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# New Types of Layered and Pillared Layered Metal Carboxylate-Phosphonates Based on the 4,4'-Bipyridine Ligand

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Hydrothermal reactions of transition metal salts with  $\text{HO}_2\text{CCH}_2\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$  ( $\text{H}_5\text{L}$ ) and 4,4'-bipyridine (bipy) lead to two new metal carboxylate-diphosphonates, namely,  $\text{Co}_3(\text{H}_2\text{L})_2(\text{H}_2\text{O})_4(\text{bipy})_2 \cdot 11\text{H}_2\text{O}$  (**1**) with a layered structure, and a blue luminescent compound,  $\text{Zn}_5\text{L}_2(\text{bipy})_2 \cdot 9\text{H}_2\text{O}$  (**2**) with a pillared layered structure. In compound **1**, three Co(II) ions are interconnected by two chelating and bridging phosphonate ligands to form a trinuclear unit, and such units are further cross-linked via bridging bipy ligands to form a 2D layer. In compound **2**, the zinc(II) ions in the trigonal bipyramidal or tetrahedral geometries are interconnected via chelating and bridging carboxylate-phosphonate ligands into 2D layers which are further cross-linked by 4,4'-bipy ligands into a pillared layered architecture. Results of luminescent studies indicate that compound **2** is a blue light luminescent material.

## Introduction

Metal phosphonates exhibit a variety of open frameworks such as layered and microporous structures.<sup>1</sup> Materials with open-framework and microporous structures are promising candidates for hybrid composite materials in electro-optical and sensing applications.<sup>2</sup> The strategy of attaching functional groups such as carboxylate ligands to the phosphonic acid has proven to be an effective route for the isolation of a variety of open-framework and microporous structures. For example, a series of metal carboxylate-phosphonates with open framework structures, using  $\text{H}_2\text{O}_3\text{PCH}_2\text{CO}_2\text{H}$  and  $\text{H}_2\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2\text{H}$  as ligands, have been independently reported by the Cheetham, Bujoli, and Sevov groups.<sup>2–4</sup> Results of our research and others indicate that amino-carboxylic-phosphonic acids are also capable of forming open frameworks.<sup>5,6</sup> Phosphonic acids at-

tached with a crown ether moiety also lead to materials with an open framework in addition to 1D "macrocyclic leaflets".<sup>7,8</sup> The use of additional bidentate metal linkers such as 1, 10-phenanthroline, 2,2'-bipyridine, piperazine, and 4,4'-bipyridine has been successful for building mixed metal hybrid structures of V and Mo as well as other transition metal hybrid compounds with chain, layered, and 3D network structures.<sup>9–11</sup> The chelating effect of the 2,2'-bipyridine and 1,10-phenanthroline

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usually results in metal phosphonates with a lower dimensionality.<sup>12</sup> The present work is based on the hypothesis that it will be possible to use a second ligand such as 4,4'-bipyridine to cross-link metal phosphonate layers into microporous pillared layered architectures. In this vein, we selected the carboxylate-phosphonate ligand, HO<sub>2</sub>CCH<sub>2</sub>N(CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub> (H<sub>5</sub>L), whose zinc(II) compound (Zn<sub>2</sub>(HL)) was previously reported by this group,<sup>6</sup> in combination with 4,4'-bipyridine (bipy) as the second metal linker. These efforts have resulted in two new metal carboxylate-phosphonate hybrids, namely, Co<sub>3</sub>(H<sub>2</sub>L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(bipy)<sub>2</sub>·11H<sub>2</sub>O (**1**), with a layered structure and Zn<sub>5</sub>L<sub>2</sub>(bipy)<sub>2</sub>·9H<sub>2</sub>O (**2**) with a pillared layered structure. Herein, we report their syntheses, crystal structures, and magnetic and luminescent properties.

