

New Types of Luminescent Lanthanide  
Squarato-Aminophosphonates

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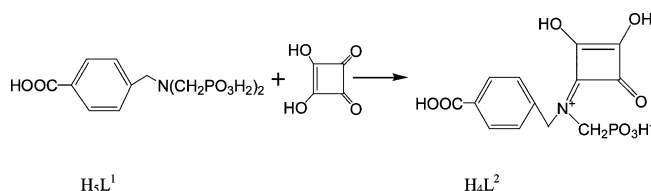
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**ABSTRACT:** Hydrothermal reactions of lanthanide nitrates with aminodiphosphonate ligand ( $(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{N}-\text{CH}_2-\text{C}_6\text{H}_4-\text{COOH}$ ,  $\text{H}_3\text{L}^1$ ) and squaric acid afforded a series of isostructural lanthanide(III) squarato-phosphonates, namely,  $\text{Ln}(\text{HL}^2)$  ( $\text{Ln} = \text{La}$ , **1**;  $\text{Pr}$ , **2**;  $\text{Nd}$ , **3**;  $\text{Eu}$ , **4**;  $\text{Gd}$ , **5**;  $\text{Tb}$ , **6**;  $\text{Er}$ , **7**) ( $\text{H}_4\text{L}^2 = \text{HOOC}-\text{C}_6\text{H}_4-\text{CH}_2-\text{N}(\text{C}_4\text{O}_3\text{H})(\text{CH}_2\text{PO}_3\text{H}_2)$ ), in which a new multifunctional squarato-phosphonate ligand ( $\text{H}_4\text{L}^2$ ) was formed by in situ condensation reaction between the two types of organic ligands. The seven-coordinated lanthanide(III) ions in these compounds are bridged by the squarato-aminophosphonate moieties of the  $\{\text{HL}^2\}^{3-}$  anions into a double layer. Each  $\{\text{HL}^2\}^{3-}$  anion acts as septadentate metal linker, bridging with seven lanthanide ions by using one carboxylate oxygen, three squarato, and three phosphonate oxygens. These double layers are further cross-linked via the coordination of the carboxylate groups into a pillared layered architecture. The  $\text{Eu}$ ,  $\text{Tb}$ , and  $\text{Nd}$  compounds exhibit strong luminescence in red light, green light, and near-IR regions, respectively.

## Introduction

Porous inorganic–organic hybrid materials are of great importance due to their potential applications such as sorbents, ion exchangers, catalysts, or charge-storage materials.<sup>1</sup> Materials with open-framework and microporous structures are also promising candidates for hybrid composite materials in electro-optical and sensing applications.<sup>2</sup> To design metal phosphonates with open-framework structures, researchers have attached a variety of functional groups such as amino acids, crown ethers, amino groups, and carboxylates to the phosphonate groups.<sup>3–10</sup> Furthermore, the introduction of a second ligand such as 4,4'-bipy and oxalate anion has been found to be an effective synthetic route, because these auxiliary ligands can act as pillars to link neighboring layers or can be incorporated into the inorganic layer to form a new hybrid layered architecture.<sup>5</sup> It is interesting to note that during the hydrothermal syntheses of coordination polymers, a few unexpected important in situ organic reactions were observed.<sup>11,12</sup> The relatively high temperatures and pressures, as well as the presence of metal ions, may facilitate some new reactions or provide facile one-pot syntheses for intriguing organic compounds that otherwise require multistep processes.<sup>12</sup> Such in situ organic reactions also provide a bridge between coordination chemistry and synthetic organic chemistry. However, in situ organic reactions are rarely reported in the chemistry of metal phosphonates.<sup>13</sup> It is reported that during the hydrothermal reactions of erbium(III) or cobalt(II) nitrate with  $(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{C}_6\text{H}_4\text{COOH}$ ,  $\text{H}_2\text{O}_3\text{PCH}_2\text{N}(\text{CHO})(\text{CH}_2\text{C}_6\text{H}_4\text{COOH})$  was formed because of the in situ oxidation of one P–C bond.<sup>13,13b</sup> During our explorations on organic–inorganic hybrids of metal aminodiphosphonates with the squaric acid as the second metal linker, a new multifunctional squarato-imino-diphosphonate ligand was formed by the condensation reaction between one C=O group of the squaric acid and the amino group of  $\text{NH}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ ; the copper(II) ion was reduced to copper(I) ion to form a novel layered compound with the newly formed ligand.<sup>13c</sup> We are curious about whether such condensation reaction can occur between squaric acid and other substituted aminodiphosphonic acids and whether the

Scheme 1. Formation of the Squarato-Phosphonic Ligand,  $\text{H}_4\text{L}^2$ 

reduction of transition metal ion is needed. As an expansion of our previous work, we selected  $(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{C}_6\text{H}_4\text{COOH}$  ( $\text{H}_3\text{L}^1$ ) as the aminodiphosphonic ligand and lanthanide salts as the metal sources. Hydrothermal reactions of lanthanide salts with  $\text{H}_3\text{L}^1$  and squaric acid afforded a series of isostructural lanthanide(III) squarato-phosphonates with a pillared-layered architecture, namely,  $\text{Ln}(\text{HL}^2)$  ( $\text{Ln} = \text{La}$ , **1**;  $\text{Pr}$ , **2**;  $\text{Nd}$ , **3**;  $\text{Eu}$ , **4**;  $\text{Gd}$ , **5**;  $\text{Tb}$ , **6**;  $\text{Er}$ , **7**) ( $\text{H}_4\text{L}^2 = \text{HOOC}-\text{C}_6\text{H}_4-\text{CH}_2-\text{N}(\text{C}_4\text{O}_3\text{H})(\text{CH}_2\text{PO}_3\text{H}_2)$ ) in which the new multifunctional  $\text{H}_4\text{L}^2$  ligand was formed by in situ condensation reaction of the two types of organic ligands (Scheme 1). Herein we report their syntheses, crystal structures, and luminescence properties.

