/A <sup>3</sup> ) | 0.613 and -0.398            | 1.038 and -0.430       | 0.469 and -0.362  |

<sup>a</sup>  $R = \sum (||F_o| - |F_c||) / \sum |F_o|.$ <sup>b</sup>  $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o)^2]^{1/2}.$ 

were carried out by using a Vario EL III Elemental Analyzer. Infrared spectra were recorded (4000-400 cm<sup>-1</sup>) as KBr disks on Shimadzu IR-440 spectrometer. Thermogravimetric analyses (TGA) were performed on an automatic simultaneous thermal analyzer (DTG-60, Shimadzu) under a flow of  $N_2$  at a heating rate of 10 °C/ min between ambient temperature and 800 °C. Powder XRD investigations were carried out on a Bruker AXS D8-Advanced diffractometer at 40 kV and 40 mA with Cu K $\alpha$  ( $\lambda$  = 1.5406 Å) radiation. Luminescence spectra and lifetime for crystalline samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter.

#### 2.2. Sorption measurements

The kinetic trap effects of water on the complexes 1-3 were monitored by TGA. Before measurements, the sample was treated at 250 °C in flowing N<sub>2</sub> overnight. After cooling to room temperature, the sample was exposed to a N<sub>2</sub> flow with water vapor at 25 °C until no weight change was observed. Then the sample was heated at a rate of 5 °C/min under a pure N<sub>2</sub> flow.

# 2.3. Synthesis

# 2.3.1. Synthesis of $[Zn_3(L1)_3(DMF)_2]_n$ (1)

A mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.15 g, 0.5 mmol), 2,5-dimethylterephthalic acid (0.097 g, 0.5 mmol) 1,3-bis(4-pyridyl)propane (0.137 g, 0.5 mmol) and 10 mL DMF was sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 120 °C for 48 h. The mixture was cooled to room temperature as a rate of 5 °C/h. Yield 0.902 g (59%). Anal. Calc. for  $C_{36}H_{38}N_2O_{14}Zn_3$ : C, 47.0; H, 4.1; N, 3.0. Found C, 47.4; H, 3.8; N, 3.2%. FTIR spectra (KBr, cm<sup>-1</sup>): 2950(m), 1678(s), 1588(s), 1407(s), 1337(m), 1281(w), 1197(m), 1112(m), 1033(w), 915(m), 845(s), 796(s), 755(s), 694(m), 545(s).

# 2.3.2. Synthesis of $[Zn(L2)(BPP)]_n$ (2)

Complex **2** was prepared by the same procedure as **1** except that 2,5-dimethylterephthalic acid was replaced by 2-aminoterephthalic acid. Yield 0.315 g (72%). Anal. Calc. for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>Zn: C, 56.9; H, 4.3; N, 9.5. Found C, 57.4; H, 4.0; N, 9.2%. FTIR spectra  $(KBr, cm^{-1}): 3415(m), 2923(m), 2858(m), 1628(s), 1569(s),$ 

1490(m), 1421(s), 1373(s), 1251(m), 1226(w), 1070(m), 1024(m), 957(w), 886(w), 831(m), 811(m), 773(s).

#### 2.3.3. Synthesis of $[Zn_2(L3)_2(BPP)]_n \cdot nDMF(3)$

Complex **3** was prepared by the same procedure as **1** except that 2,5-dimethylterephthalic acid was replaced by terephthalic acid. Yield 0.137 g (75%). Anal. Calc. for C<sub>32</sub>H<sub>29</sub>N<sub>3</sub>O<sub>9</sub>Zn<sub>2</sub>: C, 52.6; H, 4.0; N, 5.8. Found C, 52.1; H, 4.4; N, 6.2%. FTIR spectra (KBr,  $cm^{-1}$ ): 2933(m), 2851(m), 1680(m), 1626(s), 1590(w), 1504(w), 1479(w), 1417(w), 1388(s), 1290(w), 1222(m), 1067(w), 1037(w), 1016(w), 891(w), 828(s), 746(s).

