



*Dedicated to Professor Alexandru T. Balaban  
on the occasion of his 80<sup>th</sup> anniversary*

## HOMOBINUCLEAR 4f-4f COMPLEXES WITH 2,6-DIFORMYL-4-METHYL-PHENOL: INVESTIGATION OF LUMINESCENCE PROPERTIES

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We report herein the synthesis and the photophysical properties of three isomorphous homobinuclear 4f-4f complexes,  $[\text{Ln}(\text{L})_3]_2$  ( $\text{Ln}^{3+} = \text{Eu}^{3+}$  **1**,  $\text{Gd}^{3+}$  **2** and  $\text{Tb}^{3+}$  **3**;  $\text{L}^-$  is the deprotonated 2,6-diformyl-4-methylphenol ligand). The complexes were obtained as microcrystalline powders, their infrared spectra and powder X-ray diffractograms being identical. Steady-state and time resolved emission spectra of complexes **1-3** showed that the ligand, through the localisation of its triple state energy level, was an efficient quencher for the emission of both **1** and **3** complexes.

### INTRODUCTION

Numerous studies were performed on the synthesis and characterization of lanthanide complexes due to their various properties and applications (chemical sensors, luminescence, catalytic, and magnetic materials).<sup>1,2</sup>

The applications of their luminescent properties are a consequence of the narrow emission bands, with negligible environmental influences, a large Stokes shift, and relatively long photoluminescence (PL) lifetimes.<sup>3</sup> The drawback is represented by the very small molar absorption coefficient of the f-f transitions. In order to achieve high efficiency lanthanide emission, well designed chromophores, which are able to collect the UV-visible light, are employed to act as antennae to effectively transfer energy to the lanthanide ions.<sup>4</sup> These sensitizers should also be capable of protecting the Ln(III) centers from a quenching environment.

In a previous paper we presented a synthetic and magnetic study of two new homobinuclear 4f-4f complexes,  $[\text{Ln}(\text{L})_3]_2$  ( $\text{Ln}^{3+} = \text{Pr}$ ,  $\text{Gd}$ ;  $\text{L}^-$  is the deprotonated 2,6-diformyl-4-methylphenol ligand), as well as the crystal structure of the praseodymium derivative.<sup>5</sup> The crystallographic investigation of  $[\text{Pr}(\text{L})_3]_2$  revealed centrosymmetric binuclear entities with the metallic centers connected by two of the anionic ligands. The praseodymium ions are bridged by the phenoxo oxygen atoms. One carbonyl group of a bridging molecule is coordinated to one Pr(III) ion, while the other one is coordinated to the second Pr(III) ion. The other four  $\text{L}^-$  ions act as terminal chelating ligands, through the phenoxo oxygen atom and one carbonyl group. The supramolecular solid-state architecture is sustained by a system of  $\pi-\pi$  interactions. The cryomagnetic study of  $[\text{Gd}(\text{L})_3]_2$  showed a very weak antiferromagnetic interaction between the Gd(III) ions ( $J = -0.053 \text{ cm}^{-1}$ ,  $\mathbf{H} = -J\mathbf{S}_{\text{Gd1}}\mathbf{S}_{\text{Gd2}}$ ).

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The synthesis and crystal structure of an europium (III) binuclear compound obtained through a reaction between 2,6-diformyl-4-methylphenol and europium(III) perchlorate was reported.<sup>6</sup> Although it presents the same nuclearity as our studied systems, the composition is different, as two molecules of water are coordinated to the metal ions. A similar ligand, 2-hydroxyisophthalaldehyde, in reaction with various lanthanide(III) nitrates (Eu<sup>III</sup>, Tb<sup>III</sup>, Dy<sup>III</sup>, Ho<sup>III</sup>), leads to an isomorphous series of homobinuclear 4f-4f complexes, with a similar structural skeleton as the one reported by us.<sup>7</sup>

The current paper deals with a photoluminescence (PL) study performed on two homobinuclear 4f-4f complexes, [Ln(L)<sub>3</sub>]<sub>2</sub> with Ln= Eu and Tb. The europium(III) and terbium(III) ions were chosen as they are lanthanide ions that emit in the visible region, possessing a large energy gap between the emissive donor and acceptor levels and are usually sensitized by UV-absorbing chromophores containing high energy triplet excited states.<sup>8</sup> The optical measurements were performed at room-temperature and included steady-state and time resolved lamp and laser excitation and emission spectra as well as excited state dynamics.

