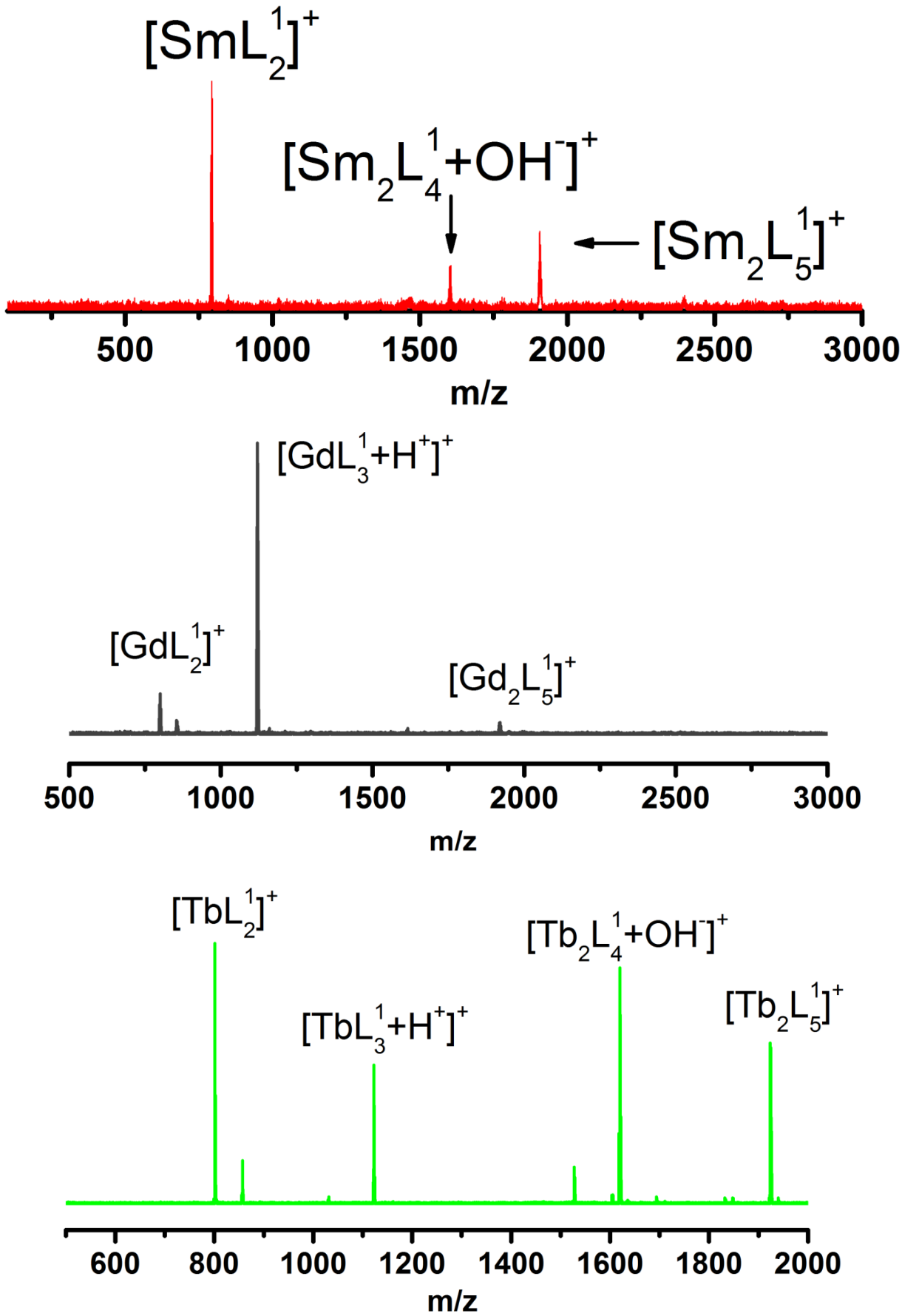

Fig.S1. LDI-TOF spectra of SmL^1_3 (above), EuL^1_3 (middle) and GdL^1_3 (below)

