

## Composition-thermometric properties correlations in homodinuclear Eu<sup>3+</sup> luminescent complexes

Luca Bellucci<sup>†§</sup>, Gregorio Bottaro<sup>†§\*</sup>, Luca Labella<sup>†\*\*</sup>, Valerio Causin<sup>§</sup>, Fabio Marchetti<sup>‡</sup>, Simona Samaritani<sup>‡</sup>, Daniela Belli Dell'Amico<sup>‡</sup>, Lidia Armelao<sup>§†</sup>.

<sup>†</sup>*CNR ICMATE and INSTM, Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, I-35131*

<sup>‡</sup>*Dipartimento di Chimica e Chimica Industriale and CIRCC, Università di Pisa, via Giuseppe Moruzzi 13, I-56124*

<sup>§</sup>*Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, I-35131*

Corresponding authors' email address:

[gregorio.bottaro@cnr.it](mailto:gregorio.bottaro@cnr.it)

[luca.labella@unipi.it](mailto:luca.labella@unipi.it)

### Abstract

A family of homodinuclear Ln<sup>3+</sup> (Ln<sup>3+</sup> = Gd<sup>3+</sup> and Eu<sup>3+</sup>) luminescent complexes with general formula [Ln<sub>2</sub>(β-diketonato)<sub>6</sub>(N-oxide)<sub>y</sub>] is developed to study the effect of the β-diketonato and N-oxide ligands on their thermometric properties. The investigated complexes are [Ln<sub>2</sub>(tta)<sub>6</sub>(pyrzMO)<sub>2</sub>] (Ln = Eu, **1**·C<sub>7</sub>H<sub>8</sub>; Gd, **5**), [Ln<sub>2</sub>(dbm)<sub>6</sub>(pyrzMO)<sub>2</sub>] (Ln = Eu, **2**; Gd, **6**), [Ln<sub>2</sub>(bta)<sub>6</sub>(pyrzMO)<sub>2</sub>] (Ln = Eu, **3**; Gd, **7**), [Ln<sub>2</sub>(hfac)<sub>6</sub>(pyrzMO)<sub>3</sub>] (Ln = Eu, **4**; Gd, **8**) (pyrzMO = pyrazine-*N*-oxide, Htta = thenoyltrifluoroacetone, Hdbm = dibenzoylmethane, Hbta = benzoyltrifluoroacetone, Hhfac = hexafluoroacetylacetone, C<sub>7</sub>H<sub>8</sub> = toluene) and their 4,4'-bipyridine-*N*-oxide (bipyMO) analogues. Europium complexes emit a bright red light under UV radiation at room temperature, whose intensity displays a strong temperature (T) dependence between 223 and 373 K. This remarkable variation is exploited to develop a series of luminescent thermometers by using the integrated intensity of <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> europium transition as the thermometric parameter (Δ). The effect of different β-diketonato and *N*-oxide ligands is investigated with particular regard to the shape of thermometer calibration (Δ vs T) and relative thermal sensitivity curves, *i.e.* the change of Δ per degree of temperature variation usually indicated as S<sub>r</sub>, % K<sup>-1</sup>. The thermometric properties are determined by the presence of two non-radiative

deactivation channels, the back energy transfer (BEnT) from  $\text{Eu}^{3+}$  to the ligand triplet levels and the ligand-to-metal charge transfer (LMCT). In the complexes bearing tta and dbm ligands, whose triplet energy is *ca.*  $20000\text{ cm}^{-1}$ , both deactivation channels are active in the same temperature range, and both contribute to determine the thermometric properties. Conversely, with bta and hfac ligands the response of the europium luminescence to temperature variation is ruled by LMCT channels since the high triplet energy ( $> 21400\text{ cm}^{-1}$ ) makes BEnT ineffective in the investigated temperature range.

Keywords: Luminescence, Europium, Pyrazine-*N*-oxide, 4,4'-Bipyridine-*N*-oxide, Molecular thermometers, Thermometry

## Introduction

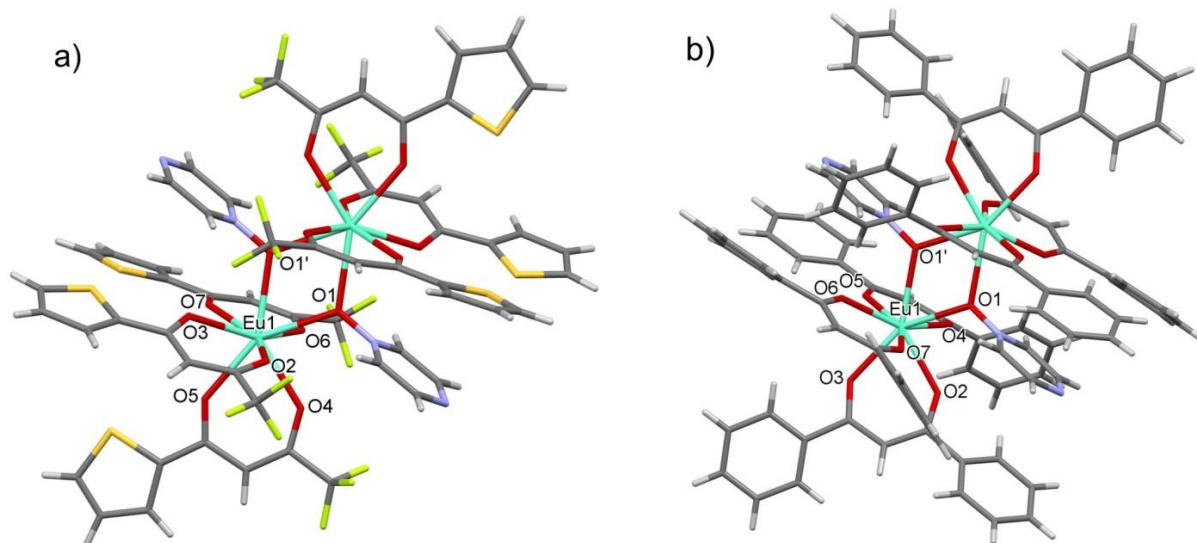
During the past decade the increasing use of non-contact techniques for temperature measurements led to many research efforts in the design of innovative lanthanide-based luminescent thermometers.<sup>1-8</sup> Lanthanide Metal Organic Frameworks (LOFs) and Coordination Polymers (CPs), in particular, due to their thermal stability<sup>2,9-17</sup> have been extensively explored as luminescent thermometers in a wide temperature range, from  $\approx 600\text{ K}$  down to cryogenic temperatures ( $< 100\text{K}$ ).<sup>12,18</sup> Moreover, the thermometric properties of these compounds can be tuned through a selective modification of the different building blocks, e.g. metal ions, spacer ligands, guest molecules.<sup>14</sup> Less extensive investigations, at variance, have been devoted to the temperature dependence of luminescent properties of discrete lanthanide  $\beta$ -diketonato complexes,<sup>19-26</sup> though these compounds, being easily processable, are suitable for the development of functional materials for temperature measurements.<sup>27-29</sup> Europium complexes with  $\beta$ -diketonato triplet energy around  $20.000 - 25.000\text{ cm}^{-1}$ ,<sup>30-33</sup> are suitable for temperature sensing between  $223$  and  $373\text{ K}$ , an interval that covers the physiological window ( $298 - 323\text{ K}$ ) and the working range of many integrated circuits.<sup>21,26,34</sup> The temperature-dependent luminescent properties of these complexes can be easily modulated by changing the lateral substituents on the  $\beta$ -diketonato ligand, as showed in a pioneering work by Sato and Wada.<sup>35</sup> Although intensity-based ratiometric luminescent thermometers are the most largely studied, the development of single emitter (single transition) thermometers is still very important for fluidodynamic and aerodynamic applications where luminescent complexes are used in the so-called Temperature Sensitive Paints (TSP) to map the surface temperature distributions. With TSP the drawbacks deriving from the use of single emitters are by-passed by using the ratio of an image taken at test conditions to an image taken at a known

reference condition.<sup>36–38</sup> Recently, we focused on lanthanide coordination chemistry with the heterotopic divergent *N*-oxide ligand 4,4'-bipyridine-*N*-oxide (bipyMO).<sup>39–41</sup> The different affinity of 4*f* metal ions towards *O*- and *N*-donor ligands affords the synthesis of lanthanide dinuclear complexes with composition [Ln<sub>2</sub>(β-diketonate)<sub>6</sub>(bipyMO)<sub>x</sub>] (x = 2 or 3 depending on the β-diketonate) where the oxygen atom of bipyMO bridges two lanthanide ions and the nitrogen donor atom is not coordinated.<sup>41</sup> 42–44 In this context, we developed a family (16 members) of homodinuclear Eu<sup>3+</sup> and Gd<sup>3+</sup> luminescent compounds to study the effect of the β-diketonato and *N*-oxide ligands on the thermometric properties of the complexes. We used four β-diketonato ligands with different steric and electronic properties commonly used for the synthesis of europium luminescent derivatives: thenoyltrifluoroacetone (Htta), dibenzoylmethane (Hdbm), benzoyltrifluoroacetone (Hbta), and hexafluoroacetylacetone (Hhfac). As *N*-oxide ancillary ligands we employed both bipyMO and pyrazine-*N*-oxide (pyrzMO), the monoaromatic ring analogue of bipyMO, only scarcely investigated in lanthanide coordination chemistry to date.<sup>45–47</sup> The studied family is composed of [Ln<sub>2</sub>(tta)<sub>6</sub>(pyrzMO)<sub>2</sub>] (Ln= Eu, **1**·C<sub>7</sub>H<sub>8</sub>; Gd, **5**), [Ln<sub>2</sub>(dbm)<sub>6</sub>(pyrzMO)<sub>2</sub>] (Ln= Eu, **2**; Gd, **6**), [Ln<sub>2</sub>(bta)<sub>6</sub>(pyrzMO)<sub>2</sub>] (Ln= Eu, **3**; Gd, **7**), [Ln<sub>2</sub>(hfac)<sub>6</sub>(pyrzMO)<sub>3</sub>] (Ln= Eu, **4**; Gd, **8**) and their bipyMO-based analogues (**1b–8b**).<sup>41</sup> All europium complexes showed an intense red emission at room temperature under UV radiation and a strong temperature (T) dependence of europium emission intensity between 223 and 373 K. This remarkable variation is exploited to develop a series of luminescent thermometers by using the integrated intensity of europium <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition as thermometric parameter (Δ). The effect of the different β-diketonato and *N*-oxide ligands on the shape of thermometer calibration (Δ vs T) curves is investigated and presented in detail.

