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Electronic Supporting Information

For

Bright Orange and Red Light-emitting Diodes of New Visible Light Excitable Tetrakis-Ln-β-Diketonate (Ln = Sm^{3+}, Eu^{3+}) Complexes

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Experimental

The Ground State Geometry Calculation

The ground state geometry was calculated using the RM1 Model.[1] In this model the basis set used is comprised of 5d, 6s, and 6p orbitals for a total of 9 orbitals. Thus, in this model, the europium trivalent ion contributes three electrons to the valence shell. Due to this more realistic description of the electronic structure, the RM1 compared with the Sparkle Models[2-6] allows to obtain more accurate structures. The calculation was carried out using the Mopac software[7]. The source code has been modified with the implementation of RM1 model parameterized to trivalent lanthanide ions. The used MOPAC keywords in all RM1 calculations were PRECISE, GNORM = 0.25, BFGS, ALLVEC (print all eigenvectors), SCFCRT = 1.D-10 (in order to increase the SCF convergence criterion) and XYZ (the geometry optimizations were performed in Cartesian coordinates).

The Judd-Ofelt Intensity Parameters

As shown in detail in reference[8] the Judd-Ofelt Intensity Parameters (Ω_λ with $\lambda = 2$, 4 and 6) are calculated by adjustment of charge factors (g) and polarizabilities (α) of each europium-ligand bond to reproduce the experimental ones. Although this procedure is appropriate until recently it had a problem that caused some discomfort. The adjustment of the intensity parameters could be accomplished obtaining different sets of charge factors, and polarizabilities associated with metal - ligand bonds. In the present work we are applied for the first time, our new procedure based on the electronic densities and superdelocalizabilities for a unique adjustment of the Ω_λ parameters[9]. This uniqueness has important consequences for the theoretical calculations of energy transfer and back-transfer rates, as well as, in the calculation of the theoretical radiative decay rate (Arad), once that the Judd-Ofelt intensity parameters, or part of these quantities are used as input in their calculations. In our opinion, there is no doubt that this procedure will allow more accurate theoretical predictions.

Luminescent Properties

The calculations of the luminescent properties were accomplished in the LUMPAC software[10]. The energy transfer and back-transfer rates were calculated by using the approach proposed by Malta in 1998[11]. All models used for us in the calculation of triplet and singlet energies, energy transfer and back-transfer rates, quantum efficiency and quantum yield are detailed in previous report[8] and in the LUMPAC homepage – http://lumpac.pro.br/theory.

Singlet and Triplet Energy Calculations

For the calculated ground state geometry, we have predicted their singlet and triplet excited states using configuration interaction single (CIS) based on the intermediate neglect of differential overlap/spectroscopic (INDO/S) technique[12,13]. The calculation was done on the ORCA software.[14] We have used a point charge of +3e to represent the trivalent lanthanide ion.

The R_L, that is the distance between the acceptor and the donor states in the energy transfer process is estimate based on the coefficients orbital molecular of the atom i (c_i) that contribute to the ligand state (triplet or singlet). The R_L has been calculated by:

$$R_L = \frac{\sum_i c_i^2 R_{L,i}}{\sum_i c_i^2}$$

where c_i and $R_{L,i}$ quantities were calculated from some data obtained using the method INDO/S implemented in the ORCA software.[14] The calculated values of R_L singlet and R_L triplet are 7.3215 Å and 8.5353 Å respectively.