## Experimental Section

**Materials and Instrumentation.** All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 15 °C/min under a nitrogen atmosphere. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the 4000–400 cm<sup>-1</sup> range. X-ray powder diffraction (XRD) patterns (Cu Kα) were collected in a sealed glass capillary on a XPERT-MPD θ–2θ diffractometer. Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer. Magnetic susceptibility measurements were carried out on a Quantum Design SQUID magnetometer with an applied field of 1000 G in the temperature range of 2–300 K. Data were corrected for diamagnetic contributions calculated from the Pascal's constants.<sup>13</sup> *N,N*-Bis(phosphonomethyl)aminoacetic acid was prepared by a Mannich-type reaction according to procedures described previously.<sup>6e</sup>

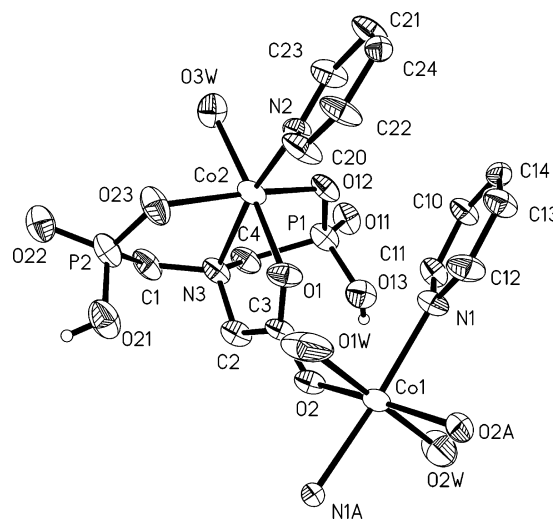
**Preparation of Co<sub>3</sub>(H<sub>2</sub>L)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(bipy)<sub>2</sub>·11H<sub>2</sub>O (**1**).** A mixture of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.24 g, 1.0 mmol), H<sub>5</sub>L (0.13 g, 0.5 mmol), and 4,4'-bipy (0.09 g, 0.5 mmol) in 10 mL of distilled water was sealed into a bomb equipped with a Teflon liner (25 mL) and then heated at 180 °C for 5 days. The resultant orange-red solution was filtered off. Ethanol was allowed to slowly diffuse into a filtrate at room temperature. After several days, orange-red block crystals of compound **1** were collected in ca. 48% yield (based on cobalt). The initial and final pH values are 4.0 and 4.5, respectively. Elemental analysis for **1**: Calcd for Co<sub>3</sub>P<sub>4</sub>O<sub>31</sub>N<sub>6</sub>C<sub>28</sub>H<sub>62</sub>: C, 26.27; H, 4.89; N, 6.57%. Found: C, 26.15; H, 5.33; N, 6.54%. IR (KBr, cm<sup>-1</sup>): 3390 br, 1605 vs, 1537 w, 1493 w, 1437 w, 1414 m, 1201 w, 1148 s, 1070 s, 1032 s, 947 w, 915 w, 820 w, 733 m, 634 m, 603 m, 573 w, 484 w.

**Preparation of Zn<sub>5</sub>L<sub>2</sub>(bipy)<sub>2</sub>·9H<sub>2</sub>O (**2**).** A mixture of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.22 g, 1.0 mmol), H<sub>5</sub>L (0.13 g, 0.5 mmol), and 4,4'-bipyridine (0.09 g, 0.5 mmol) in 10 mL of distilled water was sealed into a bomb equipped with a Teflon liner (25 mL) and then heated at 180 °C for 5 days. Colorless crystals of **2** were collected in ca. 50% yield (based on zinc). The initial and final pH values for the reaction are 4.0 and 3.5, respectively. Elemental analysis for **2**: Calcd for Zn<sub>5</sub>P<sub>4</sub>O<sub>25</sub>N<sub>6</sub>H<sub>46</sub>C<sub>28</sub>: C, 25.50; H, 3.49; N, 6.38%. Found: C, 25.65; H, 3.54; N, 6.41%. IR (KBr, cm<sup>-1</sup>): 3427 m, 1610 s, 1537 w, 1451 w, 1420 m, 1331 m, 1227 m, 1110 s, 1072 vs, 1009 m, 994 m, 821 w, 730 w, 704 w, 642 w, 604 m, 572 w, 500 w. IR spectrum of compound **2** (KBr, cm<sup>-1</sup>, after heating at 180 °C for 48 h): 1610 vs, 1537 w, 1493 w, 1437 w, 1419 s, 1331 m, 1227 m, 1110 s, 1072 vs, 1009 m, 818 w, 777 w, 731 w, 642 w, 606 m, 494 w.

