

# Dynamics of the Energy Transfer Process in Eu(III) Complexes Containing Polydentate Ligands Based on Pyridine, Quinoline, and Isoquinoline as Chromophoric Antennae

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Cite This: *Inorg. Chem.* 2022, 61, 16333–16346



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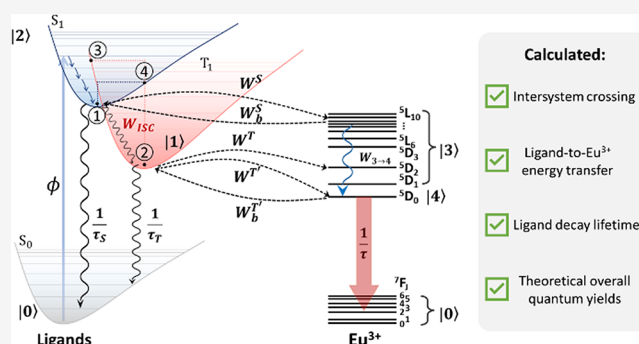
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**ABSTRACT:** In this work, we investigated from a theoretical point of view the dynamics of the energy transfer process from the ligand to Eu(III) ion for 12 isomeric species originating from six different complexes differing by nature of the ligand and the total charge. The cationic complexes present the general formula  $[\text{Eu}(\text{L})(\text{H}_2\text{O})_2]^+$  (where  $\text{L} = \text{bpcd}^{2-} = N,N'$ -bis(2-pyridylmethyl)-*trans*-1,2-diaminocyclohexane  $N,N'$ -diacetate;  $\text{bQcd}^{2-} = N,N'$ -bis(2-quinolinmethyl)-*trans*-1,2-diaminocyclohexane  $N,N'$ -diacetate; and  $\text{bisoQcd}^{2-} = N,N'$ -bis(2-isoquinolinmethyl)-*trans*-1,2-diaminocyclohexane  $N,N'$ -diacetate), while the neutral complexes present the  $\text{Eu}(\text{L})(\text{H}_2\text{O})_2$  formula (where  $\text{L} = \text{PyC3A}^{3-} = N$ -picolyl- $N,N',N'$ -*trans*-1,2-cyclohexylenediaminetriacetate;  $\text{QC3A}^{3-} = N$ -quinolyl- $N,N',N'$ -*trans*-1,2-cyclohexylenediaminetriacetate; and  $\text{isoQC3A}^{3-} = N$ -isoquinolyl- $N,N',N'$ -*trans*-1,2-cyclohexylenediaminetriacetate). Time-dependent density functional theory (TD-DFT) calculations provided the energy of the ligand excited donor states, distances between donor and acceptor orbitals involved in the energy transfer mechanism ( $R_L$ ), spin-orbit coupling matrix elements, and excited-state reorganization energies. The intramolecular energy transfer (IET) rates for both singlet-triplet intersystem crossing and ligand-to-metal (and vice versa) involving a multitude of ligand and Eu(III) levels and the theoretical overall quantum yields ( $\phi_{\text{ovl}}$ ) were calculated (the latter for the first time without the introduction of experimental parameters). This was achieved using a blend of DFT, Judd–Ofelt theory, IET theory, and rate equation modeling. Thanks to this study, for each isomeric species, the most efficient IET process feeding the Eu(III) excited state, its related physical mechanism (exchange interaction), and the reasons for a better or worse overall energy transfer efficiency ( $\eta_{\text{sens}}$ ) in the different complexes were determined. The spectroscopically measured  $\phi_{\text{ovl}}$  values are in good agreement with the ones obtained theoretically in this work.



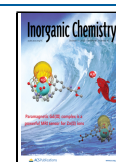
## INTRODUCTION

The nonradiative intramolecular energy transfer (IET) process (also called *antenna effect*) is broadly exploited to increase the brightness of luminescent metal complexes, in particular for trivalent lanthanide ions<sup>1</sup> when, for example, these molecules are employed as optical probes for imaging<sup>1–4</sup> and luminescent sensing.<sup>5–14</sup> For such a class of compounds, brightness is defined as  $B = \epsilon \cdot \phi_{\text{ovl}} = \epsilon \cdot \eta_{\text{sens}} \cdot \phi_{\text{int}}$ , where  $\epsilon$  is the molar absorption coefficient,  $\phi_{\text{ovl}}$  is the overall quantum yield, i.e., the ratio of emitting/absorbed photons by the matrix/ligand,  $\eta_{\text{sens}}$  is the overall energy transfer efficiency, and  $\phi_{\text{int}}$  is the intrinsic quantum yield, i.e., the ratio of emitting/absorbed photons upon direct excitation into a luminescent level of the lanthanide ion. Thus, to obtain high values of brightness, the combination of high  $\epsilon$ ,  $\eta_{\text{sens}}$ , and  $\phi_{\text{int}}$  values is required ( $\eta_{\text{sens}} = \eta_{\text{ISC}} \cdot \eta_{\text{IET}}$ ; where  $\eta_{\text{ISC}}$  and  $\eta_{\text{IET}}$  are the efficiency of the intersystem crossing (ISC)<sup>15</sup> and the IET processes, respectively). In this direction, one should avoid nonradiative

processes, which negatively impact the  $\phi_{\text{int}}$  value. These processes consist of (i) multiphonon relaxation (MPR) and (ii) backward energy transfer. They both may induce the nonradiative relaxation of the emitting levels, and the MPR process is particularly effective when high-energy vibrational modes (e.g., C–H, N–H, and O–H stretching) couple with the lanthanide electronic levels.<sup>16–18</sup> To obtain high  $\epsilon$  and  $\eta_{\text{sens}}$  values, chromophoric ligands are employed, since they are capable, at the same time, of strong absorption of light (high  $\epsilon$

Received: July 4, 2022

Published: October 6, 2022



value, usually in the UV spectral range) and efficiently transfer the excitation energy to the lanthanide ion (high  $\eta_{\text{sens}}$  values).

From Dexter's theory,<sup>19</sup> nonradiative energy transfer processes from a donor (D, in the present case the ligand) to an acceptor (A, the lanthanide ion) can occur mainly by electric dipole–dipole, electric dipole–quadrupole, and exchange interactions. To optimize the efficiency of this process, the following requirements must be satisfied: (i) selection rules in the transitions of both D and A, (ii) short D–A distance ( $R_{\text{D}}$ ), and (iii) strong spectral overlap of the emission band of D and the absorption band of A. In order to control all these features, precise knowledge of the D–A interaction is required. A complete and detailed description of the mechanism based on this interaction can be obtained by means of a combined experimental and theoretical study.<sup>20</sup> The photon absorption by D leads to an electron excitation that can result in  $S_0 \rightarrow S_1$  or  $S_0 \rightarrow T_1$  transitions. The  $S_1$  state may nonradiatively transfer energy to a triplet excited state  $T_1$  (a process known as intersystem crossing—ISC) or transfer energy to A (lanthanide ion), while the  $S_0 \rightarrow T_1$  excitation involves a spin-forbidden transition and is much less probable than a triplet state will form. Ln(III)-based complexes favor ISC as a result of their more intense spin-orbit coupling (SOC),<sup>21</sup> which grows with the fourth power of the atomic number  $Z$ . Consequently, the theoretical methodology applied to account the D–A interaction requires the proper treatment of relativistic effects, which can be included by different methodologies, namely, the zero-order regular approximation (ZORA),<sup>22,23</sup> the Douglas–Kroll–Hess (DKH)<sup>24,25</sup> Hamiltonian, or the normalized elimination of the small component (NESC) method<sup>26</sup> and its updates and new implementations.<sup>27–31</sup> These methods offer different strengths and computational costs and are scalar relativistic corrections for the contraction of *s*- or *p*-orbitals and the expansion of *d*- or *f*-orbitals.

The  $S_0 \rightarrow T_1$  and  $S_1 \rightarrow T_1$  ISC at the scalar relativistic level is spin-forbidden, but SOC induces fast ISC by mixing singlet and triplet states, enabling these processes. Thus, accurate theoretical methods that can treat excited states with SOC in the presence of heavy elements are necessary for a precise description of the D–A interaction.<sup>32</sup> While different works in literature<sup>33</sup> approach the ISC for organic and *d*-metal complexes, few works<sup>34</sup> apply this type of calculation in lanthanide spectroscopy. However, the direct utilization of ISC for  $S_1 \rightarrow T_1$  and  $T_1 \rightarrow S_0$  nonradiative energy transfer rates on the calculation of the theoretical overall quantum yield ( $\phi_{\text{ovl}}$ ), as far as we know, is not found in the literature for a big set of Eu(III) excited states.

For this reason, in this paper, we present a detailed theoretical investigation, employing a blend of density functional theory (DFT), Judd–Ofelt theory, IET theory, and rate equation modeling, aimed to determine the relevant photophysical properties for 12 isomeric species originating from six different complexes previously designed and synthesized. These results, combined with an experimental spectroscopic study, mainly carried out previously by some of us,<sup>10,12,35</sup> give a detailed picture of the energy transfer mechanism in the different compounds. In particular, for Eu(III) complexes, we have determined (i) the nature and energy of the ligand levels ( $S_1$  and  $T_1$  donors) from DFT calculations; (ii) the D–A distances; (iii) the SOC matrix elements and reorganization energies for  $S_1 \rightarrow T_1$  ( $\lambda_{\text{M}}$ ) to calculate ISC rates ( $W_{\text{ISC}}$ ); (iv) the reliable  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow$

$T_1$  (via SOC) dipole strengths to calculate  $S_0$  and  $T_1$  lifetimes; and (v) the contribution of dipole–dipole, dipole–quadrupole, and exchange mechanisms to the energy transfer process.

For the first time, the five points described above are used to perform simulations of the emitting-level populations from an appropriate rate equation model. Furthermore, these simulations permit the quantification of theoretical overall quantum yield ( $\phi_{\text{ovl}}$ ) without the introduction of experimental parameters. Thanks to this detailed study, we have been able to determine for each complex the main ligand and Eu(III) levels involved in the IET processes, the related physical mechanism, and the reasons for the better or worse overall energy transfer efficiency observed.

