A new family of lanthanide-based coordination polymers with azoxybenzene-3,3',5,5'-tetracarboxylic acid as ligand

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Univ Rennes, INSA Rennes, CNRS UMR 6226 "Institut des Sciences Chimiques de Rennes", F-35708 Rennes.

* To whom correspondence should be addressed.

ABSTRACT.

Reactions by solvothermal methods of lanthanide nitrates and azoxybenzene-3,3',5,5'-tetracarboxylic acid (H_4aobtc) lead to a family of isostructural lanthanide-based coordination polymers with general chemical formula $[Ln(Haobtc)(H_2O)_2 \cdot 2H_2O]_\infty$ with Ln = Nd-Er plus Y. The crystal structure has been solved on the basis of the Y^{3+}-derivative. It crystallizes in the triclinic system, space group *P-1* (n°2) with the following cell parameters: a = 6.6890(18) Å, b = 10.052(3) Å, c = 13.879(4) Å, α = 75.756(9)°, β = 77.551(9)°, γ = 83.964(9)° and Z = 2. The crystal structure is two-dimensional (2D). Thermal properties and luminescent properties of the Nd^{3+}-containing compound have been studied.

KEYWORDS.

Lanthanide coordination polymers – Crystal structure – Luminescent properties - azoxybenzene-3,3',5,5'-tetracarboxylic acid – Thermal analysis

HIGHLIGTHS.

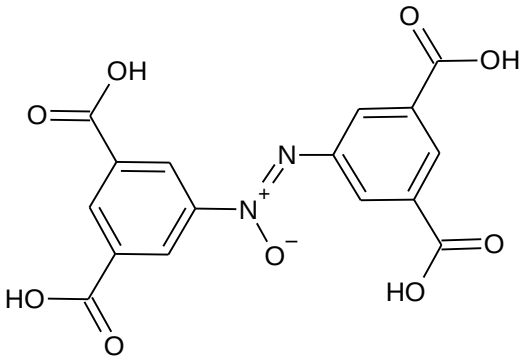
First azoxybenzene-3,3',5,5'-tetracarboxylate lanthanide coordination polymers

Excitation and emission wavelengths in the IR region

Structural characterization of a series of lanthanide coordination polymers

INTRODUCTION

Lanthanide-based coordination polymers arouse increasing interest because of their various potential applications [1] such as lighting and display [2-3], thermometric probes,[4-7] chemical sensing [8-9] or fight against counterfeiting [10-13], for instance. Our group, which is involved in that field for more than twenty years, has synthesized numerous lanthanide-based coordination polymers, playing with both the nature of the metallic nodes [14-15] or of the ligands [16], targeting new interesting porosity [17-18], magnetic [19-20] or optical [21-24] properties. Because of the unique optical properties of the lanthanide ions [25-27] much work has been devoted to the modulation of the intensity and color of the luminescence of lanthanide-based coordination polymers [28-31]. One of the challenge in that field is to produce intense white light [3, 6, 32-33]. The red and green components can be easily obtained using luminescence of the Eu^{3+} and Tb^{3+} ions respectively [34]. The blue component is more difficult to produce because it is absent from trivalent lanthanide ions emission colors. Alternatively, this blue emission can be achieved by ligand phosphorescence [3, 35]. Therefore, we have decided to investigate lanthanide coordination polymers based on azoxybenzene-3,3',5,5'-tetracarboxylic acid ligand (Scheme 1). Indeed this planar ligand presents an extended conjugated π-system that could induce blue phosphorescence. Additionally, because of its low energy excited states, efficient ligand-to-metal energy transfer is not expected, which is supposed to be favorable to ligand emission. At last its four carboxylate functions are appropriate for coordinating lanthanide ions [36] and, to the best of our knowledge, there is, to date, no example of lanthanide coordination polymer based on this ligand.

