Supporting Information

Synthesis, Structures and Photophysical Properties of Heterotrinuclear Zn_2Ln Clusters (Ln = Nd, Eu, Tb, Er, Yb)

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Table S1. Crystallographic Data of **2**–**4**.

	2	**3**	**4**
Formula	$C_{50}H_{33.50}ClF_{12}N_4NdO_{10}Zn_2$	$C_{50}H_{33.50}ClF_{12}N_4EuO_{10}Zn_2$	$C_{50}H_{33.50}ClF_{12}N_4TbO_{10}Zn_2$
M_r	1388.74	1396.46	1403.42
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
T (K)	298(2)	298(2)	298(2)
a (Å)	34.723(2)	34.725(2)	34.72(1)
b (Å)	18.470(1)	18.3371(8)	18.480(4)
c (Å)	24.125(1)	23.946(1)	24.15(1)
β (deg)	125.0233(8)	124.936(1)	125.291(2)
V (Å^3)	12670(1)	12500(1)	12645(8)
D_c (g·cm^{-3})	1.456	1.484	1.474
Z	8	8	8
μ (mm^{-1})	1.687	1.883	1.988
Reflections collected	32525	33696	43449
Unique reflections	12444	12279	12353
R_{int}	0.0276	0.0342	0.0311
Goodness-of-fit on F^2	1.027	1.047	1.144
R_1/wR_2 [$I > 2\sigma(I)$]	0.0551/0.1519	0.0514/0.1379	0.0535/0.1487
R_1/wR_2 (all data)	0.0779/0.1773	0.0798/0.1663	0.0700/0.1788
Largest diff. peak and hole (e·Å^{-3})	2.053/-0.599	1.637/-0.638	1.979/-1.505

Table S2. Selected interatomic distances (Å) and bond angles (deg) for **2–4**

	2	**3**	**4**
Ln-O1	2.363(3)	2.330(4)	2.314(3)
Ln-O2	2.503(3)	2.460(4)	2.442(3)
Ln-O3	2.478(3)	2.433(3)	2.414(2)
Ln-O4	2.376(3)	2.344(3)	2.315(2)
Ln-O7	2.429(4)	2.392(4)	2.370(3)
Ln-O8	2.436(4)	2.402(4)	2.373(3)
Zn1-N1	2.071(5)	2.063(5)	2.068(4)
Zn1-N2	2.104(4)	2.107(5)	2.114(4)
Zn1-O1	2.150(4)	2.144(4)	2.147(3)
Zn1-O2	2.136(3)	2.140(4)	2.140(2)
Zn1-O3	2.251(3)	2.263(4)	2.260(3)
Zn1-O6	2.022(4)	2.025(4)	2.026(3)
Zn2-O2	2.308(3)	2.308(3)	2.298(2)
Zn1···Zn2	3.241	3.238	3.228
Zn1···Ln	3.3540(7)	3.3238(8)	3.3099(11)
Zn2···Ln	3.3735(6)	3.3379(6)	3.3224(14)
Zn1-O1-C8	111.6(4)	112.0(4)	112.2(3)
Zn1-O2-C17	113.2(3)	112.8(3)	112.6(2)
Zn1-O2-Zn2	93.59(11)	93.35(12)	93.25(9)
O1-Ln-O2	70.48(11)	71.03(12)	71.33(8)
O1-Ln-O3	71.80(11)	72.69(12)	73.04(8)
O1-Ln-O4	135.76(12)	137.00(13)	137.71(9)