**Table 1. Crystal Data and Structure Refinements for Compounds 1 and 2**

compound	<b>1</b>	<b>2</b>
formula	Co <sub>3</sub> P <sub>4</sub> O <sub>31</sub> N <sub>6</sub> C <sub>28</sub> H <sub>62</sub>	Zn <sub>5</sub> P <sub>4</sub> O <sub>25</sub> N <sub>6</sub> H <sub>46</sub> C <sub>28</sub>
fw	1279.51	1317.44
space group	<i>P2</i> / <i>c</i>	<i>P2</i> / <i>c</i>
<i>a</i> , Å	14.8651(14)	14.3635(8)
<i>b</i> , Å	7.5694(7)	12.0029(6)
<i>c</i> , Å	22.796(2)	16.9974(9)
α, deg	90.0	90.0
β, deg	106.833(1)	113.3810(10)
γ, deg	90.0	90.0
<i>V</i> , Å <sup>3</sup>	2455.1(4)	2689.8(2)
<i>Z</i>	2	2
<i>D</i> <sub>calcd</sub> , g·cm <sup>-3</sup>	1.731	1.627
μ, mm <sup>-1</sup>	1.235	2.396
GOF on <i>F</i> <sup>2</sup>	1.040	1.080
R1, wR2 ( <i>I</i> > 2σ( <i>I</i> )) <sup>a</sup>	0.0625/0.1342	0.0565/0.1402
R1, wR2 (all data)	0.1210/0.1639	0.0811/0.1592

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w(F_o)^2 \}^{1/2}.$$



**Figure 1.** ORTEP representation of the asymmetric unit of compound **1**. The thermal ellipsoids are drawn at 50% probability. The lattice water molecules have been omitted for clarity.

**Single-Crystal Structure Determination.** Single crystals of compounds **1** and **2** were mounted on a Siemens Smart CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensity data were collected by the narrow frame method at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by SADABS program.<sup>14</sup> Both structures were solved by the direct methods and refined by full-matrix least-squares fitting on *F*<sup>2</sup> by SHELX-97.<sup>14</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. Crystallographic data and structural refinements for compounds **1** and **2** are summarized in Table 1. More details on the crystallographic studies as well as atom displacement parameters are given as Supporting Information.

