Why europium acylpyrazolonates are bad phosphors: lessons learned from the study of ionic and polymer complexes $[MLnQ_4]$, $M=NEt_4^+$, Ag^+

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Table SI1.

Compound	**Sm-1**	**Eu-1**	**Sm-2**	**Eu-2**
CCDC	2374228	2374229	2374230	2374231
Empirical formula	$C_{54}H_{48}N_7O_8Sm$, $1[C_3H_7NO]$	$C_{54}H_{48}N_7O_8Eu$, $[C_3H_7NO]$, $[C_2H_6O]$	$C_{76}H_{72}N_9O_8Sm$, $[C_2H_3N]$	$C_{76}H_{72}N_9O_8Eu$, $[C_2H_3N]$
Formula weight ($g \cdot mol^{-1}$)	1146.44	1194.11	1430.83	1432.44
T (K)	100	100	100	100
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*	$P2_1/c$	$P2_1/c$
a (Å)	26.0812(9)	26.133(4)	23.9119(19)	23.8802(6)
b (Å)	14.3916(5)	14.423(3)	14.8147(11)	14.7946(4)
c (Å)	27.6124(9)	27.726(5)	20.5360(15)	20.5168(7)
α (deg)	90	90	90	90
β (deg)	96.4560(10)	96.708(5)	107.131(2)	106.9630(10)

γ (deg)	90	90	90	90
V (Å^3)	10298.6(6)	10379(3)	6952.1(9)	6933.2(4)
Z	8	8	4	4
D_{calc} (g·cm^{-3})	1.479	1.528	1.367	1.372
ϑ_{min}-ϑ_{max} (deg)	1.62-25.00	1.57-25.00	1.64-28.35	1.64-29.00
μ (mm^{-1})	1.207	1.279	0.909	0.969
T_{min}/T_{max}	0.5273/0.6478	0.5100/0.6478	0.5923 / 0.6471	0.5691/0.6478
Reflections/ Reflection unique number	35455/9069	32435/9131	93929 / 17353	68252/18408
Reflections with $I > 2\sigma(I)$	8462	6870	12971	14303
R_{int}	0.0591	0.1294	0.1060	0.0883
GooF	1.310	1.081	1.039	1.034
R_1, wR_2 ($I > 2\sigma(I)$)	0.0701, 0.1440	0.0824, 0.1860	0.0416, 0.0912	0.0522, 0.1110
R_1, wR_2 (all data)	0.0744, 0.1460	0.1053, 0.2006	0.0639, 0.0996	0.0701, 0.1219

Compound	**Sm-3**	**Eu-3**	**Gd-3**
CCDC	2374232	2374233	2374234
Empirical formula	$C_{68}H_{52}N_8O_8AgSm$, $1.75[C_2H_3N]$	$C_{68}H_{52}N_8O_8AgEu$, $1.75[C_2H_3N]$	$C_{68}H_{52}N_8O_8AgGd$, $1.75[C_2H_3N]$
Formula weight ($g \cdot mol^{-1}$)	1439.24	1440.85	1446.14
T (K)	100	296(2)	100
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	14.0221(5)	14.0434(8)	13.9878(3)
b (Å)	29.1667(11)	29.1528(16)	29.1643(6)
c (Å)	16.7398(6)	16.7937(9)	16.7245(3)
α (deg)	90	90	90
β (deg)	113.1330(10)	112.8130(10)	113.0310(10)
γ (deg)	90	90	90
V ($Å^3$)	6295.7(4)	6337.6(6)	6278.9(2)
Z	4	4	4
D_{calc} ($g \cdot cm^{-3}$)	1.518	1.510	1.530
ϑ_{min}-ϑ_{max} (deg)	1.76-25.00	1.76-25.00	1.49-27.00
μ (mm^{-1})	1.301	1.355	1.425
T_{min}/T_{max}	0.5630/0.6478	0.5630/0.6478	0.5660/0.6478
Reflections/ Reflection unique number	41620/11078	75904/16834	53041/13696
Reflections with $I > 2\sigma(I)$	8455	12632	10643
R_{int}	0.0908	0.0751	0.0866
GooF	1.045	1.024	1.038
R_1, wR_2 ($I > 2\sigma(I)$)	0.0553, 0.1145	0.0427, 0.0841	0.0552, 0.1111
R_1, wR_2 (all data)	0.0764, 0.1266	0.0687, 0.0939	0.0734, 0.1223

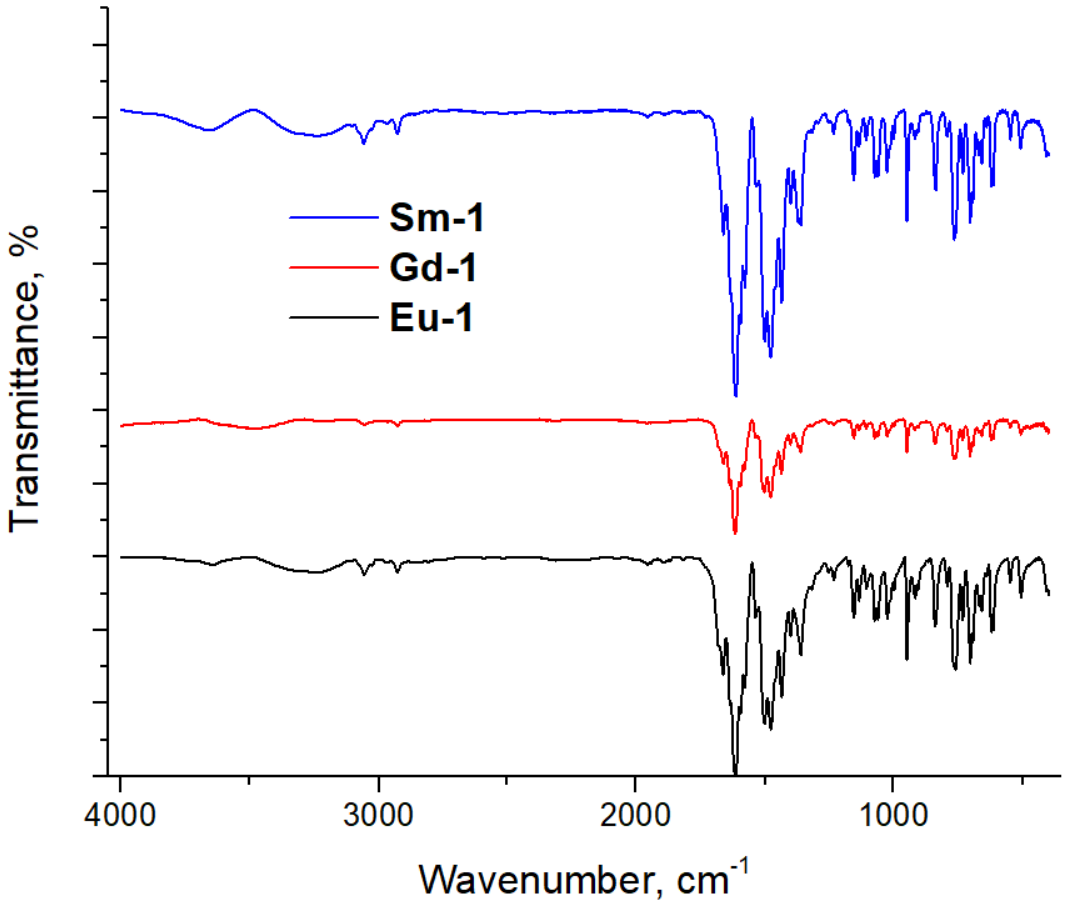


Figure S1. IR spectra of Ln-1 series.

