

## ELECTRONIC SUPPLEMENTARY MATERIAL

### Lanthanide Coordination Polymers as Luminescent Thermometers: Integrating Theoretical Modelling with Experimental Analysis to Tune the Thermal Response

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## Supplementary note S1. Synthesis and characterization

### Synthesis of the coordination polymers

The synthesis of the 1D coordination polymers was previously described elsewhere.<sup>1</sup>  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$  (**1**) and  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (**2**) (Ln = Eu, Tb) were synthesized by dissolving the  $[\text{Ln}(\text{tfa})_3(\text{H}_2\text{O})_2]$  precursor (0.2 mmol) in 20 mL of ethanol followed by the addition of the dppeo or dppbo bridge ligand (0.1 mmol). The solution was kept undisturbed for 3 days and after that, white crystals were obtained (yield of 60%). The  $\text{Eu}^{\text{III}}$  to  $\text{Tb}^{\text{III}}$  molar ratio was kept as 1:1 (50% to each other) in both systems. All the measurements were undertaken by employing the crashed crystals.

**$[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$  (**1**).** FTIR ( $\text{cm}^{-1}$ , Figure S2): 3064 (w), 2357 (w), 1654 (m), 1635 (s), 1588 (w), 1540 (w), 1517 (m), 1498 (s), 1481 (s), 1457 (m), 1436 (s), 1390 (w), 1356 (m), 1279 (s), 1216 (w), 1197 (m), 1171 (s), 1116 (s), 1081 (m), 1027 (m), 997 (m), 978 (w), 943 (m), 929 (w), 892 (w), 850 (m), 836 (m), 767 (m), 750 (m), 739 (m), 724 (s), 691 (s), 667 (m), 608 (w), 550 (s), 505 (s). Anal. Calcd (%) for  $\text{C}_{41}\text{H}_{36}\text{F}_9\text{O}_8\text{P}_2\text{Eu}_{0.5}\text{Tb}_{0.5}$  ( $1045.10 \text{ g mol}^{-1}$ ): C, 47.11; H, 3.47. Found: C, 47.24; H, 3.66.

**$[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (**2**).** FTIR ( $\text{cm}^{-1}$ , Figure S2): 3064 (w), 2357 (w), 1646 (m), 1624 (s), 1590 (w), 1545 (w), 1517 (m), 1480 (s), 1436 (m), 1424 (s), 1401 (w), 1356 (m), 1289 (s), 1212 (w), 1197 (m), 1186 (m), 1169 (s), 1132 (s), 1121 (s), 1004 (m), 1074 (m), 1029 (m), 1001 (m), 945 (m), 924 (w), 846 (w), 836 (m), 780 (m), 767 (m), 741 (m), 730 (s), 691 (s), 679 (m), 606 (w), 554 (s), 531 (s), 503 (s), 481 (s), 458 (w), 417 (w). Anal. Calcd (%) for  $\text{C}_{43}\text{H}_{40}\text{F}_9\text{O}_8\text{P}_2\text{Eu}_{0.5}\text{Tb}_{0.5}$  ( $1073.15 \text{ g mol}^{-1}$ ): C, 48.12; H, 3.76. Found: C, 47.86; H, 3.33.

### Characterization

**PXRD (powder X-ray diffraction).** PXRD within 5 - 40° was measured using a Shimadzu XRD 7000 (Cu  $K_{\alpha}$ ,  $\lambda = 1.5418 \text{ \AA}$ ) diffractometer operating at 40 kV and 30 mA, with scan rate of  $0.5^\circ \text{ min}^{-1}$ .

**FTIR (Fourier-transform infrared spectroscopy).** FTIR of complexes in solid state was recorded in an Agilent Cary 600 Series FTIR Spectrophotometer (660) in the range of 4,000 to  $400 \text{ cm}^{-1}$  with a resolution of  $2 \text{ cm}^{-1}$  using an attenuated total reflectance (ATR) accessory.

**Elemental analysis.** C, H, N, elementary analysis was measured in a model Perkin Elmer CHN2400.

**Thermogravimetry.** TG analysis for both complexes was undertaken in a TA equipment, SDT Q600 model, under an  $\text{N}_2$  atmosphere. The heating rate was set to  $10 \text{ }^\circ\text{C min}^{-1}$ , with approximately 5 mg of sample weighed into an alumina crucible.

**PL (photoluminescence).** PL were carried out in a Fluorolog-3 spectrofluorometer (Horiba FL3-22-iHR320) with double-gratings ( $1,200 \text{ grooves mm}^{-1}$ , 330 nm blaze) in the excitation monochromator and double-gratings ( $1200 \text{ grooves mm}^{-1}$ , 500 nm blaze) in the emission monochromator. An ozone-free xenon lamp of 450 W (Ushio) was used as a radiation source. A 150 W pulsed xenon lamp was used for time-resolved measurements by using a time-correlated single-photon counting (TCSPC) system. A photomultiplier (Hamamatsu R928P) operating at 950 V was used to collect the spectra in the ultraviolet and visible spectral regions, which were corrected according to the optical system of the emission monochromator and the photomultiplier response. The emission and excitation spectra were carried using the front face mode at  $22.51^\circ$ . The excitation and emission slits were kept in a position to lead to a spectral bandpass of 1 nm in all experiments.

**Luminescence thermometry.** Emission spectra from 77 K to 430 K were measured in the previously mentioned Fluorolog 3 equipment. The excitation and emission slits were kept in a position to lead to a spectral bandpass of 1 nm in all experiments. To control the temperature, a Linkam accessory (THMS600), with an optical fiber set (NA = 0.22 - Horiba-FL-3000/FM4-3000) was used. The relative thermal sensitivity of the systems was calculated from eqn S1, where  $\Delta$  is the thermometric parameter and  $T$  is the temperature. The thermometric parameter was fitted by using a logistic function (eqn S4). The temperature uncertainty ( $\delta T$ ) is calculated by eqn S2 and eqn S3, where  $\delta I/I$  is the relative uncertainty in the integrated area.<sup>2</sup>  $\delta I$  was calculated from the signal-to-noise ratio for each normalized spectrum measured within the 555 – 595 nm spectral range, which was close to 0.01 for all of them. Thus, eqn S3 can be reduced to  $\delta I/I = 0.01$  for all spectra considering the normalized spectra since  $I_{max} = 1$ .

$$S_r = \frac{1}{\Delta} \left| \frac{d\Delta}{dT} \right| \quad (S1)$$

$$\delta T = \frac{1}{S_r} \frac{\delta \Delta}{\Delta} \quad (S2)$$

$$\frac{\delta \Delta}{\Delta} = \sqrt{\left( \frac{\delta I_1}{I_1} \right)^2 + \left( \frac{\delta I_2}{I_2} \right)^2} = \sqrt{2} \frac{\delta I}{I} \quad (S3)$$

$$\Delta = A_2 + \frac{A_1 - A_2}{1 + \left( \frac{T}{T_0} \right)^p} \quad (S4)$$

## Supplementary note S2. Computational and theoretical details

### Computational protocol

All electronic structure calculations within the density functional theory (DFT) and time dependent (TD-DFT) level of theory discussed in the main text and Supporting Information were carried out with the quantum chemistry package Orca 5.0.4<sup>3</sup>.

**Geometry Optimization.** In the present work, only the position of the hydrogen atoms was optimized. This is achieved at the DFT level of theory, using the PBE0 functional<sup>4</sup> along with the D4 dispersion correction<sup>5</sup>. Aiming at an accurate optimization, we employed the Def2-TZVP basis set<sup>6</sup> with no auxiliary resolution of identity (RI) approximation.

**Excited-States calculation and frequency.** With the optimized structure of both coordination polymers, a TD-DFT calculation was performed to harness the energies of the singlets and triplets excited states, and its composition in terms of molecular orbitals. With this in mind, we employed the range-separated  $\omega$ B97x hybrid functional<sup>7</sup> with the D4 dispersion correction as well<sup>5</sup>. All atoms in the system were described with the same Def2-TZVP basis set, except Eu<sup>III</sup> and Tb<sup>III</sup>, as they were described by the Stuttgart-Cologne adapted MWB52 and MWB54 effective core potential (ECP), respectively, along with its Gaussian-type basis set<sup>8</sup>. We highlight that this ECP is widely employed for such calculations, as they allow us to consider the system's multiplicity as a singlet due to the buried nature of the  $4f$  orbitals<sup>9</sup>. The method is therefore written as  $\omega$ B97x-D4/Def2-TZVP/MWB52(54). After this step, an analytical Hessian calculation was performed to determine the energies of the molecule's vibrational modes at the ground-state using the analogous PBE0-D4/Def2-TZVP/MWB52(54) method.

### Theoretical details

This section of the paper includes finding the parameters necessary to understand the roles of energy transfer in the thermometric behavior of both compounds. Within this framework, the ligand-to-lanthanide and lanthanide-to-lanthanide energy transfer rates are determined. The first can be determined using the *JoySpectra* webplatform<sup>10</sup>, according to the data extracted from the TD-DFT calculations, while the latter is determined manually using coding scripts.

**Theoretical Judd-Ofelt intensity parameters.** These parameters are often treated as phenomenological from an experimental perspective; however, their theoretical counterparts furnish crucial information on the chemical environment surrounding the Ln<sup>III</sup>. For Eu<sup>III</sup>, they were determined by the fitting procedure detailed elsewhere<sup>11</sup>. Nevertheless, it is valuable to briefly recall the equations that describe their decomposition into forced-electric dipole (FED, Eq. S6) and dynamic coupling (DC, Eq. S7) components to determine their values for Tb<sup>III</sup>. In these equations,  $t$  and  $p$  are the ranks and components of the spherical harmonics  $(Y_p^{t*})$ , while  $\Delta E$  stands for the average energy denominator method<sup>12</sup>. The numerical factors  $\Theta(t,\lambda)$  are the relation between  $f-g$  and  $f-d$  interconfigurational transitions and  $4f$  radial integrals<sup>13</sup>, assuming values of  $\Theta(1,2) = -0.17$ ,  $\Theta(3,2) = 0.34$ ,  $\Theta(3,4) = 0.18$ ,  $\Theta(5,4) = -0.24$ ,  $\Theta(5,6) = -0.24$ ,  $\Theta(7,6) = 0.24$ .  $g_j$  is the charge factor, which is essential in this description<sup>14</sup>, which together with the overlap integral ( $\rho_j$ ) compose the overlap charge between the coordinating atom and the Ln<sup>III</sup>. Also,  $\beta_j$  is described by the by  $(1 \pm \beta_j)^{-1}$ .  $Y_p^{t*}$  represents the spherical harmonics where the site symmetry is treated by the sum over  $j$  index. Concerning the dynamic coupling mechanism,  $\alpha_{OP,j}$  and  $\alpha'_j$  represents the chemical



bond overlap polarizability and the ligand effective polarizability<sup>15</sup>, respectively. The latter is pivotal in determining the molecular region that interacts with the Ln<sup>III</sup>.

$$\Omega_{\lambda}^{theo} = (2\lambda + 1) \sum_{t,p} \frac{|B_{\lambda tp}|^2}{2t + 1}, \quad B_{\lambda tp} = B_{\lambda tp}^{FED} + B_{\lambda tp}^{DC} \quad (S5)$$

$$B_{\lambda tp}^{FED} = \frac{2}{\Delta E} \langle r^{t+1} \rangle \Theta(t, \lambda) \left( \frac{4\pi}{2t + 1} \right)^{1/2} \sum_j \frac{e^2 \rho_j g_j (2\beta_j)^{t+1}}{R_j^{t+1}} (Y_p^{t*})_j \quad (S6)$$

$$B_{\lambda tp}^{DC} = - \left[ \frac{(\lambda + 1)(2\lambda + 3)}{(2\lambda + 1)} \right]^{1/2} \langle r^{\lambda} \rangle \langle f | |C^{(\lambda)}| | f \rangle \left( \frac{4\pi}{2t + 1} \right)^{1/2} \sum_j \frac{[(2\beta_j)^{t+1} \alpha_{Op,j} + \alpha_j']}{R_j^{t+1}} (Y_p^{t*})_j \delta_{t, \lambda+1} \quad (S7)$$

Within this description, we first extracted the  $g_j$  and  $\alpha_j'$  values of the Eu<sup>III</sup> ion with the fitting. By comparing the structure of both coordination polymers, i.e, bond lengths and angles, it was reasonable to assume that both Eu<sup>III</sup> and Tb<sup>III</sup> were suffering the same influence by the ligand field. With this in mind, we employed in the calculations concerning the Tb<sup>III</sup> the same  $g_j$  and  $\alpha_j'$  values of Eu<sup>III</sup> to obtain the theoretical intensity parameters for the Tb<sup>III</sup> counterpart.

**Intramolecular energy transfer.** With the TD-DFT results, combined with the theoretical intensities parameters from the FED mechanism, we were able to calculate the rates of intramolecular energy transfer (IET) from the excited state ( $S_1$  and  $T_1$ ) of the antenna ligand to the Eu<sup>III</sup> and Tb<sup>III</sup> ions. To obtain the rates we considered three main mechanisms, the dipole-dipole ( $W_{d-d}$ ), dipole-multipole ( $W_{d-m}$ ), and exchange mechanism ( $W_{ex}$ ), as written in equations S8 – S10, where  $S_d^{Ln}$ ,  $S_{\lambda}^{Ln}$ ,  $S_{ex}^L$ , and  $S_{ex}^{Ln}$  are hidden in equations S11 – S14 for clarity<sup>16,17,18,19</sup>.

$$W_{d-d} = \frac{2\pi}{\hbar} \left( \frac{S_d^L S_d^{Ln}}{G R_L^6} \right) F \quad (S8)$$

$$W_{d-m} = \frac{2\pi}{\hbar} \left[ \frac{S_d^L}{G} \left( \sum_{\lambda} \frac{S_{\lambda}^{Ln}}{(R_L^{\lambda+2})^2} \right) \right] F \quad (S9)$$

$$W_{ex} = \frac{2\pi}{\hbar} \left( \frac{S_{ex}^L S_{ex}^{Ln}}{G R_L^4} \right) F \quad (S10)$$

$$S_d^{Ln} = \frac{2e^2(1 - \sigma_1)^2}{(2J + 1)} \sum_{\lambda} \Omega_{\lambda}^{FED} \langle \psi' | J' | |U^{(\lambda)}| | \psi \rangle^2 \quad (S11)$$

$$S_{\lambda}^{Ln} = \frac{e^2(1 - \sigma_{\lambda})^2(\lambda + 1)}{(2J + 1)} \langle r^{\lambda} \rangle^2 \langle f | |C^{(\lambda)}| | f \rangle^2 \langle \psi' | J' | |U^{(\lambda)}| | \psi \rangle^2 \quad (S12)$$

$$S_{ex}^L = \frac{4(1 - \sigma_0)^2}{3(2J + 1)} e^2 \langle \psi' | J' | |S| | \psi \rangle^2 \quad (S13)$$

$$S_{ex}^{Ln} = e^2 \sum_m \left| \left\langle \varphi \left| \sum_j \mu_z(j) s_m(j) \right| \varphi^* \right\rangle \right|^2 \quad (S14)$$

$$R_L = \frac{\sum_{i,j} a_j^2 c_i^2 R_L(i)}{\sum_{i,j} a_j^2 c_i^2} \quad (S15)$$

In all equations,  $R_L$  represents distance between the donor and acceptor states, which is obtained from the excited state calculation (Eq S15). It is noteworthy that  $R_L$  considers the individual distance between the atomic centre and the Ln<sup>III</sup> ( $R_L(i)$ ), the  $i$ -th atomic orbital coefficient contributing to the ligand donor states and incorporates the  $j$ -th orbital excitation that composes the excited state. The quantity  $\Omega_{\lambda}^{FED}$  denotes the intensity parameters regarding only the forced electric-dipole contribution. The terms  $\langle \psi'J' || U^{(\lambda)} || \psi J \rangle^2$  were obtained from reference [20], while the squared spin-operator matrix elements,  $\langle \psi'J' || S || \psi J \rangle^2$  were calculated using free-ions wave functions within the intermediate coupling scheme<sup>21, 22</sup> (**Table S1**).  $S_L$  corresponds to the dipole strength of the ligand transition involved in the IET process, with values of  $10^{-36}$  and  $10^{-40}$  esu<sup>2</sup> cm<sup>2</sup> for  $S_1$  and  $T_1$ , respectively<sup>16</sup>. Factor  $G$  represents the state degeneracy (equal 1 for  $S_1$  and 3 for  $T_1$ ), while the shielding factors  $(1 - \sigma_k)$  are also considered<sup>23</sup>.

For lanthanide-based systems, the IET process is assumed to be non-resonant<sup>16</sup>. Consequently, all equations need an energy mismatch factor ( $F$ ), represented in equation S16. Here we consider that the bandwidth of the ligands ( $\gamma_L \approx 3000 \text{ cm}^{-1}$ ) is much larger than that of the lanthanides ( $\gamma_{Ln} \approx 300 \text{ cm}^{-1}$ ),  $\gamma_L \gg \gamma_{Ln}$ .<sup>16</sup> The parameter  $\delta$  represents the maximum energy difference between donor state (D) and the acceptor state of the lanthanide ion,  $\delta = E_D - E_{Ln}$ . Forward energy transfer ( $W$ ), therefore, can be obtained by summing all mechanisms (Equation S17)<sup>19</sup>.

$$F = \frac{G(\delta, T)}{\hbar \gamma_L} \sqrt{\frac{\ln[10](2)}{\pi}} e^{-\left(\frac{\delta}{\hbar \gamma_L}\right)^2 \ln[10](2)}, \quad \text{with } G(\delta, T) = \begin{cases} 1 & \text{if } \delta \geq 0 \\ e^{\left(\frac{\delta}{k_B T}\right)} & \text{if } \delta < 0 \end{cases} \quad (S16)$$

$$W = W_{d-d} + W_{d-m} + W_{ex} \quad (S17)$$

The backward energy transfer rates ( $W^b$ ), that is, the energy returned from the acceptor to the donor state, can be obtained using the same equations, where  $k_B$  is the Boltzmann constant, with value of  $1.3806 \times 10^{-23} \text{ J K}^{-1}$ , and  $T$  is the temperature.

**Lanthanide-to-lanthanide energy transfer.** For the rates of lanthanide-to-lanthanide energy transfer, three more aspects besides the ones aforementioned must be considered, i.e, the  $W_{d-q}$ ,  $W_{q-q}$ ,  $W_{md-md}$ , which represents the dipole-quadrupole, quadrupole-quadrupole, and magnetic dipole interactions<sup>24,25</sup>. However, one can notice that  $W_{d-d}$  also changes its expression. Thus, we highlight their expressions in equations S18 – S22, where  $S_d^x$ ,  $S_q^x$ , and  $S_{md}^x$  are hidden in equations S23 – S25 for clarity, in which  $x = D$  (donor) or  $A$  (acceptor).

$$W_{d-d} = \frac{4\pi}{3\hbar} \left( \frac{S_d^D S_d^A}{R_{DA}^6} \right) F \quad (S18)$$

$$W_{dq-dq} = \frac{\pi}{\hbar} \left( \frac{S_d^D S_q^A + S_q^D S_d^A}{R_{DA}^8} \right) F \quad (S19)$$

$$W_{q-q} = \frac{28\pi}{5\hbar} \left( \frac{S_q^D S_q^A}{R_{DA}^{10}} \right) F \quad (S20)$$

$$W_{md-md} = \frac{4\pi}{3\hbar} \left( \frac{S_{md}^D S_{md}^A}{R_{DA}^6} \right) F \quad (S21)$$

$$W_{ex} = \frac{2\pi}{\hbar} \left[ \left( \frac{e^2}{R_{DA}} \right) \rho_{ij}^2 \right]^2 F \quad (S22)$$

$$S_d^x = \frac{e^2(1-\sigma_1^x)^2}{2J_x+1} \sum_{\lambda=2,4,6} \Omega_\lambda^x \langle \psi_x J_x' | |U^{(\lambda)}| | \psi_x J_x \rangle^2 \quad (S23)$$

$$S_q^x = \frac{e^2(1-\sigma_2^x)^2}{2J_x+1} \langle f | |C^{(2)}| | f \rangle^2 \langle r^2 \rangle_x^2 \langle \psi_x J_x' | |U^{(\lambda)}| | \psi_x J_x \rangle^2 \quad (S24)$$

$$S_{md}^x = \frac{\mu_B^2(1-\sigma_{md}^x)^2}{2J_x+1} \langle \psi_x J_x' | | \hat{L} + g_s \hat{S} | | \psi_x J_x \rangle^2 \quad (S25)$$

These equations are analogous to the ones presented in the IET section. The main difference between them are the adaptations required to incorporate the effects acting on each donor-acceptor Ln-Ln pair. As seen in the expression for the ET rates, their magnitude depends on the strength of the dipole-dipole, quadrupole-quadrupole and magnetic-dipole interactions (Eq S23 – S25, respectively)<sup>25</sup>. The parameters describing these strengths are also analogous to the IET case. For example,  $\Omega_\lambda^x$  represents the forced-electric dipole component of the intensity parameter for the donor or activator ( $x = D$  or  $A$ ), while  $\langle \psi_x J_x' | |U^{(\lambda)}| | \psi_x J_x \rangle^2$  signifies the square of the doubly reduced matrix elements for the excited and ground state of the donor or acceptor<sup>26</sup>.  $\langle r^t \rangle$  is the expectation value of  $r^t$  with respect to the  $4f$  radial wavefunction and the values for  $t = 2, 4$ , and  $6$  can be found in reference [27]. An interesting term that is absent in the IET case is the contribution from the magnetic-dipole interaction, which depends on the Bohr magneton ( $\mu_B$ ) and the doubly reduced matrix element of the angular  $\hat{L}$  and spin  $\hat{S}$  operators ( $\langle \psi_x J_x' | | \hat{L} + g_s \hat{S} | | \psi_x J_x \rangle$ ) calculated in the intermediate coupling scheme<sup>21,28,29</sup>, with typical values of 0.1–0.6 for states with different  $L$  and  $S$  terms. Furthermore, one can notice that as the donor-acceptor distance reduces ( $R_{DA}$ ), the rate of ET increases due to an inverse rate dependence on the distance.

For lanthanide-based systems, the ET process is non-resonant since there is an energy gap between the donor and acceptor energy levels<sup>25</sup>. Consequently, all equations need a correction factor known as the energy mismatch ( $F$ ), analogous to the IET case, assuming the unsimplified form detailed in Eq S26 – S27. To rationalize this approach, we highlight that due to the strong shielding of the  $4f$  electrons, the energy levels of the  $\text{Ln}^{3+}$  are almost invariant when changing the environment, thus, we can rely on the

energy of 4f manifolds reported for LnF<sub>3</sub> with almost no discrepancy. In contrast to the IET case, where the ligand band width was a lot broader than the Ln<sup>III</sup>, here both donor and acceptor presents the same magnitude. Therefore, for the Tb-Eu donor-acceptor pair, we will consider  $\gamma_D = \gamma_A = 350 \text{ cm}^{-1}$ , a value that has been used before for 4f transitions, yielding reasonable results.

$$F = \frac{\Upsilon}{(\gamma_D^2 + \gamma_A^2)^{1/2}} e^{-(\Delta/\gamma_D)^2 \Gamma} G(\delta, T), \text{ with } \Upsilon = \left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{1}{ch} \quad (S26)$$

$$\Gamma = \left[1 - \frac{1}{1 + (\gamma_D/\gamma_A)^2}\right] \ln 2 \quad (S27)$$

In this work we are interested in the Tb–Eu rates of energy transfer. Therefore, it is worth recalling two important aspects that should be taken into account when calculating the rates. (i) When Eu<sup>III</sup> is the acceptor, the levels <sup>7</sup>F<sub>0</sub>, <sup>7</sup>F<sub>1</sub> are thermally coupled according to the Boltzmann distribution, which depends on the energy difference between them. In the case of the pathway involving the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub> transition, the *J*-mixing between the <sup>7</sup>F<sub>0</sub> and <sup>7</sup>F<sub>2</sub> levels (of the order of 5%) was considered. (ii) When  $\delta E$  is negative, i.e., when the donor state lies below than the acceptor level in energy, the ET rates are multiplied by the

barrier factor  $e^{\left(\frac{\delta}{k_B T}\right)}$ , as it occurred in the ligand-to-Ln ET. However, the case of pathway nine (energy from the <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> to <sup>5</sup>D<sub>1</sub>→<sup>7</sup>F<sub>1</sub>) is an exception to the rule, as this state resonates between the electronic Stark levels.

