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A Comprehensive Strategy to Boost the Quantum Yield of Luminescence of Europium Complexes

SUBJECT AREAS:

METAL COMPLEXES

OPTICAL MATERIALS

COORDINATION CHEMISTRY

LIGANDS

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Lanthanide luminescence has many important applications in anion sensing, protein recognition, nanosized phosphorescent devices, optoelectronic devices, immunoassays, etc. Luminescent europium complexes, in particular, act as light conversion molecular devices by absorbing ultraviolet (UV) light and by emitting light in the red visible spectral region. The quantum yield of luminescence is defined as the ratio of the number of photons emitted over the number of UV photons absorbed. The higher the quantum yield of luminescence, the higher the sensitivity of the application. Here we advance a conjecture that allows the design of europium complexes with higher values of quantum yields by simply increasing the diversity of good ligands coordinated to the lanthanide ion. Indeed, for the studied cases, the percent boost obtained on the quantum yield proved to be strong: of up to 81%, accompanied by faster radiative rate constants, since the emission becomes less forbidden.

Lanthanide luminescence has many important applications¹, in anion sensing, pH indication and protein recognition², in nanosized phosphorescent and optoelectronic devices³, in immunoassays⁴, in ionic liquids⁵, etc. Starting with the absorption of light by the ligands, energy is subsequently transferred to the metal ion, the antenna effect, followed by the characteristic emission of the lanthanide ion^{6–10}. Luminescent europium complexes, in particular, act as light conversion molecular devices by absorbing ultraviolet (UV) light and by emitting light in the red visible spectral region. The quantum yield of luminescence is defined as the ratio of the number of photons emitted over the number of (UV) photons absorbed. Of course, the higher the quantum yields of luminescence, the higher the sensitivity of the application. Thus, being able to design lanthanide complexes with larger quantum yields is highly desirable. Recent articles describe luminescent europium complexes with so far the largest values of quantum yield in chloroform solution of 81%¹¹, and of 84%¹². It is noteworthy that quantum yields of a given complex in polymethylmethacrylate (PMMA) are larger than the corresponding yields in solution¹¹. Thus, it is not unreasonable to assume that if the quantum yield in solution is increased, the corresponding value in the solid state or in matrices should be larger.

The Laporte rule¹³ states that electronic f-f transitions in lanthanide complexes should be forbidden in centrosymmetric molecules, since they conserve parity with respect to the inversion center where the metal is located. Centrosymmetry can be broken by thermal vibrations, but most importantly, as advanced in this article, by coordinating the lanthanide ion with different ligands, leading to less forbidden transitions, which translate into a more luminescent complex.

Our assumption, that we advance in this article from a purely phenomenological perspective, is that it is not only important to simply break the centrosymmetry of the complex, but that it is essential to also take into consideration the extent by which the centrosymmetry is broken. Our guess is that the more asymmetric the complex, the less forbidden are its electronic f-f transitions. That assumption leads to our strategy we call “Escalate Coordination Anisotropy”, ECA, which states that by coordinating the lanthanide ion with all different ligands, one gives rise to complexes with luminescence quantum yields proportionately larger, when compared to the corresponding complexes with repeating ligands. Of course, this effect will be more acutely useful if each of the ligands is what we call a good ligand, i.e., a ligand whose corresponding homoleptic complex is already highly luminescent.

In order to better quantify this line of reasoning, we advance in this article the following conjecture, where $\Phi[\text{EuL}_1\text{L}_2\dots\text{L}_n]$ is the luminescent quantum yield Φ of the complex formed by a trivalent europium ion, Eu(III), coordinated to n ligands, from L_1 to L_n :



$$\Phi[\text{Eu}L_1L_2\dots L_i\dots L_j\dots L_n] \geq \{\Phi[\text{Eu}L_1L_2\dots L_i\dots L_i\dots L_n] + \Phi[\text{Eu}L_1L_2\dots L_j\dots L_j\dots L_n]\}/2 \quad \forall i,j \in [1,n] \quad (1)$$

That is, according to the conjecture, the luminescence quantum yield of a complex with any two different ligands L_i and L_j should be larger than the average of the quantum yields of two complexes: one with two identical L_i ligands and the other with two identical L_j ligands. Of course, all ligands other than L_i and L_j should be equally present in all three complexes. The equal sign is to guarantee that this inequality is also valid for the special case when L_i is already identical to L_j .

In this article, we will experimentally establish as a fact that this conjecture holds true for the special case of europium(III) ions coordinated to three identical β -diketonates and two non-ionic ligands of the general formula: $\text{Eu}(\beta\text{-diketonate})_3(L_1L_2)$. Inequality (1) then becomes:

$$\Phi[\text{Eu}(\beta\text{-diketonate})_3(L_1L_2)] \geq \{\Phi[\text{Eu}(\beta\text{-diketonate})_3(L_1)_2] + \Phi[\text{Eu}(\beta\text{-diketonate})_3(L_2)_2]\}/2 \quad (2)$$

We cannot control what will be the actual coordination positions of ligands L_1 and L_2 relative to the β -diketonates - not even if a mixture of coordination isomers will be prepared when we attempt to synthesize $\Phi[\text{Eu}(\beta\text{-diketonate})_3(L_1L_2)]$. However, we will now show that this is not important to the experimental proof of the conjecture. Indeed, by defining that these relative coordination positions are indicated by the order in which they appear in the list, note that by exchanging the roles of L_1 and L_2 in inequality (2), yields the following inequality:

$$\Phi[\text{Eu}(\beta\text{-diketonate})_3(L_2L_1)] \geq \{\Phi[\text{Eu}(\beta\text{-diketonate})_3(L_2)_2] + \Phi[\text{Eu}(\beta\text{-diketonate})_3(L_1)_2]\}/2 \quad (3)$$

By examining inequalities (2) and (3), it is possible to see that both elements in the right-hand side are identical. Therefore, we obtain, as a special case, the following, apparently more general, inequality:

$$\text{Min}\{\Phi[\text{Eu}(\beta\text{-diketonate})_3(L_1L_2)]; \Phi[\text{Eu}(\beta\text{-diketonate})_3(L_2L_1)]\} \geq \{\Phi[\text{Eu}(\beta\text{-diketonate})_3(L_1)_2] + \Phi[\text{Eu}(\beta\text{-diketonate})_3(L_2)_2]\}/2 \quad (4)$$

where $\text{Min}\{\}$ stands for the minimum value of a set $\{\}$, and which therefore states that the quantum yield of the isomer with the smallest of the quantum yields will still be larger than the average of the quantum yields of both complexes with duplicate non-ionic same ligands. Consequently, the actual relative coordinating positions of the non-ionic ligands with respect to the β -diketonates in $\Phi[\text{Eu}(\beta\text{-diketonate})_3(L_1L_2)]$, or even if a mixture of coordination isomers are present, are irrelevant with regards to the experimental proof of inequality (2).

