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A new praseodymium-based coordination polymers
with 1,10-phenantroline and glutarate ligands:
Synthesis, crystal structure and luminescent properties.

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ABSTRACT

A praseodymium-based coordination polymer with chemical formula $[\text{Pr}(\text{Hglu})(\text{glu})\text{phen}\cdot 2\text{H}_2\text{O}]_\infty$ (phen = 1,10-phenanthroline, glu = glutarate) has been hydrothermally synthesized as single crystal, structurally characterized by X-ray diffraction, IR spectroscopy and ATG measurements. This compound crystallizes in the triclinic system, space group $P\bar{1}$, with the following cell parameters: $a = 9.8254(9) \text{ \AA}$, $b = 11.0617(9) \text{ \AA}$, $c = 12.8552(12) \text{ \AA}$, $\alpha = 97.588(3)^\circ$, $\beta = 108.427(3)^\circ$, $\gamma = 112.643(3)^\circ$, $V = 1170.87(19) \text{ \AA}^3$ and $Z = 2$. The praseodymium cation is nine-fold coordinated by one chelating phenanthroline ligand, two mono-protonated glutarate ligands, and three fully de-protonated glutarate ligands. The crystal structure is 1D and can be described on the basis of double molecular chains that bridge di-nuclear units. Inside a di-nuclear unit, Pr(III)-Pr(III) distance is $4.0475(3) \text{ \AA}$. Room temperature solid-state emission spectrum has been recorded under 295 nm excitation wavelength. It shows the characteristic peaks of Pr^{3+} ion between 480 and 750 nm.

KEYWORDS: Praseodymium-based coordination polymer; Glutaric acid; Phenanthroline; Crystal structure; Luminescence.

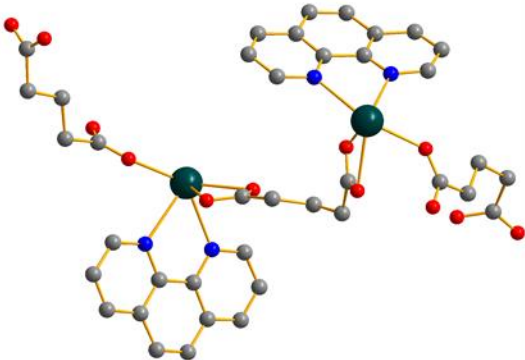
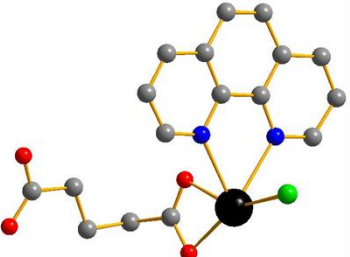
INTRODUCTION

Lanthanide-based coordination polymers have attracted much attention because of their fascinating crystal structures [1–3] and their interesting magnetic [4–6] and luminescent properties [7–10]. The design of lanthanide coordination polymers is based on the size and the rigidity of the ligands as well as on their ability to participate to inter-molecular interactions (hydrogen-bonds, π -stacking interactions...). The lanthanide ions preferentially establish bonds with ligands that present donor oxygen atoms [6], [11–12] as di-carboxylate ligands that have been widely used in coordination polymers conception [13]. In particular, aliphatic di-carboxylate ligands allow diverse conformations due to the energetically favorable rotation of the central carbon chains leading to various possible geometries and coordination modes [14–16]. In addition, the O atoms of carboxylate groups can act as hydrogen-bond acceptors.

Luminescent properties of the lanthanide ions are governed by forbidden $4f \rightarrow 4f$ transitions. Therefore, their molar absorptivity coefficients are very weak and their direct excitation is inefficient. This problem is overcome by using the so-called "antenna effect" [17]. It consists in exciting the ligand that transfers its energy to the lanthanide ion that finally de-excites radiatively. A phenomenon that is difficult to overcome in coordination compounds is the non-radiative de-excitation via O-H, C-H... vibrators in the vicinity of the lanthanide ions [18]. The use of bulky ligands prevents solvent molecules coordination. Rigid organic ligands such as 1,10-phenanthroline have proved their efficiency [19–24]. However, these bulky ligands often lead to 0D complexes. In order to obtain coordination polymers, our synthetic strategy consists of mixing rigid bulk ligands, in order to protect lanthanide ions from solvent coordination molecules and insure an efficient antenna effect, and flexible ligands for binding together the metallic centers and constructing extended molecular frameworks.

In this context, we have selected glutaric acid (HOOC-(CH₂)₃-COOH) as flexible ligand and 1,10-phenanthroline as rigid ligand. Indeed, beyond its protection aspect, 1,10-phenanthroline allows the construction of pseudo-2D or -3D frameworks via aromatic π -stacking interactions [25-27].

To the best of our knowledge, two series of ternary lanthanide complexes with glutaric acid and 1,10-phenanthroline have been reported so far. They are listed in Table 1.

Ln	Chemical formula	Perspective view of the asymmetric unit	reference
Nd			28
Pr, Eu, Er, Yb			29
Y	[Ln(glu) ₃ (phen) ₂] _∞		30
Ce, Tb, Ho			31
Dy			32
Tb, Ho			28
Y, Tm	[Ln(glu)(phen)Cl] _∞		31

Data about the luminescent properties of these compounds are very scarce. Indeed, to the best of our knowledge, only the luminescence properties of Eu₂(phen)₂(C₅H₆O₄)₃ under direct excitation ($\lambda_{\text{exc}} = 395$ nm) [29] and that of [Tb₂(phen)₂(glu)₃]_∞ and [Dy₂(phen)₂(glu)₃]_∞ via an antenna effect ($\lambda_{\text{exc}} = 280$ nm and 340 nm, respectively) [31-32] have been reported so far. Discrepancy between these two excitation wavelengths is surprising and could be related to ⁶H_{15/2} → ⁴I_{9/2}, ⁴F_{5/2} and ⁴D_{5/2} 4f→4f transitions of Dy³⁺ ion that are all located at about 340 nm [33]. Therefore it is of interest to estimate the antenna effect efficiency for lanthanide ions that present a small energy gap such as Pr³⁺.

We report here the synthesis and crystal structure of a new praseodymium coordination polymer: $[\text{Pr}(\text{Hglu})(\text{glu})\text{phen}\cdot 2\text{H}_2\text{O}]_\infty$, that has a pseudo-2D supramolecular architecture via π -stacking interactions. Its thermal behavior and luminescent properties are also reported.

EXPERIMENTAL SECTION

Materials and physical techniques

Experimental reagents were used as purchased without further purification.

IR spectrum was recorded in the solid-state, at room-temperature, on a Perkin-Elmer Spectrum II Model FT-IR spectrophotometer using ATR method in the $4000\text{-}400\text{ cm}^{-1}$ range with a 4 cm^{-1} resolution.

