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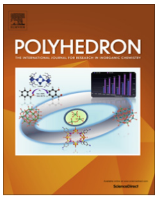

Four metal–organic frameworks constructed with hydroxylphenyl imidazole dicarboxylate: Syntheses, crystal structures and properties

Bing-Bing Shi, Shao-Feng Liu, Li Guo, Xian-Qiang Li, Gang Li *

College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, Henan, PR China

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ABSTRACT

Solvothermal reactions of 2-(3-hydroxylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid (m-OHPhH$_3$IDC) with Sr(II), Ba(II) and Zn(II) metals, respectively, lead to four metal–organic frameworks, namely, $[Sr(m\text{-}OHPhH_2IDC)_2(H_2O)_2]_n$ (**1**), $\{[Sr(m\text{-}OHPhH_2IDC)_2(H_2O)_2]\cdot H_2O\}_n$ (**2**), $\{[Zn_2(m\text{-}OHPhHIDC)_2(phen)_2]\cdot H_2O\}_n$ (phen = 1,10-phenanthroline) (**3**) and $[Ba(m\text{-}OHPhH_2IDC)_2(H_2O)_2]_n$ (**4**). According to the single-crystal X-ray structural analyses, in these polymers, the m-OHPhH$_3$IDC ligand can be singly deprotonated or doubly deprotonated, and coordinates to metal ions by diverse modes. Complexes **1**, **2** and **4** exhibit 2D layered structures with rhombic grids. Complex **3** generates a wave-like architecture by π–π interactions from a zigzag chain. The thermal and solid-state photoluminescence properties of the complexes have been investigated and discussed in detail.

1. Introduction

Over the last couple of decades, considerable attention is being bestowed on the design and self-assembly of metal–organic frameworks (MOFs), not only because of their intrinsic aesthetic appeal but also of their potentially exploitable properties [1,2]. However, the design of predetermined polymeric architectures showed limited success, therefore rational control in the construction of MOFs are still facing great challenge.

It is well established that the coordination trend of metal centers and the nature of the organic ligands used play a vital role in the construction of the MOFs [3]. In this regard, it would be highly desirable to utilize suitable organic ligands with functional groups capable of bridging metals to build up such tailored crystalline materials. Among the well employed organic ligands, a wide variety of N- and/or O-donor multidentate ligands are well explored in the literature [4], for example, Henschel's group has reported one-dimensional Ba-based polymeric structure in the case of the combination of barium cations with benzene-1,2-di(sulfonyl)amine (BSA) [5]. In addition, as compared to the reports of d-block transition metal polymers, alkaline earth polymeric complexes are underdeveloped [4,5].

In this context, the organic ligands of N-heterocyclic carboxylates can serve as excellent candidates for preparing highly connected, self-penetrating, or helical coordination frameworks due to their bent backbones and versatile bridging fashions and potential hydrogen bonding donors and acceptors [6]. Recently, imidazole-4,5-dicarboxylic acid (H$_3$IDC) and its 2-position substituted derivatives with diverse substituent groups such as methyl, ethyl, or pyridyl groups have attracted particular attention [7]. To systematically gain insight into these ligands, we endowed the backbone of H$_3$IDC with the bulky aromatic group at the 2-position of the imidazole ring. Our recent findings indicated that 2-phenyl-1*H*-imidazole-4,5-dicarboxylic acid (H$_3$PhIDC) and 2-(p-hydroxylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid (p-OHPhH$_3$IDC) are promising bridging ligands for constructing desired MOFs [8]. Meanwhile, the bulky aromatic group can supply additional stabilizing forces in controlling the assembly of related MOFs [8]. As a continuation and deepening of our former investigations, we consider that by changing the position of hydroxyl unit to reveal some new structural factors of the new ligand 2-(3-hydroxylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid (m-OHPhH$_3$IDC), and this will provide more useful information of the hydroxyl substituent effect in such a ligand. During our efforts, we successfully obtain four MOFs, $[Sr(m\text{-}OHPhH_2IDC)_2(H_2O)_2]_n$ (**1**), $\{[Sr(m\text{-}OHPhH_2IDC)_2(H_2O)_2]\cdot H_2O\}_n$ (**2**), $\{[Zn_2(m\text{-}OHPhHIDC)_2(phen)_2]\cdot H_2O\}_n$ (phen = 1, 10-phenanthroline) (**3**) and $[Ba(m\text{-}OHPhH_2IDC)_2(H_2O)_2]_n$ (**4**) under solvothermal conditions.

