Supplementary Information

Adducts of aqua complexes of Ln^{3+} with a di-hydroxylated symmetrical octamethyl-substituted cucurbituril: potential applications for isolation of heavier lanthanides

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EXPERIMENTAL SECTION

Synthesis: Chemicals, such as lanthanide nitrates was of reagent grade and was used without further purification. *t*$(OH)_2$OMeQ[6] was prepared as reported elsewhere.[1] Elemental analyses were carried out on a EURO EA-3000 elemental analyzer. A similar process was used to prepare crystals of related compounds: $Ln(NO_3)_3 \cdot xH_2O$ (0.0227 mmol) and *t*$(OH)_2$OMeQ[6] (10 mg, 0.0075 mmol) were dissolved in 3.0 mL neutral water with stirring. The solution was allowed to stand to allow slow evaporation of the volatiles in air at room temperature. X-ray quality crystals were obtained from the solution within a week. The color of crystals was dependent on the lanthanide ions. Summarizing the preparations, $\{t(OH)_2OMeQ[6] \cdot [Eu(H_2O)_8]\} \cdot 3Cl \cdot 18H_2O$ (**1**) was obtained from $Eu(NO_3)_3 \cdot 6H_2O$ (10.14 mg), Anal. calcd for $C_{44}H_{104}N_{24}O_{40}EuCl_3$ (**1**): H, 5.61; C, 28.29; N, 18.00; Found: H, 5.64; C, 28.23; N, 17.93; $\{t(OH)_2OMeQ[6] \cdot [Gd(H_2O)_8]\} \cdot 2(NO_3) \cdot Cl \cdot 8H_2O$ (**2**) was obtained from $Gd(NO_3)_3 \cdot 6H_2O$ (10.26 mg), Anal. calcd for $C_{44}H_{84}N_{26}O_{36}GdCl$ (**2**): H, 4.85; C, 30.27; N, 20.86; Found: H, 4.89; C, 30.19; N,

20.76; {*t*(OH)$_2$OMeQ[6]·[Tb(H$_2$O)$_8$]}·3Cl·10H$_2$O (**3**) was obtained from Tb(NO$_3$)$_3$·6H$_2$O (10.30 mg), Anal. calcd for $C_{44}H_{88}N_{24}O_{32}TbCl_3$ (**3**): H, 5.13; C, 30.54; N, 19.42; Found: H, 5.16; C, 30.46; N, 19.33; {*t*(OH)$_2$OMeQ[6]·[Dy(H$_2$O)$_8$]}·3Cl·11H$_2$O (**4**) was obtained from Dy(NO$_3$)$_3$·6H$_2$O (11.00 mg), Anal. calcd for $C_{44}H_{90}N_{24}O_{33}DyCl_3$ (**4**): H, 5.18; C, 30.16; N, 19.19; Found: H, 5.22; C, 30.09; N, 19.11; {*t*(OH)$_2$OMeQ[6]·[Ho(H$_2$O)$_8$]}·2(NO$_3$)·Cl·10H$_2$O (**5**) was obtained from Ho(NO$_3$)$_3$·5H$_2$O (10.02 mg), Anal. calcd for $C_{44}H_{88}N_{26}O_{38}HoCl$ (**5**): H, 4.96; C, 29.53; N, 20.35; Found: H, 4.99; C, 29.46; N, 20.26; {*t*(OH)$_2$OMeQ[6]·[Er(H$_2$O)$_8$]}·2(NO$_3$)·Cl·7H$_2$O (**6**) was obtained from Er(NO$_3$)$_3$·5H$_2$O (10.08 mg), Anal. calcd for $C_{44}H_{82}N_{26}O_{35}ErCl$ (**6**): H, 4.76; C, 30.41; N, 20.95; Found: H, 4.81; C, 30.32; N, 20.85; {*t*(OH)$_2$OMeQ[6]·[Tm(H$_2$O)$_8$]}·3Cl·19H$_2$O (**7**) was obtained from Tm(NO$_3$)$_3$·5H$_2$O (10.11 mg), Anal. calcd for $C_{44}H_{106}N_{24}O_{41}TmCl_3$ (**7**): H, 5.62; C, 27.77; N, 17.67; Found: H, 5.66; C, 27.68; N, 17.59; {*t*(OH)$_2$OMeQ[6]·[Yb(H$_2$O)$_8$]}·3Cl·19H$_2$O (**8**) was obtained from Yb(NO$_3$)$_3$·5H$_2$O (10.21 mg), Anal. calcd for $C_{44}H_{106}N_{24}O_{41}YbCl_3$ (**8**): H, 5.60; C, 27.71; N, 17.63; Found: H, 5.66; C, 27.62; N, 17.52. {*t*(OH)$_2$OMeQ[6]·[Lu(H$_2$O)$_8$]}·2(NO$_3$)·Cl·9H$_2$O (**9**) was obtained from Lu(NO$_3$)$_3$·6H$_2$O (10.66 mg), Anal. calcd for $C_{44}H_{86}N_{26}O_{37}LuCl$ (**9**): H, 4.87; C, 29.66; N, 20.44; Found: H, 4.81; C, 29.58; N, 20.33.

