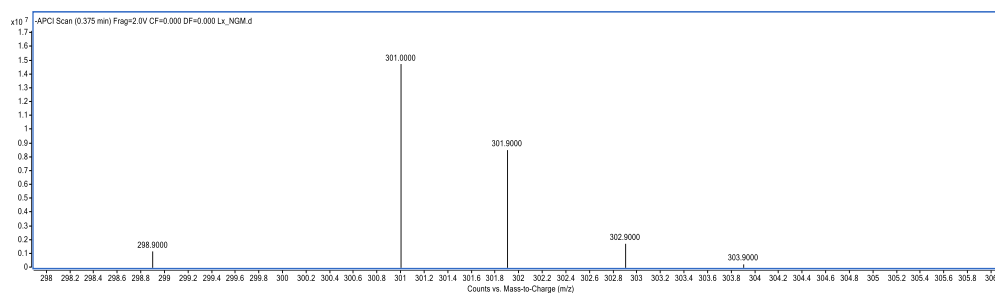


Supplementary Information

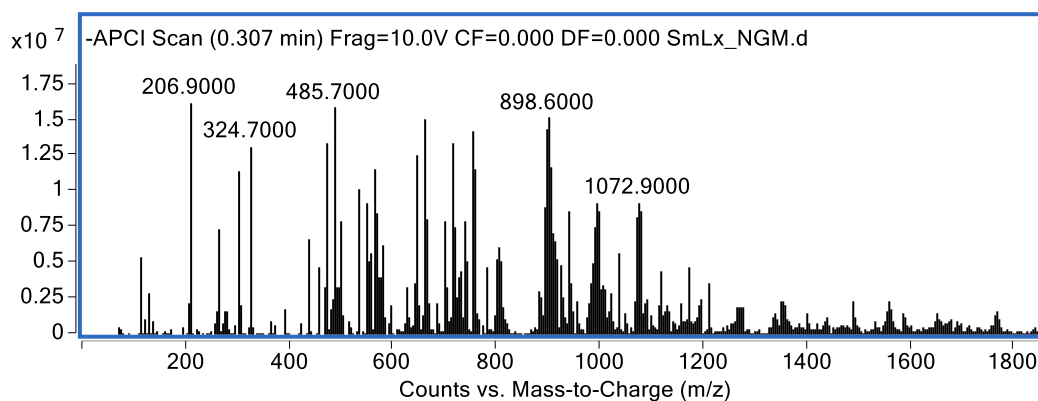
Thermal, Spectroscopic and Luminescence Properties of Lanthanide/PMMA Hybrid Materials

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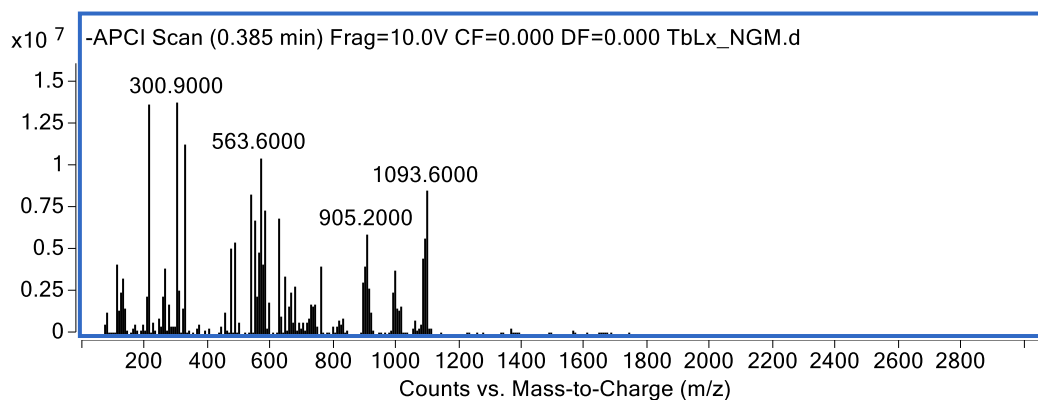
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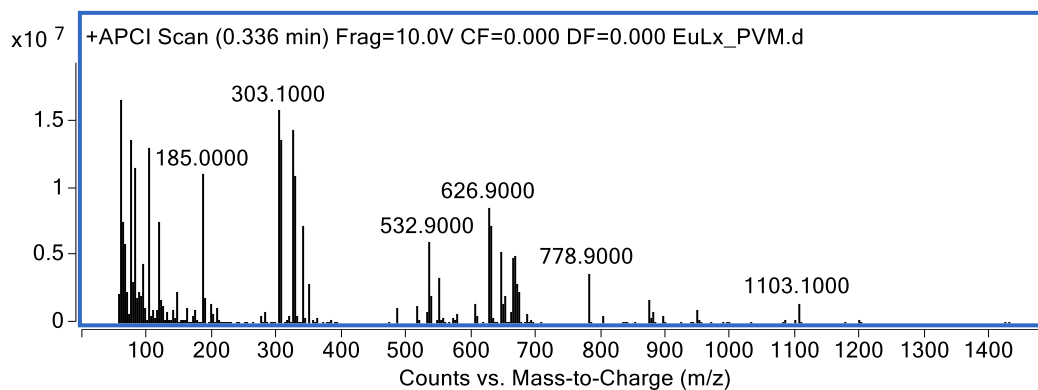
a. L



