Electronic Supplementary Information

Electroluminescent properties of lanthanide pentafluorophenolates

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Preparation of $Sm(OC_6F_5)_3(phen)$ (1(Sm))

To a solution of $Sm[N(SiMe_3)_2]_3$ (0.384 g, 0.608 mmol) in 10 ml toluene a solution of C_6F_5OH (0.336 g, 1.825 mmol) and 1.10-phenanthroline (0.108 g, 0.599 mmol) in 5 ml toluene was added. The microcrystalline precipitate was deposited from a solution in 15 h. The product was washed with hexane and dried in vacuum to give 0.498 g (93%) of **1**(Sm); m.p. in a sealed capillary >300°C (dec.). Anal. Calcd for $C_{30}SmH_8F_{15}N_2O_3$ (879.73): Sm, 17.09. Found: Sm, 17.32%. IR (Nujol, ν/sm^{-1}): 1651w, 1624w, 1592w, 1575w, 1503s, 1423m, 1346m, 1310w, 1243w, 1171m, 1142w, 1097w, 1013s, 984s, 863m, 843m, 732m, 635w, 623w.

Under the same condition were obtained $Eu(OC_6F_5)_3(phen)$ (**1**(Eu)) (yield 92%). Anal. Calcd for $C_{30}EuH_8F_{15}N_2O_3$ (881.34): Eu, 17.24. Found: Eu, 17.38%; $Dy(OC_6F_5)_3(phen)$ (**1**(Dy)) (yield 93%). Anal. Calcd for $C_{30}DyH_8F_{15}N_2O_3$ (891.87): Dy, 18.22. Found: Dy, 18.25%; $Ho(OC_6F_5)_3(phen)$ (**1**(Ho)) (yield 95%). Anal. Calcd for $C_{30}HoH_8F_{15}N_2O_3$ (894.30): Ho, 18.44. Found: Ho, 18.60%; $Tb(OC_6F_5)_3(phen)$ (**1**(Tb)) (yield 95%). Anal. Calcd for $C_{30}TbH_8F_{15}N_2O_3$ (888.30): Tb, 17.89. Found: Tb, 18.02% and $Yb(OC_6F_5)_3(phen)$ (**1**(Yb)) (yield 96%). Anal. Calcd for $C_{30}YbH_8F_{15}N_2O_3$ (902.41): Yb, 18.65. Found: Yb, 18.48%. IR spectra of **1**(Eu,Dy,Ho,Tb,Yb) are identical to that of **1**(Sm).

Preparation of $Tb(OC_6F_5)_3(bpy)$ (3)

The mixture $Tb[N(SiMe_3)_2]_3$ (0.108 g, 0.169 mmol), C_6F_5OH (0.093 g, 0.506 mmol) and 2,2'-bipyridyl (0.026 g, 0.169 mmol) was dissolved in 10 ml toluene. The formed white microcrystalline precipitate was separated from the solution by decantation, washed with toluene and dried in vacuum to give 0.138 g (95%) of **3**; m.p. in a sealed capillary >190°C (dec.). Anal. Calcd for $C_{28}TbH_8F_{15}N_2O_3$ (864.28): Tb, 18.39. Found: Tb, 18.67%. IR (Nujol, ν/sm^{-1}): 1650m, 1600m, 1577m, 1567m, 1510s, 1485m, 1320m, 1245m, 1175m, 1158m, 1117w, 1104w, 1062w, 1017s, 986s, 766m, 739m, 698w, 670w, 653w, 644w, 625w, 575w.

DFT calculations

All calculations for optimization of molecular structures were based on nonempirical PBE density functional using facilities of the Joint Supercomputer Center of Russian Academy of Sciences. The Priroda program package[S1] was used for an all-electron calculation in scalar-relativistic approximation, which is based on the full four-component one-electron Dirac equation with spin–orbit effects separated out.[S2] The extended full four-component basis: Ln [30s29p20d14f6g/9s8p6d3f1g], C,N,O [10s7p3d/3s2p1d], H [6s,2p/2s1p] was used. This level of theory allows well to describe the coordination of ligands around Ln-center in contrast to nonrelativistic calculation with the extended basis set of the same quality using pseudopotential with inner shell relativistic effects included.[S3] Calculated geometry of the tris-pentafluorophenolate complex of Tb (Fig. S2(b)) with two 1.10-phenanthroline ligands well corresponds to the experimental data. Mean deviation for Ln-O and Ln-N bonds is 0.02-0.03 Å. Ionization potential IP(cond) and electron affinity EA(cond) for the molecules embedded in condensed matter, which are directly determine HOMO and LUMO energies, are related with gas phase values by linear equations

IP(cond) = IP(gas) + E1 and

EA(cond) = EA(gas) +E2.

