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# Syntheses, Crystal Structures, and Luminescent Properties of Novel Layered Lanthanide Sulfonate–Phosphonates

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Hydrothermal reactions of lanthanide metal salts with $MeN(CH_2CO_2H)(CH_2PO_3H_2)$ ($H_3L$) and 5-sulfoisophthalic acid monosodium salt ($NaH_2BTS$) lead to four isomorphous lanthanide carboxylate–phosphonate–sulfonate hybrids, namely, $Ln(H_2L)(HBTS)(H_2O)_2\cdot H_2O$ (Ln = La (**1**), Pr (**2**), Nd (**3**), Gd (**4**)). Their structures have been established by X-ray single-crystal diffraction. The interconnection of the lanthanide(III) ions by carboxylate–phosphonate ligands results in a 1D double chain; these double chains are further bridged by bidentate bridging carboxylate–sulfonate ligands to form a ⟨011⟩ layer. The luminescent properties of compounds **3** and **4** have also been studied.

## Introduction

During the last two decades great research efforts have been devoted to the synthesis and designing of metal phosphonates with novel open-framework or microporous structures due to their potential applications in electrooptics, ion-exchange, catalysis, and sensors.[1] The strategy of attaching functional groups such as crown ether, amine, hydroxyl, and carboxylate groups to the phosphonic acid has proven to be effective for the isolation of a variety of metal phosphonates with open-framework and microporous structures.[2−7] Results from ours and other groups indicate that amino−carboxylic−phosphonic acids are also capable of forming open frameworks.[8] Most of structural studies on metal phosphonates have been focused on first row transition metals as well as main group metals such as Al(III), Ga(III), and Pb(II);[1−8] reports on lanthanide phosphonates are rather limited, and some of them are based on X-ray powder diffraction.[9−13] Lanthanide phosphonates normally have low solubil-

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ity in water and other organic solvents; hence, it is rendered difficult to obtain single crystals suitable for X-ray structural analysis. To improve the solubility and crystallinity of lanthanide phosphonates, additional function groups such as crown ether, carboxylate, hydroxyl, and amine groups have been attached to the phosphonic acid ligand.[9−13] A series of lanthanide diphosphonates with a 3D pillared-layer structure were isolated by the Ferey group.[9] Several lanthanide phosphonates with a crown ether or calixarene moiety have been reported by Clearfield, Bligh, Lukes, and Lin et al.[10] Their structures feature a chelating mononuclear unit or a layer architecture.[10] A series of one-dimensional lanthanide diphosphonates containing a hydroxyl group were reported.[11] A few 2D or 3D lanthanide phosphonates with an additional carboxylate group or amino acid moiety were obtained.[12] Lanthanide compounds with phosphonic acid attached by Ph−, $PhCH_2$−, or $NH_2CH_2CH_2$− group were obtained by the Clearfield and Legendziewicz groups.[13] The elucidation of the structures of lanthanide phosphonates is important since these compounds may exhibit useful luminescent properties.[14] Our present work is based on the hypothesis that introducing a second ligand such as 1,3,5-benzenetricarboxylic acid ($H_3BTC$) or 5-sulfoisophthalic acid ($H_3BTS$) whose lanthanide compounds have good solubility and very good crystallinity into the lanthanide−phosphonate system will result in novel lanthanide phosphonate hybrids with better solubility and crystallinity; this point has been realized by our recent works on lead(II) hybrids of di- or triphosphonic acid and 1,3,5-benzenetricarboxylic acid ($H_3BTC$) or 5-sulfoisophthalic acid ($H_3BTS$).[8] As an expansion of our work to lanthanide phosphonates, we selected one carboxylic−phosphonic acid, *N*-(phosphonomethyl)-*N*-methylglycine, $MeN(CH_2CO_2H)(CH_2PO_3H_2)$ ($H_3L$), and 5-sulfoisophthalic acid monosodium salt ($NaH_2BTS$) as the second metal linker. Hydrothermal reactions of the above phosphonate ligand with lanthanide(III) chloride (for compounds **1**, **2**, and **4**) or nitrate (for compound **3**) and 5-sulfoisophthalic acid monosodium salt ($NaH_2BTS$) afforded four novel lanthanide(III) phosphonate−sulfonate hybrids, $Ln(H_2L)(HBTS)(H_2O)_2{\cdot}H_2O$ (Ln = La (**1**), Pr (**2**), Nd (**3**), Gd (**4**)), with a layer architecture. Herein we report their syntheses, crystal structures, and characterizations.