X-ray crystallography: A suitable single crystal (~0.2 × 0.2 × 0.1 mm^3) was taken up in paraffin oil and mounted on a Bruker SMART Apex II CCD diffractometer equipped with a graphite-monochromated Mo-K_α (λ = 0.71073 Å, μ = 0.828 mm^{-1}) radiation source operating in the ω-scan mode and a nitrogen cold stream (–50 C). Data were corrected for Lorentz and polarization effects (SAINT), and semi-empirical absorption corrections based on equivalent reflections were also applied (SADABS). The structure was elucidated by direct methods and refined by the full-matrix least-squares method on F^2 with the SHELXS-97 and SHELXL-97 program packages, respectively.[2] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were introduced at calculated positions, and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent

atom. Most of the water molecules in the compounds were omitted using the SQUEEZE option of the PLATON program. The squeezed water molecules are 18, 8, 13, 10, 11, 10, 7, 19, 19 and 9 for compounds **1**–**9**, respectively. Unfortunately, whatever how hard our crystallographer has tried, the A and B kind of alerts can not be get rid of at all in CIF check reports. Moreover, Analytical expressions for neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Details of the crystal parameters, data collection conditions, and refinement parameters for the night compounds are summarized in Table SI-1. In addition, the crystallographic data for the reported structures have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1550305 (**1**), 1550306 (**2**), 1550307 (**3**), 1550308 (**4**), 1550309 (**5**), 1550310 (**6**), 1550311 (**7**), 1550312 (**8**), 1550313 (**9**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

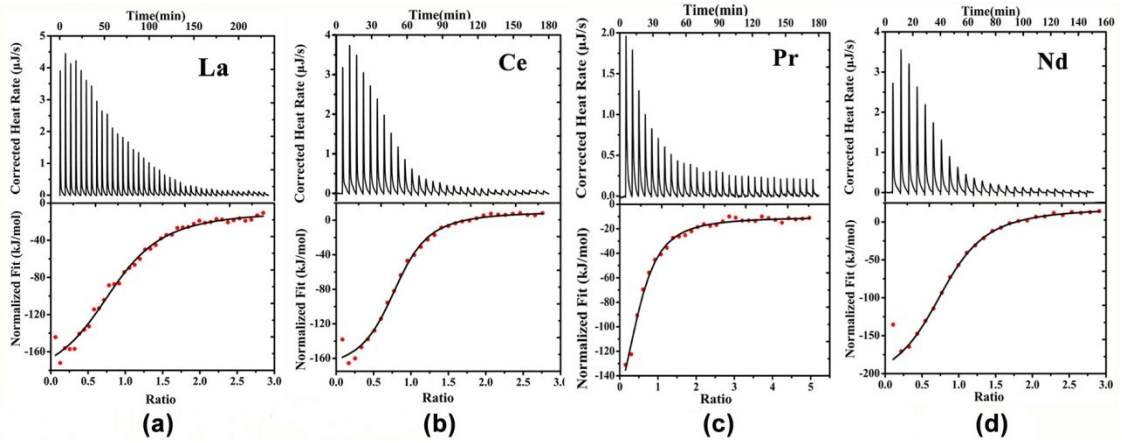
Table SI-1. Crystal Data and Structure Refinement Details for Compounds **1-9**

