

A convenient synthesis of highly luminescent lanthanide 1D-zigzag coordination chains based only on 4,4'-bipyridine as connector

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ABSTRACT

The coordination polymers $[\text{Ln}(\beta\text{-dik})_3\text{bpy}] \cdot \text{C}_7\text{H}_8$ (Ln = Eu, $\beta\text{-dik}$ = dbm, tta, hfac; Ln = Tb; $\beta\text{-dik}$ = dbm; Hdbm = dibenzoylmethane, Htta = thenoyltrifluoroacetone, Hhfac: hexafluoroacetylacetone) were easily assembled in mild conditions and high yields starting from the anhydrous lanthanide β -diketonates as nodes and 4,4'-bipyridine (bpy) as connector. X-ray single crystal studies have shown zigzag extended chains where lanthanide centres are 8-coordinated in a distorted square-antiprismatic geometry. Photoluminescence studies show bright red europium emissions and spectral features dependent on the topology of the polymeric chains.

1. Introduction

Coordination Polymers (CPs) of various dimensionality are a class of compounds that emerged and bloomed in an extraordinary way in recent years [1]. The great interest toward these compounds is due to their novel and appealing physical and chemical properties. CPs may have applications in some strategic fields as for instance chemical catalysis [2], chemical sensing [3], conversion of light to electrical energy [4].

Although rational designs and syntheses of novel derivatives have been largely achieved with *d* block transition metals [5], examples of planned synthetic strategies for *f* block metals are comparatively scarce [6], probably for the high and variable coordination numbers of these ions as well as for their lability. Nevertheless, in the recent years a flourishing literature appeared concerning coordination polymers of these centres [7], which are very attractive for their peculiar features and for their potential applications.

4,4'-bipyridine is a classical divergent ligand and it has been used to prepare a very large amount of CPs containing *d* transition metals and several different topologies ranging from one- to three-dimensional frameworks have been structurally characterized [8]. Nevertheless, examples of its use in lanthanide chemistry are surprisingly quite limited to date [9], especially as exclusive unmodified connector ligand [10]. Among the latter examples, only one crystallographic characterized monodimensional chain has appeared in the recent literature, $\infty^1[\text{LnCl}_3(\text{bpy})(\text{py})_2] \cdot \text{py}$ (Ln = Gd-Er, Yb) [9a]. Its synthesis has been carried out using anhydrous metal chlorides with 4,4'-bipyridine and pyridine under solvothermal conditions in sealed evacuated glass ampoules at 220 °C controlling the temperature to avoid the formation of the dinuclear complex $[\text{Ln}_2\text{Cl}_6(\mu_2\text{-bpy})(\text{py})_6]$ [10c] and carefully dosing the pyridine amount to prevent the crystallization of monomeric complexes $[\text{LnCl}_3(\text{py})_4] \cdot 0.5(\text{py})$ [11]. However, the presence of pyridine is essential for the formation of 1D strands, as reactions without pyridine lead to the higher-aggregated CPs $\infty^2[\text{Ln}_2\text{Cl}_6(\text{bpy})_3] \cdot 2\text{bpy}$ [10e] or $\infty^3[\text{Ln}_2\text{Cl}_6(\text{bpy})_5] \cdot 4\text{bpy}$ [9f]. For the preparation of lanthanide extended networks with nitrogen donors, it has been suggested that syntheses could largely benefit of an inert atmosphere, and of the exclusion of potential oxygen-donor ligands or oxygen containing solvents [10a].

The use of oxygen donor ligands as spacers [7] in a significantly large amount of CPs is commonly explained with the oxophilic character of the lanthanides and with their preference for anionic over neutral ligands. Nevertheless, nitrogen donor ligands are expected to be more basic than oxygen donor ones with the same charge and denticity. However, if anhydrous conditions are not guaranteed, the presence of a nitrogen donor ligand as 4,4'-bipyridine can favour deprotonation of

any coordinated water, with formation of undesired sub-products as hydroxo- or oxo-lanthanide derivatives [12].