## Experimental Section

**Materials and Instrumentation.**  $(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{N}-\text{CH}_2\text{C}_6\text{H}_4-\text{COOH}$  ( $\text{H}_3\text{L}^1$ ) was prepared by a Mannich type reaction according to procedures described previously.<sup>13</sup> 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  $\text{cm}^{-1}$ . Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer for compounds **3** and **4** or a Cary Eclipse EL06043604 fluorescence spectrometer for compound **6**.

**Preparation of  $\text{Ln}(\text{HL}^2)$  ( $\text{Ln} = \text{La}$ , **1**;  $\text{Pr}$ , **2**;  $\text{Nd}$ , **3**;  $\text{Eu}$ , **4**;  $\text{Gd}$ , **5**;  $\text{Tb}$ , **6**;  $\text{Er}$ , **7**).** These compounds were synthesized by a similar method. A mixture of  $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$  (0.5 mmol),  $\text{H}_3\text{L}^1$  (0.5 mmol), and  $\text{C}_4\text{O}_4\text{H}_2$  (0.5 mmol) in 10 mL of distilled water with the pH value adjusted to 4.5 by the slow addition of 1 M NaOH solution was sealed into an autoclave equipped with a Teflon liner (25 mL) and then heated at 165 °C for 4 days. Crystals of **1–7** were collected along with

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Table 1. Summary of Crystallographic Data and Structure Refinements for Compounds 1–7

	1	2	3	4	5	6	7
formula	C <sub>13</sub> H <sub>9</sub> NLaO <sub>8</sub> P	C <sub>13</sub> H <sub>9</sub> PrNO <sub>8</sub> P	C <sub>13</sub> H <sub>9</sub> NNdO <sub>8</sub> P	C <sub>13</sub> H <sub>9</sub> EuNO <sub>8</sub> P	C <sub>13</sub> H <sub>9</sub> NGdO <sub>8</sub> P	C <sub>13</sub> H <sub>9</sub> NTbO <sub>8</sub> P	C <sub>13</sub> H <sub>9</sub> NErO <sub>8</sub> P
fw	477.09	479.09	482.42	490.14	495.43	497.10	505.44
space group	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> (Å)	11.088(3)	11.0097(5)	10.967(2)	10.863(2)	10.8523(6)	10.809(3)	10.7793(2)
<i>b</i> (Å)	9.669(3)	9.6183(5)	9.595(2)	9.525(2)	9.5280(5)	9.470(2)	9.4896(1)
<i>c</i> (Å)	28.537(7)	28.438(1)	28.377(5)	28.298(5)	28.296(2)	28.244(6)	28.3118(2)
<i>V</i> (Å <sup>3</sup> )	3060(1)	3011.5(2)	2986.1(9)	2927.9(9)	2925.9(3)	2891.2(12)	2896.05(7)
<i>Z</i>	8	8	8	8	8	8	8
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	2.072	2.113	2.146	2.224	2.249	2.284	2.361
$\mu$ (mm <sup>-1</sup> )	2.940	3.386	3.629	4.439	4.688	5.048	6.061
GOF on <i>F</i> <sup>2</sup>	1.179	1.158	1.318	1.382	1.263	1.441	1.163
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a</sup>	0.058, 0.0961	0.0451, 0.0784	0.0336, 0.0620	0.0398, 0.0820	0.0697, 0.1115	0.0696, 0.1342	0.0402, 0.0771
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0712, 0.1025	0.0593, 0.0842	0.0355, 0.0626	0.0431, 0.0830	0.0847, 0.1170	0.0764, 0.1363	0.0427, 0.0782

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

Table 2. Selected Bond Lengths (Å) for Compounds 1–7<sup>a</sup>

	1 (La)	2 (Pr)	3 (Nd)	4 (Eu)	5 (Gd)	6 (Tb)	7 (Er)
Ln(1)–O(11)#1	2.321(5)	2.285(4)	2.272(3)	2.228(5)	2.228(6)	2.211(8)	2.172(5)
Ln(1)–O(13)	2.327(4)	2.284(4)	2.276(3)	2.234(4)	2.227(6)	2.207(7)	2.173(4)
Ln(1)–O(12)#2	2.427(5)	2.387(4)	2.372(3)	2.326(5)	2.311(6)	2.296(8)	2.248(4)
Ln(1)–O(5)#3	2.454(5)	2.408(4)	2.398(3)	2.353(4)	2.345(6)	2.335(8)	2.298(4)
Ln(1)–O(3)#4	2.486(4)	2.438(4)	2.425(3)	2.378(4)	2.362(6)	2.347(7)	2.318(4)
Ln(1)–O(4)#5	2.525(5)	2.487(4)	2.470(3)	2.431(5)	2.423(7)	2.402(8)	2.382(5)
Ln(1)–O(2)#6	2.730(5)	2.677(4)	2.654(3)	2.609(5)	2.591(7)	2.596(8)	2.539(5)
P(1)–O(11)	1.491(5)	1.498(4)	1.498(3)	1.501(5)	1.494(6)	1.499(8)	1.496(5)
P(1)–O(12)	1.528(5)	1.531(4)	1.532(3)	1.536(5)	1.540(7)	1.538(8)	1.531(4)
P(1)–O(13)	1.503(5)	1.507(4)	1.500(3)	1.501(5)	1.504(7)	1.500(7)	1.499(5)
P(1)–C(9)	1.817(7)	1.818(6)	1.824(4)	1.821(7)	1.823(9)	1.827(11)	1.820(6)

<sup>a</sup> Symmetry codes for the generated equivalent atoms: #1 *x* – 1/2, –*y* + 3/2, –*z*; #2 –*x* + 2, –*y* + 2, –*z*; #3 –*x* + 2, –*y* + 1, –*z*; #4 *x* + 1/2, –*y* + 3/2, –*z*; #5 –*x* + 3/2, *y* + 1/2, *z*; #6 *x*, –*y* + 3/2, *z* – 1/2.

