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New Zn²⁺ coordination polymers constructed from acylhydrazidate molecules: synthesis and structural characterization

Yan-Ning Wang,^a Guang-Hua Li,^a Fu-Quan Bai,^{b,*} Jie-Hui Yu^{a,*} and Ji-Qing Xu^a

^a College of Chemistry and State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Jiefang Road 2519, Changchun, 130023, P.R. China

^b State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun, Jilin, 130023, China

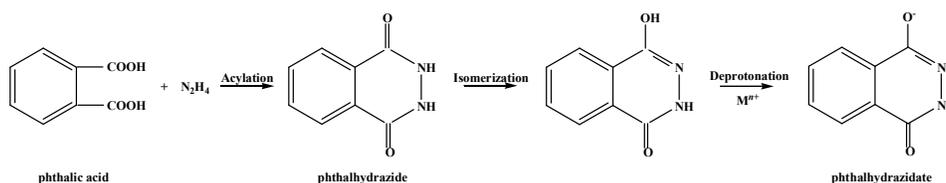
Email: jhyu@jlu.edu.cn baifq@jlu.edu.cn

By employing two types of hydrothermal *in situ* ligand reactions (acylation of N₂H₄ with aromatic polycarboxylic acids, reduction of 3-nitrophthalhydrazide by N₂H₄), three new acylhydrazidate-extended Zn²⁺ coordination polymers [Zn₂(3-apth)(atr_z)₂] (3-apth = 3-aminophthalhydrazidate; atr_z = 3-amino-1,2,4-triazolate) **1**, [Zn₂(4-apth)(atez)₂] (4-apth = 4-aminophthalhydrazidate; atez = 5-aminotetrazolate) **2**, and [Zn(3-cppth)(H₂O)] (3-cppth = 4-(3-carboxyphenoxy)phthalhydrazidate) **3** were obtained. X-ray single-crystal diffraction analysis revealed that (i) compound **1** possesses a 3-D structure. The triazolate molecules link the Zn²⁺ ions to form a 2-D layer with a (6,3) topology. Then the acylhydrazidate molecule acts as the second linker, extending the (6,3) nets into a 3-D network of compound **1**; (ii) compound **2** also exhibits a 3-D structure. The acylhydrazidate molecules first link the Zn²⁺ ions into a 1-D infinite chain. The tetrazolate molecules propagate further the chains into a 3-D (4,4)-connected net (symbol: (4·6⁴·8)₂(4²·6²·8²)); (iii) compound **3** only shows a 1-D chain structure. The photoluminescence analysis indicates that the title three compounds all emit light, especially compound **2** emits the extremely strong blue light. The side group on phthalhydrazidate molecule plays a crucial role in the emission behaviors of compounds **1-3**. At 77 K, the activated **2** can adsorb N₂ with the amount of *ca.* 41.0 cm³ g⁻¹.

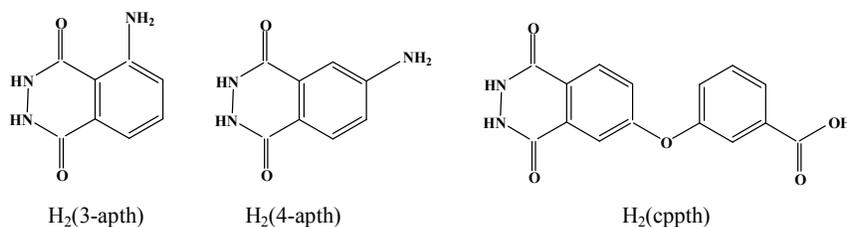
Introduction

The design and synthesis of novel metal-organic frameworks (MOFs) attracts the considerable attention in virtue of their structural diversity,¹ and the potential applications in adsorption,² optics,³ magnetism⁴ and catalysis.⁵ Through the self-assemblies of metal ions with organic N/O/S-donor ligands, a large number of MOFs have been constructed over the past two decades. However, since the self-assembling process is rather complicated, and dominated by many factors as the geometric configuration of metal ions, the nature of organic ligands (size, shape, flexibility/rigidity), and the detailed experimental conditions (solvent, pH, reaction temperature, ratio of metal-to-ligand), it is still a great challenge to get a target MOF with pre-designed structure and desirable property.⁶ N-heterocyclic molecules and polycarboxylic acid molecules have been widely employed in the construction of novel MOFs.⁷ As a kind of new-type bridging ligand, the organic acylhydrazide molecules are still less used so far.⁸ In the last five years, one of the investigations in our group is focused on the structural characterization of acylhydrazidate-coordinate compounds, where the acylhydrazidate molecules derive from the hydrothermal *in situ* acylation of N₂H₄ with aromatic polycarboxylic acids.⁹ As shown in Scheme 1, due to the acylation and isomerization, the phthalhydrazidate moiety generally has a -1 charge, and four donor atoms are nearly co-planar. So the coordination behavior of the phthalhydrazidate moiety in a complex is completely different from that of the phthalate moiety (having a -2 charge, *trans*-mode arrangement for two carboxyl groups). Based on our previous work and the related documents, we proposed a strategy of constructing acylhydrazidate-propagated MOFs in our latest report.¹⁰ Similar to the phthalate molecule, the phthalhydrazidate molecule is prone to forming an oligomer with metal ion. So a simple modification is necessary: (i) using the

diacylhydrazidate molecule as the ligand precursor. The diacylhydrazidate molecule has four acylamino groups, and they are distributed on four corners. So the diacylhydrazidate molecule possesses the potential to form an extended MOF with metal ion. This has been confirmed by the obtainment of compounds [Ba(pmdh)] (pmdh = pyromellitidihydrazidate) and [Ba(sdpth)(H₂O)₂] \cdot 0.5H₂O (sdpth = 4,4'-sulfoylidiphthalhydrazidate).¹⁰ It is noteworthy that the activated [Ba(sdpth)(H₂O)₂] \cdot 0.5H₂O can adsorb N₂ with the capacity of *ca.* 80 cm³ g⁻¹ at 77 K; (ii) incorporating the second linker into the metal-monoacylhydrazidate system. The obtainment of the 3-D compounds [Zn₂(2,3-pdh)₂(ox)] \cdot H₂O (2,3-pdh = pyridine-2,3-dicarboxylhydrazidate, ox = oxalate)¹⁰ and [Zn₂(pth)(atez)₂] (pth = phthalhydrazidate, atez = 5-aminotetrazolate)¹¹ suggests that this modulation is also effective. The organic molecule with a small size may be more easily mixed into the metal-monoacylhydrazidate system. Although the 2-fold interpenetration is observed in compound [Zn₂(2,3-pdh)₂(ox)] \cdot H₂O, it still adsorbs N₂ at 77 K (*ca.* 60 cm³ g⁻¹); (iii) using the donor atom to modify 4- or/and 5-position(s) of phthalhydrazide molecule. After being modified, the monoacylhydrazidate molecule can serve as a T-shape linker, which tends to link the metal ion into a MOF. Based on this, the 3-D compounds [Pb(3,4-pdh)] (3,4-pdh = pyridine-3,4-dicarboxylhydrazidate)¹² and [Ba₂(cpth)₂(H₂O)₂] (cpth = 4-carboxylphthalhydrazidate)¹⁰ were obtained. For 3,4-pdh, a meta-position C atom of phthalhydrazide molecule is displaced by a N heteroatom, whereas for cpth, the 4-position of phthalhydrazide molecule is modified by an additional carboxyl. In order to further investigate the relationship between structure and property, on the one hand, we keep trying to mix the triazole/tetrazole molecule into the metal-acylmonohydrazidate system. On the other hand, the carboxyphenoxy-modified phthalic acid was selected as the organic acidic resource. Luckily, three new acylhydrazidate-extended coordination polymers [Zn₂(3-apth)(atrz)₂] (3-apth = 3-aminophthalhydrazidate; atrz = 3-amino-1,2,4-triazolate) **1**, [Zn₂(4-apth)(atez)₂] (4-apth = 4-aminophthalhydrazidate) **2**, and [Zn(3-cppth)(H₂O)] (3-cppth = 4-(3-carboxyphenoxy)phthalhydrazidate) **3** were obtained. In order to explore the emission mechanism of compounds **1-3**, the density functional theory (DFT) calculations were applied to the excited state of compound **3**. Scheme 2 gives the structures of the acylhydrazide molecules appearing in compounds **1-3**.



