Electronic Supplementary Material (ESI) for New Journal of Chemistry.

SUPPLEMENTARY INFORMATION

Diglycolamide-Functionalized Resorcinarene for Rare Earths Extraction.

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Table S1: Mutual extraction of Ln (III) from nitric acid solutions (0.1 – 5M) at 25°C by 1 mM solution of CR4-DODGA in 10 % iso-octanol/toluene.

$[HNO_3]$	D(La)	D(Eu)	D(Yb)	SF(Yb/Eu)	SF(Yb/La)
0.1	0.023	0.016	0.017	1.09	0.76
1	0.017	0.02	0.04	1.80	2.51
2	0.015	0.06	0.26	4.66	16.15
3	0.074	0.21	1.22	5.93	16.26
5	0.182	1.10	15.06	13.67	82.78

$[Ln]_t$ = 1mM; equimolar concentrations of metals = 0.33mM

Table S2: Mutual extraction of Ln (III) from 5M nitric acid solution at 25°C by CR4-DODGA (0.33 – 3mM in 10 % iso-octanol/toluene).

[CR4-DODGA]	D(La)	D(Eu)	D(Yb)	SF (Yb/Eu)	SF (Yb/La)
0.33	0.03	0.11	1.08	9.82	36
1	0.18	1.1	15.06	13.67	82.78
2	0.36	3.31	78.38	23.68	217.72
3	0.59	6.82	227.47	33.35	385.54

$[Ln]_t$ = 1mM; equimolar concentrations of metals = 0.33mM

Table S3: Mutual extraction of Ln (III) from 5M nitric acid solution at 25°C by 1 mM solution of CR4-DODGA or CR4-Tz-DODGA* in 10 % iso-octanol/toluene.

[Ligand]= 1mM	D_{La} (E% La)	D_{Eu} (E% Eu)	D_{Yb} (E% Yb)	$SF_{Yb/Eu}$	$SF_{Yb/La}$
CR4-Tz-DODGA*	0.01 (1%)	0.17 (14%)	3.4 (77%)	20	340
CR4-DODGA	0.18 (15%)	1.1 (52%)	15.06 (94%)	14	83