Thermogravimetric measurements were carried out in platinum crucibles from room temperature to 1000°C under nitrogen atmosphere with $5^\circ\text{C}\cdot\text{min}^{-1}$ heating rate, using a Perkin-Elmer Pyris-Diamond thermal analyzer. At the end of the experiment, the compound was maintained for 1 h at 1000°C under synthetic air to insure complete combustion. The residual solid has been identified as Pr_2O_3 by powder X-ray diffraction.

Excitation and emission spectra were recorded in the solid-state using powder sample pasted onto copper plate with silver glue on a Horiba Jobin-Yvon Fluorolog III fluorescence spectrometer equipped with a Xe lamp 450 W and a UV-Vis PMT (Hamamatsu R928, sensitivity 185 - 900 nm). Luminescence spectrum was recorded at room-temperature in the 450-800 nm range.

Synthesis of $[\text{Pr}(\text{Hglu})(\text{glu})\text{phen}\cdot 2\text{H}_2\text{O}]_\infty$

$\text{PrCl}_3\cdot 7\text{H}_2\text{O}$ (0.0742 g, 0.2 mmol), glutaric acid (0.0396 g, 0.3 mmol), 1,10-phenanthroline (0.0595 g, 0.3 mmol) and deionized water (10 mL) were mixed and

stirred for 30 min at room temperature. The pH value was about 4.20. The mixture was placed in a 25 mL Teflon-lined stainless-steel autoclave, and heated at 150°C for 3 days under autogenous pressure. Upon cooling to room temperature, green single-crystals suitable for X-ray diffraction were obtained. They were washed with distilled water and dried under ambient temperature and pressure. IR (cm⁻¹): 3406(m, br), 2960(m), 2925(m), 2853(w), 1717(m), 1576(s), 1547(s), 1530(m), 1460(s), 1418(vs), 1307(m), 1251(m), 1193(m), 1144(m), 1102(m), 1064(m), 1042(m), 1022(m), 907(m), 851(s), 787(m), 773(m), 731(s), 687(m), 652(s), 633(s), 586(m), 526(m), 416(m) (Figure S1).

Crystallographic data collection and structure determination

A single crystal was selected for X-ray diffraction analysis. Data collection was performed, at 150 K, on a Bruker D8 Venture diffractometer, CCD area detector equipped with a graphite mono-chromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The absorption correction was done with the multi-scan method [34]. Crystallographic data and experimental details for structural analysis are summarized in Table 2.

The crystal structure was solved by direct methods with SIR2002 [35]. All the non-H atoms were refined anisotropically with SHELXL97 [36] using full matrix least squares on F² procedure from the WinGX [37] software. All the H atoms were placed at ideal positions and constrained to ride on their parent atoms.

Table 2. Crystal and final structure refinement data for $[\text{Pr}(\text{Hglu})(\text{glu})\text{phen}\cdot 2\text{H}_2\text{O}]_\infty$

Formula	$\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_{10}\text{Pr}$
Formula weight ($\text{g}\cdot\text{mol}^{-1}$)	618.35
Crystal system	Triclinic
Space group	$P\bar{1}$
a (\AA)	9.8254(9)
b (\AA)	11.0617(9)
c (\AA)	12.8552(12)
α ($^\circ$)	97.588(3)
β ($^\circ$)	108.427(3)
γ ($^\circ$)	112.643(3)
V (\AA^3)	1170.87(19)
Z	2
D_c ($\text{g}\cdot\text{cm}^{-3}$)	1.7538
T (K)	150
μ (Mo- $K\alpha$) (mm^{-1})	2.141
θ range for data collection ($^\circ$)	2.45-27.48
$F(000)$	620
R_1	0.0167
wR_2	0.0421
S	1.117
CCDC n $^\circ$	1996296

RESULTS AND DISCUSSION

Structural description of $[\text{Pr}(\text{Hglu})(\text{glu})\text{phen}\cdot 2\text{H}_2\text{O}]_\infty$

This praseodymium-based coordination polymer crystallizes in the triclinic system, space group $P\bar{1}$ with two formula units per the unit-cell. There is only one Pr^{3+} ion in the asymmetric unit. It is nine-fold coordinated by two nitrogen atoms from a chelating 1,10-phenanthroline molecule (phen), three oxygen atoms from two once protonated glutarate ligands (Hglu^-) and four oxygen atoms from three glutarate ligands (glu^{2-}) (Figure 1). The coordination polyhedron is best described as a distorted capped square antiprism (C_{4v}). It can be noticed that, in agreement with our strategy, there is no high energy vibrator (O-H or C-H) in the first coordination sphere of the lanthanide ions [38].