The deep knowledge of these photophysical properties is crucial in order to properly employ these classes of Eu(III) complexes as optical probes for the detection of important bioanalytes (i.e., citrate,<sup>10</sup> serum proteins,<sup>11</sup> hydrogen carbonate,<sup>12</sup> and lactate<sup>13</sup>).

## THEORETICAL AND COMPUTATIONAL PROCEDURES

**Computational Procedures.** All molecular structures of the complexes were obtained by means of DFT calculations run in Gaussian 16 (version A.03).<sup>36</sup> The paramagnetic Eu(III) ion has been replaced by Y(III), which is a suitable substitute as shown in a previous work<sup>13</sup> and as can be deduced from the isostructural complexes with the analogous hexa-dentate ligands ethylenediaminetetraacetic acid (EDTA) and cyclohexanediaminetetraacetic acid (CDTA). In the crystal structures with these ligands, Y(III) and Eu(III) ions are nine-coordinated with EDTA (three water molecules bound) and eight-coordinated with CDTA (two bound waters).<sup>37–39</sup>

The functional B3LYP<sup>40,41</sup> was used with the 6–31+G(d) basis set for all ligand atoms and MWB28 pseudo-potential and the valence electron basis set for the metal ion.<sup>42</sup> Geometry optimizations were carried out at the DFT level with the solvent effect accounted by the polarizable continuum model (PCM) with the parameters for water.<sup>43</sup>

The excited states ( $T_1$  and  $S_1$ ) were obtained employing the time-dependent DFT approach (TD-DFT)<sup>44</sup> using the same procedure described for the geometry optimizations (B3LYP/MWB28(Y)/6–31+G(d)/PCM).

$W_{\text{ISC}}$  was calculated using the Marcus–Levich<sup>45–47</sup> formalism. The values of  $\lambda_{\text{M}}$  were calculated utilizing the same procedure (B3LYP/MWB52(Eu)/6–31+G(d)/PCM) but selecting  $S_1$  and  $T_1$  excited states (from the TD-DFT calculations) for the geometry optimizations. The SOC matrix elements were calculated using SOC-TD-DFT<sup>48</sup> in ORCA5.0,<sup>49</sup> utilizing the B3LYP functional with ZORA<sup>23</sup> relativistic corrections. The recontracted ZORA-DEF2-TZVP<sup>50</sup> basis set for ligands and segmented all-electron relativistically contracted (SARC)-ZORA-TZVP for Eu atoms<sup>51</sup> were utilized. The calculations were done with the SARC/J auxiliary basis<sup>51,52</sup> and the resolution of the identity spin-orbit mean-field RI-SOMF<sup>53</sup> approximation. The calculated values of  $\lambda_{\text{M}}$  and SOC matrix elements, as well as the  $W_{\text{ISC}}$  rates, can be found in Table S15. Taking advantage of the SOC-TD-DFT approach, the dipole strengths of  $S_0 \rightarrow T_1$  and  $S_0 \rightarrow S_1$  excitations were obtained for calculating the  $S_1$  and  $T_1$  decay lifetimes ( $\tau_{\text{S}}$  and  $\tau_{\text{T}}$ , respectively) from Eq. S12.

**Intramolecular Energy Transfer.** The IET rates from organic ligands to Eu(III) ion were estimated taking into

consideration the dipole–dipole ( $W_{d-d}$ ), dipole–multipole ( $W_{d-m}$ ), and exchange ( $W_{ex}$ ) mechanisms:<sup>20,54–57</sup>

$$W_{d-d} = \frac{S_L(1 - \sigma_1)^2}{(2J + 1)G} \frac{4\pi}{\hbar} \frac{e^2}{R_L^6} \times \sum_{\lambda} \Omega_{\lambda}^{\text{FED}} \langle \psi'J' || U^{(\lambda)} || \psi J \rangle^2 F \quad (1)$$

$$W_{d-m} = \frac{S_L}{(2J + 1)G} \frac{2\pi e^2}{\hbar} \sum_{\lambda} (\lambda + 1) \frac{\langle r^{\lambda} \rangle^2}{(R_L^{\lambda+2})^2} \times \langle f || C^{(\lambda)} || f \rangle^2 (1 - \sigma_{\lambda})^2 \langle \psi'J' || U^{(\lambda)} || \psi J \rangle^2 F \quad (2)$$

$$W_{ex} = \frac{(1 - \sigma_0)^2}{(2J + 1)G} \frac{8\pi}{\hbar} \frac{e^2}{R_L^4} \langle \psi'J' || S || \psi J \rangle^2 \times \sum_m |\langle \phi_l | \sum_j \mu_z(j) s_m(j) | \phi^* \rangle|^2 F \quad (3)$$

where  $R_L$  is the donor–acceptor state distance and  $\Omega_{\lambda}^{\text{FED}}$  (ESI) are the intensity parameters (or Judd–Ofelt parameters) by the forced electric dipole (FED) mechanism.<sup>58,59</sup> The simple overlap model<sup>60,61</sup> was employed to calculate these quantities through the JOYSpectra web platform.<sup>62</sup> The values of the squared reduced matrix elements  $\langle \psi'J' || U^{(\lambda)} || \psi J \rangle^2$  were taken from Carnall et al.,<sup>63</sup> whereas the  $\langle \psi'J' || S || \psi J \rangle$  matrix elements were calculated using free-ion wavefunctions in the intermediate coupling scheme.<sup>64,65</sup> The values of  $\langle \psi'J' || S || \psi J \rangle$  for allowed ( $|\Delta J| = 0$  or  $1$ )  ${}^7F_0 \rightarrow {}^5D_1$ ,  ${}^7F_1 \rightarrow {}^5D_0$ ,  ${}^7F_1 \rightarrow {}^3D_1$ ,  ${}^7F_1 \rightarrow {}^5D_2$ , and  ${}^7F_1 \rightarrow {}^5G_2$  acceptor transitions are reported in Table S2 in the ESI.  $S_L$  is the dipole strength of the ligand transition involved in IET ( $10^{-36}$  and  $10^{-40}$  ( $\text{esu}^2 \cdot \text{cm}^2$ ) for  $S_1$  and  $T_1$ , respectively<sup>20</sup>),  $\langle r^{\lambda} \rangle$  are the  $4f$  radial integrals,<sup>66</sup>  $G$  is the ligand state degeneracy ( $G = 1$  or  $3$  for  $S_1$  or  $T_1$ , respectively),  $\langle f || C^{(\lambda)} || f \rangle$  is the reduced matrix element of Racah's tensor operators,<sup>67</sup> and  $(1 - \sigma_k)$  (for  $k = 1$  and  $2$ ) are the shielding factors, which have a relation with the overlap integrals between valence orbitals of the pair Ln–X ( $X$  as the ligating atom in the first coordination sphere).<sup>57,68</sup> The values of  $(1 - \sigma_k)$  for  $k = 4$  and  $6$  can be found in ref 66.  $s_m$  (in eq 3) is the spin operator in the ligand, and  $\mu_z$  is the dipole operator ( $z$  component); the value of the element matrix of these coupled operators is  $10^{-36}$  ( $\text{esu}^2 \cdot \text{cm}^2$ ).<sup>20,69</sup>

The  $F$  term in eqs 1–3 is the density of states (proportional to the spectral overlap) that considers the energy mismatch condition between donor (ligands) and acceptor states (Ln(III) ion).<sup>20,54</sup>  $F$  can be estimated by

$$F = \frac{1}{\hbar\gamma_D} \sqrt{\frac{\ln(2)}{\pi}} e^{-\left(\frac{\Delta}{\hbar\gamma_D}\right)^2 \ln(2)} \quad (4)$$

where  $\Delta$  is the energy difference between the donor barycenter state and the lanthanide ion acceptor state ( $\Delta = E_D - E_A$ ).  $\gamma_D$  is the bandwidth at half-height of the donor states ( $S_1$  and  $T_1$ ), assumed here to have a typical value of  $\gamma_D = 3000 \text{ cm}^{-1}$  for both  $S_1$  and  $T_1$  states.<sup>70,71</sup>

The forward energy transfer rates ( $W$ ) involving the Eu(III) ions as acceptors are calculated by the sum over eqs 1–3 in the same pathway:

$$W = W_{d-d} + W_{d-m} + W_{ex} \quad (5)$$

If  $\Delta$  is negative, for a given energy transfer pathway,  $W$  must be multiplied by the energy barrier factor  $\exp(\Delta/k_B T)$ , where  $k_B$  is the Boltzmann constant and  $T$  is the temperature (considered

to be 298.15 K in the present work). For example, consider that a given forward pathway  $T_1 \rightarrow [{}^7F_0 \rightarrow {}^{2S+1}L_J]$  has  $\Delta = -500 \text{ cm}^{-1}$ , then the total rate (eq 5) of this specific pathway should be multiplied by 0.09 (barrier factor). The barrier factor is not applied for the backward energy transfer [ ${}^{2S+1}L_J \rightarrow {}^7F_0$ ]  $\rightarrow T_1$  because  $\Delta = 500 \text{ cm}^{-1}$ . In addition, depending on the Eu(III) initial state involved in the energy transfer pathway (e.g.,  ${}^7F_1$  in the  $T_1 \rightarrow [{}^7F_1 \rightarrow {}^5D_1]$  pathway or  ${}^7F_0$  in the  $S_1 \rightarrow [{}^7F_0 \rightarrow {}^5L_6]$  pathway),  $W$  is multiplied by the thermal population fraction at room temperature (0.64 for  ${}^7F_0$  and 0.33 for  ${}^7F_1$ ).<sup>65,72</sup>

The IET rates from the ligands to the Eu(III) ion were calculated using both  $S_0 \leftarrow S_1$  and  $S_0 \leftarrow T_1$  decay transitions as energy donors localized in the ligands and a total of 32 energy transfer pathways involving  ${}^7F_0$  and  ${}^7F_1$  as initial states and  ${}^5D_0$ ,  ${}^5D_1$ ,  ${}^5D_2$ ,  ${}^5D_3$ ,  ${}^5L_6$ ,  ${}^5L_7$ ,  ${}^5G_2$ ,  ${}^5G_3$ ,  ${}^5G_4$ ,  ${}^5G_6$ ,  ${}^5D_4$ ,  ${}^5G_5$ ,  ${}^5L_8$ ,  ${}^5D_4$ ,  ${}^5L_9$ , and  ${}^5L_{10}$  as final states at the Eu(III) ion. Consequently, 64 IET pathways were computed for each one of the 12 studied complexes, totaling 768 IET rates analyzed (half of them are non-zero due to selection rules on the  $J$  quantum number<sup>20</sup>).

