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**The impact of composition control and energy transfer on luminescence thermometry was investigated in a  $\text{Tb}^{\text{III}}/\text{Eu}^{\text{III}}$  dual-emitting molecular cluster-aggregate, known as  $\{\text{Ln}_{20}\}$ . The study of lifetime dynamics sheds new light on how one can take advantage of rational planning to enhance thermometric performance and gaining insights into intriguing optical properties.**

Over the past decade, luminescence thermometry has emerged as a valuable tool for advancing remote temperature sensing. With its remarkable spatial resolution ( $<10\text{ }\mu\text{m}$ ), high relative thermal sensitivity ( $>1\text{ K}^{-1}$ ) and rapid acquisition times, its potential applications span from biomedicine to photonics and nanoelectronics.<sup>1</sup> This technique relies on the correlation between temperature and the luminescence properties of a material, including the intensity and spectral position of emission bands, as well as the lifetime ( $\tau$ ) of emitting states. By analysing this thermally dependent signal, a thermometric parameter ( $\Delta$ ) is obtained, and its performance can be assessed using the thermal relative sensitivity ( $S_R$ ), as expressed in eqn (1).<sup>2</sup>

$$S_R (\%) = \left| \left( \frac{\delta \Delta}{\delta T} \right) \cdot \frac{1}{\Delta} \right| \times 100 \quad (1)$$

Lanthanide ( $\text{Ln}^{\text{III}}$ )-doped materials are highly sought after in luminescence thermometry due to the distinctive optical features of 4f elements.<sup>3,4</sup> The 4f–4f electronic transitions give rise to unique emission profiles with narrow bands, displaying characteristic energy positions and long lifetimes, making them reliable thermometric parameters.<sup>1</sup> In addition, the control of luminescent processes through chemical composition and the use of established models to understand thermally induced spectral variations offer significant advantages for practical applications.<sup>5–7</sup> Among the various platforms available for designing  $\text{Ln}^{\text{III}}$ -based luminescent thermometers, molecular cluster-aggregates (MCAs) are

particularly distinguished for their tuneable architectures and outstanding luminescent performances.<sup>8</sup> Owing to their crystalline nature, MCAs possess a rigid metal core with high-nuclearity, precise coordination environment, and uniformity within a single unit. They also allow control over energy transfer (ET) processes and their influence on optical output *via* composition control. We have previously reported a highly tuneable icosanuclear MCA with the general formula  $[\text{Ln}_{20}(\text{chp})_{30}(\text{CO}_3)_{12}(\text{NO}_3)_6(\text{H}_2\text{O})_6]\cdot\text{H}_2\text{O}$ ,  $\{\text{Ln}_{20}\}$ , where chp = deprotonated 6-chloro-2-pyridinol (Fig. 1a and Fig. S1, ESI†). Through composition and ET modulation, we demonstrated fine-tuning of optical properties, including downshifting and upconversion luminescence, adjustment of colour output, and their impact on promising applications such as optical barcoding and luminescence intensity ratio thermometry.<sup>7,9,10</sup>

With these studies in mind, herein we report a series of  $\{\text{Ln}_{20}\}$  MCAs, namely  $\{\text{Eu}_1\text{Tb}_{19}\}$  (1),  $\{\text{Eu}_2\text{Tb}_{18}\}$  (2),  $\{\text{Eu}_3\text{Tb}_{17}\}$  (3) and  $\{\text{Eu}_4\text{Tb}_{16}\}$  (4), and investigate these molecular materials as  $\tau$ -based luminescent thermometers. By carefully varying the amount of  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  in the composition, we achieve precise control over intra-cluster ET processes. Our main focus is to understand how these processes impact the temperature-dependent luminescence behaviour. Specifically, we aim to provide control over the decay of  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  emitting states to enhance the potential of our MCAs as  $\tau$ -based luminescent thermometers. Using  $\tau$  as a thermometric parameter offers significant advantages for data acquisition and treatment, including insensitivity to fluctuations in excitation power, light scattering, and reflections.<sup>1,11</sup> To improve the  $S_R$  performance, we explore a ratiometric approach based on the ratio between  $\text{Eu}^{\text{III}}\text{ }^5\text{D}_0$  and  $\text{Tb}^{\text{III}}\text{ }^5\text{D}_4\text{ }\tau$  ( $\tau_{\text{Eu}}$  and  $\tau_{\text{Tb}}$ , respectively). Our dual-emitting centre MCA, with two optically active ions in the metal core, helps develop a rational understanding of  $\tau$ -based thermometry and thermal sensitivity in a molecular system. Our focus is on optimizing these features by considering variations in composition and data treatment.