Scheme 1 Acylation of N₂H₄ with phthalic acid.



Scheme 2 Structures of acylhydrazide molecules in **1-3**.

Experimental

Materials and physical measurement

All chemicals are of reagent grade quality, obtained from commercial sources without further purification. Elemental analysis was performed on a Perkin-Elmer 2400LS II elemental analyzer. Infrared (IR) spectrum was

recorded on a Perkin Elmer Spectrum *I* spectrophotometer in 4000–400 cm^{-1} region using a powdered sample on a KBr plate. Powder X-ray diffraction (XRD) data were collected on a Rigaku/max-2550 diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Thermogravimetric (TG) behavior was investigated on a Perkin-Elmer TGA-7 instrument with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in air. Fluorescence spectrum was obtained on a LS 55 fluorescence/phosphorescence spectrophotometer at room temperature. The measurement of N_2 adsorption was carried out on an asap-2010 apparatus.

Synthesis of the title compounds

[Zn₂(3-aphth)(atr_z)₂] 1. The yellow block crystals of **1** were obtained from a simple hydrothermal self-assembly of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (55 mg, 0.25 mmol), 3-nitrophthalhydrazide (52 mg, 0.25 mmol), H(atr_z) (21 mg, 0.25 mmol) and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (0.1 mL) in a 15 mL aqueous solution (pH = 8 adjusted by N_2H_4) at $160 \text{ }^\circ\text{C}$ for 4 days. Yield: *ca.* 30% based on Zn(II). Anal. Calcd $\text{C}_{12}\text{H}_{11}\text{N}_{11}\text{O}_2\text{Zn}_2$ **1**: C 30.53, H 2.35, N 32.65. Found: C 30.64, H 2.35, N 32.68%. IR (cm^{-1}): 1653 s, 1585 s, 1514 s, 1394 s, 1304 m, 1219 s, 1162 w, 1059 m, 966 m, 864 w, 698 m, 655 m.

[Zn₂(4-aphth)(atez)₂] 2. The light-yellow columnar crystals of **2** were obtained from a simple hydrothermal self-assembly of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (66 mg, 0.3 mmol), 4-aminophthalic acid (4-apha) (54 mg, 0.3 mmol), H(atez) (31 mg, 0.3 mmol) and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (0.2 mL) in a 10 mL aqueous solution (pH = 8 adjusted by N_2H_4) at $160 \text{ }^\circ\text{C}$ for 4 days. Yield: *ca.* 25% based on Zn(II). Anal. Calcd $\text{C}_{10}\text{H}_8\text{N}_{13}\text{O}_2\text{Zn}_2$ **2**: C 25.39, H 1.71, N 38.50. Found: C 25.35, H 1.68, N 38.11%. IR (cm^{-1}): 1635 m, 1623 s, 1555 s, 1446 s, 1403 s, 1324 m, 1247 m, 1082 s, 1001 w, 880 m, 839 w, 678 w.

[Zn(3-cppth)(H₂O)] 3. The colorless block crystals of **3** were obtained from a simple hydrothermal self-assembly of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (22 mg, 0.1 mmol), 4-(3-carboxyphenoxy)phthalic acid (3-cppha) (60 mg, 0.2 mmol) and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (0.1 mL) in a 15 mL aqueous solution (pH = 6 adjusted by $\text{H}_2(\text{ox})$) at $160 \text{ }^\circ\text{C}$ for 4 days. Yield: *ca.* 35% based on Zn(II). Anal. Calcd $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_6\text{Zn}$ **3**: C 47.46, H 2.66, N 7.38. Found: C 47.36, H 2.55, N 7.20%. IR (cm^{-1}): 1656 s, 1614 w, 1505 s, 1388 s, 1265 s, 1148 w, 1071 s, 955 s, 889 w, 854 s, 815 m, 772 s, 530 m.

X-ray crystallography

The data were collected with $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Rigaku R-AXIS RAPID IP diffractometer for compounds **1** and **3**, and on a Siemens SMART CCD diffractometer for compound **2**. With SHELXTL program, the structures of compounds **1-3** were solved using direct methods.¹³ The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. The H atoms on C3 in compound **2**, and on Ow1 in compound **3** were obtained from the different Fourier map. The other H atoms were treated using a riding model. The structures were then refined on F^2 using SHELXL-97.¹³ CCDC numbers are 1009502, 1009503 and 976682 for compounds **1-3**, respectively. The crystallographic data for the compounds are summarized in Table 1.

