Journal of Solid State Chemistry 260 (2018) 159–164

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Zinc-coordinated MOFs complexes regulated by hydrogen bonds: Synthesis, structure and luminescence study toward broadband white-light emission

Hui Duan, Wenyan Dan*, Xiangdong Fang*

College of Chemical Science and Engineering, Shanghai Key Laboratory of Chemical Assessment and Sustainability (CAS), Tongji University, 1239 Siping Road, Yangpu District, Shanghai 200092, People's Republic of China

ARTICLE INFO

Keywords:
Zinc complexes
Coordination polymer
Metal-organic frameworks
Hydrogen bond
Topology
Photoluminescence

ABSTRACT

Two new compounds, namely $\{[Zn(apc)_2]\cdot H_2O\}_n$ (**1**) and $[Zn(apc)_2(H_2O)_2]$ (**2**), have been designed and synthesized with a multi-functional ligand 2-aminopyrimidine-5-carboxylic acid (Hapc). Both compounds were characterized by single crystal X-ray diffraction analysis (SC-XRD), elemental analysis (EA), infrared spectroscopy (IR), and thermogravimetric analysis (TG). In solid-state structures, **1** features a two-fold interpenetrating pillared-layer 3D framework with point symbol $\{8^3\}_2\{8^6\}$, referring to tfa topology; while **2** exhibits a 3D framework based on super unit of $Zn(apc)_2(H_2O)_2$ interconnected via hydrogen bonds. Furthermore, the luminescent properties of **1** and **2** were discussed.

1. Introduction

Coordination polymers (CPs), such as porous coordination polymers (PCPs) and metal-organic frameworks (MOFs), have been extensively studied over the last decade, owing to their promising applications in the areas of gas storage and separation [1], drug delivery [2], molecular recognition [3], catalysis [4], luminescence [5], and magnetism [6]. The structure and property of CPs depend on the nature of their metal cations and ligands. Designing CPs with an eye for novel structures and utilities by sagacious choice of various metal ions and ligands always constitutes one of the most intriguing research topics of chemistry and materials science [7]. Among the factors that may influence the CP structures, the existence of hydrogen bonds are capable of gaining overall structural rigidity [8], and the stability of the corresponding molecular networks can be increased by augmenting the number or strength of the hydrogen bonds in which each tectonic subunit participates [9]. However, due to their reversible nature, hydrogen bonds are affected by various factors such as intermolecular distances, temperature, pressure and solvents [10]. As a result, the reports concerning the design and synthesis of functional CPs involving both coordination bonds and hydrogen bonds are rather scarce in the chemical literature [11].

With recent development and applications of MOF materials, manipulation of light-emitting properties of MOF materials has attracted considerable interest based on consideration of lifetime, luminous efficiency, and energy conservation [12]. In particular, white light-emitting luminophores of MOF materials stand out as a rational choice, because white light-emitting diodes (WLEDs) are favored over conventional light sources for minimizing global energy consumption. To better serve this purpose, the emission spectra of designed materials have to spread the entire visible light region and mimic the blackbody radiation of an incandescent bulb. Thus, zinc-coordinated MOF systems come into the research focus with the following advantages. First, it has been demonstrated in the literature that zinc-supported CPs with broadband white-light emission properties can be synthesized and elaborated by judicious selection of appropriate coordinating ligands in the MOF, although a traditional way to achieve the white-light emission is to combine various monochromatic emitters [12]. Secondly, Zn(II) metal centers with d^{10} electronic configuration and lack of crystal-field stabilization are suitable choices for coordination polymer materials with molecular structures simply predicted by the arrangement and binding modes of carboxylate ligands [7b]. Finally, the introduction of zinc metal ions into the MOFs materials blends in low intrinsic toxicity and excludes undesirable changes in the chromaticity of emitting phosphors [13]. Hydrogen bonds are pervasive in nature and can occur between molecules or within a single molecule, which help to lower the system energy and to stabilize the conformation of the molecule [14]. In this respect, we anticipate that the introduction of hydrogen bonds in MOF materials may further restrict the axial rotation of rigid ligand system, and hence enhance the luminescence activity of the materials by facilitating favorable intersystem crossing (ISC) and ligand-metal charge transfer (LMCT). However, the hydrogen-bonding mechanism is rather complex such that its predictable applications in MOFs materials remain largely