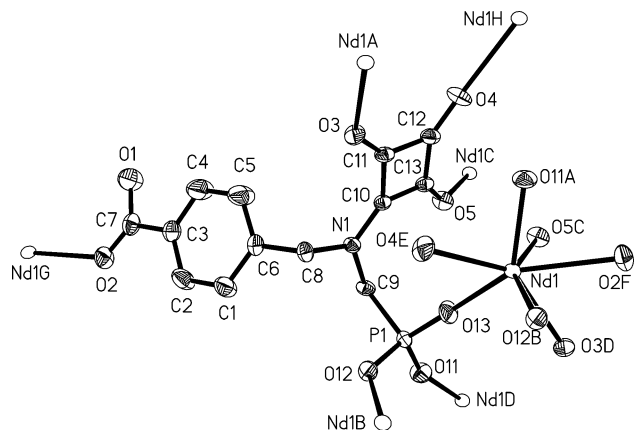
unidentified powder impurities. The final pH values of the reactions are all close to 3.0. Many efforts were made to synthesize their single-phase products by changing Ln/L ratios, pH values, and reaction temperatures but were unsuccessful. Hence samples used for elemental analyses, XRD powder diffraction studies and TGA measurements are single crystals selected on the basis of colors and shapes. Because of insufficient sample available, TGA, luminescence, and XRD powder diffraction studies for compound 7 were not performed. Anal. Calcd for C<sub>13</sub>H<sub>9</sub>NLaO<sub>8</sub>P (*M*<sub>r</sub> = 477.09): C, 32.73; H, 1.90; N, 2.94%. Found: C, 32.51; H, 1.83; N, 2.84%. IR (KBr, cm<sup>-1</sup>) for 1: 3445 (m), 2919 (w), 2342 (w), 1797 (m), 1673 (w), 1625 (m), 1542 (vs), 1505 (s), 1449 (m), 1410 (m), 1321 (m), 1298 (m), 1267 (m), 1139 (s), 1062 (s), 994 (s), 786 (w), 757 (m), 568 (m), 537 (w). Anal. Calcd for C<sub>13</sub>H<sub>9</sub>PrO<sub>8</sub>P (*M*<sub>r</sub> = 479.09): C, 32.59; H, 1.89; N, 2.92%. Found: C, 32.41; H, 1.80; N, 2.87%. IR (KBr, cm<sup>-1</sup>) for 2: 3429 (s), 2918 (w), 2340 (w), 1795 (m), 1681 (m), 1629 (s), 1535 (vs), 1491 (s), 1457 (m), 1413 (m), 1318 (m), 1310 (m), 1257 (m), 1171 (m), 1137 (s), 1067 (s), 990 (m), 955 (m), 799 (w), 747 (m), 713 (w), 625 (w), 574 (m), 539 (w), 496 (m). Anal. Calcd for C<sub>13</sub>H<sub>9</sub>NNdO<sub>8</sub>P (*M*<sub>r</sub> = 482.42): C, 32.36; H, 1.88; N, 2.90%. Found: C, 32.31; H, 1.83; N, 2.85%. IR (KBr, cm<sup>-1</sup>) for 3: 3429 (s), 2928 (w), 2079 (w), 1785 (m), 1681 (m), 1630 (s), 1535 (vs), 1491 (s), 1448 (m), 1413 (m), 1328 (m), 1292 (m), 1257 (m), 1170 (m), 1137 (s), 1051 (s), 981 (m), 963 (m), 790 (w), 747 (w), 721 (w), 635 (w), 566 (m), 513 (m), 462 (m). Anal. Calcd for C<sub>13</sub>H<sub>9</sub>NEuO<sub>8</sub>P (*M*<sub>r</sub> = 490.14): C, 31.85; H, 1.85; N, 2.86%. Found: C, 30.9; H, 1.70; N, 2.80%. IR (KBr, cm<sup>-1</sup>) for 4: 3422 (m), 3212 (m), 2346 (w), 1798 (w), 1628 (w), 1509 (vs), 1412 (w), 1321 (w), 1299 (w), 1152 (w), 1094 (m), 996 (w), 959 (w), 853 (w), 723 (w), 571 (m), 540 (w), 470 (w). Anal. Calcd for C<sub>13</sub>H<sub>9</sub>NGdO<sub>8</sub>P (*M*<sub>r</sub> = 495.43): C, 31.53; H, 1.83; N, 2.83%. Found: C, 31.10; H, 1.75; N, 2.70%. IR (KBr, cm<sup>-1</sup>) for 5: 3261 (w), 2924 (w), 2364 (w), 1802 (w), 1683 (m), 1633 (m), 1543 (vs), 1505 (s), 1453 (m), 1413 (m), 1322 (m), 1299 (m), 1271 (m), 1154 (m), 1082 (s), 997 (m), 971 (w), 758 (m), 724 (w), 632 (w), 571 (m), 545 (w), 517 (w), 473 (w). Anal. Calcd for C<sub>13</sub>H<sub>9</sub>NTbO<sub>8</sub>P (*M*<sub>r</sub> = 497.10): C, 31.41; H, 1.82; N, 2.82%. Found: C, 31.15; H, 1.78; N, 2.76%. IR (KBr, cm<sup>-1</sup>) for 6: 3420 (m), 3215 (m), 2340 (w), 1793 (w), 1625 (w), 1506 (vs), 1406 (w), 1317 (w), 1296 (w), 1155 (w), 1099 (m), 993 (w), 956 (w), 851 (w), 720 (w), 568 (m), 543 (w), 464 (w). Anal. Calcd for C<sub>13</sub>H<sub>9</sub>NErO<sub>8</sub>P (*M*<sub>r</sub> = 505.44): C, 30.89; H, 1.79; N, 2.77%. Found: C, 30.40; H, 1.71; N, 2.68%. IR (KBr, cm<sup>-1</sup>) for 7: 3264 (w), 2921 (w), 2367 (w), 1804

