

## Supporting Information

### High Red Luminescence Intensity under Sunlight Exposure of a PMMA Polymer doped with Tetrakis Eu<sup>3+</sup> $\beta$ -diketonate Complex containing Benzimidazolium Counterion

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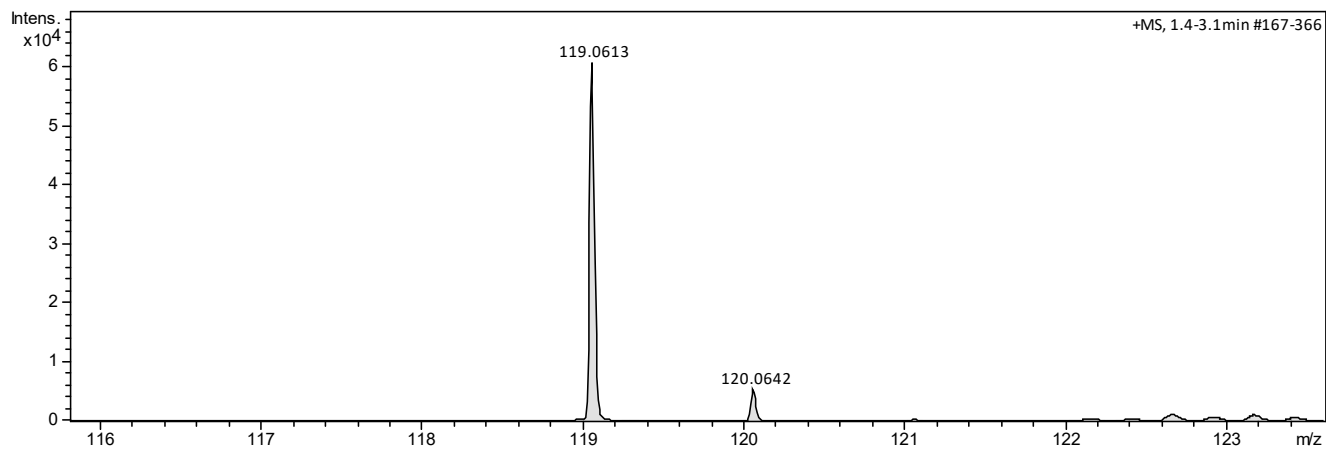
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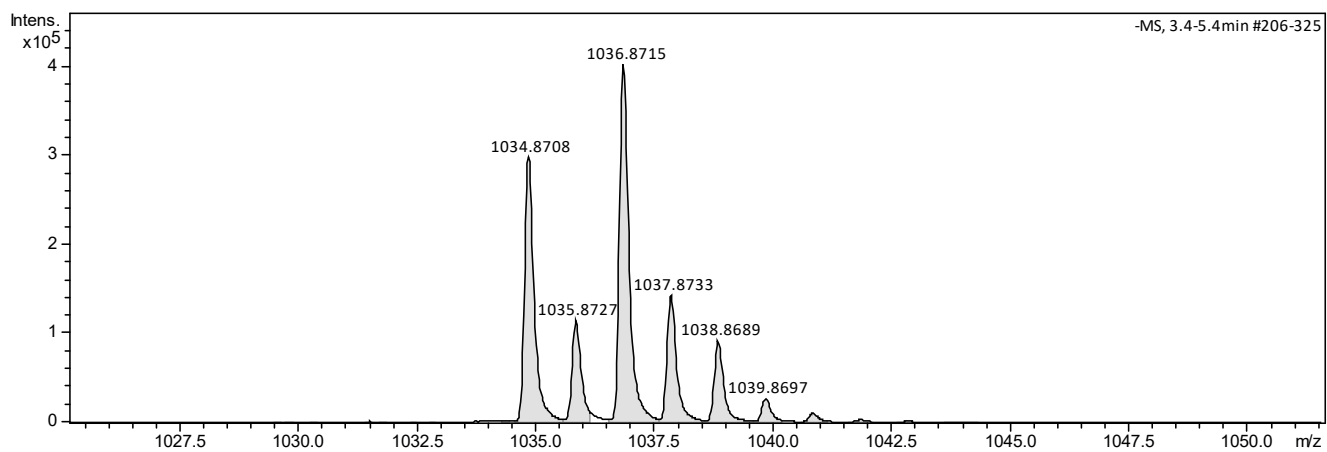
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**ESI(+), MeOH**