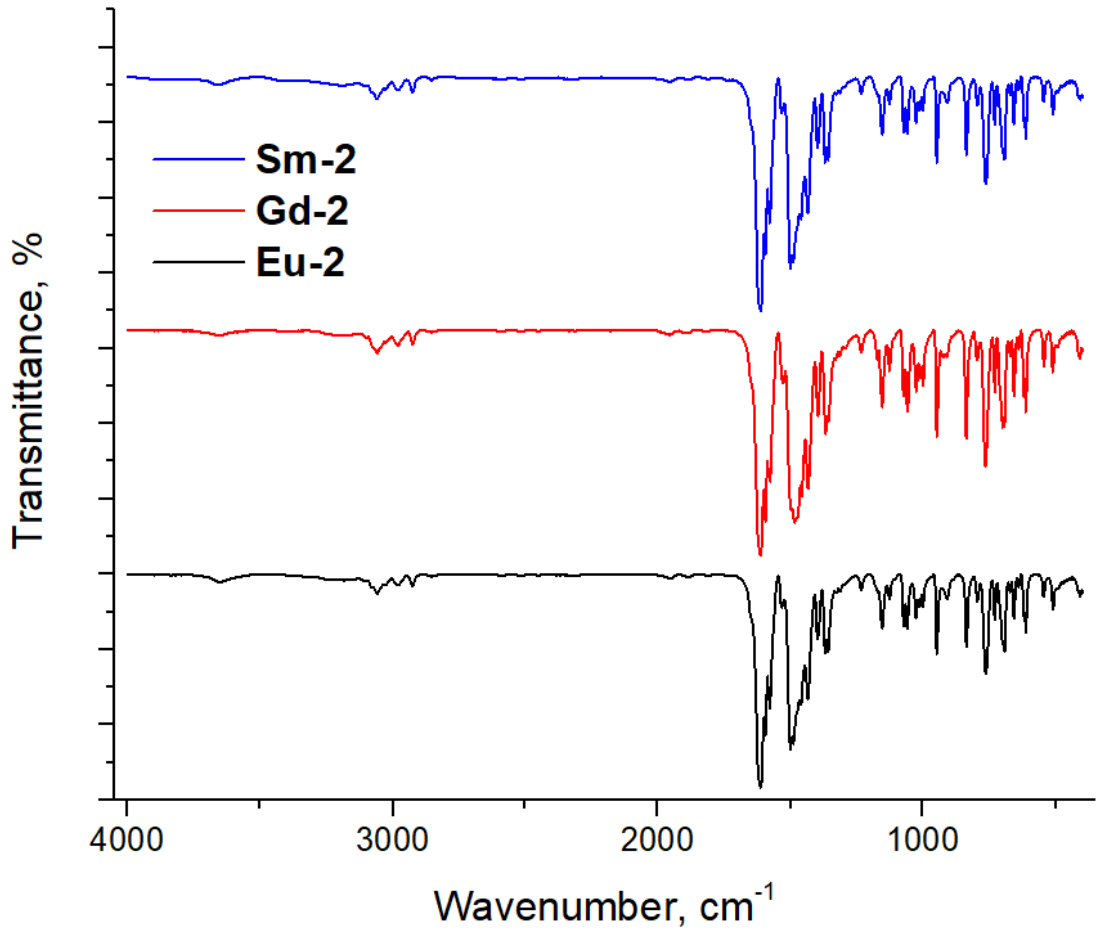


Figure S2. IR spectra of Ln-2 series.

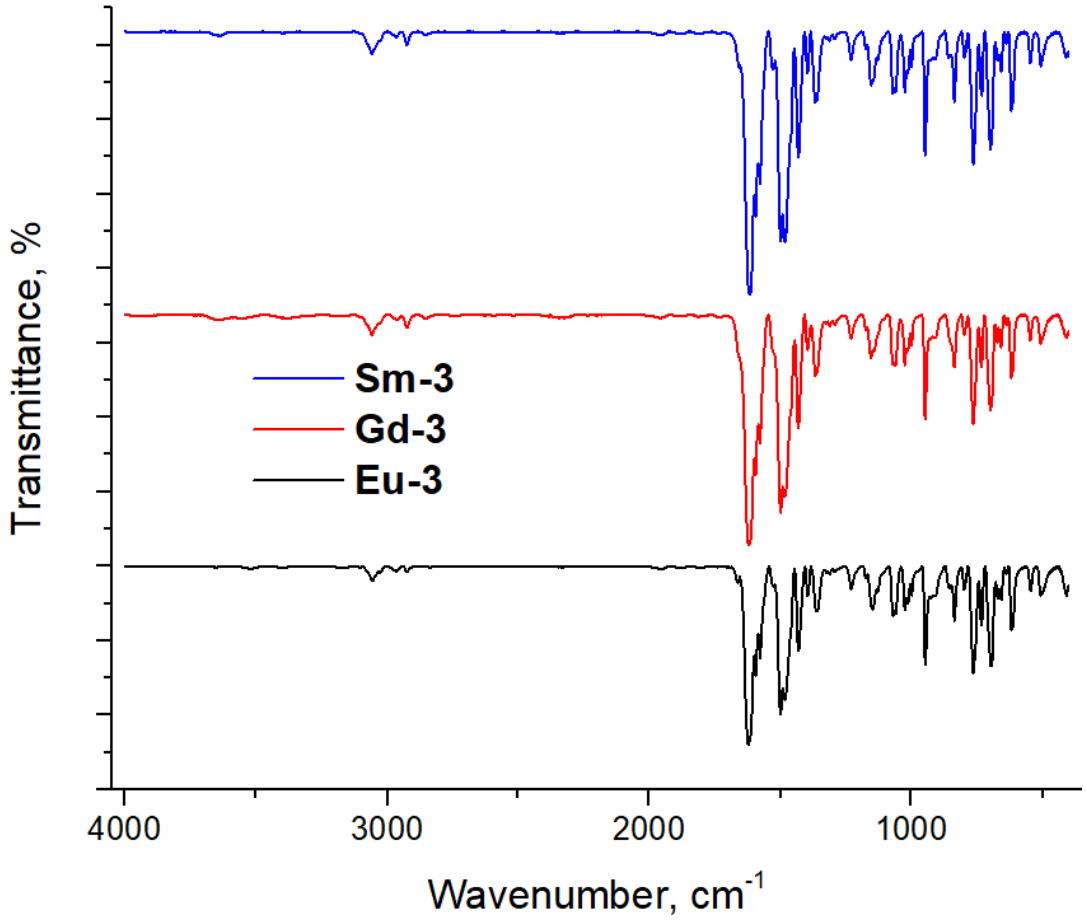


Figure S3. IR spectra of Ln-3 series.