#### 2.4. X-ray crystallographic determination

Single crystal X-ray diffraction analyses of complexes 1-3 were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data collection and reduction were performed using the APEX II software [9]. Multi-scan absorption corrections were applied for all the data sets using the APEX II program [9]. Small residual absorption effects were treated with XABS2 [10]. The structures were solved by direct methods and refined by least squares on  $F^2$  using the SHELXTL program package [11]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The free DMF molecule in 3 is disordered evenly over two positions, with occupancy ratios of 0.50(2): 0.50(2). Crystallographic data for **1–3** are listed in Table 1. Selected bond lengths and angles are given in Table 2. H-bonding parameters for 1-3 are given in Table 3.

#### 3. Results and discussion

# 3.1. Crystal structures

#### 3.1.1. Structure of complex 1

Complex **1** crystallizes in the monoclinic space group C2/c and contains two crystallographically independent zinc atoms (Zn1 and Zn2). The perspective representations of the trinuclear compound **1** is shown in Fig. 1a. The three zinc atoms in **1** form a

| Table 2     |              |         |        |      |
|-------------|--------------|---------|--------|------|
| Selected bo | nd distances | (Å) and | angles | (°). |

| Com  | plex 1                 |          |                                      |            |  |
|--|------------------------|----------|--------------------------------------|------------|--|
| Zn(1   | l)-O(1)                | 1.931(3) | O(1)-Zn(1)-O(6)                      | 121.04(12) |  |
| Zn(1   | l)–O(3) <sup>i</sup>   | 2.414(3) | $O(6)-Zn(1)-O(4)^{i}$                | 126.93(13) |  |
| Zn(1   | l)–O(4) <sup>i</sup>   | 2.015(3) | $O(1)-Zn(1)-O(3)^{i}$                | 100.57(10) |  |
| Zn(1   | l)-O(6)                | 1.939(2) | $O(4)^{i}$ -Zn(1)-O(3) <sup>i</sup>  | 57.56(10)  |  |
| Zn(1   | l)-O(7)                | 2.005(3) | $O(2)^{ii}$ -Zn(2)-O(2)              | 180.0(13)  |  |
| Zn(2   | 2)–O(2) <sup>ii</sup>  | 2.033(3) | O(2)-Zn(2)-O(5)                      | 92.74(11)  |  |
| Zn(2   | 2)–O(3) <sup>iii</sup> | 2.180(3) | $O(5)^{ii}$ -Zn(2)-O(3) <sup>i</sup> | 89.54(10)  |  |
| Zn(2   | 2)–O(5) <sup>ii</sup>  | 2.034(2) | O(2)-Zn(2)-O(3) <sup>iii</sup>       | 89.42(12)  |  |
| Com  | plex <b>2</b>          |          |                                      |            |  |
| Zn(1   | l)-N(2)                | 2.086(5) | $O(4)-Zn(1)-O(1)^{i}$                | 138.7(2)   |  |
| Zn(1   | l)–N(3)ii              | 2.057(5) | $O(4)-Zn(1)-N(3)^{ii}$               | 98.8(2)    |  |
| Zn(1   | l)–O(1)i               | 1.959(6) | O(4) - Zn(1) - N(2)                  | 106.5(2)   |  |
| Zn(1   | l)-O(4)                | 1.958(4) | $O(1)^{i}$ -Zn(1)-O(2) <sup>i</sup>  | 56.4(2)    |  |
| Com  | plex <b>3</b>          |          |                                      |            |  |
| Zn(1   | l)-O(1)                | 1.924(2) | O(1)-Zn(1)-O(3)                      | 113.43(9)  |  |
| Zn(1   | l)-O(3)                | 1.954(2) | $O(1)-Zn(1)-O(4)^{i}$                | 102.28(9)  |  |
| Zn(1   | l)-O(4)                | 1.987(2) | O(1)-Zn(1)-N(1)                      | 125.33(10) |  |
| Zn(1   | l)-N(1)                | 2.004(2) | $O(4)^{i}-Zn(1)-N(1)$                | 98.07(9)   |  |
| Symmetry codes: For <b>1</b> : $i = x, -y, 0.5 + z$ ; $ii = 0.5 - x, 0.5 - y, 1 - z$ ; $iii = 0.5 - x$ |                        |          |                                      |            |  |