## Result and Discussion

Since previous studies established a product composition [Ln<sub>2</sub>(β-diketonate)<sub>6</sub>(bipyMO)<sub>2</sub>] (β-diketonate= tta, dbm) regardless of the [Ln(β-diketonate)<sub>3</sub>] / bipyMO molar ratio (1:1 or 2:3),<sup>41</sup> the reaction between [Eu(β-diketonate)<sub>3</sub>] (β-diketonate= tta and dbm) with pyrzMO was carried out with 1:1 molar ratio in hot anhydrous toluene. Products [Eu<sub>2</sub>(tta)<sub>6</sub>(pyrzMO)<sub>2</sub>]·C<sub>7</sub>H<sub>8</sub> **1**·C<sub>7</sub>H<sub>8</sub> and [Eu<sub>2</sub>(dbm)<sub>6</sub>(pyrzMO)<sub>2</sub>] **2** were obtained in a satisfactory yield. Recrystallization of the products in toluene through diffusion of pentane vapors led to single crystals suitable for X-ray diffraction studies with composition [Eu<sub>2</sub>(β-diketonate)<sub>6</sub>(pyrzMO)<sub>2</sub>]·*n*C<sub>7</sub>H<sub>8</sub> (β-diketonate = tta, *n* = 5; β-diketonate = dbm, *n*= 0). Solvated toluene molecule in **1** are partially lost on drying but a solvent molecule was retained even after a long treatment *in vacuo* at room temperature. The structure of **1** and **2** is characterized by the [Eu<sub>2</sub>(β-diketonate)<sub>6</sub>(pyrzMO)<sub>2</sub>] dinuclear unit where pyrzMO act as a

bridging ligand only via its oxygen atom ( $\mu$ -O), leaving the nitrogen site uncoordinated (**Figure 1 a and b**).



**Figure 1:** Molecular structure of compounds **a) 1** and **b) 2**.

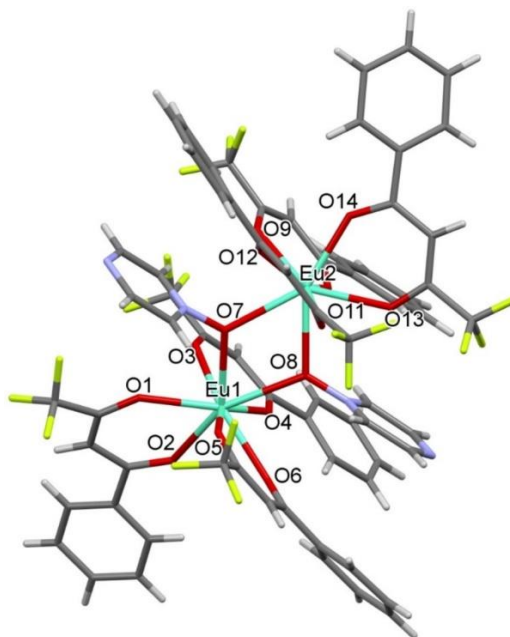
In both compounds, europium centers show a coordination number (CN) of 8 and a square antiprismatic geometry. The different substituents on the  $\beta$ -diketonato ligands slightly influence the shape of europium coordination polyhedra (see **Table S2**). Complexes **1** and **2** are centrosymmetric with the inversion center placed in the middle of the oxygen atoms of the two pyrzMO ligands.

The observed bridging  $\mu$ -O is an unprecedented coordination mode for pyrzMO, although expected for a bipyMO analogue. The molecular structures of **1** and **2** closely resemble the related bipyMO structures  $[\text{Ln}_2(\beta\text{-diketonate})_6(\text{bipyMO})_2]$ .<sup>41</sup>

Although the reactivity between  $[\text{Eu}(\text{bta})_3]$  and *N*-oxide ligands was not previously explored, we used a  $[\text{Eu}(\text{bta})_3]$  / pyrzMO molar ratio of 1:1, expecting the formation of the  $[\text{Eu}_2(\text{bta})_6(\text{pyrzMO})_2]$  complex. Indeed, Hbta has steric and electronic properties similar to Htta, having a phenyl ring instead of a thienyl group, and a  $\text{pK}_a$  value close to that of Htta ( $\text{pK}_a$  Hbta  $\approx$  6.1;  $\text{pK}_a$  Htta  $\approx$  6.3).<sup>48</sup>

Elemental analysis and single crystal XRD studies confirmed the formation of the expected compound  $[\text{Eu}_2(\text{bta})_6(\text{pyrzMO})_2]$  (**3**). As in **1** and **2**, the molecular structure presents a europium dinuclear unit with two bridging O-coordinated *N*-oxide hypodentate ligands (**Figure 2**). Each europium ion has CN = 8 and a square antiprismatic coordination geometry. However, unlike **1** and **2**, in compound **3** the two europium centers are crystallographically independent and the complex does not show an inversion center. Some geometrical parameters of the coordination polyhedron are listed in **Table S2**. Since no bipyMO analogue was previously prepared, and the number of bridging

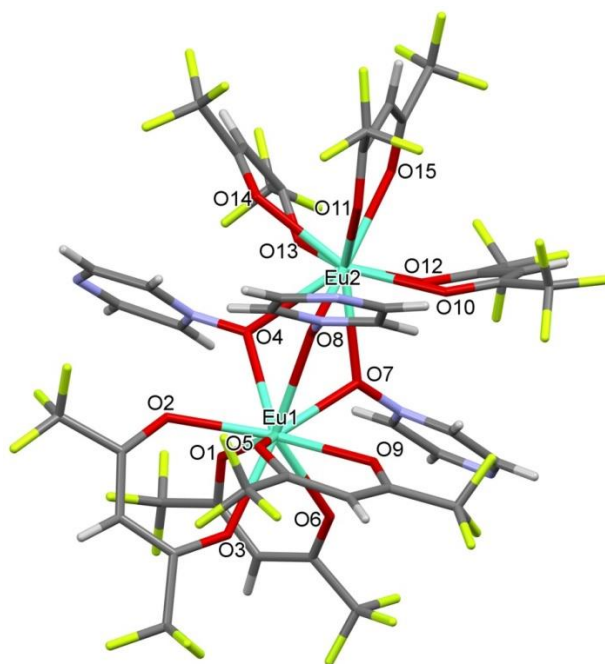
*N*-oxide ligands was not assessed, the reaction was repeated using an [Eu(bta)<sub>3</sub>]/ pyrzMO molar ratio of 2:3 and compound **3** was still obtained.



**Figure 2:** Molecular structure of compound **3**. Only the most populated positions of disordered CF<sub>3</sub> groups have been represented.

For comparison purposes we also prepared the bipyMO analogue with bta ligands: using the same stoichiometric ratio we obtained [Eu<sub>2</sub>(bta)<sub>6</sub>(bipyMO)<sub>2</sub>] (**3b** see supplementary materials)

According to previous studies,<sup>41,43,44</sup> the reaction between [Eu(hfac)<sub>3</sub>] and a *N*-oxide ligand proceeds with a 2:3 metal/ligand molar ratio. For this reason, [Eu(hfac)<sub>3</sub>] and pyrzMO were reacted using this reaction stoichiometry yielding the analytically pure compound **4** [Eu<sub>2</sub>(hfac)<sub>6</sub>(pyrzMO)<sub>3</sub>]. By cooling a toluene solution at -20 °C, single crystals suitable for X-ray diffraction have been recovered. Crystals collapsed losing solvent on standing in air. Structural studies showed a [Eu<sub>2</sub>(hfac)<sub>6</sub>(pyrzMO)<sub>3</sub>]·C<sub>7</sub>H<sub>8</sub> composition, presenting dinuclear molecules with nine-coordinate europium ions and three μ-O-bridging pyrzMO ligands (**Figure 3**).



**Figure 3:** Molecular structure of compound **4**.

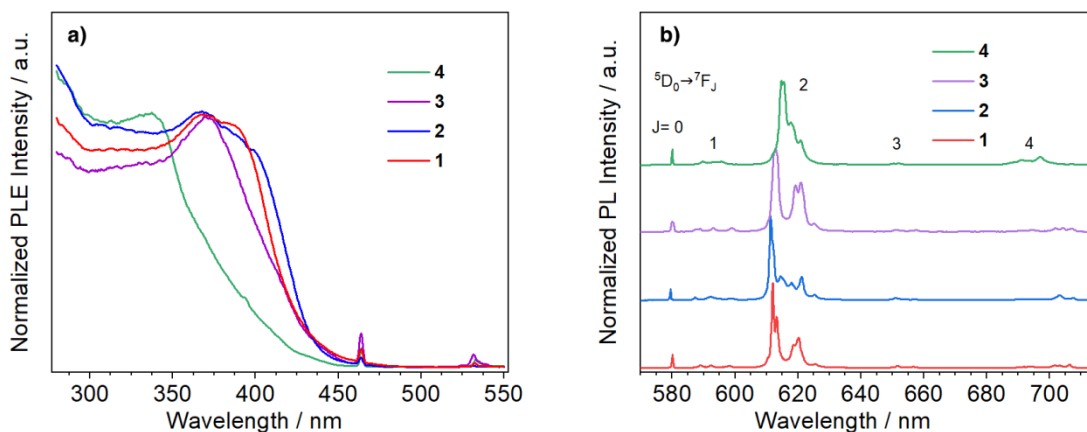
Compound **4**·toluene has no symmetry elements. Both the crystallographically independent europium atoms are in a tricapped trigonal prismatic coordination and the two polyhedra share the O4, O7, O8 face. Some geometrical parameters are listed in **Table S2**.