Table 1. Crystallographic data for **1-3**.

| | 1 | 2 | 3 |
|---------------------------|--|---|---|
| Formula | $\text{C}_{12}\text{H}_{11}\text{N}_{11}\text{O}_2\text{Zn}_2$ | $\text{C}_{10}\text{H}_8\text{N}_{13}\text{O}_2\text{Zn}_2$ | $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_6\text{Zn}$ |
| <i>M</i> | 472.06 | 473.03 | 379.62 |
| <i>T</i> (K) | 293(2) | 293(2) | 293(2) |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $C2/c$ | $C2/c$ |
| <i>a</i> (\AA) | 8.9247(18) | 12.4252(6) | 8.5477(17) |

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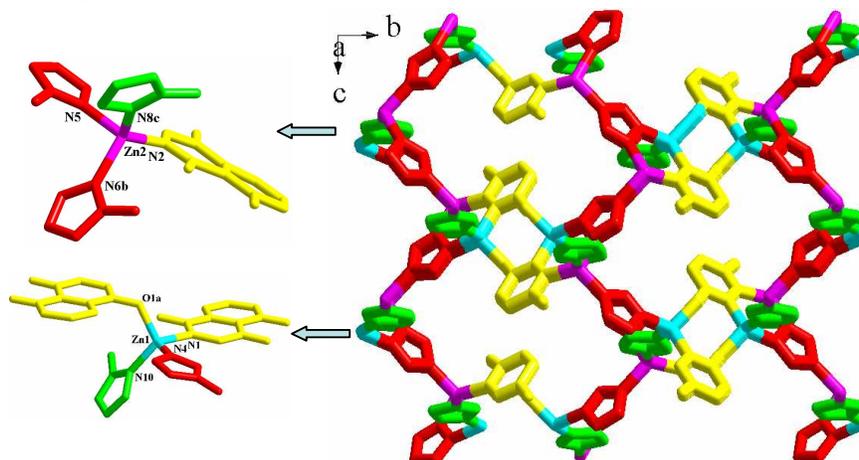
| | | | |
|-----------------------------|-----------|-------------|------------|
| b (Å) | 19.807(4) | 12.9640(9) | 18.368(4) |
| c (Å) | 9.876(2) | 10.3992(5) | 18.434(4) |
| β (°) | 104.41(3) | 117.276(3) | 94.61(3) |
| V (Å ³) | 1690.9(6) | 1487.99(14) | 2884.8(10) |
| Z | 4 | 4 | 8 |
| D_c (g cm ⁻³) | 1.854 | 2.112 | 1.748 |
| μ (mm ⁻¹) | 2.873 | 3.269 | 1.740 |
| Reflections collected | 16409 | 4136 | 13944 |
| Unique reflections | 3844 | 1328 | 3291 |
| R_{int} | 0.0449 | 0.0250 | 0.0370 |
| Gof | 1.038 | 1.064 | 1.059 |
| $R_1, I > 2\sigma(I)$ | 0.0424 | 0.0199 | 0.0318 |
| wR_2 , all data | 0.1169 | 0.0518 | 0.0786 |

Results and discussion

Synthetic analysis

All of the title compounds were obtained under the hydrothermal conditions. The reaction of Zn^{2+} , 3-nitrophthalhydrazide and H(atrz) in the presence of excessive N_2H_4 produced compound **1**. Here N_2H_4 acts as the reducer, and the $-\text{NO}_2$ group on phthalhydrazide molecule was reduced into the $-\text{NH}_2$ group. Without N_2H_4 , no crystalline product was obtained. The reactions of Zn^{2+} salt, 4-apha/3-cppha and N_2H_4 , with or without H(atrz) yielded compounds **2** and **3**. The acylhydrazidate molecules 4-apth and 3-cppth originated from the hydrothermal *in situ* acylation of N_2H_4 with corresponding polycarboxylic acid molecule. Note that the acylation of N_2H_4 with aromatic polycarboxylic acid molecules can be performed in a wide pH range (5-8), but the single-crystal growth for the title compounds was strictly controlled by pH value of the reactive system: 8 for **1**, 8 for **2**, and 6 for **3**. In the reactions, N_2H_4 is largely excessive in order to ensure the carboxyl groups to be thoroughly acylated. A series of parallel reactions have been investigated, but no satisfactory results were gained. For example, Cd^{2+} was used instead of Zn^{2+} , but the crystals suitable for X-ray single-crystal diffraction were not obtained. 4-(4-carboxyphenoxy)phthalic acid (4-cppha) was used in place of 3-cppha, but the crystal data for the as-synthesized compound $[\text{Zn}(4\text{-cppth})(\text{H}_2\text{O})]$ (4-cppth = 4-(4-carboxyphenoxy)phthalhydrazidate) did not pass the cif-checking examine.

Structure description



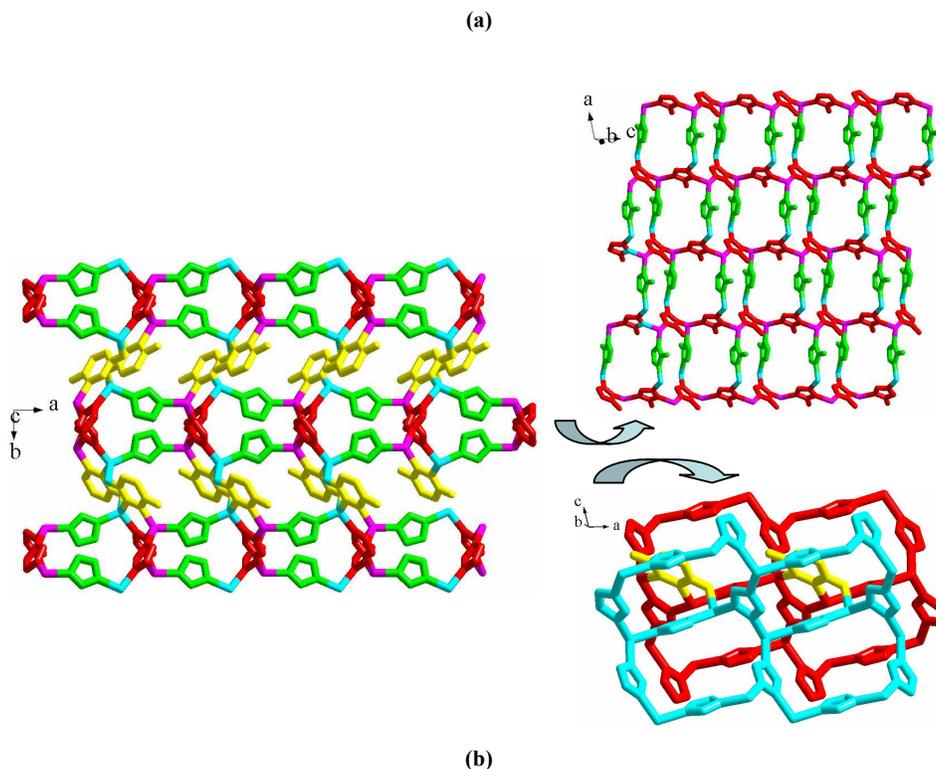


Fig. 1 Projection diagrams in (100) (a) and (001) directions (b) for **1** (a: $-x, -y+1, -z+2$; b: $x-1, y, z$; c: $x, -y+1/2, z+1/2$. $-\text{NH}_2$ and benzene ring are omitted for clarity).

