Three coordination polymers constructed from 5-(4-(tetrazol-5-yl)phenyl)isophthalic acid: Synthesis, crystal structure and properties

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ABSTRACT

Three new coordination polymers, namely, $\{[Co_2(TPA)(\mu_3\text{-}O)_3] \cdot 0.5DMA\}_n$ (**1**), $\{[Co(H_2TPA)(bibp)(H_2O)_3] \cdot H_2O\}_n$ (**2**) and $\{[Cd_3(TPA)_2(phen)_4] \cdot 4H_2O\}_n$ (**3**), (H_3TPA = 5-(4-(tetrazol-5-yl)phenyl)isophthalic acid, bibp = 4,4'-bis(imidazolyl)biphenyl, phen = 1,10-phenanthroline and DMA = N,N-dimethylacetamide), have been synthesized under solvothermal conditions and structurally characterized by elemental analysis, IR spectroscopy, powder X-ray diffraction (PXRD) and single-crystal X-ray diffraction analysis. Polymer **1** exhibits a three-dimensional (3D) structure constructed from 5-connected secondary building units (SBUs) $[Co_3(\mu_3\text{-}O)]$ and 3-connected H_3TPA ligands. Polymer **2** has a 1D zigzag polymer chain connected by H_3TPA and bibp ligands. Polymer **3** features an unusual 3D framework with a (3,4,2)-connected $\{4; 6;8\}\{4; 6^2;8^3\}$ topology. Moreover, the thermal stabilities of **1**–**3** and photoluminescence properties of **3** have been investigated. Magnetic susceptibility measurements indicate that polymers **1**–**2** display antiferromagnetic exchange properties.

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1. Introduction

The study of design and construct of novel coordination polymers is a major area of research, which has attracted increasingly interest not only due to their attractive topology but also for their promising applications in the fields of luminescence, molecular magnetism, catalysis, ion exchange [1–4]. As a matter of fact, up to now, it is still a difficult questions to design and synthesize the expected structure because there are a lot of different factors influence the final structures, for instance, central metals, inorganic/organic anions, selection of ligands, synthetic methods, pH values, reaction temperatures [5–9]. Among these factors, organic ligands have proven to be most significant to framing of coordination polymers [10,11].

Owing to their different coordination models and interesting structures with higher dimensionality [12], our group has been devoted to synthesize a lot of polymers by multi-carboxylate ligands, for instance, benzene-3,4,5-tricarboxylate (H_3BPT) ligand,

biphenyl-2,4',5-tricarboxylic acid [13,14]. But in recent decades, multifunctional ligands were enthusiastically adopted and widely welcomed because it can be used to construction of coordination polymers through versatile coordination modes [15]. Among them, bifunctional organic ligands including tetrazole and carboxylate groups, have been more widely utilized in the construction versatile coordination networks [16–23].

At this point, we have designed 5-(4-(tetrazol-5-yl)phenyl)isophthalic acid (H_3TPA) as the ligand, which is similarity to the H_3BPT and containing tetrazole and carboxylate groups. H_3TPA is a longer and rigid ligand possessing two carboxylic groups in symmetrical positions at one side of the diphenyl and a N-donor tetrazole group in the other side [24]. It may be an remarkable choice for generate highly connected, multidimensional coordination frameworks because of following purposes: (i) this ligand has eight potential coordination sites in two carboxylate groups and a tetrazole group, which assumes abundant coordination modes, leading to possess some polymers with novel structures and interesting topology; (ii) the rotation of the C—C single bond between the two phenyl rings can accommodate a variety of coordination geometries of the metal ions [25].

Herein, we have successfully synthesized three new coordination

polymers based on the H_3TPA ligand and *N*-donor auxiliary ligands (Scheme 1) under solvothermal conditions, namely, $\{[Co_2(TPA)(\mu_3\text{-}O)_3]\cdot 0.5DMA\}_n$ (**1**), $\{[Co(H_2TPA)(bibp)(H_2O)_3]\cdot H_2O\}_n$ (**2**) and $\{[Cd_3(TPA)_2(phen)_4]\cdot 4H_2O\}_n$ (**3**). In addition, the magnetic properties of **1**−**2** and photoluminescence properties of **3** have also been studied in detailed, respectively.