Results

To phenomenologically confirm the special case of the conjecture, as indicated by Eq. 2, we used two types of β -diketonates prepared from the β -diketonates TTA, 1-(2-thenoyl)-3,3,3-trifluoroacetone (Alfa Aesar, 99%), and BTFA, 4,4,4-trifluoro-1-phenyl-1,3-butanedione (Alfa Aesar, 99%), as well as three different types of non-ionic ligands: DBSO, dibenzyl sulfoxide (Aldrich, 99%), TPPO, triphenylphosphine oxide (Aldrich, 99%), and PTSO, p-tolyl sulfoxide (Aldrich, 99%). The structures of these ligands are shown in Fig. 1.

Accordingly, we prepared all six novel complexes of the type $\text{Eu}(\text{TTA})_3(\text{DBSO}, \text{TPPO})$, $\text{Eu}(\text{TTA})_3(\text{PTSO}, \text{TPPO})$, $\text{Eu}(\text{TTA})_3(\text{DSO}, \text{PTSO})$, $\text{Eu}(\text{BTFA})_3(\text{DBSO}, \text{TPPO})$, $\text{Eu}(\text{BTFA})_3(\text{PTSO}, \text{TPPO})$, and $\text{Eu}(\text{BTFA})_3(\text{DBSO}, \text{PTSO})$, as well as all corresponding six known complexes with duplicate non-ionic ligands: $\text{Eu}(\text{TTA})_3(\text{DBSO})_2^{14}$,

$\text{Eu}(\text{TTA})_3(\text{TPPO})_2^{15}$, $\text{Eu}(\text{TTA})_3(\text{PTSO})_2^{16}$, $\text{Eu}(\text{BTFA})_3(\text{DBSO})_2^{17}$, $\text{Eu}(\text{BTFA})_3(\text{TPPO})_2^{18}$, and $\text{Eu}(\text{BTFA})_3(\text{PTSO})_2^{17}$. Consequently, we now have all combinations needed to verify the special case of the conjecture, as expressed by inequality (2). In order to have complexes with low luminescent quantum yields, for comparison, we also prepared the known complexes $\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2^{14}$, and $\text{Eu}(\text{BTFA})_3(\text{H}_2\text{O})_2^{19}$.

Luminescence. Figure 2 shows a typical emission spectrum for the synthesized compounds. As usual, they are all very similar, where the hypersensitive transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ dominates the emission.

Table 1 shows all measured luminescence quantum yields Φ for all known complexes synthesized. Note that the quantum yields of the complexes measured from pure solids are always greater than or equal to their corresponding quantum yields in chloroform solution - the larger the quantum yield, the larger being this difference.

Taking the structures of these complexes into consideration, and by using a combinatorial reasoning in order to corroborate inequality (2), we then pictured six more complexes with different non-ionic ligands, which were then synthesized. If there were no synergistic effects due to the fact that two different ligands are coordinated to the europium ion when compared to complexes with duplicate ligands, one could reasonably assume that a good estimate for the luminescent quantum yield of complex $\text{Eu}(\beta\text{-diketonate})_3(L_1L_2)$ would be just Φ_{avg} , defined as the average of the luminescence quantum yields of the corresponding complexes with duplicate non-ionic ligands, as:

$$\Phi_{\text{avg}}[\text{Eu}(\beta\text{-diketonate})_3(L_1L_2)] = \{\Phi[\text{Eu}(\beta\text{-diketonate})_3(L_1)_2] + \Phi[\text{Eu}(\beta\text{-diketonate})_3(L_2)_2]\}/2 \quad (5)$$

But, according to our conjecture, inequality (1), Φ_{avg} is actually a lower bound for Φ . By using this notation, inequality (2) then becomes:

$$\Phi[\text{Eu}(\beta\text{-diketonate})_3(L_1L_2)] \geq \Phi_{\text{avg}}[\text{Eu}(\beta\text{-diketonate})_3(L_1L_2)] \quad (6)$$

Table 2 presents the values of Φ_{avg} as well as of Φ , the actual measured luminescence quantum yields for all novel complexes synthesized. From Table 2, one can easily verify that the conjecture, as expressed by Eqs. (2) and (5), holds true for all cases, since Φ is always greater than Φ_{avg} . The percent boost in the quantum yield, defined as the percent change between Φ and Φ_{avg} related to Φ_{avg} , is very significant for all six mixed ligand complexes, ranging from 81% to 33%

We further measured the lifetimes and decay rates of the emission at 612 nm, which correspond to the peak of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition for all complexes, upon an UV excitation wavelength of 360 nm at room temperature. These photophysical results are presented in Table 3.

Of course, the mean lifetimes, τ , are the inverse of the decay rates A , and the radiative decay rate, A_{rad} , can be computed from the usual formula²⁰:

$$A_{\text{rad}} = 1/\tau_{\text{rad}} = A_{\text{MD},0} \times n^3 \times (I_{\text{tot}}/I_{\text{MD}}) \quad (7)$$

where $A_{\text{MD},0}$ is the spontaneous emission probability for the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition in vacuum (14.65 s^{-1}), n is the refractive index of the solvent (1.45 for CHCl_3), and $(I_{\text{tot}}/I_{\text{MD}})$ is the ratio of the total integrated intensity of the corrected complex emission spectrum to the integrated intensity of the magnetic dipole ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition. The non-radiative decay rate can be calculated from the equation $A_{\text{obs}} = A_{\text{rad}} + A_{\text{nr,rad}}$. This implies that $1/\tau_{\text{obs}} = 1/\tau_{\text{rad}} + 1/\tau_{\text{nr,rad}}$. Consequently, the observed mean lifetime, τ_{obs} , is:

