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Supporting Information

Phase Controlled Color Tuning of the Samarium and Europium Complexes and Excellent Photostability of Their PVA Encapsulated Materials. Structural Elucidation, Photophysical Parameters and Energy Transfer Mechanism of Eu^{3+} Complex by Sparkle/PM3 Calculations

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Judd-Ofelt Intensity Parameters Calculation: Theoretical and Experimental

The Judd-Ofelt (JO) theory[1] is among one of the most successful methods for approximating the magnitude of the forced electric-dipole transitions of Ln^{3+} ions. The study of the radiative properties of the Ln^{3+} complexes are important, in exploring potential of these complexes in technological devices, which can be obtained by applying JO theory to the absorption or emission properties.

For the Eu^{3+} complex, Judd-Ofelt (JO) intensity parameters (Ω_λ, λ= 2, 4 and 6) have been theoretically evaluated using forced electric-dipole and dynamic-coupling mechanisms.[1] The dynamic-coupling mechanism, which induces stronger ligand field polarization of Ln—L (L = ligand) bonds and results in increase in the intensity of the electric-dipole transitions for non-centrosymmetric ligand fields.[1b] The Ω_2 parameter is associated with the structure of the complex and depends on the covalence behaviour of the first coordination sphere around the lanthanide ion.[2] The larger value thus indicates the significant existence of covalent bonding between the Ln^{3+} ion and the surrounding ligands. The Ω_4 parameter provides the information regarding the rigidity of the host medium in which Ln^{3+} ions are located.[3] The $^5D_0 \rightarrow {}^7F_6$ transition is not observed experimentally, thus Ω_6 experimental parameter could not be obtained, hence it is neglected in calculations.

The JO intensity parameters were calculated from the structural results obtained by Sparkle model. These JO intensity parameters are defined by eq. S1:[4]

$$\Omega_\lambda = (2\lambda + 1)\sum_{t,p}\frac{|B_{\lambda tp}|^2}{(2t+1)} \tag{S1}$$

where

$$B_{\lambda tp} = B_{\lambda tp}^{ed} + B_{\lambda tp}^{dc} \tag{S2}$$

where $B_{\lambda tp}^{ed}$ and $B_{\lambda tp}^{dc}$ correspond to the forced electric dipole(ed) and dynamic coupling (dc) mechanisms, respectively. The terms $B_{\lambda tp}^{ed}$ and $B_{\lambda tp}^{dc}$ are calculated as:

$$B^{ed}_{\lambda tp} = \frac{2}{\Delta E}\langle r^{t+1}\rangle \theta(t,\lambda)\gamma^t_p$$

(S3)

and,

$$B^{dc}_{\lambda tp} = -\left[\frac{(\lambda+1)(2\lambda+3)}{2\lambda+1}\right]^{1/2}\langle 4f\|r^\lambda\|4f\rangle(1-\sigma_\lambda)\langle f\|C^{(\lambda)}\|f\rangle\Gamma^t_p \delta_{t,\lambda+1}$$

(S4)

where γ^t_p and Γ^t_p are odd-rank ligand field parameter and ligand atom polarizability dependent terms, respectively. The quantities γ^t_p and Γ^t_p are given by:

$$\gamma^t_p = \left(\frac{4\pi}{2t+1}\right)^{\frac{1}{2}} e^2 \sum_j \rho_j (2\beta_j)^{t+1} \frac{g_j}{R_j^{t+1}} Y^{t\,*}_p(\theta_j,\varphi_j)$$

(S5)

$$\Gamma^t_p = \left(\frac{4\pi}{2t+1}\right)^{\frac{1}{2}} \sum_j \frac{\alpha_j}{R_j^{t+1}} Y^{t\,*}_p(\theta_j,\varphi_j)$$

(S6)

The γ^t_p and Γ^t_p parameters are summed over all the ligand atoms involved to take into account the nature of the chemical environment and structural aspect in the first coordination sphere of the Ln^{3+} ion. In eq. S3, the numerical factor $\theta(t,\lambda)$ is a function of the lanthanide ion, and in eq. S4 the quantities $\langle 4f\|r^\lambda\|4f\rangle$, $(1-\sigma_\lambda)$ and $\langle f\|C^{(\lambda)}\|f\rangle$ are radial integrals, shielding factors and one-electron reduced matrix elements, respectively.[5]

The values, used for the calculation of γ^t_p and Γ^t_p, respectively, were adjusted using a non-linear minimization of a four-dimensional response surface. The Generate Simulating Annealing (GSA) method was used in order to find one of the local minima, which should be global one and be chemically acceptable. During minimization stage we used the geometry obtained Sparkle/PM3 model. It has been pointed out that Ω_6 parameter could not be found experimentally, and therefore its theoretical value was not considered during the minimization procedure.