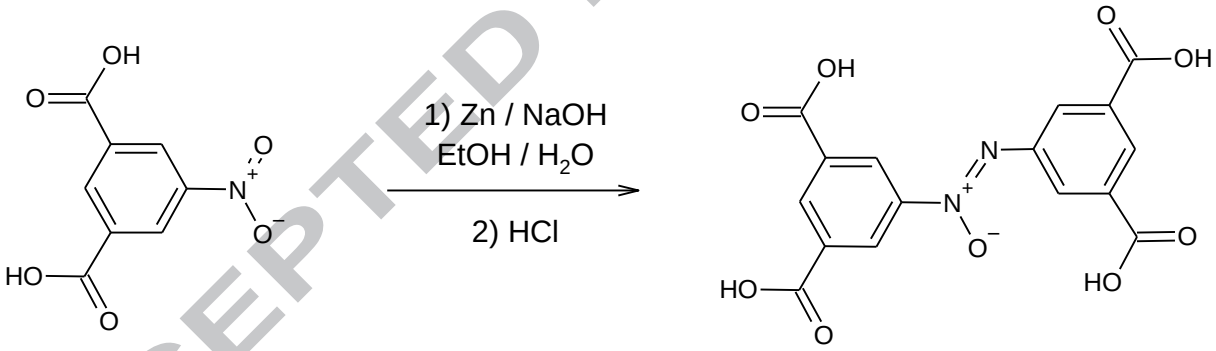


Scheme 1. Schematic representation of azoxybenzene-3,3',5,5'-tetracarboxylic acid hereafter referred as H_4aobtc.

EXPERIMENTAL SECTION.

Synthesis of the ligand azoxybenzene-3,3',5,5'-tetracarboxylic acid (H_4aobtc).

Nitro-isophthalic acid ($C_8H_5NO_6$) was purchased from Aldrich (98%) and used without any further purification. The ligand was synthesized on the basis of procedures that have previously been reported (Scheme 2) [37-39].



Scheme 2. Schematic representation of the synthetic route for H_4aobtc.

5-nitroisophthalic acid (2.10 g, 10 mmol), Zn (1.30 g, 20 mmol), and NaOH (0.80 g, 20 mmol) were suspended in a water/ethanol mixture (20 mL/50 mL) and refluxed overnight. Precipitation occurred and the yellow precipitate was filtered. It was then dissolved in 50 mL of an aqueous solution of NaOH (1 mol.L^{-1}) and the resulting solution was filtered to remove insoluble residues. Then, pH of the filtrate was adjusted to pH ≈ 3 using an aqueous solution of HCl (3 mol.L^{-1}). Precipitation of a yellow solid occurred that was filtered and dried in air.

Yield was about 80% (1.53 g). Elemental analysis for H_4aobtc (MW = 374.26 g.mol^{-1}): Found (Calc.): C 50.9% (51.3%); H 2.9% (2.7%); N 7.7% (7.5%); O 38.9% (38.5%).

IR spectrum (Figure S1) shows characteristic bands for protonated carboxylic function (1680 cm^{-1} for the ν(C=O) stretching mode), for N=N-O groups in azoxy compounds (1300 cm^{-1} and 1440 cm^{-1} for the ν_s symmetric and ν_{as} antisymmetric stretching modes, respectively) and finally for C-OH groups and water (broad band at 3350 cm^{-1} for the ν(O-H) stretching modes) [40].

Synthesis of [Ln(Haobtc)(H_2O)$_2$·2H_2O]$_\infty$ with Ln = Nd - Er plus Y.

0.2 mmol of a lanthanide nitrate (Ln(NO_3)$_3$.6H_2O), 0.1 mmol (37.4 mg) of H_4aobtc, 0.8 mL of aqueous HCl (12.5 mol.L^{-1}), 4 mL of water and 8 mL of acetonitrile were put in a 24 mL Parr autoclave. Parr autoclave was heated at 110°C during four days. Then autoclave was cooled down at a cooling rate of 3°C per hour. The obtained microcrystalline powder was filtered and dried at ambient air. Single crystals suitable for X-ray diffraction crystal structure determination were obtained with the yttrium-derivative (Figure 1).

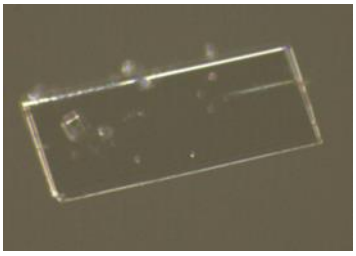


Figure 1. Picture of a single crystal of [Y(Haobtc)(H_2O)$_2$·2H_2O]$_\infty$

Isostructurality of the microcrystalline powders, that were obtained with other lanthanide ions, with [Y(Haobtc)(H_2O)$_2$·2H_2O]$_\infty$, was assumed on the basis of their powder X-ray diffraction diagrams (Figure S2).

