Supplementary Information

Synthetic procedures

Synthesis of $Eu(tta)_3(H_2O)_2$, $Eu(NO_3)_3(ephen)_2$ and $Gd(NO_3)_3(ephen)_2$ complexes

a) To synthesize $Eu(tta)_3(H_2O)_2$ complex **I** a mass of 0.6664 g (3 mmol) of Htta was dissolved in 10 mL of CH_3CH_2OH and the pH of this solution was adjusted to 6 by adding an appropriate amount of an aqueous NaOH solution (5 % w/v). Then a solution of 0.3662g of $EuCl_3.6H_2O$ in 5 mL of water was added dropwise to the ethanolic solution of Htta. After addition of 100 mL of water the mixture was vigorous stirred for 120 min at 60 ºC. The pale yellow solid product was filtrated, washed with water and dried in desiccators at room temperature. *Yield:* 80%. Anal Calcd (%) for $C_{24}H_{16}EuF_9O_8S_3$: C 33.85, H 1.89, S 11.30. Found C 33.74, H 1.88, S 10.52. IR (KBr pellets, cm^{-1}): 3651 (sh), 3610 (m), 33692 (br), 3195 (sh), 3115 w, 3092 w, 1604 s, 1584 s, 1544 s, 1513 m, 1460 m, 1446 sh, 1436 sh, 1411 s, 1358 s, 1351 sh, 1302 vs, 1290 sh, 1250 s, 1232 m, 1210 sh, 1191 s, 1140 s, 1081 m, 1062 m, 1041 sh, 1013 w, 934 m, 930m, 862 m, 850 sh, 842 vw, 795 sh, 787 m, 768 m, 752 m, 736 m, 724 m, 714 m, 695 m, 683 m, 542 m, 606 m, 582 m, 560 sh, 520 vw, 504 vw, 487 vw, 463 w, 365 w. Raman (cm^{-1}): 3091 m, 3106 sh, 3114 m, 1632 m, 1600 w, 1586 w, 1539 m, 1513 s, 1508 sh, 1444s, 1410 vs, 1358 s, 1350 sh, 1307 m,1295 sh, 1250 m, 1232 m, 1202 w, 1140 w, 1088 m, 1082 m, 1061 m, 1039 w, 1016 w, 934 m, 930 sh, 862 w, 796 w, 783 w, 769 w, 750 m, 722 m, 694 m, 685 m, 642 m, 605 m, 579 w, 561 w, 518 w, 464 w, 258 m, 218 sh, 211 m;

(b) For the synthesis of $Eu(NO_3)_3(ephen)_2$ complex **III** a mass of $Eu(NO_3)_3.6H_2O$ (0.0835 g, 0.25 mmol) in methanol (5 mL) and ephen (0.1030 g, 0.52 mmol) in methanol (5 mL) were mixed slowly. The mixture was stirred for 8h at room temperature. The solid was filtrate and dried under vacuum and afford a white power solid. *Yield:* 81%. Anal Calcd for $C_{24}H_{16}EuN_7O_{11}$: C 39.47, H 2.21, N 13.42. Found C 38.20, H 2.12, N 13.00. As it is well known that pressing a KBr pellet affects the nitrate coordination and this phenomenon has been fully discussed[1], the following results refer to ATR data. ATR (cm^{-1}): 3097 w, 3062 sh, 3027 sh, 1610 w, 1584 sh, 1574 m, 1489 sh, 1467 vs, 1435 vs, 1390 w, 1313 vs, 1283 vs, 1241 w, 1218 m, 1198 w, 1160 vw, 1134 w, 1114 vw, 1093 w, 1067 w, 1036 m, 1022 m, 993 vw, 961 vw, 893 m, 875 vw, 822 sh, 808 sh, 799 s, 745 s, 739 s, 721 s, 675 w, 642 m, 622 m, 582 w, 537 vw, 526 vw, 508 vw, 440 vw, 414 m, 359 w. Raman (cm^{-1}): 3177 w, 3070 m, 3053 m, 3039 m, 3021 m, 1589 vs, 1487 s, 1446 s, 1389 s, 1323 s, 1274 vw, 1244 w, 1224 m, 1218 sh, 1200 vw, 1137 w, 1066 s, 1037 m, 1025 sh, 892 m, 875 vw, 828 sh, 821 sh, 811 m, 801 sh, 743 w, 723 m, 710 vw, 676 vw, 642 vw, 540 vw, 530 w, 525 sh, 443 m, 415 m, 361 m, 273 m, 227 m, 193 m;

(c) The synthesis of $Gd(NO_3)_3(ephen)_2$ complex **IV** was prepared in the same way as complex **III** and a white power solid product was obtained. *Yield:* 80 %. Anal Calcd for $C_{24}H_{16}GdN_2O_7O_{11}$: C 39.18, H 2.19, N 13.33. Found C 38.10, H 2.19, N 12.79.. ATR (cm^{-1}): 3097 w, 3062 sh, 3025 sh, 1610 w, 1585 sh, 1574 m, 1490 sh, 1467 vs, 1436 vs, 1390 w, 1314 vs, 1283 vs, 1241 w, 1217 m, 1198 w, 1160 vw, 1134 w, 1114 vw, 1092 w, 1067 w, 1036 m, 1023 m, 992 vw, 960 vw, 893 m, 874 vw, 821 sh, 808 sh, 800 s, 744 s, 740 s, 722 s, 675 w, 642 m, 621 m, 582 w, 537 vw, 526 vw, 508 vw, 440 vw, 414 m, 357 w. Raman (cm^{-1}): 3177 w, 3070 m, 3052 m, 3039 m, 3021 m, 1589 vs, 1487 s, 1446 s, 1389 s, 1323 s, 1273 vw, 1244 w, 1224 m, 1218 sh, 1200 vw, 1137 w, 1066 s, 1037 m, 1025 sh, 892 m, 875 vw, 828 sh, 821 sh, 811 m, 801 sh, 743 w, 723 m, 710 vw, 676 vw, 642 vw, 539 vw, 530 w, 525 sh, 444 m, 416 m, 361 m, 274 m, 228 m, 195 m.

1. G. J. Kleywegt, W. G. R Wiesmeijer, G. J. Vandriel, W. L. Driessen, J. Reedijk and J. H. Noordik, *J. Chem. Soc.-Dalton Trans.*, 1985, 2177.

Full characterization of $Eu(tta)_3$ephen complex II

Complex **II** was obtained in good yield (83%) from the corresponding precursor $Eu(tta)_3(H_2O)_2$ complex **I** by reaction with 1 equiv of the ligand ephen. The C, H, N and S microanalysis

percentage experimental/calculated values found for Eu(tta)$_3$ephen complex **II** show that the Eu^{3+} ion has reacted with tta in a metal-to-ligand mole ratio of 1:3 and that one molecule of ephen is involved in complex **II**. High-resolution mass spectra (HR-MS) were acquired using the electrospray ionization (ESI) technique to confirm the proposed structure of complex **II** (Figure S1). Both the molecular mass and the isotopic pattern were analyzed. The *m/z* peaks correspond to the desired complex in its sodium adduct form detected at *m/z* = 1034.94472 confirming its formulation as $[C_{36}H_{20}F_9N_2O_7S_3Eu+Na]^+$. This represents an error of 5.4 ppm relatively to the expected ion at m/z = 1034.93910 which is in extremely good agreement. The composition of the first coordination sphere was also confirmed by some coordination-sensitive modes observed in both FT-IR and Raman spectra (Figures S2 and S3, respectively). The coordination of tta to Eu^{3+} was mainly indicated by the energy vibrations values of the β-diketonate chelated ring (particularly those arising from C=O and C=C stretching modes) that shift to lower wavenumbers. In the 1530-1660 cm^{-1} region, from the free tta ligand to complex **I**, the FT-IR bands at 1655/1638/not active/1581 cm^{-1} [Figure S2, trace (a)] with correspondence with the Raman bands at 1655/not active/1620/1576 cm^{-1} [Figure S3, trace (a)] shift to not active/1604/1585/1544 cm^{-1} [Figure S2, trace (b)] and to 1630/1602/1589/1540 cm^{-1} [Figure S3, trace (b)]. In turn, for complex **II**, the corresponding shifts are to 1626/1600/1579/1540 cm^{-1} [Figure S2, trace (d)] and 1624/1600/1577/1535 cm^{-1} [Figure S3, trace (d)]. The disappearance of the broad band around 3360 cm^{-1} and the medium sharp bands near 3610 and 3650 cm^{-1} for complex **II**, which are associated with the water molecules in complex **I**, suggest that water molecules have been displaced by the insertion of ephen as a coordinating unit in the first coordination sphere. The proof for the coordination of ephen is evidenced in the 1550-1650 cm^{-1} region of the Raman spectra, where the coupled C=C and C=N ring stretching vibration of ephen at 1586 cm^{-1} [Figure S3, trace (c)] shift to higher wavenumber at 1590 cm^{-1} [Figure S3, trace (d)] upon coordination.To investigate the thermal stability of the synthesized complexes **I** and **II**, termogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analyses were carried out and the results are shown in Figures S4 and S5, respectively. It is clear from the TGA data that complex **I** [Figure S4, trace (a)] undergoes a mass loss of 5%, in the 75-115 °C temperature range, which corresponds to the removal of the coordinated water molecules. In the corresponding DSC curve [Figure S5, trace (a)] this effect is manifested as an intense endothermic peak centered between 100-120 °C (an additional weaker endotherm peak associated with the melting point of the complex **I** is also observed). The sample then starts to gradually decompose. The TGA curve of complex **II** [Figure S4, trace (b)] is stable up to 225 °C, demonstrating the anhydrous character of this complex and confirming that the replacement of the water molecules by the chelating ephen ligand is clearly advantageous, as it imparts a thermal stability. Notably, no endothermic peak of melting point is observed for complex **II** in DSC analysis [Figure S5, trace (b)]. This means that complex **II** is amorphous or, at least, that it is difficult to crystallize. It should be emphasized that the presence of the epoxide group in the ephen ligand enables the existence of two isomeric Eu^{3+} complexes, since the epoxide group could be situated above or below the plane defined by the β-diketone(Eu;O3;O4).Therefore, this reaction could yield different ratios of the two isomers. When methanol solvent was used, the reaction yield was low and an orange solid was obtained from the mother solution after filtering out the mixture. With the structural characterization techniques described herein, the obtained orange solid showed the same features of the white solid. However, in respect to their photoluminescence properties, different emission quantum yields were obtained with the white solid showing the higher value. Therefore, the reaction yield was then optimized by using the solvent ethanol thus achieving the white solid that was incorporated into the tri-ureasil matrix. IR (KBr pellets, cm^{-1}): 3443 br, 1626 s, 1600 vs, 1579 s, 1540 s, 1508 m, 1477 w, 1464 m, 1436 m, 1412 s, 1357 s, 1310 vs, 1291 sh, 1248 s, 1231 s, 1201 sh, 1187 s, 1141 vs, 1132 sh, 1082 vw, 1063 m, 1036 vw, 1026 vw, 1015 vw, 933 m, 896 m, 860 m, 822 sh, 811 w, 801 sh, 789 s, 767 m, 747 m, 720 m, 714 sh, 692 w, 683 m, 642 s, 621 m, 604 m, 581 s, 522 vw, 495 w, 462 w, 413 vw, 355 w; Raman (cm^{-1}): 3107 m, 3092 m, 3019 m, 1625 m, 1606 sh, 1588 s, 1535 m, 1522 s, 1482 m, 1475 m, 1460 m, 1446 m, 1413 vs, 1390 m, 1353 m, 1321 w, 1304 m, 1287 sh, 1253 m, 1246 m, 1231 m, 1225 m, 1196 w, 1138 w, 1081 s, 1065 s, 1018 m, 933 s, 896 m, 872 w, 859 m, 843 w, 831 m, 820 m, 811 m, 795 m, 778 vw, 768 m, 750 s, 720 s, 692 sh, 683 s, 640

s, 604 m, 579 m, 559 m, 540 w, 525 sh, 520 m, 471 sh, 463 m, 444 m, 412 m, 357 m, 318 m, 300 w, 266 sh, 249 m, 223 m; HR–ESI–MS (*m/z*): calcd for $[C_{36}H_{20}F_9N_2O_7S_3Eu+Na]^+$, 1034.93910; obsd, 1034.94472; error, +5.4 ppm.

Figures and Tables captions

Figure S1 – HR-ESI-MS analysis of Eu(tta)$_3$ephen complex **II** showing the experimental (top, red line) and the predicted (bottom, black line) spectra formulated as the sodium adduct. The measured error was found to be +5.4 ppm. Both mass and isotopic patterns were analyzed.

