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 $[Zn_2(L3)_2(BPP)]_n$·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 4^4-**sql** nets interlock in parallel and give rise to a polycatenated layer (2D → 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 $[Zn_2(L3)_2(BPP)]_n$·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	$C_{36}H_{38}N_2O_{14}Zn_3$	$C_{21}H_{19}N_3O_4Zn$	$C_{32}H_{29}N_3O_9Zn_2$
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)
Z	4	8	2
D_{calc} (g/cm^3)	1.541	1.493	1.494
μ (mm^{-1})	1.870	1.279	1.534
$F(000)$	1880	1824	748
Reflections collected	10793	15311	9316
Independent reflections (R_{int})	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 [$I > 2\sigma(I)$][a]	0.0348	0.0641	0.0352
wR_2 (all data)[b]	0.0885	0.1718	0.0976
$\Delta\rho_{maximum}$ and $_{minimum}$ (e/A^3)	0.613 and −0.398	1.038 and −0.430	0.469 and −0.362

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

were carried out by using a Vario EL III Elemental Analyzer. Infrared spectra were recorded (4000–400 cm^{-1}) 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 Kα (λ = 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$_2$ overnight. After cooling to room temperature, the sample was exposed to a N$_2$ 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$_2$ flow.

2.3. Synthesis

2.3.1. Synthesis of [Zn$_3$(L1)$_3$(DMF)$_2$]$_n$ (**1**)

A mixture of Zn(NO$_3$)$_2$·6H$_2$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$_2$O$_{14}$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^{-1}): 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$_{21}$H$_{19}$N$_3$O$_4$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)]$_n$·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$_{32}$H$_{29}$N$_3$O$_9$Zn$_2$: 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 MoKα radiation (λ = 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