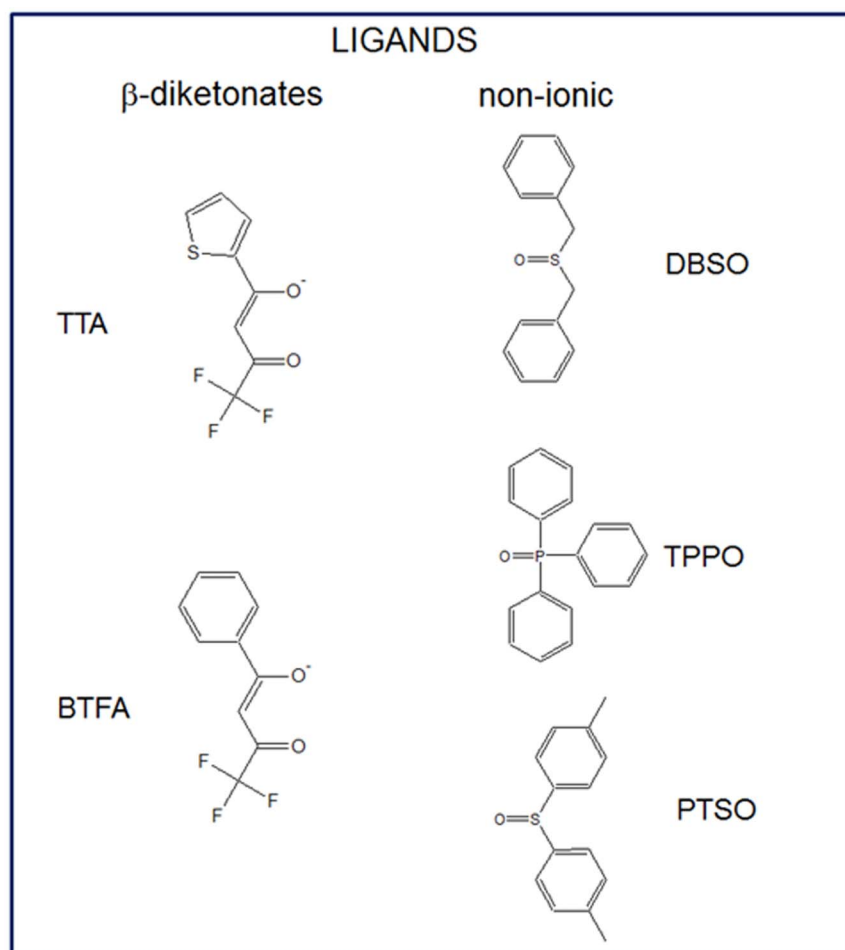


Figure 1 | Chemical structures of the ligands.

$$\tau_{obs} = \frac{\tau_{rad} \cdot \tau_{nrad}}{\tau_{rad} + \tau_{nrad}} \quad (8)$$

Table 4 presents the emission efficiencies η for the already known complexes, easily obtained from the data in Table 3, all below the corresponding values for the quantum yields, Tab. 1, for the same complexes.

That our conjecture seemingly also holds true for the emission efficiencies η , Eq. 7, can be seen in Table 5, where we show the corresponding percent boosts in the emission efficiencies, which are all positive and now range from 26% to 77%.

Discussion

As an example, Fig. 3 exhibits a graphical representation of inequality (2) for complex $\text{Eu}(\text{TTA})_3(\text{PTSO}, \text{TPPO})$. The left and right bars represent the quantum yields of the duplicate non-ionic ligand complexes $\text{Eu}(\text{TTA})_3(\text{PTSO})_2$ and $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$. The center bar, representing Φ , is divided into two sections, with the violet one representing Φ_{avg} , which for this case is equal to $21\% = (21\% + 21\%)/2$. The red part is the boost in Φ achieved by breaking the coordination isotropy of the non-ionic ligands.

Indeed, the effect of breaking the centrosymmetry even further, by coordinating the trivalent europium ion with different non-ionic ligands, boosts the value of Φ from Φ_{avg} by 67% for $\text{Eu}(\text{TTA})_3(\text{DBSO}, \text{TPPO})$. If we examine the data in Table 2, we can clearly see that these boosts range from 33% up to 81% for $\text{Eu}(\text{TTA})_3(\text{PTSO}, \text{TPPO})$. In average, they are 59%. Figure 4 displays this effect in graphical form, once again with the red parts representing

the boosts achieved for the complexes with different non-ionic ligands.

The energy transfer to the europium center is likely to be similar in cases where the same β -diketonate is used and thus changes to the energy transfer efficiency are not likely to be the source of the enhancement. That is why we measured the lifetimes and decay rates of the emission at 612 nm which corresponds to the peak of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition for all complexes. If the transitions ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ are indeed less forbidden, one would expect that a faster radiative lifetime would ensue, as indeed is the case, as reflected in our measured data in Table 3. The reader may recall that Eq. 8 for τ_{obs} is similar to the equation for the reduced mass of a two-body problem in physics. Accordingly, when one of the lifetimes is much larger than the other, the observed one will be dominated by the smallest. Such is the case of the complexes with two water molecules as non-ionic ligands: their average τ_{obs} is 0.158 ms, a value similar to their average τ_{nrad} of 0.179 ms (see Tab. 3). That happens because their average radiative lifetime τ_{rad} possesses a much larger value of 1.392 ms. This indicates that the observed lifetime is being mostly influenced by the non-radiative decay, implying that water molecules, as is well known, are not efficient ligands.

When both of the water molecules are replaced by two identical and more efficient non-ionic ligands, the average non-radiative lifetimes for the six known complexes increases to 0.497 ms, while the average radiative lifetimes decreases to 1.185 ms (see Tab. 3). Of course, their observed lifetimes then increase to an average of 0.348 ms indicating less dominance of the non-radiative decay, and the presence of more efficient non-ionic ligands.

