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Lanthanide diphosphonates based on a V-shaped ligand: syntheses, structures, experimental and theoretical luminescence properties†

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One series of isostructural lanthanide phosphonates, namely $[Ln_2(H_2L)_3] \cdot [(H_2O)_5]$ (H_4L = (5-methyl-1,3-phenylene)bis(phosphonic acid); Ln = Eu (1), Gd (2), Tb (3), and Dy (4)), have been successfully synthesized from a V-shaped rigid ligand. Systematic characterizations using single-crystal and powder X-ray diffraction (XRD), thermogravimetric analyses (TGA), and photoluminescence spectroscopy were accomplished. It was found that these compounds all crystallize in the cubic $I2_13$ space group, showing three-dimensional framework structures. The frameworks are stable up to 350 °C and show their respective characteristic metal-centered emissions. The photoluminescence properties were also theoretically investigated by using a newly developed software program – LUMPAC. The energy transfer and back energy transfer rates were estimated, and the $T_1 \rightarrow {}^5D_1$ and $T_1 \rightarrow {}^5D_0$ channels were revealed to be the dominant pathways. The combination of experimental and theoretical studies on the photoluminescence properties substantially supports the understanding and design of highly luminescent inorganic–organic hybrid materials.

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Introduction

Metal phosphonates have emerged as an important type of functional materials¹ due to their potential applications in the field of gas storage/separation,² catalysis,³ proton conduction,⁴ magnetism,⁵ luminescence,⁶ magnetic resonance imaging (MRI),⁷ and so on. But for a long time, the number of metal phosphonates was limited compared with the carboxylate analogues due to their low solubility and poor crystallinity.⁸ To overcome these obstacles, a few effective strategies have been developed, which include (1) introduction of a functional group (*e.g.*, carboxylate, hydroxyl, amine, crown ether, sulfonyl and pyridine) to the organic building blocks and (2) introduction of a second ligand (*e.g.*, oxalate, 2,2'-bipy, 4,4'-bipy and 1,10-phen) to the reaction system. By employing these strategies, more and more metal phosphonates have been successfully synthesized in the past two decades. Among these compounds, lanthanide phosphonates are of particular interest because of their diverse structures and fantastic photophysical properties.⁹

Phosphonate group has three oxygen atoms and can coordinate to metal ions with many possible coordination modes when they are in any state of protonation.^{1a} Lanthanide ions usually exhibit a high coordination number. The combination of lanthanide centers with phosphonate ligands leads to diverse structures. Meanwhile, lanthanide compounds emit intense well-defined narrow bands from the UV to near IR spectral range but suffer from low molar absorption coefficients.¹⁰ Phosphonate ligands especially rigid ones can function as “antennae”, sensitizing the emissive state of lanthanide centers *via* energy transfer.¹¹ Thus, lanthanide phosphonates are highly desirable.

Although great progress has been made, it is still necessary to synthesize more lanthanide phosphonates and characterize their structures and properties. It is believed that the structure of lanthanide phosphonates depends greatly on the size, shape and coordination mode of the ligand. The size and shape of the ligand can be tailored by varying the organic moiety attached to the phosphonic acid group. Similar ligands with different sizes would result in a myriad of architectures, either dense or porous. The ligand shape (linear or angular) would influence the extension direction and lead to different structures. For carboxylate analogues, many interesting structures have been formed from ligands with predesigned geometry (V-shaped or angular),¹² illustrating that ligand shape has significant influence on the structure formation. The coordination mode can be altered by varying the synthesis conditions (*e.g.*, pH value, temperature,

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template, and metal/ligand molar ratio). Definitely, it is very important to understand the effects of these factors on the structure formation and construct the structure–property relationship. Thereafter, new compounds for a specific function can be designed and synthesized. Meanwhile, it is also crucial to understand the mechanism of energy transfer. The luminescence properties of lanthanide phosphonates mainly depend on the first coordination sphere. With the aid of software, the coordination geometry, singlet and triplet excited state energies, Judd–Ofelt intensity parameters, energy transfer and back transfer rates, radiative and nonradiative emission rates, quantum efficiency, and overall quantum yield can be calculated. However, this kind of theoretical study is still unexplored.¹³

In this paper, we report one series of new lanthanide diphosphonates which were synthesized from one V-shaped rigid ligand. The choice of this ligand was based on the following considerations: (1) the crystal structure of lanthanide phosphonates constructed from V-shaped ligands could be very interesting because of their angular shape, but until now, the number of metal phosphonates synthesized from V-shaped ligands is still very low, especially for lanthanide phosphonates;¹⁴ (2) rigid ligands are beneficial to thermal stability; (3) rigid ligands are expected to be good sensitizers. Their structural and photoluminescence features were characterized. To have a better understanding of the energy transfer process, their photoluminescence properties were also modelled with a newly developed software program – LUMPAC.¹⁵