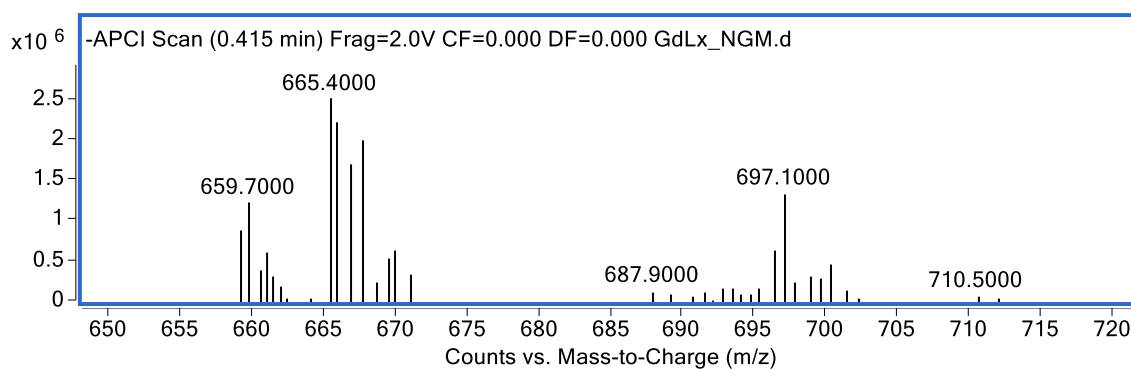
a. SmL



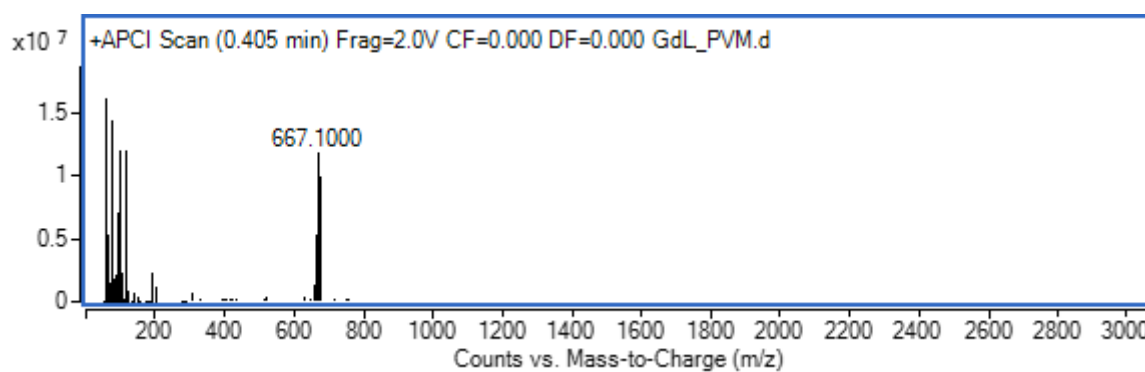
b. TbL



c. EuL



d. GdL



e. GdLN

Figure S1: Mass spectrometry spectra for ligand **L** and the **LnL** complexes in MeOH complexes.

Table S1: Mass to charge (*m/z*) of the fragments of **L** and the Ln(III) complexes.