## Experimental Section

**Materials and Instrumentation.** *N*-(Phosphonomethyl)-*N*-methylglycine, $MeN(CH_2CO_2H)(CH_2PO_3H_2)$ ($H_3L$), was prepared by a Mannich type reaction according to procedures described previously.[8a] All other 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 $cm^{-1}$. Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer.

**Preparation of $Ln(H_2L)(HBTS)(H_2O)_2{\cdot}H_2O$ (Ln = La (1), Pr (2), Gd (4)).** A mixture of $LnCl_3{\cdot}6H_2O$ (0.5 mmol), $H_3L$ (0.5 mmol), and $NaH_2BTS$ (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 120 °C for 5 days. Crystals of **1** (colorless), **2** (green), and **4** (colorless) were collected in ca. 48% (**1**), 45% (**2**), and 36% (**4**) yield (based on lanthanide), respectively. The initial and final pH values of this reaction media are close to 3.0 and 2.5, respectively. Anal. Calcd for **1**: C, 23.28; H, 3.09; N, 2.26. Found: C, 23.16; H, 3.24; N, 2.38. Calcd for **2:** C, 23.20; H, 3.08; N, 2.25. Found: C, 23.14; H, 3.24; N, 2.36. Calcd for **4**: C, 22.61; H, 3.00; N, 2.20. Found: C, 22.59; H, 3.18; N, 2.28. IR (KBr, $cm^{-1}$) for **1:** 3498 s, 3369 s, 3085 w, 2953 w, 1670 s, 1615 vs, 1444 m, 1423 w, 1406 w, 1325 w, 1291 m, 1242 m, 1178 s, 1153 s, 1106 m, 1044 s, 905 w, 831 w, 763 m, 732 w, 689 w, 620 m, 568 m, 478 w. IR (KBr, $cm^{-1}$) for **2:** 3492 s, 3367 s, 3085 w, 2952 w, 1700 m, 1616 vs, 1445 m, 1422 w, 1402 w, 1326 w, 1292 m, 1242 m, 1178 s, 1151 s, 1105 m, 1045 s, 905 w, 831 w, 795 w, 763 m, 732 w, 689 m, 668 w, 621 m, 569 m, 545 w. IR (KBr, $cm^{-1}$) for **4:** 3492 m, 3362 m, 2953 w, 1686 vs, 1612 w, 1580 w, 1453 s, 1430 m, 1324 s, 1295 s, 1105 vs, 1026 s, 995 s, 951 w, 908 w, 763 w, 719 m, 574 m.

**Preparation of $Nd(H_2L)(HBTS)(H_2O)_2{\cdot}H_2O$ (3).** The method the synthesis of the Nd(III) compound is similar to those for three other compounds; nitrate salt was used instead of the chloride. A mixture of $Nd(NO_3)_3{\cdot}6H_2O$ (0.5 mmol), $H_3L$ (1.0 mmol), and $NaH_2BTS$ (1.0 mmol) in 10 mL of distilled water was sealed into a bomb equipped with a Teflon liner (25 mL) and then heated at 130 °C for 5 days. The initial and final pH values of this reaction media are 2.0 and 1.5, respectively. Purple crystals of **3** were collected in ca. 46% yield (based on neodymium). IR (KBr, $cm^{-1}$): 3498 s, 3369 s, 3085 w, 2953 w, 1670 s, 1615 vs, 1444 m, 1423 m, 1403 m, 1292 m, 1241 m, 1201 w, 1148 s, 1070 w, 1032 s, 947 w, 915 w, 820 w, 733 m, 634 m, 603 m, 573 w, 484 w. Anal. Calcd for **3**, $C_{12}H_{18}NO_{15}PSNd$: C, 23.08; H, 3.07; N, 2.24. Found: C, 22.94.27; H, 3.22; N, 2.32.