O1-Ln-O7	115.53(14)	114.94(15)	115.02(11)
O1-Ln-O8	79.12(14)	78.68(15)	77.97(11)
O2-Ln-O3	61.56(10)	62.67(11)	63.09(8)
O2-Ln-O4	71.09(11)	71.56(12)	72.00(9)
O2-Ln-O7	81.01(12)	79.95(14)	80.10(10)
O2-Ln-O8	121.85(13)	122.50(14)	122.50(11)
O3-Ln-O4	71.16(11)	71.80(12)	72.07(8)
O3-Ln-O7	137.60(12)	137.55(13)	138.01(9)
O3-Ln-O8	147.32(13)	146.94(13)	146.33(9)
O4-Ln-O7	78.71(13)	78.11(14)	78.12(9)
O4-Ln-O8	141.42(13)	140.96(14)	141.19(10)
O7-Ln-O8	69.07(14)	70.20(15)	70.58(10)
N1-Zn1-N2	99.94(19)	99.7(2)	100.93(16)
N1-Zn1-O1	78.48(19)	78.8(2)	78.78(14)
N1-Zn1-O2	159.74(19)	159.2(2)	159.05(13)
N1-Zn1-O3	110.32(17)	110.58(18)	109.33(15)
N1-Zn1-O6	94.2(2)	94.0(2)	94.25(14)
N2-Zn1-O1	99.62(15)	99.86(15)	99.94(12)
N2-Zn1-O2	78.24(15)	78.58(17)	78.64(12)
N2-Zn1-O3	148.96(15)	148.86(16)	148.85(11)
N2-Zn1-O6	94.38(17)	94.94(18)	94.54(14)
O1-Zn1-O2	81.93(13)	81.07(14)	80.67(9)
O1-Zn1-O3	80.35(12)	79.64(13)	79.33(10)
O1-Zn1-O6	165.09(15)	164.40(16)	164.87(13)
O2-Zn1-O3	70.99(11)	70.54(12)	70.47(9)
O2-Zn1-O6	106.08(15)	106.85(16)	106.68(10)
O3-Zn1-O6	90.28(14)	90.23(15)	90.55(12)

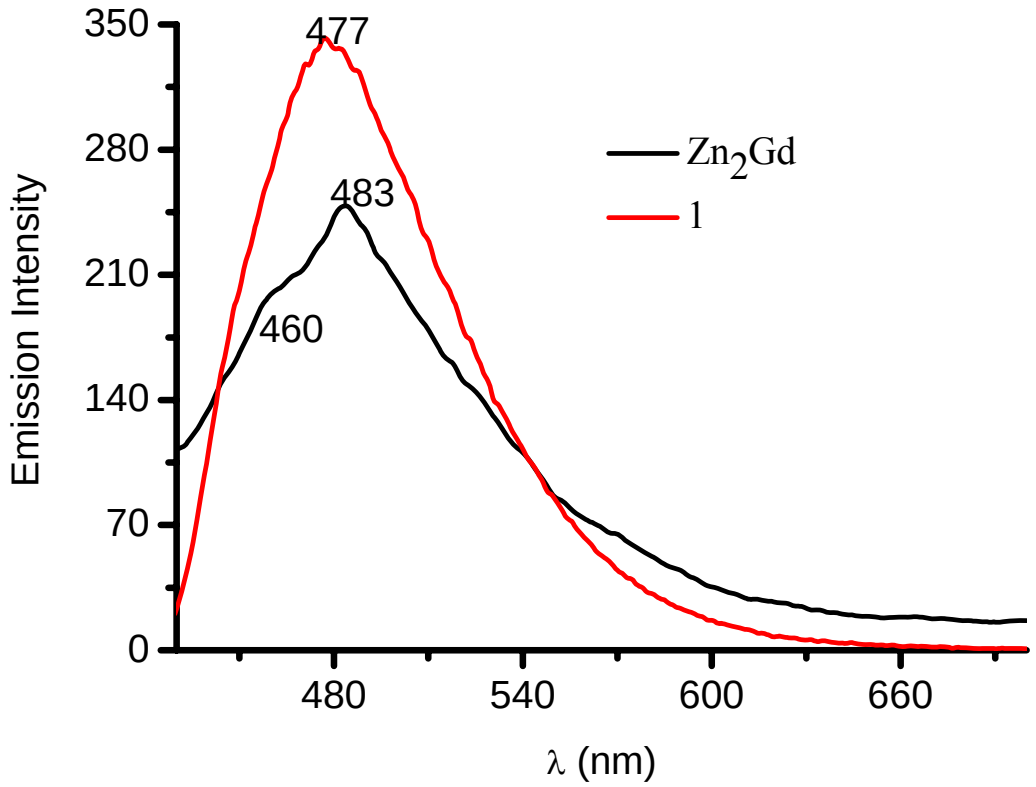

Fig. S1 The emission spectra of Zn_2Gd and complex **1** in CH_2Cl_2-CH_3CN solution at 77 K.

