

# New $Zn^{2+}$ coordination polymers with mixed triazolate/tetrazolate and acylhydrazide as linkers<sup>†</sup>

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Under hydrothermal conditions, at different pH levels adjusted by  $H_2Ox$  ( $ox = \text{oxalate}, C_2O_4^{2-}$ ) or  $N_2H_4$ , the reactions of  $Zn(CH_3COO)_2 \cdot 2H_2O$ , phthalic/3-nitrophthalic acid,  $N_2H_4 \cdot H_2O$  and triazole/tetrazole afforded four new  $Zn^{2+}$  coordination polymers as  $[Zn_5(OH)_2(Hpth)_2(pth)_2(trz)_2]$  ( $pth = \text{phthalhydrazide}$ ,  $trz = 1,2,4\text{-triazolate}$ ) **1**,  $[Zn_3(OH)_2(Hpth)_2(datrz)_2]$  ( $datrz = 3,5\text{-diamino-1,2,4-triazolate}$ ) **2**,  $[Zn_2(pth)(atez)_2]$  ( $atez = 5\text{-aminotetrazolate}$ ) **3** and  $[Zn_5(OH)_2(ox)(apth)_2(datrz)_2]$  ( $apth = 3\text{-aminophthalhydrazide}$ ) **4**. The acylhydrazide molecules  $H_2pht$  and  $H_2apth$  in compounds **1–4** originated from the hydrothermal *in situ* acylation of  $N_2H_4$  with phthalic/3-nitrophthalic acid. When preparing compound **4**, the reduction of  $-NO_2$  into  $-NH_2$  also occurred besides the acylation, creating finally a new acylhydrazide molecule  $H_2apth$ . The X-ray single-crystal diffraction analysis revealed that (i) in compounds **1**, **3** and **4**,  $Zn^{2+}$  and  $pht/apth$  aggregate into the 1D endless chains. The triazolate/tetrazolate molecules extend the  $Zn^{2+}\text{-}pht/apth$  chains into the different layer networks of compounds **1** and **4**, and a 3D network of compound **3**; (ii) in compound **2**, the datrz molecules link the  $Zn^{2+}$  ions into a 2D layer network. Pth acts as the ancillary ligand; (iii)  $ox$  from  $H_2Ox$  was introduced into the final framework of compound **4**; (iv) the acylhydrazide molecules exhibit three types of existing forms in compounds **1–4**: the diketo form, the keto-hydroxyl form, and the dihydroxyl form. Of those, the dihydroxyl form was observed for the first time. The solid-state photoluminescence analysis indicated that only compound **4** emits green light, and the others do not emit light.

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## Introduction

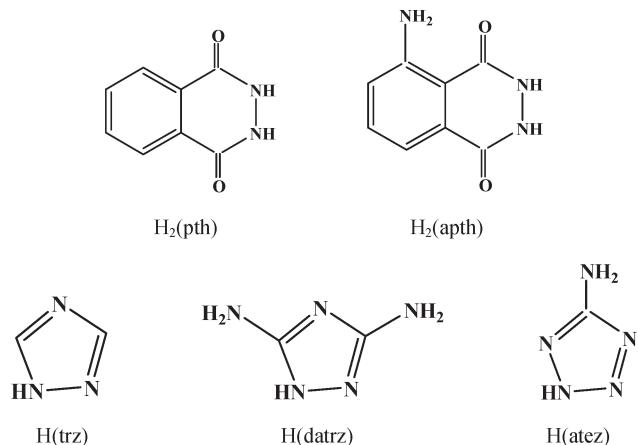
Considerable attention has been paid to the design and synthesis of novel coordination polymers due to their intriguing architectures and topologies,<sup>1</sup> and the potential applications in adsorption,<sup>2</sup> optics,<sup>3</sup> magnetism<sup>1c,4</sup> and catalysis.<sup>5</sup> Traditionally, coordination polymers were prepared through the self-assemblies of either pre-synthesized or commercially available multidentate organic N/O/S-donor ligands with metal ions. As a new and effective pathway for the preparation of both the organic ligands and coordination polymers, the *in situ* ligand synthesis technique has recently been developed rapidly.<sup>6</sup> The *in situ* ligand synthesis approach not only simplified the synthesis steps, but also created a variety of novel organic ligands and coordination polymers, in

particular those that are inaccessible through routine synthetic methods. To date, multiple types of *in situ* ligand reactions, such as the oxidative hydroxylation of aromatic rings,<sup>7</sup> the dehydrogenative coupling of carbon–carbon bonds,<sup>6a,8</sup> the cycloaddition of organic nitriles with azide or ammonia,<sup>6d,9</sup> the transformation of inorganic and organic sulfur,<sup>6e,10</sup> alkylation,<sup>11</sup> and so on, have been observed. The current investigation in our group is focused on the structural characterization of a series of metal–acylhydrazide coordination polymers by employing the *in situ* acylation of  $N_2H_4$  with aromatic polycarboxylic acids. Phthalic/pyridinedicarboxylic acids with different substituents, and biphenyl acids with different spacers have been selected to react with metal ions, affording a series of acylhydrazide-extended coordination polymers.<sup>12</sup> The substituent of phthalhydrazide/pyridinedicarboxylhydrazide and the spacer of biphenylhydrazide as well as the geometry of the metal center influence the final frameworks of the obtained compounds. More interestingly, metal–acylhydrazide compounds exhibit excellent photoluminescence properties. The mechanism study indicates that the emissions are related to the intra/inter-acylhydrazide transitions. Triazole or tetrazole have been demonstrated to be very good ligands for the construction of high-dimensional

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**Scheme 1** The structures of the organic molecules appearing in the title compounds.

coordination polymers.<sup>1a,b,13</sup> Moreover, the  $\text{M}^{n+}$ -triazolate/tetrazolate-carboxylate system has been investigated widely, in which the carboxylate molecules propagate the  $\text{M}^{n+}$ -triazolate/tetrazolate clusters, chains or layers into high-dimensional networks.<sup>14</sup> In this article, we are attempting to introduce triazole or tetrazole ligands into the metal-acylhydrazide system for the first time. Now, we report the structural characterization of four new  $\text{Zn}^{2+}$  coordination polymers as 2D  $[\text{Zn}_5(\text{OH})_2(\text{Hpth})_2(\text{pth})_2(\text{trz})_2]$  1,  $[\text{Zn}_3(\text{OH})_2(\text{Hpth})_2(\text{datrz})_2]$  2, 3D  $[\text{Zn}_2(\text{pth})(\text{atez})_2]$  3 and 2D  $[\text{Zn}_5(\text{OH})_2(\text{ox})(\text{apth})_2(\text{datrz})_2]$  4 (pth = phthalhydrazide; apth = 3-aminophthalhydrazide; trz = 1,2,4-triazole; datrz = 3,5-diamino-1,2,4-triazole; atez = 5-aminotetrazole; ox = oxalate) (see Scheme 1).