$[Ln]_t$ = 1mM; equimolar concentrations of metals = 0.33Mm

*from M. Whebie *et al.*, *Sep. Purif. Technol.*, 2016, **169**, 17-24

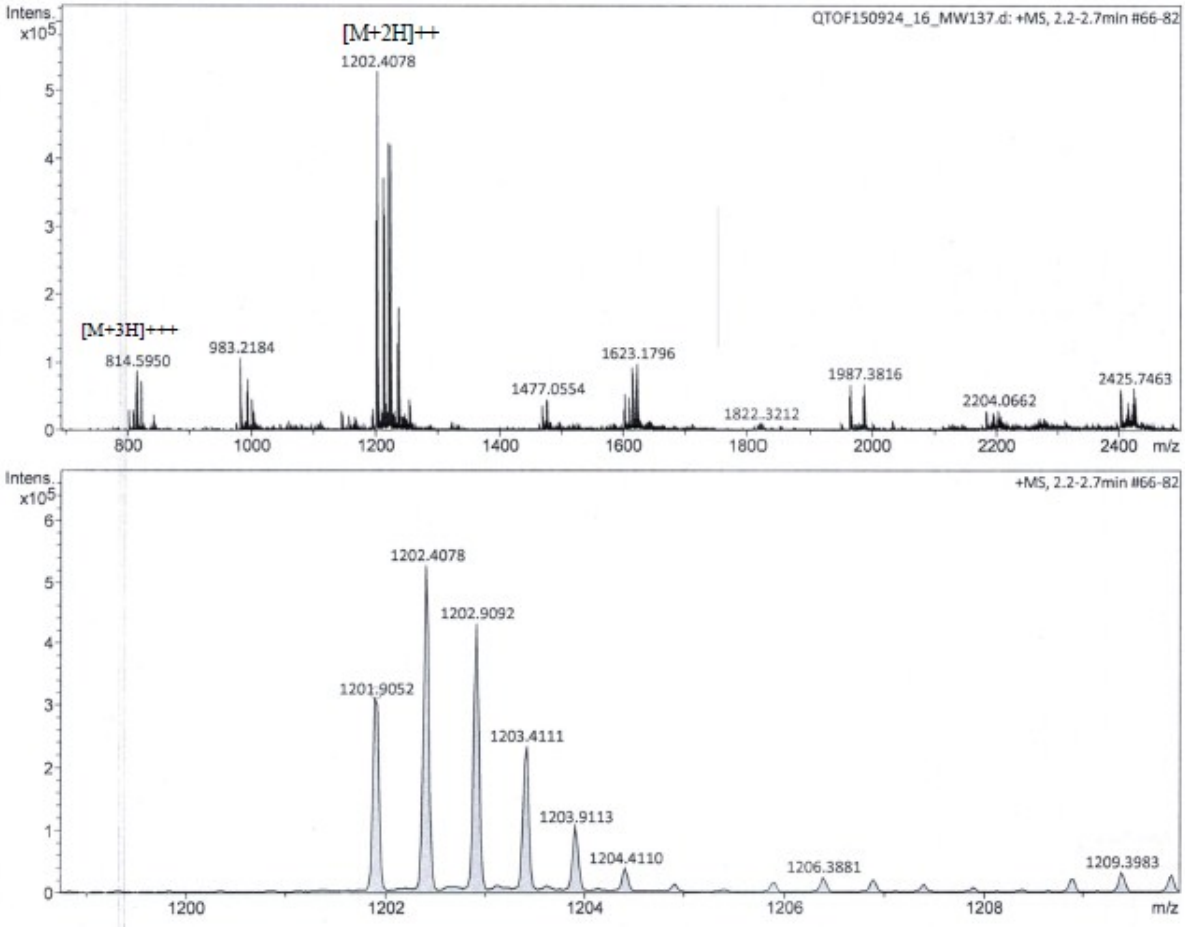
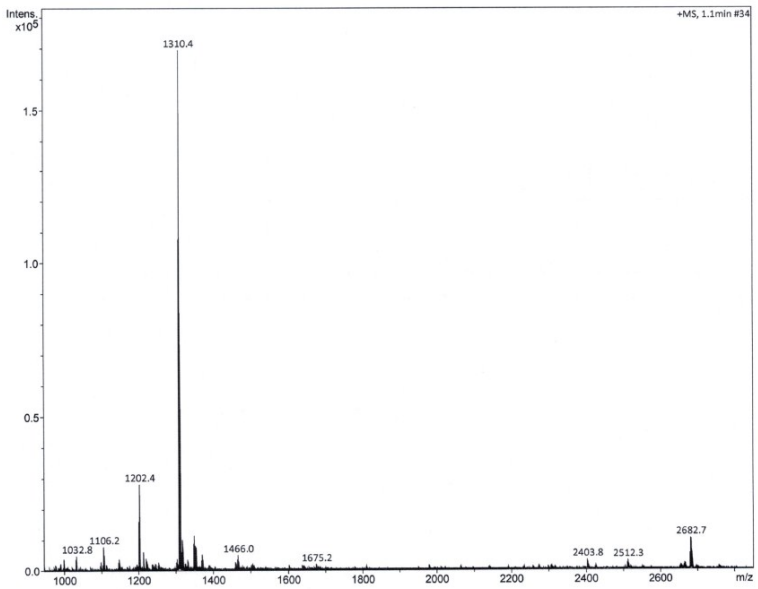
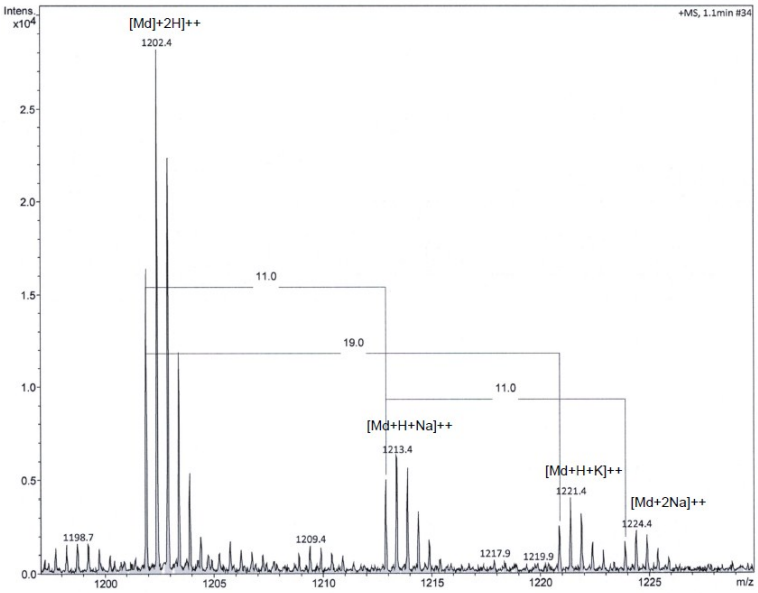