To the best of our knowledge, no examples of m-OHPhH$_3$IDC-based MOFs have been reported so far. Single-crystal X-ray diffractions reveal that the m-OHPhH$_3$IDC ligand shows a variety of coordination modes (Scheme 1) and strong coordination abilities. The molecular structures of **1**–**4** have been determined by

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* Corresponding author. Tel./fax: +86 371 67781764.
E-mail address: gangli@zzu.edu.cn (G. Li).

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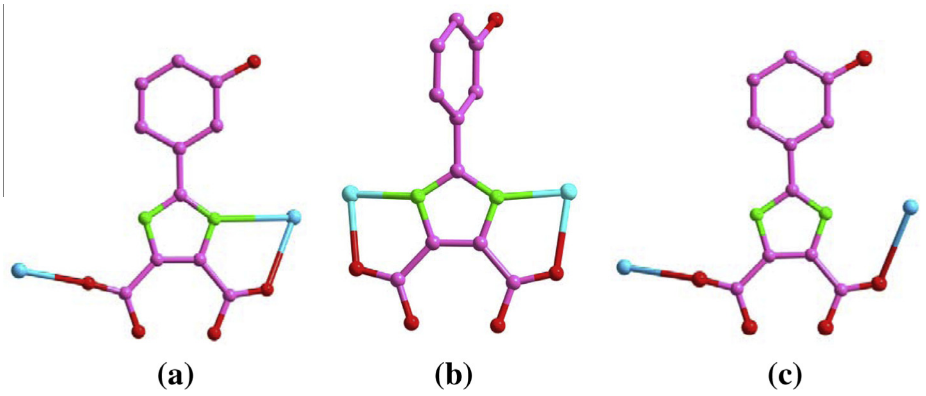

Scheme 1. Coordination modes of the imidazole dicarboxylate ligands.

single-crystal X-ray crystallography and confirmed by IR spectroscopy and elemental and differential thermal analyses. Furthermore, the solid-state photoluminescence properties of the polymers have been investigated at room temperature as well.

2. Experimental

2.1. Materials and measurements

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The organic ligand *m*-OHPhH$_3$IDC was prepared according to literature procedure [9].

The C, H and N microanalyses were carried out on a FLASH EA 1112 analyzer. IR spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets in the 400–4000 cm^{-1} region. Thermal gravimetric (TG) measurements were performed by heating the crystalline sample from 20 to 850 °C at a rate of 10 °C min^{-1} in air on a Netzsch STA 409PC differential thermal analyzer. Fluorescence spectra were characterized at room temperature by a F-4500 fluorescence spectrophotometer.

2.2. Preparation of [Sr(m-OHPhH$_2$IDC)$_2$(H$_2$O)$_2$]$_n$ (1)

A mixture of Sr(NO$_3$)$_2$ (21.2 mg, 0.1 mmol), *m*-OHPhH$_3$IDC (24.7 mg, 0.1 mmol) and CH$_3$CH$_2$OH/H$_2$O (3/4, 7 mL), Et$_3$N (0.056 mL, 0.4 mmol) were sealed in a 25 mL Teflon-lined bomb and heated at 150 °C for 96 h. The reaction mixture was then allowed to cool to room temperature at a rate of 10 °C/h. Colorless flake-shaped crystals of **1** were collected, washed with distilled water, and dried in air (65% yield based on Sr). *Anal.* Calc. for $C_{22}H_{18}N_4O_{12}Sr$: C, 42.72; H, 2.91; N, 9.06. Found: C, 42.40; H, 2.89; N, 9.18%. IR (cm^{-1}, KBr): 3489 (s), 3252 (m), 3261 (s), 1653 (m), 1464 (w), 1377 (w), 1333 (m), 1242 (m), 1210 (s), 1112 (s), 1096 (m), 997 (m), 881 (m), 795 (s), 732 (s), 667 (m), 557 (w), 533 (s).