The experimental intensity parameters Ω_2 and Ω_4 were determined by using corresponding $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions from the emission spectra of the Eu- complex. By using Judd-Ofelt theory, the values of radiative transition probability (A) and the radiative lifetime (τ_{rad}) of the lanthanide ions were calculated. The probability of radiative transition (A(ψ_J, ψ_J') or spontaneous emission coefficient corresponding to the transition $(\psi_J \rightarrow \psi_{J'})$ is given by equation S7:[6]

$$A\left(\psi_j, \psi_{j'}\right) = \frac{64\pi^4 \upsilon^3}{3h(2j+1)}\left[\chi D_{ed} + n^3 D_{md}\right] \qquad \text{(S7)}$$

Where D_{ed} and D_{md} represent the contributions from the strength of electric and magnetic dipole operators respectively, $\chi = \frac{n(n^2+2)}{9}$ is the Lorentz local field correction for electric dipole transition and 'n' is the refractive index, J and J` letters represent the total angular momentum of the ground and excited state respectively, υ is the average energy of the transition (cm^{-1}), h is Planck's constant, (2J+1) is the degeneracy of the ψ_J state. D_{ed} and D_{md} are calculated according to equations given below:[7]

$$D_{ed} = e^2 \sum_{\lambda=2,4,6} \Omega\left(\psi_j \middle\| U^\lambda \middle\| \psi_{j'}\right)^2 \qquad \text{(S8)}$$

$$D_{md} = \frac{e^2 h^2}{16\pi^2 m^2 c^2}\left(\psi_J \middle\| L+2S \middle\| \psi_{J'}\right) \qquad \text{(S9)}$$

Where Ω_λ are the Judd-Ofelt parameters, $(\psi_J // U^\lambda // \psi_J')$ and $(\psi_J || L+2S || \psi_J')$ represent the squared reduced matrix elements.[8] These reduced matrix elements account for the electronic interaction or mutual repulsion interaction between *4f* electrons. These interactions are equivalent to that of spin-orbital coupling or LS coupling and have been examined in reference.[9] A(ψ_J, ψ_J') was also calculated from the emission spectra using equation S10:[6]

$$A_{0-\lambda} = A_{0-1}\frac{S_{0-\lambda}}{S_{0-1}}\frac{\sigma_\lambda}{\sigma_1} \tag{S10}$$

Where $S_{0-\lambda}$ is the area under the curve consistent with the ($\psi_J \rightarrow \psi_{J'}$) transition acquired from the spectral data, σ_λ is the energy barycentre of the 0→λ transition and A_{0-1} is the Einstein's coefficient of the ψ_0-ψ_1 transition. By equating eq. (8) and eq. (11), we were able to determine the intensity parameters Ω_2 and Ω_4.

Non-radiative rates (A_{nrad}) were calculated from the relation:[6]

$$A_T = \frac{1}{\tau} = A_{rad} + A_{nrad} \tag{S11}$$

where (τ) is life time, (A_{rad}) is radiative rate and is equivalent to $\sum_{\psi,j'} A(\psi_j, \psi_{j'})$ and the quantum efficiency is given by the equation S12:

$$\eta = \frac{A_{rad}}{A_{rad} + A_{nrad}} \tag{S12}$$

The radiative life time of the exited state that measures the rate of depopulation of the excited state to its initial state is related to the radiative transition $A(\psi_j, \psi_{j'})$ probability as:[10]

$$\tau_{rad} = \frac{1}{\sum\psi, j' A\left(\psi_j, \psi_{j'}\right)} \tag{S13}$$

Quantum efficiency is calculated by using equation S14:

$$\Phi_{Eu} = \frac{\tau_{obs}}{\tau_{rad}} \tag{S14}$$

Where τ_{obs} is the observed lifetime and τ_{rad} is the radiative lifetime.

Energy Transfer Rates

The mechanism of energy transfer in lanthanide complexes with organic ligands can proceeds via

(a) Förster mechanism:[11] which involves dipolar or multipolar interactions between donor (ligands) and acceptor (lanthanide ion). After excitation of the lanthanide complex, the excited electron in the ^{1}S state undergoes non-radiative intersystem crossing (ISC) to ^{3}T state, then returns to the initial state (S_0) of the ligands. During this moment the transition dipole moment of the ligand and Ln(III) ion couple resulting in excitation of the later; The rate of energy transfer via this mechanism depends on (i) the spectral overlap J_{DA} , between the emission spectra of the donor (ligands) and the absorption spectra of the acceptor (Eu^{3+} ion); (ii) the luminescence quantum yield of the donor Q_D; (iii) the lifetime of the donor excited state; (iv) the relative orientation of the donor and acceptor transition dipoles k; and (v) the distance between the donor and the acceptor according to a R_L^{-6} dependence.[12]

(b) Exchange mechanism (Dexter mechanism):[13] After excitation of the ligand, the excited electron in the ^{1}S state is transferred to ^{3}T state through intersystem crossing (ISC), the electron in the ^{3}T is then transferred to the acceptor level of the Eu^{3+} ion, at the same instant , an electron from the highest occupied 4f orbital is transferred onto the ligand, filling up the hole created by the initial excitation. The rate of transfer depends on (i) the overlap integral J_{DA}, defined above; and (ii) the distance between the donor (ligand) and acceptor (Eu^{3+} ion); R_L.

