Supplementary materials

Synthesis and Characterization of Lanthanide Metal Ion Complexes of New Polydentate Hydrazone Schiff Base Ligand

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1. Scheme S1. General structures of the resulting complexes (group A and B).

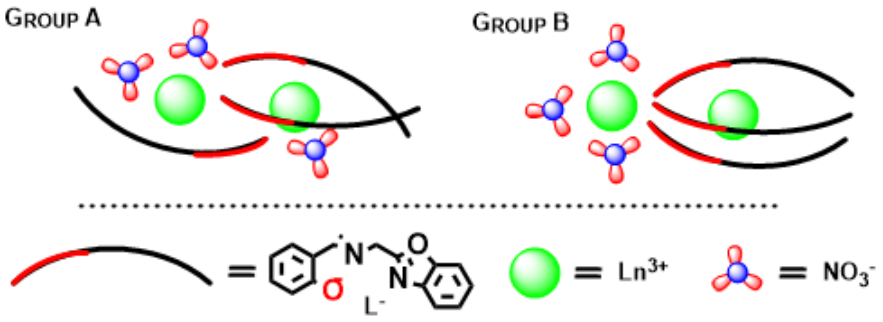
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Scheme 1. General structures of the resulting complexes (group **A** and **B**).

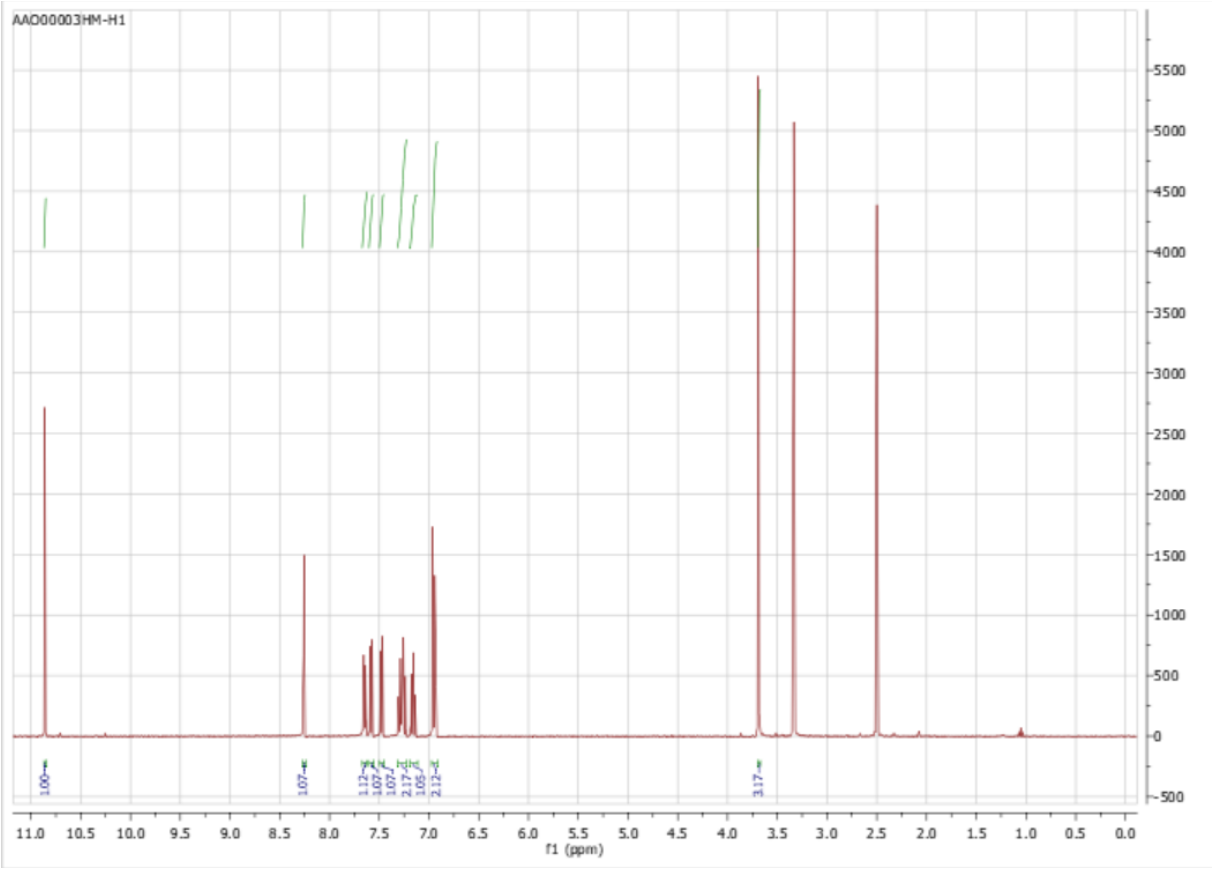


Figure S1. ^{1}H NMR spectrum of ligand in DMSO-d6.