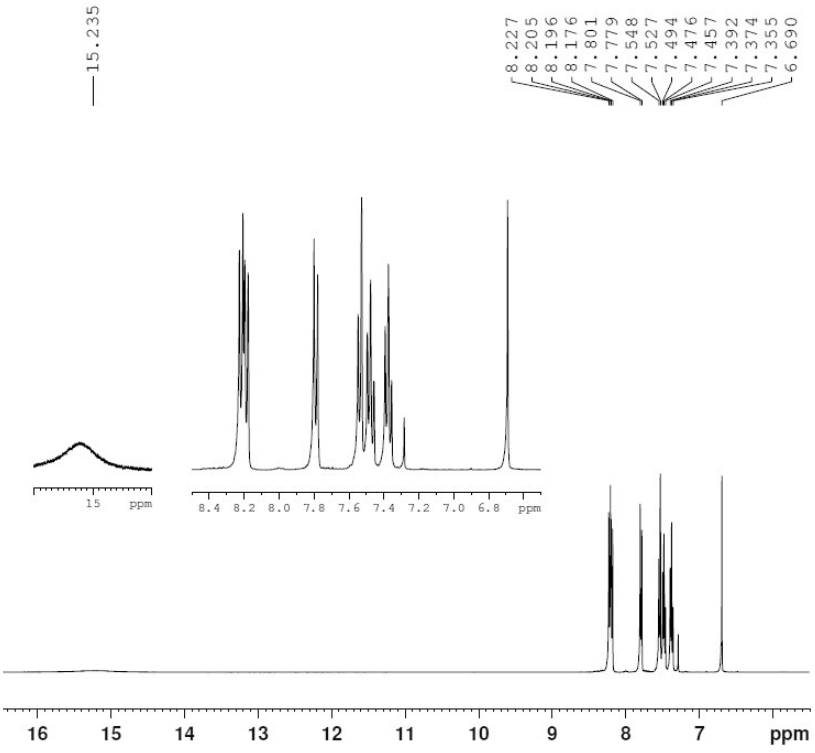


Fig. S1 ^{1}H NMR Spectrum of HL1 in $CDCl_3$

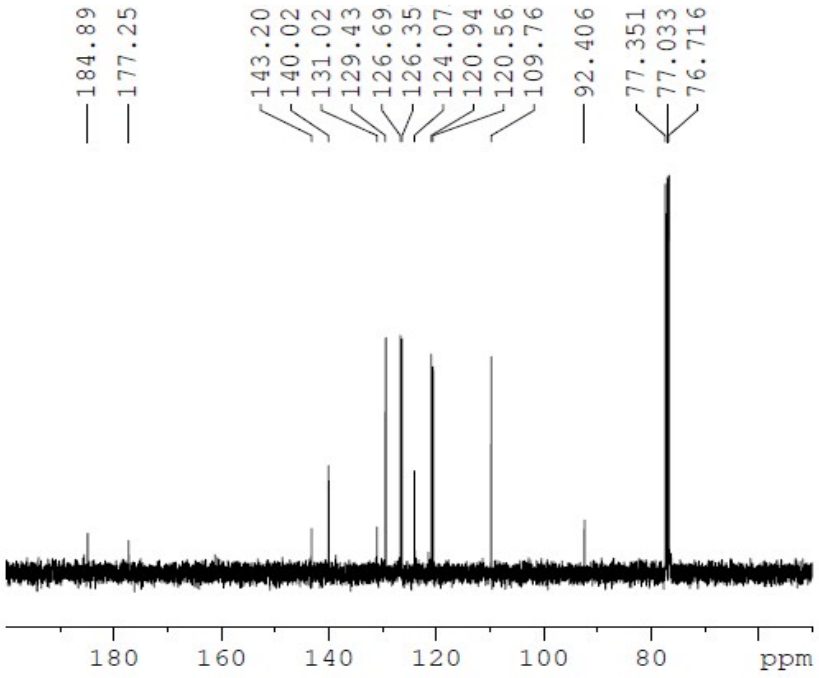


Fig. S2 ^{13}C NMR Spectrum of HL1 in $CDCl_3$