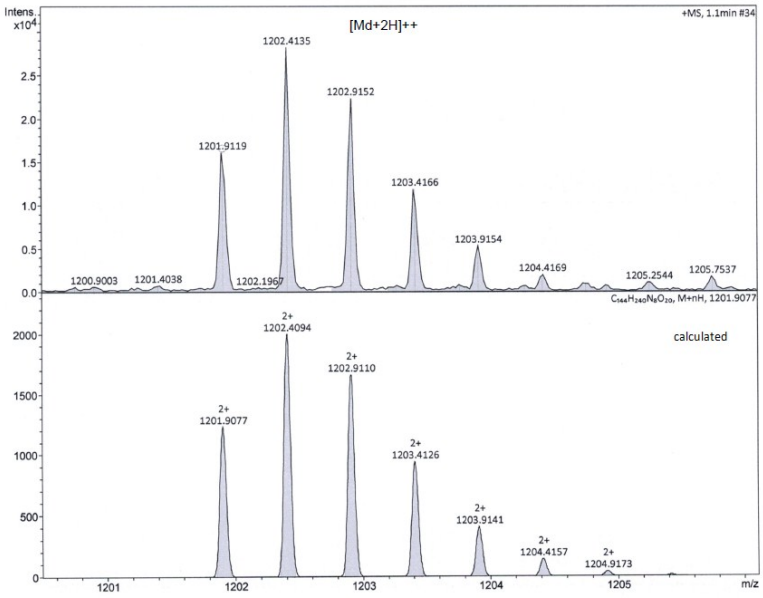
Fig. S1 HRMS of cavitand **III** (CR4-DODGA)