The complex	The fragments	<i>m/z</i> (found)
L	{[L]} ⁻	302.900
EuL	{[Eu(hfac) ₃ (MeOH)L+4H]} ⁺	1103.1000
TbL	{[Tb(hfac) ₂ (MeOH)L]} ⁻	905.200
SmL	{[Sm(hfac) ₃ L]} ⁻	1072.900
GdL	{[Gd(hfac)(MeOH)L-H]} ⁻	697.100
GdLN	{[Gd(NO ₃) ₃ (H ₂ O)L+3H]} ⁺	667.100

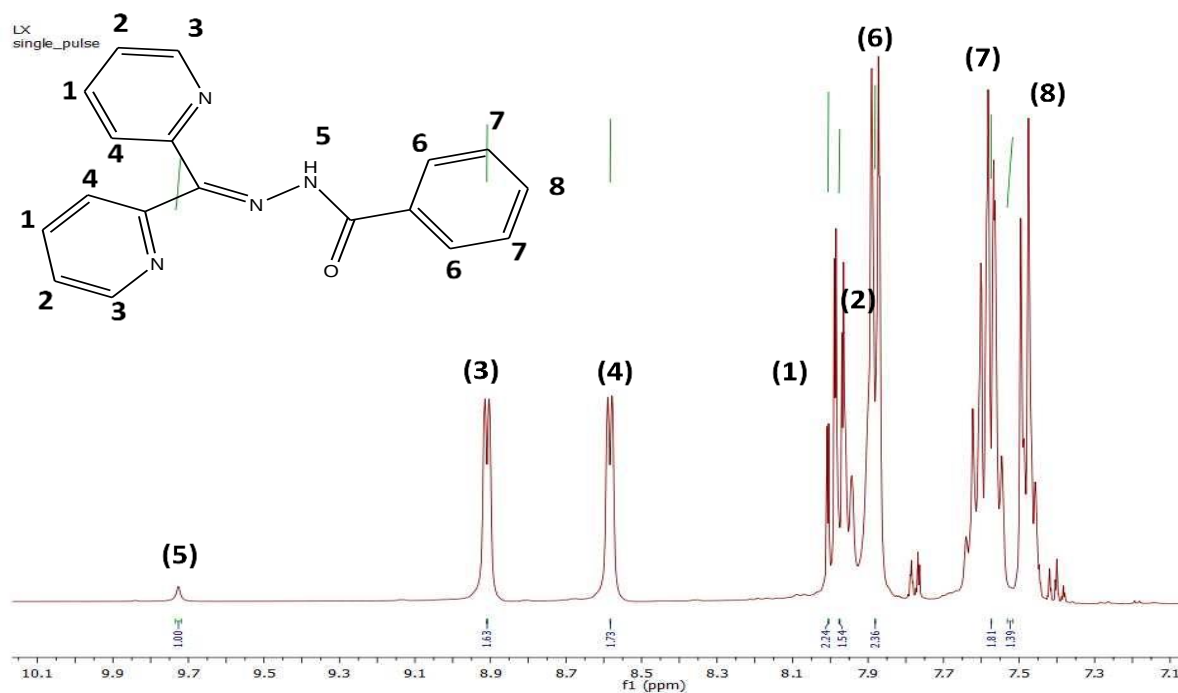


Figure S2: ^1H NMR (500 MHz) spectrum of ligand **L** in dmsd-d_6 .