0.5 + y, 0.5 - z; For **2**: i = x, 0.5 - y, 0.5 + z; ii = 1 + x, y, z; For **3**: i = 1 - x, 1 - y, 1 - z.

perfectly linear  $[Zn_3(\mu_2-OOC_{bridging})_4(\mu_2-OOC_{chelating-bridging})_2]$  unit. Zn1 is five-coordinated by four carboxylate oxygen atoms from three different L1 ligands and one oxygen atom of a DMF molecule, adopting a distorted trigonal biyramidal geometry; Zn2 is six-coordinated by six carboxylate oxygen atoms from six different L1 ligands and displays octahedral coordination. The Zn-O distances and O-Zn-O bond angles ranging from 1.931(3) to 2.414(3) Å and from 57.56(10)° to 180.00° respectively, all of which are within the range of those reported in other trinuclear zinc(II) compounds involving carboxylate ligands [12]. The  $[Zn_3(\mu_2-OOC_{bridging})_4(\mu_2-$ OOC<sub>chelating-bridging</sub>)<sub>2</sub>] unit can be regarded as a secondary building unit (SBU). The trinuclear zinc clusters in 1 are connected by rigid organic linkers (L1). Similar to [Mg<sub>3</sub>(ndc)<sub>3</sub>(dif)<sub>4</sub>] [13], the L1 ligands in compound **1** adopt two coordination modes that connect two Zn(II) atoms: a bidentate bridging mode and an asymmetric chelating bridging mode (Scheme 1a and b). Consequently, a 2D layered Metal–Organic Framework (MOF) with triangular meshes is formed (Fig. 1b). If the trinuclear zinc clusters and L1 ligands

#### Table 3

Hydrogen bonds of 1-3.

| D−H···A                                | <i>d</i> (D–H) | $d(H \cdot \cdot \cdot A)$ | $d(D \cdot \cdot \cdot A)$ | ∠(DHA) |
|--|----------------|----------------------------|----------------------------|--------|
| 1                                      |                |                            |                            |        |
| $C(3)-H(3)\cdots O(3)$                 | 0.93           | 2.40                       | 2.756(4)                   | 103    |
| $C(3)-H(3)\cdot \cdot \cdot O(5)^{iv}$ | 0.93           | 2.37                       | 3.220(5)                   | 152    |
| $C(10)-H(10C)\cdots O(4)$              | 0.96           | 2.43                       | 2.839(6)                   | 105    |
| $C(15)-H(15B)\cdots O(6)^{i}$          | 0.96           | 2.40                       | 2.905(5)                   | 113    |
| $C(16)-H(16)\cdots O(4)^{i}$           | 0.93           | 2.56                       | 3.074(5)                   | 115    |
| $C(17)-H(17C)\cdots O(6)^{v}$          | 0.96           | 2.53                       | 3.461(8)                   | 164    |
| $C(18) - H(18A) - O(7)^{i}$            | 0.96           | 2.28                       | 2.706(8)                   | 106    |
| 2                                      |                |                            |                            |        |
| $N(1)-H(1A)\cdots O(2)$                | 0.86           | 2.04                       | 2.666(7)                   | 129    |
| $C(6)-H(6)\cdots O(1)$                 | 0.93           | 2.46                       | 2.777(9)                   | 100    |
| $C(9)-H(9)\cdots N(1)^{iii}$           | 0.93           | 2.55                       | 3.438(6)                   | 161    |
| $C(16)-H(16A)\cdots O(2)^{iv}$         | 0.97           | 2.51                       | 3.245(6)                   | 132    |
| 3                                      |                |                            |                            |        |
| $C(3)-H(3A)\cdots O(1)$                | 0.93           | 2.45                       | 2.758(5)                   | 100    |
| $C(7)-H(7A)\cdots O(2)^{ii}$           | 0.93           | 2.59                       | 3.272(1)                   | 131    |
| $C(10)-H(10A) - O(1)^{iii}$            | 0.93           | 2.55                       | 3.264(8)                   | 134    |
| $C(13)-H(13A)\cdots O(2)^{ii}$         | 0.93           | 2.53                       | 3.198(6)                   | 129    |
| $C(18)-H(18A)\cdots O(5)$              | 0.96           | 2.33                       | 2.768(4)                   | 107    |