**Single-Crystal Structure Determination.** Single crystals of compounds **1**−**4** were mounted on a Siemens Smart CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ 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 the $\psi$-scan technique. All four structures were solved by the direct methods and refined by full-matrix least-squares fitting on $F^2$ by SHELX-97.[15] 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**−**4** are summarized in Table 1. Important bond distances and angles are listed in Tables 2. More details on the crystallographic studies as well as atomic displacement parameters are given as the Supporting Information.

## Results and Discussion

Compounds **1**−**4** are isomorphous and feature a complicated 2D layered structure. They are the first examples of

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**Table 1.** Crystal Data and Structure Refinements for Compounds **1**−**4**

| param | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| formula | $C_{12}H_{19}NLaO_{15}PS$ | $C_{12}H_{19}NPrO_{15}PS$ | $C_{12}H_{19}NNdO_{15}PS$ | $C_{12}H_{19}NGdO_{15}PS$ |
| fw | 619.22 | 621.22 | 624.55 | 637.56 |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$/Å | 7.6900(4) | 7.66690(10) | 7.6580(7) | 7.6465(3) |
| $b$/Å | 11.4268(5) | 11.4004(2) | 11.3929(11) | 11.3948(3) |
| $c$/Å | 12.0539(6) | 12.012 | 11.9910(11) | 11.9596(3) |
| $\alpha$/deg | 73.4210(10) | 73.3390(10) | 73.251(2) | 73.2740(10) |
| $\beta$/deg | 81.1660(10) | 81.2610(10) | 81.241(2) | 81.3400(10) |
| $\gamma$/deg | 76.8920(10) | 77.0600(10) | 77.1660(10) | 77.8140(10) |
| $V$, Å$^3$ | 984.23(8) | 975.92(2) | 972.39(16) | 970.97(5) |
| Z | 2 | 2 | 2 | 2 |
| $D_{calcd}$, g·cm$^{-3}$ | 2.089 | 2.114 | 2.133 | 2.181 |
| $\mu$, mm$^{-1}$ | 2.438 | 2.766 | 2.941 | 3.687 |
| GOF on $F^2$ | 1.123 | 1.114 | 1.130 | 1.084 |
| R1, wR2 ($I > 2\sigma(I)$)[a] | 0.0329/0.0735 | 0.0565/0.1335 | 0.0544/0.1264 | 0.0410/0.1070 |
| R1, wR2 (all data) | 0.0371/0.0770 | 0.0652/0.1421 | 0.0690/0.1380 | 0.0435/0.1107 |

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

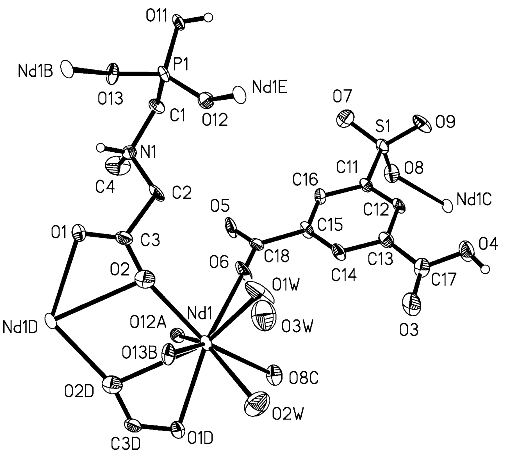

**Figure 1.** ORTEP representation of the asymmetric unit of compound **3**. Thermal ellipsoids are drawn at 50% probability. Symmetry codes for the generated atoms: (A) $x + 1, y, z$; (B) $-x, -y + 1, -z + 1$; (C) $-x + 1, -y, -z + 2$; (D) $-x + 1, -y + 1, -z + 1$; (E) $x - 1, y, z$.