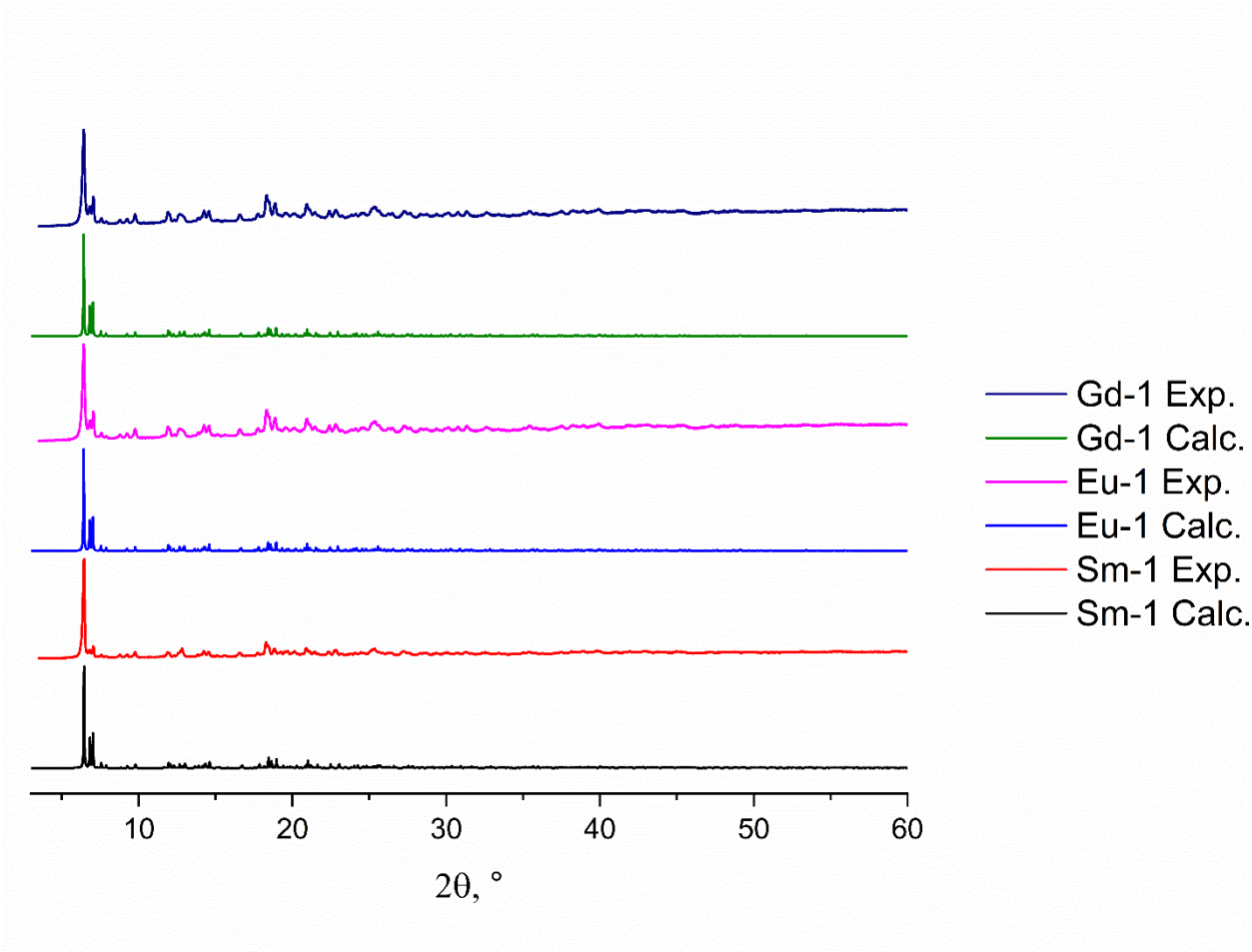


Figure S4. PXRD patterns for Ln-1 series.

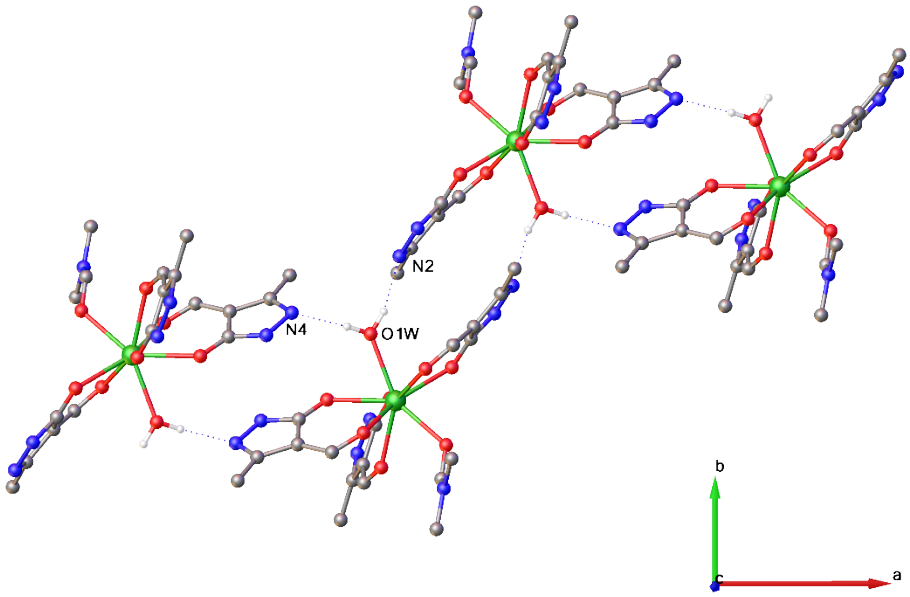


Figure S5. View of O–H…N bonds along (001) plane in **Sm-1**.

Table SI2. Selected geometrical parameters of **Sm-1**, **Eu-1** and analogous compounds.

Complex/Parameter	**Sm-1**	**Eu-1**	**[SmQ$^{CY}_3$(H$_2$O)(EtOH)](EtOH)** [64]	**[EuQ$^{CY}_3$(H$_2$O)** [29]
Ln-O(Q$^-$), average	2.3857	2.3862	2.3905	2.3323
Ln-O(Solvent)	2.409(4)(H$_2$O) 2.426(4)(DMF)	2.409(6)(H$_2$O) 2.423(5) DMF)	2.465(2)(H$_2$O) 2.485(5) (EtOH)	2.360(3) (H$_2$O)
O-Ln-O (1,3-diketone)	73.4(2), 74.7(2), 75.4(3)	73.3(2), 75.1(2), 76.7(2)	72.20(8), 72.59(8), 72.66(8)	73.25(7), 73.21(7), 74.37(7)
O1W-N2 (H-Bonded)	2.801(7)	2.803(9)	2.702(4)$^{O1W-O(EtOH)}$	2.716(3)
O1W-N4 (H-Bonded)	2.825(7)	2.85(1)	2.834(4)	2.787(4)
Symmetry of the LnO$_8$ or LnO^7 polyhedron with S_Q (p) value	Square antiprism, D$_{4d}$, 0.837	Square antiprism, D$_{4d}$, 0.763	Square antiprism, D$_{4d}$, 0.259	Capped trigonal prism, C$_{2v}$, 0.906
SAP base twist angle, °	44.8		–	–

Table SI3. Dihedral angles for Ln-1, Ln-2, and Ln-3 series.

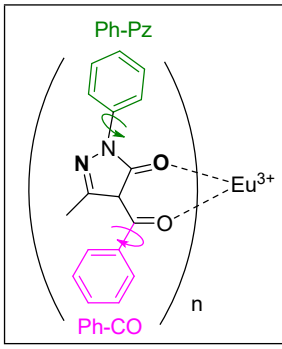
	Complex	Ph-Pz minimum	Ph-Pz average	Ph-CO minimum	Ph-CO average	Triplet energy, cm^{-1}	Singlet energy, cm^{-1}
	Eu-1	1.2	23.0	66.5	74.8	21.0	23.1
	Eu-2	18.8	27.8	41.4	57.3	19.9	22.7
	Eu-3	19.1	33.8	39.2	47.0	20.5	22.8

Figure S6. PXRD patterns for Ln-2 series

Table SI4. Selected geometrical parameters of **Sm-2**, **Eu-2** and analogous compounds.

