Europium Complexes: Luminescence Boost by a Single Efficient Antenna Ligand

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ABSTRACT: We advance the concept that a single efficient antenna ligand substituted in or added to an otherwise weakly luminescent europium complex is enough to significantly boost its luminescence. Our results, on the basis of photophysical measurements on 5 novel europium complexes and 15 known ones, point in the direction that ligand dissimilarity and ligand diversity are all concepts that clearly play a fundamental role in the luminescence of europium complexes. We show that it is important that a symmetry breaker ligand exists in the complex to enhance ligand dissimilarity and ligand diversity, all mainly affecting the nonradiative decay rate by reducing it. Because the presence of at least one antenna ligand is also obviously necessary, the optimal and the most cost-effective situation can be achieved by adding a single coordination symmetry breaker that is also an efficient antenna, such as 1-(2-thenoyl)-3,3,3-trifluoro-1-phenyl-1,3-butanedione. In such cases the quantum efficiency, \( \eta \), is decidedly boosted, as can be verified by going from complex \([\text{EuCl}_2(\text{TPPO})_4]\)Cl·3H₂O with \( \eta = 0\% \) to the novel complex \([\text{EuCl}_2(\text{BTFA})(\text{TPPO})_3]\), where TPPO stands for triphenylphosphine oxide, with \( \eta = 62\% \).

1. INTRODUCTION

Luminescence in europium complexes occurs through the so-called antenna effect: when the complexes are illuminated with ultraviolet (UV) light, the UV photons are absorbed by the ligands and the energy is then transferred to the europium ion, which subsequently decays by emitting visible light in the red-orange region.

Luminescent europium complexes can be utilized in several technologies and biological applications, such as light-emitting diode, organic light-emitting diode, bioimaging, sensing and targeting specific DNA structures, melanoma detection in milk products, and cellular imaging.

Hence, due to the innumerous applications, intensification of the brightness of luminescence by chemically modifying the europium complexes is an active area of research.

Once the europium is excited, and is equal to \( A_{\text{rad}}/(A_{\text{rad}} + A_{\text{nrad}}) \), where \( A_{\text{rad}} \) and \( A_{\text{nrad}} \) are, respectively, the radiative and the nonradiative decay rates of the excited states of the europium ion, most notably the \( ^{5}\text{D}_0 \) one. The inverse of the emission lifetime \( \tau \) is equal to \( A_{\text{rad}} + A_{\text{nrad}} \).

Recently, our research group reported a comprehensive strategy to boost luminescence in europium complexes by mixing ligands and exemplified this strategy by mixing nonionic ligands of the type phosphine oxide and sulfoxide compounds on ternary europium complexes. Results showed that increasing the coordination diversity by the presence of mixed nonionic ligands caused a boost, both in the emission quantum yield, \( \eta \), as well as on the emission quantum efficiency, \( \phi \). Later, it was also found out that mixing ligands also caused a boost in the radiative decay rates, \( A_{\text{rad}} \).

Europium \( \beta \)-diketonate complexes with repeating ligands are a well-known and highly researched class of luminescent complexes. However, europium \( \beta \)-diketonate complexes with mixed ligands are not routine compounds. Actually they are mostly novel complexes that are only now being researched for their luminescent potential and in light of our boost strategy mentioned above.

In this article, we seek to clarify the finer details and aspects influencing the luminescence of europium complexes. Accord-
Table 1. Luminescence Data for All 20 Complexes Considered<sup>a,b</sup>

