Switching to enhanced brightness: Enlightening the role of vibronic coupling in the intersystem crossing of Eu3+ complexes

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Ubiquitous technological progress has dramatically broadened the scope of optical materials research, placing trivalent lanthanide (Ln^{III}) complexes at the forefront of such endeavors[1]. Attaining high emission efficiency requires a deep understanding of the underlying photophysical processes, where the ligand-sensitization mechanism (often referred to as antenna effect) serves as the main route to harvest excitation[2]. In this mechanism, the ligand absorbs excitation to the singlet state (S_1) and then undergoes intersystem crossing (ISC) to the triplet state (T_1), which subsequently funnels energy to Ln^{III}. Current studies on the antenna effect often overlook vibronic coupling, potentially crippling the description of excited-state dynamics. Motivated by this strive, we introduce a theoretical and computational approach that leverages the impact of the vibrational modes of the S_1 and T_1 states in the antenna effect through the correlation function formalism, offering a comprehensive view of intersystem crossing for three Eu^{III} complexes: $[Eu(tta)_3(H_2O)_2]$ (**1**), $[Eu(tta)_4]^-$ (**2**) and $[Eu(PyrCF_3)_3(phen)]$ (**3**). tta = 2-thenoyltrifluoroacetate, phen = 1,10-phenantroline, and $PyrCF_3$ = 1-(1-methyl-1H-4-pyrazolyl)-4,4,4-trifluorobutane-1,3-dionate. The results achieved a desirable alignment between empirical and theoretical rates, outperforming previously employed semiclassical methods, which failed to capture the three-order-of-magnitude difference between **1** and **3**. Notably, vibrational modes within the 700 – 1600 cm^{-1} range prove critical for enhancing ISC, challenging the conventional notion of the unfavorable nature of vibronic coupling in Ln^{III} complexes. Instead, unfavorable outcomes primarily stemmed from high-energy oscillations (>3000 cm^{-1}) localized on discrete molecular fragments, as illuminated by local vibrational analysis. Consequently, this study provides a strategic roadmap for tuning the antenna effect in Ln^{III} complexes, paving the way toward brighter emitters.

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References

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