2.3. Preparation of {[Sr(m-OHPhH$_2$IDC)$_2$(H$_2$O)$_2$]·H$_2$O}$_n$ (2)

A mixture of Sr(NO$_3$)$_2$ (21.2 mg, 0.1 mmol), *m*-OHPhH$_3$IDC (24.7 mg, 0.1 mmol), 2,2′-bipy (15.6 mg, 0.1 mmol) and CH$_3$CN/H$_2$O (3/4, 7 mL), Et$_3$N (0.056 mL, 0.4 mmol) were sealed in a 25 mL Teflon-lined bomb and heated at 150 °C for 96 h. The reaction mixture was then allowed to cool to room temperature at a rate of 10 °C/h. Colorless flake-shaped crystals of **2** were collected, washed with distilled water, and dried in air (76% yield based on Sr). *Anal.* Calc. for $C_{22}H_{20}N_4O_{13}Sr$: C, 41.51; H, 3.14; N, 8.81. Found: C, 40.75; H, 3.39; N, 9.01%. IR (cm^{-1}, KBr): 3389 (m), 3091 (w), 1682 (m), 1541 (w), 1400 (s), 1376 (w), 1261 (m), 1231 (m), 1112 (s), 994 (s), 884 (s), 790 (s), 735 (s), 550 (m), 533 (m).

2.4. Preparation of {[Zn$_2$(m-OHPhHIDC)$_2$(phen)$_2$]·H$_2$O}$_n$ (3)

A mixture of Zn(NO$_3$)$_2$ (18.9 mg, 0.1 mmol), *m*-OHPhH$_3$IDC (24.7 mg, 0.1 mmol), phen (19.8 mg, 0.1 mmol), and CH$_3$CH$_2$OH/H$_2$O (3/4, 7 mL), pyridine (0.39 mL, 0.5 mmol) were sealed in a 25 mL Teflon-lined bomb and heated at 160 °C for 72 h. The reaction mixture was then allowed to cool to room temperature at a rate of 10 °C/h. Colorless flake-shaped crystals of **3** were collected, washed with distilled water and dried in air (67% yield based on Zn). *Anal.* Calc. for $C_{46}H_{32}N_8O_{11}Zn_2$: C, 54.98; H, 3.19; N, 11.16. Found: C, 55.09; H, 3.45; N, 11.04%. IR (cm^{-1}, KBr): 3426 (s), 1530 (s), 1578 (m), 1498 (w), 1427 (s), 1394 (w), 1257 (s), 1221 (m), 843 (s), 756 (s).

2.5. Preparation of [Ba(m-OHPhH$_2$IDC)$_2$(H$_2$O)$_2$]$_n$ (4)

A mixture of BaCl$_2$·2H$_2$O (24.4 mg, 0.1 mmol), *m*-OHPhH$_3$IDC (24.7 mg, 0.1 mmol), 2-picolinate (0.012 mg, 0.1 mmol) and CH$_3$CN/H$_2$O (3/4, 7 mL), pyridine (0.39 mL, 5.0 mmol) were sealed in 25 mL Teflon-lined bomb and heated at 160 °C for 96 h. The reaction mixture was then allowed to cool to room temperature at a rate of 10 °C/h. Brown crystals of **4** were collected, washed with distilled water, and dried in air (58% yield based on Ba). *Anal.* Calc. for $C_{22}H_{12}N_4O_{12}Ba$: C, 39.88; H, 1.81; N, 8.46. Found: C, 39.92; H, 1.69; N, 8.22%. IR (cm^{-1}, KBr): 3430 (m), 3222 (m), 1696 (w), 1593 (m), 1402 (w), 1473 (s), 1396 (m), 1293 (w), 1118 (s), 1030 (w), 998 (m), 843 (m), 731 (s), 683 (m), 620 (w), 550 (w), 532 (m).

2.6. Crystal structure determinations

Single-crystal data for **1**–**4** were obtained on a Bruker smart APEXII CCD diffractometer with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All data were collected at room temperature using the ω–2θ scan technique and corrected for Lorenz-polarization effects. Furthermore, a correction for secondary extinction was applied.

The four structures were solved by the direct methods and expanded using the Fourier technique. The hydrogen atoms on C were positioned geometrically and refined using a riding model. The hydrogen atoms on O were found at reasonable positions in the differential Fourier map and located there. All the hydrogen atoms were included in the final refinement. The final cycle of full-matrix least squares refinement was based on 2041 observed reflections and 192 variable parameters for **1**, and 5363 observed reflections and 394 variable parameters for **2**, 9100 observed