

# Crystal structures and spectroscopic properties of a new zinc phosphite cluster and an unexpected chainlike zinc phosphate obtained by hydrothermal reactions

Zhi-En Lin, Wei Fan, Jinlou Gu, Tatsuya Okubo\*

Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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## Abstract

A new zinc phosphite cluster,  $\text{Zn}_2(4,4'\text{-dmbpy})_2(\text{H}_2\text{PO}_3)_4$  **1**, and a new chainlike zinc phosphate,  $\text{Zn}_2(5,5'\text{-dmbpy})_2(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2$  **2**, have been synthesized under hydrothermal conditions (4,4'-dmbpy = 4,4'-dimethyl-2,2'-dipyridyl, 5,5'-dmbpy = 5,5'-dimethyl-2,2'-dipyridyl). Compound **1** is a molecular zinc phosphite constructed from  $\text{ZnO}_3\text{N}_2$  trigonal bipyramids,  $\text{H}_2\text{PO}_3$  pseudo-pyramids and 4,4'-dmbpy ligands. Compound **2** possesses a 1D chainlike framework constructed from  $\text{ZnO}_3\text{N}_2$  trigonal bipyramids,  $\text{HPO}_4$  tetrahedra,  $\text{H}_2\text{PO}_4$  tetrahedra and 5,5'-dmbpy ligands. Both compounds **1** and **2** exhibit intensive photoluminescence originated from the intraligand  $\pi$ - $\pi^*$  transitions. Crystal data: **1**, monoclinic,  $P2_1/n$ ,  $a = 8.0310(7)$  Å,  $b = 20.2301(5)$  Å,  $c = 10.8424(2)$  Å,  $\beta = 110.857(3)^\circ$ ,  $V = 1646.11(15)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_1 = 0.0297$ ,  $wR_1 = 0.0801$ ; **2**, triclinic,  $P-1$ ,  $a = 11.6875(8)$  Å,  $b = 12.3498(7)$  Å,  $c = 13.1759(8)$  Å,  $\alpha = 64.995(9)^\circ$ ,  $\beta = 65.952(9)^\circ$ ,  $\gamma = 65.296(8)^\circ$ ,  $V = 1502.99(16)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_1 = 0.0418$ ,  $wR_1 = 0.1010$ .

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**Keywords:** Hydrothermal synthesis; Crystal structure; Spectroscopic property; Zinc phosphite; Zinc phosphate

## 1. Introduction

Microporous materials are of great interest because of their widespread applications in catalysis, ion-exchange, adsorption, and host-guest assemblies [1]. Since the discovery of zeolite-like zinc phosphates by Gier and Stucky in 1991 [2], open-framework zinc phosphates have been extensively studied due to the fact that the total charges associated with them (+2 and +5) are similar to those of the aluminosilicates (+3 and +4) [3–8]. Notable examples include ND-1 with extra-large 24-ring channels [9],  $(\text{H}_3\text{deta}) \cdot \text{Zn}_4(\text{PO}_4)_3(\text{HPO}_4) \cdot \text{H}_2\text{O}$  with chiral framework [10], and NTHU-3 with the capacity of assisting molecular recognition [11]. More recently, a great deal of attention has been paid to the synthesis of zinc phosphite frameworks by the replacement of tetrahedral  $\text{PO}_4^{3-}$  units with pseudo-pyramidal  $\text{HPO}_3^{2-}$  groups

[12–25]. Because the  $\text{HPO}_3^{2-}$  group can only make three Zn–O–P bonds, the zinc phosphite frameworks are expected to be different from those formed by tetrahedral  $\text{PO}_4^{3-}$  units. For example,  $\text{Zn}(\text{en})_{0.5}(\text{HPO}_3)$  contains two independent, interpenetrating, mixed inorganic-organic hybrid networks [26]. Generally, these compounds are prepared in the presence of organic amines under hydrothermal conditions. The organic amines locate in the free voids surrounded by inorganic framework and act as the structure-directing agents. In some instances, the organic amines could also be incorporated into the frameworks, forming a new class of inorganic-organic hybrid materials. In our effort to study the effect of steric hindrance of organic amines on the structure of zinc phosphite, a new zinc phosphite cluster  $\text{Zn}_2(4,4'\text{-dmbpy})_2(\text{H}_2\text{PO}_3)_4$  **1** and an unexpected chainlike zinc phosphate  $\text{Zn}_2(5,5'\text{-dmbpy})_2(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2$  **2** have been isolated by hydrothermal reactions. In this contribution, we report their hydrothermal syntheses, crystal structures and spectroscopic properties.

\*Corresponding author. Fax: +81 3 5800 3806.

E-mail address: [okubo@chemsys.t.u-tokyo.ac.jp](mailto:okubo@chemsys.t.u-tokyo.ac.jp) (T. Okubo).

