

Organic–Inorganic Hybrids Assembled from Lanthanide and 1,4-Phenylenebis(phosphonate)

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Supporting Information

ABSTRACT: A series of novel organic-inorganic hybrids based on trivalent lanthanide (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho) and 1,4-phenylbis(phosphonate) formulated as $Ln[O_3P(C_6H_4)PO_3H]$ has been obtained as single phases under hydrothermal conditions. In the praseodymium compound (Za1), single crystals have been obtained and the crystal structure has been determined. Za1 crystallizes in the monoclinic space group, C2/c, with a = 5.6060(4) Å, b = 20.251(7) Å, c = 8.2740(6) Å, $\beta = 108.52(1)^{\circ}$. All other compounds are isostructural to Za1 as confirmed by Rietveld refinement using X-ray powder diffraction data. Compounds are characterized by thermal analyses (TG-MS and SDTA), elemental analysis, IR spectra, and X-ray thermodiffraction analysis. Their visible photoluminescence properties are also discussed.



INTRODUCTION

Organic-inorganic hybrids in general and metal-organic frameworks (MOFs) in particular constitute an important class of compounds in the exploratory research area of advanced materials design. In particular, metal phosphonates represent a particularly versatile field for investigation because of the great latitude open to the investigator. During the past two decades, a considerable amount of research attention has been devoted to the chemistry of metal phosphonates for their potential applications in ion exchange, catalysis, and sensor devices.¹⁻⁵ The wide choice of metals (mono-, di-, tri-, tetra-, penta-, and hexavalent) and the variety of organic ligands that can be utilized to prepare the metal phosphonate mean that a wide latitude of choices is possible. Because almost any desired organic compound may be converted into a phosphonic acid by known reactions, it is thus possible to introduce phosphonate ligands with different functional groups into the hybrid structure, which suggests the possibility of tailored structures for highly specific functions,⁶ and even with unusual properties.⁴ Often, metal phosphonates exhibit polymeric structures consisting of chains, layers, or threedimensional networks. By utilizing diphosphonates, it is possible to cross-link the layers and to space the cross-links by using spacer molecules, such as phosphorous or phosphoric acid, to create a porous structure. Recently, investigations of di-, tri-, and tetravalent metal phosphonates have yielded exciting structural diversity with interesting chemistries and applications, $^{7-31}$ including open framework structures $^{20-26}$ and porous pillared layered structures.^{7,8} The synthesis of lanthanide phosphonates has drawn the scientist's attention for their possible optical and

magnetic properties. However, reports on lanthanide phosphonates are rather limited because lanthanide phosphonates normally have low solubility in water and organic solvents, and hence it is difficult to obtain single crystals suitable for X-ray structural determination.²⁸ Nevertheless, the elucidation of the structures of lanthanide phosphonates is very important since these compounds may exhibit useful luminescent properties in both the visible and near IR regions. In particular, reports on the structure and photoluminescence properties of lanthanide (Ln) arylphosphonates or aryldiphosphonates are still scarce,^{28,32,33} although this kind of ligand may enhance the fluorescence of the lanthanide ions, via the so-called antenna effect.

Hydrothermal reaction of lanthanide(III) salts with 1, 4-phenylenebis(phosphonic acid), afforded a series of new isostructural compounds, with three-dimensional networks formulated as $Ln[O_3P(C_6H_4)PO_3H]$ (where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho). Herein we report their synthesis, crystal structure, thermal behavior, and luminescent properties through luminescence and excitation spectroscopy and the excitedstate lifetimes.

EXPERIMENTAL SECTION

Synthesis of 1,4-Phenylenebis(phosphonic acid) (H₄BDP). To a three-necked round-bottom flask, 5 g of 4,4'-dibromobenzene

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Figure 1. SEM images of $[Ln(HO_6P_2C_6H_4)]$, (where Ln = La (a), Ce (b), Pr (c), Nd (d), Sm (e), Eu (f), Gd (g), Tb (h), Dy (i), and Ho (j)).