We used E1 = -0.76 eV and E2 = 1.62 eV found from the comparison of the calculated IP(gas) and EA(gas) values for AlQ_3 reference system with its well known HOMO and LUMO positions.

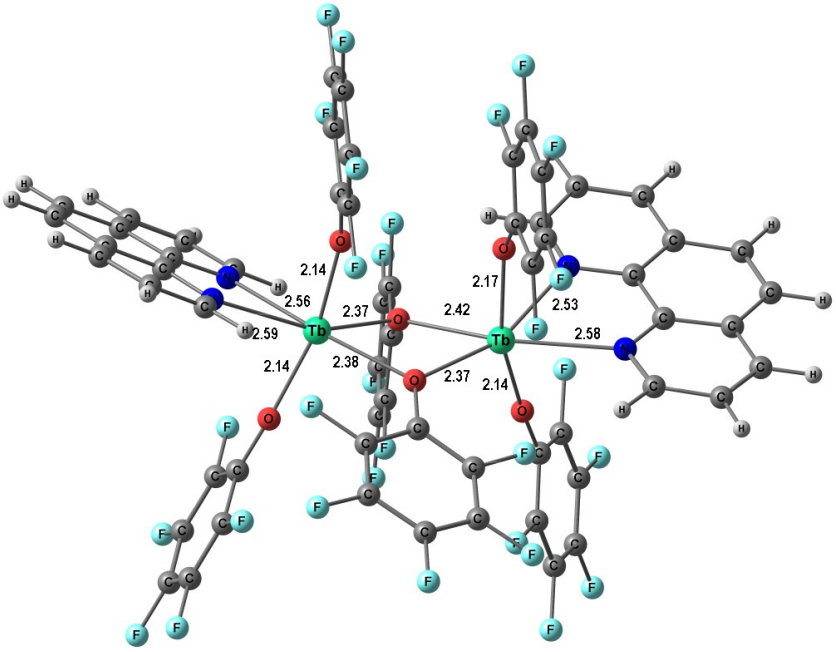
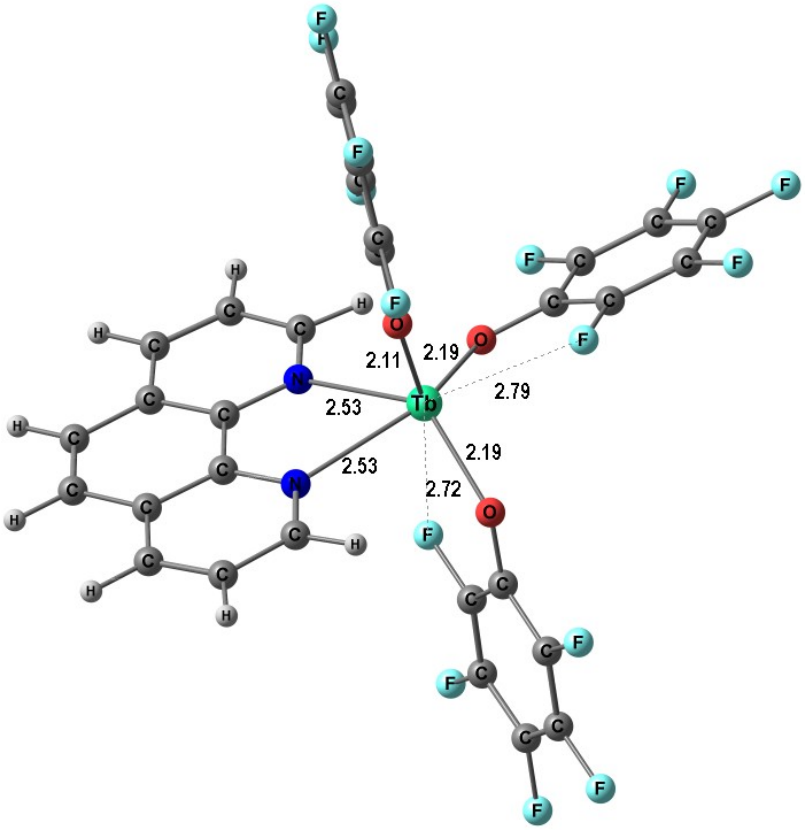