**Multiphonon relaxation.** The multiphonon decay rates involves the vibrational deactivation of the excited state by several phonon modes<sup>30</sup>. In this sense, the rates can be calculated through the energy gap law<sup>31,32</sup> by using equation S28. In this expression,  $\Delta E$  is the energy gap in units of cm<sup>-1</sup> between successive Ln<sup>III</sup> levels (*J*→*J'*), and  $W_0 \approx 10^8 \text{ s}^{-1}$  represents the decay rate extrapolated to zero energy gap ( $\Delta E \approx 0$ )<sup>33</sup>. The quantity  $\alpha$  (in units of cm) depends on the material, since it incorporates the mean phonon energy ( $\hbar\bar{\omega}$ ). With this in mind, the Miyakawa-Dexter model was employed<sup>34</sup>, represented in equation S29. In this case, *N* accounts for the number of thermally generated phonons, while *S* is the Huang-Rhys factor whose typical values are in the range of 0.02 – 0.10 for Ln<sup>III</sup> ions, while *n* is the thermally averaged phonon occupancy number (Eq S30). Concomitantly with this effect, we can also determine the nonradiative absorption rates from a lower *J'* to an upper *J* level using Boltzmann statistics (Eq. S31)<sup>35</sup>.

$$W_{J' \rightarrow J} = W_0 e^{-|\alpha| \Delta E} \quad (S28)$$

$$\alpha = \frac{1}{\hbar\bar{\omega}} \left[ \ln \left( \frac{N}{S(n+1)} \right) - 1 \right] \quad (S29)$$

$$n = \frac{1}{e^{\left(\frac{\hbar\bar{\omega}}{k_B T}\right)} - 1} \quad (S30)$$

$$W_{J' \rightarrow J} = W_{J \rightarrow J'} e^{-\left(\frac{\Delta E}{k_B T}\right)} \quad (S31)$$

The main difficulty using this method for a coordination polymer is to determine the mean phonon energy. In our approach we address this difficulty by using the weighted average of all vibrational frequencies and their intensities. Within this framework the mean phonon energy was determined to be 1572 and 1560  $\text{cm}^{-1}$  for **1** and **2**, respectively.

**Rate equations.** After computing all process that interferes with the excited state, such as the population, a system of coupled ordinary differential equations (ODEs) was generated and solved numerically by time propagation to obtain the populations of each step in the IET. The set of ODEs, obtained by directly employing Eq. S32, was solved using Radau methods<sup>36</sup>, as they have been successfully used in previous investigations, delivering reliable results at a feasible computational cost<sup>37</sup>. Each simulation was conducted over a time interval ranging from 0 – 50 ms with a step size of 1  $\mu\text{s}$ . By harvesting the population of the emitting level of  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  ( $^5\text{D}_0$  and  $^5\text{D}_4$ , respectively) as a function of temperature, we can understand the temperature influence on the emitting level, that controls the thermometric response. To completely solve the rates, we need to obtain the pumping rate ( $\phi$ ), i.e, the rate involved in populating the excited state after excitation.  $\phi$  is directly determined using the absorption cross-section ( $\sigma$ , with value of  $\sim 10^{-16}$   $\text{cm}^2$  for the ligand and  $\sim 10^{-20}$   $\text{cm}^2$  for  $f$ - $f$  transitions), the excitation wavelength ( $\lambda_{\text{exc}}$ ), Planck's constant ( $h$ ), speed of light ( $c$ ), and the power density ( $\rho$ ), assumed as 1  $\text{W cm}^{-2}$  in the following expression<sup>38</sup>:  $\phi = \sigma \rho \lambda_{\text{exc}} / hc$ .

$$\frac{dP_i(t)}{dt} = \sum_{j=1} W_{j \rightarrow i} P_j(t) - \sum_{j=1} W_{i \rightarrow j} P_i(t), i \neq j \quad (\text{S32})$$

**Theoretical thermometric parameter.** Once the theoretical intensity parameters and the population of the emissive state for each  $\text{Ln}^{\text{III}}$  have been determined, it is possible to calculate the theoretical thermometric parameter. This relation has been previously reported elsewhere [37]. However, in this paper we propose modifications to consider the excitation wavelength, i.e, considering the ligand-to-Ln and Ln-to-Ln energy transfer. The overall radiative rates can be directly harvested from the Judd-Ofelt theory (Eq. S32), by decomposing the rates into their electric and magnetic dipole strengths (Eq. S33 – S35). To perform these calculations, we applied the dataset obtained from the previous one, such as the doubly reduced matrix elements of the angular and spin operator,  $\langle l^N \psi J \mid |L + 2S| \mid l^N \psi' J' \rangle$ . However, in this step the refractive index  $n$  of the medium and the energetic barycentre of the band ( $^{\omega}_{J \rightarrow J'}$ ) needs to be considered. Herein we have chosen the value of 1.5 for  $n$ .

$$A_{J \rightarrow J'} = \frac{4e^2(\omega_{J \rightarrow J'})^3}{3\hbar c^3(2J + 1)} \left[ \frac{n(n^2 + 2)^2}{9} S_{ed} + n^3 S_{md} \right] \quad (\text{S33})$$

$$S_{ed} = \sum_{\lambda=2,4,6} \Omega_{\lambda} \langle \psi' J' \mid |U^{(\lambda)}| \mid \psi J \rangle^2 \quad (\text{S34})$$

$$S_{md} = \frac{\hbar}{4m_e^2 c^2} \langle l^N \psi J \mid |L + 2S| \mid l^N \psi' J' \rangle^2 \quad (\text{S35})$$

The emission of interest for the thermometric parameter are the  $\text{Eu}^{\text{III}}$   $^5\text{D}_0 \rightarrow ^7\text{F}_4$  and  $\text{Tb}^{\text{III}}$   $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transitions. To accurately determine the theoretical rate of the emission and its temperature dependence,  $A_{J \rightarrow J'}$  is normalized by the population of the emissive state (Eq. S36). One can note that  $P_4$  carries the excitation wavelength dependence intrinsically due to its absorption cross-section dependence<sup>39</sup>.

$$I_{J \rightarrow J'} = A_{J \rightarrow J'} P_4(Ln) \quad (S36)$$

By estimating the intensities of Eu<sup>III</sup> and Tb<sup>III</sup> emission, the theoretical thermometric parameter is

therefore the intensities ratio, analogous to the experimental formula  $\left(\Delta = \frac{I_{Tb}}{I_{Eu}}\right)$ , which is extended in Eq S37.

$$\Delta = \frac{A_{4 \rightarrow 5} P_4(Tb)}{A_{0 \rightarrow 4} P_4(Eu)} = \frac{1}{9} \left( \frac{\omega_{4 \rightarrow 5}}{\omega_{0 \rightarrow 4}} \right)^3 \left( \frac{\sum_{\lambda=2,4,6} \Omega_{\lambda} \langle 4 || U^{(\lambda)} || 5 \rangle^2}{\Omega_4 \langle 0 || U^{(\lambda)} || 4 \rangle^2} + \frac{9n^3 \hbar}{4m_e^2 c^2 (n^2 + 2)^2 \Omega_4} \left( \frac{\langle 4 || L + 2S || 5 \rangle}{\langle 0 || U^{(\lambda)} || 4 \rangle} \right)^2 \right) \frac{P_4(Tb)}{P_4(Eu)} \quad (S37)$$

It is noteworthy from Eq. S36 that only the populations are temperature dependent, since they carry the temperature variation in the energy transfer and multiphonon relaxation rates. Keeping this observation in mind, we show that the relative sensibility of the thermometer (defined in Eq. S1) depends only on the population of the emitting state within this theoretical framework (Eq. S38).

$$S_r = \frac{P_4(Eu)}{P_4(Tb)} \left| \frac{d}{dT} \left( \frac{P_4(Tb)}{P_4(Eu)} \right) \right| \quad (S38)$$

This is an elegant and unreported method that rationalizes this property even in the absence of the rates, meaning that only the populations are necessary to calculate the relative sensitivity, which can be used to predict this property. It is worth noting that the emission band of the Ln<sup>III</sup> is not being simulated, but only the intensity, which is proportional to Eq. S33. Minor deviations may arise from the different population of Stark levels. Therefore, the normalization procedure for the theoretical thermometric parameter was applied.

**Table S1.** Values of squared reduced matrix elements for Eu<sup>III</sup> ion. The values of  $\langle \psi' J' || U^{(\lambda)} || \psi J \rangle^2$  were taken from ref. [40], while the  $\langle \psi' J' || S || \psi J \rangle^2$  were calculated in a previous work using reference [21,41].

Transition	Energy / cm <sup>-1</sup>	$\langle \psi' J'    U^{(2)}    \psi J \rangle^2$	$\langle \psi' J'    U^{(4)}    \psi J \rangle^2$	$\langle \psi' J'    U^{(6)}    \psi J \rangle^2$	$\langle \psi' J'    S    \psi J \rangle^2$
<sup>7</sup> F <sub>0</sub> → <sup>7</sup> F <sub>2</sub>	1026	0.137	0	0	0
<sup>7</sup> F <sub>0</sub> → <sup>7</sup> F <sub>3</sub>	1866	0	0	0	0
<sup>7</sup> F <sub>0</sub> → <sup>7</sup> F <sub>4</sub>	2823	0	0.140	0	0
<sup>7</sup> F <sub>0</sub> → <sup>7</sup> F <sub>5</sub>	3849	0	0	0	0
<sup>7</sup> F <sub>0</sub> → <sup>7</sup> F <sub>6</sub>	4907	0	0	0.145	0
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>0</sub>	17293	0	0	0	0
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>1</sub>	19027	0	0	0	0.027
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>2</sub>	21483	0	0	0	0
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>3</sub>	24355	0	0	0	0
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> L <sub>6</sub>	25325	0	0	0.015	0
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> L <sub>7</sub>	26357	0	0	0	0
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> G <sub>2</sub>	26392	0	0	0	0
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> G <sub>3</sub>	26622	0	0	0	0
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> G <sub>4</sub>	26735	0	0	0	0
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> G <sub>6</sub>	26752	0	0	0.004	0
<sup>7</sup> F <sub>0</sub> → <sup>5</sup> G <sub>5</sub>	26763	0	0	0	0

${}^7F_0 \rightarrow {}^5L_8$	27244	0	0	0	0
${}^7F_0 \rightarrow {}^5D_4$	27586	0	0.001	0	0
${}^7F_0 \rightarrow {}^5L_9$	27960	0	0	0	0
${}^7F_0 \rightarrow {}^5L_{10}$	28427	0	0	0	0
${}^7F_1 \rightarrow {}^7F_2$	654	0.052	0	0	0
${}^7F_1 \rightarrow {}^7F_3$	1494	0.209	0.128	0	0
${}^7F_1 \rightarrow {}^7F_4$	2451	0	0.174	0	0
${}^7F_1 \rightarrow {}^7F_5$	3477	0	0.119	0.054	0
${}^7F_1 \rightarrow {}^7F_6$	4535	0	0	0.377	0
${}^7F_1 \rightarrow {}^5D_0$	16921	0	0	0	0.117
${}^7F_1 \rightarrow {}^5D_1$	18655	0.003	0	0	0
${}^7F_1 \rightarrow {}^5D_2$	21111	0	0	0	0.005
${}^7F_1 \rightarrow {}^5D_3$	23983	0	0.001	0	0
${}^7F_1 \rightarrow {}^5L_6$	24953	0	0	0.009	0
${}^7F_1 \rightarrow {}^5L_7$	25985	0	0	0.018	0
${}^7F_1 \rightarrow {}^5G_2$	26020	0	0	0	0.013
${}^7F_1 \rightarrow {}^5G_3$	26250	0	0.001	0	0
${}^7F_1 \rightarrow {}^5G_4$	26363	0	0	0	0
${}^7F_1 \rightarrow {}^5G_6$	26380	0	0	0.005	0
${}^7F_1 \rightarrow {}^5G_5$	26391	0	0	0.010	0
${}^7F_1 \rightarrow {}^5L_8$	26872	0	0	0	0
${}^7F_1 \rightarrow {}^5D_4$	27214	0	0	0	0
${}^7F_1 \rightarrow {}^5L_9$	27588	0	0	0	0
${}^7F_1 \rightarrow {}^5L_{10}$	28055	0	0	0	0

**Table S2.** Values of squared reduced matrix elements for Tb<sup>III</sup> ion. The values of  $\langle \psi'J' || U^{(\lambda)} || \psi J \rangle^2$  were taken from ref. [40], while the  $\langle \psi'J' || S || \psi J \rangle^2$  were calculated in this work using references [21,41].

Transition	Energy / cm <sup>-1</sup>	$\langle \psi'J'    U^{(2)}    \psi J \rangle^2$	$\langle \psi'J'    U^{(4)}    \psi J \rangle^2$	$\langle \psi'J'    U^{(6)}    \psi J \rangle^2$	$\langle \psi'J'    S    \psi J \rangle^2$
${}^7F_6 \rightarrow {}^7F_4$	3315	0.089	0.516	0.266	0
${}^7F_6 \rightarrow {}^7F_3$	4294	0	0.232	0.413	0
${}^7F_6 \rightarrow {}^7F_2$	4982	0.048	0.048	0.469	0
${}^7F_6 \rightarrow {}^7F_1$	5437	0	0	0.376	0
${}^7F_6 \rightarrow {}^7F_0$	5660	0	0	0.144	0
${}^7F_6 \rightarrow {}^5D_4$	20444	0.001	0.001	0.001	0
${}^7F_6 \rightarrow {}^5D_3$	26236	0	0	0.001	0
${}^7F_6 \rightarrow {}^5G_6$	26423	0.002	0.004	0.116	0.555
${}^7F_6 \rightarrow {}^5L_{10}$	26971	0	0	0.058	0
${}^7F_6 \rightarrow {}^5G_5$	27767	0.001	0.002	0.013	0.038
${}^7F_6 \rightarrow {}^5D_2$	28107	0	0	0	0
${}^7F_6 \rightarrow {}^5G_4$	28287	0	0	0.009	0
${}^7F_6 \rightarrow {}^5L_9$	28408	0	0.002	0.045	0
${}^7F_6 \rightarrow {}^5G_3$	28977	0	0	0.001	0
${}^7F_6 \rightarrow {}^5L_8$	29190	0	0	0.023	0
${}^7F_6 \rightarrow {}^5L_7$	29457	0.001	0	0.012	0
${}^7F_6 \rightarrow {}^5G_2$	29531	0	0	0	0
${}^7F_6 \rightarrow {}^5L_6$	29670	0	0	0	0.009
${}^7F_6 \rightarrow {}^5D_1$	30610	0	0	0	0
${}^7F_6 \rightarrow {}^5D_0$	31224	0	0	0	0

${}^7F_6 \rightarrow {}^5H_7$	31379	0	0	0	0.010
${}^7F_6 \rightarrow {}^5H_6$	32891	0	0	0	0.081
${}^7F_6 \rightarrow {}^5H_5$	33767	0	0	0	0
${}^7F_6 \rightarrow {}^5H_4$	34339	0	0	0	0
${}^7F_6 \rightarrow {}^5F_5$	34934	0	0	0	0.165
${}^7F_6 \rightarrow {}^5H_3$	34936	0	0	0	0
${}^7F_6 \rightarrow {}^5I_8$	35131	0	0	0	0
${}^7F_6 \rightarrow {}^5F_4$	35374	0	0	0	0
${}^7F_6 \rightarrow {}^5F_3$	36550	0	0	0	0
${}^7F_6 \rightarrow {}^5I_7$	36589	0	0	0	0.007
${}^7F_6 \rightarrow {}^5F_2$	37136	0	0	0	0
${}^7F_6 \rightarrow {}^5F_1$	37482	0	0	0	0
${}^7F_6 \rightarrow {}^5I_6$	37598	0	0	0	0.106
${}^7F_6 \rightarrow {}^5I_4$	37608	0	0	0	0
${}^7F_6 \rightarrow {}^5I_5$	37986	0	0	0	0.009
${}^7F_6 \rightarrow {}^5K_9$	39173	0	0	0	0
${}^7F_6 \rightarrow {}^5K_8$	40815	0	0	0	0
${}^7F_6 \rightarrow {}^5K_5$	41334	0	0	0	0
${}^7F_6 \rightarrow {}^5K_7$	41693	0	0	0	0
${}^7F_5 \rightarrow {}^7F_4$	1267	0.554	0.012	0.437	0
${}^7F_5 \rightarrow {}^7F_3$	2246	0.177	0.250	0.382	0
${}^7F_5 \rightarrow {}^7F_2$	2934	0	0.314	0.207	0
${}^7F_5 \rightarrow {}^7F_1$	3389	0	0.119	0.054	0
${}^7F_5 \rightarrow {}^7F_0$	3612	0	0	0	0
${}^7F_5 \rightarrow {}^7D_4$	18396	0.014	0.001	0.002	0.051
${}^7F_5 \rightarrow {}^5D_3$	24188	0.001	0.003	0.002	0
${}^7F_5 \rightarrow {}^5G_6$	24375	0.004	0.003	0.009	0.073
${}^7F_5 \rightarrow {}^5L_{10}$	24923	0	0	0.002	0
${}^7F_5 \rightarrow {}^5G_5$	25719	0	0	0.006	0.243
${}^7F_5 \rightarrow {}^5D_2$	26059	0	0.003	0.001	0
${}^7F_5 \rightarrow {}^5G_4$	26239	0.001	0	0.002	0.031
${}^7F_5 \rightarrow {}^5L_9$	26360	0	0.001	0.014	0
${}^7F_5 \rightarrow {}^5G_3$	26929	0	0	0	0
${}^7F_5 \rightarrow {}^5L_8$	27142	0	0.002	0.021	0
${}^7F_5 \rightarrow {}^5L_7$	27409	0	0	0.007	0
${}^7F_5 \rightarrow {}^5G_2$	27483	0	0	0	0
${}^7F_5 \rightarrow {}^5L_6$	27622	0	0	0	0.001
${}^7F_5 \rightarrow {}^5D_1$	28562	0	0	0	0
${}^7F_5 \rightarrow {}^5D_0$	29176	0	0	0	0
${}^7F_5 \rightarrow {}^5H_7$	29331	0	0	0	0
${}^7F_5 \rightarrow {}^5H_6$	30843	0	0	0	0.010
${}^7F_5 \rightarrow {}^5H_5$	31719	0	0	0	0.130
${}^7F_5 \rightarrow {}^5H_4$	32291	0	0	0	0.297
${}^7F_5 \rightarrow {}^5F_5$	32886	0	0	0	0.172
${}^7F_5 \rightarrow {}^5H_3$	32888	0	0	0	0
${}^7F_5 \rightarrow {}^5I_8$	33083	0	0	0	0
${}^7F_5 \rightarrow {}^5F_4$	33326	0	0	0	0.520
${}^7F_5 \rightarrow {}^5F_3$	34502	0	0	0	0
${}^7F_5 \rightarrow {}^5I_7$	34541	0	0	0	0
${}^7F_5 \rightarrow {}^5F_2$	35088	0	0	0	0
${}^7F_5 \rightarrow {}^5F_1$	35434	0	0	0	0

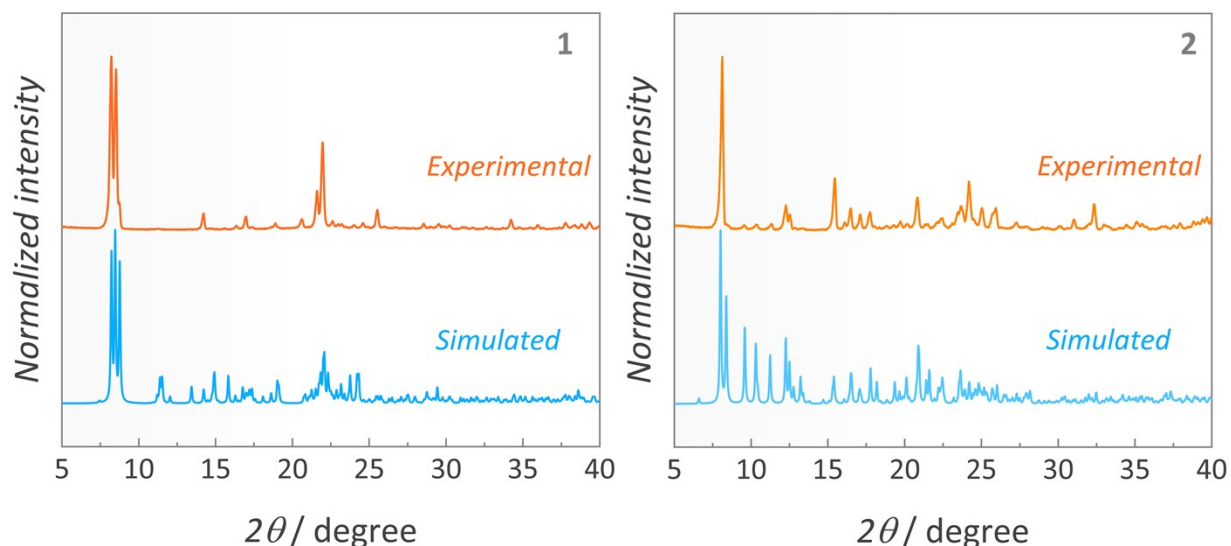


${}^7F_5 \rightarrow {}^5I_6$	35550	0	0	0	0.016
${}^7F_5 \rightarrow {}^5I_4$	35560	0	0	0	0
${}^7F_5 \rightarrow {}^5I_5$	35938	0	0	0	0.001
${}^7F_5 \rightarrow {}^5K_9$	37125	0	0	0	0
${}^7F_5 \rightarrow {}^5K_8$	38767	0	0	0	0
${}^7F_5 \rightarrow {}^5K_5$	39286	0	0	0	0
${}^7F_5 \rightarrow {}^5K_7$	39645	0	0	0	0

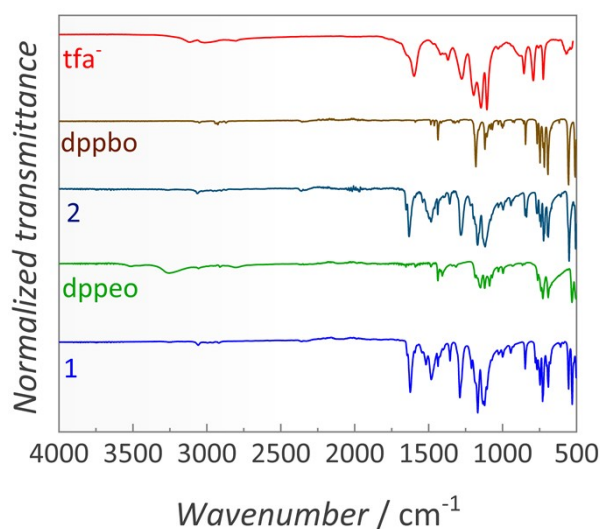
**Table S3.** Values of squared reduced matrix elements for Tb<sup>III</sup> ion used in the Ln-Ln energy transfer. The values of  $\langle \psi'J' || U^{(\lambda)} || \psi J \rangle^2$  were taken from ref. [40], while the  $\langle \psi'J' || L + gS || \psi J \rangle^2$  were calculated in this work according to reference [21,41].