IR spectrum [Y(Haobtc)(H_2O)$_2$·2H_2O]$_\infty$ (Figure S1) is similar to the one of the ligand except that it shows characteristic bands for deprotonated carboxylate function (1380 and

1590 cm^{-1}) as well as for protonated carboxylic function (1680 cm^{-1}) which suggests that at least one carboxylate group is protonated in the crystal structure [40].

Elemental analyzes of $[Ln(Haobtc)(H_2O)_2 \cdot 2H_2O]_\infty$ with Ln = Nd - Er plus Y are listed in Table S1.

Single crystal X-ray diffraction.

A single crystal of $[Y(Haobtc)(H_2O)_2 \cdot 2H_2O]_\infty$ was mounted on a Bruker D8 Venture. Crystal data collection was performed with MoK_α radiation (λ = 0.70713 Å) at 150 K. Crystal structure was solved by direct methods using the SIR97 program [41] and then refined with full matrix least-squares methods based on F^2 (SHELX97) [42] with the aid of WINGX program [43]. All non-hydrogen atoms were refined anisotropically using the SHELXL program. Hydrogen atoms bound to the organic ligand were located at ideal positions. Hydrogen atoms of water molecules were not located. Absorption correction were performed using WinGX program facilities [43-44]. Full details of the X-ray structure determination of the crystal structure have been deposited with the Cambridge Crystallographic Data Center under the depositary number CCDC- 1871493. Crystal and final structure refinement data are listed in Table 1.

Table 1. Crystal and final structure refinement data for $[Y(Haobtc)(H_2O)_2 \cdot 2H_2O]_\infty$

Molecular formula	$YC_{16}H_{15}N_2O_{13}$
System	triclinic
Space group (No.)	*P-1* (2)
a (Å)	6.6890(18)
b (Å)	10.052(3)
c (Å)	13.879(4)
α (°)	75.756(9)
β (°)	77.551(9)
γ (°)	83.964(9)
V (Å^3)	881.9(4)
Z	2
Formula weight (g.mol^{-1})	532.21
D_{calc} (g.cm^{-3})	2.004
μ (mm^{-1})	3.391
R (%)	9.03
R_W (%)	20.79
GoF	1.145
N° CCDC	1871493

Powder X-ray diffraction.

Experimental diagrams have been collected with a Panalytical X'pert Pro diffractometer equipped with a X'Celerator detector. Typical recording conditions were 45 kV, 40 mA for CuK_α (λ = 1.542Å) in θ/θ mode. Calculated pattern were produced using the Mercury and WinPLOTR software programs [45-47].

Thermal analysis.

Thermal analysis was performed with a Perkin-Elmer Pyris-Diamond analyzer in a platinum crucible between room temperature and 1000°C under N_2 atmosphere with a heating rate of 5°C.min^{-1}. The compound was maintained at 1000°C under air atmosphere for one hour to insure complete combustion.

Optical measurements.

Solid and aqueous solution UV-visible absorption spectra have been recorded with a Perkin Elmer Lambda 650 spectrometer equipped with a 60 mm integrated sphere.

Solid state luminescence measurements have been performed on a Horiba Jobin-Yvon Fluorolog III fluorescence spectrometer equipped with a Xe lamp 450 W, a UV-Vis photomultiplier (Hamamatsu R928, sensitivity 190-860 nm) and an infrared-photodiode cooled by liquid nitrogen (InGaAs, sensitivity 800-1600 nm) at room temperature. The visible phosphorescence of the ligand and the infrared emission of the Nd(III) were measured directly on powder samples introduced in quartz capillary tubes or on powder samples pasted on copper plates with a silver lacquer. The phosphorescence of the ligand has been measured at 77 K inside a small Dewar that contained liquid nitrogen. Appropriate filters were used to remove the residual excitation laser light, the Rayleigh scattered light and associated harmonics from spectra. All spectra were corrected for the instrumental response function. The lifetime for the phosphorescence was measured directly with Horiba Jobin-Yvon Fluorolog III fluorescence spectrometer coupled with an additional TCSPC module (Time-Correlated-Single-Photon-Counting) and a 320 nm pulsed Delta-Diode.

FT-IR spectra were obtained from solid samples with a Perkin Elmer Frontier FT-IR spectrometer equipped with a MIR-ATR module between 4000 cm^{-1} and 650 cm^{-1}.

RESULTS AND DISCUSSION.

Description of the crystal structure of $[Y(Haobtc)(H_2O)_2 \cdot 2H_2O]_\infty$.