## 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. The infrared (IR) spectrum was recorded on a Perkin Elmer Spectrum 1 spectrophotometer in the 4000–400  $\text{cm}^{-1}$  region using a powdered sample on a KBr plate. The powder X-ray diffraction (XRD) data were collected on a Rigaku/max-2550 diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The thermogravimetric (TG) behavior was investigated on a Perkin-Elmer TGA-7 instrument with a heating rate of 10  $^{\circ}\text{C min}^{-1}$  in air. The fluorescence spectrum was obtained on a LS 55 fluorescence/phosphorescence spectrophotometer at room temperature.

### The synthesis of the title compounds

The reactions were carried out in 30 mL Teflon-lined stainless steel vessels under autogenous pressure. The single crystals were collected by filtration, washed with distilled water and dried in air at an ambient temperature.

$[\text{Zn}_5(\text{OH})_2(\text{Hpth})_2(\text{pth})_2(\text{trz})_2]$  1. The colorless columnar crystals of 1 were obtained from a simple hydrothermal

self-assembly of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (110 mg, 0.5 mmol), phthalic acid (83 mg, 0.5 mmol),  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (0.2 mL) and  $\text{H}(\text{trz})$  (36 mg, 0.5 mmol) in a 15 mL aqueous solution (pH = 8 adjusted by  $\text{N}_2\text{H}_4$ ) at 170  $^{\circ}\text{C}$  for 4 days. Yield: ca. 20% based on  $\text{Zn}(\text{II})$ . Anal. calcd  $\text{C}_{36}\text{H}_{24}\text{N}_{14}\text{O}_{10}\text{Zn}_5$  1: C 37.94, H 2.123, N 17.21. Found: C 37.74, H 2.116, N 17.17%. IR ( $\text{cm}^{-1}$ ): 1645 m, 1577 m, 1499 s, 1442 s, 1393 m, 1220 m, 1078 m, 850 m, 693 m.

$[\text{Zn}_3(\text{OH})_2(\text{Hpth})_2(\text{datrz})_2]$  2. The colorless columnar crystals of 2 were obtained from a simple hydrothermal self-assembly of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (110 mg, 0.5 mmol), phthalic acid (83 mg, 0.5 mmol),  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (0.2 mL) and  $\text{H}(\text{datrz})$  (50 mg, 0.5 mmol) in a 15 mL aqueous solution (pH = 8 adjusted by  $\text{N}_2\text{H}_4$ ) at 170  $^{\circ}\text{C}$  for 4 days. Yield: ca. 30% based on  $\text{Zn}(\text{II})$ . Anal. calcd  $\text{C}_{20}\text{H}_{18}\text{N}_{14}\text{O}_6\text{Zn}_3$  2: C 32.17, H 2.430, N 26.27. Found: C 32.51, H 2.647, N 26.08%. IR ( $\text{cm}^{-1}$ ): 1656 s, 1621 w, 1584 s, 1510 s, 1387 s, 1163 w, 1076 s, 965 m, 846 s, 807 s, 697 s, 655 m.

$[\text{Zn}_2(\text{pth})(\text{atez})_2]$  3. The colorless columnar crystals of 3 were obtained from a simple hydrothermal self-assembly of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (110 mg, 0.5 mmol), phthalic acid (83 mg, 0.5 mmol),  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (0.2 mL) and  $\text{H}(\text{atez})$  (43 mg, 0.5 mmol) in a 15 mL aqueous solution (pH = 5 acidified by  $\text{H}_2\text{Ox}$ ) at 170  $^{\circ}\text{C}$  for 4 days. Yield: ca. 35% based on  $\text{Zn}(\text{II})$ . Anal. calcd  $\text{C}_{10}\text{H}_{8}\text{N}_{12}\text{O}_2\text{Zn}_2$  3: C 26.16, H 1.76, N 36.63. Found: C 26.54, H 1.78, N 36.33%. IR ( $\text{cm}^{-1}$ ): 1647 s, 1587 m, 1563 s, 1510 m, 1457 s, 1396 m, 1225 m, 1087 s, 1004 m, 878 m, 799 m, 709 s, 653 w.

$[\text{Zn}_5(\text{OH})_2(\text{ox})(\text{apth})_2(\text{datrz})_2]$  4. The colorless columnar crystals of 4 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), 3-nitrophthalic acid (63 mg, 0.3 mmol),  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (0.15 mL) and  $\text{H}(\text{datrz})$  (30 mg, 0.3 mmol) in a 10 mL aqueous solution (pH = 6 adjusted by  $\text{H}_2\text{Ox}$ ) at 160  $^{\circ}\text{C}$  for 4 days. Yield: ca. 15% based on  $\text{Zn}(\text{II})$ . Anal. calcd  $\text{C}_{22}\text{H}_{18}\text{N}_{16}\text{O}_{10}\text{Zn}_5$  4: C 26.60, H 1.83, N 22.57. Found: C 26.56, H 2.11, N 22.52%. IR ( $\text{cm}^{-1}$ ): 1692 w, 1646 s, 1530 s, 1467 m, 1411 s, 1279 s, 1204 m, 1086 m, 967 s, 861 s, 779 s, 736 s, 680 s.

### X-ray crystallography

The data were collected with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Rigaku R-AXIS RAPID IP diffractometer for compounds 1, 3 and 4, and on a Siemens SMART CCD diffractometer for compound 2. With the SHELXTL program, the structures of compounds 2–4 were solved using direct methods, whereas the structure of compound 1 was solved using heavy atom methods.<sup>15</sup> The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. The H atoms on O5 in compound 1, O1 in compound 3, and OH1 and OH2 in compound 4 were obtained from the difference Fourier map. The other H atoms were treated using a riding model. The structures were then refined on  $F^2$  using SHELXL-97.<sup>15</sup> The CCDC numbers are 953442–953444 for compounds 1–3, and 971308 for compound 4. The crystallographic data for the compounds are summarized in Table 1.