Our results suggest that the tendency of the *N*-oxide ligand to adopt the  $\mu$ -O bridging coordination mode is independent from the  $\beta$ -diketonato ligand,<sup>41–44</sup> while the number of *N*-oxide ligands for a dinuclear molecule is ruled by the  $\beta$ -diketonato nature.<sup>41</sup>

Gadolinium analogues of compounds **1-4** have been prepared for comparison purposes. Starting from  $[\text{Gd}(\beta\text{-diketonate})_3]$  and pyr $z$ MO in anhydrous toluene,  $\text{Gd}_2(\text{tta})_6(\text{pyr}z\text{MO})_2$  (**5**),  $[\text{Gd}_2(\text{dbm})_6(\text{pyr}z\text{MO})_2]$  (**6**),  $[\text{Gd}_2(\text{bta})_6(\text{pyr}z\text{MO})_2]$  (**7**),  $[\text{Gd}_2(\text{hfac})_6(\text{pyr}z\text{MO})_3]$  (**8**) have been obtained in satisfactory yields with IR spectra superimposable with those of the corresponding europium compounds. The related compounds  $\text{Gd}_2(\text{tta})_6(\text{bipyMO})_2$  (**5b**),  $[\text{Gd}_2(\text{dbm})_6(\text{bipyMO})_2]$  (**6b**),  $[\text{Gd}_2(\text{bta})_6(\text{bipyMO})_2]$  (**7b**),  $[\text{Gd}_2(\text{hfac})_6(\text{bipyMO})_3]$  (**8b**), have been similarly obtained using bipyMO as *N*-oxide ligand (see supplementary materials).

### *Photoluminescence studies*

All europium complexes emit bright red light upon irradiation across the UV/Vis regions, between 350 and 450 nm. Complexes bearing  $\beta$ -diketonato ligands with an increasing number of aromatic rings, present a red-shift of the excitation maximum from *ca.* 350 nm in **4** to 380 – 400 nm in **1**, **2**, and **3**, as evidenced by the photoluminescence excitation spectra (PLE) (**Figure 4a**).



**Figure 4.** a) Photoluminescence excitation spectra of compounds **1**, **2**, **3**, and **4**.  $\lambda_{em} = 611$  nm. b) Emission spectra of compound **1**, **2**, **3**, and **4**.  $\lambda_{exc} = 350$  nm.

Europium emission is achieved thanks to a ligand-mediated sensitization process, the so-called *antenna effect*.<sup>49,50</sup> The whole process is summarized as follows: *i*) light absorption *via* ligand centered transitions (chromophore) with population of the first excited singlet state, *ii*) intersystem crossing from singlet to triplet (T) level, and *iii*) energy transfer from the triplet level of the chromophore to the lanthanide excited levels, and *iv*) metal-centered emission.<sup>51</sup> The photoluminescence (PL) spectra of compounds **1-4** show the typical europium sharp bands in the 570 - 720 nm range associated to  $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_J$  ( $J = 0-4$ ) transitions (**Figure 4b**).<sup>50,52</sup> As usual for europium  $\beta$ -diketonato complexes, all spectra present a strong hypersensitive  $\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_2$  transition, which is about one order of magnitude more intense than the other  $\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_J$  ( $J = 0, 1, 3,$  and  $4$ ) emission lines.

As in bipyMO analogues<sup>39-41</sup>, the complexes show different europium coordination numbers (CNs) depending on the number of pyrZMO ligands bonded to the two metal centers: CN= 8 in **1**, **2**, and **3**; CN= 9 in **4**. The differences in the crystal field components of the  $\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_J$  multiplets observed in the PL spectra of the complexes are due to small variations in the  $\text{Eu}^{3+}$  coordination polyhedra related to CNs as well as to R and R' substituents at the  $\beta$ -diketonato moieties.

The nature of the  $\beta$ -diketonato ligands, and in particular the presence of fluorine atoms, influences the  $\ ^5\text{D}_0$  experimental lifetime ( $\tau_{obs}$ ) which progressively increases from 0.58 to 0.70 ms (**Table 1**) in the order  $\text{dbm} \approx \text{tta} < \text{bta} < \text{hfac}$ , respectively. Indeed, the introduction of an increasing number of -CF<sub>3</sub> groups diminishes the probability of a non-radiative deactivation path of the excited state.<sup>53</sup> Relevant spectroscopic data for pyrZMO- derivatives are summarized in **Table 1**. To study the effects of  $\beta$ -diketonato and *N*-oxide ligands on the PL properties of the complexes, a comparison can be made with the data for bipyMO analogues  $[\text{Eu}_2(\text{tta})_6(\text{bipyMO})_2]$  **1b**,  $[\text{Eu}_2(\text{dbm})_6(\text{bipyMO})_2]$

**2b**, [Eu<sub>2</sub>(bta)<sub>6</sub>(bipyMO)<sub>2</sub>] **3b** (Figure S2), [Eu<sub>2</sub>(hfac)<sub>6</sub>(bipyMO)<sub>3</sub>] **4b** whose room temperature PL has been previously described.<sup>41</sup> Useful spectroscopic parameters to consider in this comparison are: radiative lifetimes ( $\tau_{\text{rad}}$ ), intrinsic quantum yield ( $\Phi$ ), absolute photoluminescence quantum yields and sensitization efficiency ( $\eta$ ). Conversely to  $\tau_{\text{obs}}$ , the radiative lifetime corresponds to the luminescence lifetime of the <sup>5</sup>D<sub>0</sub> level in the absence of non-radiative processes<sup>50</sup> and it can be calculated from europium emission spectra according to equation (1):

$$\frac{1}{\tau_{\text{rad}}} = A_{MD,0} n^3 \left( \frac{I_{\text{tot}}}{I_{MD}} \right) \quad (1)$$

where  $A_{MD,0}$  is the spontaneous emission probability in vacuo of the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition (14.65 s<sup>-1</sup>),  $I_{\text{tot}}$  and  $I_{MD}$  are the integrated areas of the whole emission spectrum and the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition, and  $n$  is the refractive index ( $n \approx 1.55$  at the solid state).<sup>50</sup> The difference between  $\tau_{\text{rad}}$  and  $\tau_{\text{obs}}$  is attributed to the presence of non-radiative relaxation phenomena that cannot be directly observed.  $\tau_{\text{rad}}$  and  $\tau_{\text{obs}}$  are used to calculate the intrinsic quantum yield ( $\Phi$ , eq. 2.1) and the efficiency ( $\eta$ , eq. 2.2) of the sensitization process:

$$\Phi = \frac{\tau_{\text{obs}}}{\tau_{\text{rad}}} \cdot 100 \quad (2.1)$$

$$\eta = \frac{\text{PLQY}}{\Phi} \cdot 100 \quad (2.2)$$

where PLQY is the absolute photoluminescence quantum yield, *i.e.* an experimental evaluated quantity defined as the ratio between the number of emitted and absorbed photons ( $\text{PLQY} \leq \Phi$ ).



**Table 1:** Experimental lifetimes ( $\tau_{\text{obs}}$ ), radiative lifetimes ( $\tau_{\text{rad}}$ ), photoluminescence quantum yields (PLQY), intrinsic quantum yields ( $\Phi$ ), and sensitization efficiency ( $\eta$ ) for the europium dinuclear compounds excited at 350 nm.

Compound	T( $\text{cm}^{-1}$ ) <sup>[b]</sup>	$\tau_{\text{obs}}$ (ms)	$\tau_{\text{rad}}$ (ms)	PLQY (%)	$\Phi$ (%)	$\eta$ (%)
<b>1 (1b)</b> <sup>[a]</sup>	20200 (20500)	0.59 (0.58)	1.00 (1.02)	35 (55)	59 (57)	59 (96)
<b>2 (2b)</b> <sup>[a]</sup>	20600 (20500)	0.58 (0.45)	1.17 (0.90)	48 (42)	50 (50)	96 (84)
<b>3 (3b)</b>	21600 (21500)	0.67 (0.60)	1.00 (0.99)	22 (40)	67 (61)	33 (66)
<b>4 (4b)</b> <sup>[a]</sup>	22100 (22300)	0.70 (0.65)	1.04 (1.02)	10 (30)	67 (64)	15 (47)

<sup>[a]</sup> data from ref<sup>41</sup>. <sup>[b]</sup> Experimental values estimated from low temperature emission spectra of **5-8** and **5b-8b (Figure S3)** derivatives. A very good agreement with literature values for monomeric  $\beta$ -diketonato complexes (20400<sup>33</sup>, 20500<sup>33</sup>, 21450<sup>32</sup>, 21900<sup>31</sup>  $\text{cm}^{-1}$  for Eu(tta)<sub>3</sub>, Eu(dbm)<sub>3</sub>, Eu(bta)<sub>3</sub> and Eu(hfac)<sub>3</sub> respectively) is found. The error on the triplet energy values is  $\pm 3\%$ .

For all przMO-containing dinuclear complexes but **2**, PLQY values are lower than those of the corresponding bipyMO derivatives and range from 55 % for **1b** to 10 % for **4**. The sensitization efficiency  $\eta$  shows a similar trend and resulted near to 100 % for **1b** and **2**, and only 15 % for **4**. The data in **Table 1** show also a correlation between  $\eta$  and the  $\beta$ -diketone triplet energy. In particular, the higher the triplet energy, the greater is the difference in the sensitization efficiency between przMO and bipyMO analogues, and the lower is their absolute quantum yield. The data in **Table 1** show a close relationship between composition of the complexes and their spectroscopic properties due to the different contribution of non-radiative relaxation of excited states that plays a pivotal role in the determination of the thermometric properties of these compounds.