Figure 2. Powder XRD patterns of $[Ln(HO_6P_2C_6H_4)]$ compared with that calculated for $Pr[O_3P(C_6H_4)PO_3H]$.

Table 1. Crystallographic Data for Za1

empirical formula	$C_6H_5P_2O_6Pr$
formula weight/g mol^{-1}	375.95
temperature/K	115(2)
wavelength/Å	0.71073
crystal system	monoclinic
space group	C2/c
unit cell dimensions	
a (Å)	5.6060(4)
b (Å)	20.251(7)
c (Å)	8.2740(6)
α (°)	90
β (°)	108.522(11)
γ (°)	90
cell volume/Å ³	890.7(3)
Z	4
calc density/mg m^{-3}	2.804
absorption coefficient/mm $^{-1}$	5.833
F(000)	692
crystal size (mm ³)	$0.22\times0.09\times0.06$
theta range for data collection/ $^{\circ}$	2.01-27.1
index ranges	$-7 \le h \le 7, -25 \le k \le 25,$
	$-10 \le l \le 10$
reflections collected	4543
independent reflections	971 [$R(int) = 0.115$]
completeness to theta _{max}	98.30%
absorption correction	refined (XABS2)
max and min transmission	1 and 0.3984
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	971/5/85
goodness-of-fit on F^2	1.053
final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1=0.054,wR_2=0.122$
R indices (all data)	$R_1=0.112,wR_2=0.151$
largest diff peak and hole/ $e \cdot Å^{-3}$	1.449 and -1.914
-	

(Aldrich, 98%) and 50 mL of 1,3-diisopropylbenezene (TCI America) were added. The system was flushed with N₂ and 0.5 g of NiBr₂ (Aldrich) was added. The reaction was slowly heated to 160 °C, while 10 mL of triethyl phosphate (Aldrich, 98%) was added over a 6-h period. The system was heated to 180 °C and stirred for 24 h. NiBr₂ and triethylphosphite were sequentially added twice, with half the amount each time. After such additions, the temperature was reduced to 120 °C and the system was left open to the atmosphere for 48 h. The reaction was distilled to remove solvents and byproducts; extractions were completed using hexanes. After recrystallization from hexanes, a hydrolysis using a 1:1 ratio of H₂O and HCl was carried out at 110 °C. The product was then washed and dried.¹⁰ Yield: ca. 2 g (40%).

Synthesis of Lanthanide 1,4-Phenylenebis(phosphonate) (Ln[O₃P(C₆H₄)PO₃H]). In a typical synthesis, 0.2 mmol (0.05 g) of 1,4-phenylylenebis(phosphonic acid), 0.2 mmol of Ln(NO₃)₃·*x*H₂O (x = 5, 6) (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho), and 6 mL of water were mixed. The reaction mixture was stirred until a homogeneous gel was formed (pH = 1-2), sealed in a PTFE-lined stainless steel autoclave with an internal volume of 15 mL and heated at 180 °C for 5 days under autogenous pressure. After cooling, the resulting products were filtered off, washed with water, and dried in an oven at 80 °C. In the case of Pr[O₃P(C₆H₄)PO₃H] (Za1), the product contains a mixture of pale green powder and tiny plate-shaped crystals. A suitable single crystal was selected to perform the single-crystal X-ray diffraction studies.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for $Za1^a$

Pr1-O3	2.371 (9)
Pr1-O2	2.435 (8)
Pr1-O1	2.516 (9)
P1-O3 ⁱ	1.519 (10)
P1-O ⁱⁱ	1.542 (9)
P1-O1 ⁱⁱⁱ	1.574 (9)
Pr1-Pr1	4.2503(6)
O3 ⁱ -P1-C1	107.5 (5)
O1 ⁱⁱⁱ -P1-C1	107.9 (5)
$O2^{ii} - P1 - C1$	110.6(5)
O2 ⁱⁱ -P1-O1 ⁱⁱⁱ	103.0(5)
O3 ⁱ -P1-O1 ⁱⁱⁱ	110.7 (5)
$O3^i - P1 - O2^{ii}$	116.9 (5)
^{<i>a</i>} Symmetry codes: (i) − <i>x</i> − 1/2, − <i>y</i> + 1/2, − <i>z</i> + 1	1; (ii) $-x + 1/2, -y +$

1/2, -z + 1; (iii) -x, y, -z + 1/2.