Considering the large number of reported examples of mononuclear neutral octacoordinated $\text{Ln}(\beta\text{-dik})_3(\text{L-L})$ (where L-L is a bidentate chelating ligand, with nitrogen donor ligands included) [13], we reckoned that the use of $\text{Ln}(\beta\text{-dik})_3$ as a node and bpy as a connector in a molar ratio 1:1 could be a strategy to obtain a mono-dimensional CP without requirement of additional ligands. It is interesting to note that examples of coordination polymers containing $\text{Ln}(\text{hfac})_3$ as nodes and divergent neutral oxygen donors as connectors, $[\text{Ln}(\text{hfac})_3(\text{O}=\text{O})]_n$ (hfac = hexafluoroacetylacetone; $\text{O}=\text{O}$ = 1,4-diacetylbenzene or 1,4-dimethylterephthalate), have been reported [14]. On the other hand, attempts of synthesis of CPs by reaction of lanthanide β -diketonato complexes with 4,4'-bipyridine, or analogous N-donor divergent ligands like trans-1,2-bis(4-pyridyl)ethylene (bipyete), described in the literature afforded dinuclear complexes instead of coordination polymers [15]. Moreover, mononuclear species containing terminal 4,4'-bipyridine were obtained by reacting $\text{Ln}(\text{btfa})_3 \cdot 2\text{H}_2\text{O}$ (Ln = Gd, Eu, Eu/Tb, btfa = 4,4,4-trifluoro-1-phenyl-1,3-butanedionate) with 4,4'-bipyridine in ethanol. In the complex the octacoordinate lanthanide centre completes its coordination sphere by ligation of an ethanol molecule [16]. These results evidence how crucial the experimental conditions are to determine the nature of the product. Nevertheless, according to our project, a convenient and high yield synthesis of mono-dimensional CPs based on unfunctionalised 4,4'-bipyridine as the sole linker was developed, as reported in this paper.

2. Experimental

2.1. Materials and Instrumentation. Commercial europium and terbium oxides [Eu_2O_3 (Strem Chemicals); Tb_4O_7 (Strem Chemicals)] were used without further purification. Aqueous solutions of the lanthanide chlorides were prepared by dissolving the appropriate metal oxide in diluted hydrochloric acid. The solution was then evaporated to dryness and the solid residue was dissolved in water [17]. $[\text{Ln}(\text{dbm})_3]$ (Ln = Eu, Tb) were prepared according to the literature [18].

FTIR spectra in the solid state were recorded with a Perkin-Elmer "Spectrum One" spectrometer, with ATR technique. The metal content of the products was determined according to this procedure: each sample was treated in a platinum crucible with diluted HNO_3 and the mixture gently warmed; the resulting solution was then evaporated to dryness. After calcination, the weight of the solid residue [Eu_2O_3 or Tb_4O_7] was determined.

The luminescence spectra were recorded on solid samples at room temperature in a front-face acquisition geometry with a spectrofluorimeter (Fluorolog-3, Horiba Jobin Yvon) equipped with double-grating monochromator in both the excitation and emission sides coupled to a R928P Hamamatsu photomultiplier and a 450 W Xe arc lamp as the excitation source. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter supplied by the manufacturer. The excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. The luminescence lifetimes in the microsecond–millisecond scales were measured by a pulsed Xe lamp with variable repetition rate and elaborated with standard software fitting procedures. The experimental uncertainty on τ values is $\pm 10\%$.