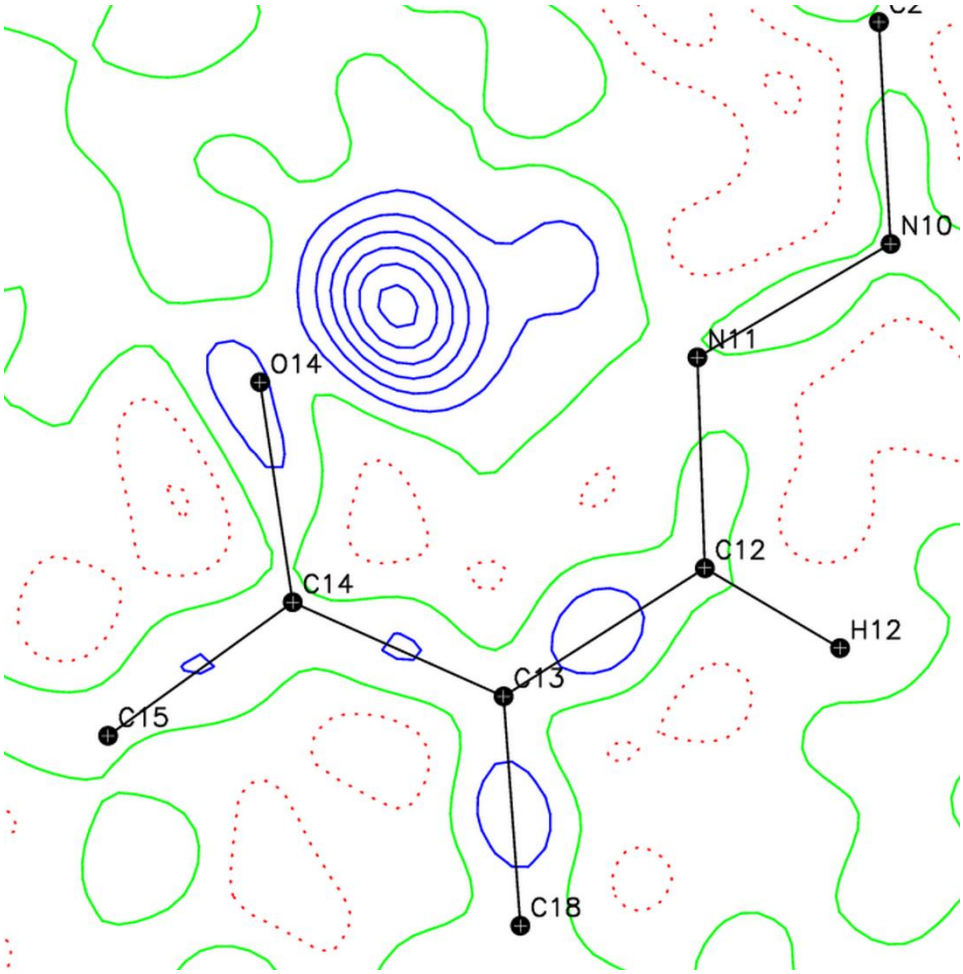


Figure S2. The difference Fourier map for the structure HL without the OH or NH hydrogen atom; the position of this hydrogen next to oxygen is clearly seen.

Table S1. Crystal data, data collection and structure refinement.