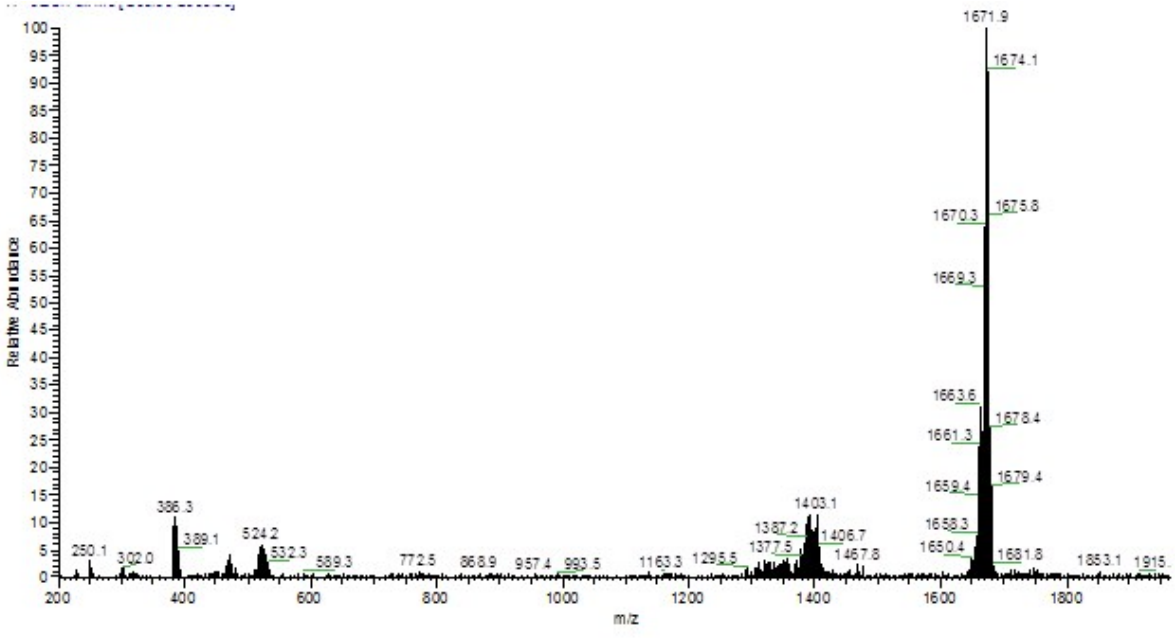


Fig. S3 ESI mass spectrum of $NBu_4[SmL_4]$.

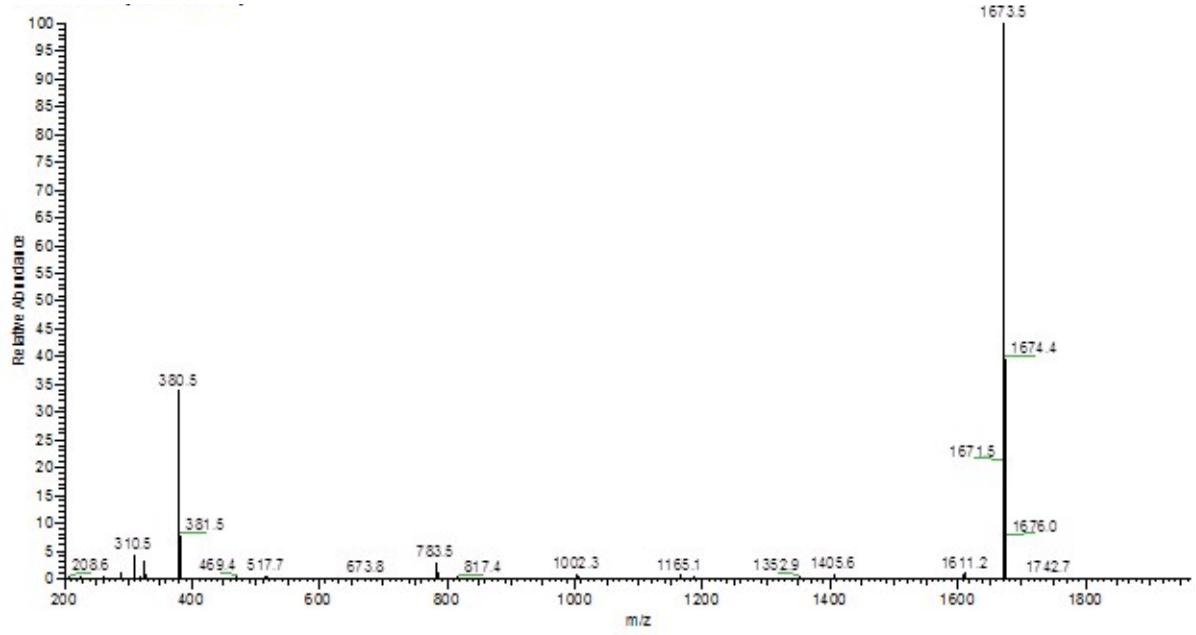


Fig. S4 ESI mass spectrum of $NBu_4[EuL_4]$.