Experimental section

Materials and instruments

Triethyl phosphite (Aldrich) and 1,3,5-trimethylbenzene (Aldrich) were dried by heating to reflux over sodium and distillation under argon atmosphere in a two-necked flask equipped with a condenser and a solvent collector. Elemental analyses were performed on a Vario EL III elemental analyzer. IR spectra were recorded on a Nicolet 6700 FTIR spectrometer as KBr pellets in the range of 4000–400 cm^{−1}. Powder X-ray patterns were obtained on a Bruker D8 Advance diffractometer using CuK α radiation (Fig. S1–S4 in the ESI†). Solution ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker AVANCE III NMR (600 MHz). For the ³¹P NMR spectrum, H₃PO₄ was used as the standard reference. Thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 449C unit at a heating rate of 10 °C min^{−1} under nitrogen atmosphere. The excitation and emission spectra of ligand H₄L and compounds 1–4 were recorded on a FluoroMax-4 spectrofluorometer. Lifetime measurements of compounds 1 and 3 were performed on an Edinburgh FLS920 fluorescence spectrometer equipped with a 450 W Xe lamp. The lifetime values were obtained by single-exponential function fit of the decay profiles using F900 analysis software. The quality of the obtained values was evaluated by “reduced chi-squared”.

Single-crystal structure determination

Single-crystal X-ray diffraction measurements of compounds 1 to 4 were carried out on a Bruker SMART APEX II CCD diffractometer (Mo K α radiation, λ = 0.71073 Å) at room temperature. SAINT was used for integration of the intensity of reflections and scaling.¹⁶ Absorption corrections were carried out with the program SADABS.¹⁷ Crystal structures were solved by direct methods using SHELXS.¹⁸ Subsequent difference Fourier analyses and least-squares refinement with SHELXL-97 (ref. 19) allowed for the location of the atom positions. In the final step of the crystal structure refinement, hydrogen atoms of idealized –CH₂ and –CH₃ groups were added and treated with the riding atom mode, and their isotropic displacement factors were chosen as 1.2 and 1.5 times the preceding carbon atoms, respectively. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the water molecules of 1–4 were located from the difference Fourier map and were not included in the refinements. The crystallographic details for compounds 1–4 are summarized in Table 1. The data have been deposited with the Cambridge Crystallographic Data Centre (CCDC), with deposition numbers CCDC 1400186–1400189 for compounds 1–4.

Synthesis of (5-methyl-1,3-phenylene)bis(phosphonic acid) (H₄L)

The ligand (5-methyl-1,3-phenylene)bis(phosphonic acid) (H₄L) was synthesized *via* the Arbuzov reaction²⁰ using 1,3-dibromo-5-methylbenzene and triethyl phosphite. Under an atmosphere of argon, a solution of 1,3-dibromo-5-methylbenzene (Energy Chemicals) and anhydrous NiBr₂ (Alfa Aesar) in 1,3,5-trimethylbenzene (Aldrich) was heated to reflux (180 °C) and triethyl phosphite was slowly added dropwise over 5 hours. After 3 days of reaction, the unreacted triethyl phosphite and 1,3,5-trimethylbenzene were removed under reduced pressure. The obtained oil was hydrolysed with conc. hydrochloric acid until a powder product was formed which was then isolated by filtration and washing with small portions of cold ethanol. ¹H NMR (DMSO-*d*₆) data for H₄L: δ = 7.61–7.57 (Ph-H, m, 2H), 2.50 (–CH₃, s, 6H) ppm. ¹³C NMR (DMSO-*d*₆) data: δ = 137.66, 133.72, 130.44, 127.99, 21.29 ppm. ³¹P NMR (D₂O) shows only one single peak at 4.65 ppm. IR (KBr, cm^{−1}): 3422.2 (w, b), 2768.2 (s, b), 2290.1 (m, b), 1636.6 (w), 1480.8 (w), 1457.0 (w), 1359.4 (m), 1219.5 (s), 1140.3 (vs), 1101.1 (s), 1031.5 (vs), 942.2 (vs), 904.6 (m), 818.4 (w), 767.7 (w), 624.6 (m), 591.0 (s), 571.5 (m), 490.9 (s), 464.3 (m).

Synthesis of compound [Ln₂(H₄L)₃][(H₂O)₅] (Ln = Eu (1), Gd (2), Tb (3) and Dy (4))

H₄L (0.063 g, 0.25 mmol), LnCl₃·6H₂O (1/6 mmol, Eu: 0.0611 g; Gd: 0.0620 g; Tb: 0.0622 g; Dy: 0.0628 g) and 10 mL of water were mixed and stirred in a Teflon-lined autoclave. The pH value of the solution was altered to about 2 with ten drops of 1 N NaOH. Afterwards, it was sealed and heated at 160 °C for 3 days and allowed to cool to room temperature in a time period of 24 hours. Colorless prismatic crystals were