---

* Corresponding authors.
E-mail addresses: wydan@tongji.edu.cn (W. Dan), xdfang@tongji.edu.cn (X. Fang).

https://doi.org/10.1016/j.jssc.2018.01.024
Received 12 November 2017; Received in revised form 13 January 2018; Accepted 25 January 2018

unexplored. Therefore, the synthesis and property studies of zinc-coordinated MOFs stabilized by internal hydrogen bonds are attractive but challenging. Herein, we used a solvothermal reaction of an aminopyrimidylcarboxylate ligand (2-aminopyrimidine-5-carboxylic acid, Hapc) and Zn^{2+} to obtain zinc-coordinated MOFs materials whose structure were stabilized by internal hydrogen bonds. The Hapc ligand is chosen based on the following reasons: (1) It is reasonable that the deprotonated carboxylate group tends to coordinate Zn^{2+} cation and 2-aminopyrimidine motif serves as the hydrogen bond linker by supplying essential donor and acceptor of hydrogen bonding; (2) Zinc-coordinated MOF structures become since rigid on the basis of π-stacking of pyrimidine rings and hydrogen bond formation, as a result of restricted axial rotation of aromatic rings; (3) Zinc-coordinated MOFs have been utilized as nontoxic, stable and highly effective light-emitting luminophores [13,15]. In this regard, a solvothermal synthesis of two zinc-coordinated MOF complexes [16], namely $\{[Zn(apc)_2]\cdot H_2O\}_n$ (**1**) and $[Zn(apc)_2(H_2O)_2]$ (**2**), has been accomplished. To the best of our knowledge, there has not even been a literature report concerning the synthesis and characterization of such types of metal complexes. Both **1** and **2** demonstrate high thermal stability, and their luminescence properties have been investigated.

2. Experimental section

2.1. Material and methods

All reagents for syntheses were purchased from commercial sources. Thermogravimetric (TGA) analyses were investigated with a NETZSCH STA 409 analyzer in N_2 atmosphere with a heating rate of 5 K min^{-1}, from 25 °C to 800 °C. Elemental analysis was measured on an Elementar Vario EL III microanalyzer. IR spectra were measured from a KBr pellets on a Thermo Scientific Nicolet IS10 FT-IR spectrometer in the range of 4000–400 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were measured using a Bruker D8 powder diffractometer at 40 kV, 40 mA for Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 0.2 s/step and a step size of 0.05° (2θ). The luminescence analyses were performed on a Hitachi F-7000 spectrofluorometer in the solid state. The lifetime measurements were measured on an Edinburgh Instruments FLS920 fluorescence spectrometer using a microsecond (100 mW) lamp.

2.2. Synthesis of compounds 1 and 1′

$\{[Zn(apc)_2]\cdot H_2O\}_n$ (**1**) were obtained by solvothermal synthesis. A mixture of Hapc (0.032 g, 0.1 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.017 g, 0.05 mmol), DMF (2.0 mL), anhydrous ethyl alcohol (2.0 mL), and deionized water (0.5 mL) was placed in a 10 mL glass bottle and stirred for 1 h at rt. After the mixture was sealed in a Pyrex tube and heated at 60 °C for 2 days, the whole apparatus is cooled to room temperature. Colorless block crystals of compound **1** were collected by filtration (yield: 45% based on $Zn(NO_3)_2\cdot 6H_2O$). Elemental analysis (%): calcd. for $\{[Zn(apc)_2](H_2O)\}_n$ (359.61): C 33.40, H 2.80, N 23.37; found: C 33.55, H 3.90, N 23.30. IR (KBr, cm^{-1}): 3407(m), 3326(m), 1654(w), 1620(m), 1544(w), 1512(w), 1411(m), 1350(m), 1301(w), 1242(w), 1173(m), 1052(w), 1003(w), 979(w), 885(w), 846(m), 804(m), 772(w), 694(m), 600(w), 556(m).

The single crystal of **1′**, $\{[Zn(apc)_2]\}_n$, as the anhydrous compound **1** was obtained when **1** was heat at 393 K for 1 h. In addition, **1′** quickly became **1** via sorption of the water molecules from air (Table 1).