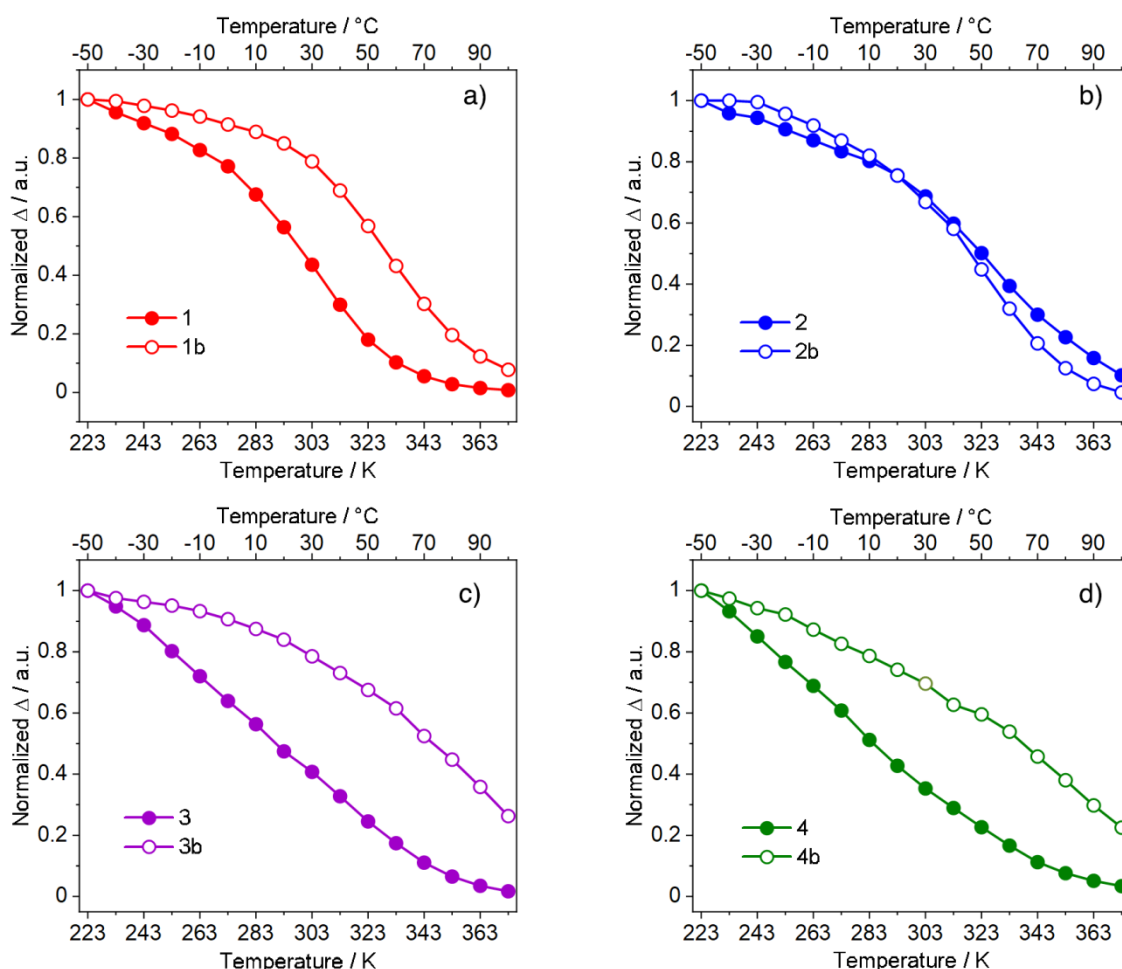
#### *Thermometric properties.*

The luminescence properties of Eu<sup>3+</sup>  $\beta$ -diketonato complexes having  $\Delta E_{T-\text{Eu}} = E(T) - E(^5D_0 \rightarrow ^7F_0)$  in the 2000 - 5000  $\text{cm}^{-1}$  range are generally more sensitive to temperature variation between 223 and 423 K.<sup>35,54</sup> On these grounds, we decided to investigate the temperature-dependent europium emission (TDE) of compounds **1-4** and **1b-4b** in order: *i*) to study the correlations between the nature of  $\beta$ -diketonato and *N*-oxide ligands with TDE modulation, *ii*) to elucidate the observed room temperature emission, and *iii*) to explore the potentiality of this family of dinuclear complexes as luminescence thermometers.

Prior to investigating the dependence of europium emission from temperature, we performed thermal analysis in air of the samples microcrystalline powders. This preliminary step is relevant to check and determine the thermal stability of the complexes in view of their use to study the TDE

behavior. The profile of weight loss for complexes **1-4** and **1b-4b**, **Figure S4**, evidenced their stability up to *ca.* 400 K. In particular **1** and **1b** present a small step around 380 K that is due to the release of toluene molecules retained in the crystals.

The intensity of the emitted light decreases as temperature increases in the range 223 - 373 K (see **Figure S5**). As thermometric parameter ( $\Delta$ ) we used the integrated area of the  $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_2$  transition that, in all compounds, gives the main contribution to the total emission (**Figure 4b**). For a better comparison,  $\Delta$  vs T curves were normalized at 223 K (**Figure 5**).



**Figure 5:** Comparison between the  $\Delta$  curves of the pyrMO and the bipyMO derivatives: **a)** **1** and **1b**, **b)** **2** and **2b**, **c)** **3** and **3b**, and **d)** **4** and **4b**.  $\lambda_{\text{exc}} = 350$  nm.

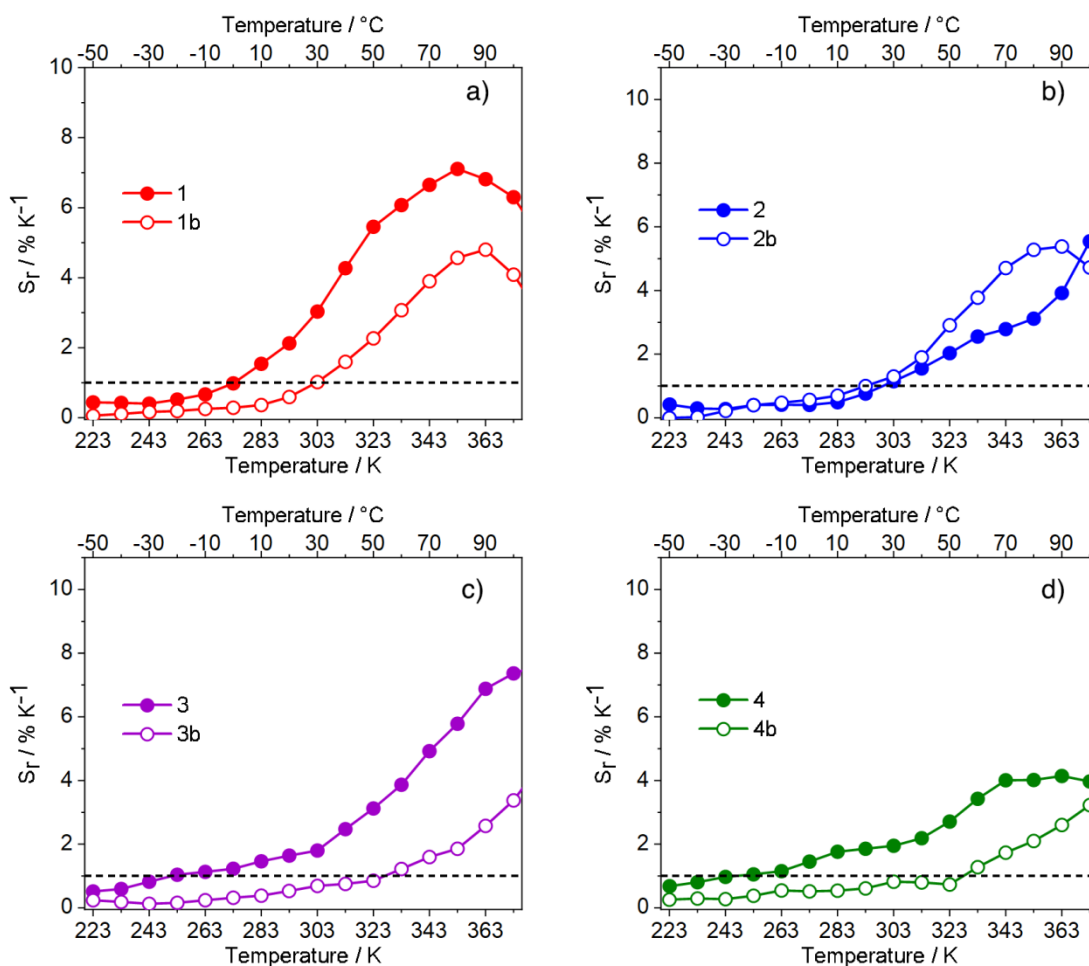
$\Delta$  curves for **1-4** and **1b-4b** complexes are a family of sigmoids having slopes sensitive to both  $\beta$ -diketonato and *N*-oxide ligands. Interestingly, for pyrMO-based compounds  $\Delta$  curves variation begins generally at a lower temperature and proceeds more quickly than that of the corresponding bipyMO derivatives. An exception is found for compounds **2** and **2b** where  $\Delta$  curves are almost overlapped. This behavior, together with large differences in the sensitization efficiency for

complexes bearing pyrzMO or bipyMO ligands, indicates a correlation between the *N*-oxide moieties and the contribution of non-radiative deactivation pathways to TDE.

