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Microwave-assisted synthesis of lanthanide coordination polymers with 2-bromobenzoic acid as ligand from hexa-lanthanide molecular precursors

Haiyun Yao<sup>a,b</sup>, Guillaume Calvez<sup>a,\*</sup>, Carole Daignebonne<sup>a</sup>, Yan Suffren<sup>a</sup>, Kevin Bernot<sup>a</sup> and Olivier Guillou<sup>a,\*</sup>

<sup>a</sup>Univ Rennes, INSA Rennes, CNRS UMR 6226 "Institut des Sciences Chimiques de Rennes", F-35708 Rennes, France

<sup>b</sup>Present address: School of Opto-electronic Engineering, Zaozhuang University, Zaozhuang 277160, China

\*To whom correspondence should be addressed.

#### Highlights

- New lanthanide-based coordination polymers crystal structure
- Straight chains are obtained from octahedral hexa-lanthanide precursors
- Strong intermetallic energy transfers between lanthanide ions

#### ABSTRACT

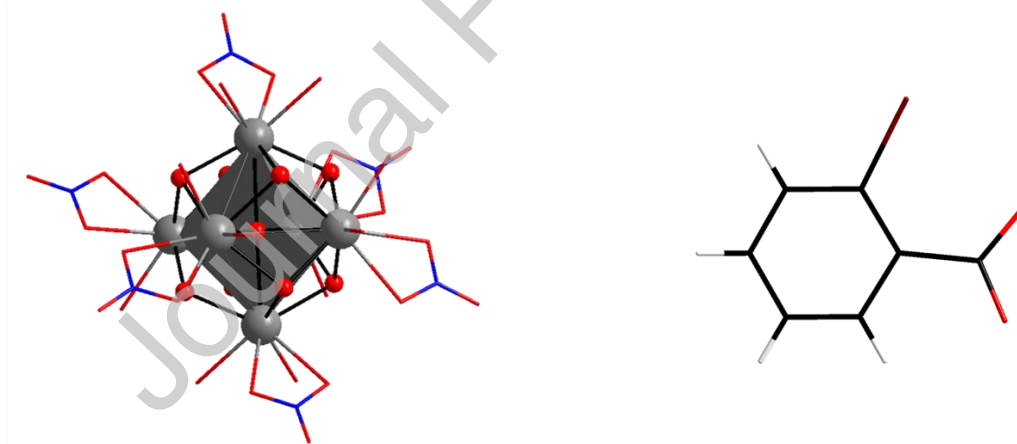
Microwave-assisted reactions, between 2-bromobenzoic acid (2-bbH) and hexa-lanthanide molecular precursors of general chemical formula

$\text{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{NO}_3)_6(\text{H}_2\text{O})_{12}\cdot 2\text{NO}_3\cdot 2\text{H}_2\text{O}$  ( $[\text{Ln}_6]$ ), lead to iso-structural 1D coordination polymers of general chemical formula  $[\text{Ln}(2\text{-bb})_3]_\infty$  with  $\text{Ln} = \text{Eu}, \text{Tb}$  or  $\text{Dy}$ . These compounds crystallize in the monoclinic system, space group  $P2_1/c$  ( $n^\circ 14$ ), with the following cell parameters (for the Dy-derivative):  $a = 12.3809(10) \text{ \AA}$ ,  $b = 21.8653(16) \text{ \AA}$ ,  $c = 7.9119(7) \text{ \AA}$ ,  $\beta = 98.709(3)^\circ$ ,  $V = 2117.2(3) \text{ \AA}^3$  and  $Z = 4$ . The influence of the hexa-nuclear precursors over the final coordination polymer is demonstrated. Indeed, while the hexa-nuclear complexes collapse during the synthetic process their progressive destruction affords a unique 1D coordination polymer that cannot be readily obtained otherwise. Additionally, some iso-structural hetero-lanthanide derivatives with general chemical formulas  $[\text{Eu}_x\text{Tb}_{1-x}(2\text{-bb})_3]_\infty$  and  $[\text{Y}_x\text{Tb}_{1-x}(2\text{-bb})_3]_\infty$  with  $0 \leq x \leq 1$  have been prepared from the corresponding hexa-nuclear complexes  $[\text{Eu}_6\text{Tb}_{6-6x}]$  and  $[\text{Y}_6\text{Tb}_{6-6x}]$ , respectively. Luminescent properties have been recorded and colorimetric coordinates have been calculated for all the compounds. These measurements indicate that the molecular chains host strong intermetallic energy transfers.

## INTRODUCTION

Lanthanide based coordination polymers<sup>1</sup> have been widely studied in the past two decades because of their interesting porous,<sup>2-6</sup> luminescent<sup>7-9</sup> or magnetic<sup>10-13</sup> properties, for instance. Indeed, because of the unique chemical and physical properties of the lanthanide ions,<sup>14-16</sup> they can find their application in various technological fields<sup>17-19</sup> such as molecular thermometry,<sup>20-25</sup> chemical sensing,<sup>9, 26-28</sup> light and display<sup>29-31</sup> or chemical tagging,<sup>32-36</sup> for examples. Therefore, the quest for new compounds with enhanced optical properties is a continuous concern.<sup>37</sup> To achieve this objective one can play both with the nature of the ligand or with the metallic centers of the coordination polymers. The more common strategy

consists on modifying the ligand<sup>21-22, 38-45</sup> but it is also possible to use polymetallic centers.<sup>18, 46-49</sup> (i) In one hand, in recent years, it has been shown that the use of a ligand that induces a large distance between the molecular motifs is beneficial because it reduces intermetallic energy transfers<sup>50-51</sup> between neighboring molecular motifs.<sup>36, 52-54</sup> Halogeno derivatives, for example, that can induce halogen bonds, have shown their efficiency.<sup>36, 52-53</sup> (ii) In the other hand, it is possible to design coordination polymers in which the metallic centers are no longer single lanthanide ions but poly-lanthanide entities. Many beautiful such compounds have been reported so far<sup>55</sup> that sometimes present metallic centers with very high nuclearities.<sup>56-58</sup> However, most of these compounds have been obtained via one-pot serendipitous syntheses. Actually, the only poly-lanthanide complexes usable as molecular precursors for the design of coordination polymers, to date, are the octahedral hexa-nuclear complexes first described by Giester *et al.*<sup>59-63</sup> (Figure 1). Several coordination compounds have been obtained using these complexes as reactants.<sup>47, 64-67</sup>



**Figure 1.** Left: Projection view of a hexa-nuclear molecular complex  $Y_6(\mu_6-O)(\mu_3-OH)_8(NO_3)_6(H_2O)_{12} \cdot 2NO_3 \cdot 2H_2O$  ( $[Y_6]$ ). Redrawn from reference 68. Right: Molecular view of 2-bromo-benzoate.