#### Rate Equations and Overall Emission Quantum Yield.

Once the IET rates are determined, the system of rate equations constituted by coupled ordinary differential equations (ODEs) can be solved to determine the relative population of each level. The set of ODEs can be solved in the analytical form, which assumes that the system is in a steady-state regime (all derivatives equal to zero) and the ground levels are very little depleted. Thus, the population of the Ln(III) emitting level is given by analytical expressions.<sup>20,65,73,74</sup> On the other hand, the set of coupled ODEs can be solved by numerical methods through time propagation. This approach was adopted in this work.

The set of ODEs can be described as follows:<sup>14,20,75</sup>

$$\frac{dP_i(t)}{dt} = \sum_{j=1} W_{j \rightarrow i} P_j(t) - \sum_{j=1} W_{i \rightarrow j} P_i(t), \text{ with } i \neq j \quad (6)$$

where both summations run all levels of the system.  $P_i$  and  $P_j$  are the populations of the levels  $|i\rangle$  and  $|j\rangle$  and  $W_{j \rightarrow i}$  and  $W_{i \rightarrow j}$  are the energy transfer rates between these states. Thus, an  $N$ -level rate equation model can be described by a set formed by  $N$ -coupled ODEs. The appropriate set of rate equations, with their respective initial conditions, can be numerically solved using several methods such as fourth-order Runge–Kutta with fixed-step or adaptive-step size, Radau, and Adams–Bashforth, among others.<sup>76</sup> We adopted the Radau method<sup>77</sup> in the simulations since it was applied in other Ln-based complexes and provided very consistent results<sup>14,78–83</sup> with a low computational cost. Each simulation was done in a time interval from 0 to 10 ms with a step-size of  $2 \mu\text{s}$ .

The solution of the rate equation model permits the estimation of the emitting level population  $P_E$  of the Ln(III) (e.g.,  ${}^5D_0$  of the Eu(III) ion), and consequently, the emission intensity  $I = A_{\text{rad}} P_E$ , where  $A_{\text{rad}}$  (Table S1) is the spontaneous emission coefficients, which can be calculated from the Judd–Ofelt intensity parameters.<sup>20,58,59,62,63,84</sup>

The overall quantum yield  $\phi_{\text{ovl}}$  is defined by the ratio of the numbers of photons emitted and absorbed by the matrix/ligand,<sup>1,20,85,86</sup>

$$\phi_{\text{ovl}} = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} = \frac{A_{\text{rad}} P_E}{\phi P_0} \quad (7)$$

where  $P_0$  is the population of the ground level and  $\phi$  is the pumping rate of the populations from this level (e.g.,  $S_0 \rightarrow S_1$  intra-ligand absorptions). The latter can be estimated by  $\phi = \sigma \rho \lambda_{\text{exc}} / hc$ , where  $\sigma$  is the absorption cross section of the ligand (in the order of  $\sim 10^{-16} \text{ cm}^2 \cdot \text{molecule}^{-1}$ ),<sup>87</sup>  $\rho$  is the power density in units of watts per square centimeter,  $\lambda_{\text{exc}}$  is the excitation wavelength,  $h$  is Planck's constant, and  $c$  is the speed of light.<sup>14,78,79,88</sup>

## EXPERIMENTAL MEASUREMENTS

The overall quantum yields  $\phi_{\text{ovl}}$  for the complexes  $[\text{Eu}(\text{bisoQcd})(\text{H}_2\text{O})_2]^+$  and  $[\text{Eu}(\text{isoQC3A})(\text{H}_2\text{O})_2]$  were experimentally obtained by secondary methods described in the literature<sup>89</sup> by measuring the visible emission spectrum of quinine bisulfate in 0.5 M  $\text{H}_2\text{SO}_4$  solution, a fluorescence quantum yield reference sample ( $\phi_s = 54.6\%$ ).  $\phi_{\text{ovl}}$  for the complexes is calculated by the equation  $\phi_{\text{ovl}} = [(A_s \cdot F_u \cdot n^2) / (A_u \cdot F_s \cdot n_0^2)] \cdot \phi_s$ , where the u subscript refers to unknown (the sample under investigation) and s to the standard, and other symbols have the following meanings:  $\phi_s$  is the overall quantum yield of the reference sample,  $A$  is the absorbance at the excitation wavelength,  $F$  is the integrated emission area across the band, and  $n$ 's are respectively the index of refraction of the solvent containing the unknown ( $n$ ) and the standard ( $n_0$ ) at the sodium D line and the temperature of the emission measurement (see ESI, Figures S16 and S17). The measurements were repeated three times, and the averaged value is provided.

## RESULTS AND DISCUSSION

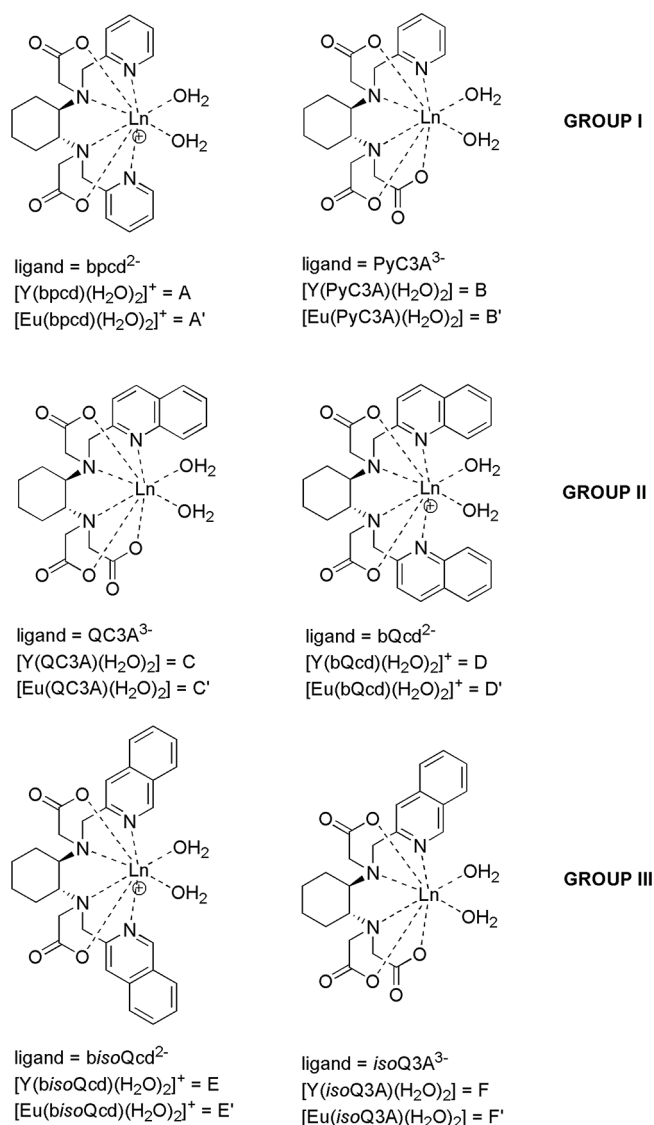
**Structural and Thermodynamic Properties of the Complexes in Aqueous Solution.** The chemical structures and the labels of the Eu(III) and Y(III) complexes described in this work are shown in Figure 1. The Eu(III) compounds were previously synthesized and spectroscopically characterized, and the Y(III) counterparts have been used exclusively as a computational structural model of the paramagnetic Eu(III) analogs, in view of the similar ionic radii of the two cations.<sup>90,91</sup>

For the sake of clarity, the investigated complexes have been divided into three groups, differing by the nature of the heteroaromatic ring: pyridine (group I), quinoline (group II), and isoquinoline (group III).

The protonation constants ( $\log K$ ) of the considered ligands are reported in Table 1. These values indicate that two fairly strong acidic and two weakly acidic sites are present. As previously discussed,<sup>10–12,35</sup> the values for the first protonation constants of the ligands are in agreement with those reported for tertiary amines ( $\log K \sim 6.9–10.7$ , depending on the substituents),<sup>92</sup> suggesting that the first protonation constant can be assigned to an aliphatic amino group, as previously reported for CDTA.<sup>93</sup> The remaining protonation constants are ascribed to heteroaromatic (pyridine, quinoline, and isoquinoline) rings and acetate moieties.<sup>10–12,35</sup>

As for the speciation in aqueous solutions of the investigated complexes, at the physiological pH = 7.4, the ML species is largely predominant in all cases (>99%), with the exception of bpcd-based complexes for which a small amount (around 5%) of the neutral hydroxo  $[\text{Eu}(\text{bpcd})(\text{OH})(\text{H}_2\text{O})]$  complex was also detected.<sup>35</sup>

Because of the strong oxophilicity of the Ln(III) ions,<sup>91</sup> the stability constants ( $\log \beta$ ) for the triacetate ligands [PyC3A, QC3A, and isoQC3A] are higher than their diacetate analogues [bpcd, bQcd, and bisoQcd, respectively]. Besides, the stability constants of the Eu(III) complexes with the quinoline- and isoquinoline-substituted ligands are lower than for their pyridine analogues (bpcd and PyC3A). This result could be



