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Achieving visible light excitation in carbazole-based Eu^{3+}-*β*-diketonate complexes *via* molecular engineering

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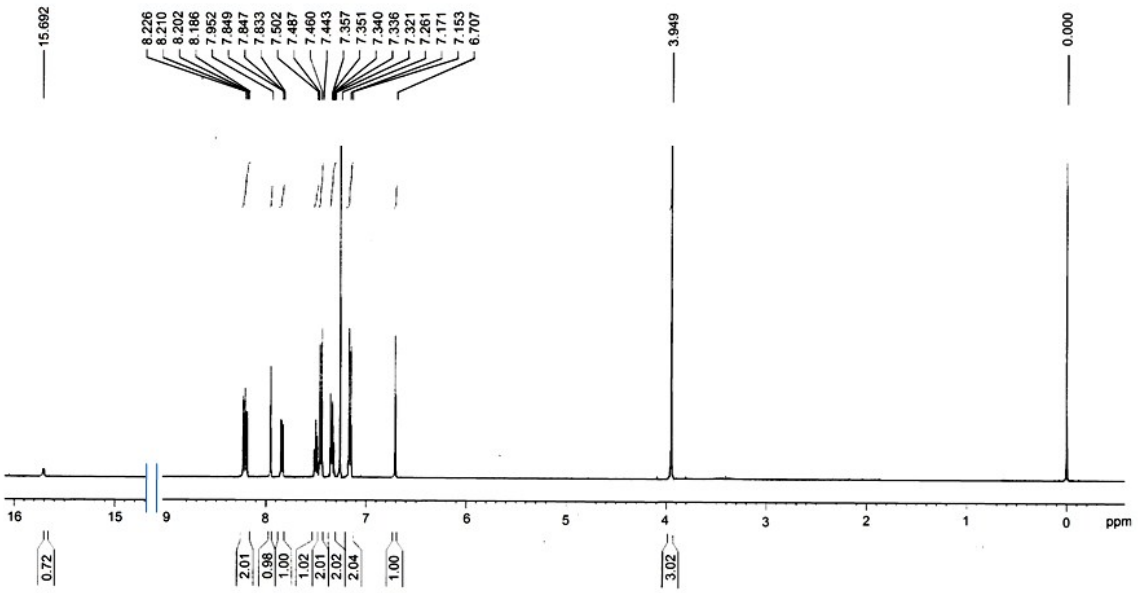