2.3. Synthesis of compound 2

The procedure for preparation of compound **2** is similar to compound **1**, 2 mL instead of 0.5 mL of deionized water was used. Light yellowish rod crystals were obtained by filtration (yield: 42% based on $Zn(NO_3)_2\cdot 6H_2O$). Elemental analysis (%): calcd. for $[Zn(apc)_2(H_2O)_2]$ (377.63): C 31.80, H 3.20, N 22.25; found: C 31.89, H 3.28, N 22.21. IR (KBr, cm^{-1}): 3427(m), 3334(m), 3198(m), 3037(w), 1660(m), 1598(w), 1564(m), 1542(w), 1517(w), 1418(m), 1362(m), 1301(w), 1244(m), 1046(w), 876(w), 857(w), 807(m), 682(w), 663(w), 547(m).

2.4. Single crystal X-ray diffraction

Single-crystal X-ray diffraction measurements were carried out on a Bruker D8 VENTURE diffractometer using Mo-Kα (λ = 0.71073 Å) and Cu-Kα (λ = 1.54178 Å) radiation at 150(2) K and 296(2) K. Data reduction was performed with the SAINT [17] and absorption corrections were applied by the SADABS program [18]. All structures were solved by using the SHELXT program and refined with SHELX-2016 program [19]. Heavy atoms and other non-hydrogen atoms are directly obtained from different Fourier maps. The final refinements were performed by the full-matrix least-square method with anisotropic thermal parameters for all non-hydrogen atoms on F^2. The hydrogen atoms of water were obtained from different Fourier maps in **1** and **2**. Other hydrogen atoms were added theoretically, which rode on the concerned atoms, and were not refined. CCDC 1281617 (**1**), 1581619 (**1′**), 1581618 (**2**), and 1584934 (Hapc) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. Crystal structures of 1 and 1′

Single-crystal X-ray diffraction measurements revealed that compounds **1** and **1′** have the same frameworks. The asymmetric unit of **1** contains one molecule of apc$^-$ ligand, a half of Zn^{2+} ion and H_2O (Fig. 1a). As shown in Fig. 1a, the Zn^{2+} ion which coordinates two carboxylate oxygen (Zn-O, 1.9570(12) Å) and two pyrimidine nitrogen atoms (Zn-N, 2.0902(14) Å) has distorted tetrahedral conformation. The carboxylate group of Hapc coordinates the zinc ion in a monodentate fashion (Fig. 1a), and is further deprotonated as suggested by similar two C-O bond lengths (1.278(2) and 1.231(2) Å). Each apc$^-$ ligand connects two zinc ions through two coordinated bonds of Zn-O and Zn-N. It is noteworthy that internal hydrogen bonds exist both between amino and water molecule ($d_{N\text{-}H\cdots O}$ = 2.958(3) Å, $d_{O\text{-}H\cdots N}$ = 2.8947(17) Å, Fig. S1), and between amino and carboxylate ($d_{N\text{-}H\cdots O}$ = 2.856(2) Å, Fig. S3). The structural stability provided by hydrogen bonding promotes the transformation from compound **1′** to **1** via water sorption from air. In addition, the structures of apc$^-$ ligands that act as bridges between Zn1 atoms become more rigid, as indicated by a small rotation of 1.2° (in **1′**, the rotation of 4.5°).

The ZnO_2N_2 tetrahedrons were corner-shared to form a 2D network along the c axis (Fig. 1b). Interestingly, a pillared-layer 3D framework was generated by internal hydrogen bonds between water and apc$^-$ ligands of 2D network (Fig. 1c). Pillared-layer frameworks were generally composed of 4, 4′-bipyridine (or analogues) and metal ions through coordinated bonds [20]. However, the hydrogen bonds between water and amino group formed the pillar-layer in **1**, which is rarely observed in CPs. ZnO_2N_2 tetrahedron was connected with four neighboring polyhedrons in the *a* and *b* directions, resulting in a one dimensional (1-D) channel with the size of 4.0 × 5.0 Å by considering the van der Waals radius (Fig. S4). Due to hydrogen bond between amino group and the uncoordinated oxygen atom of the carboxylate group ($d_{N\text{-}H\cdots O}$ = 2.953(2) Å), the other 2D network was formed by the elongated apc$^-$ ligand. (Fig. S5), the two parallel 2D planes became a two-fold interpenetrating 2D network. In the meantime, the robustness of the overall crystal formation is reinforced via relatively strong π–π interactions between the aromatic rings of the ligands (Table S3 and Figs. S6–S7). In structure of **1**, a two-fold interpenetrating 3D network