Table 1 Crystal and refinement parameters of compounds **1–4**^{a,b}

Compound	1	2	3	4
Formula	C ₂₁ H ₃₄ Eu ₂ O ₂₃ P ₆	C ₂₁ H ₃₄ Gd ₂ O ₂₃ P ₆	C ₂₁ H ₃₄ Tb ₂ O ₂₃ P ₆	C ₂₁ H ₃₄ Dy ₂ O ₂₃ P ₆
Fw	1144.22	1154.80	1158.14	1165.30
Crystal system	Cubic	Cubic	Cubic	Cubic
Space group	<i>I</i> ₂ 3	<i>I</i> ₂ 3	<i>I</i> ₂ 3	<i>I</i> ₂ 3
<i>a</i> (Å)	16.0668(9)	16.0416(9)	16.0134(11)	15.9547(8)
<i>V</i> (Å ³)	4147.5(7)	4128.0(7)	4106.3(8)	4061.3(6)
<i>Z</i>	4	4	4	4
<i>D</i> _{calcd} (g cm ^{−3})	1.832	1.858	1.873	1.906
Abs coeff (mm ^{−1})	3.305	3.495	3.728	3.966
<i>F</i> (000)	2240	2248	2256	2264
Refins collected	2970	6288	10 160	4423
Independent refins/ <i>R</i> _{int}	1221/0.0459	1222/0.0602	1219/0.0518	1204/0.0448
Completeness to theta	97.7%	97.0%	98.3%	96.8%
GOF on <i>F</i> ²	1.007	1.037	1.103	1.057
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0351, 0.0698	0.0279, 0.0559	0.0348, 0.0782	0.0243, 0.0473
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0420, 0.0731	0.0374, 0.0595	0.0438, 0.0868	0.0298, 0.0490
Largest diff. peak and hole (e Å ^{−3})	0.512, −0.599	0.475, −0.425	1.358, −0.707	0.489, −0.292

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

collected and washed with deionized water in satisfying yield. For **1** and **2**, an unknown powder can be found in the product. The obtained mixture was first sonicated in an ultrasonic oscillator for a few minutes before filtration. Elemental analysis (%) calcd for C₂₁H₃₄Eu₂O₂₃P₆ (1144.22): C 22.04, H 2.99%; found: C 21.99, H 3.08%. IR (KBr, cm^{−1}): 3588.4 (w), 3451.0 (b, m), 3134.9 (b, w), 3030.7 (w), 2921.8 (w), 2860.0 (w), 2390.3 (b, w), 1651.6 (w), 1586.1 (vw), 1406.6 (w), 1253.2 (m), 1151.0 (s), 1085.2 (s), 994.5 (w), 930.1 (m), 911.2 (sh, m), 874.6 (m), 823.0 (w), 696.0 (m), 581.3 (m), 552.3 (m), 533.9 (m), 458.6 (m). Elemental analysis (%) calcd for C₂₁H₃₄Gd₂O₂₃P₆ (1154.80): C 21.84, H 2.97%; found: C 21.89, H 3.04%. IR (KBr, cm^{−1}): 3450.7 (b, m), 2918.9 (w), 2851.4 (w), 2387.5 (w), 2290.2 (w), 2175.4 (w), 1651.8 (w), 1589.1 (w), 1413.3 (w), 1256.4 (m), 1150.6 (m), 1089.3 (s), 1035.5 (s), 1009.6 (m), 988.8 (m), 943.6 (m), 903.6 (w), 867.2 (w), 830.1 (vw), 687.4 (m), 612.2 (m), 565.3 (m), 535.2 (m), 479.1 (w), 427.2 (w). Elemental analysis (%) calcd for C₂₁H₃₄Tb₂O₂₃P₆ (1158.14): C 21.78, H 2.96%; found: C 21.86, H 3.18%. IR (KBr, cm^{−1}): 3591.6 (w), 3449.2 (m), 3031.7 (w), 2919.8 (w), 2850.4 (w), 2389.8 (w), 651.2 (w), 1587.3 (vw), 1418.2 (w), 1253.7 (m), 1153.2 (s), 1086.2 (s), 994.2 (w), 930.0 (m), 909.3 (sh, m), 874.6 (w), 822.9 (w), 695.9 (w), 581.0 (m), 552.4 (m), 533.4 (m), 458.7 (m). Elemental analysis (%) calcd for C₂₁H₃₄Dy₂O₂₃P₆ (1165.30): C 21.64, H 2.94%; found: C 21.74, H 3.17%. IR (KBr, cm^{−1}): 3596.0 (w), 3448.9 (m), 3104.2 (b, m), 3030.7 (w), 2920.8 (w), 2858.1 (w), 2391.2 (b, w), 1651.7 (w), 1586.4 (vw), 1417.0 (w), 1253.7 (m), 1154.7 (s), 1086.5 (s), 994.2 (w), 931.1 (m), 910.3 (sh, m), 875.6 (sh, w), 823.3 (w), 696.0 (w), 580.8 (m), 552.5 (m), 533.4 (m), 458.7 (m).

Results and discussion

Structural description of compounds **1–4**

The structures of compounds **1–4** are identical except that the cell volume decreases in the sequence of **1** (Eu) > **2** (Gd)

