Research Article

Structures and Spectroscopy Studies of Two M(II)-Phosphonate Coordination Polymers Based on Alkaline Earth Metals (M = Ba, Mg)

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The two examples of alkaline-earth M(II)-phosphonate coordination polymers, $[\text{Ba}_2(\text{L})(\text{H}_2\text{O})_9] \cdot 3\text{H}_2\text{O}$ (**1**) and $[\text{Mg}_{1.5}(\text{H}_2\text{O})_9] \cdot (\text{L}-\text{H}_2)_{1.5} \cdot 6\text{H}_2\text{O}$ (**2**) ($\text{H}_4\text{L} = \text{H}_2\text{O}_3\text{PCH}_2\text{N}(\text{C}_4\text{H}_8)\text{NCH}_2\text{PO}_3\text{H}_2$), *N,N'*-piperazinebis(methylenephosphonic acid), ($\text{L}-\text{H}_2 = \text{O}_3\text{PH}_2\text{CHN}(\text{C}_4\text{H}_8)\text{NHCH}_2\text{PO}_3$) have been hydrothermally synthesized and characterized by elemental analysis, FT-IR, PXRD, TG-DSC, and single-crystal X-ray diffraction. Compound **1** possesses a 2D inorganic-organic alternate arrangement layer structure built from 1D inorganic chains through the piperazine bridge, in which the ligand L^{4-} shows two types of coordination modes reported rarely at the same time. In **1**, both crystallographic distinct Ba(1) and Ba(2) ions adopt 8-coordination two caps and 9-coordination three caps triangular prism geometry structures, respectively. Compound **2** possesses a zero-dimensional mononuclear structure with two crystallographic distinct Mg(II) ions. Free metal cations $[\text{MgO}_6]_n^{2+}$ and uncoordinated anions $(\text{L}-\text{H}_2)_n^{2-}$ are joined together by static electric force. Results of photoluminescent measurement indicate three main emission bands centered at 300 nm, 378.5 nm, and 433 nm for **1** and 302 nm, 378 nm, and 434.5 nm for **2** ($\lambda_{\text{ex}} = 235$ nm), respectively. The high energy emissions could be derived from the intraligand $\pi^* \rightarrow n$ transition stations of H_4L (310 nm and 382 nm, $\lambda_{\text{ex}} = 235$ nm), while the low energy emission (>400 nm) of **1-2** may be due to the coordination effect with metal(II) ions.

1. Introduction

The design and synthesis of coordination polymers (CPs) based on phosphonates have always been the most important part of the work for the researchers. This is not only due to their complicated structural diversity but also their potential applications in optics, catalysis, magnetism, molecular sensing and separation, gas adsorption, and molecular recognition [1–4]. The choice of functionalized organic skeleton is the first important task in the construction of phosphonate CPs. The ligand H_4L , as a type of multidentate ligand (O- and/or N-donor), can be protonated and/or deprotonated to produce H_3L^- , H_2L^{2-} , HL^{3-} , and L^{4-} with versatile metal-binding and hydrogen-bonding capabilities. Most of its associated works have focused on the assembly of the transition metals, d^{10} -block metals, and lanthanides

metal-organic open frameworks [5–14]. The other important task is the choice of metal ion in the formation of CPs. Alkaline-earth metals are reasonably good candidates due to their variable stereochemical activity, flexible coordination environment, cheaper prices, and low toxicity. A series of alkaline-earth coordination compounds with novel structures and properties have been reported [15–18]. Despite many obvious advantages, some shortcomings of itself, such as the tendency of forming solvated species and their unpredictable coordination numbers, are keeping them weighted down. Therefore, our research has focused on the synthesis and photoluminescence of phosphonate CPs based on alkaline-earth metals. We hope to get further information on structures and properties of the alkaline-earth phosphonate CPs. The study on them with the ligand H_4L has rarely been reported up to now [8]. We previously reported the

SCHEME 1: The coordination modes of the ligand L^{4-} in **1**.

work of two compounds of 2D $[Pb_2(HL)] \cdot (NO_3) \cdot 2(H_2O)$ [13] and 3D $[Ba_3(btc)_2(H_2O)_4] \cdot 0.5H_2O$ [17] ($H_3btc = 1,3,5$ -benzenetricarboxylic acid) and that we have gained a great deal of skills and experiences from this work. Herein, we discuss the structures of the two alkaline-earth M(II) phosphonate CPs, namely, $[Ba_2(L)(H_2O)_9] \cdot 3H_2O$ (**1**) and $[Mg_{1.5}(H_2O)_9] \cdot (L-H_2)_{1.5} \cdot 6H_2O$ (**2**), along with their fluorescent properties.