(w), 1686 (m), 1630 (m), 1541 (vs), 1504 (s), 1458 (m), 1416 (m), 1320 (m), 1297 (m), 1274 (m), 1152 (m), 1085 (s), 994 (m), 973 (w), 760 (m), 722 (w), 635 (w), 573 (m), 548 (w), 514 (w), 470 (w).

**Single-Crystal Structure Determinations.** Single crystals of compounds 1–7 were mounted on a Mercury CCD diffractometer equipped with a graphite-monochromated Mo–K $\alpha$  radiation ( $\lambda$  = 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> The 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 isotropical thermal parameters. Crystallographic data and structural refinements for compounds 1–7 are summarized in Table 1. Important bond distances are listed in Table 2. More details on the crystallographic studies as well as atom displacement parameters are given in the Supporting Information.

## Results and Discussion

The hydrothermal reactions of the lanthanide(III) nitrate metal ions with squaric acid and (H<sub>2</sub>O<sub>3</sub>PCH<sub>2</sub>)<sub>2</sub>–N–CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>–COOH (H<sub>3</sub>L<sup>1</sup>) lead to a series of isostructural lanthanide(III) phosphonates, Ln(HL<sup>2</sup>) (Ln = La, 1; Pr, 2; Nd, 3; Eu, 4; Gd, 5; Tb, 6; Er, 7) (H<sub>4</sub>L<sup>2</sup> = HOOC–C<sub>6</sub>H<sub>4</sub>–CH<sub>2</sub>–N(C<sub>4</sub>O<sub>3</sub>H)(CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>)). The new multifunctional H<sub>4</sub>L<sup>2</sup> ligand was formed by in situ condensation reaction between the two types of organic ligands (Scheme 1). The exact mechanism of the organic reactions involved is still not clear, but the nitrate anion may play an important role since such condensation reaction does not occur using other lanthanide(III) salts. It should be noted that the condensation reaction between the square acid and NH(CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub> we reported earlier does not involve the cleavage of one N–C bond, probably because of the much larger flexibility of the NH(CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub> ligand.<sup>13c</sup> Furthermore, no reduction of the lanthanide(III) ions in Ln(HL<sup>2</sup>) occurred,

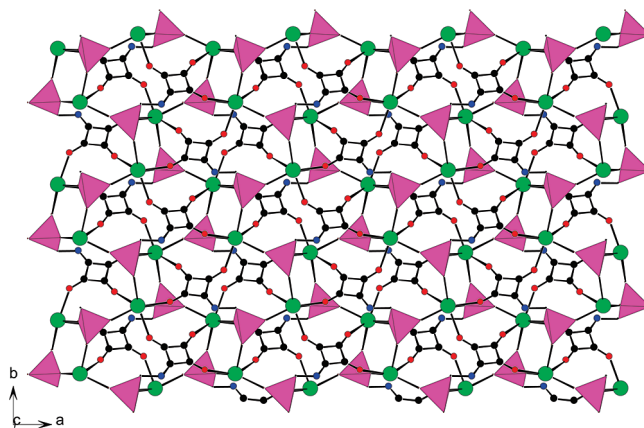


**Figure 1.** ORTEP representation of the selected unit of compound **3**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry codes for the generated atoms: (a)  $x - 1/2, -y + 3/2, -z$ ; (b)  $-x + 2, -y + 2, -z$ ; (c)  $-x + 2, -y + 1, -z$ ; (d)  $x + 1/2, -y + 3/2, -z$ ; (e)  $-x + 3/2, y + 1/2, z$ ; (f)  $x, -y + 3/2, z - 1/2$ ; (g)  $x, -y + 3/2, z + 1/2$ ; (h)  $-x + 3/2, y - 1/2, z$ .

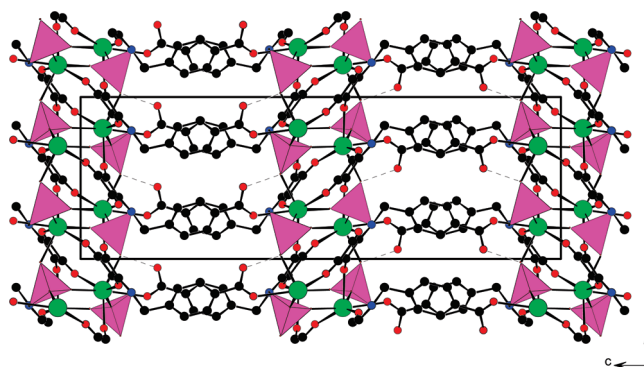
whereas the condensation reaction between the square acid and  $\text{NH}(\text{CH}_2\text{PO}_3\text{H}_2)_2$  involves the reduction of copper(II) ion to copper(I).<sup>13c</sup>