Symmetry codes: For **1**, i: x, -y, 0.5 + z; iv: 0.5 - x, -0.5 + y, 0.5 - z; v: -x, 1 - y, 1 - z. For **2**, iii: -0.5 + x, 0.5 - y, 1 - z; iv: 1.5 - x, -y, 0.5 + z. For **3**, ii: 1 - x, 1 - y, -z; iii: 2 - x, 1 - y, 1 - z.

were considered as 6-connected nodes and lines, respectively. The layer can be reduced to 6-connected **hxl** topological type with point symbol 3.3.3.3.3.4.4.4.4.4.5(2).5(2).5(2) (Fig. 1c). The thickness of the layer, given by the Zn-Zn distance between the terminal Zn atoms in the same SBU, is 6.984(2) Å. The two DMF molecules attach in a monodentate terminal mode to coordinate a trinuclear cluster, thereby separating two adjacent layers; therefore, the existence of the 2D network can be explained by the DMF-induced steric hindrance that prevents the formation of coordinative bonds between adjacent SBUs and in this way also prevents the formation of a 3D network. Neighboring layered networks are further linked into a 3D supramolecular framework through non-classical intermolecular C-H-O hydrogen bonding interactions involving the methyl hydrogen atoms of DMF molecules and carboxylate oxygen atoms (Fig. 1d, Table 3). Moreover, intramolecular  $C-H\cdots O$  hydrogen bonds are also observed.

#### 3.1.2. Structure of complex 2

Single-crystal X-ray diffraction analysis reveals that compound **2** has wave-like (4,4) layered structure, crystallizing in the space group Pbca. An ORTEP diagram view of 2 is shown in Fig. 2a. In the asymmetric unit of **2**, there is one Zn(II) cation, one **L2** anion and one BPP ligand. The Zn(II) centre is four-coordinated by two oxygen atoms from two L2 ligands, two nitrogen atoms from two BPP ligands, and displays a distorted tetrahedral coordination sphere. The Zn–O, Zn–N bond lengths and O–Zn–O, O–Zn–N bond angles range from 1.958(4) to 2.086(5) Å and 92.9(2)° to 138.7(2)°, respectively, which is within the reasonable range of observed values for other four-coordinated Zn(II) complexes with oxygen and nitrogen donating ligands [14]. The BPP ligand has TG conformation (the two pyridyl groups of BPP ligand show different *trans*(T) and *gauche*(G) orientations) [8] and adopts two end pyridyl N atoms that link to two Zn(II) atoms with a  $Zn \cdots Zn$ separation of 11.825 Å (Scheme 1f). A linear chain is formed by direct connection of Zn(II) atoms bridged by BPP ligands. The L2 ligands also bridge the Zn(II) atoms to form a zigzag chain, and the  $Zn \cdot Zn$  separation between the L2 ligands is 10.871 Å (Scheme 1c). Such parallel linear and parallel zigzag chains are perpendicularly intersected by the Zn(II) atoms at the nodes, resulting in a wave-like 2D (4,4) network (Fig. 2b). Each 4-membered ring consists of two L2 ligands, two BPP ligands and four Zn(II) atoms. The wave shape and large voids with dimensions of  $8.3 \times 7.3$  Å for each layer allow the formation of catenation between adjacent two layers in a parallel manner.

As shown in Fig. 2c, two  $4^4$ -sql nets interlock in parallel and give rise to a polycatenated layer (2D  $\rightarrow$  2D). Such parallel (4,4) layered interlocking modes are well know to belong to the parallel-parallel (p-p) class [15]. There are two crystallographically independent 4-membered rings that a 4-membered ring simply catenated by two rings of a layer (Fig. 2d). Neighboring polycatenated layers are linked into a 3D suparomolecular framework *via* C-H··· $\pi$  stacking interactions and C-H···O, C-H···N hydrogen bonds (Fig. 2e, Table 3). The H-to-centroid distance of H10···Cg1<sup>i</sup> = 2.99(2) Å [Cg1 is the centroid of the C1-C6 ring. Symmetry Code: (i) -0.5 + x, 0.5 - y, 1-z)].