2. Experiment

2.1. Materials and physical measurements

The ligands H_3TPA, bibp and phen were obtained from Jinan Camolai Trading Company; the rest of the used reagents and solvents employed were purchased commercially and were used as received without further purification. The Fourier transform infrared spectra were recorded with KBr pellets on a Bruker EQUINOX-55 FT-IR spectrometer and operated in the range of $4000-400$ cm^{-1}. Thermogravimetric analyses (TG) were measured with a NETZSCH TG 209 thermal analyzer under a nitrogen atmosphere from room temperature to 900 °C with a heating rate of 10 °C/min. Elemental analyses of C, H and N were enforced on a PerkinElmer 2400C elemental analyzer. The powder X-ray diffraction patterns were collected on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, λ = 1.5418 Å). The fluorescent spectra for polymer 3 were measured at room temperature with a Hitachi F-4500 fluorescence spectrophotometer. Magnetism properties for polymers **1**−**2** were tested on a Quantum Design MPMS-XL-7 SQUID magnetometer.

2.2. Syntheses of polymers 1−3

2.2.1. Synthesis of $\{[Co_2(TPA)(\mu_3\text{-}O)_3]\cdot 0.5DMA\}_n$ (1)

A mixture of $CoSO_4\cdot 7H_2O$ (0.0056 g, 0.02 mmol) and H_3TPA (0.0031 g, 0.01 mmol) was dissolved in 6 mL of DMA/H$_2$O (5:1, v/v). The solution was placed into the Teflon-lined stainless steel vessel (25 mL), sealed and heated up to 160 °C under autogenously pressure, maintained for three days. Pink crystals were obtained when it was cooled to room temperature. Yield 46% (based on H_3TPA). *Anal.* Calcd for $C_{17}H_{11.5}Co_2N_{4.5}O_{7.5}$; C, 39.52; H, 2.24; N, 12.20%. Found: C, 39.40; H, 2.25; N, 12.28%. IR (KBr cm^{-1}): 3929.23(w), 3742.61(w), 3049.64(s), 3038.69(m), 2807.86(w), 2397.30(w), 2269.65(w), 2137.07(w), 2027.49(w), 1918.66(w), 1887.66(w), 1843.43(w), 1509.60(m), 1459.17(s), 1159.54(w), 1030.40(w), 1012.47(m), 957.29(w), 919.64(m), 733.76(m), 665.02(w), 636.93(w).
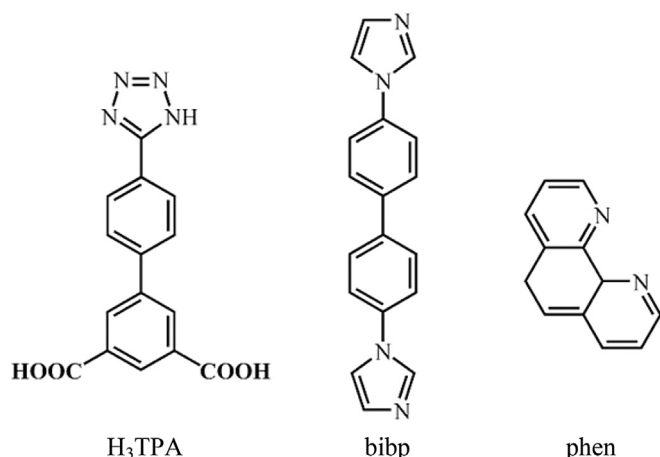
2.2.2. Synthesis of $\{[Co(H_2TPA)(bibp)(H_2O)_3]\cdot H_2O\}_n$ (2)

2 was synthesized in a similar way to that described for **1**, except that bibp (0.0028 g, 0.01 mmol) was added, yellow crystals were obtained. Yield 52% (based on H_3TPA). *Anal.* Calcd for $C_{33}H_{21}CoN_8O_8$; C, 55.31; H, 2.95; N, 15.64%. Found: C, 55.24; H, 2.98; N, 15.60%. IR (KBr cm^{-1}): 3994 (w), 3930 (w), 3559 (w), 3027 (s), 2795 (w), 2353 (w), 2321 (w), 2184 (w), 2074 (w), 1847 (w), 1646 (w), 1609 (m), 1578 (w), 1562 (m), 1536 (m), 1515 (m), 1478 (m), 1399 (s), 1314 (w), 1299 (m), 1272 (w), 1246 (m), 1220 (w), 1135 (s), 1109 (s), 626.93 (w).