2. Experimental

2.1. Materials and General Methods. N,N' -piperazine-bis(methylenephosphonic acid) (H_4L) was synthesized according to the literature's methods [19, 20]. All other chemical reagents were obtained from commercial sources and used without further purification. The elemental analysis was conducted on a Perkin-Elmer 2400 LC II elemental analyzer. IR spectrum was carried out on a Nicolet Impact 410 FI-IR spectrometer with KBr pellets in the 400 cm^{-1} – 4000 cm^{-1} region. UV-Vis spectrum was carried out on a UV-3600 UV-Vis-NIR spectrophotometer by SHIMADZU with $BaSO_4$ pellets in the 200 nm–800 nm region. Thermal analysis (TG-DSC) was performed on a STA 449 F3 Jupiter analyzer by NETZSCH Co., of Germany in N_2 environment at a heating rate of $10\text{ K} \cdot \text{min}^{-1}$. Emission and excitation spectra were recorded on a PerkinElmer LS 55 fluorescence spectrometer. The powder X-ray diffraction (PXRD) pattern was collected on an ARL X'TRA diffractometer using graphite-monochromated $Cu\ K\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$) in the angular range $2\theta = 4^\circ$ – 40° with stepping size of 0.02° and counting time of 4 s per step.

2.2. The Preparation of $[Ba_2(L)(H_2O)_9] \cdot 3H_2O$ **1.** A mixture of 0.53 g (2.0 mmol) $BaCl_2 \cdot 2H_2O$, 0.11 g (0.4 mmol) H_4L , 0.06 g (0.4 mmol) 4,4'-bipyridine, and 10.0 mL (555 mmol) deionized water was sealed in a 23 mL Teflon-lined stainless steel autoclave, and then heated at 160°C for 120 h. The crystals of (**1**) (colorless block shaped) were collected by

vacuum filtration, washed thoroughly with deionized water and dried in air (yield 81% based on barium atom). Elemental analysis, $C_6H_{36}Ba_2N_2O_{18}P_2$: C 9.54, H 4.86, N 3.81. Calcd.: C 9.46, H 4.73, N 3.68%. IR data (cm^{-1}): 3239 (m), 2960 (w), 2927 (w), 2848 (w), 2813 (w), 1673 (w), 1625 (w), 1459 (w), 1421 (w), 1375 (w), 1261 (w), 1213 (w), 1140 (w), 1099 (s), 1060 (s), 972 (s), 817 (m), 781 (m), 638 (w), 569 (m), 484 (m).

2.3. The Preparation of $[Mg_{1.5}(H_2O)_9] \cdot (L-H_2)_{1.5} \cdot 6H_2O$ **2.** A mixture of 0.096 g (0.8 mmol) $MgSO_4$, 0.22 g (0.8 mmol) H_4L , 0.01 g (0.04 mmol) 4,4'-bipyridine, and 10.0 mL (555 mmol) deionized water was sealed in a 23 mL Teflon-lined stainless steel autoclave, and then heated at 160°C for 168 h. The crystals of (**2**) (colorless block-shaped) were collected by vacuum filtration, washed thoroughly with deionized water, and dried in air (yield 75% based on magnesium atom). Elemental analysis, $C_6H_{34}N_2O_{16}P_2Mg$: C 15.11, H 7.13, N 5.87. Calcd.: C 15.04, H 7.06, N 5.79%. IR data (cm^{-1}): 3288 (m), 3233 (w), 3010 (m), 2981 (w), 2912 (w), 1687 (w), 1584 (w), 1456 (w), 1436 (w), 1386 (w), 1265 (w), 1211 (w), 1147 (s), 1076 (s), 1025 (s), 921 (m), 825 (w), 761 (m), 601 (m), 553 (m), 505 (m), 434 (w).