Complex/Parameter	Sm-2	Eu-2	$(H_3O)[SmQ^{CY}_4]$ [64]	$(H_3O)[EuQ^{CY}_4]$ [52]
Ln-O	2.3973	2.3865	2.3990	2.354 (4)–2.436 (4)
O-Ln-O (1,3-diketone)	72.13(7), 71.37(7), 72.54(7), 72.46(7)	72.79(9), 72.80(9), 71.87(9), 72.54(9)	71.3(1), 71.5(1)	71.14 (13), 72.13 (14)
Symmetry of the LnO_8 polyhedron with $S_Q(p)$ value	Square antiprism, D_{4d}, 0.497	Square antiprism, D_{4d}, 0.461	Square antiprism, D_{4d}, 0.891	Square antiprism, D_{4d}, 0.322

[a]				
SAP base twist angle, °	45.1		–	–

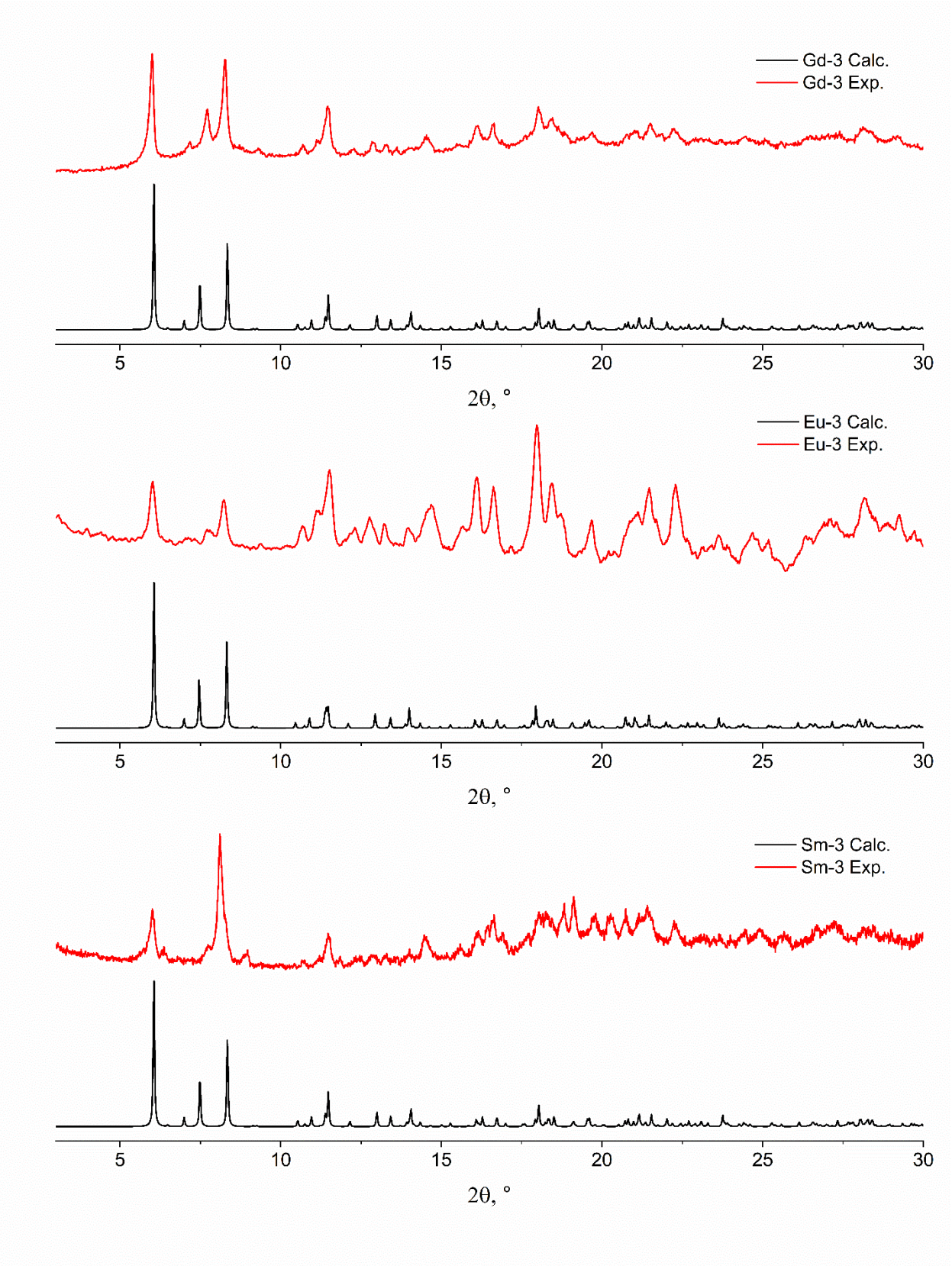


Figure S7. PXRD patterns for Ln-3 series

Table SI5**.** Selected geometrical parameters of **Sm-3**, **Eu-3** and analogous compounds.

Complex/Parameter	**Sm-3**	**Eu-3**	**Gd-3**	**{AgGdQ$^{CY}_4$}** [52]
Ln-O	2.3994	2.3909	2.3770	2.287 (8)–2.448 (9)
O-Ln-O (1,3-diketone)	71.8(1), 71.6(1), 72.8(1), 72.1(3)	71.88(9), 73.28(9), 71.52(8), 72.1(1)	72.4(1), 72.2(1), 73.5(1), 72.2(4)	68.1 (3)–70.8 (3)
Ag-N	2.123(6), 2.116(6)	2.123(3), 2.128(3)	2.113(5), 2.126(5),	2.229 (11)–2.403 (9)
N-Ag-N	163.5(2)	163.2(1)	164.0(2)	99.4 (4), 129.3 (4), 131.2 (4)
Symmetry of the LnO_8 polyhedron with $S_Q(p)$ value [a]	Square antiprism, D_{4d}, 0.304	Square antiprism, D_{4d}, 0.279	Square antiprism, D_{4d}, 0.269	Square antiprism, D_{4d}, 0.322
SAP base twist angle, °	45.1			–

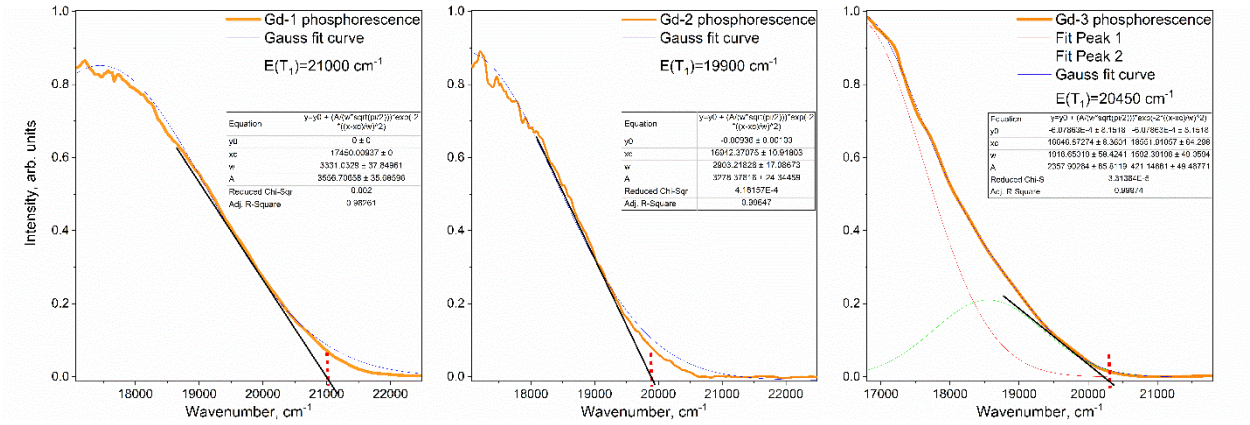


Figure S8. Phosphorescence spectra of **Gd-1**, **Gd-2**, and **Gd-3**

Table SI6**.** The energies of Stark components corresponding to the respective transitions

