Supporting Information

Heteroleptic β-diketonate Ln(III) complexes decorated by pyridyl substituted pyridazine ligand: synthesis, structure and luminescent properties.

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Content

Table S1. The crystallographic details for **1-8**, **10**, and **12**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{38}H_{22}N_4O_6F_9S_3Pr$	$C_{38}H_{22}N_4O_6F_9S_3Nd$	$C_{38}N_4O_6F_9S_3SmH_{22}$	$C_{38}H_{23}N_4O_6F_9S_3Eu$	$C_{38}H_{22}N_4O_6F_9S_3Gd$
Formula weight	1038.68	1042.01	1048.12	1050.74	1055.03
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	P2/c	P2/c
a/Å	15.0472(7)	17.4079(7)	14.8835(3)	24.2613(11)	24.2809(13)
b/Å	18.9230(10)	12.7965(5)	18.8542(4)	10.2407(5)	10.2995(7)
c/Å	15.2845(8)	19.1081(7)	15.3188(3)	16.5383(6)	16.5074(8)
α/°	90	90	90	90	90.00
β/°	95.551(4)	92.492(4)	94.9294(17)	93.893(4)	94.050(6)
γ/°	90	90	90	90	90.00
Volume/Å^3	4331.7(4)	4252.5(3)	4282.83(14)	4099.5(3)	4117.9(4)
Z	4	4	4	4	4
ρ_{calc}g/cm^3	1.593	1.628	1.626	1.702	1.702
μ/mm^{-1}	1.356	1.456	1.605	1.774	1.854
F(000)	2056.0	2060.0	2068.0	2076.0	2076.0
Crystal size/mm^3	0.28 × 0.24 × 0.22	0.28 × 0.24 × 0.18	0.34 × 0.22 × 0.16	0.28 × 0.24 × 0.18	0.34 × 0.22 × 0.16
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.356 to 55	5.892 to 55	5.664 to 54.998	6.342 to 54.998	5.2 to 55
Index ranges	$-19 \le h \le 19$, $-24 \le k \le 22$, $-18 \le l \le 19$	$-13 \le h \le 22$, $-16 \le k \le 16$, $-24 \le l \le 23$	$-19 \le h \le 10$, $-23 \le k \le 24$, $-19 \le l \le 19$	$-31 \le h \le 24$, $-12 \le k \le 13$, $-20 \le l \le 21$	$-31 \le h \le 31$, $-13 \le k \le 13$, $-21 \le l \le 11$
Reflections collected	40312	39898	19971	26576	20182
Independent reflections	9738 [R_{int} = 0.0473, R_{sigma} = 0.0393]	9743 [R_{int} = 0.0414, R_{sigma} = 0.0356]	9421 [R_{int} = 0.0296, R_{sigma} = 0.0491]	9364 [R_{int} = 0.0753, R_{sigma} = 0.0737]	9306 [R(int) = 0.0481]
Data/restraints/parameters	9738/33/499	9743/31/499	9421/34/499	9364/9/460	9306/9/476
Goodness-of-fit on F^2	1.074	1.048	1.024	1.166	1.063
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0429, wR_2 = 0.0951	R_1 = 0.0334, wR_2 = 0.0702	R_1 = 0.0356, wR_2 = 0.0716	R_1 = 0.0988, wR_2 = 0.2146	R_1 = 0.0565, wR_2 = 0.1180
Final R indexes [all data]	R_1 = 0.0615, wR_2 = 0.1125	R_1 = 0.0422, wR_2 = 0.0755	R_1 = 0.0509, wR_2 = 0.0788	R_1 = 0.1165, wR_2 = 0.2257	R_1 = 0.0767, wR_2 = 0.1287
Largest diff. peak/hole / e Å^{-3}	1.26/−1.12	1.24/−1.22	1.08/−1.15	5.51/−5.06	2.69/−1.41
CCDC number	**1530858**	**1535871**	**1530856**	**1818856**	**1818862**

	6	7	8	10	12
Empirical formula	$C_{38}H_{22}N_4O_6F_9S_3Tb$	$C_{38}H_{22}N_4O_6F_9S_3Dy$	$C_{38}H_{22}N_4O_6F_9S_3Ho$	$C_{38}H_{22}N_4O_6F_9S_3Tm$	$C_{38}H_{22}N_4O_6F_9S_3Lu$
Formula weight	1056.70	1060.27	1062.70	1066.70	1072.75
Temperature/K	100 (2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	10.2761(3)	10.2806(8)	10.3064(4)	14.7870(4)	14.7615(6)
b/Å	21.4121(9)	21.385(3)	21.3468(7)	18.7993(5)	18.7778(9)
c/Å	18.9121(7)	18.8697(16)	18.8868(7)	15.3065(3)	15.287(2)
α/°	90.00	90	90	90	90.00
β/°	104.036(4)	103.894(10)	104.004(4)	95.358(2)	94.459(8)
γ/°	90.00	90	90	90	90.00
Volume/Å^3	4037.1(3)	4027.1(7)	4031.8(3)	4236.41(17)	4224.6(6)
Z	4	4	4	4	4
ρ_{calc}g/cm^3	1.739	1.749	1.751	1.672	1.687
μ/mm^{-1}	10.903	12.221	5.957	6.103	2.574
F(000)	2080.0	2084.0	2088.0	2096.0	2104.0
Crystal size/mm^3	0.30 × 0.24 × 0.16	0.28 × 0.22 × 0.14	0.18 × 0.14 × 0.10	0.32 × 0.24 × 0.18	0.32 × 0.18 × 0.14
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.34 to 139.98	6.354 to 139.984	6.356 to 139.996	7.468 to 144.98	5.34 to 55
Index ranges	$-11 \le h \le 12$, $-26 \le k \le 26$, $-23 \le l \le 20$	$-12 \le h \le 10$, $-26 \le k \le 26$, $-23 \le l \le 23$	$-12 \le h \le 11$, $-20 \le k \le 26$, $-23 \le l \le 21$	$-18 \le h \le 17$, $-23 \le k \le 22$, $-18 \le l \le 9$	$-19 \le h \le 17$, $-24 \le k \le 14$, $-19 \le l \le 17$
Reflections collected	29434	28131	12909	17128	19260
Independent reflections	7605 [R(int) = 0.0986]	7578 [R_{int} = 0.2303, R_{sigma} = 0.2197]	7284 [R_{int} = 0.1050, R_{sigma} = 0.0978]	8235 [R_{int} = 0.0543, R_{sigma} = 0.0582]	9544 [R(int) = 0.0373]
Data/restraints/parameters	7605/24/475	7578/21/493	7284/438/523	8235/30/499	9544/5/485
Goodness-of-fit on F^2	1.151	1.026	1.832	1.048	1.058
Final R indexes [I ≥ 2σ (I)]	R_1 = 0.0920, wR_2 = 0.1996	R_1 = 0.0976, wR_2 = 0.2099	R_1 = 0.1593, wR_2 = 0.4291	R_1 = 0.0522, wR_2 = 0.1373	R_1 = 0.0470, wR_2 = 0.1133
Final R indexes [all data]	R_1 = 0.1047, wR_2 = 0.2061	R_1 = 0.1922, wR_2 = 0.2691	R_1 = 0.1849, wR_2 = 0.4484	R_1 = 0.0622, wR_2 = 0.1439	R_1 = 0.0591, wR_2 = 0.1201
Largest diff. peak/hole / e Å^{-3}	2.59/−1.52	2.08/−2.05	4.55/−6.69	2.18/−1.39	2.40/−1.78
CCDC number	**1818863**	**1818872**	**1851088**	**1530857**	**1818883**

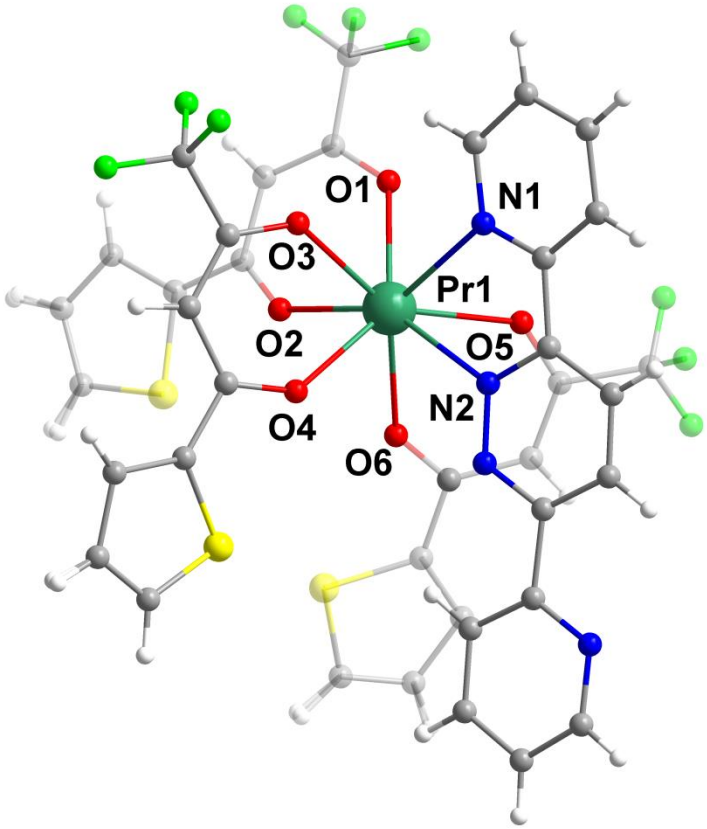


Figure S1. Molecular structure of **1** (colour legend: praseodymium sea green, oxygen red, nitrogen blue, carbon grey, sulphur yellow, fluorine bright green, hydrogen white). Selected structure parameters (bond lengths, Å; angles, °): Pr1–O1 2.415(3); Pr1–O2 2.399(3); Pr1–O3 2.438(3); Pr1–N1 2.667(3); Pr1–O4 2.416(3); Pr1–O5 2.426(3); Pr1–O6 2.420(3); Pr1–N2 2.623(3); O1–Pr1–O2 71.15(10); O3–Pr1–O4 69.82(10); O5–Pr1–O6 70.46(9); N1–Pr1–N2 59.96(11).

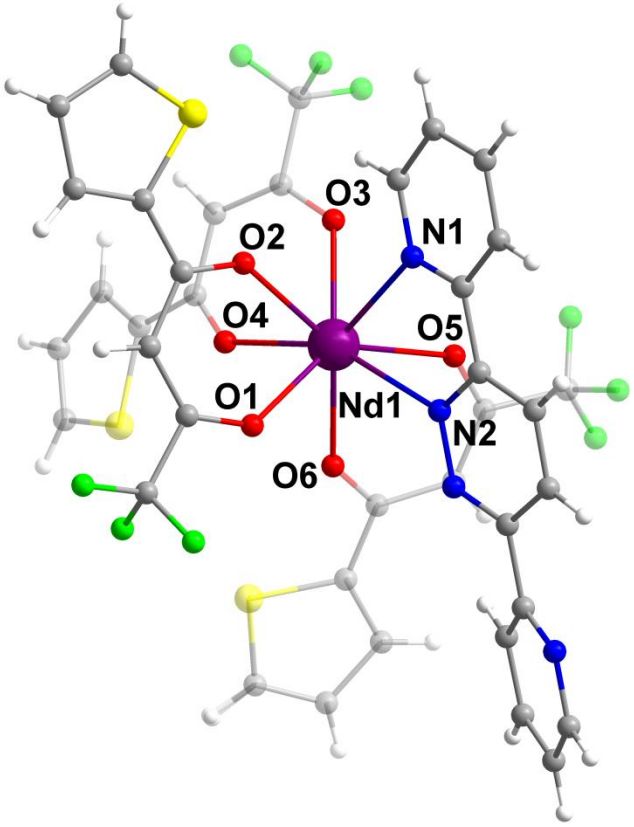


Figure S2. Molecular structure of **2** (colour legend: neodymium violet, oxygen red, nitrogen blue, carbon grey, sulphur yellow, fluorine bright green, hydrogen white). Selected structure parameters (bond lengths, Å; angles, °): Nd1–O1 2.376(2); Nd1–O2 2.439(2); Nd1–O3 2.409(2); Nd1–N1 2.654(2); Nd1–O4 2.403(2); Nd1–O5 2.414(2); Nd1–O6 2.3995(19); Nd1–N2 2.650(2); O1–Nd1–O2 70.31(7); O3–Nd1–O4 71.39(7); O5–Nd1–O6 70.86(7); N1–Nd1–N2 60.42(7).