| Class | Complex | τ (ms) | A<sub>rad</sub> (s⁻¹) | τ<sub>nrad</sub> (ms) | A<sub>nrad</sub> (s⁻¹) | τ<sub>tot</sub> (ms) | A<sub>tot</sub> (s⁻¹) | η (%) |
|-------|---------|--------|----------------------|---------------------|----------------------|---------------------|----------------------|-------|
| (i)   | [EuCl₂(TPPO)₄]Cl·3H₂O<sup>20</sup> | ----- | ----- | ----- | ----- | ----- | ----- | ~0 |
| (ii)  | [EuCl₂(DBM)(TPPO)₃]<sup>21</sup> | 0.465 | 2151 | 0.943 | 1061 | 0.917 | 1090 | 49 |
| (iii) | [EuCl₂(TTA)(TPPO)₂]<sup>21</sup> | 0.583 | 1715 | 0.941 | 1063 | 1.531 | 652 | 62 |
| (iv)  | [EuCl₂(DBM)(BTFA)(TPPO)₃]<sup>21</sup> | 0.131 | 7634 | 0.779 | 1283 | 0.157 | 6351 | 17 |
| (v)   | [EuCl₂(TTA)(TPPO)₂]<sup>21</sup> | 0.425 | 2352 | 1.229 | 814 | 0.650 | 1539 | 35 |
| (vi)  | [EuCl₂(BTFA)(TPPO)₂]<sup>21</sup> | 0.503 | 1987 | 0.876 | 1142 | 1.183 | 845 | 57 |
| (vii) | [EuCl₂(TTA)(TPPO)₂]<sup>21</sup> | 0.393 | 2545 | 1.193 | 838 | 0.586 | 1707 | 33 |
| (viii) | [EuCl₂(BTFA)(TPPO)₂]<sup>21</sup> | 0.420 | 2380 | 1.241 | 806 | 0.635 | 1574 | 34 |
| (ix)  | [EuCl₂(TTA)(BTFA)(TPPO)₂]<sup>21</sup> | 0.423 | 2364 | 1.215 | 823 | 0.649 | 1541 | 35 |
| (x)   | [EuCl₂(DBM)(TPPO)₃]<sup>21</sup> | 0.583 | 1715 | 0.941 | 1063 | 1.531 | 652 | 62 |
| (xi)  | [EuCl₂(BTFA)₂(DBM)(TPPO)₂]<sup>21</sup> | 0.367 | 2725 | 1.088 | 919 | 0.554 | 1806 | 34 |
| (xii) | [EuCl₂(DBM)(BTFA)(TPPO)₂]<sup>21</sup> | 0.415 | 2410 | 0.924 | 1082 | 0.765 | 1307 | 45 |
| (xiii) | [EuCl₂(BTFA)(TPPO)₂]<sup>21</sup> | 0.424 | 2359 | 0.951 | 1052 | 0.741 | 1349 | 43 |
| (xiv) | [EuCl₂(BTFA)(TPPO)₂]<sup>21</sup> | 0.473 | 2114 | 0.884 | 1131 | 1.017 | 983 | 53 |
| (xv)  | [EuCl₂(TTA)(BTFA)(TPPO)₂]<sup>21</sup> | 0.435 | 2299 | 0.915 | 1093 | 0.829 | 1206 | 48 |
| (xvi) | [EuCl₂(BTFA)(TPPO)₂]<sup>21</sup> | 0.438 | 2184 | 0.945 | 1058 | 0.888 | 1126 | 45 |
| (xvii) | [EuCl₂(TTA)(BTFA)(TPPO)₂]<sup>21</sup> | 0.434 | 2303 | 0.967 | 1034 | 0.788 | 1269 | 45 |

<sup>a</sup>Lifetimes, τ; total decay rates, A<sub>tot</sub>; radiative lifetimes, τ<sub>rad</sub>; radiative decay rates, A<sub>rad</sub>; nonradiative lifetimes, τ<sub>nrad</sub>; nonradiative decay rates, A<sub>nrad</sub>; and quantum efficiency, η.  
<sup>b</sup>A sequence of dashes, -----, indicates that data could not be measured due to very poor luminescence.

*Table 1. Luminescence Data for All 20 Complexes Considered*
Clearly, for luminescence to emerge, it is important that at least one good antenna ligand be present in the structure. However, our results indicate that adding more than one antenna does not necessarily improve the quantum efficiency further, as can be seen in Table 1, when complexes with only one antenna ligand display the largest quantum efficiencies $\eta$.

Indeed, the fact that adding more of the same antenna ligand to a complex does not necessarily improve the quantum efficiency indicates that there are more factors at play, factors that deserve a closer and more detailed examination.

2.1. Coordination Centrosymmetry Breaking Ligands.

The Laporte rule\textsuperscript{25} states that atomic $f-f$ transitions are forbidden in centrosymmetric chemical environments. Therefore, to make radiative decay less forbidden and thus more likely to occur, relaxation of centrosymmetry must take place. This, in itself, is well-known.\textsuperscript{26} Only recently, it was advanced that, for example, by thermal vibrations.

The reduction in quantum efficiency displayed in Table 1, when more antennae are added to the complex, can be understood in terms of which ligands make centrosymmetry happen and which ligands break the centrosymmetry.

Triphenylphosphine oxide (TPPO), with its three phenyl groups attached to a phosphine oxide, is a very bulky ligand, so when there are only two of them attached to the europium ion, they prefer to place themselves opposite to each other, thereby enhancing the centrosymmetry of the complex, as in Figure 1.

This preference for opposite placements with respect to the europium ion, predicted by Sparkle/RM1,\textsuperscript{27} had already been established by crystallography for two of the complexes $[\text{Eu(TTFA)}_3\text{(TPPO)}_2]$\textsuperscript{22} and $[\text{Eu(BTFA)}_3\text{(TPPO)}_2]$.\textsuperscript{23}

Moreover, in complexes of the type $[\text{Eu(}\beta\text{-diketonato)}_3\text{(TPPO)}_2]$, the three $\beta$-diketonates tend to place themselves in a triangular positioning around the europium ion in the equatorial plane, as can also be seen in Figure 1.

On the other hand, when there are three TPPOs, Sparkle/RM1 predicts quite logically that two of these remain relatively opposite to each other, but the third is necessarily placed in another position without a counterpart. This removes some symmetry, which occurs when several identical $\beta$-diketonates are all coordinated to a single center. Therefore, centrosymmetry is necessarily reduced because TPPO is very different from the other ionic ligands, as can be seen in Figure 2. This explains why complexes with three TPPOs have larger quantum efficiencies when compared with complexes with two TPPOs, as shown in Table 1. Clearly, complexes with three TPPOs cannot be centrosymmetric and, provided the requirement that at least one antenna should be present in the complex is satisfied, luminescence ensues.

