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Supplementary Information

Intermolecular Energy Transfer and Photostability of Luminescence-tuneable Multicolour PMMA Films Doped with Lanthanide β-diketonate Complexes

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1. Infrared Spectroscopy

The infrared spectroscopy showed a significant displacement of the C=O stretching band from 1665 cm^{-1}, for the free tta ligand, to 1608 cm^{-1} in the IR spectra of the compounds, indicating that the lanthanide ion is coordinated through the oxygen atoms (**Fig. S1**). Besides, this band presents higher intensity with increasing doping concentration from 0.1 to 15 % (weight percentage, w/w) (**Fig. S1**), confirming the successful incorporation of the Ln^{3+}-complexes in the polymer matrix. The same spectroscopic behavior was observed in the case of the $[Tb(acac)_3(H_2O)_3]$ complex (**Fig. S2**).

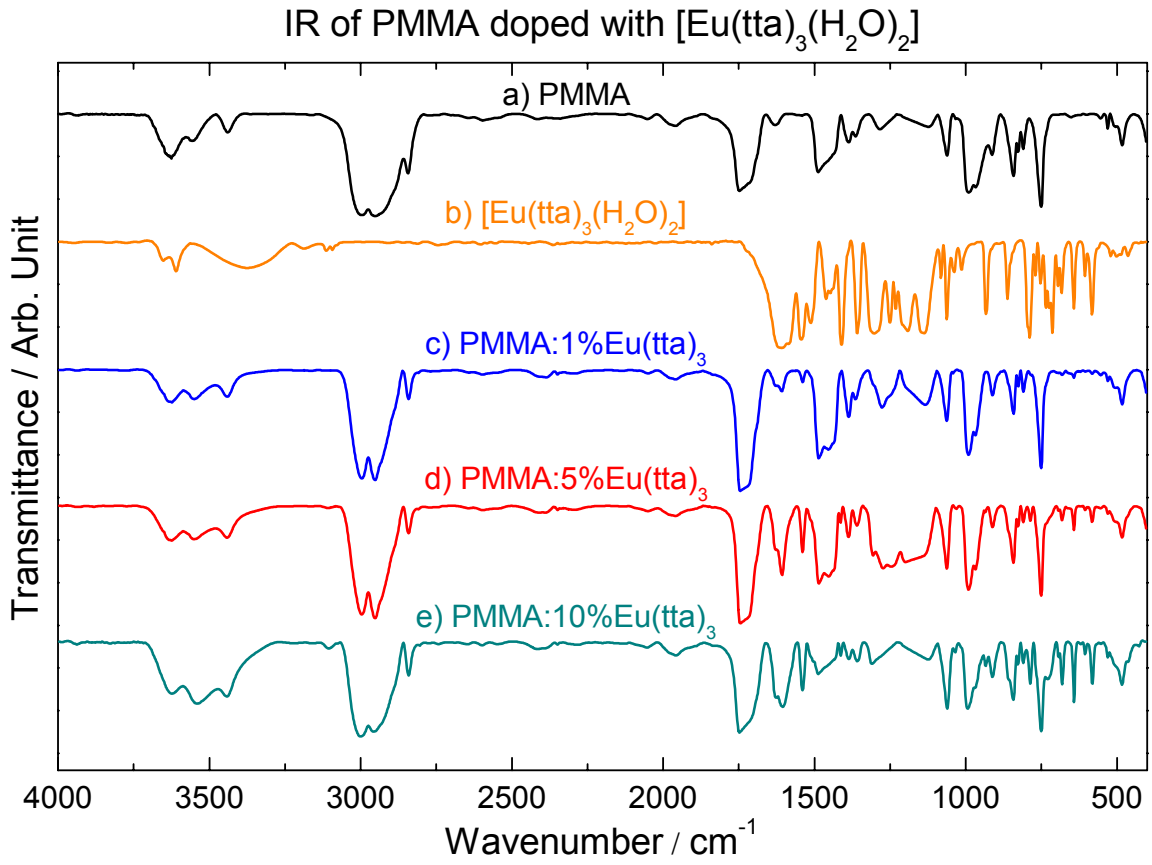

Figure S1. Infrared absorption spectra of: a) PMMA, b) $[Eu(tta)_3(H_2O)_2]$, c) PMMA:1%$Eu(tta)_3$ d) PMMA:5%$Eu(tta)_3$ and e) PMMA:10%$Eu(tta)_3$.