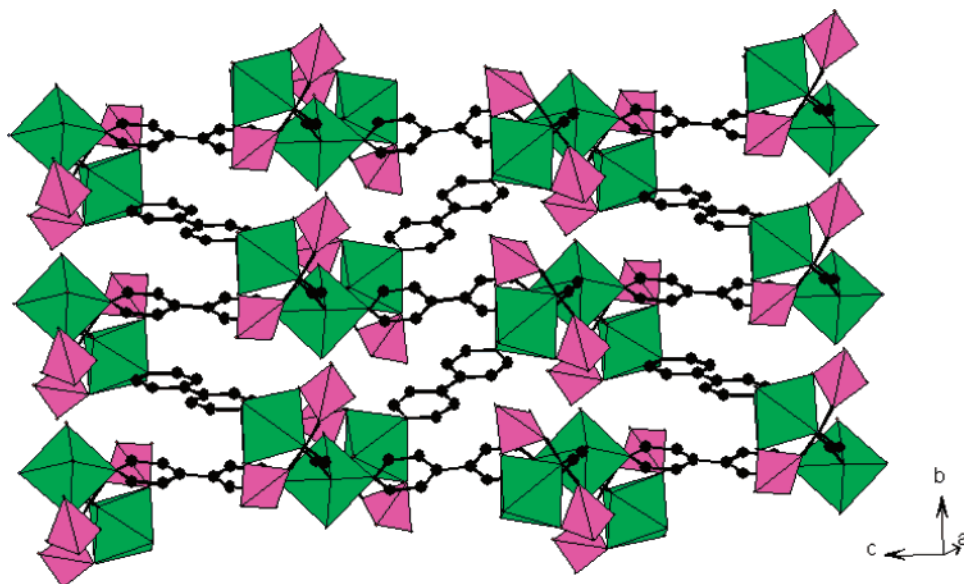
## Results and Discussion

**Crystal Structure Descriptions of Compounds 1 and 2.** Compound **1** features a layered structure in which there are two unique Co(II) ions in the asymmetric unit (Figure 1). The Co(1) center is located on a 2-fold axis and is octahedrally coordinated by two

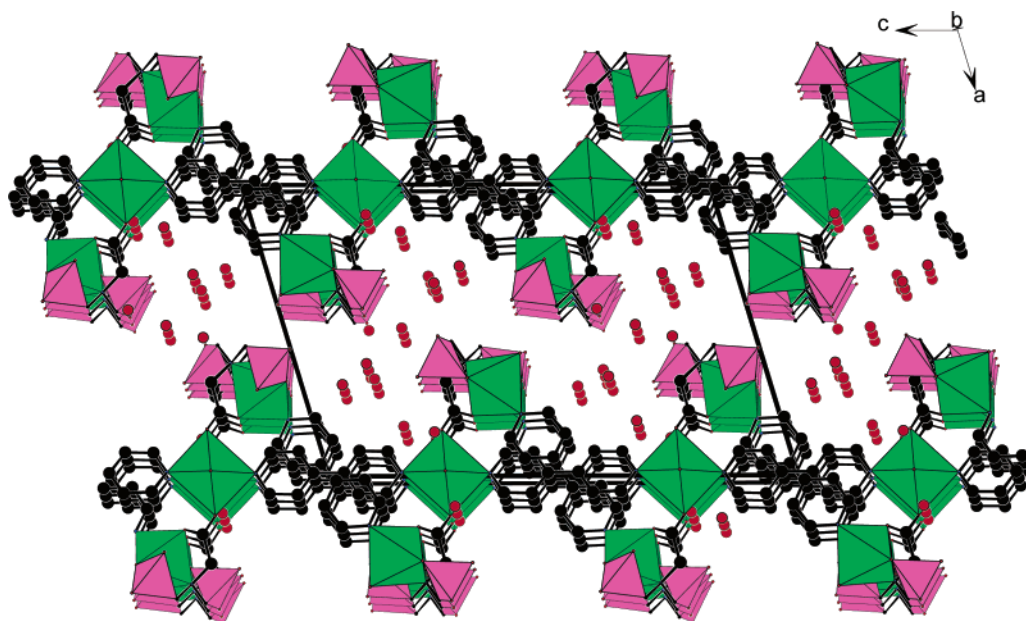
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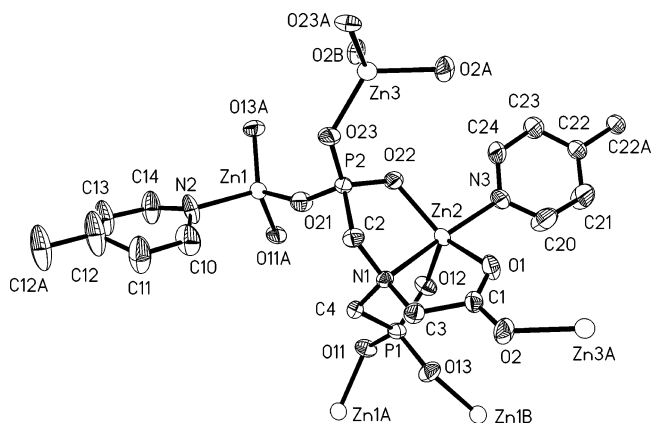


**Figure 2.** Polyhedral representation of a  $\langle 100 \rangle$  cobalt(II) carboxylate-phosphonate layer in compound **1**. The cobalt(II) octahedra and phosphonate tetrahedra are shaded in green and pink. C atoms are drawn as black circles.