**Figure 1.** Chemical structures of the Ln(III) complexes studied in this work. Ln = Y(III) and Eu(III).

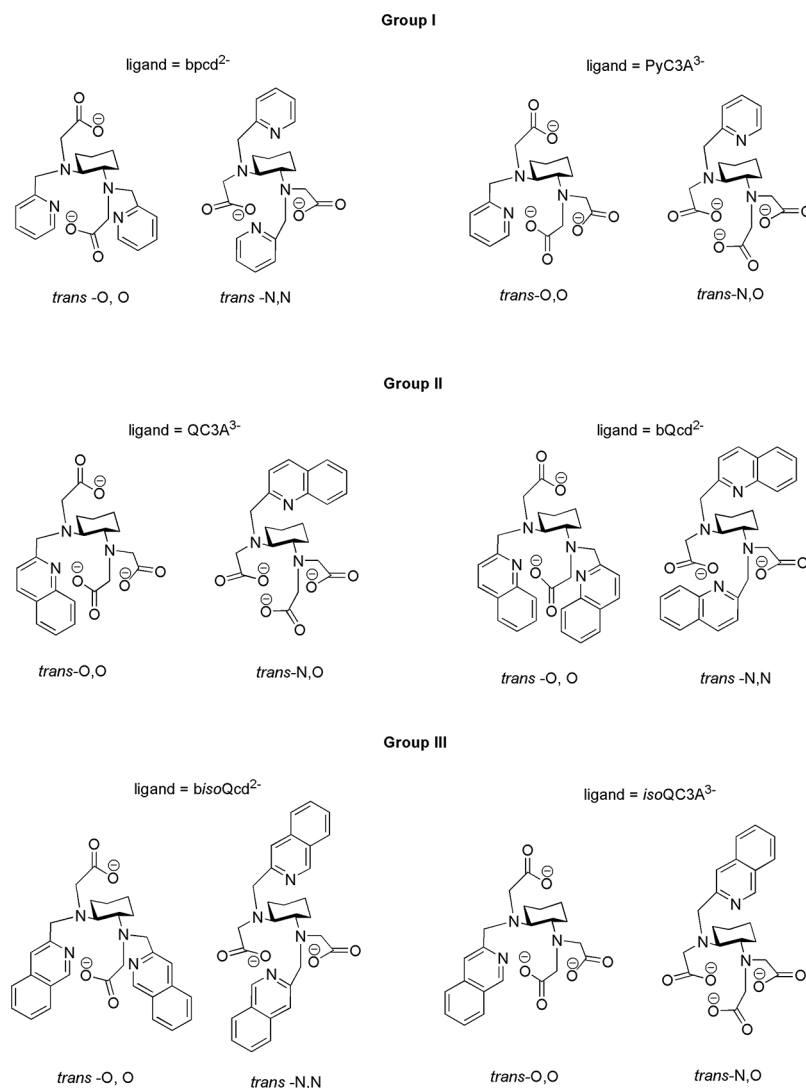
due to a weaker interaction of the quinoline moieties with the metal ion with respect to the pyridine ones and to the increased steric hindrance. From the perspective of the biological applications, the values of  $\log \beta$  appear promising, in particular for the triacetate-based ligands (PyC3A, QC3A, and isoQC3A) whose stability is close to that of macrocyclic ligands possessing a similar coordination ability and already employed in molecular imaging applications (i.e., DO3A derivatives with  $\log \beta$  values in the 18–21 range<sup>94</sup>).

Molecular models obtained from DFT calculations on the Y(III) counterparts (complexes A–F) of Eu(III) complexes show that Y(III) is in all cases eight-fold coordinated with six donor atoms belonging to the ligand and two oxygen atoms to coordinated water molecules, the general formula being  $[\text{Y}(\text{L})(\text{H}_2\text{O})_2]$ , as illustrated in Figure 1. As two different coordination geometries, differing by the stereochemistry of the sp<sup>3</sup> nitrogen atoms, are possible for each ligand (Figure 2), DFT calculations are performed on 12 species, whose labeling is reported in Table 2 while the minimum energy structures are shown in Figure 3.

**Table 1. Protonation Constants ( $\log K_i$ ) and Formation Constants ( $\log \beta$ ) for the Complexes with Eu(III) Described in This Work at 298.15 K and  $\mu = 0.1$  M NaCl<sup>a</sup>**

reaction	bpcd <sup>b</sup>	PyC3A <sup>c</sup>	bQcd <sup>d</sup>	QC3A <sup>c</sup>	bisoQcd <sup>d</sup>	isoQC3A <sup>e</sup>	CDTA <sup>f</sup>
	$\log K_i$						
L + H $\rightleftharpoons$ HL	9.72	10.26	9.37	10.53	9.27	9.43	9.43
HL + H $\rightleftharpoons$ H <sub>2</sub> L	5.87	6.33	5.85	6.29	5.86	7.37	6.01
H <sub>2</sub> L + H $\rightleftharpoons$ H <sub>3</sub> L	2.94	3.67	3.46	3.60	3.43	3.32	3.68
H <sub>3</sub> L + H $\rightleftharpoons$ H <sub>4</sub> L	2.22	2.01	1.79	2.81	1.62	2.16	2.51
	$\log \beta$						
L + Eu $\rightleftharpoons$ EuL	11.19	15.68	9.97	12.55	10.53	14.63	19.60

<sup>a</sup>Additional protonation and formation constants data of the analog CDTA ligand are also reported for comparison. Charges are omitted for simplicity. <sup>b</sup>Data from ref 35. <sup>c</sup>Data from ref 12. <sup>d</sup>Data from ref 11. <sup>e</sup>Data from ref 10. <sup>f</sup>CDTA: cyclohexanediaminetetraacetic acid; data taken from ref 95.

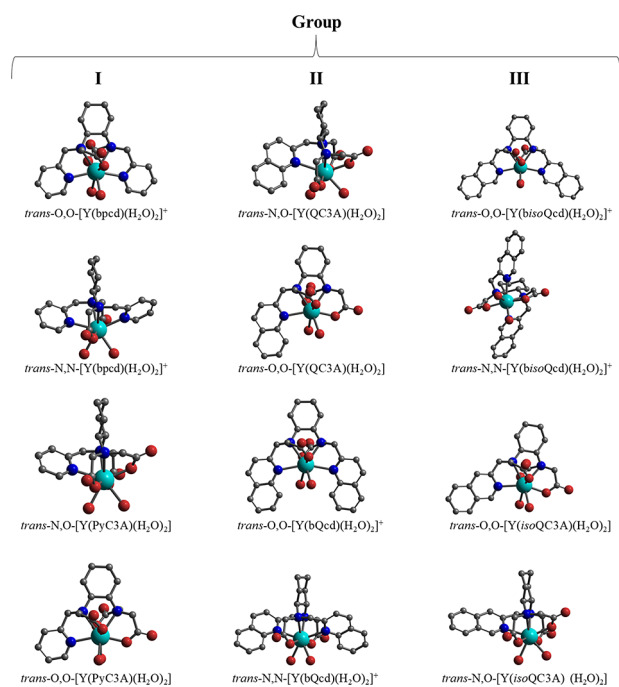
**Figure 2.** Possible coordination geometries of the ligands in this paper.

From a structural point of view, the increase in steric crowding when passing from pyridine- to the quinoline-substituted ligands is clearly seen upon inspection of the structures shown in Figure 3. This steric increase may reflect the change in Judd–Ofelt intensity parameters, more precisely in the general interpretation that  $\Omega_4$  and  $\Omega_6$  parameters correlate with the rigidity of a compound.<sup>96,97</sup> Accordingly, an increase in the average  $\bar{\Omega}_4$  and  $\bar{\Omega}_6$  (Table S1) between groups is observed:  $\bar{\Omega}_{4,6}(\text{I}) < \bar{\Omega}_{4,6}(\text{II}) < \bar{\Omega}_{4,6}(\text{III})$ .

From the resulting bond distances (Table 3), it emerges that the substitution of pyridine by quinoline or isoquinoline has nearly no effect on the Y(III)–O<sub>acetate</sub> bonds (average variation,  $\Delta\text{Py} \rightarrow \text{Q} \sim -0.001$  and  $+0.005$  Å for the di- and tri-acids, respectively), and the Y(III)–N<sub>amine</sub> distances are marginally affected ( $\Delta\text{Py} \rightarrow \text{Q} \sim -0.019$  and  $-0.006$  Å). It can also be noted that Y(III)–O<sub>water</sub> bonds are slightly longer in the pyridine triacid isomers as could be expected on the basis of the decreased charge on the metal ion, while in the quinoline

**Table 2.** Labels, Group Membership, and Formula of the Complexes in This Paper

complex	isomer	formula	group
A	1	<i>trans</i> -O,O-[Y(bpcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	I
	2	<i>trans</i> -N,N-[Y(bpcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	
A'	1'	<i>trans</i> -O,O-[Eu(bpcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	
	2'	<i>trans</i> -N,N-[Eu(bpcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	
B	3	<i>trans</i> -N,O-[Y(PyC3A)(H <sub>2</sub> O) <sub>2</sub> ]	
	4	<i>trans</i> -O,O-[Y(PyC3A)(H <sub>2</sub> O) <sub>2</sub> ]	
B'	3'	<i>trans</i> -N,O-[Eu(PyC3A)(H <sub>2</sub> O) <sub>2</sub> ]	
	4'	<i>trans</i> -O,O-[Eu(PyC3A)(H <sub>2</sub> O) <sub>2</sub> ]	
C	5	<i>trans</i> -N,O-[Y(QC3A)(H <sub>2</sub> O) <sub>2</sub> ]	II
	6	<i>trans</i> -O,O-[Y(QC3A)(H <sub>2</sub> O) <sub>2</sub> ]	
C'	5'	<i>trans</i> -N,O-[Eu(QC3A)(H <sub>2</sub> O) <sub>2</sub> ]	
	6'	<i>trans</i> -O,O-[Eu(QC3A)(H <sub>2</sub> O) <sub>2</sub> ]	
D	7	<i>trans</i> -O,O-[Y(bQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	
	8	<i>trans</i> -N,N-[Y(bQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	
D'	7'	<i>trans</i> -O,O-[Eu(bQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	
	8'	<i>trans</i> -N,N-[Eu(bQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	
E	9	<i>trans</i> -O,O-[Y(bisoQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	III
	10	<i>trans</i> -N,N-[Y(bisoQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	
E'	9'	<i>trans</i> -O,O-[Eu(bisoQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	
	10'	<i>trans</i> -N,N-[Eu(bisoQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup>	
F	11	<i>trans</i> -O,O-[Y(isoQC3A)(H <sub>2</sub> O) <sub>2</sub> ]	
	12	<i>trans</i> -N,O-[Y(isoQC3A)(H <sub>2</sub> O) <sub>2</sub> ]	
F'	11'	<i>trans</i> -O,O-[Eu(isoQC3A)(H <sub>2</sub> O) <sub>2</sub> ]	
	12'	<i>trans</i> -N,O-[Eu(isoQC3A)(H <sub>2</sub> O) <sub>2</sub> ]	