2.4. Crystallography. Single crystals of both **1** and **2** were mounted on a Siemens Smart CCD diffractometer equipped with graphite-monochromated $Mo\ K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 293 K using the ω - 2θ scan technique. Their structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXL-97. All nonhydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms were either located by difference Fourier maps or calculated geometrically and their contributions in structural factor calculations were included. The crystallographic data and structural refinements are summarized in Table 1. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) of **1-2** are listed in Table S1 (see supplementary material available online at <http://dx.doi.org/10.1155/2013/378379>). The hydrogen bond lengths ($\text{\AA}$) and angles ($^\circ$) of **1-2** are given in Table S2 (see Supplementary material). CCDC nos. 852680 and 852681 contain the supplementary crystallographic data for this paper, respectively. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

3.1. Description of Structures. The asymmetric unit of **1** (Figure 1(a)) contains two crystallographically independent $Ba(II)$ ions, one L^{4-} ligand, nine coordinated water molecules, and three lattice water molecules. $Ba(1)$ ion is 8 coordinated with two phosphonate oxygen atoms (μ_2 -O(1) and μ_2 -O(4)) and six coordinated water molecules (μ_2 -O(7), O(8), μ_2 -O(9), O(10), μ_2 -O(11), and O(12)) to give rise to its two caps triangular prism coordination geometry. $Ba(2)$ ion shows the layout of 9-coordination with three caps triangular prism geometry, surrounded by three phosphonate oxygen atoms (μ_2 -O(1), μ_2 -O(4), and O(2)) and six water oxygen atoms (μ_2 -O(7), O(13), O(14), O(15),

FIGURE 1: (a) Molecular structure of **1** showing the atom-labeling scheme (50% thermal ellipsoids). (b) 2-D layer built from inorganic chains and organic linker in the *bc* plane (left), and the 3-D supramolecular network of **1** stacked by hydrogen bonds along the *y*-axis (right) (Green: Ba, Pink: P, Grey: C, Red: O, Blue: N, White: H).

μ_2 -O(9A), and μ_2 -O(11A)). Ba–O bond lengths are in the range of 2.634(3)–3.172(4) Å, which are in consonance with those of Ba(II) compounds [17, 18]. There are two types of coordination patterns for the ligand L^{4-} in **1** (Scheme 1). One is the form of hexadentate ligand. Each phosphonate group of the ligand L^{4-} , as both a bi- and monodentate ligand, uses two of three oxygen atoms to coordinate with two Ba(II) atoms in $\mu_2:\eta^2\eta^1\eta^0$ mode. This mode has only been found in the compound $\text{Nd}_2(\text{H}_2\text{L})_3 \cdot 9\text{H}_2\text{O}$ reported by Groves et al. [6]. It is similar to those of the reported compounds $\text{KCeL}_4 \cdot 4\text{H}_2\text{O}$ and $\text{La}_2\text{L} \cdot \text{H}_2\text{L} \cdot 4.5\text{H}_2\text{O}$ [7]. Most of the reported cases act as monodentate donors to bridge with metal centers [8–11]. The other is only a bidentate ligand, in which one of three oxygen atoms is in service to bridge with two Ba(II) atoms in $\mu_2:\eta^2\eta^0\eta^0$ mode. The pure coordination mode has never been observed in all the H_4L -compounds; however, the complicated coordination modes containing this manner have been reported for a phosphonate group [5]. The uncoordinated phosphonate oxygen atoms and nine coordinated water oxygen atoms are involved in

the formation of hydrogen bonds. The highdimensional materials could be developed harmoniously with the multidirectional coordination strategy adopted. Regarding it as the secondary building unit (SBU), the combinatorial polyhedra $[\text{Ba}(1)\text{Ba}(2)\text{O}_{14}]_n$, made of a two caps triangular prism $[\text{Ba}(1)\text{O}_8]$ and a three caps triangular prism $[\text{Ba}(2)\text{O}_9]$ via planar-shared three oxygen atoms (O(1), O(4), and O(7)), are connected with each other by edge-shared two oxygen atoms (O(9), O(11)) to result in a 1D inorganic single chain viewed along the *b*-axis. Under the action of piperazine moiety (N(1)) of H_4L , a 1D ladder-chain is born out from the single chain. Then the ladder-chains further expand to a 2D layer with inorganic-organic alternative arrangement through bridging piperazine moiety (N(2)) in the *bc* plane (Figure 1(b) left). Layer of this type is analogous to those in 3D metal- H_4L frameworks such as $[\text{Sr}(\text{H}_2\text{L})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ [8] and $[\text{M}(\text{H}_2\text{L})] \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}$) [14]. All the lattice water molecules are located in the inter-layers. There are many complicated hydrogen bonds in the structure, in which hydrogen bonds formed among the lattice water molecules. The hydrogen bonds play an