To the best of our knowledge, there is only one lanthanide coordination polymer based on 2-bbH reported so far:  $[Eu(2-bb)_3 \cdot H_2O]_\infty$ .<sup>69</sup> As expected, in this 1D crystal structure, the 2-bb<sup>-</sup> ligands act both as antenna<sup>70</sup> and spacers.

Our group has developed the use of hexa-lanthanide complexes as molecular precursors for almost 20 years<sup>71-72</sup> and, in this article, we describe the microwave-assisted synthesis, the crystal structure and the luminescent properties of new lanthanide coordination polymers obtained from 2-bromo-benzoic acid (2-bbH) and hexa-lanthanide complexes ([Ln<sub>6</sub>]).

## EXPERIMENTAL SECTION.

### Synthesis of [Ln(2-bb)<sub>3</sub>]<sub>∞</sub> with Ln = Eu, Tb or Dy.

2-bbH was purchased from TCI (>98%) and used without further purification. Lanthanide oxides were purchased from Ampère (4N) and used without further purification. Lanthanide nitrates and hexa-nuclear complexes [Ln<sub>6</sub>] were prepared as previously described.<sup>68, 73</sup>

5.10<sup>-3</sup> mmol of hexa-lanthanide complexes ([Ln<sub>6</sub>]) with Ln = Eu, Tb or Dy, 5.10<sup>-3</sup> mmol of 2-bromobenzic acid (2-bbH) and 2 mL of acetonitrile were mixed under magnetic stirring in a 10 mL tube. The suspension was then microwave heated at 100°C (CEM Discover microwave heater; power setting 150 W; maximum pressure 2 bars) for 15 min. Then the mixture was filtered and allowed to cool down to room temperature. The resulting limpid solution was then left for several days at room temperature in a closed vessel. After a few days, single crystals appeared. They were collected, rinsed with acetonitrile and dried in air. Each batch produces only about 300 µg of single crystals which makes difficult some measurements. Iso-structurality of the samples was assumed on the basis of their powder X-ray diffraction diagrams and IR spectra. They were all similar and only those of the Tb-derivative are reported (Figures S1 and S2). Measurements have been made on crushed single crystals.

**Single crystal X-ray diffraction.**

The crystal structure has been solved on the basis of the dysprosium-derivative. Single crystals were mounted on a Bruker D8 Venture diffractometer. Crystal data collection were performed at 150 K with Mo  $K_{\alpha}$  radiation ( $\lambda = 0.70713 \text{ \AA}$ ). The crystal structure was solved, using SIR 97,<sup>74</sup> by direct methods. It was refined, using SHELX-2017<sup>75-76</sup> with the aid of WINGX program.<sup>77-78</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at ideal positions. Absorption corrections were performed using the facilities of WINGX program.<sup>79</sup> There is some residual density near the  $\text{Dy}^{3+}$  ion. Selected crystal and final structure refinement data are gathered in Table 1. Full details of the crystal structure have been deposited with the Cambridge Crystallographic Data Centers under the depositary number CCDC-1871218.

**Table 1.** Crystallographic data for  $[\text{Dy}(\text{2-bb})_3]_{\infty}$ .

Chemical formula	$\text{C}_{21}\text{H}_{12}\text{Br}_3\text{DyO}_6$
System	Monoclinic
Space group ( $n^{\circ}$ )	$P2_1/c$ ( $n^{\circ}14$ )
Formula weight ( $\text{g}\cdot\text{mol}^{-1}$ )	762.51
$a$ ( $\text{\AA}$ )	12.3809(10)
$b$ ( $\text{\AA}$ )	21.8653(16)
$c$ ( $\text{\AA}$ )	7.9119(7)
$\beta$ ( $^{\circ}$ )	98.709(3)

$V (\text{\AA}^3)$	2117.2(3)
$Z$	4
$D_{calc} (\text{g}\cdot\text{cm}^{-3})$	2.392
$R (\%)$	4.26
$R_w (\%)$	11.27
$GoF$	1.067
CCDC number	1871218

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### Electronic microscopy and Energy Dispersive Spectroscopy (EDS).

EDS measurements have been performed with a Hitachi TM-1000, Tabletop Microscope version 02.11 (Hitachi High-Technologies, Corporation Tokyo Japan) with EDS analysis system (SwiftED-TM, Oxford Instruments Link INCA). Reproducibility of the elemental analyses has been checked by repeating the measurements several times. Results, expressed in atom percentages, are average values of different spots. These experiments support the homogeneity of the samples.

### Optical measurements.

Solid-state emission and excitation spectra have been measured on a Horiba Jobin-Yvon Fluorolog III fluorescence spectrometer equipped with a Xe lamp 450 W, an UV-Vis photomultiplier (Hamamatsu R928, sensitivity 190 - 860 nm). The emission/excitation spectra recordings were realized on powder samples in 700  $\mu\text{L}$  quartz cuvettes. The quantum yields were measured with the same device using an integrating sphere, extending its correction curve in the 290-330 nm range by measuring standards in this range (the Eu tris-dipicolinate in *tris* (tris(hydroxymethyl)aminomethane) buffer solution as proposed by Chauvin *et al*<sup>80</sup>). The quantum yield was estimated measuring the ratio between absorbed photons around the excitation wavelength without and with the sample (the

difference between respectively  $L_a$  and  $L_c$  values for corresponding integrated spectra) and the emitted photons with and without the sample (the difference between respectively  $E_c$  and  $E_a$  values for corresponding integrated spectra). The lifetime values were measured with the same device, using a pulsed Xenon source and measuring the intensity emitted after increasing time delay. The decay time was then fitted using a mono-exponential decay function. 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. Colorimetric coordinates have been calculated on the basis of the emission spectra.<sup>81-82</sup>