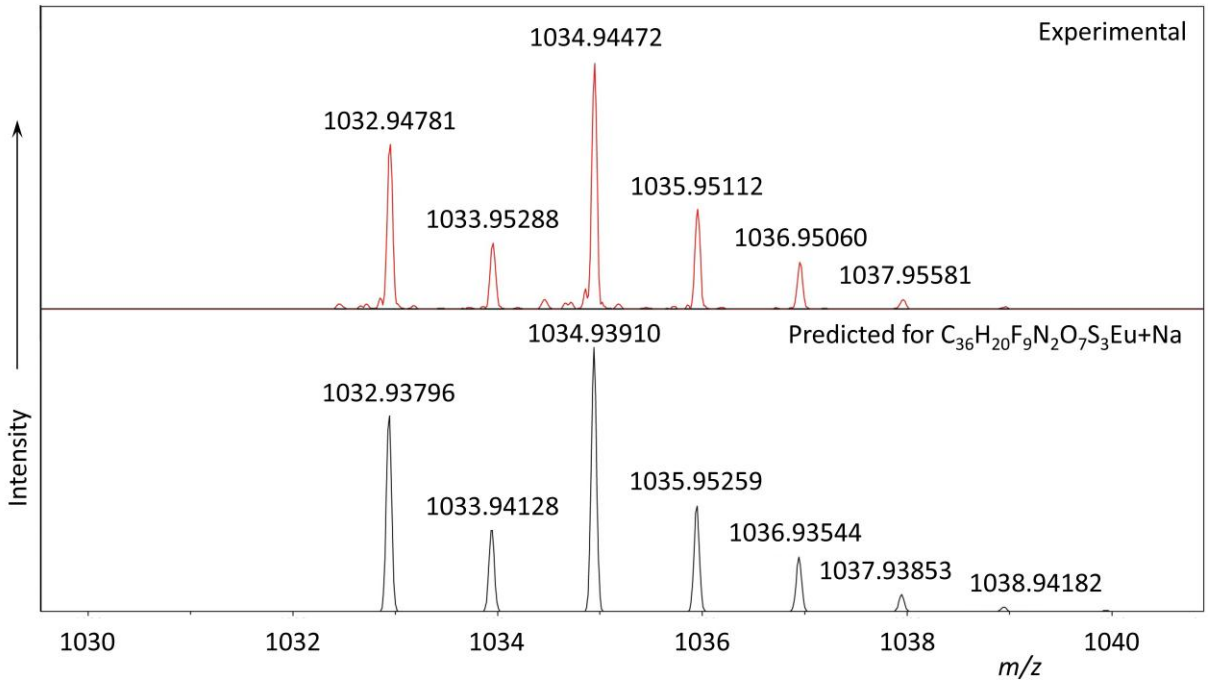


Figure S2 – FT-IR spectra of the tta ligand (a), $Eu(tta)_3(H_2O)_2$ complex **I** (b), ephen ligand (c) and $Eu(tta)_3$ephen complex **II** (d).

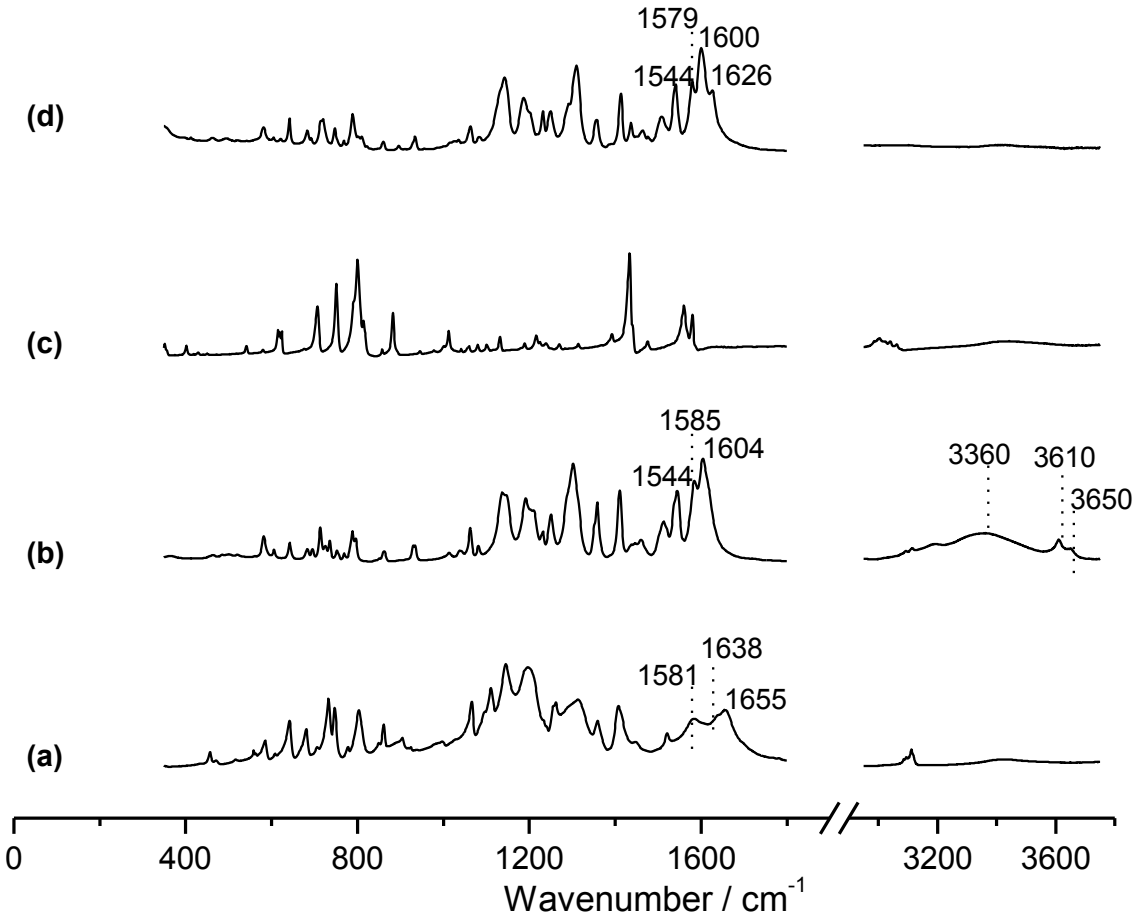


Figure S3 – Raman spectra of the tta ligand (a), $Eu(tta)_3(H_2O)_2$ complex **I** (b), ephen ligand (c) and $Eu(tta)_3$ephen complex **II** (d).

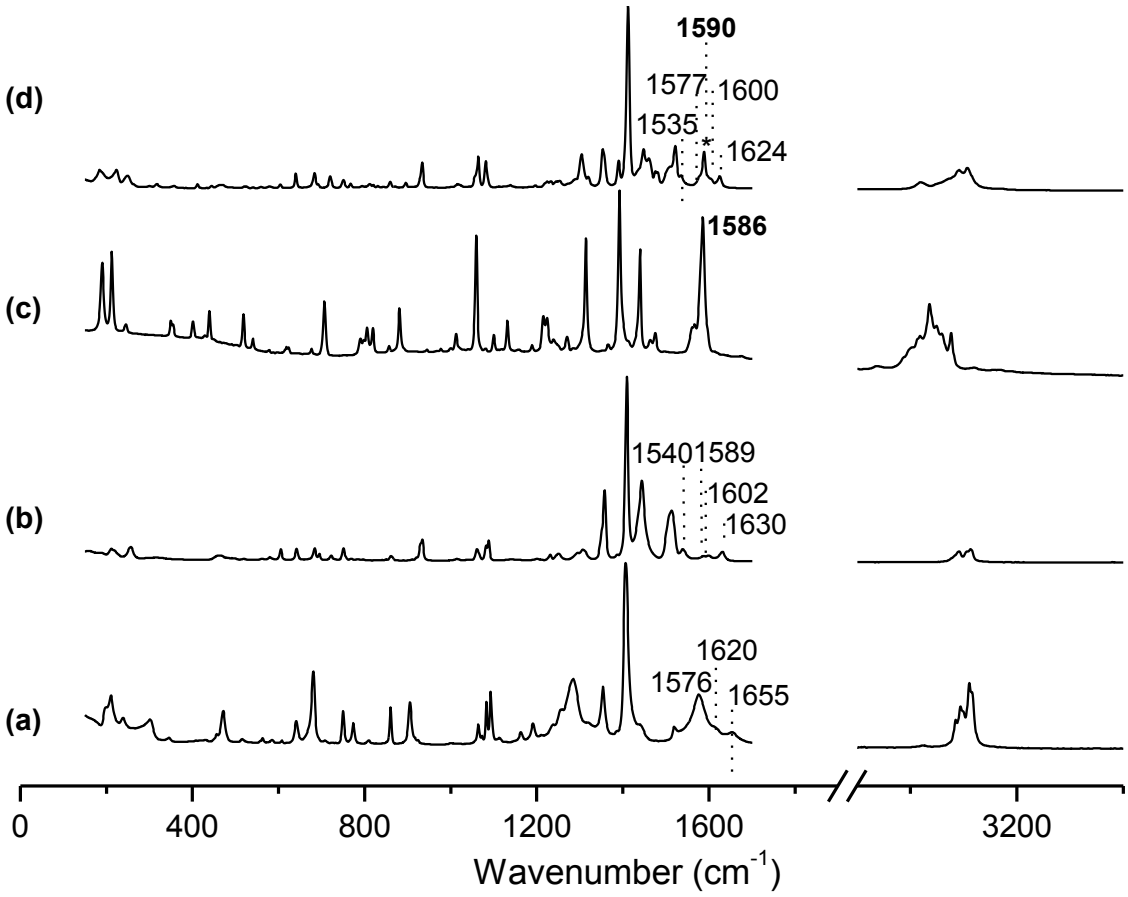


Figure S4 – TGA curves of the $Eu(tta)_3(H_2O)_2$ complex **I** (a) and $Eu(tta)_3$ephen complex **II** (b).

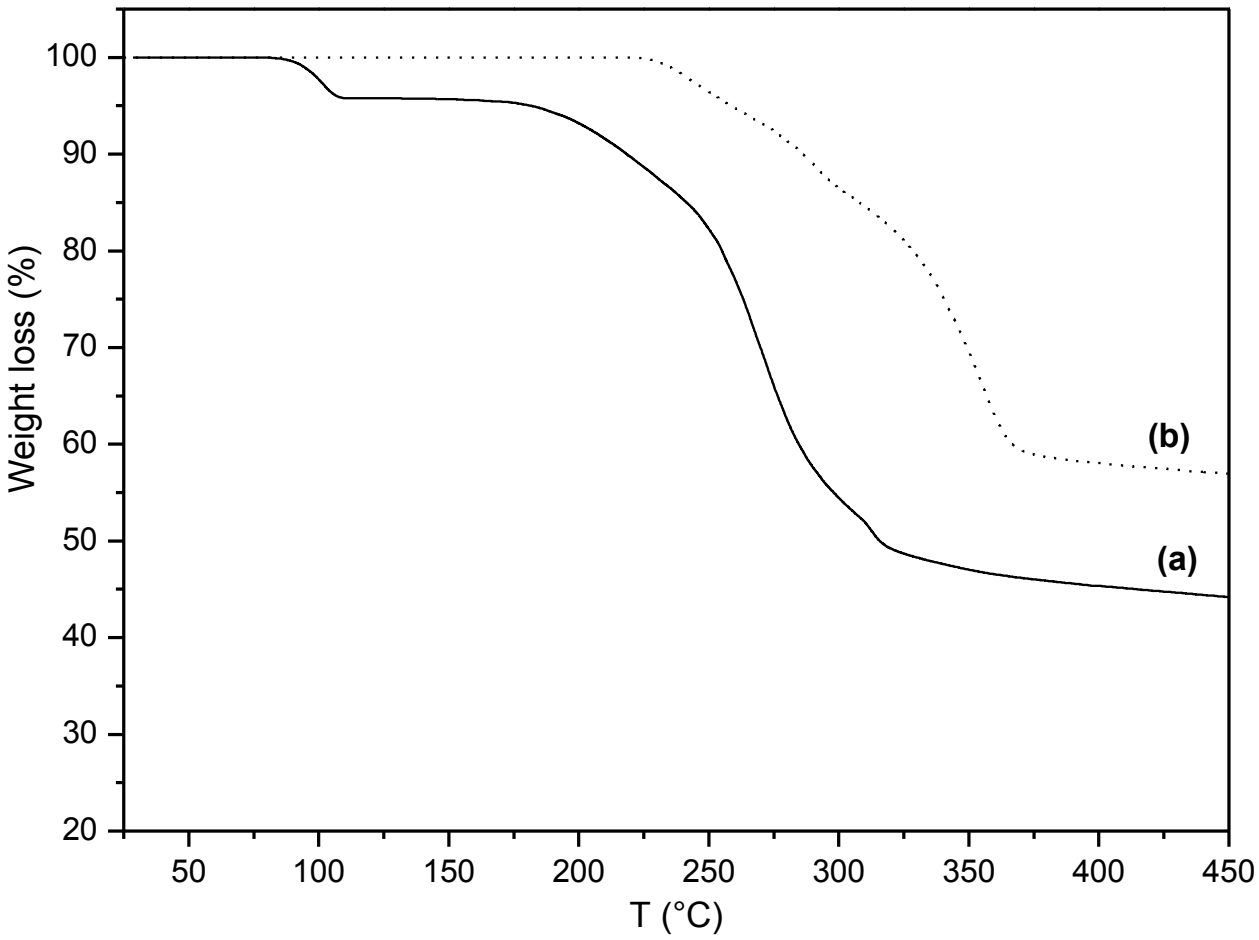


Figure S5 – DSC curves of the $Eu(tta)_3(H_2O)_2$ complex **I** (a) and $Eu(tta)_3$ephen complex **II** (b).

