

Short communication

An iodine-containing metal-organic framework: Synthesis, structure and luminescent properties

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ABSTRACT

Presented here is a three-dimensional structure $[\text{Cd}_3(\text{IN})_5] \cdot \text{I}_3^-$ (**1**) based on isonicotinic acid. Compound **1** has been characterized by single crystal X-ray diffraction, powder crystal X-ray diffraction, infrared spectrum, thermogravimetric analysis, element analysis and scanning electron microscopy. The structure of compound **1** shows a 3D framework constructed by rod-shaped metal chains together with IN anions, while the channels are occupied by triiodide ions. The luminescent properties of **1** have also been investigated.

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In recent years, iodine-containing metal-organic frameworks (IMOFs) have gained large interests [1–7]. IMOFs not only possess the potential applications of normal MOFs, such as gas storage/separation, catalysis, chemical sensors, and magnetism, but also have some unique advantages [8–14]. First, the particular chemistry properties of iodine, such as oxidizability and conductivity, can be introduced into IMOFs [15,16]. Another attractive aspect is that iodine can be absorbed or removed easily by MOFs because of its low melting point and good solubility [17]. Therefore, IMOFs have attracted more and more attention recently. However, most reported IMOFs are based on guest exchange by diffusion in iodine vapor or solution [18–20]. But these methods are time-consuming and strenuous. Therefore, it is necessary to develop new methods. There are few reports on the introduction of iodine as precursor template because of their poorly crystallinity [21,22]. Su and coworkers reported a series of unprecedented 3d-4f metal-organic frameworks using iodine as a versatile precursor template [21].

Interestingly, almost all IMOFs reported are constructed by N-donor ligands. It may be due to the existence of the weak interaction of N⋯I, which gives us an idea to construct IMOFs. Isonicotinic acid (HIN), as a common ligand, has been used widely to construct many MOFs [23–28]. Pyridine group of HIN may immobilize iodine efficiently in

reaction progress. In addition, the length of HIN is appropriate to form the channel with iodine or polyiodide ion. Lu and coworker reported a novel open-channel MOFs $[\text{Cu}_2(\text{IN})_3] \cdot \text{I}_5^- \cdot 2/3\text{I}_2 \cdot \text{H}_2\text{O}$ with an included fused-polyiodine ring based on HIN [29].

Based on the above considerations, an IMOF based on isonicotinic acid, namely $[\text{Cd}_3(\text{IN})_5] \cdot \text{I}_3^-$ (**1**), has been prepared under hydrothermal conditions. To obtain IMOFs with polyiodide anions, iodine and potassium iodine were used simultaneously in the reaction system. Compound **1** has been characterized by single crystal X-ray diffraction, powder crystal X-ray diffraction, infrared spectrum, thermogravimetric analysis, element analysis and scanning electron microscopy (Table 1). The structure of compound **1** shows a 3D framework constructed by rod-shaped metal chains together with IN anions, while the channels are occupied by triiodide ions. The luminescent properties of **1** have also been investigated).

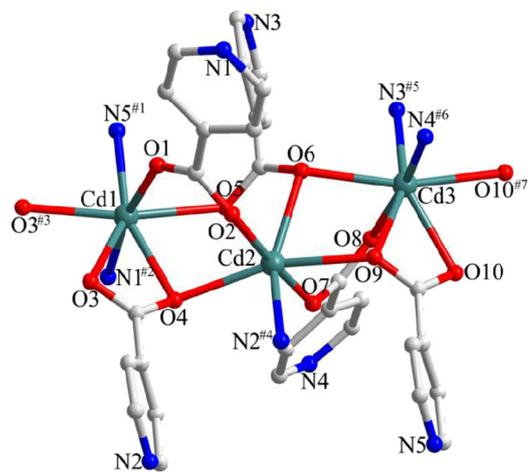
The X-ray crystal structure reveals that the asymmetric unit of compound **1** contains three Cd(II) ions, five IN anions and one triiodide ion. Three Cd(II) ions are all seven-coordinated in distorted pentagonal bipyramid spheres, but their coordination environments are entirely different (Fig. 1a). Each Cd1 and Cd3 is connected by five carboxyl oxygen atoms (For Cd1: O1, O3, O3^{#3}, O4, O5; For Cd2: O6, O8, O9, O10, O10^{#7}) and two nitrogen atoms (For Cd1: N1^{#2}, N5^{#1}; For Cd2: N3^{#5}, N4^{#6}), while Cd2 is coordinated by six carboxyl oxygen atoms (O2, O4, O5, O6, O7, O9) and one nitrogen atom (N2^{#4}). All bond lengths of Cd—O and Cd—N are in the normal range [30–32]. These Cd(II) ions are linked by carboxylate groups of IN anions to form an infinite rod-

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Table 1
Crystal data and structure refinements for compound **1**.