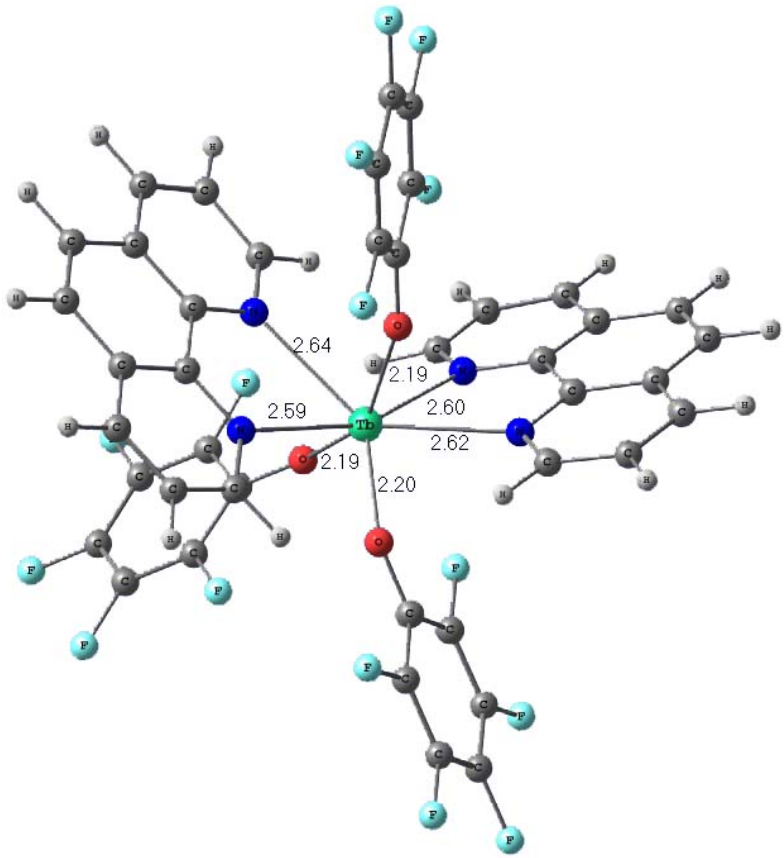
Fig. S1. Calculated molecular structure of dimer (phen)Tb$(OC_6F_5)_2$ (μ-$OC_6F_5)_2$Tb$(OC_6F_5)_2$(phen).

Table S1. Calculated distances [Å] in molecules (phen)Ln$(OC_6F_5)_2$ (μ-$OC_6F_5)_2$Ln$(OC_6F_5)_2$(phen).

distance	Pr	Nd	Sm	Yb
Ln_1-(μ-O)	2.50; 2.45	2.49; 2.45	2.36; 2.37	2.31; 2.38
Ln_2-(μ-O)	2.42; 2.45	2.43; 2.43	2.42; 2.35	2.33; 2.32
Ln_1 –O	2.19; 2.20	2.19; 2.18	2.14; 2.14	2.14; 2.13
Ln_2 –O	2.19; 2.25	2.19; 2.25	2.14; 2.20	2.14; 2.17
Ln_1 –N	2.64; 2.62	2.63; 2.62	2.56; 2.55	2.51; 2.49
Ln_2 –N	2.64; 2.67	2.63; 2.66	2.56; 2.59	2.52; 2.56



a



b

Fig. S2. Calculated molecular structure of $Tb(OC_6F_5)_3(phen)$ (a) and $Tb(OC_6F_5)_3(phen)_2$ (b).

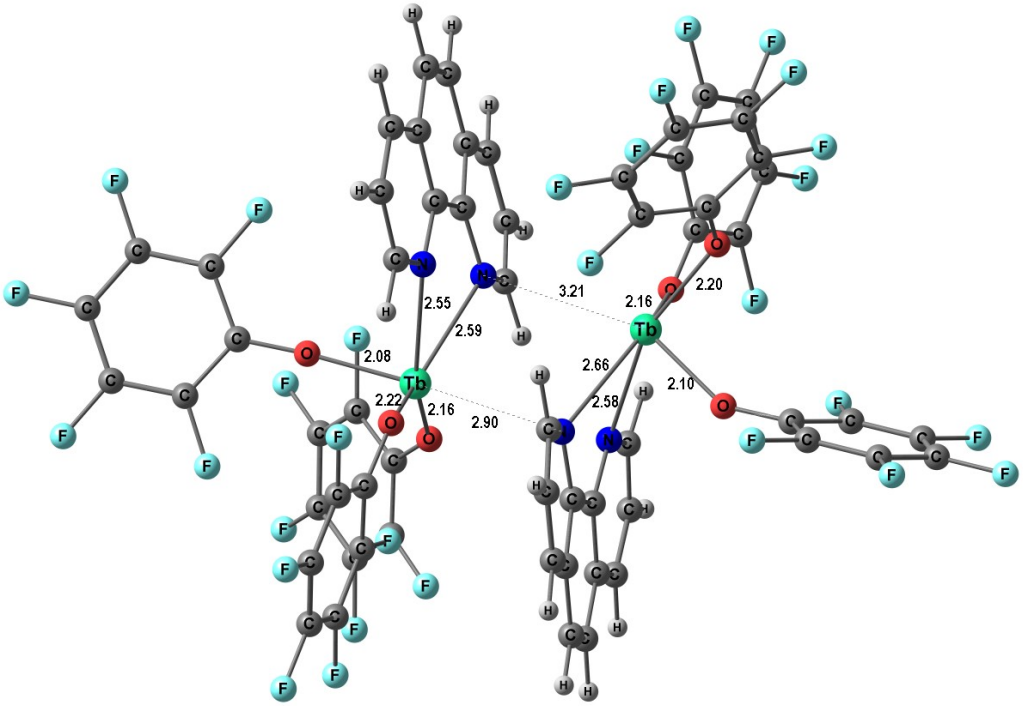


Fig. S3. Calculated molecular structure of dimer $(C_6F_5O)_3Tb(\mu\text{-phen})_2Tb(OC_6F_5)_3$.