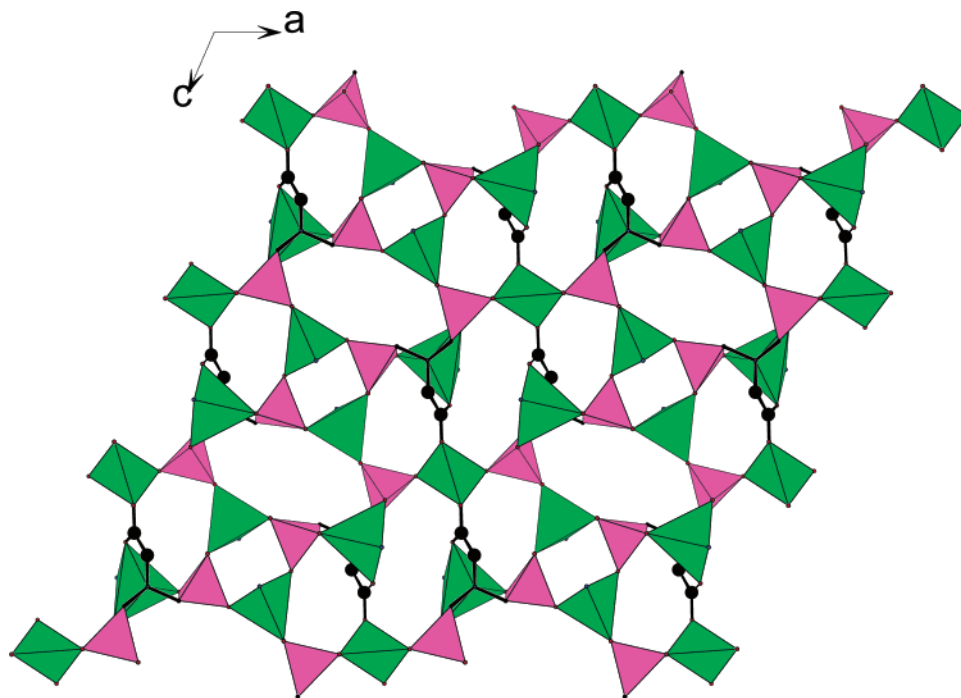
**Figure 3.** View of the structure of compound **1** down the  $b$ -axis. The cobalt(II) octahedra and phosphonate tetrahedra are shaded in green and pink. C and O atoms are drawn as black and red circles, respectively.

carboxylate oxygen atoms from two carboxylate ligands, as well as two nitrogen atoms from 4,4'-bipy ligands and two aqua ligands. The Co(2) ion occupies a general position and is in an octahedral environment composed of a tetradentate chelating carboxylate ligand (1 N and 3 O), a 4,4'-bipy nitrogen atom, and an aqua ligand. The Co–N distances range from 2.132(5) to 2.254(5) Å, and the Co–O bonds are in the range 2.041(4)–2.158(5) Å. These distances are comparable to those reported for other Co(II) phosphonates.<sup>3–5</sup> Two Co(1)(H<sub>2</sub>L) chelating units are bridged by a Co(2)N<sub>2</sub>O<sub>4</sub> octahedron to form a trinuclear unit, and such units are cross-linked by 4,4'-bipy ligands into a  $\langle 100 \rangle$  2D layer (Figure 2). The carboxylate-phosphonate ligand is pentadentate, and each phosphonate group is unidentate and singly protonated; the carboxylate group is bidentate bridging. The noncoordinated phosphonate oxygen atoms are involved in hydrogen bonding with aqua ligands and



**Figure 4.** ORTEP representation of the asymmetric unit of compound **2**. The thermal ellipsoids are drawn at 50% probability. The lattice water molecules have been omitted for clarity.