**Table 1** The crystallographic data for the title compounds

	1	2	3	4
Formula	C <sub>36</sub> H <sub>24</sub> N <sub>14</sub> O <sub>10</sub> Zn <sub>5</sub>	C <sub>20</sub> H <sub>18</sub> N <sub>14</sub> O <sub>6</sub> Zn <sub>3</sub>	C <sub>10</sub> H <sub>8</sub> N <sub>12</sub> O <sub>2</sub> Zn <sub>2</sub>	C <sub>22</sub> H <sub>18</sub> N <sub>16</sub> O <sub>10</sub> Zn <sub>5</sub>
M	1139.54	746.59	459.02	993.37
T (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P $\bar{1}$	C2/c	C2/c	C2/m
a (Å)	7.6058(6)	13.7823(7)	12.354(3)	18.923(4)
b (Å)	10.2154(7)	9.7678(7)	12.473(3)	11.121(2)
c (Å)	12.2851(12)	20.5088(17)	10.449(2)	15.759(3)
$\alpha$ (°)	102.799(5)			
$\beta$ (°)	97.934(5)	96.553(4)	116.92(3)	102.63(2)
$\gamma$ (°)	98.974(5)			
V (Å <sup>3</sup> )	904.52(13)	2742.5(3)	1435.5(5)	3236.5(11)
Z	1	4	4	4
D <sub>c</sub> (g cm <sup>-3</sup> )	2.092	1.808	2.124	2.039
$\mu$ (mm <sup>-1</sup> )	3.353	2.668	3.383	3.733
Reflections collected	5047	7500	6966	15 933
Unique reflections	3140	2405	1640	3876
R <sub>int</sub>	0.0249	0.0436	0.0193	0.0463
Gof	1.183	1.050	1.070	1.077
R <sub>1</sub> , I > 2σ(I)	0.0373	0.0297	0.0209	0.0431
wR <sub>2</sub> , all data	0.1310	0.0816	0.0542	0.1105

## Results and discussion

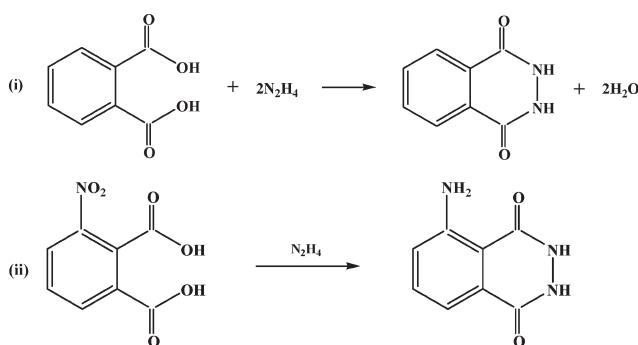
### Synthetic analysis

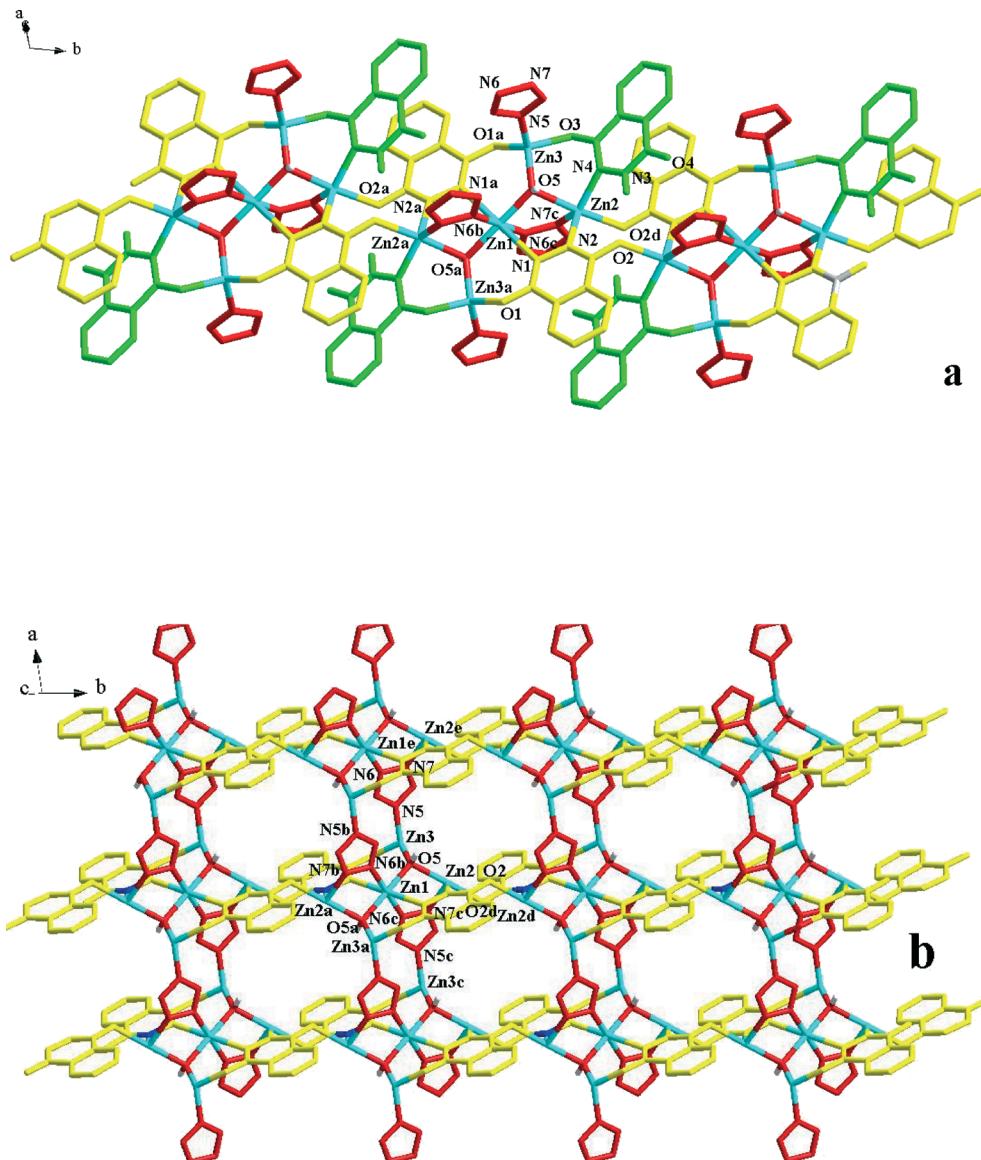
All of the reactions were performed under hydrothermal conditions. In the different pH levels adjusted by H<sub>2</sub>Ox or N<sub>2</sub>H<sub>4</sub>, the reactions of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, phthalic/3-nitrophthalic acid, N<sub>2</sub>H<sub>4</sub> and triazole/tetrazole yielded the title compounds 1–4. As shown in Scheme 2(i), the hydrothermal *in situ* acylation of N<sub>2</sub>H<sub>4</sub> with phthalic acid yielded H<sub>2</sub>pht. Scheme 2(ii) displays the reaction of N<sub>2</sub>H<sub>4</sub> with 3-nitrophthalic acid. Apart from the acylation, the reduction of -NO<sub>2</sub> into -NH<sub>2</sub> also occurred in the presence of N<sub>2</sub>H<sub>4</sub>, creating finally another new acylhydrazide molecule H<sub>2</sub>aphth. Note that the acylation of N<sub>2</sub>H<sub>4</sub> with phthalic/3-nitrophthalic acid can be carried out in a wide pH range, but the single-crystal growth for compounds 1–4 was strictly controlled by the pH level of the reactive system: 8 for 1, 8 for 2, 5 for 3 and 6 for 4. H<sub>2</sub>Ox can be used to acidify the reactive system. Sometimes it can also appear in the resulting framework of the compound, as observed in compound 4. In the reactions, N<sub>2</sub>H<sub>4</sub> is largely

excessive in order to ensure that the carboxyls are thoroughly acylated. Other metal ions such as Pb<sup>2+</sup> and Cd<sup>2+</sup> have been used instead of Zn<sup>2+</sup>, but crystals suitable for X-ray single-crystal diffraction were not obtained.