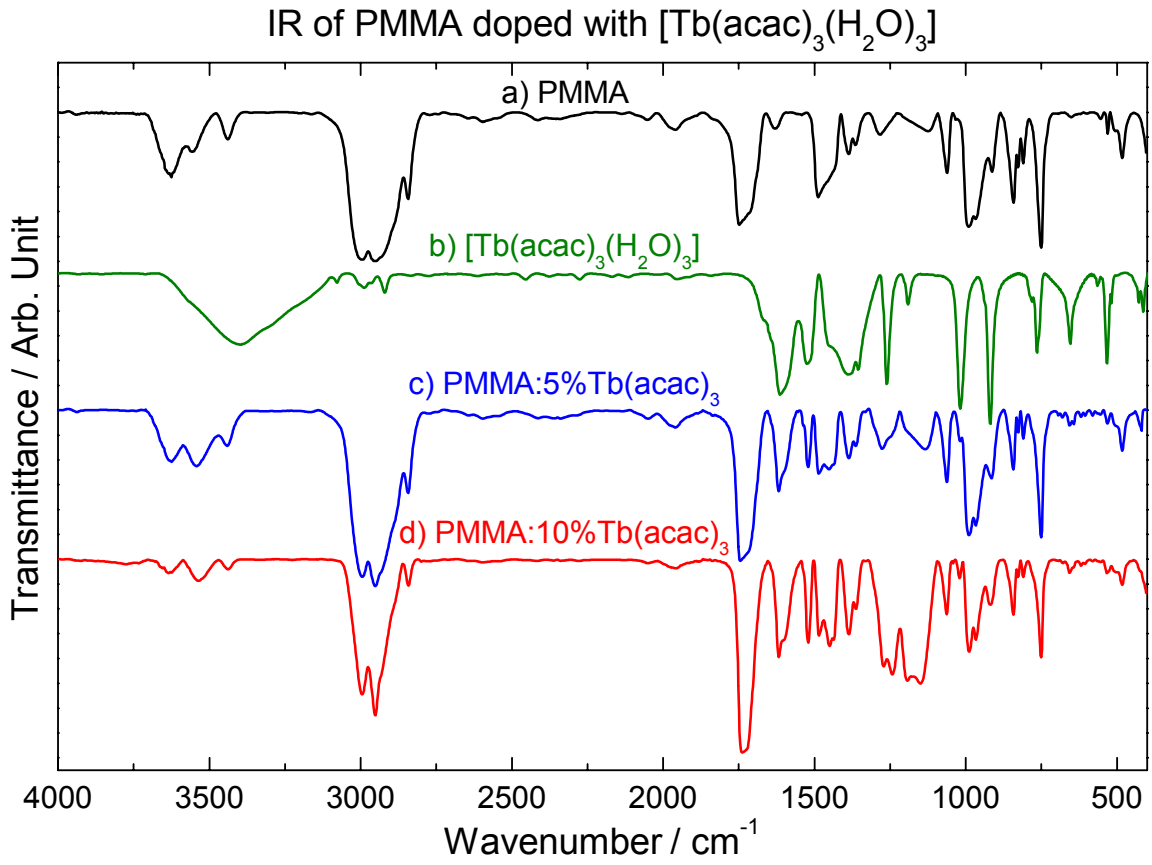

Figure S2. Infrared absorption spectra of: a) PMMA, b) $[Tb(acac)_3(H_2O)_3]$, c) PMMA:5%$Tb(acac)_3$ and d) PMMA:10%$Tb(acac)_3$.

2. Thermogravimetry

Table S1. The thermal analysis for the PMMA-Ln^{3+}-complexes prepared in this work.

Sample	T_1 (°C)	T_2 (°C)	Δm (%)	Residue (%)
PMMA	304	418	91.5	2.08
PMMA:5%$Tb(acac)_3$	299	425	84.3	6.71
PMMA:10%$Tb(acac)_3$	297	422	83.9	10.1
PMMA:15%$Tb(acac)_3$	298	419	76.4	14.1
PMMA:1%$Eu(tta)_3$	297	415	92.9	4.27
PMMA:5%$Eu(tta)_3$	296	419	87.3 (26.8+60.5)	3.03
PMMA:10%$Eu(tta)_3$	293	426	92.2 (34.5+57.7)	5.34