The crystal structure contains only one independent Y^{3+} ion. This ion is linked to eight oxygen atoms that form a slightly distorted dodecahedron. Two out of these oxygen atoms belong to coordination water molecules. The six other belong to carboxylate groups from five different ligands: one according to a bidentate mode and the four other according to a monodentate one. The crystal structure presents only one independent ligand that is

coordinated to five lanthanide ions (see Figure 2). One out of the four carboxylic functions is protonated. This is supported by the IR spectrum (Figure S1) that shows the characteristic peak of a protonated carboxylic acid (1680 cm^{-1}). In the ligand, oxygen atoms bound to the nitrogen atoms have 0.5 occupancy factors. Surprisingly, this crystal structure is very close to that of a Dy^{3+}-based coordination polymer with azobenzene-3,3',5,5'-tetracarboxylic acid (H_4abtc) as ligand that has been recently reported (CCDC-1855292) [48].

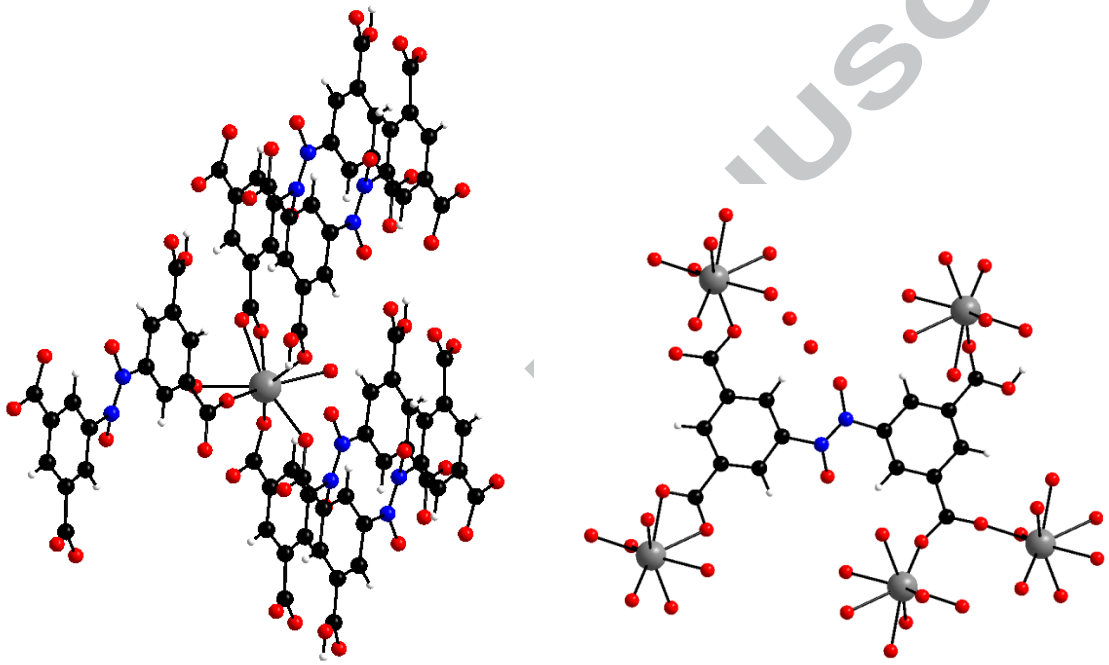


Figure 2. Projection views of coordination modes of the Y^{3+} ion (left) and of the $Haobtc^{3-}$ ligand (right) in $[Y(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$.

This crystal structure can be described as the superimposition of double-planes that spread perpendicular the *a* axis. In the double-plane molecular motif, there are four different Ln-Ln distances depending on the ligand coordination: 5.452 Å between two lanthanide ions linked by the same carboxylate group, 10.052 Å or 8.997 Å between lanthanide ions linked by two different carboxylate groups bound to the same benzene ring and 8.996 Å between lanthanide ions linked by two carboxylate groups bound to two different benzene rings (See Figure 3). Between two adjacent double-plans, the shortest Ln-Ln distance is 6.689 Å.