We prepared MCAs 1, 2, 3 and 4 according to the previously reported procedure (Table S1, ESI†).<sup>9</sup> Powder X-ray diffractograms (PXRD) confirm that the compounds are isostructural to

Department of Chemistry and Biomolecular Sciences, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, K1N 6N5, Canada. E-mail: [m.murugesu@uottawa.ca](mailto:m.murugesu@uottawa.ca)  
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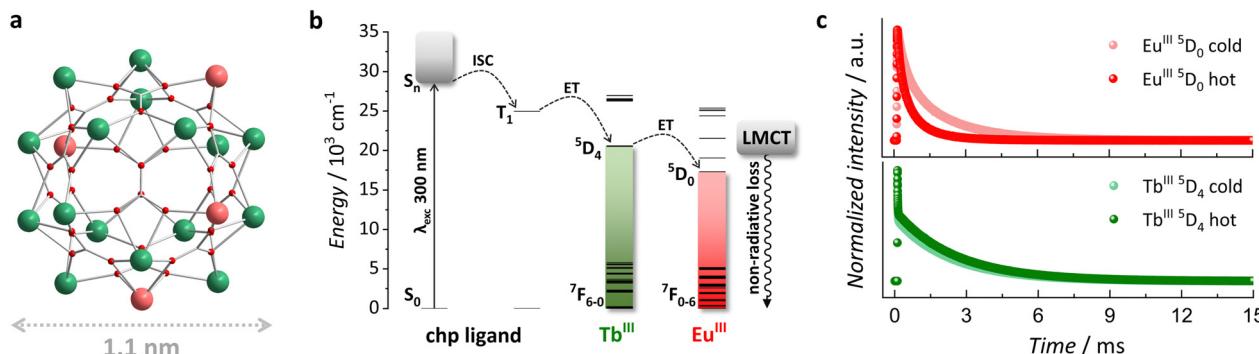


Fig. 1 (a) Molecular core of  $\{Ln_{20}\}$  MCAs. Structure shown refers to  $\{Eu_4Tb_{16}\}$ .  $Ln^{III}$  are randomly assigned. Color code: green for  $Tb^{III}$ , salmon for  $Eu^{III}$  and red for oxygen. (b) Partial energy level diagram of  $\{Ln_{20}\}$  MCAs. ISC = intersystem crossing; ET = energy transfer; LMCT = ligand-to-metal charge transfer. (c) Emission decay curves of  $Eu^{III} 5D_0$  (700 nm) and  $Tb^{III} 5D_4$  (545 nm) of  $\{Eu_4Tb_{16}\}$ , obtained at -5 °C (cold) and 60 °C (hot),  $\lambda_{exc} = 300$  nm.

the icosanuclear  $\{Ln_{20}\}$ , which crystallizes in the  $R\bar{3}$  space group (Fig. S2, ESI†). Fourier transform infrared (FTIR) spectra show the expected molecular vibrations (Fig. S3, ESI†), while energy-dispersive X-ray spectroscopy (EDS) data qualitatively confirm the presence of  $Ln^{III}$  ions in each MCA (Fig. S4, ESI†). ICP-OES supports the nominal chemical composition, with a good agreement between theoretical and experimental  $Ln^{III}$  ratio. Photoluminescent studies were carried out in acetonitrile (0.1 mg mL<sup>-1</sup>), as the stability of the  $\{Ln_{20}\}$  MCA in this solvent has been demonstrated by NMR spectroscopy in previous works.<sup>12</sup> Further experimental details are available in the ESI.†