[Zn₂(3-aph)(atr_z)₂] **1**. X-ray single-crystal diffraction analysis revealed that compound **1** is a new 3-D Zn²⁺ MOF extended by 3-aph and atr_z. It crystallizes in the space group $P2_1/c$, and the asymmetric unit is found to be composed of two types of Zn²⁺ ions (Zn1, Zn2), two types of atr_z molecules (atr_z I, atr_z II) and one 3-aph molecule. As shown in Fig. 1a (the inserted plots), Zn1 and Zn2 are both in a tetrahedral site, but the detailed environments are different. Zn1 is coordinate with two atr_z N atoms (N4, N10), one hydroxylimino O atom (O1a) and one hydroxylimino N atom (N1), whereas Zn2 is surrounded by three atr_z N atoms (N5, N6b, N8c) and one hydroxylimino N atom (N2). The Zn-N distances span a narrow range of 1.986(3)-2.048(3) Å, and the Zn-O bond length is short (1.967(3) Å). Two types of atr_z molecules are involved in the different coordination modes. Atr_z I adopts a double-bridged mode, while atr_z II adopts a triple-bridged mode. The μ₃-mode 3-aph molecule utilizes two N atoms and one O atom to serve as the donors. Each donor atom monodentately bonds to one Zn²⁺ ion (see Scheme 3). Bridged by atr_z and 3-aph, compound **1** shows a 3-D network structure (see Fig. 1a). Fig. 1b is the projection diagram of compound **1** in (001) direction. As displayed in Fig. 1b (the inserted plot above), two types of Zn²⁺ ions and two types of atr_z molecules aggregate to form a 2-D layer. The atr_z II molecules with 2- and 4-position N atoms link first the Zn2 ions into a 1-D zigzag-shape chain, running down the *c*-axial direction. On the other hand, atr_z I and Zn1 aggregate into a new linear unit [Zn(atr_z)]⁺. This linear unit acts as the linker, extending the 1-D zigzag chains into this 2-D layer network. Based on the topological method, this 2-D layer possesses a (6,3) topology. The inserted diagram below in Fig. 1b shows the inter-layer interactions. The 3-aph molecules occupy the space between the 2-D layers. Two hydroxylimino N atoms bidentately bond to two Zn²⁺ ions, whereas one hydroxylimino O atom monodentately interacts with another Zn²⁺ ion from the neighboring layer. In this kind of linking way, the 3-aph molecules as the connectors propagate the 2-D (6,3) nets into a 3-D network of compound **1**. The shortest Zn...Zn contact of 3.752 Å is that between Zn1 and Zn2.

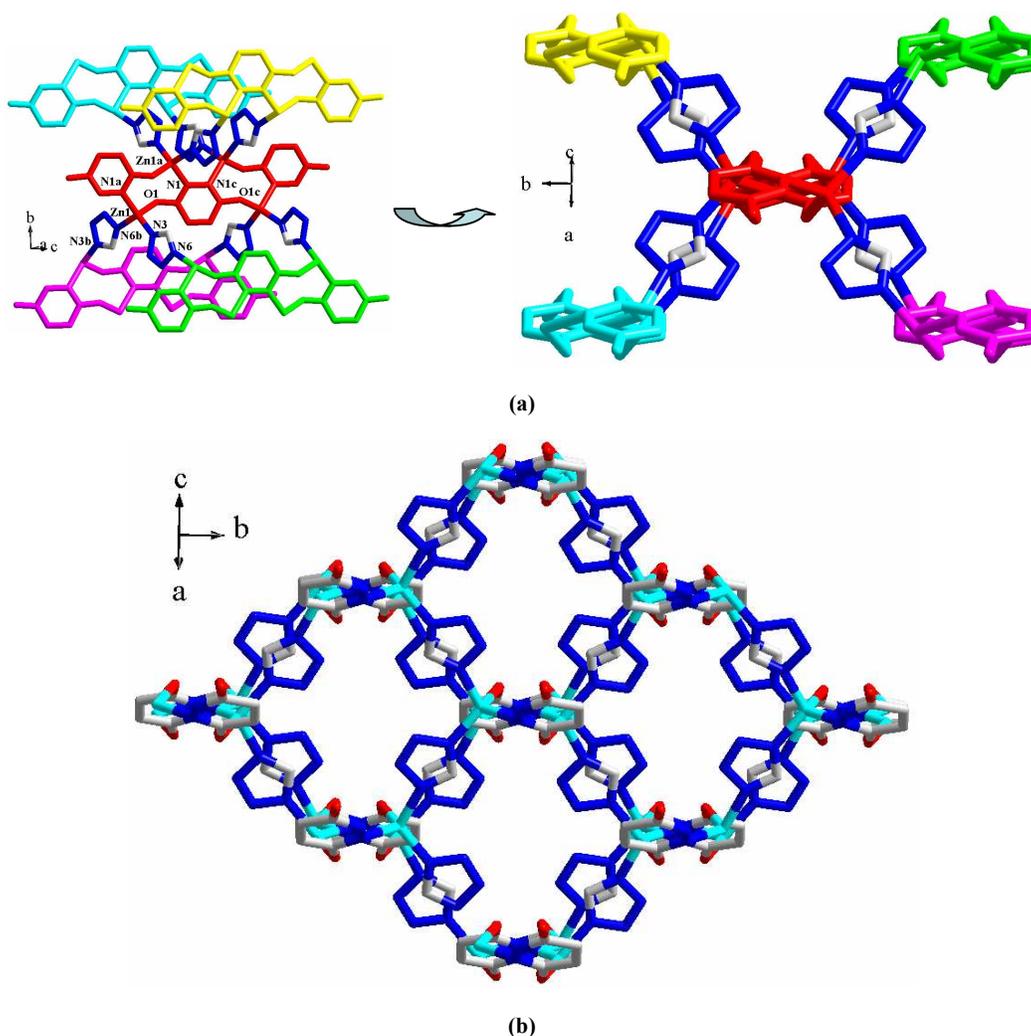


Fig. 2 1-D chain (left), interactions between chains (right) (a), and 3-D network (b) for **2** (a: $-x+1/2, -y+1/2, -z+2$; b: $x, -y, z+1/2$; c: $-x, y, -z+3/2$. $-\text{NH}_2$ and benzene ring are omitted for clarity).

[Zn₂(4-apth)(atez)₂] 2. Compound **2** is another 3-D Zn(II) MOF propagated by 4-apth and atez. It crystallizes in the space group $C2/c$, and the asymmetric unit is found to be composed of one Zn^{2+} ion (Zn1), one atez molecule and a half 4-apth molecule. As shown in Fig. 2a (left), the 4-apth molecules with two hydroxylimino groups as the donors link the Zn^{2+} ions into a 1-D endless chain, which is based on the 8-membered loops. The $\text{Zn}_2(\text{CON})_2$ ring shows a chair-mode configuration, stabilizing the chain structure. The $\text{Zn1}\cdots\text{Zn1a}$ contact is 3.777 Å. The crystallographically unique Zn1 center in the chain is involved in a tetrahedral site. Around each Zn^{2+} center, two positions are occupied by hydroxylimino N and O atoms. The remaining two positions are occupied by the atez N atoms. As shown in Fig. 2a (right), via the linkage of atez, each $\text{Zn}_2(4\text{-apth})^{2+}$ chain interacts with the adjacent four $\text{Zn}_2(4\text{-apth})^{2+}$ chains. In this way, 4-apth and atez link the Zn(II) centers into a 3-D network of compound **2** (see Fig. 2b). The 1-D channel with the size of $ca. 7 \times 3.5 \text{ \AA}$ is observed. Based on the topological method, the Zn^{2+} center can be regarded as a 4-connected node. Note that this node adopts a tetrahedral geometric configuration. The 4-apth molecule can be considered as a planar 4-connected node, while the μ_2 -mode atez acts as the linker. So compound **3** exhibits a 3-D (4,4)-connected net (symbol: $(4\cdot 6^4\cdot 8)_2(4^2\cdot 6^2\cdot 8^2)$). The tetrahedral Zn1 is surrounded by