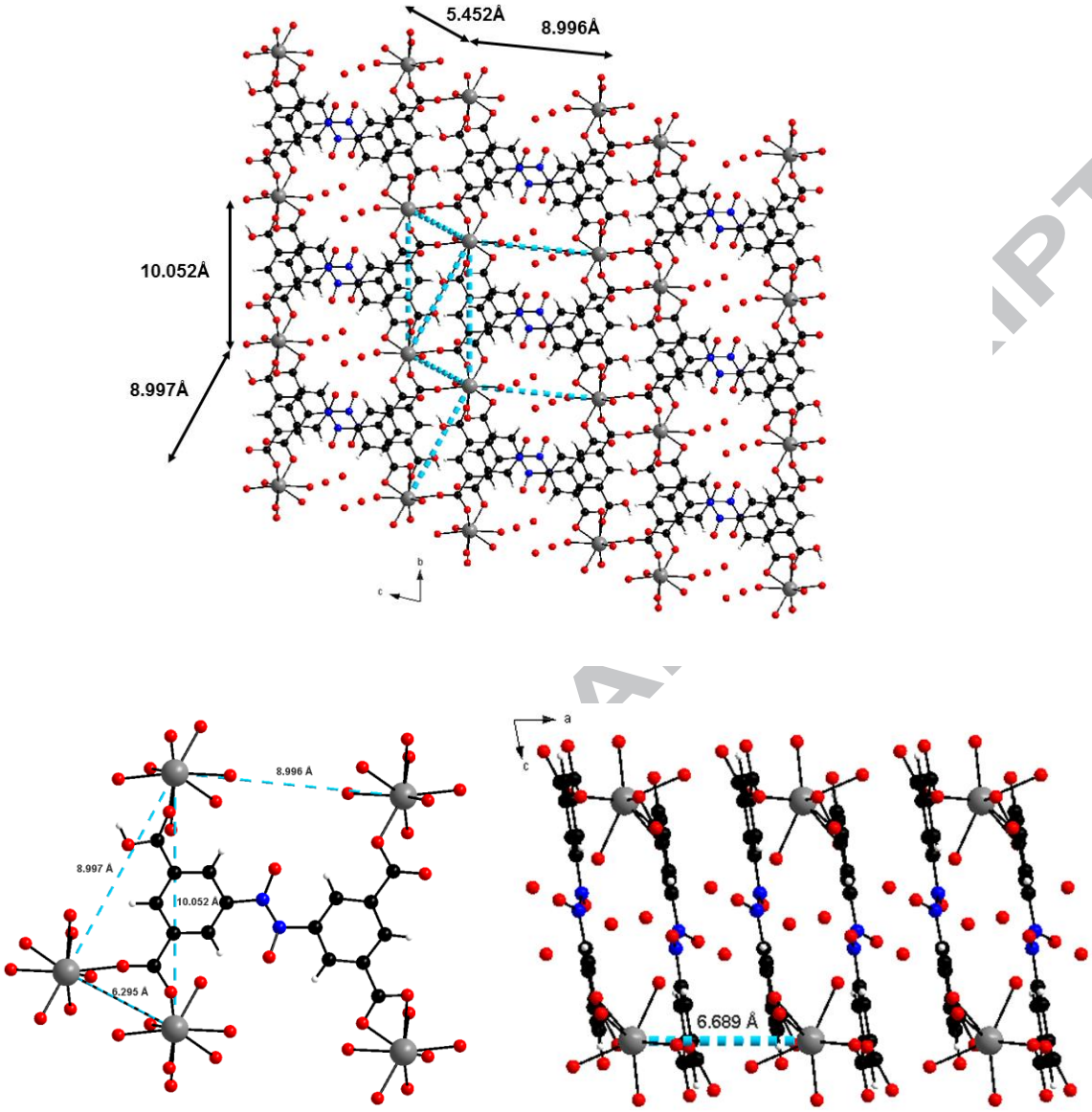


Figure 3. Lanthanide distances in a double-plane molecular motif (top), between two adjacent double-planes (bottom right) and depending on the ligand coordination modes (bottom left) in $[Y(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$.

The crystal structure presents channels, that spread along the *a* and *b* axes, in which crystallization water molecules are located. These crystallization water molecules are strongly bound to the molecular framework via a hydrogen-bonds network that involve crystallization and coordination water molecules, oxygen atoms of the carboxylate groups and of the azoxy groups of the ligands (Figure 4 and Table S2).