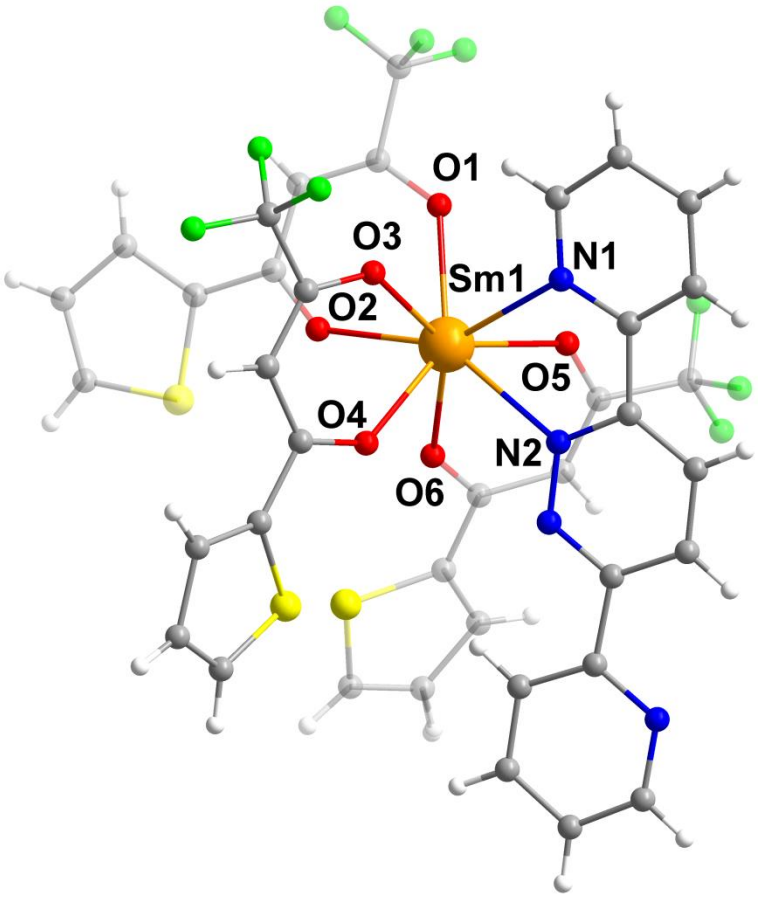


Figure S3. Molecular structure of **3** (colour legend: samarium light orange, oxygen red, nitrogen blue, carbon grey, sulphur yellow, fluorine bright green, hydrogen white). Sm1–O1 2.356(2); Sm1–O2 2.349(2); Sm1–O3 2.392(2); Sm1–N1 2.600(3); Sm1–O4 2.365(2); Sm1–O5 2.380(2); Sm1–O6 2.365(2); Sm1–N2 2.571(3); O1-Sm1-O2 72.59(8); O3-Sm1-O4 71.24(8); O5-Sm1-O6 72.12(8);N1-Sm1-N2 61.67(9).

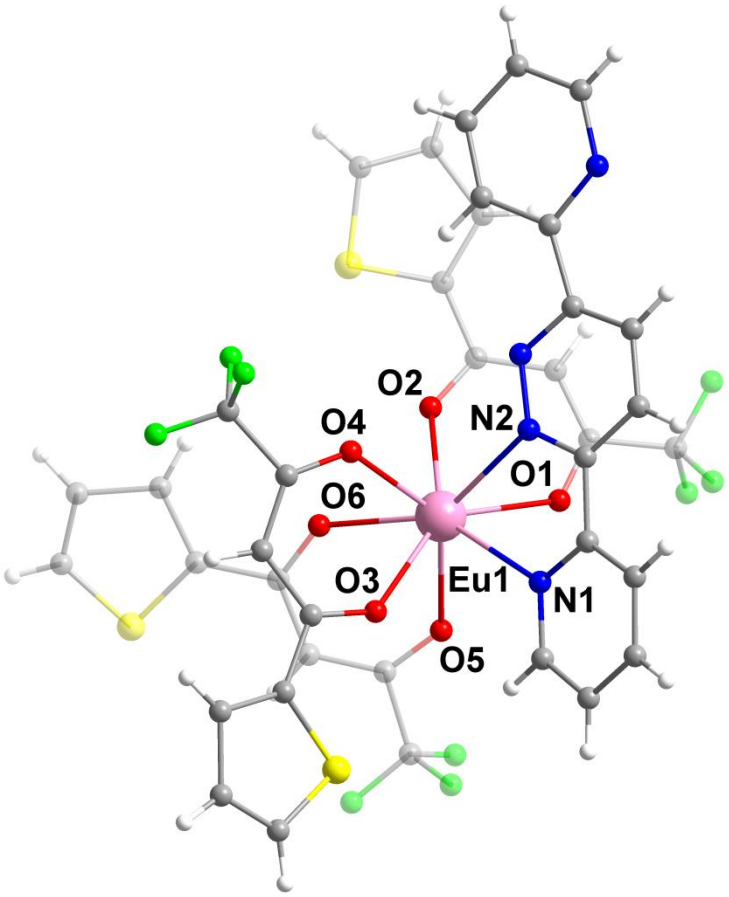


Figure S4. Molecular structure of **4** (colour legend: europium rose, oxygen red, nitrogen blue, carbon grey, sulphur yellow, fluorine bright green, hydrogen white). Eu1–O1 2.408(7); Eu1–O2 2.351(7); Eu1–O3 2.388(7); Eu1–N1 2.590(8); Eu1–O4 2.392(7); Eu1–O5 2.384(7); Eu1–O6 2.385(7); Eu1–N2 2.579(8); O1–Eu1–O2 70.8(2); O3–Eu1–O4 71.9(2); O5–Eu1–O6 71.9(2);N1–Eu1–N2 61.8(3).

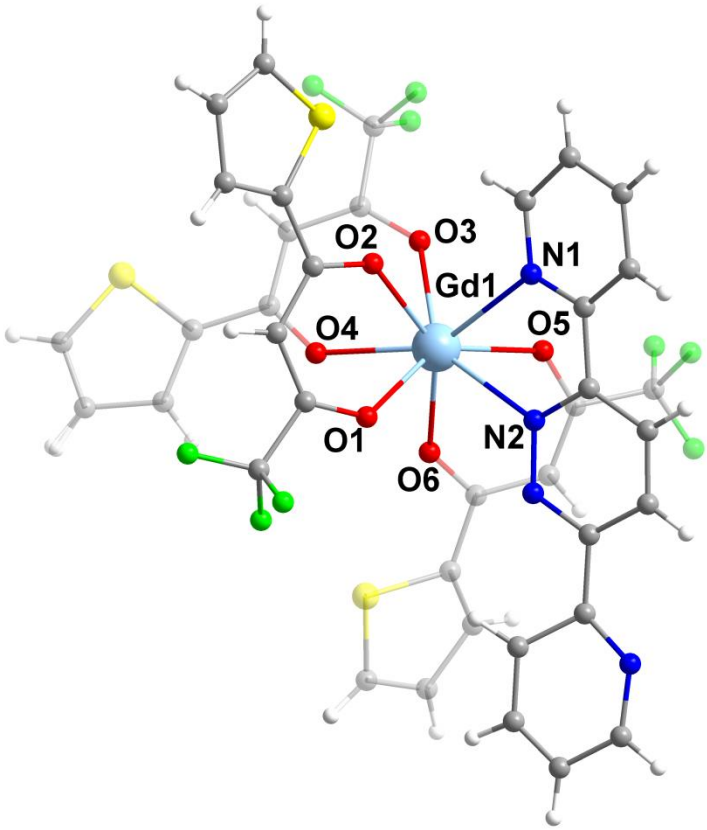


Figure S5. Molecular structure of **5** (colour legend: gadolinium pale blue, oxygen red, nitrogen blue, carbon grey, sulphur yellow, fluorine bright green, hydrogen white). Selected structure parameters (bond lengths, Å; angles, °): Gd1–O1 2.358(4); Gd1–O2 2.368(4); Gd1–O3 2.346(7); Gd1–N1 2.580(4); Gd1–O4 2.368(4); Gd1–O5 2.405(4); Gd1–O6 2.328(4); Gd1–N2 2.566(5); O1–Gd1–O2 72.54(13); O3–Gd1–O4 72.95(13); O5–Gd1–O6 71.64(13); N1–Gd1–N2 62.39(15).

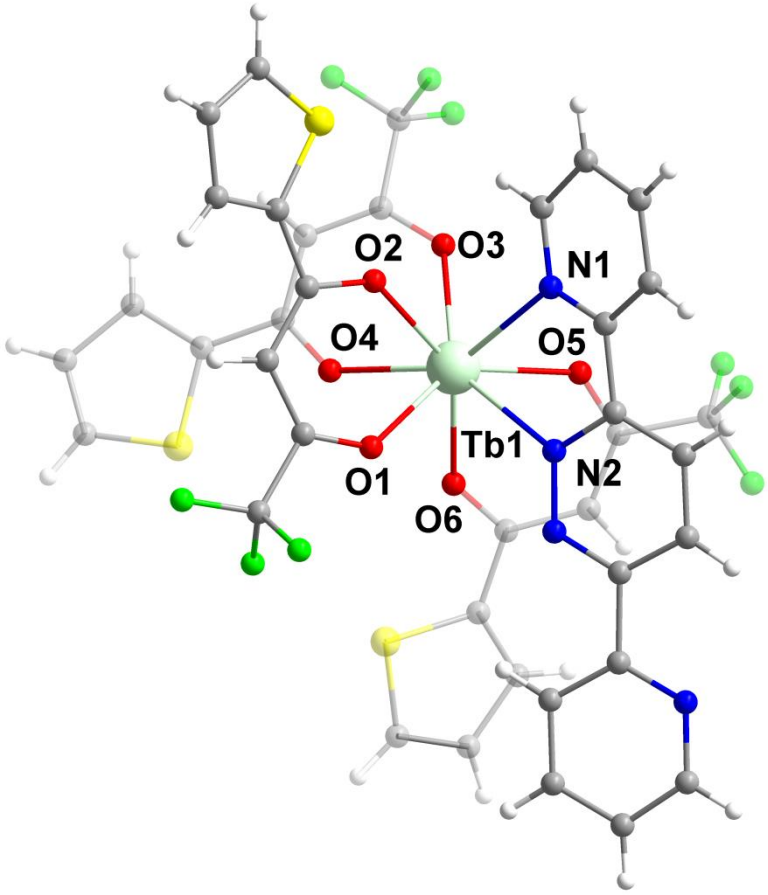


Figure S6. Molecular structure of **6** (colour legend: terbium light green, oxygen red, nitrogen blue, carbon grey, sulphur yellow, fluorine bright green, hydrogen white). Selected structure parameters (bond lengths, Å; angles, °): Tb1–O1 2.324(7); Tb1–O2 2.351(6); Tb1–O3 2.346(7); Tb1–N1 2.550(9); Tb1–O4 2.346(7); Tb1–O5 2.355(7); Tb1–O6 2.265(6); Tb1–N2 2.594(9); O1–Tb1–O2 71.8(2); O3–Tb1–O4 71.8(2); O5–Tb1–O6 73.7(2); N1–Tb1–N2 63.3(3).

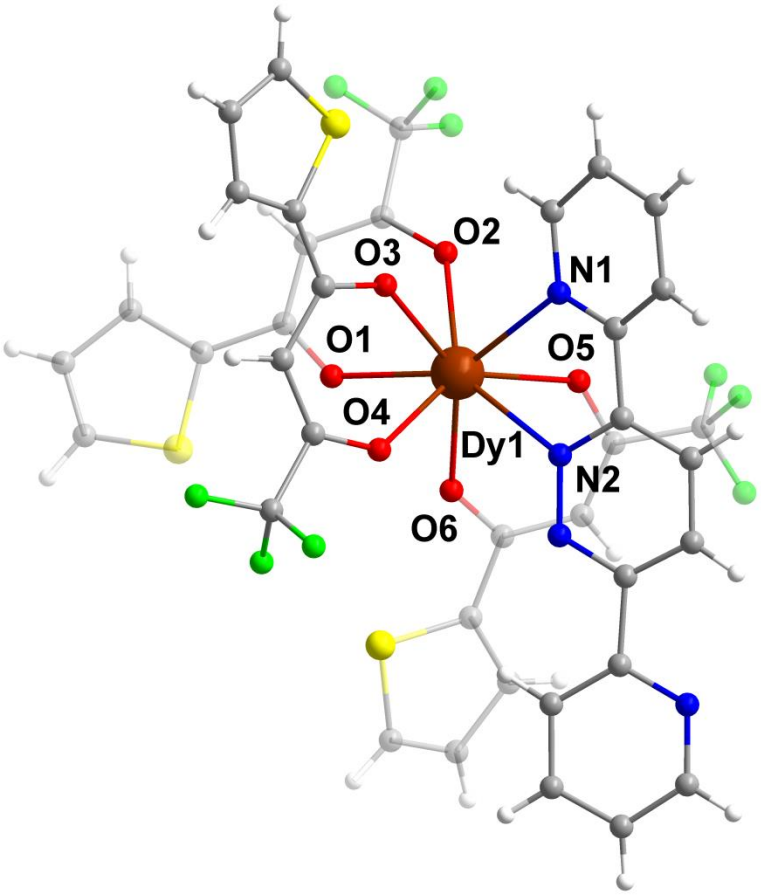


Figure S7. Molecular structure of **7** (colour legend: dysprosium brown, oxygen red, nitrogen blue, carbon grey, sulphur yellow, fluorine bright green, hydrogen white). Selected structure parameters (bond lengths, Å; angles, °): Dy1–O1 2.331(10); Dy1–O2 2.355(10); Dy1–O3 2.335(8); Dy1–N1 2.527(11); Dy1–O4 2.338(9); Dy1–O5 2.348(8); Dy1–O6 2.282(9); Dy1–N2 2.588(11); O1–Dy1–O2 73.2(3); O3–Dy1–O4 71.6(3); O5–Dy1–O6 73.9(3); N1–Dy1–N2 63.5(4).