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_{44}H_{104}N_{24}O_{40}EuCl_3$	$C_{44}H_{84}N_{26}O_{36}GdCl$	$C_{44}H_{88}N_{24}O_{32}TbCl_3$	$C_{44}H_{90}N_{24}O_{33}DyCl_3$	$C_{44}H_{88}N_{26}O_{38}HoCl$	$C_{44}H_{82}N_{26}O_{35}ErCl$	$C_{44}H_{106}N_{24}O_{41}TmCl_3$	$C_{44}H_{106}N_{24}O_{41}YbCl_3$	$C_{44}H_{86}N_{26}O_{37}LuCl$
Formula weight	1867.82	1746.07	1730.65	1752.25	1789.78	1738.07	1902.81	1906.92	1781.81
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C 2/m	C 2/c	C 2/m	C 2/m	C 2/c	C 2/c	C 2/m	C 2/m	C 2/c
a (Å)	22.377(11)	22.316(5)	22.215(5)	22.190(2)	22.377(4)	22.449(18)	22.267(2)	22.245(3)	22.20(2)
b (Å)	12.519(6)	12.427(3)	12.391(5)	12.2997(12)	12.440(2)	12.430(10)	12.3118(11)	12.3258(13)	12.287(13)
c (Å)	14.991(7)	26.976(6)	14.675(5)	14.6385(15)	26.896(7)	26.83(2)	14.6937(14)	14.7424(19)	26.75(3)
α(°)	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
β (°)	108.190(10)	112.573(5)	108.468(5)	108.175(3)	111.367(3)	112.018(11)	108.292(3)	108.334(4)	111.489(17)
γ(°)	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
T (K)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)
V (Å^3)	3990(3)	6908(3)	3831(2)	3796.0(6)	6973(2)	6940(10)	3824.6(6)	3837.0(8)	6790(13)
Z	2	4	2	2	4	4	2	2	4

Dc (g·cm^{-3})	1.555	1.679	1.500	1.533	1.705	1.663	1.652	1.651	1.743
μ (mm^{-1})	0.991	1.113	1.123	1.188	1.290	1.359	1.376	1.434	1.611
F(000)	1940	3596	1784	1806	3688	3572	1972	1974	3664
Data collected	4095	5781	4713	4636	6785	5942	4510	4564	5777
Independent data	3578	4781	4604	4457	6094	5379	4199	3664	4677
R_{int}	0.0622	0.0563	0.0517	0.0410	0.0663	0.0410	0.0390	0.0499	0.0752
GOFs	1.042	1.125	1.133	1.095	1.060	1.123	1.081	1.032	1.027
R_1 [I>2σ (I)]	0.0559	0.0983	0.0504	0.0466	0.0592	0.0563	0.0509	0.0576	0.0510
wR_2 [I>2σ (I)]	0.1418	0.2462	0.1460	0.1360	0.1528	0.1735	0.1270	0.1330	0.1347
R_1 (all data)[a]	0.0654	0.1145	0.0515	0.0491	0.0659	0.0615	0.0556	0.0763	0.0665
wR_2 (all data)[b]	0.1484	0.2541	0.1479	0.1391	0.1577	0.1842	0.1304	0.1401	0.1445

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = (F_o^2 + 2F_c^2)/3$.

Isothermal titration calorimetry (ITC): Microcalorimetric experiments were performed using an isothermal titration calorimeter Nano ITC 2G (TA, USA). Each consecutive injection (6 μL) of a solution ($Ln(NO_3)_3 \cdot 5$ or $6H_2O$ respectively: 1×10^{-3} M) into the microcalorimetric reaction cell (1mL) charged with a solution of $t(OH)_2$OMeQ[6] (1×10^{-4} M). The heat of reaction was corrected for the heat of dilution of the guest solution determined in the separate experiments. All solutions were degassed prior to titration experiment by sonication. Computer simulations (curve fitting) were performed using the Nano ITC ananlyze software.