2.2. Syntheses

2.2.1. $^1[\text{Tb}(\text{dbm})_3(\text{bpy})]\cdot\text{C}_7\text{H}_8$, **1**. To a suspension of $[\text{Tb}(\text{dbm})_3]$ (0.29 g; 0.35 mmol) in toluene (20 mL) 4,4'-bipyridine (bpy) was added (0.057 g; 0.36 mmol). After 2 h stirring at 60 °C a yellow solution was obtained. Precipitation of a yellow solid occurred overnight. The suspension was filtered and the product was dried *in vacuo* 0.26 g; 0.24 mmol; 66.7 % yield. El. Anal. Calcd for $[\text{Tb}(\text{dbm})_3(\text{bpy})]\cdot\text{C}_7\text{H}_8$, $\text{C}_{62}\text{H}_{49}\text{N}_2\text{O}_6\text{Tb}$, %: C, 69.1; H, 4.6; N, 2.6; Tb, 14.8. Found: C, 69.3; H, 4.5; N, 2.6; Tb, 14.7. ATR IR, cm^{-1} : 3057w, 3027 w, 1594 s, 1548 vs, 1514 vs, 1478 s, 1454 vs, 1404 vs, 1384 vs, 1305 m, 1220m, 1177 w, 1156 w, 1127 w, 1100 w, 1067 m, 1043 w, 1023 m, 1002 w, 941 w. The product was crystallized from a toluene solution by vapour diffusion of pentane. The product shows a modest solubility in toluene and appears to be air stable in the solid state (IR control).

2.2.2. $^1[\text{Eu}(\text{dbm})_3(\text{bpy})]\cdot\text{C}_7\text{H}_8$, **2**. To a suspension of $[\text{Eu}(\text{dbm})_3]$ (0.82 g; 1.00 mmol) in toluene (50 mL) and 4,4'-bipyridine (bpy) was added (0.17 g; 1.00 mmol). After 2 h stirring at 60 °C a yellow solution was obtained. Precipitation of a yellow solid occurred overnight at room temperature. The suspension was filtered and the product was dried *in vacuo* 0.81 g; 0.76 mmol; 74.1 % yield. El. Anal. Calcd for $[\text{Eu}(\text{dbm})_3(\text{bpy})]\cdot\text{C}_7\text{H}_8$, $\text{C}_{62}\text{H}_{49}\text{EuN}_2\text{O}_6$: C, 69.6; H, 4.6; Eu, 14.2; N, 2.6 %. Found: C, 69.5; H, 4.6; Eu, 14.5; N, 2.7 %. ATR IR, cm^{-1} : 3056 (w), 3027 (w) 1593 (s), 1556 (s), 1512 (s), 1477 (s), 1454 (s), 1404 (s), 1380 (s), 1304 (m), 1219 (m), 1176 (w), 1155 (w), 1067 (m), 1022 (m), 1002 (w), 940 (w).

The product is air stable as inferred by monitoring through IR spectroscopy a solid microcrystalline sample after exposition to air for 2, 3, 6, 24 h, 1 week, 1 month and 1 year. The product shows a modest solubility in toluene; a solution prepared at 60 °C was slowly cooled to room temperature with formation of single crystals suitable for X-ray diffraction studies.

2.2.3. ${}^1\infty[\text{Eu}(\text{tta})_3(\text{bpy})] \text{C}_7\text{H}_8$, **3**. $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$, (1.61g; 1.89 mmol) was introduced in a weighed vial. The vial was put into a Schlenk tube and treated in vacuo at 70 °C for 24 h. The weight loss proceeded smoothly and stopped at a value corresponding to the complete H₂O loss. A portion of $[\text{Eu}(\text{TfA})_3]$ (0.74g; 0.90 mmol) was dissolved in toluene (45 mL) and 4,4'-bipyridine (bpy) was added (0.14g; 0.90 mmol). After 3 h stirring at room temperature the solution was slowly concentrated up to incipient precipitation, and cooled at -20 °C overnight. The suspension was filtered and the solid product was dried *in vacuo*; 70.3 % yield. El. Anal. Calcd for $[\text{Eu}(\text{tta})_3(\text{bpy})]$, C₃₄H₂₀EuN₂F₉O₆S₃: C, 42.0, H, 2.1; Eu, 15.7; N 2.9; S 9.9 %. Found: C, 42.8; H, 2.7; Eu, 17.0; N, 3.0; S, 9.5 %. The product was crystallized from a toluene solution by vapour diffusion of pentane. ATR IR: cm⁻¹) 2962 (w), 1598 (s), 1537 (ms), 1505 (m), 1455 (mw), 1411 (ms), 1352 (mw), 1301 (s), 1247 (m), 1230 (m), 1184 (ms), 1135 (s), 1083 (m), 1061 (ms), 1015 (m), 934 (mw), 859 (mw), 809 (m), 787 (s), 750 (mw), 716 (ms).