structurally characterized lanthanide sulfonate−phosphonates. Only the structure of compound **3** will be described in detail as an example. As shown in Figure 1, the asymmetric unit of compound **3** is composed of one neodymium(III) ion, one $H_2L$ anion, one HBTS anion, two aqua ligands, and one lattice water molecule. The Nd(III) ion is 9-coordinated by three carboxylate oxygens from two $H_2L$ anions, two phosphonate oxygens from two other $H_2L$ anions, one carboxylate oxygen atom from a $HBTS^{2-}$ anion, and one sulfonate oxygen atom from another $HBTS^{2-}$ anion as well as two aqua ligands. The Nd−O distances range from 2.376(6) to 2.826(7) Å, which are comparable to those reported for other lanthanide(III) phosphonates.[9−13] The $H_2L$ anion is pentadentate; it chelates with one Nd(III) ion bidentately by using its carboxylate group and bridges with four other Nd(III) centers. O2 of the carboxylate group is a $\mu_2$-metal linker. Two of three phosphonate oxygens are unidentate, whereas the remaining one (O11) is protonated and noncoordinated. The amine group is also protonated and noncoordinated. This type of coordination mode is different from that reported in its zinc cluster cage compound where the phosphonate ligand is deprotonated completely and hexadentate (chelates with a zinc tridentately and bridges with three other zinc).[8a] The $HBTS^{2-}$ anion is bidentate and bridges with two Nd(III) ions. The sulfonate group is unidentate (O8). One carboxylate group is also unidentate (O6). The second carboxylate group (O3−C17−O4) is protonated (O4) and noncoordinated. This type of coordination mode is different from that in its lead(II) hybrid where the completely deprotonated BTS ligand is pentadentate and bridges with three metal centers.[8e] The BTS anion in its two-dimensional lanthanide coordination polymers is also pentadentate and totally deprotonated; each carboxylate group chelates with a lanthanide ion and the sulfonate group is unidenate.[16] On the basis of the requirement of charge balance as well as P−O, C−O, and S−O distances, the $H_2L$ anion is −1 and the HBTS anion is −2 in charge.

The interconnection of Nd(III) atom by the carboxylate phosphonate $H_2L$ ligands resulted in a $Nd_2(HL)_2$ unit, and such a neighboring unit is bridged by the carboxylate groups to form a 1D double chain along the $a$-axis (Figure 2a). These double chains are cross-linked by bridging HBTS anions to form a ⟨011⟩ lanthanide phosphonate−sulfonate hybrid layer (Figures 2b and 3). The lattice water molecule O3W is hydrogen bonded to the aqua ligand (O1w) with O···O separation of 2.756(12) Å and the amine group with N···O separation 2.879(11) Å (symmetry code: $-x, 1 - y, 1 - z$). The noncoordinated phosphonate oxygen (O11) forms a hydrogen bond with carboxylate O4 (symmetry code: $x + 1, y - 1, z$) and O5 (symmetry code: $x - 1, y, z$) of HBTS anion, and the O···O separations are 2.623(9) and 2.495(9) Å, respectively.

The other three compounds are isostructural with the Nd(III) compound. It is observed that most of the Ln−O bond lengths are decreased from La to Gd due to the so-called "lanthanide contraction" (Table 2); the Ln−O2 (symmetry code: $1 - x, 1 - y, 1 - z$) bond is significantly longer (and much weaker) than those of the remaining Ln−O bonds, and this bond is significantly elongated when Ln = Gd. This indicates that the coordination number tends to be 8 for heavier lanthanide(III) ions. It is noticed that the cell volume contracts about 1.35% when the lanthanide ion changes from La to Gd.