Fig. S1 ^{1}H NMR Spectrum of ligand **L2**

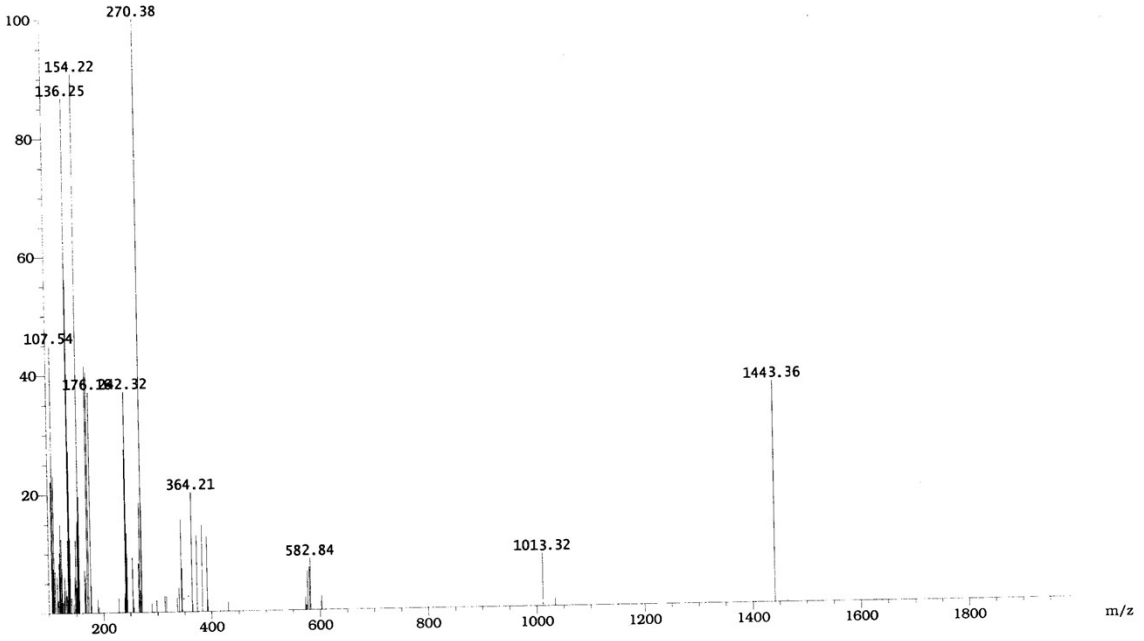

Fig. S2 MS(FAB) Spectrum of complex **1**

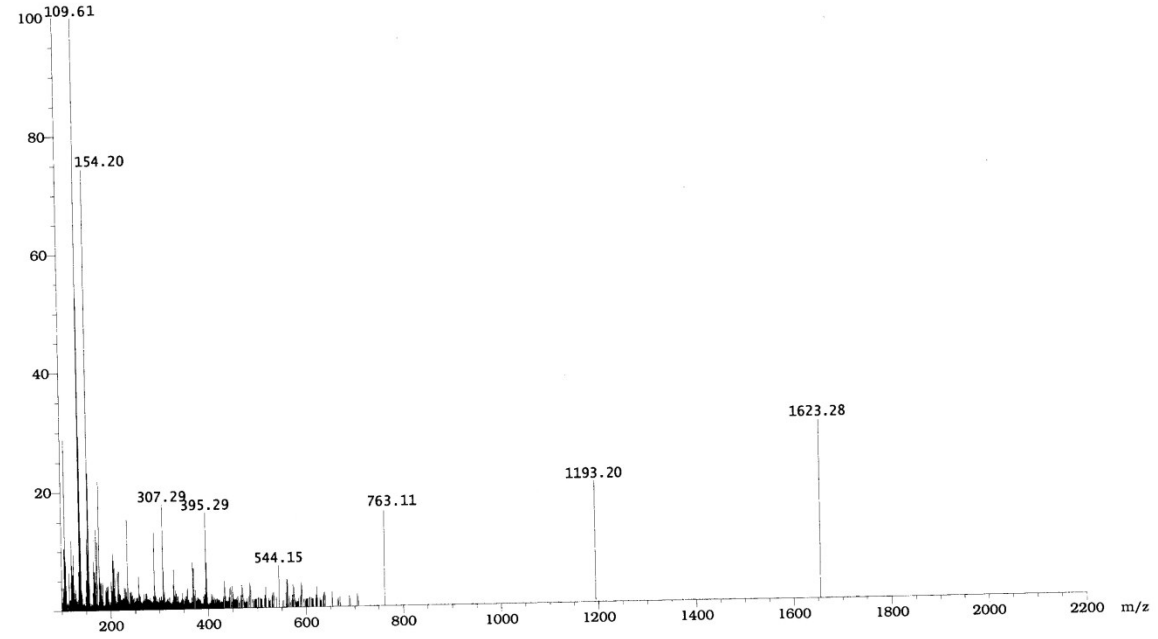

Fig. S3 MS(FAB) Spectrum of complex **2**

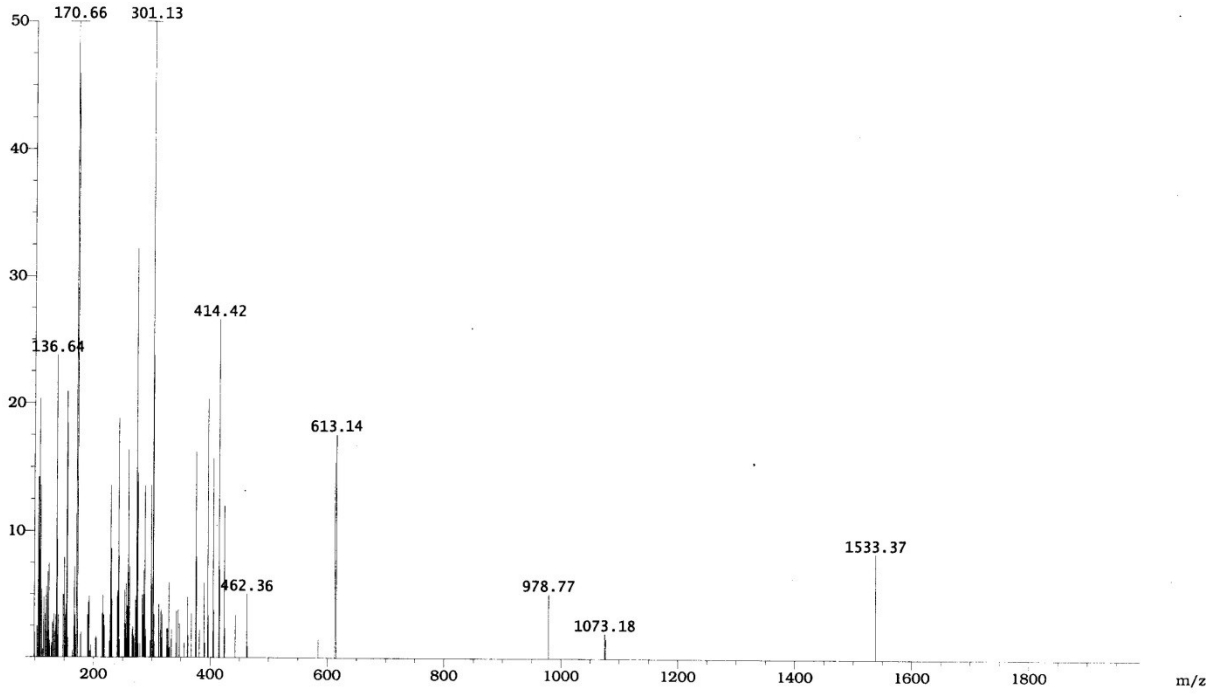

Fig. S4 MS(FAB) Spectrum of complex **3**

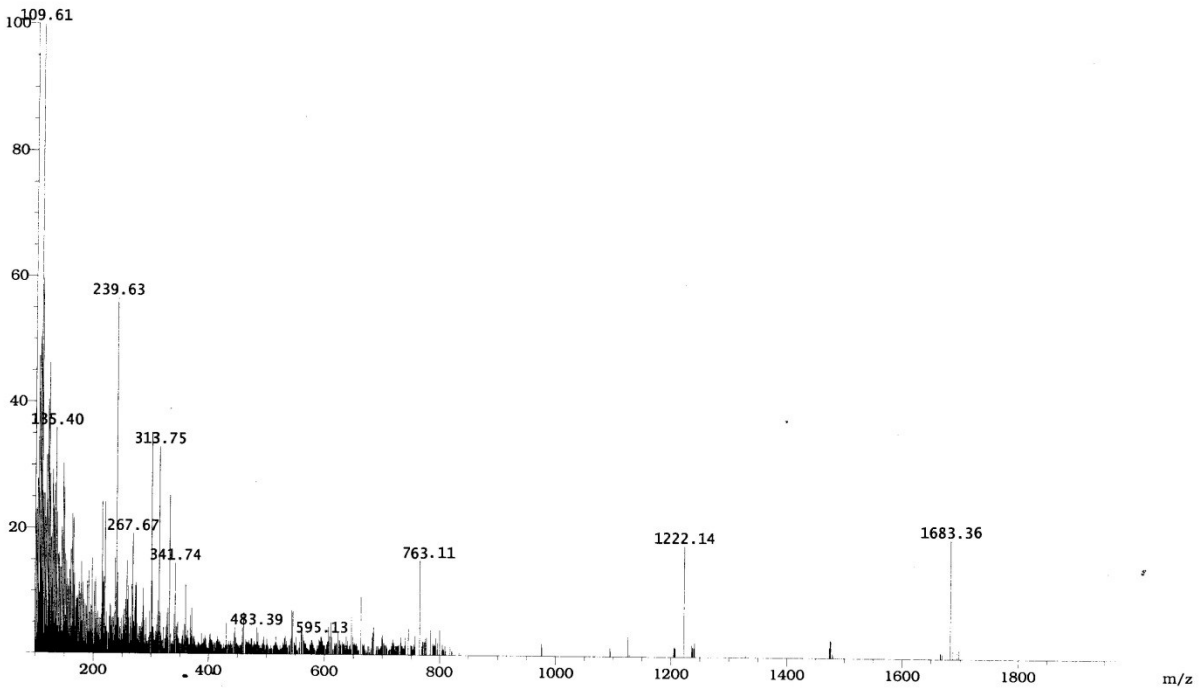