### 3.1.3. Structure of complex 3

X-ray crystallography shows that complex **3** crystallizes in the monoclinic space group  $P2_1/m$ , with one Zn atom, half a BPP ligand, two halves of an **L3** ligand and one DMF molecule in the asymmetric unit. The four-coordinated Zn(II) center is surrounded by three oxygen atoms from three **L3** ligands and one nitrogen atom from a BPP ligand, which exhibits a distorted tetrahedral coordination geometry (Fig. 3a), with Zn–O, Zn–N distances and O–Zn–O, O–Zn–N bond angles ranging from 1.924(2) to 2.004(2) Å and



**Fig. 1.** View of structure **1**. (a) ORTEP diagram showing the coordination environment for Zn(II) ions in **1**. All H atoms are omitted for clarity (symmetry codes: (ii) 0.5–*x*, 0.5–*y*, 1–*z*); (b) View of the layered network of **1**; (c) View of the **hxl**-type 6-connected architecture of **1** (Zn cations, dark red balls; **L1** ligands, yellow sticks); (d) View of the 3D framework of **1** formed by C–H…O hydrogen bonds (pink dash lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

98.07(9)° to 125.33(10)°, respectively, all of which are within the range of those found in other four-coordinated Zn(II) complexes with oxygen and nitrogen donating ligands [16]. In the polymeric structure of **3**, the **L3** ligands adopt two different bridging modes: one acts as bridging mode  $\mu_2$  to link two Zn(II) ions, whereas the other has bridging mode  $\mu_4$  connecting four Zn(II) ions (Scheme 1d, e). The BPP ligand has TG conformation [8] and acts as a trans bidentate bridging ligand to link two Zn(II) ions, with the Zn $\cdots$ Zn separation being 10.921 Å. In this manner, each  $\mu_4$ -L3 ligand links four Zn atoms in  $\mu_2$ -bridging bidentate coordination mode to result in an interesting neutral chain of linear  $[Zn_2(L3)_2]_n$ with Zn...Zn separation of 10.306 Å. The adjacent neutral chains are bridged by flexible  $\mu_2\text{-BPP}$  and rigid  $\mu_2\text{-}\text{L3}$  spacers to form a 2D framework with bimetallic  $[Zn_2(COO)_2N_2O_2]$  building units in which the Zn1···Zn1<sup>i</sup> distance is 3.603 Å (Fig. 3b). The 2D framework can be topologically recognized as a (4,4) net where the dinuclear [Zn<sub>2</sub>(COO)<sub>2</sub>N<sub>2</sub>O<sub>2</sub>] unit is regarded as quadruply-connected node. In these 2D sheets each bimetallic [Zn<sub>2</sub>(COO)<sub>2</sub>N<sub>2</sub>O<sub>2</sub>] building unit is connected to six others, two of them by  $\mu_4$ -L3 ligands, four of them by two  $\mu_2$ -L3 and two  $\mu_2$ -BPP spacers. Adjacent 2D networks connect to form a 3D framework through C-H···O hydrogen bonds and a  $\pi \cdots \pi$  stacking interaction between the parallel phenyl ring of a  $\mu_4$ -L3 ligand and a pyridyl ring of  $\mu_2$ -BPP ligand of neighboring complexes, with a centroid to centroid distance of 3.563(4) Å (Fig. 3c, Table 3).

#### 3.2. Discussion

# 3.2.1. Effect of the 1,4-benzenedicarboxylate ligands on the grometries of **1–3**

From the structures descriptions above, we can see that the choice of 1,4-benzenedicarboxylate anions is critical in determining the structures of the resultant complexes. In this work, the role of 1,4-benzenedicarboxylate anions can be explained in terms of their different substituents. Complexes 1-3 show the effects of substituents of the 1,4-benzenedicarboxylate ligands on the structures. Although the 1,4-benzenedicarboxylate anions L1, L2 and L3 have the same carboxylate groups, L1 has two substituents (methyl), whereas L2 and L3 have one (amino) and none, respectively. As a result,  $[Zn_3(L_1)_3(DMF)_2]_n$  (1), in which the Zn atom was only coordinated by L1 and DMF, shows a 2D layer structure with trinuclear units,  $[Zn(L_2)(BPP)]_n$  (2) displays a 2D polycatenated layer structure constructed by L2 and BPP ligands, whereas  $[Zn_2(L_3)_2(BPP)]_n \cdot nDMF$  (3) has a different 2D structure involving L3 and BPP ligands with dinuclear units. Obviously, the substituents of the 1,4-benzenedicarboxylate anions are in large part responsible for the structural differences of 1-3.