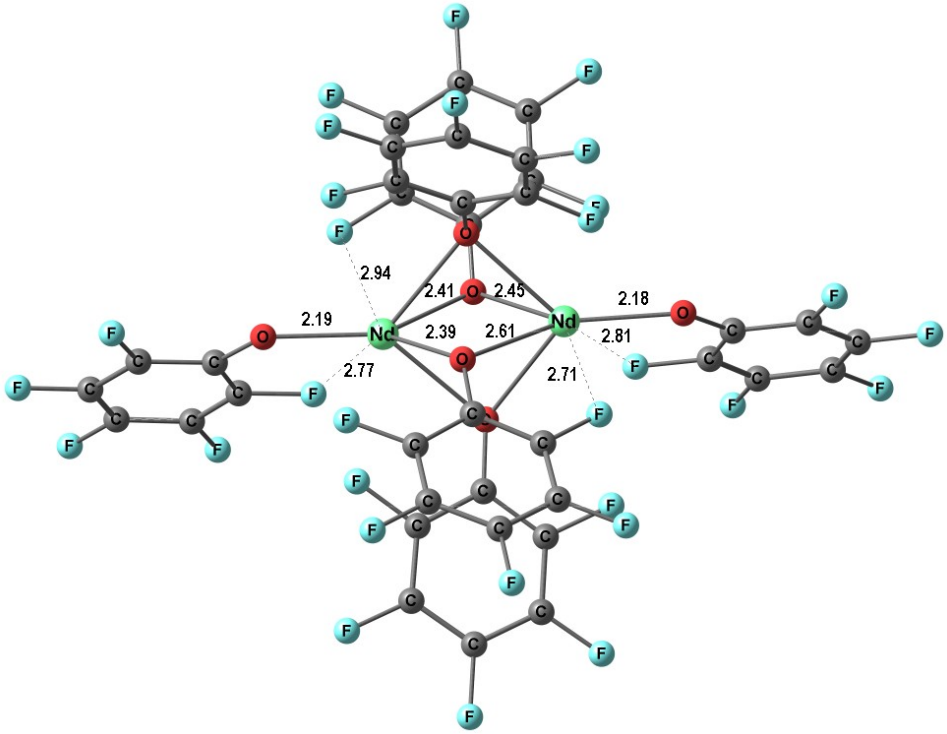


Fig. S4. Calculated molecular structure of dimer $(C_6F_5O)Nd(\mu\text{-}OC_6F_5)_4Nd(OC_6F_5)_3$.

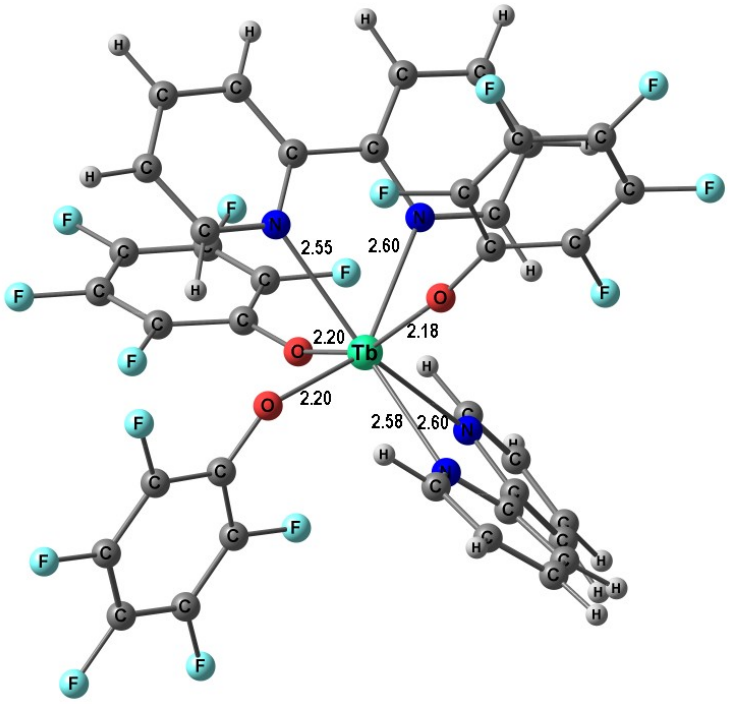


Fig. S5. Calculated molecular structure of $Tb(OC_6F_5)_3(bpy)_2$.