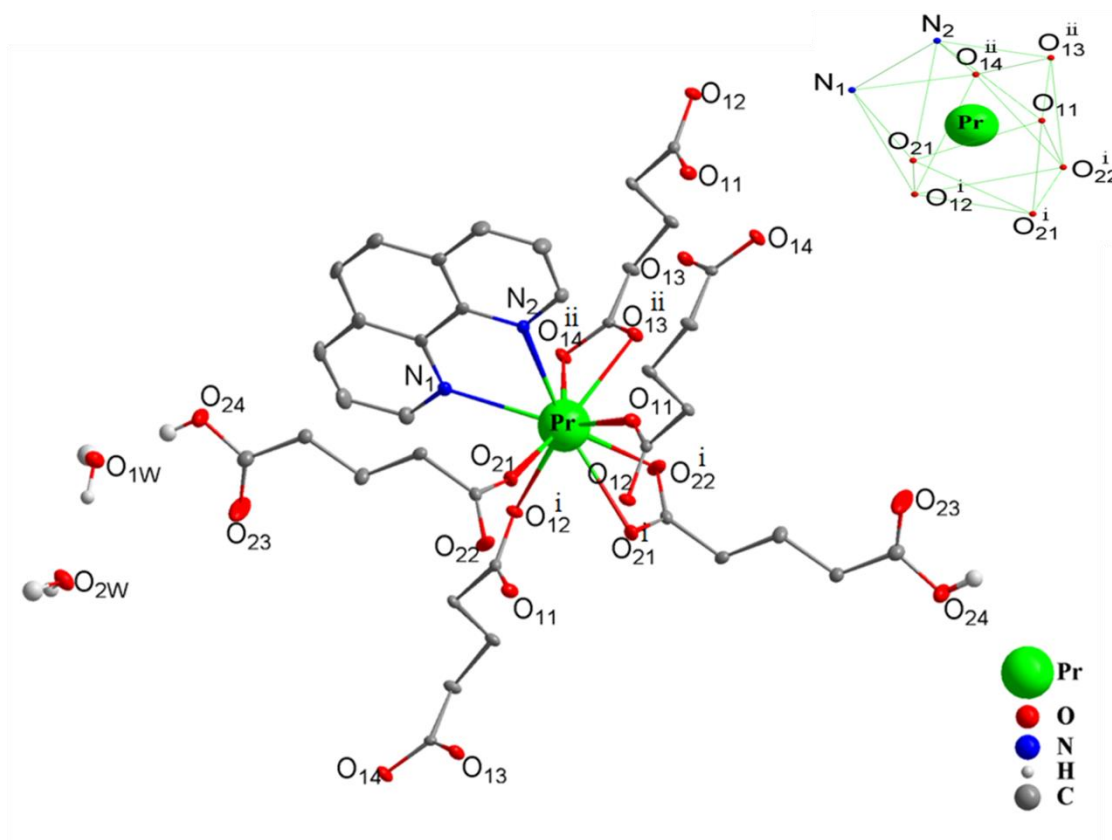


Figure 1. Projection view of an extended asymmetric unit and coordination polyhedron of the Pr^{3+} ion (in inset) of $[\text{Pr}(\text{Hglu})(\text{glu})\text{phen}\cdot 2\text{H}_2\text{O}]_{\infty}$. Symmetry codes: (i) $x + 2, y + 1, z + 2$; (ii) $x + 1, y + 1, z + 2$.

The glu^{2-} ligand exhibits one bidentate chelating carboxylate group. Its second carboxylate group bridges two lanthanide ions in a monodentate fashion (Figure 2 left). The once protonated Hglu^{-} ligand acts as a bridging-chelating tridentate ligand by its deprotonated carboxylate function while its protonated carboxylate function is free (Figure 2 right) and points toward the inter-molecular space.

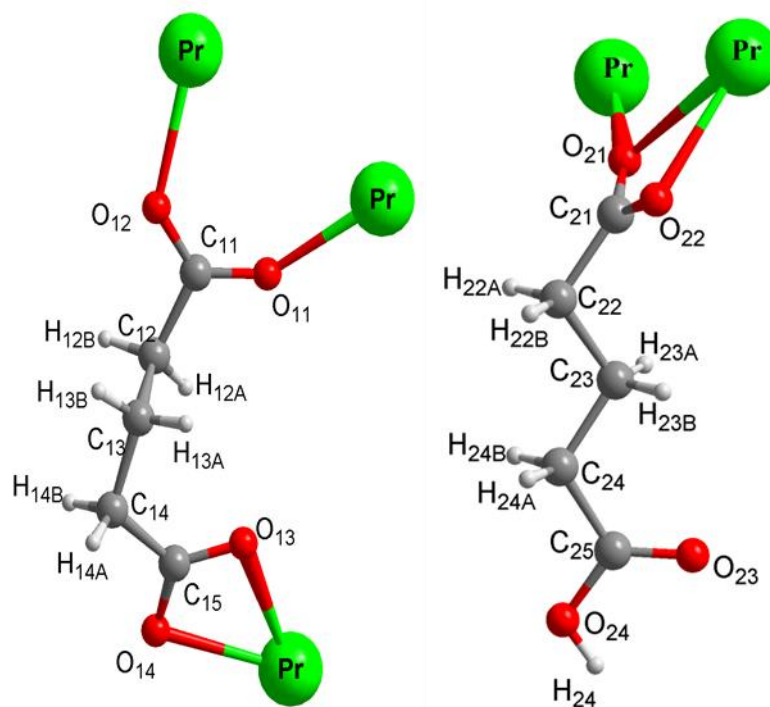


Figure 2. Coordinating modes of the fully deprotonated (glu^{2-} left) and once deprotonated (Hglu^- right) glutarate ligands in $[\text{Pr}(\text{Hglu})(\text{glu})\text{phen}\cdot 2\text{H}_2\text{O}]_\infty$.

The Pr–N bond lengths are 2.647(1) and 2.714(1) Å. The Pr–O bond lengths range from 2.410(1) to 2.732(1) Å. The mean Pr–O distance is 2.512 Å (Table 3), in agreement with what has been reported before for dicarboxylate rare-earths complexes [39-42].

Table 3. Selected bond lengths (Å) and angles (°) in [Pr(Hglu)(glu)phen·2H ₂ O] _∞ .					
Pr-O11	2.410(1)	Pr-O21	2.410(1)	Pr-N1	2.714(1)
Pr-O12ⁱ	2.479(1)	Pr-O22ⁱ	2.523(1)	Pr-N2	2.647(1)
Pr-O13ⁱⁱ	2.527(1)	Pr-O21ⁱ	2.732(1)		
Pr-O14ⁱⁱ	2.504(1)				
O21-Pr1-O12ⁱ	79.54(4)	O21-Pr1-O14ⁱⁱ	150.79(4)	O21-Pr1-O22ⁱ	125.36(4)
O21-Pr1-O21ⁱ	76.36(4)	O21-Pr1-O13ⁱⁱ	143.26(4)	O22ⁱ-Pr1-O21ⁱ	49.10(4)
O22ⁱ-Pr1-O13ⁱⁱ	72.82(4)	O12ⁱ-Pr1-O22ⁱⁱ	79.19(4)	O12ⁱ-Pr1-O21ⁱ	70.07(4)
O12i-Pr1-O14ⁱⁱ	91.86(4)	O12ⁱ-Pr1-O13ⁱⁱ	137.18(4)	O11-Pr1-O22ⁱ	86.71(5)
O11-Pr1-O13ⁱⁱ	76.21(4)	O11-Pr1-O21ⁱ	67.88(4)	O13ⁱⁱ-Pr1-O21ⁱ	111.03(4)
O14ⁱⁱ-Pr1-O13ⁱⁱ	51.89(4)	O14ⁱⁱ-Pr1-O21ⁱ	127.01(4)	O14ⁱⁱ-Pr1-O22ⁱ	79.30(4)
O11-Pr1-O12ⁱ	134.21(4)	O11-Pr1-O14ⁱⁱ	128.10(4)	O11-Pr1-O21	73.79(4)
N2-Pr1-N1	61.64(4)	Pr1-O21-Pr1ⁱ	103.64(4)		
O22-C21-O21	120.30(15)	O13-C15-O14	120.42(15)		
	glu²⁻		Hglu⁻		
O12-C11	1.276(2)	O21-C21	1.271(2)		
O11-C11	1.255(2)	O22-C21	1.257(2)		
O13-C15	1.254(2)	O23-C25	1.205(2)		
O14-C15	1.282(2)	O24-C25	1.316(2)		
C11-C12	1.517(2)	C21-C22	1.514(2)		
C12-C13	1.541(2)	C22-C23	1.533(2)		
C14-C13	1.530(2)	C23-C24	1.525(2)		
C15-C14	1.513(2)	C24-C25	1.508(2)		
			Phen		
N2-C10	1.329(2)	C1-C2	1.405(3)	C7-C8	1.410(3)
N2-C32	1.365(2)	C3-C2	1.372(3)	C9-C8	1.371(3)
N1-C1	1.327(2)	C4-C3	1.406(3)	C10-C9	1.405(2)
N1-C31	1.370(2)	C4-C5	1.439(3)	C31-C4	1.411(2)
		C5-C6	1.352(3)	C32-C7	1.408(2)
		C7-C6	1.435(2)	C31-C32	1.448(2)