**Figure 3.** Group assignment, formula, and minimum energy DFT structure of the possible isomers of the Y(III) counterparts of the investigated Eu(III) complexes. Hydrogen atoms are removed for clarity.

complexes, they are only slightly affected. However, the most remarkable finding is that the average Y(III)–N<sub>heterocycle</sub> bond distance increases in the Py → isoQ → Q order. In the case of quinoline-based complexes, the increase of this bond distance is 0.11 Å with respect to the pyridine ligands ( $\Delta$ Py → Q ~ +0.11 Å), indicating the weaker interaction of quinoline with

the metal ion; this possibly contributes to the drop of stability of the quinoline complexes compared to the pyridine analogues (on average ~1.4 and 3.4 log units for the di- and tri-acetate ligands). However, it is expected that quinoline also has a notable impact on the solvation properties of the complex, which often have a strong influence on the stability.

**Spectroscopic Properties of the Complexes.** As reported in Table 4, the experimental spectroscopic study on the Eu(III) complexes shows low to moderate intrinsic quantum yields ( $\phi_{\text{int}}$  in the 5–10% range) for all compounds, which reflect the presence of MPR quenching, induced by water molecules in the proximity of the metal ion (hydration number  $q$  calculated by the Horrocks equation<sup>98–100</sup>), which is detrimental for the luminescence efficiency. This number, in the 2.5–2.8 range (Table 4), even if slightly larger than that found by DFT calculation ( $q = 2$ ), is still in agreement with it. It must be pointed out that the  $q$  number is also sensitive to the presence of water in the outer coordination sphere of the metal ion. On the other hand, the presence of water molecules bound to Eu(III) is required to use these metal complexes as optical probes to sense biomolecules or bioanalytes. In fact, some of us reported how the displacement of this bound water by the target molecule is based on the optical sensing mechanism of important bioanalytes such as HCO<sub>3</sub><sup>–</sup>,<sup>12</sup> citrate,<sup>10</sup> and bovine serum albumin (BSA).<sup>11</sup>

As for the overall quantum yield ( $\phi_{\text{ovl}}$ ), we noticed a significant drop in its value in the case of the quinoline- and isoquinoline-based complexes (group II and III molecules) due to a worse efficiency of the sensitization process ( $\eta_{\text{sens}}$ ), which includes the ISC and the IET phenomena.  $\eta_{\text{sens}}$  is about 25% in the case of [Eu(bisoQcd)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> (9' + 10') complexes (Table 4), corresponding to an overall quantum yield of around 1%. The reasons for this behavior will be discussed in detail in the next sections of the paper. Finally, upon excitation into the ligand absorption bands (Figure 4), the luminescence of Eu(III) is sensitized and the emission spectra of the related complexes are all compatible with an emitting ion located in a non-centrosymmetric site. As it is well known in this case, the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> hypersensitive transition dominates the spectra<sup>101</sup> (Figure 4). Nevertheless, the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>4</sub> transitions are also very strong in comparison to <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> (used as a reference), suggesting that the Eu(III) ion is in a distorted cubic symmetry.<sup>102,103</sup> The theoretical intensity parameters  $\Omega_{\lambda}$  (Table S1) agree with the spectra in Figure 4.

Furthermore, all complexes exhibit a relatively strong <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>0</sub> transition (particularly in the case of quinoline-based complexes). This feature is compatible with an axial character of the Eu(III) point symmetry.<sup>101</sup> C<sub>nv</sub>, C<sub>nv</sub>, and C<sub>s</sub> are the only possible point symmetries in the presence of sizeable intensity of the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>0</sub> transition,<sup>104,105</sup> even if the C<sub>s</sub> symmetry can be ruled out due to the presence of the chiral ligand. The relatively high intensity of <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>0</sub> suggests that the studied compounds experience a strong  $J$ -mixing effect.<sup>106–109</sup>

**Excited States of the Ligands.** From TD-DFT calculations, donor energy levels (S<sub>1</sub> and T<sub>1</sub>) were obtained together with their respective donor–acceptor distances, fundamental quantities used in eq 4 ( $\Delta$  value in  $F$ ) and eqs 1–3 ( $R_L$ ), respectively.

Table 5 summarizes the calculated S<sub>1</sub> and T<sub>1</sub> energy positions, and Figures S1–S12 show the main compositions of these excited states. Once S<sub>1</sub> and T<sub>1</sub> states are both characterized as an electronic density displacement to the same portion in the compound (see unoccupied molecular

Table 3. Selected Bond Distances (Å) of the Complexes in Table 2

group	formula (isomer)	Y–O <sub>acetate</sub>	Y–N <sub>amine</sub>	Y–N <sub>heterocycle</sub>	Y–O <sub>water</sub>
I	[Y( <i>trans</i> -O,O bpdc)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (1)	2.262	2.550	2.525	2.448
	[Y( <i>trans</i> -N,N bpdc)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (2)	2.292	2.610	2.503	2.492
	[Y( <i>trans</i> -O,O PyC3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (3)	2.286	2.568	2.550	2.474
	[Y( <i>trans</i> -N,O PyC3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (4)	2.300	2.595	2.546	2.539
II	[Y( <i>trans</i> -O,O QC3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (5)	2.286	2.574	2.654	2.458
	[Y( <i>trans</i> -N,O QC3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (6)	2.290	2.576	2.642	2.478
	[Y( <i>trans</i> -O,O bQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (7)	2.268	2.557	2.661	2.464
	[Y( <i>trans</i> -N,N bQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (8)	2.284	2.567	2.594	2.482
III	[Y( <i>trans</i> -O,O bisoQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (9)	2.262	2.577	2.526	2.451
	[Y( <i>trans</i> -N,N bisoQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (10)	2.283	2.565	2.614	2.463
	[Y( <i>trans</i> -O,O isoQC3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (11)	2.297	2.594	2.581	2.509
	[Y( <i>trans</i> -N,O isoQC3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (12)	2.297	2.579	2.553	2.471

Table 4. Experimental Intrinsic  $\phi_{\text{inv}}$  Overall  $\phi_{\text{ovl}}$  Quantum Yields (in %), and  $\eta_{\text{sens}}$  (in %) Reported for the Investigated Eu(III) Complexes<sup>e</sup>

group	complex	formula	$\phi_{\text{int}}$	$\eta_{\text{sens}}$	$\phi_{\text{ovl}}$	$q$
I	A'	[Eu(bpdc)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (1' + 2')	10.0(1) <sup>b</sup>	61 <sup>b</sup>	6.1(3) <sup>b</sup>	2.7(1) <sup>a</sup>
	B'	[Eu(PyC3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (3' + 4')	9.0(1) <sup>b</sup>	67 <sup>b</sup>	6.0(3) <sup>b</sup>	2.7(1) <sup>b</sup>
II	C'	[Eu(QC3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (5' + 6')	9.9(1) <sup>b</sup>	40 <sup>b</sup>	4.0(2) <sup>b</sup>	2.5(1) <sup>b</sup>
	D'	[Eu(bQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (7' + 8')	9.0(1) <sup>b</sup>	29 <sup>b</sup>	2.6(3) <sup>b</sup>	2.8(1) <sup>b</sup>
III	E'	[Eu(bisoQcd)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (9' + 10')	5.0(1) <sup>c</sup>	26	1.3(1) <sup>d</sup>	2.8(1) <sup>c</sup>
	F'	[Eu(isoQC3A)(H <sub>2</sub> O) <sub>2</sub> ] <sup>+</sup> (11' + 12')	5.4(1) <sup>c</sup>	40	2.2(2) <sup>d</sup>	2.8(1) <sup>c</sup>

<sup>a</sup>Ref 35. <sup>b</sup>Ref 12. <sup>c</sup>Ref 10. <sup>d</sup>The data were determined in this work by using the reference standard. <sup>e</sup> $q$  is the calculated number of water molecules.

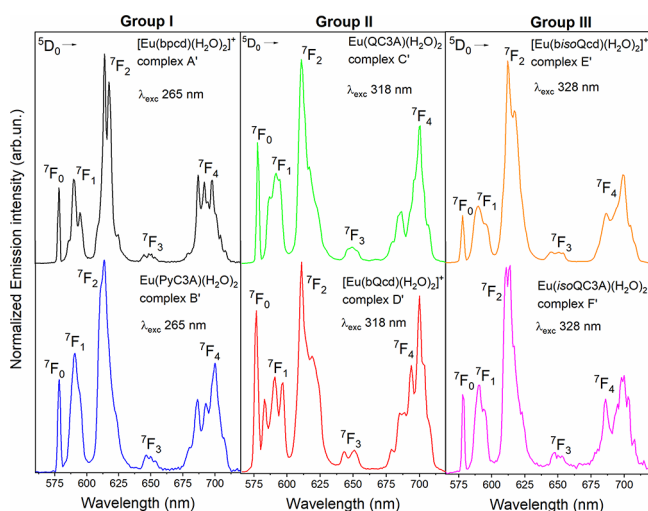


Figure 4. Room temperature luminescence emission spectra of the investigated Eu(III) complexes in aqueous solution (100 mM) upon excitation of the ligand (the  $\lambda_{\text{exc}}$  values are reported in the figure).

orbitals in Figures S1–S12 in the ESI), the values of donor–acceptor distances ( $R_L$ , the distance from the unoccupied molecular orbitals centroid to the Eu(III) ion) for IET involving  $S_1$  and  $T_1$  states can be considered the same for each compound (Table 5). For example, Figure S1 shows that the unoccupied molecular orbitals of the *trans*-O,O-[Y(bpdc)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> (1) are localized at pyridine group for both  $S_1$  and  $T_1$  states. Thus,  $R_L$  is the distance between the center of the pyridine group to Y(III).