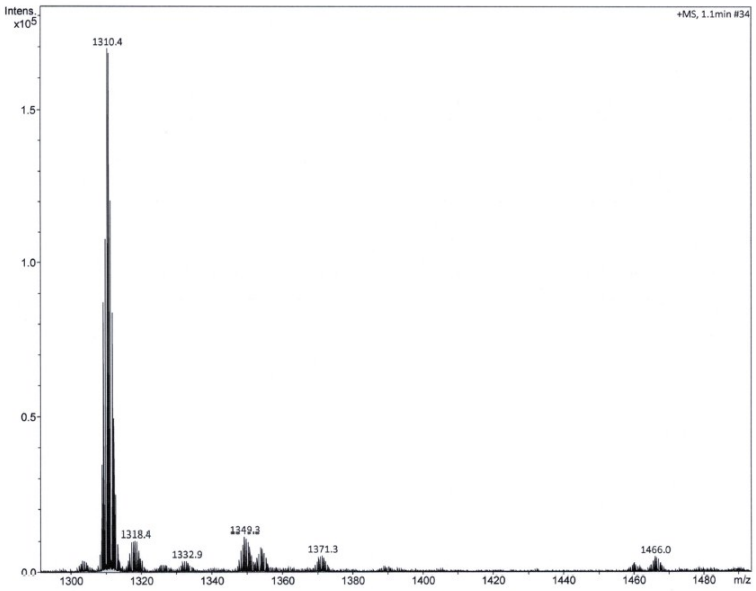
Fig. S2

Experimental and calculated isotopic pattern for $Yb(NO_3)_3$: CR4-DODGA 1:1 complexes








Intens.
x10^5
+MS, 1.1min #34
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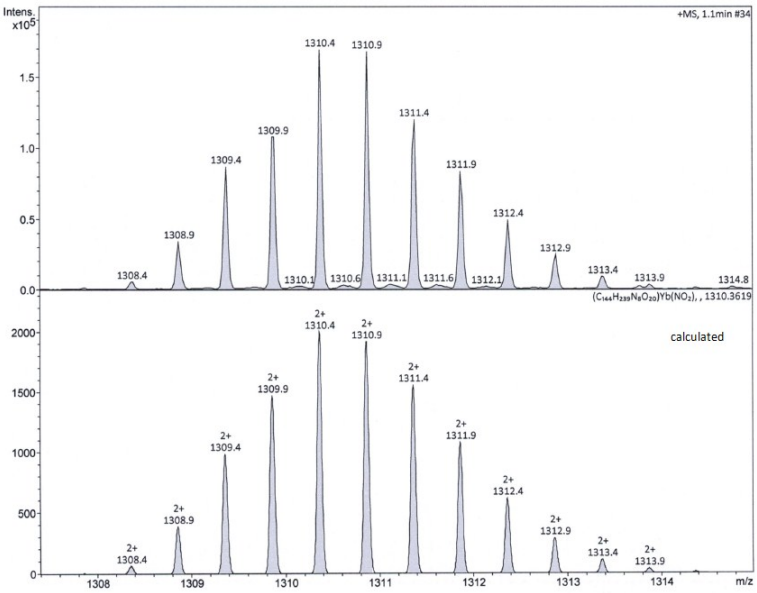
1318.4
1332.9
1349.3
1371.3
1466.0
m/z