Complex/transition	Range, nm	Energy, cm^{-1}
Sm^{3+} ion complexes		
$^4G_5 \rightarrow {}^6H_{5/2}$	560-575	17880
$^4G_5 \rightarrow {}^6H_{7/2}$	590-615	16820
$^4G_5 \rightarrow {}^6H_{9/2}$	635-660	15160
$^4G_5 \rightarrow {}^6H_{11/2}$	705-715	14270
Eu^{3+} ion complexes		
$^5D_0 \rightarrow {}^7F_0$	577-580	17290
$^5D_0 \rightarrow {}^7F_1$	588-600	16290
$^5D_0 \rightarrow {}^7F_2$	611-628	16270
$^5D_0 \rightarrow {}^7F_3$	647-660	15430
$^5D_0 \rightarrow {}^7F_4$	690-710	14470

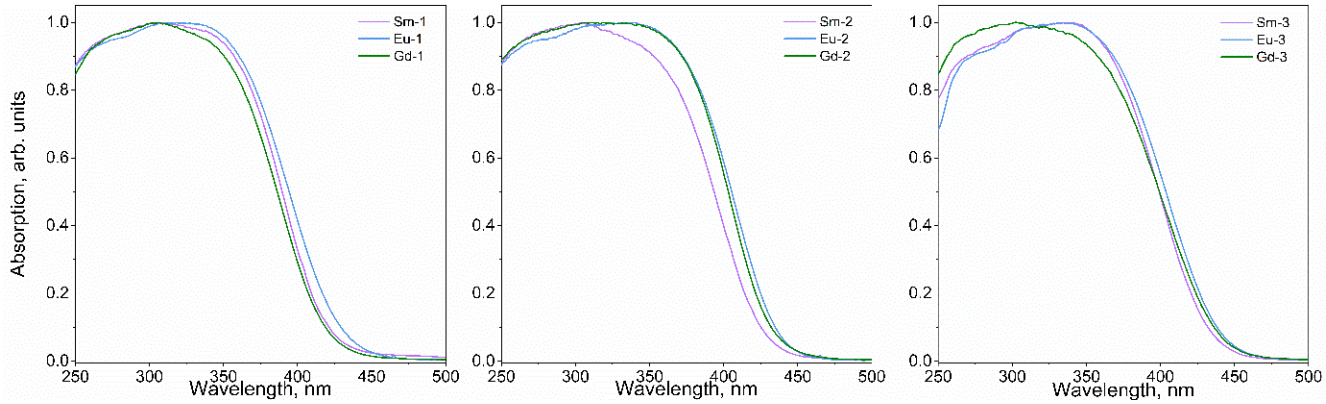


Figure S9. Diffuse reflectance spectra of complexes.

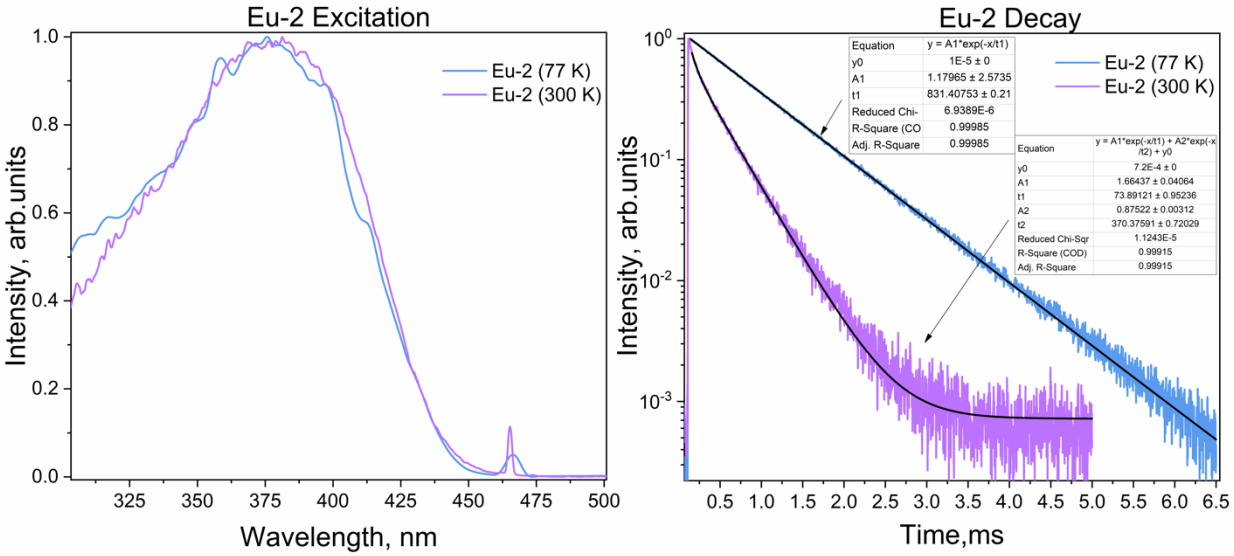


Figure S10. (left) Eu-2 excitation spectra at 77 and 300 K. (right) Eu-2 photoluminescence decays at 77 and 300 K (λ_{em}=612 nm and λ_{ex}=345 nm).

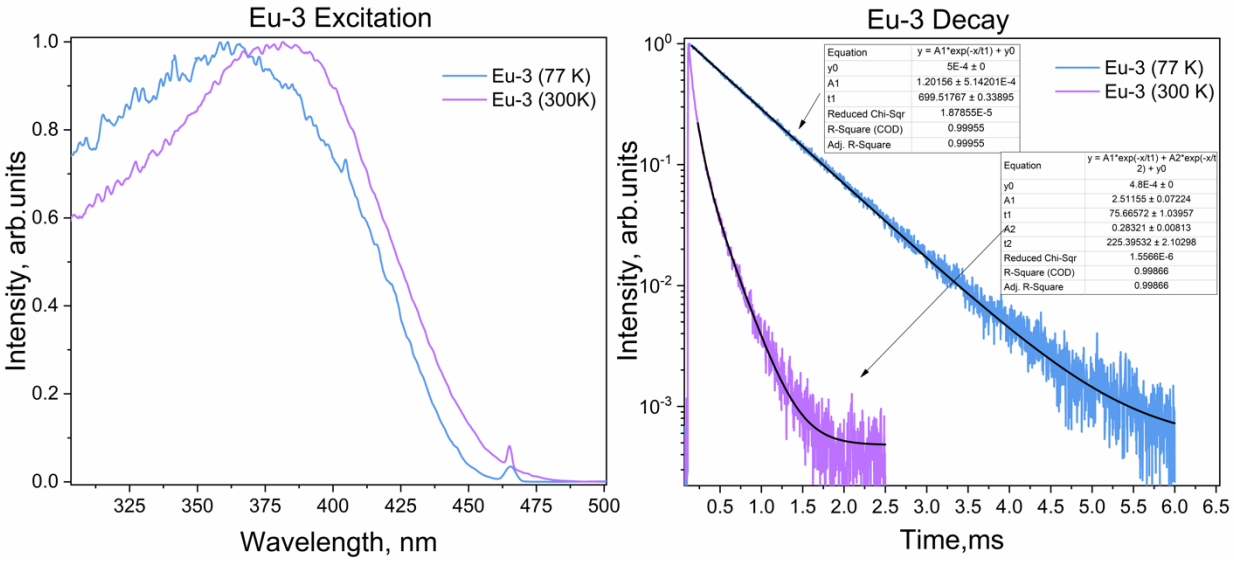


Figure S11. (left) Eu-3 excitation spectra at 77 and 300 K. (right) Eu-3 photoluminescence decays at 77 and 300 K (λ_{em}=612 nm and λ_{ex}=345 nm).