## EXPERIMENTAL

### Syntheses

All solvents and chemicals were of analytical grade and were used as received. 2, 6-Diformyl-4-methyl-phenol (HL) was prepared according to reference.<sup>9</sup> The three complexes were obtained following a procedure already reported by the authors.<sup>5</sup>

An aqueous solution (5 ml) of the corresponding lanthanide(III) nitrate (1 mmol) was added to a stirred mixture containing a warm ethanol-acetonitrile (1/1) solution (10 ml) of 2,6-diformyl-4-methylphenol (0.49 g, 3 mmol) and an aqueous solution (5 ml) of LiOH·H<sub>2</sub>O (0.12 g, 3 mmol). A yellow precipitate formed slowly. The mixture was stirred for an hour and then filtered to isolate the solid. The yellow microcrystalline solid was washed with warm ethanol and dried. [Eu(L)<sub>3</sub>]<sub>2</sub> **1**: IR data (KBr, cm<sup>-1</sup>) 3430 lw, 2833vw, 1668vs, 1649vs, 1533vs, 1451m, 1402m, 1328w, 1302w, 1264vw, 1225s, 1158vw, 1042w, 995w, 964m, 885w, 829m, 774w, 712vw, 637m, 502m. *Anal. Calc.* for C<sub>54</sub>H<sub>42</sub>Eu<sub>2</sub>O<sub>18</sub>: C, 50.54; H, 3.27%; Found: C, 50.27; H, 3.44%. [Gd(L)<sub>3</sub>]<sub>2</sub> **2**: 3421 lw, 2833vw, 1668vs, 1649vs, 1533vs, 1452m, 1403m, 1328w, 1304w, 1264vw, 1225s, 1158vw, 1043w, 994w, 964m, 885w, 830m, 774w, 713vw, 637m, 502m. *Anal. Calc.* for C<sub>54</sub>H<sub>42</sub>Gd<sub>2</sub>O<sub>18</sub>: C, 50.13; H, 3.25%; Found: C, 51.42; H, 3.46%. [Tb(L)<sub>3</sub>]<sub>2</sub> **3**: 3447 lw, 2832vw, 1669vs, 1649vs, 1534vs, 1452m, 1403m, 1328w, 1303w, 1265vw, 1226s, 1158vw, 1044w, 996w, 965m, 886w, 831m, 774w, 713vw, 638m, 504m. *Anal. Calc.* for C<sub>54</sub>H<sub>42</sub>Tb<sub>2</sub>O<sub>18</sub>: C, 50.00; H, 3.24%; Found: C, 51.37; H, 3.53%.

### Physical measurements

The IR spectrum (KBr) pellets was recorded on a Bruker Tensor 37 spectrophotometer in the 4000 - 400 cm<sup>-1</sup> region. The UV-Vis spectrum (diffuse reflectance technique) was recorded with a Jasco V-670 spectrophotometer.

### Photoluminescence measurements

The emission measurements were also carried out at 20 °C using a Fluoromax 4P spectrofluorometer (Jobin Yvon), operated in both fluorescence and phosphorescence mode. The repetition rate of the flash lamp was 25 Hz, the integration window 0.5-1 ms, the delay after flash was set to 0.03- 0.1 ms, and up to 150 flashes were accumulated per data point. The slits were set to 1-10 nm in excitation as well as emission. The PL decays were measured by using the "decay by delay" feature. Time resolved emission spectra (TRES) were also recorded by a nitrogen laser (λ<sub>ex</sub> = 337 nm) and wavelength tunable Nd:YAG-laser/OPO system (Spectra Physics/GWU) operating at 20 Hz as excitation light sources and an intensified CCD camera (Andor Technology) coupled to a spectrograph Shamrock 303i (Andor Technology). The TRES were collected using the box car technique. The initial gate delay (delay after laser pulse) was set to a few μs and the gate width was adjusted to 50 μs. The photoluminescence (PL) was detected in the spectral range of 500 nm < λ<sub>em</sub> < 750 nm (Eu<sup>3+</sup>) or 450 < λ<sub>em</sub> < 650 (Tb<sup>3+</sup>). All PL measurements were performed at room temperature. The PL decays were fitted with a multi-exponential function *f(t)* using a commercial software (Origin, version 7.1):