(c) Multipolar (Dipole - multipole 2^λ) mechanism[14] also plays a significant role in energy transfer process.

The Förster (dipole-dipole) mechanism along with dipole-2^λ pole mechanism and Dexter (exchange) mechanisms are two of the mechanisms taken into account in the kinetic treatment of energy transfer by Malta et al.[15] The intramolecular energy transfer rates were calculated from the approach developed by Malta and collaborators.[15] According to their theoretical model, the ligand-lanthanide energy transfer(ET) rate, W_{ET} can be inferred from the sum of two terms:

$$W_{ET} = W_{ET}^{mm} + W_{ET}^{em} \qquad \text{(S15)}$$

where W^{mm}_{ET} corresponds to the energy transfer rate obtained from the multipolar mechanisms and W^{em}_{ET} corresponds to the energy transfer rate obtained from the exchange mechanism. The term W^{mm}_{ET} is given as

$$W^{mm}_{ET} = \frac{2\pi}{\hbar}\frac{e^2 S_L}{(2J+1)G}F\sum_{\lambda}\gamma_\lambda\langle\alpha'\|U^{(\lambda)}\|\alpha J\rangle^2 + \frac{2\pi}{\hbar}\frac{e^2 S_L}{(2J+1)GR_L^6}F\sum_{\lambda}\Omega^{e.d.}_{\lambda}\langle\alpha'\|U^{(\lambda)}\|\alpha J\rangle^2 \tag{S16}$$

In the above eq. S16, the first term corresponds to the dipole-2^λ pole mechanism, with λ = 2, 4 and 6 and second part represents the dipole-dipole mechanism, also with λ = 2, 4 and 6; the term G is the degeneracy of the ligand initial state and α specifies a given 4f spectroscopic term, S_L is the dipole strength associated with transition $\varnothing \rightarrow \varnothing'$ in the ligand, *J* is the total angular momentum quantum number of the Ln^{3+} ion. The quantities $\langle\alpha'\|U^{(\lambda)}\|\alpha J\rangle$ are reduced matrix elements, in the intermediate coupling scheme, of the unit tensor operator $U^{(\lambda)}$ and R_L is the distance from the Ln^{3+} ion to the region of the molecule in which the ligand donar (or acceptor) state is localized. The $\Omega^{e.d.}_{\lambda}$ term is related to forced electric dipole contribution to 4f-4f intensity parameters and the γ_λ is given by:

$$\gamma_\lambda = (\lambda+1)\frac{\langle r^\lambda\rangle^2}{(R_L^{\lambda+2})^2}\langle 3\|C^{(\lambda)}\|3\rangle^2(1-\sigma_\lambda)^2 \tag{S17}$$

where $\langle r^\lambda\rangle$ is the radial expectation value of r^λ for 4f electrons, $\langle 3\|C^{(\lambda)}\|3\rangle$ is a reduced matrix element of the Racah tensor opertor $C^{(\lambda)}$ and σ_λ represents the screening factors due to the 5s and 5p filled sub-shells of the Ln^{3+} ion.

The quantity F is given by:

$$F = \frac{1}{\hbar\gamma_L}\sqrt{\frac{ln2}{\pi}}exp\left[-\left(\frac{\Delta}{\hbar\gamma_L}\right)^2 ln2\right] \tag{S18}$$

where γ_L is the ligand state bandwidth-at -half-maximum and Δ is the transition nergy difference between the donor and acceptor involved in the transfer process.The second part, W_{ET}^{em} of the eq. S15, corresponds to the energy transfer rate obtained from the exchange mechanism and is given as

$$W_{ET}^{em} = \frac{8\pi e^2(1 - \sigma_0)^2}{3\hbar(2J + 1)R_L^4} F\langle \alpha' J' \| S^{(\lambda)} \| \alpha J\rangle^2 \sum_m \left| \left\langle \emptyset \left| \sum_k \mu_z(k) s_m(k) \right| \emptyset' \right\rangle \right|^2 \quad \text{(S19)}$$

where S is the total spin operator of the lanthanide ion, μ_z is the z-component of the electric dipole operator and s_m (*m* = 0, ±1) is a spherical component of the spin operator (both for the ligand electrons) and σ_0 is a distance depend screening factor.[16] The percentage (%) contribution of each pathway to the resultant energy transfer is as:

$$Contribution(\%) = \left[\frac{W_{ET} + W_{BT}}{\sum_{i=1}^{3} (W_{ET} - W_{BT})_i} \right] \times 100 \quad \text{(S20)}$$