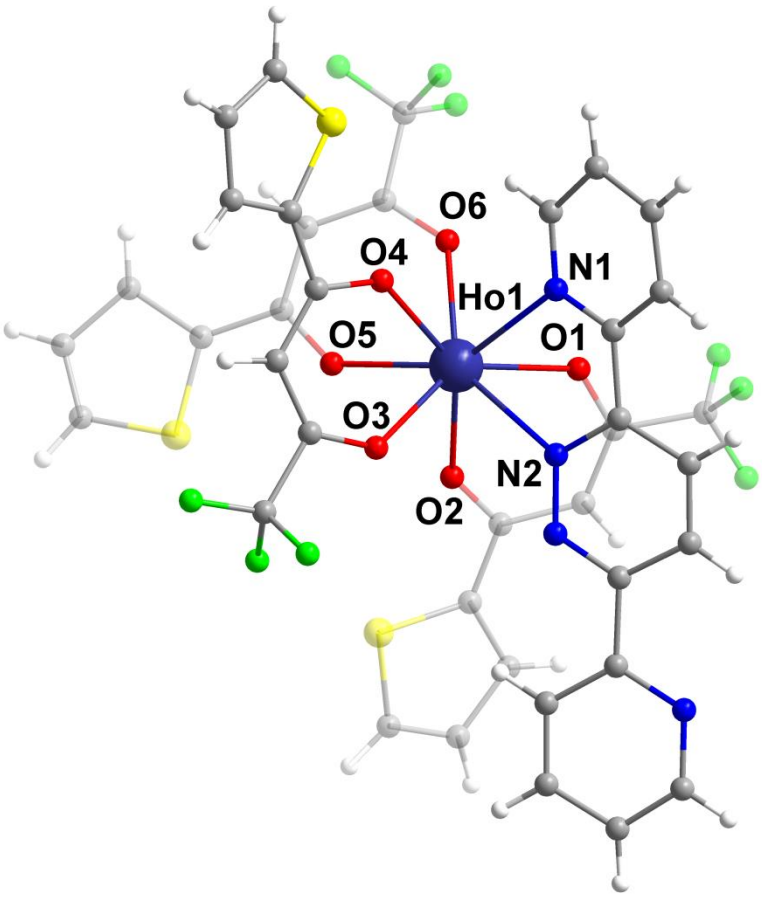


Figure S8. Molecular structure of **8** (colour legend: holmium indigo, oxygen red, nitrogen blue, carbon grey, sulphur yellow, fluorine bright green, hydrogen white). Selected structure parameters (bond lengths, Å; angles, °): Ho1–O1 2.330(9); Ho1–O2 2.245(9); Ho1–O3 2.310(9); Ho1–N1 2.524(12); Ho1–O4 2.346(9); Ho1–O5 2.312(8); Ho1–O6 2.334(9); Ho1–N2 2.570(11); O1–Ho1–O2 73.5(3); O3–Ho1–O4 72.5(3); O5–Ho1–O6 73.4(3); N1–Ho1–N2 64.8(4).

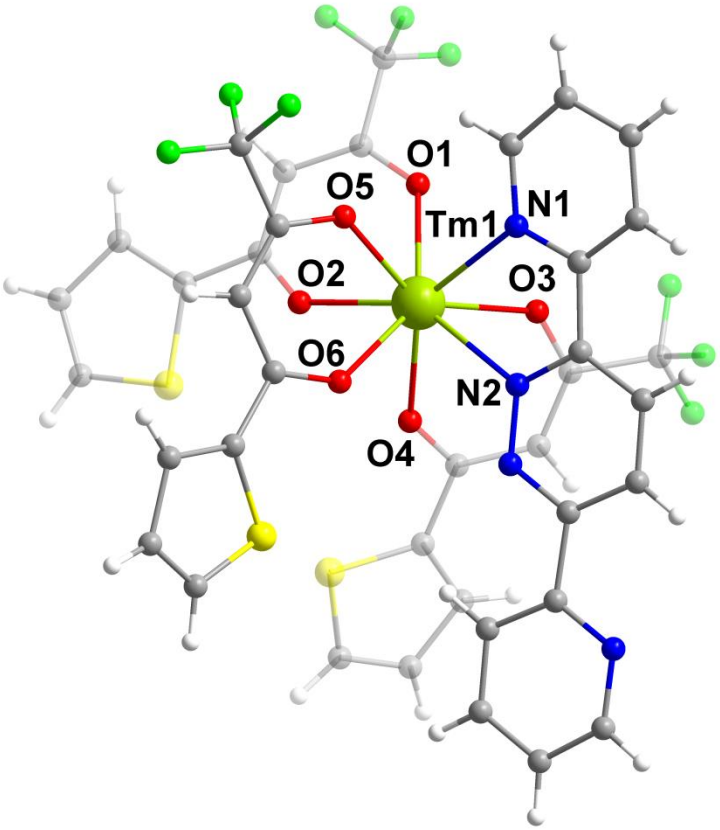


Figure S9. Molecular structure of **10** (colour legend: thulium lime, oxygen red, nitrogen blue, carbon grey, sulphur yellow, fluorine bright green, hydrogen white). Selected structure parameters (bond lengths, Å; angles, °): Tm1–O1 2.280(3); Tm1–O2 2.281(3); Tm1–O3 2.311(3); Tm1–N1 2.492(4); Tm1–O4 2.279(3); Tm1–O5 2.310(3); Tm1–O6 2.297(3); Tm1–N2 2.498(4); O1–Tm1–O2 74.64(12); O3–Tm1–O4 74.50(11); O5–Tm1–O6 72.67(12); N1–Tm1–N2 63.67(13).

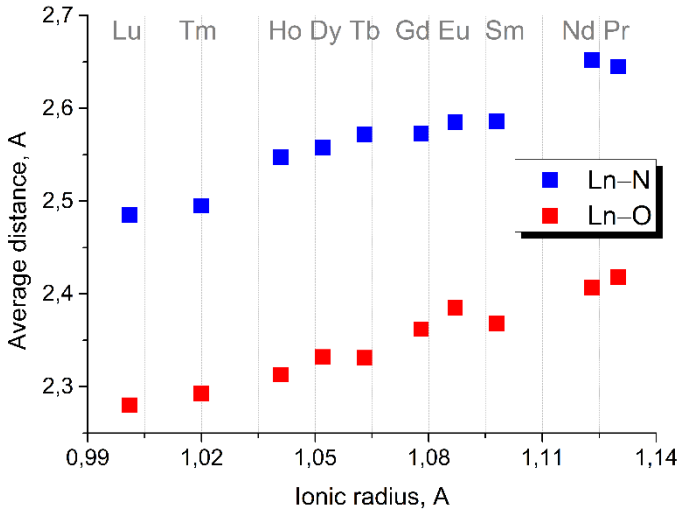
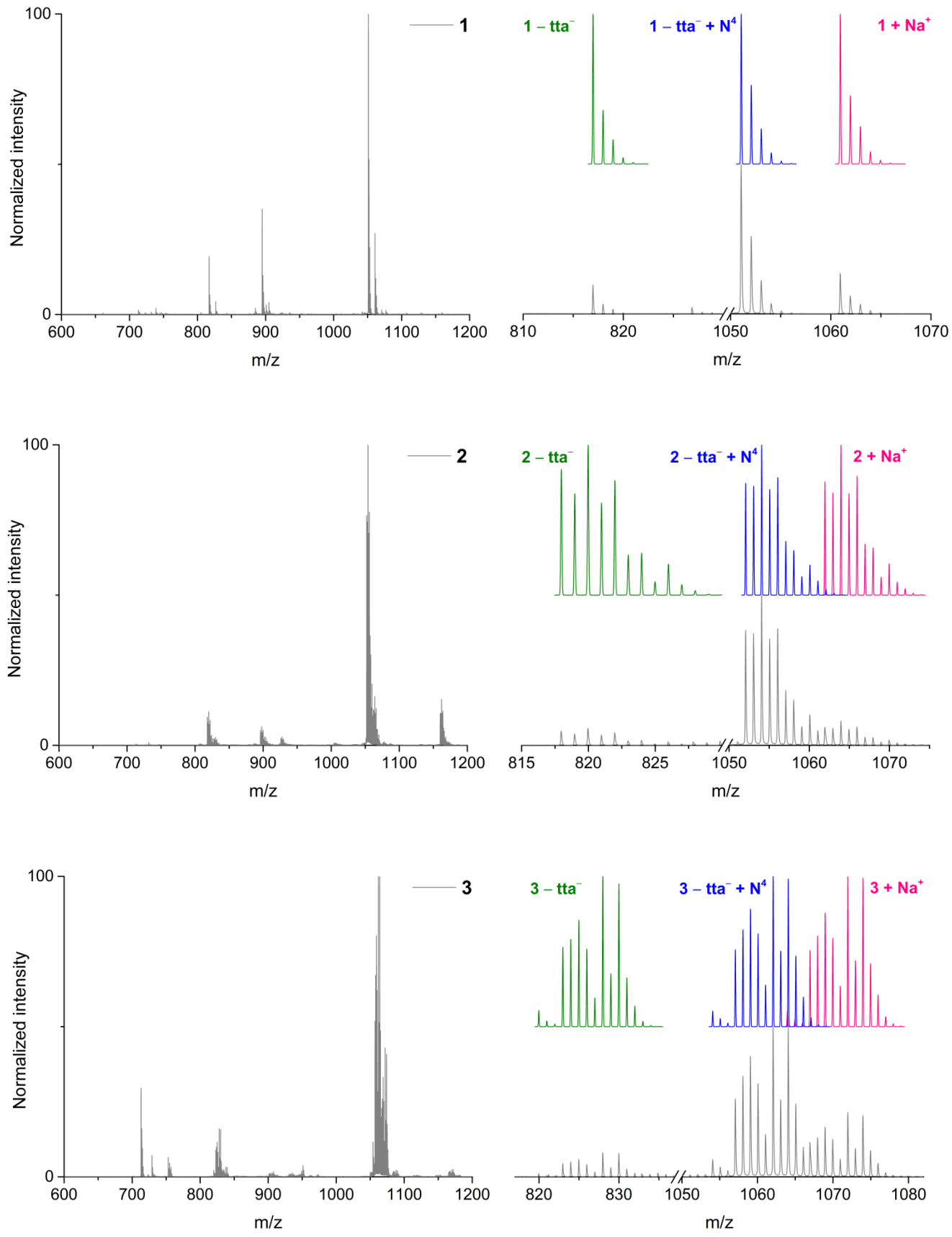
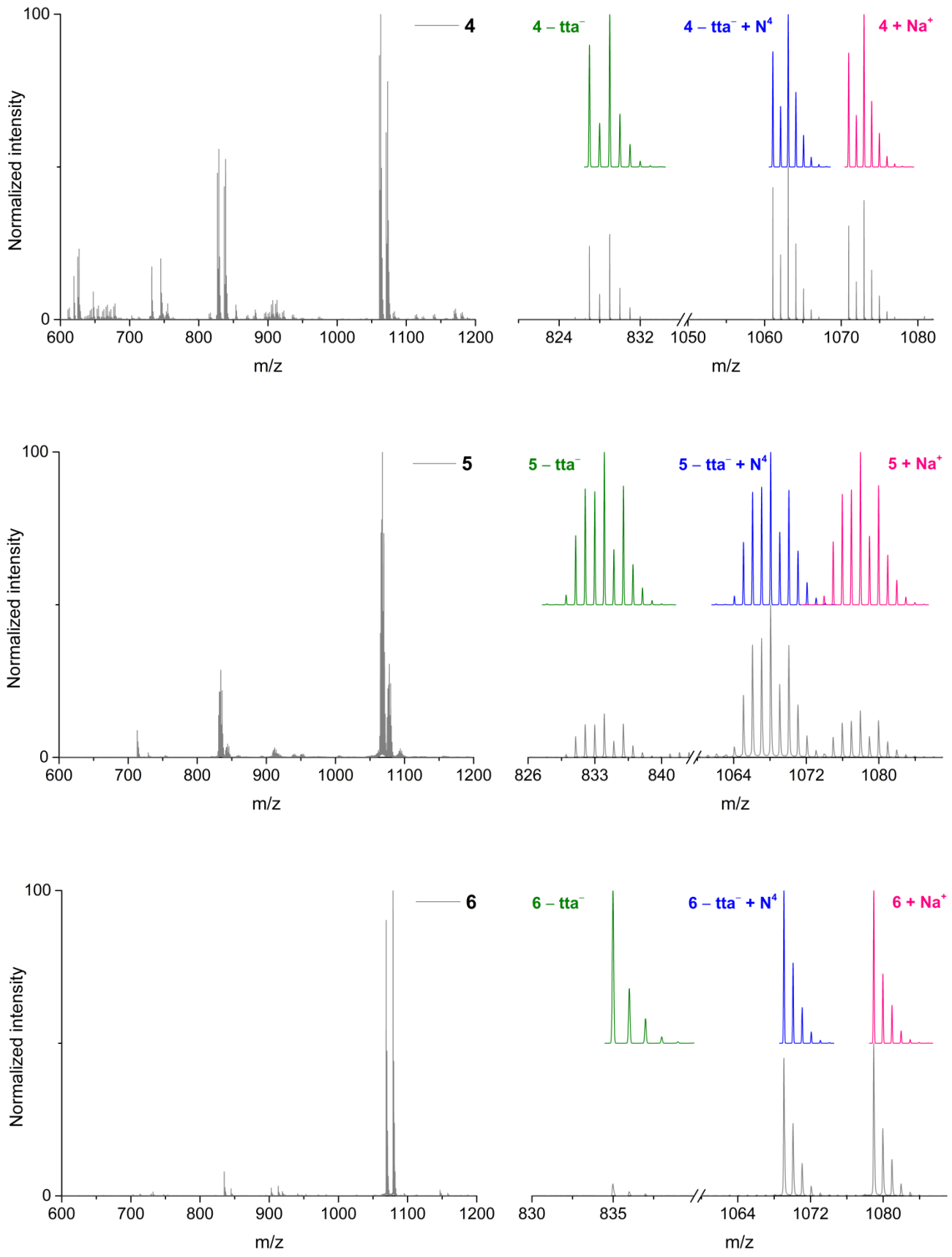
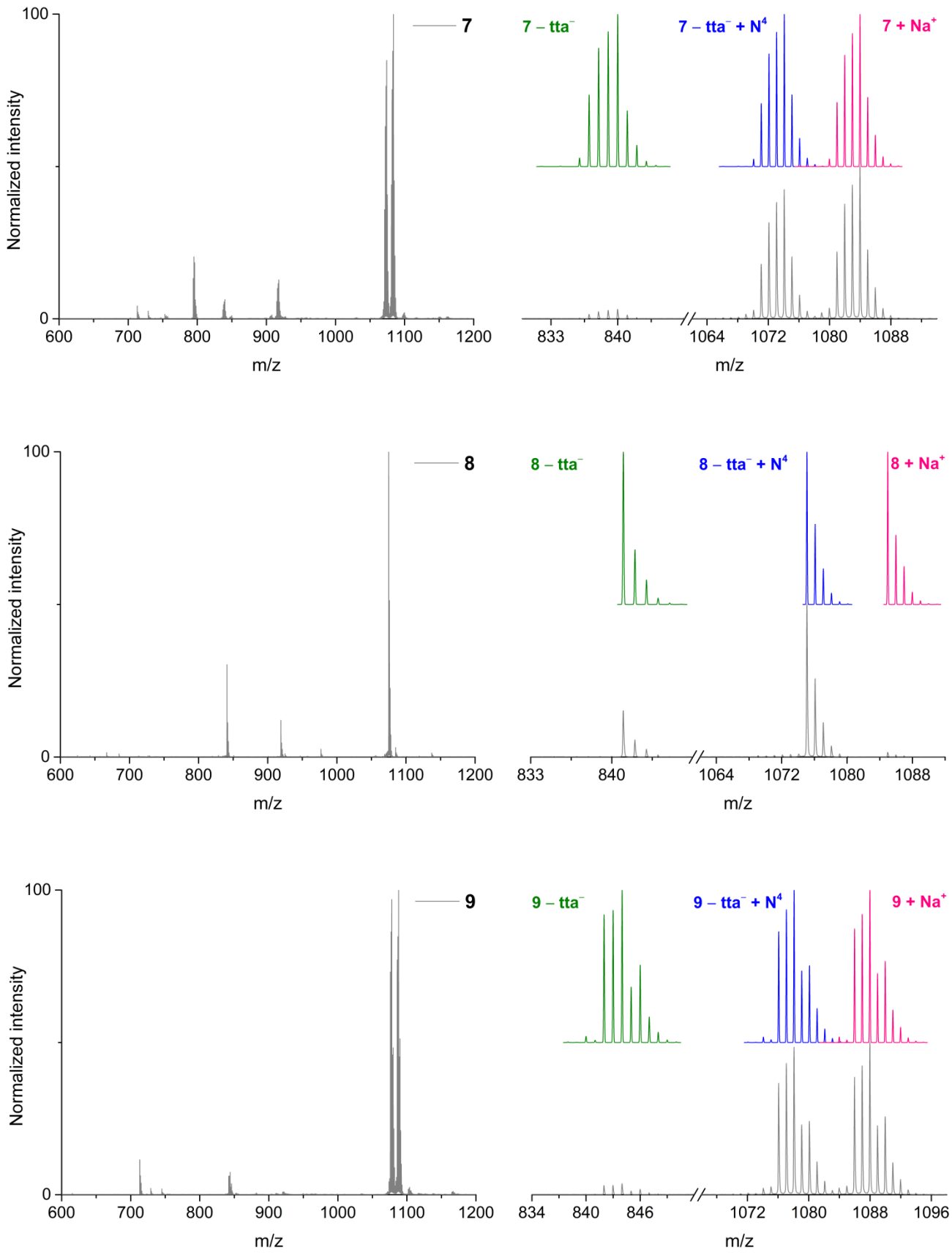