For a better comparison of the thermometric properties we calculated the relative thermal sensitivity ( $S_r$ , expressed in % K<sup>-1</sup>, eq. 3), *i.e.* the figure of merit usually employed for thermometers comparison.<sup>55</sup>

$$S_r = \frac{1}{\Delta} \left| \frac{\delta\Delta}{\delta T} \right| \quad (3)$$

where  $\Delta$  is the thermometric parameter and  $\delta\Delta$  is the variation of the thermometric parameter per temperature variation ( $\delta T$ ). A value of  $S_r \geq 1$  is assumed as the quality criterion for using these compounds as highly sensitive luminescent thermometers (**Figure 6**).<sup>3</sup>



**Figure 6:**  $S_r$  curves of compounds a) 1 and 1b, b) 2 and 2b, c) 3 and 3b, and d) 4 and 4b.

All the complexes displayed an overall good thermometric response, with  $S_r \geq 1$ , over T ranges from about 40 K up to 130 K. As a general observation, pyrzMO-based complexes show wider

applicative temperature intervals (up to 70 K for **4** and **4b**) and higher  $S_r$  values than their corresponding bipyMO analogues. Compound **3**, instead, displayed the highest  $S_r$  maximum of 7.4 % K<sup>-1</sup> at 373 K. These results, summarized in **Table 2**, show that the design of the complex chemical composition is a practical and effective route to tune TDE of the systems.

**Table 2** Applicative temperature range,  $S_r$  maximum values and its corresponding temperature ( $T S_r$  max) of compounds **1**, **1b**, **2**, **2b**, **3**, **3b**, **4**, and **4b**.

Sample	T $S_r >1$ (K)	Applicative range (K)	$S_r$ max (% K <sup>-1</sup> )	T $S_r$ max (K)
<b>1</b>	273	100	7.1	353
<b>1b</b>	303	70	4.8	363
<b>2</b>	293	80	4.9	373
<b>2b</b>	293	80	4.9	343
<b>3</b>	253	120	7.4	373
<b>3b</b>	333	40	3.4	373
<b>4</b>	243	130	4.1	363
<b>4b</b>	333	40	3.2	373

The Mott-Seitz (MS) model is commonly used to determine the temperature effect on the quenching of lanthanide luminescence and it can be used to rationalize the obtained results. The experimental data were fitted to find the number and the activation energies of the main non-radiative deactivation channels:<sup>56,57</sup>

$$\Delta(T) = \frac{\Delta_0}{1 + \sum_i \alpha_i e^{\left(\frac{-\Delta E_i}{k_B T}\right)}} \quad (4)$$

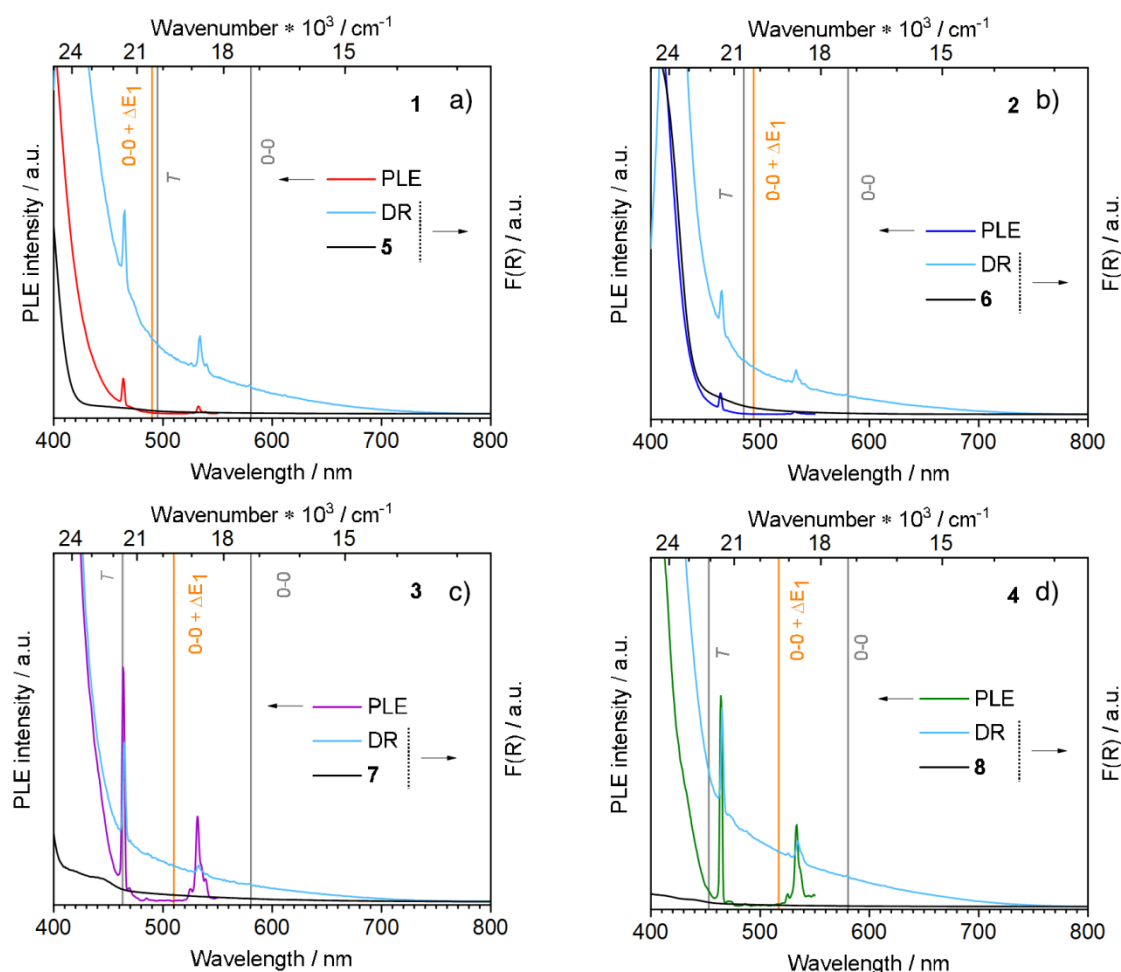
where  $\Delta_0$  is the value of  $\Delta$  at 0 K,  $\Delta E_i$  the activation energy,  $\alpha_i$  the ratio between the non-radiative and radiative deactivation probabilities for the considered path,  $k_B$  the Boltzmann constant, and T temperature in K.<sup>58</sup>

As showed in **Figure S6**, the one-term MS equation is a good model to reproduce our  $\Delta$  vs T experimental curves.

**Table 3:**  $\Delta E_{T-Eu}$ , and  $\Delta E_1$  energy values for the studied compounds. In the second column is reported the triplet energy level of the  $\beta$ -diketonato ligand.

Compound	$\Delta E_{T-Eu}$ ( $\text{cm}^{-1}$ )	$\Delta E_1$ ( $\text{cm}^{-1}$ )
<b>1</b>	$2980 \pm 606$	$3109 \pm 499$
<b>1b</b>	$3280 \pm 615$	$3409 \pm 392$
<b>2</b>	$3380 \pm 618$	$3021 \pm 379$
<b>2b</b>	$3330 \pm 616$	$2876 \pm 390$
<b>3</b>	$4480 \pm 651$	$2377 \pm 350$
<b>3b</b>	$4350 \pm 647$	$2602 \pm 286$
<b>4</b>	$4880 \pm 663$	$2116 \pm 247$
<b>4b</b>	$5080 \pm 669$	$2109 \pm 327$

The most common non-radiative deactivation pathways usually considered in the MS model are:<sup>59,60</sup> (i) back energy transfer (BEnT) from  $\text{Eu}^{3+} {}^5\text{D}_0$  level to the ligand triplet levels, (ii) ligand-to-metal charge transfer (LMCT), and (iii) multiphonon relaxations. For tta (**1**, **1b**) and dbm-based (**2**, **2b**) compounds, MS activation energies ( $\Delta E_1$ , eq. 4 **Table 3**) are comparable to the  $\Delta E_{T-Eu}$  energy gap indicating that BEnT is the most active channel in determining the temperature dependency of europium emission. Conversely, the values of  $\Delta E_1$  and  $\Delta E_{T-Eu}$  for compounds **3**, **3b**, **4**, and **4b** are quite different suggesting a different mechanism for the non-radiative depopulation of the excited states. The comparison in the visible region of solid-state absorption spectra (diffuse reflectance) and excitation spectra (**Figure 7** and **Figure S7**) aided to shine some light on this behavior.



**Figure 7:** Overlap between the photoluminescence excitation (PLE, left axis) and the absorption (DR, right axis) spectra of: **a) 1**, **b) 2**, **c) 3**, and **d) 4**. To better evidence the presence of LMCT transitions the absorption spectra of Gd-complexes **5**, **6**, **7**, **8** are reported as well. The label “0-0” refers to the energy of  $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_0$  transition,  $T$  is the energy of the  $\beta$ -diketonato triplet level, while  $\Delta E_1$  is the activation energy determined with the MS equation.

The absorption spectra of all compounds have extended tails in the visible up to 700 nm. These signals overlap with  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  manifolds but they are not able to sensitize  $\text{Eu}^{3+}$  emission, as evidenced in PLE spectra where ligand-centered transitions occur below 500 nm. This suggests the existence of not yet considered low-energy levels, able to act as further non-radiative deactivation channel. This situation is often encountered in presence of low-energy LMCT states ( $E_{\text{LMCT}} < 25000 \text{ cm}^{-1}$ ).<sup>50,57,61–63</sup> A commonly accepted method to reveal such transitions in lanthanoid complexes is the comparison of the absorption spectra of  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$  compounds. In fact, being the gadolinium first excited state at *ca.*  $32000 \text{ cm}^{-1}$ , LMCT transitions in the visible are not observed. The spectra of Gd-complexes **5**, **6**, **7** and **8** reported in **figure 7** (black curves) do not show bands at  $\lambda > 400 \text{ nm}$  thus confirming the presence of LMCT transitions in the absorption spectra of  $\text{Eu}^{3+}$  complexes. A similar behaviour is found for bipyMO-bearing complexes (**Figure S7**).

