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$_2$O)$_3$] complex (Fig. S2).

![IR of PMMA doped with [Eu(tta)$_3$(H$_2$O)$_2$]]

**Figure S1.** Infrared absorption spectra of: a) PMMA, b) [Eu(tta)$_3$(H$_2$O)$_2$], 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$_2$O)$_3$], 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T$_1$ (°C)</th>
<th>T$_2$ (°C)</th>
<th>Δm (%)</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>304</td>
<td>418</td>
<td>91.5</td>
<td>2.08</td>
</tr>
<tr>
<td>PMMA:5%Tb(acac)$_3$</td>
<td>299</td>
<td>425</td>
<td>84.3</td>
<td>6.71</td>
</tr>
<tr>
<td>PMMA:10%Tb(acac)$_3$</td>
<td>297</td>
<td>422</td>
<td>83.9</td>
<td>10.1</td>
</tr>
<tr>
<td>PMMA:15%Tb(acac)$_3$</td>
<td>298</td>
<td>419</td>
<td>76.4</td>
<td>14.1</td>
</tr>
<tr>
<td>PMMA:1%Eu(tta)$_3$</td>
<td>297</td>
<td>415</td>
<td>92.9</td>
<td>4.27</td>
</tr>
<tr>
<td>PMMA:5%Eu(tta)$_3$</td>
<td>296</td>
<td>419</td>
<td>87.3 (26.8+60.5)</td>
<td>3.03</td>
</tr>
<tr>
<td>PMMA:10%Eu(tta)$_3$</td>
<td>293</td>
<td>426</td>
<td>92.2 (34.5+57.7)</td>
<td>5.34</td>
</tr>
</tbody>
</table>
Figure S3. Thermogravimetry (TG) and differential thermogravimetry (DTG) curves registered under dynamic N₂ 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(H₂O)₂]

The emission spectra of the PMMA:x%Eu(tta)₃ films (x = 1, 5, 10 and 15) and [Eu(tta)₃(H₂O)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 Ln³⁺ ions in the polymer matrix. The doped polymer films show the characteristic ⁵D₀→⁷F₉ (J = 0, 1, 2, 3 and 4) transitions of the Eu³⁺ ion, with the hypersensitive ⁵D₀→⁷F₂ transition (614 nm) as the most prominent one (Fig. S4).

Figure S4a–d presents the inhomogeneous line broadening effect for the ⁵D₀→⁷F₉ 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 Eu³⁺ ion upon incorporation into the polymer.[1]

![Emission spectra of PMMA:Eu(tta)₃](image)

**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(H₂O)₂] complex (e) recorded in the spectral range from 420 to 720 nm under excitation at 350 nm.

References