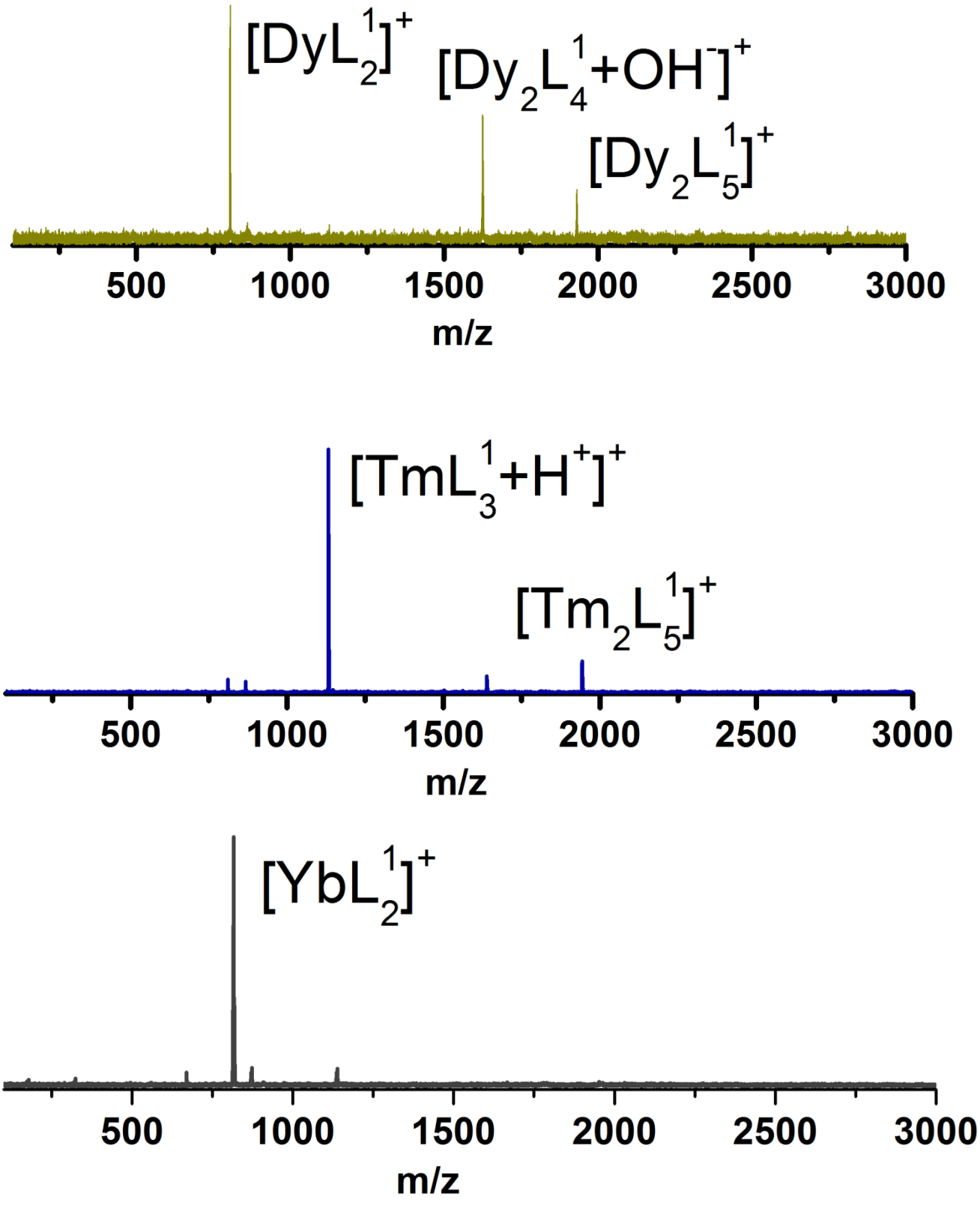

Fig.S2. LDI-TOF spectra of DyL^1_3 (above), TmL^1_3 (middle) and YbL^1_3 (below)