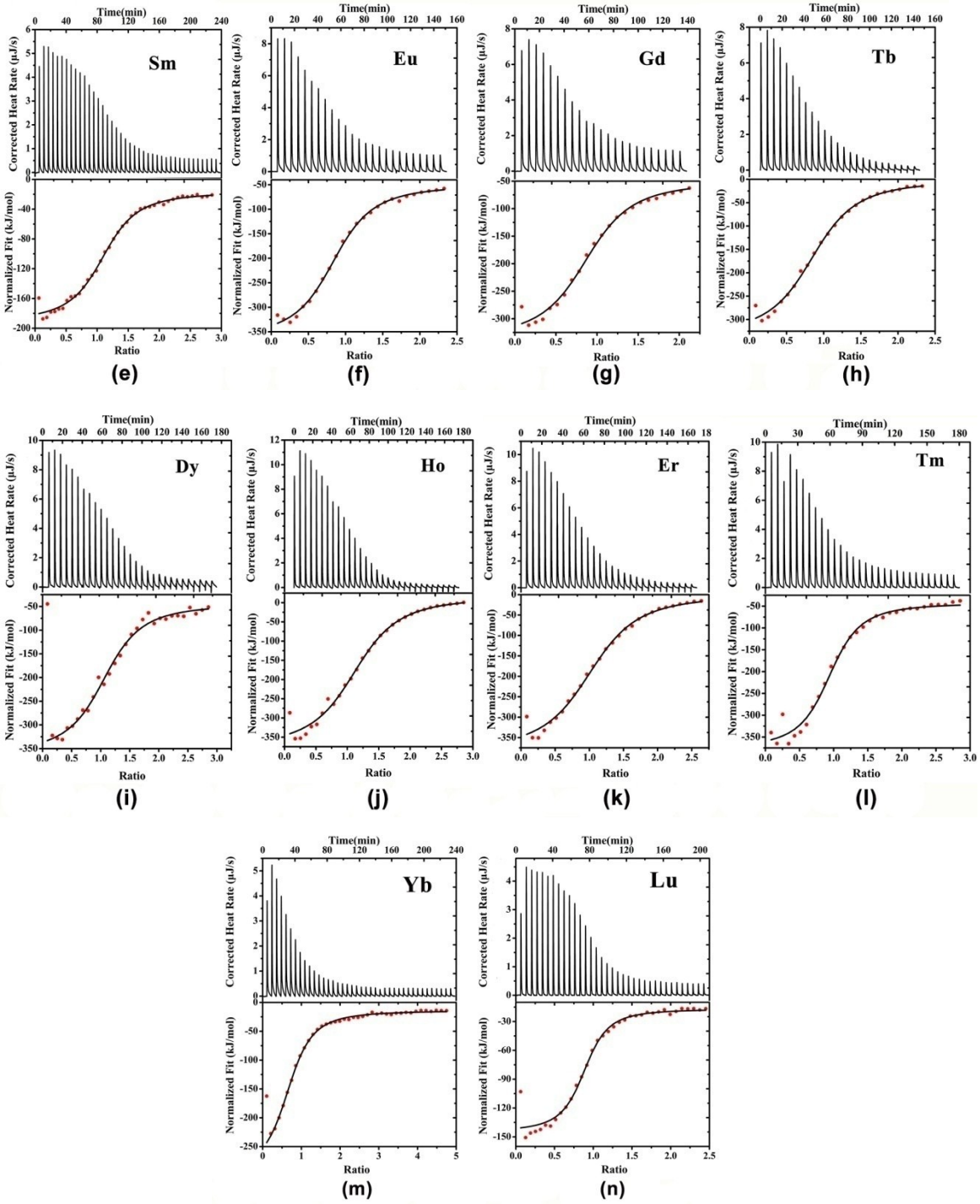


Figure SI-1 ITC profile of $t(OH)_2$OMeQ[6] with $Ln(NO_3)_3$ at 298.15 K: Ln = (a) La; (b) Ce; (c) Pr; (d) Nd; (e) Sm; (f) Eu; (g) Gd; (h) Tb; (i) Dy; (j) Ho; (k) Er; (l) Tm; (m) Yb; (n) Lu.

