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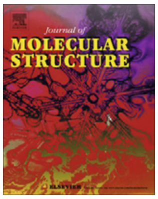

Synthesis, crystal structure and photoluminescent property of a novel indium (III) supramolecular 3D framework

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ABSTRACT

A new metal–organic framework $[In_2(OH)_2(1,3\text{-BDC})_2(2,2'\text{-bipy})_2]$ **1** (1,3-benzenedicarboxylate = 1,3-BDC, 2,2′-bipyridine = 2,2′-bipy) has been hydrothermally synthesized from the reaction of $In(NO_3)_3$, 1,3-BDC and 2,2′-bipy. Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the triclinic space group *P*-1 (No. 2), $a = 8.6461$ Å, $b = 9.9234$ Å, $c = 10.1799$ Å, $\alpha = 78.1801°$, $\beta = 75.1646°$, $\gamma = 72.7427°$, $V = 798.40$ Å^3, $Z = 2$. Compound **1** contains double-chain-like ribbons which are constructed by $[In_2(OH)_2(2,2'\text{-bipy})_2]_\infty^{2+}$ units and 1,3-BDC ligands. The adjacent ribbons are packed and exhibit interesting 3D supramolecular networks. The further characterizations of compound **1** have been performed by fluorescent spectroscopy, powder X-ray diffraction, IR spectroscopy, thermogravimetric analysis (TGA), ICP-AES and elemental analyses.

1. Introduction

In recent years, metal–organic frameworks (MOFs) as promising new materials have attracted much interest for their rich structural chemistry and potential applications in catalysis, separations, gas storage and so forth [1–3]. The crystal structure of MOFs is formed by a metal ion or a metallic cluster and coordinated multidendate organic ligands. Transition-metal-based MOFs are most studied, and the research of main group metal based MOFs is significantly less explored. At present, the research field has been extended to using main group metal as framework polyhedral node because of the fact that main group metal based MOFs present interesting opportunities with respect to their intriguing structures and many applications [4], such as in catalysis [5,6]. Among main group metal based MOFs, the design and synthesis of indium (III)-based MOFs attracts a special attention due to the change of valence in trivalent metal centers may produce obviously diverse structures different from those containing divalent transition metal centers. Moreover, indium (III)-based MOFs with thermally stable framework can be used as Lewis acid catalysts in the green chemistry [6]. To the best of our knowledge, so far, only a few of In(III)-based MOFs have been described which mainly focused on using 1,4-benzenedicarboxylate [3a,7], 1,3,5-benzenetricarboxylic acid [8] and 1,2,4,5-benzenetetracarboxylate [9] as organic ligands.

1,3-benzenedicarboxylate (1,3-BDC) as an extensively used organic ligand, has constructed many non-interpenetrating open frameworks of transition and rare earth metals with variable cavities or channels [10], however, it is rarely employed in the design and synthesis of indium (III)-based MOFs [11]. With the aim of synthesizing the novel MOFs, we conducted our studies on the hydrothermal synthesis of In-based MOFs using the 1,3-BDC as ligand. Finally, in the presence of 2,2′-bipy as the secondary ligand, a new indium (III)-based MOFs, $[In_2(OH)_2(1,3\text{-BDC})_2(2,2'\text{-bipy})_2]$ (**1**), has been successfully prepared. Introducing 2,2′-bipy as the secondary ligand not only due to 2,2′-bipy as a versatile ligand can construct appealing structure of varying dimensions, but also shows the different photoluminescent property [12]. The compound **1** shows a double stranded chain structure which is constructed by dimeric $[In_2(OH)_2(2,2'\text{-bipy})_2]_\infty^{2+}$ units and 1,3-BDC ligands. Finally, these chains form the interesting 3D supramolecular framework by strong π–π interactions of the organic ligands. To our knowledge, the one-dimensional double-chain-like ribbons framework is rarely reported in In-benzenemulticarboxylate systems [13]. Herein, we describe the synthesis, crystal structure and characterization of compound **1** along with its fluorescent property.

2. Experimental

2.1. Materials and instrumentation

All chemicals were obtained from commercial sources and used without further purification. Powder X-ray diffraction (XRD) data

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were obtained using SHIMADAZU XRD-6000 diffractometer with Cu Kα radiation (λ = 1.5418 Å), with the step size and the count time of 0.02° and 4 s, respectively. The elemental analysis was conducted on a Perkin Elmer 2400 elemental analyzer. ICP-AES (inductively coupled plasma-atomic emission spectroscope) analysis was performed on a Perkin Elmer Optima 3300DV ICP instrument. FT-IR spectrum was recorded on a Nicolet Impact 410 spectrometer between 400 and 4000 cm^{-1} using the KBr pellet method. Thermogravimetric analysis (TGA) was conducted on a Perkin–Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 °C min^{-1} from room temperature to 800 °C. The fluorescence measurement was performed on a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source.

2.2. Synthesis

A mixture of 2,2′-bipy (0.156 g, 1.0 mmol), 1,3-BDC (0.045 g, 0.27 mmol) and In(NO_3)$_3$ (0.05 g, 0.17 mmol) were added to 8 ml of distilled water in a Teflon-lined stainless steel vessel (23 ml), and then the pH value was adjusted to 6 by NaOH (0.5 M). The mixture was sealed and heated at 160 °C for 3 days. Finally, the autoclave was slowly cooled down to ambient temperature. The resulting colorless block-shaped crystals of compound **1** were collected by filtration, washed with distilled water and air-dried. The yield of product was 51% in weight based on indium.