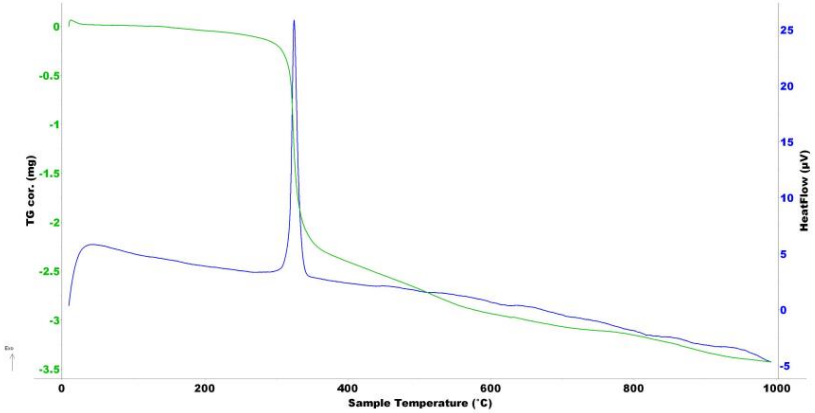
Compound	HL	1 (Sm)	2 (Eu)	3a (Tb)
Formula	$C_{15}H_{13}N_3O_2$	$C_{45}H_{36}Sm_2N_{12}O_{15}\cdot C_2H_3N$	$C_{45}H_{36}Eu_2N_{12}O_{15}\cdot C_2H_3N\cdot C_6H_{14}O$	$C_{45}H_{36}N_{12}O_{15}Tb_2\cdot C_7H_8\cdot C_2H_3N\cdot CH_4O$
Formula weight	267.28	1326.61	1432.03	1467.92
	/c		/c	
Crystal system	orthorhombic	monoclinic	triclinic	triclinic
Space group	Pbcn	$P2_1/c$	P-1	P-1
a(Å)	22.6342(4)	11.5200(5)	14.2703(4)	11.5819(7)
b(Å)	8.59955(12)	14.8132(5)	14.2792(4)	12.9463(7)
c(Å)	12.8361(2)	29.8965(9)	16.8854(4)	19.4420(7)
α(°)	90	90	87.661(2)	74.414(4)
β(º)	90	91.509(3)	65.209(2)	87.335(4)
γ(°)	90	90	65.232(3)	86.059(5)
V(Å^3)	2498.47(7)	5100.0(3)	2798.08(15)	2800.2(3)
Z	8	4	2	2
D_x(g cm^{-3})	1.421	1.728	1.700	1.741
F(000)	1120	2624	1432	1460
μ(mm^{-1})	0.795	2.361	2.303	2.588
Reflections:				
collected	5790	20471	46097	32225

unique (R_{int})	2503 (0.0173)	9788 (0.0399)	12597 (0.0273)	11795 (0.0494)
with I>2σ(I)	2277	7629	11266	9539
R(F) [I>2σ(I)]	0.0387	0.0518	0.0198	0.0436
wR(F^2) [I>2σ(I)]	0.1003	0.1218	0.0434	0.1017
R(F) [all data]	0.0425	0.0716	0.0248	0.0581
wR(F^2) [all data]	0.1042	0.1357	0.0456	0.1126
Goodness of fit	1.023	1.072	1.060	1.036
max/min Δ ($e \cdot Å^{-3}$)	0.19/-0.31	2.82/-2.02	0.64/-0.61	1.89/-1.66
CCDC number	1542869	2062743	2062744	1542870