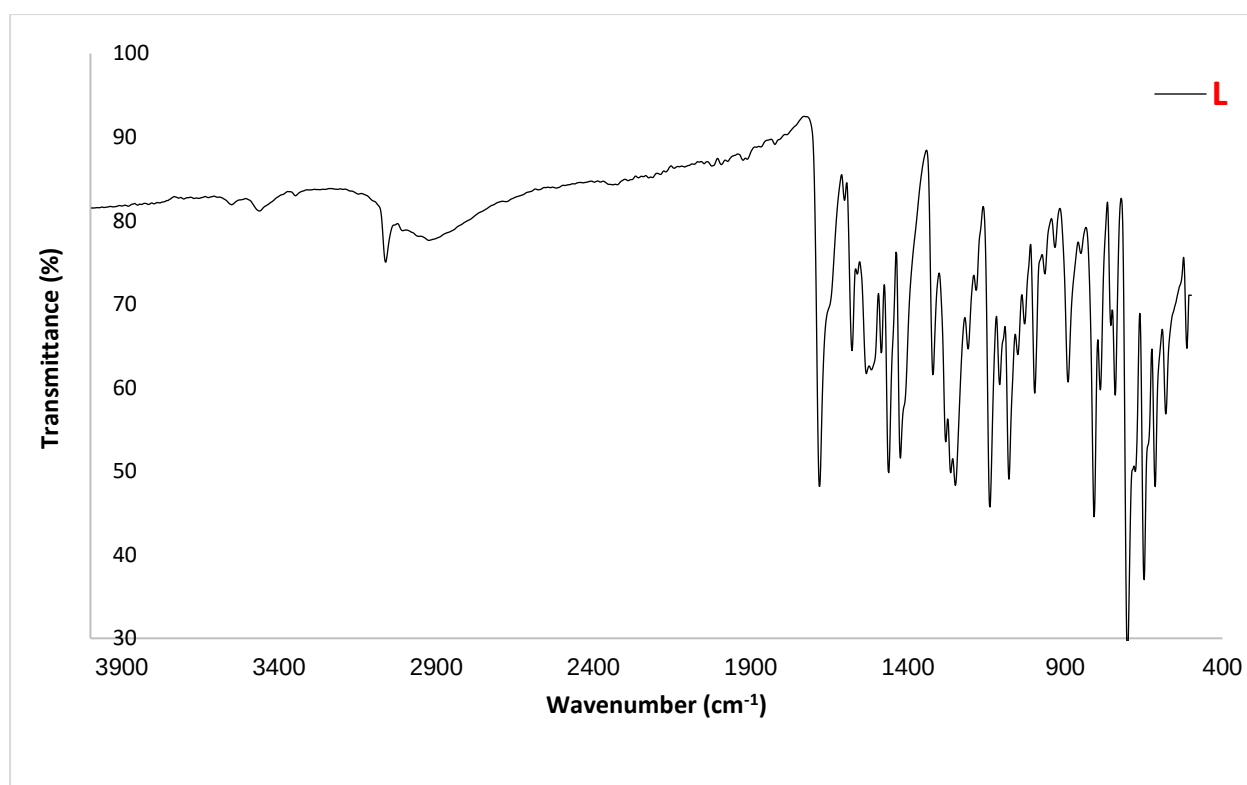


Figure S3: The IR spectra for the ligand **L** in the solid state at RT.