one hydroxylimino O atom (O1), one hydroxylimino N atom (N1a) and two atez N atoms (N3, N6b). The Zn-O distance of 1.9726(15) Å and the Zn-N range of 1.9715(18)-2.0032(18) Å are comparable with those observed in compound 1. 4-Apth is involved in a tetra-bridged coordination mode: each donor atom monodentately coordinates to one Zn²⁺ ion (see Scheme 3). The double-bridged atez molecule utilizes 1- and 4-position N atoms to act as the donors.

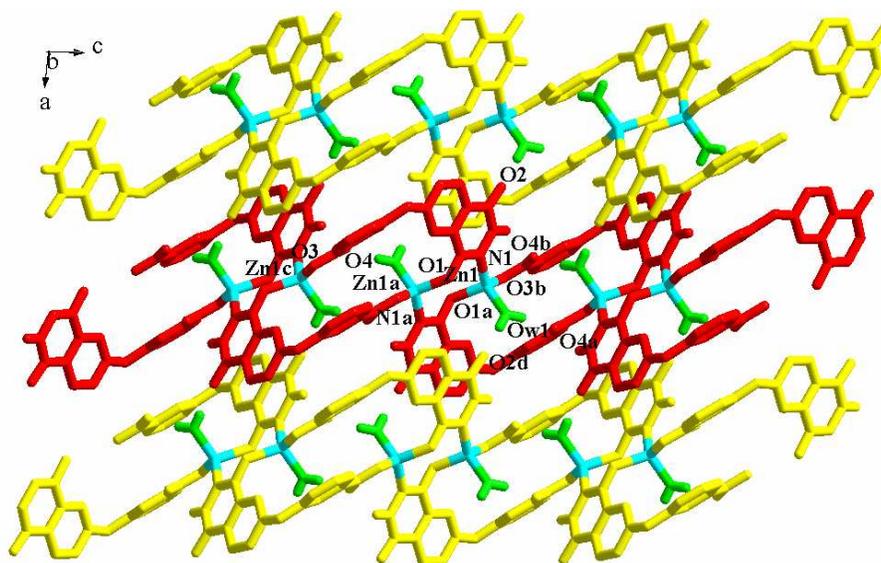
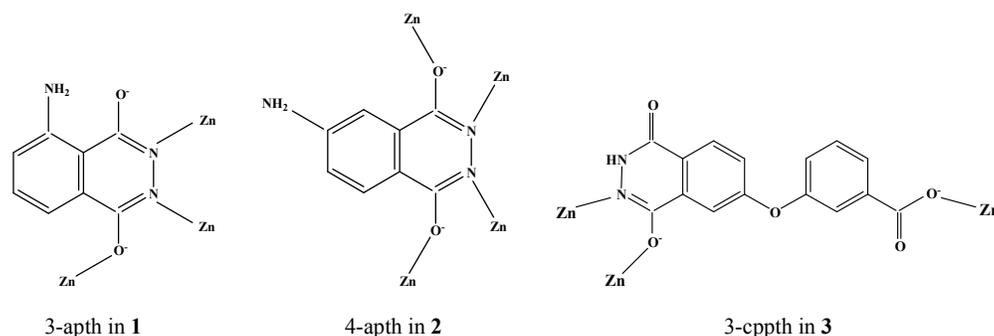


Fig. 3 1-D chain of **3**, also showing interactions between chains (a: $-x+1, -y, -z+1$; b: $x, -y, z+1/2$; c: $x, -y, z-1/2$; d: $x+1, y, z$. Hydrogen-bonded interactions are omitted for clarity).

[Zn(3-cppth)(H₂O)] 3. Compound **3** is a 3-cppth-extended chained Zn²⁺ coordination polymer. It crystallizes in the space group C2/c, and the asymmetric unit is found to be composed of one Zn²⁺ ion (Zn1), one 3-cppth molecule and one coordinate water molecule (Ow1). Zn1 with a tetrahedral geometry is completed by one hydroxylimino N atom (N1), one hydroxylimino O atom (O1a), one carboxyl O atom (O3b) and one water molecule (Ow1). 3-cppth adopts a triple-bridged coordination mode: the carboxyl with one O atom monodentately coordinates to one Zn²⁺ ion, while the phthalhydrazidate ring with the hydroxylimino N and O atoms bidentately bridges two Zn²⁺ ions (see Scheme 3). As displayed in Fig. 3, the μ_3 -mode 3-cppth molecules link the tetrahedral Zn(II) ions into a 1-D infinite chain. First of all, two 3-cppth molecules with the hydroxylimino groups alternately link two Zn(II) ions into a dinuclear units with a composition [Zn₂(3-cppth)₂]. The 8-membered Zn₂(CON)₂ ring is also observed, and it also adopts a chair-mode configuration. The Zn...Zn separation is 4.000 Å. Through using the carboxyl O atom to coordinate to the Zn(II) ion from the neighboring dinuclear unit, the dinuclear units are further linked together into a 1-D infinite chain of compound **3**. Synchronously, a big 24-membered cyclic loop is formed. The 1-D chain extends along the *c*-axial direction. Between the 1-D chains, four types of weak interactions are observed: (i) the coordinate water molecule (Ow1) forms the intermolecular hydrogen bond to the neighboring uncoordinate acylamino O atom (O2d). The Ow1...O2d separation is short (2.625(3) Å); (ii) the coordinate water molecule (Ow1) hydrogen bonds to the adjacent uncoordinate carboxyl O atom (O4a). The Ow1...O4a contact is 2.684(3) Å; (iii) along the *a*-axial direction, the neighboring benzene rings stack via the π ... π interaction (separation: *ca.* 3.31 Å); (iv) two adjacent phthalhydrazidate rings form the π ... π packing with a contact of *ca.* 3.44 Å. Via these weak interactions, compound **3** self-assembles into a 2-D supramolecular layer network. Fig. S2

illustrates the hydrogen-bonded interactions between the chains in **3**.



Scheme 3 Coordination modes of acylhydrazidate molecules in **1-3**.