### Structural description

[Zn<sub>5</sub>(OH)<sub>2</sub>(Hpth)<sub>2</sub>(pth)<sub>2</sub>(trz)<sub>2</sub>] 1. Compound 1 is a trz-extended 2D Zn<sup>2+</sup>-pth coordination polymer. It crystallizes in the space group of P $\bar{1}$ , and the asymmetric unit is found to be composed of three types of Zn<sup>2+</sup> ions (Zn1, Zn2, Zn3; occupancy ratio: 0.5 for Zn1, 1 for Zn2 and Zn3), one hydroxyl group (O5), two types of pth molecules (pth I, pth II) and one trz molecule. As shown in Fig. 1a, Zn1, Zn2 and Zn3 are involved in the different sites. The octahedral Zn1 lies at an inversion center, coordinated with two hydroxyl O atoms (O5, O5a), two trz N atoms (N6b, N6c) and two hydroxylimino N atoms (N1, N1a). Zn2 adopts a trigonal bipyramidal configuration. The equatorial plane is occupied by one hydroxylimino N atom (N2), one acylamino N atom (N4) and one trz N atom (N7c), while the axial positions are occupied by one hydroxyl O atom (O5) and one hydroxylimino O atom (O2d). The tetrahedral Zn3 is completed by two hydroxylimino O atoms (O3, O1a), one trz N atom (N5) and one hydroxyl O atom (O5). The two types of pth molecules exhibit different coordination modes. Pth I adopts a  $\mu_4$  coordination mode. All of the potential coordination atoms for pth I participate in the coordination, bonding to four Zn<sup>2+</sup> ions. This kind of coordination mode for pth is a new one, which has never been observed in the previous reports. The  $\mu_2$ -mode pth II utilizes the hydroxylimino N and O atoms to coordinate to two Zn<sup>2+</sup> ions. Trz adopts a  $\mu_3$  coordination modes: each N atom interacts with one Zn<sup>2+</sup> ion. Compound 1 possesses a 2D layer structure. First of all, one hydroxyl

**Scheme 2** The *in situ* reactions of N<sub>2</sub>H<sub>4</sub> with phthalic/3-nitrophthalic acid.

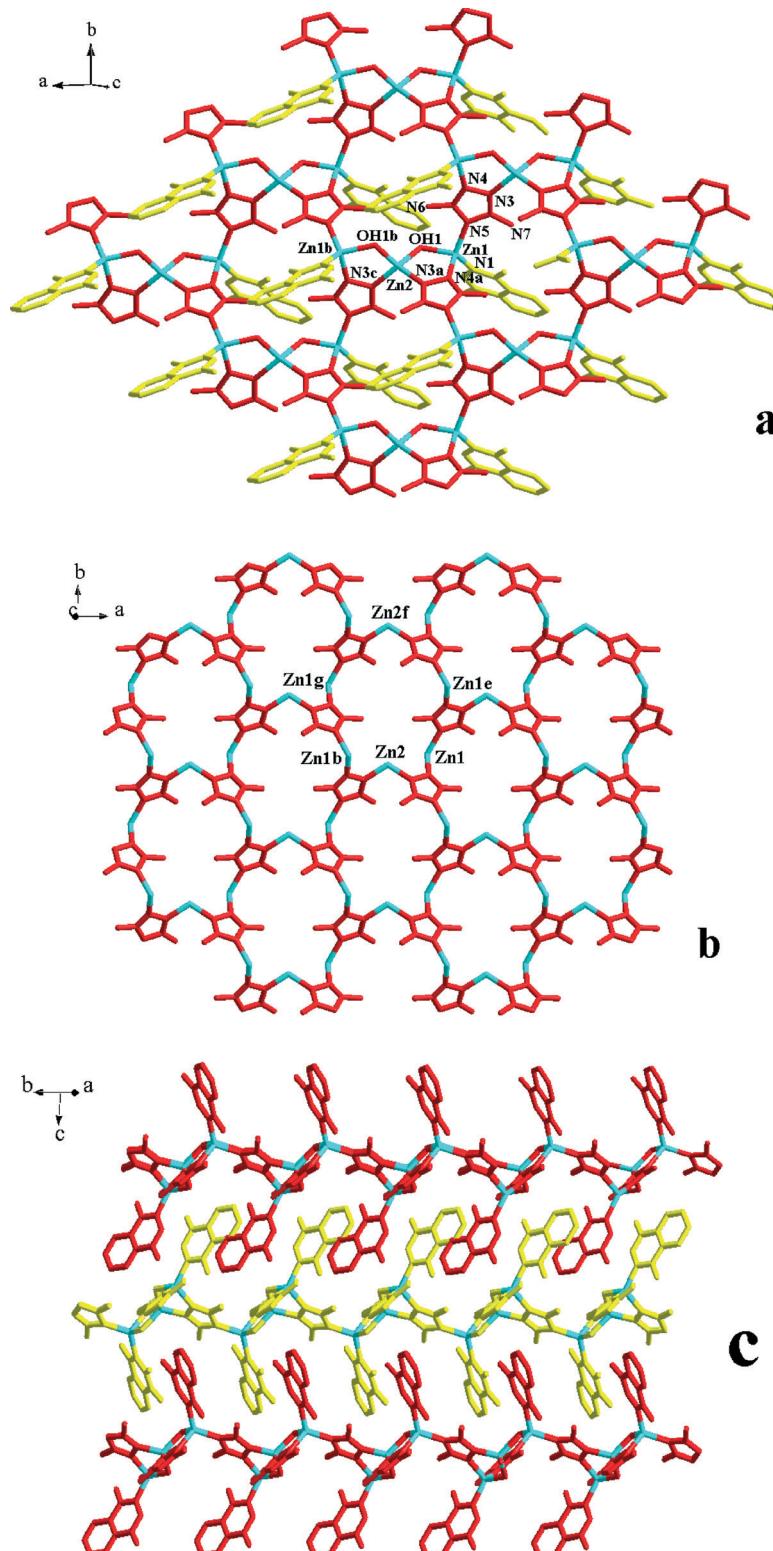


**Fig. 1** The  $\text{Zn}_5(\text{OH})_2(\text{ptb}^{\text{I}})_2(\text{Hptb}^{\text{II}})_2^{2+}$  chain (a) and the 2D layer (b) for compound 1 (pth II is omitted in b).