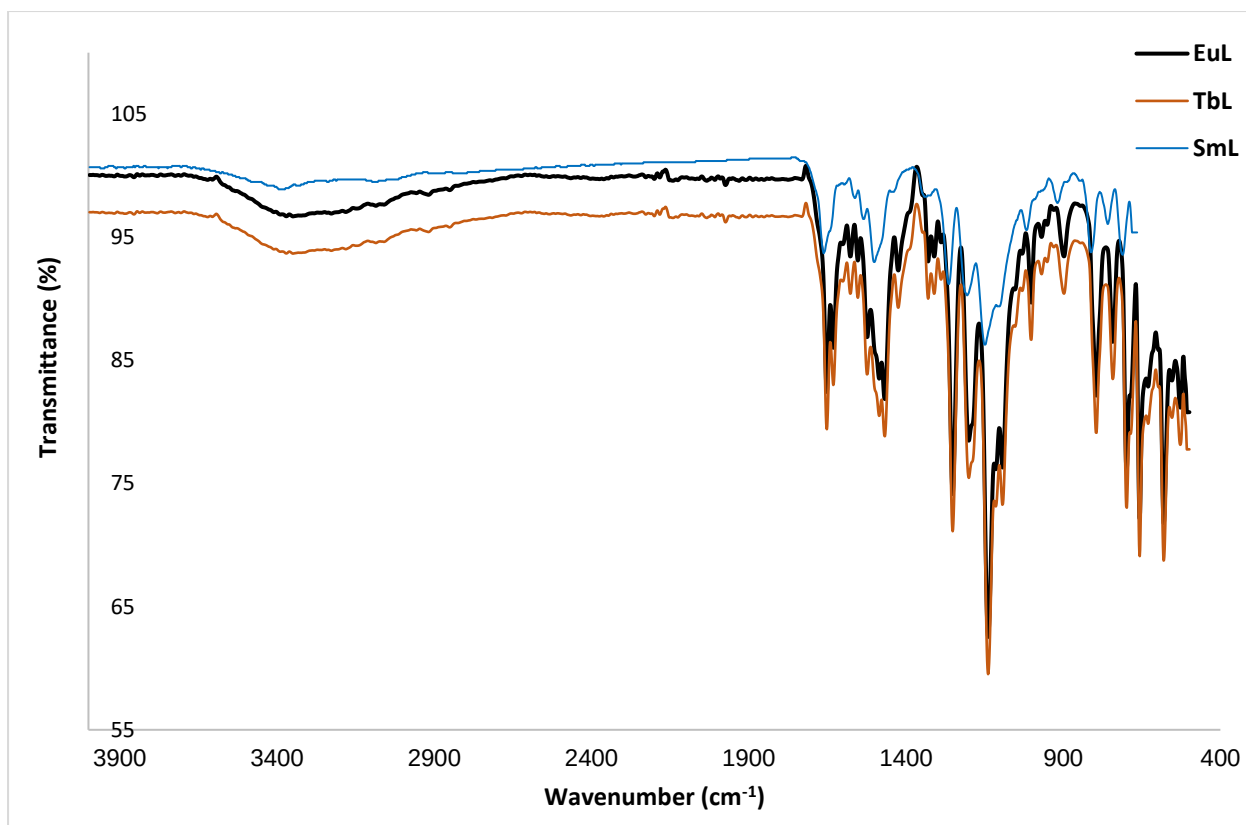


Figure S4: The IR spectra for the **Ln(III)** complexes in the solid state at RT.

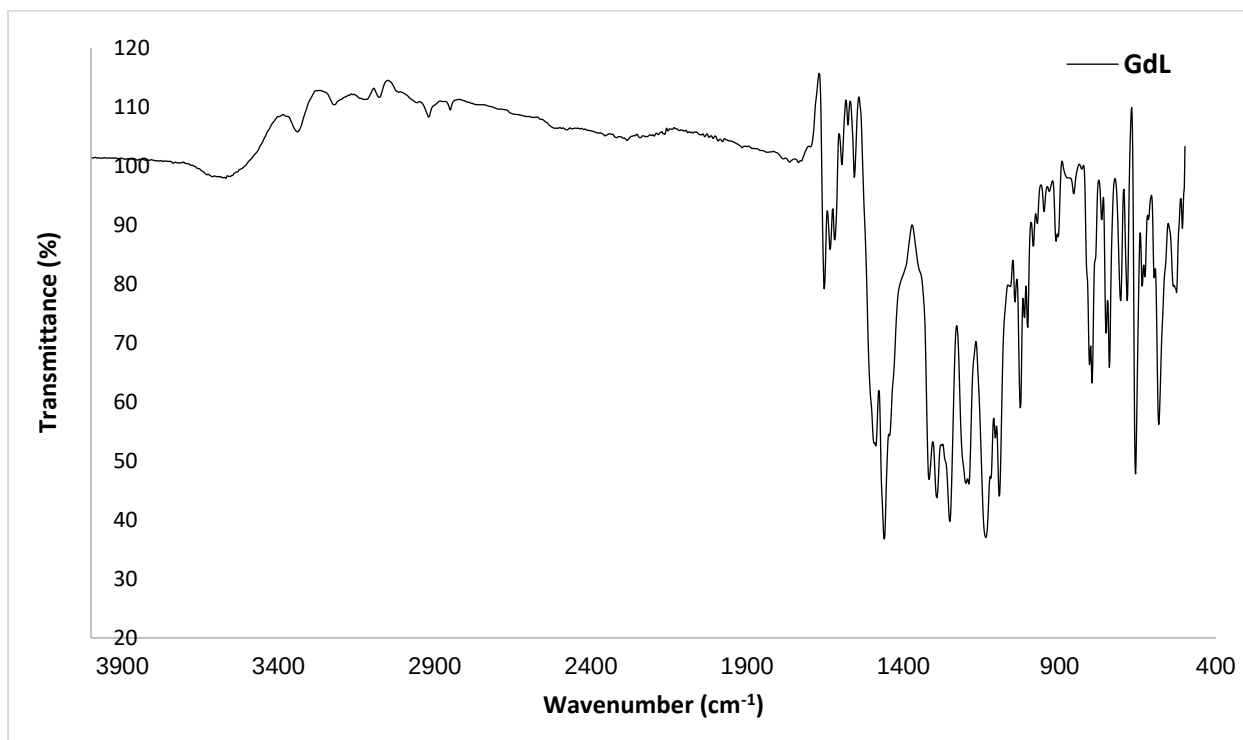


Figure S5: The IR spectra for **GdL** in the solid state at RT.