## RESULTS AND DISCUSSION.

### Crystal structure of $[\text{Ln}(\text{2-bb})_3]_\infty$ with Ln = Eu, Tb or Dy.

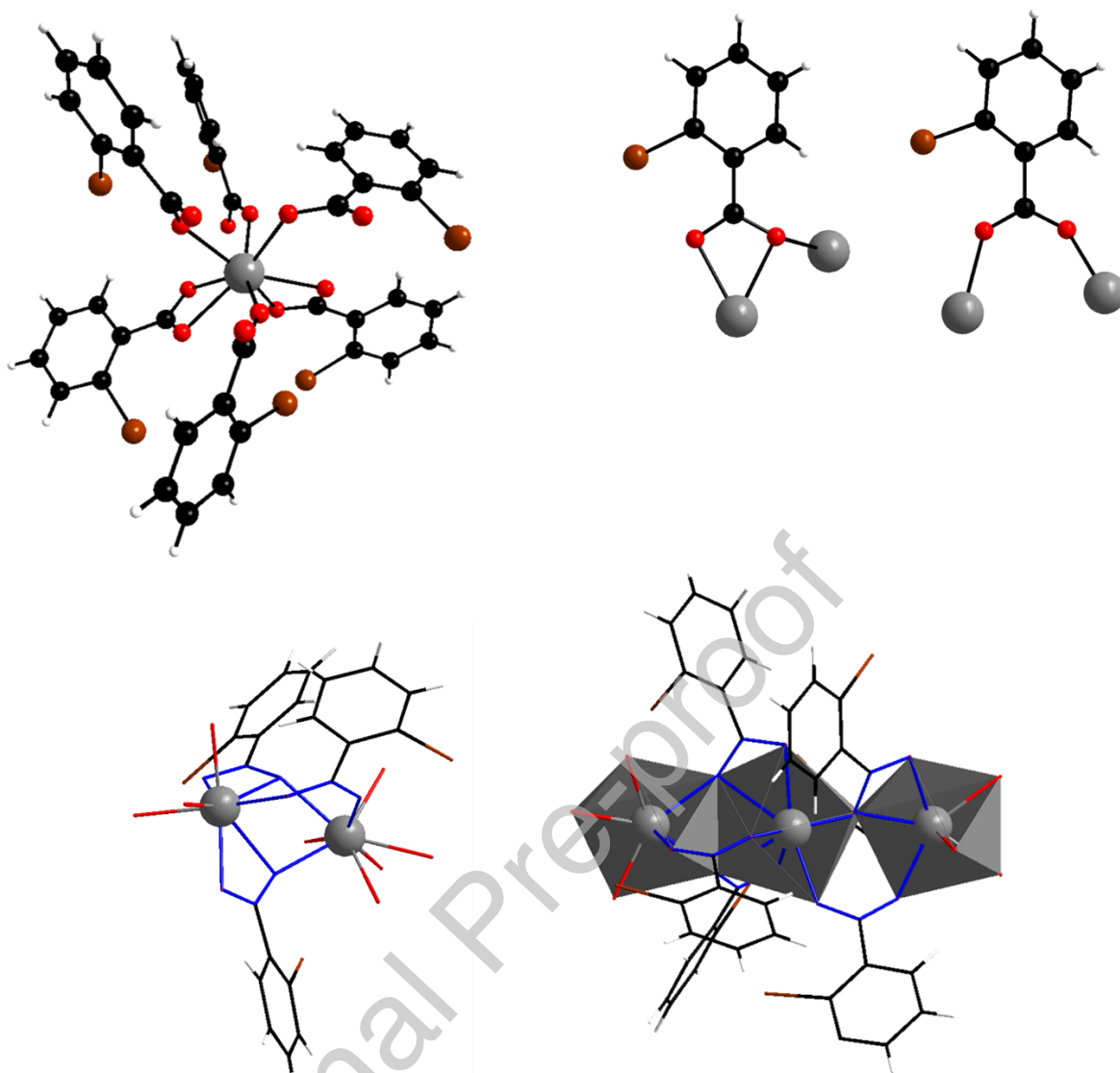
Microwave-assisted reactions in acetonitrile between a hexa-lanthanide complex ( $[\text{Ln}_6]$  with Ln = Eu, Tb or Dy) and 2-bromobenzoic acid lead to isostructural lanthanide coordination polymers with general chemical formula  $[\text{Ln}(\text{2-bb})_3]_\infty$  with Ln = Eu, Tb or Dy. The crystal structure has been solved on the basis of the Dy-derivative. It can be described as the juxtaposition of almost linear molecular chains that spread parallel to the  $c$ -axis. The chain is situated at the  $c$  glide plane, which means it obeys sub-periodic rod group symmetry  $pc11$  (No. R5).<sup>83</sup> Position of the Dy atom above the plane makes Dy...Dy distance a bit longer than half of the  $c$  axis:  $3.9584(3) \text{ \AA}$  vs  $3.9119(4) \text{ \AA} = c/2$ .

There is only one  $\text{Dy}^{3+}$  ion in the asymmetric unit. It is eight coordinated by eight oxygen atoms from six different 2-bb<sup>-</sup> ligands that form a bi-capped trigonal prism (Figure 2). There are three independent ligands in the asymmetric unit that present two different coordination modes: in the first one, the two oxygen atoms of the carboxylate function are monodentate while in the second one, one oxygen atom is monodentate and the second is