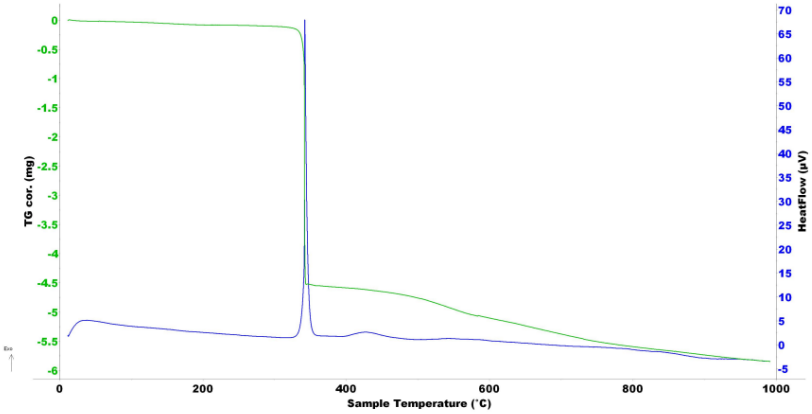
Compound	**3b (Tb)**	**4 (Dy)**	**5 (Ho)**
Formula	$C_{45}H_{36}N_{12}O_{15}Tb_2 \cdot C_2H_3N \cdot C_6H_{16}N^+ \cdot NO_3^-$	$C_{45}H_{36}Dy_2N_{12}O_{15} \cdot C_2H_3N$	$C_{45}H_{36}Ho_2N_{12}O_{15} \cdot 3(C_2H_3N) \cdot CH_4O$
Formula weight	1507.96	1350.91	1469.92
Crystal system	cubic	monoclinic	monoclinic
Space group	$P2_13$	$P2_1/c$	$P2_1/n$
a(Å)	17.90482(15)	11.4753(3)	13.4899(4)
b(Å)	17.90482(15)	14.7637(4)	21.7608(8)
c(Å)	17.90482(15)	29.7478(8)	20.2951(9)
α(°)	90	90	90
β(º)	90	91.904(2)	108.887(4)
γ(°)	90	90	90
V($Å^3$)	5739.97(14)	5037.0(2)	5636.9(4)
Z	4	4	4
D_x(g cm^{-3})	1.745	1.781	1.732
F(000)	3008	2656	2912
μ(mm^{-1})	2.531	3.026	2.879
Reflections:			
collected	20848	19321	27295
unique (R_{int})	4349 (0.0277)	9636 (0.0250)	10885 (0.0267)
with I>2σ(I)	4189	8460	9573
R(F) [I>2σ(I)]	0.0154	0.0256	0.0340
wR(F^2) [I>2σ(I)]	0.0311	0.0538	0.0780
R(F) [all data]	0.0174	0.0321	0.0417
wR(F^2) [all data]	0.0317	0.0563	0.0809
Goodness of fit	1.024	1.028	1.071
max/min Δ ($e \cdot Å^{-3}$)	0.23/-0.28	0.74/-1.18	1.35/-1.17
CCDC number	2062745	2062746	1542871

Compound	**6 (Er)**	**7 (Tm)**	**8 (Yb)**
Formula	$C_{45}H_{36}N_{12}O_{15}Er_2 \cdot C_2H_3N$	$C_{45}H_{36}N_{12}O_{15}Tm_2 \cdot 4(C_2H_3N)$	$C_{45}H_{36}N_{12}O_{15}Yb_2 \cdot 4(C_2H_3N)$
Formula weight	1359.42	1482.90	1495.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a(Å)	11.51739(10)	13.6208(5)	13.60755(17)
b(Å)	14.79757(11)	21.8908(8)	21.86269(19)
c(Å)	29.90397(19)	20.4587(6)	20.4089(2)
α(°)	90	90	90
β(º)	91.6300(7)	109.062(4)	109.0172(14)

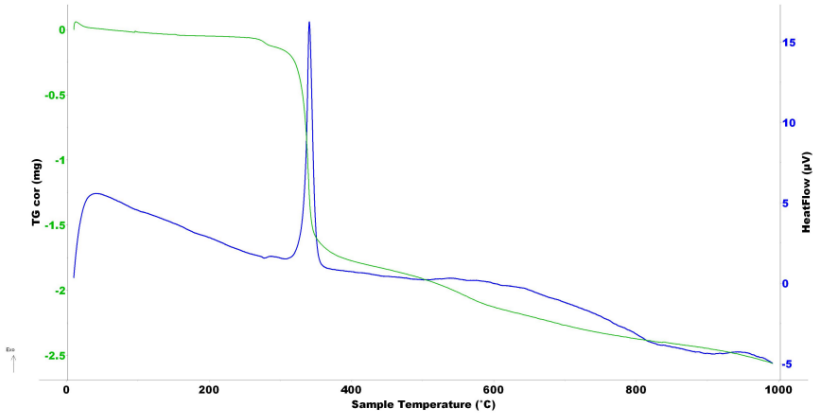
γ(°)	90	90	90
V(Å^3)	5094.45(7)	5765.7(4)	5740.21(11)
Z	4	4	4
D_x(g cm^{-3})	1.772	1.708	1.730
F(000)	2668	2928	2952
μ(mm^{-1})	6.631	3.138	3.320
Reflections:			
collected	41037	13286	110666
unique (R_{int})	9157 (0.0546)	8402 (0.0317)	12102 (0.0272)
with I>2σ(I)	8032	6490	11455
R(F) [I>2σ(I)]	0.0522	0.0418	0.0248
wR(F^2) [I>2σ(I)]	0.1321	0.0848	0.0974
R(F) [all data]	0.0612	0.0646	0.0272
wR(F^2) [all data]	0.1359	0.0963	0.0997
Goodness of fit	1.102	1.045	1.019
max/min Δ (e·Å^{-3})	3.82/-1.00	1.13/-1.04	2.52/-1.61
CCDC number	2062747	2062748	2062749