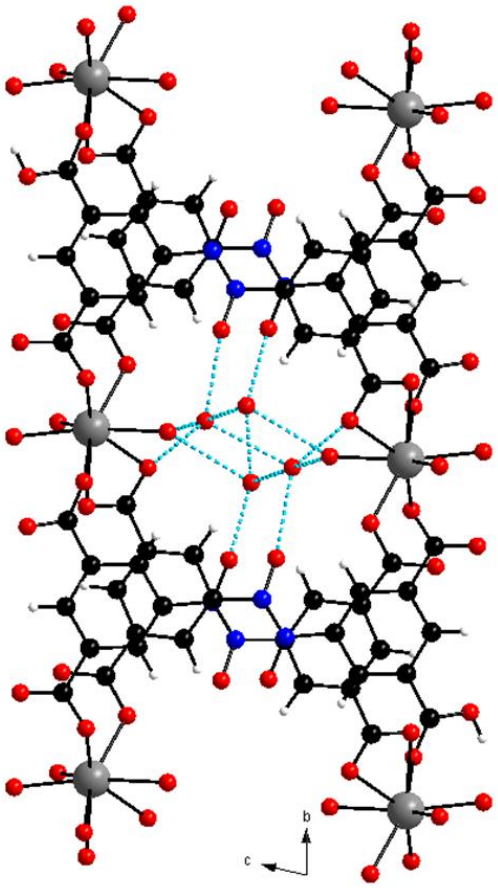


Figure 4. Hydrogen-bonds network (light blue broken lines) in $[Y(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$.

Thermal analysis of $[Y(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$.

Thermal analysis of the coordination polymer (Figure 5) shows a first weight loss before 200°C (14%) that can be attributed to the departure of the four crystallization and coordination water molecules (calc. 13.7%). Then, the anhydrous compound $[Y(Haobtc)]_\infty$ is stable between 200°C and 350°C. Above this temperature the decomposition of the ligand occurs. At 1000°C, the yttrium oxide is obtained. This result is confirmed by the powder X-ray diffraction diagram of the residual solid (Figure S3) that can be indexed by JCPDS-05-0574.

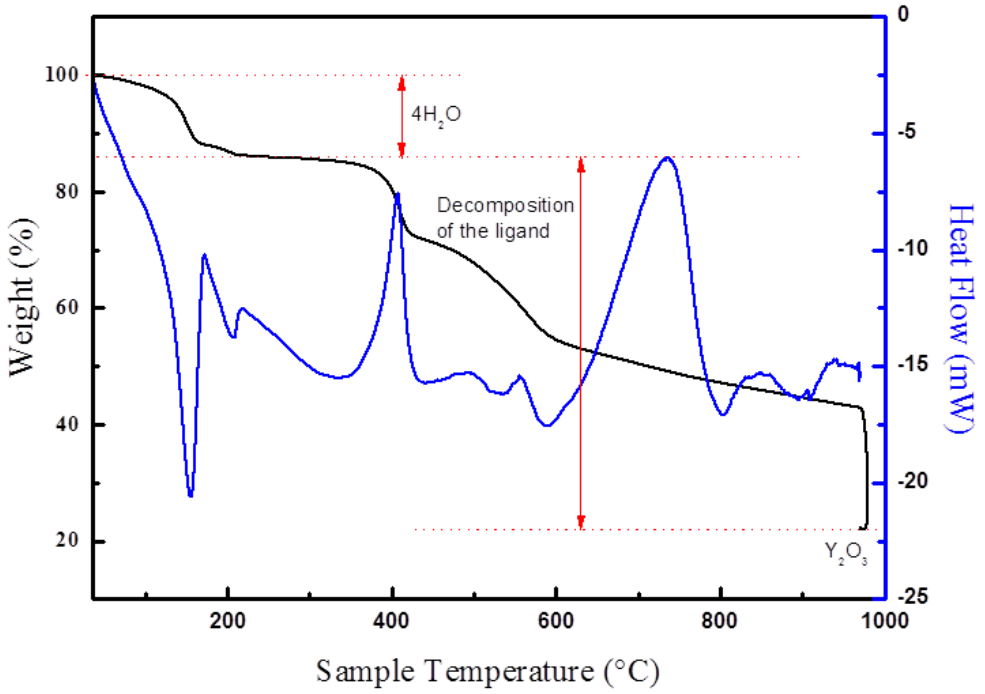


Figure 5. Thermal analysis of $[Y(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$.

Optical measurements.