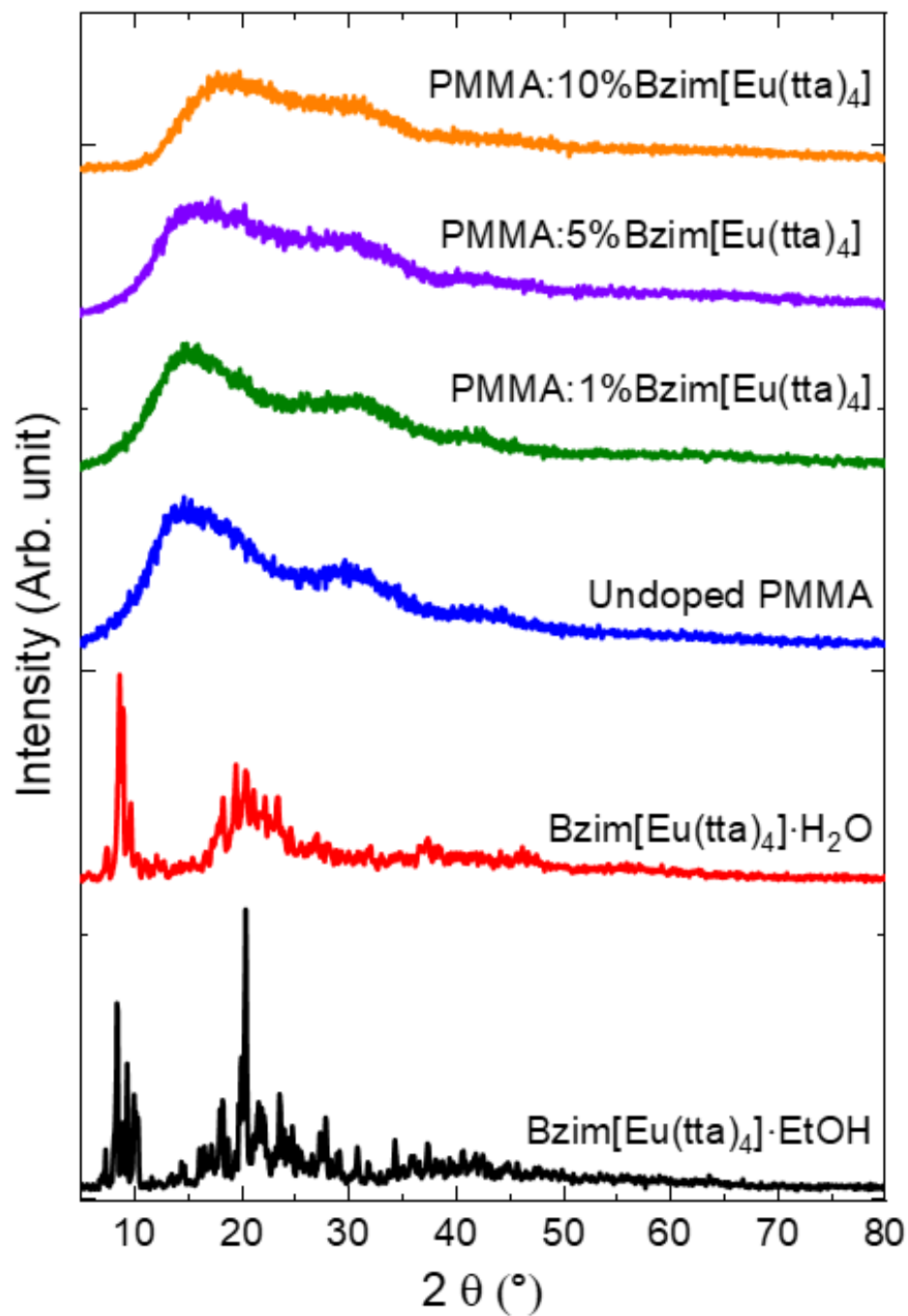


**Figure S1:** ESI(+)-MS Spectrum of Bzim[Eu(tta)<sub>4</sub>], *m/z* corresponds to Bzim<sup>+</sup>.

**ESI(-), MeOH**

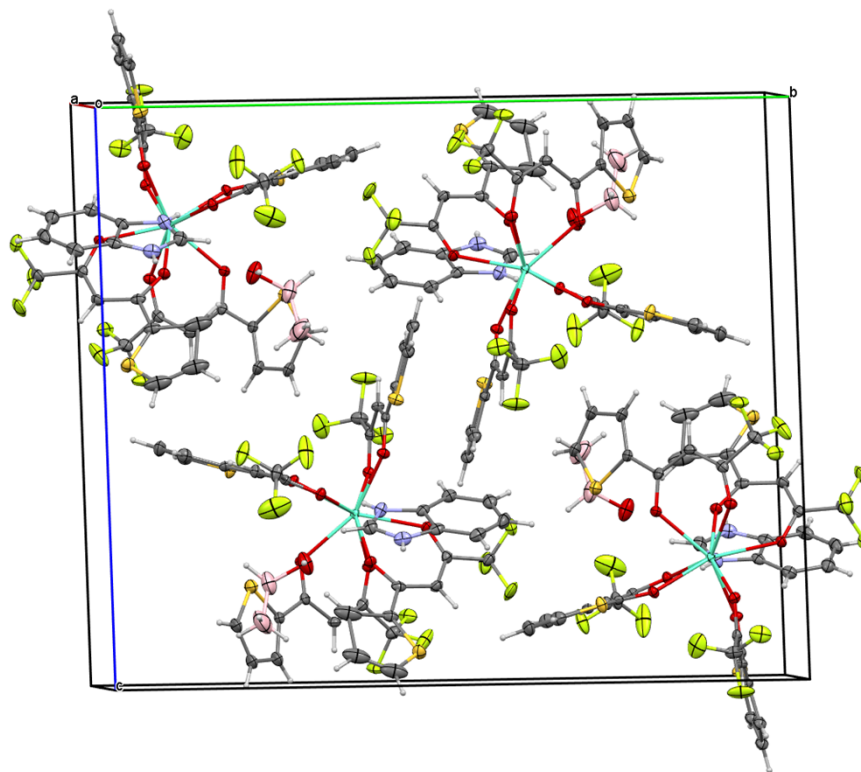


**Figure S2:** ESI(-)-MS Spectrum of Bzim[Eu(tta)<sub>4</sub>], *m/z* corresponds to [Eu(tta)<sub>4</sub>]<sup>-</sup>.

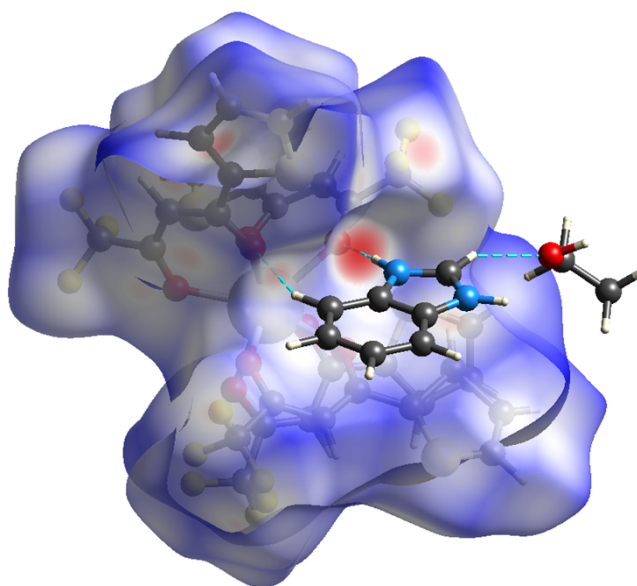


**Figure S3.** X-ray powder diffraction patterns (XPD) of the Bzim[Eu(tta)<sub>4</sub>]·EtOH (black line), Bzim[Eu(tta)<sub>4</sub>]·H<sub>2</sub>O (red line), undoped PMMA (blue line) and PMMA:x% Bzim[Eu(tta)<sub>4</sub>], where x: 1 (green line), 5 (purple line) and 10% (orange line) w/w. All data were recorded at room temperature in the 5–80° range.