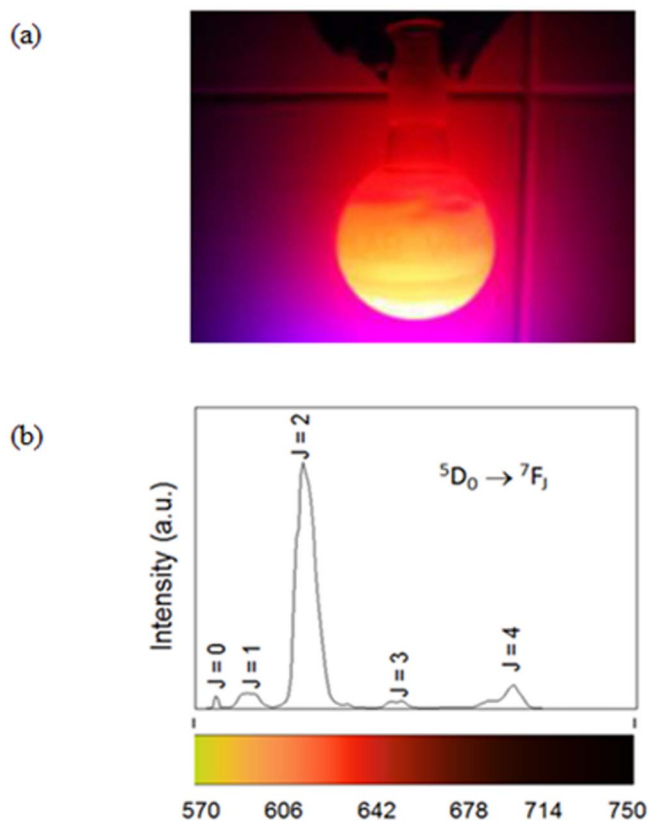


Figure 2 | (a) Film of complex $\text{Eu}(\text{TTA})_3(\text{DBSO}, \text{TPPO})$ deposited in a round bottom flask, illuminated by a black light (ultraviolet light) lamp; (b) Emission spectrum for the complex $\text{Eu}(\text{TTA})_3(\text{DBSO}, \text{TPPO})$. The transitions from ${}^5\text{D}_0$ to ${}^7\text{F}_j$ are identified by their respective J values. The bottom part displays the corresponding colors as perceived by the human eye.

Further enhancement can be done by reducing the radiative lifetime and increasing the non-radiative one to the point that they become identical, for example, to the same value τ . In this case, the observed lifetime, τ_{obs} , would be equal to half of either of them. Indeed, from Eq. (8), $\tau_{\text{obs}} = \tau / (\tau + \tau) = \tau/2$. This is approximately what we achieved with our six novel mixed-ligand complexes, when the radiative lifetimes were substantially reduced to an average of 0.961 ms; and, simultaneously, the average non-radiative lifetimes were also substantially increased to the average value of 0.713 ms. Since both lifetimes are somewhat similar in magnitude to each other, the observed average lifetime is now 0.407 ms, around one half of both average radiative and non-radiative lifetimes.

These results do reinforce our hypothesis that the transitions ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ are indeed less forbidden in the novel mixed-ligand complexes because the boost in the quantum yield due to the increased diversity of good ligands coordinated to the europium ion is accompanied by faster radiative rate constants.

The quantum yield that we measured is the ratio of the number of emitted photons by the number of absorbed photons and results from a number of steps, including energy losses by non-radiative channels in both the ligand and the lanthanide ion. The last step of this light conversion process is the emission of visible light by the europium complex. The emission efficiency of this last step, η , also called intrinsic quantum yield, $Q_{\text{Eu}}^{\text{Eu}}$, is given by $\eta = A_{\text{rad}} / (A_{\text{rad}} + A_{\text{nrad}}) = A_{\text{rad}} / A_{\text{obs}}$. Therefore, the quantum yield Φ cannot be larger than the emission efficiency η for any given complex, even in the hypothetical situation in which every photon absorbed by the ligand is converted into a photon emitted by the europium ion in the complex²¹.

Table 1 | Luminescence quantum yields Φ for all known complexes synthesized, measured by other authors from pure solids, and in 1×10^{-4} M chloroform solutions, as measured in the present article. The excitation wavelength was 360 nm and measurements were carried out at room temperature (~ 300 K), with a slit width of 1.0 nm for the excitation, and 1.0 nm for the emission

Complex	Φ (%) Pure solid	Φ (%) CHCl_3 sol.
$\text{Eu}(\text{TTA})_3(\text{DBSO})_2$	85 ¹⁴	27
$\text{Eu}(\text{TTA})_3(\text{TPPO})_2$	73 ¹⁵	21
$\text{Eu}(\text{TTA})_3(\text{PTSO})_2$	57 ¹⁶	21
$\text{Eu}(\text{BTFA})_3(\text{DBSO})_2$	-	19
$\text{Eu}(\text{BTFA})_3(\text{TPPO})_2$	-	21
$\text{Eu}(\text{BTFA})_3(\text{PTSO})_2$	-	20
$\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2$	23 ¹⁴	9
$\text{Eu}(\text{BTFA})_3(\text{H}_2\text{O})_2$	22 ¹⁹	8

Since the emission efficiencies η are upper bounds of the quantum yields, Φ , and both, of course, cannot be larger than unity (or 100%), it is not unreasonable to assume that our conjecture, Eq. 1, is, by extension, also valid for the emission efficiencies according to Eq. 9, below.

$$\eta[\text{Eu}L_1L_2\dots L_i\dots L_j\dots L_n] \geq \{ \eta[\text{Eu}L_1L_2\dots L_i\dots L_i\dots L_n] + \eta[\text{Eu}L_1L_2\dots L_j\dots L_j\dots L_n] \} / 2 \quad \forall i, j \in [1, n] \quad (9)$$

By comparing the %Boosts in Tables 2 and 5, one can verify that %Boost[Φ] is always larger than %Boost[η], for each and every one of the six mixed ligand complexes synthesized. One may wonder if this fact comes as a byproduct of our conjecture. In order to check that, we describe, in the supplementary information, a simulation we carried out to determine the likelihood that %Boost[Φ] \geq %Boost[η] based solely on the following facts: (i) that both Φ and η can only assume values between zero and unity (or between 0% and 100%); (ii) that $\eta \geq \Phi$; and (iii) that the conjecture defined in Eqs. 1 and 9 are valid. The obtained result does indicate that %Boost[Φ] will be, in average, larger than %Boost[η] for 5 out of 7 complexes. Consequently, for the majority of cases, one can preliminarily determine the boost in η , which is much easier to measure, with the understanding that the corresponding boost in the much more useful quantum yield will be likely larger, thus expanding the applicability and usefulness of our conjecture.