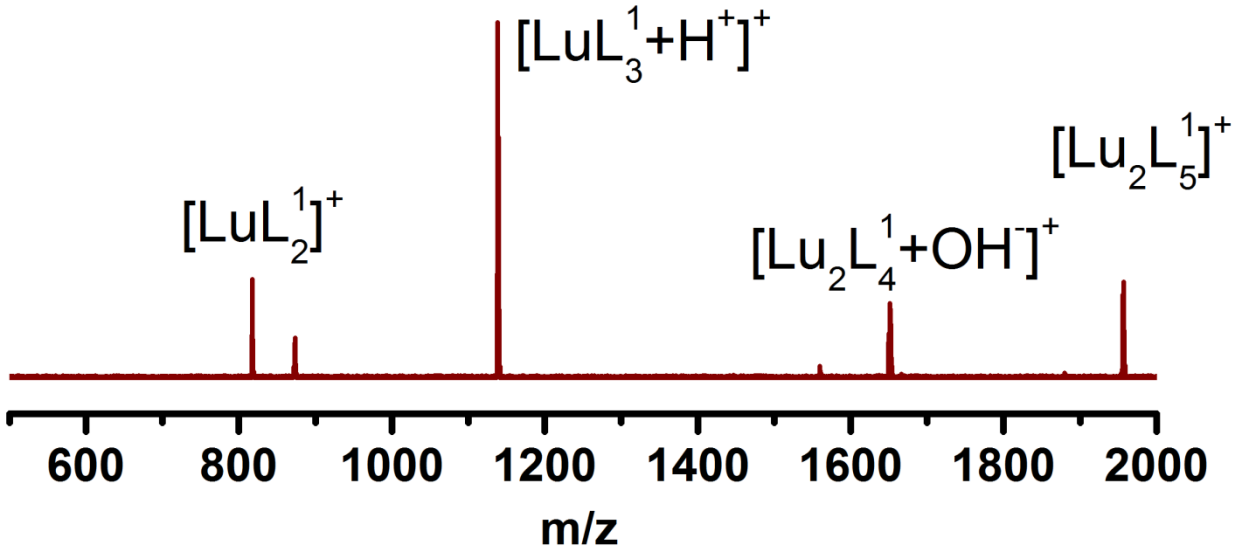

Fig.S3. LDI-TOF spectra of LuL^{1}_{3}

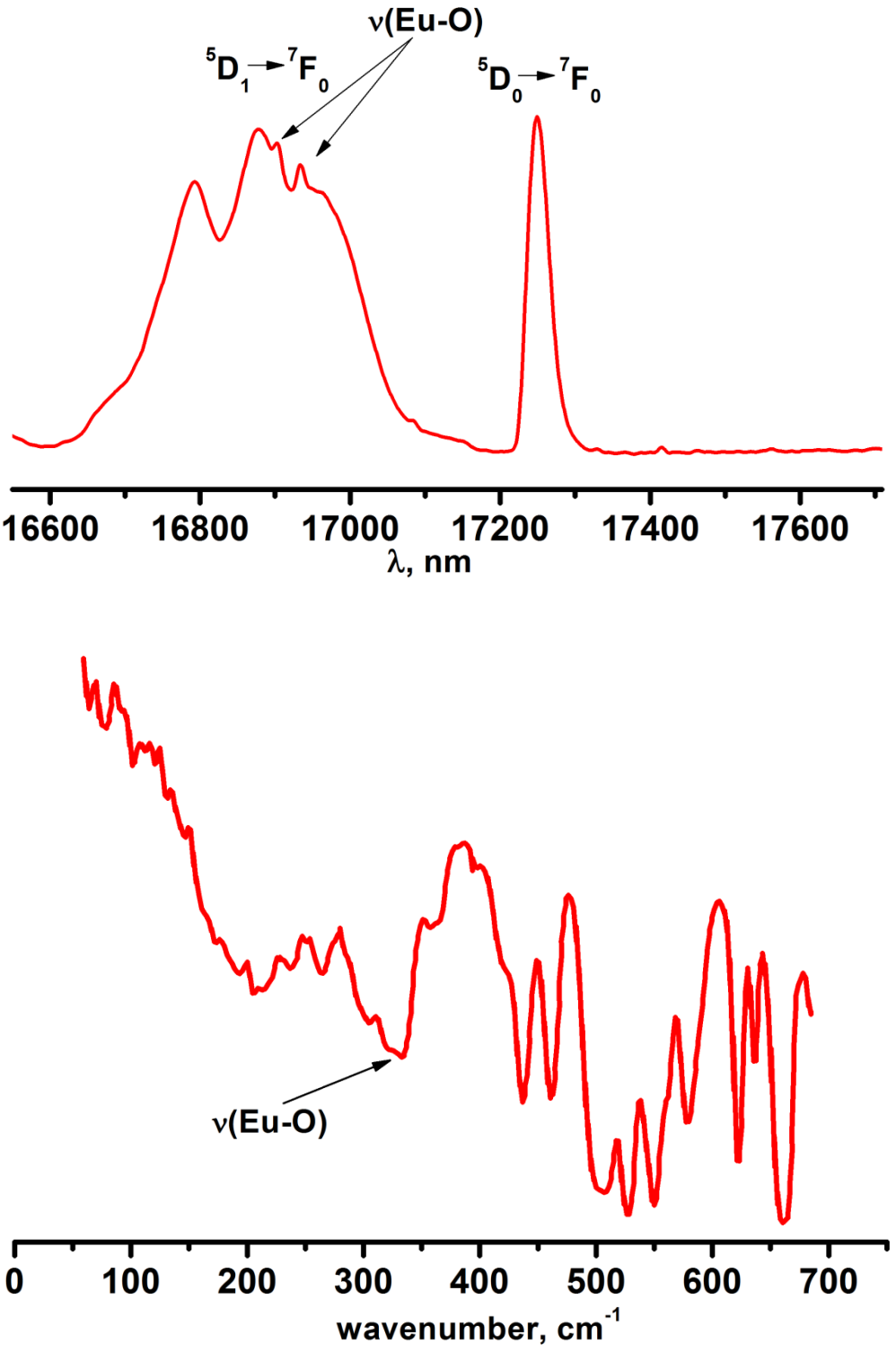

Fig. S4. Luminescence spectrum of EuL^1_3 (above) and low-frequency IR spectrum of the same sample (below)