Symmetry codes: (i) $x + 2, y + 1, z + 2$; (ii) $x + 1, y + 1, z + 2$

A bi-nuclear praseodymium cage is formed by two bridging oxygen atoms (O21), from two once protonated glutarate ligands (Hglu⁻), that form a four-membered Pr1-O21-Pr1-O21 ring. The two praseodymium ions are further linked to each other by two bridging carboxylate clips (Pr1-O11-C11-O12-Pr1) from two fully deprotonated glutarate ligands. Inside this bi-nuclear unit, the Pr(III)···Pr(III) distance is equal to 4.0475(3) Å. The binuclear unit consists of two edge-sharing polyhedrons. The fully deprotonated glutarate ligand play the role of the linker between these bi-nuclear units (Figure 3). This ligand adopts

the anti-gauche conformation: the torsions angles are $[-167.84(15)^\circ]$ for C11-C12-C13-C14 and $[69.93(20)^\circ]$ for C12-C13-C14-C15.

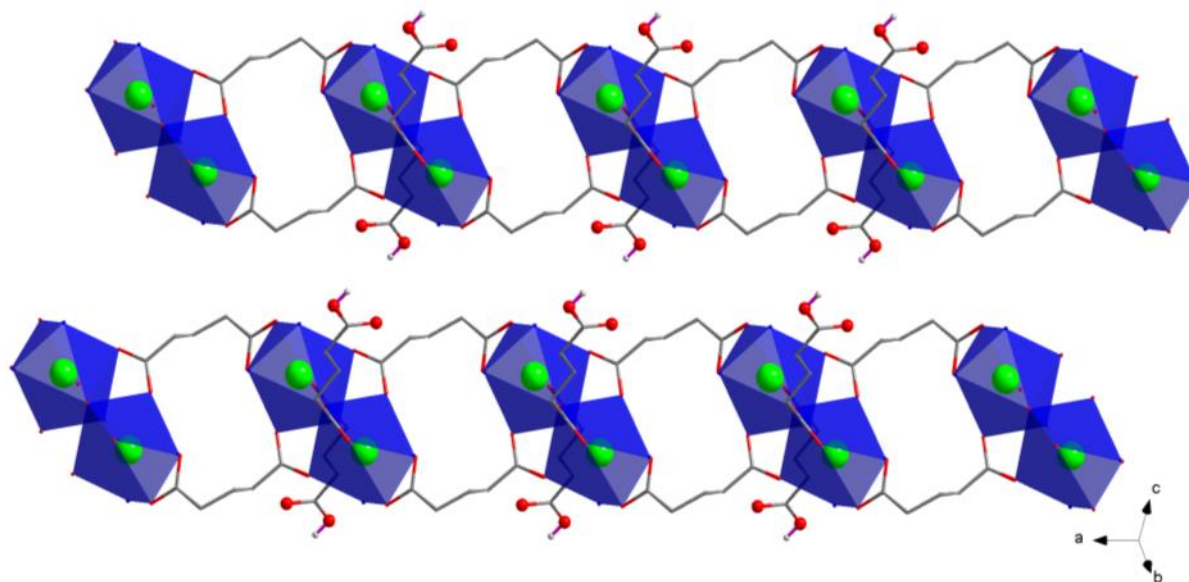


Figure 3. Projection view of the 1D molecular double-chains of $[\text{Pr}(\text{Hglu})(\text{glu})\text{phen}\cdot 2\text{H}_2\text{O}]_\infty$. The phen ligands have been omitted for clarity.

The crystal structure can be described on the basis of double-molecular chains that spread parallel to the a -axis. These double chains are made of di-nuclear units linked to each other by fully deprotonated glutarate ligands. The molecular double chains are decorated by phen ligands that point toward the inter-chains space. π -stacking interactions along the b -axis, with 4.26 \AA centroid-to-centroid mean distance, between adjacent parallel opposite phen ligands generate a pseudo-2D network (Figure 4). The once protonated Hglu^- ligand bridges the two lanthanide ions of the dimeric units by its tridentate COO^- function. The protonated other carboxylate function points toward the inter-chain space and form strong H-bonds (Table 4) with crystallization water molecules (Figure 4). Hglu^- ligand adopts anti-anti conformation, the torsion angles are $[179.29(16)^\circ]$ for C21-C22-C23-C24 and $[-176.26(16)^\circ]$ for C22-C23-C24-C25.

D–H···A	D–H (Å)	H···A (Å)	D···A(Å)	D–H···A (°)
O1W–H2W···O2W	0.84(3)	1.87(3)	2.713(2)	173(3)
O2W–H3W···O14 ⁱ	0.90(3)	1.85(3)	2.7369(18)	172(3)
O2W–H4W···O22 ⁱⁱ	0.86(4)	1.93(4)	2.7804(19)	174(3)
O1W–H1W···O12 ⁱⁱⁱ	0.84(4)	2.06(4)	2.8956(19)	175(3)
O24–H24···O1W	0.84(2)	1.77(2)	2.62(2)	173(2)

Symmetry codes: (i) $1 + x, y, -1 + z$; (ii) $2 - x, -y, 1 - z$; (iii) $x, y, -1 + z$