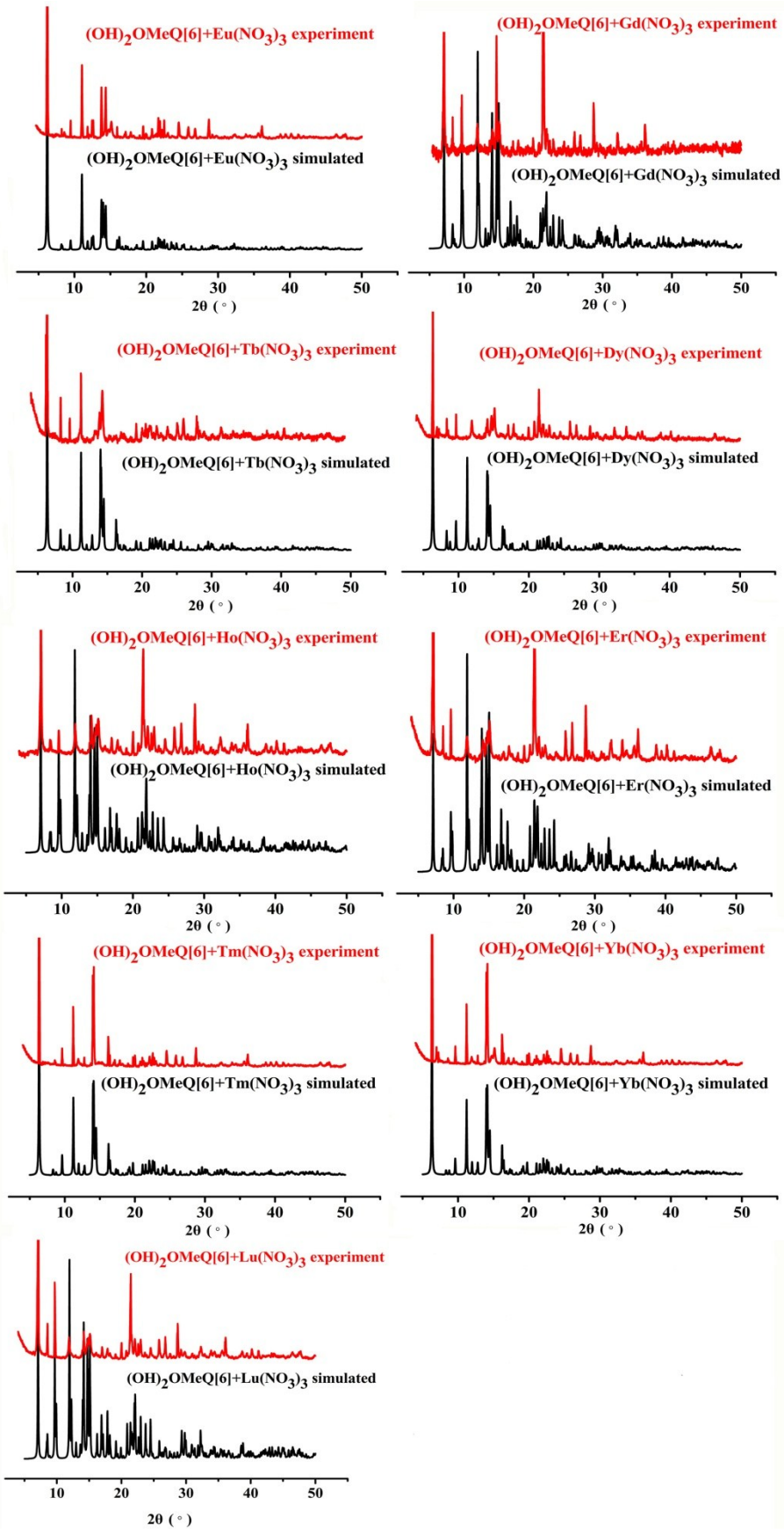


Figure SI-2 Powder X-ray diffraction (PXRD) of the adducts from nine isomorphous group respectively