Tb <sup>III</sup>	Energy / cm <sup>-1</sup>	$\langle \psi'J'    U^{(2)}    \psi J \rangle^2$	$\langle \psi'J'    U^{(4)}    \psi J \rangle^2$	$\langle \psi'J'    U^{(6)}    \psi J \rangle^2$	$\langle \psi'J'    L + gS    \psi J \rangle^2$
${}^5D_4 \rightarrow {}^7F_6$	20444	0.0009	0.0008	0.0013	0
${}^5D_4 \rightarrow {}^7F_5$	18396	0.0142	0.0013	0.0022	0.1618
${}^5D_4 \rightarrow {}^7F_4$	17129	0.0002	0.0022	0.0014	0.0620
${}^5D_4 \rightarrow {}^7F_3$	16145	0.0022	0.0005	0.0006	0.6835

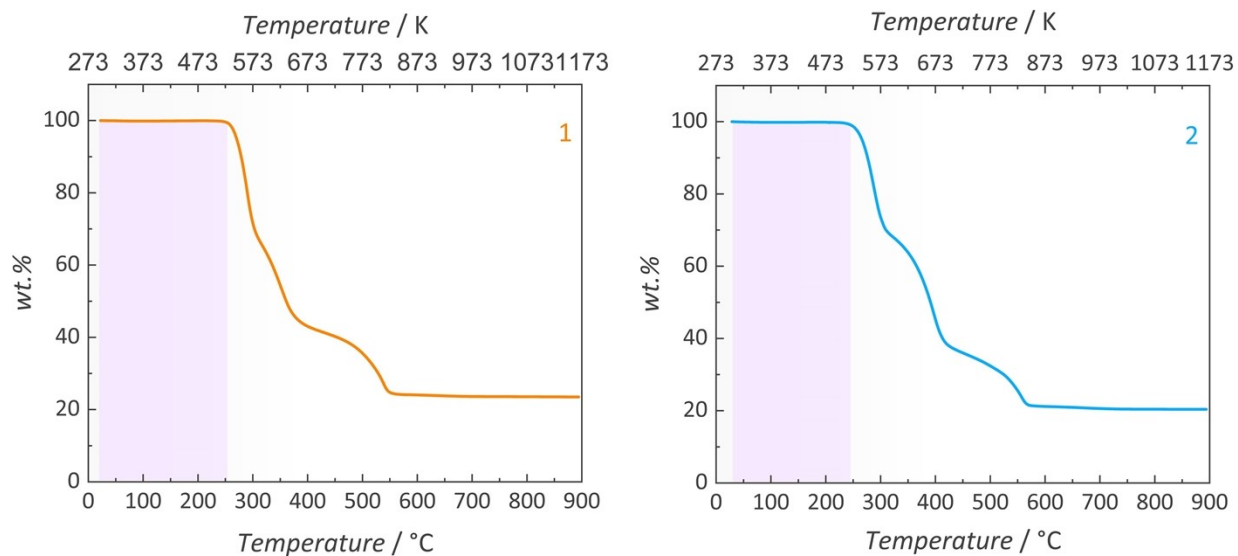
### Supplementary note S3 – Experimental structural characterization



**Figure S1.** Powder XRD of crashed crystals of **1** and **2** compared to the simulated pattern determined from the SC-XRD previously reported by us elsewhere<sup>1</sup> (CCDC code 2219225 and 2219224). **1** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$ ; **2** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (Ln = Eu, Tb). The peaks in the experimental PXRD matches the ones simulated from the SC-XRD analysis. Although the crystals were crashed before undertaking the PXRD data, the crystals were obtained as needles, which presents preferential growth in a specific crystallographic direction. Moreover, needles can also assume a preferential orientation in the sample holder. These effects can lead to changes in the relative peak intensity of the experimental PXRD (measured as a crashed crystal) compared to the PXRD simulated from the SC-XRD analysis (measured for the needle-shaped crystals).<sup>42</sup> These changes in the relative intensity of the peaks are mainly observed for **2**.

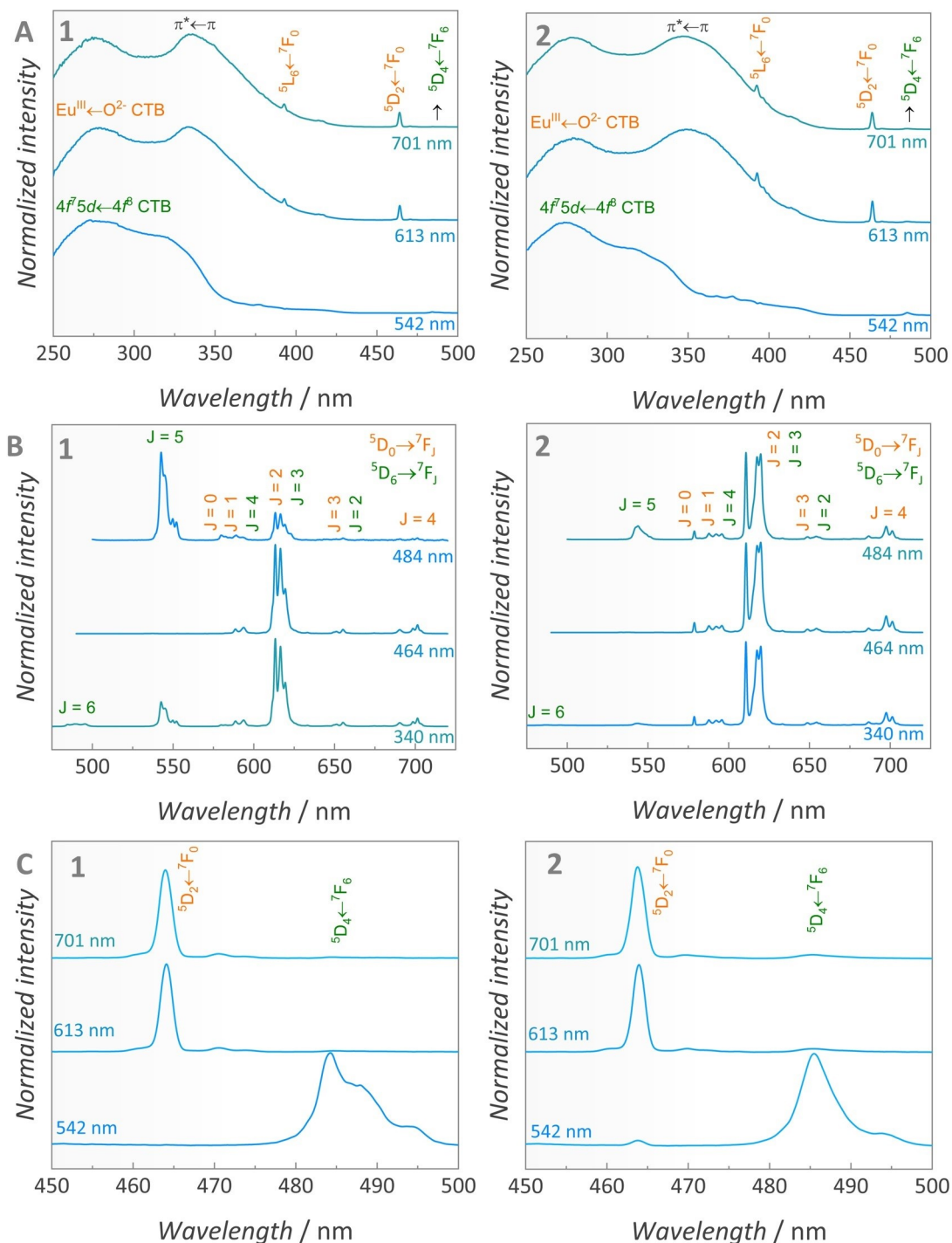


**Figure S2.** FTIR spectra of **1** and **2** compared to the dppeo, dppbo, and  $\text{tfa}^-$  ligands. **1** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$ ; **2** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (Ln = Eu, Tb).

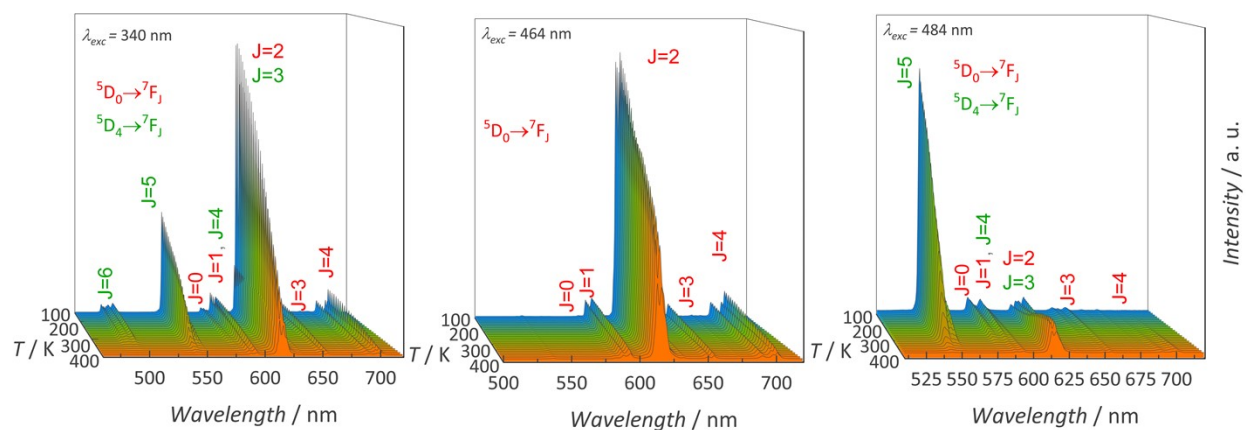


**Figure S3.** Thermogravimetric analyses (TG) of **1** and **2**. The thermal events after 250 °C correspond to the  $\beta$ -diketone decomposition and the bridge ligand thermolysis. Moreover, after 600 °C, the plateau in the TG curves corresponds to  $\text{Eu}_2\text{O}_3$  and  $\text{Tb}_4\text{O}_7$  formation. The residual mass is in accordance with the expected theoretical value for **1** (18%) and **2** (17%). **1** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$ ; **2** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (Ln = Eu, Tb).

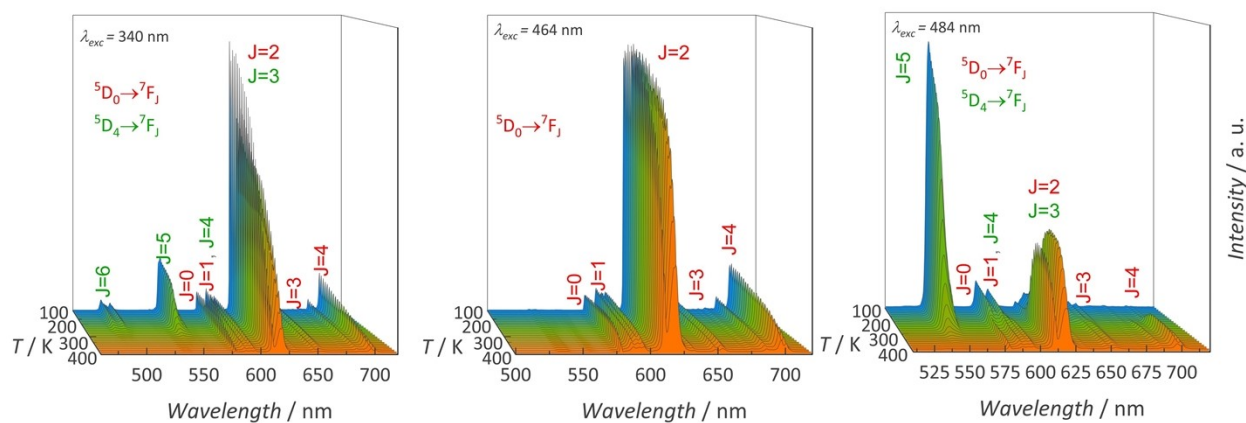
Supplementary note S4 – Additional experimental photoluminescence data



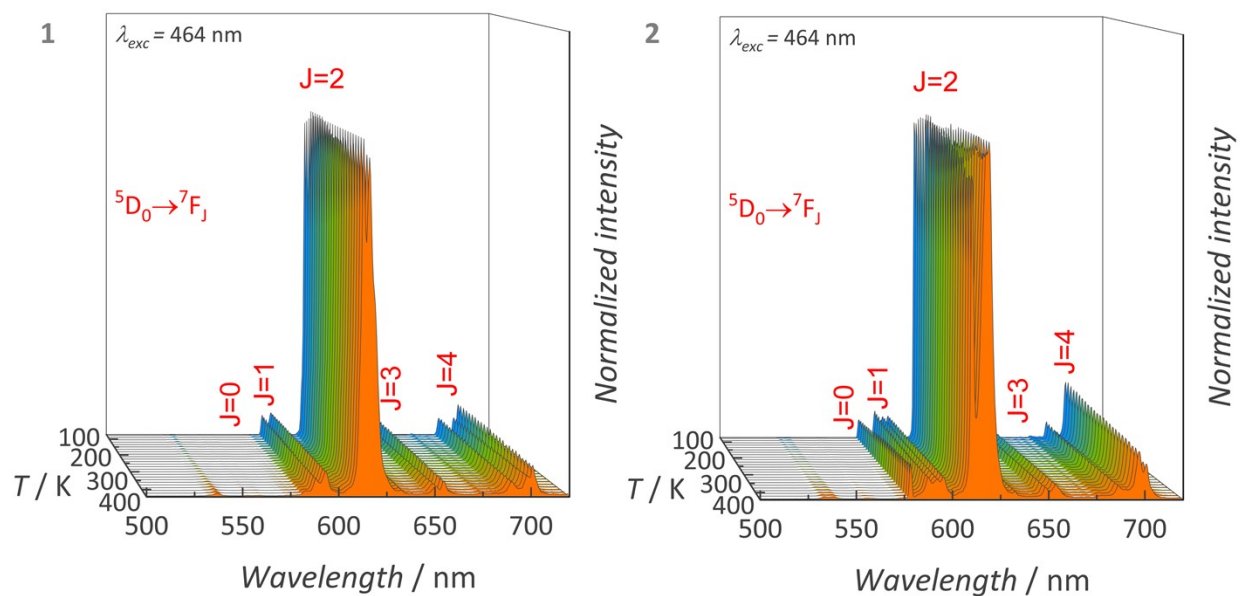
**Figure S4.** Selective (a) excitation and (b) emission spectra of **1** and **2** measured at 298 K. (c) Magnification of the excitation spectra within the 450 – 500 nm. The monitored excitation or emission wavelength is displayed in the spectra. Tb<sup>III</sup> transition assignments are shown in green and Eu<sup>III</sup> ones in orange. **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).



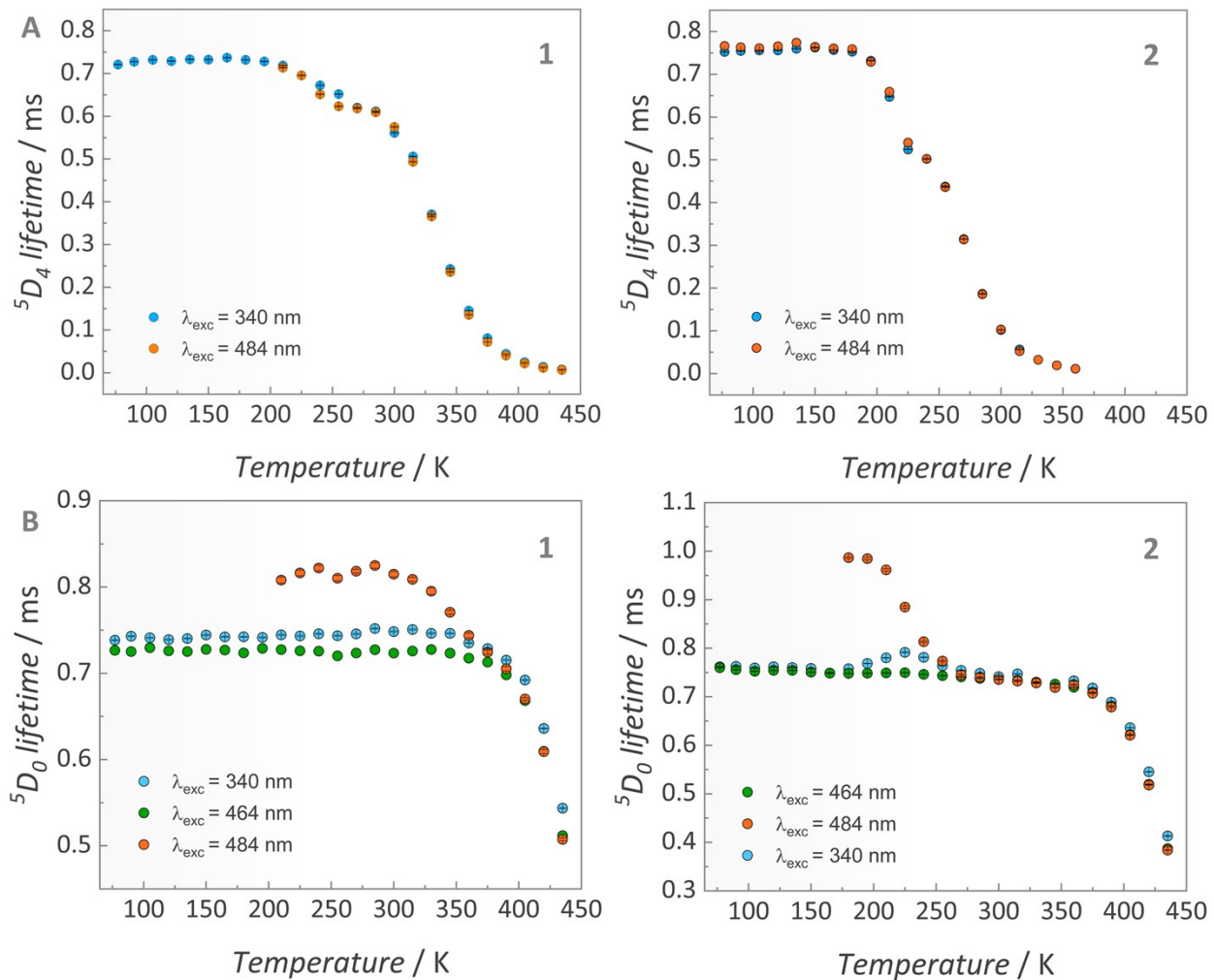
**Figure S5.** Temperature-dependent emission spectra of **1** under different excitation wavelengths. **1** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$  (Ln = Eu, Tb).



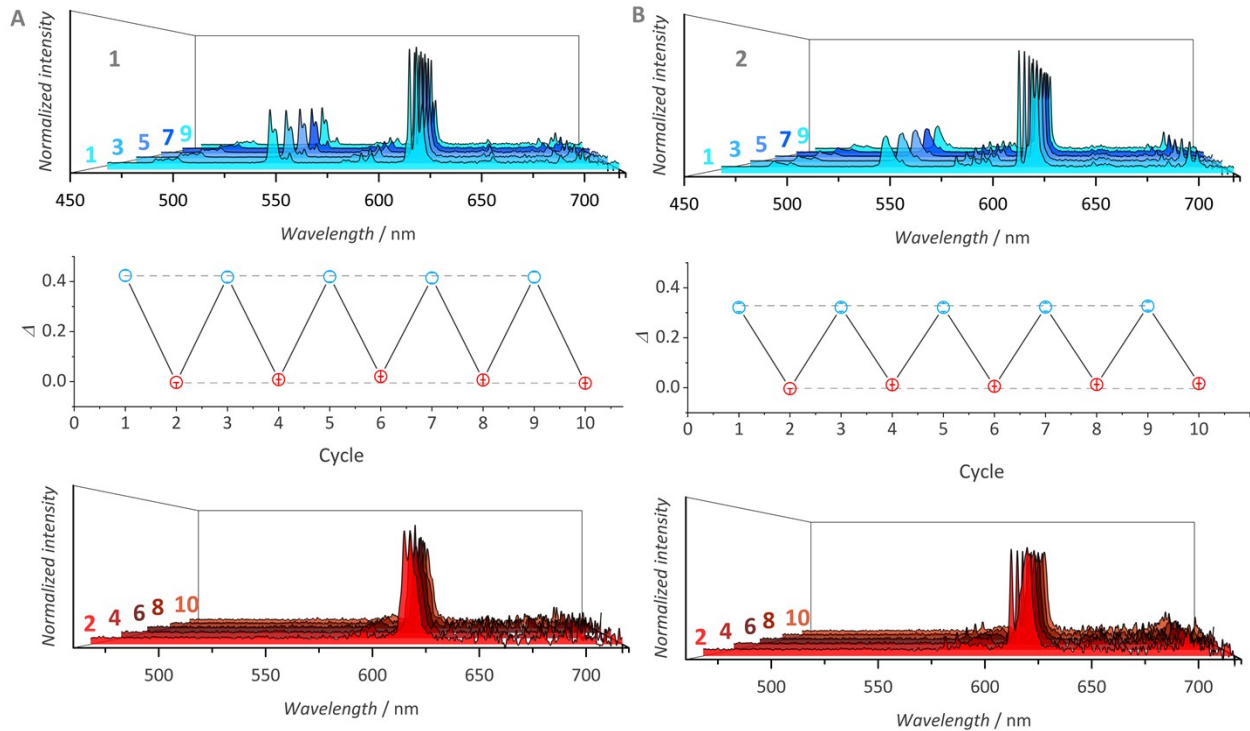
**Figure S6.** Temperature-dependent emission spectra of **2** under different excitation wavelengths. **2** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (Ln = Eu, Tb).



**Figure S7.** Temperature-dependent emission spectra of **1** and **2** under 464 nm excitation ( $\text{Eu}^{\text{III}} \text{}^7\text{F}_0 \rightarrow \text{}^5\text{D}_2$ ). **1** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$ ; **2** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (Ln = Eu, Tb).



**Figure S8.** (a)  $\text{Tb}^{\text{III}}$   ${}^5D_4$  and (b)  $\text{Eu}^{\text{III}}$   ${}^5D_0$  emitting state lifetime dependence on the temperature and excitation wavelengths. **1** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$ ; **2** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (Ln = Eu, Tb).