## 2. Experimental

### 2.1. Synthesis

Compound **1** was hydrothermally synthesized under autogenous pressure. Typically, a mixture of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.221 g), 4,4'-dmbpy (0.184 g),  $\text{H}_3\text{PO}_3$  (0.164 g), and  $\text{H}_2\text{O}$  (4 ml) in a molar ratio of 1:1:2:222 was sealed in a Teflon-lined steel autoclave and heated at 160 °C for 7 days and then cooled to room temperature. The initial and final pH of the reaction mixture was about 4. The solid product, consisting of single crystals in the form of light-yellow prisms, was recovered by filtration, washed with distilled water and dried in air (83% yield based on Zn). Yellow block crystals of compound **2** were obtained in a yield of 72% (based on Zn) by reacting  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.219 g), 5,5'-dmbpy (0.184 g),  $\text{H}_3\text{PO}_3$  (0.166 g), and  $\text{H}_2\text{O}$  (4 ml) under the same reaction condition as used for **1**. The initial pH of the reaction mixture was about 4 and there was no appreciable change in the pH after the reaction.

### 2.2. Characterization

The CHN analyses were carried out on an Elementar Vario EL III analyzer. The inductively coupled plasma (ICP) analyses were carried out on a Perkin-Elmer Optima 3300 DV spectrometer. Powder X-ray diffraction (XRD) data were obtained using an M03X-HF22 (MAC Science Co.) with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The step size was  $0.02^\circ$  and the count time was 4 s. IR spectra (KBr pellet) were recorded on a Nicolet Magna 560 spectrometer. The thermogravimetric analyses were performed on a Thermoplus TG 8120 (Rigaku) analyzer in 10%  $\text{O}_2$ /90% He atmosphere from 30 to 800 °C. Diffusive reflection spectra (DRS) were taken on a U-4100 (Hitachi) diffuse reflection spectrometer at room temperature. Fluorescent spectra were measured on a Jasco FP-6500 fluorescence spectrophotometer.

### 2.3. Crystal structure determination

A suitable single crystal of each compound with the dimensions of  $0.40 \times 0.40 \times 0.20 \text{ mm}$  for **1** and  $0.30 \times 0.25 \times 0.10 \text{ mm}$  for **2** was carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. Crystal structure determination by XRD was performed on a Siemens SMART CCD diffractometer with graphite-monochromated  $\text{MoK}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation in the  $\omega$  and  $\varphi$  scanning mode at room temperature. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods using the SHELX97 program package [27,28]. The zinc and phosphorus atoms were first located, and the carbon, nitrogen, and oxygen atoms were found in the final difference Fourier maps. All hydrogen atoms were found in the final difference Fourier maps, except the hydrogen atoms attached to O(3), C(11), C(12), C(23), and C(24) atoms in compound **2** were

Table 1  
Crystal data and structure refinement for **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{24}\text{H}_{32}\text{N}_4\text{O}_{12}\text{P}_4\text{Zn}_2$	$\text{C}_{24}\text{H}_{29}\text{N}_4\text{O}_{12}\text{P}_3\text{Zn}_2$
Formula weight	823.16	789.16
Temperature (K)	293(2)	293(2)
Wavelength ( $\text{\AA}$ )	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P-1$
$a$ ( $\text{\AA}$ )	8.0310(7)	11.6875(8)
$b$ ( $\text{\AA}$ )	20.2301(5)	12.3498(7)
$c$ ( $\text{\AA}$ )	10.8424(2)	13.1759(8)
$\alpha$ (deg)	90	64.995(9)
$\beta$ (deg)	110.857(3)	65.952(9)
$\gamma$ (deg)	90	65.296(8)
Volume ( $\text{\AA}^3$ )	1646.11(15)	1502.99(16)
$Z$	2	2
$\rho_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.661	1.744
$\mu$ ( $\text{mm}^{-1}$ )	1.716	1.825
Reflections collected	11987	11681
Independent reflections	3770 [ $R(\text{int}) = 0.0231$ ]	6772 [ $R(\text{int}) = 0.0222$ ]
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0297$ , $wR_2 = 0.0801$	$R_1 = 0.0418$ , $wR_2 = 0.1010$
$R$ indices (all data)	$R_1 = 0.0331$ , $wR_2 = 0.0826$	$R_1 = 0.0543$ , $wR_2 = 0.1094$

Table 2  
Select bond lengths ( $\text{\AA}$ ) for **1** and **2**

Compound <b>1</b>			
Zn(1)–O(4)	1.988(2)	P(1)–O(3)	1.568(2)
Zn(1)–O(1)	2.006(2)	P(1)–H(1)	1.29(3)
Zn(1)–O(2)	2.007(2)	P(2)–O(4)	1.494(2)
Zn(1)–N(1)	2.133(2)	P(2)–O(6)	1.498(2)
Zn(1)–N(2)	2.139(2)	P(2)–O(5)	1.558(2)
P(1)–O(1)	1.482(2)	P(2)–H(2)	1.31(3)
P(1)–O(2)	1.493(2)		
Compound <b>2</b>			
Zn(1)–O(6)	1.954(2)	P(1)–O(2)	1.513(2)
Zn(1)–O(9)	2.006(2)	P(1)–O(3)	1.572(3)
Zn(1)–O(5)	2.059(2)	P(1)–O(4)	1.576(3)
Zn(1)–N(1)	2.118(3)	P(2)–O(8)	1.494(2)
Zn(1)–N(2)	2.164(3)	P(2)–O(5)	1.529(2)
Zn(2)–O(1)	1.943(2)	P(2)–O(6)	1.543(3)
Zn(2)–O(10)	1.998(2)	P(2)–O(7)	1.592(3)
Zn(2)–O(2)	2.108(2)	P(3)–O(10)	1.500(3)
Zn(2)–N(3)	2.118(3)	P(3)–O(9)	1.516(2)
Zn(2)–N(4)	2.185(3)	P(3)–O(11)	1.554(3)
P(1)–O(1)	1.485(3)	P(3)–O(12)	1.556(3)