To enhance the absorption coefficient of  $Ln^{III}$  ions, molecular systems often utilize organic ligands as “antennas” to absorb photons. Subsequently, the ligands transfer the absorbed energy to the  $Ln^{III}$  emitting centre, populating its 4f excited states. In the  $\{Ln_{20}\}$  MCA, the chp ligand plays the role of a sensitizing antenna, with triplet state ( $T_1$ ) energy reported at  $24\,961 \text{ cm}^{-1}$ . From that level, the luminescent processes expected for the  $Eu^{III}/Tb^{III}$  pair are well-known (Fig. 1b).<sup>9</sup> Due to the favourable position of  $Tb^{III} 5D_4$  excited state ( $\approx 20\,500 \text{ cm}^{-1}$ ) relative to chp  $T_1$ , an efficient  $T_1 \rightarrow Tb^{III}$  ET takes place, resulting in emission bands within the visible range characteristic of  $Tb^{III}$ . However, direct sensitization of  $Eu^{III} 5D_0$  excited state ( $\approx 17\,500 \text{ cm}^{-1}$ ) by chp  $T_1$  is not efficient, leading to non-radiative deactivation through an  $Eu$ -based ligand-to-metal charge transfer (LMCT) state at  $20\,492 \text{ cm}^{-1}$ .<sup>12</sup> The characteristic  $Eu^{III}$  emission bands are only observed due to an efficient  $Tb^{III} \rightarrow Eu^{III}$  ET, which leads to the population of  $Eu^{III} 5D_0$ . Thus,  $Tb^{III}$  acts as a bridging pathway that allows the electronic population to reach  $Eu^{III}$  emitting state.

By changing the  $Tb^{III}/Eu^{III}$  composition in our MCAs series, we can assess the influence of  $Tb^{III} \rightarrow Eu^{III}$  ET and the efficiency of this process, along with side non-radiative deactivation pathways (such as the LMCT state), on the population of both  $Tb^{III} 5D_4$  and  $Eu^{III} 5D_0$  emitting states targeted for  $\tau$  thermometry (Fig. 1c). The observed  $\tau$  reflects the contribution of all radiative (emission of light) and non-radiative processes (vibration, energy transfer, charge-transfer state, etc.) leading to the deactivation of an emitting state. Therefore, accounting for these processes is critical for understanding the emission dynamics,  $\tau$  behaviour with temperature, and the impact on thermometric performance.

The excitation and emission spectra of all MCAs were collected at 20 °C. The presence of an intense broad band centred at 300 nm, assigned to the chp excited singlet state ( $S_1$ ), and the absence of noticeable 4f–4f transition bands indicate an efficient antenna effect (Fig. S5, ESI†). Under 300 nm excitation, MCAs exhibit characteristic sharp bands assigned to  $Tb^{III}$  ( $^5D_4 \rightarrow ^7F_J, J = 6-0$ ) and  $Eu^{III}$  ( $^5D_0 \rightarrow ^7F_J, J = 0-4$ ) electronic transitions (Fig. S6, ESI†). While **1** shows a higher intensity of  $Tb^{III}$  emission bands, the rest of the series displays a higher intensity of  $Eu^{III}$  components. This impacts the colour output of each MCA. MCA **1** displays a yellow-greenish output, while **4** exhibits an orange-red emission (Fig. S7, ESI†), which agrees with the change in  $Tb^{III}/Eu^{III}$  ion ratio in the composition. Emission decay curves of  $Tb^{III} 5D_4$  and  $Eu^{III} 5D_0$  emitting states collected at 20 °C (Fig. 2a and b) show a multiexponential decay profile due to the presence of four different crystallographic sites occupied by  $Ln^{III}$  ions within the  $\{Ln_{20}\}$  asymmetric unit. Average  $\tau$  ( $\langle\tau\rangle$ ) values were calculated from decay curves as expressed by eqn (2), where  $t_0$  is the time at which the curve hits its maximum intensity ( $I$ ), and  $t_1$  is the time when it reaches the background.<sup>13</sup>

$$\langle\tau\rangle = \frac{\int_{t_0}^{t_1} t \cdot I(t) \cdot dt}{\int_{t_0}^{t_1} I(t) \cdot dt} \quad (2)$$

At a constant temperature (20 °C), the  $\tau$  of both emitting centres shortens with an increase in  $Eu^{III}$  content. In either case, the radiative process accounted by the observed  $\tau$  is the emission of light. Regarding  $\tau_{Tb}$ , the  $Tb^{III} \rightarrow Eu^{III}$  ET is the

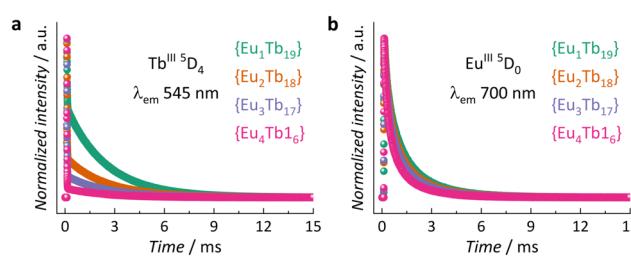


Fig. 2 Emission decay curves of  $\{Eu_1Tb_{19}\}$  (**1**),  $\{Eu_2Tb_{18}\}$  (**2**),  $\{Eu_3Tb_{17}\}$  (**3**) and  $\{Eu_4Tb_{16}\}$  (**4**) MCAs monitoring (a)  $Tb^{III} 5D_4$  (545 nm) and (b)  $Eu^{III} 5D_0$  (700 nm) emitting states. Collected at 20 °C,  $\lambda_{exc} = 300$  nm.