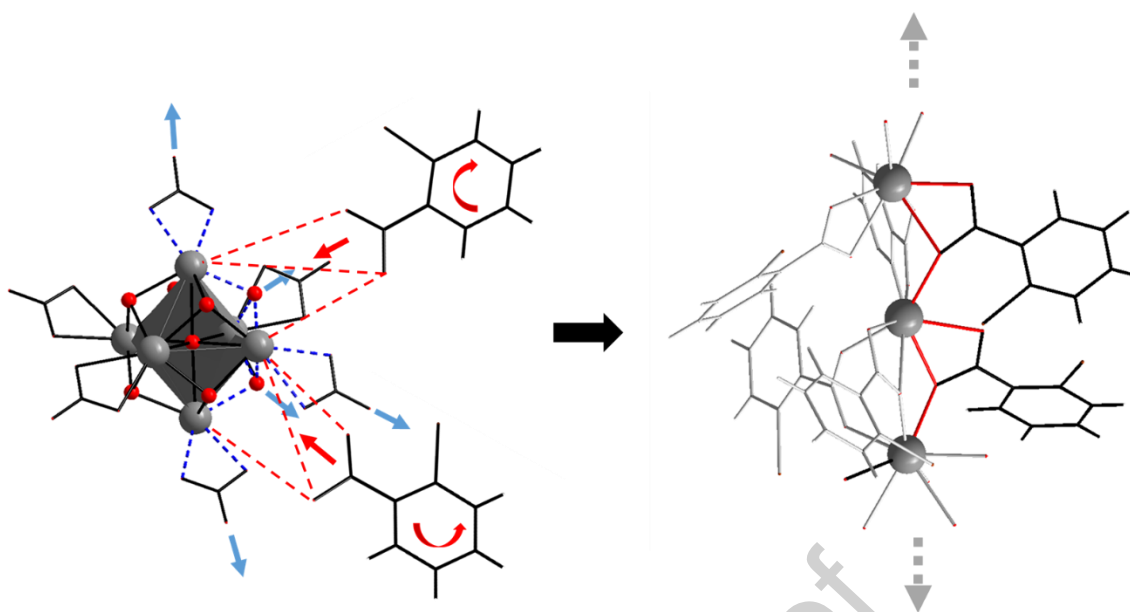


bidentate (Figure 2). There are three bridging ligands between two adjacent Dy<sup>3+</sup> ions, which leads to a short intermetallic distance in the molecular chains:  $d_{\text{Dy-Dy}} = 3.9584(3) \text{ \AA}$ . This crystal structure presents a 1D inorganic sub-lattice (coordination polyhedrons share edges) which constitutes an asset as far as strong intermetallic energy transfers<sup>52-53</sup> and high luminance are targeted.

It has been previously shown, that the octahedral complexes used as molecular precursors may present a structuring effect and may lead to crystal structures that cannot be obtained from simple mono-nuclear lanthanide salts.<sup>64-65, 84-85</sup> This is, once more, the case here and despite several attempts, it has not been possible to obtain these compounds using other precursors. Moreover, the quasi-linearity of the molecular chains (Dy-Dy-Dy angle is 175.9(1)°) strongly suggests that the carboxylate functions of the ligands clip and connect neighboring lanthanide ions of hexa-nuclear complexes while nitrate ions, hydroxides and coordination water molecules are simultaneously removed (Scheme 1). This synthetic mechanism has already been proposed recently.<sup>86</sup>

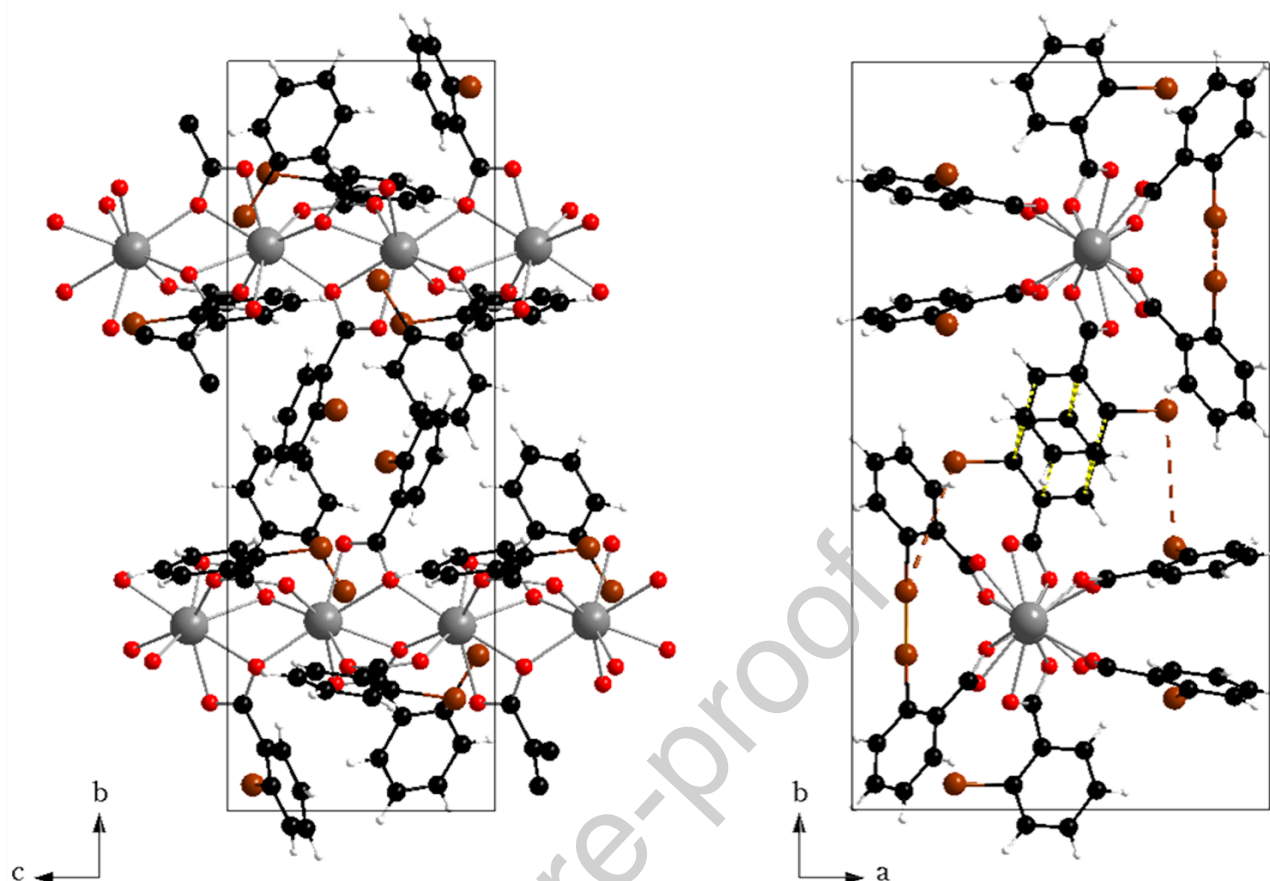


**Figure 2.** Neighborhood of the Dy<sup>3+</sup> ion (top left), coordination modes of the 2-bb<sup>-</sup> ligands (top right), triple Dy-Dy bridge (binding bonds are drawn in blue) (bottom left) and Dy<sup>3+</sup> polyhedrons (bottom right) of [Dy(2-bb)<sub>3</sub>]<sub>∞</sub>.