geometrically placed. All none hydrogen atoms were refined anisotropically. Experimental details for the structural determinations of the compounds are presented in Table 1. Selected bond distances are listed in Table 2. CCDC reference number 621670/621671 (1/2).

## 3. Results and discussion

### 3.1. Characterization

The powder XRD patterns of compounds **1** and **2** are shown in Fig. 1. Except for those marked peaks, the

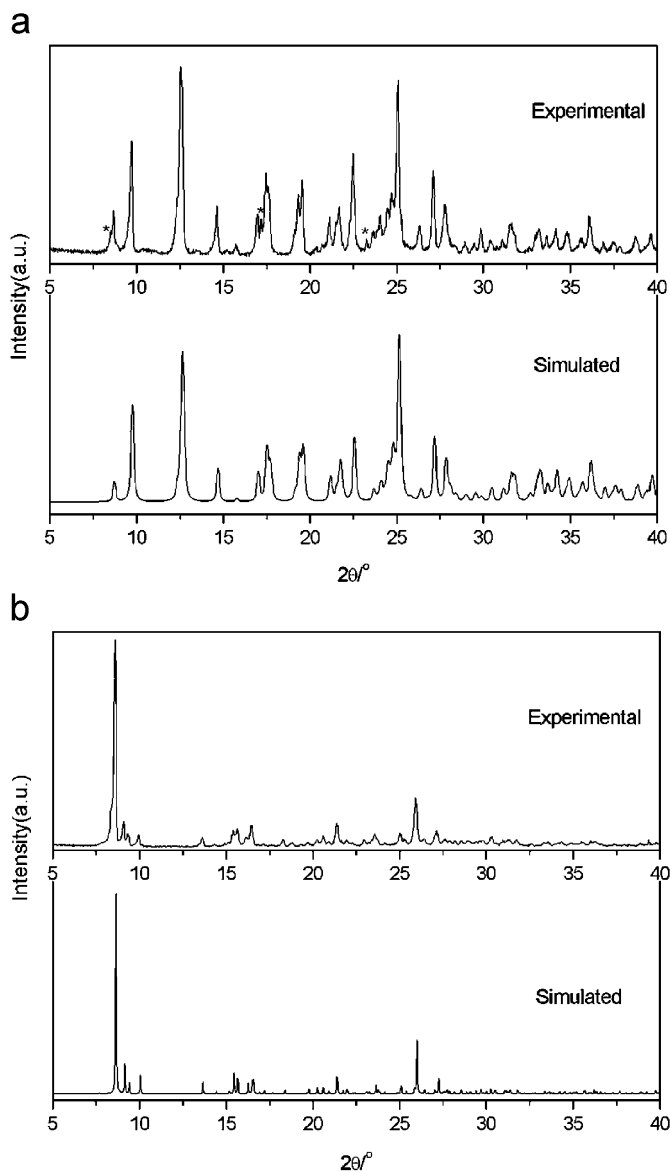


Fig. 1. Simulated and experimental powder X-ray diffraction patterns of **1** (a) and **2** (b).

experimental XRD pattern of **1** is in agreement with the simulated one based on the single crystal structure, indicating the presence of minor impurity phase in the product. In the case of **2**, the diffraction peaks on simulated and experimental patterns correspond well in position, indicating the phase purity of the as-synthesized compound **2**. The ICP and elemental analysis results are listed as follows: Calcd. for **1**: Zn, 15.88%; P, 15.05%; C, 35.02%; H, 3.92%; N, 6.81%. Anal. found: Zn, 15.21%; P, 14.87%; C, 34.53%; H, 3.75%; N, 6.74%. Calcd. for **2**: Zn, 16.57%; P, 11.77%; C, 36.53%; H, 3.70%; N, 7.10%. Anal. found: Zn, 16.14%; P, 11.26%; C, 35.86%; H, 3.61%; N, 6.95%.