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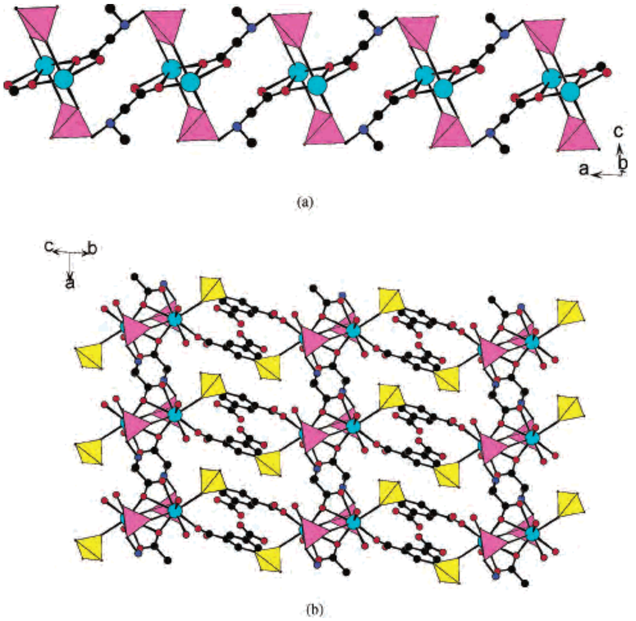

**Figure 2.** (a). A 1D double chain of Nd(III) carboxylate phosphonate along the *a*-axis. (b). A ⟨011⟩ layer of Nd(III) phosphonate−sulfonate in compound **3**. The phosphonate and sulfonate tetrahedra are shaded in pink and yellow, respectively. Nd, N, C, and O atoms are drawn as cyan, blue, black, and red circles, respectively.

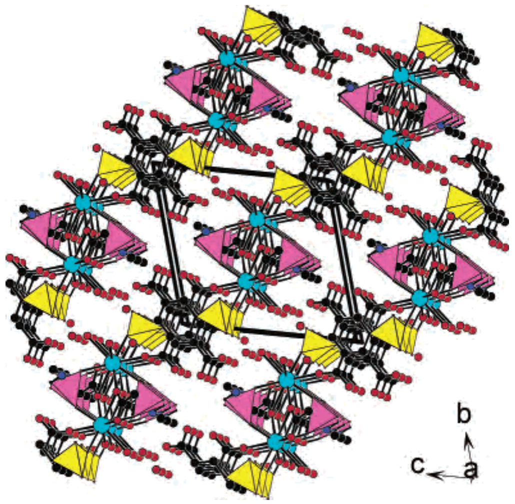

**Figure 3.** View of the structure of **3** down the *a*-axis. The phosphonate and sulfonate tetrahedra are shaded in pink and yellow, respectively. Nd, N, C, and O atoms are drawn as cyan, blue, black, and red circles, respectively.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Compounds **1**−**4**