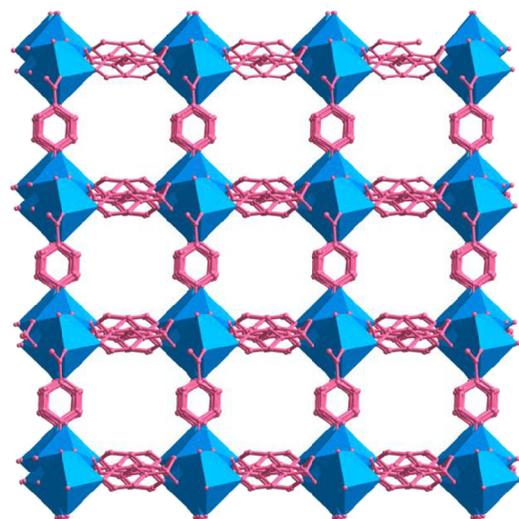
	1
Formula	C ₃₀ H ₂₀ Cd ₃ I ₃ N ₅ O ₁₀
Fw	1328.41
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	9.5870(6)
<i>b</i> /Å	11.3820(11)
<i>c</i> /Å	16.4430(18)
α /°	88.872(8)
β /°	79.149(8)
γ /°	82.684(7)
<i>V</i> /Å ³	1747.8(3)
<i>Z</i>	2
<i>D_c</i> /g cm ⁻³	2.524
<i>F</i> (000)	1236
<i>R</i> (int)	0.0442
GOF on <i>F</i> ²	1.122
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0956
<i>wR</i> ₂ (all data)	0.2185



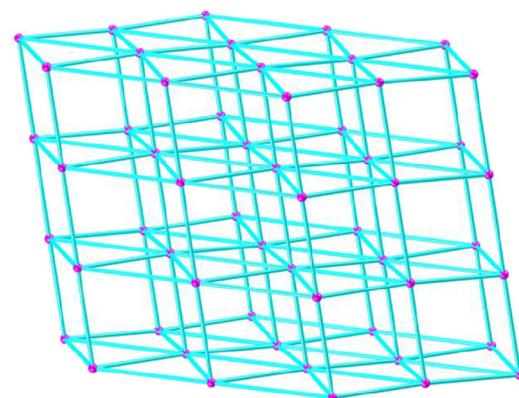
(a)



(b)



(c)



(d)

shaped metal chain (Fig. 1b). The metal chains are further connected by IN anions to obtain a 3D framework with channels (Fig. 1c). The channels are occupied by triiodide ions (Fig. S1).

Topologically, if the trinuclear units (Cd1, Cd2 and Cd3) are viewed as 8-connected nodes and IN anions as linkers, the whole framework can be symbolized as an 8-connected net with (3⁶·4¹⁸·5³·6) topology (Fig. 1d).

To investigate the purity of compound **1**, powder X-ray diffraction (PXRD) was conducted at 2θ ranging from 5 to 50° (Fig. S2). The PXRD pattern of as-synthesized sample is consistent with the simulate one. The result reveals that the sample of compound **1** is pure. Thermal behavior of compound **1** was studied by thermogravimetric analysis. As shown in Fig. S3, the weight loss corresponding to the decomposition of organic composition and triiodide ion is observed from room temperature to 330 °C. The residue can be considered as CdO (obsd 28.8%, calcd 29.0%). The morphologies of compound **1** were characterized by scanning electron microscopy (Fig. 2). In addition, compound **1** has potential channels, so the BET surface was confirmed by measuring the N₂ adsorption experiments (Fig. S4). The N₂ sorption isotherm at 77 K shows a characteristic type III behavior, which exhibits that there is not micropore in compound **1** before removing triiodide ions.

The photoluminescence properties of compound **1** have been investigated at room temperature. The emission and excitation peaks of **1** are shown in Fig. 3, and the main emission peak is at 444 nm ($\lambda_{ex} = 322$ nm). Meanwhile, the emission spectrum of organic ligand HIN has been also investigated (Fig. S5), and the main emission peak is located at 456 nm. Compared with HIN, the emission peak of **1** is blue-shifted by 12 nm. It may be attributed to the coordination effects of organic ligand to Cd(II) cations, which increases the ligand conformational rigidity and reduces the nonradiative decay of the intraligand [33]. In addition, the maximum emission peak for compound **1** is similar to the reported compounds without iodine {454 nm for [Cd(IN)₂·(H₂O)] and 457 for [Cd₂(IN)₂(SO₄)(DMF)₂] [34]. The results show the emission peak of compound **1** is probably caused by the π^* -n or π^* - π of HIN, and may be not affected by triiodide ions.

In summary, an IMOF with the interesting 3D structural motif has been synthesized by using iodine and potassium iodide as templates. The structure of compound **1** shows a 3D framework constructed by rod-shaped metal chains together with IN anions and triiodide ion located in the channel. The luminescent properties of **1** have also been investigated. The result demonstrates that rational synthesis using a target template, such as iodine, provides a progressive evolution for the construction of MOFs with fascinating structural topologies and excellent properties.

Fig. 1. (a) The local coordination environments of Cd(II) ions in **1**. Symmetry codes: #1 *x*, *y* - 1, *z*; #2 *x* - 1, *y*, *z*; #3 -*x* + 1, -*y*, -*z* + 1; #4 -*x* + 1, -*y* + 1, -*z* + 1; #5 -*x* + 1, -*y*, -*z* + 2; #6 *x* + 1, *y*, *z*; #7 -*x* + 1, -*y* + 1, -*z* + 2. (b) The rod-shaped Cd(II) chain (c) View of the 3D framework. (d) The (3⁶·4¹⁸·5³·6) topology of **1**.

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