FIGURE 2: (a) ORTEP view of **2** showing the atom-labeling scheme (30% thermal ellipsoids). (b) The 2-D layer in the *bc* plane and the 3-D supramolecular network of **2** stacked by hydrogen bonds. (Green: Mg, Pink: P, Grey: C, Red: O, Blue: N, White: H).

FIGURE 3: FT-IR spectra of **1-2** and the ligand H_4L .

important role in the construction of the 3D supramolecular network (Figure 1(b) right). They are $O(3W) \cdots O(1W)$ ($3.006(6) \text{ \AA}$, 174.1°), $O(1W) \cdots O(3W)$ ($2.796(6) \text{ \AA}$, 161.8°), $O(2W) \cdots O(5)$ ($2.802(5) \text{ \AA}$, 169.4°), $O(2W) \cdots O(15)$ ($2.945(6) \text{ \AA}$, 170.8°), $O(8) \cdots O(1W)$ ($2.788(5) \text{ \AA}$, 162.9°), $O(12) \cdots O(3W)$ ($2.792(6) \text{ \AA}$, 153.0°) and $O(14) \cdots O(2W)$ ($2.795(6) \text{ \AA}$, 146.7°), respectively. The weak intermolecular interactions not only take part in the construction of a 3-D supramolecular network but also stabilize the structure. Accordingly, existence of the molecular weak interactions might bring about the peculiar properties for compounds.

Single-crystal X-ray diffraction analysis reveals that compound **2** possesses a zero-dimensional mononuclear structure, in which the asymmetric unit (Figure 2(a)) contains one and a half crystallographically independent metal cations $Mg(II)$, one and a half ligand anions $(L-H_2)^{2-}$, and nine aqua ligands along with six lattice water molecules. $Mg(1)$ centre adopts octahedral configuration $[MgO_6]^{2+}$ to coordinate with six oxygen atoms from six lattice water molecules, so is $Mg(2)$ centre. $Mg(II)-O$ bond lengths fall in a narrow range of $2.0321(2) \sim 2.0996(2) \text{ \AA}$, basically close to those of $Mg(II)$ compounds [18]. The *cis*- and *trans*-angles of $O-Mg(II)-O$ are $84.92(7)^\circ \sim 95.80(9)^\circ$ and $170.86(9)^\circ \sim 178.33(8)^\circ$, respectively, which slightly deviate from those of the ideal octahedron. The ligand $(L-H_2)^{2-}$ is a trend for loneliness as a result of $Mg(II)$ ions surrounded by water molecules. In consideration of extremely strong hydration of the Mg^{2+} ion, anhydrous $MgSO_4$ is used during the synthesis. Although different kinds of solvent have been used in the synthesis process, the compound **2** can only be obtained in aqueous solution under the same conditions. A systemic research on looking for solvents that benefit the crystal growth will continue to do so in future. For the sake of charge balance, both nitrogen atoms ($N(1)$, $N(2)$) of the ligand L^{4-} are protonated in **2**. All the phosphonate oxygen atoms are deprotonated and participate in the formation of hydrogen bonds. Both the octahedral cation $[MgO_6]^{2+}$ and the ligand anion $(L-H_2)^{2-}$ are alternately arranged and are connected with each other by hydrogen bonds, $O(13) \cdots O(2)$ ($2.749(2) \text{ \AA}$, 166.4°), $O(13) \cdots O(5W)$ ($2.772(3) \text{ \AA}$, 163.3°),

FIGURE 4: Experimental and simulated powder X-ray diffraction patterns of **1** (a) and **2** (b).

FIGURE 5: The TGA-DSC curves of **1** (a) and **2** (b).