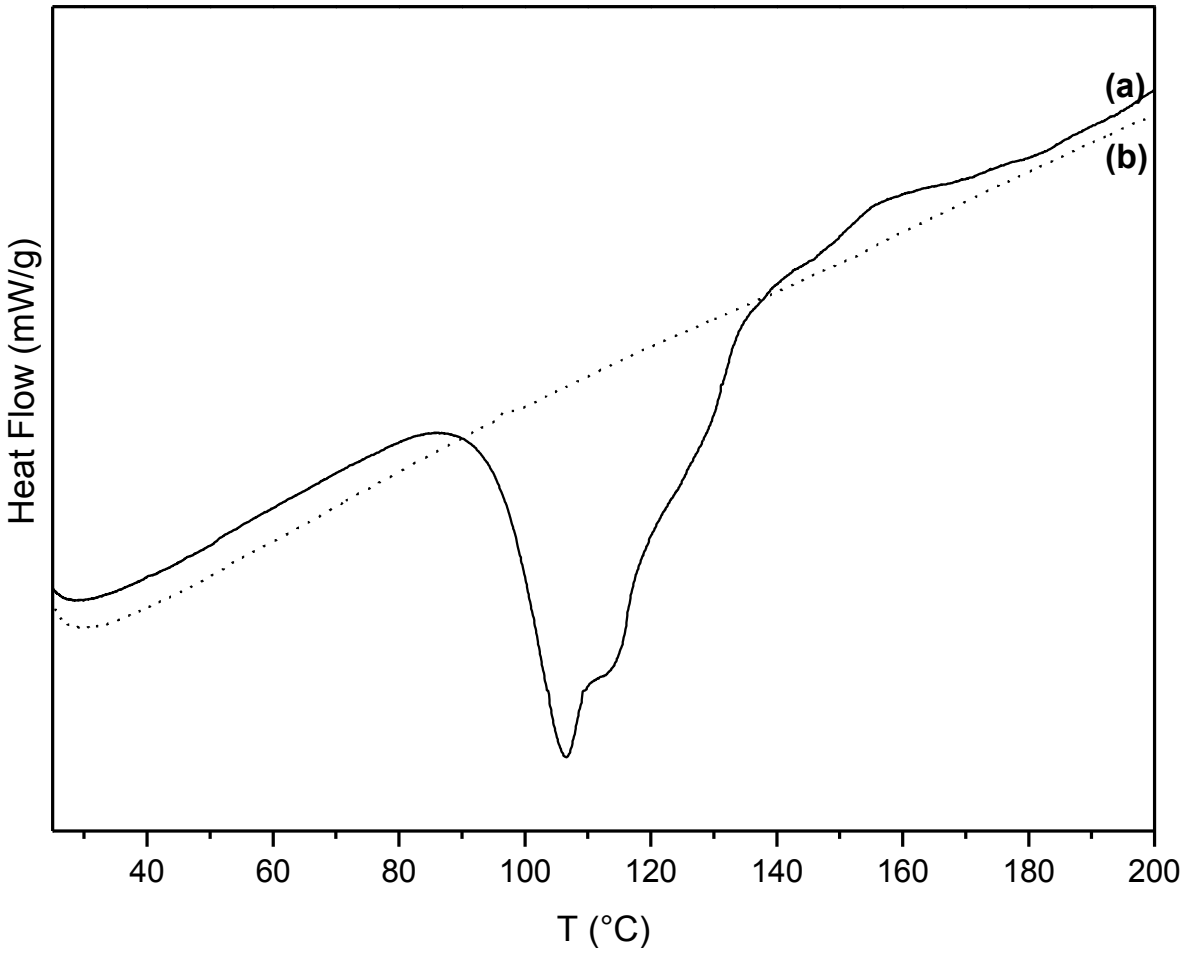


Figure S6 – Refractive index variation as function of the wavelength of **FtU5Eu-II**.

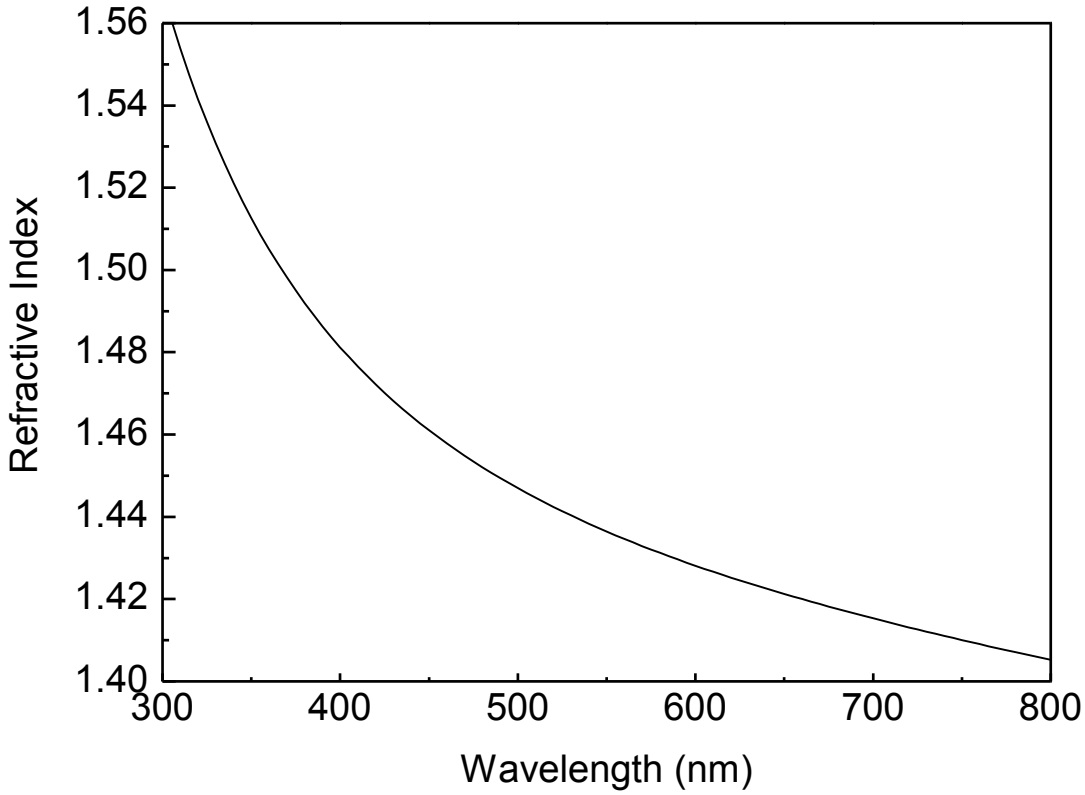


Figure S7 – (A) Structure model and (B) ellipsometric parameters I_s (red circles) and I_c (blue triangles) of **FtU5Eu-II**. The solid lines correspond to the data best fit ($\chi^2_{red}=1.2\times10^{-3}$).

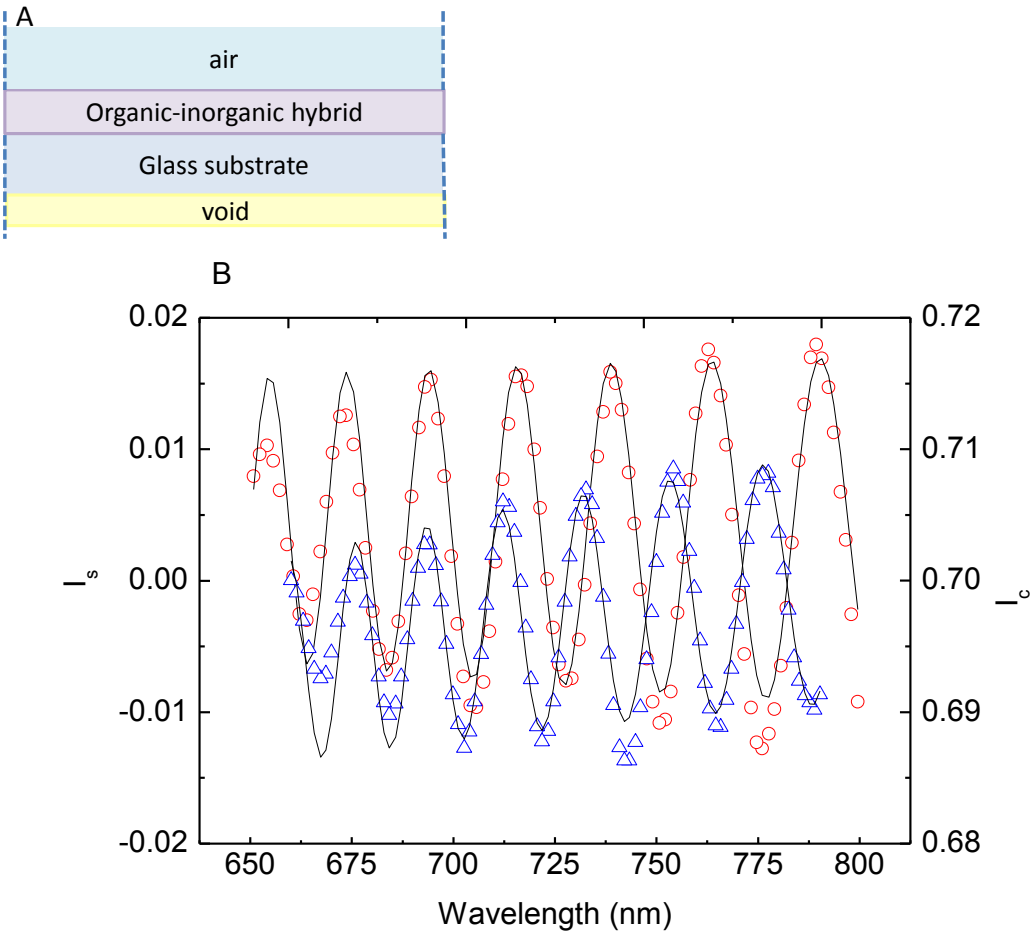


Figure S8 – FT-IR spectra of the nondoped **t-U(5000)** (a) and **MtU5Eu-II** (b).