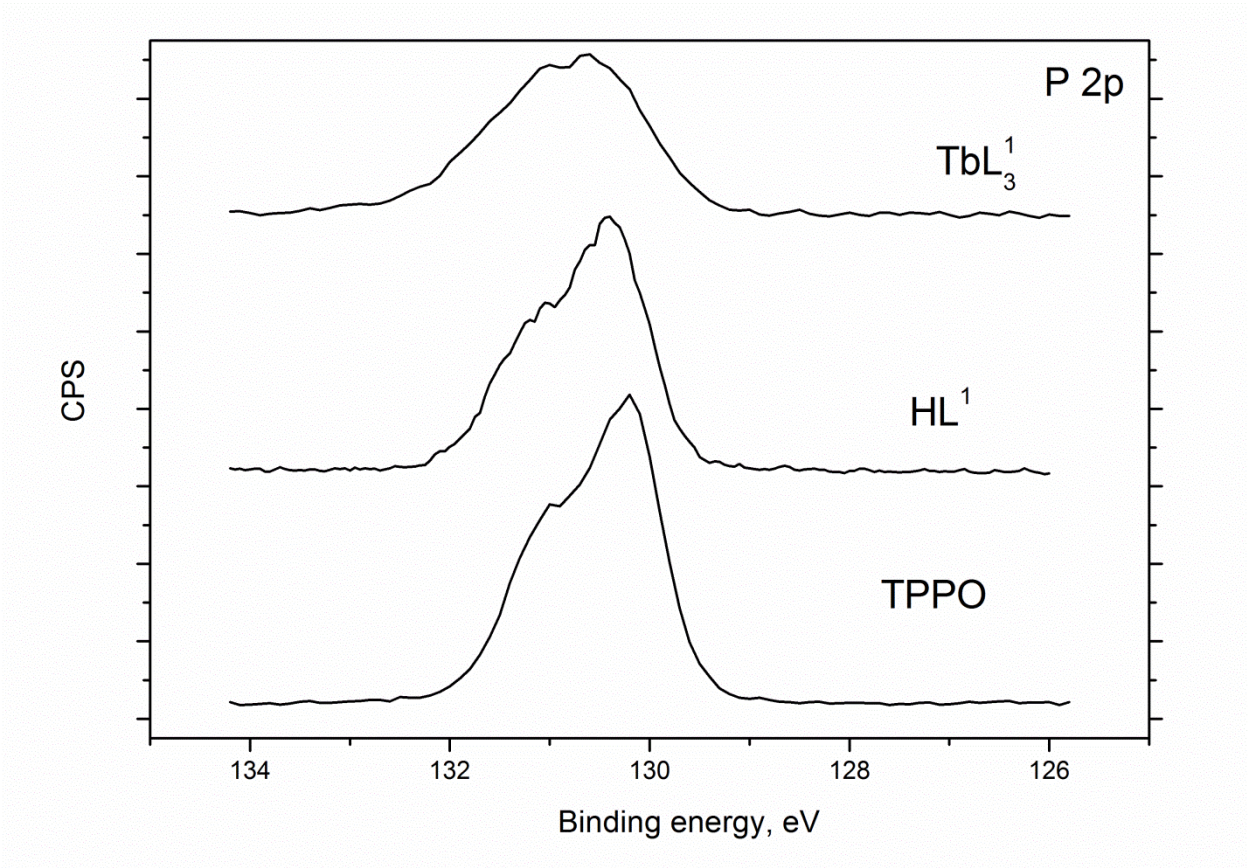

Fig. S5. P 2p photoelectron spectra of TPPO, HL^1 and TbL$^1_3$

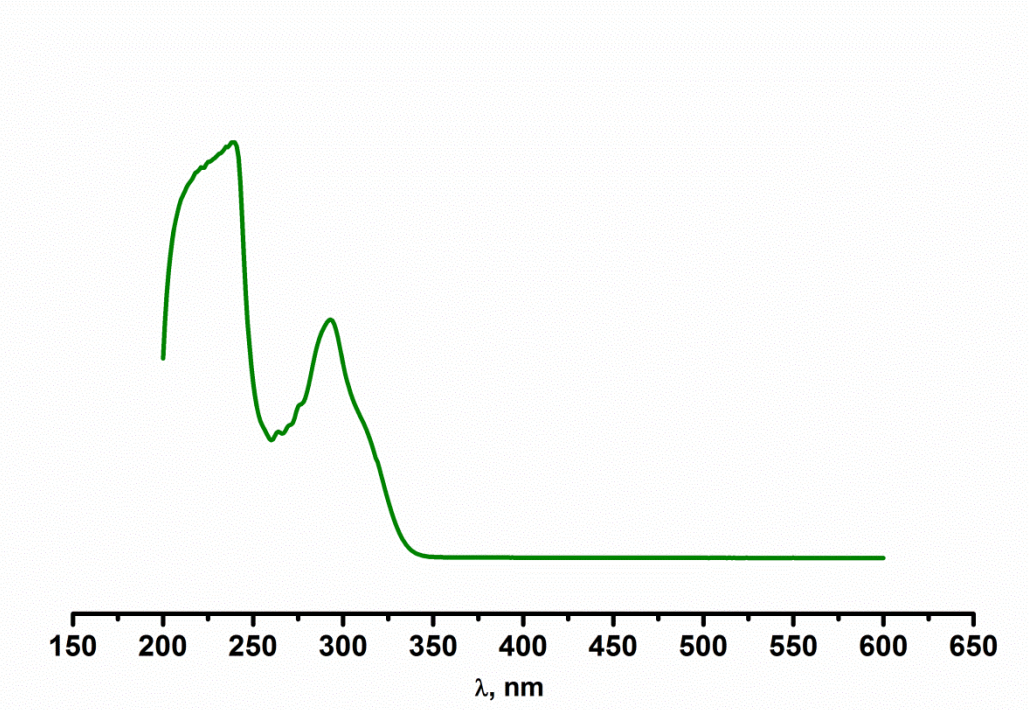

Fig. S6. Luminescence excitation spectrum of TbL$^1_3$ in toluene.