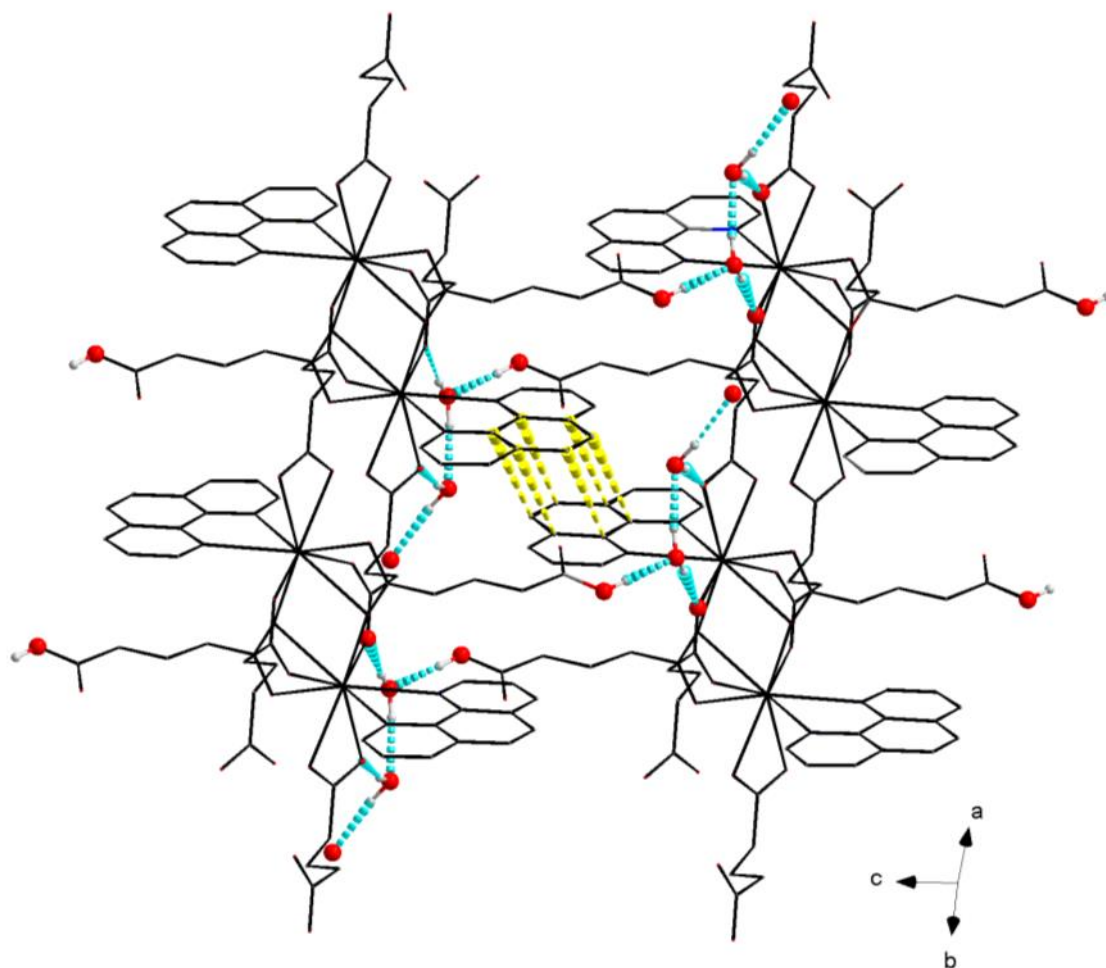


Figure 4. Projection view of the pseudo-2D molecular network of $[\text{Pr}(\text{Hglu})(\text{glu})\text{phen}\cdot 2\text{H}_2\text{O}]_\infty$. π -stacking interactions and H-bonds are symbolized by broken lines in yellow and blue respectively.

In this crystal structure shortest inter-metallic distances between Pr^{3+} ions that belong to different binuclear units are $7.6250(7)$ Å if the lanthanide ions belong to the same molecular chain and $10.343(1)$ Å for lanthanide ions that belong to adjacent molecular motifs. These quite long inter-metallic distances are in agreement with our synthetic strategy.

Infrared spectroscopy

The IR spectrum (Figure S1) shows the characteristic bands of the COO^- groups: the asymmetric stretching appears in the range of $1516\text{-}1576\text{ cm}^{-1}$, and the symmetric stretching are observed in the range of $1307\text{-}1460\text{ cm}^{-1}$ [27]. The band at 1717 cm^{-1} is characteristic of the asymmetric stretching of COOH group, in accordance with partial protonation of glutarate ligands (Hglu^-) [25, 42, 43]. A broad band is observed at 3406 cm^{-1} that is assigned to O–H stretching vibration of crystallization water molecules and of the hydroxyl group of Hglu^- ligand. The presence of 1,10-phenanthroline ligand is confirmed by the characteristic (C–H) out of plane bending vibrations that are observed at 731 and 851 cm^{-1} [27, 43], while (C–H) in plane bending vibrations are observed around 1040 cm^{-1} . Weak sharp peaks that can be assigned to Ln–O and Ln–N vibrations appear at lower wavenumbers (around 416 cm^{-1}), supporting the coordination of the ligands [44].

Thermal analyses (TG/TDA)

The thermogravimetric curve is shown in (Figure 5). The compound starts to lose two crystallization water molecules from about 45°C to about 130°C in two steps, with an overall weight loss of 5.6% (calcd. 5.7%). Then, both glutarate ligands are successively removed: (i) Between 140°C and 340°C , an overall weight loss of 16.1% (calcd. 15.9%) is observed that probably corresponds to the departure in two steps of the Hglu^- ligand. These two steps can be related to the fact that one carboxylate function is bound to a lanthanide ion while the other is free. Indeed the first weight loss at 230°C (6.9%) corresponds to the departure of a CO_2 molecule (calcd. 7.2%) while the second at 320°C (9.2%-Calcd. 8.7%) corresponds to the departure of the alkyl chain (C_4H_6). (ii) Then, between 360°C and 400 , the glu^{2-} ligand departure is observed associated with a 23.9% weight loss (Calcd. 23.8%). At last, the phen

ligand decomposes between 410°C and 900°C finally leading to Pr₂O₃ (27.4% weight loss; Calcd. 27.9%) [29].