> **3** (Tb) > **4** (Dy) due to the effect of lanthanide contraction. Here, only the structure of **1** will be depicted in detail. Compound **1** crystallizes in the cubic space group *I*₂3 with four molecules in each unit cell. Each asymmetric unit is composed of one europium(III) ion located at a three-fold axis, one lattice water molecule lying at a three-fold axis, one lattice water molecule lying at a two-fold axis and half diphosphonate ligand (H₂L)^{2−}, suggesting a formula of [Eu₂(H₂L)₃](H₂O)₅. The diphosphonate ligand is doubly deprotonated and adopts a tetradentate coordination mode. The coordination mode can be described as μ⁴:η¹:η⁰:η¹:η¹:η⁰:η¹, which means that each diphosphonate ligand bridges four symmetry-related europium ions in total with its four phosphonate oxygen atoms (see Scheme 1 and Fig. 1). The europium ion (Eu1) is octahedrally coordinated to six phosphonate oxygen atoms (O2 and O3) of six phosphonate ligands. These oxygen atoms are arranged in a *fac* coordination geometry (see Fig. S5 in the ESI†) with the O–Eu–O angles found in the range of 89.8(3)–90.1(3)° (see Table S1†) and the Eu–O distances in the range of 2.2748(18)–2.2869(19) Å (see Table 2), which are comparable to those found for other europium phosphonates.²¹ As far as we know, the octahedral coordination geometry is rarely observed in hydrothermally synthesized lanthanide compounds.²¹ The europium ions are interconnected by the

Scheme 1 Schematic representation of the coordination environment of ligand H₂L^{2−}.

Fig. 1 XPREP diagram of **1** (thermal ellipsoids are given at 50% probability). A: $1 + z, x, -1 + y$; B: $y, 1 + z, -1 + x$; C: $x, 2.0 - y, 0.5 - z$; D: $1.5 - z, x, 1.0 - y$; E: $2.0 - y, 1.5 - z, -1 + x$.

tetradentate diphosphonate ligands into a three-dimensional network (see Fig. 2a). Topological analysis reveals an unknown 2-nodal (4,6)-connected net featured by the Schläfli symbol $\{4^3, 6^2, 8\}_3\{4^9, 6^6\}_2$, wherein the $\{4^3, 6^2, 8\}$ and $\{4^9, 6^6\}$ notations correspond to the 4-connected diphosphonate ligands and the 6-connected Eu(III) ion nodes, respectively (see Fig. 2b). With the aid of the PLATON program, the free solvent-accessible volumes are estimated to be about 4.8–6.6% for compounds **1–4**, indicating that these frameworks are quite dense.

Until now, only very few lanthanide diphosphonates based on rigid diphosphonate ligands have been reported.²² Among these limited compounds, 2D layered or 3D pillar layered structures have been observed. A closer look at the bond distances of compound **1** reveals that all Eu...Eu distances of two neighboring europium ions are about 5.729 Å. Definitely, this can be ascribed to the bent shape of the diphosphonate ligand, which reduces the Eu...Eu distance between two neighboring phosphonate groups. The symmetrical structure of the ligand, identical coordination geometry and distance between neighboring metals make it possible to form a highly symmetrical 3D crystal structure, illustrating that the predesigned ligand geometry has a major effect on the structure formation.

TGA analyses

The TGA diagrams of compounds **1–4** are shown in Fig. 3. As expected, they exhibited similar thermal behaviors which

Table 2 Selected bond lengths found in compounds **1–4**

Ln–O	1 (Eu)	2 (Gd)	3 (Tb)	4 (Dy)
Ln(1)–O(2)#1	2.2748(18)	2.2667(15)	2.250(2)	2.2339(12)
Ln(1)–O(2)#2	2.2748(18)	2.2667(15)	2.250(2)	2.2340(12)
Ln(1)–O(2)	2.2748(18)	2.2667(15)	2.250(2)	2.2340(12)
Ln(1)–O(3)#3	2.2869(19)	2.2744(16)	2.259(2)	2.2506(13)
Ln(1)–O(3)#4	2.2869(19)	2.2744(16)	2.259(2)	2.2506(13)
Ln(1)–O(3)#5	2.2869(19)	2.2744(16)	2.259(2)	2.2506(13)

Symmetry transformations used to generate equivalent atoms: #1 $z + 1, x, y - 1$; #2 $y, z + 1, x - 1$; #3 $x, -y + 2, -z + 1/2$; #4 $-y + 2, -z + 3/2, x - 1$; #5 $-z + 3/2, x, -y + 1$.

(a)

(b)

Fig. 2 Three-dimensional packing (a) and topology (b) diagrams of compound **1** viewed along the *a*-axis.

underwent two major weight losses. The first ones in the temperature range of 30–135 °C could be ascribed to the removal of lattice water molecules (for **1**: calculated 7.8%, observed 7.5%; for **2**: calculated 7.7%, observed 7.5%; for **3**: calculated 7.7%, observed 7.8%; for **4**: calculated 7.6%, observed 7.5%). These frameworks remained stable until 350 °C, suggesting their good thermal stability. It was also confirmed by PXRD measurements that these samples retained their crystallinity after heating at 100 °C for 3 hours in an oven (see Fig. S1–S4 in the ESI†). Further heating led to the collapse of the frameworks and decomposition of the organic ligands.

Photoluminescence studies

The rigid diphosphonate ligand (H_2L^{2-}) possesses a delocalized π -electron conjugated system and could be a good

Fig. 3 TGA diagrams of compounds 1–4.

absorbing chromophore to sensitize Ln(III) emission. To examine its ability as an “antenna” for sensitizing Ln(III) emission, the steady-state emission spectra of the free ligand H_4L and compounds 1–4 in the solid state were measured at room temperature and the results are shown in Fig. 4–7.