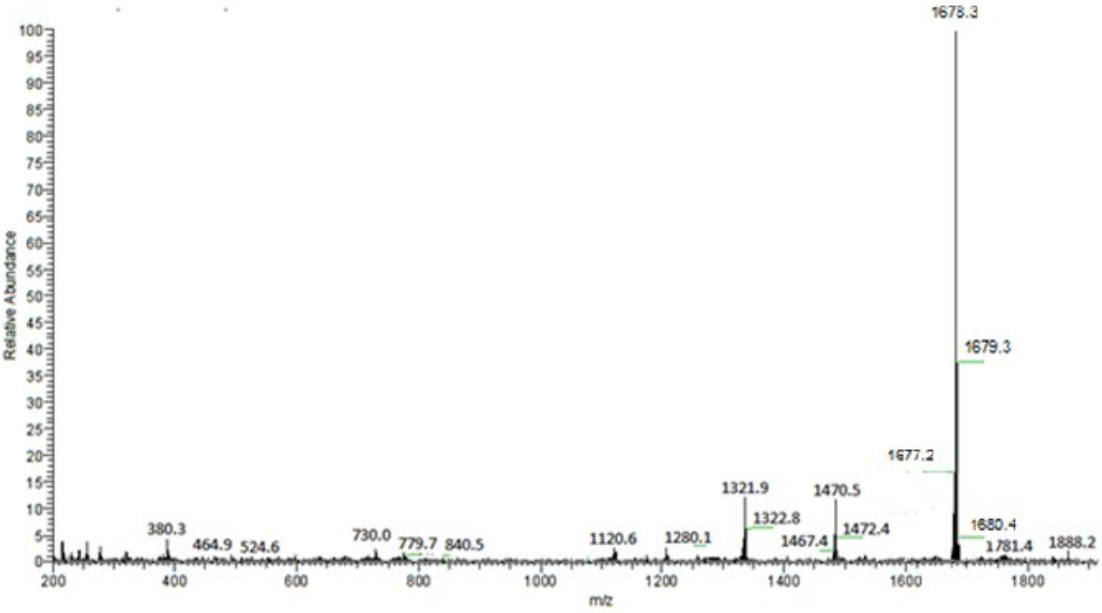


Fig. S5 ESI mass spectrum of $NBu_4[GdL_4]$.

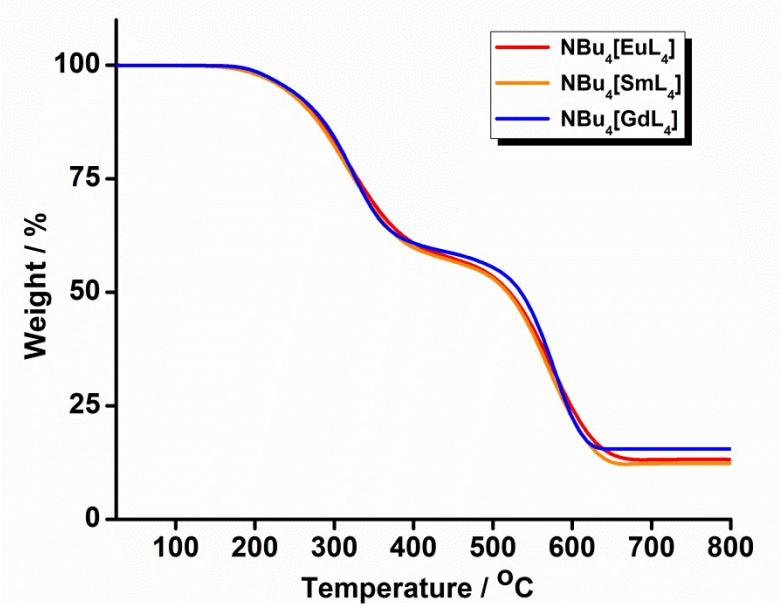


Fig. S6 Thermogravimetric curves of Ln^{3+}-complexes.

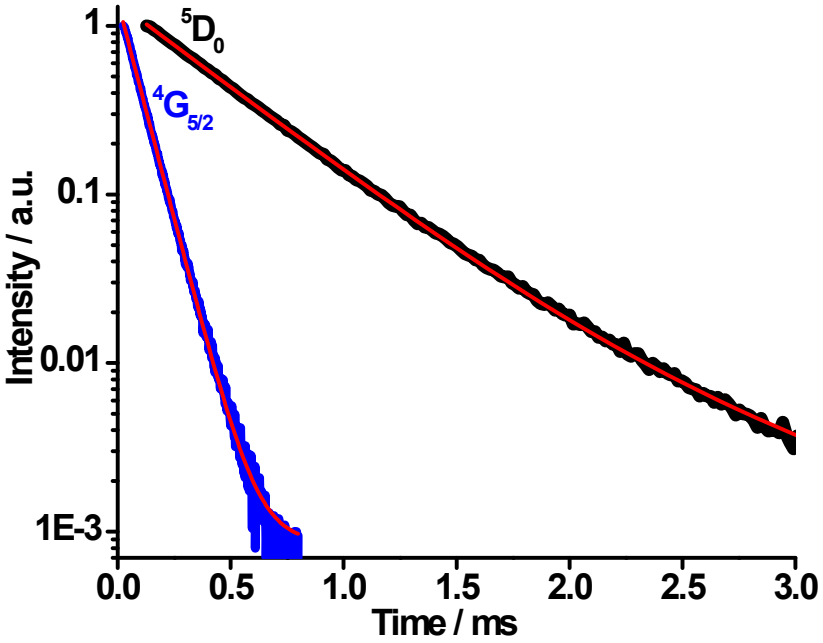


Fig. S7 $^5D_0$, $^4G_{5/2}$ decay profiles of $NBu_4[LnL_4]$ complexes, λ_{em} = 612 nm for Eu^{3+} and 648 nm for Sm^{3+} (λ_{ex} = 410 nm).