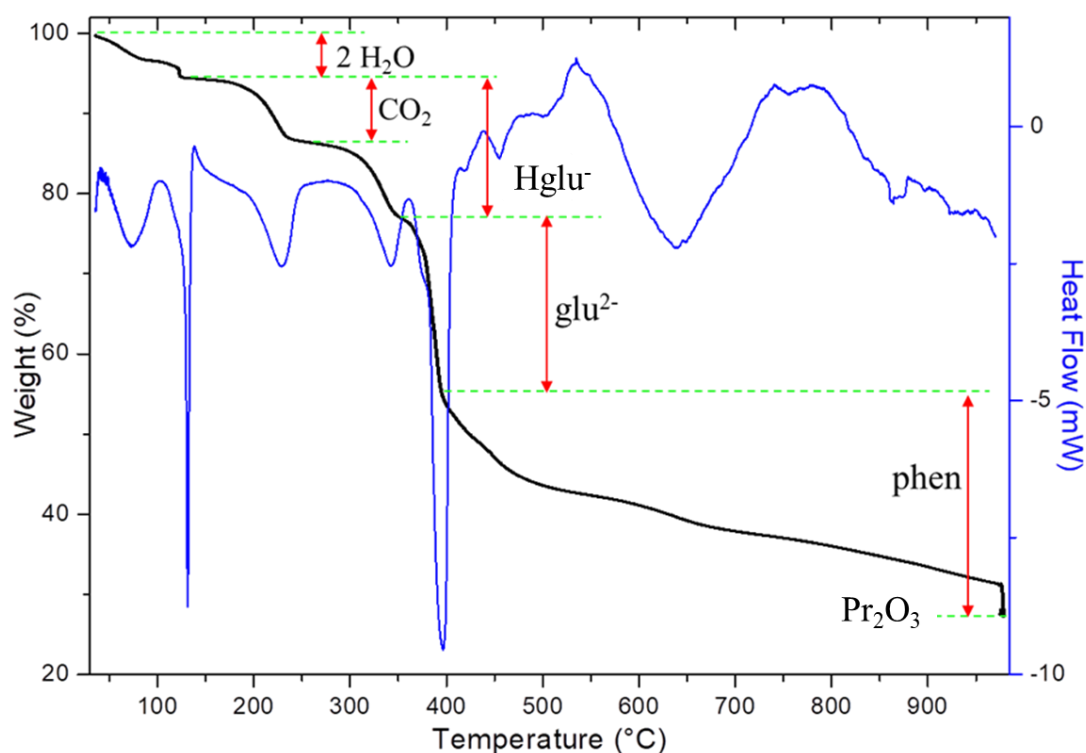


Figure 5. Thermal analysis (TG/TDA) of [Pr(Hglu)(glu)phen·2H₂O]_∞.

Photoluminescence properties

Room-temperature solid-state excitation and emission spectra of [Pr(Hglu)(glu)phen·2H₂O]_∞ have been recorded (Figure 6). The excitation spectrum strongly suggests that there is an efficient antenna effect from phen ligand to the Pr³⁺ ion [43].

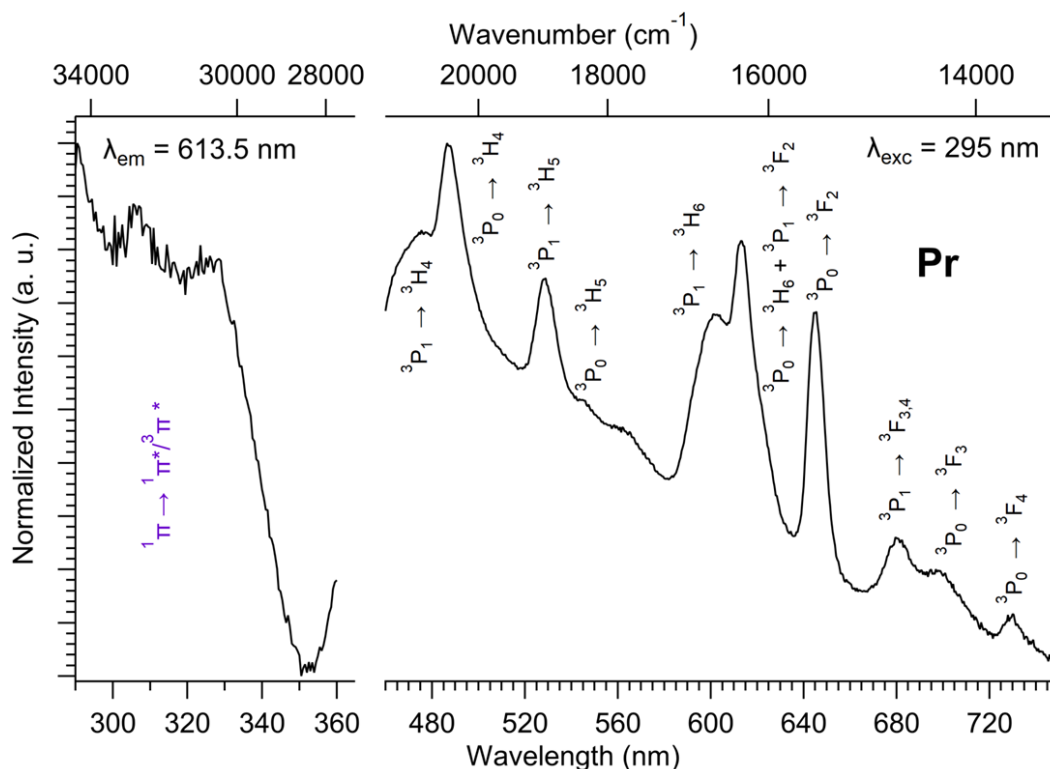


Figure 6. Room temperature solid-state excitation ($\lambda_{\text{em}} = 613.5 \text{ nm}$) and emission ($\lambda_{\text{exc}} = 295 \text{ nm}$) spectra of $[\text{Pr}(\text{Hglu})(\text{glu})\text{phen} \cdot 2\text{H}_2\text{O}]_{\infty}$.

The emission spectrum ($\lambda_{\text{exc}} = 295 \text{ nm}$) presents nine emission peaks with maxima centered at 486.5, 529, 545.5, 601, 613.5, 645.5, 679.5, 698 and 730 nm, respectively. These peaks can be attributed to the Pr^{3+} f-f transitions: ${}^3\text{P}_1 \rightarrow {}^3\text{H}_4 + {}^3\text{P}_0 \rightarrow {}^3\text{H}_4$, ${}^3\text{P}_1 \rightarrow {}^3\text{H}_5$, ${}^3\text{P}_0 \rightarrow {}^3\text{H}_5$, ${}^3\text{P}_1 \rightarrow {}^3\text{H}_6$, ${}^3\text{P}_0 \rightarrow {}^3\text{H}_6 + {}^3\text{P}_1 \rightarrow {}^3\text{F}_2$, ${}^3\text{P}_0 \rightarrow {}^3\text{F}_2$, ${}^3\text{P}_1 \rightarrow {}^3\text{F}_{3,4}$, ${}^3\text{P}_0 \rightarrow {}^3\text{F}_3$, ${}^3\text{P}_0 \rightarrow {}^3\text{F}_4$, respectively [45-46]. The spectrum is dominated by the ${}^3\text{P}_0 \rightarrow {}^3\text{H}_6 + {}^3\text{P}_1 \rightarrow {}^3\text{F}_2$ transitions (maximum at 613.5 nm). It can be noticed that the dominant peak is unusually strong. Indeed, most often, this is the ${}^3\text{P}_0 \rightarrow {}^3\text{F}_2$ transition, centered at about 640 nm that dominates the emission spectrum [47]. However, a major peak centered at 620 nm has already been reported [48]. The low quality of the emission spectrum doesn't allow any explanation.

CONCLUSION AND OUTLOOK.

In this paper we have described the synthesis and the crystal structure of a new lanthanide-based coordination polymer with a bulky ligand (phen) and a flexible ligand (glutarate). The role of the bulky ligand is to provide an antenna effect and to avoid the presence of coordination water molecules in the first coordination sphere of the lanthanide ion

in order to prevent vibrational non-radiative de-excitation. The role of the flexible ligand is to connect the metallic centers to form an extended molecular framework. Results reported here demonstrate that this synthetic strategy is efficient. Indeed, a lanthanide based coordination polymer is obtained and an antenna effect toward Pr^{3+} ion is observed. Unfortunately, to date, despite great synthetic effort, we didn't succeed in obtaining isostructural compounds involving other luminescent lanthanide ions, such as Sm^{3+} , Eu^{3+} , Tb^{3+} or Dy^{3+} , that could exhibit brighter luminescence in the visible region. Our group is currently working along this line.