Excitation spectra that have been recorded for the homo-lanthanide compounds, **[**$Ln(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ with Ln = Nd-Er plus Y, show that none of them present antenna effect [49]. Commonly, energy of the first excited triplet state is estimated on the basis of the first edges of the phosphorescence spectrum of the Gd^{3+}-derivative. This spectrum has been recorded at 77 K (Figure S4). The lowest wavelength emission edge of the spectrum is about 360 nm (27780 cm^{-1}) which does not favor an efficient ligand-to-metal energy transfer according to Latva's empirical rules [50] that are commonly evoked for Tb^{3+}- and Eu^{3+}-based compounds. Moreover, luminescence decay of **[**$Gd(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ has been measured. It is bi-exponential with τ_1 = 3.50(2) µs and τ_2 = 18.9(4) µs. These lifetimes are very short for phosphorescence that is three to four orders of magnitude smaller than what is usually observed for lanthanide-based coordination polymers.[51]

Additionally, except for the Nd^{3+}-derivative (Figure 6), no luminescence is observed by direct excitation of the lanthanide ion. This can be related to the optical properties of the

ligand. Indeed, absorption spectrum of the Gd^{3+}-based compound has been recorded (Figure S5). It shows that the ligand absorbs up to 550 nm (18180 cm^{-1}) which prevents direct excitation of lanthanide ions that present absorption bands below 400 nm such as Eu^{3+}, Tb^{3+} or Dy^{3+}, for instance. Furthermore, we observe a significant overlap between the absorption band (singlet states) and the phosphorescence band (triplet states). This indicates that energy levels of the triplet are lower than the energy levels of the different lanthanides that emit in the visible (Sm, Eu, Tb, Dy). So, a back transfer probably occurs and quenches any luminescence of the rare earth in the visible.

On the opposite, the Nd^{3+}-derivative emission spectrum shows sizeable luminescence in the IR domain: the energy of the excited state of the Nd(III) (11400 cm^{-1}) is lower than the energy state of the ligand and the IR emission occurs without significant back transfer. The three classical emissions for the Nd(III) are observed at 878, 1059 and 1338 nm (assigned $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$, respectively), under direct excitation at 586 nm ($^4I_{9/2} \rightarrow {}^2G_{7/2}$, $^2G_{5/2}$), 747 nm ($^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4S_{3/2}$) and 805 nm ($^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^2H_{9/2}$) (Figure 6).