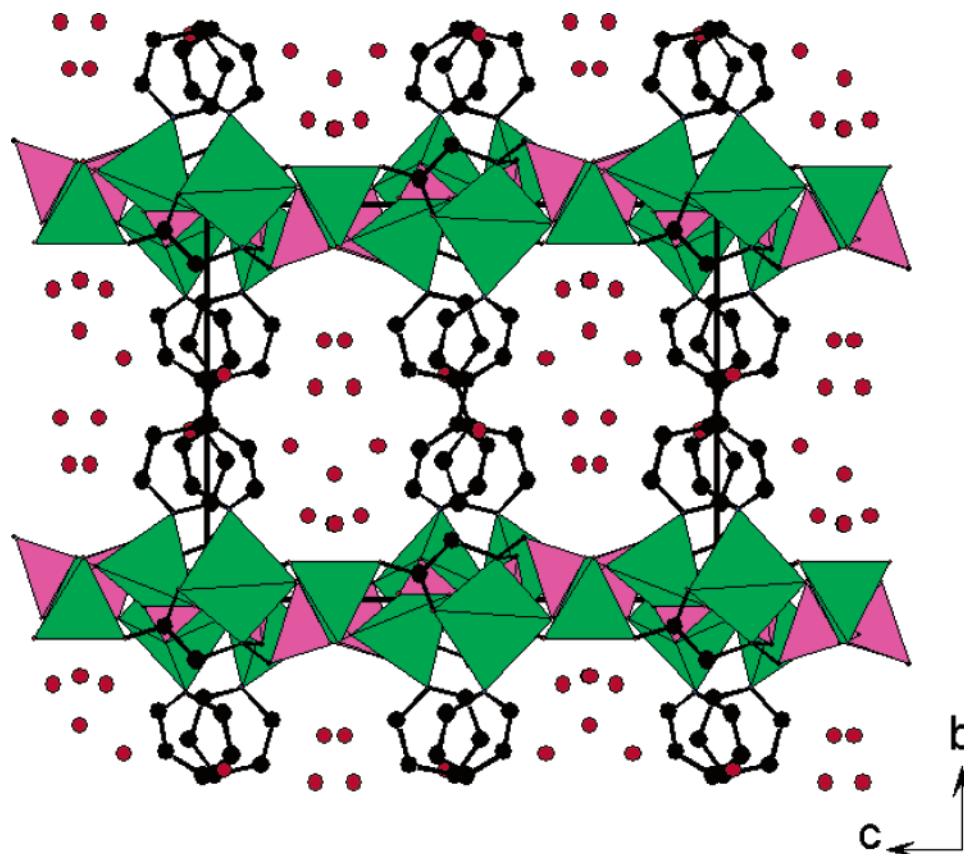
**Figure 5.** A (010) zinc(II) carboxylate-phosphonate layer in compound **2**. The zinc(II) polyhedra and phosphonate tetrahedra are shaded in green and pink, respectively. C and O atoms are drawn as black and red circles, respectively.

interstitial water molecules, which further increases the stability of the structure (Figure 3).