Sparkle PM3 calculations for EuL^1_3

Table S1: Spherical Atomic Coordinates for the Sparkle/PM3 Coordination Polyhedron of monomeric complex EuL^1_3, Charge Factors (g) and the Polarizability (α) of the Coordinated Atom

Atom	*R/Å*	θ/°	ϕ/°	g^a	α^a
O (Ligand 1)	2.42154	75.305	143.746	0.0101	3.4640×10^{-24}
O (Ligand 1)	2.39837	53.831	217.024	0.0101	3.4640×10^{-24}
O (Ligand 2)	2.42407	107.924	47.329	0.0101	3.4640×10^{-24}
O (Ligand 2)	2.39866	44.171	19.932	0.0101	3.4640×10^{-24}
O (Ligand 3)	2.42240	111.168	300.280	0.0101	3.4640×10^{-24}
O (Ligand 3)	2.39648	161.624	215.132	0.0101	3.4640×10^{-24}

[a] Obtained using a nonlinear minimization technique.

Table S2: Spherical Atomic Coordinates for the Sparkle/PM3 Coordination Polyhedron of dimeric complex EuL^1_3, Charge Factors (g) and the Polarizability (α) of the Coordinated Atom

Atom	*R/Å*	θ/°	ϕ/°	g^a	α^a
O (Ligand 1)	2.41271	80.716	121.674	0.0142	4.1236×10^{-24}
O (Ligand 1)	2.43465	122.602	66.263	0.0142	4.1236×10^{-24}
O (Ligand 2)	2.41926	141.641	216.443	0.0142	4.1236×10^{-24}
O (Ligand 2)	2.43605	77.344	205.992	0.0142	4.1236×10^{-24}
O (Ligand 3)	2.41735	19.676	280.456	0.0142	4.1236×10^{-24}
O (Ligand 3)	2.48857	60.321	23.278	0.0103	6.4998×10^{-24}
O (Ligand 4)	2.47074	108.337	326.986	0.0103	6.4998×10^{-24}

Table S3. Calculated values of intramolecular energy transfer and back-transfer rates for Europium EuL^13 compounds. The RL value is the distance from the donor state located at the organic ligands and the Eu^{3+} ion nucleus

	Ligand State (cm^{-1})		4f – State (cm^{-1})	R_L (Å)	Transfer Rate (s^{-1})	Back-Transfer Rate (s^{-1})
Sparkle/PM3 Monomer Structure	Singlet (34263.3)	→	$^5D_4$(27586)	5.2602	1.75×10^{3}	2.16×10^{-11}
	Triplet (22501.3)	→	$^5D_1$(19027)	4.9063	7.98×10^{9}	5.48×10^{2}
	Triplet (22501.3)	→	$^5D_0$(17293)	4.9063	5.62×10^{9}	7.79×10^{-2}
Sparkle/PM3 Dimer Structure	Singlet (37633.2)	→	$^5D_4$(27586)	5.0746	6.72×10^{1}	7.63×10^{-20}
	Triplet (23756.3)	→	$^5D_1$(19027)	5.8775	1.99×10^{9}	3.27×10^{-1}
	Triplet (23756.3)	→	$^5D_0$(17293)	5.8775	1.04×10^{9}	3.47×10^{-5}