Fig. S5 MS(FAB) Spectrum of complex **4**

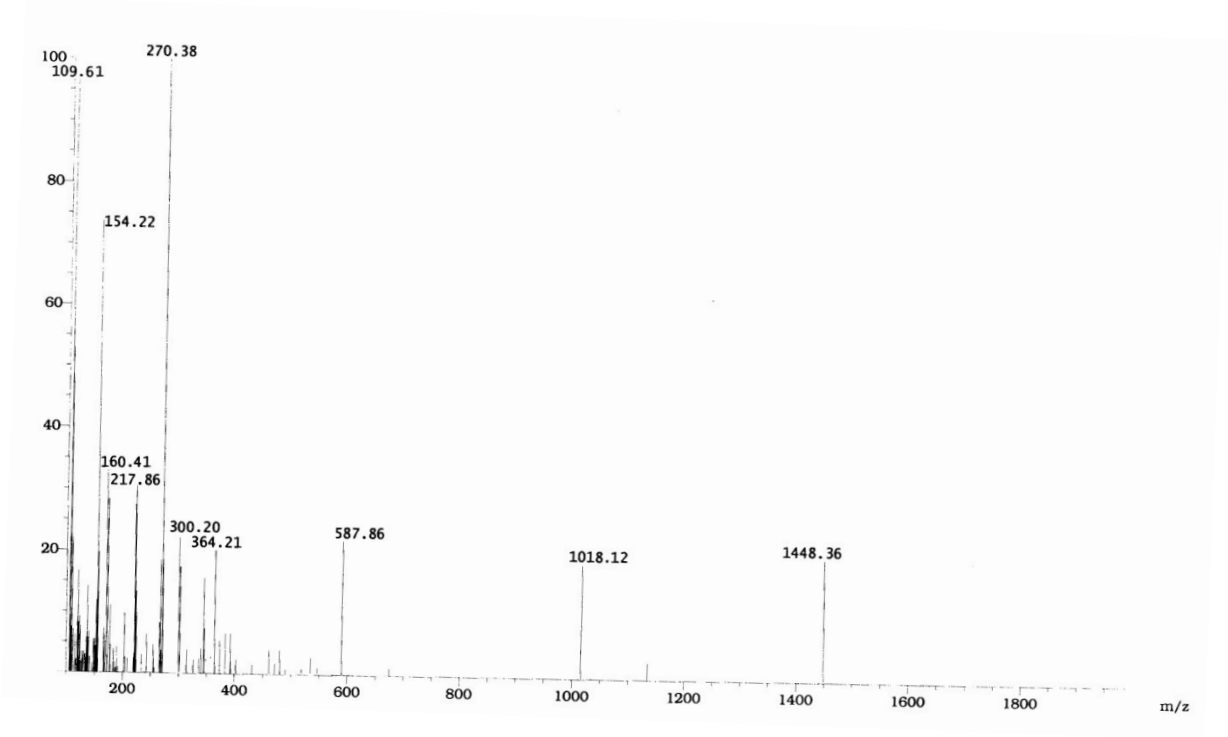

Fig. S6 MS(FAB) Spectrum of complex **5**

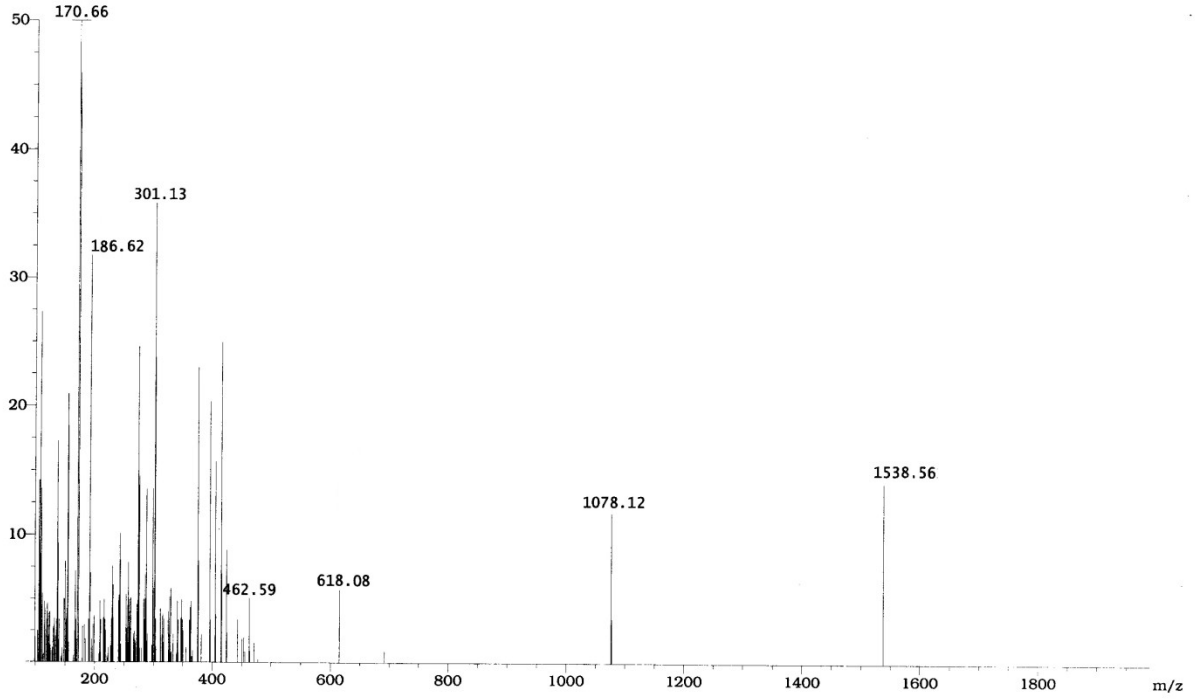

Fig. S7 MS(FAB) Spectrum of complex **6**

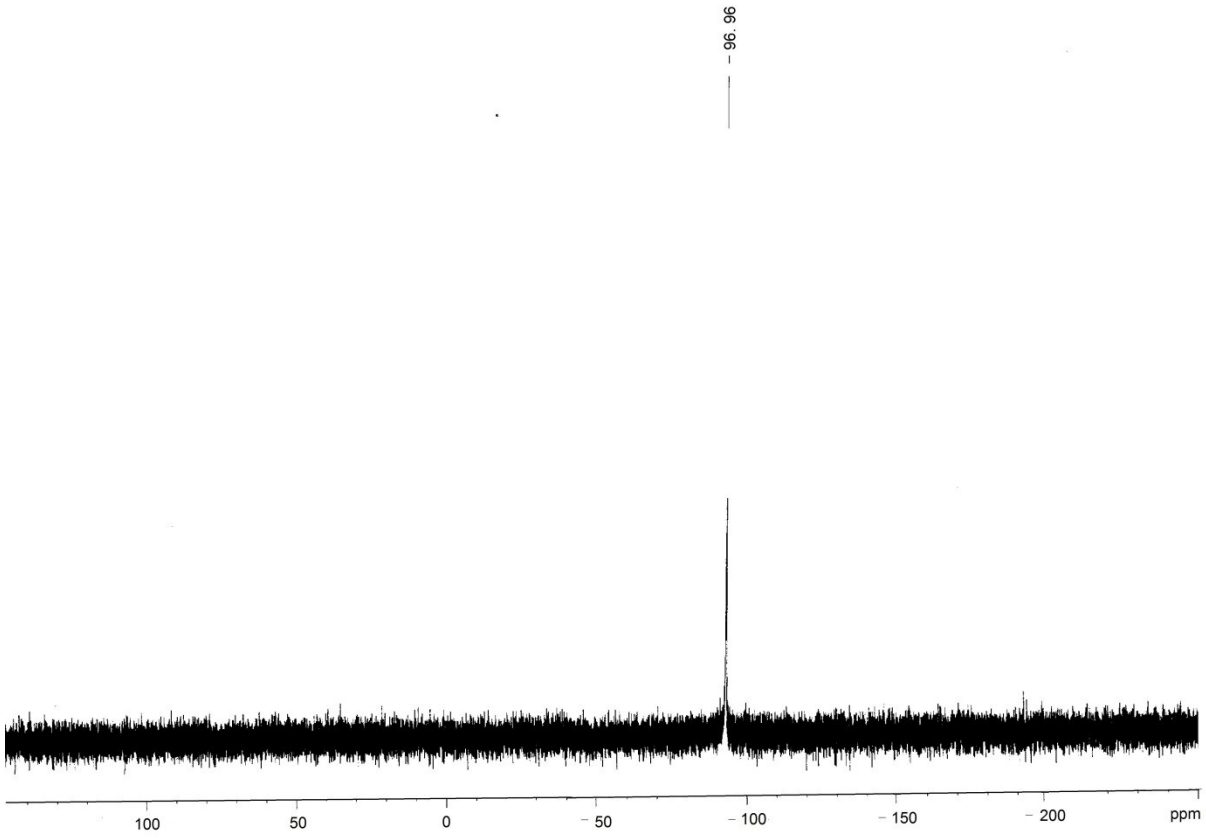

Fig. S8 ^{31}P NMR Spectrum of complex **4**

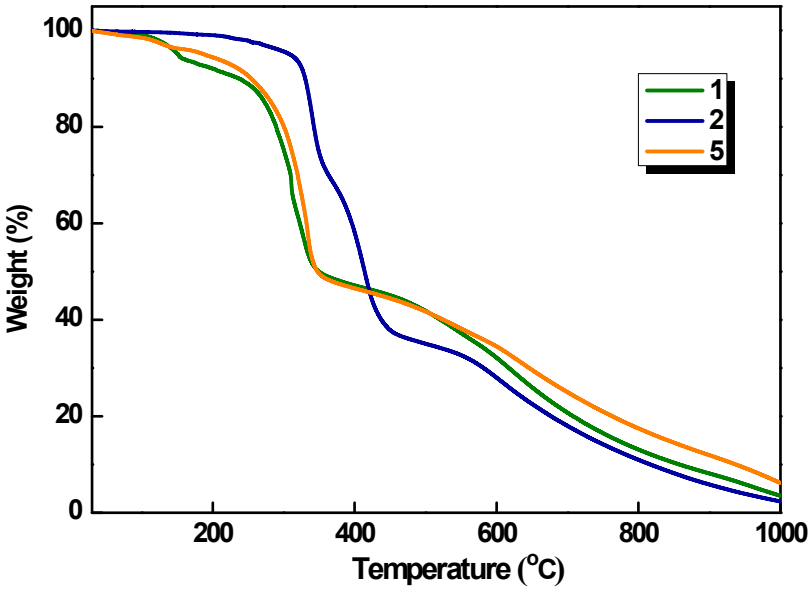