Table 3. Hydrogen-Bond Geometry in Za1 (Å, $^{\circ}$)^{*a*}

$D-H\cdots A$	D-H [Å]	$H{\boldsymbol{\cdot}}{\boldsymbol{\cdot}}{\boldsymbol{\cdot}}A\left[\mathring{A}\right]$	$D \cdots A \left[{\rm \mathring{A}} \right]$	$D-H\cdots A\left[deg ight]$			
$O1-H10\cdots O1$ ^I	1.0(1)	1.54(8)	2.47(1)	151(14)			
^{<i>a</i>} Symmetry codes: (i) $-x + 1, +y, -z + 1/2$.							

Single-Crystal X-ray Diffraction Studies. Data collection was performed at 115 K on a Bruker Smart APEX-II CCD diffractometer with a Mo K α source operated at 40 kV and 40 mA. The crystal structure was solved by direct methods. The refinement was performed using full-matrix least-squares on F^2 . All non-H atoms were anisotropically refined. All H atoms were either geometrically placed riding on their parent atoms or located from the difference Fourier map, with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached. Crystallographic calculations were carried out using the following programs: APEX2³⁴ for data collection, SAINT³⁴ for cell refinement and data reduction, SADABS³⁵ for empirical absorption correction, SHELXS-97³⁶ for structure solution, XABS2³⁷ for refined absorption correction, SHELXL-97³⁶ for structure refinement and to prepare materials for publication, PLATON³⁸ for the geometrical calculations, and Diamond³⁹ for molecular graphics.

Thermal Characterization. A Mettler-Toledo TGA/SDTA851^e and a DSC822^e were used for the thermal analyses in an oxygen dynamic atmosphere (50 mL/min) at a heating rate of 10 °C/min. In all cases, ca. 10 mg of powder sample was thermally treated, and blank runs were



Figure 3. (a) Asymmetric unit of $[Pr(HO_6P_2C_6H_4)]$. (b) Coordination modes of 1,4-phenylbis(phosphonate) ligand $[\mu_6 - 2(\eta^1: \eta^2: \eta^1)]$. (c, d) Perspective view of the coordination environment of Pr^{3+} . (e) Perspective view of the inorganic layer along the *b*-axis. (f, g) Projection of the structure along the *a*-axis (g) and *c*-axis (f), respectively.

performed. In TG tests, a Pfeiffer Vacuum ThermoStar GSD301T mass spectrometer was used to determine the evacuated vapors. The masses 18 (H₂O), 44 (CO₂), and 78 (C_6H_6) were tested by using a detector C-SEM, operating at 1200 V, with a time constant of 1 s.

Morphological Characterization. Micrographs and X-ray microanalysis (SEM/EDX) were recorded with a JEOL JSM-6100 electron microscope operating at 20 kV coupled with an INCA Energy-200 energy dispersive X-ray microanalysis system (EDX) with a PentaFET ultrathin window detector. SEM images show that the particles are nanoplates with diameters between 200–400 nm (see Figure 1), and EDX confirmed that the ratio Ln/P is ca. 1:2.

Infrared Absorption Spectra. The infrared data were collected at room temperature (RT) using a FT-IR Bruker Tensor-27 spectrometer from KBr pellets. The spectra were collected over the range $4000-400 \text{ cm}^{-1}$ by averaging 15 scans at a maximum resolution of 4 cm⁻¹.