2.2.4. ${}^1\infty[\text{Eu}(\text{hfac})_3(\text{bpy})] \text{C}_7\text{H}_8$, **4**. $[\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2]$, (1.09g; 1.35 mmol) was introduced in a weighed vial. The vial was put into a Schlenk tube and treated in vacuo at 50 °C for 48 h. The weight loss proceeded smoothly and stopped at a value corresponding to the complete H₂O loss. A portion of the anhydrous $[\text{Eu}(\text{hfac})_3]$ (0.61g; 0.78 mmol) was dissolved in toluene (90 mL) and 4,4'-bipyridine (0.13g; 0.80 mmol) was added. After 1 h stirring at about 100 °C, the yellow solution was slowly cooled to room temperature. A suspension of a crystalline solid was obtained that was filtered. The solid was formed by single crystals suitable for X-ray diffraction studies. Some crystals were selected in atmosphere saturated with toluene and sealed in capillaries to perform X-ray diffraction studies. The remaining solid was dried *in vacuo*; 75 % yield. El. Anal. Calcd for $[\text{Eu}(\text{hfac})_3(\text{bpy})]$, C₂₅H₁₁EuF₁₈O₆N₂: C, 32.3; H, 1.2; Eu, 16.4; N, 3.0 %. Found: C, 32.6; H, 1.3; Eu, 16.6; N, 2.8 %. ATR IR: (range: 700-1700 cm⁻¹) 1647 (s), 1608 (mw), 1558 (mw), 1534 (m), 1461 (ms), 1418 (mw), 1251 (s), 1199 (s), 1141 (s), 1101 (s), 1069 (m), 1047 (mw), 1005 (mw), 972 (w), 951 (w), 858 (w), 800 (ms), 767 (w), 733 (m).

2.3. Single-crystal X-ray Diffraction.

X-ray diffraction studies were carried out with a Bruker Smart Breeze CCD diffractometer. Crystals of the products **1-4** were selected under toluene saturated N₂ atmosphere and sealed in capillaries. Crystal data and structure refinements details are reported in Table 1.

Table 1. Crystal Data and Structure Refinement details for products 1-4.

Compounds	1	2	3	4
formula	C ₆₂ H ₄₉ N ₂ O ₆ Tb	C ₆₂ H ₄₉ N ₂ O ₆ Eu	C ₄₁ H ₂₈ F ₉ N ₂ O ₆ S ₃ Eu	C ₃₂ H ₁₉ F ₁₈ N ₂ O ₆ Eu
F w	1076.95	1069.99	1063.79	1021.45
T (K)	100	296	296	296
λ (Å)	1.54184	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.2439(2)	10.4113(5)	36.2560(8)	13.3199(6)
<i>b</i> (Å)	21.7900(4)	21.9845(9)	11.2353(2)	23.5333(12)
<i>c</i> (Å)	23.0178(5)	23.2634(12)	23.2827(5)	13.3714(6)
β (°)	95.893(2)	96.860(4)	101.5280(10)	105.3190(10)
<i>V</i> (Å ³)	5110.8(2)	5286.6(4)	9292.8(3)	4042.5(3)
<i>Z</i>	4	4	8	4
<i>D</i> _{calc} (g/cm ³)	1.400	1.344	1.521	1.678
μ (mm ⁻¹)	7.238	1.239	1.565	1.676
θ _{max} (°)	72.586	21.692	25.816	26.159
collected reflns	37928	19661	33807	31507
unique reflns	9935	6166	8922	8071
parameters	485	430	431	345
GOF	1.052	0.976	1.076	1.026
<i>R</i> _{int}	0.0713	0.0954	0.0400	0.0407
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0525	0.0519	0.0593	0.0655
w <i>R</i> ₂ ^b	0.1281	0.1122	0.1520	0.1720