Compounds **1–7** are isostructural and feature a novel 3D pillared layered structure. The structure of compound **3** will be described as an example. As shown in Figure 1, Nd(1) is 7-coordinated by three phosphonate oxygens, three squarato oxygens, and one carboxylate oxygen from seven  $\{\text{HL}^2\}^{3-}$  anions. The Nd–O distances range from 2.272(3) to 2.654(3) Å, which are comparable to those reported for other Nd(III) phosphonates.<sup>5,13</sup> The  $\{\text{HL}^2\}^{3-}$  anion is septadentate and bridges with seven Nd(III) ions via one carboxylate oxygen, three squarato, and three phosphonate oxygens. The other carboxylate oxygen is protonated and remains uncoordinated (O(1)), the C(7)–O(1) bond length of 1.328(5) Å is significantly longer than the C(7)–O(2) bond (1.228(6) Å). The N(1)–C(10) bond that connects the squarato group with the amino-phosphonate moiety is double bond in character with a bond distance of 1.328(5) Å,<sup>15</sup> which is close to that in the copper(I) squarato-amino-diphosphonate we reported previously.<sup>13c</sup> The C–O bonds within the squarato moiety are also double bonds with distances ranging from 1.239(5) to 1.248(5) Å, which are very close to the C=O bonds in 1,3,5-tris(4-cyanobenzoyl)benzene (1.222(2) Å).<sup>16</sup>

It is interesting to mention that the neodymium(III) ions are interconnected by the squarato-amino-phosphonate moieties (excluding the phenyl-carboxylic acid groups) of the  $\{\text{HL}^2\}^{3-}$  anions into double layers (Figure 2). The interlayer distance is about 14.2 Å. Neighboring such layers are further cross-linked through the coordination the phenyl carboxylate groups of the  $\{\text{HL}^2\}^{3-}$  anions with long-narrow shaped tunnels along *a*-axis (Figure 3). The noncoordination carboxylate oxygens are oriented toward the tunnels, and hence there is no free space available for the solvent molecules. Hydrogen bonds are formed between noncoordination carboxylate oxygen (O1) and phosphonate oxygen (O12). The O(1)–H(1B)···O(12) (symmetry code:  $-x + 2, y - 1/2, -z + 1/2$ ) hydrogen bond distance is 2.535(5) Å and the angle is 168.2°. It should be mentioned that in lanthanide(III) complexes with  $\text{H}_5\text{L}^1$ , the carboxylate group of the phosphonate ligand remains uncoordinated and is involved in the interlayer hydrogen bonding.<sup>13</sup> It should also be noted that the squarato-amino-diphosphonate ligand in the copper(I) complex bears an additional phosphonate group, but it bridges



**Figure 2.** A 2D double layer of neodymium(III) squarato-amino-phosphonate parallel to the *ab* plane in **3**. The phosphonate groups are shaded in pink. Nd, N, C, and O atoms are represented by green, blue, black, and red circles, respectively.



**Figure 3.** View of the structure of **3** down the *a*-axis. The phosphonate tetrahedra are shaded in pink. Nd, N, C, and O atoms are represented by green, blue, black, and red circles, respectively. Hydrogen bonds are drawn as dashed lines.

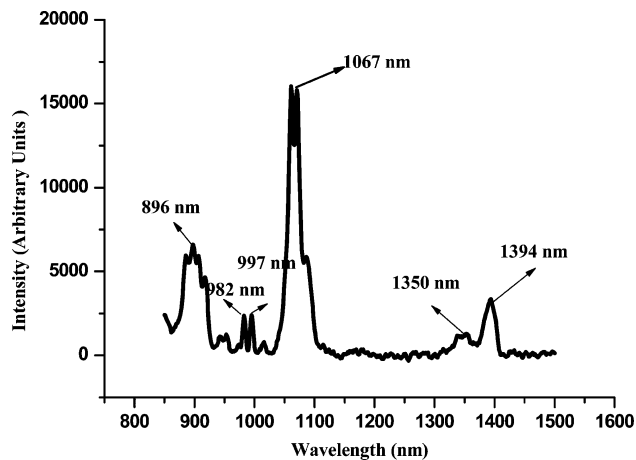
only with two metal centers by using one squarato oxygen and one phosphonate oxygen.<sup>13c</sup>

The Ln–O distances and cell volumes decrease with the “lanthanide contraction” (Tables 1 and 2); the contraction rates of Ln–O bonds and cell volumes from  $\text{La}^{3+}$  to  $\text{Er}^{3+}$  are about 6.61 and 5.36%, respectively.

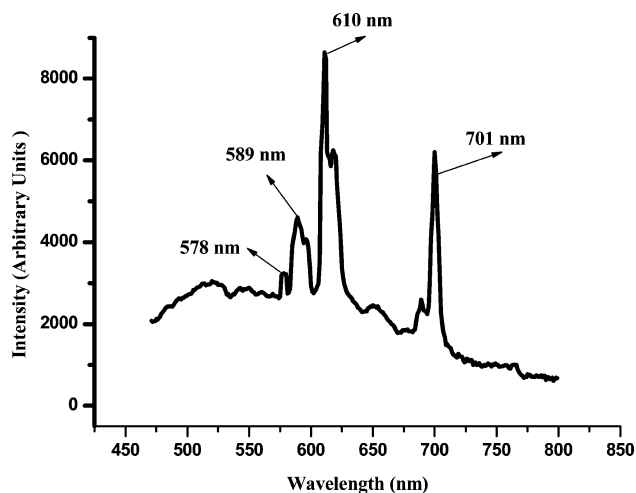
The IR Spectra of compounds **1–7** are similar. The broadband at ca. 3420  $\text{cm}^{-1}$  indicates the presence of surface water molecules in all compounds. The band at around 2340  $\text{cm}^{-1}$  can be assigned to the OH-stretching vibrations of P–OH group. The strong bands at around 1630 and 1440  $\text{cm}^{-1}$  can be assigned to the C=O and C–O stretching vibration of the carboxylate group. The vibrations of the phosphonate groups appear as a set of sharp bands in the region between 1200 and 1000  $\text{cm}^{-1}$ . These assignments are in agreement with those reported in the literature.<sup>13b,17</sup>