Figure S10. Dependence of average Ln−N and Ln−O distances on ionic radii of Ln(III) in [Ln(**tta**)$_3$(**dppn**)].


1
1 – tta⁻
1 – tta⁻ + N⁴
1 + Na⁺
2
2 – tta⁻
2 – tta⁻ + N⁴
2 + Na⁺
3
3 – tta⁻
3 – tta⁻ + N⁴
3 + Na⁺
Normalized intensity
m/z


4
4 – tta⁻
4 – tta⁻ + N⁴
4 + Na⁺
5
5 – tta⁻
5 – tta⁻ + N⁴
5 + Na⁺
6
6 – tta⁻
6 – tta⁻ + N⁴
6 + Na⁺
Normalized intensity
m/z


7
7 – tta⁻
7 – tta⁻ + N⁴
7 + Na⁺
8
8 – tta⁻
8 – tta⁻ + N⁴
8 + Na⁺
9
9 – tta⁻
9 – tta⁻ + N⁴
9 + Na⁺
Normalized intensity
m/z

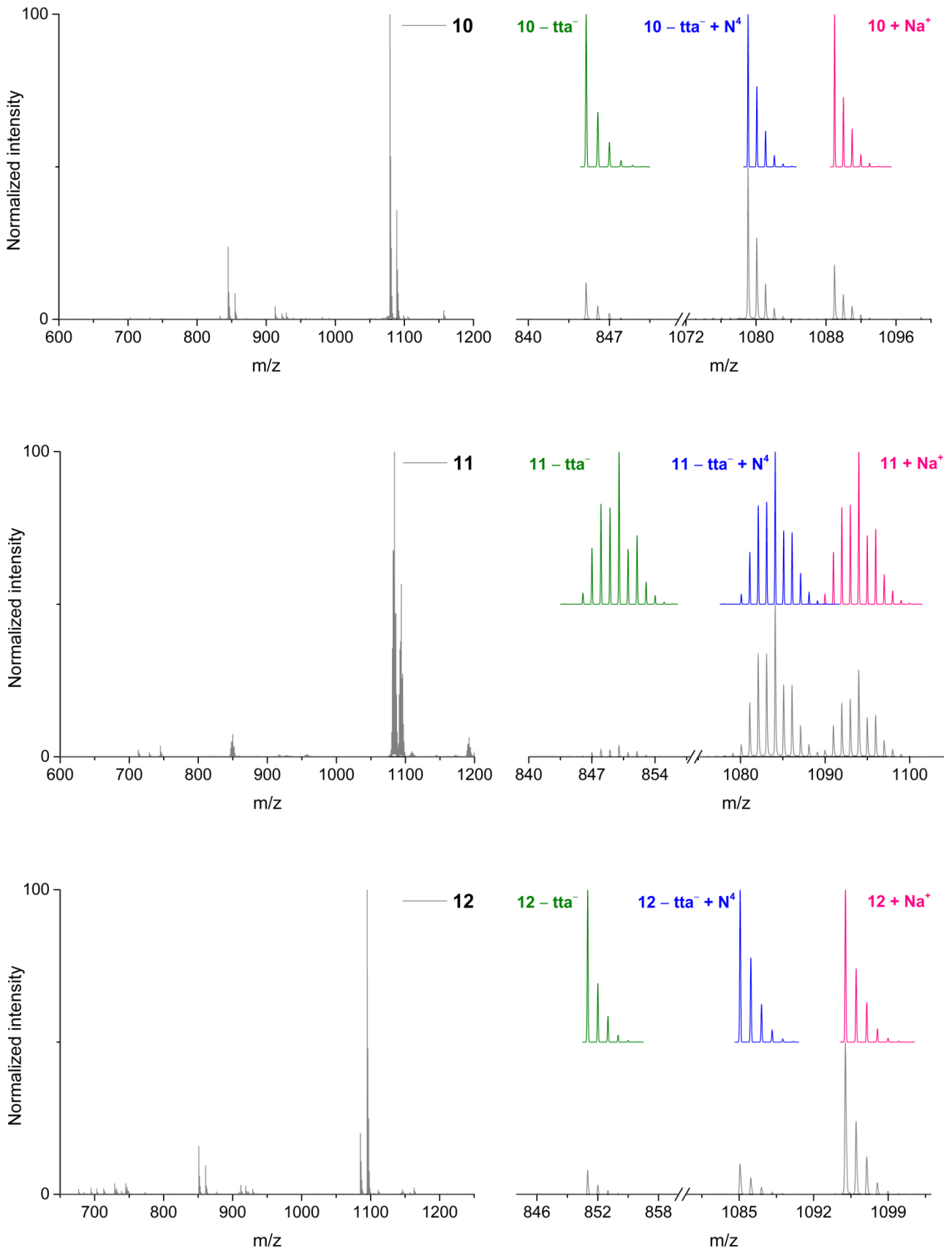


Figure S11. Experimental (grey) ESI$^+$ MS spectra of **1-12** and simulated (olive, blue, and pink) isotopic patterns of the most intensive signals; **N^4** = **dppn**.

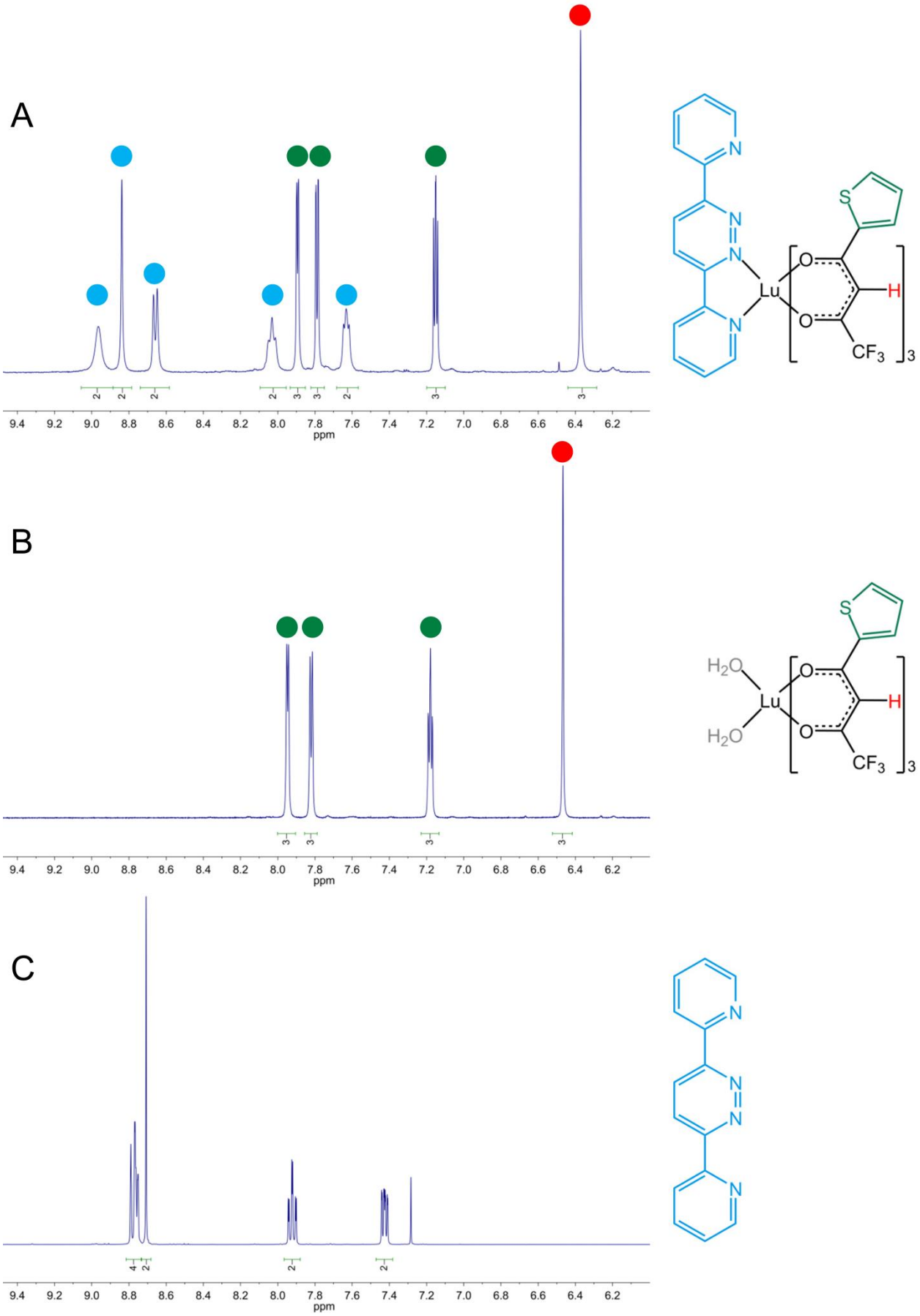


Figure S12. ^{1}H NMR spectra of (A) **12** (d_6-acetone), (B) [Lu(**tta**)$_3$(H_2O)$_n$] (d_6-acetone), and (C) free **dppn** ($CDCl_3$).