2.2. Chloride as a Ligand Dissimilarity Enhancer. In complexes of the kind $[\text{EuCl}(\beta\text{-diketonato)}_3\text{(TPPO)}_2]$, chloride now replaces one of the $\beta$-diketonates in the equatorial plane, as in Figure 3. Given the fact that it consists of a single atom, the chloride dramatically increases ligand dissimilarity and makes the situation in the equatorial plane significantly less centrosymmetric, as can be seen in Figure 3.

Chloride, by being a single atom, turns out to be a very efficient ligand dissimilarity enhancer and coordination symmetry breaker, which can boost luminescence in a significant manner. Indeed, from Table 1, the average quantum efficiency of the complexes $[\text{Eu(}\beta\text{-diketonato)}_3\eta\text{(TPPO)}_2]$, of $\eta = 31\%$\textsuperscript{23} (with $\beta$ ligand being either TTA or BTFA) is boosted by 48% in complexes with a single chloride ligand $[\text{EuCl(}\beta\text{-diketonato)}_3\eta\text{(TPPO)}_2]$ to $\eta = 46\%$.

As mentioned above, DBM, being a $\beta$-diketonate, is an antenna, albeit with a very low efficiency. We then decided to examine whether the replacement of a DBM by a chloride would also significantly boost the quantum efficiency of the luminescence of $[\text{Eu(DBM)}_3\eta\text{(TPPO)}_2]$, which is immeasurably low. Indeed, that was the case, as can be verified by examining Table 1. The quantum efficiency jumped from essentially 0% for $[\text{Eu(DBM)}_3\eta\text{(TPPO)}_2]$ to 17% for $[\text{EuCl(DBM)}_3\eta\text{(TPPO)}_2]$.

2.3. $\beta$-Diketonate as a Coordination Symmetry Breaker. If a simple single-atom ligand, as chloride, is capable of 6788
breaking the coordination symmetry of europium complexes and boosting luminescence, then a different \( \beta \)-diketonate should play a similar role as a ligand dissimilarity enhancer and coordination symmetry breaker.

As such, let us consider the difference in luminescence in going from complexes \([\text{Eu}(\beta)_2(\text{TPPO})_2] \) to complexes \([\text{Eu}(\beta)_2(\beta')(\text{TPPO})_2] \), where \( \beta' \) behaves as a ligand dissimilarity enhancer and coordination symmetry breaker. Results are summarized in Table 1 for \( \beta = \text{TTA} \) and BTFA.

Again, the average quantum efficiency of complexes of the type \([\text{Eu}(\beta)_2(\text{TPPO})_2] \) is \( \eta = 31\% \), whereas by adding a different \( \beta \)-diketonate as a ligand dissimilarity enhancer and coordination symmetry breaker, \([\text{Eu}(\beta)_2(\beta')(\text{TPPO})_2] \), the quantum efficiency is boosted by 52% to an average of \( \eta = 47\% \), quite similar to the boost of 48% obtained by employing chloride as a coordination symmetry breaker. The chemical nature of the coordination symmetry breaking ligand per se is thus seemingly not relevant. It is important, though, that a symmetry breaker ligand exists so that ligand dissimilarity and ligand diversity are enhanced.

2.4. Antennae as Ligand Dissimilarity Enhancers.

Because we established the need for at least one efficient antenna ligand and also one ligand dissimilarity enhancer and coordination symmetry breaker ligand, let us now examine the cases when the antenna and the ligand dissimilarity and coordination symmetry breaker roles are played out, simultaneously, by a single ligand. That could turn out to be perhaps an optimal condition.

Now, let us first consider complex \([\text{Eu(DBM)}_3(\text{TPPO})_2] \), which does not contain any highly efficient antennae. By replacing a DBM with either a BTFA or a TTA, which behave as good antennae, as ligand dissimilarity enhancers and as coordination symmetry breaker ligands, the boost in luminescence is dramatic, from essentially zero to an average of \( \eta = 44\% \).

Likewise, consider now the complex \([\text{EuCl}_2(\text{TPPO})_4]\text{Cl}_2\cdot 3\text{H}_2\text{O} \), which also does not have any antennae in its formula and therefore displays a quantum efficiency of essentially zero. The addition of a DBM as a symmetry breaker, leading to \([\text{EuCl}_2(\text{DBM})(\text{TPPO})_3] \), does not help because DBM is not an efficient antenna. Indeed, the quantum efficiency remains immeasurably low. However, by adding a symmetry breaker, which is also a very effective antenna, such as TTA or BTFA, the quantum efficiency is boosted tremendously, to a maximum of \( \eta = 62\% \) for \([\text{EuCl}_2(\text{BTFA})(\text{TPPO})_3] \). The fact that this recordist complex has two chloride ions as ligands adds to the reality that the chemical nature of the other ligands that are neither antennae nor ligand dissimilarity enhancers or coordination symmetry breakers plays only a supportive role in the luminescence phenomenon, not a protagonist one.