FIGURE 6: The solid state UV-Vis spectra (a) and fluorescent spectra (b) of the two compounds and the ligand H_4L under the excitation of 235 nm. Note: the fluorescent intensity decay for H_4L is 1% T attenuation and those of the other two are normal.

TABLE 1: Crystallographic data for 1-2.

	1	2
Empirical formula	C ₆ H ₃₆ Ba ₂ N ₂ O ₁₈ P ₂	C ₉ H ₅₁ N ₃ O ₂₄ P ₃ Mg _{1.5}
Formula weight	760.97	714.9
Temperature (K)	296(2) K	296(2) K
Wavelength (Å)	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	Pī	Pī
Unit cell dimensions		
<i>a</i> (Å)	6.9479(8)	5.7894(1)
<i>b</i> (Å)	8.6291(1)	11.803(3)
<i>c</i> (Å)	21.850(2)	22.685(5)
α (°)	82.7950(1)	76.850(2)
β (°)	81.3570(1)	89.656(2)
γ (°)	68.7620(1)	81.516(2)
Volume (Å ³)	1203.6(2)	1492.3(6)
<i>Z</i>	2	3
Calculated density (g/cm ³)	2.100	1.591
Absorption coefficient (mm ⁻¹)	3.462	0.329
<i>F</i> (000)	744	762
Theta range for data collection (°)	0.95°–24.99°	0.92°–25.00°
	–8 ≤ <i>h</i> ≤ 8	–6 ≤ <i>h</i> ≤ 6
Limiting indices	–9 ≤ <i>k</i> ≤ 10	–14 ≤ <i>k</i> ≤ 13
	–25 ≤ <i>l</i> ≤ 25	–26 ≤ <i>l</i> ≤ 26
Unique (<i>R</i> (int))	8512/4182 (<i>R</i> (int) = 0.0258)	10567/5248 (<i>R</i> (int) = 0.0226)
Maximum and minimum transmission	0.354 and 0.260	0.952 and 0.924
Data/restraints/parameters	4182/0/271	5248/0/367
Goodness-of-fit on <i>F</i> ²	1.137	1.059
Final <i>R</i> indices (<i>I</i> > 2σ (<i>I</i>))	<i>R</i> ₁ = 0.0267, <i>wR</i> ₂ = 0.0725	<i>R</i> ₁ = 0.0379, <i>wR</i> ₂ = 0.1106
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0310, <i>wR</i> ₂ = 0.0854	<i>R</i> ₁ = 0.0438, <i>wR</i> ₂ = 0.1149
Largest different peak and hole (e · Å ⁻³)	0.598 and –0.659 e · Å ⁻³	0.445 and –0.358 e · Å ⁻³

Note: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2 \}^{1/2}$.

O(17)···O(3W) (2.694(3) Å, 167.7°), O(2W)···O(1) (2.693(2) Å, 162.0°), O(3W)···O(7) (2.765(2) Å, 155.2°), O(6W)···O(1) (2.776(3) Å, 177.8°), and O5W···O(3) (2.724(2) Å, 166.7°), to build a 1-D fishbone chain along the *c*-axis. The above hydrogen bonds are formed among the phosphonate oxygen atoms (O(1), O(2), O(3), O(7), O(8)) and the water oxygen atoms (O(13), O(15), O(17), O(2W), O(3W), O(5W), O(6W)). A great number of the adjacent 1-D fishbone chains further spread out through the hydrogen bond interactions in the *bc* plane to give rise to a 2-D supramolecular layer (Figure 2(b) left), in which the lattice water molecules are situated at interlayers. The complicated hydrogen bonds carry 2-D supramolecular layer forward into a 3-D supramolecular network unceasingly (Figure 2(b) right). The hydrogen bonds should be contributed enormously to the construction of the supramolecular structure and some of the most important potential application performance.