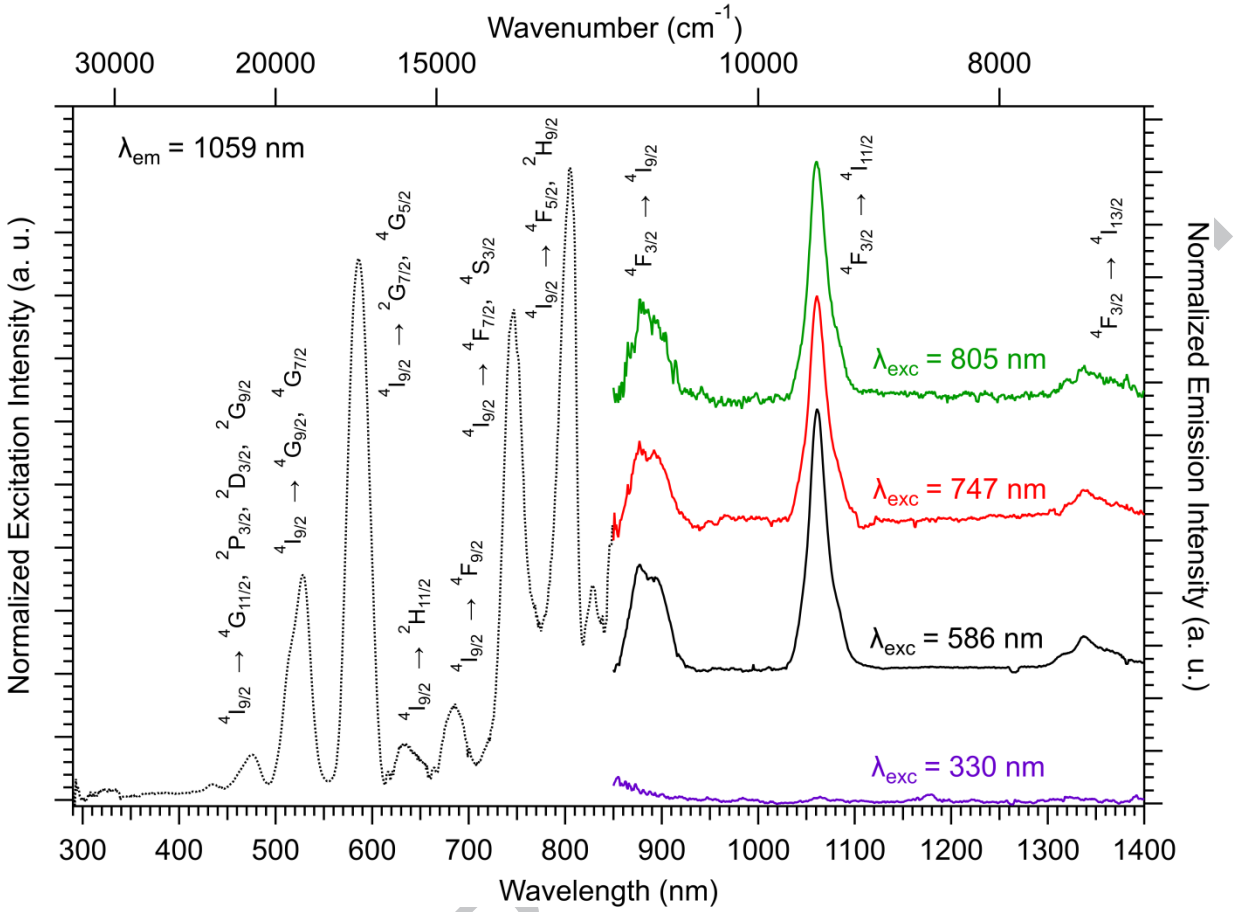


Figure 6. Solid state excitation and emission spectra of $[Nd(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ measured at room temperature under different excitation wavelengths in the visible and the IR.

Excitation bands for $[Nd(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ are observed beyond 450 nm and the more efficient excitation wavelength is 586 nm. This is in agreement with the absorption spectrum of $[Gd(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ (Figure S5) that shows that the main absorption band is observed before 450 nm and that absorption becomes almost zero at about 550 nm.

CONCLUSION AND OUTLOOKS

A series of lanthanide-based coordination polymers with azoxybenzene-3,3',5,5'-tetracarboxylic acid as ligand has been synthesized and structurally characterized. Compounds that constitute this family don't show luminescence in the visible region. However the Nd^{3+}-derivative shows sizeable emission band in the IR region, under

excitation wavelengths comprised between 586 nm and 805 nm that are compatible with potential applications in biological media.

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SUPPORTING INFORMATION

Infra-Red Spectra of $[Ho(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ and H_4aobtc; Experimental powder X-ray diffraction diagrams of $[Ln(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ with Ln = Nd-Er except Pm plus Y and simulated powder X-ray diffraction diagram of $[Y(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ from its crystal structure; Experimental powder X-ray diffraction diagram of the residual solid after ATG-TD analysis indexed by Y_2O_3 (JCPDS-05-0574); Solid state emission spectrum of $[Gd(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ recorded at 77 K; Solid state absorption spectrum of $[Gd(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ recorded at room temperature; Elemental analyzes for $[Ln(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ with Ln = Nd - Er plus Y; Hydrogen-bonds network in $[Y(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$.

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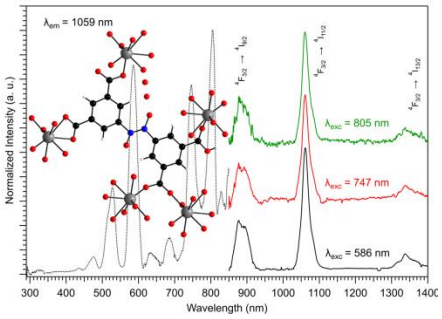

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Reactions by solvothermal methods of lanthanide nitrates and azoxybenzene-3,3',5,5'-tetracarboxylic acid (H_4aobtc) lead to a family of isostructural lanthanide-based coordination polymers with general chemical formula $[Ln(Haobtc)(H_2O)_2{\cdot}2H_2O]_\infty$ with Ln = Nd-Er plus Y. Luminescent properties of the Nd^{3+}-containing compound could be of interest as far as biological applications are targeted.

HIGHLIGTHS.

First azoxybenzene-3,3',5,5'-tetracarboxylate lanthanide coordination polymers;

Excitation and emission wavelengths in the IR region;

Structural characterization of a series of lanthanide coordination polymers.