2.3. Crystal structure determinations

A block single crystal with dimensions of 0.10 mm × 0.1 mm × 0.1 mm was selected for single-crystal X-ray diffraction analysis. The intensity data were collected on a Rigaku RAXIS-RAPID IP diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at a temperature of 293(2) K. No significant decay was observed during the data collection. Data processing was accomplished with the RAPID AUTO processing program. The structure was solved by direct method using the SHELXTL crystallographic software package [14,15]. The In atom was first located, and then the C, N, and O atoms were found from the difference Fourier map. All the H atoms attached to the carbon were placed geometrically, and the remaining H atoms in the O–H group in the compound were located in the difference Fourier map. Experimental details for the structural determination of compound **1** are summarized in Table 1, while the selected bond lengths and angles data are presented in Table 2. CCDC-759,777 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1
Crystal data and structure refinement for the compound **1**.

Empirical formula	$C_{18}H_{13}InN_2O_5$
Formula weight	452.12
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
a (Å)	8.6461(17)
b (Å)	9.923(2)
c (Å)	10.180(2)
α (°)	78.18(3)
β (°)	75.17(3)
γ (°)	72.74(3)
Volume (Å^3)	798.4(3)
Z	2
Calculated density (Mg m^{-3})	1.881
Absorption coefficient (mm^{-1})	1.515
F(0 0 0)	448
Theta range for data collection (°)	3.02–27.43
Limiting indices	$-11 \le h \le 11$, $-12 \le k \le 11$, $-13 \le l \le 11$
Reflections collected/unique	7878/3596
R(int)	0.0457
Completeness to theta = 27.43	98.7%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3596/0/239
Goodness-of-fit on F^2	1.115
Final *R* indices [$I > 2\mathrm{sigma}(I)$]	$R_1 = 0.0421$, $wR_2 = 0.0783$
R indices (all data)	$R_1 = 0.0548$, $wR_2 = 0.0869$
Largest diff. peak and hole (e TÅ^3)	0.747 and −1.247

Table 2
Selected bond lengths (Å) and angles (°) for compound **1**.

In(1)–O(2)	2.122(3)	In(1)–O(1)^a	2.150(3)
In(1)–O(1)	2.148(3)	In(1)–O(5)^b	2.154(3)
In(1)–N(1)	2.291(4)	In(1)–N(2)	2.329(4)
O(2)–In(1)–O(1)	166.23(13)	O(1)^a–In(1)–N(1)	97.71(14)
O(2)–In(1)–O(1)^a	93.90(13)	O(5)^b–In(1)–N(1)	158.13(13)
O(1)–In(1)–O(1)^a	75.33(14)	O(2)–In(1)–N(2)	96.25(13)
O(2)–In(1)–O(5)^b	83.03(12)	O(1)–In(1)–N(2)	95.83(13)
O(1)–In(1)–O(5)^b	91.02(12)	O(1)^a–In(1)–N(2)	166.29(12)
O(1)^a–In(1)–O(5)^b	103.31(13)	O(5)^b–In(1)–N(2)	87.08(13)
O(2)–In(1)–N(1)	101.63(13)	N(1)–In(1)–N(2)	71.24(14)
O(1)–In(1)–N(1)	88.50(13)	In(1)–O(1)–In(1)^a	104.67(14)

Symmetry transformations used to generate equivalent atoms.
[a] $-x + 1, -y, -z + 1$.
[b] $-x + 1, -y, -z$.

3. Results and discussion

3.1. Synthesis

Through the systematic experiments to find out the optimum reaction condition, we believe that the formation of the coordination framework is extremely dependent on the pH value of the reaction system. 2,2′-bipy molecules are added to adjust the pH value and also act as chelating ligands. So the amount of 2,2′-bipy molecules plays an important role in the resulting structure. The appropriate pH value favoring the generations of compound **1** is ca. 6. With pH value less than 6 the reaction system generated an unknown phase together with **1** while the reactions would not produce crystal but powder when the pH scale ranges from 6 to 6.5. Thus, excessive 2,2′-bipy is required to ensure the purity of compound **1**.

3.2. Characterization

The powder X-ray diffraction pattern for compound **1** is consisted with the simulated on the basis of the single-crystal structure, indicating the phase purity of the as-synthesized sample (as shown in Fig. 1). The difference in reflection intensities between the simulated and experimental patterns was due to the variation in crystal orientation for the powder sample. The elemental analysis results are listed as follows: anal. calc. for $C_{36}H_{26}N_4O_{10}In_2$: In 25.39%; C 47.77%; H 2.87% N 6.19%; Found: In 25.33%; C 47.83%; H 2.96%; N 6.15%.

The infrared spectrum (IR) for compound **1** exhibits a broad peak in the area 3390 cm^{-1} corresponding to the vibrations of the O–H groups. The absence of any strong absorption bands in the region 1690–1730 cm^{-1} confirms the complete deprotonation of the carboxyl groups of 1,3-BDC in compound **1** [16]. The bands 1632, 1593 cm^{-1} and 1365, 1319 cm^{-1} correspond to a bound