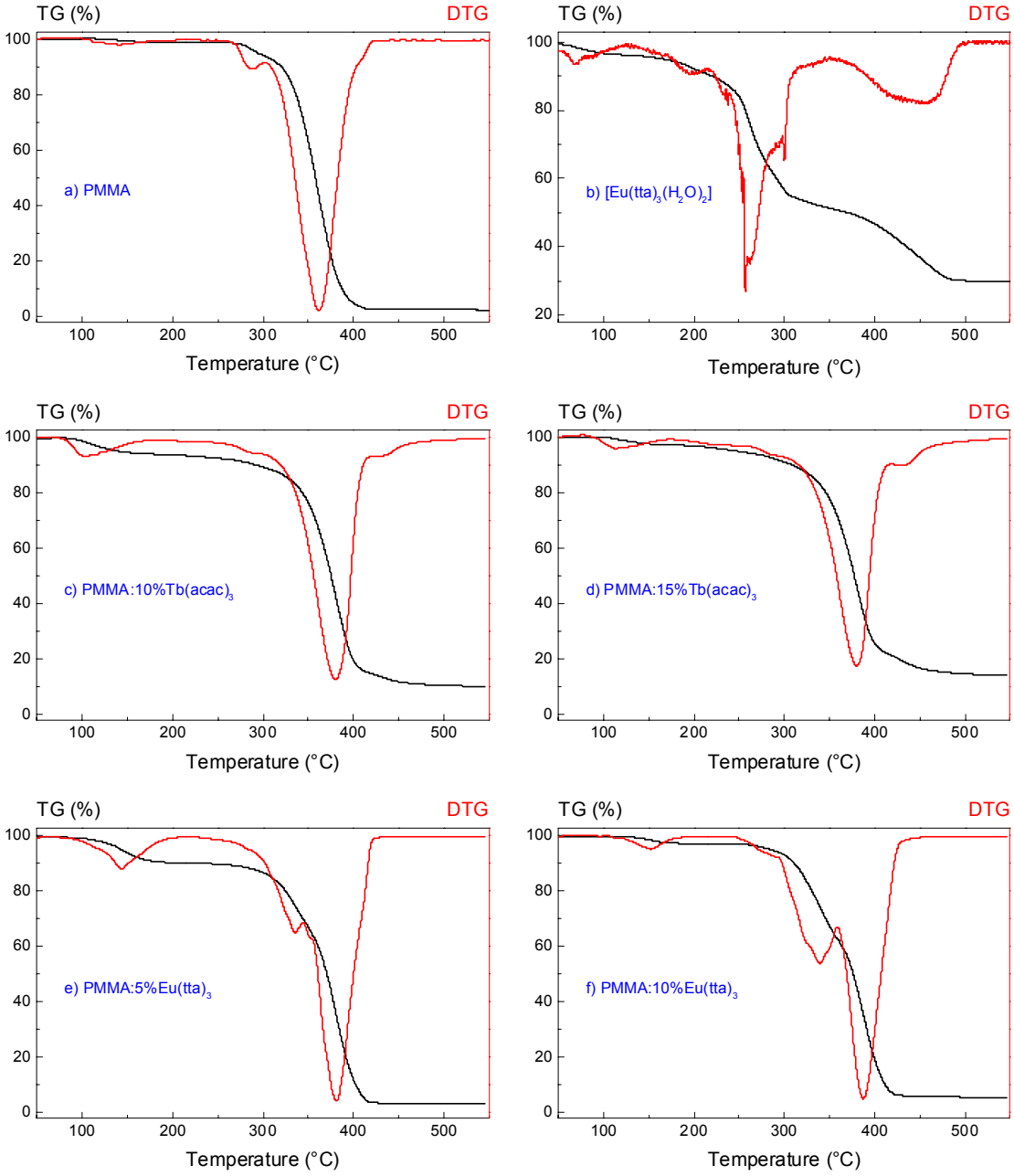

Figure S3. Thermogravimetry (TG) and differential thermogravimetry (DTG) curves registered under dynamic N_2 atmosphere of: a) PMMA, b) PMMA:5%Tb(acac)$_3$, c) PMMA:10%Tb(acac)$_3$, d) PMMA:15%Tb(acac)$_3$, e) PMMA:5%Eu(tta)$_3$ and f) PMMA:10%Eu(tta)$_3$.

3. Emission spectra of PMMA doped with $[Eu(tta)_3(H_2O)_2]$

The emission spectra of the PMMA:x%$Eu(tta)_3$ films (x = 1, 5, 10 and 15) and $[Eu(tta)_3(H_2O)_2]$ complex were recorded in the range from 470 to 720 nm, under excitation on the organic moiety at 350 nm in order to investigate the chemical environment around Ln^{3+} ions in the polymer matrix. The doped polymer films show the characteristic $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3 and 4) transitions of the Eu^{3+} ion, with the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition (614 nm) as the most prominent one (**Fig. S4**).

Figure S4a–d presents the inhomogeneous line broadening effect for the $^5D_0 \rightarrow {}^7F_J$ transitions of the PMMA:$Eu(tta)_3$ system compared with those narrow emission lines of the hydrated complex precursor (**Fig. S4e**). This is a consequence of a distribution of slightly different symmetry sites occupied by the Eu^{3+} ion upon incorporation into the polymer.[1]

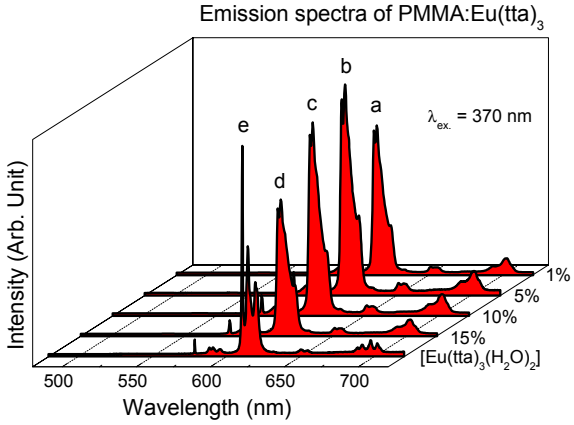

Figure S4. Emission spectra of PMMA:x%$Eu(tta)_3$ films where x = 1 (a), 5 (b), 10 (c) and 15 % (d) and $[Eu(tta)_3(H_2O)_2]$ complex (e) recorded in the spectral range from 420 to 720 nm under excitation at 350 nm.

References

[1] O. L. Malta, L. D. Carlos, *Quim. Nova* **2003**, *26*, 889.