a)



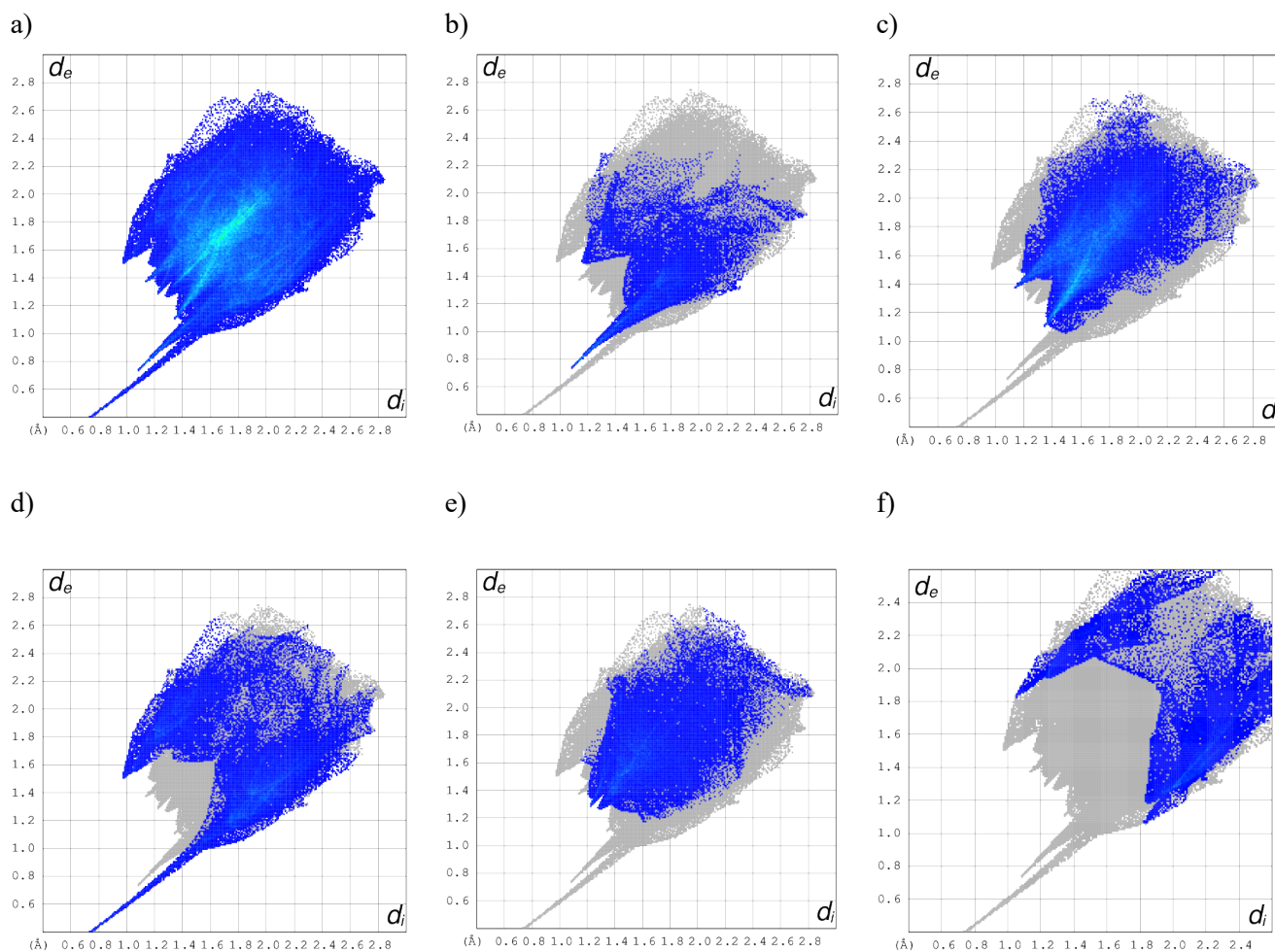
b)