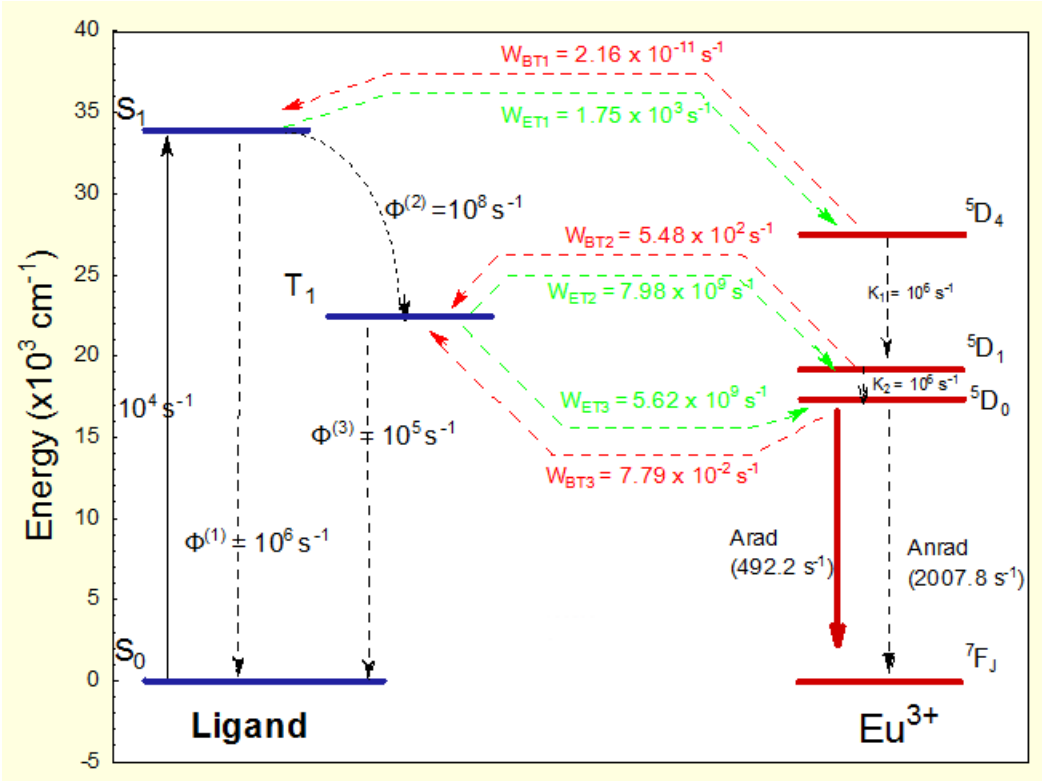

Fig.S7 Energy level diagram for EuL$^1_3$ monomeric species showing the most probable channels for the intramolecular energy transfer process

Sparkle PM3 calculations for EuL$^2_3$

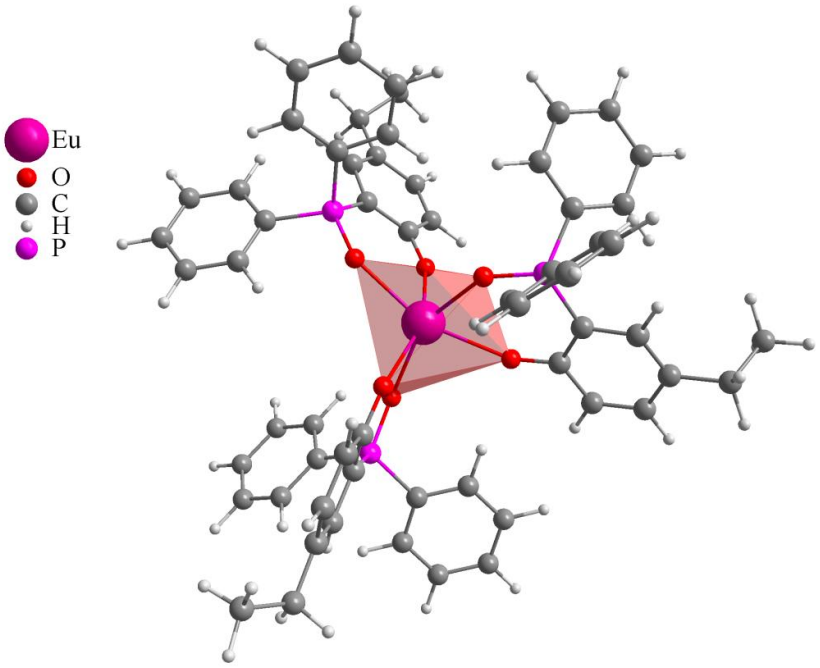

Fig.S8. Calculated ground state geometries of the monomeric molecular structure of EuL$^2_3$ using the Sparkle/PM3 model

Table S4: Spherical Atomic Coordinates for the Sparkle/PM3 Coordination Polyhedron of monomeric complex EuL^2_3, Charge Factors (g) and the Polarizability (α) of the Coordinated Atom

Atom	*R/Å*	θ/°	ϕ/°	g^a	α^a
O (Ligand 1)	2.42129	73.135	144.292	0.0104	3.2505×10^{-24}
O (Ligand 1)	2.39847	53.863	218.943	0.0104	3.2505×10^{-24}
O (Ligand 2)	2.42390	107.042	47.912	0.0104	3.2505×10^{-24}
O (Ligand 2)	2.39884	44.714	16.853	0.0104	3.2505×10^{-24}
O (Ligand 3)	2.42239	113.690	300.227	0.0104	3.2505×10^{-24}
O (Ligand 3)	2.39656	162.042	207.343	0.0104	3.2505×10^{-24}

[a] Obtained using a nonlinear minimization technique.

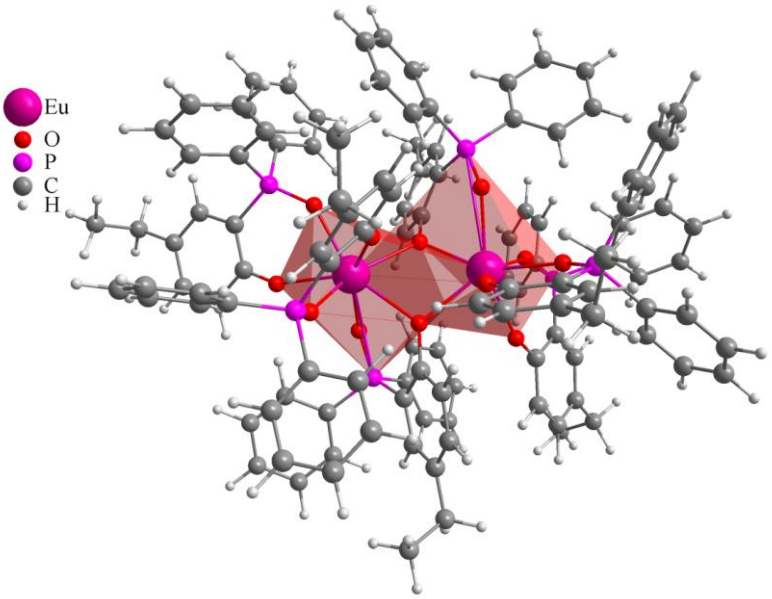

Fig.S9. Calculated ground state geometries of the dimeric molecular structure of EuL^2_3 using the Sparkle/PM3 model