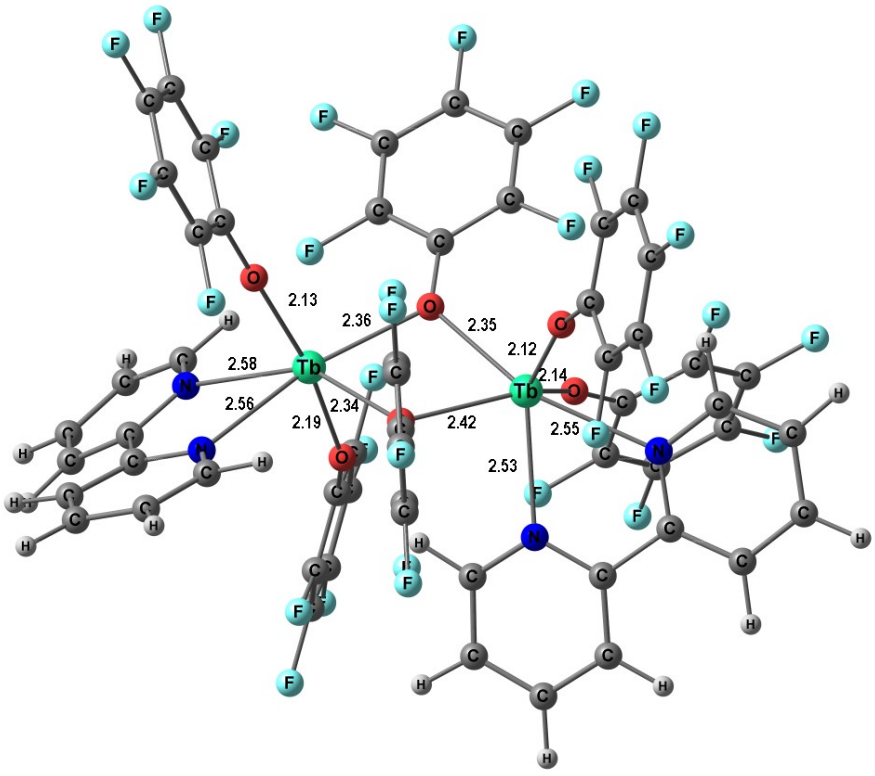


Fig. S6. Calculated molecular structure of dimer $(bpy)Tb(OC_6F_5)_2$ $(\mu\text{-}OC_6F_5)_2Tb(OC_6F_5)_2(bpy)$.

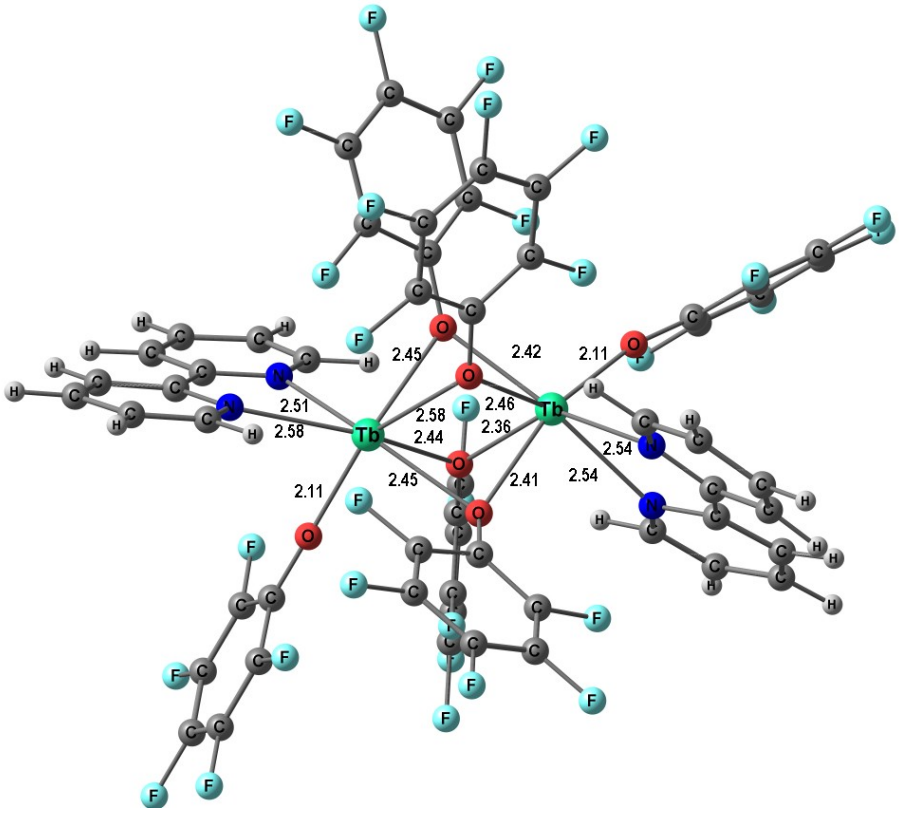


Fig. S7. Calculated molecular structure of dimer (bpy)Tb(OC_6F_5)(μ-OC_6F_5)$_4$Tb(OC_6F_5)(bpy).