(a)

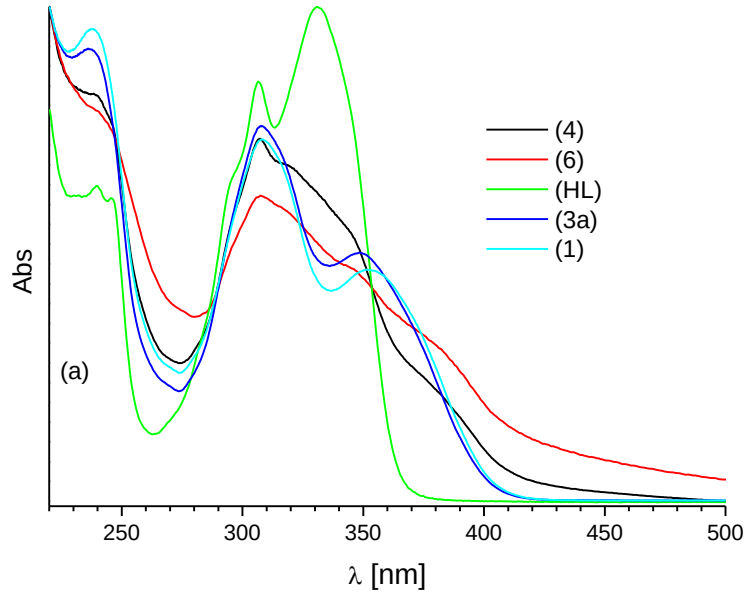


(b)



(c)

Figure S3. Thermogravimetric analysis (TGA) curves of representative of complexes (a) **2**, (b) **3**, (c) **6**.



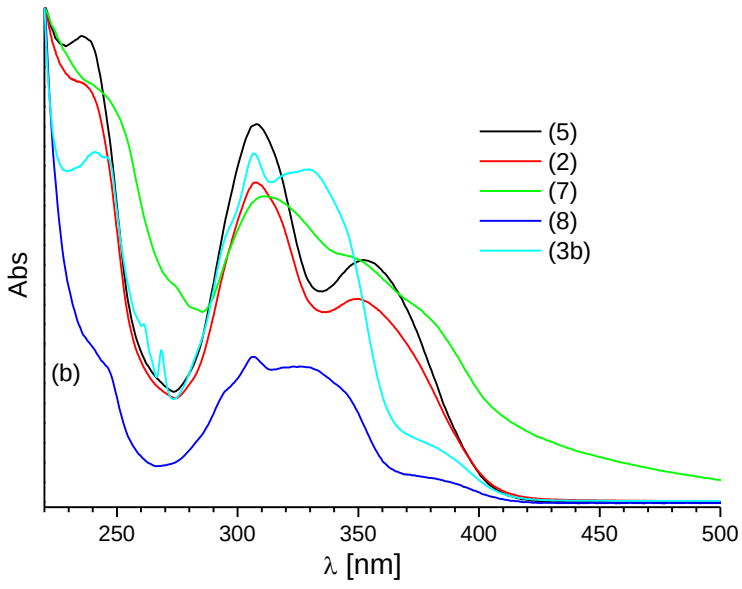


Figure S4. The UV-Vis spectra of group **A** (a) and **B** (b) compounds in acetonitrile solution.

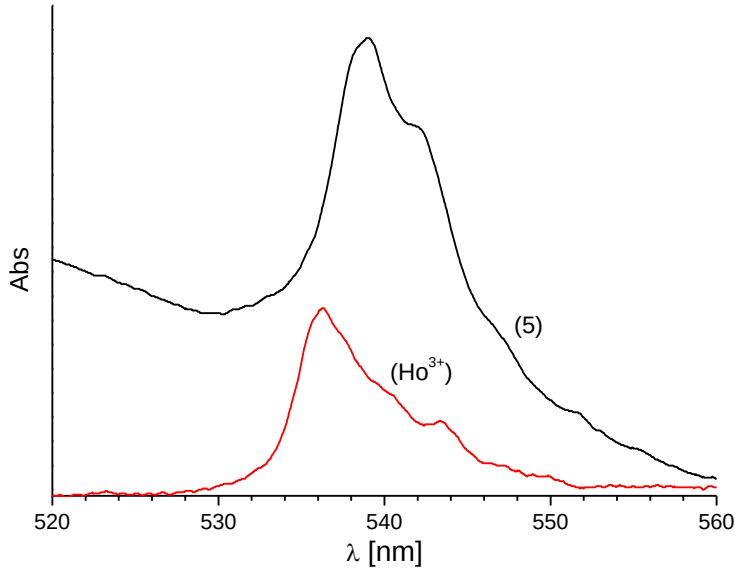


Figure S5. The absorption spectrum of Ho^{3+} ion in acetonitrile solution in $Ho(OTf)_3$ and (Ho)**5** in range $^5I_8$-$^5F_4$,$^5S_2$, c=2·× 10^{-3}.