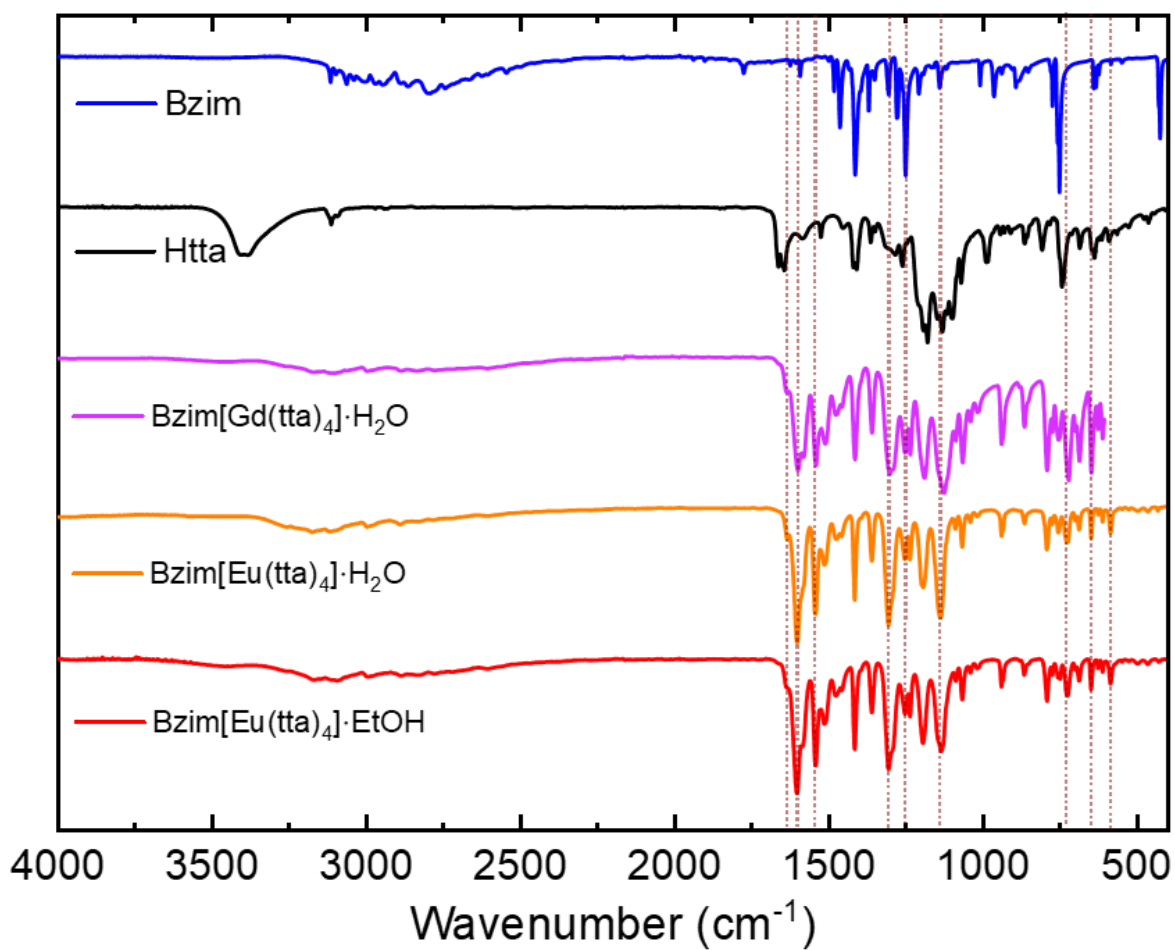
**Figure S4.** Crystal packing diagram (one unit cell) for the Bzim[Eu(tta)<sub>4</sub>]·EtOH structure. The packing diagram is viewed approximately along the crystallographic a-axis, EtOH solvent molecules highlighted in pink for clarity (a) and Hirshfeld surfaces mapped with  $d_{\text{norm}}$  for the Bzim[Eu(tta)<sub>4</sub>]·EtOH (b)

**Table S1.** Single crystal data and structure refinement for Bzim[Eu(tta)<sub>4</sub>] $\cdot$ EtOH complex.

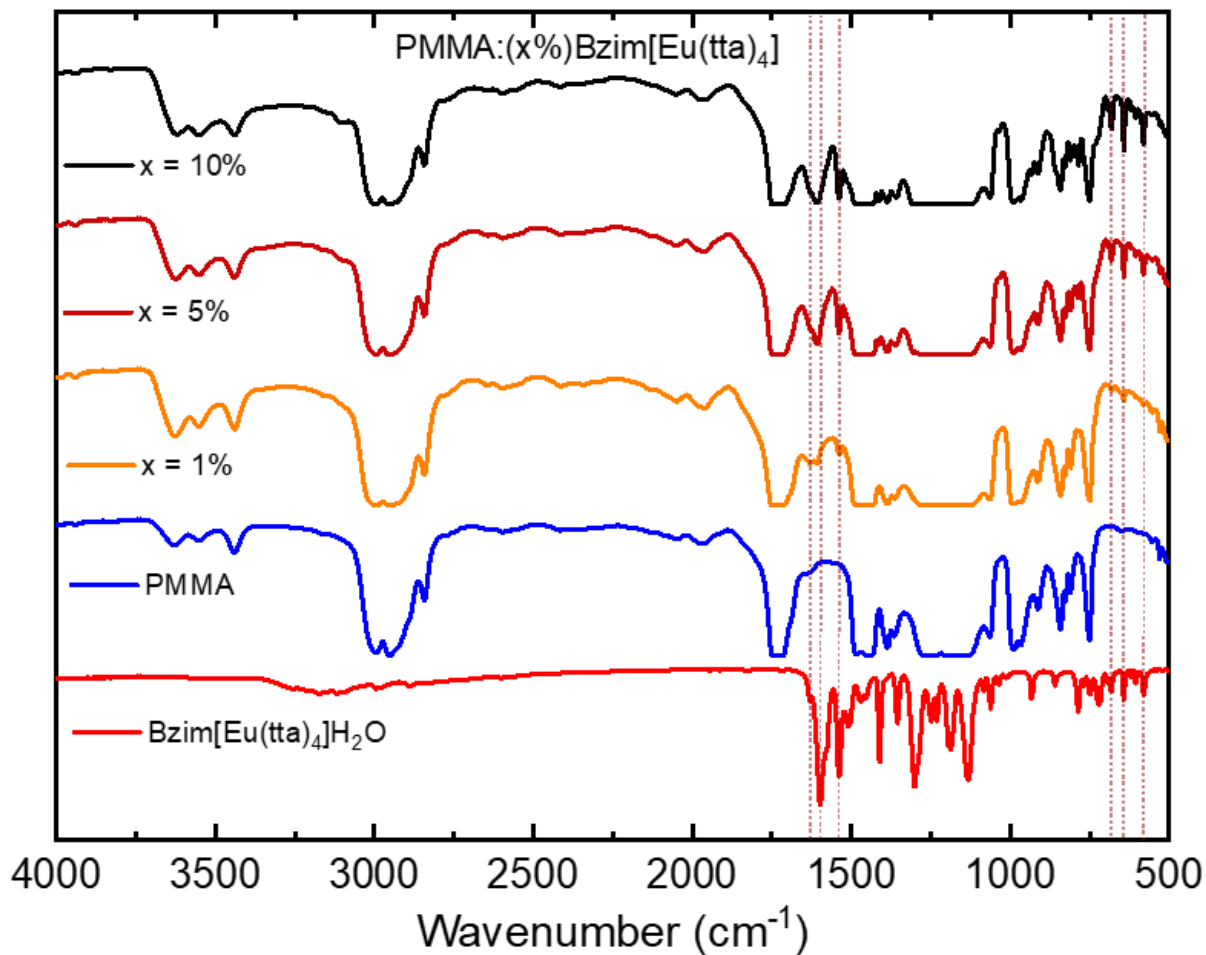
<b>Complex</b>	<b>Bzim[Eu(tta)<sub>4</sub>]<math>\cdot</math>EtOH</b>	
Empirical formula	C <sub>41</sub> H <sub>29</sub> EuF <sub>12</sub> N <sub>2</sub> O <sub>9</sub> S <sub>4</sub>	
Formula weight	1201.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.2374(4) Å	$\alpha = 90^\circ$ .
	b = 23.0415(9) Å	$\beta = 104.5740(10)^\circ$ .
	c = 19.8634(8) Å	$\gamma = 90^\circ$ .
Volume/Å <sup>3</sup>	4534.7(3)	
Z	4	
Density (calculated)	1.760 Mg/m <sup>3</sup>	
Absorption coefficient	1.673 mm <sup>-1</sup>	
F(000)	2384	
Crystal size	0.260 x 0.060 x 0.030 mm <sup>3</sup>	
Theta range for data collection	1.379 to 26.412°.	
Index ranges	-12 $\leq$ h $\leq$ 8, -28 $\leq$ k $\leq$ 28, -24 $\leq$ l $\leq$ 24	
Reflections collected	59993	
Independent reflections	9297 [R(int) = 0.0454]	
Completeness to theta = 25.242°	100.0 %	
Max. and min. transmission	0.7454 and 0.6243	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	9297 / 6 / 614	
Goodness-of-fit on F <sup>2</sup>	1.038	
Final R indices [I $\geq$ 2 $\sigma$ (I)]	R1 = 0.0289, wR2 = 0.0616	
R indices (all data)	R1 = 0.0366, wR2 = 0.0645	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.032 and -0.856 e.Å <sup>-3</sup>	