2.5. Several Ligand Dissimilarity Enhancers.

If a single coordination symmetry breaker is capable of significantly boosting the quantum efficiency of luminescence of europium complexes, one could guess that perhaps several coordination symmetry breakers would lead to an even more luminescent complex. However, we verified that the presence of several symmetry breakers not only quickly exhausts their effect on the luminescence, but also starts to slowly interfere negatively, one with the other. From Table 1, the quantum efficiencies of the fully mixed ionic ligand complexes of the formulae \([\text{EuCl}(\beta)_2(\beta')(\text{TPPO})_2] \) have an average \( \eta = 34\% \), a value which is equivalent to the average \( \eta = 36\% \) of complexes \([\text{EuCl}_2(\beta)(\text{TPPO})_2] \). Likewise, the quantum efficiency of the fully mixed ionic ligand complex \([\text{Eu(DBM)}(\text{BTFA})(\text{TTA})(\text{TPPO})_2] \) is \( \eta = 45\% \), a value which is equivalent to the average \( \eta = 47\% \) of all six complexes of the type \([\text{Eu}(\beta)_2(\beta')(\text{TPPO})_2] \). Thus, the chemical difficulty involved in the synthesis of a fully mixed-ligand complex does not translate into further luminescence boost and is therefore not justified.

2.6. Chemical Partition of \( A_{\text{rad}} \).

The radiative decay rate \( A_{\text{rad}} \) of a given complex is a more direct measure of how less forbidden the \( f \rightarrow f \) transitions become in the presence of the ligands. Recently, our research group introduced the chemical partition of \( A_{\text{rad}} \), where \( A_{\text{rad}} = 2 \), and the values of \( \Omega_{\text{rad,C}} \) for each ligand as a facilitator of the radiative decay in the complex. The larger the value of \( A_{\text{rad}} \) and \( A_{\text{rad}} \), the more is the complex luminescence via radiative channels.

Accordingly, to calculate the chemical partition, we first fully optimized the geometries of the complexes with the Sparkle/RMI model. The quality of the obtained geometries was then assessed from the values of the \( Q, D, \) and \( C \) parameters, \( \text{as arrived at by the LUMPAC software from the emission spectra of the europium complexes. LUMPAC adjusts these parameters for each europium complex to reproduce the various experimentally obtained intensity parameters} \end{document}
Table 2. Values of $A_{\text{rad}}$ and the Average Values of Their Chemical Partitions Per Type of Ligand

| complex | $A_{\text{rad}}$ ($s^{-1}$) | Cl$^-$ | $\beta$-diketonate | average $A_{\text{rad}}$ ($s^{-1}$) |
|---------|-----------------|--------|-----------------|---------------------------------|
| $[\text{EuCl}_2(\text{BTFA})(\text{TPPO})_3]^{21}$ | 974 | 29 | 179 | 246 |
| $[\text{EuCl}_2(\text{TFA})(\text{TPPO})_3]^{13}$ | 981 | 90 | 131 | 224 |
| $[\text{EuCl}_3(\text{DBM})(\text{TPPO})_3]^{21}$ | 1160 | 152 | 363 | 141 |
| $[\text{EuCl}_2(\text{BTFA})(\text{TPPO})_3]^{21}$ | 1048 | 23 | 445 | 68 |
| $[\text{EuCl}_3(\text{DBM})(\text{TPPO})_3]^{21}$ | 807 | 11 | 396 | 2 |
| $[\text{EuCl}_2(\text{DBM})(\text{TTA})(\text{TPPO})_3]^{21}$ | 775 | 56 | 331 | 29 |
| $[\text{EuCl}_3(\text{DBM})(\text{DBM})(\text{TPPO})_2]^{19}$ | 736 | 73 | 324 | 8 |
| $[\text{EuCl}_2(\text{TFA})(\text{TTA})(\text{TPPO})_3]^{21}$ | 740 | 47 | 263 | 84 |

“Ionic (either chloride or $\beta$-diketonate) $A_{\text{rad}}^{\text{ionic}}$, or nonionic $A_{\text{rad}}^{\text{nonionic}}$ coordinated to europium(III) for each of the eight chloride containing europium(III) complexes.

Table 3. Effect of a Single Ionic Coordination Symmetry Breaker on Nonradiative and Radiative Decay Rates, $A_{\text{rad}}$ and $A_{\text{rad},n}$ of Europium Complexes $[\text{Eu(BTFA)}_3(\text{TPPO})_3]^{13}$ and $[\text{Eu(TTA)}_3(\text{TPPO})_3]^{13}$