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

3. Results and discussion

We have carried out the reactions between the lanthanide β-diketonato complexes [Ln(β-dik)₃] (Ln = Eu, β-dik = dbm, tta, hfac; Ln = Tb, β-dik = dbm) [18] with 4,4'-bipyridine, in a molar ratio 1:1, in toluene under anhydrous conditions at about 60 °C. The solutions, slowly cooled at room temperature, separated out crystals of the coordination polymers ¹[Ln(β-dik)₃bpy]·C₇H₈ (Ln = Tb: β-dik = dbm, **1**; Ln = Eu, β-dik = dbm, **2**; tta, **3**; hfac, **4**). The products were characterized by elemental analysis, IR, single crystal X-ray diffraction and photoluminescence (PL) studies.

The modest solubility of the products in toluene significantly increases by addition of free 4,4'-bipyridine, suggesting a partial fragmentation of the polymers, potentially up to a mononuclear species [Ln(dbm)₃(bpy)₂] if the 4,4'-bipyridine concentration is sufficiently high. Nevertheless, also in presence of a 4,4'-bipyridine excess, only the coordination polymer precipitated out by concentrating and/or cooling the solution.

The terbium and europium derivatives **1** and **2**, ¹[Ln(dbm)₃bpy]·C₇H₈, are isostructural. The crystal structures of the compounds show a significant disorder in the orientation of the external phenyl groups. The disorder is not removed by collecting data at low temperature (100 K). The structures of both compounds **1** and **2** contain zigzag chains as shown in Figure 1. Toluene molecules are

hosted between the bipyridine linkers of two parallel chains almost exactly in the middle. The phenyl plane of toluene is perpendicular to the nearest pyridine planes as shown in Fig. 2 at a distance which may suggest edge-on π - π interactions [19]. This finding is in agreement with the observation that toluene is not removed by treatment of the sample under vacuum at room temperature. Each lanthanide is octa-coordinated in a distorted square anti-prismatic geometry (Fig. 3). Six coordination sites are occupied by the oxygen atoms of the chelating β -diketones and the other two by the nitrogen atoms of two bpy ligands. The Ln–N bond lengths, close to 2.64 Å, are in keeping with the mean value of 2.60(4) Å found in the {EuO₆N₂} coordination examples contained in the Cambridge Crystallographic Database [20]. The N–Ln bonds, however, are tilted with respect to the pyridine planes by 9.6 - 12.5° and 9.5 - 11.9°, for **1** and **2**, respectively.