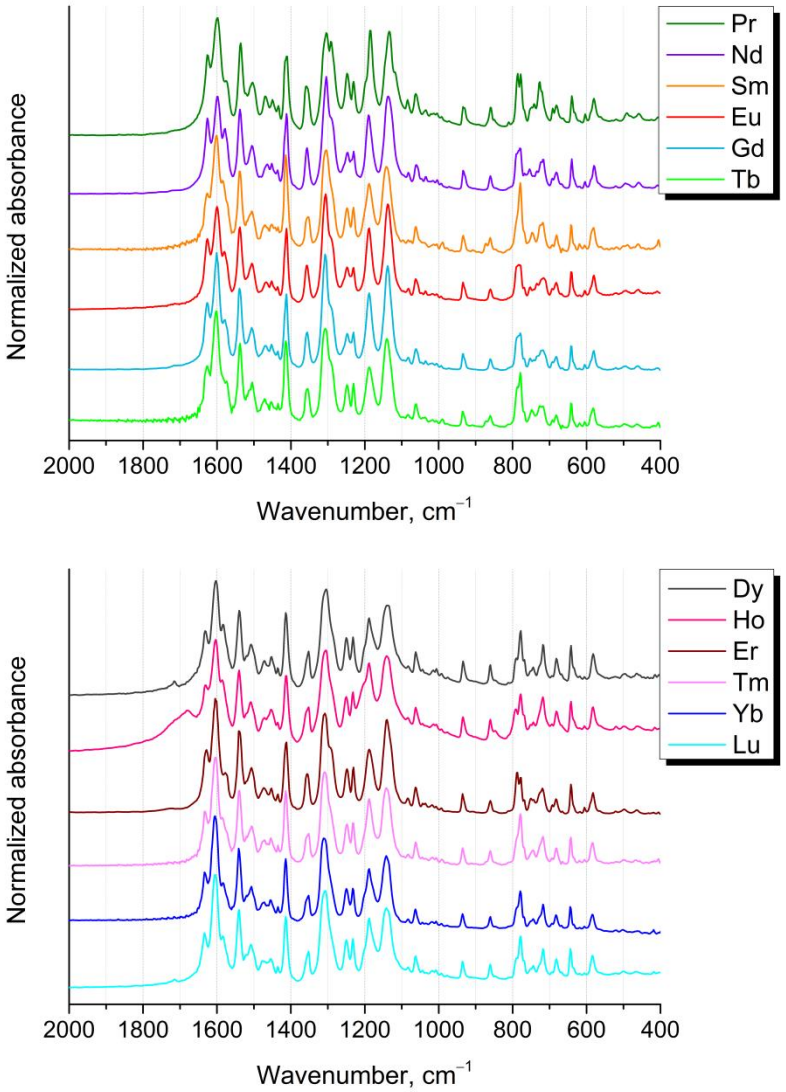


Figure S13. FTIR spectra of **1-12** in fingerprint region (KBr pills).

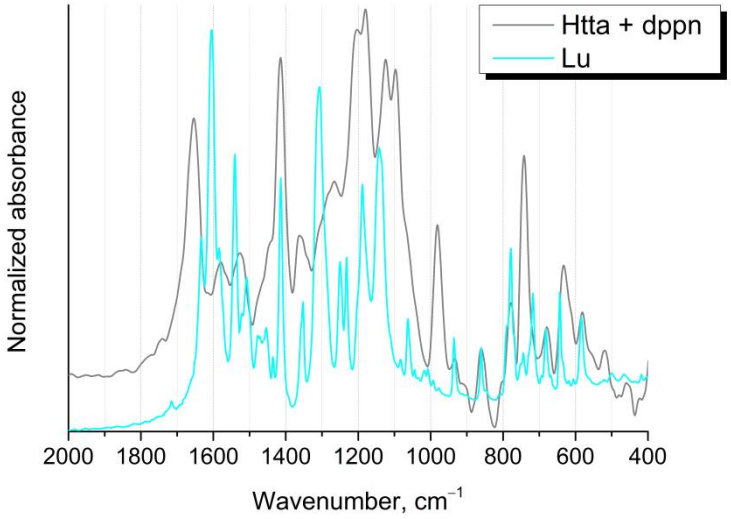


Figure S14. FTIR spectra of **12** and mixture of free ligands H**tta** + **dppn** in fingerprint region (KBr pills).

Table S2. The lifetime of the excited states and the quantum yield of **2-4**, **11** (powder samples, λ_{exct} = 351 nm).

	Ln(III)	Level	Energy of level, cm^{-1}	τ_{av}, µs		Φ_{exp}, %
				r.t.	77 K	(r.t.)
3	Sm	$^4G_{5/2}$	17860	69±3	62±3	18±1
4	Eu	$^5D_1$	18590	0.65±0.03	1.7±0.1	37±3
		$^5D_0$	17210	650±40*	660±40*	
2	Nd	$^4F_{3/2}$	11490	1.19±0.05	1.20±0.05	0.6±0.1
11	Yb	$^2F_{5/2}$	10260	10.2±0.5	10.4±0.5	0.47±0.1

* There is a growing portion on the afterglow curve. For details, see the main text.

Table S3. The relative contribution to the emission spectrum of **4** from the Eu(III) transitions spectral lines.

Transition	Relative intensity
$^5D_0 \rightarrow {}^7F_0$	0.14
$^5D_0 \rightarrow {}^7F_1$	1
$^5D_0 \rightarrow {}^7F_2$	10.8
$^5D_0 \rightarrow {}^7F_3$	0.55
$^5D_0 \rightarrow {}^7F_4$	2.8
$^5D_0 \rightarrow {}^7F_5$	0.15
$^5D_0 \rightarrow {}^7F_6$	0.06
$^5D_1 \rightarrow {}^7F_0$	0.006
$T_1 \rightarrow S_0$	<0.01

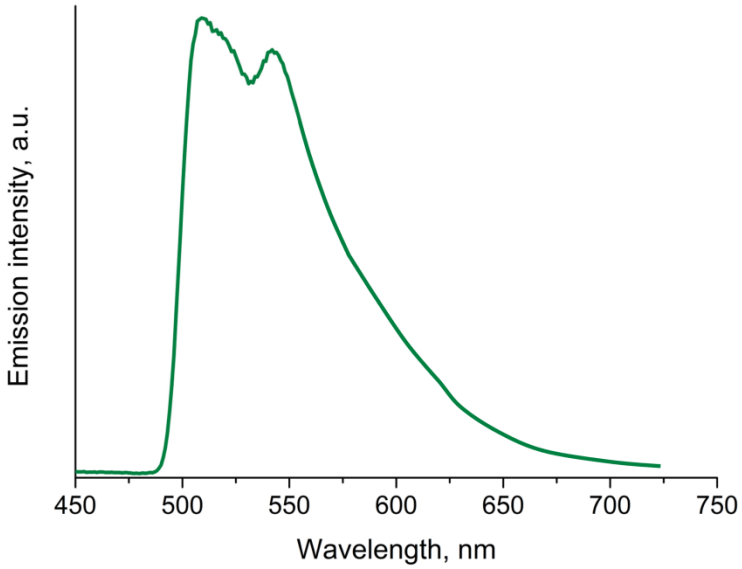


Figure S15. Emission spectra of [Gd(NO_3)$_3$(**dppn**)] in solid state at 78 K, λ_{exct} = 351 nm.

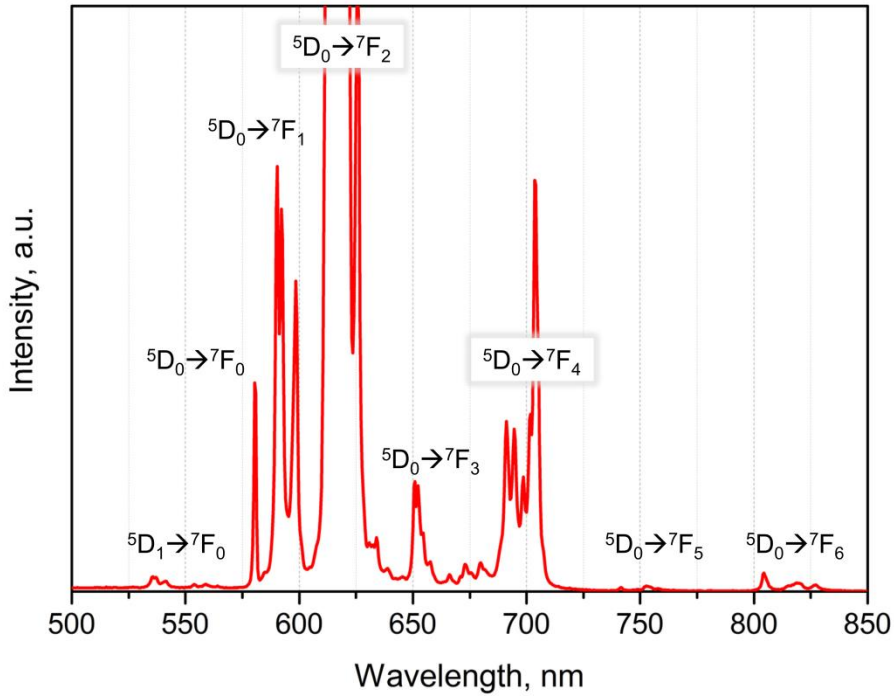


Figure S16. Eu(III) f-f transitions in photoemission spectrum of **4**, 78 K, λ_{exct} = 351 nm.

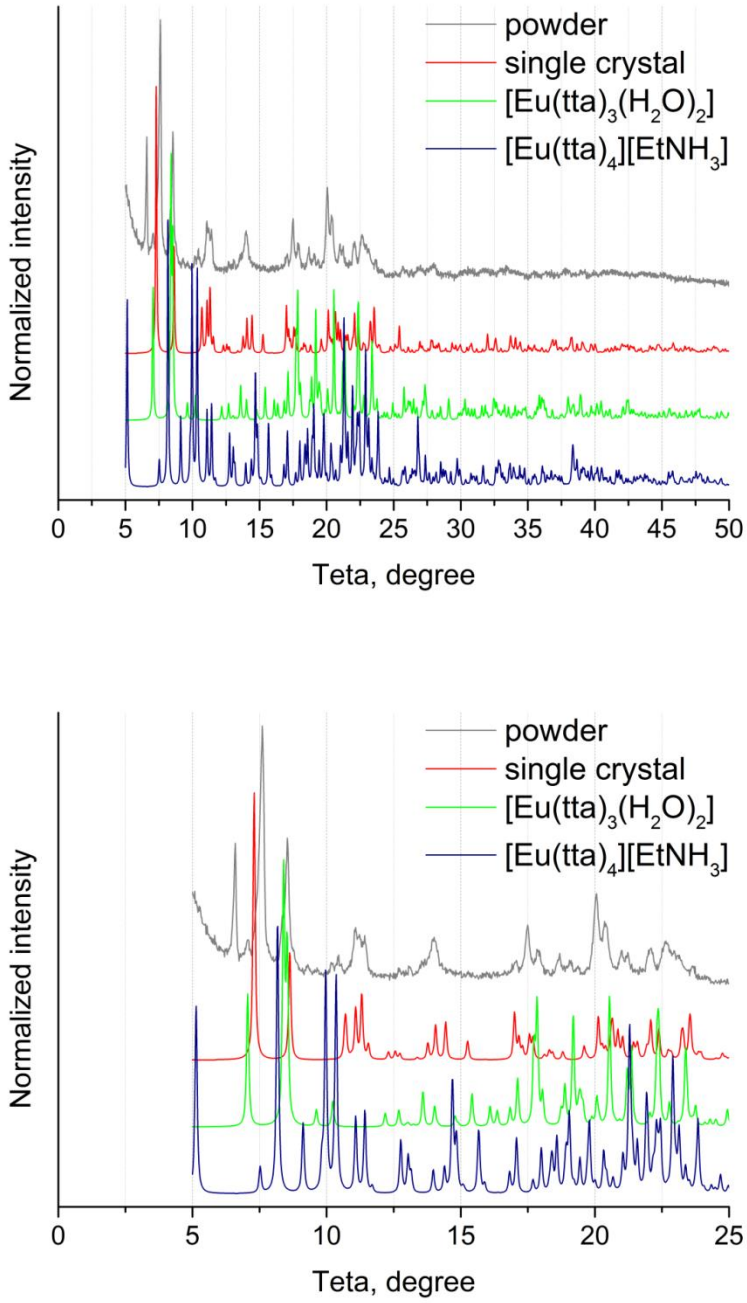


Figure S17. Powder patterns for **4** (powder and single crystal), $[Eu(tta)_3(H_2O)_2]$[1] and $[Eu(tta)_4][EtNH_3]$.[2]