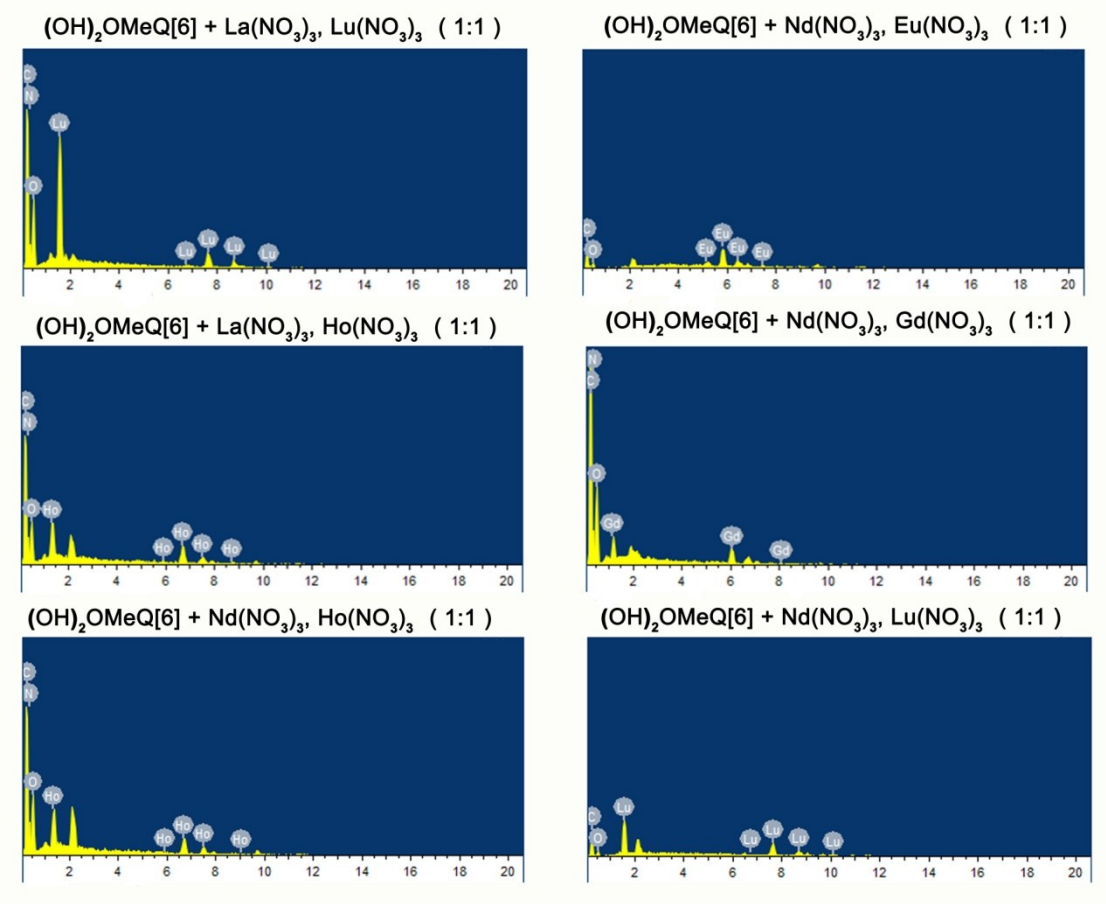


Figure SI-3 the electron spectroscopy of the representative adducts with 1:1 ratios of Ln_{light}:Ln_{heavy}

References

1 Fang-Fang Shen, Kai Chen, Yun-Qian Zhang, Qian-Jiang Zhu, Zhu Tao, and Hang Cong, Org. Lett. **2016**, *18*, 5544–5547.

2 (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112; (b) G. M. Sheldrick, SHELXL-97 Program for the Solution and Refinement of Crystal structures, University of Göttingen, Germany, 1997.