Powder X-ray Diffraction Studies. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance powder X-ray diffractometer with $Cu-K\alpha$ radiation. The samples were gently ground in an agate mortar in order to minimize the preferred orientation. Routine XRD data were collected at room temperature over the angular 2θ range $4{-}40^\circ$ with a step of 0.009° and a counting time of 0.15 s/step. High-resolution X-ray diffraction (XRD) measurement collected at RT over the angular 2θ range $4-90^\circ$ with a step of 0.013° and a counting time of 7 s. The PXRD patterns of the compounds were compared with the calculated one (see Figure 2), indicating that the products have been successfully obtained as isostructural pure crystalline phases. Rietveld refinement was carried out by the FullProf program.⁴⁰ Single crystal structure of Za1 was used as the initial model in all cases. The PXRD profiles have been modeled as a Cauchy (Lorentzian) function in the range $2\theta = 6-70^{\circ}$. The zero offset, the scale factor, six background terms, fwhm parameters, the unit cell, asymmetry correction for peaks below $2\theta = 20^\circ$, and the positions of Ln, O, and P atoms (excepting C and H) were refined.

Powder X-ray Thermodiffraction Studies. Powder X-ray thermodiffraction studies were performed in air. The sample was placed in an Anton Paar XRK 900 reactor chamber on a Bruker D8 Advance diffractometer with *DAVINCI* design, using Cu K α radiation, equipped with a LynxEye detector. Each powder pattern was recorded in the 7–60° range (2 θ) from RT to 900 °C with a step of 0.02° and a counting time of 0.4 s. The temperature ramp between two consecutive temperatures was 10 °C/min.

Gas Adsorption Study. Nitrogen adsorption data were performed volumetrically at 77 K using a Micromeritics ASAP 2020 analyzer.

Luminescence and Excitation Measurements. RT luminescence and excitation spectra were measured using a standard spectrofluorometer (Jobin-Yvon Fluorolog-2). The sample was excited with a 150 W Xe-lamp by an excitation monochromator and the dispersed emitted light was detected with a photomultiplier (Hamamatsu R928) at a 90° configuration to minimize direct light from the lamp. Excitation spectra were corrected for the lamp response at different wavelengths. Luminescence spectra were not corrected for the detection system response (monochromator + detector). Emission lifetimes were measured in a FLSP920 fluorescence spectrometer (Edinburgh Inst.), equipped with a microsecond xenon flashlamp and a cooled R928P photomultiplier (Hamamatsu), based on the multichannel scaling technique (repetition rate 50 Hz and pulse width of 1 μ s).

RESULTS AND DISCUSSION

The detailed crystallographic data of and the structure refinement parameters of Pr-compound (Za1) are summarized in Table 1. Selected bond distances, angles, and hydrogen bonds are given in Tables 2 and 3. The asymmetric unit of Za1 is relatively



Figure 4. Topological representation of the binodal frameworks of [Ln(HBDP)]: P corresponds to 4-connected nodes and Pr is 6-connected nodes. Internodal distances: $P \rightarrow P 6.44 \text{ Å}$; $P \rightarrow Pr 3.24 \text{ Å}$, 3.78 Å, and 3.84 Å.