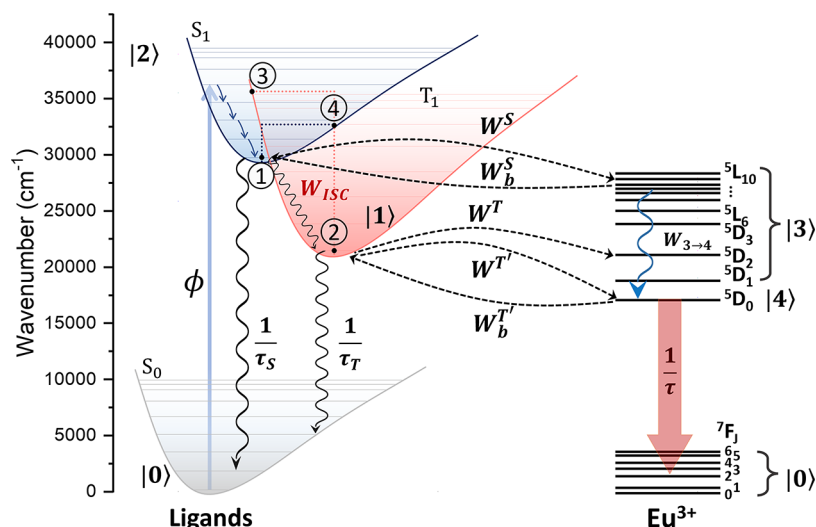
As discussed above, the 12 studied isomers were separated into three groups according to their distinct chemical characteristics (i.e., the nature of the heteroaromatic ring). This classification also finds parallelism in the values of the electronic level energy of the ligands involved in the IET

Table 5. Donor–Acceptor Distances  $R_L$  (in Å) and Energies of the  $S_1$  and  $T_1$  States (in  $\text{cm}^{-1}$ ) Estimated from TD-DFT Calculations

group	formula (isomer)	$R_L$	$S_1$	$T_1$
I	1	3.91	39,412	31,435
	2	3.89	38,185	31,361
	3	3.93	38,546	31,368
	4	3.93	39,818	31,415
II	5	4.33	32,445	22,198
	6	4.32	33,271	22,696
	7	4.32	33,391	22,859
	8	4.28	31,818	22,052
III	9	5.04	32,087	21,843
	10	5.03	32,136	21,817
	11	5.08	32,000	21,995
	12	5.06	32,235	21,863

process ( $S_1$  and  $T_1$  states; see Table 5): group I is composed of complexes 1–4 where both  $S_1$  and  $T_1$  are at higher energy ( $S_1$  around 38,900  $\text{cm}^{-1}$  and  $T_1$  around 31,400  $\text{cm}^{-1}$ ) than the complexes in groups II (complexes 5–8) and III (complexes 9–12). However, the complexes in group I present  $R_L$  shorter than complexes in groups II and III. As expected, this finding is connected to the shorter Y–N<sub>heterocycle</sub> observed in the DFT structures of the [Y(bpdc)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> and [Y(PyC3A)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> complexes (Table 3). The complexes in groups II and III have similar donor energies ( $S_1$  around 32,400  $\text{cm}^{-1}$  and  $T_1$  around 21,100  $\text{cm}^{-1}$ ), but they are distinguished from each other by the value of  $R_L$  (Table 5), where complexes in group III present the highest values of  $R_L$  among all groups.

The calculated values of  $\lambda_M$  and SOC matrix elements allow estimating the  $W_{\text{ISC}}$  rates (Table S15) through the Marcus–Levich formalism.<sup>45–47</sup> In addition, from the spin-orbit interaction, the decay lifetimes  $\tau_S$  and  $\tau_T$  were estimated (Eq.



**Figure 5.** Schematic energy level diagrams for Eu-based complexes in this work. The  $S_1$  and  $T_1$  states for compounds 1'–4' (group I) range from 38,185 to 39,818  $\text{cm}^{-1}$  and from 31,361 to 31,435  $\text{cm}^{-1}$ , respectively, while those for 5'–12' (groups II and III) range from 31,818 to 33,391  $\text{cm}^{-1}$  and 22,052 to 22,859  $\text{cm}^{-1}$ , respectively (see Table S5).  $S_0$  is the ligand ground level.  $\phi$  is the pumping rate.  $W_{ISC}$  is the  $S_1 \rightarrow T_1$  ISC rate (Table S15). The blue wavy arrow represents the non-radiative decay from higher levels of Eu(III) to the emitting  $^5D_0$  while the black ones are the ligand's decay lifetimes ( $\tau_S$  and  $\tau_T$ , Table S16).  $W^S$  and  $W^T$  are the forward energy transfer rates from the  $S_1$  and  $T_1$  states, respectively. Compounds 5'–12' present significant backward energy transfer rates to the  $T_1$  state ( $W_b^T$ ). The notation  $|N\rangle$  ( $N = 0, 1, \dots, 5$ ) represents levels (or set of levels), and they will be used in the rate equation modeling to determine the theoretical value of the overall quantum yield ( $\phi_{ovl}$ ). The points 1, 2, 3, and 4 in the  $S_1$  and  $T_1$  states are related to the Marcus reorganization energies to estimate the ISC rate for each group (see the Supporting Information file).

$S_{12}$ ) from the dipole strengths of  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow T_1$  excitations ( $S_S$  and  $S_T$  in Table S16).

A trend between the average of experimental  $\bar{\phi}_{ovl}$  and computationally obtained  $W_{ISC}$ ,  $1/\tau_S$ , and  $1/\tau_T$  for the studied compounds can be observed (Figure S15). As these Eu(III) complexes present IET dominated by the  $T_1$  channel, a more effective  $W_{ISC}$  is expected to produce a higher  $\phi_{ovl}$ . On the same hand, a smaller  $1/\tau_T$  rate induces a higher  $T_1$  population to be transferred to Eu(III), also increasing the overall quantum yield (Figure S15). For these cases,  $1/\tau_S$  rates do not follow such trends. These results make clear the importance of the proper computation of  $W_{ISC}$ ,  $\tau_S$ , and  $\tau_T$  quantities, highlighting the importance of the improvements shown in the present work.

**Intramolecular Energy Transfer.** With the energy values of the  $S_1$  and  $T_1$  states and their donor–acceptor distances ( $R_L$ ) presented in Table 5, the IET rates can be calculated for each studied compound using eqs 1–5.

Figure 5 shows energy level diagrams that illustrate the ligand-to-Eu(III) energy transfer process. A total of 768 IET rates (64 for each complex, of which 32 for the forward and 32 for backward energy transfer) were obtained with non-zero contributions (see Tables S3–S14). The complete data for forward ( $W^S$  and  $W^T$ ) and backward ( $W_b^S$  and  $W_b^T$ ) IET rates, including the  $W_{d-d}$ ,  $W_{d-mv}$  and  $W_{ex}$  mechanisms contributions (eqs 1–3), are presented in Tables S3–S14 while Figure 6 summarizes all IET rates.

Pathways from 1 to 16 (see Tables S3–S14) represent the contributions from  $S_1$ , while pathways from 17 to 32 represent the  $T_1$  contributions.  $W^S$  and  $W^T$  are the sum over all forward pathways (ligand-to-Eu(III)) while  $W_b^S$  and  $W_b^T$  are the rates for the backward ones (Eu(III)-to-ligand).

The IET results indicate that the channel  $T_1 \rightarrow \text{Eu(III)}$  is the most effective energy transfer channel for all complexes. For group I, pathway 29 (from  $T_1$  to  $^7F_1 \rightarrow ^5G_2$ ) has the

highest forward IET rate, the exchange mechanism ( $W_{ex}$ ) being the dominating one in the overall IET process. Also, the backward IET rates (from Eu(III) levels to  $T_1$ ) can be neglected due to a high energy barrier involved (large values of  $|\Delta|$ ). Groups II and III have the forward rate dominated by pathway 18 (from  $T_1$  to  $^7F_0 \rightarrow ^5D_1$ , also governed by the exchange mechanism) and present a considerable  $W_b^T$  rate dominated by pathway 29 (from  $^7F_1 \rightarrow ^5G_2$  to  $T_1$ ). Thus, a consequence of these energy differences in the donor states, particularly regarding the  $T_1$  states, is reflected in the backward energy transfer, where the complexes in group I do not have a significant rate while groups II and III do ( $W_b^T$  is around one order of magnitude lower than  $W^T$ ); see Figure 6. Compounds in Groups II and III also have a great contribution to the energy transfer directly to the Eu(III)  $^5D_0$  emitting level (sum of pathways 17 and 23, represented by the quantity  $W^{T'}$ ), which is a reflection of the  $^7F_1$  participation in the IET process.<sup>110</sup>

**Rate Equations and Overall Quantum Yield.** Based on schematic energy level diagrams in Figure 5, the population kinetics can be described by the following general rate equations model for all complexes:

$$\text{ODE} \quad \frac{dP_0}{dt} = -\phi P_0 + \frac{1}{\tau_S} P_2 + \frac{1}{\tau_T} P_1 + \frac{1}{\tau} P_4 \quad \text{Level} \quad \text{Ground-level} \quad (8)$$

$$\frac{dP_1}{dt} = -\left(\frac{1}{\tau_T} + W^T + W^{T'}\right) P_1 + W_{ISC} P_2 + W_b^T P_3 + W_b^{T'} P_4 \quad T_1 \quad (9)$$