**Figure S5.** Fingerprint plots: a) all (100%), b) [O $\cdots$ H]/[H $\cdots$ O] (9.4% ), c) [F $\cdots$ H]/[H $\cdots$ F] (32.4%), d) [C $\cdots$ H]/[H $\cdots$ C] (18.2%), e) [H $\cdots$ H]/[H $\cdots$ H] (15.7%), and f) [S $\cdots$ H]/[H $\cdots$ S] (7.4%) contacts for Bzim[Eu(tta)<sub>4</sub>] $\cdot$ EtOH displaying percentages of contacts contributed to the total Hirshfeld surface area of the complex.

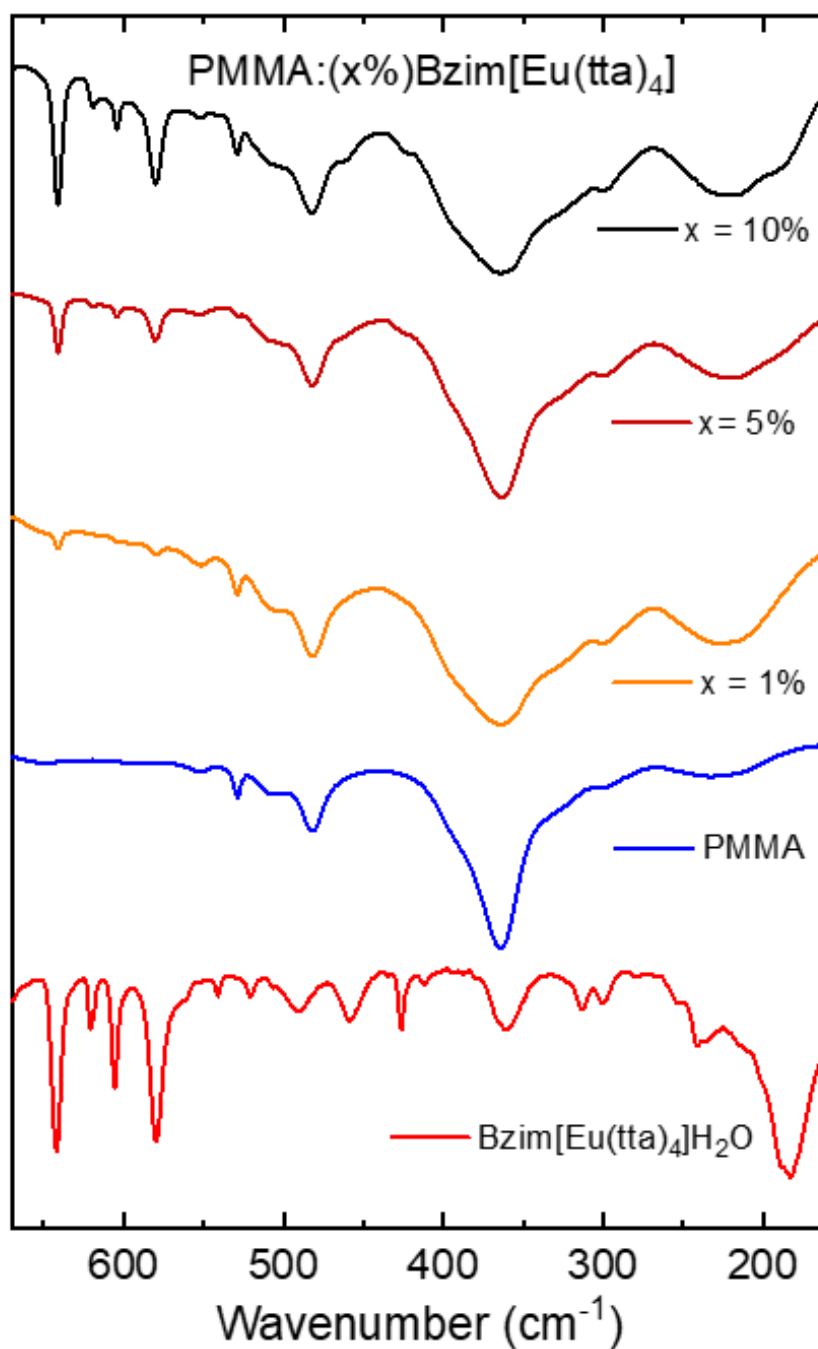


**Figure S6.** Infrared absorption spectra (FTIR) of the Bzim (blue line), Htta ligand (black line) and Bzim[Ln(tta)<sub>4</sub>]·H<sub>2</sub>O, where Ln<sup>3+</sup>: Gd (purple line) and Eu (red line) complexes, besides the Bzim[Eu(tta)<sub>4</sub>]·EtOH. All spectra were registered using ATR mode with a spectral resolution of 2.0 cm<sup>-1</sup> in the range of 4000-400 cm<sup>-1</sup>.