As stated earlier, this article advances the “Escalating Coordination Anisotropy” strategy from a purely phenomenological viewpoint. A better clarification of all of the mechanisms involved to arrive to a more accurate theoretical understanding of the phenomenon is beyond the scope of this article. Future work by our group will involve, for example, measurements of the triplet levels

Table 2 | Average luminescence quantum yields Φ_{avg} ; actual measured quantum yields Φ for all novel complexes synthesized, in 1×10^{-4} M chloroform solutions; and the percent boost in the quantum yield, defined as the percent change between Φ and Φ_{avg} related to Φ_{avg} . The excitation wavelength was 360 nm and measurements were carried out at room temperature (~ 300 K), with a slit width of 1.0 nm for the excitation, and 1.0 nm for the emission

Complex	Φ_{avg} (%)	Φ (%)	%Boost [Φ]
$\text{Eu}(\text{TTA})_3(\text{DBSO}, \text{TPPO})$	24	40	67
$\text{Eu}(\text{TTA})_3(\text{PTSO}, \text{TPPO})$	21	38	81
$\text{Eu}(\text{TTA})_3(\text{DBSO}, \text{PTSO})$	24	37	54
$\text{Eu}(\text{BTFA})_3(\text{DBSO}, \text{TPPO})$	20	33	65
$\text{Eu}(\text{BTFA})_3(\text{PTSO}, \text{TPPO})$	21	31	51
$\text{Eu}(\text{BTFA})_3(\text{DBSO}, \text{PTSO})$	20	26	33



Table 3 | Observed lifetimes, τ_{obs} , and decay rates A_{obs} ; radiative lifetimes, τ_{rad} , and decay rates A_{rad} ; non-radiative lifetimes, τ_{nrad} , and decay rates A_{nrad} ; and $(I_{\text{tot}}/I_{\text{MD}})$, the ratio of the total integrated intensity of the corrected complex emission spectrum to the integrated intensity of the magnetic dipole ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition

Complex	τ_{obs} (ms)	A_{obs} (s^{-1})	τ_{rad} (ms)	A_{rad} (s^{-1})	τ_{nrad} (ms)	A_{nrad} (s^{-1})	$I_{\text{tot}}/I_{\text{MD}}$
Eu(TTA) ₃ (DBSO,TPPO)	0.436	2294	0.909	1100	0.838	1194	24.63
Eu(TTA) ₃ (PTSO,TPPO)	0.436	2294	0.933	1072	0.818	1222	24.01
Eu(TTA) ₃ (DBSO,PTSO)	0.391	2558	0.963	1038	0.658	1520	23.24
Eu(BTFA) ₃ (DBSO,TPPO)	0.398	2513	1.017	983	0.654	1530	22.01
Eu(BTFA) ₃ (PTSO,TPPO)	0.399	2506	0.952	1050	0.687	1456	23.50
Eu(BTFA) ₃ (DBSO,PTSO)	0.382	2618	0.989	1011	0.622	1607	22.63
Averages	0.407	2464	0.961	1042	0.713	1422	23.34
Eu(TTA) ₃ (DBSO) ₂	0.379	2639	1.182	846	0.558	1793	18.94
Eu(TTA) ₃ (TPPO) ₂	0.350	2857	1.256	796	0.485	2061	17.83
Eu(TTA) ₃ (PTSO) ₂	0.327	3058	1.330	752	0.434	2306	16.85
Eu(BTFA) ₃ (DBSO) ₂	0.341	2933	1.209	827	0.475	2106	18.51
Eu(BTFA) ₃ (TPPO) ₂	0.367	2725	1.088	919	0.554	1806	20.58
Eu(BTFA) ₃ (PTSO) ₂	0.326	3067	1.046	956	0.474	2111	21.40
Averages	0.348	2880	1.185	849	0.497	2031	19.02
Eu(TTA) ₃ (H ₂ O) ₂	0.187	5357	1.387	721	0.216	4636	16.15
Eu(BTFA) ₃ (H ₂ O) ₂	0.129	7752	1.397	716	0.142	7036	16.03
Averages	0.158	6555	1.392	719	0.179	5836	16.09

of the sensitizers, using Gd complex analogues, to assess the impact of making the complexes more asymmetric on the modulation of the energy transfer between the ligand triplet state and the excited Eu accepting level (${}^5\text{D}_1$ or ${}^5\text{D}_0$), a key intramolecular energy transfer step.

Finally, it is important to mention that a high luminescence quantum yield is not directly related to the brightness of a complex, or to its perceived brightness. The brightness is actually proportional to the probability of absorption of UV photons by the complex, multiplied by its luminescence quantum yield:

$$\text{Brightness} \propto \frac{\# \text{absorbed photons}}{\# \text{incident photons}} \cdot \frac{\# \text{emitted photons}}{\# \text{absorbed photons}} \quad (10)$$

where $(\# \text{emitted photons}/\# \text{absorbed photons}) = \Phi/100\%$. Thus, a complex may be very bright due to a high probability of absorption of UV photons, while possessing a modest quantum yield. But, of course, even in this case, augmenting the luminescence quantum yield by using our ECA strategy should make a bright complex brighter.

If the complexes synthesized in this article are representative of several of the situations that may arise when studying the luminescence of europium complexes, then our ECA strategy of increasingly breaking the coordination isotropy of the complexes, in steps, from the homoleptic coordination to a fully heteroleptic one, is both simple and comprehensive. Of course, we expect that, as we increase

further and further the coordination anisotropy of the complexes, for example, by going from 3 identical β -diketonates and two different non-ionic ligands to an all different ligand and fully heteroleptic complex, the boost in the luminescent quantum yield will still happen, but will become increasingly smaller, mainly due to the fact that a quantum yield cannot go above 100%.

Although we could not find any assertion in the literature that luminescent quantum yields in solution will be always smaller than in solids, or in matrices such as PMMA, that apparently seems to be the case as indicated from the data in Table 1 and also from other studies¹¹. We can rationalize this reduction in terms of the higher non-radiative dissipating ability of liquid phases when compared to solid phases and matrices. That is because of the vibrational energy transfer from the Eu(III) excited state to nearby energy matched oscillators; whereas in the solid state this is less effective as local motion is constrained. Actually, in many cases the presence of low amounts of water in the solvent may become an issue as the OH oscillator, like the amine or amide NH oscillator, is a good quencher of the Eu(III) ${}^5\text{D}_0$ state²². Therefore, we expect, subject to further experimental proof, that our conjecture, inequality (1), will also hold true in solids, in matrices, etc, amplifying the range of applications of our ECA strategy.