main non-radiative deactivation pathway present in all systems. Thus, a higher number of  $\text{Eu}^{\text{III}}$  ions in the MCA leads to a higher probability of ET, resulting in a faster depopulation of  ${}^5\text{D}_4$ . In the case of  $\tau_{\text{Eu}}$ , besides the non-radiative contribution of the LMCT state, the higher number of  $\text{Eu}^{\text{III}}$  ions leads to concentration quenching and increases the likelihood of  $\text{Eu}^{\text{III}}$  occupying different crystallographic sites, which impacts the average  $\tau$ .

To better understand these photophysical properties and assess the MCAs' potential as  $\tau$ -based luminescent thermometers, we collected variable temperature emission decay curves of  $\text{Tb}^{\text{III}} {}^5\text{D}_4$  and  $\text{Eu}^{\text{III}} {}^5\text{D}_0$ , ranging from  $-5$  °C to  $60$  °C (Fig. S8 and S9, ESI<sup>†</sup>). As illustrated in Fig. 3a and b,  $\tau_{\text{Tb}}$  increases with rising temperature, while  $\tau_{\text{Eu}}$  decreases under the same conditions. The trend for  $\text{Tb}^{\text{III}}$  suggests that at higher temperatures excited vibrational levels coupled with the  $\text{Tb}^{\text{III}} {}^5\text{D}_4$  have a higher probability of being occupied, as expected according to Boltzmann distribution, leading to a slower depopulation of this emitting state. Conversely,  $\text{Eu}^{\text{III}} {}^5\text{D}_0$  becomes more easily deactivated at higher temperatures since it increases the probability of energy loss through non-radiative routes.

To gain a deeper understanding of these characteristics and assess the efficiency ( $\eta_{\text{ET}}$ ) of  $\text{Tb}^{\text{III}} \rightarrow \text{Eu}^{\text{III}}$  ET in each system, structurally analogous MCAs were prepared by replacing the emitting  $\text{Eu}^{\text{III}}$  ions with  $\text{Gd}^{\text{III}}$ . As the first excited 4f level of  $\text{Gd}^{\text{III}}$  ( ${}^6\text{P}_{7/2}$ ,  $32\,200\text{ cm}^{-1}$ ) is too high in energy relative to both chp  $\text{T}_1$  and  $\text{Tb}^{\text{III}} {}^5\text{D}_4$ , it is an optically inactive ion in this system. Thus, we were able to compare the  $\tau$  of the donor ion ( $\text{Tb}^{\text{III}}$ ) in the presence ( $\tau_a$ ) and the absence ( $\tau_0$ ) of the acceptor ion ( $\text{Eu}^{\text{III}}$ ) (Fig. S10 ESI<sup>†</sup>), and calculate  $\eta_{\text{ET}}$  using eqn (3).<sup>14</sup>

$$\eta_{\text{ET}} (\%) = \left[ 1 - \left( \frac{\tau_a}{\tau_0} \right) \right] \times 100 \quad (3)$$

As depicted in Fig. 3c, at a constant temperature (20 °C), the increase of  $\text{Eu}^{\text{III}}$  content in the MCA results in the enhancement