The structure of compound **2** is a pillared layered architecture in which the Zn(II) ions are interconnected by carboxylate-phosphonate ligands to form a 2D layer; the layers are further cross-linked by 4,4'-bipy ligands to form a pillared layered structure. As shown in Figure 4, there are three unique Zn(II) ions in the asymmetric unit. The Zn(3) atom occupying a position of the 2-fold symmetry is in a tetrahedral environment consisting of two phosphonate oxygens and two carboxylate oxygens from four L ligands. The Zn(1) center is in a tetrahedral environment composed of three phosphonate oxygen atoms and a 4,4'-bipy nitrogen atom. The Zn(2) ion is five-coordinate by a tetradentate L ligand and a nitrogen atom from a 4,4'-bipy ligand. Its coordination geometry can be described as a trigonal bipyramid. The Zn–O (1.898(4)–2.045(5) Å) and Zn–N (2.047(6)–2.283(5) Å) distances are comparable to those reported for other zinc(II) phosphonates.<sup>2–5</sup> All Zn(II) ions in Zn<sub>2</sub>(HL) with a 3D network structure we reported previously are tetrahedrally coordinated.<sup>5</sup> Unlike those in compound **1**, the carboxylate-phosphonate ligands in compound **2** are fully deprotonated. Each L ligand is nonadentate; it chelates to a Zn(2) (1 N, 3 O) atom tetradentately and also bridges with 3 Zn(1) and 2 Zn(3) ions. This type of coordination mode is also different from that in Zn<sub>2</sub>(HL) in that the amine group of the ligand in Zn<sub>2</sub>(HL) is protonated and remains uncoordinated. The zinc polyhedra in the aforementioned structure are interconnected via chelating and bridging carboxylate-phosphonate ligands into (010) 2D layers (Figure 5), which are further cross-linked by 4,4'-bipy ligands into a pillared layered structure. The size of the long-narrow shaped cavity thus formed is estimated to be 2.0 × 6.0 Å<sup>2</sup>. The lattice water molecules are located in the cavities of the structure (Figure 6).

**TGA Study.** The TGA diagrams of **1** indicate three main steps of weight losses, the first of which corresponds to the loss of 11 interstitial water molecules. The weight loss begins at 60 °C and is completed at 185 °C. The observed weight loss of 17.0% is slightly larger than the calculated value (15.5%), indicating the presence of a small amount of surface water, which is also supported by the low temperature (60 °C) required for the release of water molecules and TGA curves. The second weight occurs in the range of 192–453 °C, which can be attributed to the decomposition of bipy as well as the carboxylate groups and release of four aqua ligands as well as the water molecules formed by the condensation of hydrogen phosphonate groups. The third step is further decomposition of the phosphonate ligands. The final product is a mixture of Co(PO<sub>3</sub>)<sub>2</sub> and CoP<sub>2</sub>O<sub>7</sub> in a 1:1 molar ratio based on X-ray powder diffraction. The total weight loss of 41.2% is much less than the calculated value (60.2%) due to the fact that the thermal decomposition process is not complete at 800 °C, as evidenced by the slope of the curves. TGA curves of compound **2** also indicate three main steps of weight losses. The first step is loss of nine interstitial water molecules from 64 to 190 °C, with the observed weight loss of 11.6% being in good agreement with the calculated value (12.3%). The second step in the temperature range of 200–494 °C corresponds to the loss of 4,4'-bipyridine and diphosphonate ligands. The third step, which overlaps with the second one, corresponds to further decomposition of organic groups. The final product is a mixture of Zn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and ZnO in a 2:1 molar ratio based on the X-ray powder diffraction patterns. The total weight loss of 48.9% is close to the calculated value (47.6%).

**X-ray Powder Diffraction Study.** Results of XRD powder diffraction for compound **2** indicate that the measurement XRD powder pattern (see Supporting

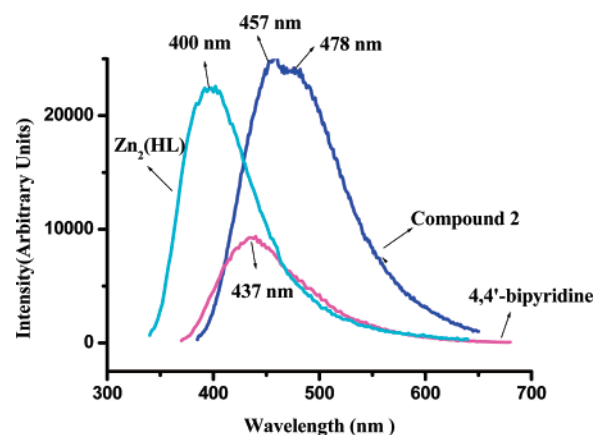


**Figure 6.** View of the structure of **2** down the *a*-axis. The zinc(II) polyhedra and phosphonate tetrahedra are shaded in green and pink, respectively. C and O atoms are drawn as black and red circles, respectively.