(O5) links three  $\text{Zn}^{2+}$  ions (Zn1, Zn2, Zn3) to form a  $\text{Zn}_{2.5}(\text{OH})^{4+}$  unit. Then through the interactions between Zn1 and N1, Zn2 and N2, and Zn3a and O1, the  $\text{Zn}_{2.5}(\text{OH})^{4+}$  unit further combines with a pth molecule (pth I) into a new  $\text{Zn}_{2.5}(\text{OH})(\text{ptb}^{\text{I}})^{2+}$  units. Furthermore, another new unit  $\text{Zn}_5(\text{OH})_2(\text{ptb}^{\text{I}})_2^{4+}$  forms via an inversion center. The remaining hydroxylimino O atom (O2) for pth I interacts with Zn2d from the neighboring  $\text{Zn}_5(\text{OH})_2(\text{ptb}^{\text{I}})_2^{4+}$  unit. Via this kind of interaction, the  $\text{Zn}_5(\text{OH})_2(\text{ptb}^{\text{I}})_2^{4+}$  units self-assemble into a 1D endless chain, running down the *b*-axial direction. In the formation of a layer network of compound 1, trz plays an important role. As shown in Fig. 1b, the N5 of trz interacts with Zn1, while N6 and N7 interact respectively with Zn1e and Zn2e from the adjacent chain. Via the Zn–N interactions, the trz molecules double support the 1D chains into a 2D layer network. In compound 1, pth II has two roles: (i) it balances the systematic charge; (ii) it satisfies the coordination

of Zn2 and Zn3. Based on the topological viewpoint, the entire multinuclear cluster is treated as a node itself, and thus the 2D net is that of a simple (4,4) grid. The Zn–N, Zn–O and Zn–OH distances all span wide ranges: 2.006(5)–2.418(5) Å for Zn–N, 1.904(4)–2.180(4) Å for Zn–O, and 1.946(4)–2.190(4) Å for Zn–OH.

[ $\text{Zn}_3(\text{OH})_2(\text{Hptb})_2(\text{datrz})_2$ ] 2. Compound 2 is a datrz-extended 2D  $\text{Zn}^{2+}$ –pth coordination polymer. It crystallizes in the space group *C*2/c. The asymmetric unit is found to be composed of two types of  $\text{Zn}^{2+}$  ions (Zn1, Zn2; occupancy ratio: 1 for Zn1, 0.5 for Zn2), one hydroxyl group and one pth molecule together with one datrz molecule. As shown in Fig. 2a, both  $\text{Zn}^{(n)}$  ions are in a tetrahedral site, but the detailed environments are different. Zn1 is coordinated with one hydroxylimino N atom (N1), two datrz N atoms (N5, N4a) and one hydroxyl group (OH1), whereas Zn2 lies at an inversion center, surrounded by two hydroxyl groups (OH1, OH1b) and



**Fig. 2** The 2D layer network (a), the simplified layer network (b) and the 3D supramolecular network (c) for compound 2.

two datrz N atoms (N3a, N3c). As shown in Fig. 2b, in the formation of the layer structure, OH and pth do not play a role. The  $\mu_3$ -mode datrz molecules link the  $Zn^{2+}$  ions into the 2D layer of compound 2. The layer is based on the 22-membered

loops. Each loop consists of six  $Zn^{(II)}$  ions and six datrz molecules.  $Zn2$  and two datrz form a  $Zn(\text{datrz})_2$  unit, which can be viewed as a linker. Two  $Zn(\text{datrz})_2$  units and two datrz molecules alternately link four  $Zn1$  ions into this 22-membered

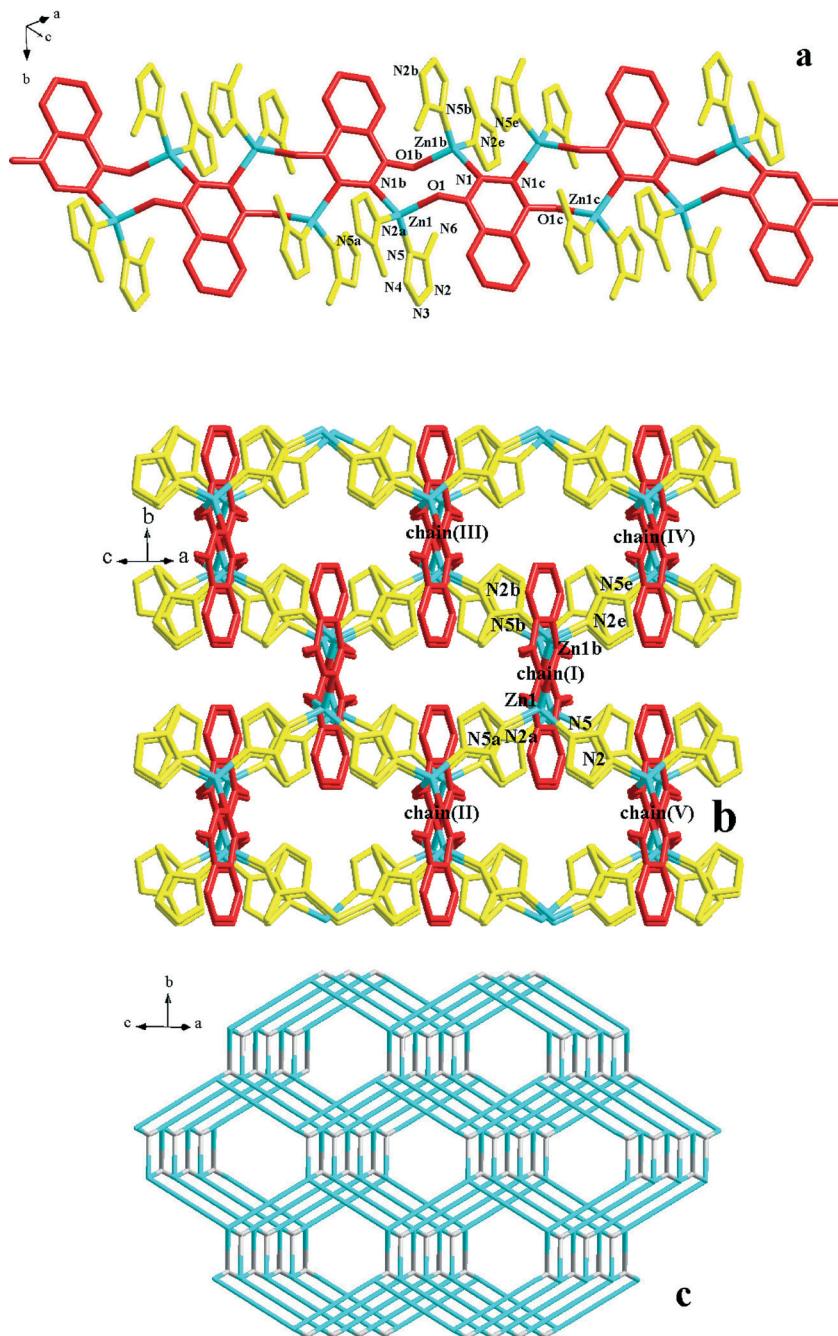
loop. OH serves as another linker between Zn1 and Zn2, stabilizing the 2D layer network. The pth molecules protrude from the layer and are distributed on both sides of the layer. *Via* the  $\pi \cdots \pi$  interactions between the adjacent pth molecules (contact: 3.46 Å), the 2D layers self-assemble into a 3D supramolecular network (see Fig. 2c). Based on the topological method, compound 2 affords a simple (6,3) hexagonal net. All of the Zn–N bond lengths are comparable with each other with a narrow range of 1.994(2)–2.013(2) Å. The Zn–OH range is 1.9627(19)–1.9892(17) Å. The shortest Zn···Zn contact within the layer is Zn1···Zn2 = 3.299 Å.