The excitation spectrum of ligand H_4L recorded by monitoring at an emission wavelength of 468 nm exhibits a broad band in the range of 250–400 nm with a maximum at 305 nm. With the excitation wavelength fixed at 305 nm, the free ligand H_4L exhibits a broad emission band containing four components (450, 468, 480.5 and 491.5 nm), which can be assigned to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions of the aromatic ring in the ligand (see Fig. 4).

Under excitation, compounds 1 (Eu), 3 (Tb) and 4 (Dy) show the characteristic metal-centered luminescence of Eu, Tb and Dy, respectively. The excitation spectra of compounds 1, 3 and 4 are all dominated by a broad band in the range of 230–320 nm with a maximum at about 280 nm, confirming the existence of the ligand sensitizing process. Meanwhile, some characteristic transitions of the Eu(III), Tb(III) and Dy(III) energy levels can be observed in the excitation spectra. The blue shift of the maximum in comparison with that of the

Fig. 4 Normalized excitation and emission spectra of ligand H_4L (left) and compound 2 (right) at room temperature.

Fig. 5 Normalized excitation (left) and emission (right) spectra of compound 1 at room temperature obtained by exciting at 280 (red) and 393 nm (cyan), respectively.

free ligand should be caused by the coordination of lanthanide ions.

For compound 1, the emission spectra were recorded by excitation into the ligand ($\lambda_{ex} = 280$ nm) and the $^7F_0 \rightarrow ^5L_6$ transition band of the Eu(III) ion ($\lambda_{ex} = 393$ nm) (see Fig. 5). In both cases, a series of sharp lines originated from the transitions between the lowest emitting state 5D_0 and different 7F_J ($J = 0-4$) levels of the fundamental Eu(III) septet at 578 ($^5D_0 \rightarrow ^7F_0$), 589 ($^5D_0 \rightarrow ^7F_1$), 612, 617, 622 ($^5D_0 \rightarrow ^7F_2$), 649 ($^5D_0 \rightarrow ^7F_3$) and 701 nm ($^5D_0 \rightarrow ^7F_4$) can be observed. Only one component is found for the $^5D_0 \rightarrow ^7F_0$ transition, verifying that there is only one crystallographic independent Eu(III) ion in the compound.²³ The change of the incident wavelength from 280 to 393 nm leads to peak splitting and variation of the intensity ratio of $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$ from 2.07 to 1.43. The small asymmetry parameter implies a slightly distorted octahedral geometry around the Eu(III) center. The decay curve ($\lambda_{ex,em} = 393, 612$ nm) can be well fitted by a single exponential function, confirming the presence of only one kind of emissive Eu^{3+} center in the crystal lattice.

Fig. 6 Normalized excitation (left) and emission (right) spectra of compound 3 at room temperature.

Fig. 7 Normalized excitation (left) and emission (right) spectra of compound 4 at room temperature.

Table 3 Charge factors and polarizabilities of compound 1

Charge factors	Polarizabilities ($\times 10^{-24} \text{ \AA}^3$)
$g(2) = 0.0108$	$\alpha(2) = 3.1942$
$g(3) = 1.9998$	$\alpha(3) = 2.2256$
$g(4) = 1.9998$	$\alpha(4) = 2.2256$
$g(5) = 0.0108$	$\alpha(5) = 3.1942$
$g(6) = 1.9998$	$\alpha(6) = 2.2256$
$g(7) = 0.0108$	$\alpha(7) = 3.1942$

The 5D_0 lifetime is long (1.95 ms), implying the absence of coordinated water in the first coordination sphere.²⁴

As expected, both the excitation and emission spectra of compound 2 resemble those of ligand H_4L (see Fig. 4). For a Gd-containing compound, the ligand-to-metal energy transfer and metal-centered (MC) luminescence cannot take place because the MC electronic levels of the Gd^{3+} ion (31 000 cm^{-1}) are well above the ligand-centered electronic levels of typical organic ligands.²⁵ The small red shift of the emission maxima could be attributed to the coordination of the ligand to Gd(III) ions which could enhance the delocalization of electron density from the ligand to the metal and reduce the energy gap between the $\pi^*-\pi$ molecular orbital of the diphosphonate ligand.²⁶

Under excitation at 280 nm, sharp characteristic emission bands from Tb^{3+} cations are observed for compound 3 (see Fig. 6), which can be assigned to the $^5D_4 \rightarrow ^7F_J$ ($J = 6-3$) transitions at 494 ($J = 6$), 548 ($J = 5$), 594 ($J = 4$) and 620 nm ($J = 3$). The luminescence lifetime (1.30 ms) was investigated by

Table 5 Theoretical values of the intramolecular energy transfer and back-transfer rates (s^{-1}) calculated for compound 1

	Transfer rate	Back-transfer rate
$S_1 \rightarrow ^5D_4$	2.84×10^1	2.61×10^{-19}
$T_1 \rightarrow ^5D_1$	5.38×10^5	3.21×10^{-3}
$T_1 \rightarrow ^5D_0$	3.37×10^5	4.06×10^{-7}

excitation at 350 nm and monitoring at 542 nm. In the emission spectrum of compound 4 ($\lambda_{\text{ex}} = 280 \text{ nm}$), typical intense emission bands at about 480, 574 and 660 nm can be observed, corresponding to the $^4F_{9/2} \rightarrow ^6H_J$ ($J = 15/2, 13/2$, and $11/2$) transitions of the Dy^{3+} ion, respectively (see Fig. 7). No emission bands originating from the ligands are detected, indicating efficient ligand-to-lanthanide energy transfer.