simple containing half Pr³⁺ cation and half the HBDP³⁻ ligand as displayed in Figure 3a. This is a consequence of the fact that Pr³⁺ cation is situated on a crystallographic 2-fold axis along the *b*-direction, while $HBDP^{3-1}$ resides on an inversion center. The coordination mode of the $HBDP^{3-}$ ligand is depicted in Figure 3b. We should mention that this coordination mode has not yet been reported. However, the same coordination mode has been reported with another similar ligand.²⁹ The Pr³⁺ cation is bonded to eight oxygen atoms that come from six phosphonate crystallographically equivalent groups (Figure 3c). Its coordination geometry may be described as a distorted bicapped trigonal-prism, ${PrO_8}$ (Figure 3d), out of six phosphonate groups surrounding Pr^{3+} : (i) two of them are coordinated in chelating modes via the oxygen atoms O1 and O2, (ii) the other two act as a bridge between two adjacent Pr^{3+} cations within the oxygen atom O2, (iii) and the two remaining are bonded via oxygen atom O3. The distances Pr-O range from 2.371(9) to 2.516(9) Å, with average values of 2.44(1) Å. The Pr^{3+} polyhedra alternate in a chain edge-to-edge parallel to the [101] direction, and the distance between adjacent Pr^{3+} cations in the chain is 4.2503(6) Å. These chains are in turn connected via phosphonate groups along the [101] direction forming the inorganic layer (see Figure 3e). Connection between adjacent layers is ensured by HBDP³⁻ organic pillars leading to an alternation along c-axis of organic and inorganic fragments as depicted in Figure 3f,g, forming channels running along the *a*- and *c*-axis, with approximate dimensions of 6.5×4.2 Å² and 6.5×5.6 Å². Gas (N₂/77 K) adsorption study

Table 4. Refinement Indexes of Agreement	, Cell Parameters (<i>a</i> ,	<i>b</i> , <i>c</i> , β , and Volume)), and Distances Ln—	Ln and Ln−O of the
Ln-Compounds Compared with Single-Crys	stal Data of Za1			

Ln	Pr (single-crystal)	La	Ce	Pr	Nd	Sm
R _{Shannon} /Å	1.126	1.16	1.143	1.126	1.109	1.079
$R_{ m Bragg}$		2.62	4.41	3.48	4.91	3.92
$R_{\rm f}$		2.37	3.62	2.30	3.67	3.41
a (Å)	5.6060(4)	5.6184(4)	5.5897(9)	5.5746(6)	5.555(1)	5.5196(9)
b (Å)	20.251(7)	20.149(1)	20.073(3)	20.056(2)	20.050(4)	19.973(3)
c (Å)	8.2740(6)	8.3824(5)	8.325(1)	8.2868(8)	8.244(2)	8.179(1)
β (°)	108.52(1)	108.674(3)	108.573(7)	108.588(4)	108.496(8)	108.469(7)
cell volume/Å 3	890.7(3)	898.9(1)	885.4(2)	878.2(2)	870.7(3)	855.3(2)
Ln-Ln	4.2503(6)	4.2901(5)	4.2682(9)	4.2505(8)	4.223(1)	4.1970(9)
Ln-O(1)	2.516(9)	2.621(9)	2.65(2)	2.49(1)	2.54(3)	2.53(2)
Ln-O(2)	2.435(8)	2.501(8)	2.52(1)	2.48(1)	2.59(2)	2.44(2)
Ln-O(2)	2.650(9)	2.669(9)	2.74(2)	2.66(2)	2.66(2)	2.61(2)
Ln-O(3)	2.370(9)	2.33(1)	2.32(2)	2.21(2)	2.29(3)	2.41(2)
Ln	Pr (single-crystal)	Eu	Gd	Tb	Dy	Но
R _{Shannon} /Å	1.126	1.066	1.053	1.04	1.027	1.015
R _{Bragg}		3.13	6.03	4.56	6.70	8.14
$R_{\rm f}$		2.13	4.15	3.92	4.67	5.09
a (Å)	5.6060(4)	5.4997(7)	5.480(1)	5.4735(7)	5.4462(9)	5.4309(5)
b (Å)	20.251(7)	19.955(3)	19.943(4)	19.894(2)	19.869(3)	19.844(2)
c (Å)	8.2740(6)	8.158(1)	8.132(2)	8.116(1)	8.086(1)	8.0629(6)
β (°)	108.52(1)	108.353(5)	108.367(8)	108.323(5)	108.237(6)	108.208(3)
cell volume/Å ³	890.7(3)	849.8(2)	843.5(3)	838.9(2)	831.1(2)	825.4(1)
Ln-Ln	4.2503(6)	4.1904(9)	4.173(1)	4.1764(9)	4.169(1)	4.1512(9)
Ln-O(1)	2.516(9)	2.53(2)	2.59(3)	2.51(2)	2.48(2)	2.49(2)
Ln-O(2)	2.435(8)	2.52(2)	2.62(2)	2.47(1)	2.26(2)	2.28(1)
Ln-O(2)	2.650(9)	2.62(2)	2.69(2)	2.61(2)	2.64(2)	2.56(1)