Table S5: Spherical Atomic Coordinates for the Sparkle/PM3 Coordination Polyhedron of dimeric complex EuL^2_3, Charge Factors (g) and the Polarizability (α) of the Coordinated Atom

Atom	*R/Å*	θ/°	ϕ/°	g^a	α^a
O (Ligand 1)	2.40794	71.991	117.928	0.0137	4.0736×10^{-24}
O (Ligand 1)	2.43179	119.449	66.997	0.0137	4.0736×10^{-24}
O (Ligand 2)	2.41539	149.746	217.591	0.0137	4.0736×10^{-24}
O (Ligand 2)	2.43891	86.292	197.720	0.0137	4.0736×10^{-24}
O (Ligand 3)	2.41085	38.127	267.857	0.0137	4.0736×10^{-24}
O (Ligand 3)	2.47745	51.240	14.036	0.0101	6.4995×10^{-24}
O (Ligand 4)	2.47714	105.933	329.812	0.0101	6.4995×10^{-24}

Table S6. Calculated values of intramolecular energy transfer and back-transfer rates for Europium EuL^2_3 compounds. The RL value is the distance from the donor state located at the organic ligands and the Eu^{3+} ion nucleus

	Ligand State (cm^{-1})		4f – State (cm^{-1})	R_L (Å)	Transfer Rate (s^{-1})	Back-Transfer Rate (s^{-1})
Sparkle/PM3 Monomeric Structure	Singlet (33037.8)	→	$^5D_4$(27586)	5.2752	4.49×10^3	1.99×10^{-8}
	Triplet (21417.3)	→	$^5D_1$(19027)	5.0543	1.07×10^{10}	1.34×10^5
	Triplet (21417.3)	→	$^5D_0$(17293)	5.0543	9.68×10^9	24.60
Sparkle/PM3 Dimeric Structure	Singlet (39914.2)	→	$^5D_4$(27586)	4.7630	5.07	9.96×10^{-26}
	Triplet (23379.7)	→	$^5D_1$(19027)	5.4132	3.45×10^9	3.47
	Triplet (23379.7)	→	$^5D_0$(17293)	5.4132	1.98×10^9	4.02×10^{-4}

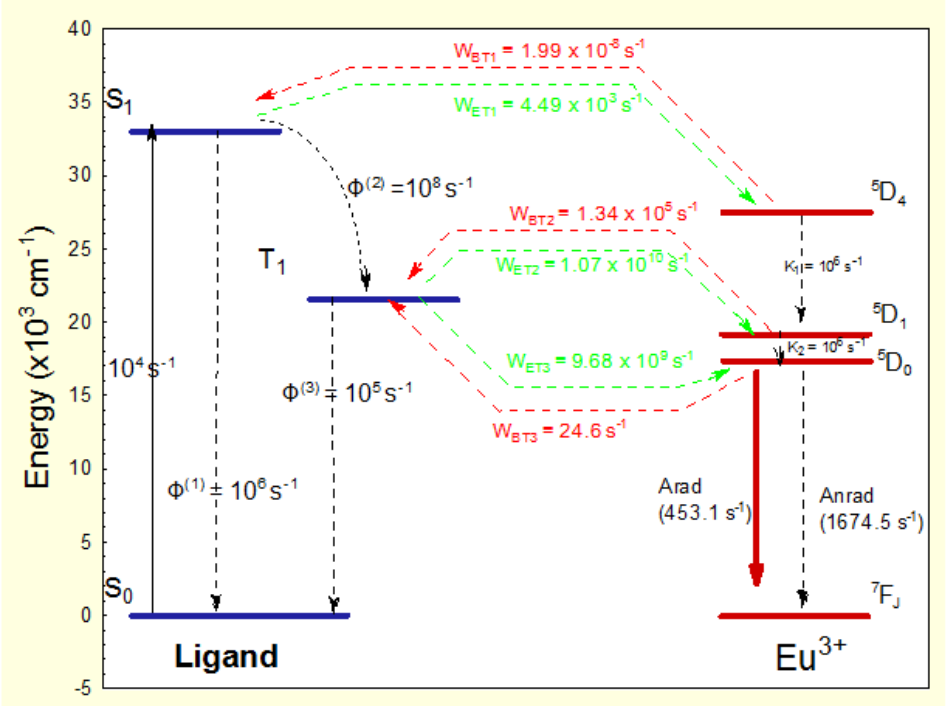

Fig.S10 Energy level diagram for EuL^2_3 monomeric species showing the most probable channels for the intramolecular energy transfer process