**Luminescence Properties.** The optical properties of compounds **1–6** were investigated at room temperature. Compounds **1**, **2**, and **5** did not exhibit emission bands in the visible or near IR region at room temperature. The emission spectra of compounds **3**, **4**, and **6** are shown in Figures 4–6. Under excitation at 826 nm, compound **3** displays a weak emission band at 896 nm ( $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ ), a strong emission band at 1067 nm ( $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ ), and a very weak band at 1394 nm ( $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$ ) in the near-IR region.<sup>8–10,18</sup> Because of the ligand field effect and the very low symmetry of the

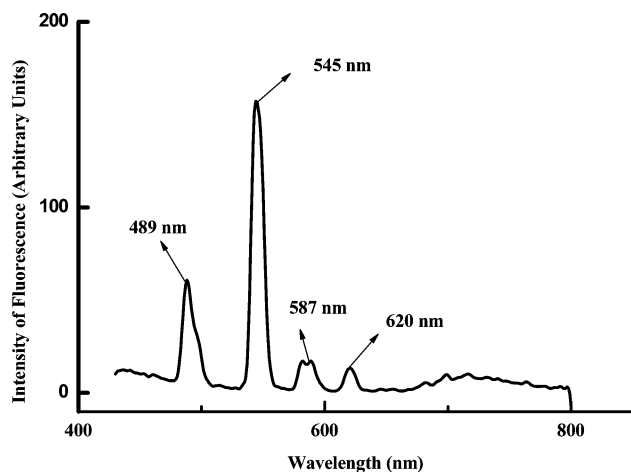




**Figure 4.** Solid-state emission spectrum of compound **3** at room temperature.



**Figure 5.** Solid-state emission spectrum of compound **4** at room temperature.



**Figure 6.** Solid-state emission spectrum of compound **6** at room temperature.

Nd(III) site (C1), each transition band shows several sub-bands or shoulder bands. Compound **4** exhibits one weak and three very strong characteristic emission bands of the Eu(III) ion in the visible region under excitation at 394 nm (Figure 5). These emission bands are 578 nm ( $^5D_0 \rightarrow ^7F_0$ ),

589 nm ( $^5D_0 \rightarrow ^7F_1$ ), 610 nm ( $^5D_0 \rightarrow ^7F_2$ ), and 701 nm ( $^5D_0 \rightarrow ^7F_4$ ). The Eu ( $^5D_0$ ) lifetime of **4** for  $\lambda_{\text{ex, em}} = 392, 612$  nm is 0.27 ms. The observation of the weak  $^5D_0 \rightarrow ^7F_0$  transition band indicates the very low symmetry of the Eu(III) site (C1). The emission spectrum of compound **6** exhibit characteristic emission bands of the Tb(III) ion, and the emission peaks are at 489 nm ( $^5D_4 \rightarrow ^7F_6$ ), 545 nm ( $^5D_4 \rightarrow ^7F_5$ ), 587 nm ( $^5D_4 \rightarrow ^7F_4$ ), and 620 nm ( $^5D_4 \rightarrow ^7F_3$ ), respectively. The Tb ( $^5D_4$ ) lifetime of **6** for  $\lambda_{\text{ex, em}} = 256, 543$  nm is 1.63 ms.

**TGA Studies.** Compounds **1–6** are subjected to TGA studies under a nitrogen atmosphere (See Supporting Information). Their thermal behaviors are quite similar and display mainly three steps of weight losses. The slight weight loss before 250 °C for compound **1** or 400 °C for other compounds may be due to the slight amount of surface water absorbed in the sample, which is also confirmed by IR studies. The weight loss in 250–550 °C for compound **4** and 400–550 °C for other compounds correspond to the partial decomposition of the two types of organic ligands. The second step overlaps with the first one, during which the compounds are further decomposed. The total observed weight losses at 1000 °C are 36.3, 34.7, 25.5, 23.3, 26.7, and 25% for compounds **1–6**, respectively. The final residuals were not characterized because of the corrosive reactions of the final residuals with the TGA baskets made of  $\text{Al}_2\text{O}_3$ . From the slope of the TGA curve, it is known that the decomposing process is not completed at 1000 °C.

## Conclusion

In summary, the hydrothermal syntheses, crystal structures, and luminescence properties of seven novel rare-earth squarato-aminophosphonates have been described. Under the hydrothermal reactions, one N–C bond of the  $(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{N}-\text{CH}_2\text{C}_6\text{H}_4-\text{COOH}$  ( $\text{H}_5\text{L}^1$ ) was broken and a new multifunctional squarato-phosphonate ligand was formed by the condensation reaction between one C=O group of the squaric acid and the amino group of  $-\text{NH}(\text{H}_2\text{O}_3\text{PCH}_2)_2$ . Their structures feature a novel 3D pillared layered structure. Compounds **3**, **4**, and **6** display red, green, or near-infrared emission bands. Results of this study indicate that in situ condensation reactions between squaric acid and aminophosphonate under hydrothermal conditions are not uncommon. These types of organic reactions are very interesting because they could lead to not only new functional ligands that otherwise could not be synthesized by conventional organic syntheses but also new organic–inorganic hybrids with unusual physical properties. However, it is still a great challenge to understand the mechanisms of these reactions. Our future research efforts will be devoted to the further investigations of other related systems and try to establish possible mechanisms for such in situ organic reactions under hydrothermal reactions.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for compounds **1–7**; simulated and experimental XRD powder patterns and TGA curves for compounds **1–6** (PDF). These materials are available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Clearfield, A. *Metal Phosphonate Chemistry in Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons: New York, 1998;