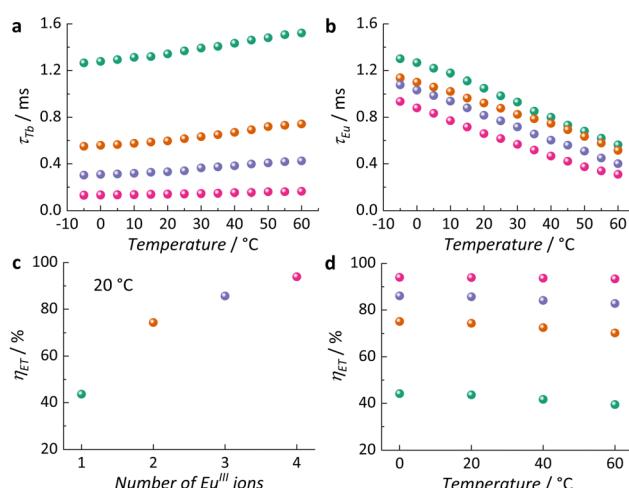


Fig. 3 Average  $\tau$  values of (a)  $\text{Tb}^{\text{III}} {}^5\text{D}_4$  (545 nm) and (b)  $\text{Eu}^{\text{III}} {}^5\text{D}_0$  (700 nm) emitting states of  $\{\text{Eu}_1\text{Tb}_{19}\}$  (1) (green),  $\{\text{Eu}_2\text{Tb}_{18}\}$  (2) (orange),  $\{\text{Eu}_3\text{Tb}_{17}\}$  (3) (purple) and  $\{\text{Eu}_4\text{Tb}_{16}\}$  (4) (pink) MCAs, as well as  $\text{Tb}^{\text{III}} \rightarrow \text{Eu}^{\text{III}}$  ET efficiency ( $\eta$ ) at (c) 20 °C and (d) variable temperatures.

of  $\eta_{\text{ET}}$ , which corroborates  $\text{Tb}^{\text{III}} \rightarrow \text{Eu}^{\text{III}}$  ET as the main pathway of non-radiative depopulation of  $\text{Tb}^{\text{III}} {}^5\text{D}_4$ . This leads to the population of  $\text{Eu}^{\text{III}} {}^5\text{D}_0$  at the expense of  $\text{Tb}^{\text{III}} {}^5\text{D}_4$ . In general, the efficiency of ET processes is highly influenced by temperature, with significant effects typically observed at lower temperatures ( $< 0$  °C).<sup>15</sup> In our study, as the temperature increases, the efficiency decreases (Fig. 3d and Table S2, ESI<sup>†</sup>). This effect is more pronounced in 1, where  $\eta_{\text{ET}}$  decreases from 44.2% to 39.4%, and less evident in 4, where it changes from 94.0% to 93.4%. The varying behaviour is attributed to the more noticeable increase in  $\tau_{\text{Tb}}$  with temperature in 1 compared to 4.

Based on these results, we explored the tuning of intra-cluster  $\text{Tb}^{\text{III}} \rightarrow \text{Eu}^{\text{III}}$  ET of our series of MCAs to investigate their potential as  $\tau$ -based thermometers. More specifically, we decided to take advantage of the two  $\tau$  with different tendencies in our systems to investigate their suitability for ratiometric thermometry. We chose as  $\Delta$  the ratio between  $\tau_{\text{Tb}}/\tau_{\text{Eu}}$ , and also  $\tau_{\text{Eu}}$  itself for comparison purposes, on the premise that the opposite trends of  $\text{Tb}^{\text{III}}$  and  $\text{Eu}^{\text{III}}$ , where  $\tau_{\text{Tb}}$  increases and  $\tau_{\text{Eu}}$  decreases according to temperature, would have a positive impact on sensitivity and favour a higher  $S_R$ .

The temperature dependence of  $\Delta$  is shown in Fig. 4a and b. A logistic function (eqn (S1), ESI<sup>†</sup>) was used for the mathematical fitting of  $\Delta$  values. It is valid to point out that this function has no physical meaning and was used just for fitting purposes. To evaluate the thermometric performance,  $S_R$  curves were obtained by applying the fitted function to eqn (1). Further details about thermometry data treatment, including thermal resolution (Fig. S11, ESI<sup>†</sup>), are available in the ESI<sup>†</sup>.

Using only  $\tau_{\text{Eu}}$  as a  $\Delta$ , we observe an enhancement of  $S_R$  according to the increase of  $\text{Eu}^{\text{III}}$  ions in the MCA composition. While 1 shows a maximum  $S_R$  ( $S_{R\text{max}}$ ) value of  $1.7\text{ °C}^{-1}$  at  $60$  °C, at this same temperature, 4 displays an  $S_{R\text{max}}$  of