The IR spectra of **1** and **2** clearly show the existence of organic ligands in the region  $1380\text{--}1610\text{ cm}^{-1}$ , and the broad bands at ca.  $1000\text{--}1200\text{ cm}^{-1}$  are associated with the stretching vibrations of P–O bonds. The IR spectrum of **1**

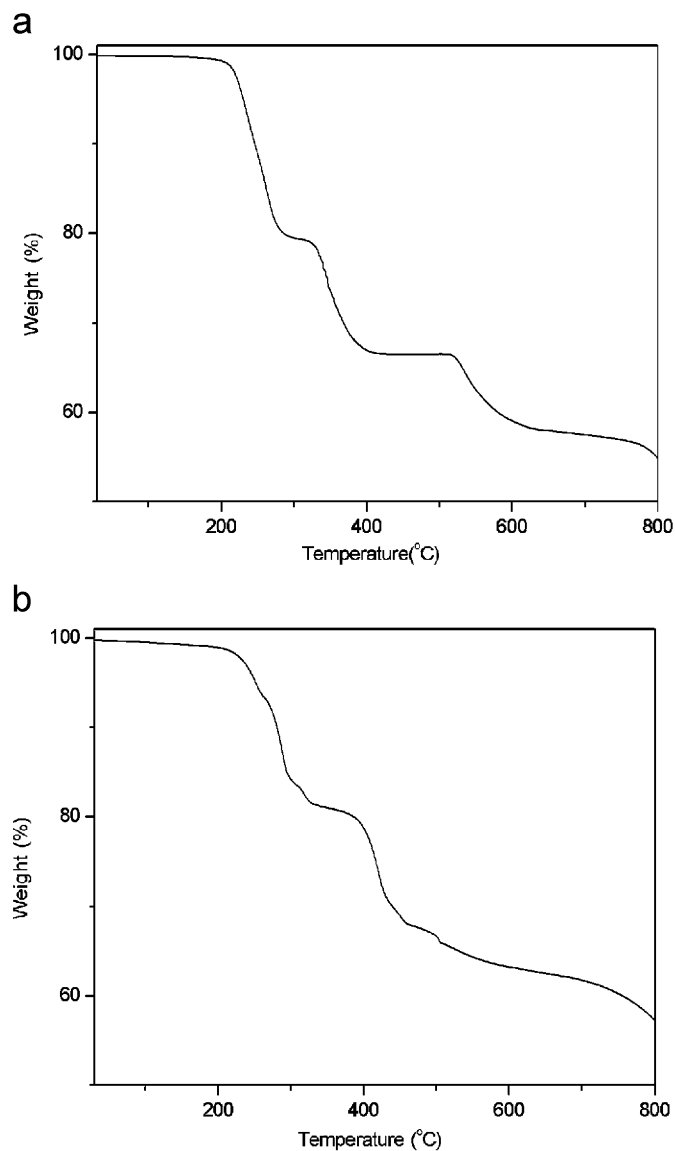


Fig. 2. The TG curves of **1** and **2** with a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ .

contains a strong band at  $2390\text{ cm}^{-1}$ , in good agreement with the existence of P–H bond in the crystal structure. However, no characteristic peak of P–H bond was found in the IR spectrum of **2**, indicating that the initial  $\text{H}_3\text{PO}_3$  source used in the synthesis of **2** could be oxidized or disproportionated into  $\text{PO}_4^{3-}$  anions under hydrothermal conditions. Such phenomenon has been also observed in the synthesis of organically templated zinc phosphate–phosphite frameworks [29,30].

Initial thermogravimetric analyses of **1** and **2** were carried out under  $\text{He}/\text{O}_2$  atmosphere with a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ . As shown in Fig. 2a and b, the structure of **1** and **2** keep stable up to  $200\text{ }^{\circ}\text{C}$ . The weight losses between  $200$  and  $800\text{ }^{\circ}\text{C}$  are attributed to the decomposition of organic molecules. For compound **1**, the total weight loss of 45.74% corresponds well to the expected value

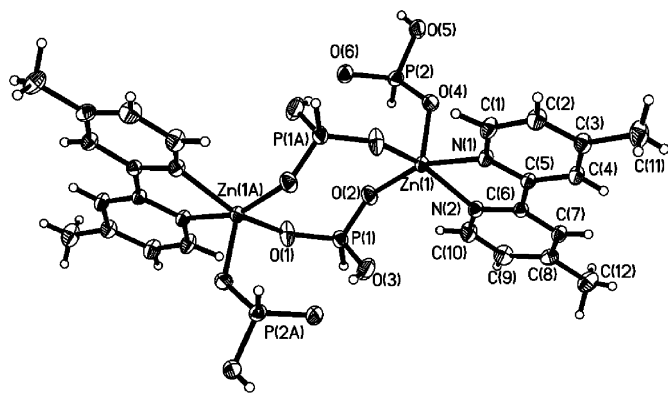


Fig. 3. View of the coordination environments of the zinc and phosphorus atoms in the molecular structure of **1**, showing the atom-label scheme and 30% thermal ellipsoids.

(44.76%). For compound **2**, the observed weight loss of 42.56% is less than the calculated value (46.69%), which is due to the retention of carbon in the solid residue (black in color). The similar thermal decomposition phenomenon was also observed in an organically ligated indium phosphate compound [31].