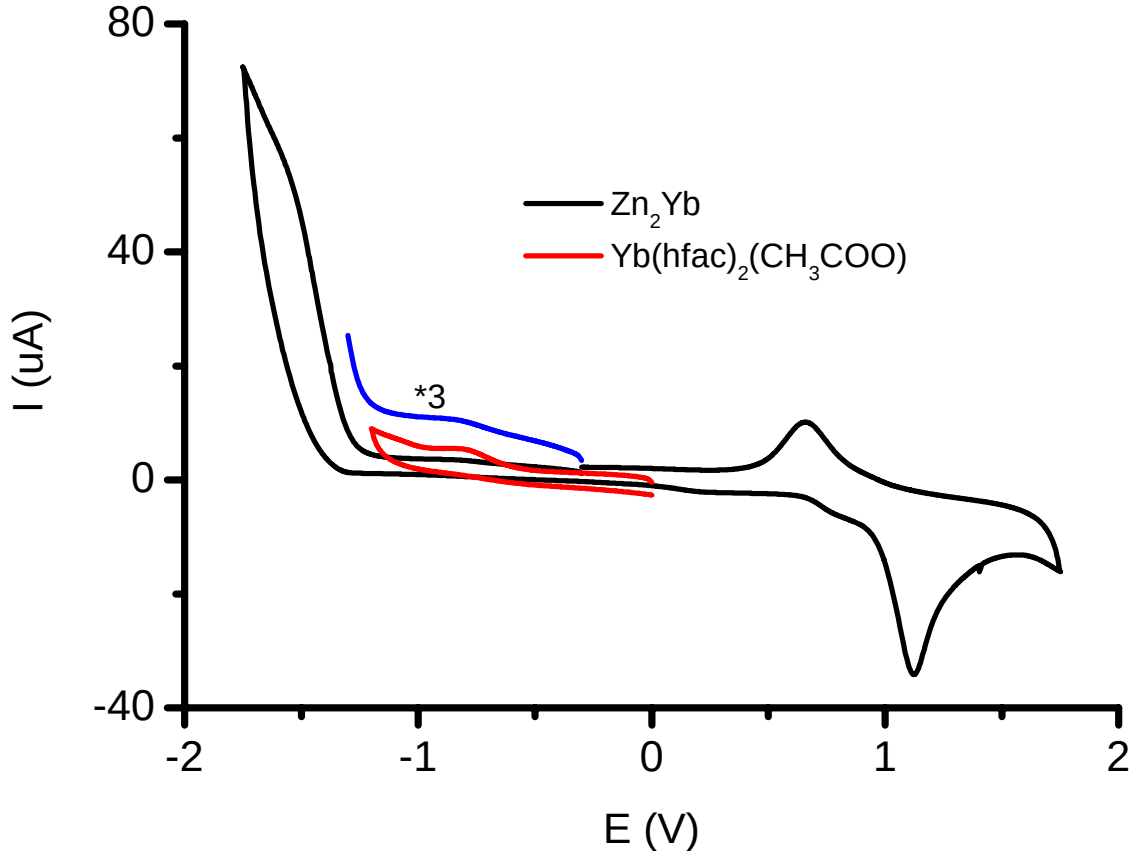

Fig. S2 The cyclic voltammogram of **6** in dichloromethane at 298 K

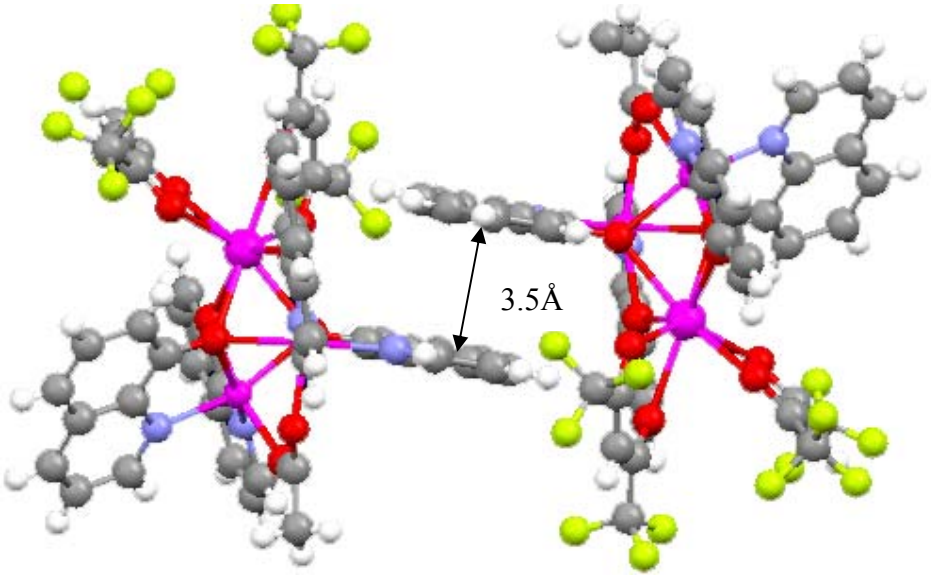

Fig. S3 The intermolecular π–π stacking of q ligands

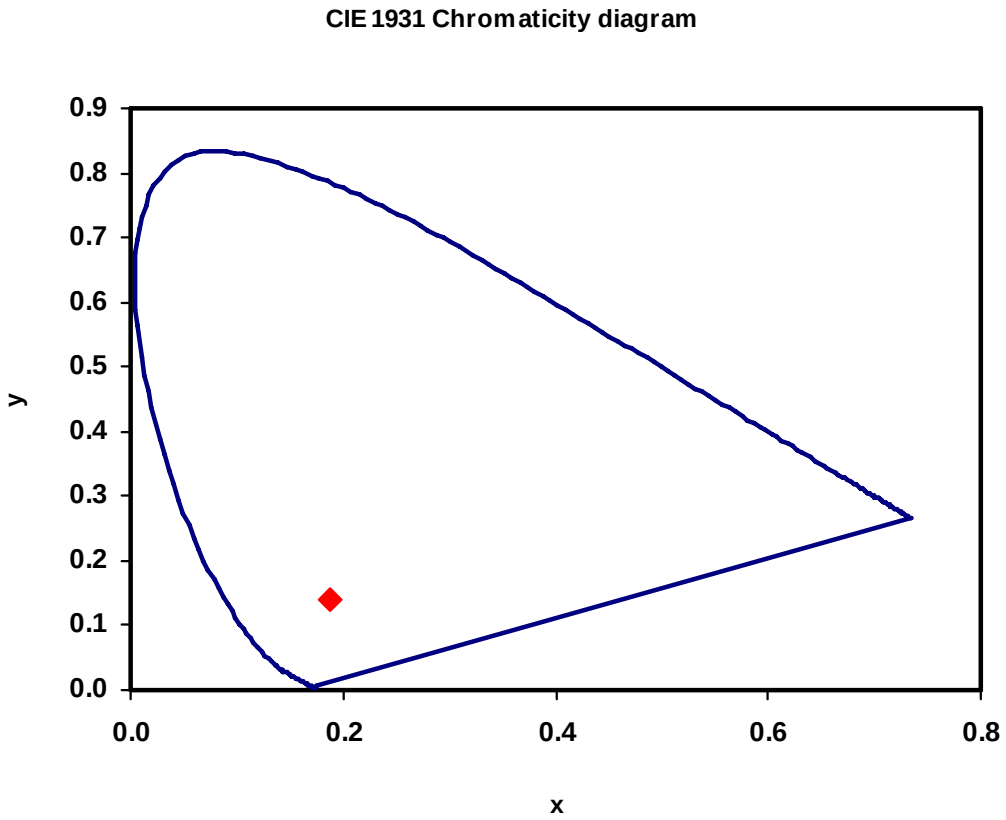

Fig. S4 The chromaticity coordinates of **3** once irradiation with 360 nm in dichloromethane at 298 K

Experimental Section

Synthesis of$Ln(hfac)_2(CH_3COO)(H_2O)_2$ (Ln = Nd, Eu, Tb, Er, Yb): Ln_2O_3 were dissolved in CH_3COOH, after dissolved, the filtrates were evacuated to afford $Ln(CH_3COO)_3$. To an aqueous solution of lanthanide(III) acetates (pH = 5–7) were added dropwise 2.2 equiv of Hhfac with stirring at room temperature for 3 hrs. The precipitates were filtered, washed with excess of water, and dried under vacuum to afford the products without further purification.