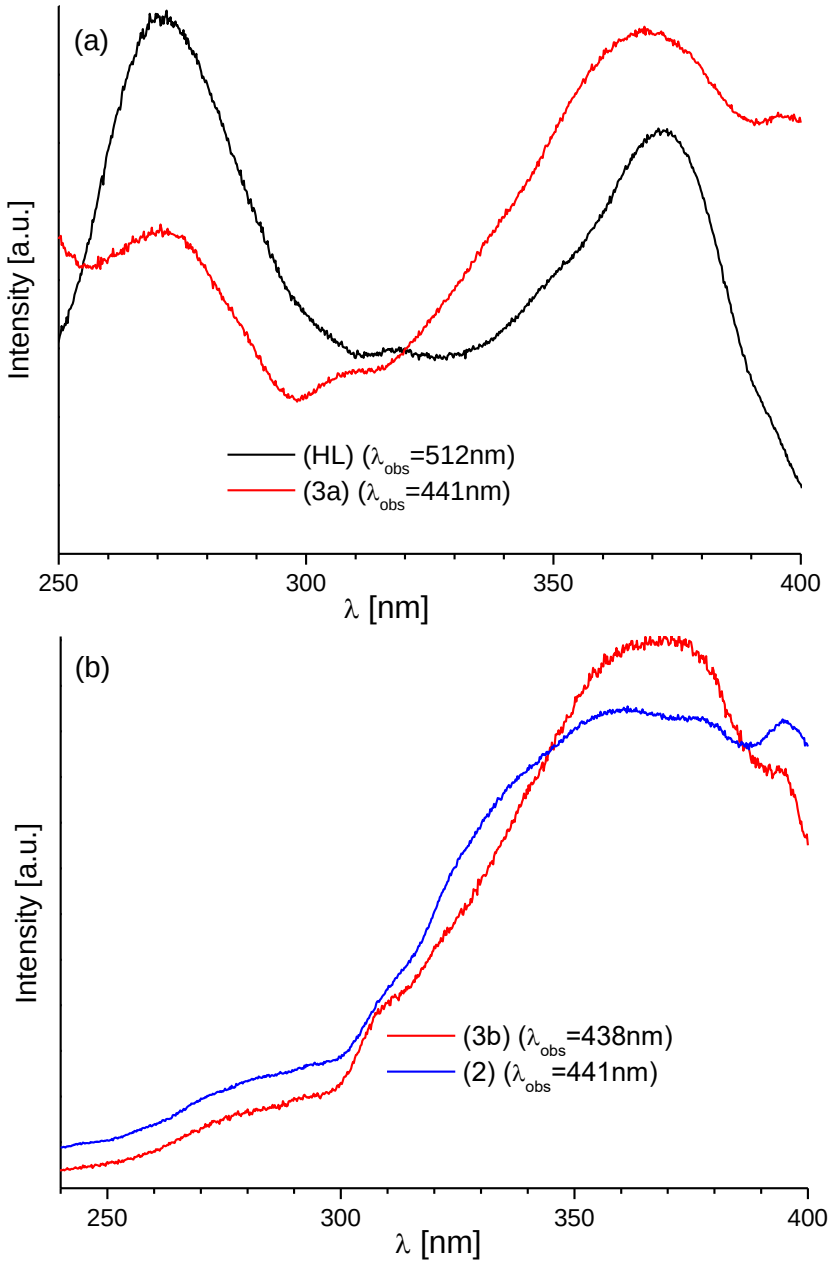


Figure S6. a–b. The excitation spectra of solid samples: (a) **HL**, **3a** and (b) **2**, **3b**.