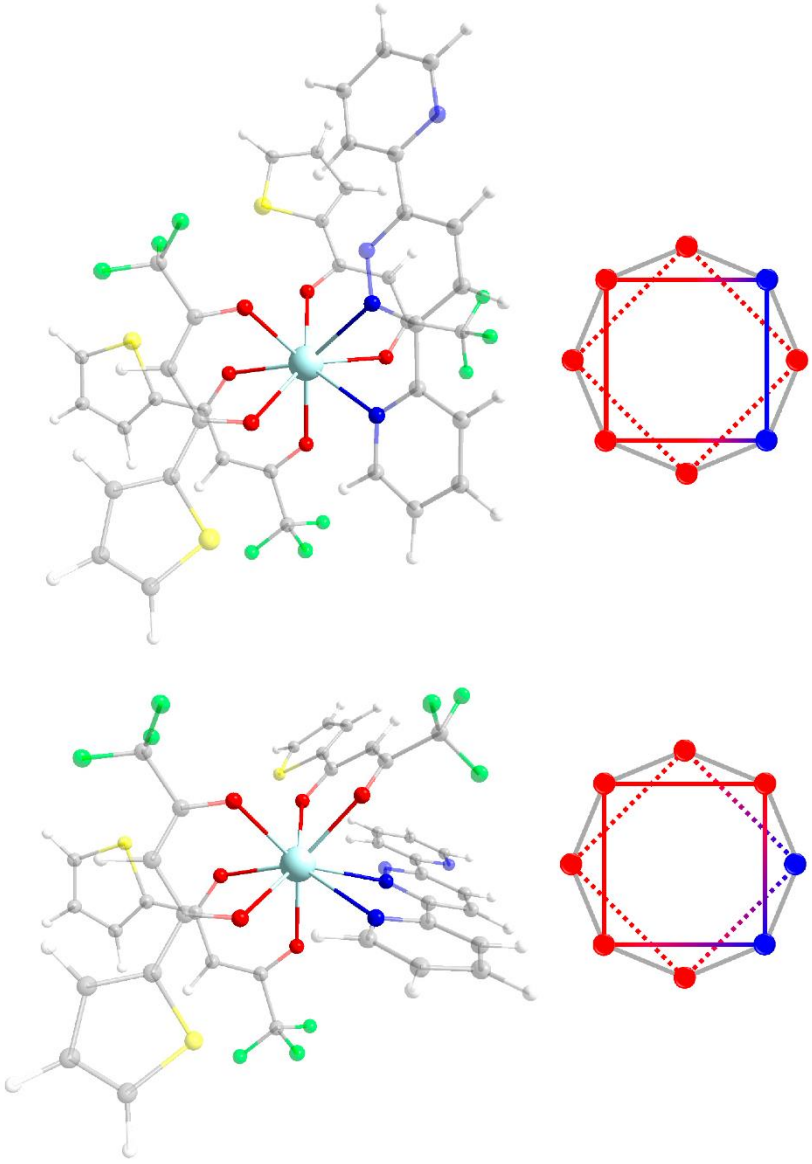
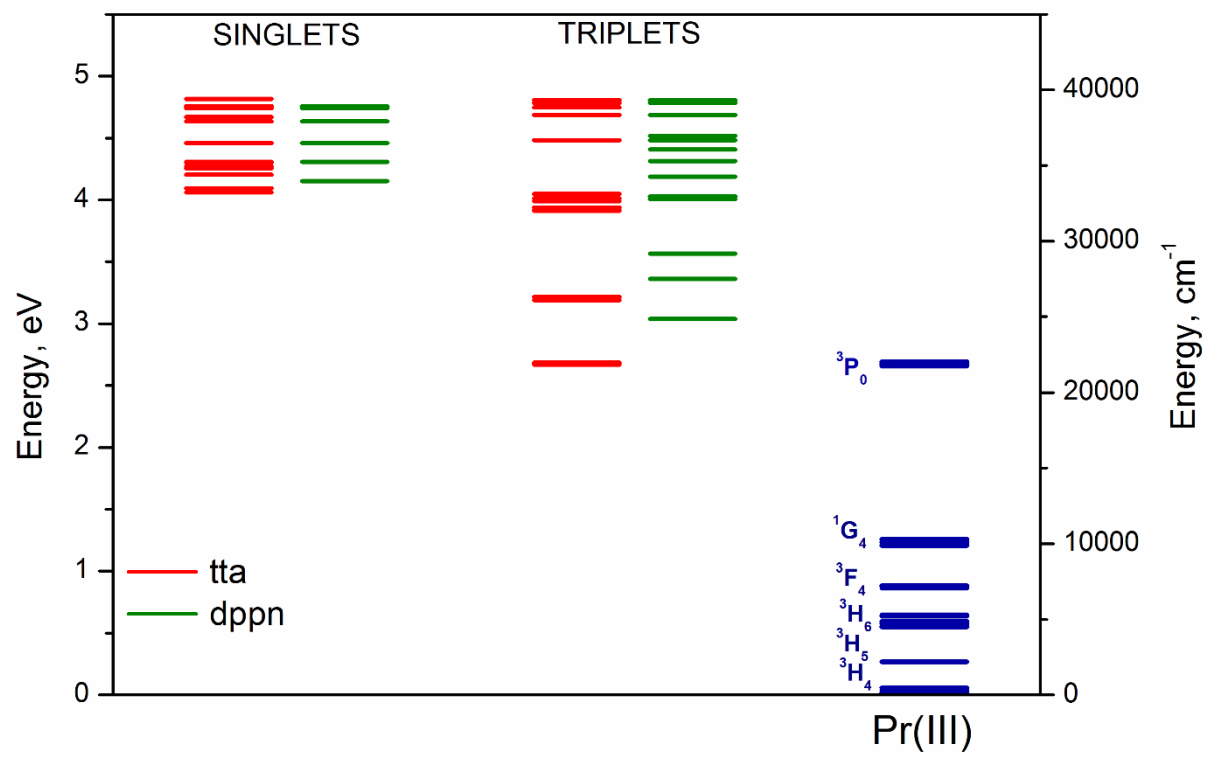
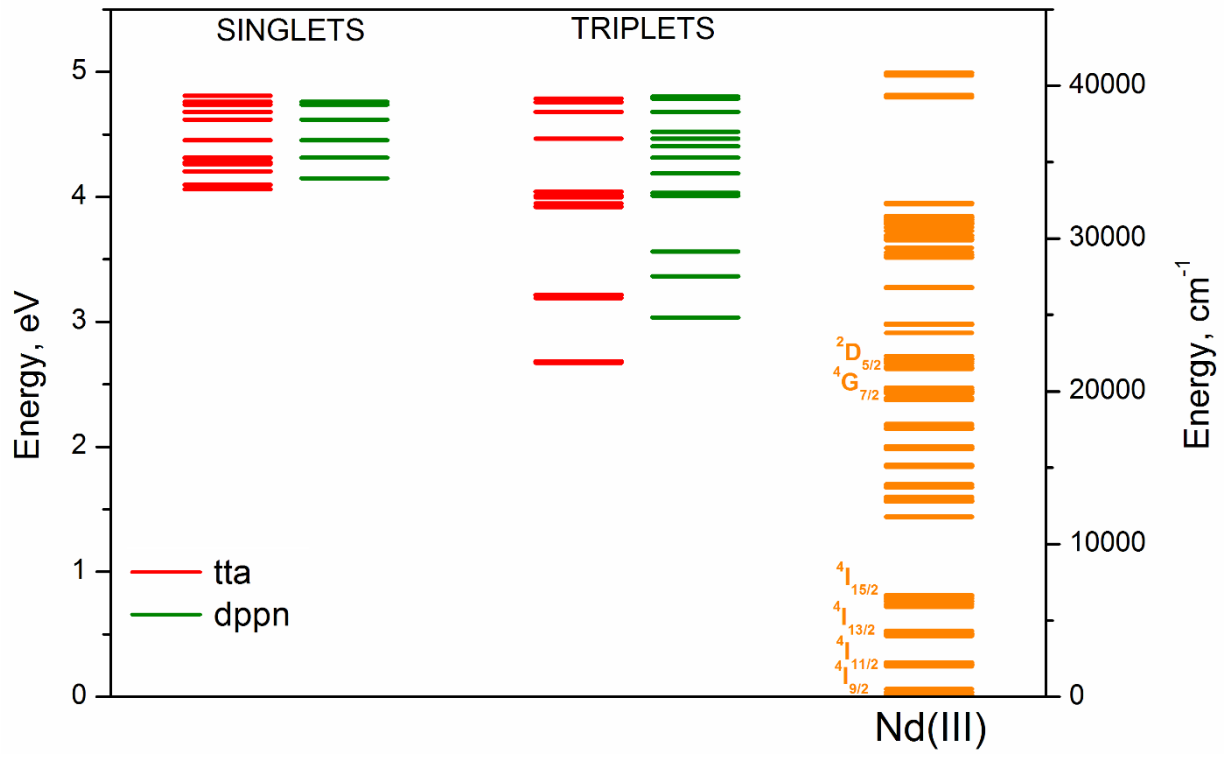


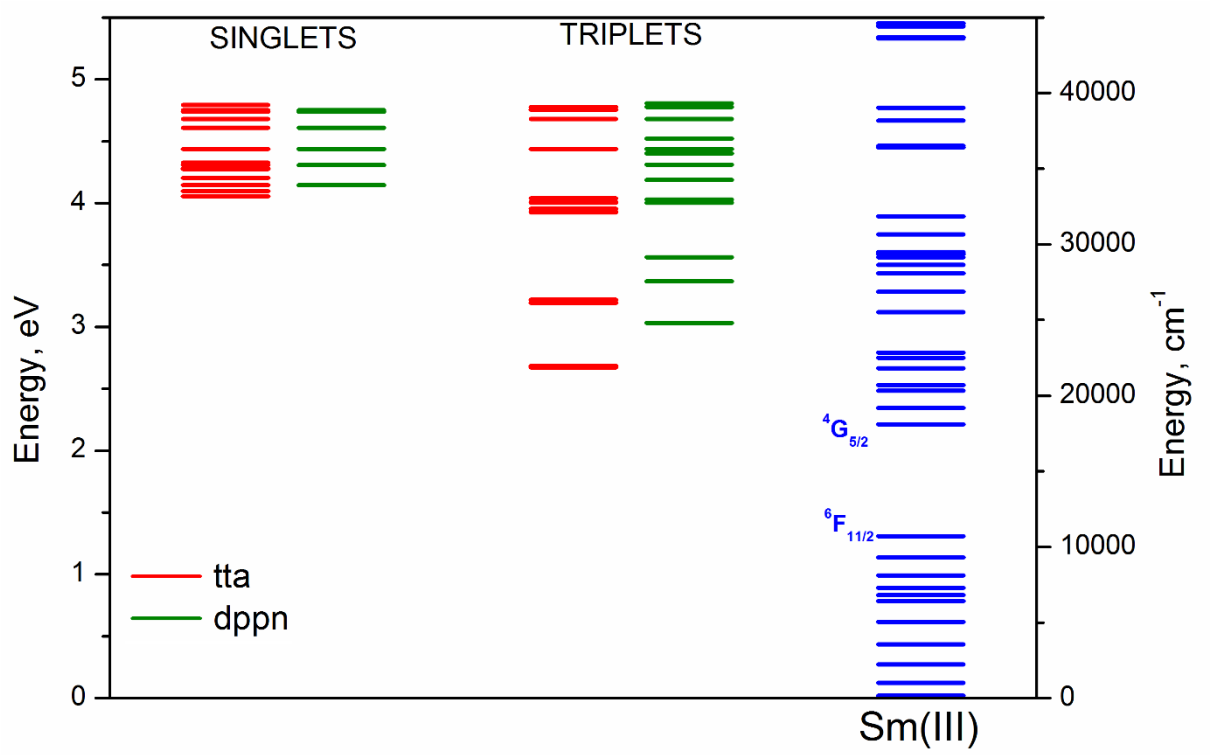
Figure S18. Calculated structure of possible isomers [Eu(**tta**)$_3$(**dppn**)] and the schematic representation of the coordination polyhedron (colour legend: europium light turquoise, oxygen red, nitrogen blue, carbon grey, sulphur yellow, fluorine bright green, hydrogen white).