Luminescence modeling

It is very important to understand the mechanism of photoluminescence; therefore, theoretical calculation was performed on compound 1 with a newly developed software program – LUMPAC.¹⁵ To date, theoretical modeling of the photoluminescence properties of extended solids is still very rare.²⁷ Considering that the photoluminescence properties of lanthanide compounds mainly depend on the first coordination sphere, straightforward approximation was carried out to obtain a mononuclear motif. In this case, one Eu(III) ion and six doubly deprotonated diphosphonate ligands were selected to obtain the optimized geometry using Sparkle PM3 implemented in MOPAC 2012 (ref. 28) software (Fig. S6†). The polarizability (α) and charge factor (g) values of the oxygen atoms directly bonded to the europium center are shown in Table 3.

Based on these polarizability (α) and charge factor (g) values, the theoretical JO intensity parameters were calculated in models 2 and 3 of LUMPAC. The obtained Ω_2 , Ω_4 and Ω_6 values are listed in Table 4. The slight deviation between the experimental and calculated JO intensity parameters might be due to the oversimplified process of the mononuclear motif. These theoretical parameters were further used to calculate the theoretical 5D_0 transition probabilities (k_r and k_{nr}), quantum efficiency (η) and quantum yield (q), which were found to be very close to the experimental values. The singlet (S_1) and triplet (T_1) energies were calculated to be 37 197.9 and 23 009.3 cm^{-1} , respectively, which are greater than those for the low-lying excited state of Eu^{3+} (5D_1 : 18 674 cm^{-1} ; 5D_0 : 17 500 cm^{-1}). It is well known that an optimal

Table 4 Experimental (excitation wavelength 280 nm) and calculated intensity parameters (Ω), radiative (k_r) and nonradiative (k_{nr}) transition probabilities, emission quantum efficiency (η) and quantum yield (q) values of the 5D_0 emitting level

	Intensity parameters (10^{-20} cm^2)			$k_r (\text{s}^{-1})$	$k_{nr} (\text{s}^{-1})$	$\eta (\%)$	$q (\%)$
	Ω_2	Ω_4	Ω_6				
Experimental	2.52	1.60	—	149.57	363.25	29.17	—
Theoretical	2.65	0.34	0.43	135.0	377.82	26.32	12.16

Scheme 2 Schematic energy transfer process in compound 1.

ligand-to-metal energy transfer process for Eu(III) needs 2500–3500 cm^{-1} .²⁹ The energy gaps $\Delta E(^3\pi\pi^* \rightarrow ^5D_1)$ and $\Delta E(^3\pi\pi^* \rightarrow ^5D_0)$ are calculated to be 4335.3 and 5509.3 cm^{-1} , respectively, which are too large to sensitize the luminescence of Eu^{3+} . Therefore, the ligand-to-metal energy transfer is inefficient. The distances from the donor centre (located in the organic part) to the acceptor (Eu^{3+}) of electron density (R_L) are determined to be 5.8898 Å for $R_L(\text{singlet})$ and 5.8537 Å for $R_L(\text{triplet})$. The larger values of the nonradiative transition probability (k_{nr}) and distance R_L also signify that the energy transfer is inefficient.²⁷

The energy transfer rates were also calculated with model 3 of LUMPAC (Table 5). It is obvious that the values for the ligand singlet state are quite low compared with those for the processes through ligand triplet states, implying its weak effect on the luminescence process. The energy transfer channels through the ligand triplet state to the 5D_1 and 5D_0 states ($T_1 \rightarrow ^5D_1$ and $T_1 \rightarrow ^5D_0$) are the dominant pathways and all the back-transfer rates are almost negligible. Thus, it can be deduced that the most efficient luminescence pathway is $S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow (^5D_1, ^5D_0) \rightarrow ^7F_{0-6}$. The intramolecular energy transfer processes taking place in compound 1 are presented in Scheme 2.

Conclusions

In summary, we have synthesized one series of lanthanide diphosphonates from a V-shaped diphosphonic acid ligand. The structural analyses reveal that interesting structures can be obtained from the symmetric V-shaped ligand. The rigidity of the ligand leads to the high thermal stability of the obtained compounds. The experimental and theoretical luminescence properties were investigated and compared. With the aid of software, scientists can have a better understanding of the mechanism of energy transfer which provides effective inspiration for the design of luminescent hybrid materials. The present work is a rare example of luminescence modeling of extended lanthanide phosphonates which provides insight into the design of luminescent inorganic-organic hybrid materials.