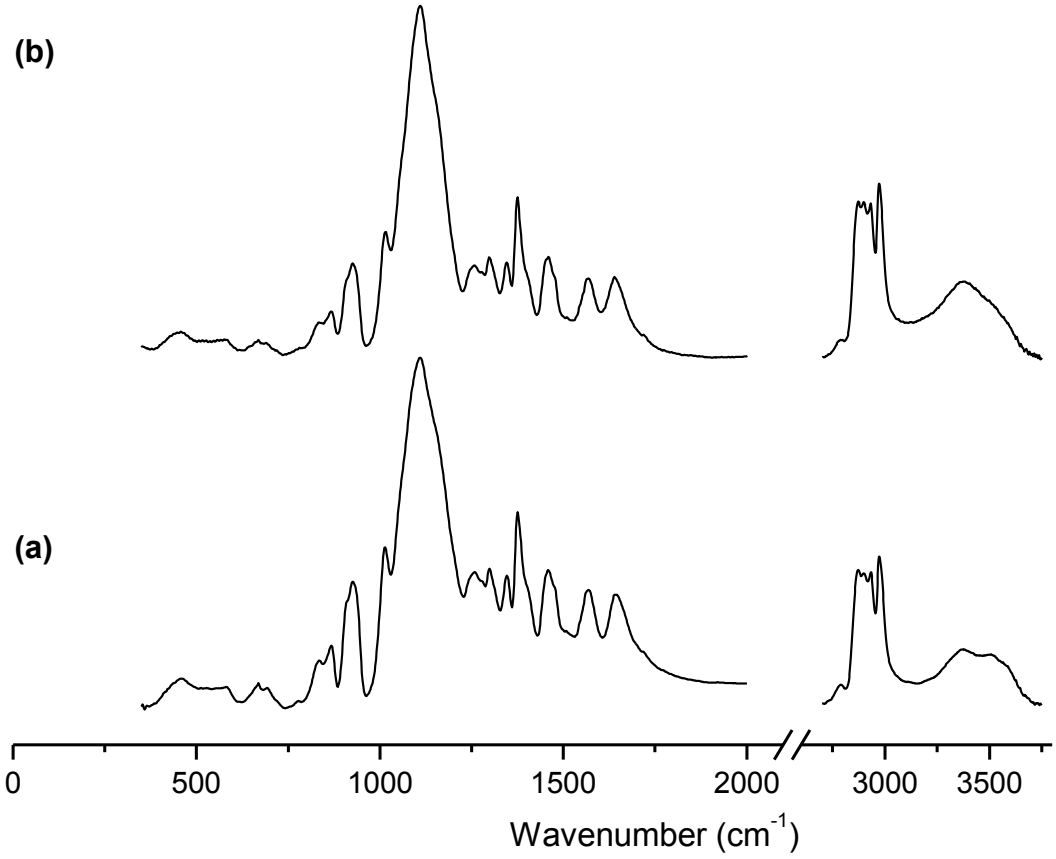


Figure S9 – Raman spectra of the **t-U(5000)** (a) and **MtU5Eu-II** (b).

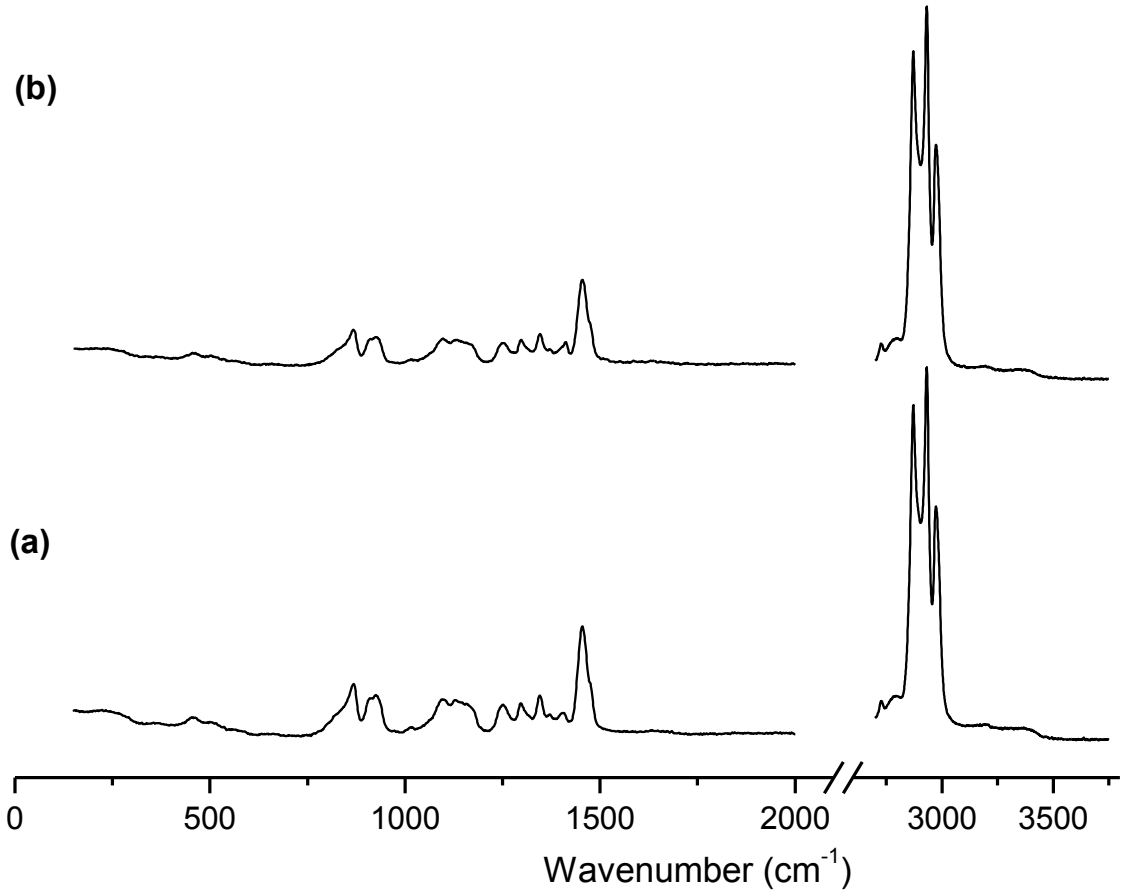


Figure S10 – Optimized molecular geometry obtained from DFT calculations (B3LYP) for the Eu(tta)$_3$ephen complex **II** (form A).

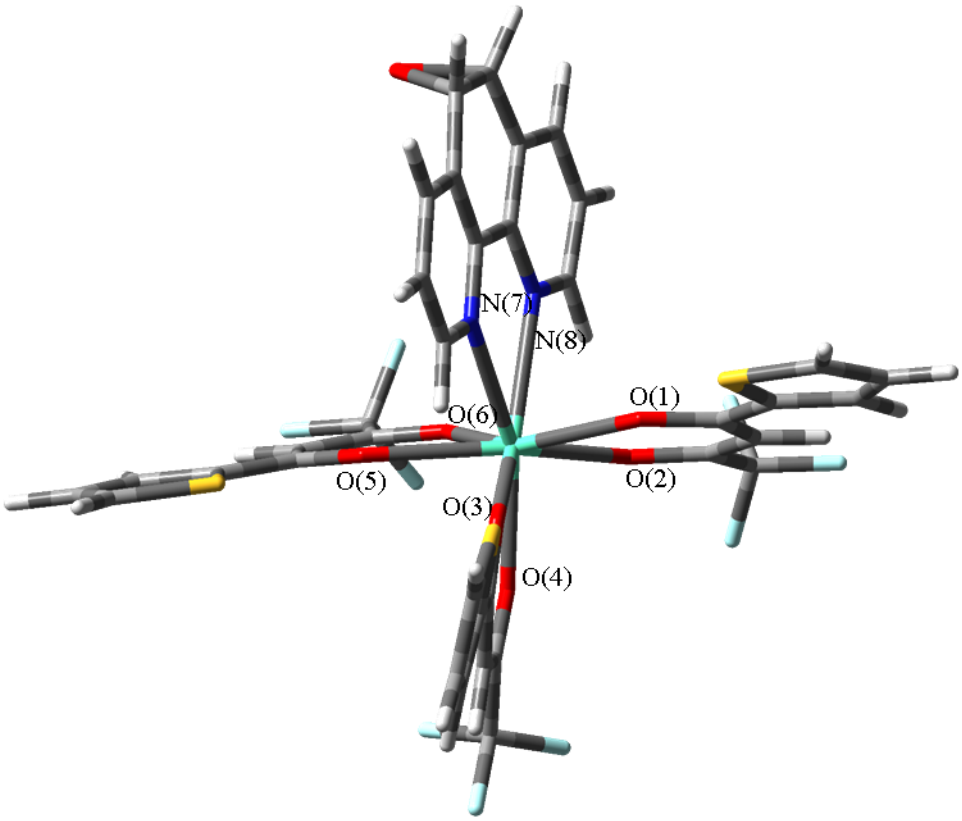
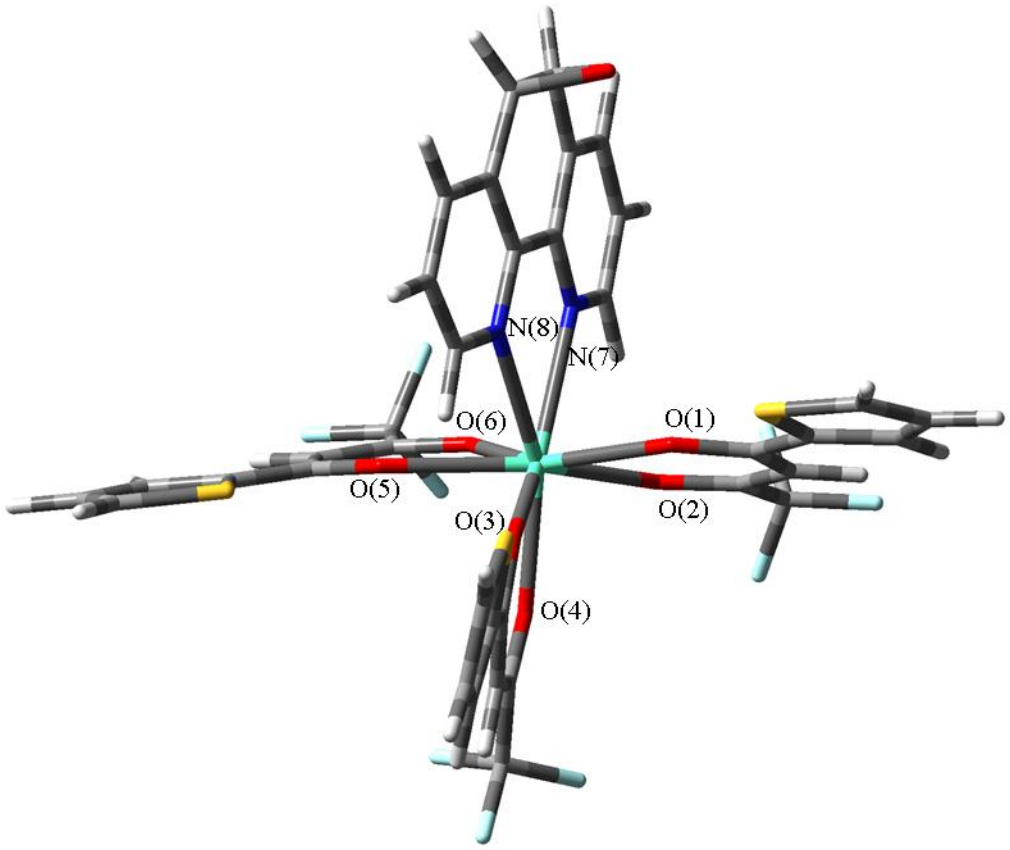


Figure S11 – Optimized molecular geometry obtained from DFT calculations (B3LYP) for the Eu(tta)$_3$ephen complex **II** (form B) together with the calculated metal-bond distances (bottom).



Eu-O(1)	Eu-O(2)	Eu-O(3)	Eu-O(4)	Eu-O(5)	Eu-O(6)	Eu-N(7)	Eu-N(8)
2.420	2.383	2.446	2.357	2.437	2.385	2.669	2.643

Figure S12 – Schematic diagram showing the energies and electronic density contours for the HOMO (H) and LUMO (L) frontier molecular orbitals of the Eu(tta)$_3$ephen complex **II** obtained in ethanolic solution. The energy diagram (left) represents the HOMO-LUMO energy gap (in eV).