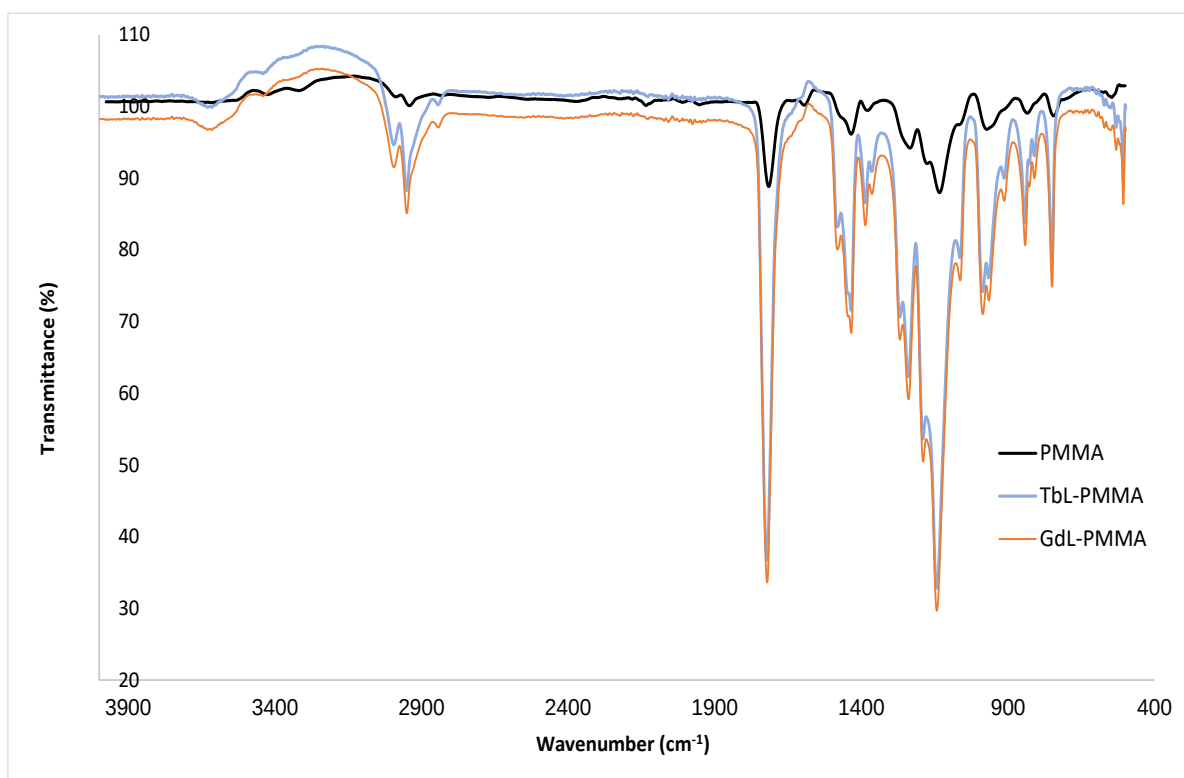


Figure S6: The IR spectra for the **Ln(III)-PMMA** polymers in the solid state at RT.

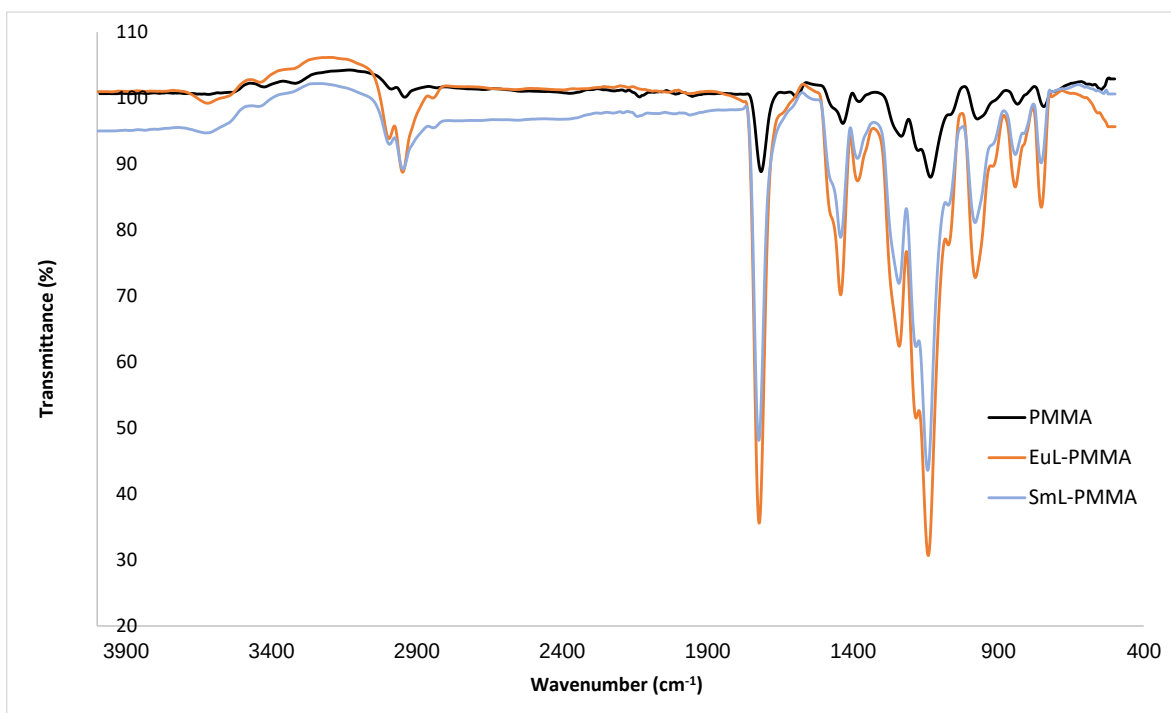
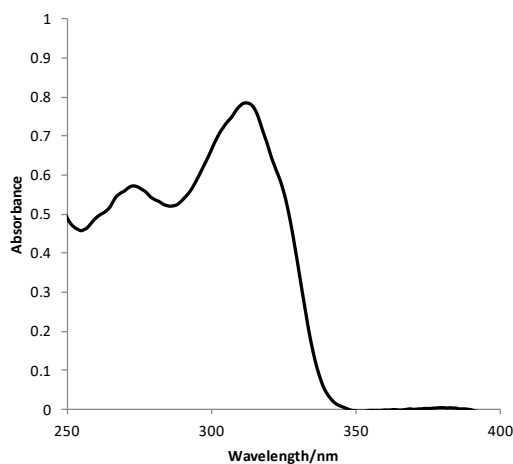