2.2.3. Synthesis of $\{[Cd_3(TPA)_2(phen)_4]\cdot 4H_2O\}_n$ (3)

A mixture of $CdSO_4\cdot 8H_2O$ (0.0154 g, 0.02 mmol), H_3TPA (0.0062 g, 0.02 mmol) and phen (0.0040 g, 0.02 mmol) was dissolved in 6 mL of DMA/H$_2$O (5:1, v/v). The solution was placed into the Teflon-lined stainless steel vessel (25 mL), sealed and heated up to 180 °C under autogenously pressure, maintained for three days. Colorless crystals were obtained when it was cooled to room temperature. Yield 59% (based on H_3TPA). *Anal.* Calcd for $C_{78}H_{46}Cd_3N_{16}O_{12}$; C, 53.95; H, 2.67; N, 12.91%. Found: C, 54.171; H, 2.85; N, 12.80%. IR (KBr cm^{-1}): 3743 (w), 3047 (s), 2473 (w), 2378 (w), 2362 (w), 2336 (w), 2183 (w), 2073 (w), 1915 (w), 1825 (w), 1598 (m), 1525 (m), 1398 (s), 1256 (m), 997 (w), 632.93 (w). The Fourier transform infrared spectra for **1**−**3** are illustrated in Fig. S1.

2.3. X-ray crystallography

X-ray crystallographic data for the three polymers were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296(2) K. The structure was solved by direct methods and refined with full-matrix least-squares on F^2 with the SHELXL-97 program package and OLEX-2 suite [26,27]. All non-hydrogen atoms were located with difference Fourier synthesis, and the hydrogen atoms were generated geometrically. Crystal data and refinement parameters of polymers 1−3 are listed in Table 1, and the selected bond lengths and angles are reported in Table S1. CCDC reference numbers of polymers **1**−**3** is 1469165, 1469163 and 1473887,

Scheme 1. Structures of H_3TPA, bibp and phen ligands.

Table 1
Crystal and structure refine data for polymers **1**−**3**.

Polymers	1	2	3
Formula	$C_{17}H_{11.5}Co_2N_{4.5}O_{7.5}$	$C_{33}H_{21}CoN_8O_8$	$C_{78}H_{46}Cd_3N_{16}O_{12}$
Fw	516.67	716.51	1736.51
T(K)	296 (15)	296 (2)	296 (2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*P2$_1$/c*	*C2/c*
A (Å)	34.791 (18)	16.088 (3)	36.304 (13)
B (Å)	10.290 (4)	24.143 (5)	10.291 (4)
C (Å)	13.669 (5)	8.2258 (17)	23.003 (8)
α (°)	90.00	90	90.00
β (°)	112.964 (12)	90.223 (4)	120.885 (6)
γ (°)	90.00	90	90.00
Volume (Å^3)	4506 (3)	3195.0 (11)	7375 (5)
Z	8	4	4
Dc (mg/m^3)	1.523	1.490	1.564
μ (mm^{-1})	1.519	0.603	0.931
F (000)	2072.0	1464.0	3464.0
Reflns collected	11750	17101	19223
Independ reflections	4472	6305	7186
R_{int}	0.1388	0.0794	0.0508
Goodness-of-fit on F^2	1.040	0.986	1.260
R_1^a, wR_2^b [$I > 2\sigma(I)$]	0.1474	0.0604	0.0785
	0.3642	0.1542	0.1998
R_1, wR_2 (all data)	0.2501	0.1046	0.0937
	0.4284	0.1917	0.2118

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma(F_o^2)^2\}^{1/2}$.