| $\beta$-diketonate | coordination symmetry breaker | complex | $A_{\text{rad}}$ ($s^{-1}$) | $A_{\text{rad},n}$ ($s^{-1}$) |
|-------------------|-----------------------------|---------|-----------------|-----------------|
| BTFA              | Cl                          | $[\text{Eu(BTFA)}_3(\text{TPPO})_3]^{13}$ | 919 | 1806 |
|                   | $[\text{EuCl}_2(\text{BTFA})(\text{TPPO})_3]^{13}$ | 1142 | 845 |
|                   | $[\text{EuCl}_2(\text{TFA})(\text{TPPO})_3]^{13}$ | 1063 | 652 |
|                   | $[\text{EuCl}_2(\text{BTFA})(\text{TPPO})_2]^{19}$ | 1058 | 1126 |
|                   | $[\text{EuCl}_3(\text{DBM})(\text{TPPO})_2]^{19}$ | 1093 | 1206 |
|                   | $[\text{EuCl}_2(\text{DBM})(\text{TTA})(\text{TPPO})_3]^{21}$ | 1131 | 983 |
|                   | $[\text{EuCl}_2(\text{DBM})(\text{DBM})(\text{TPPO})_2]^{19}$ | 1015 | 1349 |
|                   | average                      | 1084 | 1027 |
| TTA               | Cl                          | $[\text{Eu(TTA)}_3(\text{TPPO})_3]^{13}$ | 796 | 2061 |
|                   | $[\text{EuCl}_2(\text{TFA})(\text{TPPO})_3]^{13}$ | 814 | 1539 |
|                   | $[\text{EuCl}_2(\text{TTA})(\text{TPPO})_3]^{21}$ | 1061 | 1090 |
|                   | $[\text{EuCl}_2(\text{DBM})(\text{TTA})(\text{TPPO})_3]^{19}$ | 1093 | 1206 |
|                   | $[\text{EuCl}_2(\text{TFA})(\text{DBM})(\text{TPPO})_2]^{19}$ | 1058 | 1126 |
|                   | $[\text{EuCl}_2(\text{DBM})(\text{DBM})(\text{TPPO})_2]^{19}$ | 1052 | 1307 |
|                   | average                      | 1082 | 1328 |
|                   | average                      | 1027 | 1266 |

The optimized geometry of the europium complex is deemed not to be consistent with the experimental intensity parameters $\Omega_{\text{rad},\text{exp}}$. From Table S1, all D/C values for all studied complexes are greater than 1. So, all $\Omega_{\text{rad},\text{obs}}$ values are compatible with the corresponding experimental values $\Omega_{\text{rad},\text{exp}}$. For example, the D/C ratio calculated for the $[\text{EuCl}_2(\text{TTA})(\text{TPPO})_3]^{21}$ complex was 1.51.

The $\Omega_{\text{rad},\text{exp}}$ with $\lambda = 2$ and 4 obtained from the emission spectrum of the complex were $32.64 \times 10^{-20}$ and $6.75 \times 10^{-20}$ cm$^2$, respectively, and compare with the corresponding fitted values obtained from LUMPAC, that were $32.62 \times 10^{-20}$ and $6.76 \times 10^{-20}$ cm$^2$, respectively. Therefore, the theoretical model can be considered adjusted to the experimental data. It was further possible to calculate the $\Omega_0$ value, which could not be measured from the experimental emission spectrum.

Finally, using LUMPAC software, we performed the actual calculations of the chemical partition of radiative decay rates, $A_{\text{rad}}$. For example, Figure 4 shows the effects of each of the ligands on $A_{\text{rad}},$ according to the chemical partition for the complexes $[\text{EuCl}_2(\text{BTFA})(\text{TPPO})_3]$, $[\text{EuCl}_2(\text{BTFA})(\text{TPPO})_2]$, and $[\text{EuCl}_2(\text{TTA})(\text{BTFA})(\text{TPPO})_3]$.

Now, we are in position to evaluate the effects of types of ligands, such as chlorides, $\beta$-diketonates, and nonionic (TPPO), on the radiative decay rates of luminescence of the novel europium complexes studied in this article. Table 2 shows the average effects per ligand according to the chemical partition, categorized by types of ligands on the radiative decay rates corresponding to $5D_0 \rightarrow 7F_j$ where $J = 2$, 4, and 6 electronic transitions.

From Table 2 it is possible to immediately verify that the chloride ligand effects on the radiative decay rates are very small, around 60 s$^{-1}$, reinforcing their role as essentially symmetry breaking species, not as forthright facilitators of radiative decay.

As mentioned in the previous sections, the presence of three TPPOs, two of them opposite to each other, and the third adjacent to one of them, breaks the centrosymmetry of the complex in a significant manner. That is why the average effect of the TPPOs in the complexes of type $[\text{EuCl}_2(\beta)(\text{TPPO})_3]$, is 235 s$^{-1}$, which is much larger than that in complexes of the types $[\text{EuCl}_2(\beta)(\text{TPPO})_2]$ and $[\text{EuCl}(\beta')(\text{TPPO})_2]$, where this value is 55 s$^{-1}$.

In complexes of the type $[\text{EuCl}_2(\beta)(\text{TPPO})_3]$, $A_{\text{rad}}$, is dominated by the contributions of the three TPPOs, each supplying 235 s$^{-1}$, for an average total of 705 s$^{-1}$. On the other hand, for complexes of the types $[\text{EuCl}(\beta')(\text{TPPO})_3]$ and $[\text{EuCl}(\beta')(\text{TPPO})_2]$, $A_{\text{rad}}$ is now governed by the $\beta$-diketonate ligands, whose total contributions average 707 s$^{-1}$. Once again, this inversion of preponderance can be understood in geometric terms. Because the bulky TPPOs are opposite to each other due to the presence of the chloride ligand. Hence, the $\beta$-diketonate ligands are forced into a non-centrosymmetric arrangement, thus dominating the effect of making the radiative...
transition less forbidden. The chemical partition thus clarifies the otherwise unexpected role of the ligand dissimilarity enhancer chloride.

2.7. Effect of Ligand Dissimilarity on $A_{\text{rad}}$. Nonradiative decay processes tend to depopulate the excited levels of the Eu(III) complexes, most notably the $^5D_0$ state, thus reducing luminescence. Lessening the nonradiative decay rate is therefore highly desirable and a very important research goal.