Figure S7: The IR spectra for the **Ln(III)-PMMA** polymers in the solid state at RT.

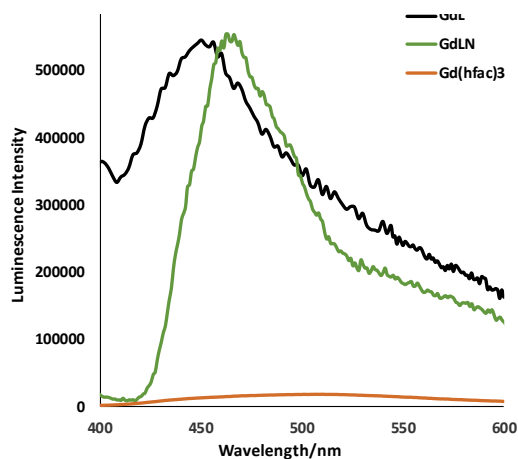
Table S2: Summary of the important IR stretching frequencies for the **LnL** complexes and the **LnL-PMMA** polymers, in the solid state at RT.

Bond	N-H	C-H (PMMA)	C=O (PMMA)	C=O (Nitrile)	C=N	C=N (Py)	C-O PMMA	Ln-O	Ln-N
L	3421	–	–	1682	1526	1249	–	–	–
TbL	3362	–	–	1651	1518	1251	–	580	656
EuL	3341	–	–	1653	1536	1251	–	580	565
SmL	3420	–	–	1661	1501	1263	–	681	711
GdL	3357	–	–	1653	1557	1251	–	582	656
PMMA	–	2944	1695	–	–	–	1138	–	–
TbL- PMMA	3440	2948	1719	1458	1434	1287	1196	510	748
EuL- PMMA	3426	2937	1721	1452	1442	1239	1138	746	837
SmL- PMMA	3428	2942	1723	1462	1440	1241	1140	748	839
GdL- PMMA	3430	2950	1724	1460	1434	1251	1141	751	841

(a)



(b)



(c)

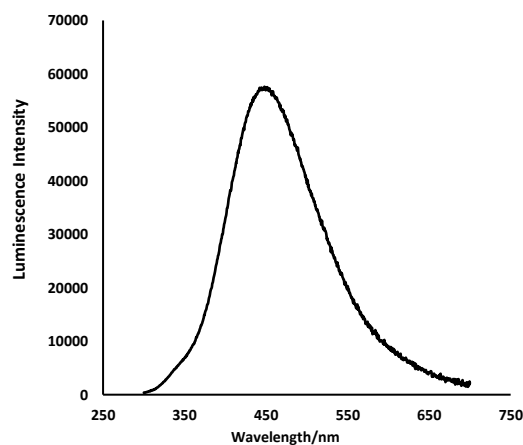


Figure S8: (a) The Absorption spectrum of $[\text{Gd}(\text{hfac})_3(\text{H}_2\text{O})_2]$ in EtOH. (b) The phosphorescence spectra of: **GdL**, **GdLN** and $[\text{Gd}(\text{hfac})_3(\text{H}_2\text{O})_2]$. (c) The phosphorescence spectra of the **GdL**-PMMA polymer ($\lambda_{\text{ex}} = 385 \text{ nm}$), all recorded at $\lambda_{\text{ex}} = 385 \text{ nm}$ in ethanol at 77K.