**Figure S9.** Thermometric parameter ( $\lambda_{\text{exc}} = 340 \text{ nm}$ ) recorded in 10 heating-cooling temperature cycles for (a) **1** and (b) **2**.  $\Delta = I_{\text{Tb}}/I_{\text{Eu}}$ , where  $I_{\text{Tb}}$  is the area above the  $\text{Tb}^{\text{III}} \text{ } ^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition band (530 - 570 nm) while  $I_{\text{Eu}}$  is the area above the  $\text{Eu}^{\text{III}} \text{ } ^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition (605 - 635 nm, with some contribution of  $\text{Tb}^{\text{III}}$ , overlapped  $^5\text{D}_4 \rightarrow ^7\text{F}_3$  band). The bottom and top of each figure represent the emission spectra collected in each cycle. The repeatability ( $R$ ) of a thermometer's readout upon temperature cycling is quantified by Equation S39, where  $\Delta_c$  is the mean thermometric parameter (extracted from the repeatability curve) and  $\Delta_i$  is the value of each measurement of the thermometric parameter. Both systems present repeatability ( $R$ ) higher than 99.2%.

$$R = 1 - \frac{\max|\Delta_c - \Delta_i|}{\Delta_c} \quad (\text{S39})$$

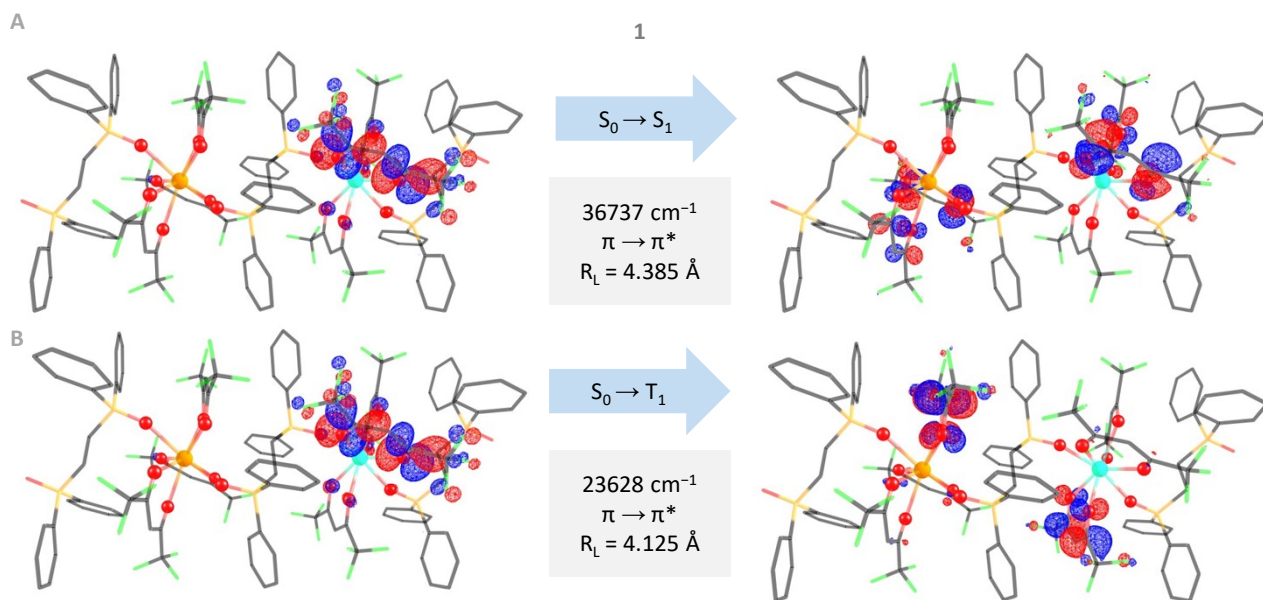


## Supplementary Note S5. Electronic structure and photophysical parameters of Ln<sup>III</sup>-based compounds

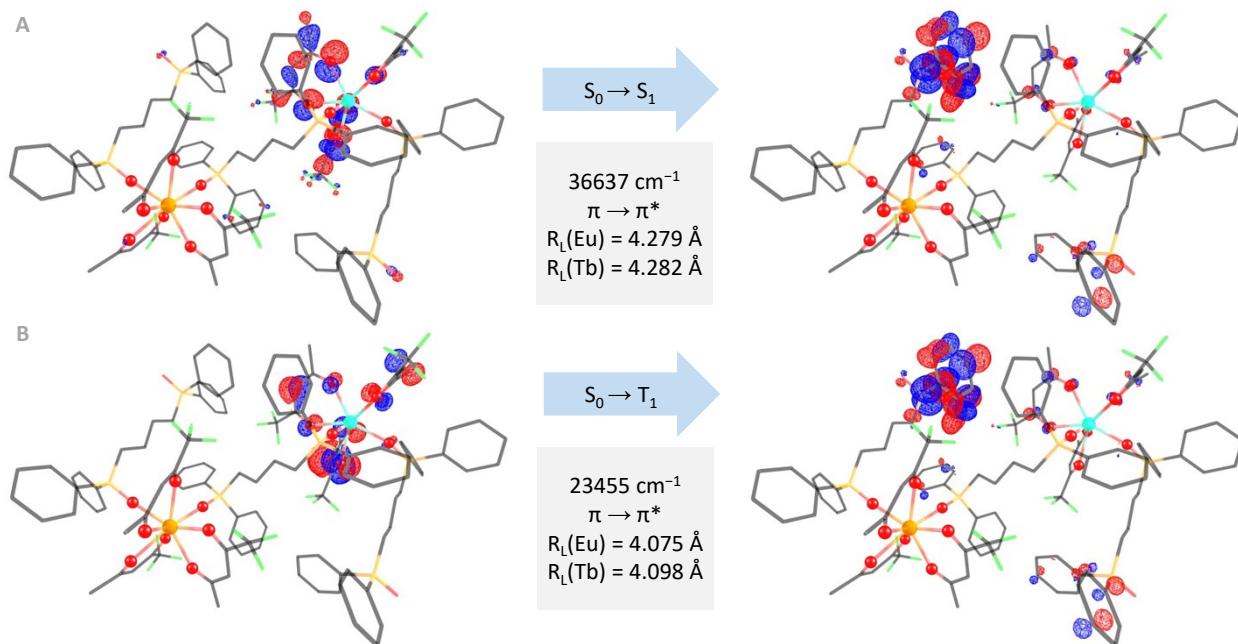
The time-dependent density functional theory (TD-DFT) calculation was used to acquire the distance between the ligand's centroid position and the Ln<sup>III</sup>. This quantity allows us to estimate the rates of intramolecular energy transfer from the antenna ligand to the Ln<sup>III</sup>. However, information such as the forced electric dipole component of the Judd-Ofelt intensity parameters is still required, which can be determined using the same geometry as the one used in the TD-DFT. Thus, in this section we summarize by parts each step of the calculation and its role in the overall mechanism.

### Electronic structure

Starting from the electronic structure of both coordination polymers, the outcomes from the TD-DFT calculation are illustrated in Fig S10 – S11.



**Fig S10.** Monoelectronic states involved in the (a) singlet-singlet and (b) singlet-triplet excitation transitions for **1**. Green = fluorine, grey = carbon, orange = europium, cyan = terbium, bright orange = phosphorus, red = oxygen. **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub> (Ln = Eu, Tb). It should be mentioned that the excited states (S1 and T1) are a combination of different transitions and different molecular orbitals, and we chose to represent only the molecular orbital with the highest contribution for the S<sub>1</sub>/T<sub>1</sub>.



**Fig S11.** Monoelectronic states involved in the (a) singlet-singlet and (b) singlet-triplet excitation transitions for **2**. Green = fluorine, grey = carbon, orange = europium, cyan = terbium, bright orange = phosphorus, red = oxygen. **2** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (Ln = Eu, Tb). The excited states ( $S_1$  and  $T_1$ ) are formed by a combination of different molecular orbitals and transitions, and we chose to represent only the molecular orbital with the highest contribution for the  $S_1/T_1$ .

#### Photophysical parameters

The determination of the experimental Judd-Ofelt intensity parameters for  $\text{Eu}^{\text{III}}$  is quite straightforward from the emission spectrum. However, for  $\text{Tb}^{\text{III}}$  this is not true, as a high contribution from the magnetic dipole strength is observed, inhibiting their direct determination from the emission spectrum. Thus, in this paper we determined the experimental parameters for  $\text{Eu}^{\text{III}}$ , then calculate the theoretical ones using the Monte-Carlo fitting algorithm to extract the ligand field parameters and use the same parameters to calculate the intensity parameters of the  $\text{Tb}^{\text{III}}$  counterpart. In this sense, Tables S4 – S6 were obtained. The parameters considering only the forced-electric dipole were used to harvest the IET pathways, since they are accounted for the dipole-dipole strength. For further information regarding the protocol to calculate the rates, proceed to supplementary note S2 – Intramolecular energy transfer.

**Table S4.** Experimental and theoretical Judd-Ofelt intensity parameters for the  $\text{Eu}^{\text{III}}$  component of each coordination polymer. All values are in the order of  $\times 10^{-20} \text{ cm}^2$ . **1** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$ ; **2** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (Ln = Eu, Tb).

Compound	$\Omega_2^{(exp)}$	$\Omega_2^{(theo)}$	$\Omega_4^{(exp)}$	$\Omega_4^{(theo)}$	$\Omega_6^{(theo)}$
<b>1</b>	25.87	25.87	6.150	6.470	0.820
<b>2</b>	23.25	23.24	7.090	7.080	1.650

**Table S5.** Values of bond length ( $R_j$ ), charge factor ( $g_j$ ), effective polarizability ( $\alpha'_j$ ), and bond overlap polarizability ( $\alpha_{OP,j}$ ) for each atom in the Eu<sup>III</sup> coordination polyhedron derived by the Adaptive Guided Stochastic optimization algorithm. The quantities  $g_j$  and  $\alpha'_j$  were employed for the determination of the Judd-Ofelt parameters for the Tb<sup>III</sup> counterpart. **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).

1	$R_j / \text{Å}$	$g_j$	$\alpha'_j$	$\alpha_{OP,j} / \times 10^{-26} \text{ cm}^3$
<b>O(18)</b>	2.327	0.347	0.925	4.231
<b>O(26)</b>	2.312	0.243	0.050	4.349
<b>O(27)</b>	2.392	0.502	2.287	3.769
<b>O(28)</b>	2.376	0.312	0.050	3.879
<b>O(29)</b>	2.402	0.248	0.066	3.700
<b>O(30)</b>	2.402	0.289	0.155	3.703
<b>O(31)</b>	2.392	0.441	0.200	3.767
<b>O(32)</b>	2.401	0.293	0.050	3.705
<b>2</b>				
<b>O(2)</b>	2.300	0.288	0.812	4.434
<b>O(3)</b>	2.347	0.460	0.493	4.082
<b>O(4)</b>	2.395	0.303	0.133	3.752
<b>O(5)</b>	2.408	0.327	0.136	3.663
<b>O(6)</b>	2.380	0.349	0.164	3.850
<b>O(7)</b>	2.411	0.329	0.149	3.640
<b>O(8)</b>	2.355	0.340	1.045	4.026
<b>O(9)</b>	2.379	0.431	1.857	3.855

**Table S6.** Decomposition of the theoretical intensity parameters into their forced electric dipole (FED) and dynamic coupling (DC) counterparts for both coordination polymers. The decomposition follows the procedure reported in the Theoretical Judd-Ofelt Parameters of Supplementary Note S2. All  $\Omega_{2,4,6}$  are in  $10^{-20} \text{ cm}^2$  units. **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).

Compound	Intensity parameters					
	$\Omega_2^{(FED)}$	$\Omega_2^{(DC)}$	$\Omega_4^{(FED)}$	$\Omega_4^{(DC)}$	$\Omega_6^{(FED)}$	$\Omega_6^{(DC)}$
<b>1</b>						
<b>Eu<sup>III</sup></b>	0.00595	25.26	0.0589	5.324	0.104	0.512
<b>Tb<sup>III</sup></b>	0.0141	25.47	0.0922	4.754	0.157	0.371
<b>2</b>						
<b>Eu<sup>III</sup></b>	0.00520	22.75	0.0657	5.817	0.135	1.093
<b>Tb<sup>III</sup></b>	0.00695	18.11	0.0406	4.517	0.0813	0.725

### Supplementary note S6. Intramolecular energy transfer (Ligand-to-Ln<sup>III</sup>)

Employing equations S8 – S16, we were able to determine the rates of intramolecular energy transfer, after computing the forced-electric dipole counterpart of the Judd-Ofelt parameters. To decompose the rates for each Ln<sup>III</sup> separately, calculations were performed for each moiety. In the case of **2**, where distinct values of  $R_L$  were found for Tb<sup>III</sup> and Eu<sup>III</sup>, the corresponding value for each Ln<sup>III</sup> was used (Fig S11).

**Table S7.** Energy transfer rates (in s<sup>-1</sup>) for **1** considering the ligand-to-Eu<sup>III</sup> process.  $\delta$  is the donor-acceptor (singlet/triplet-Eu<sup>III</sup>) energy difference (in cm<sup>-1</sup>). We summarize in this table only the pathways contributing more than 0.001% of the total 40 pathways (1 – 40).  $W_{d-d}$ ,  $W_{m-d}$ ,  $W_{ex}$  are the dipole-dipole, dipole-multipole, and exchange rates, respectively.  $W$  and  $W^b$  are the total forward and backward energy transfer rates (sum of each component), respectively at 300.15 K. **1** = [Ln(tfa)<sub>3</sub>( $\mu$ -dppeo)]<sub>n</sub> (Ln = Eu, Tb).

Pathway	Donor	Acceptor	$\delta$	$W_{d-d}$	$W_{m-d}$	$W_{ex}$	$W$	$W^b$
<b>7</b>	S <sub>1</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>1</sub>	17710	0	0	1.522×10 <sup>3</sup>	1.522×10 <sup>3</sup>	7.905×10 <sup>-35</sup>
<b>10</b>	S <sub>1</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> L <sub>6</sub>	11412	1.254×10 <sup>3</sup>	9.212×10 <sup>1</sup>	0	1.346×10 <sup>3</sup>	2.116×10 <sup>-22</sup>
<b>15</b>	S <sub>1</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> G <sub>6</sub>	9985	1.138×10 <sup>3</sup>	8.362×10 <sup>1</sup>	0	1.222×10 <sup>3</sup>	1.802×10 <sup>-19</sup>
<b>18</b>	S <sub>1</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>4</sub>	9151	3.803×10 <sup>3</sup>	5.973×10 <sup>3</sup>	0	6.354×10 <sup>3</sup>	7.388×10 <sup>-17</sup>
<b>26</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>0</sub>	19816	0	0	1.430×10 <sup>1</sup>	1.430×10 <sup>1</sup>	1.361×10 <sup>-39</sup>
<b>27</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>1</sub>	18082	1.560×10 <sup>-4</sup>	1.168×10 <sup>1</sup>	5.920×10 <sup>-2</sup>	1.174×10 <sup>1</sup>	1.522×10 <sup>-36</sup>
<b>28</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>2</sub>	15626	0	0	3.484×10 <sup>2</sup>	3.484×10 <sup>2</sup>	3.356×10 <sup>-30</sup>
<b>29</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>3</sub>	12754	9.448×10 <sup>-1</sup>	2.318×10 <sup>3</sup>	0	2.319×10 <sup>3</sup>	1.613×10 <sup>-23</sup>
<b>30</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>6</sub>	11784	3.453×10 <sup>1</sup>	2.537×10 <sup>0</sup>	0	3.707×10 <sup>1</sup>	1.455×10 <sup>-23</sup>
<b>31</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>7</sub>	10752	1.881×10 <sup>2</sup>	1.382×10 <sup>1</sup>	0	2.019×10 <sup>2</sup>	9.691×10 <sup>-21</sup>
<b>32</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>2</sub>	10717	0	0	2.639×10 <sup>5</sup>	2.639×10 <sup>5</sup>	4.493×10 <sup>-17</sup>
<b>33</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>3</sub>	10487	9.109×10 <sup>0</sup>	1.143×10 <sup>4</sup>	0	1.144×10 <sup>4</sup>	4.193×10 <sup>-18</sup>
<b>35</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>5</sub>	10357	7.309×10 <sup>1</sup>	5.368×10 <sup>0</sup>	0	7.845×10 <sup>1</sup>	2.888×10 <sup>-20</sup>
<b>36</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>6</sub>	10346	1.495×10 <sup>2</sup>	6.400×10 <sup>1</sup>	0	2.135×10 <sup>2</sup>	9.792×10 <sup>-20</sup>
<b>Total</b>							2.890×10 <sup>5</sup>	1.233×10 <sup>-16</sup>
<b>7</b>	T <sub>1</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>1</sub>	4601	0	0	3.162×10 <sup>8</sup>	3.162×10 <sup>8</sup>	3.308×10 <sup>-2</sup>
<b>26</b>	T <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>0</sub>	6707	0	0	3.250×10 <sup>7</sup>	3.250×10 <sup>7</sup>	6.225×10 <sup>-6</sup>
<b>27</b>	T <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>1</sub>	4973	3.644×10 <sup>-3</sup>	3.082×10 <sup>2</sup>	1.877×10 <sup>4</sup>	1.908×10 <sup>4</sup>	4.981×10 <sup>-6</sup>
<b>28</b>	T <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>2</sub>	2517	0	0	6.787×10 <sup>6</sup>	6.787×10 <sup>6</sup>	1.387×10 <sup>2</sup>
<b>32</b>	T <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>2</sub>	-2392	0	0	2.029×10 <sup>2</sup>	2.029×10 <sup>2</sup>	6.959×10 <sup>7</sup>
<b>Total</b>							3.555×10 <sup>8</sup>	6.959×10 <sup>7</sup>

**Table S8.** Energy transfer rates (in s<sup>-1</sup>) for **1** considering the ligand-to-Tb<sup>III</sup> process.  $\delta$  is the donor-acceptor (singlet/triplet-Eu<sup>III</sup>) energy difference (in cm<sup>-1</sup>). We summarize in this table only the pathways contributing more than 0.001% of the total 78 pathways (1 – 78).  $W_{d-d}$ ,  $W_{m-d}$ ,  $W_{ex}$  are the dipole-dipole, dipole-multipole, and exchange rates, respectively.  $W$  and  $W^b$  are the total forward and backward energy transfer rates (sum of each component), respectively at 300.15 K. **1** = [Ln(tfa)<sub>3</sub>( $\mu$ -dppeo)]<sub>n</sub> (Ln = Eu, Tb).

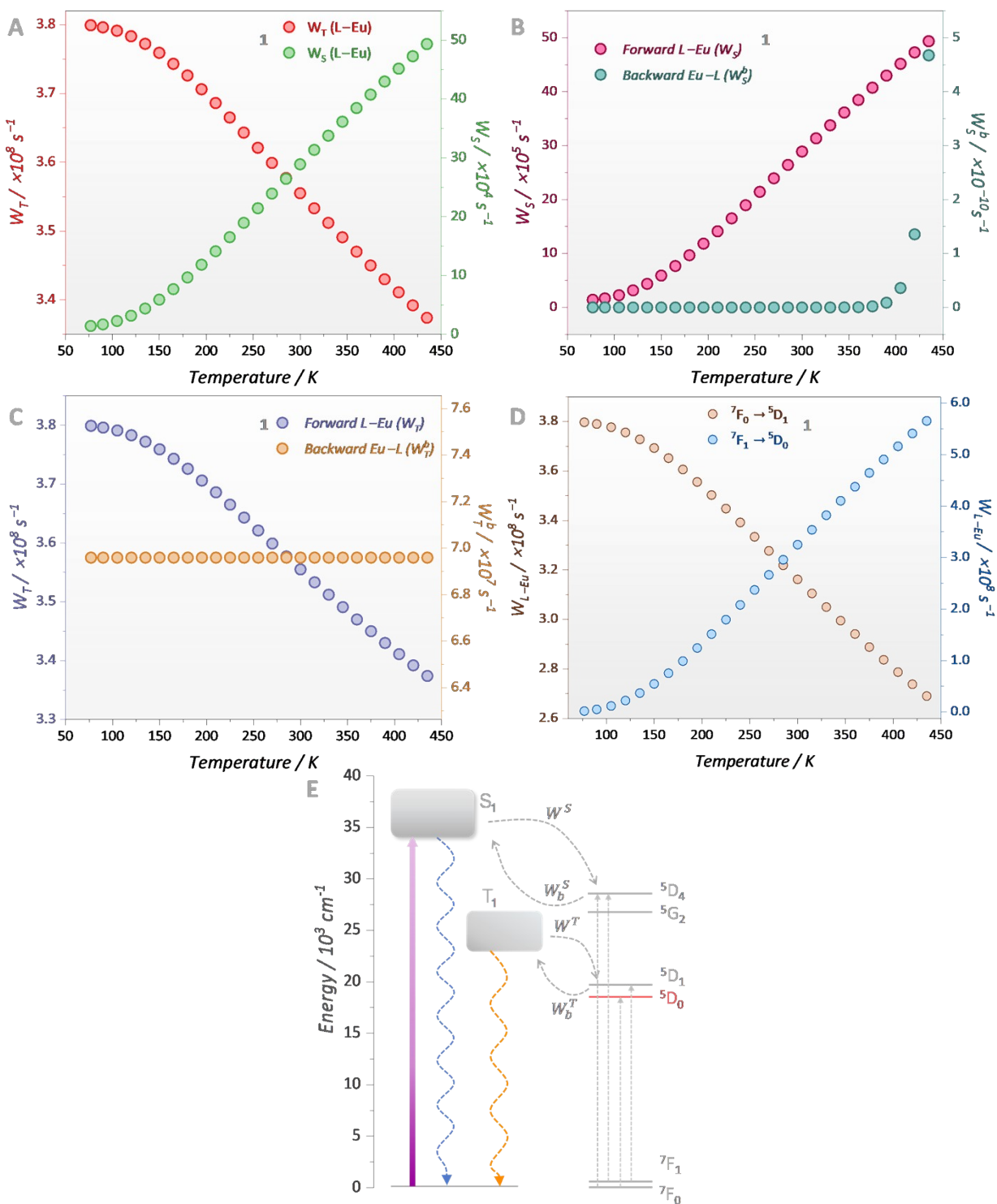
Pathway	Donor	Acceptor	$\delta$	$W_{d-d}$	$W_{m-d}$	$W_{ex}$	$W$	$W_b$
8	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>6</sub>	10314	4.539×10 <sup>3</sup>	1.419×10 <sup>5</sup>	2.647×10 <sup>7</sup>	2.662×10 <sup>7</sup>	8.765×10 <sup>-8</sup>
10	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>5</sub>	8970	1.676×10 <sup>3</sup>	3.262×10 <sup>5</sup>	5.586×10 <sup>5</sup>	5.913×10 <sup>6</sup>	1.450×10 <sup>-12</sup>
12	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>4</sub>	8450	1.546×10 <sup>3</sup>	4.036×10 <sup>4</sup>	0	4.191×10 <sup>4</sup>	1.512×10 <sup>-13</sup>
16	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>7</sub>	7280	4.716×10 <sup>3</sup>	5.350×10 <sup>5</sup>	1.879×10 <sup>2</sup>	5.399×10 <sup>5</sup>	3.214×10 <sup>-10</sup>
18	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>6</sub>	7067	0	0	4.992×10 <sup>5</sup>	4.992×10 <sup>6</sup>	9.391×10 <sup>-9</sup>
21	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>7</sub>	5358	0	0	1.377×10 <sup>7</sup>	1.377×10 <sup>7</sup>	8.259×10 <sup>-5</sup>
22	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>6</sub>	3846	0	0	2.030×10 <sup>8</sup>	2.030×10 <sup>8</sup>	1.981×10 <sup>0</sup>
25	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> F <sub>5</sub>	1803	0	0	6.859×10 <sup>8</sup>	6.859×10 <sup>8</sup>	1.424×10 <sup>5</sup>
30	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>7</sub>	148	0	0	3.490×10 <sup>7</sup>	3.490×10 <sup>7</sup>	1.488×10 <sup>7</sup>
33	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>6</sub>	-861	0	0	7.907×10 <sup>6</sup>	7.907×10 <sup>6</sup>	4.913×10 <sup>8</sup>
35	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>5</sub>	-1249	0	0	1.000×10 <sup>5</sup>	1.000×10 <sup>5</sup>	4.721×10 <sup>7</sup>
47	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>6</sub>	12362	6.831×10 <sup>1</sup>	5.585×10 <sup>4</sup>	5.496×10 <sup>5</sup>	6.055×10 <sup>5</sup>	9.151×10 <sup>-21</sup>
49	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>5</sub>	11018	1.562×10 <sup>2</sup>	5.460×10 <sup>3</sup>	7.147×10 <sup>6</sup>	7.153×10 <sup>6</sup>	8.048×10 <sup>-17</sup>
51	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>4</sub>	10498	8.210×10 <sup>1</sup>	4.418×10 <sup>4</sup>	1.471×10 <sup>6</sup>	1.515×10 <sup>6</sup>	2.523×10 <sup>-16</sup>
55	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>7</sub>	9328	7.104×10 <sup>2</sup>	4.839×10 <sup>4</sup>	0	4.910×10 <sup>4</sup>	1.342×10 <sup>-15</sup>
57	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>6</sub>	9115	0	0	1.887×10 <sup>5</sup>	1.887×10 <sup>5</sup>	1.652×10 <sup>-14</sup>
61	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>6</sub>	5894	0	0	1.306×10 <sup>7</sup>	1.306×10 <sup>7</sup>	5.850×10 <sup>-6</sup>
62	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>5</sub>	5018	0	0	2.470×10 <sup>8</sup>	2.470×10 <sup>8</sup>	8.730×10 <sup>-3</sup>
63	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>4</sub>	4446	0	0	7.135×10 <sup>8</sup>	7.135×10 <sup>8</sup>	4.788×10 <sup>-1</sup>
64	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> F <sub>5</sub>	3851	0	0	5.117×10 <sup>8</sup>	5.117×10 <sup>8</sup>	4.875×10 <sup>0</sup>
67	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> F <sub>4</sub>	3411	0	0	1.777×10 <sup>9</sup>	1.777×10 <sup>9</sup>	1.707×10 <sup>2</sup>
72	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>6</sub>	1187	0	0	8.461×10 <sup>7</sup>	8.461×10 <sup>7</sup>	2.413×10 <sup>5</sup>
74	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>5</sub>	799	0	0	5.997×10 <sup>6</sup>	5.997×10 <sup>6</sup>	1.299×10 <sup>5</sup>
<b>Total</b>							4.346×10 <sup>9</sup>	5.562×10 <sup>8</sup>
6	T <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>4</sub>	3184	2.201×10 <sup>-1</sup>	2.796×10 <sup>2</sup>	0	2.799×10 <sup>2</sup>	9.438×10 <sup>-5</sup>
8	T <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>6</sub>	-2795	2.355×10 <sup>-5</sup>	8.331×10 <sup>-4</sup>	1.865×10 <sup>3</sup>	1.865×10 <sup>3</sup>	1.236×10 <sup>9</sup>
45	T <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> D <sub>4</sub>	5232	2.825×10 <sup>-1</sup>	2.468×10 <sup>3</sup>	5.765×10 <sup>7</sup>	5.765×10 <sup>7</sup>	8.293×10 <sup>-4</sup>
47	T <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>6</sub>	-747	6.691×10 <sup>-2</sup>	6.183×10 <sup>1</sup>	7.307×10 <sup>6</sup>	7.307×10 <sup>6</sup>	2.224×10 <sup>-8</sup>
49	T <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>5</sub>	-2091	5.277×10 <sup>-5</sup>	2.087×10 <sup>-3</sup>	3.277×10 <sup>4</sup>	3.277×10 <sup>4</sup>	7.426×10 <sup>8</sup>
<b>Total</b>							6.499×10 <sup>7</sup>	2.529×10 <sup>9</sup>

**Table S9.** Energy transfer rates (in  $s^{-1}$ ) for **2** considering the ligand-to-Eu<sup>III</sup> process.  $\delta$  is the donor-acceptor (singlet/triplet-Eu<sup>III</sup>) energy difference (in  $cm^{-1}$ ). We summarize in this table only the pathways contributing more than 0.001% of the total 40 pathways (1 – 40).  $W_{d-d}$ ,  $W_{m-d}$ ,  $W_{ex}$  are the dipole-dipole, dipole-multipole, and exchange rates, respectively.  $W$  and  $W^b$  are the total forward and backward energy transfer rates (sum of each component), respectively at 300.15 K. **2** = [Ln(tfa)<sub>3</sub>( $\mu$ -dppbo)]<sub>n</sub> (Ln = Eu, Tb).