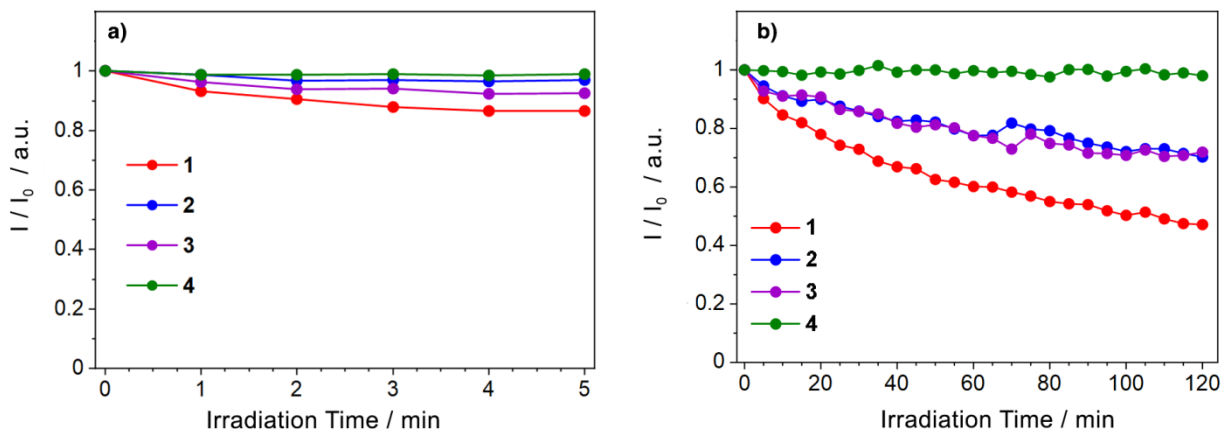
The vertical lines in **Figures 7** and **Figure S7** highlight the energy of: *i*) ligand-centered triplet (T), *ii*)  $^5D_0 \rightarrow ^7F_0$  transitions labelled as 0-0 and *iii*)  $E_{MS} = ^5D_0 \rightarrow ^7F_0 + \Delta E_1$ .

In compounds **1**, **1b**, **2**, and **2b** (cfr. **Figure 7 a** and **b**, and **Figure S7 a** and **b**)  $E_{MS}$  and T values are very close indicating the primary role of back energy transfer in  $\text{Eu}^{3+}$  luminescence quenching, as already mentioned. Although we cannot exactly determine the energy of LMCT transitions, there are experimental evidences of their contribution from the  $\Delta$  vs T curves (**Figure 5**). In fact, the observed  $\Delta$  difference between pyrzMO-bearing complexes (**1** and **2**) and their analogues with bipyMO- (**1b** and **2b**) are due to the LMCT that are more effective in **1** and **2** as also highlighted by the lower  $\eta$  values for pyrzMO derivatives (**Figure 5** and **6** and **Table 1**).

Instead, in compounds **3**, **3b**, **4**, and **4b** (cfr. **Figure 7 c** and **d**, and **Figure S7 c** and **d**) bearing  $\beta$ -diketonato ligands with high triplet energy, BEnT is less effective and LMCT becomes the quenching channel that rules the thermometric properties.

### *Photostability studies*

In luminescent thermometers based on the intensity of a single transition, the photochemical stability of the complex represents a further relevant parameter to be evaluated. Indeed, since  $\Delta$  corresponds to the integrated intensity of the transition (*i.e.*  $\text{Eu}^{3+} ^5D_0 \rightarrow ^7F_2$  transition in our case), all phenomena that can modulate the intensity, excluding temperature, are potential sources of uncertainty or error. Photodegradation involves the organic part of the metal complex that is unstable towards oxidation in its excited state in presence of dioxygen,<sup>64</sup> thus influencing the service-life of the luminescent thermometer. We tested the photostability of our samples in air by monitoring the intensity of europium  $^5D_0 \rightarrow ^7F_2$  transition ( $I$ ) in two different time lapses of continuous irradiation (**Figure 8** and **Figure S8**): *i*) 5 minutes, that correspond to the total sample irradiation time during the three cooling/heating cycles (collection of ca. 50 emission spectra), and *ii*) 2 hours, to simulate harsh working conditions for the luminescent thermometer.



**Figure 8:** Photostability of the complexes **1**, **2**, **3**, and **4** during **a)** 5 min and **b)** 120 min of continuous irradiation.  $\lambda_{\text{exc}}=350$  nm.

As visible from **Figure 8a**, we do not observe for any of the samples a relevant intensity decrease upon irradiation during the first five minutes ( $\Delta I < 10\%$ ) indicating their photostability in this time-lapse. Looking instead at the overall temporal stability of the complexes (**Figure 8b**) we clearly observe its dependence from the nature of the  $\beta$ -diketonato ligands. In particular, compounds **4** does not show relevant photodegradation during the exposition time due to the high stability of C-F bonds.<sup>65</sup> At variance, complexes **2** and **3** show analogous photodegradation curves and a good photostability, independently from the number of  $-\text{CF}_3$  groups. The intensity of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition in these complexes decreased by about 30 % of the initial value after two hours of continuous irradiation. Finally, compounds **1** shows the highest fading tendency, keeping only 50 % of the initial emission intensity. In this case, the poorer photostability can be attributed to the thienyl ring which can be easily oxidized in these conditions, as also reported in the literature.<sup>66</sup>

The effect of *N*-oxide ligands does not clearly show up in complexes bearing tta and hfac because it is shadowed by the photodecomposition paths involving  $\beta$ -diketonato groups. Instead, it can be appreciated only in the **2-2b** and **3-3b** pairs (**Figure S7**) where bipyMO-derivatives show a lower photobleaching stability than pyrZMO analogues. It is likely that the absorption properties of the two *N*-oxides play an active role in determining this behavior being the absorption spectrum of bipyMO red shifted respect to those of pyrZMO (**Figure S9**).

## Conclusions

We studied the correlations between temperature dependent emission and chemical composition in a family of homodinuclear  $\text{Eu}^{3+}$  complexes of general formula  $[\text{Eu}_2(\beta\text{-diketonato})_6(\text{pyrZMO})_x]$  or  $[\text{Eu}_2(\beta\text{-diketonato})_6(\text{bipyMO})_x]$   $x=2$  for  $\beta$ -diketonato= dbm, bta, and tta, and  $x=3$  for  $\beta$ -diketonato



= hfac. The large difference in affinity between nitrogen and oxygen donors in *N*-oxides<sup>41,43</sup> dictates the reaction outcome for lanthanides. Irrespective of the employed  $\beta$ -diketonate, *N*-oxide ligands adopted the  $\mu$ -O bridging coordination mode. Conversely, the number of *N*-oxide molecules coordinated to  $\text{Eu}^{3+}$  ions is determined by  $\beta$ -diketonate. These coordination differences for  $\text{Eu}^{3+}$  ions are closely related to the spectroscopic (absorption and emission) and thermometric properties. Concerning room temperature photoluminescence, we observed a strong relationship between complex composition and emission behavior. The values of absolute PLQY and sensitization efficiency  $\eta$  are significantly higher, up to 55 % and 96 % respectively, in bipyMO-containing dinuclear complexes. Moreover, we found that the higher the ligand triplet energy, the lower the absolute quantum yields and the greater the  $\eta$  difference between pyrzMO and bipyMO derivatives. These results indicate that non-radiative deactivation processes are more efficient in pyrzMO-based compounds and suggest that they can play a prominent role in TDE. All the complexes were characterized by a relevant temperature dependence of their photoluminescence properties in the range 223 - 373 K and displayed a very good thermometric response with  $S_r \geq 1$  over an interval of 40K up to 130 K depending on both the  $\beta$ -diketonato and *N*-oxide ligands. In general, pyrzMO-based complexes show wider exploitable temperature ranges than their bipyMO analogues. Compound **4** has the largest applicative temperature range (from 243 to 373 K, 130 K temperature interval) and **3** the highest  $S_r$  maximum value, i.e. 7.4 %  $\text{K}^{-1}$  at 373 K. The thermometric properties were characterized by two non-radiative deactivation channels, the back-energy transfer (BEnT) from  $\text{Eu}^{3+} \ ^5\text{D}_0$  level to the ligand triplet levels and the ligand-to-metal charge transfer (LMCT). In **1**, **2**, **1b** and **2b** BEnT and LMCT channels are close in energy and both contribute to the quenching of europium emission. For complexes **3**, **4**, **3b** and **4b**, the high ligand triplet energy ( $\geq 21500 \text{ cm}^{-1}$ ) hampers the BEnT mechanism and the LMCT path results the most effective in deactivating the luminescence signal.

## Experimental

### Materials and instrumentation.

Anhydrous toluene was purchased from Merck and used as received.  $[\text{Ln}(\text{dbm})_3]$ ,  $[\text{Ln}(\text{tta})_3]$ ,  $[\text{Ln}(\text{hfac})_3]$  ( $\text{Ln}^{3+} = \text{Eu}^{3+}$  and  $\text{Gd}^{3+}$ ) were prepared according to the literature;<sup>67</sup>  $[\text{Ln}(\text{bta})_3]$  was prepared similarly treating  $[\text{Ln}(\text{bta})_3(\text{H}_2\text{O})_2]$ <sup>68</sup> ( $\text{Ln}^{3+} = \text{Eu}^{3+}$  and  $\text{Gd}^{3+}$ ) under reduced pressure at 70° C over  $\text{P}_4\text{O}_{10}$ . PyrzMO was synthesized according to the literature.<sup>69</sup> FTIR spectra in solid phase were recorded with a Perkin–Elmer “Spectrum One” spectrometer, equipped with an ATR accessory. Elemental analysis (C, H, N) was performed at the Dipartimento di Chimica e Chimica

Industriale, Università di Pisa (Italy). Thermogravimetric analysis (TGA) was performed with a TA Instruments SDT 2960 with simultaneous TGA/DSC system. We followed the mass loss associated to degradation mechanisms as a function of temperature, together with the heat flow. Scans were recorded at a heating rate of 10 °C/min in a temperature range from 293 to 1063 K. Experiments were performed in air weighing about 10 mg of microcrystalline sample previously treated under vacuum at room temperature to remove the toluene molecules occluded in the structure. The onset temperature ( $T_{\text{onset}}$ ), i.e. the temperature value where the weight loss begins, was defined as the intersection point between the baseline and the tangent to the point of maximum slope of the curve oblique side.