$$f(t) = \sum_{i=1}^n A_i \exp(-t/\tau_i) + B \quad (1)$$

where *A<sub>i</sub>* is the decay amplitude, *B* is a constant (the baseline offset) and τ<sub>*i*</sub> is the time constant of the decay *i*. The average decay times were calculated using the following formula:

$$\langle \tau \rangle = \frac{\sum_{i=1}^n A_i \tau_i}{\sum_{i=1}^n A_i} \quad (2)$$

PL decay times τ<sub>*i*</sub> (uncertainty ≤10%) are the average values obtained from at least three separate measurements.

### Crystallographic measurements

X-ray powder diffraction measurements were performed at room temperature on a Shimadzu XRD-7000 diffractometer (Bragg-Brentano geometry) using CuKα radiation, operated at 40 kV and 30 mA in the 2θ range 5-50° with steps of 0.02° and a counting time of 0.60 s/step. The sample was spinned at 15 rpm.

## RESULTS AND DISCUSSION

### IR spectroscopy and solid state structure analyses

The reaction between 2,6-diformyl-4-methylphenol, LiOH·H<sub>2</sub>O and Eu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O in a 3:3:1 molar ratio, leads to a neutral homobinuclear

europium(III) complex, with the formula  $[\text{Eu}(\text{L})_3]_2$  **1**. The gadolinium (**2**) and terbium (**3**) derivatives have been obtained following the same procedure.

The IR spectra of compounds **1** ÷ **3** were found to be basically identical. The two strong bands located between  $1620$  and  $1670\text{ cm}^{-1}$  are due to the carbonyl groups arising from the organic ligand,  $\nu(\text{C}=\text{O})$ . The bands assigned to the uncoordinated carbonyl groups are located at  $1668\text{ cm}^{-1}$  for **1**,  $1665\text{ cm}^{-1}$  for **2**, and  $1669\text{ cm}^{-1}$  for **3**, while those belonging to the coordinated carbonyl groups are located at  $1631\text{ cm}^{-1}$  (**1**),  $1632\text{ cm}^{-1}$  (**2** and **3**). The bands corresponding to the aromatic part of the ligand are observed at  $1533, 1451, 1402\text{ cm}^{-1}$  (**1**),  $1533, 1452, 1403\text{ cm}^{-1}$  (**2**) and  $1534, 1452, 1403\text{ cm}^{-1}$  (**3**). The phenoxo group vibration is represented by a band located at  $1225\text{ cm}^{-1}$  in all three cases.

We were not able to grow single crystals for compounds **1** - **3**, but the powder X-ray diffraction patterns of compounds **1** ÷ **3** match the diffraction pattern obtained from single-crystal data of the praseodymium(III) derivative (Supplementary

material). We give here a short recount of that crystalline structure, shown in Fig. 1.

The molecular unit is centrosymmetric. Two out of the six 2,6-diformyl-4-methylphenolato ions act as tridentate bridging ligands, connecting the two praseodymium(III) ions through the phenoxo oxygen atom. One carbonyl group of a bridging molecule is coordinated to a Pr(III) ion, while the other one is coordinated to the second Pr(III) ion. The other four  $\text{L}^-$  ions function as terminal bidentate ligands, coordinating through one carbonyl group and the phenoxo oxygen atom (two  $\text{L}^-$  terminal ligands for each praseodymium atom). The uncoordinated carbonyl group of the terminal ligands has a *transoid* disposition with respect to the coordinated one. Each praseodymium atom is coordinated by eight oxygen atoms: two phenoxo and two carbonyl oxygen atoms belonging to the terminal ligands, two phenoxo bridging oxygens, and two carbonyl oxygen atoms arising from the bridging 2,6-diformyl-4-methylphenolato ions. The coordination polyhedron of the praseodymium atom may be described as a distorted square antiprism (Fig. 2).