Intens.
x10^5
+MS, 1.1min #34
1310.4
1310.9
1311.4
1309.9
1309.4
1311.9
1312.4
1308.9
1312.9
1313.4
1308.4
1313.9
1314.8
(C144H288N4O38)Yb(NO3)3, , 1310.3619
calculated
2+
1310.4
2+
1310.9
2+
1311.4
2+
1309.9
2+
1309.4
2+
1311.9
2+
1312.4
2+
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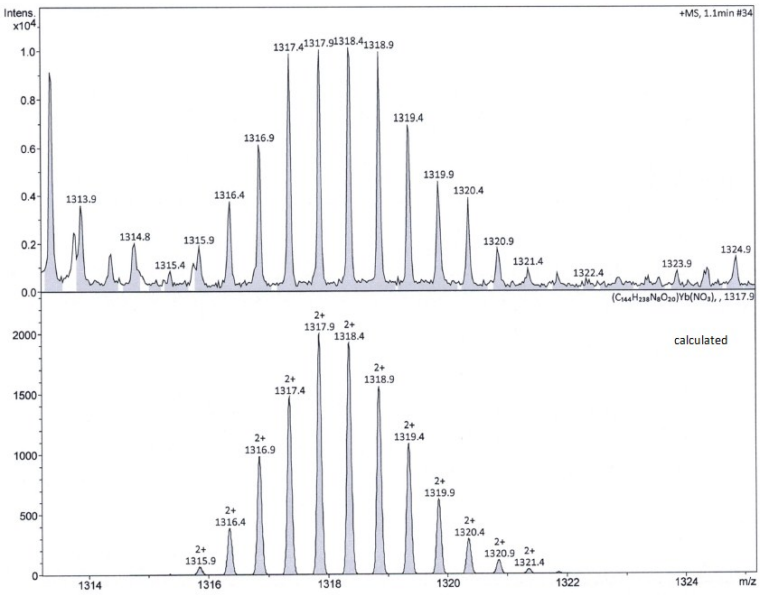
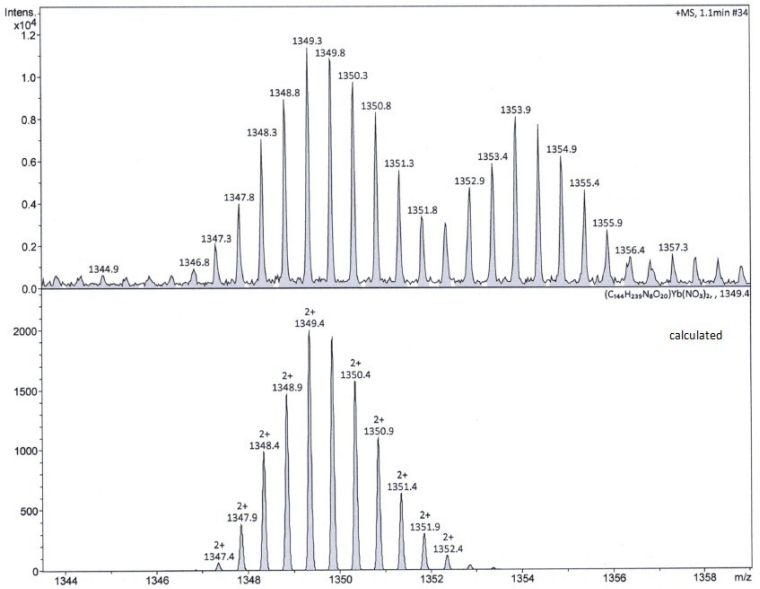
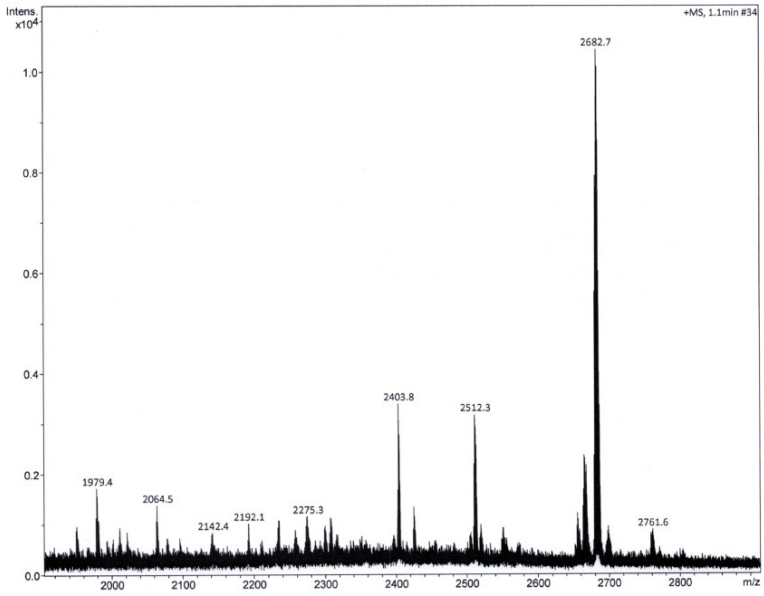
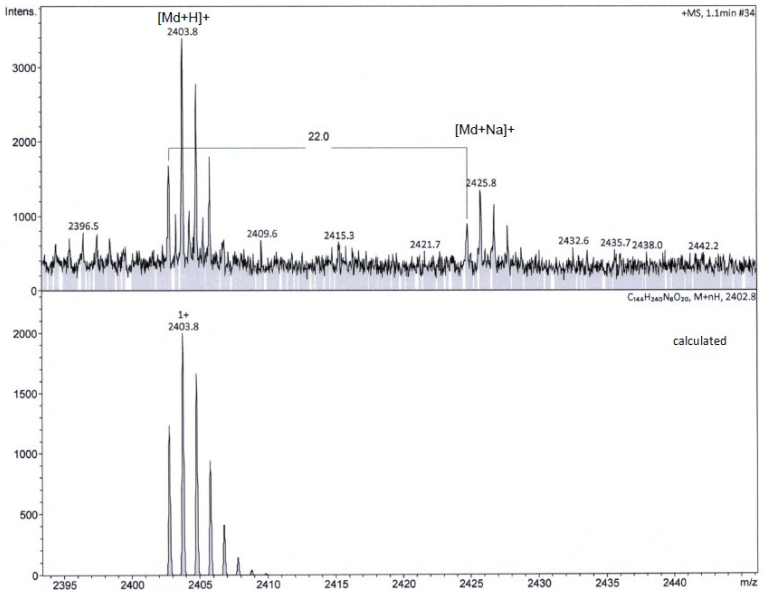
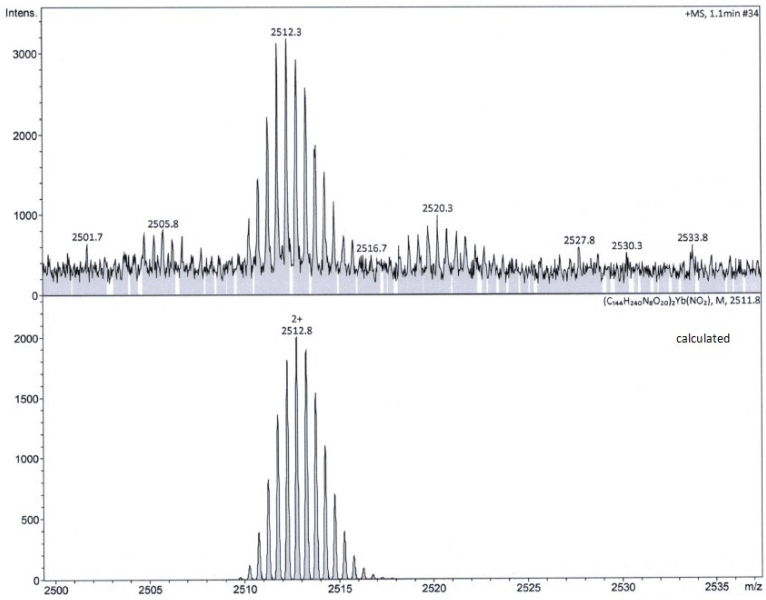
2+
1312.9
2+
1313.4
2+
1308.4
2+
1313.9
m/z