Absorption spectra of powder samples were recorded using a *Cary 5000 UV-Vis-Spectrometer* equipped with an integrating sphere. The spectra were normalized and plotted as  $F(R)$  vs wavelength.  $F(R)$  is the Kubelka-Munk function.<sup>63</sup>

Room temperature luminescence spectra of sample powders were recorded with a Horiba JobinYvon *Fluorolog-3* spectrofluorimeter. Absolute photoluminescence quantum yields (PLQY) were calculated from corrected emission spectra obtained by means of an integrating sphere. Estimated errors on PLQY and excited state lifetimes are  $\pm 20$  and 10 %, respectively. A full description of the employed set-up can be found in a previous paper.<sup>41</sup>

Since low temperature (77 K) emission spectra of Gd-complexes **5-8** and **5b-8b** (**Figure S3**) do not show a well resolved vibronic progression, i.e. 0-phonon band cannot be clearly identified, triplet energy was estimated from the crossing point of the tangent line on the high energy side of the spectra and x axis.<sup>70,71</sup> In literature, the tangent method and the peak fitting procedure were used to evaluate the triplet energy in  $\beta$ -diketonato ligands providing results differing of *ca.* 3 %, therefore we give accordingly an uncertainty of  $\pm 3$  % on these values.<sup>23,72</sup>

Temperature dependent experiments (223–373 K) were carried using a Horiba T64000 triple spectrometer and a Linkam THMS600 heating/freezing microscope stage having temperature stability  $< 0.1$  K over a 83 - 873 K temperature range. A full description of the employed set-up has been previously reported.<sup>63</sup> Mott-Seitz fitting was performed with MATLAB; the curves with  $R^2 \geq 0.991$  were considered as best fitting curves.

Photostability experiments were conducted in air on solid samples gently pressed on KBr pellets irradiated at 350 nm for 5 minutes and 2 hours alternatively. The integrated intensity of europium  $^5D_0 \rightarrow ^7F_2$  transition was recorded every 1 and 5 minutes, respectively. The power of the excitation beam was  $60 \mu\text{W} / \text{cm}^2$ .

**Synthesis of [Eu<sub>2</sub>(tta)<sub>6</sub>(pyrzMO)<sub>2</sub>] $\cdot$ C<sub>7</sub>H<sub>8</sub> (1) $\cdot$ C<sub>7</sub>H<sub>8</sub>.** To a solution of [Eu(tta)<sub>3</sub>] (0.208 g, 0.26 mmol) in anhydrous toluene (20 mL) pyrzMO (0.025 g, 0.26 mmol) was added. The yellow solution was stirred overnight at room temperature and then concentrated under reduced pressure until precipitation of a yellowish solid which was filtered and dried *in vacuo* for 5 h (0.15 g, 60.2 % yield as [Eu<sub>2</sub>(tta)<sub>6</sub>(pyrzMO)<sub>2</sub>] $\cdot$ C<sub>7</sub>H<sub>8</sub>). El. Anal. Calcd for [Eu<sub>2</sub>(tta)<sub>6</sub>(pyrzMO)<sub>2</sub>] $\cdot$ C<sub>7</sub>H<sub>8</sub>, C<sub>63</sub>H<sub>40</sub>Eu<sub>2</sub>F<sub>18</sub>N<sub>4</sub>O<sub>14</sub>S<sub>6</sub>, %: Teor: C, 39.5; H, 2.1; N, 2.9. Found: C, 39.6; H, 1.8; N, 3.1. IR-ATR (range: 1700-700 cm<sup>-1</sup>): 1596s, 1540s, 1507m, 1471m, 1430w, 1411s, 1359m, 1303s, 1061m, 1013w, 934m, 855m, 832w, 784s, 766w, 746w, 716s. Well-shaped single crystals were obtained through diffusion of pentane vapors in a toluene solution of the product. X-Ray diffraction studies showed the composition [Eu<sub>2</sub>(tta)<sub>6</sub>(pyrzMO)<sub>2</sub>] $\cdot$ 5C<sub>7</sub>H<sub>8</sub>.

The Gd<sup>3+</sup> derivative [Gd<sub>2</sub>(tta)<sub>6</sub>(pyrzMO)<sub>2</sub>] (5) has been obtained following a similar procedure: [Gd(tta)<sub>3</sub>] (0.504 g, 0.61 mmol), pyrzMO (0.059 g, 0.61 mmol). (5): 0.376 g, 59.8 % yield as [Gd<sub>2</sub>(tta)<sub>6</sub>(pyrzMO)<sub>2</sub>]. El. Anal. Calcd for [Gd<sub>2</sub>(tta)<sub>6</sub>(pyrzMO)<sub>2</sub>], C<sub>56</sub>H<sub>32</sub>F<sub>18</sub>Gd<sub>2</sub>N<sub>4</sub>O<sub>14</sub>S<sub>6</sub>, %: Teor: C, 39.3; H, 2.1; N, 2.9. Found: C, 39.0; H, 1.7; N, 3.1. IR-ATR (range: 1700-700 cm<sup>-1</sup>): 1596s, 1540s, 1507m, 1471m, 1430w, 1411s, 1359m, 1303s, 1061m, 1013w, 934m, 855m, 832w, 784s, 766w, 746w, 716s.

**Synthesis of [Eu<sub>2</sub>(dbm)<sub>6</sub>(pyrzMO)<sub>2</sub>] (2).** A suspension of [Eu(dbm)<sub>3</sub>] (0,192 g, 0.23 mmol) and pyrzMO (0.024 g, 0.235 mmol) in anhydrous toluene (20 mL) was heated at 60 °C for 1 h. The obtained yellow solution was slowly cooled to -20 °C. The crystalline solid precipitated out, was decanted and dried *in vacuo* for 3 h (0.119 g, yield 56.4 % as [Eu<sub>2</sub>(dbm)<sub>6</sub>(pyrzMO)<sub>2</sub>]). El. Anal. Calcd for [Eu<sub>2</sub>(dbm)<sub>6</sub>(pyrzMO)<sub>2</sub>], C<sub>98</sub>H<sub>74</sub>Eu<sub>2</sub>N<sub>4</sub>O<sub>14</sub>, %: Teor: C, 64.1; H, 4.1; N, 3.0. Found: C, 64.4; H, 4.0; N, 2.8. IR-ATR (range: 1700-700 cm<sup>-1</sup>): 1592s, 1550s, 1515s, 1473s, 1457s, 1414s,sh, 1305m, 1261w, 1247w, 1218m, 1176w, 1156w, 1068m, 1021m, 1010m, 939w, 850m, 829m, 781w, 757s, 725s. Crystals suitable to single crystal X-Ray diffraction studies were obtained through diffusion of pentane vapors in a toluene solution of the product.

[Gd<sub>2</sub>(dbm)<sub>6</sub>(pyrzMO)<sub>2</sub>] (6): [Gd(dbm)<sub>3</sub>] (0.373 g, 0.45 mmol), pyrzMO (0.043 g, 0.45 mmol). (6): 0. 205 g, 50.4 % yield as [Gd<sub>2</sub>(dbm)<sub>6</sub>(pyrzMO)<sub>2</sub>]. El. Anal. Calcd for [Gd<sub>2</sub>(dbm)<sub>6</sub>(pyrzMO)<sub>2</sub>], C<sub>98</sub>H<sub>74</sub>Gd<sub>2</sub>N<sub>4</sub>O<sub>14</sub>, %: Teor: C, 63.8; H, 4.0; N, 3.0. Found: C, 63.6; H, 3.9; N, 2.9 IR-ATR (range: 1700-700 cm<sup>-1</sup>): 1592s, 1550s, 1515s, 1473s, 1457s, 1414s,sh, 1305m, 1261w, 1247w, 1218m, 1176w, 1156w, 1068m, 1021m, 1010m, 939w, 850m, 829m, 781w, 757s, 725s.

**Synthesis of [Eu<sub>2</sub>(bta)<sub>6</sub>(pyrzMO)<sub>2</sub>] (3).** To a solution of [Eu(bta)<sub>3</sub>] (0.463 g, 0.58 mmol) in anhydrous toluene (30 mL) pyrzMO (0.056 g, 0.58 mmol) was added. The pale-yellow solution was

stirred at room temperature for 4 h, concentrated under reduced pressure and then cooled to -20 °C. The formed colorless solid was filtered and dried *in vacuo* for 7 h. (0.32 g, yield 62.0% as [Eu<sub>2</sub>(bta)<sub>6</sub>(pyrzMO)<sub>2</sub>]). El. Anal. Calcd for [Eu<sub>2</sub>(bta)<sub>6</sub>(pyrzMO)<sub>2</sub>], C<sub>68</sub>H<sub>44</sub>Eu<sub>2</sub>F<sub>18</sub>N<sub>4</sub>O<sub>14</sub>, %: Teor: C, 45.7; H, 2.5; N, 3.1. Found: C, 45.7; H, 2.5; N, 3.5. IR-ATR (range: 1700-700 cm<sup>-1</sup>): 1632m, 1608s, 1574m, 1532m, 1473m, 1431w, 1319m, 1292s, 1242m, 1189m, 1130s, 1077m, 1025w, 1011w, 945w, 848m, 833m, 810w, 767m, 716m, 700m. Crystals suitable to single crystal X-Ray diffraction studies were obtained through diffusion of pentane vapours in a toluene solution of the product. Repeating the reaction using an [Eu(bta)<sub>3</sub>]/ pyrzMO molar ratio of 2:3, compound **3** was still obtained.