As expected, the triazole/tetrazole molecules are successfully introduced into the metal-monoacylhydrazidate system, and compounds **1-2** show the 3-D network structures. In compound **2** and the report compounds $[Zn_5(OH)_2(Hpht)_2(pth)_2(trz)_2]$ ($trz = 1,2,4$ -triazolate), $[Zn_3(OH)_2(Hpht)_2(datrz)_2]$ ($datrz = 3,5$ -diamino-1,2,4-triazolate), $[Zn_2(pth)(atez)_2]$ and $[Zn_5(OH)_2(ox)(3-apth)_2(datrz)_2]$, the metal ions and the monoacylhydrazidate molecules first form an oligomer. The triazole/tetrazole molecules act as the second linkers, extending the oligomers into a high-D network.¹¹ But compound **1** shows a special situation. The monoacylhydrazidate molecule serves as the second connector, while the triazole molecules link first the Zn^{2+} ions into a 2-D layer network. As a linker, the monoacylhydrazidate molecule generally utilizes two acylamino/hydroxylimino groups or two acylamino/hydroxylimino O atoms to donor the metal ions, as observed in compound **2**.⁹ So the monoacylhydrazidate molecule can be viewed as a rod-like connector. In compound **1**, another special situation is found. The monoacylhydrazidate molecule adopts an unusual bridging mode. Although only one hydroxylimino O atom interacts with the metal ion, the hydrazino group as the donors interacts with the metal ions. This kind of bridging mode for monoacylhydrazidate molecule has never been observed in the past reports.⁹ The 4-position of the phthalhydrazide is modified by a carboxyphenoxy group, so 3-cppth can be regarded as a potential T-shape linker. But only one acylamino group for 3-cppth joins in the coordination, so compound **3** exhibits a 1-D chain structure. The side group on triazolate/tetrazolate molecule impacts the final network structures. For example, the datrz-extended compound $[Zn_5(OH)_2(ox)(3-apth)_2(datrz)_2]$ exhibits a 2-D layer network, whereas the atrz-propagated compound **1** shows a 3-D network structure. The existence of the 5-position $-NH_2$ group on triazole molecule should play a key role. As mentioned in introduction section, the acylhydrazidate molecule generally exists in a keto-hydroxyl form in a complex, which is verified by two different C-O distances.⁹ In compound **3**, 3-cppth also exists in a keto-hydroxyl form (C7-O1 = 1.288(2) Å; C8-O2 = 1.237(3) Å). However, two C-O distances are comparable with each other, and both are larger than 1.275 Å (C1-O1 = 1.314(5) Å, C4-O2 = 1.277(5) Å for **1**; C1-O1 = 1.301(3) Å for **2**), suggesting that 3-apth and 4-apth exist in a dihydroxyl form in compounds **1** and **2**. When interacting with the metal ion, the hydroxyl group deprotonates to balance the metal charge, so the acylhydrazidate molecules in compounds **1-3** all have a -2 charge. The triazole or tetrazole ligands show a -1 oxidation state in compounds **1-2**.

Characterization

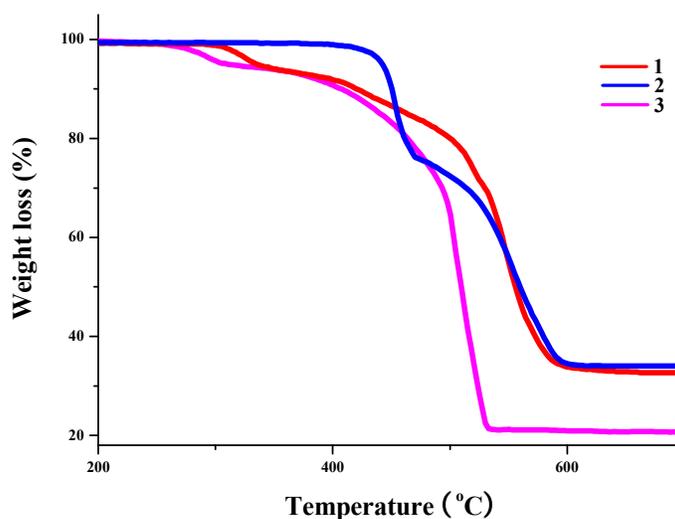


Fig. 4 TG curves of 1-3.

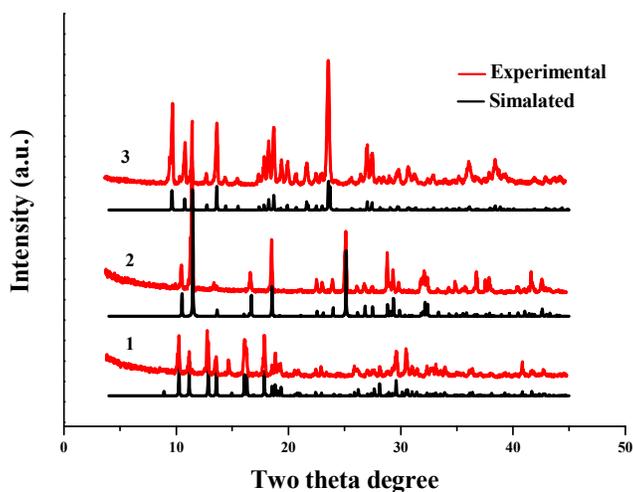


Fig. 5 Experimental (red) and simulated (black) powder XRD patterns for 1-3.

The TG behaviors of the title compounds were investigated. As depicted in Fig. 4, compounds **1** and **3** possess the similar thermal stability, because the temperatures for the onset of decomposition are comparable with each other (300 °C for **1**, 270 °C for **3**). Both underwent two steps of weight loss. For compound **3**, the first step of *ca.* 5.2% weight loss should be assigned to the sublimation of the coordination water (Calcd: 4.7%). Since the coordinate water forms two types of strong hydrogen bonds to the neighboring acylamino and carboxyl O atoms, it is very stable, and the temperature for the onset of removal is slightly high. In the second step, the organic molecule decomposed, and the Zn²⁺ synchronously combined with O₂. So the final residue was ZnO (Calcd: 21.4%; Found: *ca.* 21.0%). For compound **1**, *ca.* 4.5% of weight loss for the first step should correspond to the removal of the amino group on tetrazole molecule (Calcd: 3.5%). After the second step of weight loss, the remaining was proved

also to be ZnO (Calcd: 34.4%; Found: *ca.* 33.0%). Compound **2** also underwent two-steps of weight loss. Although the rational attribution can not be given, we can know based on the TG curve of compound **2**: (i) compound **2** possesses the best thermal stability, and can be thermal stable up to *ca.* 410 °C; (ii) the final residue was ZnO (Calcd: 34.4%; Found: *ca.* 34.0%). The experimental powder X-ray diffraction (XRD) pattern for each compound is in accord with the simulated one generated on the basis of structural data, confirming that the as-synthesized product is pure phase (see Fig. 5). The $\nu(\text{COO})$ peaks are generally either larger than 1680 cm^{-1} or smaller than 1610 cm^{-1} , whereas the $\nu(\text{CONH})$ peaks appear in the range of $1625\text{--}1675\text{ cm}^{-1}$.¹⁴ So the appearance of the strong peaks at 1635 cm^{-1} for **2** and 1656 cm^{-1} for **3** in the IR spectra of compounds **2** and **3** implies that the acylation of N_2H_4 with 4-apha or 3-cppha has occurred. For compound **1**, $\nu(\text{CONH})$ is at 1653 cm^{-1} (see Fig. S1).