SUPPORTING INFORMATION

Room-temperature solid-state IR spectrum of $[\text{Pr}(\text{Hglu})(\text{glu})\text{phen}\cdot 2\text{H}_2\text{O}]_\infty$

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REFERENCES.

- [1]. J. C. G. Bünzli. Lanthanide coordination chemistry: From old concepts to coordination polymers. *J. Coord. Chem.*, 67 (2014) 3706–3733.
- [2]. R. Janicki, A. Mondry, P. Starynowicz. Carboxylates of rare earth elements. *Coord. Chem. Rev.*, 340 (2017) 98–133.
- [3]. Y. Robin, K. M. Fromm. Coordination polymer networks with O- and N-donors: What they are, why and how they are made? *Coord. Chem. Rev.*, 250 (2006) 2127–2157.
- [4]. O. Kahn. *Molecular Magnetism*, VCH, Weinheim, 1993.
- [5]. C. Benelli, D. Gatteschi. Magnetism of Lanthanides in Molecular Materials with Transition-Metal Ions and Organic Radicals. *Chem. Rev.*, 102, (2002) 2369-2387.
- [6]. S. Cotton. *Lanthanide and Actinide Chemistry*. England: Hoboken, 2006.
- [7]. M. Pan, B. B. Du, Y. X. Zhu, M. Q. Yue, Z. W. Wei, C. Y. Su. Highly Efficient Visible-to-NIR Luminescence of Lanthanide(III) Complexes with Zwitterionic Ligands Bearing Charge-Transfer Character: Beyond Triplet Sensitization. *Chem. Eur. J.*, 22 (2016), 2440–2451.
- [8]. J. Wang, Y. Suffren, C. Daiguebonne, O. Guillou. Multi-Emissive Lanthanide-Based Coordination Polymers for Potential Application as Luminescent Bar-Codes. *Inorg. Chem.*, 58 (2019) 2659–2668.
- [9]. J. Heine, K. Müller-Buschbaum. Engineering metal-based luminescence in coordination polymers and metal–organic frameworks. *Chem. Soc. Rev.*, 42 (2013) 9232-9242.
- [10]. O. Guillou, C. Daiguebonne, G. Calvez, K. Bernot. A Long Journey in Lanthanide Chemistry: From Fundamental Crystallogenesis Studies to Commercial Anticounterfeiting Taggants. *Acc. Chem. Res.*, 49 (2016) 844–856.
- [11]. J. G. Bunzli, C. Piguet. Lanthanide-Containing Molecular and Supramolecular Polymetallic Functional Assemblies. *Chem. Rev.*, 102 (2002) 1897-1928.
- [12]. R. G. Pearson. Hard and Soft Acids and Bases. *J. Am. Chem. Soc.*, 85 (1963) 3533–3539.
- [13]. O. Guillou, C. Daiguebonne. Lanthanide ions containing coordination polymers. In *Handbook on the Physics and Chemistry of Rare Eaths*. Elsevier., V. K. Gschneider, K. A.; Bünzli, J. C. G.; Pecharsky, Ed. Amsterdame, 2005, pp. 349–404.
- [14]. T .K. Kim, K. J. Lee, M. Choi, N. Park, D. Moon, H. R. Moon. Metal-organic frameworks constructed from flexible ditopic ligands: Conformational diversity of an aliphatic ligand. *New J. Chem.*, 37 (2013) 4130–4139.
- [15]. B. Benmerad, A. Guehria-Laidoudi, S. Dahaoui, C. Lecompte. A Polynuclear coordination glutarate of lanthanum (III) with uncommon cage feature. *Acta Crystallogr. Sect. C Cryst. Struct. Commun.*, C60 (2004) 119–122.
- [16]. F. S. Delgado, P. L. Luis, J.Pasan, L.C. Delgado, O. Fabelo, M. Hernandez-Molina, A. D. Lozano-Gorriñ, F. Lloret, M. Julve, C. R-Perez. Crystal growth and structural remarks on malonate-based lanthanide coordination polymers. *Cryst. Eng. Comm.*, 18 (2016) 7831–7842, 2016.
- [17]. S.I. Weissman. Intramolecular energy transfer the fluorescence of complexes of Europium. *J. Chem. Phys.*, 10 (1942) 214-217.
- [18]. J.C. Bünzli, S. V Eliseeva. Basics of lanthanides photophysics. In *Lanthanide Luminescence*,” *Springer Berlin Heidelberg*. 7, 2010, pp. 1-45.