### 3.2. Description of the structure

Compound **1** is a simple molecular solid, which consists of two zinc centers, four H<sub>2</sub>PO<sub>3</sub> units, and two 4,4'-dmbpy ligands. As seen in Fig. 3, the two zinc centers are bridged by two H<sub>2</sub>P(1)O<sub>3</sub> groups to form a four-membered ring unit, and the other two H<sub>2</sub>P(2)O<sub>3</sub> units are terminal and hang from the zinc centers as pendants. The 4,4'-dmbpy ligands bonded directly with the zinc centers to complete their coordination spheres. The Zn–O bond distances are in the region 1.988(2)–2.007(2) Å, the Zn–N bond lengths are between 2.133(2) and 2.139(2) Å, and the P–O bond distances vary from 1.482(2) to 1.568(2) Å. Bond valence sum values clearly indicate that P(1)–O(3), P(2)–O(5) with the distance of 1.568(2) and 1.558(2) Å are hydroxyl bonds [32]. These assignments are also in agreement with the proton positions observed near the oxygen atoms in the difference Fourier map.

Compound **1** possesses a similar molecular structure with that of Zn<sub>2</sub>(2,2'-bipy)<sub>2</sub>(H<sub>2</sub>PO<sub>3</sub>)<sub>4</sub> [33], however, these inorganic–organic hybrid clusters exhibit different supramolecular interactions, including hydrogen bond interaction between H<sub>2</sub>PO<sub>3</sub> units and  $\pi$ – $\pi$  interactions between organic ligands. As a result, the stacking of these zinc phosphite clusters is quite different. In the case of Zn<sub>2</sub>(2,2'-bipy)<sub>2</sub>(H<sub>2</sub>PO<sub>3</sub>)<sub>4</sub>, the hydrogen bonds involving H<sub>2</sub>PO<sub>3</sub><sup>−</sup> groups connect adjacent zinc phosphite clusters into infinite layers. The organic amines protrude into the interlamellar region and are parallel with each other. The adjacent layers are stable packed together and exhibit 3D supramolecular arrays through  $\pi$ – $\pi$  interactions between 2,2'-bipy molecules. While in the instance of compound **1**, the molecular structure is stabilized by the

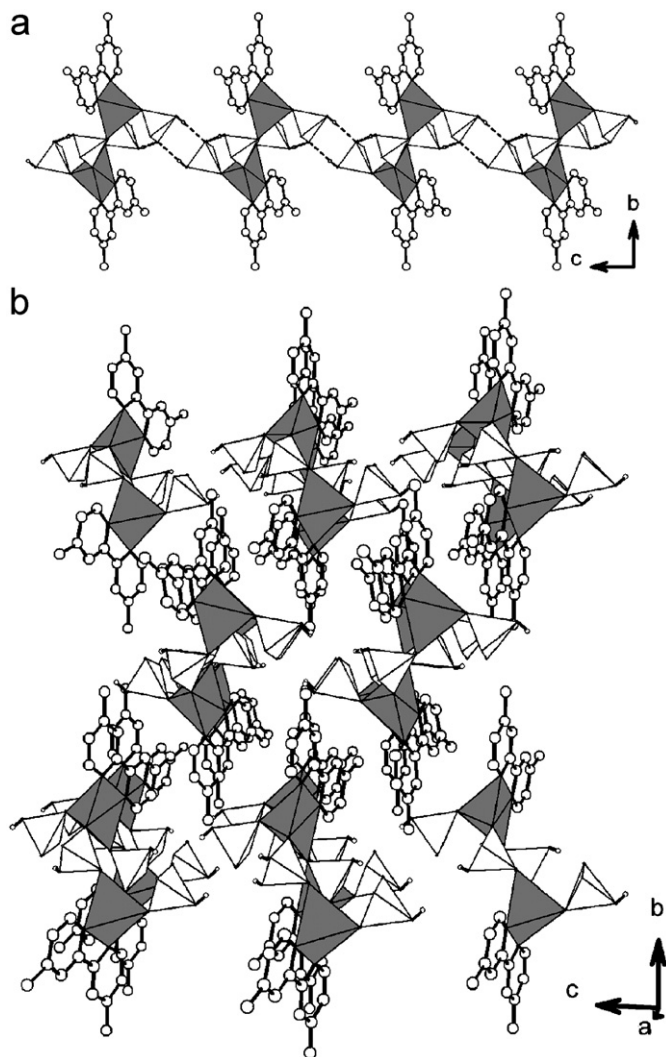


Fig. 4. (a) View of structure of **1** showing the H-bonds between adjacent clusters. (b) Packing drawing of the structure of **1** along [100] direction. ZnO<sub>3</sub>N<sub>2</sub> trigonal bipyramids, medium gray; HPO<sub>3</sub> pseudo-pyramids, white.

extensive hydrogen bonds, forming a chainlike network running along the [001] direction, as shown in Fig. 4a. The O...O distances between adjacent H<sub>2</sub>PO<sub>3</sub><sup>−</sup> groups are in the range of 2.586(3)–2.597(2) Å. The important hydrogen bonds of compound **1** are listed in Table 3. Each chain structure interact with four adjacent chains via  $\pi$ – $\pi$  interactions between 4,4'-dmbpy molecules to generate an interesting 3D supramolecular network, as shown in Fig. 4b.