Fig. S9. Thermogravimetric curves for complexes **1**, **2** and **5**

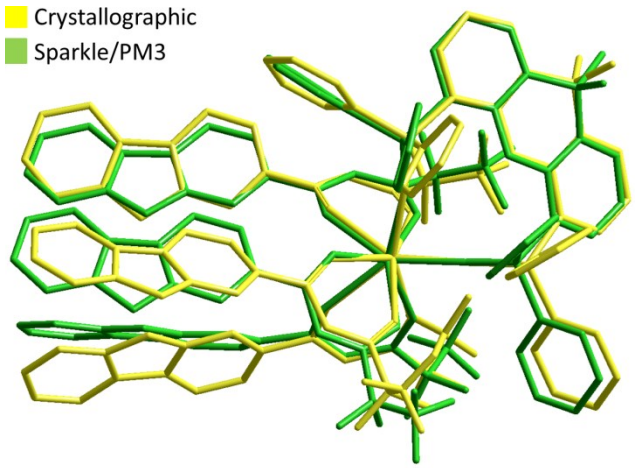

Fig. S10 Overlay of crystal structure and Sparkle/PM 3 model optimized structure of complex **A**

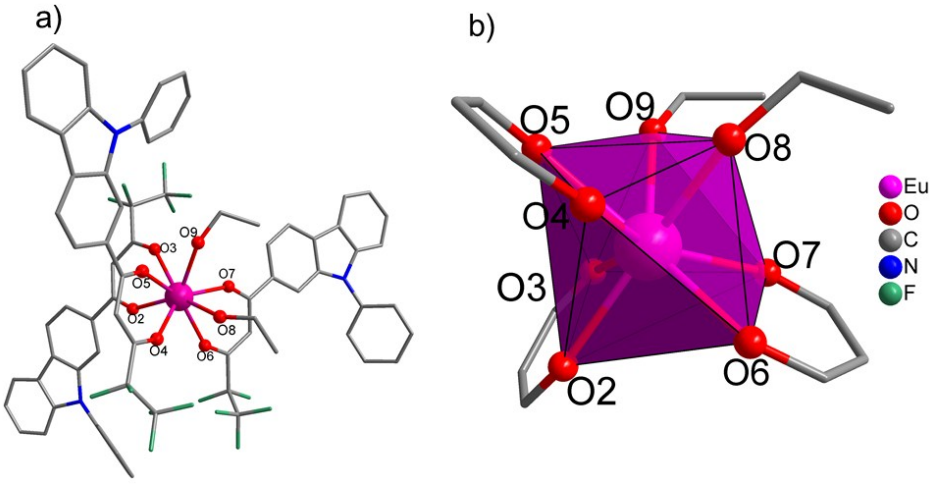

Fig. S11 (a) The ground state geometry of the complex **1** optimized by the