**[Zn<sub>2</sub>(pth)(atez)<sub>2</sub>]** 3. Compound 3 is an atez-extended 3D Zn(<sup>II</sup>)-pth coordination polymer. It crystallizes in the space group *C*2/c, and the asymmetric unit is found to be composed of one Zn<sup>2+</sup> ion (Zn1), half of a pth molecule and one atez molecule. The crystallographically unique Zn1 center adopts a tetrahedral geometry, completed by one hydroxylimino O atom (O1), one hydroxylimino N atom (N1b) as well as two atez N atoms (N5, N2a). The Zn1–N2a<sub>atez</sub> distance of 1.9895(15) is slightly longer than that of Zn1–N5<sub>atez</sub> (1.9632(15) Å), but comparable with that of Zn1–N1b<sub>hydroxylimino</sub> (1.9937(14) Å). The Zn1–O1 bond length is normal (1.9678(14) Å). Pth adopts the same coordination mode as that of pth I in compound 1: each N/O donor monodentately coordinates to one Zn<sup>2+</sup> ion. Atez is involved in a double-bridged coordination mode: the N atoms at 1,4-positions act as the donors. Linked by pth and atez, compound 3 exhibits a 3D network structure. The pth molecules with two hydroxylimino groups link first the tetrahedral Zn<sup>2+</sup> ions into a 1D infinite chain structure, running down the *a* axial direction (see Fig. 3a). The chain is based on 8-membered rings consisting of two Zn<sup>2+</sup> ions and two hydroxylimino groups. The ring adopts the chair-mode configuration, making the chain structure more stable. The Zn···Zn separation within the ring is 3.955 Å. Around each tetrahedral Zn<sup>2+</sup> ion, two positions are occupied by hydroxylimino N/O atoms. The remaining two positions are occupied by atez N atoms. As shown in Fig. 3b, *via* the linkage of atez, each Zn<sub>2</sub>(pth)<sup>2+</sup> chain (I) interacts with the neighboring four Zn<sub>2</sub>(pth)<sup>2+</sup> chains (II, III, IV, V), producing a 3D network of compound 3. A 1D channel with the size of 7.5 × 3.7 Å<sup>2</sup> is observed. Fig. 3c shows the topology of the 3D network of compound 3. The Zn<sup>2+</sup> ion is regarded as a 4-connected node. Note that this node adopts a tetrahedral geometric configuration. The  $\mu_4$ -mode pth is considered as a 4-connected node, while the  $\mu_2$ -mode atez acts as the linker. The 3D compound 3 exhibits a (4·6<sup>4</sup>·8)<sub>2</sub>(4<sup>2</sup>·6<sup>2</sup>·8<sup>2</sup>)-topology.

**[Zn<sub>5</sub>(OH)<sub>2</sub>(ox)(aphth)<sub>2</sub>(datrz)<sub>2</sub>]** 4. Compound 4 is a datrz-extended layered Zn<sup>2+</sup>-aphth coordination polymer. It crystallizes in the space group *C*2/m, and the asymmetric unit is found to be composed of three types of Zn<sup>2+</sup> ions (Zn1, Zn2, Zn3; occupancy ratio: 1 for Zn1 and Zn2, 0.5 for Zn3), two types of OH<sup>−</sup> groups (OH1, OH2; occupancy ratio: 0.5 for each), one ox group (occupancy ratio: 0.5 for each atom) and one datrz molecule as well as two types of aphth molecules (aphth I and aphth II). For each aphth molecule, only a half appears in an asymmetric unit of compound 4. Zn1 and Zn2

are both in the tetrahedral sites, completed by one hydroxylimino O atom (O1 for Zn1, O2 for Zn2), one hydroxylimino N atom (N7a for Zn1, N9 for Zn2), one datrz N atom (N3 for Zn1, N1 for Zn2), and one OH group (OH2 for Zn1, OH1 for Zn2). While Zn3 is in a trigonal bipyramidal site with two datrz N atoms (N2, N2c) and one ox O atom (O6) occupying the equatorial plane, and OH1 and another ox O atom (O5) occupying the axial positions. Both aphth I and aphth II adopt the  $\mu_4$  coordination modes, which are the same as that adopted by pth in compounds 1 and 3. Fig. 4 illustrates the layer structure of compound 4. Aphth I and Zn1 aggregate to form a 1D infinite chain, namely chain I (red). Aphth II and Zn2 aggregate to form another chain, namely chain II (green). Both chains extend along the *c*-axial direction. The datrz molecules with N1 and N3 as the donors link alternately two types of chains into a 2D layer network of compound 4. Chain I is further modified by OH1. The neighboring two Zn1 ions (Zn1, Zn1d) are linked by OH2, which makes the chain structure more stable. Similarly, chain II is further modified by OH1. Differently, due to the presence of the 2-position N atom (N2) for datrz, two symmetry-related datrz N atoms (N2, N2c) together with OH1 further coordinate to a new Zn<sup>2+</sup> ion (Zn3). So OH1 and OH2 adopt different coordination modes: the  $\mu_2$  mode for OH2 and the  $\mu_3$  mode for OH1. Ox with two O atoms (O5, O6) chelates to Zn3, completing the 5-fold coordination of Zn3. Fig. S1† illustrates the projection plot of compound 4 in the (010) direction for better understanding its layer structure. The Zn–N distances (1.990(4)–2.023(4) Å) are basically comparable with each other, while the Zn–O/OH range of 1.923(3)–2.132(4) is slightly wide. A short Zn···Zn interaction (Zn2···Zn2c = 3.160 Å) is found in compound 4.