| | La (**1**) | Pr (**2**) | Nd (**3**) | Gd (**4**) |
|---|---|---|---|---|
| Ln1−O12$^{\#1}$ [a] | 2.436(3) | 2.393(6) | 2.376(6) | 2.335(4) |
| Ln1−O13$^{\#2}$ | 2.463(3) | 2.433(6) | 2.393(6) | 2.356(4) |
| Ln1−O2 | 2.505(3) | 2.462(6) | 2.439(7) | 2.376(5) |
| Ln1−O8$^{\#3}$ | 2.500(3) | 2.457(6) | 2.439(6) | 2.386(5) |
| Ln1−O1W | 2.519(4) | 2.469(7) | 2.457(8) | 2.404(5) |
| Ln1−O1$^{\#4}$ | 2.613(4) | 2.573(7) | 2.547(7) | 2.473(5) |
| Ln1−O6 | 2.586(4) | 2.554(6) | 2.546(6) | 2.518(5) |
| Ln1−O2W | 2.638(4) | 2.605(7) | 2.582(8) | 2.548(5) |
| Ln1−O2$^{\#4}$ | 2.827(4) | 2.822(7) | 2.826(7) | 2.932(6) |
| O12$^{\#1}$−Ln1−O13$^{\#2}$ | 135.69(11) | 136.0(2) | 135.4(2) | 133.74(16) |
| O12$^{\#1}$−Ln1−O8$^{\#3}$ | 81.96(12) | 81.6(2) | 81.9(2) | 81.89(16) |
| O13$^{\#2}$−Ln1−O8$^{\#3}$ | 136.39(12) | 136.1(2) | 135.9(2) | 136.56(16) |
| O12$^{\#1}$−Ln1−O2 | 77.49(12) | 77.8(2) | 77.7(2) | 77.96(16) |
| O13$^{\#2}$−Ln1−O2 | 72.74(12) | 73.2(2) | 73.3(2) | 73.31(16) |
| O8$^{\#3}$−Ln1−O2 | 149.29(12) | 149.2(2) | 149.4(2) | 148.87(16) |
| O12$^{\#1}$−Ln1−O1W | 135.40(13) | 136.0(2) | 136.3(2) | 137.16(18) |
| O13$^{\#2}$−Ln1−O1W | 74.95(13) | 75.2(2) | 75.2(3) | 76.84(19) |
| O8$^{\#3}$−La1−O1W | 92.17(15) | 91.9(3) | 92.3(3) | 91.8(2) |
| O2−Ln1−O1W | 86.78(15) | 87.4(3) | 87.1(3) | 87.2(2) |
| O12$^{\#1}$−Ln1−O6 | 69.80(12) | 70.2(2) | 70.3(2) | 71.18(16) |
| O13$^{\#2}$−Ln1−O6 | 130.36(12) | 130.8(2) | 131.5(2) | 132.26(18) |
| O8$^{\#3}$−Ln1−O6 | 75.93(12) | 75.7(2) | 75.6(2) | 75.55(17) |
| O2−Ln1−O6 | 75.67(12) | 75.9(2) | 76.2(2) | 75.61(18) |
| O1W−Ln1−O6 | 65.91(13) | 66.0(2) | 66.4(2) | 66.23(17) |
| O12$^{\#1}$−Ln1−O1$^{\#4}$ | 80.93(13) | 80.6(2) | 80.3(2) | 79.18(17) |
| O13$^{\#2}$−Ln1−O1$^{\#4}$ | 85.28(13) | 85.2(2) | 84.7(2) | 83.42(18) |
| O8$^{\#3}$−Ln1−O1$^{\#4}$ | 79.81(12) | 79.3(2) | 79.5(2) | 80.33(17) |
| O2−Ln1−O1)$^{\#4}$ | 118.54(12) | 118.9(2) | 118.5(2) | 118.23(18) |
| O1W−Ln1−O1$^{\#4}$ | 141.67(14) | 141.1(3) | 141.3(3) | 141.65(19) |
| O6−Ln1−O(1)$^{\#4}$ | 144.05(13) | 143.8(2) | 143.5(2) | 143.88(18) |
| O12$^{\#1}$−Ln1−O2W | 142.44(13) | 142.2(2) | 141.7(2) | 141.28(18) |
| O13$^{\#2}$−Ln1−O2W | 66.95(13) | 66.7(2) | 67.1(2) | 67.90(17) |
| O8$^{\#3}$−Ln1−O2W | 69.44(13) | 69.4(2) | 68.9(2) | 68.77(17) |
| O2−Ln1−O2W | 137.78(13) | 137.8(2) | 138.3(2) | 138.55(18) |
| O1W−Ln1−O2W | 71.39(15) | 70.6(3) | 71.0(3) | 70.5(2) |
| O6−Ln1−O2W | 122.81(14) | 122.2(2) | 122.1(3) | 121.83(18) |
| O1$^{\#4}$−Ln1−O2W | 70.91(15) | 70.8(3) | 70.8(3) | 71.6(2) |
| O12$^{\#1}$−Ln1−O2$^{\#4}$ | 70.13(11) | 70.06(19) | 69.7(2) | 68.51(15) |
| O13$^{\#2}$−Ln1−O2$^{\#4}$ | 69.50(11) | 69.50(19) | 69.1(2) | 68.29(15) |
| O8$^{\#3}$−Ln1−O2$^{\#4}$ | 122.63(11) | 122.4(2) | 122.6(2) | 122.28(15) |
| O2−Ln1−O2$^{\#4}$ | 70.85(12) | 71.0(2) | 70.6(2) | 71.24(18) |
| O1W−Ln1−O2$^{\#4}$ | 142.16(14) | 142.5(2) | 142.0(3) | 142.86(18) |
| O6−Ln1−O2$^{\#4}$ | 132.02(11) | 132.41(19) | 132.2(2) | 131.85(15) |
| O1$^{\#4}$−Ln1−O2$^{\#4}$ | 47.70(11) | 48.0(2) | 47.9(2) | 47.00(15) |
| O2W−Ln1−O2$^{\#4}$ | 105.03(13) | 105.2(2) | 105.5(2) | 106.10(17) |

[a] Symmetry transformations used to generate equivalent atoms: (#1) $x + 1, y, z$; (#2) $-x, -y + 1, -z + 1$; (#3) $-x + 1, -y, -z + 2$; (#4) $-x + 1, -y + 1, -z + 1$.