Sparkle/PM3 model (b) Coordination environment of complex **1**. All hydrogen atoms are omitted for clarity.

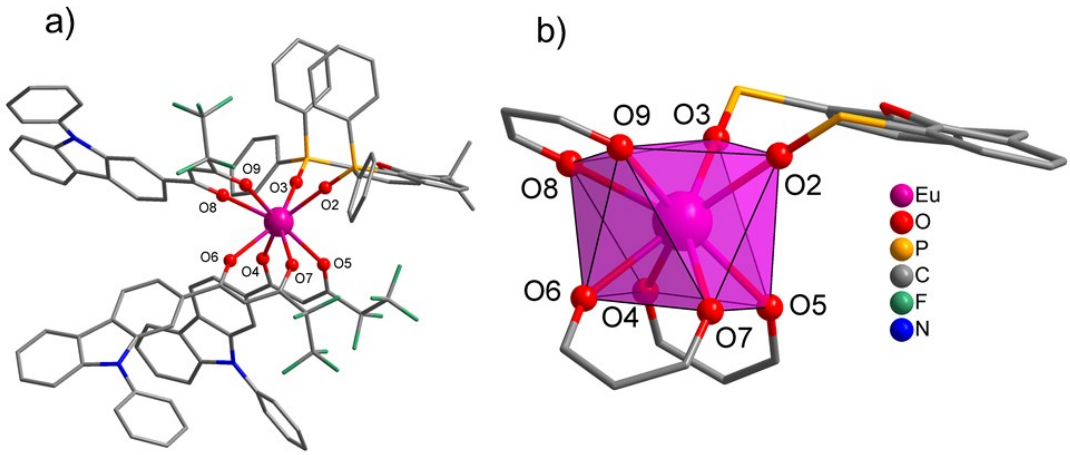

Fig. S12 (a) The ground state geometry of the complex **2** optimized by the Sparkle/PM3 model (b) Coordination environment of complex **2**. All hydrogen atoms are omitted for clarity.