Pathway	Donor	Acceptor	$\delta$	$W_{d-d}$	$W_{m-d}$	$W_{ex}$	$W$	$W_b$
<b>7</b>	S <sub>1</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>1</sub>	17610	0	0	8.953×10 <sup>-2</sup>	8.953×10 <sup>-2</sup>	7.513×10 <sup>-39</sup>
<b>10</b>	S <sub>1</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> L <sub>6</sub>	11312	3.836×10 <sup>1</sup>	2.689×10 <sup>0</sup>	0	4.105×10 <sup>1</sup>	1.043×10 <sup>-23</sup>
<b>15</b>	S <sub>1</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> G <sub>6</sub>	9885	9.532×10 <sup>1</sup>	6.680×10 <sup>0</sup>	0	1.020×10 <sup>2</sup>	2.430×10 <sup>-20</sup>
<b>18</b>	S <sub>1</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>4</sub>	9051	4.659×10 <sup>1</sup>	7.314×10 <sup>2</sup>	0	7.780×10 <sup>2</sup>	1.461×10 <sup>-17</sup>
<b>26</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>0</sub>	19716	0	0	6.062×10 <sup>-5</sup>	6.062×10 <sup>-5</sup>	9.316×10 <sup>-45</sup>
<b>27</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>1</sub>	17982	4.738×10 <sup>-2</sup>	4.274×10 <sup>-4</sup>	2.236×10 <sup>-6</sup>	4.296×10 <sup>-4</sup>	8.999×10 <sup>-41</sup>
<b>28</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>2</sub>	15526	0	0	2.062×10 <sup>-1</sup>	2.062×10 <sup>-1</sup>	3.381×10 <sup>-33</sup>
<b>29</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>3</sub>	12654	8.504×10 <sup>-3</sup>	1.983×10 <sup>1</sup>	0	1.984×10 <sup>1</sup>	2.229×10 <sup>-25</sup>
<b>30</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>6</sub>	11684	7.944×10 <sup>-1</sup>	5.568×10 <sup>-2</sup>	0	8.501×10 <sup>-1</sup>	5.389×10 <sup>-25</sup>
<b>31</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> L <sub>7</sub>	10652	9.326×10 <sup>0</sup>	6.536×10 <sup>-1</sup>	0	9.980×10 <sup>0</sup>	7.736×10 <sup>-22</sup>
<b>32</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>2</sub>	10617	0	0	1.130×10 <sup>4</sup>	1.130×10 <sup>4</sup>	3.109×10 <sup>-18</sup>
<b>33</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>3</sub>	10387	4.689×10 <sup>-1</sup>	5.576×10 <sup>-2</sup>	0	5.581×10 <sup>2</sup>	3.304×10 <sup>-19</sup>
<b>35</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>5</sub>	10257	4.769×10 <sup>0</sup>	3.343×10 <sup>-1</sup>	0	5.104×10 <sup>0</sup>	3.035×10 <sup>-21</sup>
<b>36</b>	S <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>6</sub>	10246	9.800×10 <sup>0</sup>	3.703×10 <sup>0</sup>	0	1.350×10 <sup>1</sup>	1.000×10 <sup>-20</sup>
<b>Total</b>							1.283×10 <sup>4</sup>	1.809×10 <sup>-17</sup>
<b>7</b>	T <sub>1</sub>	<sup>7</sup> F <sub>0</sub> → <sup>5</sup> D <sub>1</sub>	4428	0	0	3.863×10 <sup>8</sup>	3.863×10 <sup>8</sup>	9.265×10 <sup>-2</sup>
<b>26</b>	T <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>0</sub>	6534	0	0	4.097×10 <sup>7</sup>	4.097×10 <sup>7</sup>	1.800×10 <sup>-5</sup>
<b>27</b>	T <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>1</sub>	4800	3.826×10 <sup>-3</sup>	3.805×10 <sup>2</sup>	2.306×10 <sup>4</sup>	2.344×10 <sup>4</sup>	1.403×10 <sup>-5</sup>
<b>28</b>	T <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> D <sub>2</sub>	2344	0	0	8.037×10 <sup>6</sup>	8.037×10 <sup>6</sup>	3.766×10 <sup>2</sup>
<b>32</b>	T <sub>1</sub>	<sup>7</sup> F <sub>1</sub> → <sup>5</sup> G <sub>2</sub>	-2565	0	0	9.739×10 <sup>1</sup>	9.739×10 <sup>1</sup>	7.655×10 <sup>7</sup>
<b>Total</b>							4.353×10 <sup>8</sup>	7.656×10 <sup>7</sup>

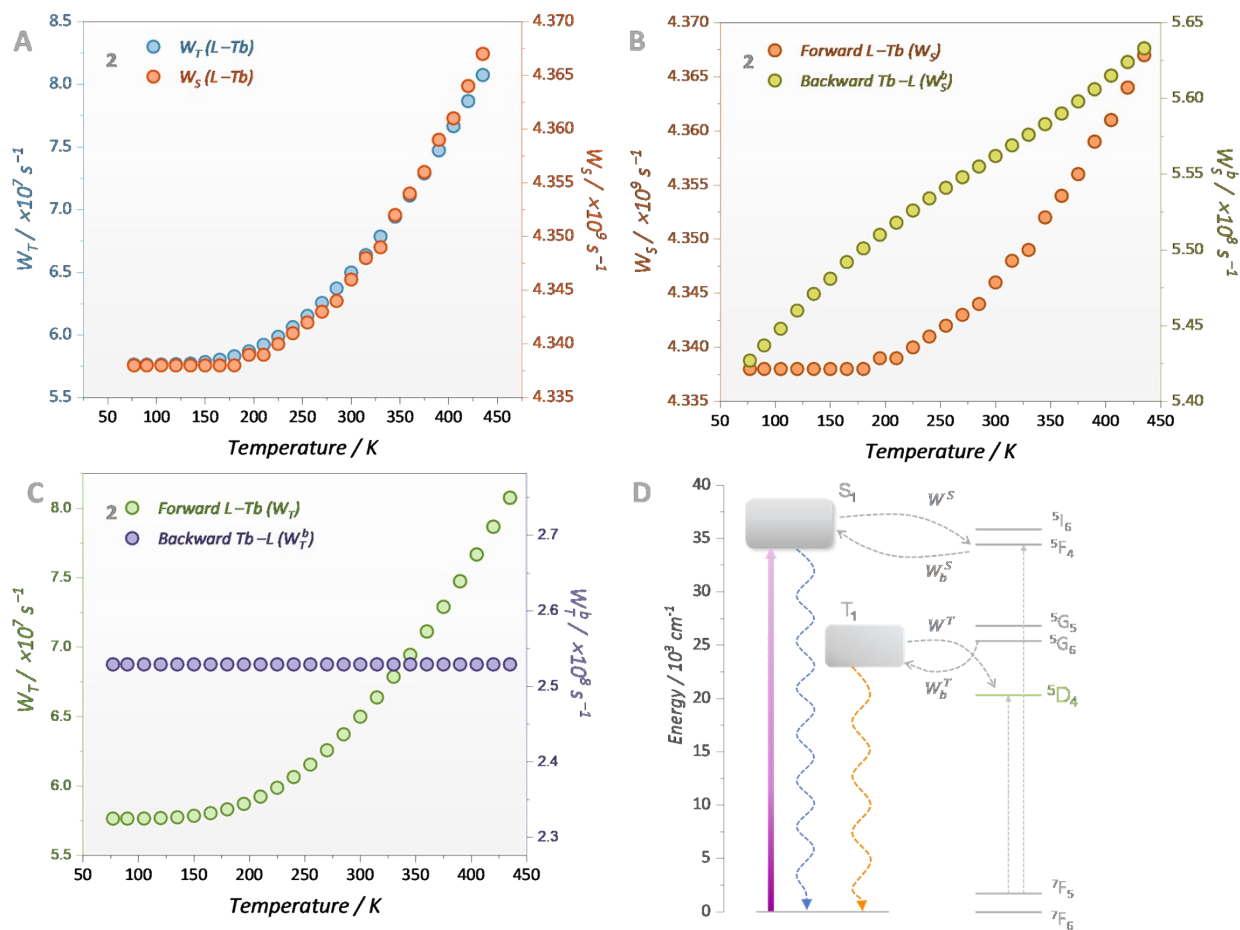
**Table S10.** Energy transfer rates (in  $s^{-1}$ ) for **2** considering the ligand-to-Tb<sup>III</sup> process.  $\delta$  is the donor-acceptor (singlet/triplet-Eu<sup>III</sup>) energy difference (in  $cm^{-1}$ ). We summarize in this table only the pathways contributing more than 0.001% of the total 78 pathways (1 – 78).  $W_{d-d}$ ,  $W_{m-d}$ ,  $W_{ex}$  are the dipole-dipole, dipole-multipole, and exchange rates, respectively.  $W$  and  $W^b$  are the total forward and backward energy transfer rates (sum of each component), respectively at 300.15 K. **2** = [Ln(tfa)<sub>3</sub>( $\mu$ -dppbo)]<sub>n</sub> (Ln = Eu, Tb).

Pathway	Donor	Acceptor	$\delta$	$W_{d-d}$	$W_{m-d}$	$W_{ex}$	$W$	$W_b$
8	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>6</sub>	10214	9.902×10 <sup>1</sup>	7.551×10 <sup>3</sup>	1.435×10 <sup>6</sup>	1.442×10 <sup>6</sup>	7.671×10 <sup>-16</sup>
10	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>5</sub>	8870	8.494×10 <sup>1</sup>	1.204×10 <sup>1</sup>	7.100×10 <sup>5</sup>	7.508×10 <sup>5</sup>	2.973×10 <sup>-13</sup>
12	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>4</sub>	8350	1.052×10 <sup>2</sup>	6.785×10 <sup>3</sup>	0	6.891×10 <sup>3</sup>	4.039×10 <sup>-14</sup>
16	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>7</sub>	7180	5.935×10 <sup>2</sup>	1.642×10 <sup>5</sup>	5.870×10 <sup>1</sup>	1.648×10 <sup>5</sup>	1.585×10 <sup>-10</sup>
18	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> L <sub>6</sub>	6967	0	0	1.699×10 <sup>6</sup>	1.699×10 <sup>6</sup>	5.236×10 <sup>-9</sup>
21	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>7</sub>	5258	0	0	9.469×10 <sup>6</sup>	9.469×10 <sup>6</sup>	9.174×10 <sup>-5</sup>
22	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> H <sub>6</sub>	3746	0	0	2.179×10 <sup>8</sup>	2.179×10 <sup>8</sup>	3.435×10 <sup>0</sup>
25	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> F <sub>5</sub>	1703	0	0	1.053×10 <sup>9</sup>	1.053×10 <sup>9</sup>	3.530×10 <sup>5</sup>
30	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>7</sub>	48	0	0	5.823×10 <sup>7</sup>	5.823×10 <sup>7</sup>	4.009×10 <sup>7</sup>
33	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>6</sub>	-961	0	0	7.847×10 <sup>6</sup>	7.847×10 <sup>6</sup>	7.876×10 <sup>8</sup>
35	S <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> I <sub>5</sub>	-1349	0	0	9.596×10 <sup>4</sup>	9.596×10 <sup>4</sup>	7.318×10 <sup>7</sup>
47	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>6</sub>	12262	3.120×10 <sup>-1</sup>	6.415×10 <sup>2</sup>	6.428×10 <sup>3</sup>	7.070×10 <sup>3</sup>	1.726×10 <sup>-22</sup>
49	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>5</sub>	10918	2.078×10 <sup>0</sup>	1.772×10 <sup>2</sup>	2.360×10 <sup>5</sup>	2.360×10 <sup>5</sup>	4.294×10 <sup>-18</sup>
51	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>4</sub>	10398	1.569×10 <sup>0</sup>	2.072×10 <sup>3</sup>	7.025×10 <sup>4</sup>	7.233×10 <sup>4</sup>	1.946×10 <sup>-17</sup>
55	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>7</sub>	9228	2.928×10 <sup>1</sup>	4.872×10 <sup>3</sup>	0	4.901×10 <sup>3</sup>	2.163×10 <sup>-16</sup>
57	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> L <sub>6</sub>	9015	0	0	2.200×10 <sup>4</sup>	2.200×10 <sup>4</sup>	3.112×10 <sup>-15</sup>
61	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>6</sub>	5794	0	0	7.389×10 <sup>6</sup>	7.389×10 <sup>6</sup>	5.346×10 <sup>-6</sup>
62	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>5</sub>	4918	0	0	1.903×10 <sup>8</sup>	1.903×10 <sup>8</sup>	1.086×10 <sup>-2</sup>
63	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> H <sub>4</sub>	4346	0	0	6.538×10 <sup>8</sup>	6.538×10 <sup>8</sup>	7.088×10 <sup>-1</sup>
64	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> F <sub>5</sub>	3751	0	0	5.487×10 <sup>8</sup>	5.487×10 <sup>8</sup>	8.445×10 <sup>0</sup>
67	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> F <sub>4</sub>	3311	0	0	2.107×10 <sup>9</sup>	2.107×10 <sup>9</sup>	3.270×10 <sup>2</sup>
72	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>6</sub>	1087	0	0	1.369×10 <sup>8</sup>	1.369×10 <sup>8</sup>	6.305×10 <sup>5</sup>
74	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> I <sub>5</sub>	699	0	0	9.897×10 <sup>6</sup>	9.897×10 <sup>6</sup>	3.464×10 <sup>5</sup>
75	S <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> K <sub>5</sub>	-2649	0	0	5.088×10 <sup>0</sup>	5.088×10 <sup>0</sup>	1.675×10 <sup>6</sup>
<b>Total</b>							5.005×10 <sup>9</sup>	9.046×10 <sup>8</sup>
6	T <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> D <sub>4</sub>	3011	1.013×10 <sup>-1</sup>	3.229×10 <sup>2</sup>	0	3.230×10 <sup>2</sup>	2.497×10 <sup>-4</sup>
8	T <sub>1</sub>	<sup>7</sup> F <sub>6</sub> → <sup>5</sup> G <sub>6</sub>	-2968	1.013×10 <sup>-6</sup>	3.869×10 <sup>-4</sup>	8.526×10 <sup>2</sup>	8.526×10 <sup>2</sup>	1.296×10 <sup>9</sup>
45	T <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> D <sub>4</sub>	5059	6.816×10 <sup>-2</sup>	1.684×10 <sup>3</sup>	3.872×10 <sup>7</sup>	3.872×10 <sup>7</sup>	1.374×10 <sup>-3</sup>
47	T <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>6</sub>	-920	1.704×10 <sup>-4</sup>	3.873×10 <sup>1</sup>	4.505×10 <sup>6</sup>	4.505×10 <sup>6</sup>	3.143×10 <sup>8</sup>
49	T <sub>1</sub>	<sup>7</sup> F <sub>5</sub> → <sup>5</sup> G <sub>5</sub>	-2264	1.176×10 <sup>-5</sup>	1.109×10 <sup>-3</sup>	1.714×10 <sup>4</sup>	1.714×10 <sup>4</sup>	8.906×10 <sup>8</sup>
<b>Total</b>							4.324×10 <sup>7</sup>	2.680×10 <sup>9</sup>

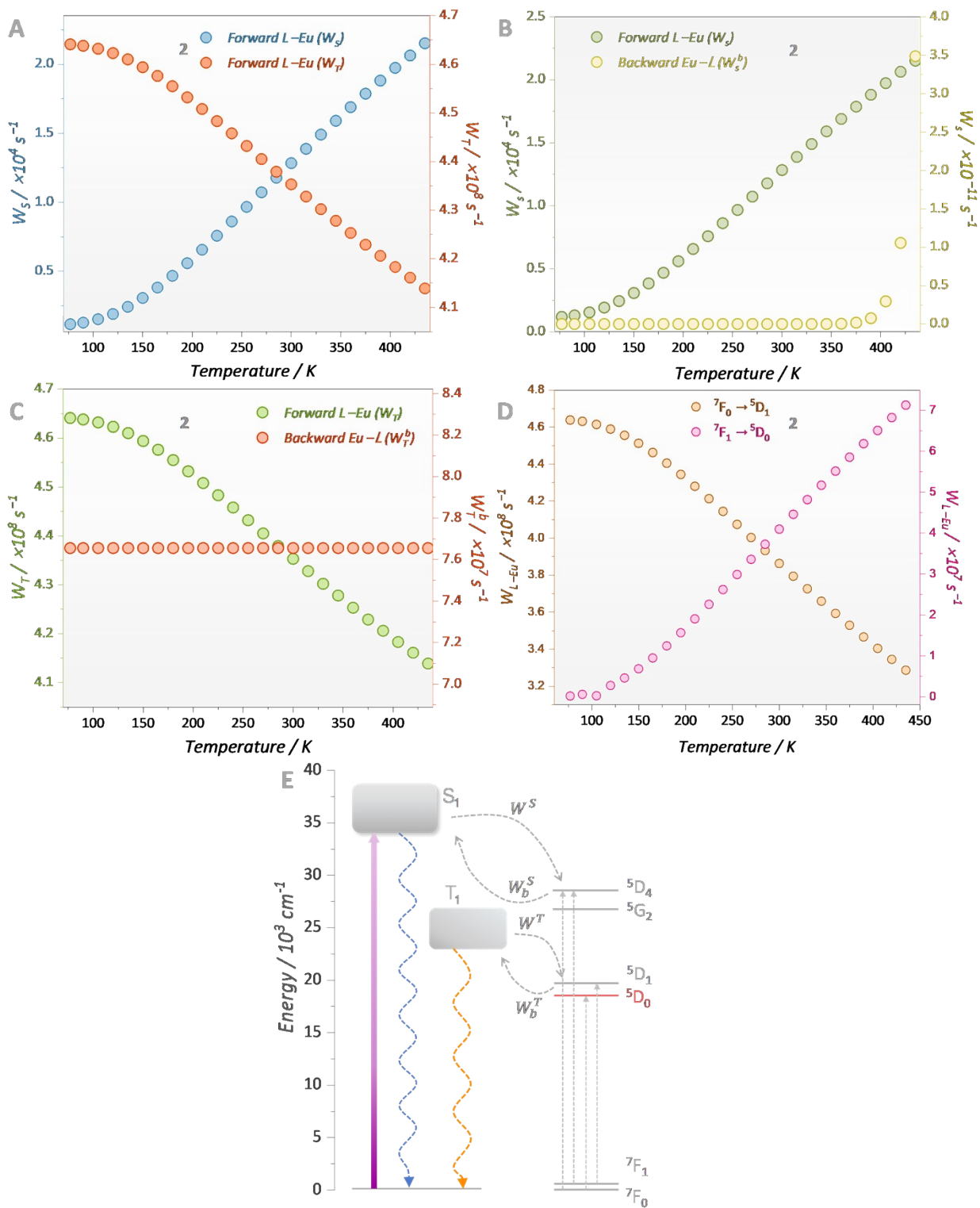


**Fig S12.** Temperature dependent IET ligand-to-Eu<sup>III</sup> rates for coordination polymer **1** focusing on (a) energy transfer arising from the singlet and triplet state to Eu<sup>III</sup>; (b) the forward and backward energy transfer rates (Eu<sup>III</sup>-Ligand) from the singlet state and (c) from the triplet state; (d) temperature dependence of the energy transfer from the triplet state concerning the <sup>7</sup>F<sub>0</sub> and <sup>7</sup>F<sub>1</sub> manifold; (e) Partial energy transfer diagram highlighting the process described in Fig. S13 a,b,c,d. **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub> (Ln = Eu, Tb).