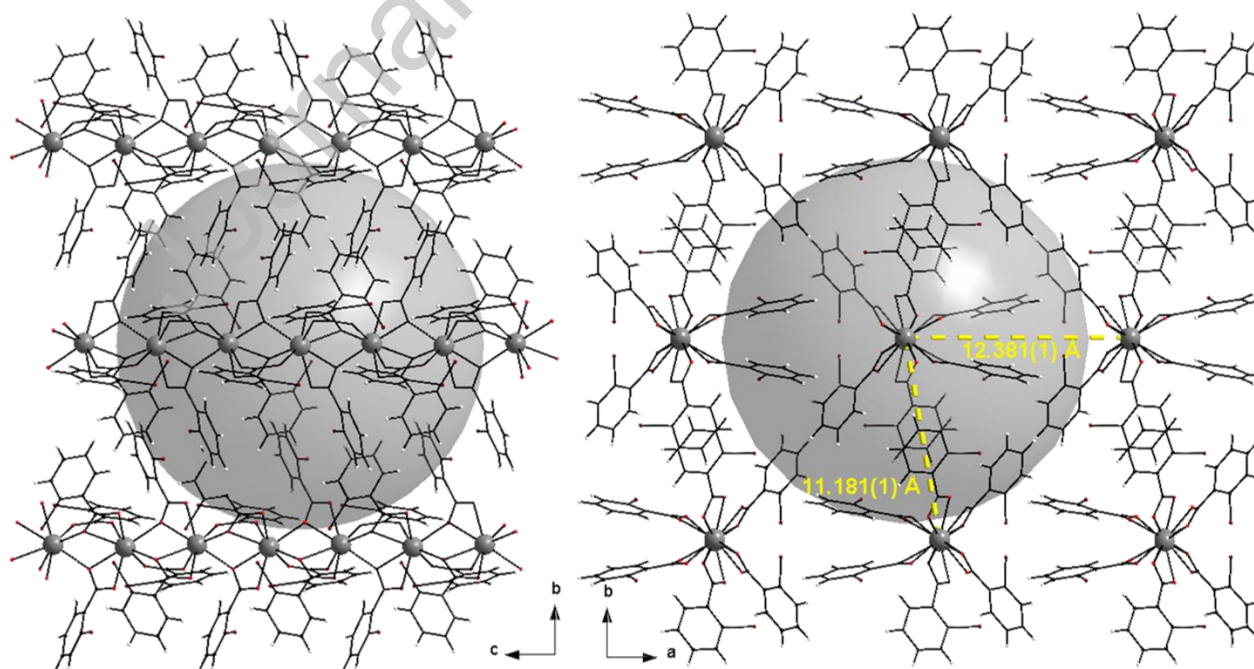


**Scheme 1.** Schematic representation of the proposed synthetic mechanism: Carboxylate functions of 2-bb<sup>-</sup> ligands connect (in red) neighboring atoms of a hexa-lanthanide complex while nitrates and hydroxides are removed (in blue). Then the linked ligands rotate because of  $\pi$ -stacking and halogen-bonds driving forces. Labile coordination water molecules of the starting complex (left) have been omitted for clarity.

The stability of the crystal packing is insured by  $\pi$ -stacking interactions (centroid-to-centroid distance of C16-C21 ring and its equivalent, by inversion at  $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ , is 3.676(3) Å) and halogen-bonds (the shortest distance between halogen atoms, 4.054(1) Å, is found for Br1...Br3 with the valence angle C17-Br3...Br1 equal to 89.6(2)°) (Figure 3). It can be noticed that, in this crystal structure, there is no coordination or crystallization solvent molecule. This is an asset as far as strongly luminescent coordination polymers are targeted. Indeed it implies the absence of O-H or C-H vibrators in the vicinity of the lanthanide ions that are known for favoring non-radiative de-excitation of the lanthanide ions, especially of Eu<sup>3+</sup> ions.<sup>87</sup> Intermetallic distances between lanthanide ions that belong to adjacent molecular chains are greater than 10 Å (Scheme 2) that is the threshold above which intermetallic energy transfers are expected to be less efficient.<sup>87-88</sup> On a global point of view, there are four lanthanide ions closer than 10 Å from a given Dy<sup>3+</sup> ions (Scheme 2).



**Figure 3.** Projection views along the  $a$ - (left) and  $c$ -axes (right) of an extended unit cell of  $[\text{Dy}(\text{2-bb})_3]_\infty$ . Halogen bonds and  $\pi$ -stacking interactions are drawn in brown and yellow dotted lines, respectively (right).