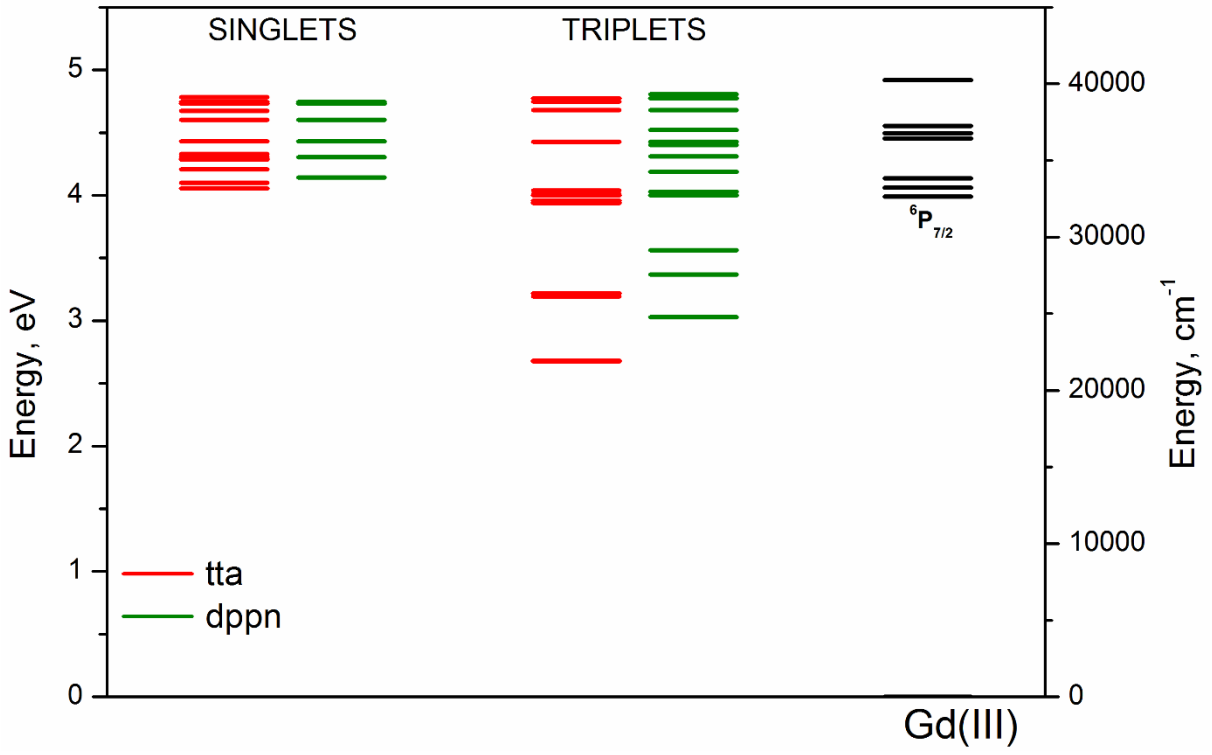
Table S4. Average values of experimental and calculated bond lengths (Å) Ln–O and Ln–N in **1-12**.

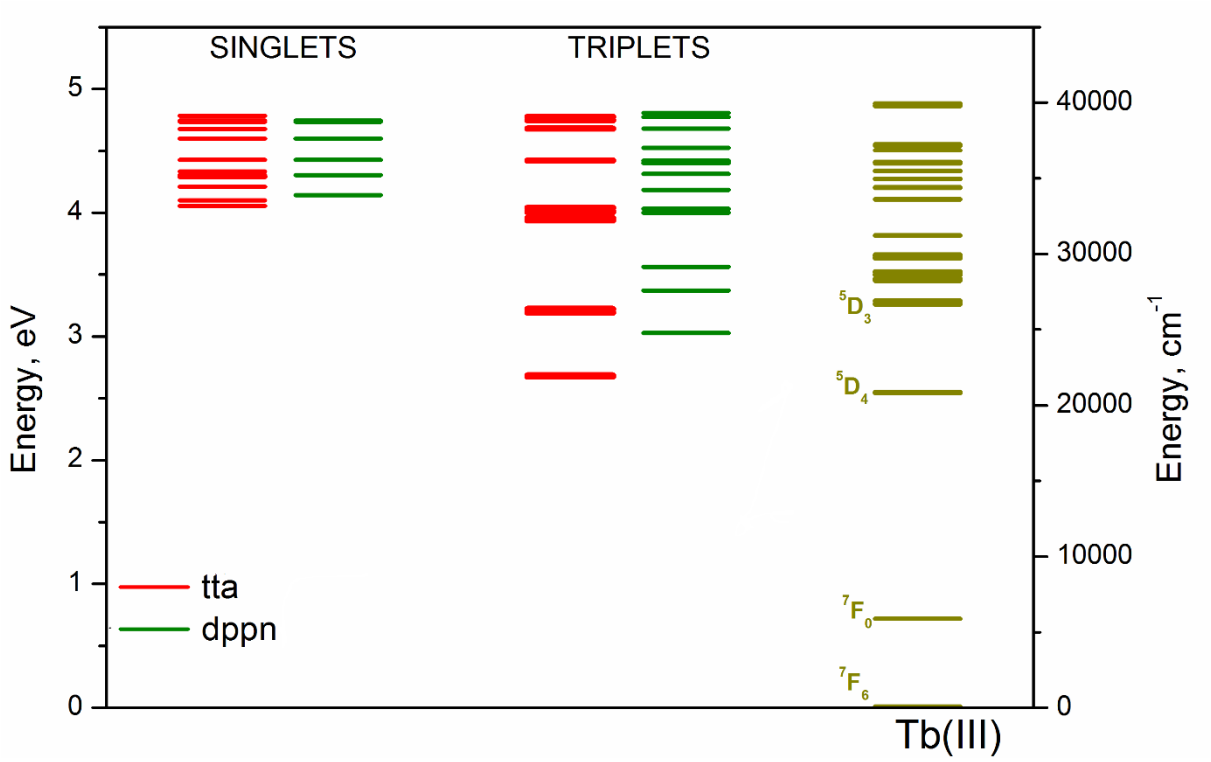
Complex	Ln	Experimental		Calculated	
		Ln–O	Ln–N	Ln–O	Ln–N
1	Pr	2.425	2.645	2.435	2.662
2	Nd	2.407	2.652	2.416	2.642
3	Sm	2.368	2.586	2.385	2.608
4	Eu	2.385	2.585	2.370	2.594
5	Gd	2.364	2.573	2.357	2.581
6	Tb	2.331	2.572	2.343	2.568
7	Dy	2.332	2.558	2.331	2.555
8	Ho	2.313	2.547	2.318	2.543
9	Er	-	-	2.306	2.530
10	Tm	2.293	2.495	2.295	2.519
11	Yb	-	-	2.284	2.508
12	Lu	2.280	2.485	2.273	2.498

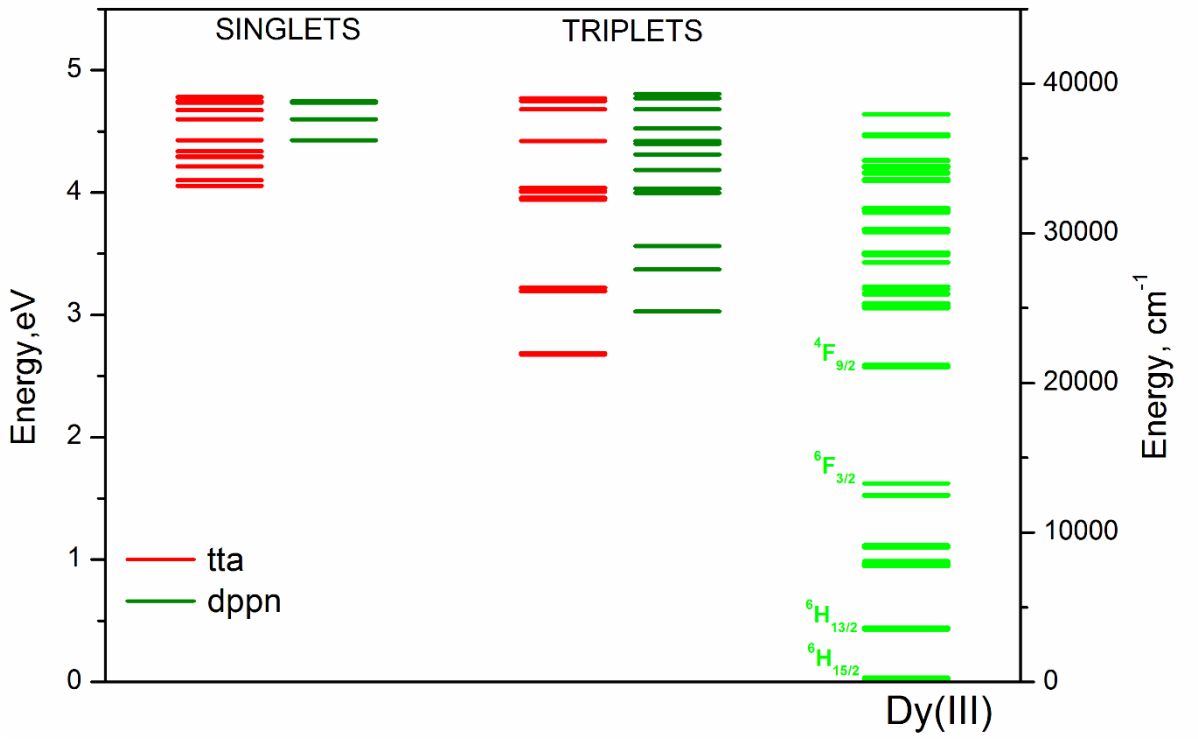

SINGLETS
TRIPLETS
Energy, eV
Energy, cm-1
tta
dppn
3P0
1G4
3F4
3H6
3H5
3H4
Pr(III)

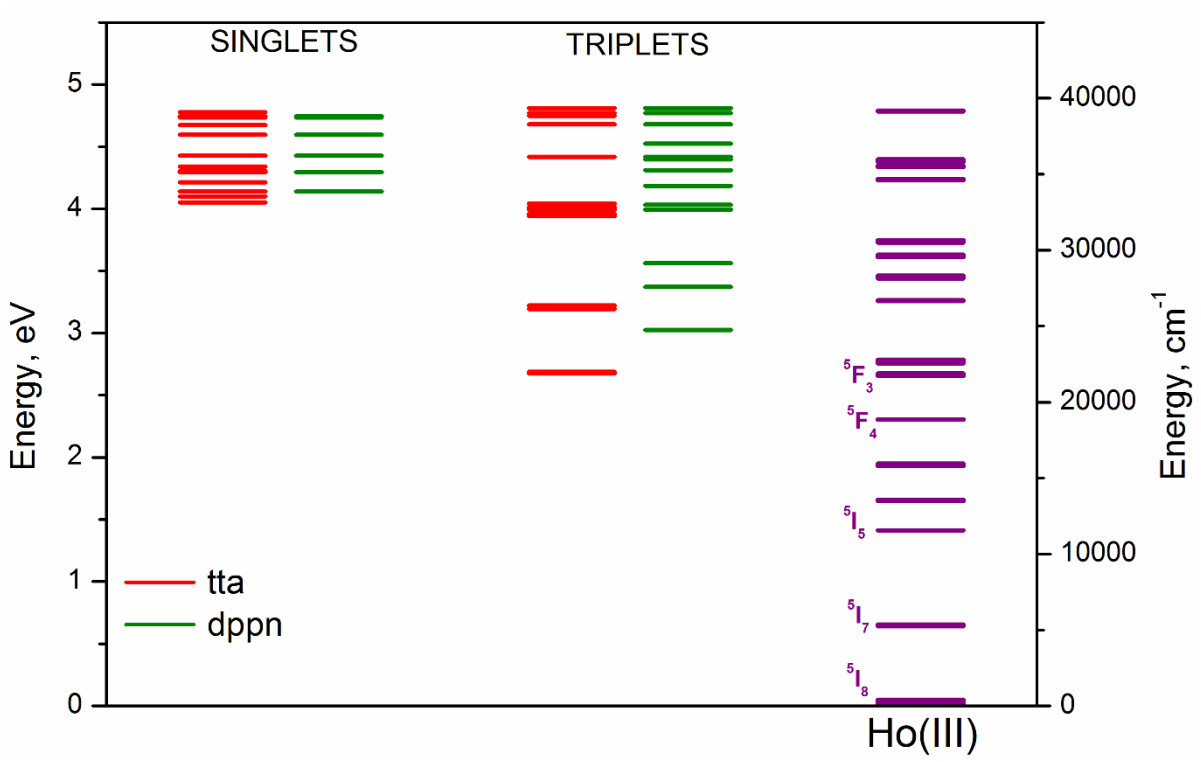

SINGLETS
TRIPLETS
Energy, eV
Energy, cm-1
tta
dppn
2D5/2
4G7/2
4I15/2
4I13/2
4I11/2
4I9/2
Nd(III)