Compound **2** was obtained unexpectedly because of the phosphorous acid was oxidized or disproportionated into PO<sub>4</sub><sup>3−</sup> anions under hydrothermal conditions. Unlike compound **1** with a molecular structure, compound **2** possesses a chainlike framework. The asymmetric unit of **2** consists of two Zn centers, one HPO<sub>4</sub> and two H<sub>2</sub>PO<sub>4</sub> tetrahedra, and two neutral 5,5'-dmbpy ligands, as depicted by Fig. 5. Each Zn atom is coordinated by three framework oxygen atoms and two nitrogen atoms from a 5,5'-bmbpy

Table 3  
Hydrogen bonds for **1**

D–H...A <sup>a</sup>	<i>d</i> (D–H) (Å)	<i>d</i> (H...A) (Å)	<i>d</i> (D...A) (Å)	Angle D–H...A (deg)
O3–H3...O6#1	0.71(4)	1.88(4)	2.586(3)	172(5)
O5–H4...O6#2	0.65(3)	1.95(3)	2.597(2)	178(4)

<sup>a</sup>Symmetry transformations used to generate equivalent atoms: #1–*x*, –*y* + 1, –*z* + 1; #2–*x*, –*y* + 1, –*z*.

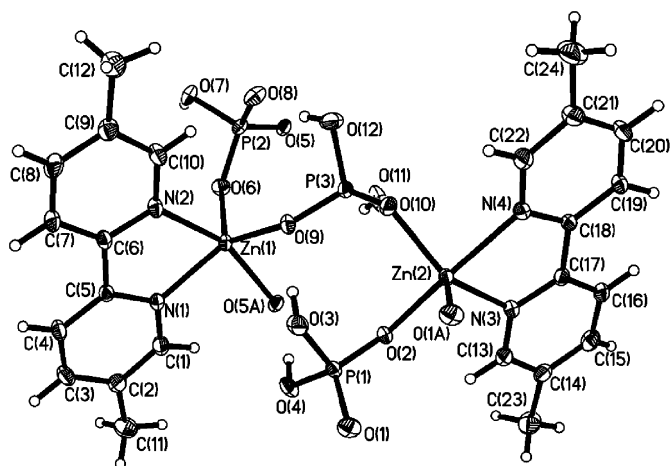


Fig. 5. ORTEP drawing of the asymmetric unit of **2** showing the atom-label scheme and 30% thermal ellipsoids. Atom labels having “a” refer to symmetry-generated atoms.

molecule to form a distorted trigonal bipyramidal geometry. The Zn–O(N) bond distances are in the range of 1.943(2)–2.185(3) Å, with an average value of 2.065 Å. Of the three crystallographically distinct P atoms, P(1) and P(3) each share two oxygen atoms with adjacent Zn atoms and possess two terminal P–OH bonds. P(2) makes two P–O–Zn links and possesses one terminal P–OH bonds and one terminal P=O bond (1.494(2) Å). The P–O<sub>bridging</sub> and P–OH bond lengths are between 1.485(3)–1.543(3) Å and 1.554(3)–1.592(3) Å, respectively. The 5,5'-dmbpy molecules possess typical geometry and connected to Zn centers through Zn–N bonds.

The structure of **2** contains of neutral zinc phosphate chains decorated with neutral 5,5'-dmbpy ligands, as shown in Fig. 6a. There are two types of four-membered rings in the hybrid zinc phosphate chains. Type I is constructed from the alternative linkages of two Zn(1)O<sub>3</sub>N<sub>2</sub> and two HP(2)O<sub>4</sub> moieties, while type II is made up of two Zn(2)O<sub>3</sub>N<sub>2</sub> and two H<sub>2</sub>P(1)O<sub>4</sub> groups. The two types of four-membered rings repeat alternating in the chain structure with H<sub>2</sub>P(3)O<sub>4</sub> tetrahedra acting as the bridges to connect them. The organic amine is incorporated into the framework and serves as a bidentate ligand rather than a structure-directing agent. It is noteworthy that the distance between the least-squares planes of adjacent pyridine rings of the organic molecules is less than 3.5 Å, indicating the presence of intermolecular  $\pi$ – $\pi$  interactions. Thus, the one-dimensional (1D) chains are