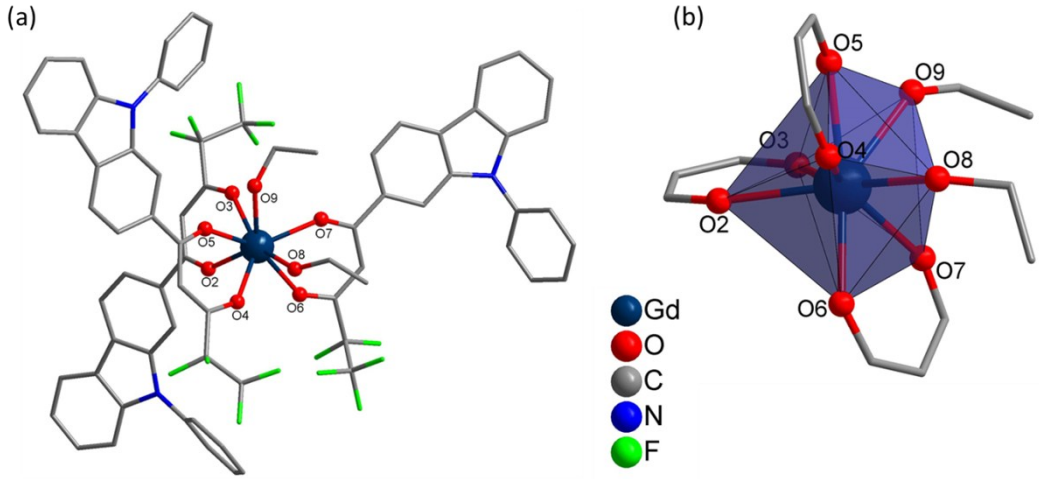

Fig. S13(a) The ground state geometry of the complex **5** optimized by the Sparkle/PM3 model (b) Coordination environment of complex **5**. All hydrogen atoms are omitted for clarity.

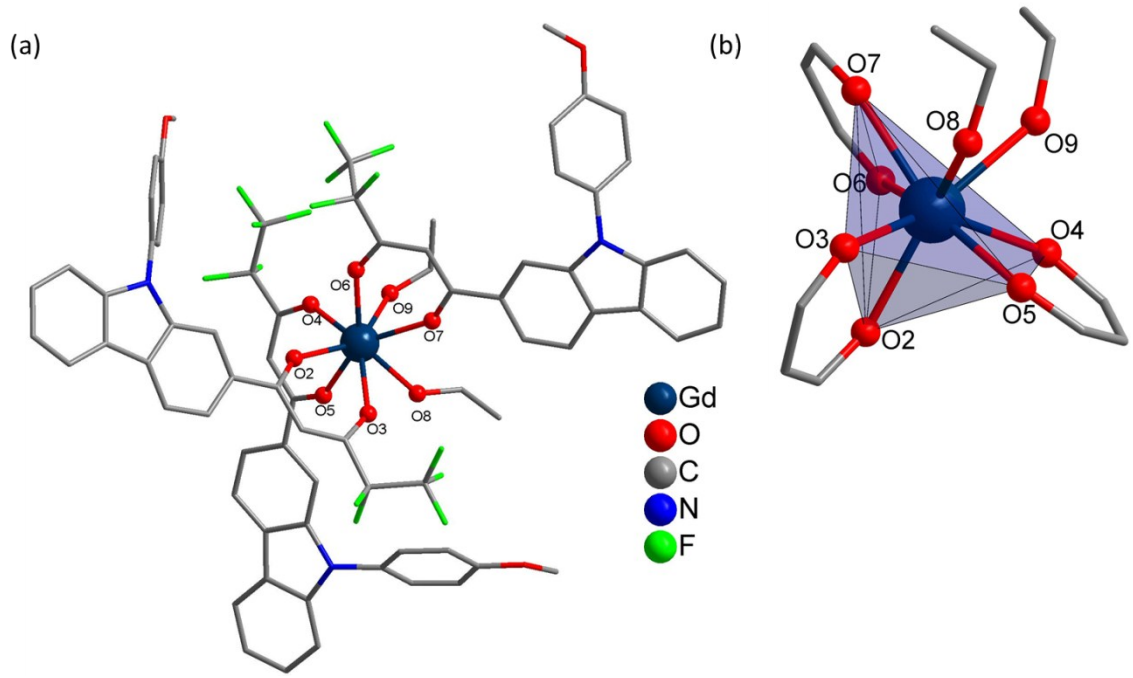

Fig. S14 (a) The ground state geometry of the complex **6** optimized by the Sparkle/PM3 model (b) Coordination environment of complex **6**. All hydrogen atoms are omitted for clarity.

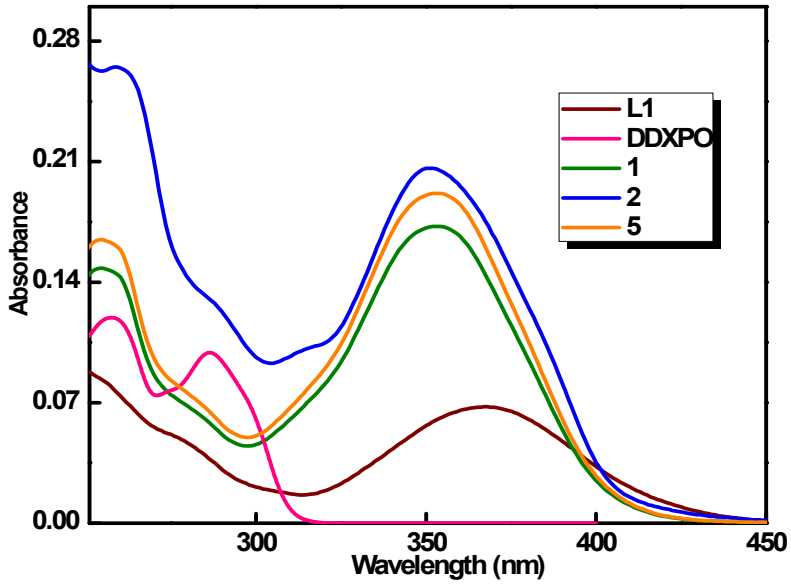

Fig. S15 UV-vis absorption spectra of the ligands **L1** and **DDXPO** and complexes **1**, **2** and **5** in $CHCl_3$ solution ($c = 2 \times 10^{-6}$ mol L^{-1}).