The boost in the quantum yield of luminescence of these tris- β -diketonate europium complexes, achieved by breaking through their

Table 4 | Luminescence emission efficiencies η for all known complexes synthesized, measured by other authors from pure solids, and in 1×10^{-4} M chloroform solutions, as measured in the present article at room temperature (~ 300 K)

Complex	η (%) Pure solid	η (%) CHCl ₃ sol
Eu(TTA) ₃ (DBSO) ₂	70 ¹⁴	32
Eu(TTA) ₃ (TPPO) ₂	72 ¹⁵	28
Eu(TTA) ₃ (PTSO) ₂	66 ¹⁶	25
Eu(BTFA) ₃ (DBSO) ₂	-	28
Eu(BTFA) ₃ (TPPO) ₂	-	34
Eu(BTFA) ₃ (PTSO) ₂	-	31
Eu(TTA) ₃ (H ₂ O) ₂	29 ¹⁴	13
Eu(BTFA) ₃ (H ₂ O) ₂	13 ¹⁹	9

Table 5 | Average luminescence emission efficiencies η_{avg} , defined as in Eq.5; actual measured emission efficiencies η for all novel complexes synthesized in 1×10^{-4} M chloroform solutions at room temperature (300 K); and the percent boost in the emission efficiency, defined as the percent change between η and η_{avg} related to η_{avg}

Complex	η_{avg} (%)	η (%)	%Boost [η]
Eu(TTA) ₃ (DBSO,TPPO)	30	48	60
Eu(TTA) ₃ (PTSO,TPPO)	27	47	77
Eu(TTA) ₃ (DBSO,PTSO)	29	41	44
Eu(BTFA) ₃ (DBSO,TPPO)	31	39	26
Eu(BTFA) ₃ (PTSO,TPPO)	33	42	29
Eu(BTFA) ₃ (DBSO,PTSO)	30	39	32

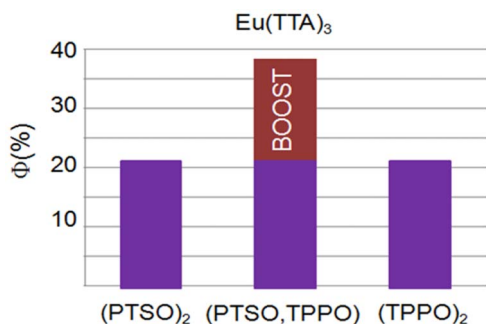


Figure 3 | Luminescence quantum yields Φ for complexes $\text{Eu}(\text{TTA})_3(\text{PTSO})_2$, left bar, $\text{Eu}(\text{TTA})_3(\text{PTSO},\text{TPPO})$, centerbar, and $\text{Eu}(\text{TTA})_3(\text{TPPO})_2$, right bar. The oblique line is shown to indicate the average Φ_{avg} between the Φ values of the duplicate ligands complexes. The red part of the centerbar represents the boost in the quantum yield obtained.

non-ionic homoleptic coordination, seems to be indeed a significant effect.

Methods

Preparation of $\text{Eu}(\beta\text{-diketonate})_3(\text{L}_1\text{L}_2)$. The already known precursor complexes $\text{Eu}(\beta\text{-diketonate})_3(\text{H}_2\text{O})_2$ and $\text{Eu}(\beta\text{-diketonate})_3(\text{L}_1)_2$ were prepared by standard procedures, improved for this article, as described in the supporting information. Complexes of the type $\text{Eu}(\beta\text{-diketonate})_3(\text{L}_1\text{L}_2)$ were prepared according to the following procedure also developed for this article: always stirring, make a solution of 0.175 mmol of $\text{Eu}(\beta\text{-diketonate})_3(\text{H}_2\text{O})_2$ in 20 mL of pure ethanol. Very slowly, and always stirring, add 30 mL of an ethanolic solution of two equivalents, 0.350 mmol, of the non-ionic ligand L_1 ; then, leave the system being stirred under reflux condensation for eight hours. Extremely slowly, and always stirring, add 15 mL of an ethanolic solution of one equivalent, 0.175 mmol, of the non-ionic ligand L_2 ; then, leave the system being stirred under reflux condensation for another eight hours. Subsequently, allow the solvent to slowly evaporate at room temperature, until its complete evaporation. This evaporation may take a week or more. A pale yellow solid of $\text{Eu}(\beta\text{-diketonate})_3(\text{L}_1\text{L}_2)$ is obtained. Wash the solid three times, each time with 5 mL of hexane, to remove any excess amount of ligands, mainly L_1 , and dry under vacuum for 24 h. Finally, recrystallize the complex with an hexane/acetone solution (10:1). Note that L_2 must be able to displace L_1 in the complex. We observed empirically that TPPO is capable of displacing both PTSO, and DBSO. In turn, PTSO is capable of displacing DBSO.

Characterizations. All prepared europium complexes synthesized, both novel and known, have been characterized by elemental analysis (Perkin-Elmer CHN 2400, and, for sulfur, an IC-AES Spectro Ciros CCD), infrared spectroscopy (samples of the complexes were prepared as KBr disks and the spectra were measured in a Bruker model IFS 66 spectrophotometer, 4000 cm^{-1} – 400 cm^{-1}), and by ^1H NMR, ^{19}F NMR, and ^{31}P NMR (all NMR spectra of all complexes were obtained in CDCl_3 solutions via a Varian Unity Plus 300 MHz, tuning the probe to each of the nuclei studied). The novel complexes were further characterized, Table 6, by MALDI-TOF mass spectroscopy taken on an Autoflex 3 Smart Beam Vertical spectrometer by Bruker Daltonics, with α -cyano-4-hydroxycinnamic acid as the matrix.

The Supplementary Information presents all details of the experimental characterizations, data, spectra and all relevant spectral attributions for all complexes synthesized in this article.

We now proceed to describe the most relevant aspects of the characterizations.

IR spectroscopy. We observed that, in general, all values of the signals in the IR spectra, corresponding to the coordinating groups of the ligands (C=O, S=O and P=O), had their stretchings shifted to lower values upon coordination. By examining

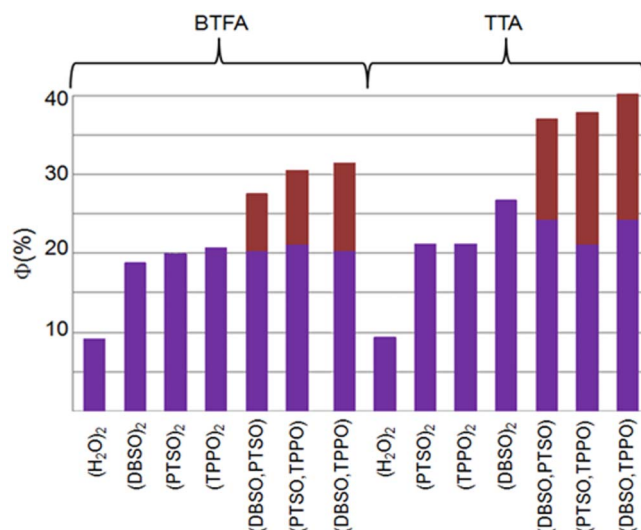


Figure 4 | Luminescence quantum yields Φ for all synthesized complexes. Complexes with two different non-ionic ligands are represented by two colored bars, where the bottom violet part represents the average Φ_{avg} between the Φ values of the duplicate ligands complexes, and the top red part is the boost in the luminescence due to the further breaking of the symmetry by coordinating the europium ion with different non-ionic ligands.