#### 3.2.2. IR spectra

FT-IR spectra of complexes **1–3** were recorded as KBr pellets (Fig. S1). In the IR spectrum, the moderate absorption band



Scheme 1. The coordination modes of L1, L2, L3 and BPP ligands in 1-3.



**Fig. 2.** View of structure **2**. (a) ORTEP diagram of the asymmetry unit of **2**. All H atoms omitted for clarity (Symmetry codes: (i) x, 0.5–y, 0.5 +z; (ii) 1 +x, y, z); (b) View of the (4,4) layer in **2**; (c) 2D parallel polycatenation in **2**; (d) The type of interlocking mode in **2**; (e) View of the 3D framework of **2** formed by C–H… $\pi$  stacking interactions and hydrogen bonds (pink dash lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

observed at 2950 cm<sup>-1</sup> for **1** is attributed to the  $v(C_{methyl}-H)$  vibration of **L1** ligand. The moderate absorption band centered at 3415 cm<sup>-1</sup> is assigned to the v(N-H) vibration of N–H group of **L2** ligand. The moderate absorption bands at 2923, 2858 cm<sup>-1</sup> for **2**, 2933, 2851 cm<sup>-1</sup> for **3** may be assigned to the  $v(C_{methenyl}-H)$ vibration of BPP ligands. The strong and sharp bands at 1678 and 1680 cm<sup>-1</sup> are assigned to the carbonyl group of the DMF molecule. The features at 1588 and 1407 cm<sup>-1</sup> for **1**, 1628 and 1569, 1421 cm<sup>-1</sup> for **2**, 1626 and 1479, 1417 cm<sup>-1</sup> for **3**, are associated with the asymmetric (C-O-C) and symmetric (C-O-C) stretching vibrations. The  $\Delta v(v_{as}(COO^{-})-v_{s}(COO^{-}))$  values are 181 cm<sup>-1</sup> for **1**, 59 and 207 cm<sup>-1</sup> for **2**, 147 and 209 cm<sup>-1</sup> for **3**, indicating the coordination of **L1**, **L2**, **L3** with zinc in bridging, unidentate and chelating, bridging and unidentate modes, respectively [17], which is well consistent with the X-ray diffraction structural analysis.



**Fig. 3.** View of structure **3.** (a) ORTEP diagram showing the coordination environment for Zn(II) ions in **3.** All H atoms are omitted for clarity (symmetry codes: (i) 1–x, 1–y, 1–z); (b) View of the (4,4) layer in **3**; (c) View of the 3D framework of **3** formed by π…π stacking interactions and hydrogen bonds (pink dash lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

# 3.2.3. Thermal analyses

The thermogravimetric anslyses (TGA) of complexes **1–3** were performed in a N<sub>2</sub> atmosphere wherein the sample was heated to 800 °C at a rate of 10 °C/min. The TG curves are shown in Fig. 4. Complex **1** shows two weight loss steps. The first corresponding to the release of two DMF molecules is observed from 250 °C to 300 °C (obsd 16.1%, calcd 15.9%). The weight-loss step occurred above 400 °C which corresponds to the decomposition of the framework structure. Complex **2** has thermal stability as no strictly clean weight loss step occurs below 360 °C. Then a sharp weight loss occurred above 360 °C due to the decomposition of the structure. Complex **3** also shows two weight loss steps. The first corresponding to release of one free DMF molecule is observed from 30 °C to 120 °C (obsd 10.2%, calcd 10%). The compound begins to decompose when the temperature is raised to 350 °C.

#### 3.2.4. Luminescent properties

The solid-state photoluminescent properties of the free ligands and complexes **1–3** have been investigated at room temperature. The emission peaks of **L1**, **L2**, **L3** and complexes **1–3** are shown in Fig. 5.