- Vol. 47, pp 371–510 (and references therein). (b) Mao, J.-G. *Coord. Chem. Rev.* **2007**, 251, 1493. (c) Matczak-Jon, E.; Videnova-Adrabinska, V. *Coord. Chem. Rev.* **2005**, 249, 2458.
- (2) Cheetham, A. K.; Ferey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, 38, 3269. (b) Zhu, J.; Bu, X.; Feng, P.; Stucky, G. D. *J. Am. Chem. Soc.* **2000**, 122, 11563. (c) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, 43, 1466.
- (3) Kong, D. Y.; Li, Y.; Xiang, O. Y.; Prosvirin, A. V.; Zhao, H. H.; Ross, J. H.; Dunbar, K. R.; Clearfield, A. *Chem. Mater.* **2004**, 16, 3020. (b) Gomez-Alcantara, M. M.; Cabeza, A.; Martinez-Lara, M.; Aranda, M. A. G.; Suau, R.; Bhuvanesh, N.; Clearfield, A. *Inorg. Chem.* **2004**, 43, 5283. (c) Kong, D. Y.; Clearfield, A. *Chem. Commun.* **2005**, 1005. (d) Kong, D. Y.; Medvedev, D. G.; Clearfield, A. *Inorg. Chem.* **2004**, 43, 7308. (e) Kong, D.; Zon, J.; McBee, J.; Clearfield, A. *Inorg. Chem.* **2006**, 45, 977. (f) Konar, S.; Bhuvanesh, N.; Clearfield, A. *J. Am. Chem. Soc.* **2006**, 128, 9604. (g) Konar, S.; Zon, J.; Prosvirin, A. V.; Dunbar, K. R.; Clearfield, A. *Inorg. Chem.* **2007**, 46, 5229. (h) Konar, S.; Clearfield, A. *Inorg. Chem.* **2008**, 47, 3489. (i) Konar, S.; Clearfield, A. *Inorg. Chem.* **2008**, 47, 3492.
- (4) Bao, S. S.; Ma, L. F.; Wang, Y.; Fang, L.; Zhu, C. J.; Li, Y. Z.; Zheng, L. M. *Chem.—Eur. J.* **2007**, 13, 2333. (b) Cao, D. K.; Xiao, J.; Tong, J. W.; Li, Y. Z.; Zheng, L. M. *Inorg. Chem.* **2007**, 46, 428. (c) Liu, B.; Yin, P.; Yi, X. Y.; Gao, S.; Zheng, L. M. *Inorg. Chem.* **2006**, 45, 4205. (d) Bao, S. S.; Chen, G. S.; Wang, Y.; Li, Y. Z.; Zheng, L. M.; Luo, Q. H. *Inorg. Chem.* **2006**, 45, 1124. (e) Yin, P.; Gao, S.; Wang, Z. M.; Yan, C. H.; Zheng, L. M.; Xin, X. Q. *Inorg. Chem.* **2005**, 44, 2761. (f) Ma, Y.-S.; Li, H.; Wang, J. J.; Bao, S.-S.; Cao, R.; Li, Y.-Z.; Ma, J.; Zheng, L. M. *Chem.—Eur. J.* **2007**, 13, 4759. (g) Liu, B.; Li, B.-L.; Li, Y.-Z.; Chen, Y.; Bao, S.-S.; Zheng, L.-M. *Inorg. Chem.* **2007**, 46, 8524. (h) Liu, X.-G.; Bao, S.-S.; Li, Y.-Z.; Zheng, L.-M. *Inorg. Chem.* **2008**, 47, 5525.
- (5) Mao, J.-G.; Wang, Z.-K.; Clearfield, A. *Inorg. Chem.* **2002**, 41, 6106. (b) Mao, J.-G.; Clearfield, A. *Inorg. Chem.* **2002**, 41, 2319. (c) Song, J.-L.; Zhao, H.-H.; Mao, J.-G.; Dunbar, K. R. *Chem. Mater.* **2004**, 16, 1884. (d) Song, J. L.; Mao, J.-G. *Chem.—Eur. J.* **2005**, 11, 1417. (e) Song, J. L.; Lei, C.; Mao, J. G. *Inorg. Chem.* **2004**, 43, 5630. (f) Du, Z. Y.; Xu, H. B.; Mao, J.-G. *Inorg. Chem.* **2006**, 45, 9780. (g) Yang, B.-P.; Prosvirin, A. V.; Guo, Y.-Q.; Mao, J.-G. *Inorg. Chem.* **2008**, 47, 1453. (h) Du, Z. Y.; Prosvirin, A. V.; Mao, J.-G. *Inorg. Chem.* **2007**, 46, 9884.
- (6) Stock, N.; Bein, T. *Angew. Chem., Int. Ed.* **2004**, 43, 749. (b) Serre, C.; Stock, N.; Bein, T.; Ferey, G. *Inorg. Chem.* **2004**, 43, 3159. (c) Forster, P. M.; Stock, N.; Cheetham, A. K. *Angew. Chem. Int. Ed.* **2005**, 44, 7608. (d) Bauer, S.; Muller, H.; Bein, T.; Stock, N. *Inorg. Chem.* **2005**, 44, 9464. (e) Serre, C.; Groves, J. A.; Lightfoot, P.; Slawin, A. M. Z.; Wright, P. A.; Stock, N.; Bein, T.; Haouas, M.; Taulelle, F.; Ferey, G. *Chem. Mater.* **2006**, 18, 1451. (f) Sonnauer, A.; Nather, C.; Hoppe, H. A.; Senker, J.; Stock, N. *Inorg. Chem.* **2007**, 46, 9968. (g) Bauer, S.; Marrot, J.; Devic, T.; Ferey, G.; Stock, N. *Inorg. Chem.* **2007**, 46, 9998. (h) Bauer, S.; Stock, N. *Angew. Chem., Int. Ed.* **2007**, 46, 6857.