was performed in order to check the accessibility of channels, and the results prove they are not accessible ($S_{BET} = 29 \text{ m}^2/\text{g}$). Taking as network nodes the phosphorus atoms and Ln^{3+} cations, Ln-compounds can be envisaged as binodal frameworks built-up from one type of 4-(P-atom) and 6-connected (Ln^{3+} cation) nodes (Figure 4).

All the other members of the family have been obtained as microcrystalline powders. Rietveld refinement shows the isostructurality of all Ln-compounds, tuned by the influence of the Ln^{3+} cations (see Table 4). The final values obtained of figures of merit are within acceptable ranges,⁴¹ as the model used adjusts very well with the experimental data. The final Rietveld refinements plots for all compounds are shown in Figure 5. The variation of unit cell parameters show dependency to the Shannon's effective ionic radii,⁴² and the expected tendencies are observed: the ionic radii decrease linearly as the unit cell parameters (*a*, *b*, *c*, β , and volume) and distances Ln–Ln do. These tendencies are illustrated in Figure 6.

Selected IR spectra of Ln-compounds are depicted in Figure S1 (see Supporting Information). The presence of the HBDP³⁻ ligand in the Ln-compounds is confirmed by two bands at 1140 cm⁻¹ (strong) and 1046 cm⁻¹(medium) characteristic of the stretching vibrations of the phophonate $P-O_3$ groups, as well as the broad band at around 1634 cm⁻¹ characteristic of P=O stretching vibrations. The band at 1260 cm⁻¹ may attributed to P=O deformation vibration. Bands between

600 cm⁻¹ and 400 cm⁻¹ main correspond to the bending modes of the PO₃ group. However, the band at 538 cm⁻¹ may be assigned to Ln—O stretching vibration. The band at 975 cm⁻¹ is characteristic of P–C stretching vibrations. Bands at 1385 cm⁻¹ and 663 cm⁻¹ are, respectively, characteristic of C–C stretching vibrations of the phenylene group and in-plane deformation vibrations of para-disubstituted aromatic ring with identical groups. Bands at 836 cm⁻¹ and 819 cm⁻¹ are attributed to the C–H out-of-plane vibrations for para-disubstituted phenylene rings. The broad bands around 3600 and 3000 cm⁻¹, arising from the O–H stretching vibrations of the protonated phosphonate oxygens O(1), suggest that extensive hydrogen bonds are present in the Ln-compounds because of the absence of O–H deformation band around 1568 cm⁻¹, as they do not contain either coordinated or lattice water molecules.^{10,11,43–46}

The thermal stability in air of Ln-compounds was investigated. The TG curves, and some typical mass spectrometry analysis curves, are depicted in Figure S2a,b (see Supporting Information). According to the difference in their thermal stability, TG curves may be divided into two groups named **hs** (high stability) and **ms** (medium stability). TG curves of Ln-compounds reveal the observed total mass losses, presented in the Table 5, from room temperature up to 1200 °C, and a 1:1 mixture of LnPO₄ and Ln(PO₃)₃ as the final product. The TG curves of Ln-compounds very closely resemble each other and show that this series of compounds is characterized by high

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Figure 5. Observed (red) and calculated (black) profiles for the final Rietveld refinement of $[Ln(HO_6P_2C_6H_4)]$ compounds (Ln = La, Ce, Pr, Nd, Eu, Dy, Ho). The difference plot (blue) is on the same intensity scale.