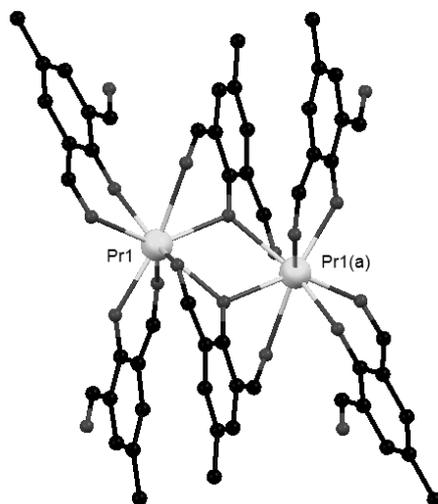


Fig. 1 – View of the molecular structure of the homobinuclear Pr(III) entity in crystal  $[\text{Pr}(\text{L})_3]_2$ .

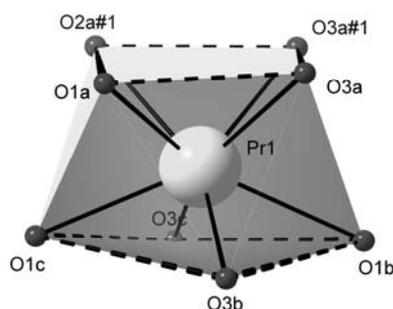


Fig. 2 – The coordination environment of the praseodymium ion in  $[\text{Pr}(\text{L})_3]_2$ .

The Pr – O distances fall in the range 2.301(2) and 2.622(2) Å. The intramolecular distance between the praseodymium atoms is 4.0711(4) Å. The Pr - O(Ph) – Pr angle is 111.37(9)°.

## Photoluminescence

### 1. [Eu(L)<sub>3</sub>]<sub>2</sub>

Following steady-state lamp excitation within the spectral range of  $\lambda_{\text{ex}} = 350\text{--}420$  nm weak europium  $D_0 - ^7F_{0,1,2,3,4}$  emission transitions are observed superimposed on a broad 510 nm centered luminescence (Fig. 3).

Time resolved lamp excitation spectra measured at the strongest transition ( $^5D_0 - ^7F_2$ , 614 nm) could reveal only some weak intensity narrow spectral features assigned to the f-f absorptions at 394 nm ( $^7F_0 - ^5L_6$ ) and 464 nm ( $^7F_0 - ^5D_2$ ) which were comparable in intensity to a broad band peaked around 410–420 nm.

Using the laser excitation at 394 nm the PL spectrum displays the  $^5D_0 - ^7F_J$  ( $J = 0,1,2,3,4$ ) transitions at about  $\lambda_{\text{em}} = 579$  nm, 582 nm, 614 nm, 653 nm, and 698 nm, respectively (Fig. 3). Very weak  $^5D_{1,2}$  related luminescence could also be detected in the spectral range of  $\sim 510\text{--}560$  nm. Another feature of interest besides the observance of the electric and the magnetic forbidden transition ( $^5D_0 - ^7F_0$ ) transition, is the high intensity of the  $^5D_0 - ^7F_2$  transition, relative to the  $^5D_0 - ^7F_1$  lines ( $R \sim 5.2$ ) indicating that the Eu ions are coordinated in a local site without an inversion center. According to X-ray data, the CN for Eu complex is eight and the polyhedron around the

lanthanide's ions can be described as a distorted square antiprism.

For Eu (III) ions located at a strictly square antiprism ( $D_{4d}$ ) site the Eu transitions ( $^5D_0 - ^7F_j$ ) ( $j = 0, 2, 3$ ) transitions are forbidden.<sup>10</sup> For the [Eu(L)<sub>3</sub>]<sub>2</sub>, the so-called hypersensitive Eu ( $^5D_0 - ^7F_2$ ) transition dominates the emission spectra while the electric and the magnetic dipole forbidden transition ( $^5D_0 - ^7F_0$ ) transition, though weak, is also noticeable. Overall, the luminescence data indicates that the actual coordination polyhedron is close to a bicapped trigonal prism (symmetry  $C_{2v}$ ) than to a square antiprism. Indeed, while the arrangement of the oxygen atoms around europium in **1** is close to  $D_{4d}$ , the individual contributions of the oxygen donor atoms (related to carbonyl and phenoxo ligands) could significantly differ leading to a net crystal field at europium sites of lower symmetry, probably  $C_{2v}$ .