The R_L parameter (eq. S21) has been calculated by:

$$R_L = \frac{\sum_i c_i^2 R_{L,i}}{\sum_i c_i^2} \quad \text{(S21)}$$

where c_i being the molecular orbital coefficient of the atom i contributing to the ligand state (triplet or singlet) involved in the energy transfer, $R_{L,i}$ relates to the distance from atom i to the Eu^{3+} ion.

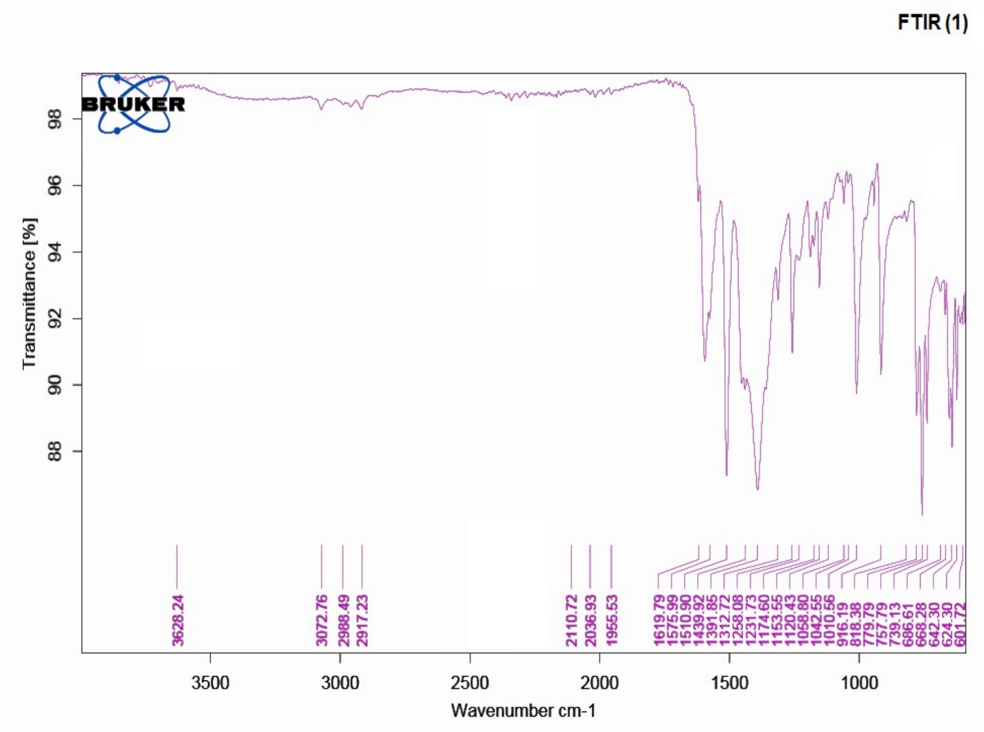

Fig. S1. FTIR spectra of [Sm(acac)$_3$(pyz)$_2$]