the infrared spectra of the complexes, it is possible to identify the presence of some key groups. For example, in all cases there are signals associated with the stretching of C=O in the region from 1582 cm^{-1} to 1689 cm^{-1} . It is noteworthy that these C=O stretches for the β -diketonates have two signals. We were also able to identify signals corresponding to the CF_3 group of the β -diketonates appearing in the interval from 1114 cm^{-1} to 1324 cm^{-1} . Analyzing the signals of the stretchings of non-ionic ligands (DBSO, PTSO and TPPO), we can find signals associated with the S=O and P=O stretchings. For example, in the case of $\text{Eu}(\text{BTFA})_3(\text{DBSO},\text{TPPO})$, the frequencies of these stretchings appear in 945 cm^{-1} and 1015 cm^{-1} , respectively. On the other hand, if the complex has the PTSO ligand in its structure, the signals associated to the CH_3 stretchings can be found. As an example, for $\text{Eu}(\text{BTFA})_3(\text{PTSO},\text{TPPO})$, the CH_3 stretchings occur at 2974 cm^{-1} and 2931 cm^{-1} .

^1H NMR spectroscopy. By analyzing the ^1H NMR spectra (CDCl_3 , 300 MHz), all the signals appear broadened, indicating that the europium complex was formed. The signals associated to the vinylic hydrogen of the β -diketonates range from δ 8.90 ppm to δ 15.81 ppm. The presence of the methylene group (CH_2) in DBSO in complex $\text{Eu}(\text{BTFA})_3(\text{DBSO},\text{TPPO})$, appears as two broadened signals from δ 6.10 ppm to δ 5.81 ppm. The same reasoning applies when TTA is used instead of BTFA, in which case these values in the complex appear as two broadened signals at δ 5.53 ppm and δ 5.29 ppm. Considering complexes of the type $\text{Eu}(\beta\text{-diketonate})_3(\text{PTSO},\text{TPPO})$, the methyl group (CH_3) chemical shifts, present at the PTSO sulfoxide group, can be detected either for complexes with BTFA or TTA, at δ 2.50 ppm and δ 2.47 ppm, respectively. For comparison, the corresponding signals for the uncoordinated PTSO occur at δ 2.35 ppm. Additionally, when the complexes contain two coordinated sulfoxides: PTSO and DBSO, then their ^1H NMR spectra show signals associated to both the CH_3 group in PTSO, and the CH_2 group in DBSO; ascertaining that these groups are part of the complex structure.

For $\text{Eu}(\text{BTFA})_3(\text{DBSO},\text{PTSO})$, the CH_3 signal appears at δ 2.49 ppm, whereas the signals of the CH_2 hydrogens appear at δ 6.10 ppm and δ 5.81 ppm. The corresponding values for $\text{Eu}(\text{TTA})_3(\text{DBSO},\text{PTSO})$ are δ 2.51 ppm, and from δ 6.03 ppm to δ 5.75 ppm, respectively. Indeed, ^1H NMR spectra do seem to be useful in characterizing the coordination of ligands to lanthanide ions.

Table 6 | Mass spectroscopy (MALDI-TOF) and elemental analysis data for the novel mixed non-ionic ligand complexes. Empirical values, in parenthesis, are presented besides the experimental results

Complex		$[\text{M}+\text{H}]^+ (m/z)$	%C	%H	%S
$\text{Eu}(\text{TTA})_3(\text{DBSO},\text{TPPO})$	$\text{EuC}_{56}\text{H}_{41}\text{F}_9\text{O}_8\text{PS}_4$	1324.9 (1325.1)	50.80 (50.76)	3.29 (3.10)	9.52 (9.67)
$\text{Eu}(\text{TTA})_3(\text{PTSO},\text{TPPO})$	$\text{EuC}_{56}\text{H}_{41}\text{F}_9\text{O}_8\text{PS}_4$	1325.2 (1325.1)	50.79 (50.76)	3.16 (3.10)	9.61 (9.67)
$\text{Eu}(\text{TTA})_3(\text{DBSO},\text{PTSO})$	$\text{EuC}_{52}\text{H}_{40}\text{F}_9\text{O}_8\text{S}_5$	1277.1 (1277.0)	48.78 (48.90)	3.14 (3.13)	12.42 (12.54)
$\text{Eu}(\text{BTFA})_3(\text{DBSO},\text{TPPO})$	$\text{EuC}_{62}\text{H}_{47}\text{F}_9\text{O}_8\text{PS}$	1307.0 (1307.2)	57.20 (56.96)	3.89 (3.60)	2.22 (2.45)
$\text{Eu}(\text{BTFA})_3(\text{PTSO},\text{TPPO})$	$\text{EuC}_{62}\text{H}_{47}\text{F}_9\text{O}_8\text{PS}$	1307.1 (1307.2)	56.97 (56.96)	3.65 (3.60)	2.37 (2.45)
$\text{Eu}(\text{BTFA})_3(\text{DBSO},\text{PTSO})$	$\text{EuC}_{58}\text{H}_{46}\text{F}_9\text{O}_8\text{S}_2$	1259.2 (1259.2)	55.41 (55.33)	3.81 (3.66)	4.92 (5.09)