### 2. [Tb(L)<sub>3</sub>]<sub>2</sub>

In contrast to **1**, lamp excitation within 300–420 nm of [Tb(L)<sub>3</sub>]<sub>2</sub> gave only the broad emission centered at about 505 nm, the terbium related transitions being absent. Under laser excitation at 337 nm, the terbium emission was detected (Fig. 4) and assigned to the  $^5D_4 - ^7F_3, F_4, F_5, F_6$  transitions spanning from 450 to 650 nm. The most intense PL band is located at 545 nm and corresponds to the  $^5D_4 - ^7F_5$  transition. Three other peaks are observed at 491 nm ( $^5D_4 \rightarrow ^7F_6$ ), 586 nm ( $^5D_4 \rightarrow ^7F_4$ ) and 624 nm ( $^5D_4 \rightarrow ^7F_3$ ).

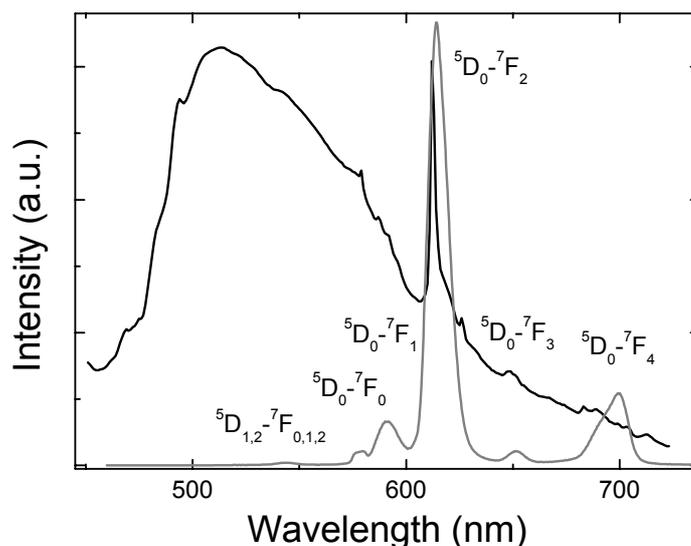


Fig. 3 – PL spectra of [Eu(L)<sub>3</sub>]<sub>2</sub> following steady state lamp within  $\lambda_{\text{ex}} = 300\text{--}420$  nm (black line) and laser excitation (grey line) at  $\lambda_{\text{ex}} = 394$  nm.

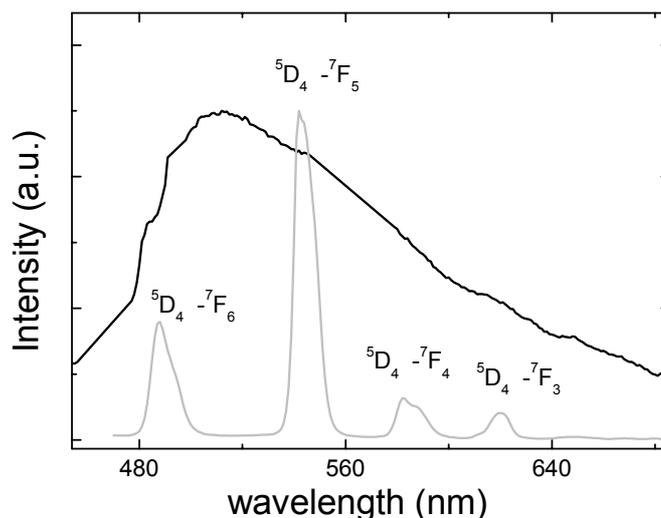


Fig. 4 – PL spectra of  $[\text{Tb}(\text{L})_3]_2$  following steady state lamp within  $\lambda_{\text{ex}} = 300\text{--}420$  nm (black line) and laser excitation (grey line) at  $\lambda_{\text{ex}} = 337$  nm.