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Notes and references

- (a) K. J. Gagnon, H. P. Perry and A. Clearfield, *Chem. Rev.*, 2012, **112**, 1034–1054; (b) *Metal phosphonate chemistry: From synthesis to application*, ed. A. Clearfield and K. D. Demadis, The Royal Society of Chemistry, London, 2012.
- (a) S. R. Miller, G. M. Pearce, P. A. Wright, F. Bonino, S. Chavan, S. Bordiga, I. Margiolaki, N. Guillou, G. Férey, S. Bourrelly and P. L. Llewellyn, *J. Am. Chem. Soc.*, 2008, **130**, 15967–15981; (b) M. Taddei, F. Costantino, A. Ienco, A. Comotti, P. V. Daud and S. M. Cohen, *Chem. Commun.*, 2013, **49**, 1315–1317.
- (a) M. Angeloni, O. Piermatti, F. Pizzo and L. Vaccaro, *Eur. J. Org. Chem.*, 2014, **79**, 1716–1726; (b) Y.-P. Zhu, Y.-L. Liu, T.-Z. Ren and Z.-Y. Yuan, *RSC Adv.*, 2014, **4**, 16018–16021; (c) A. Dutta, A. K. Patra, H. Uyama and A. Bhaumik, *ACS Appl. Mater. Interfaces*, 2013, **5**, 9913–9917.
- (a) M. Bazaga-García, R. M. P. Colodrero, M. Papadaki, P. Garczarek, J. Zoń, P. Olivera-Pastor, E. R. Losilla, L. León-Reina, M. A. G. Aranda, D. Choquesillo-Lazarte, K. D. Demadis and A. Cabeza, *J. Am. Chem. Soc.*, 2014, **136**, 5731–5739; (b) A. Donnadio, M. Nocchetti, F. Costantino, M. Taddei, M. Casciola, F. da Silva Lisboa and R. Vivani, *Inorg. Chem.*, 2014, **53**, 13220–13226; (c) M. Bazaga-García, M. Papadaki, R. M. P. Colodrero, P. Olivera-Pastor, E. R. Losilla, B. Nieto-Ortega, M. Á. G. Aranda, D. Choquesillo-Lazarte, A. Cabeza and K. D. Demadis, *Chem. Mater.*, 2015, **27**, 424–435.
- X. Yang, S.-S. Bao, M. Ren, N. Hoshino, T. Akutagawa and L.-M. Zheng, *Chem. Commun.*, 2014, **50**, 3979–3981.
- (a) C. Maxim, D. G. Branzea, C. Tiseanu, M. Rouzières and R. Clérac, *Inorg. Chem.*, 2014, **53**, 2708–2717; (b) R. M. P. Colodrero, K. E. Papathanasiou, N. Stavgianoudaki, P. Olivera-Pastor, E. R. Losilla, M. A. G. Aranda, L. León-Reina, J. Sanz, I. Sobrados, D. Choquesillo-Lazarte, J. M. García-Ruiz, P. Atienzar, F. Rey, K. D. Demadis and A. Cabeza, *Chem. Mater.*, 2012, **24**, 3780–3792; (c) R. Janicki, M. Monteil, M. Lecouvey and A. Mondry, *Opt. Mater.*, 2013, **36**, 259–264.
- M. Elhabiri, S. Abada, M. Sy, A. Nonat, P. Choquet, D. Esteban-Gomez, C. Cassino, C. Platas-Iglesias, M. Botta and L. J. Charbonnière, *Chem. – Eur. J.*, 2015, **21**, 6535–6546.
- J.-G. Mao, *Coord. Chem. Rev.*, 2007, **251**, 1493–1520.
- (a) T. Araki, A. Kondo and K. Maeda, *Chem. – Eur. J.*, 2015, **21**, 6257–6264; (b) A. R. Patterson, W. Schmitt and R. C. Evans, *J. Phys. Chem. C*, 2014, **118**, 10291–10301; (c) S. M. F. Vilela, D. Ananias, A. C. Gomes, A. A. Valente, L. D. Carlos, J. A. S. Cavaleiro, J. Rocha, J. P. C. Tomé and F. A. A. Paz, *J. Mater. Chem.*, 2012, **22**, 18354–18371; (d) S. M. F. Vilela, A. D. G. Firmino, R. F. Mendes and J. A. Fernandes, *Chem. Commun.*, 2013, **49**, 6400–6402; (e) F.-N. Shi, T. Trindade, J. Rocha and F. A. A. Paz, *Cryst. Growth Des.*,