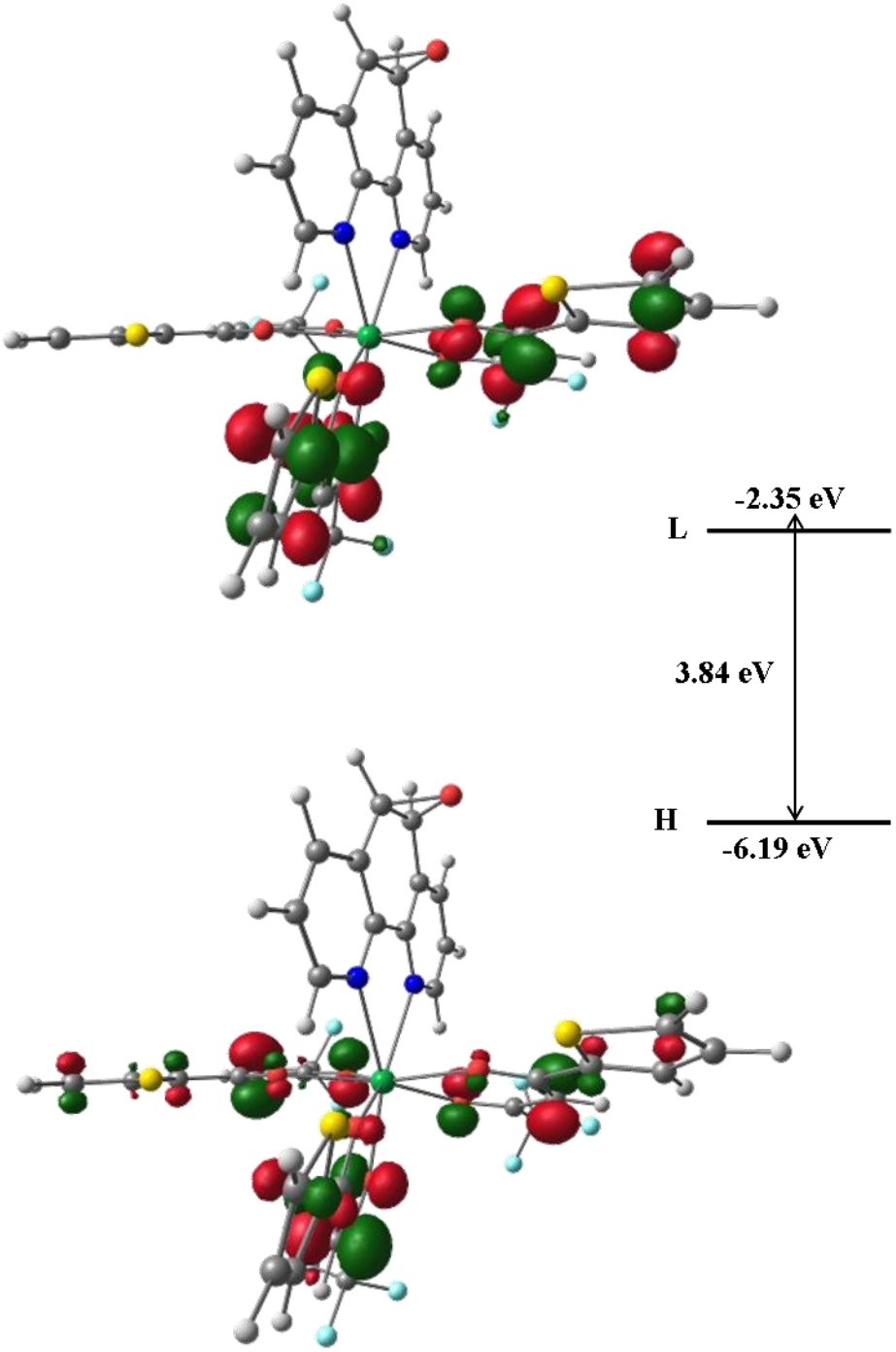


Figure S13 - UV-Vis absorption spectra of tta (solid line) and ephen ligands (dot line) in ethanolic solutions (10^{-5} mol L^{-1}).

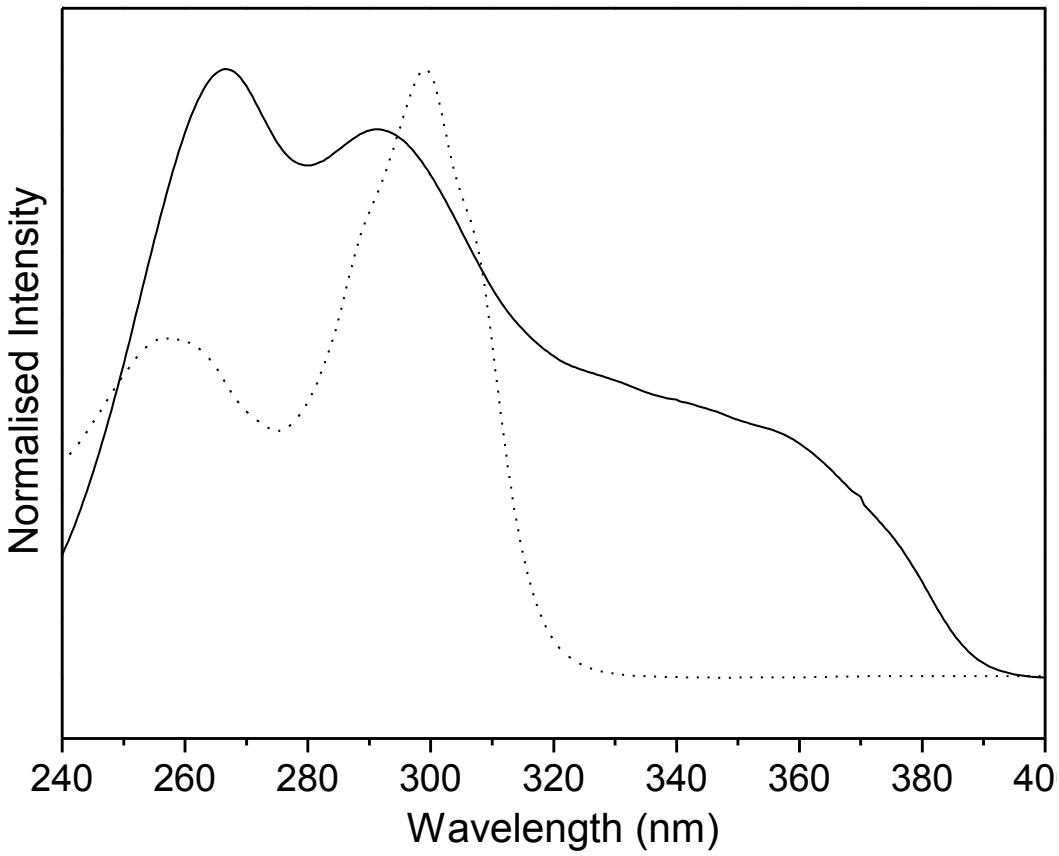


Figure S14 – UV-Vis absorption spectra of $Eu(NO_3)_3(ephen)_2$ complex **III** (black line) and $Eu(tta)_3(H_2O)_2$ complex **I (**red line) in ethanolic solution (10^{-5} and 10^{-4} M, respectively)

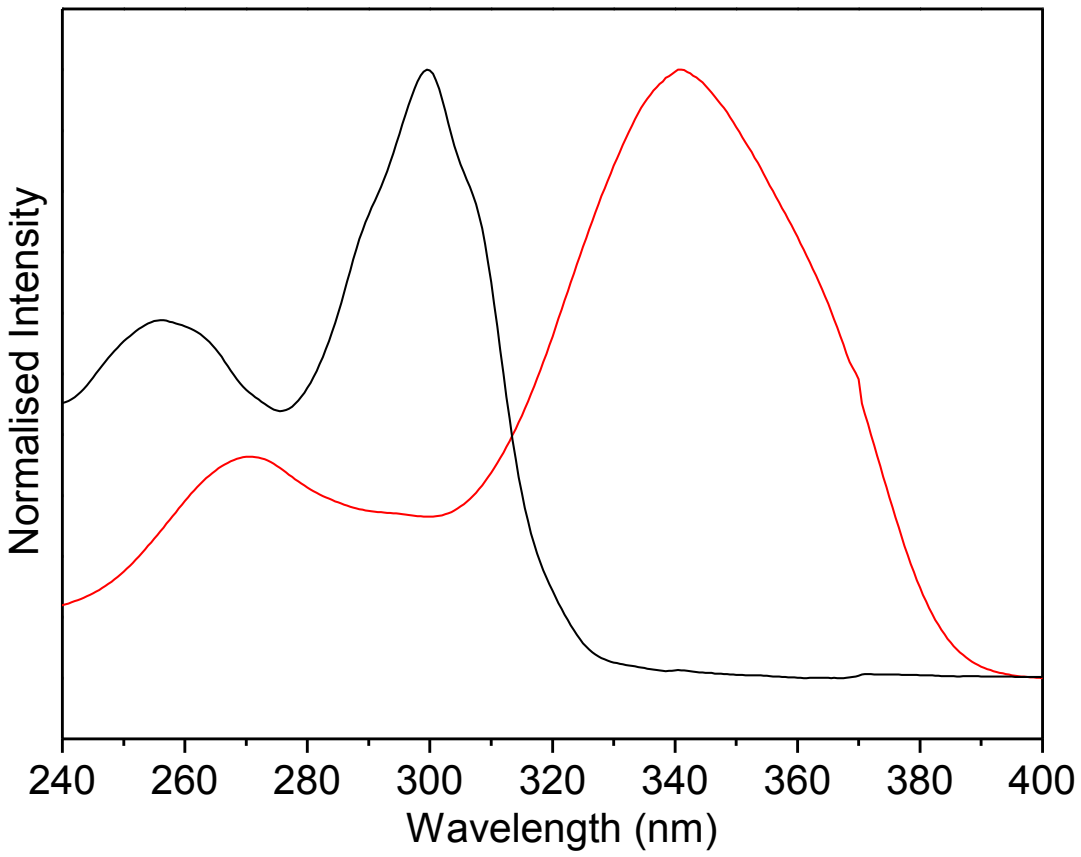


Figure S15 – Time-resolved emission spectra (10K) of $Gd(NO_3)_3(ephen)_2$ complex **IV** excited at 340 nm and acquired at SD=0.05 ms. The integration window was 20.00 ms. The triplet state energy peak position (455 nm) is also assigned.

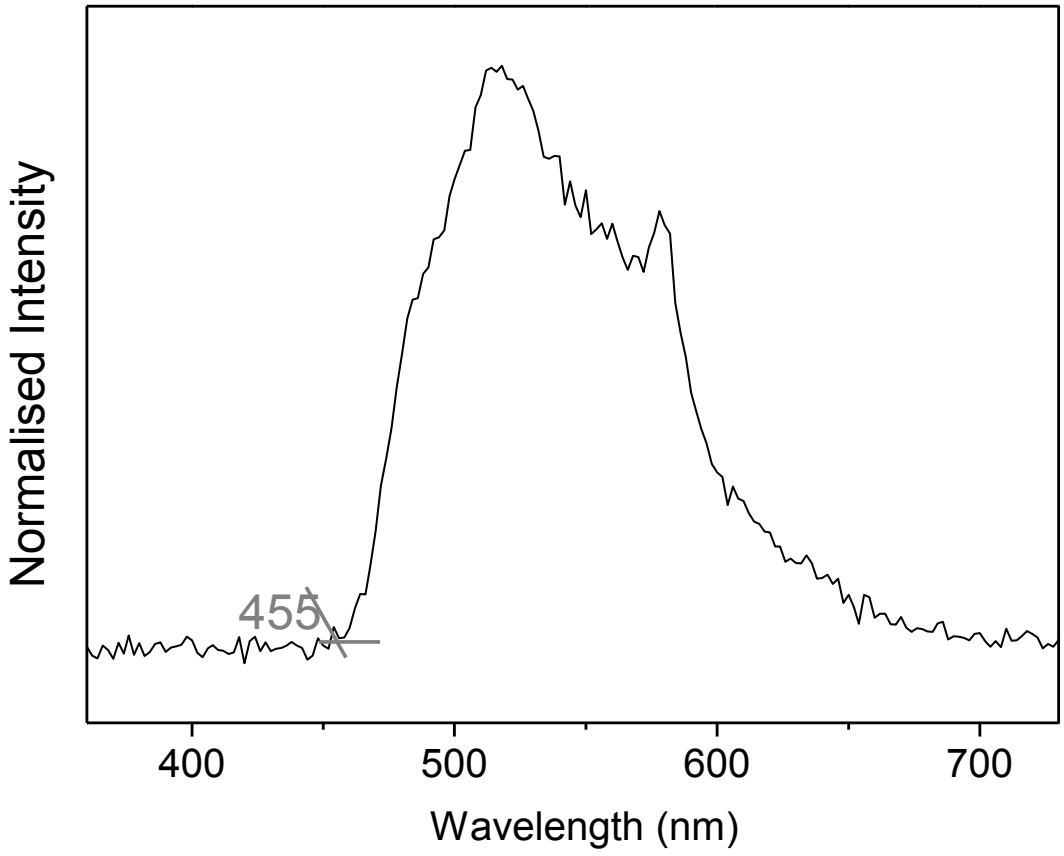


Figure S16 – Excitation spectra (300K) of $Eu(NO_3)_3(ephen)_2$ complex **III** (black line) and $Eu(tta)_3(H_2O)_2$ complex **I** **(**red line) in ethanolic solution (10^{-5} and 10^{-4} M, respectively) monitored at *ca.* 612 nm.