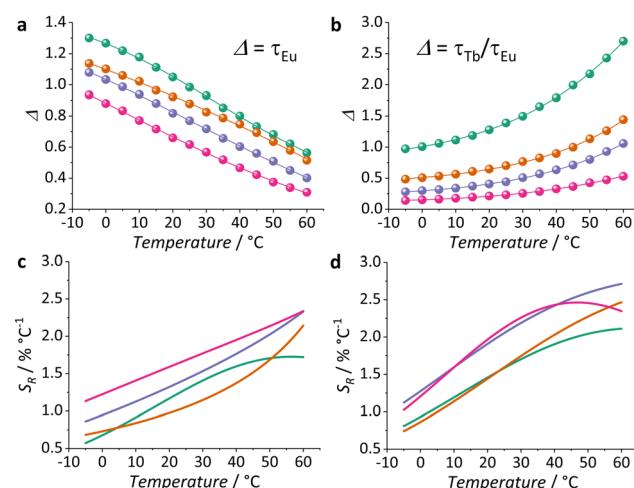


Fig. 4 Temperature dependence of (a)  $\tau_{\text{Eu}}$  and (b)  $\tau_{\text{Tb}}/\tau_{\text{Eu}}$  ratio as thermometric parameters ( $\Delta$ ) of MCAs  $\{\text{Eu}_1\text{Tb}_{19}\}$  (1) (green),  $\{\text{Eu}_2\text{Tb}_{18}\}$  (2) (orange),  $\{\text{Eu}_3\text{Tb}_{17}\}$  (3) (purple) and  $\{\text{Eu}_4\text{Tb}_{16}\}$  (4) (pink). Inserted lines show the mathematical fitting of logistic function. Relative thermal sensitivities ( $S_R$ ) of (c)  $\tau_{\text{Eu}}$  and (d)  $\tau_{\text{Tb}}/\tau_{\text{Eu}}$  ratio are also given for the MCAs with the same color scheme.

2.3%  $^{\circ}\text{C}^{-1}$ . This behaviour is somehow expected once the LMCT state quenching depends on the number of  $\text{Eu}^{\text{III}}$  present. Since this is the main non-radiative deactivation pathway of  $\text{Eu}^{\text{III}}\ ^5\text{D}_0$ , it will govern the temperature dependence of  $\tau_{\text{Eu}}$ . On top of that, the increase of  $\eta_{\text{ET}}$  seems to favor a higher  $S_{\text{R}}$ . However, a beneficial impact on thermometry is observed only to a certain extent, as **3** and **4** exhibit the same trend and  $S_{\text{Rmax}}$  values.

When we consider the  $\tau_{\text{Tb}}/\tau_{\text{Eu}}$  ratiometric approach and compare it to  $\tau_{\text{Eu}}$  data (single approach), an interesting improvement of  $S_{\text{Rmax}}$  is observed. While **1** displays  $S_{\text{Rmax}}$  of 2.1%  $^{\circ}\text{C}^{-1}$ , **3** shows a value of 2.7%  $^{\circ}\text{C}^{-1}$ , both at 60  $^{\circ}\text{C}$ . This represents an enhancement higher than 22% for **1** and 15% for **3** in comparison to the single approach. Within the ratiometric approach and considering the trend observed for the other MCAs, **4** shows a slight reduction in performance, with  $S_{\text{Rmax}}$  of 2.5%  $^{\circ}\text{C}^{-1}$  at 45  $^{\circ}\text{C}$ . In this case, in addition to the thermally-driven effect of LMCT on  $\tau_{\text{Eu}}$ , we also have to consider the behaviour of  $\tau_{\text{Tb}}$  itself. For all compositions,  $\tau_{\text{Tb}}$  exhibits a considerable increase according to temperature. The highest increase is observed for **3** (37%), while **4** (22%) has the lowest. Therefore, the degree of  $\tau_{\text{Tb}}$  temperature susceptibility greatly impacts the ratiometric approach outcome. While  $\tau_{\text{Tb}}/\tau_{\text{Eu}}$  improves the thermometric performance, one must consider how much advantage can be practically derived from each specific system being explored.

The values of  $S_{\text{Rmax}}$  obtained in this study are comparable to those observed for other  $\tau$ -based thermometers (Table S4, ESI<sup>†</sup>), ranging from nanoparticles to molecular compounds. Notably, our MCAs exhibit significantly better performance than other reported molecular systems. To the best of our knowledge, this is the first time  $\tau$  has been employed as a thermometric parameter for a  $\text{Ln}^{\text{III}}$ -based MCA. This result highlights the unique advantages of MCAs as they strike a balance between nanoparticles and molecular systems, combining high nuclearity in a nanometric size with precise control over composition and coordination environment. We anticipate that the insights gained from this study will pave the

way for the development of other dual-centre systems with potential for  $\tau$ -based thermometry.

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## Conflicts of interest

There are no conflicts to declare.

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