The broad band in the range 3492−3498 cm$^{-1}$ indicates the presence of water molecules in all four compounds. The asymmetric vibration absorption band of the sulfonate group appeared around 1201 cm$^{-1}$. The absorption band around 634 cm$^{-1}$ is characteristic band for $\nu_{S-O}$ of the sulfonate group. The strong bands around 1615 cm$^{-1}$ correspond to the antisymmetric stretching bands of the carboxylate groups. The symmetric stretching bands of the carboxylate group appeared in the range 1430−1437 cm$^{-1}$. The bands from 900 to 1100 cm$^{-1}$ are due to the stretching vibrations of the tetrahedral $CPO_3$ group.

TGA diagrams of **1**−**4** are similar and reveal three main weight losses. Compound **1** is used as an example. The first step corresponds to the loss of one lattice water molecule and two aqua ligands. The weight loss started at 79 °C and was completed at 236 °C. The observed weight loss of 8.1% is close to the calculated value (8.7%). The process of this dehydration is irreversible as supported by XRD powder patterns taken after dehydration, which show several new peaks and some of old peaks disappeared, indicating a structural change. The second step covers a temperature range from 236 to 570 °C, during which two processes occurred: the release of water formed by the condensation of $CPO_2$-(OH) groups and the decomposing of both phosphonate and BTS ligands. The third step overlapped with the second one and continued up to 1000 °C, during which the compound was further decomposed. The total weight loss is ca. 48.8%. The final products were not identified; however, we expect the residual is mainly composed of $LaPO_4$ and $La_2O_2(SO_4)$.

**Luminescent Properties** The solid-state luminescent spectra of compounds **3** and **4** were investigated at room temperature. The emission spectra of $NaH_2BTS$ phosphonate