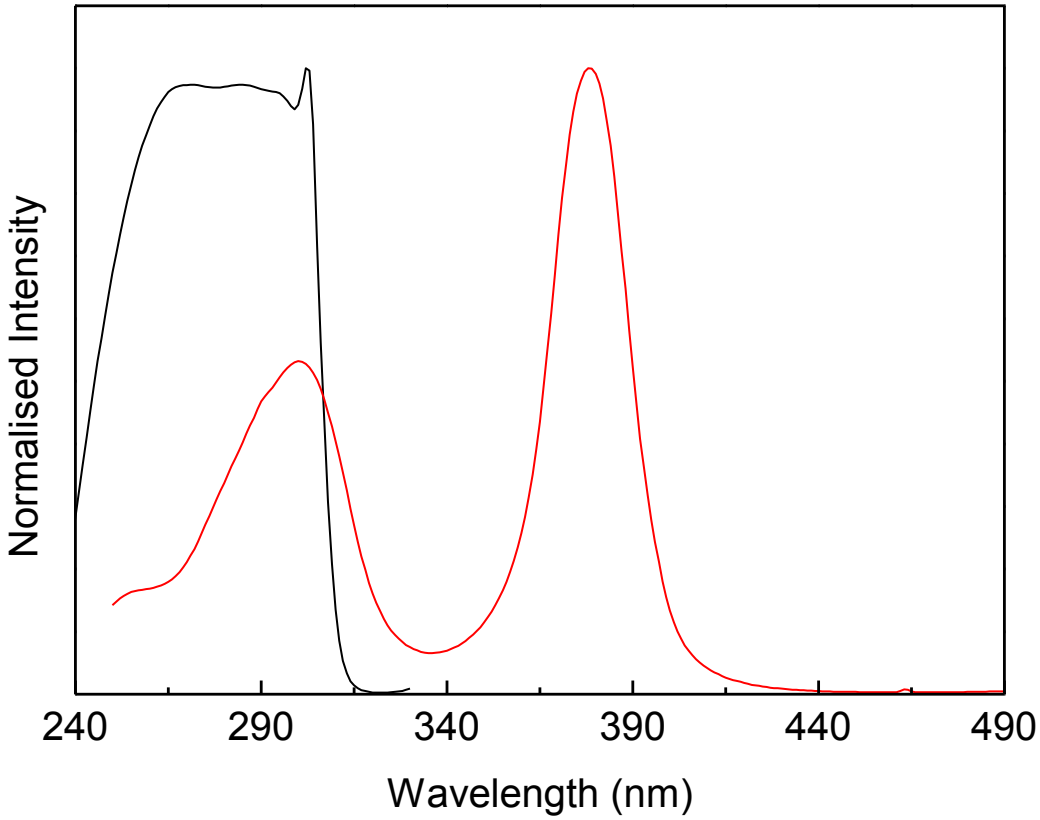


Figure S17 – Emission spectra (300K) of (A) complex **II**, (B) **MtU5Eu-II** and (C) **FtU5Eu-II** excited between 270 and 464 nm.

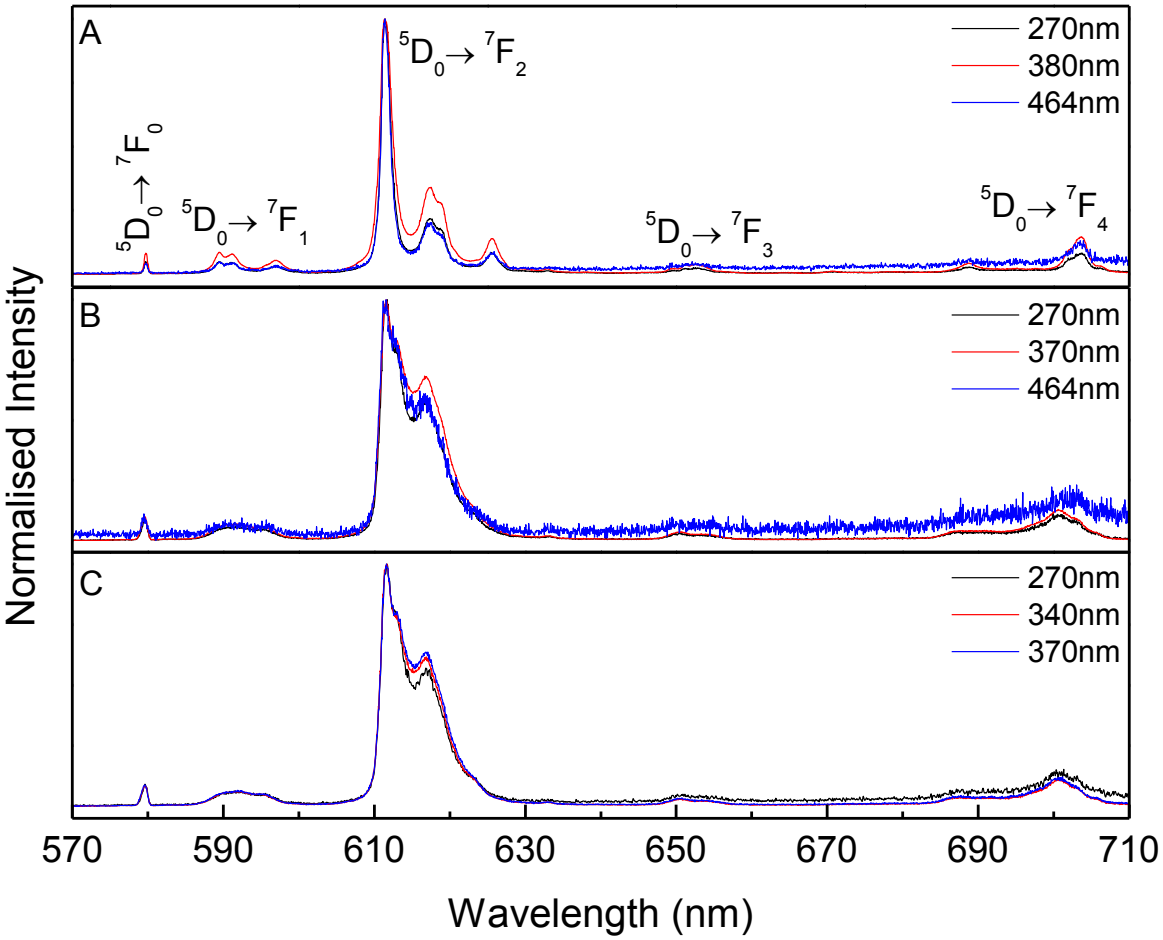


Figure S18 - Low temperature (12K) emission spectra of (A) complex **II** and of (B) **MtU5Eu-II** excited between 270 and 464 nm.

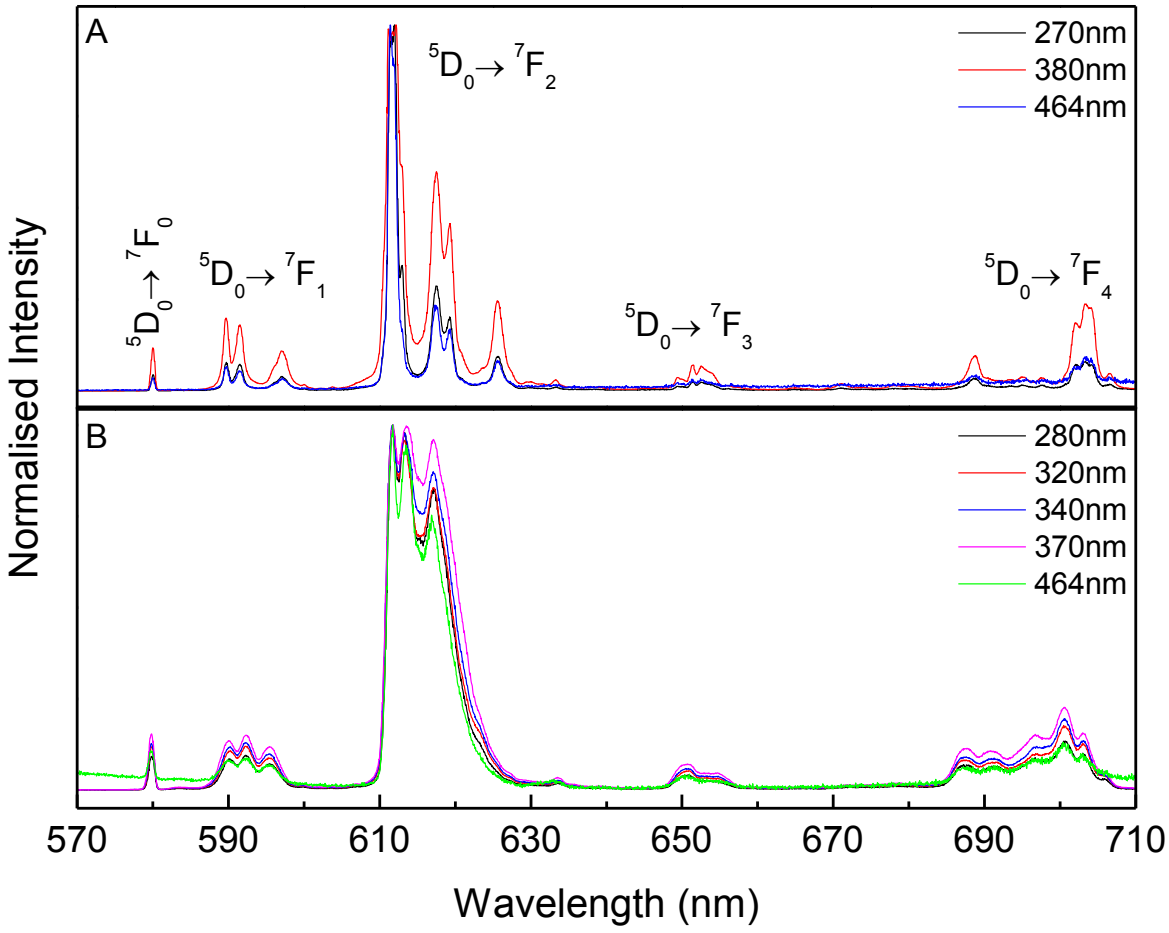


Figure S19 – Room temperature (300K) emission decay curves excited at 270, 380 and 464 nm and monitored at 612 nm of complex **II**. The solid lines correspond to the data best fit using a single exponential function. On the right side the respective residual plots and the reduced-χ^2 (χ^2_{red}) values are displayed.

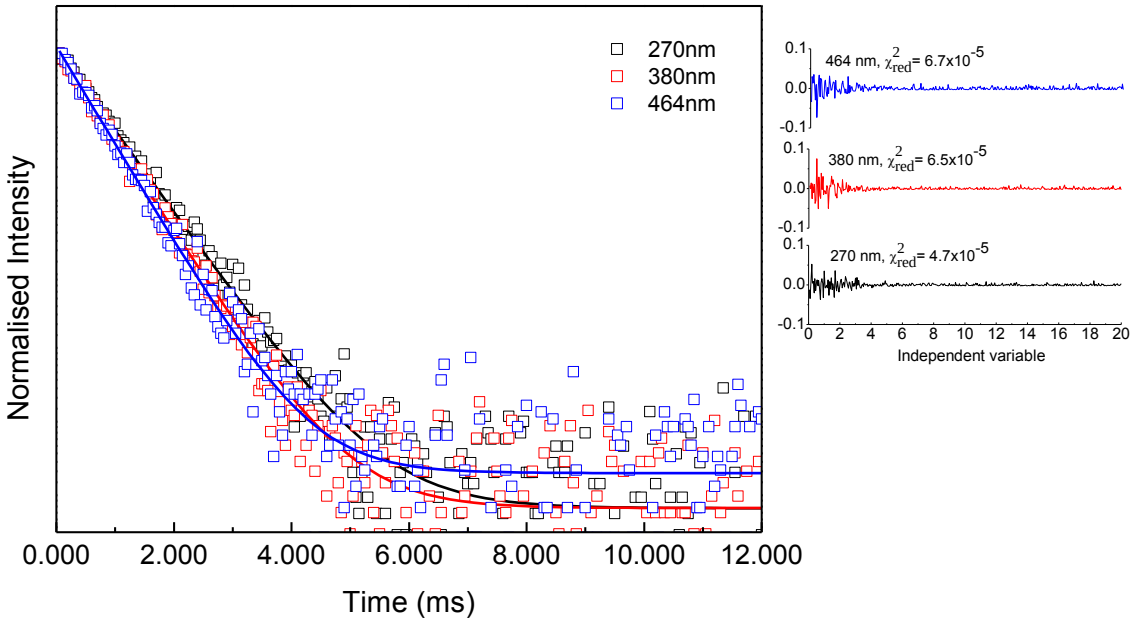


Figure S20 – Room temperature (300K) emission decay curves excited at 270, 370 and 464 nm and monitored at 612 nm of **MtU5Eu-II**. The solid lines correspond to the data best fit using a single exponential function. On the right side the respective residual plots and the reduced-χ^2 (χ^2_{red}) values are displayed.