thermal stability. A noticeable increase in thermal stability has been observed in the case of Dy- and Ho-compounds. From room temperature to ca. 600 °C in the case of **hs**, and to ca. 500 °C in the case of **ms**, no noticeable mass loss (or a slight mass loss of ca. 3%) was detected. Between ca. 600 and 1100 °C in the case of **hs**, and between ca. 500 and 1000 °C in the case of **ms**, the mass loss proceeds in continuous and overlapping stages and corresponds to the loss of the phenyl group. The associated mass spectrometry m/z 18 (H₂O), 44 (CO₂), and 78 (C₆H₆) curves are in a good agreement with TG curves. The very slight mass loss below 600 and 500 °C for hs and ms, respectively, is explained by the m/z 78 curve which shows the desorption of the phenyl group in the ranges 500–750 °C (hs) and 400–700 °C (ms), with first maxima at around 560 °C (hs) and 528 °C (ms). After 600 °C (hs) or 500 °C (ms), the mass loss increases rapidly due to the combustion of phenyl groups and that is manifested by a series of bands on the m/z 18 and 44 curves in the ranges of 600–1100 °C (hs) and 500–1000 °C (ms).

The X-ray thermodiffraction analysis of the Ho-compound carried out under air heating up to 900 $^{\circ}$ C (Figure 7) has confirmed that no significant structural change occurs up 600 $^{\circ}$ C. At 650 $^{\circ}$ C, a noticeable diffraction intensities drop is



Figure 6. Variation of cell parameters (*a*, *b*, *c*, and β), volume, and distance Ln–Ln versus Shannon's ionic radii (Å) of Ln³⁺ cations in the isostructural Ln-compounds.

observed and peak broadening is observed, and continues decreasing and broadening until 850 °C. At 900 °C, practically no diffraction peaks have been observed. Nevertheless, by maintaining the temperature at 900 °C for a longer time as well as after cooling down to 30 °C, two new phases have been formed characterized by a series of broad diffraction peaks corresponding to the formation of HoPO₄ and Ho(PO₃)₃.^{47,48} The X-ray thermodiffraction study is consistent with TG analysis and confirms the very high thermal stability of the Ln-compounds reported in this paper.

The RT luminescence and excitation spectra of the Eu- and Tb-compounds as powders are shown in Figure 8a,b. The emission peaks in the luminescence spectra are assigned to the electronic transitions from the ⁵D₀ and ⁵D₄ multiplet to lower energy states ⁷F_J of Eu³⁺ and Tb³⁺, respectively. The excitation spectra correspond to transitions from the ground states — ⁷F₀ and ⁷F₆Eu³⁺ and Tb³⁺, respectively — to excited states according to the Dieke's diagram (see insets of Figure 8a,b).⁴⁹ In addition to these f—f transitions, the excitation spectra show strong bands at wavelengths smaller than 340 nm, which are tentatively assigned to an energy transfer process from the ligand. The presence of organic ligands usually leads to an absence of luminescence due to the strong competition with nonradiative relaxation processes

Table 5. Calculated and Found Percentages of C-H and Total Mass Losses of $[Ln(HO_6P_2C_6H_4)]$ Compounds

	calculated				experime	ntal	
compound	$M_{\rm r}$ (g/mol)	C (%)	H (%)	weight loss (%)	C (%)	H (%)	weight loss (%)
$La[O_3P(C_6H_4)PO_3H]$	373.95	19.25	1.34	20.62	19.1	1.2	21.8
$Ce[O_3P(C_6H_4)PO_3H]$	375.16	19.19	1.33	20.55	19.4	1.1	21.2
$Pr[O_3P(C_6H_4)PO_3H]$	375.95	19.15	1.33	20.51	18.7	1.4	21.3
$Nd[O_3P(C_6H_4)PO_3H]$	379.29	18.98	1.32	20.33	19.2	1.3	20.8
$Sm[O_3P(C_6H_4)PO_3H]$	385.41	18.86	1.30	20.01	18.7	1.2	21.0
$Eu[O_3P(C_6H_4)PO_3H]$	387.01	18.60	1.29	19.92	18.9	1.1	20.4
$Gd[O_3P(C_6H_4)PO_3H]$	392.30	18.35	1.27	19.65	18.1	1.3	20.2
$Tb[O_3P(C_6H_4)PO_3H]$	393.97	18.27	1.27	19.57	18.6	1.2	20.4
$Dy[O_3P(C_6H_4)PO_3H]$	397.55	18.11	1.26	19.40	18.2	1.3	19.6
$Ho[O_3P(C_6H_4)PO_3H]$	399.98	18.00	1.25	19.28	18.1	1.2	18.7