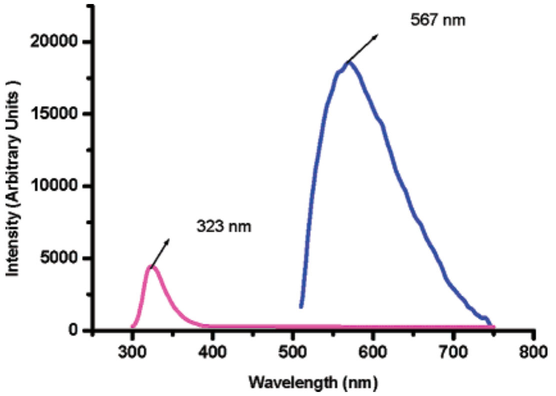

**Figure 4.** Solid-state emission spectra of BTS (pink) and phosphonate ligand (blue).

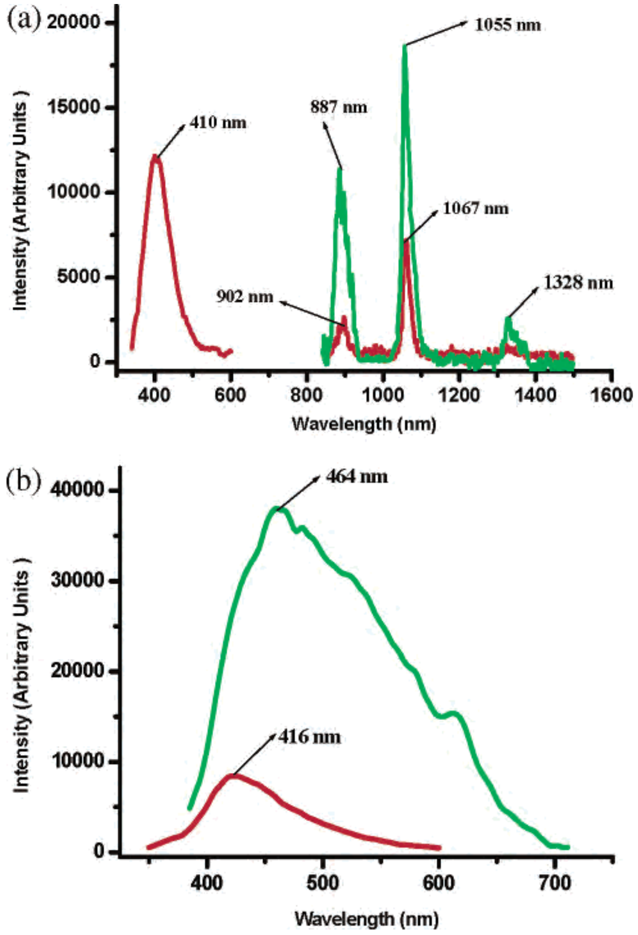

**Figure 5.** Solid-state emission spectra of compounds **3** (a) and **4** (b) before (red) and after dehydration (green).

ligands are shown in Figure 4. The free 5-sulfoisophthalic acid monosodium salt ($NaH_2BTS$) ligand shows only a weak emission band 323 nm ($\lambda_{ex} = 270$ nm), whereas the MeN($CH_2CO_2H$)($CH_2PO_3H_2$) ($H_3L$) ligand shows a very strong fluorescent emission band at 567 nm ($\lambda_{ex} = 482$ nm) (Figure 4). Upon complexion of both ligands with the lanthanide(III) ions, the luminescent spectra of the compounds formed exhibit emission bands characteristic of the corresponding lanthanide(III) ions (Figure 5). Upon excitation at 310 nm, compound **3** displays a strong blue fluorescent emission band at 410 nm, which can be assigned to the $^4D_{3/2} \rightarrow {}^4I_{13/2}$ transition. Under excitation of 356 nm compound **3** displays a strong emission band at 902 ($^4F_{3/2} \rightarrow {}^4I_{9/2}$), an emission band with much lower intensity at 1067 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$), and a very weak band at 1328 nm ($^4F_{3/2} \rightarrow {}^4I_{13/2}$) in the near-IR region (Figure 5a).[17] The spectrum of compound **4** only shows a strong fluorescent emission band at 416 nm ($\lambda_{ex} = 318$ nm) (Figure 5b). Upon removal of the lattice water and two aqua ligands, the emission band at 410 nm of compound **3** disappeared whereas other emission bands have been slightly shifted to lower wavelengths and their intensities were enhanced greatly. The emission band for compound **4** has been shifted to 464 nm, and its intensity is also significantly enhanced after dehydration (Figure 5b). The lower intensities of emission bands for compounds **3** and **4** compared with those for the corresponding dehydrated species are due to the quenching effect of the luminescent state by high-frequency vibrating water molecules. The shifts of emission bands are probably due to the structural changes after dehydration. These results indicate that compounds **3** and **4** are capable of producing blue light in electroluminescent devices, and compound **3** is a luminescent material in the near-IR region.

## Conclusion

In summary, four novel rare-earth sulfonate−phosphonates have been synthesized by hydrothermal reactions and structurally characterized. This demonstrates that by using a second metal linker such as carboxylic acids and sulfonic acids whose lanthanide complexes have good solubility in water and other solvent, we can greatly improve the solubility and crystallinity of lanthanide phosphonates, which allows us to determinate their structures accurately and easily. Also it is possible for us to design new types of lanthanide complexes with novel structures. We believe that a wide range of new lanthanide open-framework and microporous materials can be developed by self-assembly or structural directed synthesis using a similar technique. Compound **3** and **4** are new examples of luminescent rare-earth phosphonate−sulfonates characterized with a significant blue luminescent and near-infrared emission. More detailed and systematic studies are needed to understand the luminescent properties of lanthanide phosphonates, about which little is known heretofore.

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**Supporting Information Available:** X-ray crystallographic files for compounds **1**−**4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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