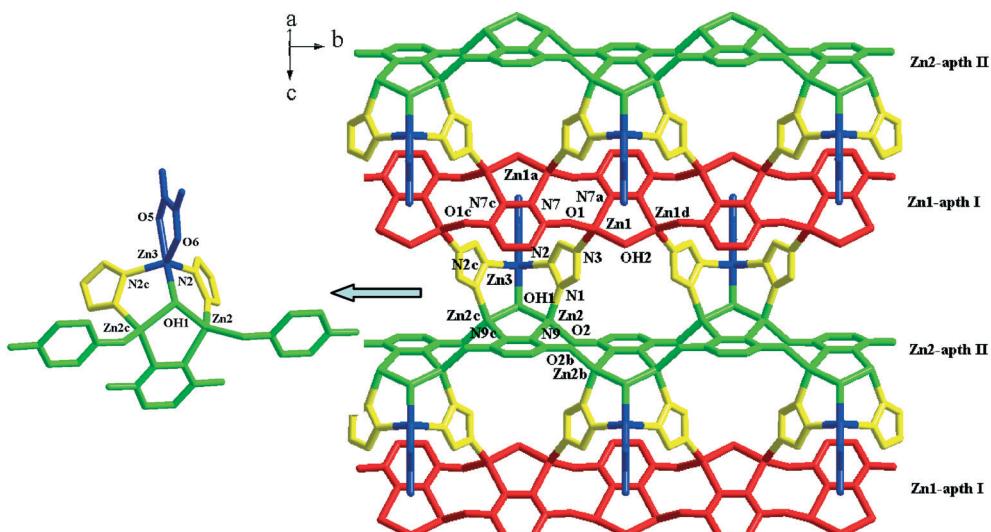
In compounds 1–4, the acylhydrazide molecules exhibit three types of existing forms (Scheme 3). (i) The diketo form. Pth in compound 2 exists in a diketo form, which is confirmed by two short and equivalent C–O distances (C7–O1 = 1.260(4) Å, C8–O2 = 1.259(4) Å). The diketo form is not the stable existing form for the acylhydrazide molecule. Only in compounds [pmdh] (pmdh = pyromellittidihydrozide)<sup>16</sup> and [Pb<sub>2</sub>(epdh)<sub>4</sub>(H<sub>2</sub>O)] (epdh = 5-ethylpyridine-2,3-dicarboxylhydrazide),<sup>12b</sup> was the diketo form ever observed. (ii) The keto-hydroxyl form. One C–O distance of 1.286(7) Å is longer than the other one (1.241(7) Å), suggesting that pth II in compound 1 exists in a keto-hydroxyl form. As shown in Scheme 2, the keto-hydroxyl form should originate from the isomerization of the diketo-form pth. One acylamino group isomerized into the hydroxylimino group. The other did not. The keto-hydroxyl form has been theoretically conformed to be the most stable existing form for the acylhydrazide molecule,<sup>17</sup> and a majority of acylhydrazide molecules exist in this kind of form.<sup>12</sup> (iii) The dihydroxyl form. This kind of existing form for the acylhydrazide molecule has never been observed in the previous reports. The C–O distances for pth I in compound 1 (C7–O1 = 1.313(7) Å, C8–O2 = 1.300(7) Å), pth in compound 3 (C1–O1 = 1.295(2) Å), and aphth in compound 4 (C8–O1 = 1.311(5) Å, C12–O2 = 1.313(5) Å) are rather longer



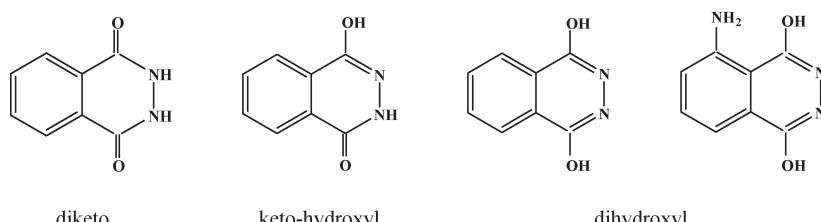
**Fig. 3** The  $\text{Zn}_2(\text{ptb})^{2+}$  chain (a), 3D network (b) and topology (c) for compound 3.

( $>1.29 \text{ \AA}$ ), indicating that the bond between C and O is a single one, not a double one. That is to say, the isomerization for the other acylamino group also occurred. The triazole or tetrazole ligands show a -1 oxidation state in compounds 1–4. However, the acylhydrazide molecules exhibit different oxidation states. The acylhydrazide molecule existing in a dihydroxyl form has a -2 charge, whereas the acylhydrazide molecule existing in a diketo/keto-hydroxyl form has a -1 charge. As exemplified by compounds 1–4, the triazole or tetrazole ligands were successfully introduced into the metal-acylhydrazide system. In compounds 1, 3 and 4, the triazole

and tetrazole ligands act as the second linker, extending the metal-acylhydrazide oligomers into the 2D or 3D networks. This situation is different from that of the widely studied  $\text{M}^{n+}$ -carboxylate-triazolate/tetrazolate system, in which  $\text{M}^{n+}$  and triazolate/tetrazolate aggregate into the cluster, chain or layer, while the carboxylate serves as the second linker. Compounds 1–3 exhibit distinct network structures and the triazole or tetrazole ligands play a crucial role: (i) they influence the existing form, oxidation state and the coordination mode for pth; (ii) they influence the geometry of  $\text{Zn}^{2+}$ , (iii) they influence the interactions between  $\text{Zn}^{2+}$  and pth; (iv) they



**Fig. 4** The 2D layer network of compound 4 (the aromatic ring of apth is omitted for clarity).



**Scheme 3** The three types of existing forms for the acylhydrazide molecules in compounds 1–4.

influence the linkage with the  $Zn^{2+}$ -pth aggregate. Compounds 2 and 4 show different layer networks, which should be due to the presence of the substituted  $-NH_2$  group on the pth molecule.