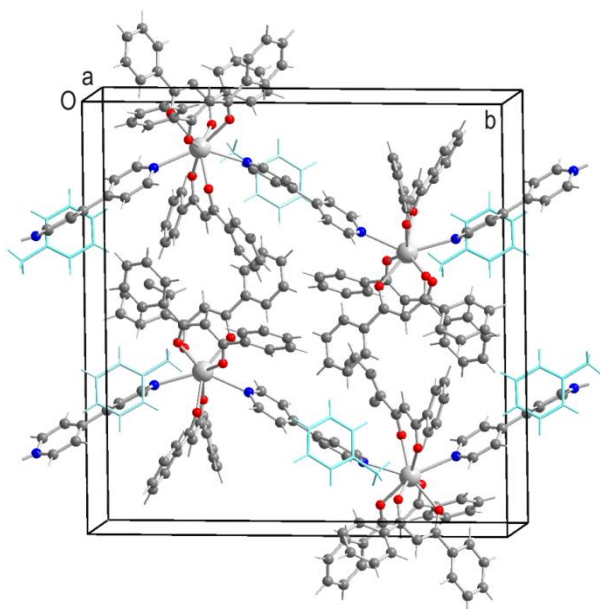


Fig. 1 The structure of portion of the chains in $[\text{Ln}(\text{dbm})_3\text{bpy}] \cdot \text{C}_7\text{H}_8$. Ln = Tb, **1**; Eu, **2**. Only the most populated positions of the disordered phenyl groups are represented.

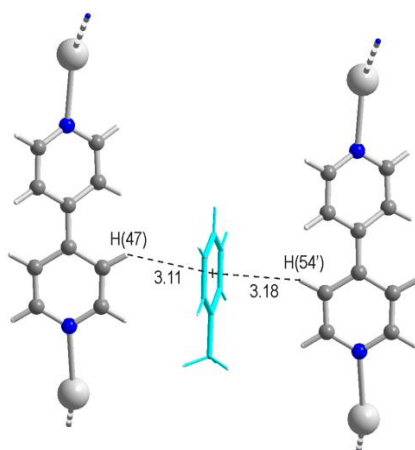


Fig. 2 View the solvent hosted within the chains in the crystal structure of **2**.

The chains show Ln...Ln...Ln angles of about 127°. In the solid state the polymers appear to be air stable. IR spectra recorded after several days of exposition to the air appeared unmodified.

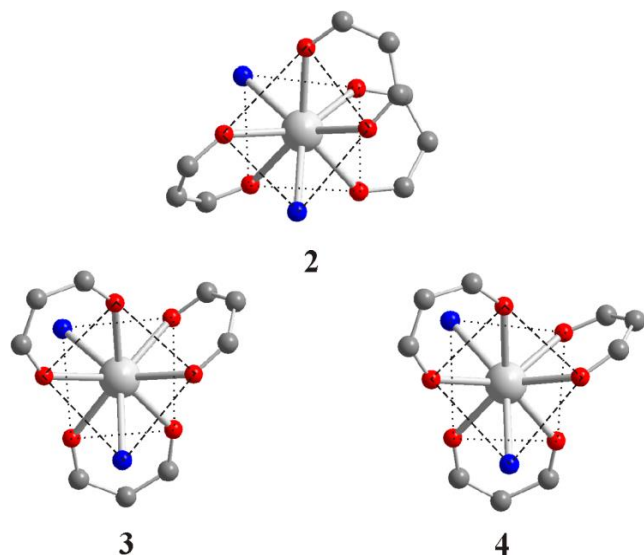


Fig. 3. The geometry of the metal coordination. The N–Eu–N angle amounts to 139°, 141° and 147° for **2**, **3** and **4**, respectively. The corresponding angle in an ideal semiregular square antiprism is 141.5°.

Also the europium derivatives **3** and **4**, ${}^1_2[\text{Eu}(\text{tta})_3\text{bpy}] \cdot \text{C}_7\text{H}_8$ and ${}^1_2[\text{Eu}(\text{hfac})_3\text{bpy}] \cdot \text{C}_7\text{H}_8$ in the solid state are arranged in zigzag chains as shown in Figure 4.