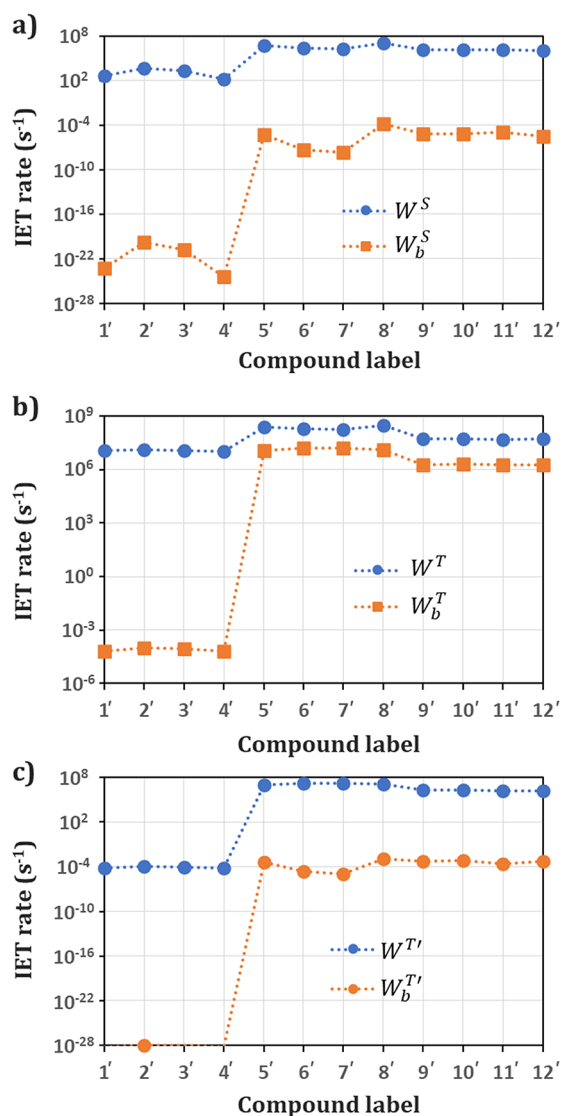
$$\frac{dP_2}{dt} = -\left(\frac{1}{\tau_S} + W^S + W_{ISC}\right) P_2 + W_b^S P_3 + \phi P_0 \quad S_1 \quad (10)$$

$$\frac{dP_3}{dt} = -(W_b^S + W_b^T + W_{3 \rightarrow 4}) P_3 + W^S P_2 + W^T P_1 \quad ^5D_1 \text{ to } ^5L_{10} \quad (11)$$

$$\frac{dP_4}{dt} = -\left(\frac{1}{\tau} + W_b^{T'}\right) P_4 + W^T P_1 + W_{3 \rightarrow 4} P_3 \quad ^5D_0 \quad (12)$$

with  $P_N$  representing the population of the  $|N\rangle$  level as depicted in Figure 5.  $\tau_S$ ,  $\tau_T$ , and  $\tau$  are the decay lifetimes of the





**Figure 6.** IET rates involving  $S_1$  (a) and  $T_1$  (b, c) states. Involvement of the  ${}^5D_0$  level is reported in (c). The blue circles represent forward rates ( $W^S$ ,  $W^T$ , and  $W^{T'}$ ) and the orange squares represent the backward rates ( $W_b^S$ ,  $W_b^T$ , and  $W_b^{T'}$ ). With exception of  $W_b^T$  for groups II and III (compounds from  $5'$  to  $12'$ ), backward IET rates can be neglected in the rate equation model.

$S_1$ ,  $T_1$ , and  ${}^5D_0$  levels. The values of these quantities for Ln-based complexes range from  $10^{-9}$  to  $10^{-6}$  s for  $\tau_S$ ,  $10^{-6}$  to  $10^{-3}$  s for  $\tau_T$ , and  $\sim 10^{-3}$  s for  $\tau_{{}^5D_0}$ .

Table S16 shows the values of  $\tau_S$  and  $\tau_T$  obtained from DFT calculations. As stressed before,  $W_{ISC}$  is the  $S_1 \rightarrow T_1$  ISC rate, and this rate was obtained for one complex of each group due to the complexity of the computational process. Hence, the  $W_{ISC}$  for isomers  $1'$ ,  $5'$ , and  $11'$  were considered as representative examples of their respective groups (see Table S15 and related discussions in the Supporting Information file). These values were estimated according to the Marcus–Levich framework.<sup>45–47</sup>

$W^T$  and  $W^S$  are the forward ligand-to-Eu(III) energy transfer rates while  $W_b^T$  and  $W_b^S$  are their respective backward energy transfer (Figure 6).

To obtain estimates of the Eu(III)  ${}^5D_0$  emitting level population, the  ${}^5D_0$  state (4) in Figure 5) was separated from Eu(III) upper levels (state 13) in Figure 5). Thus, the quantities  $W_b^{T'}$  and  $W^{T'}$  represent the backward energy transfer rates involving only the Eu(III) emitting level  ${}^5D_0$  and they are obtained by the sum of pathways 17 and 23 in Tables S3–S14.

The population simulations using eqs 8–12 consider the boundary conditions, which guarantee that the sum of the populations on all energy levels should be constant at any time  $t$ .<sup>85,110</sup> Thus, the following relationship must be preserved (eq 13):

$$\sum_N P_N(t) = 1 \quad (13)$$

where  $P_N(t)$  is the population of state  $N$  at time  $t$  ( $0 \leq t \leq t_f$ ).

Table 6 summarizes all rates used in eqs 8–12. Since all compounds present  $T_1$  above the  ${}^5D_0$  level, the values of  $W_b^{T'}$  (energy transfer from  ${}^5D_0$  to  $T_1$ ) are very low and can be neglected. On the other hand, the lower energy position of  $T_1$  provided high values of  $W^{T'}$  (energy transfer rates from  $T_1$  to  ${}^5D_0$  level) for compounds in groups II and III. The sensitizing process of the Eu(III) ion for all compounds is via the  $T_1$  state.

Figure S13 shows the transient curves of  ${}^5D_0$  and the ground levels for all 12 complexes. It can be noted that group I (complexes  $1'$ ,  $2'$ ,  $3'$ , and  $4'$ ) has the highest  ${}^5D_0$  populations in comparison to the others. This is related to a higher  $W_{ISC}$  rate due to a lower  $S_1$ – $T_1$  energy gap ( $\Delta E_{ST}$ ) and the absence of significant backward energy transfer ( $W_b^S$ ,  $W_b^T$ , and  $W_b^{T'}$ ). Despite the complexes in group I having shorter donor–acceptor distances (Table 5), they presented relatively low rates among the groups. However, the complexes in group I

**Table 6.** IET Rates (in Units of  $S^{-1}$ ) Used in eqs 8–12 for each Eu(III) Complex

group	isomer	$W^S$	$W_b^S$	$W^T$	$W^{T'}$	$W_b^T$	$W_b^{T'}$
I	$1'$	$3.9 \times 10^2$	$10^{-24}$	$1.2 \times 10^7$	$9.6 \times 10^1$	$6.1 \times 10^{-5}$	$10^{-29}$
	$2'$	$4.5 \times 10^3$	$10^{-20}$	$1.3 \times 10^7$	$1.2 \times 10^2$	$1.0 \times 10^{-4}$	$10^{-28}$
	$3'$	$2.0 \times 10^3$	$10^{-21}$	$1.2 \times 10^7$	$1.1 \times 10^2$	$8.5 \times 10^{-5}$	$10^{-29}$
	$4'$	$1.6 \times 10^2$	$10^{-25}$	$1.1 \times 10^7$	$9.4 \times 10^1$	$6.5 \times 10^{-5}$	$10^{-29}$
II	$5'$	$5.1 \times 10^6$	$4.8 \times 10^{-6}$	$2.5 \times 10^8$	$4.1 \times 10^7$	$1.2 \times 10^7$	$4.1 \times 10^{-4}$
	$6'$	$2.2 \times 10^6$	$5.0 \times 10^{-8}$	$2.0 \times 10^8$	$2.8 \times 10^7$	$1.6 \times 10^7$	$2.6 \times 10^{-5}$
	$7'$	$1.9 \times 10^6$	$2.4 \times 10^{-8}$	$1.8 \times 10^8$	$2.3 \times 10^7$	$1.7 \times 10^7$	$1.0 \times 10^{-5}$
	$8'$	$1.0 \times 10^7$	$1.6 \times 10^{-4}$	$3.0 \times 10^8$	$5.2 \times 10^7$	$1.3 \times 10^7$	$1.1 \times 10^{-3}$
III	$9'$	$1.4 \times 10^6$	$6.9 \times 10^{-6}$	$5.5 \times 10^7$	$1.0 \times 10^7$	$2.0 \times 10^6$	$5.7 \times 10^{-4}$
	$10'$	$1.4 \times 10^6$	$6.7 \times 10^{-6}$	$5.6 \times 10^7$	$1.1 \times 10^7$	$2.0 \times 10^6$	$6.7 \times 10^{-4}$
	$11'$	$1.5 \times 10^6$	$1.2 \times 10^{-5}$	$4.8 \times 10^7$	$8.3 \times 10^6$	$1.9 \times 10^6$	$2.3 \times 10^{-4}$
	$12'$	$1.2 \times 10^6$	$3.2 \times 10^{-6}$	$5.2 \times 10^7$	$9.6 \times 10^6$	$1.9 \times 10^6$	$4.9 \times 10^{-4}$

presented very high energies of the  $T_1$  state ( $\sim 31,300 \text{ cm}^{-1}$ ), and this interesting condition allows the uncommon  $T_1 \rightarrow [{}^7F_1 \rightarrow {}^5G_2]$  pathway to be the dominating route (see pathway 29 in Tables S3–S5, and S6) and suppressing the Eu-to-ligand backward transfer. On the other hand, the complexes in groups II and III presented higher  $W^T$  rates (also the backward ones) due to  $T_1$  lower energies ( $\sim 22,000 \text{ cm}^{-1}$ ) being in good resonance with the  ${}^5D_1$  level (see pathway 18 in Tables S7–S14).