It has the energy on 12.1 kcal/mol higher than the isomer structure in Fig S6.

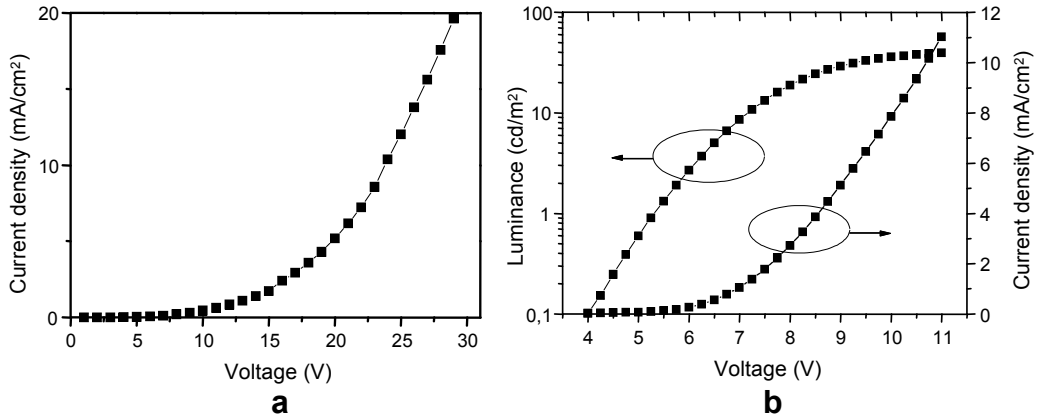


Fig. S8. I-V characteristic of device ITO/**1**(Pr)/Yb (a) and I-L-V characteristics of device ITO/TPD/**1**(Pr)/Yb (b). The data for **1**(Nd, Sm, Dy, Ho, Er) are similar.

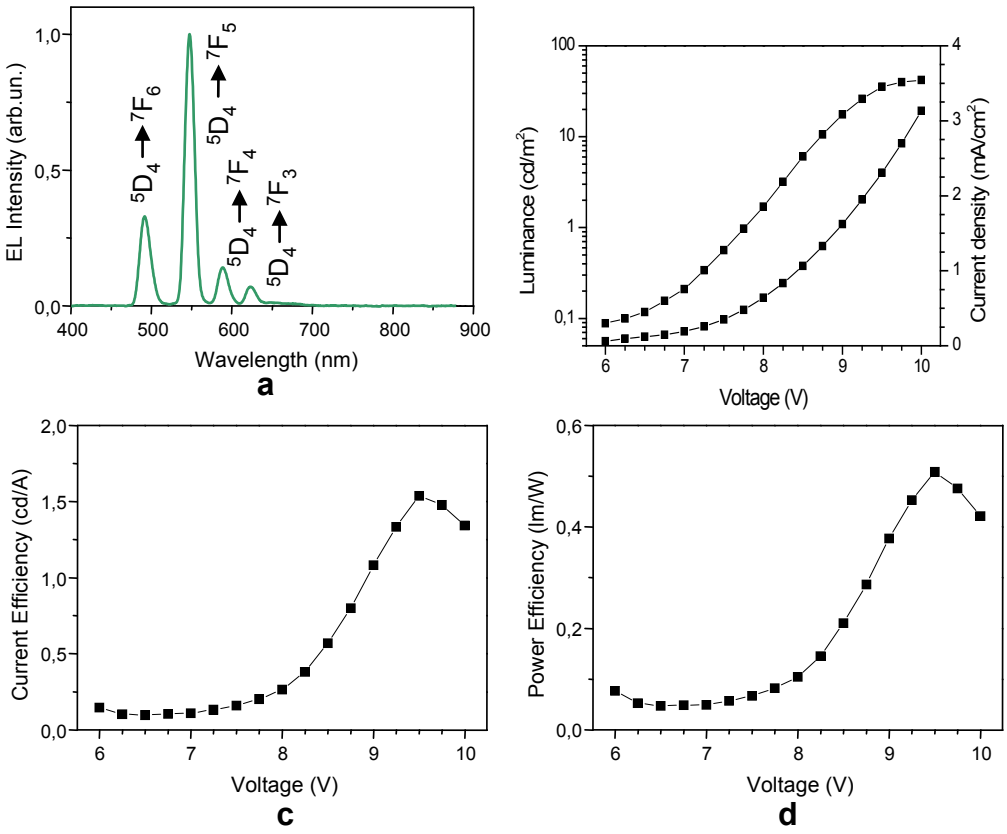


Fig. S9. EL spectrum (a), L-V and J-V curves (b), current efficiency vs voltage (c) and power efficiency vs voltage (d) of the device ITO/**2**(Tb)/Yb.