Table S3: Summary of the CIE1931 chromaticity coordinates for the **LnL** complexes and the **LnL**-PMMA polymers, in the solid state at RT.

Sample	x	y	Intensity	Color
EuL	0.56692	0.41914	19780	red
TbL	0.34263	0.43616	62000	Bright green
SmL	0.53354	0.45743	25330	yellow
Eu-PMMA	0.43313	0.30910	68420	Red
Tb-PMMA	0.26557	0.42116	85440	Green
Sm-PMMA	0.35077	0.38002	34500	Orange

Summary of TD DFT results

The ligand **L** is optimized from ground state geometries at the UAPFD function 6-311+g(2d,p) basis in the gas-phase.

Singlet Excitation energies									
HOMO is 7		79							
No.	Energy (eV)	Wavelength (nm)	Osc. Streng.	Symmetry	Major con Minor con Minor contribs				
1	18901.6	529.0557	0	3.000-A	HOMO(A)->LUMO(A) (44%), HOMO(B)->LUMO(B) (44%)				
2	27418.82	364.713	0	3.000-A	H-1(A)->L1 H-4(A)->L1 H-4(A)->LUMO(A) (2%), H-1(A)->LUMO(A) (5%)				
3	27922.91	358.1288	0	3.000-A	H-5(A)->L1 H-6(A)->L1 H-7(A)->LUMO(A) (2%), H-6(A)->L+2(A) (3%)				
4	28381.84	352.3379	0	3.000-A	HOMO(A)->H-9(A)->L+1 H-7(A)->L+1(A) (2%), H-6(A)->L+1(A) (2%), H-8(A)->L1 H-3(A)->LUMO(A) (5%), H-3(B)->LUMO(B) (5%)				
5	29550.54	338.4033	0.4096	1.000-A	HOMO(A)->LUMO(A) (44%), H-2(A)->LUMO(A) (2%), H-2(B)->LUMO(B) (2%)				
6	30022.38	333.0849	0	3.000-A	H-1(A)->L1 H-5(A)->L1 H-2(A)->L+2(A) (2%), H-1(A)->L+7(A) (3%), H-4(A)->L+2(A) (4%)				
7	30396.62	328.984	0	3.000-A	HOMO(A)->H-9(A)->L+1 H-4(A)->LUMO(A) (2%), H-4(A)->L+2(A) (4%)				
8	31655.65	315.8994	0.0124	1.000-A	H-1(A)->L1 H-4(A)->L1 H-3(A)->LUMO(A) (6%), H-2(A)->LUMO(A) (8%)				
9	32036.34	312.1455	0	3.000-A	HOMO(A)->H-6(A)->L+1 H-5(A)->L+2(A) (2%), H-4(A)->L+3(A) (3%), H-8(A)->L1 H-3(A)->LUMO(A) (5%), H-3(B)->LUMO(B) (5%)				
10	32237.98	310.1931	0	3.000-A					
S1									
3.6638 eV									
E T	-987.944 Eh								
E S	-988.02 Eh								
DE	0.076568 Eh								
T1	2.183535 eV								

Comments on Checkcif alerts

- PLAT234_ALERT_4_B Large Hirshfeld Difference F10 --C28 . 0.28 Ang.
 PLAT234_ALERT_4_B Large Hirshfeld Difference F17B --C33 . 0.26 Ang.

Response: These alerts are generated because there is a large amount of disorder of many fluoride atoms in the complex. A disorder model for the atoms: F10 was not successful. These atoms were refined isotropically with high thermal motions to keep the refinement stable. However, the high MainResAtom does not indicate an incorrect atom-type assignment.
- PLAT241_ALERT_2_B High MainResAtom Ueq as Compared to Neighbours F13 Check
 PLAT241_ALERT_2_B High MainResAtom Ueq as Compared to Neighbours F18 Check

Response: Due to disorder of these fluoride atoms and hence were refined isotropically with high thermal motions. Any attempts to refine the atoms anisotropically would make the refinement unstable.