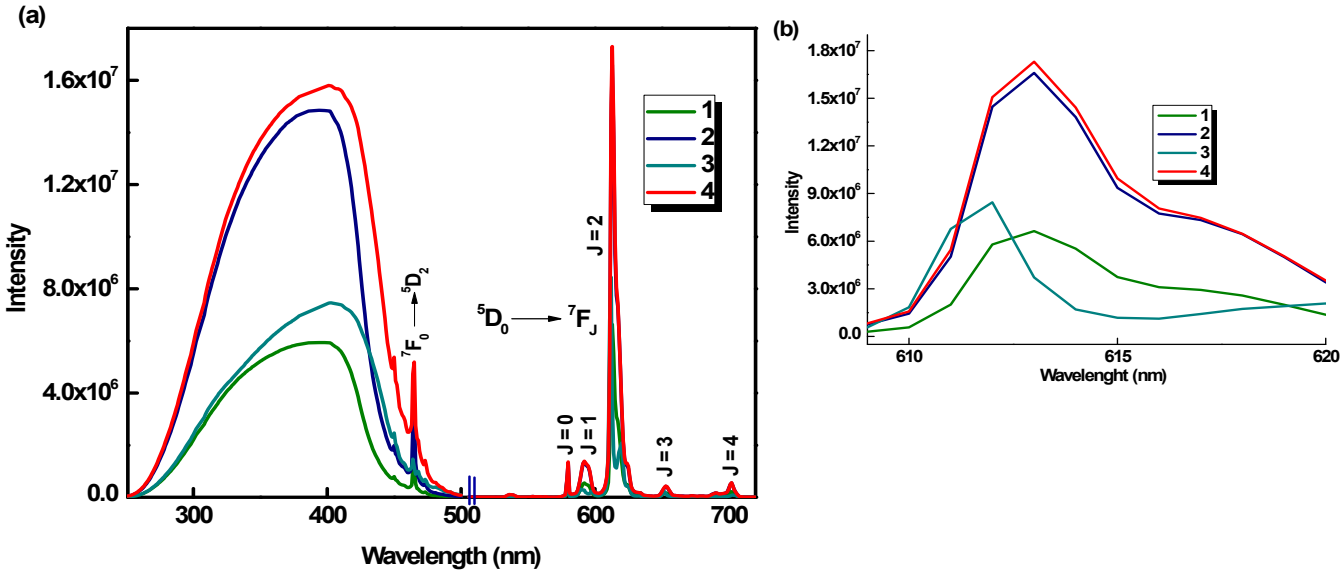

Fig. S16(a) Solid-state room-temperature excitation (λ_{em} = 612 nm) and emission (λ_{em} = 612 nm) spectra for complexes **1-4**. (b) $^5D_0 \rightarrow {}^7F_2$ transitions of complexes **1-4**

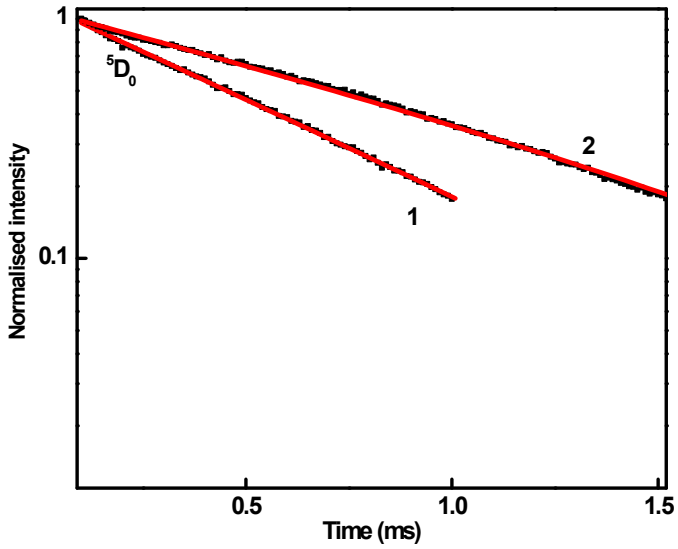

Fig. S17 Solid state luminescence decay profiles of complexes **1** and **2** monitored at 612 nm.

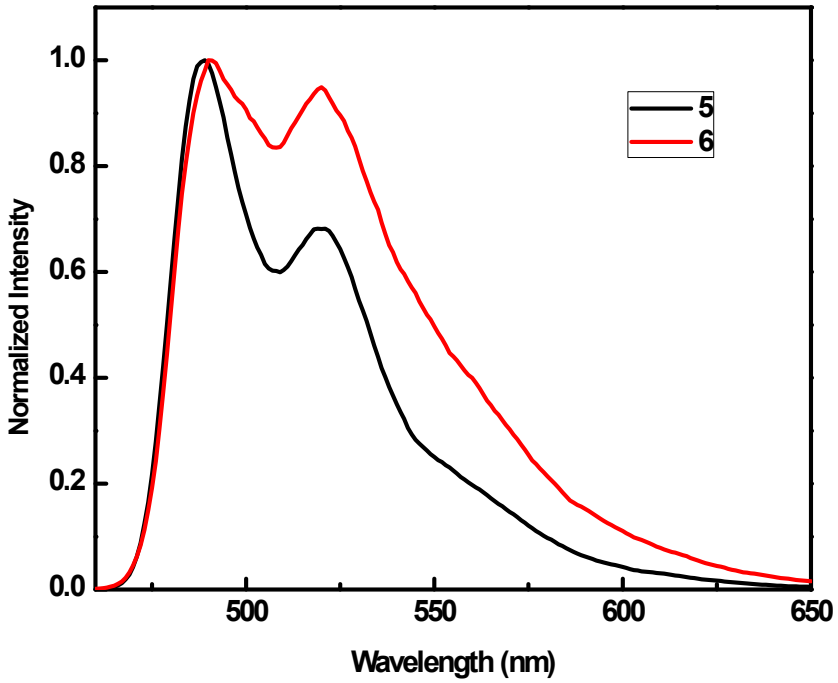

Fig. S18 77 K Phosphorescence spectra of complexes Gd(**L1**)$_3$(C_2H_5OH)$_2$ (**5**) and Gd(**L2**)$_3$(C_2H_5OH)$_2$ (**6**)