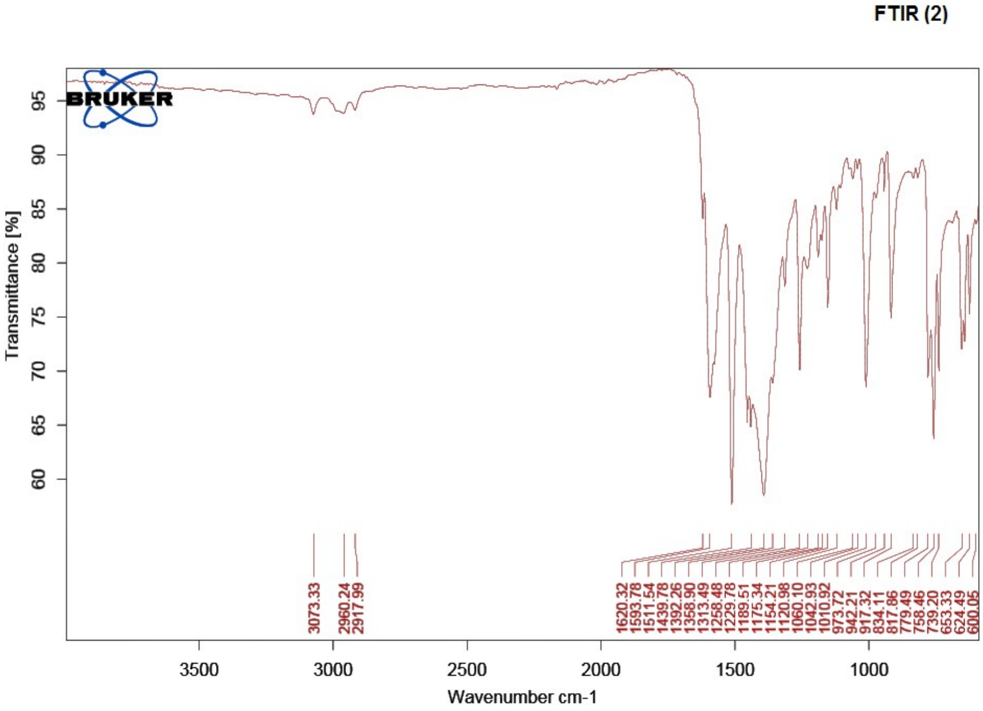

Fig. S2. FTIR spectra of [Eu(acac)$_3$(pyz)$_2$]

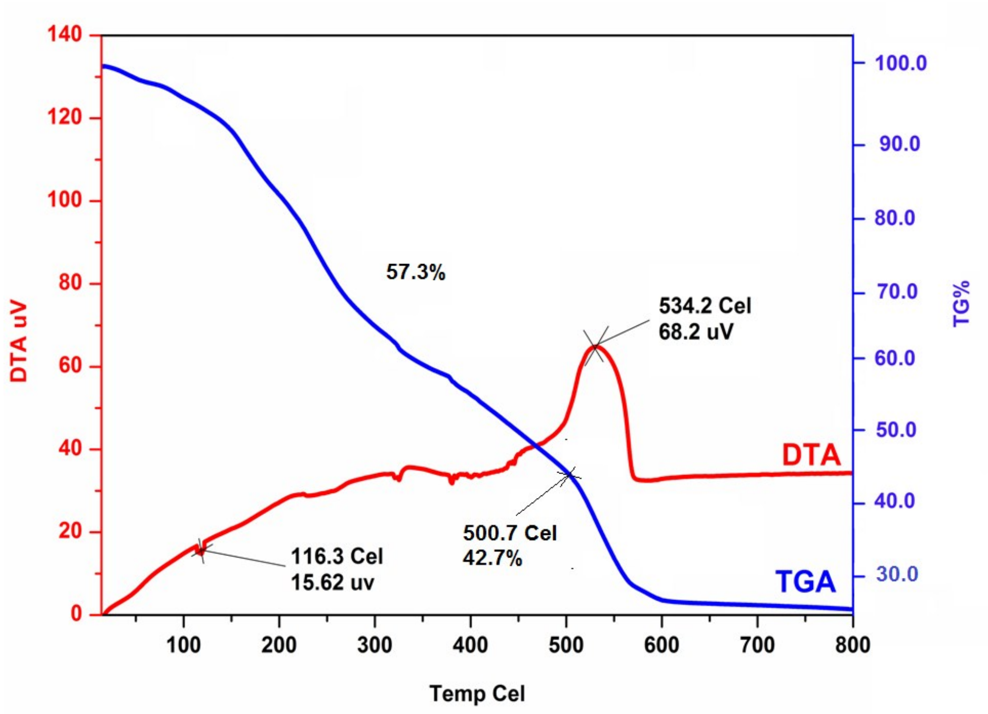

Fig. S3. TG and DTA plots of [Sm(acac)$_3$(pyz)$_2$]