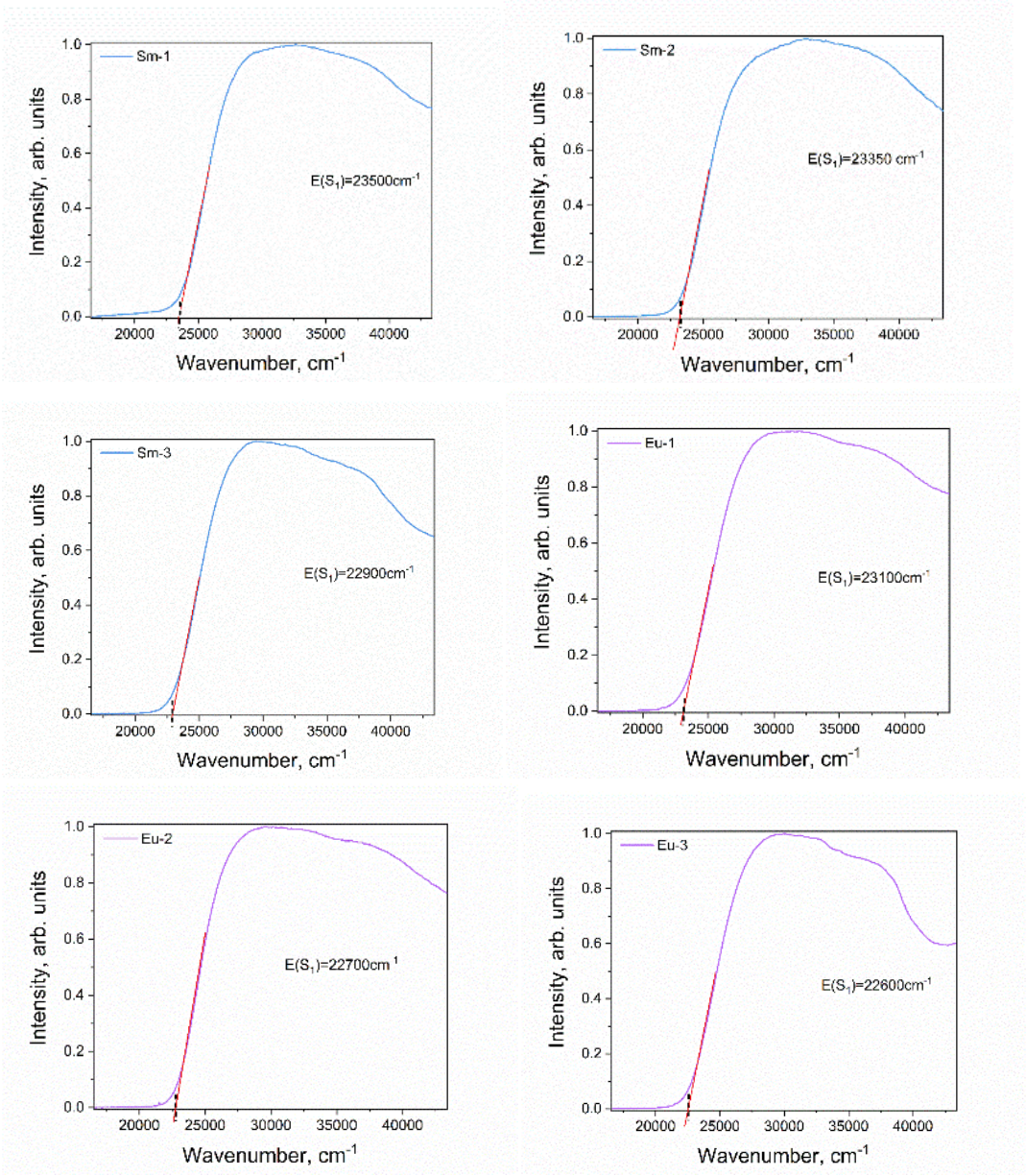


Figure S12. First excited singlet state energy evaluation by the diffuse reflectance spectra.