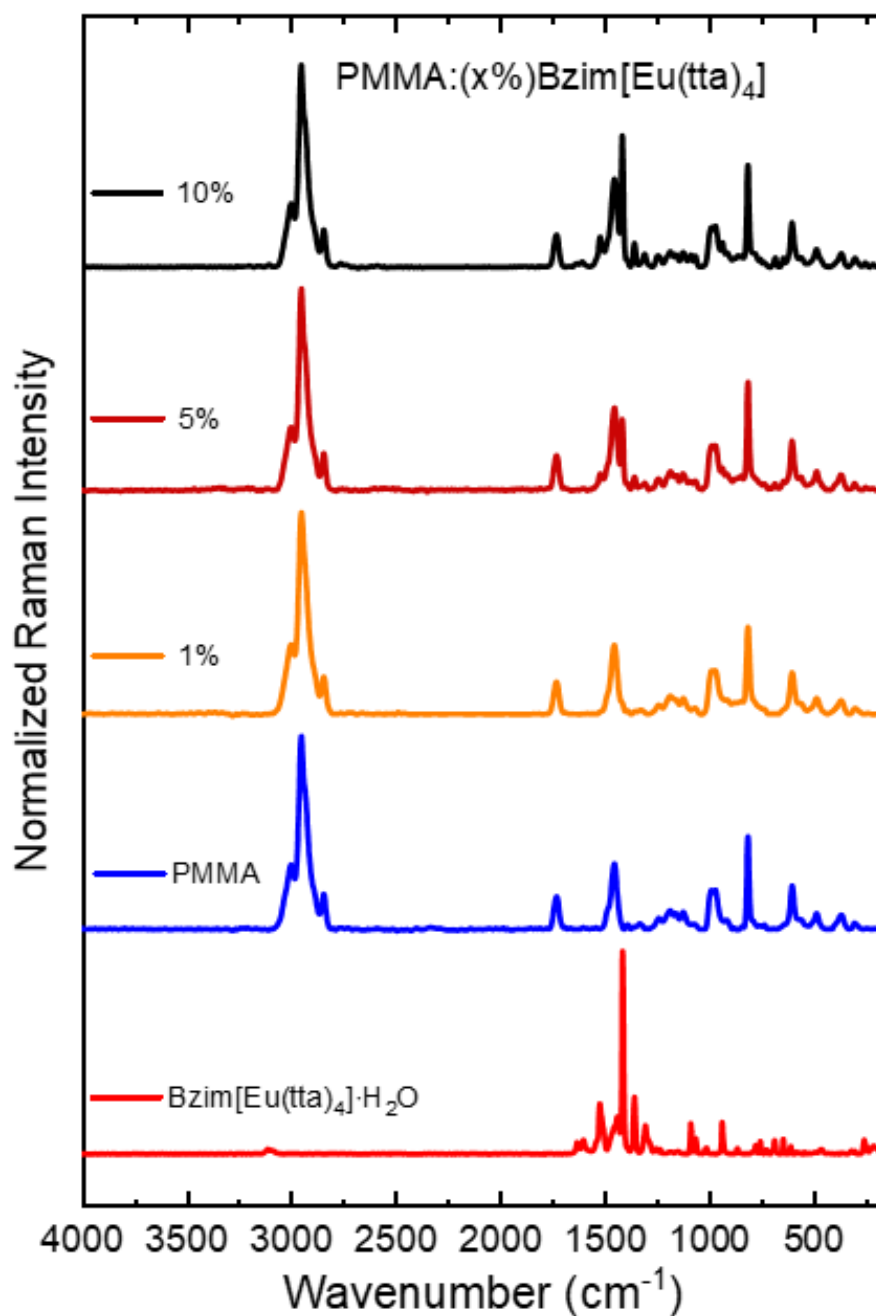


**Figure S7.** FTIR spectra for the Bzim[Eu(tta)<sub>4</sub>]·H<sub>2</sub>O (red line) complex, non-doped PMMA (blue line) and their corresponding PMMA:(x%)Bzim[Eu(tta)<sub>4</sub>] doped films, where x = 1 (orange line), 5 (dark red line), and 10 (black line). All data were recorded in the spectral interval of 4000 to 400 cm<sup>-1</sup> with a spectral resolution of 2.0 cm<sup>-1</sup>.