With the values of populations in the steady-state regime (i.e., the  ${}^5D_0$  and ground-level populations at  $t > 2 \text{ ms}$  in Figure S13,  $P_4$  and  $P_0$  respectively), the pumping rate, and radiative rates (Table S1), we obtain the theoretical value of the overall quantum yield ( $\phi_{\text{ovl}}$ , eq 7). All these values are summarized in Table 7.

**Table 7. Populations of the  ${}^5D_0$  ( $P_4$ ) and Ground ( $P_0$ ) Levels (Unitless), Pumping ( $\phi$ ), and Radiative ( $A_{\text{rad}}$ , Table S1) rates (in Units of  $\text{S}^{-1}$ ), and the Overall Quantum Yield  $\phi_{\text{ovl}}$  (in %) for Each Eu(III) Complex**

group	isomer	$P_4$	$P_0$	$\phi$	$A_{\text{rad}}$	$\phi_{\text{ovl}}$
I	1'	$3.0 \times 10^{-2}$	0.969	128.2	152.6	3.7
	2'	$3.1 \times 10^{-2}$	0.968	132.4	188.4	4.6
	3'	$3.3 \times 10^{-2}$	0.967	131.1	250.2	6.5
	4'	$3.2 \times 10^{-2}$	0.968	126.9	207.9	5.4
II	5'	$3.8 \times 10^{-2}$	0.962	155.8	207.1	5.2
	6'	$3.6 \times 10^{-2}$	0.964	151.9	204.4	5.0
	7'	$3.6 \times 10^{-2}$	0.964	151.4	179.3	4.4
	8'	$4.3 \times 10^{-2}$	0.957	158.8	120.4	3.4
III	9'	$6.9 \times 10^{-3}$	0.993	157.5	132.1	0.6
	10'	$1.1 \times 10^{-2}$	0.989	157.3	186.4	1.4
	11'	$2.2 \times 10^{-2}$	0.978	157.9	263.7	3.7
	12'	$8.3 \times 10^{-3}$	0.992	156.8	236.2	1.3

It is important to mention that the  $\phi_{\text{ovl}}$  value, in downconversion systems, is independent of the excitation power density since if  $\phi$  (the pumping rate) is  $n$ -fold increased, the emitting level population  $P_4$  increases while the ground state is more depleted  $P_0$ , but the ratio  $P_4/P_0$  is also  $n$ -fold increased. In other words, the  $\phi$  value in the rate equation model does not affect the  $\phi_{\text{ovl}}$  calculations.<sup>14</sup>

It can be noted that the compounds in group I present higher values of theoretical  $\phi_{\text{ovl}}$ , as compound 3' reaches  $\phi_{\text{ovl}} = 6.5\%$ . On the other hand, compounds 9' and 10' have lower values of  $\phi_{\text{ovl}}$  among all compounds due to a low radiative rate ( $A_{\text{rad}}$ ) and  ${}^5D_0$  population ( $P_4$ ), quantities ascribed to the small values of  $\Omega_i$  (mainly the  $\Omega_2$ , Table S1) and high backward IET rates, respectively. These results are in complete agreement with those determined experimentally for complexes 9' and 10' (Table 4). As for the values of the  $\phi_{\text{ovl}}$  for the different complexes, we also noticed a good agreement between theoretical and experimental data (see Tables 4 and 7), which confirms the effectiveness of the theoretical modeling without the inclusion of experimental data. A question can be raised regarding whether a better luminescent performance of these compounds could be obtained in the direct excitation of the  $\text{Eu}^{3+}$  levels (e.g.,  ${}^5D_0$  and  ${}^5D_1$ ). Of course, this avoids non-radiative losses in the process and the  $\phi_{\text{ovl}}$  values tend to  $\phi_{\text{int}}$ . However, this kind of excitation involves a drastic decrease by order of magnitudes of the molar absorption extinction coefficient  $\epsilon$ . In this way, the brightness ( $B = \epsilon \cdot \phi_{\text{ovl}}$ ) is lower in comparison to the excitation through singlet states of

the ligands. While  $\phi_{\text{ovl}}$  varies between 0 and 1,  $\epsilon$  may vary by orders of magnitude. Therefore, it is convenient to optimize energy transfer processes beneficially for the sake of higher brightness.

## CONCLUSIONS

In the present work, we have theoretically analyzed 12 Eu(III)-based complexes (all the possible geometric isomers were considered) with the general formula  $[\text{Eu}(\text{L})(\text{H}_2\text{O})_2]^+$  (where  $\text{L} = \text{bpqd}^{2-}$ ;  $\text{bQcd}^{2-}$  and  $\text{bisQcd}^{2-}$ ) and  $\text{Eu}(\text{L})(\text{H}_2\text{O})_2$  (where  $\text{L} = \text{PyC3A}^{3-}$ ;  $\text{QC3A}^{3-}$  and  $\text{isoQC3A}^{3-}$ ). TD-DFT calculations revealed the ligand excited donor states and the donor–acceptor distance ( $R_L$ ). Thus, a total of 768 Ligand $\leftrightarrow$ Eu(III) IET rates were calculated considering the transition of both  $S_1$  and  $T_1$  as donor states (localized in the ligands) and 16 acceptors, involving  ${}^7F_0$  and  ${}^7F_1$  as initial states and  ${}^5D_0$ ,  ${}^5D_1$ ,  ${}^5D_2$ ,  ${}^5D_3$ ,  ${}^5L_6$ ,  ${}^5L_7$ ,  ${}^5G_2$ ,  ${}^5G_3$ ,  ${}^5G_4$ ,  ${}^5G_6$ ,  ${}^5D_4$ ,  ${}^5G_5$ ,  ${}^5L_8$ ,  ${}^5D_4$ ,  ${}^5L_9$ , and  ${}^5L_{10}$  as final states. The IET rates are affected by (i) donor–acceptor distances ( $R_L$ ); (ii) the donor ( $S_1$  and  $T_1$ ) state energy position; and (iii) selection rules on  $J$  quantum numbers ( $|J - J'| \leq \lambda \leq J + J'$  for dipolar and  $\Delta J = J - J' = 0, \pm 1$  for exchange mechanisms). Once (i) and (ii) are associated with the donor excited states, good theoretical treatment is necessary for an appropriate description of IET rates and, therefore, a rate equation model, which enables the prediction of the emitting level population. The energy transfer process for all studied compounds is dominated via the  $T_1$  state, with  $W^T$  in some cases more than  $10^4$  times higher than  $W^S$  (compounds 1' and 4', Figure 6). The reason for the higher efficiency of the sensitization process ( $\eta_{\text{sens}}$ ), around 60–65% in the case of the complexes of group I is connected to a shorter  $R_L$  combined with a high ISC rates ( $W_{\text{ISC}}$ ) and a negligible backward energy transfer from Eu(III) to  $S_1$  and  $T_1$  level of the ligands. On the contrary, the worst sensitization efficiency (around 25%) recorded in the case of group II and III complexes (in particular for  $[\text{Eu}(\text{bisQcd})(\text{H}_2\text{O})_2]^+$ , isomers 9' and 10') seems to be due to a significant rate of the Eu(III)-to- $T_1$  backward energy transfer process ( $W_{\text{b}}^T \approx 2 \times 10^6 \text{ s}^{-1}$ ) to a lower  $W_{\text{ISC}}$  and to a larger  $R_L$ . To sum up, the forward IET mechanisms mainly involve the Eu(III)  ${}^5G_2$  level for the compounds of the group I and  ${}^5D_1$  and  ${}^5D_0$  levels for the compounds of groups II and III. The backward IET process, significant only for these last complexes, mainly involves the  ${}^5G_2$  level. All the IET processes are dominated by the exchange mechanism.

For the first time, theoretical overall quantum yields ( $\phi_{\text{ovl}}$ ) were calculated without the introduction of experimental parameters (e.g., decay lifetimes, Judd–Ofelt parameters, energy levels). This was achieved using a blend of DFT, Judd–Ofelt theory, IET theory (including calculated ISC from SOC-TD-DFT), and rate equation modeling. The present work represents a milestone in a detailed description of the luminescence properties of Ln-based chelates. Such a combined experimental/computational study provides deep knowledge of all the variables governing the IET mechanism, and we believe that its extension to other luminescent Ln(III) complexes can make easier the design of new and ever more efficient chromophoric antennae to sensitize the Ln(III) luminescence.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c02330>.

Calculation of the intensity parameters and radiative rates, the matrix elements, the IET and ISC rates, and the decay lifetimes of  $S_1$  and  $T_1$  states; pictures of the molecular orbitals composition of  $S_1$  and  $T_1$  states; and luminescence emission spectra for the calculation of the experimental quantum yields (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was developed within the scope of the projects CICECO-Aveiro Institute of Materials, UIDB/50011/2020,

UIDP/50011/2020, and LA/P/0006/2020, and The Shape of Water (PTDC/NAN-PRO/3881/2020) financed by national funds through the FCT/MCTES (PIDDAC). F.P., A.M., M.S., S.R., and M.B. thank the Italian Ministry of University and Research for the received funds in the frame of PRIN (Progetti di Ricerca di Rilevante Interesse Nazionale) project “CHIR-ALAB,” Grant No. 20172M3K5N). Also, COST Action CA18202, NECTAR—Network for Equilibria and Chemical Thermodynamics Advanced Research, supported by COST (European Cooperation in Science and Technology), is acknowledged. R.T.M., Jr. and E.K. thank SMU’s Center for Scientific Computing for providing generous computational resources. This work was financially supported by the National Science Foundation (Grant CHE 2102461).

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