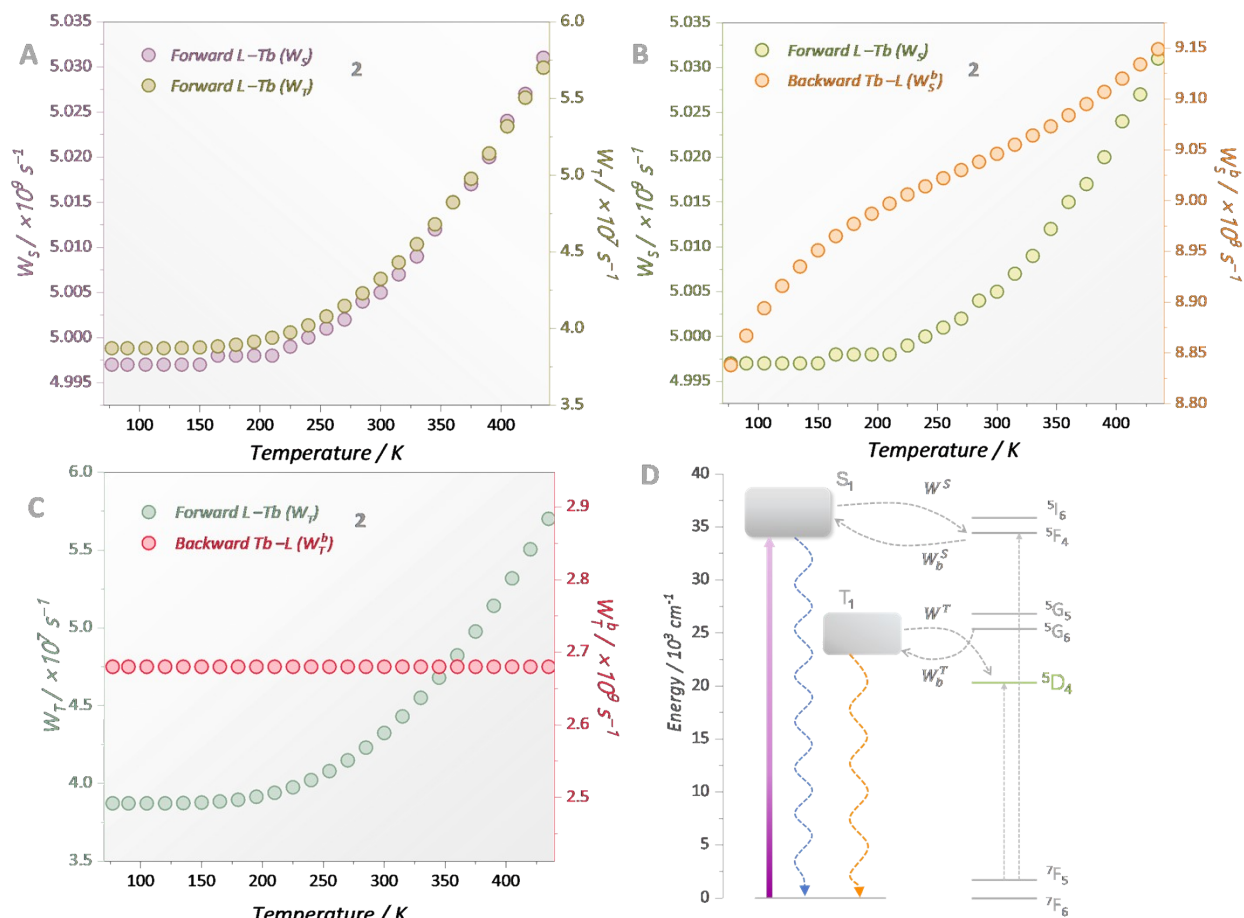




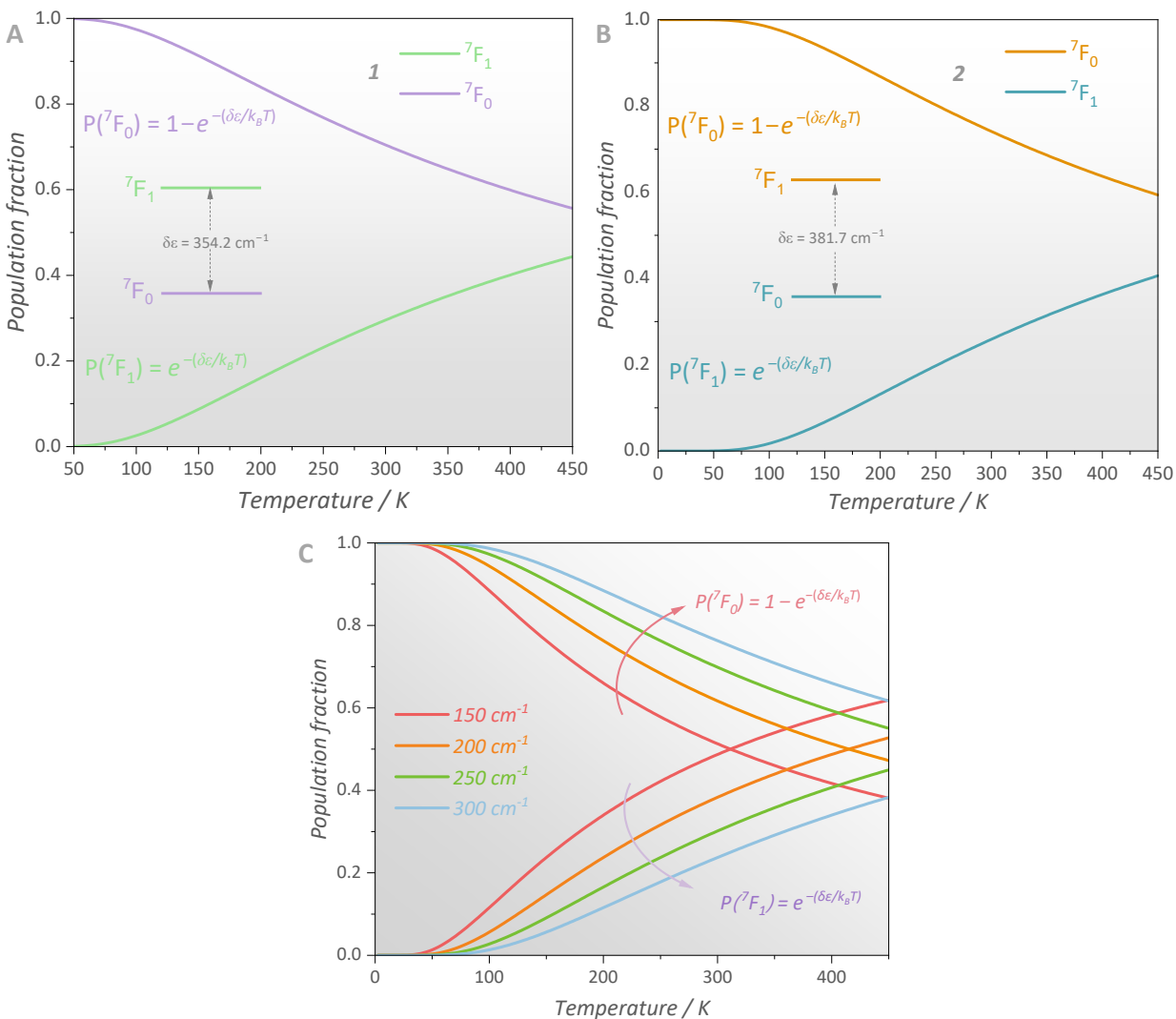
**Fig S13.** Temperature dependent IET ligand-to-Tb<sup>III</sup> rates for coordination polymer **1** focusing on (a) energy transfer arising from the singlet and triplet state to Eu<sup>III</sup>; (b) the forward and backward energy transfer rates from the singlet state and (c) from the triplet state; (d) Partial energy transfer diagram highlighting the process described in Fig. S10 a,b,c. **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub> (Ln = Eu, Tb).



**Fig S14.** Temperature dependent IET ligand-to- $Eu^{III}$  rates for coordination polymer **2** focusing on (a) energy transfer arising from the singlet and triplet state to  $Eu^{III}$ ; (b) the forward and backward energy transfer rates from the singlet state and (c) from the triplet state; (d) Partial energy transfer diagram highlighting the process described in Fig. S11 a,b,c,d. **2** =  $[Ln(tfa)_3(\mu\text{-dppbo})]_n$  ( $Ln = Eu, Tb$ ).



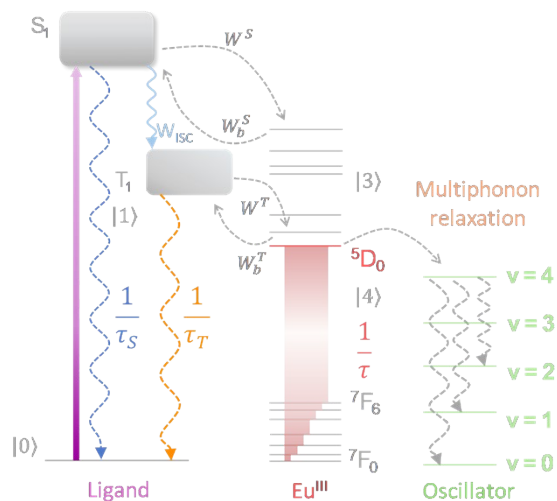
**Fig S15.** Temperature dependent IET ligand-to-Tb<sup>III</sup> rates for coordination polymer **2** focusing on (a) energy transfer arising from the singlet and triplet state to Eu<sup>III</sup>; (b) the forward and backward energy transfer rates from the singlet state and (c) from the triplet state; (d) Partial energy transfer diagram highlighting the process described in Fig. S12 a,b,c,d. **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).



**Fig S16.** Thermal population of the  ${}^7F_0$  and  ${}^7F_1$  manifolds for (a) **1** and (b) **2**. The energy difference between the two levels ( $\delta\varepsilon$ ) was obtained by the difference of the emission band's barycenter in the experimental spectra. (c) Trend in the thermal population of  ${}^7F_1$  level for various energies difference. **1** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$ ; **2** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (Ln = Eu, Tb).

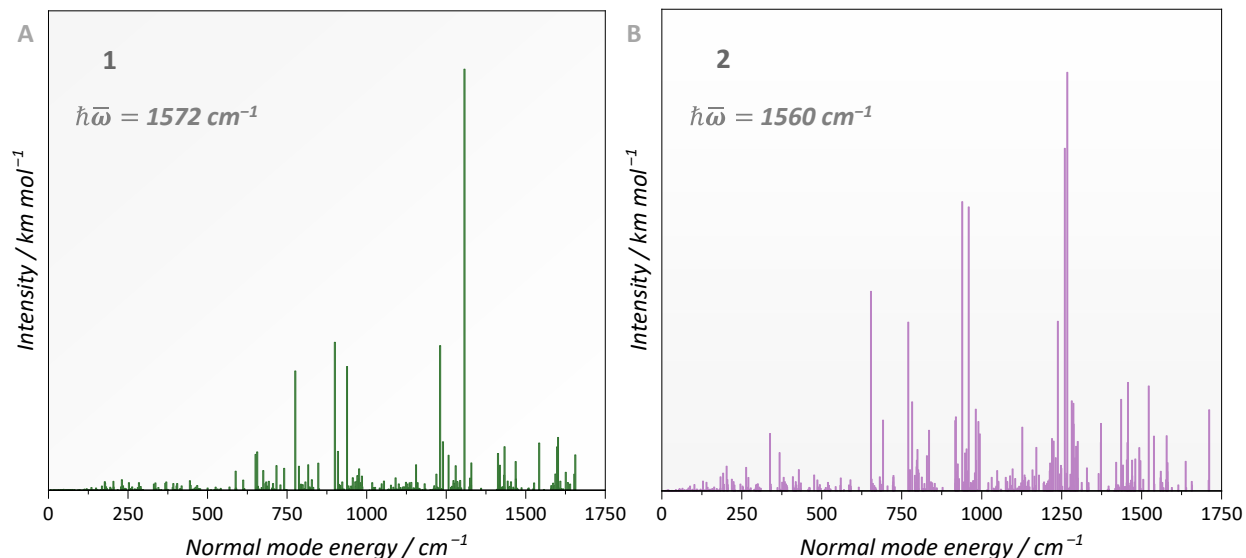
## Supplementary note S7 – Multiphonon relaxation

Among the relaxation pathways that can occur in a Ln<sup>III</sup>-based compound, the non-radiative decay is often associated with the multiphonon relaxation, i.e, the sequential absorption and emission of a phonon to bridge the energy gap between two electronic states (Fig S17 for the Eu<sup>III</sup> part).

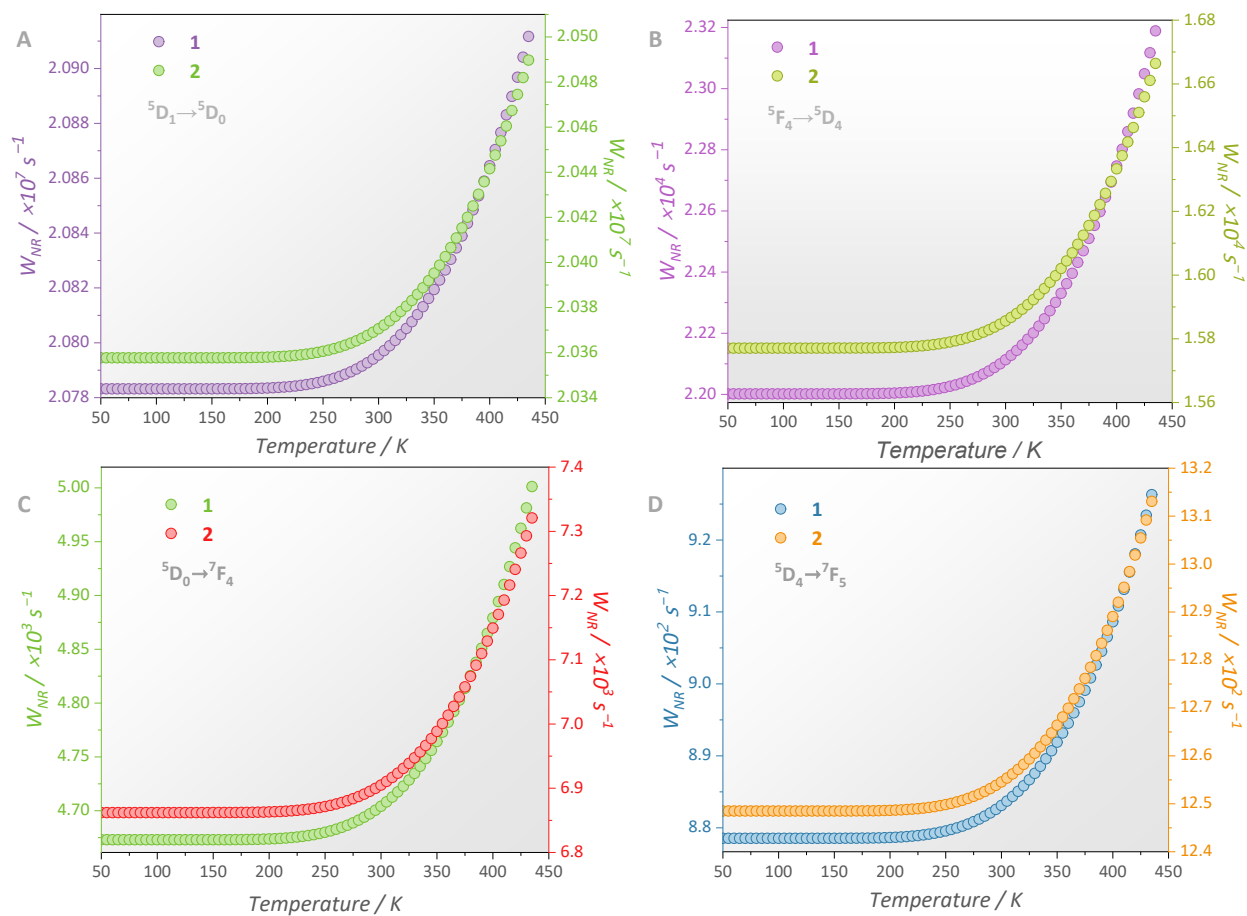


**Fig S17.** Representation of the multiphonon relaxation for the Eu<sup>III</sup> counterpart.

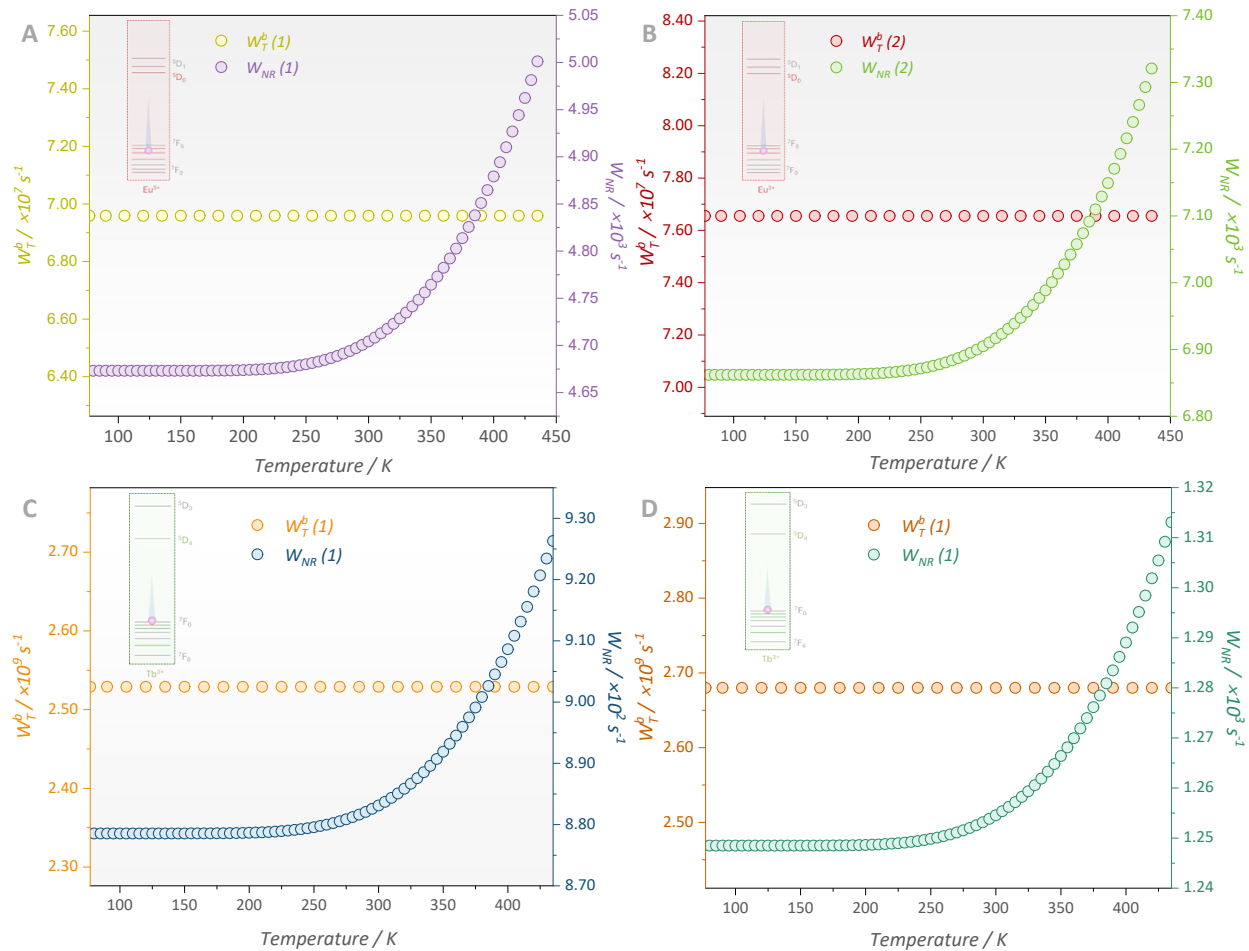
For the determination of the multiphonon relaxation rates by the Miyakawa-Dexter model<sup>34</sup>, the mean phonon energy is needed. Instead of using the energy of the maximum vibrational normal mode, previous studies on thermally activated delayed fluorescent materials shows that all normal modes do not contribute the same to the mean phonon energy<sup>43,44</sup>. Therefore, we employed the weighted energy by the vibrational intensity (Fig S18).



**Fig S18.** Normal mode energies highlight the mean phonon energy weighted by its intensity for (a) **1** and (b) **2**. **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).



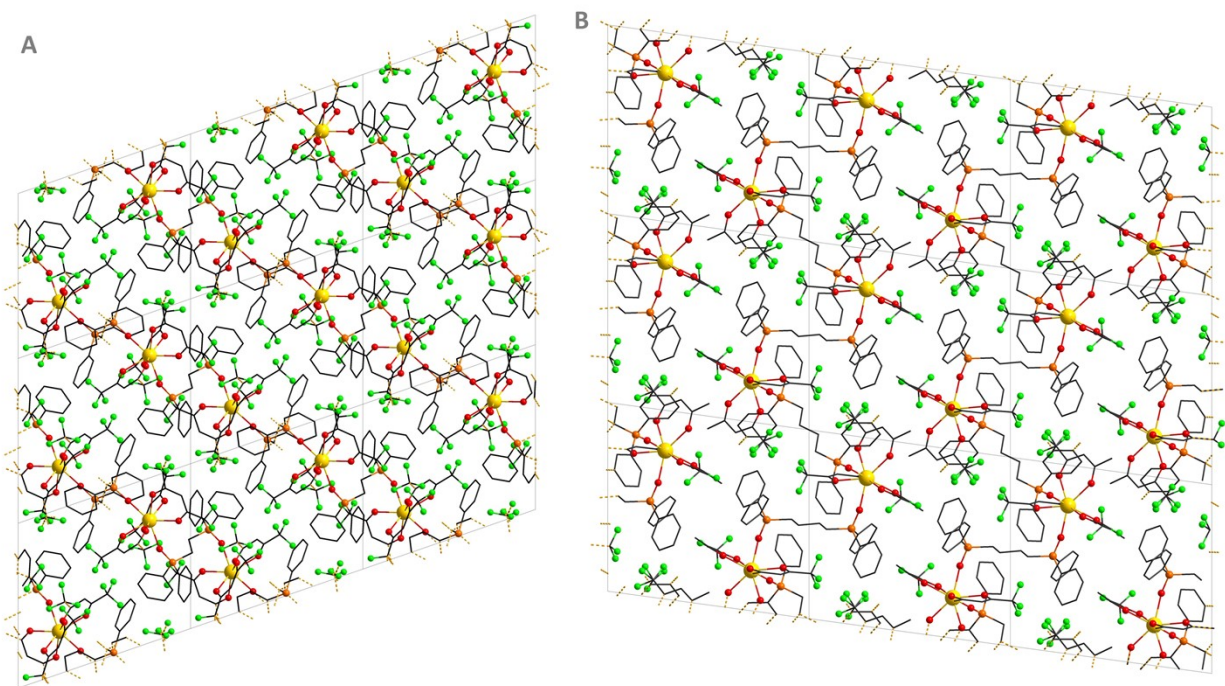
**Fig S19.** Rates of multiphonon relaxation for **1** and **2** considering the Huang-Rhys factor of 0.1. The decay from upper emitting levels to the  ${}^5D_0$  and  ${}^5D_4$  of  $\text{Eu}^{III}$  and  $\text{Tb}^{III}$ , respectively are represented in item (a) and (b), respectively. The multiphonon decay rates considering the relaxation from the emitting level to the ground state are displayed in item (c) for  $\text{Eu}^{III}$  ( ${}^5D_0 \rightarrow {}^7F_4$ ) and (d) for  $\text{Tb}^{III}$  ( ${}^5D_4 \rightarrow {}^7F_5$ ). **1** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$ ; **2** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppbo})]_n$  (Ln = Eu, Tb).



**Fig S20.** Comparison of Ligand-to-Ln<sup>III</sup> backward ET and multiphonon relaxation dependence with temperature regarding the excited state. Considering Eu<sup>III</sup> for (a) **1** and (b) **2**, and Tb<sup>III</sup> for (c) **1** and (d) **2**. **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).

### Supplementary note S8 – Ln<sup>III</sup>-to-Ln<sup>III</sup> energy transfer

Analogous to the case of ligand-to-Ln<sup>III</sup> energy transfer, the Ln<sup>III</sup>-to-Ln<sup>III</sup> process is pivotal when considering all photophysical phenomenon occurring in the coordination compound. For this reason, we determined the rates of ET between Eu<sup>III</sup> and Tb<sup>III</sup> varying the distance between both centers considering the Tb<sup>III</sup> 4*f* excitation. The calculations were performed for all inter- and intramolecular distances between both ions (Fig 2), however, for sake of clarity we will only highlight the table for one of the intramolecular distances for complexes **1** and **2**, since the process is the same for each calculation. We emphasize that the population of the acceptor ground-state needs to be considered in the determination, therefore, this factor is represented in Fig S16. To ensure that only these distances need consideration, a 3x3x3 supercell of **1** and **2** are represented in Fig. S22, demonstrating that the structures are ordered. Hence, precluding the necessity to simulate multiple distances. It is noteworthy that all energy transfer rates for each distance as a function of temperature are highlighted directly in Fig. S23.



**Figure S21.** Packing diagram of (a) **1** and (b) **2**. Representation along the *a* axis. H atoms have been omitted for the sake of clarity. **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).



**Table S11.** Tb<sup>III</sup>-to-Eu<sup>III</sup> energy transfer rates at 300 K considering the intramolecular distance ( $R_{\text{Tb-Eu}} = 8.298 \text{ \AA}$ ) for **1**.  $W_{d-d}$ ,  $W_{d-q}$ ,  $W_{q-q}$ ,  $W_{ex}$ , and  $W_{md-md}$  are the dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, exchange, and magnetic dipole-magnetic dipole mechanisms in  $\text{s}^{-1}$ , respectively.  $W$  is the sum of each pathway and the  $W_{\text{Tb} \rightarrow \text{Eu}}$  is the sum of all pathways.  $\delta$  is the energy difference (in  $\text{cm}^{-1}$ ) between donor and acceptor states. **1** =  $[\text{Ln}(\text{tfa})_3(\mu\text{-dppeo})]_n$  (Ln = Eu, Tb).