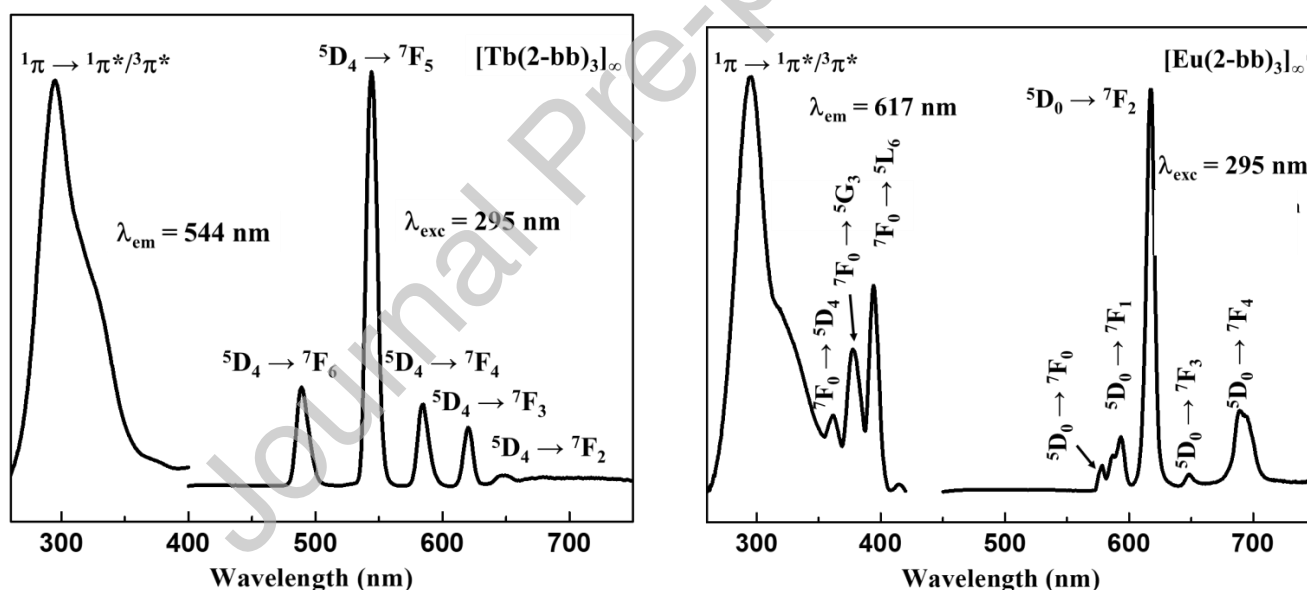


**Scheme 2.** Projection views along the  $a$ -axis (left) and along the  $c$ -axis (right) of the crystal packing of  $[\text{Dy}(\text{2-bb})_3]_\infty$ . A 10 Å radius gray sphere centered on a given  $\text{Dy}^{3+}$  ion is drawn.

Shortest intermetallic distances between Dy<sup>3+</sup> ions that belong to different molecular chains are indicated. In a given molecular chain, shortest intermetallic distance is 3.9584(3) Å.

### Luminescence properties of [Ln(2-bb)<sub>3</sub>]<sub>∞</sub> with Ln = Eu, Tb or Dy.

Emission and excitation spectra of [Ln(2-bb)<sub>3</sub>]<sub>∞</sub> with Ln = Eu or Tb have been recorded (Figure 4). Quantum yields and luminescence lifetimes have been measured and colorimetric coordinates calculated (Table 2). From Table 2, it can be noticed that overall quantum yields and luminescent lifetimes are sizeable and compare well with what is usually reported for lanthanide-based coordination polymers.<sup>54</sup> This may be related with the presence of an inorganic sub-lattice and with the absence of C-H or O-H vibrators in the vicinity of the lanthanide ions.<sup>87</sup> On the opposite, the luminescence of the Dy<sup>3+</sup>-derivative is very weak and difficult to record with our setup.



**Figure 4.** Room temperature solid state excitation and emission spectra of [Tb(2-bb)<sub>3</sub>]<sub>∞</sub> (left) and [Eu(2-bb)<sub>3</sub>]<sub>∞</sub> (right).

**Table 2.** Quantum yields, luminescent lifetimes and colorimetric coordinates of [Tb(2-bb)<sub>3</sub>]<sub>∞</sub> and [Eu(2-bb)<sub>3</sub>]<sub>∞</sub>.

	$Q_{Ln}^{Ligand} (\%)^{\dagger}$	$\tau (ms)^{\dagger}$	$Q_{Ln}^{Ln} (\%)^{\ddagger}$	Colorimetric coordinates <sup>†</sup>	
				x	y
[Tb(2-bb) <sub>3</sub> ] <sub>∞</sub>	35(3)	2.0(2)	-	0.328	0.570
[Eu(2-bb) <sub>3</sub> ] <sub>∞</sub>	11(1)	0.97(9)	32(3)	0.617	0.353

<sup>†</sup>  $\lambda_{exc} = 295 \text{ nm}$

<sup>‡</sup>  $\lambda_{exc} = 394 \text{ nm}$

Both excitation spectra show a broad excitation band centered at 295 nm that can be attributed to the  ${}^3\pi^*/{}^1\pi^* \leftarrow {}^1\pi$  transition of the ligand and confirm an efficient antenna<sup>70</sup> effect toward both lanthanide ions. This efficiency ( $\eta_{sens}$ ) has been estimated for the Eu<sup>3+</sup>-derivative according to the following relationship:<sup>87</sup>

$$Q_{Eu}^{Ligand} = \eta_{sens} \cdot Q_{Eu}^{Eu} \quad (1)$$

where  $Q_{Eu}^{Ligand}$  and  $Q_{Eu}^{Eu}$  are the overall and intrinsic quantum yields, respectively.  $Q_{Eu}^{Eu}$  has been measured under 394 nm excitation wavelength that corresponds to the  ${}^5L_6 \leftarrow {}^7F_0$  Eu<sup>3+</sup> transition because this transition doesn't significantly overlap the ligand excitation band. This leads to a moderate value of  $\eta_{sens} = 34.5 \%$ . This moderate value is in agreement with the quite high intensity of the  ${}^5L_6 \leftarrow {}^7F_0$  Eu<sup>3+</sup> transition compared with the  ${}^3\pi^*/{}^1\pi^* \leftarrow {}^1\pi$  transition. This feature can be related to the presence of a PET (Photo-induced Electron Transfer) effect that arises when a donor group (such as Br) is present near an easily reducible metallic ion (such as Eu<sup>3+</sup>).<sup>89-93</sup>

The emission spectrum of [Tb(2-bb)<sub>3</sub>]<sub>∞</sub> shows the characteristic  ${}^5D_4 \rightarrow {}^7F_{6-0}$  transitions<sup>94</sup> of the Tb<sup>3+</sup> ion centered at 489, 544, 584, 621, 648, 669 and 681 nm,

respectively. It is dominated by the  $^5D_4 \rightarrow ^7F_5$  transition and therefore  $[Tb(2-bb)_3]_\infty$  exhibits green emission under UV excitation.

The emission spectrum of  $[Eu(2-bb)_3]_\infty$  shows the characteristic  $^5D_0 \rightarrow ^7F_{0-4}$   $Eu^{3+}$  transitions<sup>95</sup> centered at 578, 593, 617, 649 and 689 nm, respectively. The  $^5D_0 \rightarrow ^7F_1$  transition dominates the emission spectrum and induces a red emission of  $[Eu(2-bb)_3]_\infty$  under UV excitation.