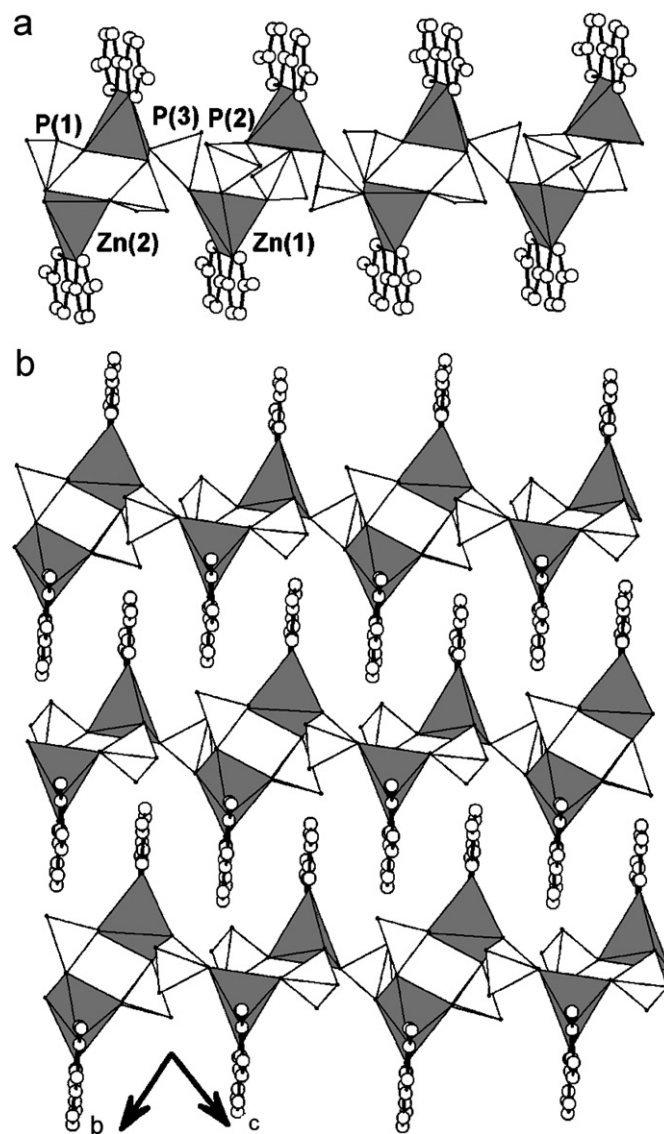


Fig. 6. (a) View of the chainlike structure of **2**. (b) Packing drawing of the structure of **2** along [100] direction. ZnO<sub>3</sub>N<sub>2</sub> trigonal bipyramids, medium gray; PO<sub>4</sub> tetrahedra, white.

extended into a two-dimensional (2D) framework through the  $\pi$ – $\pi$  interactions between adjacent 5,5'-dmbpy molecules, as shown in Fig. 6b.

It should be noted here that the structure of compound **2** is reminiscent of another hybrid zinc phosphate, Zn<sub>2</sub>(2,2'-bpy)<sub>2</sub>(HPO<sub>4</sub>)(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> [34]. The structure topology within the zinc phosphate chains is the same in both

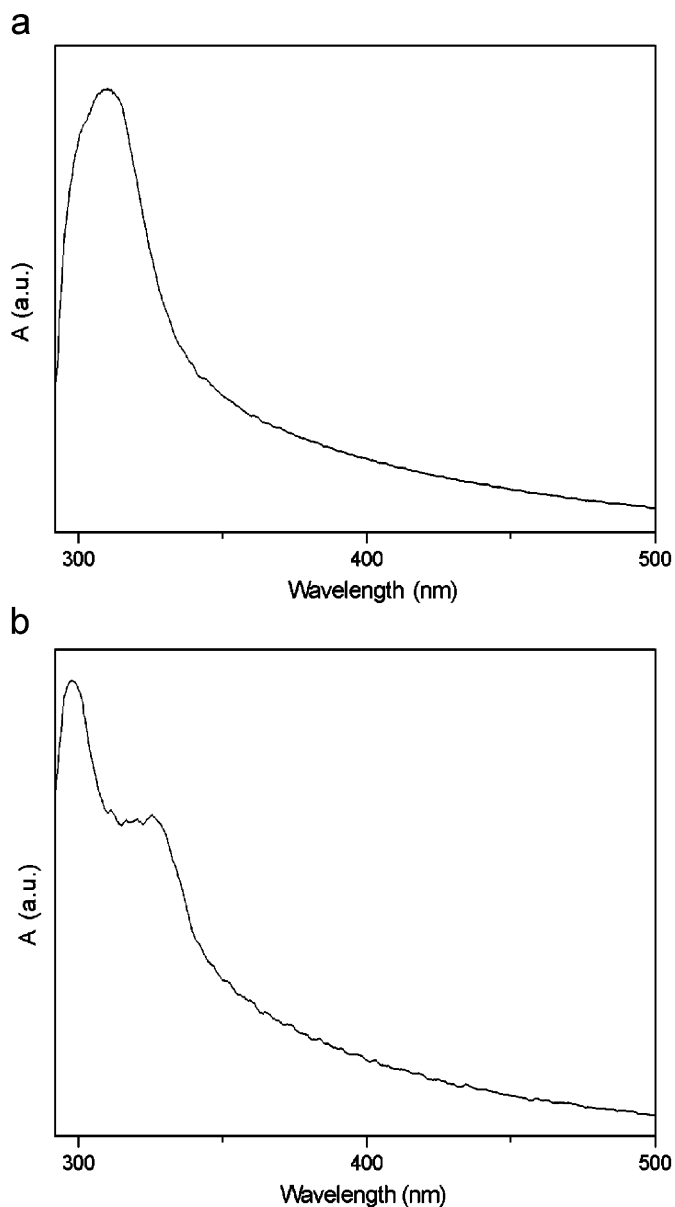


Fig. 7. DRS spectra of (a) **1** and (b) **2**.

compounds, except that the 2,2'-bipy ligands are replaced by 5,5'-dmbpy ligands. The two organic ligands play the same structural role in the formation of the two compounds, however, the interchain distances are different in the two compounds due to the size differences of the 2,2'-bipy ligand and 5,5'-dmbpy ligand.