### 3. $[\text{Gd}(\text{L})_3]_2$

#### (Ligand related photophysical properties)

In order to understand the emission mechanism of the new complexes **1** and **3**, we determined the singlet and triplet energy levels of the ligand, HL by using the Gd complex,  $[\text{Gd}(\text{L})_3]_2$ , **2**. Following steady-state excitation within spectral range of  $\lambda_{\text{ex}} = 300\text{--}420$  nm, weak broad band fluorescence was measured with a maximum at 500 nm (FWHM at ca. 90 nm). This greenish emission was quenched following short delay,  $\delta t$ , after the lamp pulse (30  $\mu\text{s}$ ) which ascertains the ligand singlet origin. A broad and structured red-shifted emission was measured at room-temperature with lifetime in the range of hundreds of  $\mu\text{s}$  (Fig. 5). The long-lived emission is peaked at about 670 nm and has a marked spectral shoulder at about 590 nm, the latter being assigned to the ligand triplet states  ${}^3\pi\pi^*$  (as phosphorescence). The energy gap between the  ${}^1\pi\pi^* \rightarrow {}^3\pi\pi^*$  transitions of the lowest singlet and triplet state of the ligand should be at least  $5000\text{ cm}^{-1}$  to generate an efficient intersystem crossing process.<sup>11</sup> The ligand singlet–triplet gap, taken as the difference between the maximum of ligand fluorescence (500 nm) and the high-energy spectral feature of ligand phosphorescence (590 nm) gives a smaller value, of ca.  $3000\text{ cm}^{-1}$ .

Besides the inefficient population of the triplet level, a critical parameter for an efficient energy-transfer from the ligand to the lanthanide's ions is the location of the triplet level<sup>12</sup> at about 590 nm ( $\sim 16950\text{ cm}^{-1}$ ). The triplet energy is smaller than those of the excited levels of europium  ${}^5\text{D}_1$  ( $\sim 525$  nm or  $\sim 19476\text{ cm}^{-1}$ ) and  ${}^5\text{D}_0$  (579 nm or  $\sim 17270\text{ cm}^{-1}$ ) or terbium  ${}^5\text{D}_4$  (490 nm or

$\sim 20408\text{ cm}^{-1}$ ). For **1**, the observance of europium emission upon excitation into the ligand absorption (300–420 nm, Fig. 3) and the ligand absorption as broad band centered at 420 nm in the excitation spectrum (see also Fig. 5) certify for some weak sensitization of the europium PL via the ligand (*antenna* effect). For **3**, the antenna effects were absent, the terbium emission being excited only via the direct excitation into UV f-f absorptions (at 337 nm, Fig. 4).

The PL decays measured at  $\lambda_{\text{em}} =$  at 614 nm (**1**), 545 nm (**3**) and 670 nm (**2**) are non-exponential (Fig. 6) being satisfactorily fitted with two exponentials (Eq. 1).

For europium compound (**1**) a short decay time is measured around 20  $\mu\text{s}$  accounting for ca. 50% of the total signal amplitude and a long decay time of 130  $\mu\text{s}$ . For terbium compound (**2**) a short decay time of 30  $\mu\text{s}$  accounts for almost 75 % of the total decay amplitude with a long decay time at 365  $\mu\text{s}$ . The average emission lifetimes obtained with Eq. 2 were  $\tau_{\text{av}} = 75\text{ }\mu\text{s}$  (**1**), 298  $\mu\text{s}$  (**2**) and 114  $\mu\text{s}$  (**3**). In the absence of any non-radiative deactivation processes induced by the presence of bound -OH ligands in the first coordination sphere of europium and terbium (Fig. 2) the lifetimes are expected to fall in the ms range. However, due to the low energy of the triplet level, this acts mainly as an acceptor state *via* the back-transfer from the excited levels of europium and terbium. On the other side, the absence of bound -OH oscillators and the low energy triplet states of the ligand may be well-suited for the efficient sensitization of the near-infrared lanthanide emitting ions, such as Nd (III), Er (III) or Yb (III) [1a] and this will be further investigated.