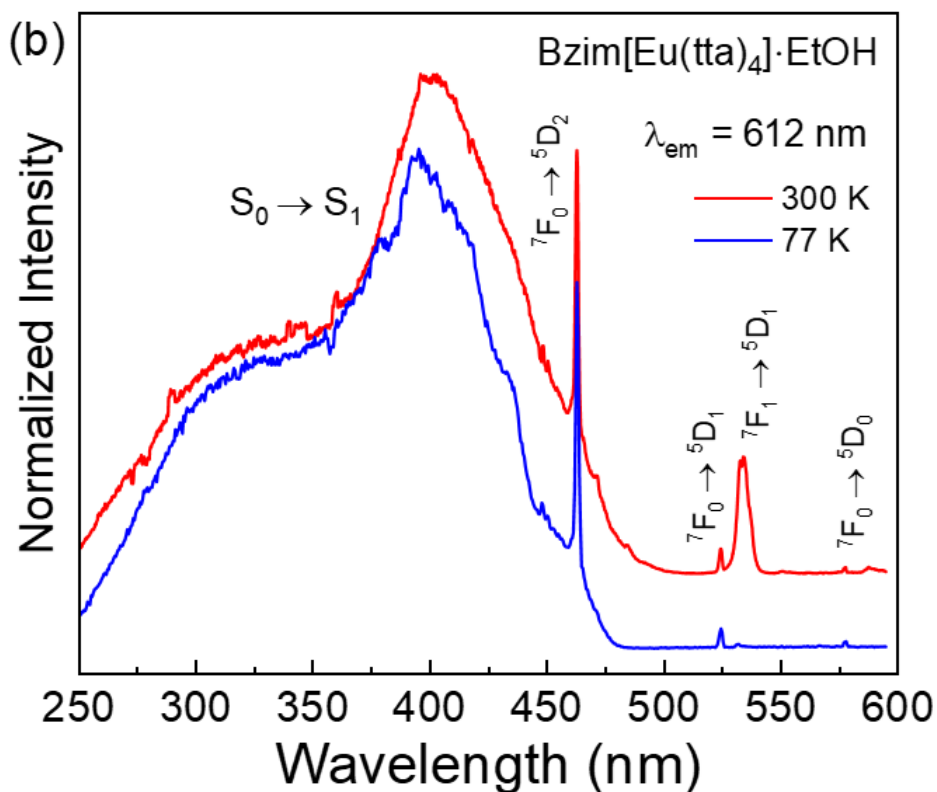
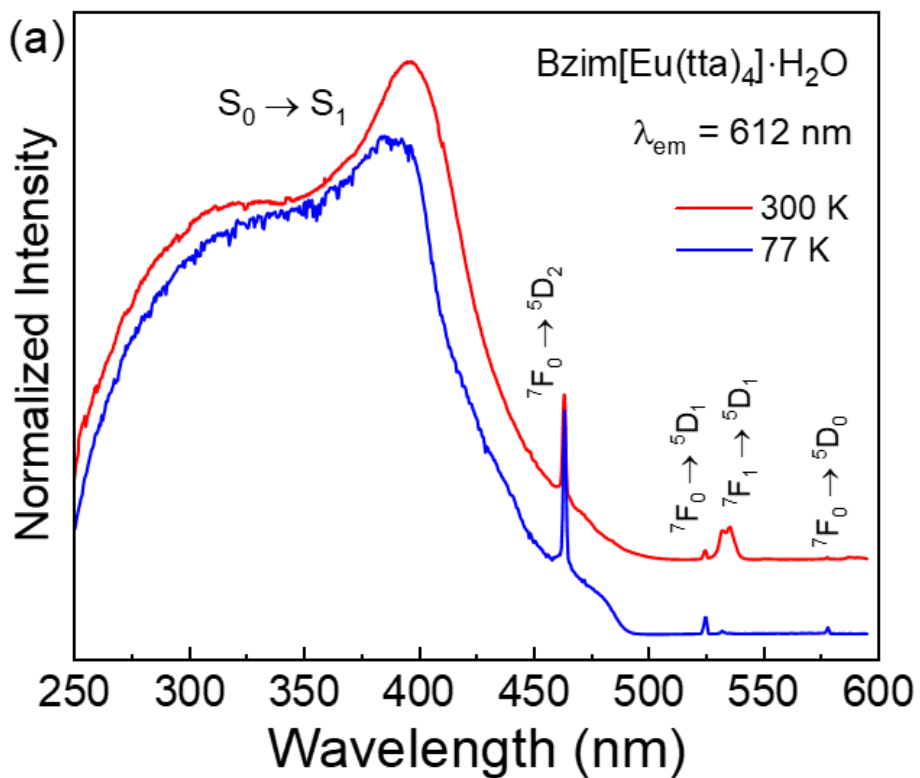




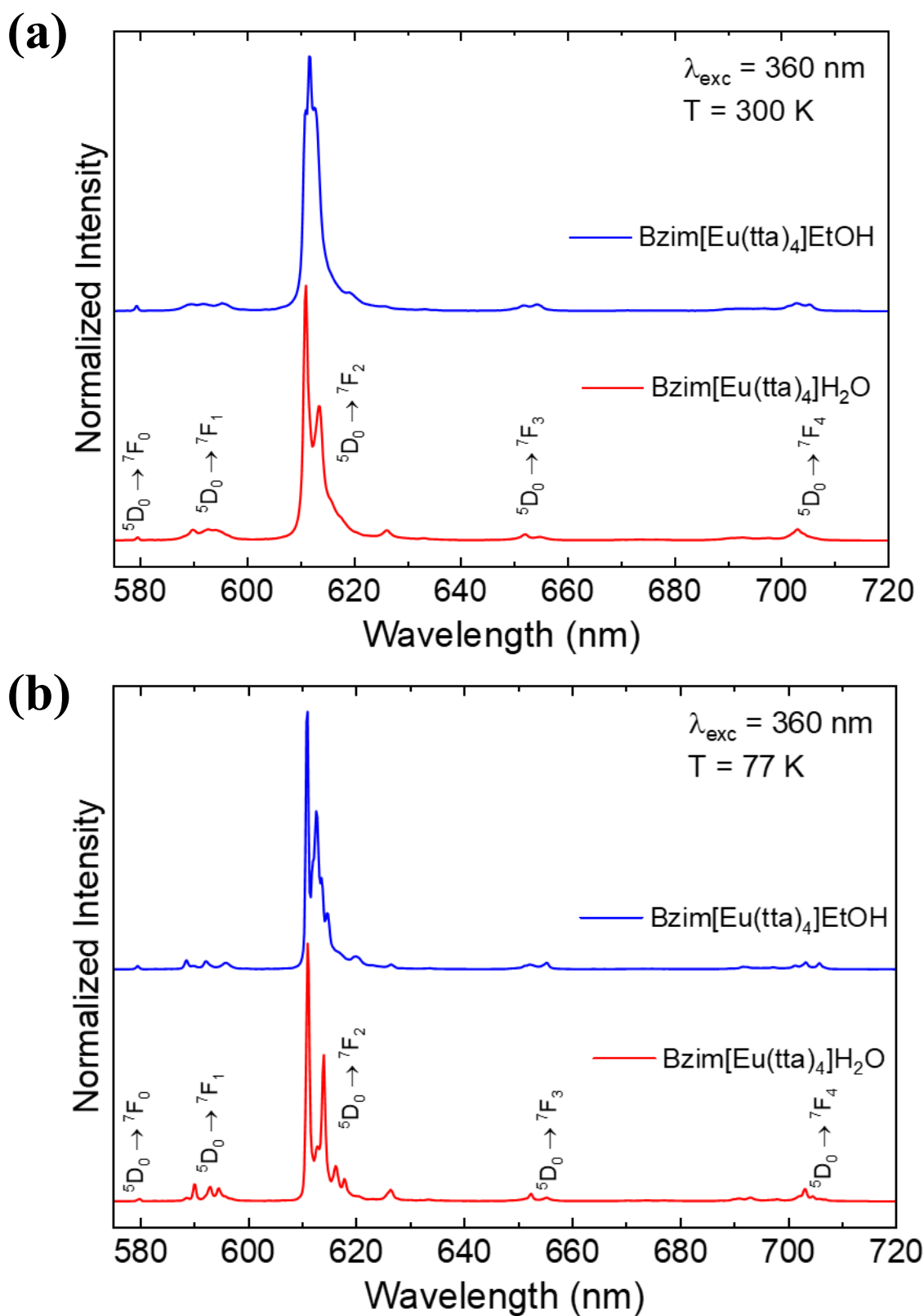
**Figure S8.** Far-FTIR spectra for the Bzim[Eu(tta)<sub>4</sub>]·H<sub>2</sub>O (red line) complex, non-doped PMMA (blue line) and their corresponding PMMA:(x%)Bzim[Eu(tta)<sub>4</sub>] doped films, where x = 1 (orange line), 5 (dark red line), and 10 (black line). All data were recorded in the spectral interval of 670 to 150 cm<sup>-1</sup> with a spectral resolution of 2.0 cm<sup>-1</sup>.