Starting materials of $Nd(hfac)_2(CH_3COO)(H_2O)_2$: IR (KBr, cm^{-1}): 1651s (C=O, hfac); 1552(C=O, CH_3COO). C, 22.06; H, 1.39; Nd, 22.07. Found: C, 22.13; H, 1.28; Nd, 22.13.

Starting materials of $Eu(hfac)_2(CH_3COO)(H_2O)_2$: IR (KBr, cm^{-1}): 1652s (C=O, hfac); 1557(C=O, CH_3COO). C, 21.80; H, 1.37; Eu, 22.98. Found: C, 21.88; H, 1.38; Eu, 22.99.

Starting materials of $Tb(hfac)_2(CH_3COO)(H_2O)_2$: IR (KBr, cm^{-1}): 1652s (C=O, hfac); 1557(C=O, CH_3COO). C, 21.57; H, 1.36; Tb, 23.79. Found: C, 21.56; H, 1.33; Tb, 24.06.

Starting materials of $Er(hfac)_2(CH_3COO)(H_2O)_2$: IR (KBr, cm^{-1}): 1652s (C=O, hfac); 1567(C=O, CH_3COO). C, 21.31; H, 1.34; Er, 24.73. Found: C, 20.99; H, 1.22; Er, 24.99

Starting materials of $Yb(hfac)_2(CH_3COO)(H_2O)_2$: IR (KBr, cm^{-1}): 1652s (C=O, hfac); 1535(C=O, CH_3COO). C, 21.13; H, 1.33; Yb, 25.36. Found: C, 21.06; H, 1.36; Yb, 25.24.

Electrospray mass spectra (ESI–MS)

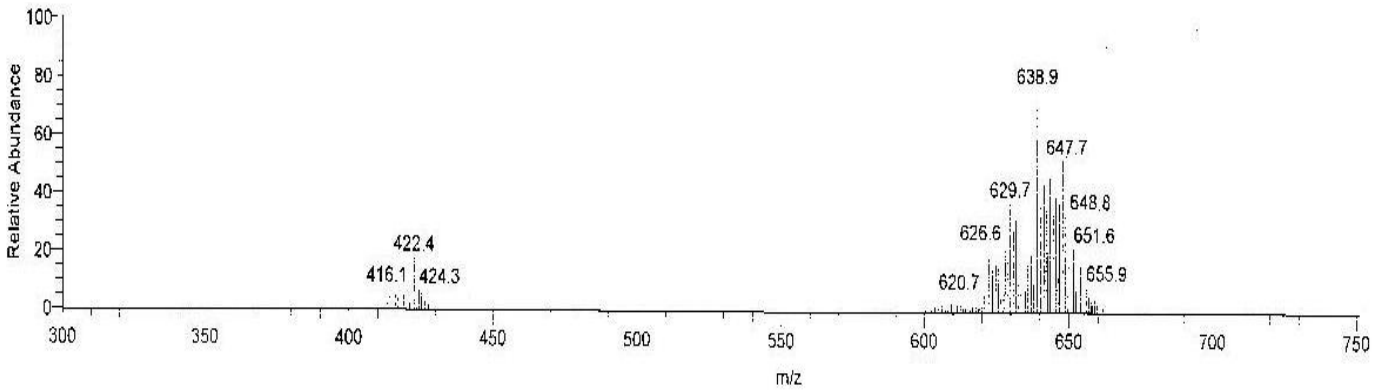

Fig. S2. ESI–MS spectra of Nd(III) Complex

ESI–MS (CH_3OH): m/z (%) 654-618 $[Nd(hfac)_2(CH_3COO)(H_2O)_n+H]^+$, (n=0, 1, 2).