**[Gd<sub>2</sub>(bta)<sub>6</sub>(pyrzMO)<sub>2</sub>] (7)**: [Gd(bta)<sub>3</sub>] (0.498 g, 0.62 mmol), pyrzMO (0.060 g, 0.62 mmol). (**7**): 0.377 g, 67.7 % yield as [Gd<sub>2</sub>(bta)<sub>6</sub>(pyrzMO)<sub>2</sub>]. El. Anal. Calcd for [Gd<sub>2</sub>(bta)<sub>6</sub>(pyrzMO)<sub>2</sub>], C<sub>68</sub>H<sub>44</sub>F<sub>18</sub>Gd<sub>2</sub>N<sub>4</sub>O<sub>14</sub>, %: Teor: C, 45.4; H, 2.5; N, 3.1. Found: C, 45.3; H, 2.3; N, 3.0. IR-ATR (range: 1700-700 cm<sup>-1</sup>): 1632m, 1608s, 1574m, 1532m, 1473m, 1431w, 1319m, 1292s, 1242m, 1189m, 1130s, 1077m, 1025w, 1011w, 945w, 848m, 833m, 810w, 767m, 716m, 700m.

**Synthesis of [Eu<sub>2</sub>(hfac)<sub>6</sub>(pyrzMO)<sub>3</sub>] (4)**. To a suspension of [Eu(hfac)<sub>3</sub>] (0.766 g; 0.99 mmol) in toluene (30 mL) pyrzMO was added (0.143 g; 1.49 mmol). The colorless mixture was refluxed for 1 h. The resulting pale-yellow solution was cooled to room temperature, concentrated under reduced pressure and finally cooled to -20 °C. Precipitation of a colorless crystalline solid occurred. The suspension was filtered and the solid was dried *in vacuo* for 4 h (0.52 g; 57.3% yield as [Eu<sub>2</sub>(hfac)<sub>6</sub>(pyrzMO)<sub>3</sub>]). El. Anal. Calcd for [Eu<sub>2</sub>(hfac)<sub>6</sub>(pyrzMO)<sub>3</sub>], C<sub>42</sub>H<sub>18</sub>Eu<sub>2</sub>F<sub>36</sub>N<sub>6</sub>O<sub>15</sub>, %: Teor: C, 27.5; H, 1.0; N, 4.6. Found: C, 27.5; H, 1.4; N, 4.4. IR-ATR (range: 1700-700 cm<sup>-1</sup>): 1648m, 1577w, 1533w, 1495m, 1473m, 1435m, 1253m, 1202m, 1138s, 1098m, 1012m, 848m, 801m, 734w, 716w. Recrystallization from toluene at -20 °C afforded crystals suitable for X-Ray diffraction studies showing the composition [Eu<sub>2</sub>(hfac)<sub>6</sub>(pyrzMO)<sub>3</sub>]·C<sub>7</sub>H<sub>8</sub>. The crystals were treated under atmosphere saturated with toluene to avoid collapse due to the loss of the crystallization solvent.

**[Gd<sub>2</sub>(hfac)<sub>6</sub>(pyrzMO)<sub>3</sub>] (8)**: [Gd(hfac)<sub>3</sub>] (0.498 g, 0.64 mmol), pyrzMO (0.093 g, 0.96 mmol). (**8**): 0.356 g, 60.3 % yield as [Gd<sub>2</sub>(hfac)<sub>6</sub>(pyrzMO)<sub>3</sub>]. El. Anal. Calcd for [Gd<sub>2</sub>(hfac)<sub>6</sub>(pyrzMO)<sub>3</sub>], C<sub>42</sub>H<sub>18</sub>F<sub>36</sub>Gd<sub>2</sub>N<sub>6</sub>O<sub>15</sub>, %: Teor: C, 27.3; H, 1.0; N, 4.6. Found: C, 27.0; H, 1.1; N, 4.5. IR-ATR (range: 1700-700 cm<sup>-1</sup>): 1648m, 1577w, 1533w, 1495m, 1473m, 1435m, 1253m, 1202m, 1138s, 1098m, 1012m, 848m, 801m, 734w, 716w.

**X-Ray diffraction study.** Crystals of **2** and **3** and were glued at the end of glass fibers, those of **1**, **3b** and **4** were closed in Lindeman capillaries under toluene saturated nitrogen atmosphere. Diffractions were studied at room temperature by means of a Bruker SMART Breeze CCD diffractometer equipped with graphite monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal data are listed in Table 4. Intensity data collections were carried out for all samples within a maximum  $2\theta$  of about 52 deg, because the diffractions besides this limit was very weak. All the structure solutions were found using the automated direct methods contained in SHELXS-97 program.<sup>63</sup> Crystal structures of **1**, **3b** and **4** contained, in addition to the dinuclear molecule, also toluene solvate. In the case of **3b**, the solvent molecules were so disordered that it was impossible to localize the exact position, and their contribution was subtracted from the electron density map by the SQUEEZE procedure.<sup>64</sup> In the crystal structure of **1** the toluene molecules for each dinuclear metal complex were 5, one of them being placed on an inversion center. The disorder present in a  $\text{CF}_3$  group of the crystal structure of **3** made it necessary to consider it as distributed in two limit positions. The reliability factors obtained in the final refinement cycles are listed in Table 4. Supplementary crystallographic data for this paper have been deposited with The Cambridge Crystallographic Data Centre and can be obtained free of charge from it. The deposition numbers for each compound are listed in Table 4.

**Table 4:** Crystal data and refinement summaries for **1**, **2**, **3** and **4**.

Identification code	1·5 toluene	2	3	4·toluene
CCDC number	2008931	2008932	2008933	2008935
Empirical formula	$\text{C}_{91}\text{H}_{72}\text{Eu}_2\text{F}_{18}\text{N}_4\text{O}_{14}\text{S}_6$	$\text{C}_{98}\text{H}_{74}\text{Eu}_2\text{N}_4\text{O}_{14}$	$\text{C}_{68}\text{H}_{44}\text{Eu}_2\text{F}_{18}\text{N}_4\text{O}_{14}$	$\text{C}_{49}\text{H}_{26}\text{Eu}_2\text{F}_{36}\text{N}_6\text{O}_{15}$
Formula weight	2283.80	1835.58	1786.99	1926.68
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
$a$ [Å]	12.69(3)	14.2487(7)	21.1218(10)	13.474(3)
$b$ [Å]	24.14(6)	19.861(1)	15.6107(7)	20.621(4)
$c$ [Å]	17.14(4)	16.1236(8)	22.8947(10)	25.124(5)
$\beta$ [°]	102.76(4)	111.021(1)	106.864(2)	97.30(3)
Volume [Å <sup>3</sup> ]	5121(22)	4259.2(4)	7224.3(6)	6924(3)
$Z$	2	2	4	4
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.481	1.431	1.643	1.848
$\mu$ [mm <sup>-1</sup> ]	1.427	1.526	1.831	1.955
$F(000)$	2284	1856	3520	3728
Data/restraints/parameters	9848 / 126 / 595	10560 / 0 / 532	14508 / 280 / 993	14310 / 755 / 923
Goodness-of-fit on $F^2$	1.185	1.126	1.173	1.062
Final $R_1$ [ $I \geq 2\sigma(I)$ ]	0.0861	0.0359	0.0699	0.0900
Final $wR_2$ [ $I \geq 2\sigma(I)$ ]	0.1882	0.0755	0.1045	0.2602
Final $R_1$ [all data]	0.1234	0.0473	0.1192	0.1109
Final $wR_2$ [all data]	0.2102	0.0807	0.1210	0.2844

## ASSOCIATED CONTENT

### Supporting Information

The syntheses of bipyMO-based compounds, (**3b**, **5b-8b**) crystallographic data for **3b**, thermogravimetric analyses, Gd<sup>3+</sup> derivatives PL measurements, and additional thermometric studies can be found in the Supplementary Information.

### Notes

The authors declare no competing financial interest.

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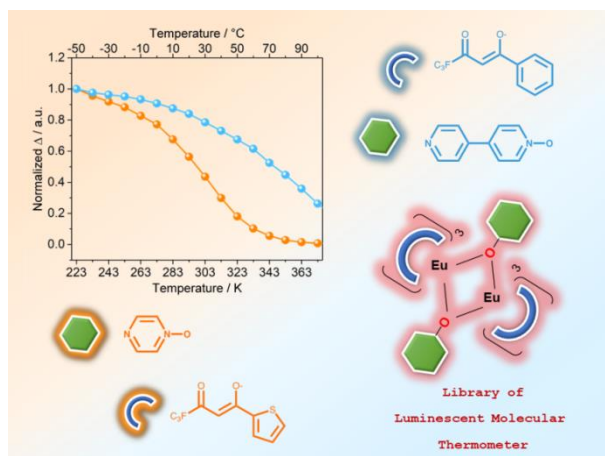
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# Inorganic Chemistry

## Table of Contents synopsis



A family of homodinuclear Eu<sup>3+</sup> luminescent complexes with general formula [Ln<sub>2</sub>( $\beta$ -diketonate)<sub>6</sub>(N-oxide)<sub>y</sub>] (y = 2 or 3) was developed to study the effect of the  $\beta$ -diketonato and N-oxide ligands on their thermometric properties. In this way, an effective tuning of the system's thermometric properties can be achieved.