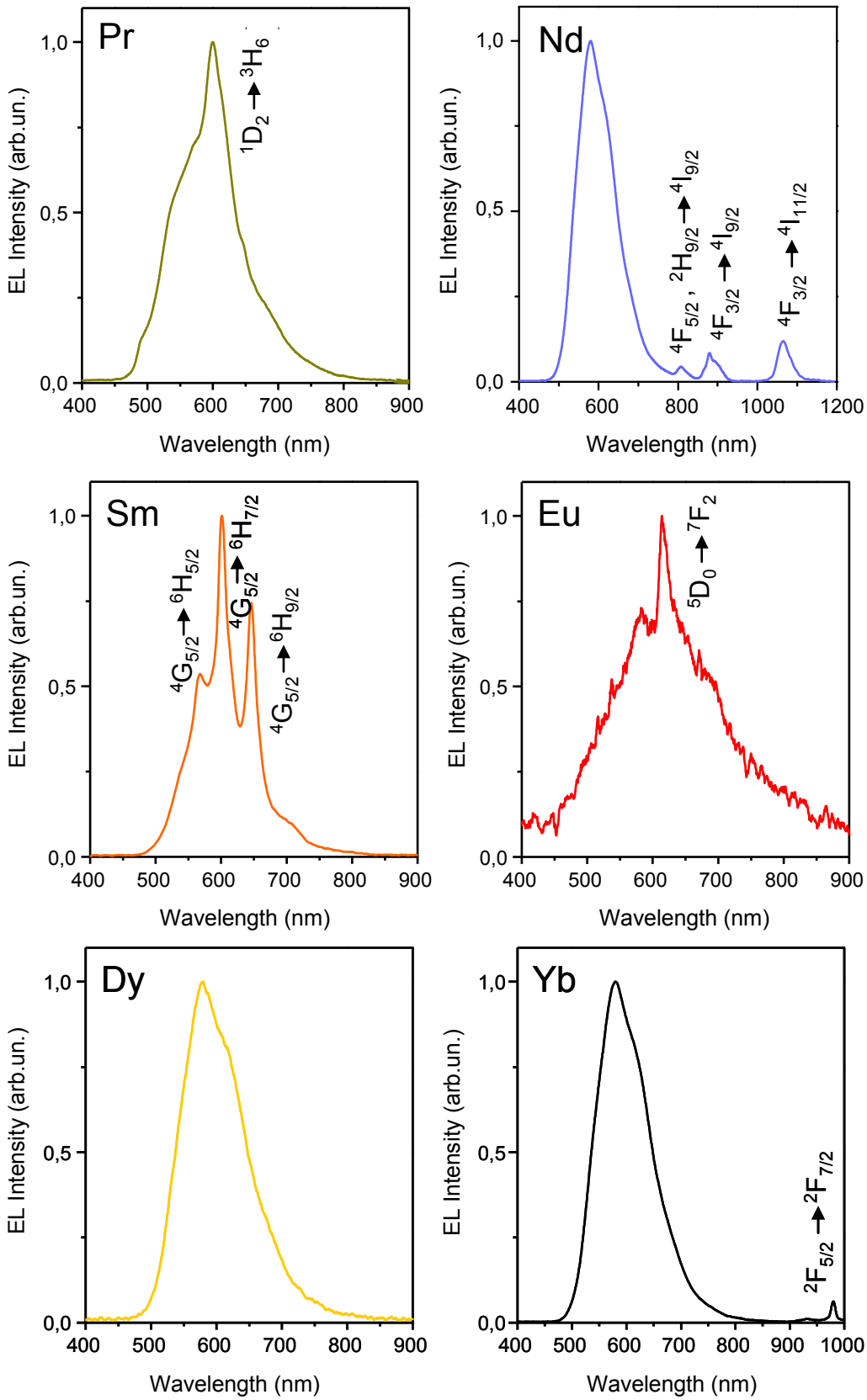


Fig. S10. EL spectra of devices ITO/TPD/**1**(Ln)/Yb at 12 V (**1**(Eu) at 27 V). The spectra of the devices with **1**(Gd, Ho, Er) are similar to that of **1**(Dy).