Photoluminescence and sorption property

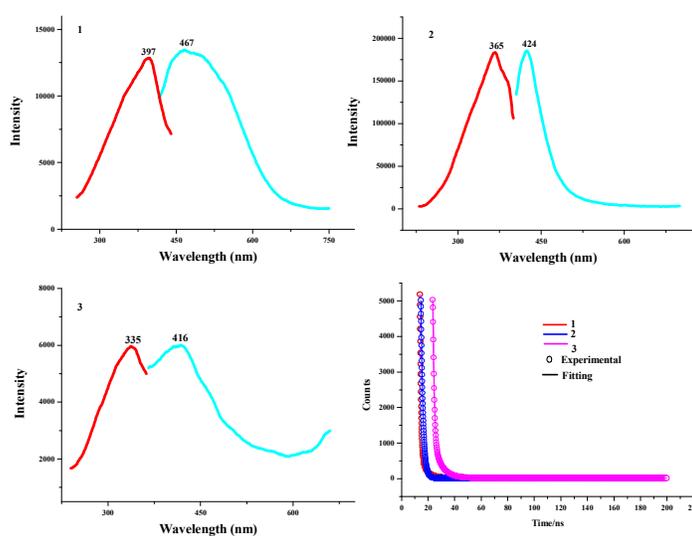


Fig. 6 Emission and excitation spectra as well as decay curves for 1-3.

The photoluminescence properties of the title compounds in the solid state were studied. As shown in Fig. 6, the title three compounds all possess the photoluminescence properties. Upon excitation, compounds **2** and **3** emit the similar blue light, and the peaks appear at 424 nm for **2** and 416 nm for **3**, respectively ($\lambda_{\text{ex}} = 365\text{ nm}$ for **2**, $\lambda_{\text{ex}} = 335\text{ nm}$ for **3**). Compound **1** also exhibits a blue-light emission, but the maximum is at 467 nm when excited at 397 nm. The emission intensities for compounds **1** and **3** are comparable, whereas compound **2** shows an extremely strong emission. Under the ultraviolet lamp, the blue light for compound **2** can be seen clearly. In order to understand its emission mechanism, the DFT calculations were carried out to the excited state of compound **3**. The DFT calculations indicate that (i) the effective emission appears at 427 nm ($f = 0.1540$), which is comparable with that of the observed (416 nm); (ii) the emission corresponds to the electronic transitions from orbital 183 to orbital 186, from orbital 183 to orbital 187 as well as from orbital 184 to orbital 188 ($E = 2.90\text{ eV}$) (see Fig. S3). Fig. 7 exhibits the characteristics of orbitals 183, 184, 186, 187 and 188. Based on the characteristics of these orbitals, the emission of compound **3** should be ascribed to a combination of two charge transfer paths: the charge transfer from the benzene ring moiety to the acylhydrazidate ring moiety (path I); the charge transfer from the 3-carboxyphenoxy group to the acylhydrazidate ring moiety (path II). The carboxyl group and the centric O atom for 3-cppth molecule do not directly provide the orbitals for electronic transition. The centric O atom serves as the

role of the intermediate. Based on our previous reports, most of the acylhydrazidate-coordiante compounds emit green light, and the maximum emissions appear within a range of 500-530 nm. The DFT calculations suggest that the green-light emission should be attributed to the charge transfer from the benzene ring moiety to the acylhydrazidate ring moiety, namely the path I found in compound **3**. Since the orbitals for the carboxyphenoxy group are involved in the charge transfer, a big blue shift by *ca.* 100 nm occurs, and compound **3** actually emits blue light. Compound **2** exhibits a similar emission to that of compound **3**. Here the tetrazole molecule should provide the orbitals for electronic transition. So the path II in compound **2** is the charge transfer from the tetrazole molecule to the acylhydrazidate ring moiety. The Zn²⁺ center acts as the bridge role. In compound **1**, the proportion of involvement for the path II is low, so only a slight blue-shift by *ca.* 50 nm is observed. On the other hand, the substituted -NH₂ group on pth molecule also play a crucial role in the emissions of compounds **1** and **2**. Three examples of pth-containing compounds as [Zn₃(OH)₂(Hpth)₂(pth)₂(trz)₂], [Zn₃(OH)₂(Hpth)₂(datrz)₂] and [Zn₂(pth)(atez)₂] have been reported, but they all do not emit light.¹¹ A 3-apth-containing compound [Zn₅(OH)₂(ox)(3-apth)₂(datrz)₂] has also been reported.¹¹ It emits green light. At that time, the mixed ox molecule was thought to be a key role in determining its emission behavior. The emission behaviors of compounds **1** and **2** indicate that the role of the substituted -NH₂ group is unnegligible. The presence of the substituted -NH₂ group is helpful for electronic transition. The decay curves for compounds **1** and **3** fit into a double exponential function, and the lifetimes were calculated to be $\tau_1 = 0.87$ ns, $\tau_2 = 5.82$ ns for compound **1**, and $\tau_1 = 0.89$ ns, $\tau_2 = 6.04$ ns for compound **3**, respectively. The luminescence lifetime for compound **2** was calculated to be $\tau_1 = 1.44$ ns. To assess the porosity property of the as-synthesized MOFs, the N₂ adsorption isotherm of compound **2** at 77 K was measured. Fig. 8 illustrates the corresponding adsorption-desorption isotherms. The N₂ uptake of compound **2** does not show a typical type-I, but follows an increasing trend. This implies that the pore or porous portal for compound **2** is not big, and only under the pressure, the activated **2** can adsorb N₂. The capacity of compound **2** to adsorb N₂ at 77 K and 1 bar is *ca.* 41.0 cm³ g⁻¹. The adsorption and desorption isotherm curves do not overlap with each other with small hysteresis. The BET surface area is estimated to be 31.84 m² g⁻¹, and the measured pore volume is *ca.* 0.0635 cm³ g⁻¹ for compound **2**. The adsorption uptake of N₂ is small, and sorption profile is non-typical. Maybe only a surface adsorption or capillary condensation occurs in the sample.