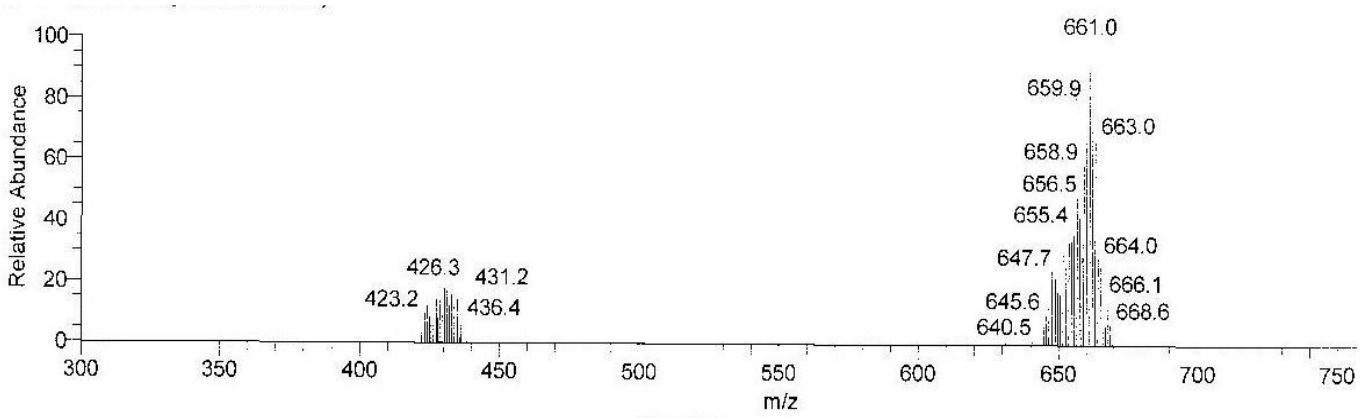

Fig. S3. ESI–MS spectra of Eu(III) Complex

ESI–MS (CH_3OH): m/z (%) 662-626 $[Eu(hfac)_2(CH_3COO)(H_2O)_n+H]^+$, (n=0, 1, 2).

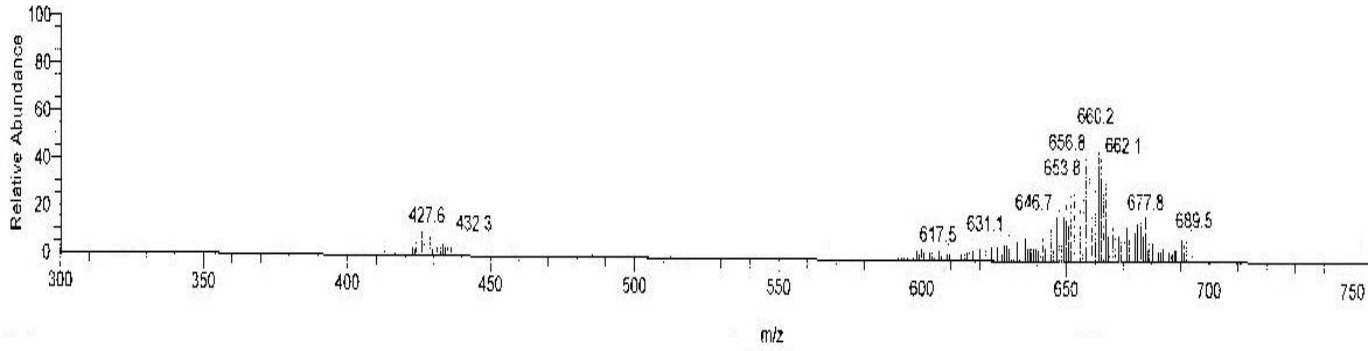

Fig. S4. ESI–MS spectra of Tb(III) Complex

ESI–MS (CH_3OH): m/z (%) 668-633 $[Tb(hfac)_2(CH_3COO)(H_2O)_n+H]^+$, (n=0, 1, 2).