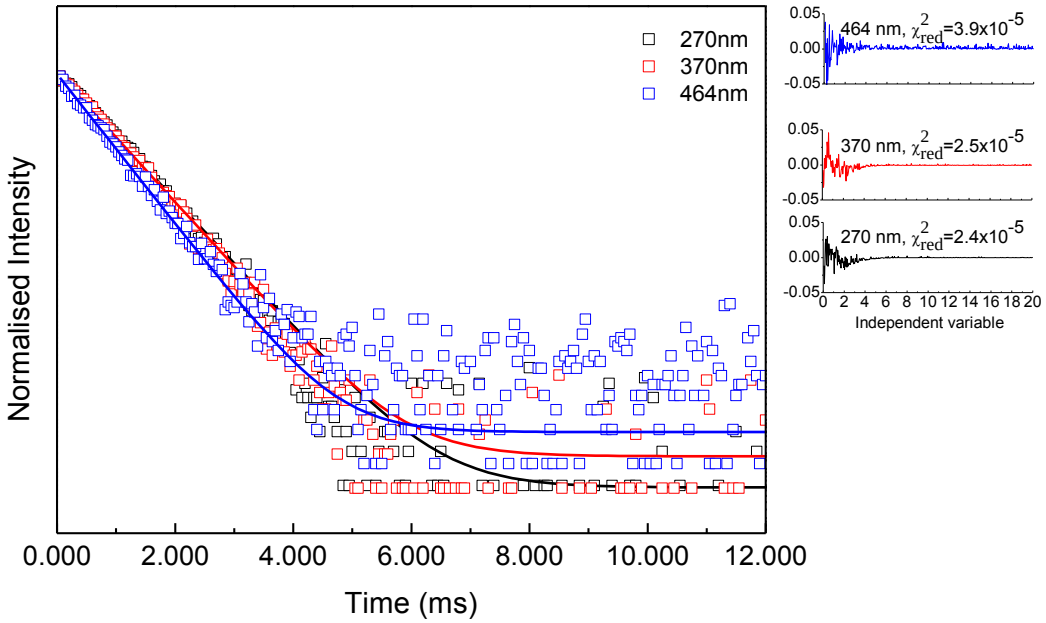


Figure S21 - Room temperature (300K) emission decay curves excited at 270, 340 and 370 nm and monitored at 612 nm of **FtU5Eu-II**. The solid lines correspond to the data best fit using a single exponential function. On the right side the respective residual plots and the reduced-χ^2 (χ^2_{red}) values are displayed.

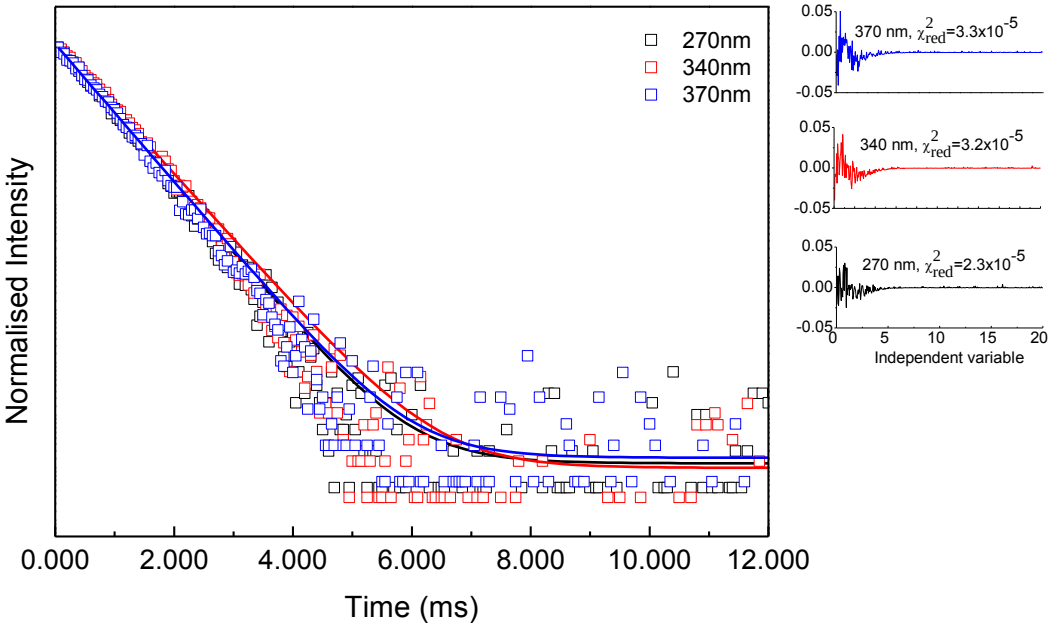


Figure S22 – UV-Vis absorption spectrum of **FtU5Eu-II**.

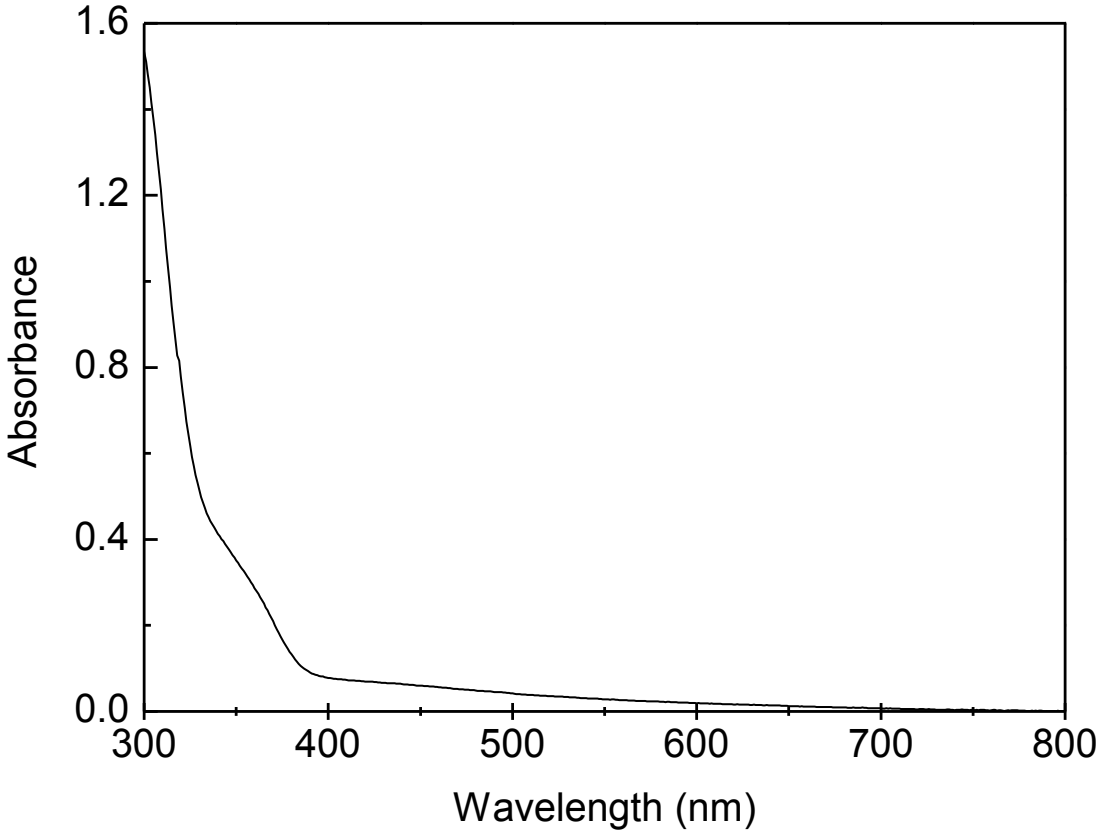


Table S1. Cartesian coordinates (Å) of B3LYP optimized $Eu(tta)_3(H_2O)_2$ complex **I** .

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.012505	-0.818959	-2.026084
2	6	0	5.564502	-3.969371	-0.340188
3	6	0	5.073986	-2.774355	-0.932805
4	6	0	3.710932	-2.595894	-0.745656
5	6	0	2.830368	-1.517323	-1.184853
6	6	0	3.369374	-0.404225	-1.891976
7	6	0	2.590273	0.626143	-2.386167
8	6	0	3.264134	1.743606	-3.167943
9	6	0	4.524823	1.589320	3.635215
10	6	0	3.928179	2.759772	4.056584
11	6	0	2.697236	3.007710	3.391126
12	6	0	-7.339923	-1.354230	-0.798403
13	6	0	2.370201	2.023262	2.470321
14	6	0	1.208910	1.903118	1.594880
15	6	0	0.190915	2.902516	1.622307
16	6	0	-0.918416	2.853441	0.801560
17	6	0	-1.941213	3.975153	0.873947
18	6	0	-6.202597	-1.526328	0.038278
19	6	0	-5.020829	-1.119595	-0.560797
20	6	0	-3.650113	-1.127409	-0.052333
21	6	0	-3.385185	-1.611579	1.259095
22	6	0	-2.106063	-1.671915	1.786155
23	6	0	-1.914818	-2.246363	3.182579
24	6	0	4.569992	-4.687831	0.291425
25	63	0	-0.342493	-0.165133	-0.735380
26	9	0	-1.113567	-3.381339	3.152348
27	9	0	-3.113899	-2.613969	3.790936
28	9	0	-1.297875	-1.331391	4.023607
29	9	0	3.132543	2.961466	-2.510224
30	9	0	4.623743	1.536322	-3.374046
31	9	0	2.680027	1.897244	-4.420883
32	9	0	-2.111193	4.572460	-0.372219
33	9	0	-3.186707	3.497768	1.263738
34	9	0	-1.594801	4.984731	1.765089
35	8	0	-1.000316	-1.296496	1.228405
36	8	0	-2.724702	-0.696207	-0.852658
37	8	0	1.308657	0.790224	-2.267653
38	8	0	1.567255	-1.644375	-0.918952
39	8	0	-1.229220	1.941805	-0.070813
40	8	0	1.162452	0.874698	0.810762
41	8	0	-1.219810	1.084361	-2.711895
42	8	0	-0.747696	-2.046803	-2.260430
43	16	0	-5.315917	-0.512814	-2.179756
44	16	0	3.025252	-3.919351	0.177678
45	16	0	3.597334	0.773121	2.425856
46	1	0	0.293112	3.738976	2.296384
47	1	0	-4.206002	-1.957896	1.867881
48	1	0	-7.684247	-0.586473	-2.839844
49	1	0	-8.349555	-1.611923	-0.505310
50	1	0	-6.257165	-1.931495	1.040349
51	1	0	5.700443	-2.078312	-1.475519
52	1	0	6.600146	-4.281886	-0.377970
53	1	0	4.674514	-5.624170	0.820577
54	1	0	4.432079	-0.370156	-2.077710
55	1	0	5.459357	1.170628	3.980145
56	1	0	4.350708	3.413026	4.809123

57	1	0	2.080124	3.875492	3.584606
58	1	0	-1.833046	1.787307	-2.426634
59	1	0	-0.390180	1.443900	-3.094289
60	1	0	-1.619854	-2.214128	-2.653590
61	1	0	-0.090448	-2.744089	-2.416540