### Luminescence properties of $[Y_xTb_{1-x}(2-bb)_3]_\infty$ and $[Eu_xTb_{1-x}(2-bb)_3]_\infty$ with $0.1 \leq x \leq 0.5$ .

Isostructural hetero-lanthanide derivatives ( $[Y_xTb_{1-x}(2-bb)_3]_\infty$  and  $[Eu_xTb_{1-x}(2-bb)_3]_\infty$  with  $0.1 \leq x \leq 0.5$ ) have been prepared from the corresponding hexa-lanthanide molecular precursors ( $[Y_{6x}Tb_{6-6x}]$  and  $[Eu_{6x}Tb_{6-6x}]$ ). Their isostructurality with  $[Eu(2-bb)_3]_\infty$  has been assumed on the basis of their powder X-ray diffraction diagrams and relative contents of the different lanthanide ions have been measured by EDS (Table S1). The  $x$  value has been limited to 0.5 because afterwards the  $[Y_xTb_{1-x}(2-bb)_3]_\infty$  molecular alloys were no longer isostructural to  $[Dy(2-bb)_3]_\infty$  and because when  $x$  is greater than 0.5, the  $Tb^{3+}$  luminescence completely vanishes in the  $[Eu_xTb_{1-x}(2-bb)_3]_\infty$  series.

$Tb^{3+}$  overall quantum yields and luminescence lifetimes have been measured and colorimetric coordinates have been calculated for  $[Y_xTb_{1-x}(2-bb)_3]_\infty$  with  $0.1 \leq x \leq 0.5$  (Table 3). Emission spectra are reported in Figure S3.

**Table 3.** Overall quantum yield, luminescence lifetime and colorimetric coordinates for  $[Y_xTb_{1-x}(2-bb)_3]_\infty$  with  $0.1 \leq x \leq 0.5$ .

$x$	$Q_{Tb}^{Ligand}$ (%)	$\tau_{Tb}$ (ms)	Colorimetric coordinates	
			$x$	$y$
0.1	42(4)	1.9(2)	0.354	0.566
0.15	50(5)	2.0(2)	0.349	0.570

0.3	74(5)	2.0(2)	0.337	0.577
0.5	29(3)	1.7(2)	0.350	0.570

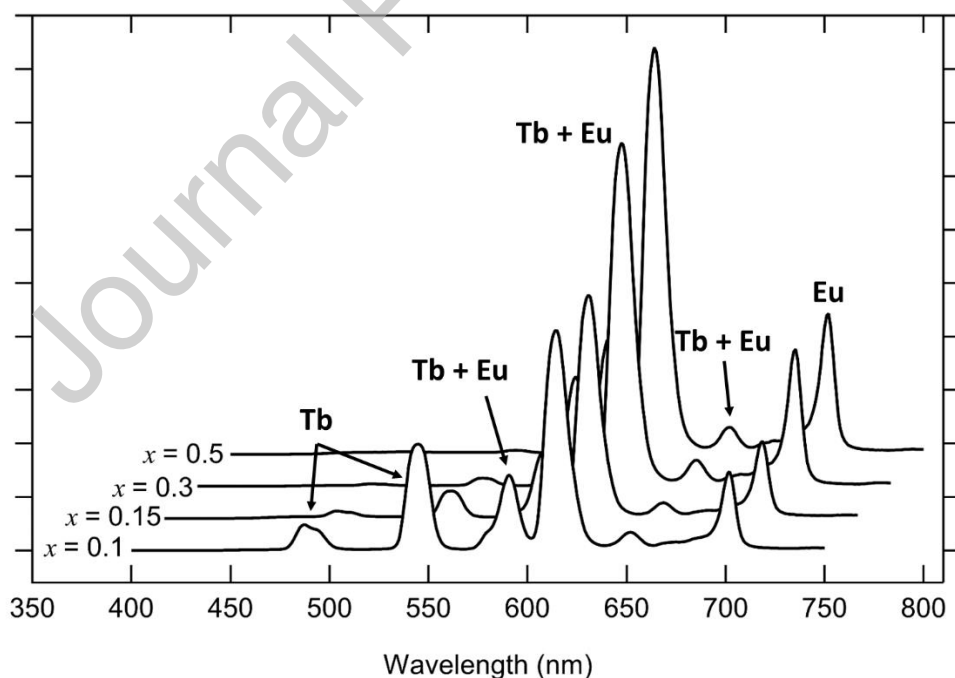
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$\lambda_{\text{exc}} = 295 \text{ nm}$

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The measurements indicate that there is a sizeable concentration quenching effect in this system. Indeed, dilution of the optically active  $\text{Tb}^{3+}$  ion by the optically no-active  $\text{Y}^{3+}$  provokes an enhancement of the  $\text{Tb}^{3+}$  overall quantum yield even at low dilution rate ( $x = 10\%$ ). The maximum overall quantum yield is observed for  $x \approx 0.3$ . Then the dilution effect does not compensate anymore the decrease of the number of optically active lanthanide ions.

Emission spectra of the corresponding  $[\text{Eu}_x\text{Tb}_{1-x}(\text{2-bb})_3]_\infty$  compounds have been recorded (Figure 5), colorimetric coordinates have been calculated (Figure 6) and the  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  overall quantum yields and luminescence lifetimes have been measured (Table 4).



**Figure 5.** Room temperature solid-state emission spectra ( $\lambda_{\text{exc}} = 295 \text{ nm}$ ) of  $[\text{Eu}_x\text{Tb}_{1-x}(\text{2-bb})_3]_\infty$  with  $0.1 \leq x \leq 0.5$ .



These spectra strongly suggest that there are efficient Tb<sup>3+</sup>-to-Eu<sup>3+</sup> intermetallic energy transfers. Indeed, the Tb<sup>3+</sup> component rapidly decreases and almost completely vanishes for  $x = 0.5$  while the Eu<sup>3+</sup> component increases. This is in agreement with the evolutions *versus*  $x$  of the quantum yields and of the luminescence lifetimes that are observed (Table 4) and with the observed strong concentration quenching effect.<sup>96</sup>

**Table 4.** Tb<sup>3+</sup> and Eu<sup>3+</sup> overall quantum yields and luminescence lifetimes for [Eu <sub>$x$</sub> Tb <sub>$1-x$</sub> (2-bb)<sub>3</sub>] <sub>$\infty$</sub>  with  $0.1 \leq x \leq 0.5$ .