### Characterization

The TG behaviors of the title compounds have been investigated. Fig. S2<sup>†</sup> presents the temperature *vs.* weight-loss curves. Based on the TG curves, we can find that compounds 1, 3 and 4 possess a good thermal stability, and can be thermally stable up to *ca.* 390 °C for 1, *ca.* 420 °C for 3 and *ca.* 390 °C for 4. Compound 1 underwent two steps of weight loss. The *ca.* 13.7% weight loss for the first step should be ascribed to the loss of the trz molecule (calcd: 12.0%). After the second step of weight loss, the remaining was proved to be  $Zn(OH)_2$  (The residue content: calcd 43.6%, found *ca.* 42.2%), suggesting that the pth molecule decomposed in the second step. Compound 2 underwent three steps of weight loss. The first step of minor weight loss of *ca.* 7% should be assigned to the removal of the  $NH_2$  group on datrz (calcd: 8.6%). In a temperature range of 430–570 °C, compound 2 underwent two steps of continuous weight loss, corresponding to the sublimation of trz and pth, respectively. Synchronously,  $Zn^{2+}$  interacted with  $O_2$  into  $ZnO$ , and  $Zn(OH)_2$  thermally decomposed to  $ZnO$ . So the final residue was  $ZnO$ .

(the residue content: calcd 32.7%, found *ca.* 31.5%). Compound 3 underwent two steps of weight loss. The first step of a *ca.* 30% weight loss indicates that in this step the pth molecules were lost (calcd: 34.9%), and  $Zn^{2+}$  isochronously combined with  $O_2$ . The intermediate is  $[Zn_2O(atez)_2]$  (calcd: 31.4%). In the second step, the atez molecule was lost, and the final residue was  $ZnO$  (calcd: 35.5%, found: *ca.* 34.8%). Compound 4 underwent two steps of weight loss. The first step should be assigned to the loss of OH and datrz (calcd: 23.2%). In the second step, the sublimation of apth and ox occurred. The final residue was  $ZnO$  (calcd: 40.8%; found: *ca.* 40%).

In the IR spectra of compounds 1–4 (see Fig. S3<sup>†</sup>), the appearance of the strong peaks at 1645  $\text{cm}^{-1}$  for 1, 1656  $\text{cm}^{-1}$  for 2, 1647  $\text{cm}^{-1}$  for 3 and 1646  $\text{cm}^{-1}$  for 4 implies that the acylation of  $N_2H_4$  with phthalic/3-nitrophthalic acid has occurred. By the way, the  $\nu(\text{COO})$  peaks are generally either larger than 1680  $\text{cm}^{-1}$  or smaller than 1610  $\text{cm}^{-1}$ , whereas the  $\nu(\text{CONH})$  peaks appear in the range of 1625–1675  $\text{cm}^{-1}$ .<sup>18</sup> The experimental powder XRD pattern for each compound is in accordance with the simulated one generated on the basis of the structural data, confirming that the as-synthesized product is pure phase (see Fig. S4<sup>†</sup>).

### Photoluminescence property

The photoluminescence properties of the title compounds in the solid state were investigated. Fig. 5 presents the related

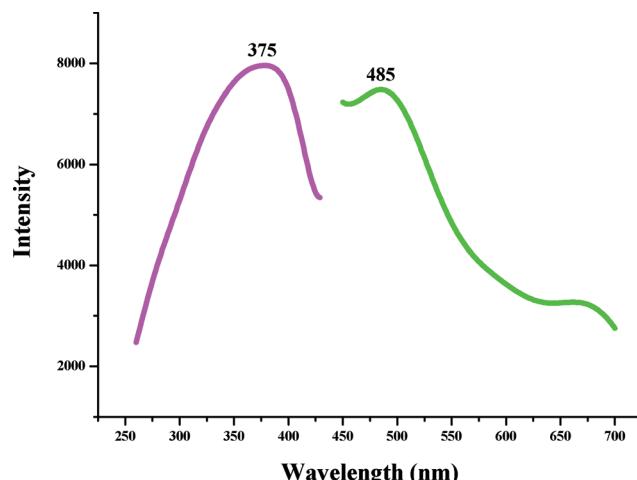


Fig. 5 The excitation and emission spectra of compound 4 in the solid state.

excitation and emission spectra. Regrettfully, only the layered compound 4 emits light. The other three compounds do not emit light. Upon excitation at 375 nm, compound 4 exhibits a green-light emission, and the peak appears at 485 nm. Based on the previous emission mechanism study,<sup>12</sup> the emission close to 500 nm should be attributed to the charge transfer within the apth molecule, which corresponds to the charge transfer from the  $\pi^*$  orbitals of the benzene ring moiety to the  $\pi$  orbitals of the acylhydrazide ring moiety. The fact that compounds 1–3 do not emit light should be due to the close packing of the molecules. The close packing of the molecules is prone to leading to the luminescence quenching. Compounds 1, 2 and 4 all possess the 2D layer structures. But in compounds 1 and 2, the neighboring acylhydrazide molecules form the  $\pi\cdots\pi$  packing, which makes the molecular stacking closer. So compounds 1 and 2 do not emit light. In compound 4, ox plays a key role. On the one hand, ox interacts with Zn<sup>2+</sup> in a chelating way, preventing the 2D layer network from the further extension. On the other hand, the ox molecules are distributed on both sides of the layer, and protrude from the layer, weakening the interactions between the neighboring 2D layers, in particular hindering the formation of the  $\pi\cdots\pi$  packing of the neighboring apth molecules.

## Conclusion

In summary, we have reported the synthesis and structural characterization of four new Zn<sup>2+</sup> coordination polymers with the mixed pth/apth and triazolate/tetrazolate ligands. They are obtained by the reactions of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, phthalic/3-nitrophthalic acid, N<sub>2</sub>H<sub>4</sub> and triazole/tetrazole under hydrothermal conditions. H<sub>2</sub>pth/H<sub>2</sub>apth originated from the *in situ* acylation of N<sub>2</sub>H<sub>4</sub> with phthalic/3-nitrophthalic acid. The reduction of -NO<sub>2</sub> into -NH<sub>2</sub> was also observed when preparing compound 4. The pH level of the reactive system and the N<sub>2</sub>H<sub>4</sub> amount influence the crystal growth of compounds

1–4. The X-ray single-crystal diffraction analysis revealed that the triazole/tetrazole molecules were successfully introduced into the metal-acylhydrazide system. As observed in compounds 1, 3 and 4, the Zn<sup>2+</sup> ions first interact with the pth/apth molecules it form an aggregate. The triazolate or tetrazolate ligands serve as the second linkers, propagating further the Zn<sup>2+</sup>-pth/apth aggregates into the 2D or 3D networks. Three types of existing forms for pth/apth are observed in compounds 1–4: the diketo form, keto-hydroxyl form and dihydroxyl form. Of these, the dihydroxyl form for the acylhydrazide molecule is found for the first time. Only compound 4 emits light. The introduced ox molecule directly influences the structure of compound 4, indirectly influencing its emission behavior.

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