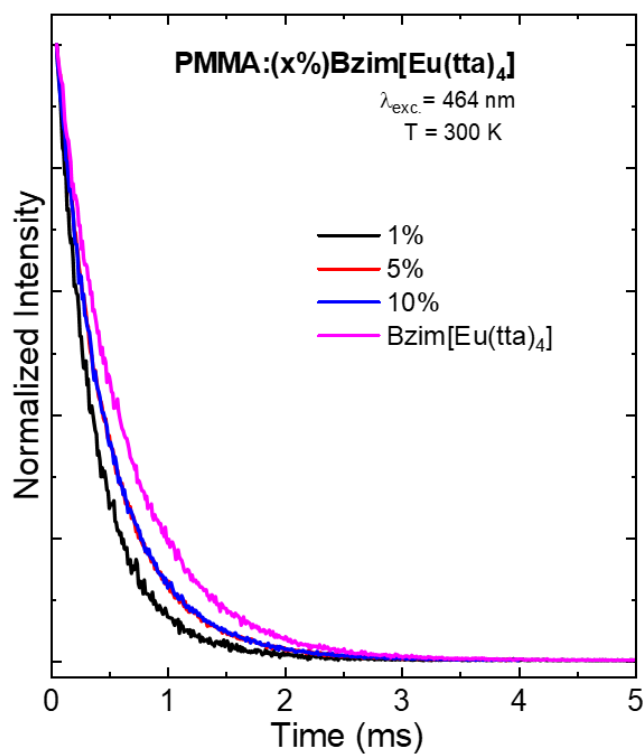
**Figure S9.** Raman Scattering spectra for Bzim[Eu(tta)<sub>4</sub>]·H<sub>2</sub>O (red line) complex, non-doped PMMA (blue line) and their corresponding PMMA:(x%)Bzim[Eu(tta)<sub>4</sub>] doped films, where x = 1 (orange line), 5 (dark red line), and 10 (black line). All data were collected in the spectral interval of 4000 to 200 cm<sup>-1</sup>, at 1064 nm excitation laser.



**Figure S10.** Excitation spectra of the solid-state Bzim[Eu(tta)<sub>4</sub>] L, L: H<sub>2</sub>O (a) or EtOH (b) complexes, recorded under 300 (red line) and 77 K (blue line) in the 250 – 600 nm range monitoring the emission at the hypersensitive  ${}^5D_0 \rightarrow {}^7F_2$  transition ( $\lambda_{em} = 612 \text{ nm}$ ) of the Eu<sup>3+</sup> ion.



**Figure S11.** Emission spectra of the solid-state Bzim[Eu(tta)<sub>4</sub>] L, L:EtOH (blue line) or H<sub>2</sub>O (red line) complexes with excitation at 360 nm. The spectra were recorded under 300 (a) and 77 K (b) in the range of 575 to 720 nm.



**Figure S12.** Luminescence decay curves of the [Bzim][Eu(tta)<sub>4</sub>] complex and their corresponding PMMA:(x%)Bzim[Eu(tta)<sub>4</sub>] doped films, where x = 1, 5 and 10. All data were determined under 300 K with excitation at the <sup>7</sup>F<sub>0</sub>→<sup>5</sup>D<sub>2</sub> transition at 464 nm.

**Table S2.** CIE diagram coordinates of the PMMA:(x%)Bzim[Eu(tta)<sub>4</sub>] doped films, where x = 1, 5 and 10. All data were determined under 300 K with excitation at 254 (UVC), 310 (UVB), 405 (UVA) nm and under sunlight radiation.

$\lambda_{\text{ex.}}(\text{nm})$	254		310		405		Sunlight	
	x	y	x	y	x	y	x	y
PMMA:(1%)Bzim[Eu(tta)]	0.668	0.332	0.669	0.331	0.669	0.330	0.655	0.345
PMMA:(5%)Bzim[Eu(tta)]	0.668	0.332	0.668	0.332	0.669	0.331	0.678	0.322
PMMA:(10%)Bzim[Eu(tta)]	0.668	0.331	0.668	0.332	0.668	0.332	0.669	0.331