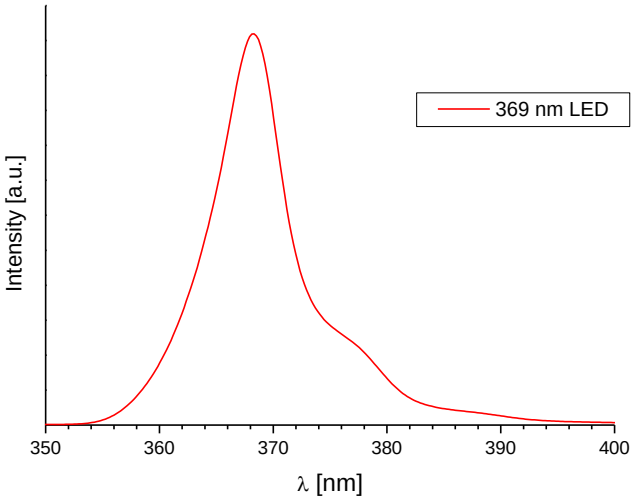


Figure S7. Spectroscopic characteristics of a 369 LED.

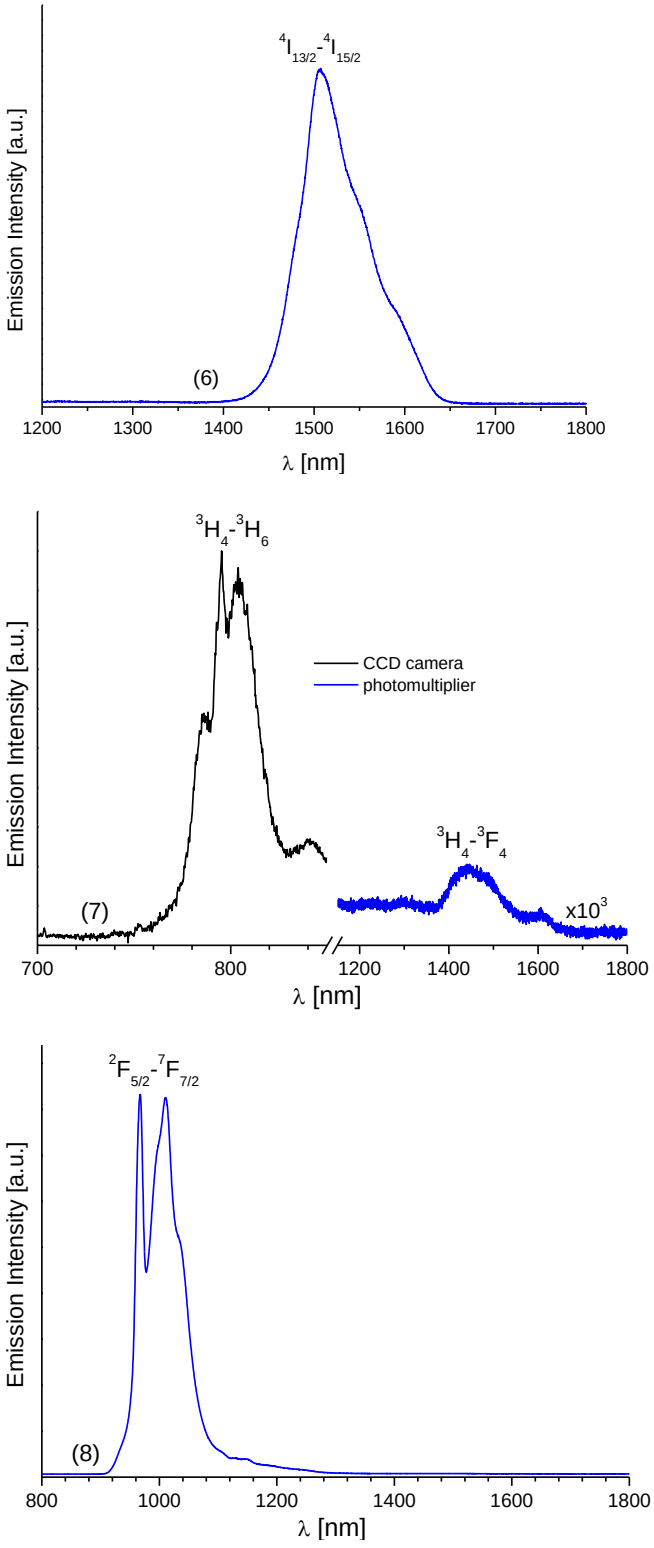


Figure S8. Photoluminescence spectra of solid samples **6**, **7** and **8** in NIR region.