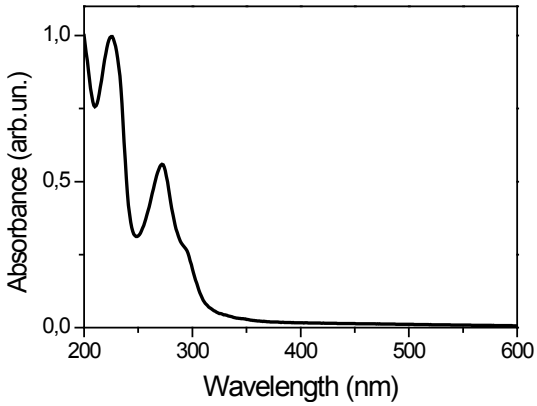


Fig. S11. Absorption spectra of films of **1**(Sm, Dy, Tb).

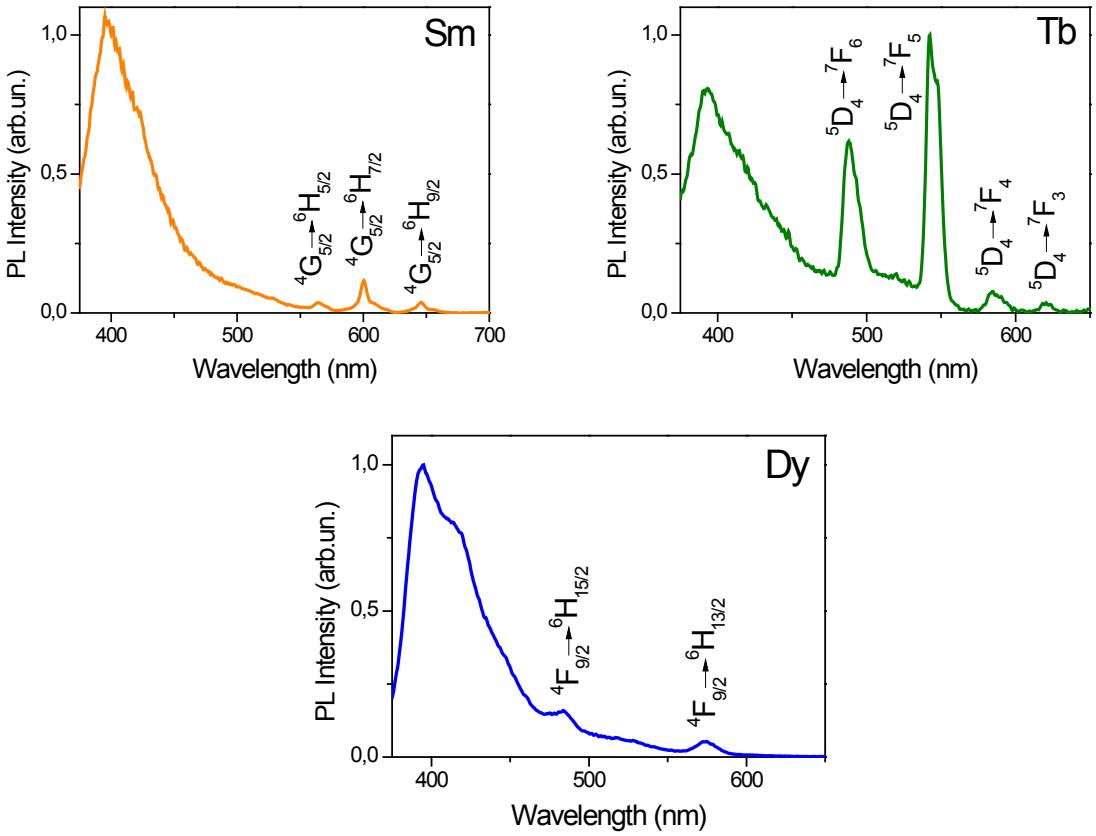


Fig. S12. PL spectra of the double layer samples of TPD(50 nm)/**1**(Ln)(100 nm), λ_{ex} = 270 nm.

Table S2. Energy levels (eV) of HOMO and LUMO of Sm and Tb complexes.

Complex	HOMO		LUMO	
	Experiment	Calculated	Experiment	Calculated
$SmL_3(phen)$	- 5.87	- 5.98 (-5.53, dimer)	- 2.69	- 4.14 (-4.53, dimer)
$SmL_3(phen)_2$	- 6.05	-5.48	- 2.79	- 3.84
$TbL_3(phen)$	- 6.03	- 5.68 (-5.29, dimer)	- 2.85	- 3.89 (-4.11, dimer)
$TbL_3(phen)_2$	- 5.77	- 5.08	- 2.51	- 3.63
$TbL_3(bpy)_2$	- 6.01	- 5.10	- 2.47	- 3.60

References

S1 D.N. Laikov, Chem. Phys. Lett. **281** (1997) 151; **416** (2005) 116.

S2 K.G. Dyall, J. Chem. Phys. **100** (1994) 2118.

S3 A. F. Shestakov and N. S. Emelyanova, J. Mol. Structure: THEOCHEM **124** (2010) 954.