Unfortunately, despite the insights provided by earlier research,22–34 many factors involved in determining the nonradiative decay rate still elude us.

As a matter of fact, $A_{\text{rad}}$ values display much wider variations among complexes than $A_{\text{rad}}$ values. In Table 1, the standard deviation of all $A_{\text{rad}}$ values present is 209 s$^{-1}$, whereas the same quantity for $A_{\text{rad}}$ is 1266 s$^{-1}$, which is 6 times larger. In addition, although the difference between the largest $A_{\text{rad}}$ value in Table 1 from its lowest is 948 s$^{-1}$, the same for $A_{\text{rad}}$ is a whopping 5699 s$^{-1}$, again 6 times larger.

Therefore, detecting what affects $A_{\text{rad}}$ is truly more important for luminescence than controlling what affects $A_{\text{rad}}$.

Our present results point in the direction that ligand dissimilarity is seemingly even more important for nonradiative decays than for radiative ones.

Take, for example, the data in Table 3, which evidence what happens to $A_{\text{rad}}$ and $A_{\text{rad}}$ when going from complexes with three identical ionic ligands to complexes with two identical and a third different ionic ligand. For BTFA complexes with one coordination symmetry breaker, the average value of $A_{\text{rad}}$ is 1084 s$^{-1}$, whereas the corresponding value for the complex without a coordination symmetry breaker, $[\text{Eu(BTFA)}_3\text{(TPPO)}_2]$13, $A_{\text{rad}}$ is 919 s$^{-1}$, which is a difference of only +165 s$^{-1}$. That the coordination symmetry breaker species does seem to affect more intensively the nonradiative decay rates, $A_{\text{rad}}$, can be verified by the fact that the average value of $A_{\text{rad}}$ is 1027 s$^{-1}$ for these BTFA complexes with one coordination symmetry breaker, whereas the corresponding value of $A_{\text{rad}}$ without a coordination symmetry breaker, $[\text{Eu(BTFA)}_3\text{(TPPO)}_2]$, is 1806 s$^{-1}$, for a difference of −779 s$^{-1}$. Note that the absolute value of −779 s$^{-1}$ is almost 5 times that of +165 s$^{-1}$.

Similar figures for TTA complexes are 1027 and 796 s$^{-1}$ for $A_{\text{rad}}$ for a difference of +231 s$^{-1}$. Likewise, for $A_{\text{rad}}$, the figures are 1266 and 2061 s$^{-1}$, for a difference of −795 s$^{-1}$. Again, please note that the absolute value of −795 s$^{-1}$ is more than 3 times that of +231 s$^{-1}$.

Clearly, ligand dissimilarity has a double desirable effect by both increasing $A_{\text{rad}}$ and at the same time, by reducing $A_{\text{rad}}$.

However, the effect of ligand dissimilarity on reducing $A_{\text{rad}}$ is much stronger.

Following this reasoning, we could presume that a fully mixed ionic ligand complex would then display even lower values of $A_{\text{rad}}$. From the data in Table 4, for both the BTFA and TTA cases, $A_{\text{rad}}$ is indeed lowered by going from the nonmixed ionic ligand complexes to the fully mixed ones. However, the lowest $A_{\text{rad}}$ values occur for intermediary complexes of the type $[\text{Eu(L)}_2(L')(\text{TPPO})_2]$, as is clear from Table 3, and not for the fully mixed ones of the type $[\text{Eu(L)}_2(L')(\text{TPPO})_2]$ in Table 4. Too much diversity does not seem to be advantageous for $A_{\text{rad}}$.

Now, we are faced with a choice, we can either increase ligand dissimilarity by going from the three $\beta$-diketonates to either (i) one $\beta$-diketone and two chlorides, to (ii) two $\beta$-diketonates and one chloride, or (iii) two identical $\beta$-diketonates and a third different one. Our present results indicate that it is much better to choose (i), that is, the situation of one single antenna with high efficiency, which we suspect might probably have more to do with the radiative processes, and two chlorides, which we suspect have more to do with the nonradiative processes, and the reason might possibly be because a chloride is much more dissimilar to a $\beta$-diketone than another $\beta$-diketone.

3. CONCLUSIONS

Our intention in this article was not to arrive at complexes with excellent efficiencies but rather to unveil factors and aspects affecting luminescence to further strengthen knowledge of this phenomenon on a more fundamental level.

Results point in the direction that ligand dissimilarity, ligand diversity, and centrosymmetry are all concepts that seemingly play a fundamental role in the luminescence of eurpium complexes. Indeed, in a previous article, we had already shown that luminescence could be boosted13 by moving from a homoleptic to a heteroleptic coordination.

Our results further revealed that the effects of chloride ligands on the radiative decay rates are indeed very small, around 60 s$^{-1}$ (according to the chemical partition of $A_{\text{rad}}$), reinforcing their role as essentially ligand dissimilarity enhancers and not as forthright facilitators of radiative decay.