Path	Donor	Acceptor	$\delta$	$W_{d-d}$	$W_{d-q}$	$W_{q-q}$	$W_{ex}$	$W_{md-md}$	$W$
1	$^5\text{D}_4 \rightarrow ^7\text{F}_6$	$^7\text{F}_0 \rightarrow ^5\text{D}_0$	3151	$5.212 \times 10^{-19}$	$5.368 \times 10^{-15}$	$5.918 \times 10^{-12}$	$2.066 \times 10^{-43}$	0	$4.144 \times 10^{-11}$
2	$^5\text{D}_4 \rightarrow ^7\text{F}_6$	$^7\text{F}_0 \rightarrow ^5\text{D}_1$	1417	0	0	0	$1.116 \times 10^{-33}$	0	$7.810 \times 10^{-33}$
3	$^5\text{D}_4 \rightarrow ^7\text{F}_6$	$^7\text{F}_0 \rightarrow ^5\text{D}_2$	-1039	0	0	0	$1.06 \times 10^{-34}$	0	$7.417 \times 10^{-34}$
4	$^5\text{D}_4 \rightarrow ^7\text{F}_6$	$^7\text{F}_1 \rightarrow ^5\text{D}_0$	3523	0	0	0	$2.890 \times 10^{-45}$	0	$8.669 \times 10^{-45}$
5	$^5\text{D}_4 \rightarrow ^7\text{F}_6$	$^7\text{F}_1 \rightarrow ^5\text{D}_1$	1789	$2.510 \times 10^{-11}$	$2.585 \times 10^{-7}$	$2.850 \times 10^{-4}$	$3.820 \times 10^{-35}$	0	$8.557 \times 10^{-5}$
6	$^5\text{D}_4 \rightarrow ^7\text{F}_6$	$^7\text{F}_1 \rightarrow ^5\text{D}_2$	-667	0	0	0	$3.790 \times 10^{-33}$	0	$1.137 \times 10^{-33}$
7	$^5\text{D}_4 \rightarrow ^7\text{F}_5$	$^7\text{F}_0 \rightarrow ^5\text{D}_0$	1103	$2.016 \times 10^{-8}$	$2.254 \times 10^{-4}$	$1.577 \times 10^0$	$1.046 \times 10^{-32}$	0	$4.730 \times 10^0$
8	$^5\text{D}_4 \rightarrow ^7\text{F}_5$	$^7\text{F}_0 \rightarrow ^5\text{D}_1$	-631	0	0	0	$5.141 \times 10^{-33}$	$3.323 \times 10^{-3}$	$2.326 \times 10^{-3}$
9	$^5\text{D}_4 \rightarrow ^7\text{F}_5$	$^7\text{F}_0 \rightarrow ^5\text{D}_2$	-3087	0	0	0	$2.394 \times 10^{-49}$	0	$1.676 \times 10^{-48}$
10	$^5\text{D}_4 \rightarrow ^7\text{F}_5$	$^7\text{F}_1 \rightarrow ^5\text{D}_0$	1475	0	0	0	$6.940 \times 10^{-34}$	$6.398 \times 10^{-4}$	$1.919 \times 10^{-4}$
11	$^5\text{D}_4 \rightarrow ^7\text{F}_5$	$^7\text{F}_1 \rightarrow ^5\text{D}_1$	-259	$1.175 \times 10^{-7}$	$1.314 \times 10^{-3}$	$9.193 \times 10^1$	$7.811 \times 10^{-32}$	$5.539 \times 10^{-4}$	$3.758 \times 10^1$
12	$^5\text{D}_4 \rightarrow ^7\text{F}_5$	$^7\text{F}_1 \rightarrow ^5\text{D}_2$	-2715	0	0	0	$6.348 \times 10^{-46}$	$2.301 \times 10^{-17}$	$6.903 \times 10^{-18}$
13	$^5\text{D}_4 \rightarrow ^7\text{F}_4$	$^7\text{F}_0 \rightarrow ^5\text{D}_0$	-164	$5.099 \times 10^{-7}$	$5.187 \times 10^{-3}$	$8.790 \times 10^{-1}$	$1.380 \times 10^{-31}$	0	$6.190 \times 10^{-1}$
14	$^5\text{D}_4 \rightarrow ^7\text{F}_4$	$^7\text{F}_0 \rightarrow ^5\text{D}_1$	-1898	0	0	0	$1.365 \times 10^{-39}$	$3.375 \times 10^{-10}$	$2.362 \times 10^{-10}$
15	$^5\text{D}_4 \rightarrow ^7\text{F}_4$	$^7\text{F}_0 \rightarrow ^5\text{D}_2$	-4354	0	0	0	$1.423 \times 10^{-63}$	0	$9.959 \times 10^{-64}$
16	$^5\text{D}_4 \rightarrow ^7\text{F}_4$	$^7\text{F}_1 \rightarrow ^5\text{D}_0$	208	0	0	0	$2.893 \times 10^{-31}$	$1.020 \times 10^{-1}$	$3.100 \times 10^{-2}$
17	$^5\text{D}_4 \rightarrow ^7\text{F}_4$	$^7\text{F}_1 \rightarrow ^5\text{D}_1$	-1667	$2.872 \times 10^{-13}$	$2.921 \times 10^{-9}$	$4.948 \times 10^{-7}$	$2.985 \times 10^{-37}$	$8.110 \times 10^{-10}$	$1.496 \times 10^{-7}$
18	$^5\text{D}_4 \rightarrow ^7\text{F}_4$	$^7\text{F}_1 \rightarrow ^5\text{D}_2$	-4123	0	0	0	$5.472 \times 10^{-59}$	$7.599 \times 10^{-31}$	$2.280 \times 10^{-31}$
19	$^5\text{D}_4 \rightarrow ^7\text{F}_3$	$^7\text{F}_0 \rightarrow ^5\text{D}_0$	-1143	$4.750 \times 10^{-11}$	$5.116 \times 10^{-7}$	$2.236 \times 10^{-3}$	$3.193 \times 10^{-35}$	0	$1.565 \times 10^{-3}$
20	$^5\text{D}_4 \rightarrow ^7\text{F}_3$	$^7\text{F}_0 \rightarrow ^5\text{D}_1$	-2877	0	0	0	$2.025 \times 10^{-47}$	$5.519 \times 10^{-27}$	$3.864 \times 10^{-27}$
21	$^5\text{D}_4 \rightarrow ^7\text{F}_3$	$^7\text{F}_0 \rightarrow ^5\text{D}_2$	-5333	0	0	0	$2.430 \times 10^{-77}$	0	$1.701 \times 10^{-77}$
22	$^5\text{D}_4 \rightarrow ^7\text{F}_3$	$^7\text{F}_1 \rightarrow ^5\text{D}_0$	-912	0	0	0	$1.440 \times 10^{-33}$	$5.608 \times 10^{-3}$	$1.682 \times 10^{-3}$

23	$^5D_4 \rightarrow ^7F_3$	$^7F_1 \rightarrow ^5D_1$	-2646	$1.361 \times 10^{-20}$	$1.466 \times 10^{-16}$	$6.407 \times 10^{-13}$	$3.513 \times 10^{-44}$	$1.052 \times 10^{-15}$	$1.926 \times 10^{-13}$
24	$^5D_4 \rightarrow ^7F_3$	$^7F_1 \rightarrow ^5D_2$	-5102	0	0	0	$7.416 \times 10^{-72}$	$1.135 \times 10^{-43}$	$3.406 \times 10^{-43}$
<b>Total</b>								$W_{Tb \rightarrow Eu}$	$4.8835 \times 10^1$

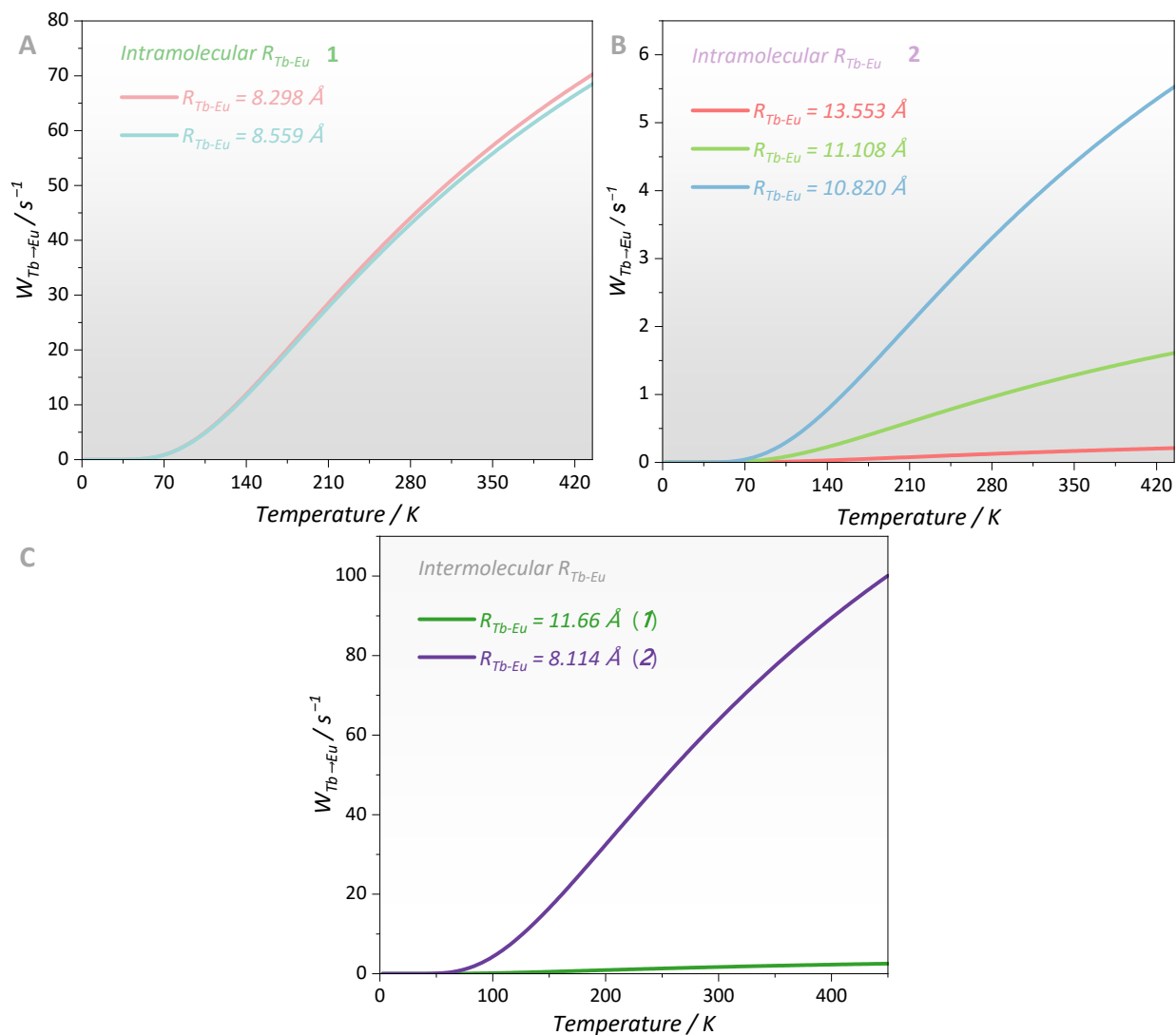
**Table S12.** Tb<sup>III</sup>-to-Eu<sup>III</sup> energy transfer rates at 300 K considering the intramolecular distance ( $R_{Tb-Eu} = 10.820 \text{ \AA}$ ) for **2**.  $W_{d-d}$ ,  $W_{d-q}$ ,  $W_{q-q}$ ,  $W_{ex}$ , and  $W_{md-md}$  are the dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, exchange, and magnetic dipole-magnetic dipole mechanisms (in  $s^{-1}$ ), respectively.  $W$  is the sum of each pathway and the  $W_{Tb \rightarrow Eu}$  is the sum of all pathways.  $\delta$  is the energy difference (in  $cm^{-1}$ ) between donor and acceptor states. **2** =  $[Ln(tfa)_3(\mu-dppbo)]_n$  ( $Ln = Eu, Tb$ ).

Path	Donor	Acceptor	$\delta$	$W_{d-d}$	$W_{d-q}$	$W_{q-q}$	$W_{ex}$	$W_{md-md}$	$W$
1	$^5D_4 \rightarrow ^7F_6$	$^7F_0 \rightarrow ^5D_0$	3151	$4.607 \times 10^{-20}$	$3.228 \times 10^{-16}$	$4.165 \times 10^{-13}$	$4.672 \times 10^{-75}$	0	$2.751 \times 10^{-13}$
2	$^5D_4 \rightarrow ^7F_6$	$^7F_0 \rightarrow ^5D_1$	1417	0	0	0	$2.523 \times 10^{-65}$	0	$1.665 \times 10^{-65}$
3	$^5D_4 \rightarrow ^7F_6$	$^7F_0 \rightarrow ^5D_2$	-1039	0	0	0	$2.390 \times 10^{-66}$	0	$1.578 \times 10^{-66}$
4	$^5D_4 \rightarrow ^7F_6$	$^7F_1 \rightarrow ^5D_0$	3523	0	0	0	$4.159 \times 10^{-78}$	0	$2.745 \times 10^{-78}$
5	$^5D_4 \rightarrow ^7F_6$	$^7F_1 \rightarrow ^5D_1$	1789	$2.219 \times 10^{-12}$	$1.555 \times 10^{-8}$	$2.006 \times 10^{-5}$	$8.639 \times 10^{-67}$	0	$6.624 \times 10^{-6}$
6	$^5D_4 \rightarrow ^7F_6$	$^7F_1 \rightarrow ^5D_2$	-667	0	0	0	$8.572 \times 10^{-65}$	0	$2.829 \times 10^{-65}$
7	$^5D_4 \rightarrow ^7F_5$	$^7F_0 \rightarrow ^5D_0$	1103	$5.337 \times 10^{-9}$	$4.298 \times 10^{-5}$	$2.330 \times 10^{-1}$	$2.366 \times 10^{-64}$	0	$1.200 \times 10^0$
8	$^5D_4 \rightarrow ^7F_5$	$^7F_0 \rightarrow ^5D_1$	-631	0	0	0	$1.163 \times 10^{-64}$	$6.750 \times 10^{-4}$	$4.455 \times 10^{-4}$
9	$^5D_4 \rightarrow ^7F_5$	$^7F_0 \rightarrow ^5D_2$	-3087	0	0	0	$\approx 0$	0	$\approx 0$
10	$^5D_4 \rightarrow ^7F_5$	$^7F_1 \rightarrow ^5D_0$	1475	0	0	0	$1.570 \times 10^{-65}$	$1.302 \times 10^{-4}$	$4.296 \times 10^{-5}$
11	$^5D_4 \rightarrow ^7F_5$	$^7F_1 \rightarrow ^5D_1$	-259	$1.037 \times 10^{-8}$	$8.355 \times 10^{-5}$	$6.740 \times 10^{-1}$	$1.766 \times 10^{-63}$	$1.127 \times 10^{-4}$	$2.140 \times 10^0$
12	$^5D_4 \rightarrow ^7F_5$	$^7F_1 \rightarrow ^5D_2$	-2715	0	0	0	$1.436 \times 10^{-77}$	$4.681 \times 10^{-18}$	$1.545 \times 10^{-18}$
13	$^5D_4 \rightarrow ^7F_4$	$^7F_0 \rightarrow ^5D_0$	-164	$4.360 \times 10^{-8}$	$2.990 \times 10^{-4}$	$6.200 \times 10^{-2}$	$3.122 \times 10^{-63}$	0	$4.100 \times 10^{-1}$
14	$^5D_4 \rightarrow ^7F_4$	$^7F_0 \rightarrow ^5D_1$	-1898	0	0	0	$3.101 \times 10^{-71}$	$6.898 \times 10^{-11}$	$4.552 \times 10^{-11}$
15	$^5D_4 \rightarrow ^7F_4$	$^7F_0 \rightarrow ^5D_2$	-4354	0	0	0	$\approx 0$	0	$\approx 0$
16	$^5D_4 \rightarrow ^7F_4$	$^7F_1 \rightarrow ^5D_0$	208	0	0	0	$6.543 \times 10^{-63}$	$2.100 \times 10^{-2}$	$6.862 \times 10^{-3}$
17	$^5D_4 \rightarrow ^7F_4$	$^7F_1 \rightarrow ^5D_1$	-1526	$2.464 \times 10^{-14}$	$1.690 \times 10^{-10}$	$3.495 \times 10^{-8}$	$6.775 \times 10^{-69}$	$1.656 \times 10^{-10}$	$1.164 \times 10^{-8}$
18	$^5D_4 \rightarrow ^7F_4$	$^7F_1 \rightarrow ^5D_2$	-3982	0	0	0	$\approx 0$	$1.561 \times 10^{-31}$	$5.151 \times 10^{-32}$

19	${}^5D_4 \rightarrow {}^7F_3$	${}^7F_0 \rightarrow {}^5D_0$	-1148	$4.171 \times 10^{-12}$	$3.158 \times 10^{-8}$	$1.578 \times 10^{-4}$	$7.240 \times 10^{-67}$	0	$1.042 \times 10^{-3}$
20	${}^5D_4 \rightarrow {}^7F_3$	${}^7F_0 \rightarrow {}^5D_1$	-2882	0	0	0	$4.611 \times 10^{-79}$	$1.131 \times 10^{-17}$	$7.463 \times 10^{-18}$
21	${}^5D_4 \rightarrow {}^7F_3$	${}^7F_0 \rightarrow {}^5D_2$	-5338	0	0	0	$\approx 0$	0	$\approx 0$
22	${}^5D_4 \rightarrow {}^7F_3$	${}^7F_1 \rightarrow {}^5D_0$	-776	0	0	0	$3.263 \times 10^{-65}$	$1.143 \times 10^{-3}$	$3.772 \times 10^{-4}$
23	${}^5D_4 \rightarrow {}^7F_3$	${}^7F_1 \rightarrow {}^5D_1$	-2510	$1.199 \times 10^{-21}$	$9.080 \times 10^{-18}$	$4.537 \times 10^{-14}$	$7.993 \times 10^{-76}$	$2.154 \times 10^{-16}$	$1.504 \times 10^{-14}$
24	${}^5D_4 \rightarrow {}^7F_3$	${}^7F_1 \rightarrow {}^5D_2$	-4966	0	0	0	$\approx 0$	$2.338 \times 10^{-43}$	$7.715 \times 10^{-44}$
								$W_{Tb \rightarrow Eu}$	$0.4369 \times 10^1$

**Table S13.** Total Tb<sup>III</sup>-Eu<sup>III</sup> energy transfer rates considering both intra- and intermolecular Tb<sup>III</sup>-Eu<sup>III</sup> distances at 300.15 K. **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).

	Intramolecular		Intermolecular	
	$R_{Tb-Eu} / \text{Å}$	$W_{Tb \rightarrow Eu} / s^{-1}$	$R_{Tb-Eu} / \text{Å}$	$W_{Tb \rightarrow Eu} / s^{-1}$
<b>1</b>	8.298	$4.883 \times 10^1$	11.66	$1.696 \times 10^0$
	8.559	$4.604 \times 10^1$	-	-
<b>2</b>	10.82	$0.4369 \times 10^1$	8.114	$6.402 \times 10^1$
	11.10	$0.1062 \times 10^1$	-	-
	13.55	$0.1389 \times 10^0$	-	-



**Fig S22.** Temperature dependent rates of Tb<sup>III</sup>-to-Eu<sup>III</sup> energy transfer for the intramolecular Tb<sup>III</sup>-Eu<sup>III</sup> distances in (a) **1** and (b) **2**. The rates of energy transfer considering the intermolecular Tb<sup>III</sup>-Eu<sup>III</sup> distances were also determined in (c). For all calculations, the direct Tb<sup>III</sup> excitation (481 nm) was considered. **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).

### Supplementary note S9 – Population dynamics and theoretical thermometry

With the ligand-to-Ln<sup>III</sup> intramolecular energy transfer and Ln<sup>III</sup>-to-Ln<sup>III</sup> energy transfer rates, as well as with the emission lifetime of both Tb<sup>III</sup> and Eu<sup>III</sup>, and the multiphonon decay rates, the next step to accurately describe the photophysical dynamics involves in obtaining the population of each emitting state. To do so, we can construct a set of coupled ordinary differential equations (ODEs), as evinced in Eq. S31. This system can be solved numerically through time propagation, enabling the obtention of the population dynamics of each level. From this perspective, Eq. S40 and S41 were constructed and solved using Radau methods<sup>36</sup>.

#### Under ligand excitation (340 nm)

$$|0\rangle: \frac{d}{dt}P_0 = -\phi P_0(t) + \frac{1}{\tau_T}P_1(t) + \frac{1}{\tau_S}P_2(t) + \frac{1}{\tau}P_4(t) \quad (S40a)$$

$$|1\rangle: \frac{d}{dt}P_1 = -\left(\frac{1}{\tau_T} + W^T\right)P_1(t) + W_{ISC}P_2(t) + W_b^T P_3(t) \quad (S40b)$$

$$|2\rangle: \frac{d}{dt}P_2 = -\left(\frac{1}{\tau_S} + W^S + W_{ISC}\right)P_2(t) + W_b^S P_3(t) + \phi P_0(t) \quad (S40c)$$

$$|3\rangle: \frac{d}{dt}P_3 = -(W_b^S + W_b^T + W_{3\rightarrow4})P_3(t) + W^T P_1(t) + W^S P_2(t) \quad (S40d)$$

$$|4\rangle: \frac{d}{dt}P_4 = -\left(\frac{1}{\tau}\right)P_4(t) + W_{3\rightarrow4}P_3(t) + W^T P_1(t) \quad (S40e)$$

#### Under Tb<sup>III</sup> intra-4f excitation (481 nm)

$$|0\rangle: \frac{d}{dt}P_0 = -\phi P_0(t) + \frac{1}{\tau_{Tb}}P_1(t) + \frac{1}{\tau_{Eu}}P_3(t) \quad (S41a)$$

$$|1\rangle: \frac{d}{dt}P_1 = -\left(\frac{1}{\tau_{Tb}} + W_{1\rightarrow2} + W_{1\rightarrow3}\right)P_1(t) + \phi P_0(t) \quad (S41b)$$

$$|2\rangle: \frac{d}{dt}P_2 = -W_{2\rightarrow3}P_2(t) + W_{1\rightarrow2}P_1(t) \quad (S41c)$$

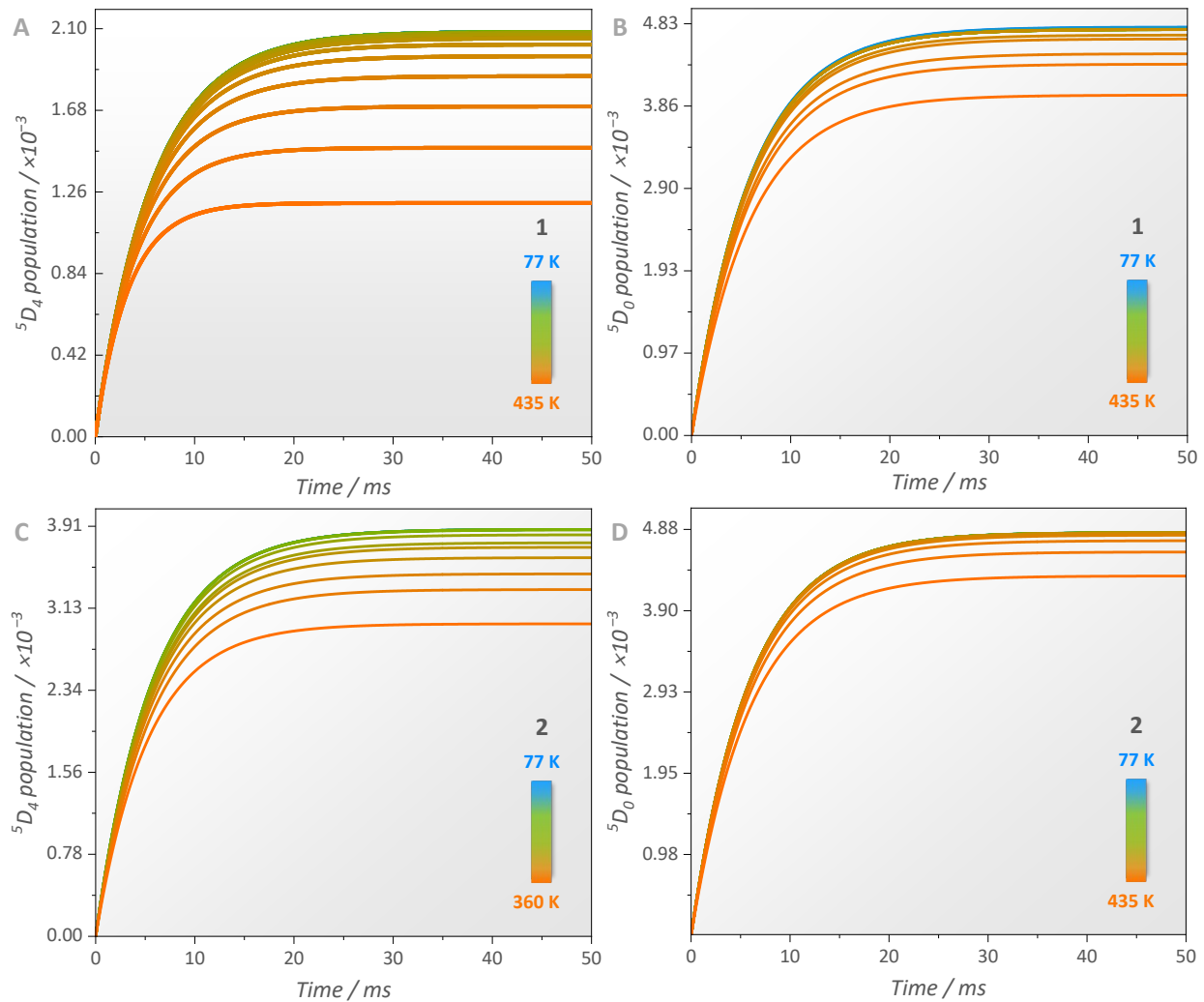
$$|3\rangle: \frac{d}{dt}P_3 = -\left(\frac{1}{\tau_{Eu}}\right)P_3(t) + W_{1\rightarrow3}P_1(t) + W_{2\rightarrow3}P_2(t) \quad (S41d)$$