Intens.
x10^4
+MS, 1.1min #34
1317.4
1317.9
1318.4
1318.9
1316.9
1319.4
1319.9
1320.4
1313.9
1316.4
1314.8
1315.9
1315.4
1320.9
1321.4
1322.4
1323.9
1324.9
(C144H238N8O20)Yb(NO3)3 , 1317.9
calculated
2+ 1317.9
2+ 1318.4
2+ 1317.4
2+ 1318.9
2+ 1316.9
2+ 1319.4
2+ 1316.4
2+ 1319.9
2+ 1320.4
2+ 1315.9
2+ 1320.9
2+ 1321.4
m/z


Intens.
x10^4
+MS, 1.1min #34
1349.3
1349.8
1350.3
1348.8
1350.8
1353.9
1348.3
1354.9
1353.4
1351.3
1352.9
1355.4
1347.8
1351.8
1355.9
1347.3
1356.4
1357.3
1344.9
1346.8
(C144H238N8O20)Yb(NO3)2 , 1349.4
calculated
2+ 1349.4
2+ 1348.9
2+ 1350.4
2+ 1348.4
2+ 1350.9
2+ 1351.4
2+ 1347.9
2+ 1351.9
2+ 1347.4
2+ 1352.4
m/z


Intens.
x10^4
+MS, 1.1min #34
2682.7
2403.8
2512.3
1979.4
2064.5
2142.4
2192.1
2275.3
2761.6
m/z


Intens.
+MS, 1.1min #34
[Md+H]+
2403.8
22.0
[Md+Na]+
2425.8
2396.5
2409.6
2415.3
2421.7
2432.6
2435.7
2438.0
2442.2
C144H240N8O20, M+nH, 2402.8
1+
2403.8
calculated
m/z


Intens.
+MS, 1.1min #34
2512.3
2501.7
2505.8
2516.7
2520.3
2527.8
2530.3
2533.8
(C144H240N8O20)2Yb(NO3), M, 2511.8
2+
2512.8
calculated
m/z