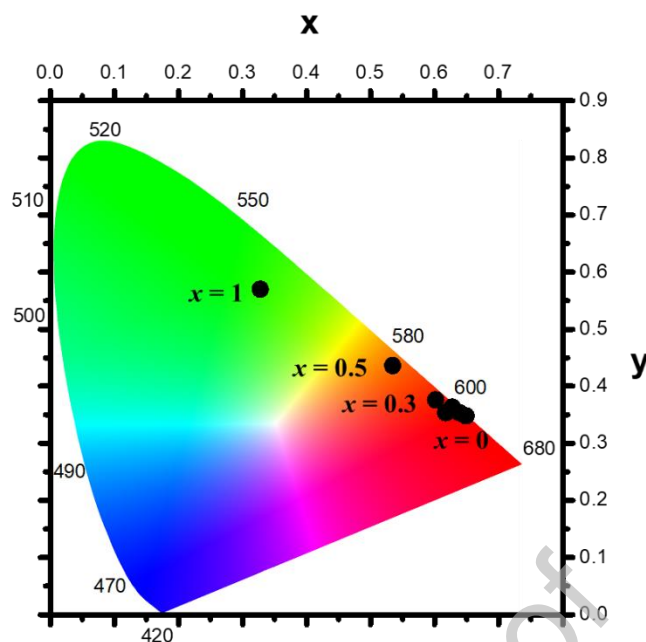
$x$	$Q_{\text{Tb}}^{\text{Ligand}}$ (%)	$\tau_{\text{Tb}}$ (ms)	$Q_{\text{Eu}}^{\text{Ligand}}$ (%)	$\tau_{\text{Eu}}$ (ms)	$\eta_{\text{ET}}$ (%)
0.1	10(1)	0.6(1)	28(3)	1.8(2)	69
0.15	2.3(2)	0.2(1)	47(4)	2.0(2)	88
0.3	1.9(2)	0.2(2)	40(4)	1.6(2)	94
0.5	0.04(1)	0.12(2)	29(3)	1.3(1)	96

$\lambda_{\text{exc}} = 295 \text{ nm}$

The intermetallic energy transfers have been quantified by the following relationship:<sup>87</sup>

$$\eta_{\text{ET}} = 1 - \frac{\tau_{\text{obs}}}{\tau_0} \quad (2.)$$

where  $\tau_{\text{obs}}$  and  $\tau_0$  are the luminescent lifetimes of the Tb<sup>3+</sup> in presence (Table 4) and in absence (Table 3) of an acceptor Eu<sup>3+</sup> ion, respectively. These calculations confirm the efficiency of the Tb<sup>3+</sup>-to-Eu<sup>3+</sup> intermetallic energy transfers (Figure 6).



**Figure 6.** Colorimetric coordinates of  $[\text{Eu}_x\text{Tb}_{1-x}(\text{2-bb})_3]_\infty$  with  $x = 0, 0.05, 0.1, 0.15, 0.3, 0.5$  and 1. Colorimetric coordinates have been calculated from emission spectra ( $\lambda_{\text{exc}} = 295 \text{ nm}$ ).

## CONCLUSIONS AND OUTLOOK.

In this article, we have structurally described a new series of 1D lanthanide coordination polymers obtained from hexa-lanthanide complexes by a microwave-assisted synthesis. These compounds cannot be obtained from simple mono-nuclear salts of lanthanide ions and a mechanism is proposed for explaining the synthetic process that leads from octahedral hexa-nuclear complexes to straight molecular chains. Although there are many “catena type” lanthanides containing coordination polymers reported to date, this one is special and can be called “hybrid inorganic chain”<sup>97</sup> because metal ions are linked by bridging oxygen atoms and the organic part is not involved in propagation of the chain. Luminescence properties of the  $\text{Tb}^{3+}$ - and  $\text{Eu}^{3+}$ -derivatives and of some hetero-lanthanide derivatives have been studied. This study suggests that the molecular chains host strong intermetallic energy transfers.

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#### **SUPPORTING INFORMATION.**

Experimental X-ray powder diffraction pattern of  $[\text{Tb}(2\text{-bb})_3]_\infty$  and calculated from the crystal structure X-ray powder diffraction diagram of  $[\text{Dy}(2\text{-bb})_3]_\infty$ ; IR spectrum of  $[\text{Tb}(2\text{-bb})_3]_\infty$ ; Metallic relative contents in  $[\text{Y}_x\text{Tb}_{1-x}(2\text{-bb})_3]_\infty$  and  $[\text{Eu}_x\text{Tb}_{1-x}(2\text{-bb})_3]_\infty$  with  $0.1 \leq x \leq 0.5$ ; Room temperature solid state emission spectra of  $[\text{Y}_x\text{Tb}_{1-x}(2\text{-bb})_3]_\infty$  with  $0.1 \leq x \leq 0.5$  ( $\lambda_{\text{exc}} = 295 \text{ nm}$ ).

**Credit Author statement**

**Haiyun Yao:** Investigation. **Guillaume Calvez:** Supervision. **Carole Daiguebonne:** Supervision, Investigation. **Yan Suffren:** Validation. **Kevin Bernot:** Writing. **Olivier Guillou:** Writing, Review and Editing.

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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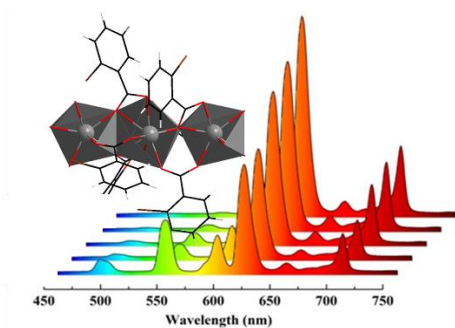


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**TABLE OF CONTENT.**

A new series of lanthanide coordination polymers obtained from hexa-lanthanide complexes by a microwave assisted synthesis with a strong intermetallic energy transfer.



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