### 3.3. Photoluminescence properties

As shown in Fig. 7, the DRS spectrum of **1** shows a strong absorption band at 310 nm, and the DRS spectrum of **2** exhibits dominant absorption at 298 and 325 nm, which are assigned to the intraligand  $\pi-\pi^*$  transition of the organic ligands. Fig. 8 presents the emission spectra of compounds **1** and **2** at room temperature. When excited at 310 nm, **1** gives

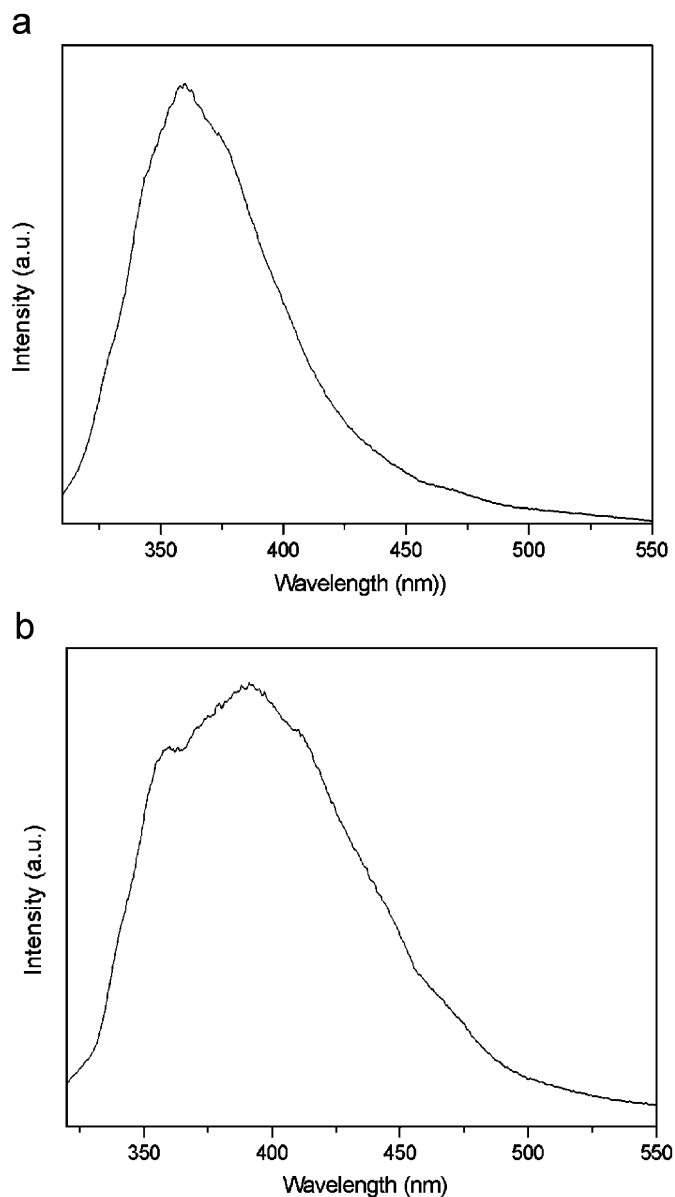


Fig. 8. The solid state photoluminescent spectra of **1** ( $\lambda_{\text{ex}} = 310$  nm) and **2** ( $\lambda_{\text{ex}} = 298$  nm) at room temperature.

a strong emission with the maximum wavelength centered at 360 nm. For **2**, a strong fluorescent emission band centered at 360 and 391 nm is observed, when excited at 298 nm. Compared to  $\text{Zn}_2(2,2'\text{-bipy})_2(\text{H}_2\text{PO}_3)_4$  with an emission band centered at 456 nm [33], the emission band of **1** dramatically blue-shifted despite they possess the same molecular structure, suggesting that photoluminescent materials with a wide range of emission characteristics may be developed by tuning their organic ligands.

## 4. Conclusions

A new zinc phosphite and a new zinc phosphate,  $\text{Zn}_2(\text{H}_2\text{PO}_3)_4(4,4'\text{-dmbpy})_2$  **1** and  $\text{Zn}_2(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2(5,5'\text{-dmbpy})_2$  **2**, were obtained as good quality single crystals

under hydrothermal conditions. Structural analyses indicate that compound **1** has a molecular structure and compound **2** owns a chainlike structure. Both of the compounds possess neutral frameworks with the organic amines bonded directly to the zinc centers. The two compounds exhibit intensive photoluminescence originated from the intraligand  $\pi$ - $\pi^*$  transitions.

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