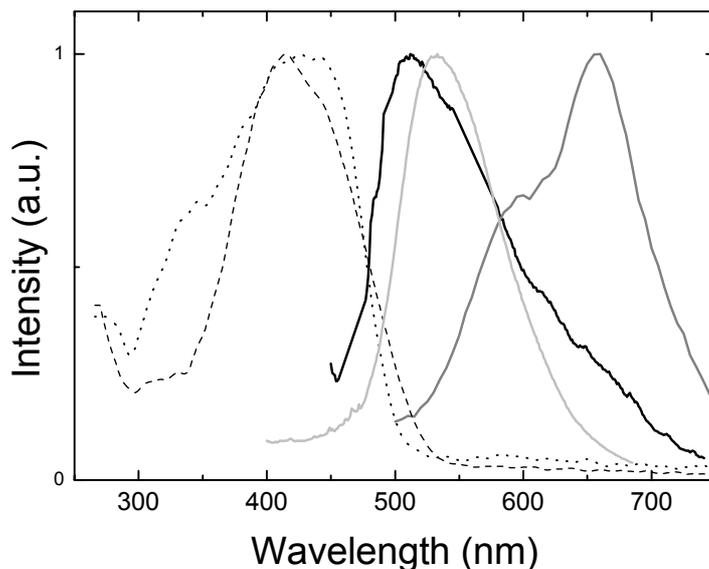


Fig. 5 – DR-UV/Vis of  $[\text{Gd}(\text{L})_3]_2$  (dotted line) and HL (dashed line). Fluorescence of  $[\text{Gd}(\text{L})_3]_2$  (black line) and HL (light grey line) and phosphorescence (dark grey line) of  $[\text{Gd}(\text{L})_3]_2$ . Fluorescence and phosphorescence spectra were measured following steady-state Xe lamp and pulsed lamp excitation (delay after the lamp pulse of 0.1 ms), respectively, at  $\lambda_{\text{ex}} = 420$  nm.

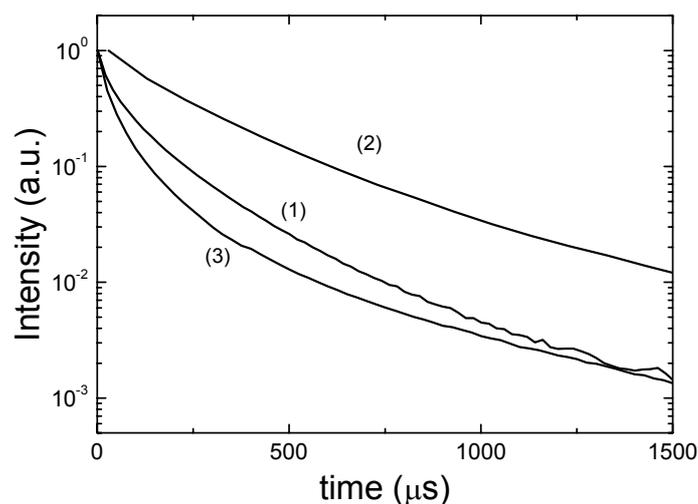


Fig. 6 – Emission decays of 1 ( $\lambda_{\text{ex}} = 394$  nm,  $\lambda_{\text{em}} = 614$  nm), 2 ( $\lambda_{\text{ex}} = 400$  nm,  $\lambda_{\text{em}} = 670$  nm) and 3 ( $\lambda_{\text{ex}} = 337$  nm,  $\lambda_{\text{em}} = 545$  nm).

## CONCLUSIONS

Homobinuclear 4f-4f complexes,  $[\text{Ln}(\text{L})_3]_2$  ( $\text{Ln} = \text{Eu}(\text{III}), \text{Gd}(\text{III})$  and  $\text{Tb}(\text{III})$ , with  $\text{L}^-$  the deprotonated 2,6-diformyl-4-methylphenol) were characterised by means of optical spectroscopy. The data point to the inefficient sensitization *via* the ligand of europium complex emission. For the terbium complex, the sensitization *via* the ligand was absent, the emission occurring only *via* the direct excitation into the UV f-f absorption transitions. Further studies consider the derivatives of the ligand with the near-infrared emitting lanthanide ions.

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