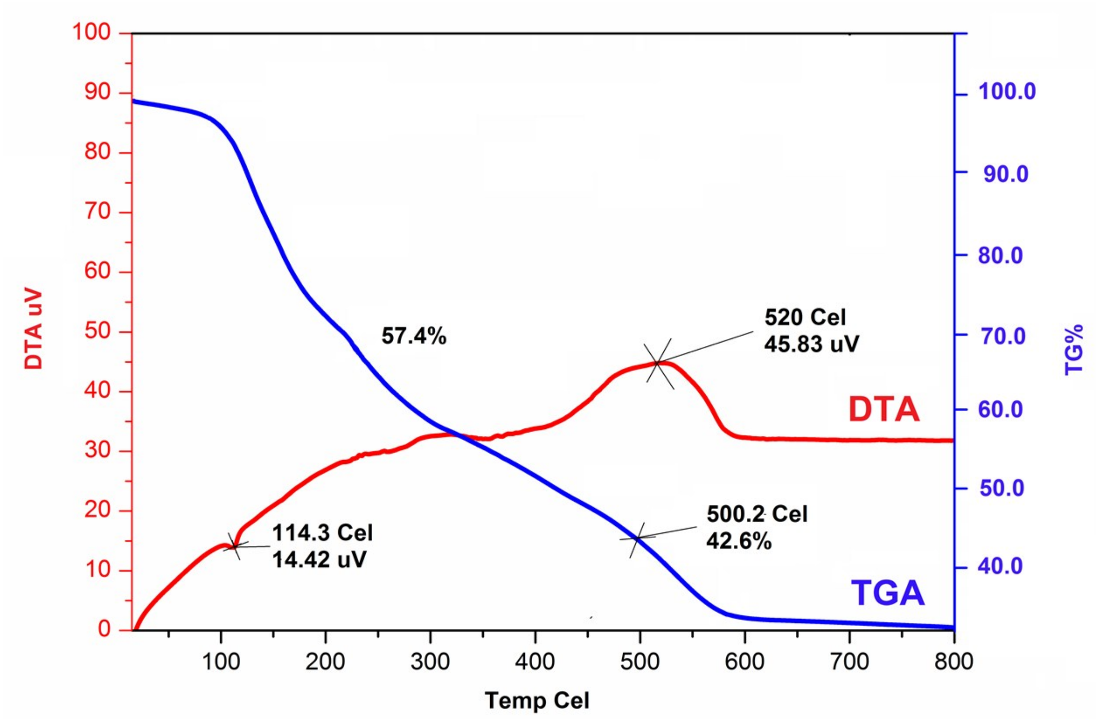

Fig. S4. TG and DTA plots of [Eu(acac)$_3$(pyz)$_2$]