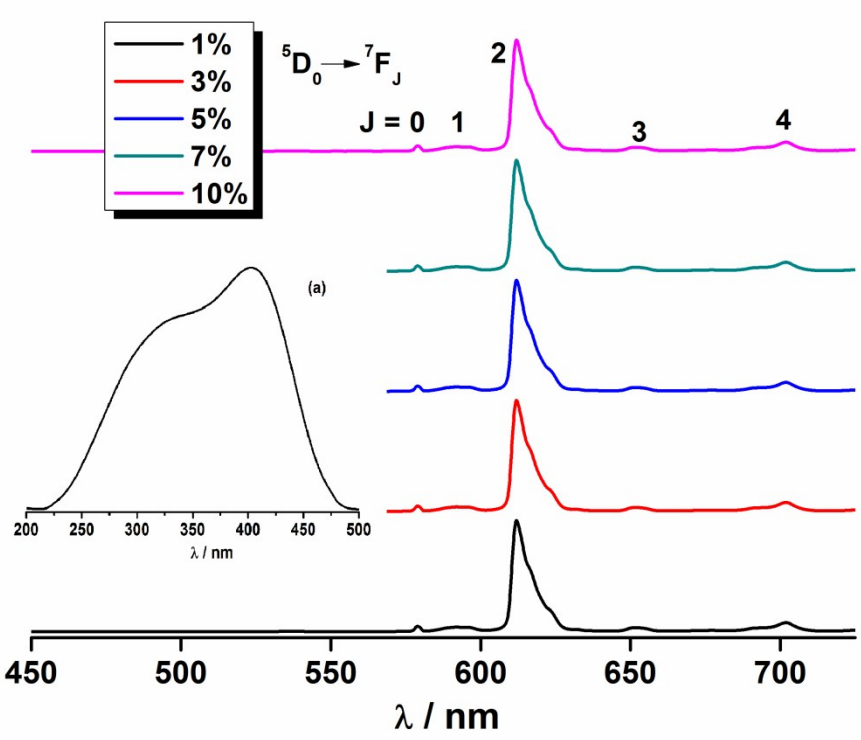


Fig. S8 Corrected, normalized emission (λ_{ex}= 410 nm) spectra of $NBu_4[EuL_4]$ at 298 K in PMMA films (1-10%), (a) excitation spectrum of 5% $NBu_4[EuL_4]$ doped PMMA film (λ_{em}= 612 nm); vertical scales being arbitrary units.