3.2. FTIR Spectroscopy. The IR spectra for the title compounds and the ligand H₄L were recorded in the region from 4000 to 400 cm⁻¹ (Figure 3). The broad bands at 3239 cm⁻¹ for **1** and 3288 cm⁻¹, 3233 cm⁻¹ for **2** are due to the H–OH stretching vibration of the water molecule, while the band at 3428 cm⁻¹ for the ligand H₄L is attributed to P–OH stretching vibration. The weak band in **2** appeared at 3010 cm⁻¹ can be due to N–H group stretching; however, in **1** and H₄L it is absent as these contain no protonated nitrogen atoms. The bands, at 2960 cm⁻¹, 2927 cm⁻¹, 2848 cm⁻¹, and 2813 cm⁻¹ for **1**, 2981 cm⁻¹, 2912 cm⁻¹ for **2**, and 3002 cm⁻¹, 2941 cm⁻¹ for H₄L, can be attributed to the asymmetric and symmetric C–H stretching vibrations of the –CH₂– groups, respectively. The bands in the region of 2700–2200 cm⁻¹ are ν(PO–H) for H₄L, which are characteristic of hydrogen phosphonate groups. However, there are no peaks in this region for **1-2**, which means the change of configuration of H₄L in **1-2**. The peaks at 1673 cm⁻¹ for **1**, 1687 cm⁻¹ for **2**, and 1689 cm⁻¹

for H_4L may be due to an overtone or combination band of the $C-PO_3$ stretching vibrations, slightly blue-shifting than that of H_4L . The weak bands at 1625 cm^{-1} for **1** and 1584 cm^{-1} for **2** are due to the $\delta(H-OH)$ vibration, but there is missing data in this region for H_4L . The corresponding $\delta(-CH_2-)$ deformation bands appear at 1459 cm^{-1} , 1421 cm^{-1} , and 1375 cm^{-1} for **1**, 1456 cm^{-1} , 1436 cm^{-1} , and 1386 cm^{-1} for **2**, and 1448 cm^{-1} , 1440 cm^{-1} , and 1382 cm^{-1} for H_4L . The weak bands at 1261 cm^{-1} for **1**, 1265 cm^{-1} for **2** and 1267 cm^{-1} for H_4L can be assigned to the $\omega(-CH_2-)$ vibration. The $P=O$ stretching vibrations are observed at 1213 cm^{-1} , 1140 cm^{-1} for **1**, 1211 cm^{-1} , 1147 cm^{-1} for **2** and 1213 cm^{-1} , 1160 cm^{-1} for H_4L . The classic strong $-PO_3$ vibrations (typically $1200-900\text{ cm}^{-1}$) [21] are at 1099 (vs), 1060 (vs), and 972 cm^{-1} (vs) for **1**, 1076 (vs), 1025 (s), and 921 cm^{-1} (ms) for **2**, and 1103 (s), 1031 (s) and 923 cm^{-1} (s) for H_4L . All of these peaks can be assigned to the stretching vibrations associated with the $N-C$ bonds and the CPO_3 tetrahedra. Compared with H_4L , the changes of the IR spectra in the $\nu(PO)$ region show the coordination of oxygen atoms in phosphonic group with barium atoms in **1**. The broad band at 923 cm^{-1} $\nu(P-OH)$ disappeared, but a new sharp band were observed at 971 cm^{-1} that can be attributed to $\nu(P-O^-)$ for **1**. In addition, the intensity differences and shifts of peaks from infrared spectra can bring us to the conclusion that the surrounding environment of the H_4L unit has been modified when coordinating with metal ions. Additional middle strong bands at low energy are found at 569 cm^{-1} and 484 cm^{-1} for **1**, 553 cm^{-1} and 505 cm^{-1} for **2**, and 572 cm^{-1} and 509 cm^{-1} for H_4L . These bands are probably due to bending vibrations of the tetrahedral O_3PC groups and $Ba-O$ (for **1**) stretching vibrations.

3.3. PXRD and Thermal Characteristics. The powder XRD patterns of **1-2** indicate that as-synthesized products are the new materials, and the patterns are entirely consistent with the simulated those from the single-crystal X-ray diffractions (Figure 4).