In Eq. S40(a-e), various states such as the ground state ( $S_0$  at  $t = 0$ , transitioning to  ${}^7F_J$  at  $t \neq 0$ ),  $T_1$ , and  $S_1$  were defined as  $|0\rangle$ ,  $|1\rangle$  and  $|2\rangle$ , respectively.  $|3\rangle$  represents any Eu<sup>III</sup> manifold other than  ${}^5D_0$ , while  $|4\rangle$  is the  ${}^5D_0$  level. The decay lifetime values of  $S_1$ ,  $T_1$ , and  ${}^5D_0$  state, assigned as  $\tau_S$ ,  $\tau_T$ , and  $\tau$ , respectively, assume values in the range of 1 ns – 1  $\mu$ s for  $\tau_S$ , 1  $\mu$ s – 1 ms for  $\tau_T$ , and 1 ms for

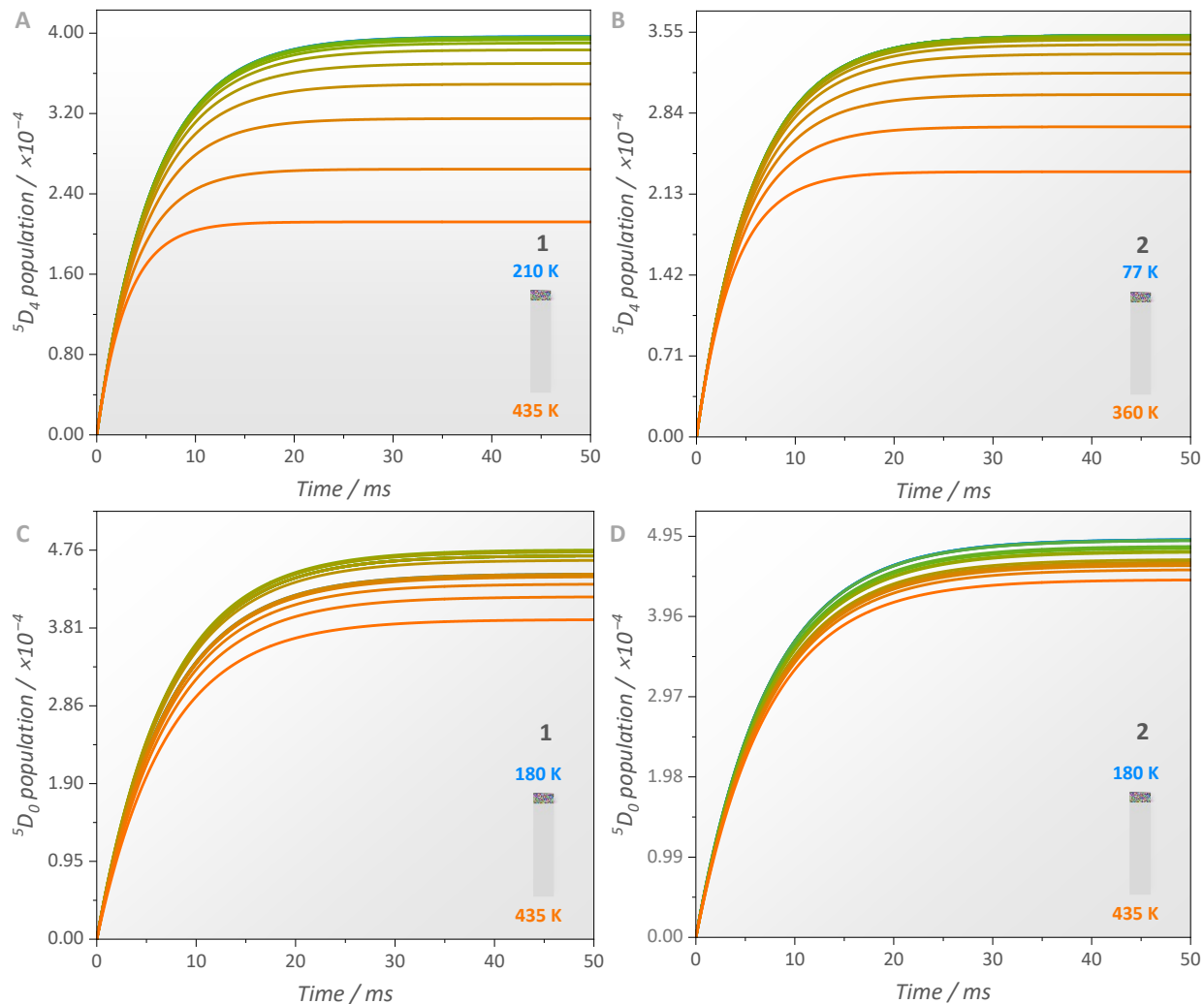
<sup>45</sup>. The intersystem crossing (ISC) rates denoted as  $W_{ISC}$  were estimated to be around  $10^8 \text{ s}^{-1}$ , considering energy gaps between  $S_1$  and  $T_1$  within 10000 to 15000  $\text{cm}^{-1}$ ,<sup>46</sup> consistent with the system under study.

It is worth noting that considering only the  $\text{Ln}^{\text{III}}$ -to- $\text{Ln}^{\text{III}}$  energy transfer, a few adaptations were made based on the experimental investigations. For example, no evidence of  $\text{Eu}^{\text{III}}$ - $\text{Tb}^{\text{III}}$  energy transfer was observed. Therefore, we neglected the process of backward energy transfer when exciting the  $\text{Tb}^{\text{III}}$ , since it would account for  $P_{1,2,3}$  in the coupled ODEs. Also, the  ${}^5D_1$  thermal population from  ${}^5D_0$  was also neglected, due to the large energy gap between the levels and rapid multiphonon deactivation of  ${}^5D_1 \rightarrow {}^5D_0$  and  ${}^5D_0 \rightarrow {}^7F_4$ .

The population dynamics for both cases are heavily reliant on the chosen boundary conditions, ensuring that the total population across all energy levels remains constant at any given time  $t$  within the employed interval<sup>47</sup>.



**Fig S23.** Population dynamics of (a) Tb<sup>III</sup> <sup>5</sup>D<sub>4</sub> and (b) Eu<sup>III</sup> <sup>5</sup>D<sub>0</sub> manifolds for **1**; (c) Tb<sup>III</sup> <sup>5</sup>D<sub>4</sub> and (d) Eu<sup>III</sup> <sup>5</sup>D<sub>0</sub> states for **2**. All calculations were performed considering the ligand's excitation (340 nm). **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).



**Fig S24.** Population dynamics of (a) Tb<sup>III</sup> <sup>5</sup>D<sub>4</sub> and (b) Eu<sup>III</sup> <sup>5</sup>D<sub>0</sub> manifolds for **1**; (c) Tb<sup>III</sup> <sup>5</sup>D<sub>4</sub> and (d) Eu<sup>III</sup> <sup>5</sup>D<sub>0</sub> states for **2**. All calculations were performed considering the direct 4f Tb<sup>III</sup> excitation (484 nm). **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).

**Table S14.** Normalized experimental and theoretical parameters for **1** and **2** under ligand excitation (340 nm). **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).

Temperature / K	$\Delta_{\text{exp}}(\mathbf{1})$	$\Delta_{\text{theo}}(\mathbf{1})$	$\Delta_{\text{exp}}(\mathbf{2})$	$\Delta_{\text{theo}}(\mathbf{2})$
77	1	1	1	1
90	0.9679	0.9634	0.9652	0.9752
105	0.9465	0.9447	0.9505	0.9586
120	0.9246	0.9277	0.9368	0.9437
135	0.9061	0.9116	0.9254	0.9272
150	0.8929	0.8828	0.9163	0.9093
165	0.8772	0.8689	0.9092	0.8949
180	0.8617	0.8555	0.8893	0.8784
195	0.8439	0.8310	0.8459	0.8391
210	0.8294	0.8085	0.7467	0.7528
225	0.8053	0.7823	0.5908	0.6107
240	0.7731	0.7670	0.4244	0.4688
255	0.7384	0.7380	0.2865	0.3277
270	0.6981	0.6853	0.1785	0.2443
285	0.6589	0.6360	0.1025	0.1405
300	0.6041	0.5984	0.0543	0.0973
315	0.5157	0.4182	0.0269	0.0629
330	0.3930	0.2933	0.0119	0.0382
345	0.2638	0.1938	0.0044	0.0314
360	0.1554	0.0951	0.0010	0.0235
375	0.0867	0.0577	0.0006	0.0184
390	0.0422	0.0089	4.4151×10 <sup>-4</sup>	0.0115
405	0.0175	0.0039	0.0029	0.0058
420	0.0074	0.0021	0.0067	0.0041
435	0.0048	0.0014	0.0129	0.0032



**Table S15.** Normalized experimental and theoretical parameters for **1** and **2** under Tb<sup>III</sup> excitation (484 nm). **1** = [Ln(tfa)<sub>3</sub>(μ-dppeo)]<sub>n</sub>; **2** = [Ln(tfa)<sub>3</sub>(μ-dppbo)]<sub>n</sub> (Ln = Eu, Tb).

Temperature / K	$\Delta_{\text{exp}}(\mathbf{1})$	$\Delta_{\text{theo}}(\mathbf{1})$	$\Delta_{\text{exp}}(\mathbf{2})$	$\Delta_{\text{theo}}(\mathbf{2})$
77	1	1	1	1
90	0.9604	0.9932	0.9629	0.9664
105	0.9742	0.9671	0.9422	0.9314
120	0.9229	0.9411	0.9243	0.9028
135	0.9056	0.9134	0.8945	0.8808
150	0.8454	0.8554	0.8555	0.8537
165	0.8005	0.8077	0.7974	0.8108
180	0.7496	0.7538	0.7026	0.7138
195	0.6864	0.6957	0.5444	0.5540
210	0.6183	0.6378	0.3502	0.3695
225	0.5482	0.5695	0.1981	0.2519
240	0.4786	0.4954	0.1121	0.1483
255	0.4092	0.4332	0.0661	0.0799
270	0.3408	0.3742	0.0385	0.0498
285	0.2836	0.3197	0.0210	0.0256
300	0.2260	0.2671	0.0111	0.0097
315	0.1713	0.2061	0.0056	0.0056
330	0.1159	0.1617	0.0028	0.0039
345	0.0689	0.1179	0.0014	0.0011
360	0.0371	0.0676	5.872×10 <sup>-4</sup>	8.948×10 <sup>-4</sup>
375	0.0180	0.0044	2.283×10 <sup>-4</sup>	7.675×10 <sup>-4</sup>
390	0.0082	0.0260	4.228×10 <sup>-5</sup>	6.035×10 <sup>-4</sup>
405	0.0034	0.0143	3.876×10 <sup>-5</sup>	3.698×10 <sup>-4</sup>
420	0.0016	0.0066	3.106×10 <sup>-5</sup>	1.125×10 <sup>-4</sup>
435	0.0025	0.0190	2.377×10 <sup>-5</sup>	6.082×10 <sup>-5</sup>

### Supplementary note S10 – Tutorial to calculate the matrix elements

The doubly reduced matrix elements  $(\langle \psi_{xJ_x}' | \hat{L} + g_s \hat{S} | \psi_{xJ_x} \rangle)$  of the angular  $\hat{L}$  and spin  $\hat{S}$  operators determined in Tables S1 – S3 were previously calculated in reference [24,47]. However, their calculation procedure was recently reviewed with corrections pointed out by Carneiro Neto *et al*<sup>25</sup>. Since they are present in the expressions for the energy transfer rates (Eq S13 and S25), their correct determination is pivotal. Considering the selection rules, the non-null contributions are regarding transitions that obey  $\Delta J = J - J' = 0, \pm 1$  (with  $J = J' \neq 0$ ). With this in mind, the aforementioned matrix elements can be separated into two contributions (Eq S42).

$$\langle \psi'J' | \hat{L} + g_s \hat{S} | \psi J \rangle = \langle \psi'J' | \hat{L} | \psi J \rangle + g_s \langle \psi'J' | \hat{S} | \psi J \rangle = \sum_{i,L,S} a_i \langle \psi'J' | \hat{L} | \psi J \rangle + g_s \sum_{i,L,S} b_i \langle \psi'J' | \hat{S} | \psi J \rangle \quad (S42)$$

In these expressions,  $g_s$  is the electron  $g$ -factor, with value of 2.0023. Therefore, calculating the doubly reduced matrix elements reduces to obtaining the states' matrix elements considering the angular and spin operators. This can be accomplished by using the Ofelt's intermediate coupling wavefunctions<sup>21</sup>, obtaining the product into the same LS term, and applying Eq. S43 – S44. In these equations,  $J$  is the total angular momentum, composed by the total orbital angular momentum ( $L$ ) and total spin angular momentum ( $S$ ). The term in brackets  $\{\}$  stands for the Wigner 6- $j$  symbol.

$$\langle LSJ | \hat{L} | LSJ' \rangle = (-1)^{L+S+J+1} [(2J+1)(2J'+1)(L+1)L(2L+1)]^{1/2} \left\{ \begin{matrix} J & 1 & J' \\ L & S & L \end{matrix} \right\} \quad (S43)$$

$$\langle LSJ | \hat{S} | LSJ' \rangle = (-1)^{L+S+J'+1} [(2J+1)(2J'+1)(S+1)S(2S+1)]^{1/2} \left\{ \begin{matrix} S & J & L \\ J' & S & 1 \end{matrix} \right\} \quad (S44)$$

It is possible to evaluate Eq S42 and obtain the values of the matrix elements.

## Supplementary note S11 – Input data for the computational part

### MWB52 ECP for Eu<sup>III</sup> in Orca software

NewGTO Eu

S 5

1	70059.42000	0.000097
2	10776.23500	0.000707
3	2482.49010	0.003362
4	702.15260	0.010206
5	216.79260	0.016597

S 1

1	41.49500	1.0
---	----------	-----

S 1

1	29.49690	1.0
---	----------	-----

S 1

1	15.03090	1.0
---	----------	-----

S 1

1	3.77720	1.0
---	---------	-----

S 1

1	1.92190	1.0
---	---------	-----

S 1

1	0.71310	1.0
---	---------	-----

S 1

1	0.30970	1.0
---	---------	-----

S 1

1	0.05490	1.0
---	---------	-----

S 1

1	0.02270	1.0
---	---------	-----

P 6

1	4058.02070	0.000048
2	1023.32590	0.000357
3	339.38520	0.001687
4	122.34850	0.005693
5	29.05580	0.072398
6	20.62690	-0.046807

P 1		
1	14.61790	1.0
P 1		
1	5.44440	1.0
P 1		
1	2.74140	1.0
P 1		
1	1.22830	1.0
P 1		
1	0.57690	1.0
P 1		
1	0.24890	1.0
P 1		
1	0.08000	1.0
D 6		
1	389.08410	0.000534
2	117.76020	0.004258
3	44.98690	0.017160
4	22.85990	0.012427
5	7.83310	0.270416
6	4.11340	0.445272
D 1		
1	2.09990	1.0
D 1		
1	1.00430	1.0
D 1		
1	0.34220	1.0
D 1		
1	0.10510	1.0
F 5		
1	128.23410	0.003424
2	46.26850	0.034313
3	20.73660	0.123194
4	9.44790	0.251824

```

5  4.31490      0.351292
F 1
1  1.91210      1.0
F 1
1  0.78970      1.0
F 1
1  0.28590      1.0
G 4
1  20.73660     0.026516
2  9.44790      0.099066
3  4.31490      0.213378
4  1.91210      0.453713
G 1
1  0.78970      1.0
G 1
1  0.28590      1.0
end
NewECP Eu
N_core 52
lmax g
s 2
1  4.742100  125.972804  2
2  2.371100  -5.265472  2
p 2
1  4.059200  86.395920  2
2  2.029600  -1.042461  2
d 2
1  2.840700  40.156495  2
2  1.420400  -0.099115  2
f 1
1  5.883800  -68.468426  2
g 1
1  1.000000  0.000000  2
end

```

### MWB54 ECP for Tb<sup>III</sup> in Orca software

NewGTO Tb

S 5

1	70059.42000	0.000097
2	10776.23500	0.000707
3	2482.49010	0.003362
4	702.15260	0.010206
5	216.79260	0.016597

S 1

1	41.49500	1.0
---	----------	-----

S 1

1	29.49690	1.0
---	----------	-----

S 1

1	15.03090	1.0
---	----------	-----

S 1

1	3.77720	1.0
---	---------	-----

S 1

1	1.92190	1.0
---	---------	-----

S 1

1	0.71310	1.0
---	---------	-----

S 1

1	0.30970	1.0
---	---------	-----

S 1

1	0.05490	1.0
---	---------	-----

S 1

1	0.02270	1.0
---	---------	-----

P 6

1	4058.02070	0.000048
2	1023.32590	0.000357
3	339.38520	0.001687
4	122.34850	0.005693
5	29.05580	0.072398
6	20.62690	-0.046807

P 1

1	14.61790	1.0
P 1		
1	5.44440	1.0
P 1		
1	2.74140	1.0
P 1		
1	1.22830	1.0
P 1		
1	0.57690	1.0
P 1		
1	0.24890	1.0
P 1		
1	0.08000	1.0
D 6		
1	389.08410	0.000534
2	117.76020	0.004258
3	44.98690	0.017160
4	22.85990	0.012427
5	7.83310	0.270416
6	4.11340	0.445272
D 1		
1	2.09990	1.0
D 1		
1	1.00430	1.0
D 1		
1	0.34220	1.0
D 1		
1	0.10510	1.0
F 5		
1	128.23410	0.003424
2	46.26850	0.034313
3	20.73660	0.123194
4	9.44790	0.251824
5	4.31490	0.351292

```

F 1
1 1.91210 1.0
F 1
1 0.78970 1.0
F 1
1 0.28590 1.0
G 4
1 20.73660 0.026516
2 9.44790 0.099066
3 4.31490 0.213378
4 1.91210 0.453713
G 1
1 0.78970 1.0
G 1
1 0.28590 1.0
end
NewECP Tb
N_core 54
lmax g
s 2
1 4.742100 125.972804 2
2 2.371100 -5.265472 2
p 2
1 4.059200 86.395920 2
2 2.029600 -1.042461 2
d 2
1 2.840700 40.156495 2
2 1.420400 -0.099115 2
f 1
1 5.883800 -68.468426 2
g 1
1 1.000000 0.000000 2
end
end

```



## Supplementary note S12 – Python script for the population rates

Considering the ligand-to-Ln<sup>III</sup> energy transfer:

```
# Population extractor
# Created by Leonardo F. Saraiva

from scipy.integrate import solve_ivp
import numpy as np

# define the rate equations. Here it is defined the populations P0, P1, P2, P3,
P4

# Considering Ligand-to-Ln ET.

# AT = 1/t(triplet); WT = forward energy transfer rate from the triplet;

# WT1 = forward energy transfer (W') from the triplet

# WI = intersystem crossing rate;

# AS = 1/t(singlet); WS = forward energy transfer rate from the singlet;

# phi = pump, defined as: (sigma*power*lambda) / h * c
# (cross-section * power density * exc wavelength) / planck constant * speed of
light

# W34 = multiphonon relaxation rates from the upper levels to the 5D0

# A = 1/t, where t is the lifetime of the emitting level

def f(t, y, w):
    p0, p1, p2, p3, p4 = y

    AT, WT, WI, WTb, AS, WS, WSb, phi, W34, A = w

    dp0dt = -phi*p0 + AT*p1 + AS*p2 + A*p4

    dp1dt = -(AT + WT)*p1 + WI*p2 + WTb*p3

    dp2dt = -(AS + WS + WI)*p2 + WSb*p3 + phi*p0

    dp3dt = -(WSb + WTb + W34)*p3 + WS*p2

    dp4dt = -A*p4 + W34*p3 + WT*p1
```

```

    return [dp0dt, dp1dt, dp2dt, dp3dt, dp4dt]

# Set the initial conditions and time range

# At t = 0, only the ground level is populated (p0 = 1).

y0 = [1.0, 0.0, 0.0, 0.0, 0.0]

#define the time range (0, tf). For Eu(III) complexes, usually 10 ms is
sufficient.

# Substitute the tf value in the t_eval=[] (try block).

t_span = (0, 50e-3)

# Set the values of wij (scaled down)

# w = [(1/t(triplet)), WT, WI, WTb, (1/t(singlet)), WS, WSb, phi, W34, (1/t(Eu))]

# Remove the # signal from the prior line

try:
    # Solve the system of equations numerically using Radau method
    sol = solve_ivp(f, t_span, y0, method='Radau', t_eval=np.linspace(0, 50e-3,
2000), args=(w,))

    if sol.success:
        # Extract the x and y values
        x = sol.t
        y = sol.y.T # Transpose y to match the dimensions

        # Save the values to a file
        np.savetxt('popEu105.csv', np.column_stack((x, y)), delimiter=',',
header='x,p0,p1,p2,p3,p4', comments='')

        # Alternatively, you can save them as separate arrays
        # x = sol.t
        # p0 = sol.y[0]
        # p1 = sol.y[1]
        # p2 = sol.y[2]
        # p3 = sol.y[3]
        # p4 = sol.y[4]

        # Plot the results if desired
        # import matplotlib.pyplot as plt

```

```

    # plt.plot(x, p0, label='p0')
    # plt.plot(x, p1, label='p1')
    # plt.plot(x, p2, label='p2')
    # plt.plot(x, p3, label='p3')
    # plt.plot(x, p4, label='p4')
    # plt.xlabel('Time')
    # plt.ylabel('Values')
    # plt.title('System of Equations')
    # plt.legend()
    # plt.show()
else:
    print('Integration failed.')
except Exception as e:
    print('Error during integration:', str(e))

```

Considering the Ln<sup>III</sup>-to-Ln<sup>III</sup> ET:

```

# Population extractor
# Created by Leonardo F. Saraiva

from scipy.integrate import solve_ivp
import numpy as np

# define the rate equations. Here it is defined the populations P0, P1, P2, P3.

# Considering Ln-to-Ln ET.

# phi = pumping rate.

# Atb = 1/tTb (inverse of Tb lifetime)

# AEu = 1/Eu (inverse of Eu lifetime)

# W12 = Rates of ET from 5D4 to 5DJ states, where J := 0;

# W13 = Rates of ET from 5D4 to 5D0 state;

# W23 = Rates of multiphonon decay.

def f(t, y, w):
    P0, P1, P2, P3 = y

    phi, Atb, Aeu, W12, W13, W23 = w

    dp0dt = -phi*P0 + Atb*P1 + Aeu*P3

```

```

dp1dt = -(Atb + W12 + W13)*P1 + phi*P0

dp2dt = -W23*P2 + W12*P1

dp3dt = -Aeu*P3 + W13*P1 + W23*P2

return [dp0dt, dp1dt, dp2dt,dp3dt]

# Set the initial conditions and time range

# At t = 0, only the ground level is populated (p0 = 1).

y0 = [1.0, 0.0, 0.0, 0.0]

#define the time range (0, tf). Usually 10 - 50 ms.

# Substitute the tf value in the t_eval=[] (try block).

t_span = (0, 50e-3)

# Set the values of wij (scaled down)

# w = [phi, (1/tTb), (1/tEu), W12, W13, W23]

# Remove # from the previous line.

try:
    # Solve the system of equations numerically using Radau method
    sol = solve_ivp(f, t_span, y0, method='Radau', t_eval=np.linspace(0, 50e-3,
2000), args=(w,))

    if sol.success:
        # Extract the x and y values
        x = sol.t
        y = sol.y.T # Transpose y to match the dimensions

        # Save the values to a file
        np.savetxt('pop.csv', np.column_stack((x, y)), delimiter=',',
header='x,P0,P1,P2,P3', comments='')

        # Alternatively, you can save them as separate arrays
        # x = sol.t
        # p0 = sol.y[0]
        # p1 = sol.y[1]

```

```
# p2 = sol.y[2]
# p3 = sol.y[3]

# Plot the results if desired
# import matplotlib.pyplot as plt
# plt.plot(x, p0, label='p0')
# plt.plot(x, p1, label='p1')
# plt.plot(x, p2, label='p2')
# plt.plot(x, p3, label='p3')
# plt.plot(x, p4, label='p4')
# plt.xlabel('Time')
# plt.ylabel('Values')
# plt.title('System of Equations')
# plt.legend()
# plt.show()
else:
    print('Integration failed.')
except Exception as e:
    print('Error during integration:', str(e))
```

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