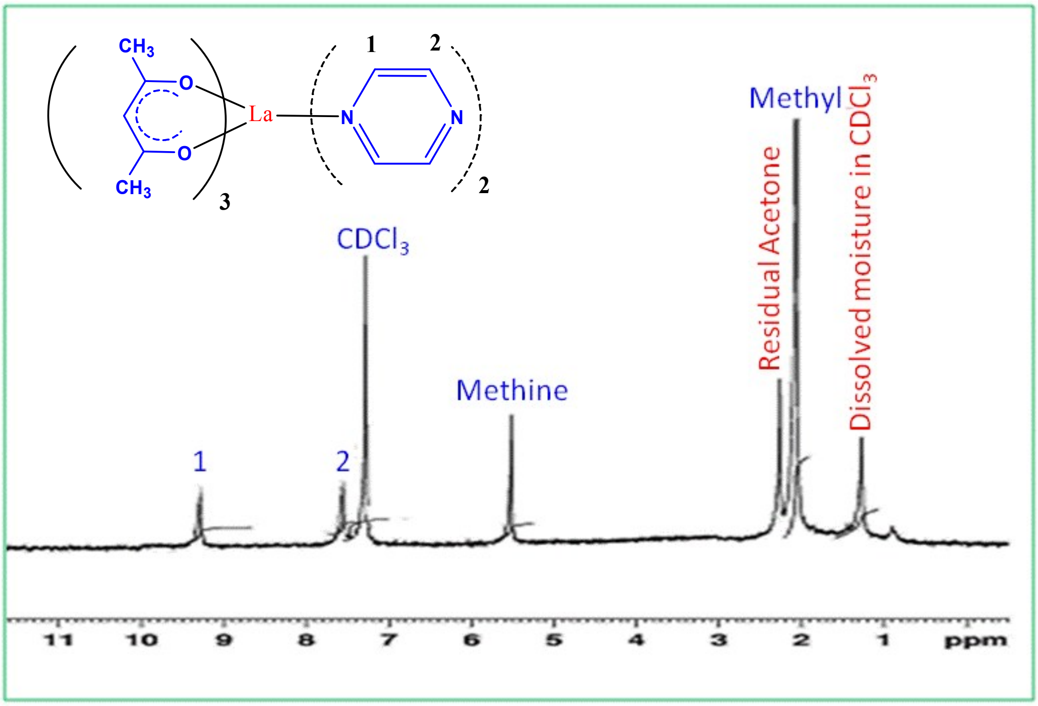

Fig S5. 400 MHz ^{1}H NMR spectrum of [La(acac)$_3$(pyz)$_2$] in CDCl$_3$

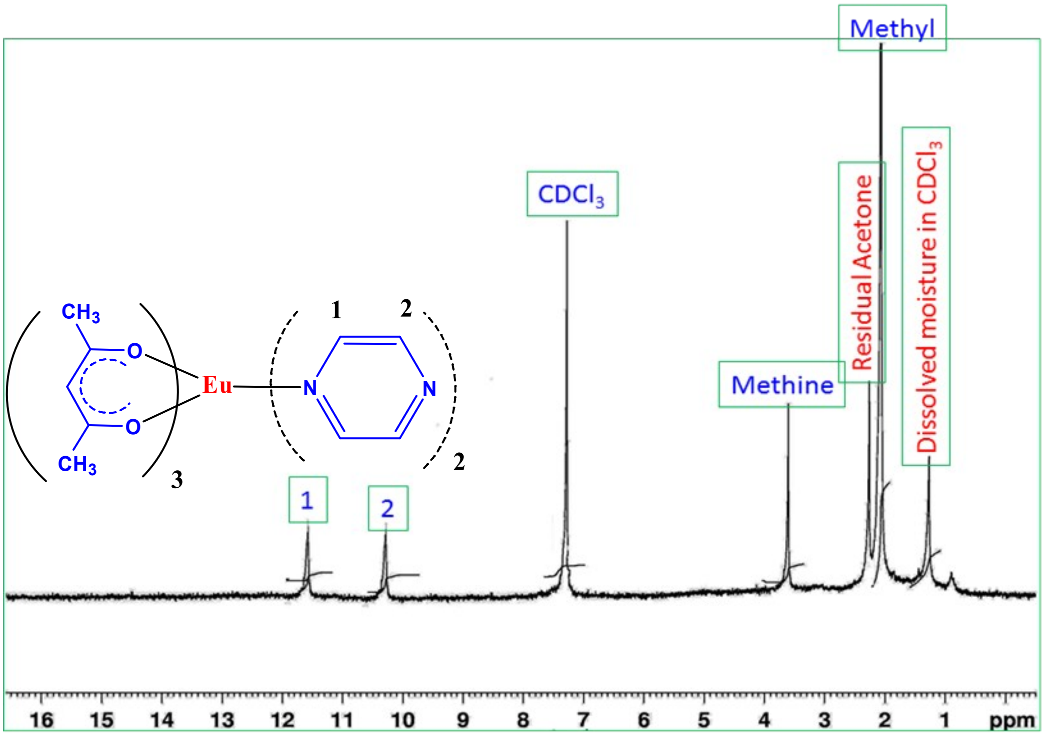

Fig.S6. 400 MHz ^{1}H NMR spectrum of [Eu(acac)$_3$(pyz)$_2$] in CDCl$_3$.

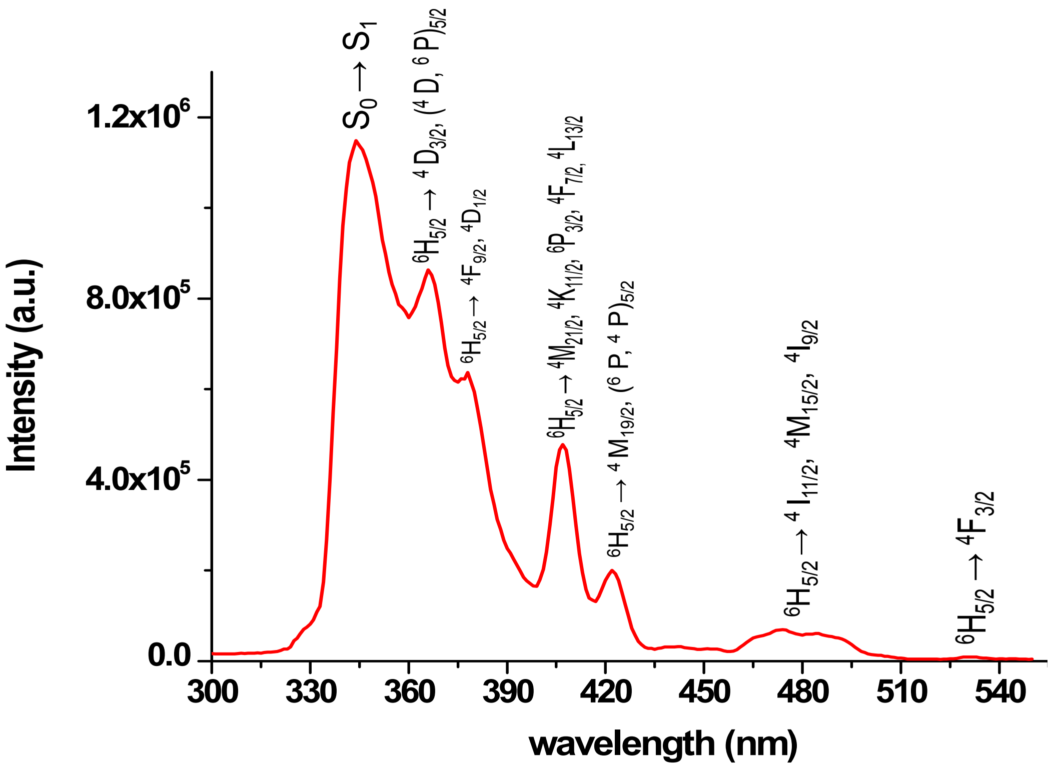

Fig.S7. Excitation spectra of $[Sm(acac)_3(pyz)_2]$ monitered at $\lambda_{emission}$ = 646 nm.