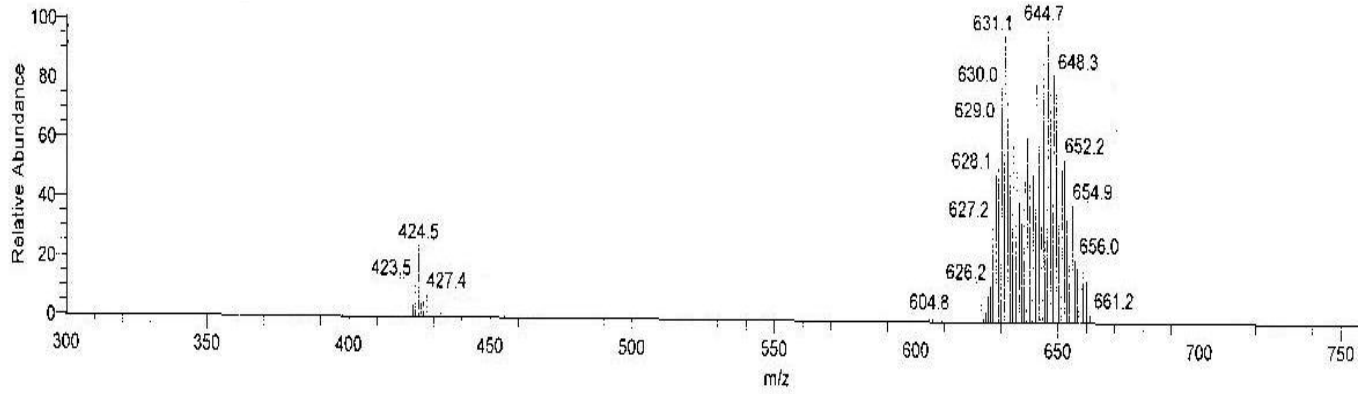

Fig. S5. ESI–MS spectra of Er(III) Complex

ESI–MS (CH_3OH): m/z (%) 677-641 $[Er(hfac)_2(CH_3COO)(H_2O)_n+H]^+$, (n=0, 1, 2).

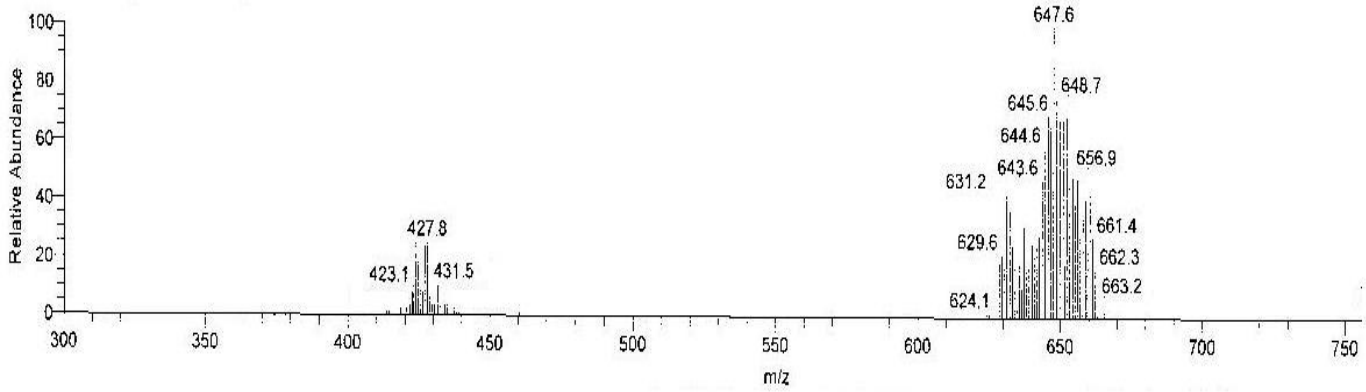

Fig. S6. ESI–MS spectra of Yb(III) Complex

ESI–MS (CH_3OH): m/z (%) 682-647 $[Yb(hfac)_2(CH_3COO)(H_2O)_n+H]^+$, (n=0, 1, 2).