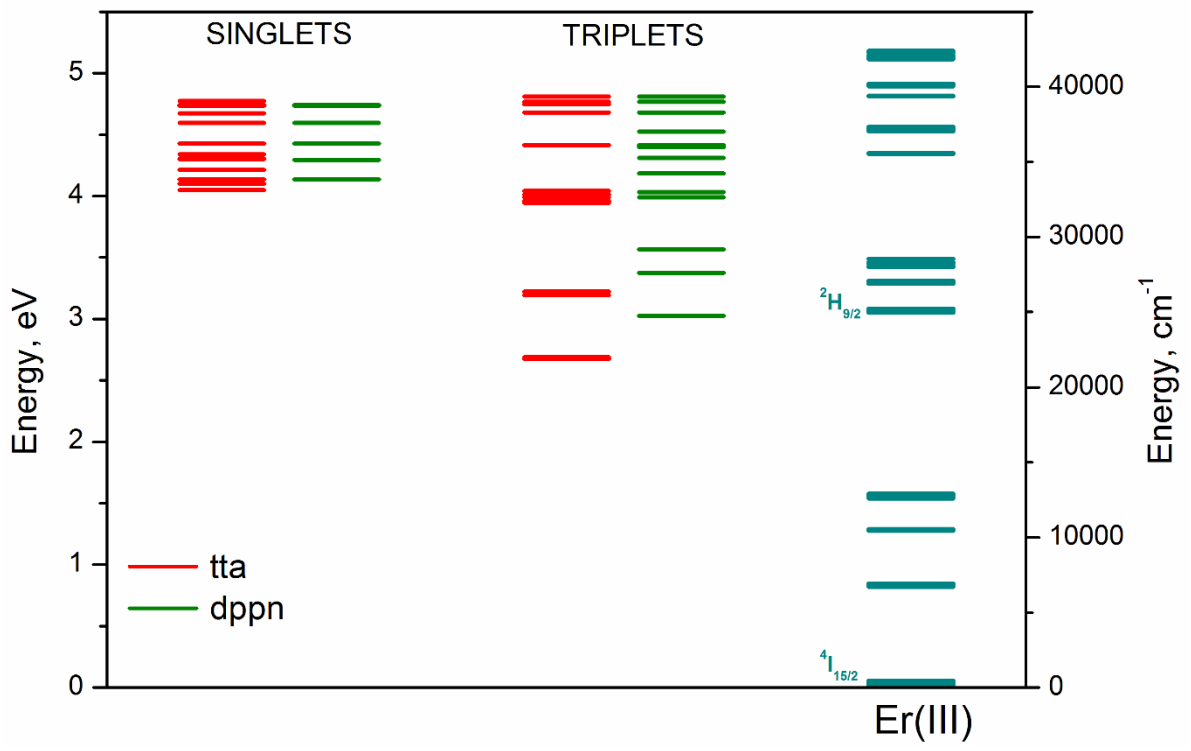

SINGLETS
TRIPLETS
Energy, eV
Energy, cm-1
tta
dppn
4G5/2
6F11/2
Sm(III)

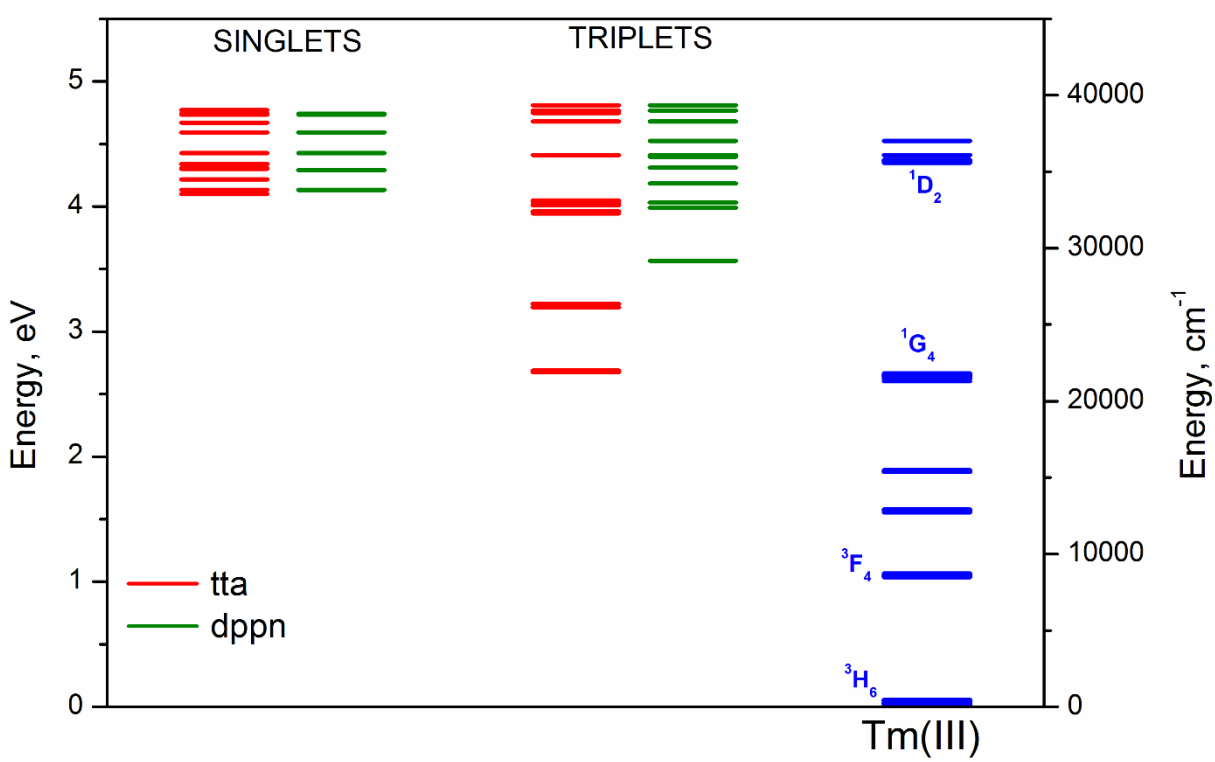

SINGLETS
TRIPLETS
Energy, eV
Energy, cm-1
tta
dppn
6P7/2
Gd(III)

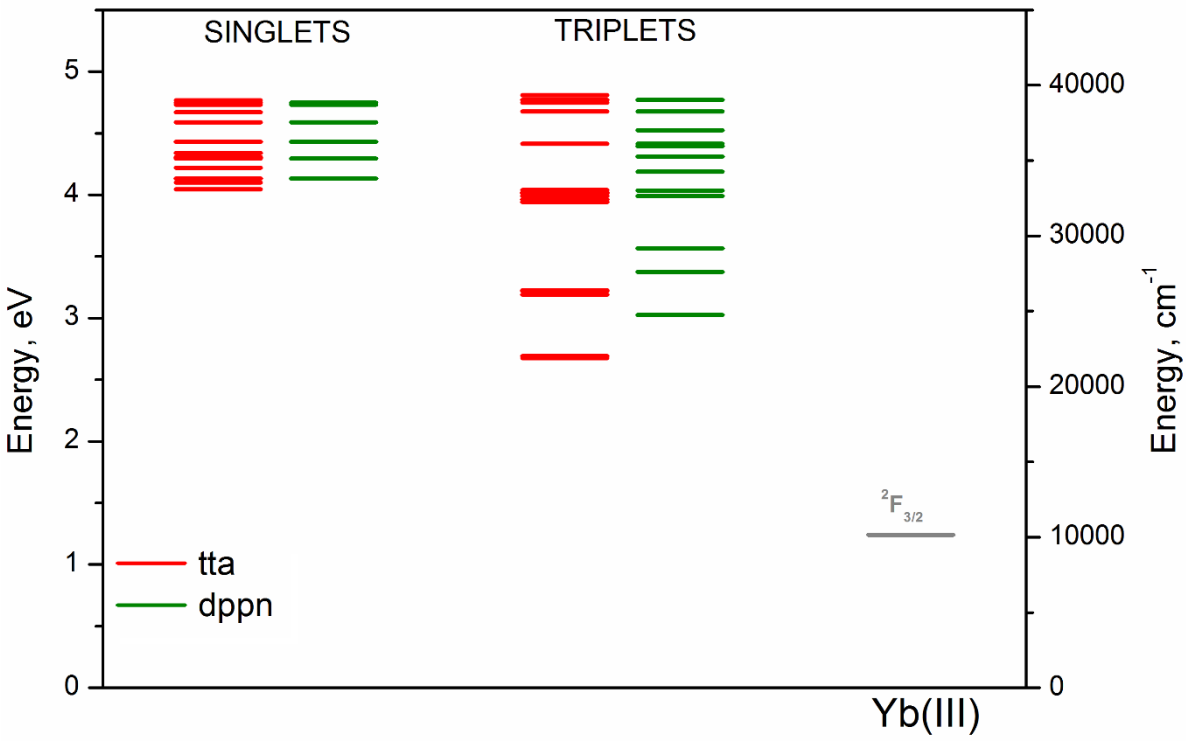

SINGLETS
TRIPLETS
Energy, eV
Energy, cm-1
tta
dppn
5D3
5D4
7F0
7F6
Tb(III)


SINGLETS
TRIPLETS
Energy,eV
Energy, cm-1
tta
dppn
4F9/2
6F3/2
6H13/2
6H15/2
Dy(III)


SINGLETS
TRIPLETS
Energy, eV
Energy, cm-1
tta
dppn
5F3
5F4
5I5
5I7
5I8
Ho(III)


SINGLETS
TRIPLETS
Energy, eV
Energy, cm-1
tta
dppn
2H9/2
4I15/2
Er(III)


SINGLETS
TRIPLETS
Energy, eV
Energy, cm-1
tta
dppn
1D2
1G4
3F4
3H6
Tm(III)


SINGLETS
TRIPLETS
Energy, eV
Energy, cm-1
tta
dppn
2F3/2
Yb(III)

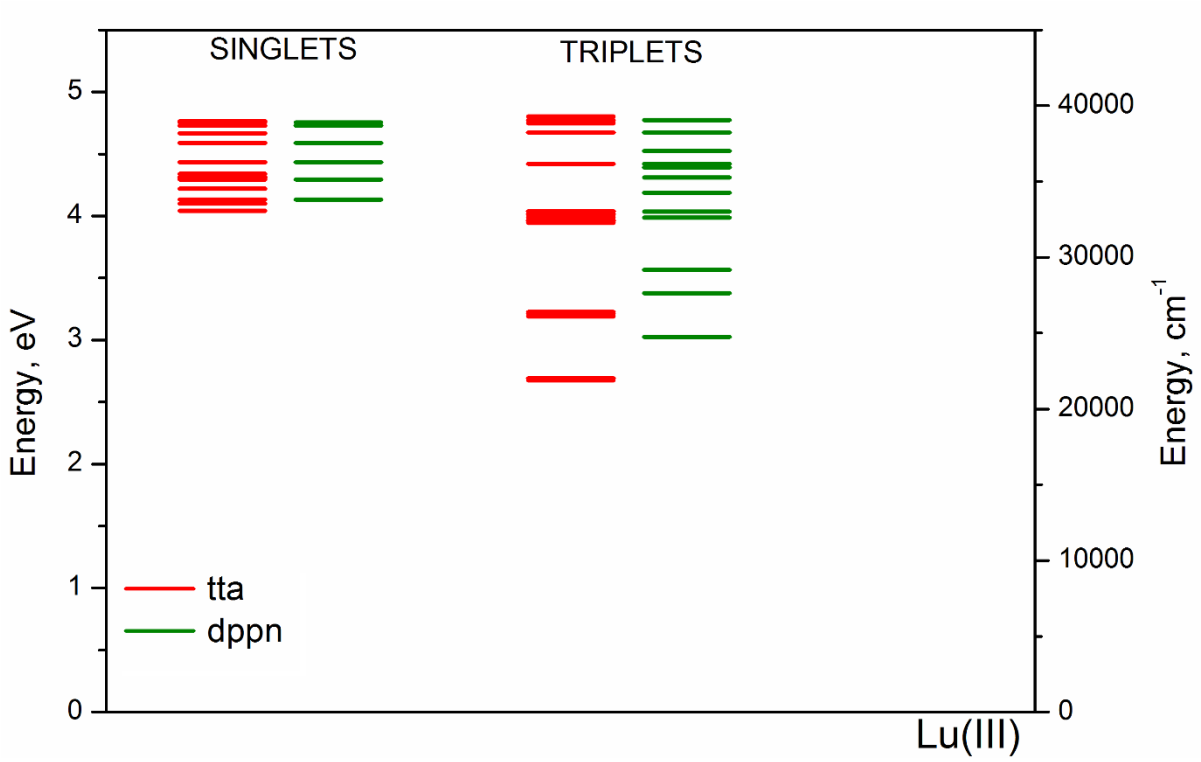


Figure S19. Excited state diagrams for **1-12** obtained from TDDFT calculations. Energy levels of the corresponding Ln(III) ions are provided for comparison.[3]

References

1 V. Vallet, A. Fischer, Z. Szabó and I. Grenthe, *Dalton Trans.*, 2010, **39**, 7666–7672.

2 S. Yi, M. Yao, J. Wang and X. Chen, *Phys. Chem. Chem. Phys.*, 2016, **18**, 27603–27612.

3 W. T. Carnall, G. L. Goodman, K. Rajnak and R. S. Rana, *J. Chem. Phys.*, 1989, **90**, 3443–3457.