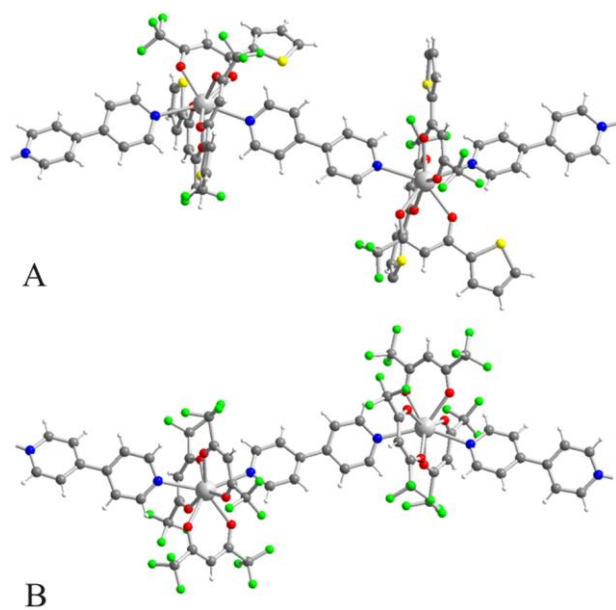


Fig. 4. The structures of portion of the chains in ${}^1_2[\text{Eu}(\text{tta})_3\text{bpy}] \cdot \text{C}_7\text{H}_8$, **3**, A and ${}^1_2[\text{Eu}(\text{hfac})_3\text{bpy}] \cdot \text{C}_7\text{H}_8$, **4**, B. Only the most populated positions of the disordered CF_3 groups are represented.

The crystal structures of **3** and **4** show a significant disorder in the orientation of the CF₃ groups and in the trapped solvent. The chains show Ln···Ln···Ln angles of about 142° and 148°, respectively. The coordination around europium is still distorted square antiprismatic (Fig. 3) with a reduced tilt of the N–Eu bonds with respect to the pyridine plane.

At variance with the products **1** and **2**, the embedded toluene can be easily removed from compound **3** by treatment under vacuum at room temperature, while **4** must be stored in toluene saturated atmosphere to prevent release of the crystallization solvent. This fact reveals that the involved van der Waals interactions become progressively weaker by varying the β-diketonato ligand in the order dbm > tta > hfac. The presence of scarcely polarisable fluorine atoms in tta and hfac can justify this behaviour.

Compounds **2**, **3** and **4** were investigated by photoluminescence studies since europium is particularly interesting as structural probe. Beside information on the different geometrical arrangements around europium ions in the polymeric chains, these derivatives emit red light also detectable at the naked eye. The corresponding PL spectra, reported in Figure 5, show the characteristic sharp bands associated to ⁵D₀ → ⁷F_J, J = 0–4 transitions of Eu³⁺ ions.

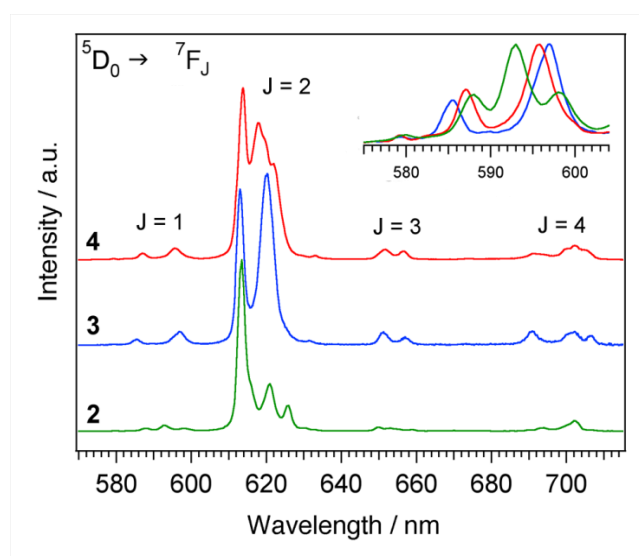


Fig. 5. PL spectra of **2**, **3** and **4** excited at 370 nm. Inset: magnification of the ⁵D₀ → ⁷F₁ transition.