Figure 7. X-ray thermodiffractogram of Ho-compound recorded in air heating up from 50 to 900 °C. Color code corresponding to the structural changes.



Figure 8. RT emission (up) and excitation (down) spectra of (a) Euand (b) Tb-compounds. Emission spectrum was obtained upon excitation at 464 and 376 nm, while excitation spectrum was performed detecting luminescence at 615 and 545 nm, for Eu- and Tb-compounds, respectively. Energy level scheme of Eu^{3+} and Tb^{3+} ion with the transitions responsible for the luminescence and excitation spectra are depicted in the inset.

induced by high energy ligand vibrations. Moreover, it is wellknown that a strong quenching of luminescence occurs for high concentration of lanthanide ions due to energy migration of the excitation to quenching impurities (killer traps).⁵⁰ This is especially relevant for two- or three-dimensional lattices. Therefore, the observation of visible luminescence in a solid form in concentrated lanthanide compounds at room temperature is an outstanding result itself. Additionally, the sharp lines observed in luminescence and excitation spectra are a clear demonstration of the good crystalline quality of the samples. The absence of emission from the excited state ${}^{5}D_{1}$ and ${}^{5}D_{3}$ to the ground state in Eu³⁺ and Tb³⁺, respectively, can be explained by the energy gap's law taking into account the maximum phonon energy of the lattice or by resonant energy transfer processes between adjacent Eu³⁺ or Tb³⁺ ions. In this process the excited electron in ⁵D₁ can relax to ⁵D₀ multiplet and excites the ground state ${}^{7}F_{0}$ electron to the ${}^{7}F_{3}$ state in a neighboring Eu³⁺ ion since the energy difference between these states is the same. In the same manner, a Tb³⁺ ion can relax from the ${}^{5}D_{3}$ level to the ${}^{5}D_{4}$ and excites a near neighbor Tb³⁺ from the ${}^{7}F_{6}$ to the ${}^{7}F_{1,0}$. ⁵¹ The same process can be responsible for the lack of visible emission in all the other members of the series. Temporal dependence of Tb³⁺ and Eu³⁺ luminescence, corresponding to transitions from the ${}^{5}D_{4}$ and ${}^{5}D_{0}$ to lower energy levels, shows a single exponential behavior

(Figure S3, see Supporting Information) with lifetimes of 1.89 ± 0.02 ms and 1.397 ± 0.015 ms, respectively.

CONCLUSIONS

The hydrothermal synthesis and the structural characterization of a series of novel isostructural metal—organic hybrids based on lanthanide and 1,4-phenylenebis(phosphonate) $Ln[O_3P(C_6H_4)PO_3H]$ (where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Ho) have been reported. These compounds have been obtained as single phases and exhibit very high thermal stability, and their photoluminescence properties are also discussed. Currently, our work is focused on using the extended analogue 1,4-biphenylenebis(phosphonate) and spacer molecules as a second ligand, such as phosphorous or phosphoric acid, to create porous structures, as these may be promising materials in the fields of gas storage and photoluminescence.

ASSOCIATED CONTENT

Supporting Information. IR spectra of Ln(HBDP) compounds, TG curves of Ln(HBDP) with representative MS curves for Ho-compound and La-compound, room temperature of Eu³⁺ emission decay curve, and X-ray crystallographic information (CIF files) for the Ln(HBDP) compounds can be obtained free of charge via the Internet at http://pubs.acs.org.

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