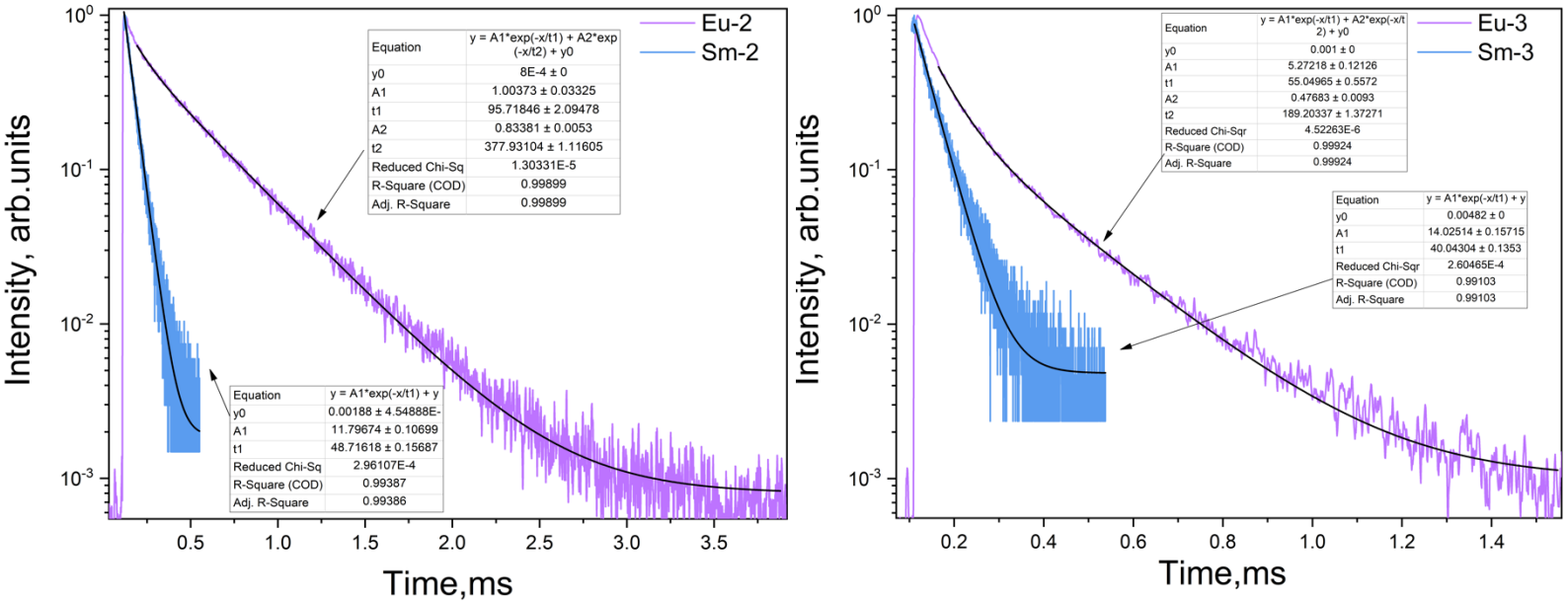
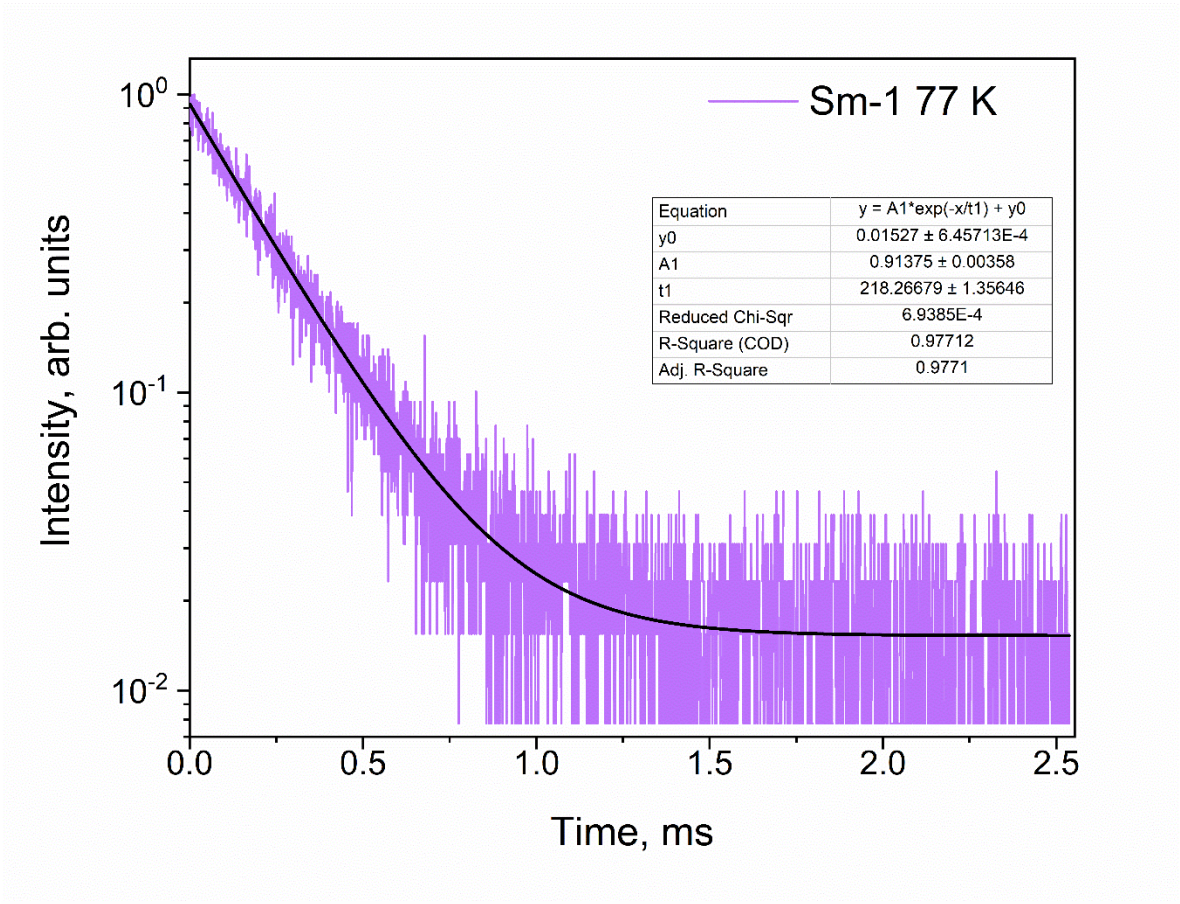
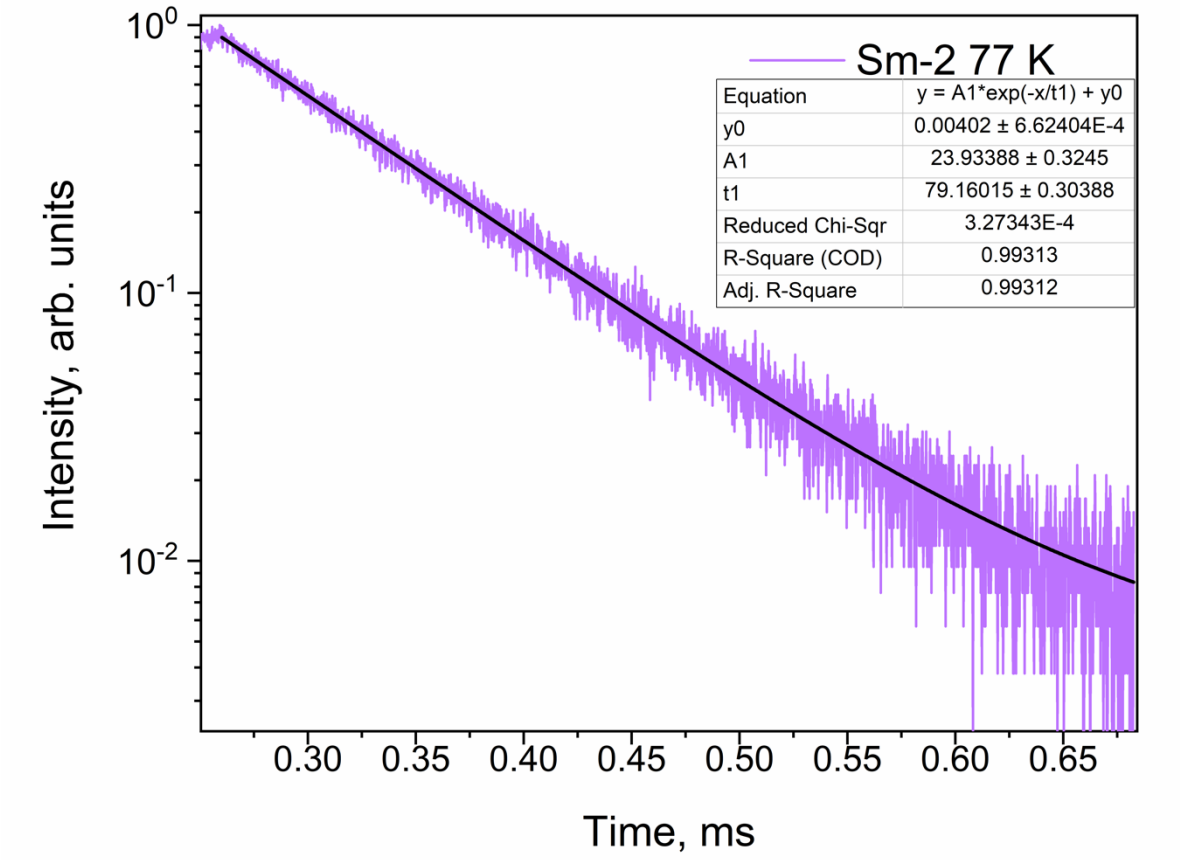


Figure S13. Comparison of PL decays at 300 K of (left) Eu-2 and Sm-2, (right) Eu-3 and Sm-3.