- (7) Groves, J. A.; Miller, S. R.; Warrender, S. J.; Mellot-Draznieks, C.; Lightfoot, P.; Wright, P. A. *Chem. Commun.* **2006**, 3305. (b) Groves, J. A.; Wright, P. A.; Lightfoot, P. *Dalton Trans.* **2005**, 2007. (c) Devi, R. N.; Wormald, P.; Cox, P. A.; Wright, P. A. *Chem. Mater.* **2004**, 16, 2229.
- (8) Zhang, X. M.; Hou, J. J.; Zhang, W. X.; Chen, X. M. *Inorg. Chem.* **2006**, 45, 8120. (b) Tsao, C. P.; Sheu, C. Y.; Nguyen, N.; Lii, K. H. *Inorg. Chem.* **2006**, 45, 6361. (c) Burkholder, E.; Golub, V.; O'Connor, C. J.; Zubietta, J. *Inorg. Chem.* **2004**, 43, 7014. (d) Lin, C. H.; Lii, K. H. *Inorg. Chem.* **2004**, 43, 6403. (e) Murugavel, R.; Shanmugan, S. *Chem. Commun.* **2007**, 1257.
- (9) Fredoueil, F.; Evain, M.; Massiot, D.; Bujoli-Doeuff, M.; Janvier, P.; Clearfield, A.; Bujoli, B. *J. Chem. Soc., Dalton Trans.* **2002**, 1508. (b) Rabu, P.; Janvier, P.; Bujoli, B. *J. Mater. Chem.* **1999**, 9, 1323. (c) Drumel, S.; Janvier, P.; Bujoli-Doeuff, M.; Bujoli, B. *J. Mater. Chem.* **1996**, 6, 1843.
- (10) Distler, A. S.; Sevov, S. C. *Chem. Commun.* **1998**, 959. (b) Lohse, D. L.; Sevov, S. C. *Angew. Chem., Int. Ed.* **1997**, 36, 1619. (c) Turner, A.; Jaffres, P. A.; MacLean, E. J.; Villemain, D.; McKee, V.; Hix, G. B. *Dalton Trans.* **2003**, 1314. (d) Hartman, S. J.; Todorov, E.; Cruz, C.; Sevov, S. C. *Chem. Commun.* **2000**, 1213. (e) Hix, G. B.; Wragg, D. S.; Wright, P. A.; Morris, R. E. *J. Chem. Soc., Dalton Trans.* **1998**, 3359.
- (11) Hu, S.; Chen, J.-C.; Tong, M.-L.; Wang, B.; Yan, Y.-X.; Batten, S.-R. *Angew. Chem., Int. Ed.* **2005**, 44, 5471–5475. (b) Zhang, J.-P.; Zheng, S.-L.; Huang, X.-C.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2004**, 43, 206–209. (c) Liu, C.-M.; Gao, S.; Kou, H.-Z. *Chem. Commun.* **2001**, 1670–1671.
- (12) Zhang, X.-M.; Hou, J.-J.; Wu, H.-S. *Dalton Trans.* **2004**, 3437–3439. (b) Zhang, X.-M. *Coord. Chem. Rev.* **2005**, 249, 1201–1219. (c) Cheng, L.; Zhang, W. X.; Ye, B. H.; Lin, J. B.; Chen, X. M. *Inorg. Chem.* **2007**, 46, 1135–1143.
- (13) Tang, S. F.; Song, J. L.; Mao, J. G. *Eur. J. Inorg. Chem.* **2006**, 2011. (b) Bauer, S.; Bein, T.; Stock, N. *Inorg. Chem.* **2005**, 44, 5882. (c) Yang, B. P.; Mao, J. G. *Inorg. Chem.* **2005**, 44, 566.
- (14) Sheldrick, G. M. *SHELXTL, Crystallographic Software Package, version 5.1*; Bruker-AXS: Madison, WI, 1998.
- (15) Palenik, G. J.; Rendle, D. F.; Carter, W. S. *Acta Crystallogr., Sect. B* **1974**, 30, 2390. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* **1987**, S1.
- (16) Kumar, V. S. S.; Pigge, F. C.; Rath, N. P. *Cryst. Growth Des.* **2004**, 4, 651.
- (17) Bauer, S.; Bein, T.; Stock, N. *J. Solid State Chem.* **2006**, 179, 145.
- (18) Hebbink, G. A.; Grave, L.; Woldering, L. A.; Reinhoudt, D. N.; van Vegel, F. C. J. M. *J. Phys. Chem.* **2003**, A107, 2483. (b) Faulkner, S.; Pope, S. J. A. *J. Am. Chem. Soc.* **2003**, 125, 10526. (c) Pope, S. J. A.; Kenwright, A. M.; Boote, V. A.; Faulkner, S. *J. Chem. Soc., Dalton Trans.* **2003**, 3780.