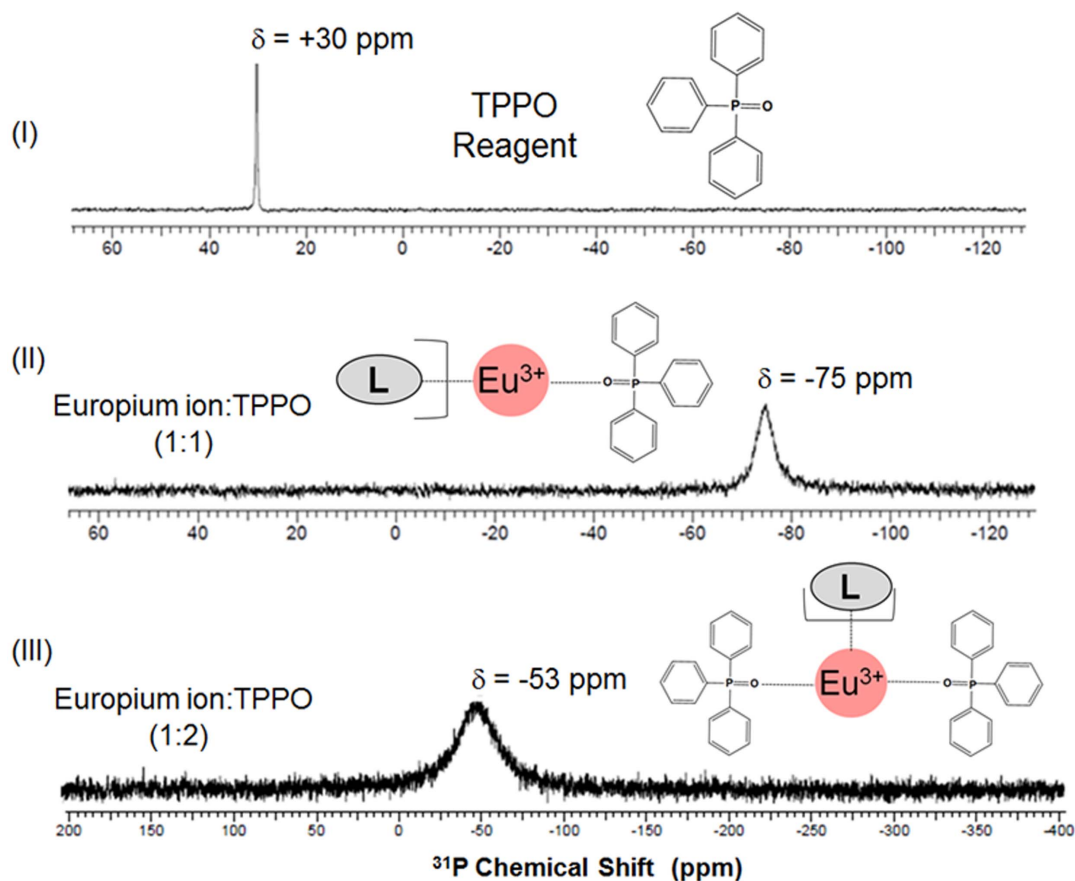


Figure 5 | ^{31}P NMR spectra of TPPO in three situations: (I) as a reagent; (II) in the novel complex $\text{Eu}(\text{TFA})_3(\text{PTSO}, \text{TPPO})$; (III) in the known complex $\text{Eu}(\text{TFA})_3(\text{TPPO})_2$.

^{31}P NMR spectroscopy. By analyzing the ^{31}P NMR spectra of the complexes that contain the ligand TPPO in the proportions of 1 : 1 or 1 : 2 (Eu:TPPO), we observed for both cases only one very broad signal that can be associated to the phosphorus nuclei. For the novel complexes with TPPO in the proportion 1 : 1 (Eu:TPPO), the chemical shifts range from $\delta -74$ ppm to $\delta -77$ ppm.

On the other hand, for the known complexes with TPPO in the proportion of 1 : 2 (Eu:TPPO), the chemical shift appeared at $\delta -53$ ppm. However, for the uncoordinated TPPO, this value is $\delta +30$ ppm. Consequently, these results show that the phosphorus nuclei are greatly affected by coordination.

Figure 5 illustrates the markedly different signals of the phosphorus nuclei of TPPO in the three situations: (I) as a pure reagent; (II) as ligand in the novel complexes; and (III) as ligands in the known complexes. Note that the width of the signal for the 1 : 2 complex is about 5 times larger than the previous case, 1 : 1, and more than 30 times the width for the pure reagent. Broadening is seemingly a strong evidence of coordination, particularly in the case of ^{31}P NMR spectra.

Luminescence measurements. The luminescence spectra and quantum yield measurements were obtained with a Fluorolog-3 Horiba Jobin Yvon equipped with a Hamamatsu R928P photomultiplier with a SPEX 1934 D phosphorimeter and a 150 W pulsed xenon lamp. The absolute quantum yields were measured, at room temperature, from 1×10^{-4} M chloroform solutions at an excitation wavelength of 360 nm, with a slit width of 1.0 nm for the excitation, and 1.0 nm for the emission, with a Horiba Quanta- ϕ F-3029 integrating sphere mounted in the sample compartment of the spectrofluorimeter. Data was processed by software supplied by Horiba-Jobin-Yvon, from which the quantum yield of the complexes in solution, Φ , were calculated via the usual formula:

$$\Phi = (E_{\text{solution}} - E_{\text{solvent}}) / (R_{\text{solvent}} - R_{\text{solution}}) \quad (11)$$

where E_{solution} and E_{solvent} are the areas under the emission spectra of the solution, and of the pure solvent, respectively. Likewise, R_{solvent} and R_{solution} are the areas under the reflectance spectra of the solvent, and of the solution, respectively. All areas were calculated by taking into account the sphere correction factors. The procedures for calculating all these quantities are explained thoroughly in the supporting information. Data for all terms in Eq. (3) were obtained from the integrating sphere.

In order to determine the precision of our experiments, we measured the quantum yields for five different samples of each of two chosen complexes: the ones with the highest and with the lowest measured quantum yields, respectively,

$\text{Eu}(\text{TFA})_3(\text{DBSO}, \text{TPPO})$ and $\text{Eu}(\text{BTFA})_3(\text{H}_2\text{O})_2$. For $\text{Eu}(\text{TFA})_3(\text{DBSO}, \text{TPPO})$, the measured values of the quantum yield for the five samples were: 40.4%; 40.8%; 39.5%; 40.4%; and 40.2%, for a mean of 40.3%, and a sample standard deviation of 0.5%. The 95% confidence interval for the mean is therefore $(40.3 \pm 0.6)\%$. For $\text{Eu}(\text{BTFA})_3(\text{H}_2\text{O})_2$, the measured values of quantum yield for the five samples were 8.7%; 8.6%; 8.9%; 8.7%; and 8.8%, for a mean value of 8.7%, and a sample standard deviation of 0.1%. The 95% confidence interval for the mean is therefore $(8.7 \pm 0.2)\%$. And since these errors are of the order of 1% of the measurement, they are much smaller than the boosting effect we describe, which is of the order of 60% of the quantum yield, thus ensuring that the effect discovered is veritably real. These measurements are absolute ones and usually more precise than relative measurements by comparison with a fluorescence standard.

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Author contributions

N.B.D.L. performed the synthetic, analytical and luminescence experiments. A.M.S. and N.B.D.L. conceptualized the conjecture, proposed the project, designed the experiments and wrote the article. S.M.C.G. and N.B.D.L. designed the synthetic methodology for obtaining the novel complexes, and analyzed the characterization data. N.B.D.L., A.M.S. and S.A.J. analyzed the luminescence data. All authors reviewed the manuscript.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

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