Fig. 4. Thermogravimetric curves for 1-3.

The photoluminescent spectra of **L1**, **L2** and **L3** show emission maxima at 383 nm ( $\lambda_{ex}$  = 330 nm), 345 nm ( $\lambda_{ex}$  = 317 nm) and 329 nm ( $\lambda_{ex}$  = 296 nm), respectively. The emission bands of these



Fig. 5. Solid-state emission spectra of L1-L3 and compounds 1-3 at room temperature.



Fig. 6. PXRD patterns for (a) 1, (b) 2 and (c) 3.

free ligands are probably attributable to the  $\pi^*$ -n or  $\pi^*$ - $\pi$  transition. Upon complexation of these ligands with Zn(II) ions, the emis-



**Fig. 7.** TGA of **1–3** with water absorbate.

sion peaks occur at 535 nm ( $\lambda_{ex} = 421$  nm) for **1**, 487 nm ( $\lambda_{ex} = 340$  nm) for **2**, 502 nm ( $\lambda_{ex} = 407$  nm) for **3**, all of which are clearly red-shifted compared with the free ligands. The emissions of **1–3** probably originate from a ligand-to-metal charge transfer (LMCT) [18] excited state, because the **L1**, **L2**, **L3**, and BPP ligands with their extended aromaticity are regarded as good candidates for enhancement of emissive properties. The luminescent lifetimes of solids **1–3** measured using an Edinburgh FLS920 phosphorimeter with a 450 W xenon lamp as excitation source were, 28.04, 3.08, 2.43 ns, respectively (Fig. S2).

#### 3.2.5. Stability of the complexes

To investigate the stability of complexes **1–3**, the kinetic trap effects of water on the samples were monitored by TGA. The TGA curve shows that the partially decomposed **3** still adsorbed large numbers of water molecules, and the structure mostly collapsed with the removal of water upon heating (Fig. 7). **2** exhibits enhanced hydrophobicity as compared to **3** and adsorbed up to 10 wt.% water at room temperature. Increasing the water repellent groups, **1** displays a different TG curve from **2**. **1** adsorbed up to 7.5 wt.% water at 25 °C, and there is no additional weight loss upon heating up to 300 °C. The weight-loss step occurred below 105 °C which corresponds to the release of free water molecules inside the pores (~3 wt.%) and two coordinated water molecules replacing the two DMF molecules of the unit cell (obsd 4.5%, calcd 4.4%).

The samples of **1–3** were treated under high vacuum at 120 °C for 12 h, then were exposed to air (relative humidity of 80-90%) and examined using PXRD to provide insight on the structural integrity of the materials under ambient conditions. PXRD shows that **3** was unstable in air and its structure mostly collapsed after moisture exposure for 7 days (Fig. 6c). After exposing to air 7 days, no new peaks appear for 2, but all of the peak intensities for 2 decrease (Fig. 6b). In contrast, PXRD patterns of 1 remain essentially unchanged up to 30 days, with no new peaks and apparent loss in peak intensity (Fig. 6a). Compared to 3, the results indicate that the incorporation of the water repellent groups of the ligand (methyl for L1, amino for L2) enhance the stability of 1 and 2 under standard atmospheric conditions. It has been demonstrated that the introduction of water repellent functional groups (e.g. methyl) within the frameworks can largely enhance the hydrophobic properties of MOFs [1c].

#### 4. Conclusion

In conclusion, three new zinc-organic frameworks based on structurally related 1,4-benzenedicarboxylate with or without 1,3-bis(4-pyridyl)propane have been prepared under solvothermal conditions. These compounds display interesting and versatile 2D coordination features. The structural diversities of the complexes show that the organic anions play important roles in the formation of the MOFs. Complexes 1-3 exhibit strong blue photoluminescence in the solid state at room temperature, which may have potential applications as luminescent materials in blue light-emitting devices. The moisture-stability results of 1-3 reveal that the introduction of water repellent groups (e.g. methyl, amino) of the organic ligands in a MOF could efficiently enhance the water resistance of MOF materials.

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#### **Appendix A. Supplementary material**

CCDC Nos. 884819-884821 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.ica.2012.10.006.

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