Truly, more than centrosymmetry breaking, it is ligand diversity and ligand dissimilarity that enhance luminescence, mainly by reducing the nonradiative decay rate, and the classical parity rule and its relaxation have very little to do with nonradiative decays, but the fact is that nonradiative decay rates are much more affected by ligand dissimilarity than by radiative decay rates, by an order of magnitude.

On the other hand, chloride, by being a single atom, turned out to be a very efficient coordination symmetry breaker and ligand dissimilarity enhancer, capable of boosting luminescence in a significant manner due to its unexpected strong effect on the nonradiative decay rate $A_{\text{rad}}$.

Indeed, we found out that the chemical nature of the coordination symmetry breaking ligand per se is seemingly not relevant. It is important, however, that a symmetry breaker ligand exists and that ligand dissimilarity, or ligand diversity, is enhanced, all affecting mainly $A_{\text{rad}}$ by reducing it.

The presence of at least one antenna ligand is nevertheless obviously necessary. Therefore, the optimal and the most cost-effective situation can be achieved by adding a single symmetry breaker that is also an efficient antenna, such as TTA or BTFA. In such cases, the quantum efficiency is boosted tremendously.
to a maximum of $\eta = 62\%$ for the novel complex $[\text{EuCl}_2(\text{BTFA})(\text{TPPO})_3]$. The cost effectiveness of this unprecedented strategy is due to the fact that chloride ions are much less expensive than any efficient antenna ligand.

These are easy to use chemical ideas, independent of the chemical nature of the ligands, that we devised and proved experimentally.

In summary, our results indicate that a single ligand dissimilarity enhancer antenna of high efficiency substituted in, or added to, an otherwise weakly luminescent europium complex is enough to significantly boost its luminescence.

4. Experimental Section and Computational Methods

4.1. Materials. Table 5 shows the reagents and solvents used, their sources, and purity degrees.

The structures of both types of ligands considered in this work are shown in Figure 5.

![Figure 5. Structures of the ligands considered in this work: DBM, BTFA, TTA, and TPPO.](image)

4.2. Syntheses of the Novel Chloride Europium Complexes. Previously, our research group reported a strategy for the synthesis of mixed-ligand europium complexes with chloride and $\beta$-diketonate ligands, exemplified by the synthesis of $[\text{EuCl}_2(\text{TTA})(\text{TPPO})_3]$ from $[\text{EuCl}_2(\text{TPPO})_4]\text{-}3\text{H}_2\text{O}$. This same strategy was followed for the syntheses of all five novel complexes $[\text{EuCl}_2(\text{BTFA})(\text{TPPO})_3]$, $[\text{EuCl}(\text{TTA})(\text{TPPO})_2]$, $[\text{EuCl}(\text{BTFA})(\text{TPPO})_2]$, $[\text{EuCl}(\text{DBM})(\text{TPPO})_2]$, and $[\text{EuCl}(\text{DBM})(\text{TTA})(\text{TPPO})_2]$, all starting from 1 mmol of $[\text{EuCl}_2(\text{TPPO})_4]\text{-}3\text{H}_2\text{O}$ as well. In all cases, after the first addition of 1 equiv of a ligand, we let the mixture sit under reflux for 16 h and after the addition of another equivalent of either the same ligand or of another ligand, we let the mixture sit under stirring and reflux for 24 more hours. The differences were as follows: (i) for the synthesis of $[\text{EuCl}_2(\text{BTFA})(\text{TPPO})_3]$, 1 equiv of BTFA was used; (ii) for $[\text{EuCl}_2(\text{TTA})(\text{TPPO})_2]$, $[\text{EuCl}($BTFA$)_2(\text{TPPO})_2]$, and $[\text{EuCl}(\text{DBM})(\text{TPPO})_2]$, 2 equiv of the ligands, either TTA, BTFA, or DBM, were used; and (iii) for $[\text{EuCl}(\text{DBM})(\text{TTA})(\text{TPPO})_2]$, we first used 1 equiv of DBM and then 1 equiv of TTA.

4.3. Characterization. Table 6 shows the characterization techniques carried out in this article, together with the respective equipment used.

![Table 5. Reagents and Solvents Employed in the Synthesis Procedures](image)

| reagent/solvent | source          | purity (%)       |
|----------------|-----------------|-----------------|
| 1,3-diphenylpropane-1,3-dione (DBM) | Alfa Aesar | 99 |
| 4,4,4-trifluoro-1-phenyl-1,3-butanedione (BTFA) | Alfa Aesar | 99 |
| 1-(2-thienyl)-3,3,3-trifluorocetone (TTA) | Alfa Aesar | 99 |
| triphenylphosphine oxide (TPPO) | Sigma-Aldrich | 98 |
| ethanol | J.T. Baker | 99 | (high-performance liquid chromatography (HPLC)) |
| chloroform | J.T. Baker | 99 | (HPLC) |

All samples for infrared spectroscopy experiments were prepared as disks of KBr. $^1$H NMR, $^{31}$P NMR, and $^{19}$F NMR spectroscopy experiments were carried out in CDCl$_3$ solutions. All characterization assignments of these IR, and $^1$H, $^{31}$P, and $^{19}$F NMR spectra are presented in the Supporting Information.