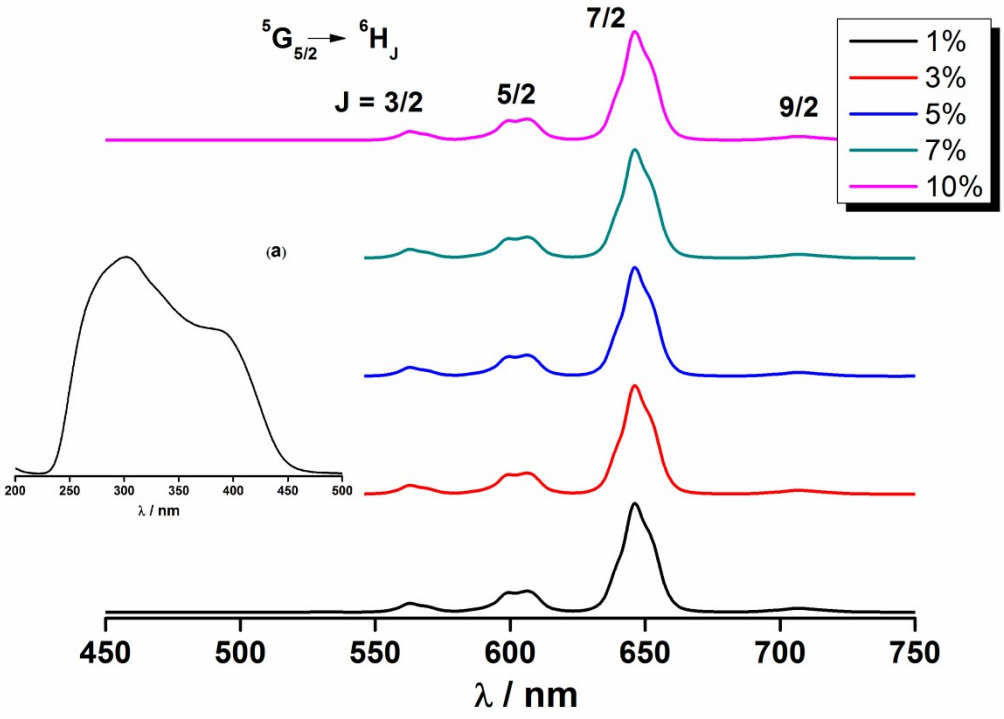
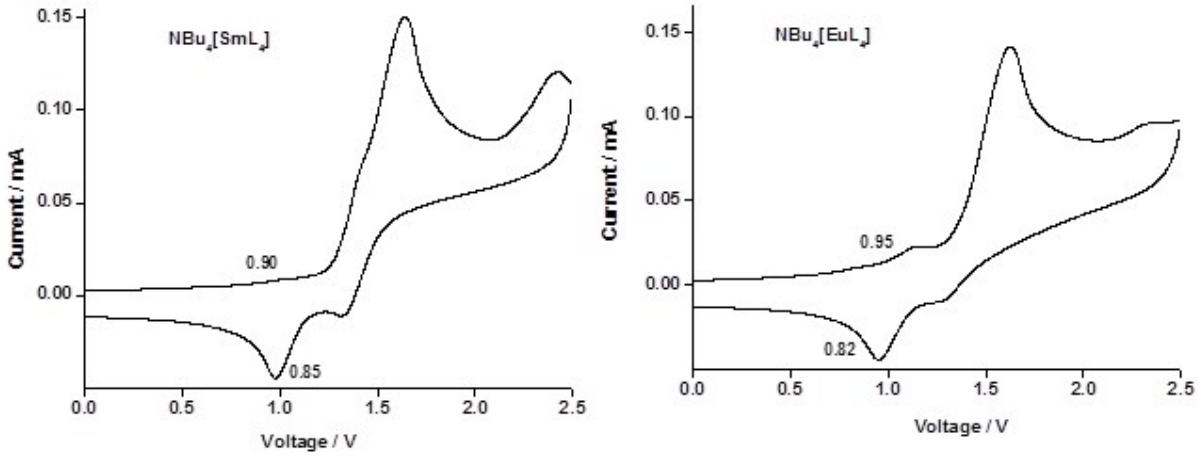


Fig. S9 Corrected, normalized emission (λ_{ex}= 410 nm) spectra of $NBu_4[SmL_4]$ at 298 K in PMMA films (1-10%), (a) excitation spectrum of 5% $NBu_4[SmL_4]$ doped PMMA film (λ_{em}= 648 nm); vertical scales being arbitrary units.

Table S1. ϕ_{ov} (%) and τ_{obs} (μs) values of PMMA thin films doped with 1-10% $NBu_4[LnL_4]$ (Ln = Sm^{3+}, Eu^{3+}) at 298 K.

Concentration (Wt. %)		1%	3%	5%	7%	10%
ϕ_{ov} / %	$NBu_4[SmL_4]$	9 ± 1	10 ± 1	11 ± 1	10 ± 1	10 ± 1
	$NBu_4[EuL_4]$	79 ± 8	77 ± 8	85 ± 9	80 ± 8	78 ± 8
τ_{obs} / μs	$NBu_4[SmL_4]$	115 ± 4	108 ± 2	104 ± 1	100 ± 2	101 ± 3
	$NBu_4[EuL_4]$	811 ± 3	805 ± 6	796 ± 6	790 ± 4	785 ± 4



Complex	**$E_{1/2}^{ox}$(V)**	**Eg (eV)[a]**	**HOMO**	**LUMO**
$NBu_4[SmL_4]$	0.875	3.123	-5.615	-2.492
$NBu_4[EuL_4]$	0.885	3.123	-5.625	-2.502

[a]Obtained from UV-Vis absorption spectra

Fig. S10 Cyclic-Voltagrams and HOMO, LUMO values of $NBu_4[LnL_4]$ (Ln = Sm^{3+}, Eu^{3+}).

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