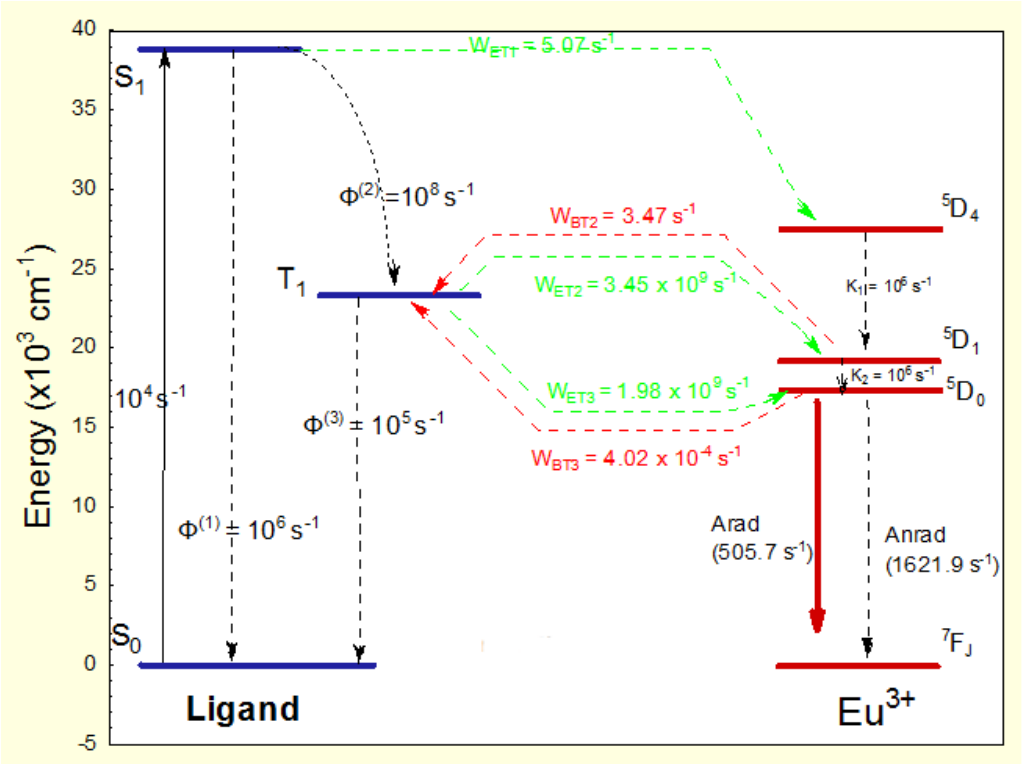

Fig.S11 Energy level diagram for EuL^2_3 dimeric species showing the most probable channels for the intramolecular energy transfer process

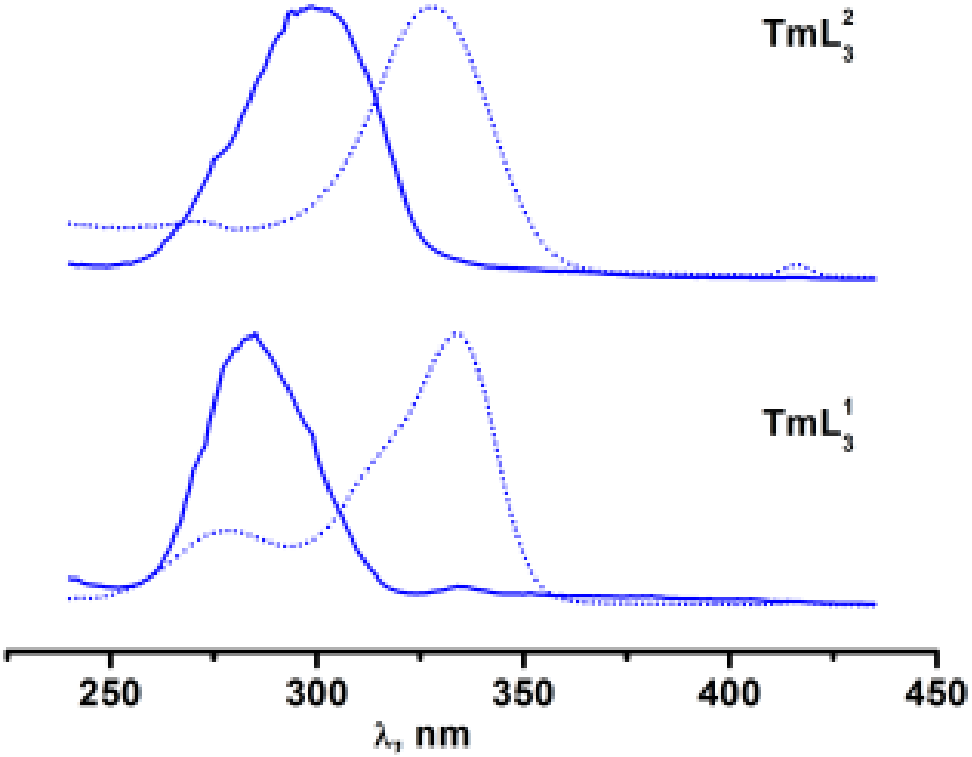

Fig.S12. Excitation luminescence spectra taken at 298 K (solid line) and 77 K (dotted line)