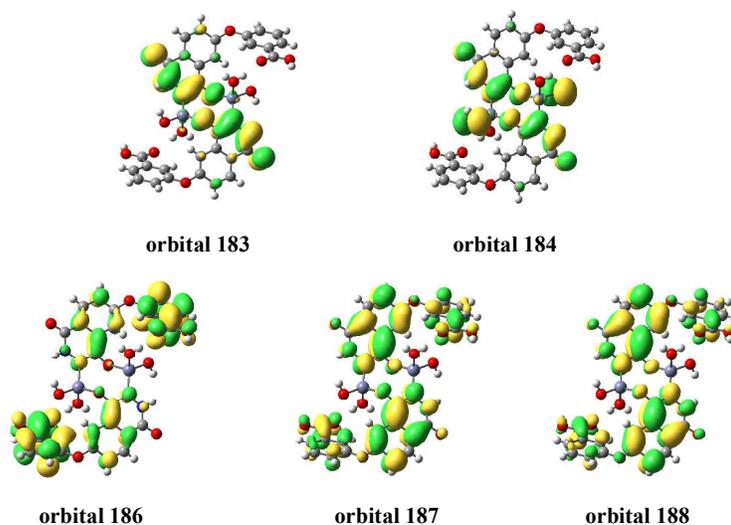


Fig. 7 Electron density contours of frontier molecular orbitals for **3**.

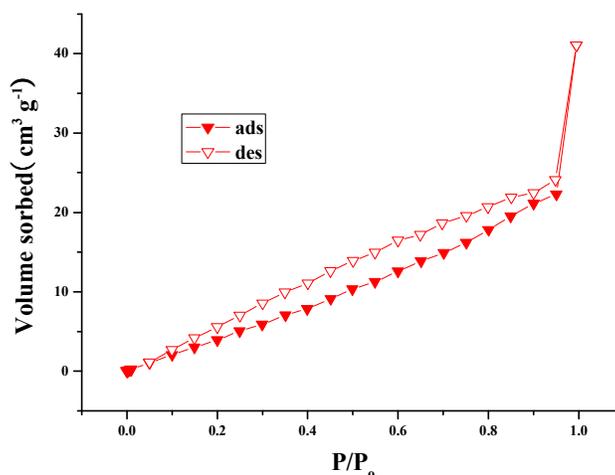


Fig. 8 N₂ adsorption-desorption of **2** at 77 K.

Conclusion

In summary, we reported the synthesis, structural characterization as well as the photoluminescence and adsorption properties of three new acylhydrazidate-extended coordination polymers **1-3**. The acylhydrazidate molecules in **1-3** originated from two types of hydrothermal *in situ* ligand reactions: the acylation of N₂H₄ with aromatic polycarboxylic acids; the reduction of -NO₂ into -NH₂ by N₂H₄. The obtainment of the 3-D compounds **1** and **2** further confirms that the strategy of incorporating the triazole/tetrazole molecule into the metal-monoacylhydrazidate system to construct the MOF is feasible. A special bridging mode for acylhydrazidate molecule is observed in compound **1**, namely the hydrazino group instead of the other O atom acts as the donors. Besides the keto-hydroxyl form, the acylhydrazidate molecule can also exist in a dihydroxyl form in a complex, as observed in compounds **1** and **2**. The meta-position of pth molecule is modified by a carboxyphenoxy group, and the 3-cppth molecule can serve as a T-shape linker. The 3-cppth-extended compound **3** only exhibits a 1-D chain structure, since the acylamino group is non-coordinate in compound **3**. The title three compounds all emit blue-light. The carboxyphenoxy group in compound **3** does not assist the pth molecule to link the Zn²⁺ ions into a 3-D MOF, but it contributes to the blue-light emission of compound **3**, based on the DFT calculations. The introduced triazole and tetrazole molecules in compounds **1** and **2** play the same role as that of the carboxyphenoxy group in compound **3**. The -NH₂ group on pth molecule is verified to be another important factor of determining the emissions of compounds **1** and **2**. It is noteworthy that compound **2** emits the extremely strong blue light, and can serve as the light source. The N₂ adsorption-desorption isotherms indicate that the activated **2** can adsorb a small quantity of N₂ at 77 K.

Acknowledgements

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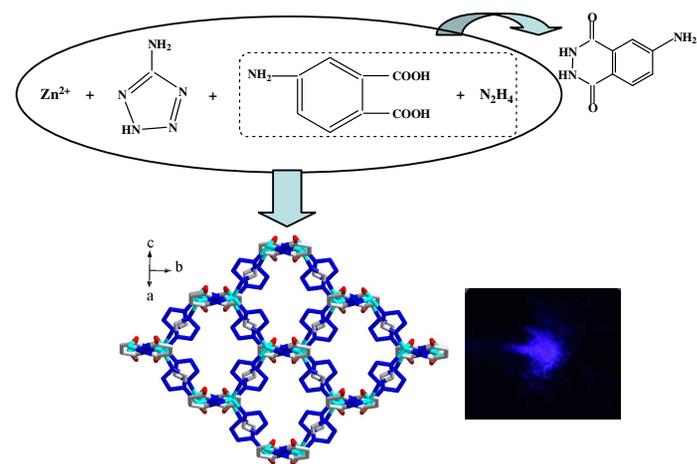
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New Zn²⁺ coordination polymers constructed from acylhydrazidate molecules: synthesis and structural characterization

Yan-Ning Wang, Guang-Hua Li, Fu-Quan Bai,* Jie-Hui Yu,* Ji-Qing Xu



By employing two types of hydrothermal *in situ* ligand reactions (acylation of N₂H₄ with aromatic polycarboxylic acids, reduction of 3-nitrophthalhydrazide by N₂H₄), three new acylhydrazidate-extended Zn²⁺ coordination polymers [Zn₂(3-apth)(atr_z)₂] (3-apth = 3-aminophthalhydrazidate; atr_z = 3-amino-1,2,4-triazolate) **1**, [Zn₂(4-apth)(atez₂)₂] (4-apth = 4-aminophthalhydrazidate; atez = 5-aminotetrazolate) **2**, and [Zn(3-cppth)(H₂O)] (3-cppth = 4-(3-carboxyphenoxy)phthalhydrazidate) **3** were obtained. X-ray single-crystal diffraction analysis revealed that (i) compound **1** possesses a 3-D structure. The triazolate molecules link the Zn²⁺ ions to form a 2-D layer with a (6,3) topology. Then the acylhydrazidate molecule acts as the second linker, extending the (6,3) nets into a 3-D network of compound **1**; (ii) compound **2** also exhibits a 3-D structure. The acylhydrazidate molecules first link the Zn²⁺ ions into a 1-D infinite chain. The tetrazolate molecules propagate further the chains into a 3-D (4,4)-connected net (symbol: (4⁶·8)₂(4²·6²·8²)); (iii) compound **3** only shows a 1-D chain structure. The photoluminescence analysis indicates that the title three compounds all emit light, especially compound **2** emits the extremely strong blue light. The side group on phthalhydrazidate molecule plays a crucial role in the emission behaviors of compounds **1-3**. At 77 K, the activated **2** can adsorb N₂ with the amount of *ca.* 41.0 cm³ g⁻¹.