Table S2. Cartesian coordinates (Å) of B3LYP optimized Eu(tta)$_3$ephen complex **II** (form A).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	63	0	-0.061038	-0.228447	-0.347528
2	16	0	-3.670817	3.127012	1.220312
3	16	0	0.724623	4.659943	1.415940
4	16	0	4.471992	0.684077	1.940719
5	9	0	-2.613267	-1.535690	-4.527120
6	9	0	-4.703803	-1.174543	-3.825529
7	9	0	-3.513659	-2.866047	-2.971472
8	9	0	1.243998	1.168411	-5.061452
9	9	0	3.127918	0.368770	-4.161630
10	9	0	2.911660	2.561685	-4.539374
11	9	0	1.628980	-4.336007	-2.764204
12	9	0	0.973508	-5.179774	-0.802370
13	9	0	3.152302	-5.045713	-1.291103
14	8	0	-2.130356	1.024095	-0.099467
15	8	0	-1.686571	-0.982588	-1.925344
16	8	0	0.650009	2.100902	-0.057305
17	8	0	0.988516	0.529679	-2.318319
18	8	0	2.172912	-0.466158	0.554635
19	8	0	0.819629	-2.371906	-0.896389
20	6	0	-5.171069	3.990348	1.230986
21	6	0	-6.028083	3.565415	0.238125
22	6	0	-5.469123	2.519800	-0.548076
23	6	0	-4.192771	2.160091	-0.145572
24	6	0	-3.283761	1.145367	-0.679657
25	6	0	-3.690281	0.339112	-1.777405
26	6	0	-2.878932	-0.657364	-2.297681
27	6	0	-3.425507	-1.542434	-3.409368
28	6	0	1.431190	6.240582	1.459954
29	6	0	2.229140	6.483607	0.363656
30	6	0	2.275561	5.377402	-0.530877
31	6	0	1.515048	4.299816	-0.107772
32	6	0	1.307988	2.990056	-0.735272
33	6	0	1.819683	2.765198	-2.040691
34	6	0	1.631124	1.573025	-2.722254
35	6	0	2.225437	1.422590	-4.116158
36	6	0	6.124913	0.437769	2.392339
37	6	0	6.615151	-0.770850	1.946087
38	6	0	5.641592	-1.517946	1.226146
39	6	0	4.420182	-0.870708	1.131986
40	6	0	3.177203	-1.285955	0.481579
41	6	0	3.107746	-2.541419	-0.177503
42	6	0	1.948380	-2.988271	-0.793524
43	6	0	1.935624	-4.378041	-1.414799
44	1	0	-5.347879	4.768618	1.959462
45	1	0	-7.013672	3.982466	0.075032
46	1	0	-5.987849	2.055591	-1.376821
47	1	0	-4.666974	0.487513	-2.211536
48	1	0	1.219156	6.911100	2.280198

49	1	0	2.760187	7.412844	0.201263
50	1	0	2.855874	5.376678	-1.444127
51	1	0	2.359507	3.556271	-2.537131
52	1	0	6.654238	1.190960	2.958075
53	1	0	7.627509	-1.111210	2.122621
54	1	0	5.837494	-2.490896	0.794628
55	1	0	3.975696	-3.182361	-0.189099
56	1	0	-0.653704	0.480936	6.102831
57	6	0	-0.558654	0.353618	5.028991
58	6	0	-1.057522	-0.805251	4.420848
59	6	0	0.072289	1.323219	4.250590
60	6	0	-1.668497	-1.891265	5.214609
61	6	0	-0.930577	-0.936473	3.021187
62	1	0	0.478673	2.223424	4.695062
63	6	0	0.185930	1.112692	2.873036
64	8	0	-0.924330	-3.199212	5.203359
65	6	0	-2.249638	-3.064285	4.503066
66	1	0	-2.047339	-1.624936	6.196424
67	7	0	-0.314332	0.012819	2.272168
68	6	0	-1.516847	-2.088742	2.317882
69	1	0	0.665870	1.826200	2.216728
70	6	0	-2.203127	-3.097054	3.027110
71	1	0	-3.041584	-3.633947	4.979252
72	7	0	-1.416312	-2.111736	0.965929
73	6	0	-2.805634	-4.129516	2.296476
74	6	0	-1.976400	-3.126937	0.272863
75	6	0	-2.688864	-4.150174	0.907036
76	1	0	-3.345994	-4.913289	2.817963
77	1	0	-1.851629	-3.094803	-0.800879
78	1	0	-3.130993	-4.943532	0.317359

Table S3. Cartesian coordinates (Å) of B3LYP optimized Eu(tta)$_3$ephen complex **II** (form B).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	63	0	-0.031503	-0.279227	-0.315692
2	16	0	-3.426339	3.484769	0.657209
3	16	0	1.024144	4.616361	1.211524
4	16	0	4.504054	0.517217	2.046149
5	9	0	-2.415132	-1.822833	-4.506492
6	9	0	-4.508064	-1.230678	-3.995108
7	9	0	-3.520367	-2.912239	-2.897339
8	9	0	1.552668	0.734276	-5.038587
9	9	0	3.342121	-0.135358	-4.019080
10	9	0	3.292869	2.040862	-4.528853
11	9	0	1.380469	-4.747334	-2.223114
12	9	0	0.650394	-5.309917	-0.187999
13	9	0	2.836715	-5.395178	-0.656762
14	8	0	-1.992943	1.137622	-0.335912
15	8	0	-1.607727	-1.073251	-1.917457
16	8	0	0.843532	1.997239	-0.123072
17	8	0	1.162000	0.272014	-2.272182
18	8	0	2.159798	-0.595433	0.702726
19	8	0	0.713060	-2.525280	-0.615631
20	6	0	-4.850296	4.452307	0.483238
21	6	0	-5.685971	3.983789	-0.508769
22	6	0	-5.171908	2.819519	-1.143186
23	6	0	-3.950586	2.414388	-0.627690
24	6	0	-3.099683	1.284012	-0.996419
25	6	0	-3.505513	0.399590	-2.033043
26	6	0	-2.746955	-0.701018	-2.398590
27	6	0	-3.294480	-1.651160	-3.454192
28	6	0	1.793996	6.167247	1.178710
29	6	0	2.618293	6.316272	0.084880
30	6	0	2.634049	5.160025	-0.744999
31	6	0	1.823631	4.139638	-0.275107
32	6	0	1.568837	2.806513	-0.830519
33	6	0	2.111373	2.471719	-2.100010
34	6	0	1.879700	1.250336	-2.712681
35	6	0	2.514062	0.977773	-4.069793
36	6	0	6.127832	0.203457	2.558293
37	6	0	6.542832	-1.069587	2.231066
38	6	0	5.533785	-1.811994	1.556092

39	6	0	4.360945	-1.096791	1.376446
40	6	0	3.104282	-1.484749	0.733702
41	6	0	2.959520	-2.791413	0.197096
42	6	0	1.785762	-3.211504	-0.409855
43	6	0	1.675161	-4.656953	-0.874267
44	1	0	-5.003423	5.316082	1.114145
45	1	0	-6.626030	4.450638	-0.773695
46	1	0	-5.682688	2.304390	-1.946286
47	1	0	-4.440217	0.573208	-2.543421
48	1	0	1.596585	6.891432	1.955893
49	1	0	3.188191	7.213500	-0.120276
50	1	0	3.226046	5.084857	-1.647713
51	1	0	2.714988	3.197876	-2.621651
52	1	0	6.697097	0.967979	3.067182
53	1	0	7.526978	-1.458429	2.459469
54	1	0	5.671779	-2.829506	1.214118
55	1	0	3.776935	-3.491234	0.277073
56	1	0	-3.788665	-4.455791	3.033098
57	6	0	-3.182071	-3.747519	2.477529
58	6	0	-2.649132	-2.627801	3.129842
59	6	0	-2.939722	-3.933473	1.117012
60	6	0	-2.925690	-2.357430	4.554794
61	6	0	-1.851756	-1.735642	2.381995
62	1	0	-3.345092	-4.784980	0.584898
63	6	0	-2.161995	-2.992510	0.433649
64	8	0	-3.687851	-1.091789	4.842828
65	6	0	-2.235926	-1.213278	5.215977
66	1	0	-3.253601	-3.198305	5.157844
67	7	0	-1.623997	-1.922671	1.058600
68	6	0	-1.167891	-0.607366	3.034365
69	1	0	-1.952739	-3.079212	-0.623701
70	6	0	-1.299436	-0.391036	4.423193
71	1	0	-2.072170	-1.241116	6.288771
72	7	0	-0.352839	0.163559	2.270137
73	6	0	-0.541683	0.628670	5.012985
74	6	0	0.352561	1.159832	2.845825
75	6	0	0.291541	1.415751	4.219082
76	1	0	-0.617369	0.805455	6.081353
77	1	0	0.966059	1.746240	2.175509
78	1	0	0.881300	2.217359	4.646372

Table S4. Cartesian coordinates (Å) of B3LYP optimized $Eu(NO_3)_3(ephen)_2$ complex **III**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	63	0	-0.000054	0.852119	0.000330
2	8	0	0.712428	3.098161	-0.852293
3	8	0	-0.001723	5.056141	-0.001055
4	8	0	-1.763409	1.510096	-1.722084
5	8	0	0.076510	0.560063	-2.536573
6	8	0	-1.564585	1.195883	-3.942901
7	7	0	-0.001063	3.819223	-0.000484
8	7	0	-1.110044	1.100114	-2.790895
9	8	0	-0.713799	3.098168	0.851971
10	8	0	1.763868	1.510887	1.721887
11	8	0	-0.075538	0.560470	2.537103
12	8	0	1.566473	1.195609	3.942678
13	7	0	1.111196	1.100452	2.790914
14	6	0	4.190097	1.318679	-2.418560
15	6	0	5.046954	0.326855	-1.946240
16	6	0	2.887992	1.386995	-1.910822
17	1	0	4.517087	2.037648	-3.159360
18	6	0	4.591710	-0.575011	-0.975215
19	1	0	6.066390	0.255197	-2.311759
20	7	0	2.432875	0.510536	-0.990739
21	1	0	2.190062	2.145995	-2.232754
22	6	0	5.483786	-1.602522	-0.401503
23	6	0	3.259237	-0.459084	-0.527410
24	6	0	4.919642	-2.585978	0.565319
25	8	0	5.780569	-1.462680	1.066643
26	1	0	6.355576	-1.876160	-0.987416
27	6	0	2.697677	-1.435951	0.418699
28	7	0	1.386646	-1.312249	0.751412

29	6	0	3.485864	-2.499546	0.912351
30	1	0	5.386422	-3.560852	0.666722
31	6	0	0.830286	-2.210053	1.593827
32	6	0	2.884098	-3.441675	1.754696
33	6	0	1.542750	-3.294703	2.109193
34	1	0	-0.204212	-2.037968	1.858433
35	1	0	3.470422	-4.268708	2.142191
36	1	0	1.059258	-3.993571	2.780554
37	1	0	-6.066280	0.254245	2.312297
38	6	0	-5.046839	0.325950	1.946800
39	6	0	-4.591700	-0.575522	0.975365
40	6	0	-4.189876	1.317476	2.419573
41	6	0	-5.483862	-1.602667	0.401122
42	6	0	-3.259211	-0.459535	0.527615
43	6	0	-2.887780	1.385910	1.911835
44	1	0	-4.516802	2.036126	3.160709
45	6	0	-4.919804	-2.585688	-0.566205
46	8	0	-5.780592	-1.462033	-1.066958
47	1	0	-6.355688	-1.876524	0.986879
48	6	0	-2.697720	-1.436059	-0.418877
49	7	0	-2.432764	0.509808	0.991350
50	1	0	-2.189769	2.144704	2.234079
51	6	0	-3.485995	-2.499290	-0.913121
52	1	0	-5.386713	-3.560448	-0.668117
53	7	0	-1.386626	-1.312372	-0.751298
54	6	0	-2.884242	-3.441095	-1.755846
55	6	0	-0.830239	-2.209882	-1.594004
56	1	0	-3.470634	-4.267838	-2.143857
57	6	0	-1.542810	-3.294163	-2.110028
58	1	0	0.204344	-2.037875	-1.858311
59	1	0	-1.059311	-3.992786	-2.781641

Table S5 - Molecular orbital compositions in the ground-state for the Eu(tta)$_3$ephen complex **II,** obtained in ethanolic solution. H and L are the highest occupied and the lowest unoccupied molecular orbitals, respectively.

Orbital	**Eu**	**tta**	**ephen**
H – 12	1.08	96.35	2.57
H – 11	0.61	96.98	2.42
H – 10	0.48	98.14	1.38
H – 9	0.74	96.73	2.53
H – 8	0.40	99.03	0.57
H – 7	1.04	93.79	5.17
H – 6	0.71	89.15	10.14
H – 5	0.18	21.8	78.03

H – 4	0.59	97.58	1.83
H – 3	0.19	98.89	0.92
H – 2	0.84	98.12	1.04
H – 1	0.61	97.61	1.78
H	0.25	98.64	1.12
L	1.54	96.38	2.07
L + 1	1.49	91.56	6.94
L + 2	1.08	84.98	13.94
L + 3	0.44	19.30	80.26
L + 4	0.70	2.87	96.43
L + 5	0.32	2.14	97.54