TG-DSC measures were conducted to examine the stabilities of two compounds (Figure 5). The combined TG-DSC analysis of **1** shows three major weight losses in N_2 atmosphere. The first and the second mass losses of 28.35% from 50°C to 260°C , with an endothermic peak centered at 94°C , correspond to the losses of three lattice water molecules and nine aqua ligands (calc. 28.38%). The third step of about 12.63% (calc. 12.69%), in the range of $400-640^\circ\text{C}$, can be assigned to the pyrolysis of the organic moieties of the ligand H_4L . Two exothermic peaks centered at 463°C and 555°C indicate structural changes. From 640°C , thermal decomposition is still continuing, and the final residue is mainly $Ba_2P_2O_6$ at 1000°C . The TGA curve of **2** consists of four weight losses in N_2 atmosphere. The first loss of 15.19% with an endothermic peak centered at 94°C starts from 55°C and completes at about 110°C , owing to the release of four lattice water molecules (calc. 15.11%). The second weight loss of 22.56%, from 110°C to 350°C , can be attributed to nine coordinated water molecules (calc. 22.66%). The third

step from 350°C is the process of the decomposition of organic group until 820°C , corresponding two exothermic peaks centered at 367°C and 732°C . The last step with a small exothermic peak centered at 950°C covers a temperature range of $820^\circ\text{C}-1000^\circ\text{C}$, which corresponds to the continuous pyrolysis of the organic group of the ligand H_4L . The final product is MgP_2O_6 and MgO (1 : 1.3). The total weight losses of 67.27% agree with the calculated value (67.13%).

3.4. Photophysical Properties. The solid-state UV-Vis spectra of both **1-2** and H_4L are shown in Figure 6(a). The three absorption bands observed at 213 nm, 229 nm and 296 nm for the free ligand H_4L , 228 nm, 272 nm, and 298 nm for **1** and 227 nm, 277 nm, and 304 nm for **2**, respectively. These bands may be the electron-releasing character of the N -substituent attached to the $-PO_3$ group and caused by the $n \rightarrow \pi^*$ transition from the nitrogen atom to the $P=O$ group. The absorption bands of **1-2** can manifest a little red shift in the UV spectra, compared with those of the free ligand H_4L . This may be that the total energy of system decreases after the coordination with $Ba(II)$ ions for **1** and after the formation of a salt with $Mg(II)$ ions for **2** along with hydrogen bonds.

Photoluminescent properties of alkaline earth metal complexes are not well studied as compared with those of transition metal and rare earth complexes [22]. The solid-state fluorescent properties of both **1-2** and H_4L were investigated at room temperature (Figure 6(b)). The free ligand H_4L emits two strong fluorescent bands (1%T attenuation) centered at 310 and 382 nm under the excitation of 235 nm, which derived from the photo-induced electron transfer (PET). The compound **1** with $Ba(II)$ ion displays two main fluorescent bands centred at 378.5 and 433 nm with a shoulder peak at 300 nm, and the compound **2** with $Mg(II)$ ion also exhibits two strong fluorescent bands centred at 378 and 434.5 nm with a weak peak at 302 nm under the excitation of 235 nm. These fluorescent bands could come from the intraligand $\pi^* \rightarrow n$ transition state of H_4L . The emission intensity of H_4L is 1%T attenuation in the test and those of the other two are normal. Compared with those of the free ligand H_4L , the high energy emission bands ($<400\text{ nm}$) of **1-2** are blue-shifted slightly and show significant decreases in intensity. Moreover, the fluorescent intensity of **2** is less than that of **1**. They are probably related to $O-H\cdots N$ hydrogen bond interactions, the protonation of nitrogen atoms of H_4L as well as specific coordination environment around metal ions. The low energy emission bands ($>400\text{ nm}$) of **1-2** are most likely because of the coordination effect with metal (II) ions [23, 24]. Investigation and consideration of N -heterocyclic systems in future may yield effective path for the preparation of luminescent materials.

4. Conclusions

We have firstly reported the preparation of two novel alkaline-earth phosphonate CPs, $[Ba_2(L)(H_2O)_9]\cdot 3H_2O$ (**1**) and $[Mg_{1.5}(H_2O)_9]\cdot (L-H_2)_{1.5}\cdot 6H_2O$ (**2**), by using a hydrothermal technique. Hydrogen bonds and static electric forces have typically led to the 3-D supramolecular networks.

Results of photoluminescence measurement indicate that the two compounds display three emission peaks, derived from the organic ligand and coordination effect. There are slight blueshift and the significant reduction in intensity in the high energy region for **1-2** as compared with the free ligand H_4L . The behavior may be attributed to specific coordination environment around metal ions and lots of hydrogen bond interactions involving nitrogen atoms in the structure. So the work on the application of optical functional materials including alkaline-earth metals and d^{10} -metals is now in progress.

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