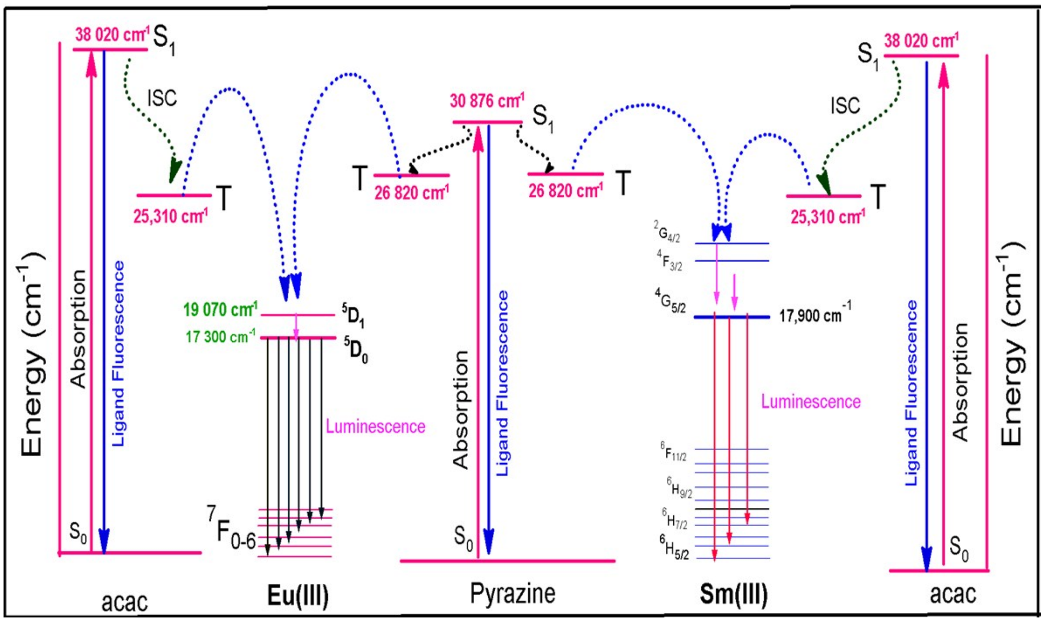

Fig. S8. Schematic energy level diagram and energy transfer processes for the Eu^{3+} and Sm^{3+} complex: S_1 represents the first excited singlet state and T represents the first excited triplet state.

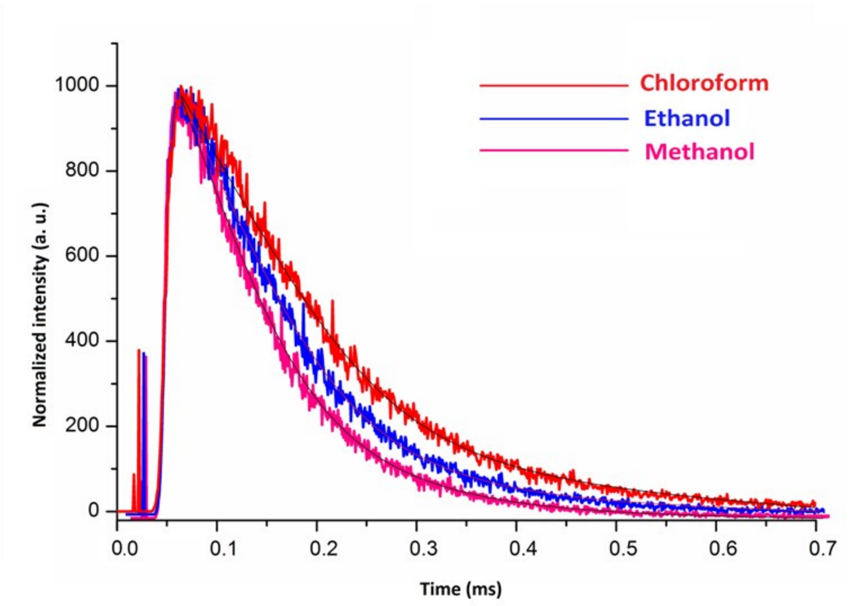

Fig. S9: Luminescence decay curves of [Eu(acac)$_3$(pyz)$_2$] by monitoring the hypersensitive ($^5D_0 \rightarrow {}^7F_2$) transition at 613nm upon excitation at 375 nm.

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