Table S1. Comparison of selected bond lengths (Å) from crystal structure and Sparkle/PM3 model geometry for complex **A**

	Bond lengths (Å)		**Difference**
	Crystal Structure	Sparkle/PM3 Model	
Eu-O2	2.300	2.418	0.118
Eu-O3	2.372	2.422	0.051
Eu-O4	2.399	2.469	0.071
Eu-O5	2.358	2.471	0.113
Eu-O6	2.399	2.463	0.064
Eu-O7	2.411	2.469	0.058
Eu-O8	2.344	2.474	0.129
Eu-O9	2.414	2.473	0.058
			Average 0.083

Table S2. Selected bond lengths (Å) for complexes **1-4** by Sparkle/PM 3 model

	1	**2**	**3**	**4**
Eu-O2	2.4496	2.4190	2.4506	2.4194
Eu-O3	2.4478	2.4221	2.4500	2.4224
Eu-O4	2.4574	2.4673	2.4562	2.4665
Eu-O5	2.4494	2.4721	2.4533	2.4737
Eu-O6	2.4482	2.4653	2.4482	2.4643
Eu-O7	2.4481	2.4668	2.4492	2.4674
Eu-O8	2.4481	2.4717	2.4492	2.4710
Eu-O9	2.4509	2.4712	2.4497	2.4706

Table S3. Selected bond angles (º) for complexes **1-4** by Sparkle/PM 3 model

	1	**2**	**3**	**4**
Eu-O2-O3	63.836	77.953	63.981	77.947
Eu-O2-O4	91.884	145.014	93.140	144.765
Eu-O2-O5	95.925	89.430	89.775	89.164
Eu-O2-O6	84.492	136.549	83.904	136.713
Eu-O2-O7	109.227	83.862	113.823	84.090
Eu-O2-O8	148.444	122.685	129.569	122.899
Eu-O2-O9	133.400	77.442	150.847	77.520
Eu-O3-O4	134.288	80.238	138.919	80.178
Eu-O3-O5	80.679	88.550	81.973	88.632
Eu-O3-O6	126.024	142.588	123.528	142.359
Eu-O3-O7	86.084	152.342	87.600	152.598
Eu-O3-O8	146.579	75.318	67.704	75.277
Eu-O3-O9	73.004	105.440	144.205	105.283
Eu-O4-O5	63.053	62.904	63.302	62.942
Eu-O4-O6	85.659	74.118	83.877	74.210
Eu-O4-O7	139.601	104.416	133.480	104.244
Eu-O4-O8	60.677	132.332	114.963	76.719
Eu-O4-O9	106.899	90.515	60.393	135.332
Eu-O5-O6	148.712	103.020	146.206	103.269
Eu-O5-O7	142.657	70.459	146.662	70.430
Eu-O5-O8	85.542	138.592	69.793	138.632
Eu-O5-O9	59.249	158.080	88.592	158.002
Eu-O6-O7	63.529	62.573	63.558	62.552
Eu-O6-O8	78.543	72.626	137.059	72.337
Eu-O6-O9	137.824	76.207	81.419	76.192
Eu-O7-O8	86.732	132.332	76.941	132.121
Eu-O7-O9	83.519	90.515	81.579	90.615
Eu-O8-O9	73.770	62.694	76.615	62.762

Table S4. Selected bond lengths (Å) for complexes **5** and **6** by Sparkle/PM 3 model

	5	**6**
Gd-O2	2.4047	2. 4066
Gd-O3	2.3993	2.4006
Gd-O4	2.4150	2.4114
Gd-O5	2.4124	2.4084
Gd-O6	2.3999	2.4011
Gd-O7	2.4021	2.4038
Gd-O8	2.4315	2.4586
Gd-O9	2.4416	2.4329

Table S5. Selected bond angles (º) for complexes **5** and **6** by Sparkle/PM 3 model

	5	**6**
Gd-O2-O3	66.942	67.336
Gd-O2-O4	88.182	91.390
Gd-O2-O5	91.475	85.824
Gd-O2-O6	83.675	80.623
Gd-O2-O7	122.462	117.926
Gd-O2-O8	141.861	132.648
Gd-O2-O9	127.778	145.048
Gd-O3-O4	143.756	142.354
Gd-O3-O5	87.067	80.794
Gd-O3-O6	115.792	119.775
Gd-O3-O7	82.838	85.107
Gd-O3-O8	150.388	69.689
Gd-O3-O9	73.198	146.908
Gd-O4-O5	66.824	66.439
Gd-O4-O6	85.364	84.387
Gd-O4-O7	133.406	132.468
Gd-O4-O8	55.830	111.683
Gd-O4-O9	106.526	56.798
Gd-O5-O6	151.939	147.475
Gd-O5-O7	136.155	144.826
Gd-O5-O8	85.684	68.456
Gd-O5-O9	53.483	92.920
Gd-O6-O7	66.637	66.463
Gd-O6-O8	81.417	139.828
Gd-O6-O9	145.672	82.029
Gd-O7-O8	82.696	76.448
Gd-O7-O9	82.809	81.656
Gd-O8-O9	79.451	77.752