Europium emission can be excited in a wide wavelength range, from UV to visible, up to ≈ 500 nm. The sensitized emission is achieved thanks to the light absorption of both 4,4'-bipyridine and β-diketonato ligands, although their different contributions can not be separated due to spectral overlap. The PL spectra of **2**, **3** and **4** have a similar shape and are characterized by the presence of a strong *hypersensitive* ⁵D₀ → ⁷F₂ transition which is *ca.* one order of magnitude more intense than the ⁵D₀ → ⁷F_J J = 1, 3 and 4 emissions. The spectra display a marked difference in the splitting of

the ${}^5D_0 \rightarrow {}^7F_J$ multiplets, as well as a small variation in their relative intensity ratios and peak positions. An example of this behaviour is evidenced in the inset of Figure 5 for the ${}^5D_0 \rightarrow {}^7F_1$ transitions. These changes are related to the different distortions of the square anti-prismatic geometry of europium ions in the polymeric chains (Figures 1, 3 and 4). 5D_0 lifetime values progressively increased from 0.31 to 0.52 ms by changing the nature of β -diketonato ligands in the order $\text{dbm} < \text{tta} < \text{hfac}$ (Table 2). The mono-exponential profile of the decay curves indicates the presence of a single spectroscopic site for europium ions in all the samples. A better comparison of the emission properties of the three polymers can be performed by evaluating radiative lifetimes, intrinsic quantum yields and Judd-Ofelt parameters Ω_2 and Ω_4 (Table 2). Following a well established procedure [21], these parameters can be calculated from the emission spectra using as an internal standard the ${}^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition which is not influenced by the ligand field acting on Eu^{3+} sites.

Table 2. Experimental lifetimes, radiative lifetimes, intrinsic quantum yields and JO parameters for **2**, **3** and **4**.

	τ (ms)	τ_{rad} (ms) ^a	Φ_{Ln}^{Ln} (%)	Ω_2 (10^{-20} cm^2) ^a	Ω_4 (10^{-20} cm^2) ^a
2	0.31	0.95	33	25.8	3.2
3	0.45	1.08	42	22.7	4.6
4	0.52	0.92	56	27.6	4.4

^ain the calculations a refractive index of 1.5 in agreement with literature data [22] have been employed.

In agreement with the similar chemical environment of Eu^{3+} ions in **2**, **3** and **4**, the values of Ω_2 and Ω_4 are only slightly affected by the structural differences in the 1D-zigzag chains. Conversely, we observe a remarkable decrease of the intrinsic quantum yields, with an evident inverse correlation between Φ_{Ln}^{Ln} values and the hindrance of the organic ligands. The steric and inductive properties of the employed β -diketonates are probably responsible for the structural modifications around europium centres, *i.e.* straightening of the 1D-zigzag chains and deviations of the metal centres from the pyridine planes. These variations heavily influence not only the profiles of the emission spectra but also the competition between radiative and non-radiative relaxation pathways. The use of less sterically hindered β -diketonato ligands and the introduction of $-\text{CF}_3$ groups seem to hamper the non radiative deactivation channels thus originating longer lifetimes and higher intrinsic quantum yield values.

4. Conclusions

The design of a convenient and high yield synthesis for quite stable mono-dimensional lanthanide CPs based on unfunctionalised 4,4'-bipyridine as linker has been here presented. Such a synthesis, carried out in mild conditions, was successful with all the β -diketonato ligands we have used, despite their difference in the steric and electronic properties. The synthesis appears to be adaptable to other lanthanide centers as showed in the present report by the characterization of the isotopic $^1_\infty[\text{Ln}(\text{dbm})_3\text{bpy}] \cdot \text{C}_7\text{H}_8$ (Ln = Eu, Tb). Since β -diketonato ligands are commonly used in lanthanide chemistry for the synthesis of highly luminescent materials, the present results pave the way to the general synthesis of 1D highly luminescent coordination polymers where it is possible to properly choose diketonato ligands suitable as sensitizers for any lanthanide used. Luminescence properties may be modulated also changing the spacer nature or using different monoanionic bidentate ligands with a high preference toward a chelate coordination mode. Further studies in this area are in progress in our labs.

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Appendix A. Supplementary data

CCDC 1471964-1471967 contain the supplementary crystallographic data for the compounds described in this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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