During our theoretical modeling of the structures, we could construct several possible coordination isomers for the synthesized complexes. By analyzing the lifetime curves for the complexes, we could not detect any summation of two or more different exponential decays. Therefore, from the perspective of luminescence, all solutions behave as if there is only one compound present in each one. Indeed, if there are two, or even more coordination isomers present, they all have identical luminescent properties within the resolution of our equipment. Hence, possible mixes of very similar isomers, evidenced mainly in some of the $^{19}$F and $^{31}$P NMR spectra present in the Supporting Information, do not invalidate our results and conclusions that focus on photophysical properties and luminescence. So far, no techniques have been developed by our group to isolate several very similar coordination isomers of a given europium complex from each other. Future research must address this issue.

4.3.1. Complex $[\text{EuCl}_2(\text{BTFA})(\text{TPPO})_3]$. 4.3.1.1. Characterization. Calc. MALDI-TOF MS $[\text{M + H}]^+$ $(m/z)$ 1274.16, found $(m/z)$ 1274.31; elemental analysis calc $C$ 60.34%, $H$ 4.11%, found $C$ 59.97%, $H$ 4.06%; IR (KBr): $\nu$C–H 3035 cm$^{-1}$, $\nu$C=O 1625 cm$^{-1}$, $\nu$P=O 1180–1185 cm$^{-1}$, and $\nu$C–F 1075 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.55–6.71 ppm (m, Ar); $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28 and –74 ppm;
and $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −80 and −82 ppm. Yield: 84%.

4.3.2. Complex [EuCl(TTA)$_2$(TPPO)$_2$]. 4.3.2.1. Characterization. Calcd MALDI-TOF MS [M + H$^+$] (m/z) 1189.05, found (m/z) 1189.13; elemental analysis calcld C 52.56%, H 3.39%, found C 52.39%, H 3.30%; IR (KBr): $\nu$C−H 3055 cm$^{-1}$, $\nu$C=O 1680 cm$^{-1}$, $\nu$P=O 1180−1120 cm$^{-1}$, $\nu$C−F 1075 cm$^{-1}$, and $\nu$S=C 1070 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.66−7.32 ppm (m, Ar) and $\delta$ 7.01−6.27 ppm (m, Th); $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28 ppm; and $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −84 and −87 ppm. Yield: 70%.

4.3.3. Complex [EuCl(BTFA)$_2$(TPPO)$_2$]. 4.3.3.1. Characterization. Calcd MALDI-TOF MS [M + H$^+$] (m/z) 1177.14, found (m/z) 1176.98; elemental analysis calcld C 57.18%, H 3.37%, found C 57.42%, H 3.93%; IR (KBr): $\nu$C−H 3055 cm$^{-1}$, $\nu$C=O 1680 cm$^{-1}$, $\nu$P=O 1180−1120 cm$^{-1}$, and $\nu$C−F 1070 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.55−7.33 ppm (m, Ar); $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 25 and −64 ppm; and $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −80 ppm. Yield: 81%.

4.3.4. Complex [EuCl(DBM)$_2$(TPPO)$_2$]. 4.3.4.1. Characterization. Calcd MALDI-TOF MS [M + H$^+$] (m/z) 1193.23, found (m/z) 1193.34; elemental analysis calcld C 66.47%, H 4.56%, found C 66.62%, H 4.65%; IR (KBr): $\nu$C−H 3054 cm$^{-1}$, $\nu$C=O 1595 cm$^{-1}$, and $\nu$P=O 1120−1115 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.98−7.35 ppm (m, Ar); and $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 31 ppm. Yield: 90%.

4.3.5. Complex [EuCl(DBM)(TTA)(TPPO)$_2$]. 4.3.5.1. Characterization. Calcd MALDI-TOF MS [M + H$^+$] (m/z) 1191.14, found (m/z) 1191.20; elemental analysis calcld C 59.53%, H 3.98%, found C 59.55%, H 4.09%; IR (KBr): $\nu$C−H 3055 cm$^{-1}$, $\nu$C=O 1600 cm$^{-1}$, $\nu$P=O 1120−1180 cm$^{-1}$, and $\nu$C−F 1070 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15−7.32 ppm (m, Ar) and $\delta$ 7.00−6.00 ppm (m, Th); $^{19}$F NMR (162 MHz, CDCl$_3$): $\delta$ 29 ppm; and $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −75 and −79 ppm. Yield: 74%.

4.4. Luminescence. The photophysical properties emission quantum efficiency, $\eta$, radiative decay rates, $A_{rad}$ and non-radiative decay rates, $A_{nrad}$ determined from excitation spectra, emission spectra, and lifetime curves. These measurements were carried out by using $10^{-4}$ M chloroform solutions of the europium complexes with chloride ligands considered in this work. The maxima in the excitation spectra for all samples were found in the region from 362 to 400 nm for emissions at a wavelength of 612 nm, corresponding to the hypersensitive transition from $^5$D$_0$ to $^7$F$_2$ for the trivalent europium ion.

The slit used in the experiments was 1.0 nm for both emission and excitation spectroscopic measurements. All photophysical experiments were performed at room temperature, close to 25 °C, using a Fluorolog-3 Horiba Jobin Yvon Photophysical Study. A Red Light-Emitting Ionic Europium (III) Complex Applied in near UV LED. Synth. Met. 2016, 221, 236–241.

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