Information) is in good agreement with the one simulated from single-crystal data; hence, it is a pure phase. Furthermore, after heating compound **2** at 180 °C for 24 h, its XRD powder pattern collected is still close to the one taken before heating, indicating that the framework of compound **2** is retained after the removal of lattice water molecules. This is also supported by the IR spectrum recorded after heating compound **2** at 180 °C for 48 h, which shows that except for the disappearance of the broad absorption band associated with the water molecules its IR spectrum is similar to the one taken without heating. The XRD powder pattern for compound **1** was not measured since it was obtained by a diffusion method; hence, we assume that it is a monophasic which is supported by results from other measurements.

**Magnetic and Luminescent Properties.** Magnetic measurements in the temperature range of 2–300 K revealed that the moment at 300 K is  $\mu_{\text{eff}}$  of 9.46  $\mu_{\text{B}}$  per formula unit, which corresponds to three isolated high-spin Co(II) ( $d^7$ ) ions. As the temperature is decreased, the  $\mu_{\text{eff}}$  value decreases to 6.46  $\mu_{\text{B}}$ , indicating antiferromagnetic interactions between Co(II) ions within the trinuclear  $\text{Co}_3(\text{H}_2\text{L})_2$  unit (Co...Co 5.317(1) Å) as well as zero-field splitting effects.

The free carboxylate-diphosphonate  $\text{H}_3\text{L}$  ligand shows no emission in the visible region, whereas the 4,4'-bipy ligand shows a fluorescent emission band at  $\lambda_{\text{max}} = 437$  nm ( $\lambda_{\text{excitation}} = 350$  nm). The zinc(II) phosphonate,  $\text{Zn}_2(\text{HL})$ , shows a fluorescent emission band at  $\lambda_{\text{max}} = 400$  nm ( $\lambda_{\text{excitation}} = 330$  nm). Upon complexation of the two types of ligands with the zinc(II) ion, compound **2**



**Figure 7.** Comparison of the solid-state fluorescent spectrum of compound **2** (blue line) with those of 4,4'-bipyridine (pink line) and  $\text{Zn}_2(\text{HL})$  (green line).

(excited at 370 nm) displays a very strong blue fluorescent emission band in the solid state at  $\lambda_{\text{max}} = 457$  nm with a shoulder at 478 nm as shown in Figure 7. The lifetime of the fluorescence was measured to be  $\sim 6.0$  ns. The emission spectrum of **2** is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature, but rather is attributed to an intraligand emission state, as reported for other zinc(II) complexes with *N*-donor ligands.<sup>15</sup> The fluorescent intensity of compound **2** is more than

(15) (a) Wang, S. *Coord. Chem. Rev.* **2001**, 215, 79. (b) Ghedini, M.; Deda, M. L.; Aiello, I.; Grisolia, A. *J. Chem. Soc., Dalton Trans.* **2002**, 3406. (c) Yang, W.; Schmider, H.; Wu, Q.; Zhang, Y.-S.; Wang, S. *Inorg. Chem.* **2000**, 39, 2397.

2 times larger than that of the free bipy ligand which can be attributed to the coordination of the bipy ligands to zinc ions, which effectively increases the rigidity of the 4,4'-bipy ligand and reduces the loss of energy via radiationless decay of the intraligand emission excited state. The fluorescent spectrum of compound **2** also shows a significant enhancement in intensity and a large shift to higher wavelength in emission band compared with that of the zinc phosphonate,  $\text{Zn}_2(\text{HL})$ , indicating that the use of the second ligand (4,4'-bipy) may be an effective way to prepare blue light luminescent materials. Thus, results from our present investigation indicate that compound **2** is

capable of producing blue light in electro-luminescent devices.

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**Supporting Information Available:** X-ray crystallographic files for compounds **1** and **2** in CIF format; XRD powder patterns of compound **2** taken before and after removal of lattice water molecules (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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