- [19]. G. Zucchi, O. Maury, P. Thuéry, F. Gumy, J. C. G. Bünzli, M. Ephritikhine. 2,2'-bipyrimidine as efficient sensitizer of the solid-state luminescence of lanthanide and uranyl ions from visible to near-infrared. *Chem. Eur. J.*, 15 (2009) 9686–9696.
- [20]. R. Maouche, S. Belaid, B. Benmerad, S. Bouacida, S. Freslon, C. Daiguebonne, Y. Suffren, G. Calvez, K. Bernot, C. Roiland, L. Le Pollès, O. Guillou. Luminescence properties of lanthanide complexes-based molecular alloys. *Inorg. Chim. Acta*, 501 (2020) 119309.
- [21]. R. An, H. Zhao, H.-M. Hu, X. Wang, M.-L. Yang, G. Xue. Synthesis, Structure, White-Light Emission, and Temperature Recognition Properties of Eu/Tb Mixed Coordination Polymers. *Inorg. Chem.*, 55 (2016) 871–876.
- [22]. C.-T. Li, Y.-F. Zhao, H.-M. Hu, H. Zhao, X. Wang, G. Xue. Lanthanide coordination frameworks constructed from 3,3',4,4'-diphenylsulfonetetracarboxylic and 1,10-phenanthroline: synthesis, crystal structures and luminescence properties. *Dalton Trans.* 45 (2016) 15436-15444.
- [23]. B. Xu, Y. Cheng, H.-M. Hu, C. Bai, X. Wang, M.-L. Yang, G. Xue. Syntheses, crystal structures and luminescence properties of lanthanide-based coordination polymers constructed from a functionalized terpyridyl carboxylate ligand. *CrystEngComm*, 18 (2016) 4613-4626.
- [24]. Y.-C. Hu, C. Bai, H.-M. Hu, C.-T. Li, T.-H. Zhang, W. Liu. Lanthanide coordination polymers based on designed bifunctional 2-(2,2':6',2''-terpyridin-4'-yl)benzenesulfonate ligand: syntheses, structural diversity and highly tunable emission. *Acta Cryst. B*75 (2019) 855–864.
- [25]. L. Zhang, Y. Zhao, L. Qu, L. Huang, K. Wang, A. Normal. Hydrothermal synthesis and structural characterization of three lanthanide coordination polymers with adipic acid and 1,10-phenanthroline. *J. Coord. Chem.*, 61 (2008) 2157–2166.
- [26]. C. B. Liu, H. L. Wen, S. S. Tan. First examples of ternary lanthanide succinate complexes: hydro-solvothermal syntheses and structures of lanthanide coordination polymers of succinic acid and 1,10-phenanthroline. *J. Mol. Struct.*, 794 (2006) 190–195.
- [27]. L. Huang, L. P. Zhang, L. P. Jin. Hydrothermal synthesis and structural characterization of new lanthanide coordination polymers with pimelic acid and 1,10-phenanthroline. *J. Mol. Struct.*, 692 (2004) 169–175.
- [28]. L. P. Zhang, Y. H. Wan, L. P. Jin. Hydrothermal synthesis and crystal structures of three novel lanthanide coordination polymers with glutarate. *646 (2003) 169–178.*
- [29]. D. Y. Wei, H.Z. Xie, S.J. Huang, J. Zhou, G. X. Lu. Hydrothermal syntheses and characterization of four 2-D lanthanide coordination polymers with glutarate and 1,10-phenanthroline. *J. Coord. Chem.*, 64 (2011) 424–430.
- [30]. L. Jin, H.L. Zhu. Poly[μ_4 -glutarato-di- μ_3 -glutarato-bis(1,10-phenanthroline)diyttrium(III)]. *Acta Cryst. E*67 (2011) m1088.
- [31]. X. F. Tan, J. Zhou, H. H. Zou, L. Fu, Q. Tang, P. Wang. A series of lanthanide glutarates: lanthanide contraction effect on crystal frameworks of lanthanide glutarates. *RSC Adv.*, 7 (2017) 17934–17940.
- [32]. L. Xing, Z. Jian, Z. Hua-hong, F. Lianshe. A 2-D dysprosium glutarate exhibiting slow magnetic relaxation and luminescent properties. *J. Coord. Chem.*, 71 (2018) 2722-2731.
- [33]. Carnall, W. T.; Fields, P. R.; Rajnak, K., Spectral intensities of the trivalent lanthanides and actinides in solution. II. Pm^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} and Ho^{3+} . *J. Chem. Phys.* 49, (1968), 4412-4423.
- [34]. Bruker. APEX2 and SAINT. Bruker AXS Ins., Madison, Wisconsin, USA 2015.
- [35]. M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. D. Caro, C. Giacovazzo, G. Polidoria, R. Spagna. SIR2004: An improved tool for crystal structure determination and refinement. *J. Appl. Crystallogr.*, 38 (2005) 381–388.

- [36]. G. M. Sheldrick. A short history of SHELX. *Acta Crystallogr. Sect. A Found. Crystallogr.*, 64 (2008) 112–122.
- [37]. L. G. Farrugia. WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.*, 45 (2012) 849–854.
- [38]. R. An, X. Wang, H. Hu, Z. Zhao, C. Bai, G. Xue. Controllable synthesis of four series of lanthanide coordination polymers: synthesis, structures, luminescent and magnetic properties. *Cryst. Eng. Comm.*, 17 (2015) 8289–8299.
- [39]. B. Benmerad, A. Guehria-laidoudi. Metal-organic compounds polymeric aqua (glutarato)(hydrogen glutarato) lanthanum (III) monohydrate. *Acta Cryst.*, C56 (2000) 789–792.
- [40]. M. Kumar, C. Q. Qiu, J. K. Zareba, A. Frontera, A. K. Jassal, S. C. Sahoo, S. J. Liu, H. N. Sheikh. Magnetic, luminescence, topological and theoretical studies of structurally diverse supramolecular lanthanide coordination polymers with flexible glutaric acid as a linker. *New J. Chem.*, 43 (2019) 14546–14564.
- [41]. B. Benmerad, A. Guehria-Laïdoudi, S. Dahaoui, C. Lecomte. The first suberate lanthanum(III) complex without uncoordinated water. *Acta Crystallogr. Sect. C Cryst. Struct. Commun.*, 60 (2004) m407–m409.
- [42]. C. Bromant, W. Nika, I. Pantenburg and G. Meyer. Rare-Earth-Metal Coordination Polymers: Syntheses and Crystal Structures of Three New Glutarates, $[\text{Pr}_2(\text{Glu})_3(\text{H}_2\text{O})_4] \cdot 10.5\text{H}_2\text{O}$, $[\text{Pr}(\text{Glu})(\text{H}_2\text{O})_2]\text{Cl}$ and $[\text{Er}(\text{Glu})(\text{GluH})(\text{H}_2\text{O})_2]$. *Z. Anorg. Allg. Chem.* 631 (2005), 2416–2422.
- [43]. X. Li, Y.-B. Zhang, and Y.-Q. Zou. Hydrothermal synthesis, crystal structure, and luminescence of lanthanide(III) coordination polymers with tetrafluorosuccinate and 1,10-phenanthroline. *J. Mol. Struct.* 919 (2009) 277–283.
- [44]. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, Applications in Coordination, Organometallic, and Bioinorganic Chemistry*. Hoboken, New Jersey, 2009.
- [45]. U.P. Singh, N. Goel, G. Singh, P. Srivastava. Syntheses, structural and thermal studies of Eu(III) and Gd(III) complexes with 2,6-dinitrophenol and 1,10-phenanthroline/2,2'-bipyridine ligands. *Inorganica Chimica Acta* 387 (2012) 294–307.
- [46]. W. T. Carnall, P. R. Fields, and B. G. Wybourne. Spectral Intensities of the Trivalent Lanthanides and Actinides in Solution. I. Pr^{3+} , Nd^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+} . *J. Chem. Phys.* 42, (1965) 3797–3806..
- [47]. M. Pan, B.-B. Du, Y.-X. Zhu, M.-Q. Yue, Z.-W. Wei, C.-Y. Su. Highly Efficient Visible-to-NIR Luminescence of Lanthanide(III) Complexes with Zwitterionic Ligands Bearing Charge-Transfer Character: Beyond Triplet Sensitization. *Chemistry-a European Journal* 22 (2016) 2440–2451.
- [48]. Y. Pointel, Y. Suffren, C. Daignebonne, F. Le Natur, S. Freslon, G. Calvez, K. Bernot, O. Guillou. Rational design of dual IR and visible highly luminescent light-lanthanides-based coordination polymers. *Inorg. Chem.* 59 (2020)10673–10687.

GRAPHICAL ABSTRACT

A new Pr^{3+} -coordination polymers with rigid and flexible ligand that emits under UV Excitation.