Sm-1 77 K
Equation | y = A1*exp(-x/t1) + y0
y0 | 0.01527 ± 6.45713E-4
A1 | 0.91375 ± 0.00358
t1 | 218.26679 ± 1.35646
Reduced Chi-Sqr | 6.9385E-4
R-Square (COD) | 0.97712
Adj. R-Square | 0.9771
Intensity, arb. units
Time, ms


Sm-2 77 K
Equation | y = A1*exp(-x/t1) + y0
y0 | 0.00402 ± 6.62404E-4
A1 | 23.93388 ± 0.3245
t1 | 79.16015 ± 0.30388
Reduced Chi-Sqr | 3.27343E-4
R-Square (COD) | 0.99313
Adj. R-Square | 0.99312
Intensity, arb. units
Time, ms

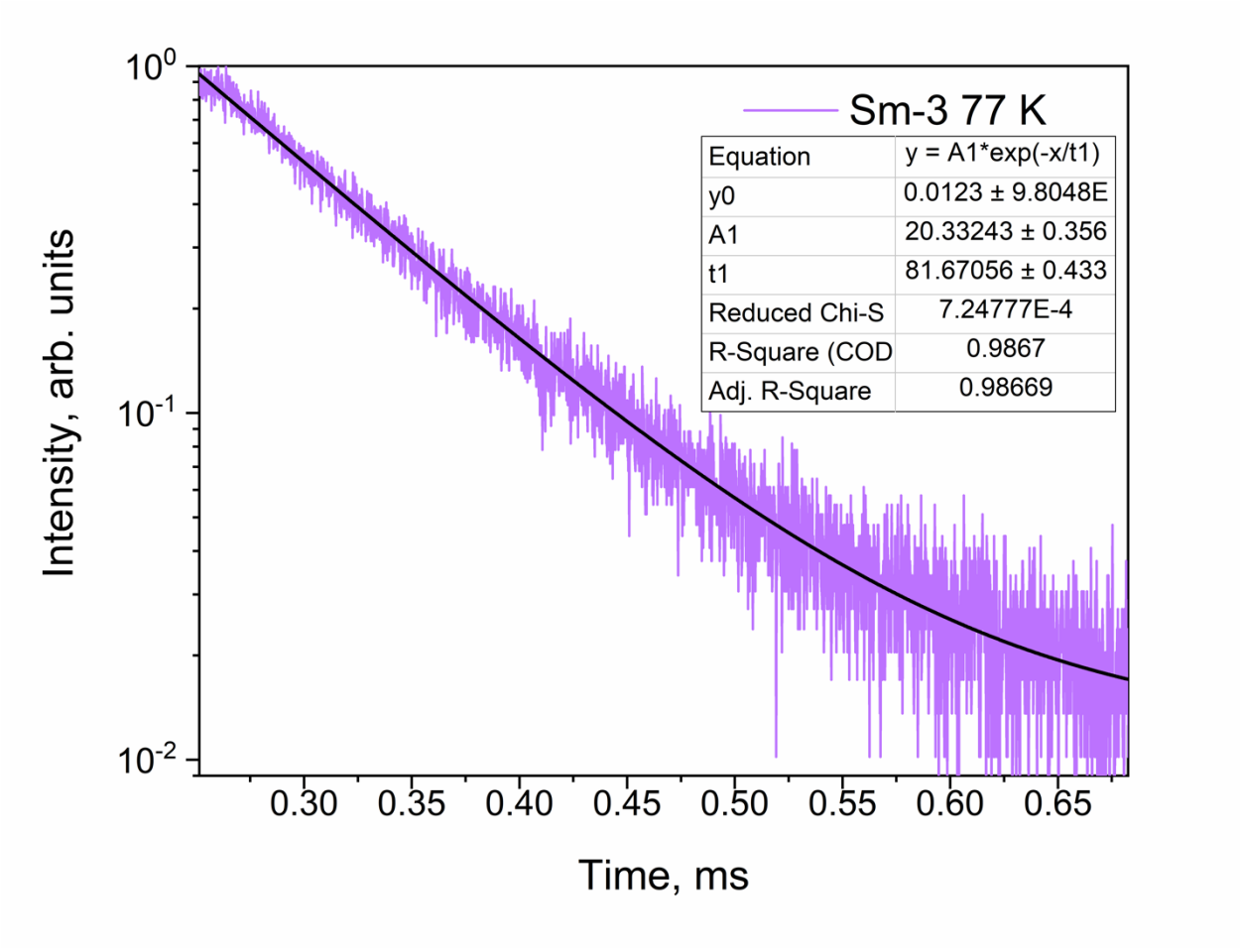


Figure S14. PL decays of Sm^{3+} ion complexes at 77 K.

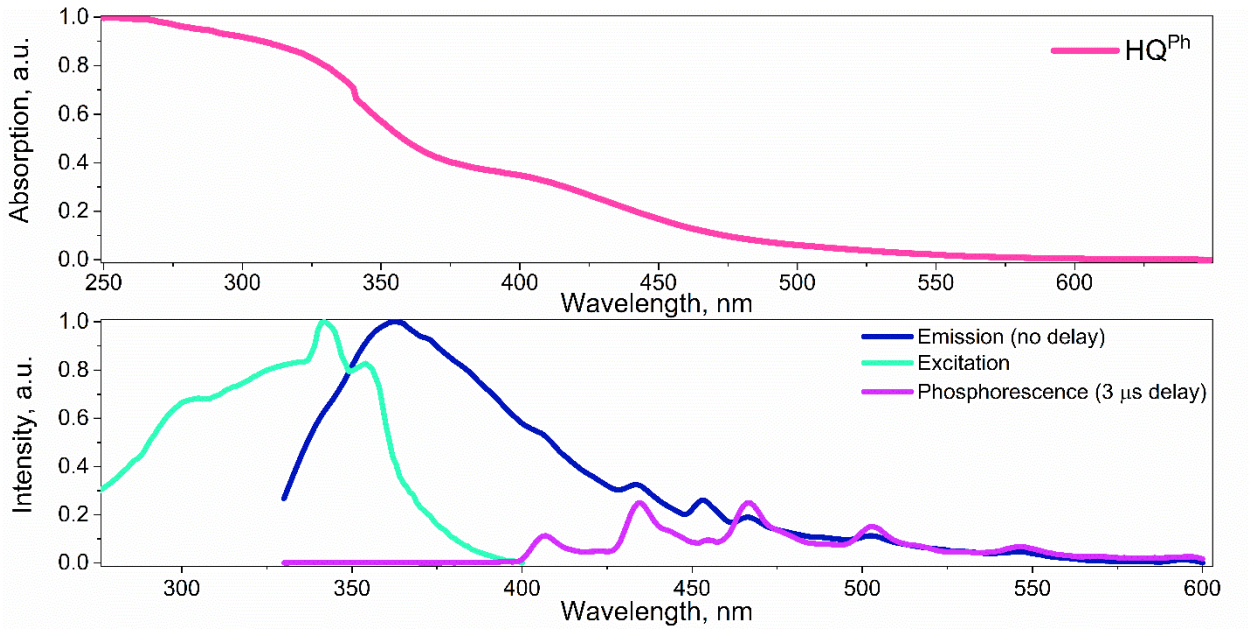


Figure S15. HQ^{Ph} optical properties.