- 2008, **8**, 3917–3920; (f) F. A. A. Paz, S. M. F. Vilela and J. P. C. Tomé, *Cryst. Growth Des.*, 2014, **14**, 4873–4877.
- 10 J.-C. G. Bünzli and S. V. Eliseeva, Lanthanide Luminescence, in *Springer Series on Fluorescence*, ed. P. Hänninen and H. Härmä, SpringerVerlag, Berlin, 2010, vol. 7, p. 1.
 - 11 M. P. Placidi, J. Engelmann, L. S. Natrajan and N. K. Logothetis, *Chem. Commun.*, 2011, **47**, 11534–11536.
 - 12 (a) J.-R. Li, D. J. Timmons and H.-C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 6368–6369; (b) J.-R. Li, A. A. Yakovenko, W. Lu, D. J. Timmons, W. Zhuang, D. Yuan and H.-C. Zhou, *J. Am. Chem. Soc.*, 2010, **132**, 17599–17610; (c) Z.-Q. Shi, Z.-J. Guo and H.-G. Zheng, *Dalton Trans.*, 2014, **43**, 13250–13258; (d) Y. Liu, J.-R. Li, W. M. Verdegaal, T.-F. Liu and H.-C. Zhou, *Chem. – Eur. J.*, 2013, **19**, 5637–5643.
 - 13 (a) S. Biju, R. O. Freire, Y. K. Eom, R. Scopelliti, J.-C. G. Bünzli and H. K. Kim, *Inorg. Chem.*, 2014, **53**, 8407–8417; (b) J. H. S. K. Monteiro, A. de Bettencourt-Dias, I. O. Mazalia and F. A. Sigoli, *New J. Chem.*, 2015, **39**, 1883–1891; (c) M. R. Felício, T. G. Nunes, P. M. Vaz, A. M. P. Botas, de P. Ribeiro-Claro, R. A. S. Ferreira, R. O. Freire, P. D. Vaz, L. D. Carlos, C. D. Nunes and M. M. Nolasco, *J. Mater. Chem. C*, 2014, **2**, 9701–9711.
 - 14 (a) X. Lv, S.-F. Tang, L. Li, X. Xu and X. Zhao, *Z. Anorg. Allg. Chem.*, 2013, **639**, 1845–1849; (b) X. Lv, L. Li, X. Sun, H. Zhang, J. Cai, C. Wang, S. Tang and X. Zhao, *Chem. – Asian J.*, 2014, **9**, 901–907; (c) W. Ouellette, G. Wang, H. Liu, G. T. Yee, C. J. O'Connor and J. Zubietta, *Inorg. Chem.*, 2009, **48**, 953–963; (d) Y.-F. Liu, G.-F. Hou, Y.-H. Yu, P.-F. Yan and G.-M. Li, *New J. Chem.*, 2014, **38**, 1328–1335.
 - 15 J. D. L. Dutra, T. P. Bispo and R. O. Freire, *J. Comput. Chem.*, 2014, **35**, 772–775.
 - 16 SAINT, Version 6.45; Bruker Analytical X-ray Systems Inc., 2003.
 - 17 G. M. Sheldrick, *SADABS*, Version 2.10, Bruker AXS Inc., Madison, WI, 2003.
 - 18 G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution and Refinement*, University of Göttingen, 1997.
 - 19 G. M. Sheldrick, *SHELXTL, Crystallographic Software Package*, SHELXTL, Version 5.1, Bruker-AXS, Madison, WI, 1998.
 - 20 (a) D. Kong and A. Clearfield, *Cryst. Growth Des.*, 2005, **5**, 1767–1773; (b) D. Kong, J. Zou, J. McBee and A. Clearfield, *Inorg. Chem.*, 2006, **45**, 977–986.
 - 21 (a) S.-F. Tang, J.-L. Song, X.-L. Li and J.-G. Mao, *Cryst. Growth Des.*, 2007, **7**, 360–366; (b) Y.-S. Ma, H. Li, J.-J. Wang, S.-S. Bao, R. Cao, Y.-Z. Li, J. Ma and L.-M. Zheng, *Chem. – Eur. J.*, 2007, **13**, 4759–4769.
 - 22 (a) Z. Amghouz, S. García-Granda, J. R. García, A. Clearfield and R. Valiente, *Cryst. Growth Des.*, 2011, **11**, 5289–5297; (b) M. J. Bialek, J. Janczakb and J. Zon, *CrystEngComm*, 2013, **15**, 390–399.
 - 23 E. Guillet, D. Imbert, R. Scopelliti and J.-C. G. Bünzli, *Chem. Mater.*, 2004, **16**, 4063–4070.
 - 24 A.-S. Chauvin, S. Comby, M. Baud, C. De Piano, C. Duhot and J.-C. G. Bünzli, *Inorg. Chem.*, 2009, **48**, 10687–10696.
 - 25 W.-K. Wong, H. Liang, J. Guo, W.-Y. Wong, W.-K. Lo, K.-F. Li, K.-W. Cheah, Z. Zhou and W.-T. Wong, *Eur. J. Inorg. Chem.*, 2004, 829.
 - 26 (a) W.-G. Lu, L. Jiang, X.-L. Feng and T.-B. Lu, *Cryst. Growth Des.*, 2006, **6**, 564; (b) Q.-L. Zhu, T.-L. Sheng, C.-H. Tan, S.-M. Hu, R.-B. Fu and X.-T. Wu, *Inorg. Chem.*, 2011, **50**, 7618–7624.
 - 27 M. M. Nolasco, R. F. Mendes, P. P. Lima, F. A. A. Paz, L. D. Carlos and J. Rocha, *Eur. J. Inorg. Chem.*, 2015, 1254–1260.
 - 28 (a) MOPAC2012, James J. P. Stewart, Stewart Computational Chemistry, Version 15.027W web: [HTTP://OpenMOPAC.net](http://OpenMOPAC.net); (b) J. D. C. Maia, G. A. U. Carvalho, C. P. Manguiera, S. R. Santana, L. A. F. Cabral and G. B. Rocha, *J. Chem. Theory Comput.*, 2012, **8**, 3072–3081.
 - 29 M. Latva, H. Takalo, V. M. Mukkala, C. Matachescu, J. C. Rodriguez-Ubis and J. Kankare, *J. Lumin.*, 1997, **75**, 149–169.