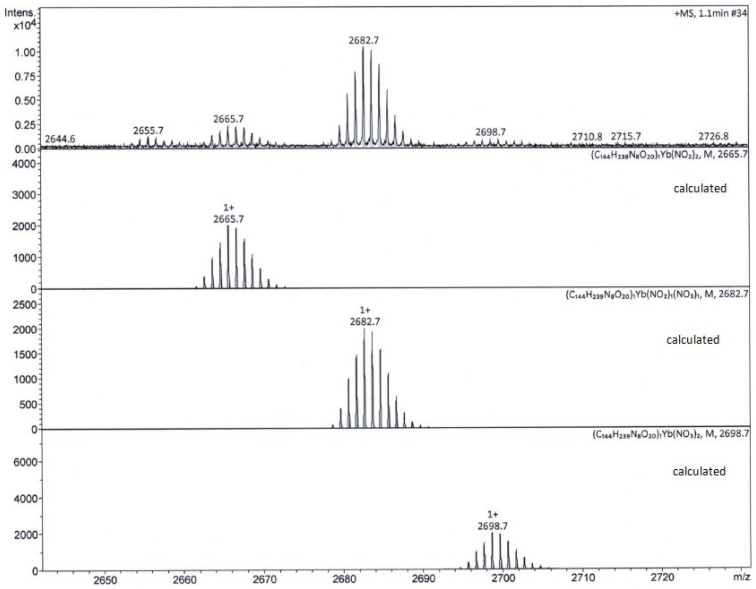
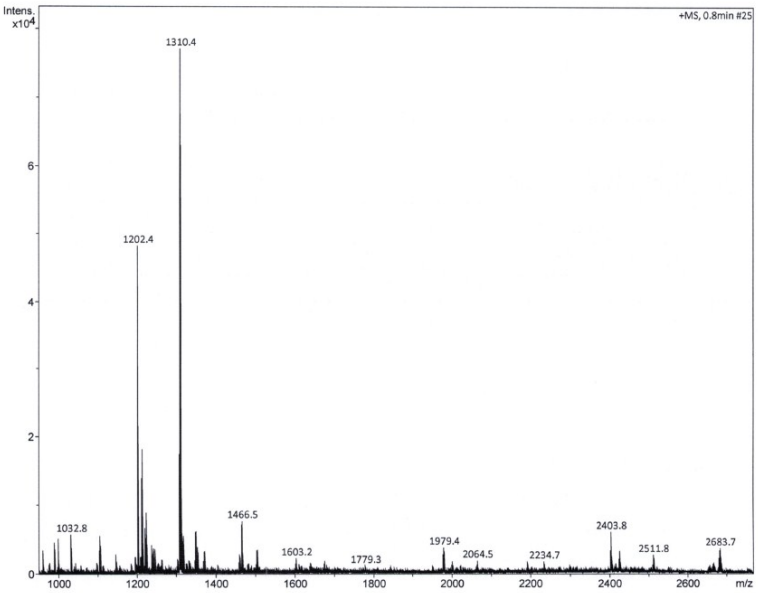
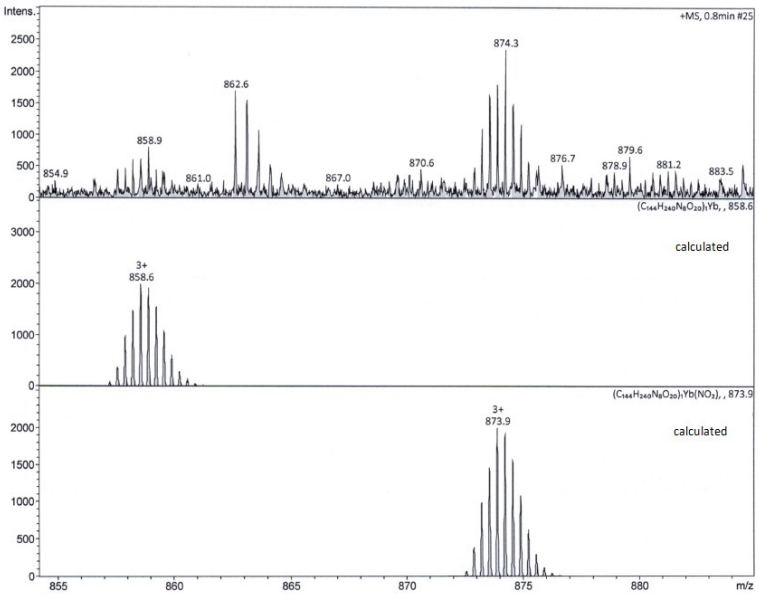
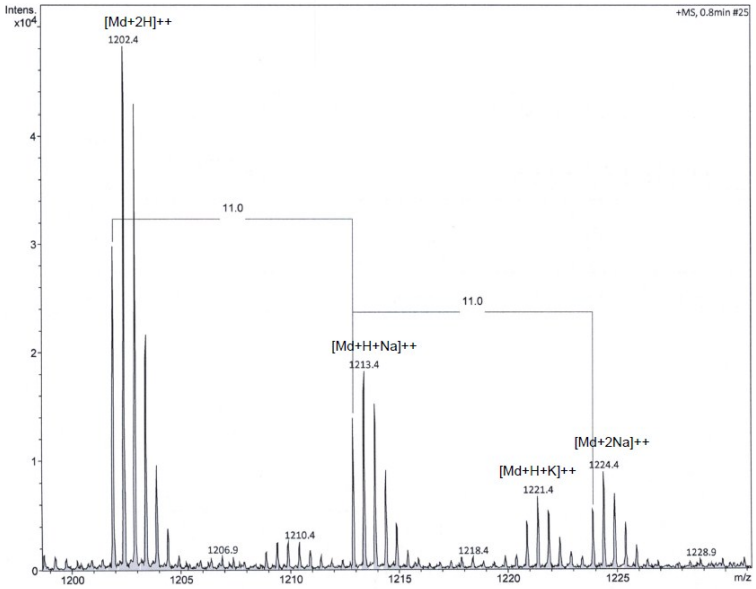

Intens.
x10^4
+MS, 1.1min #34
2682.7
2644.6
2655.7
2665.7
2698.7
2710.8
2715.7
2726.8
(C144H238N8O20)2Yb(NO3)2, M, 2665.7
calculated
1+
2665.7
(C144H239N8O20)2Yb(NO3)(NO3)2, M, 2682.7
1+
2682.7
calculated
(C144H239N8O20)2Yb(NO3)2, M, 2698.7
calculated
1+
2698.7
m/z

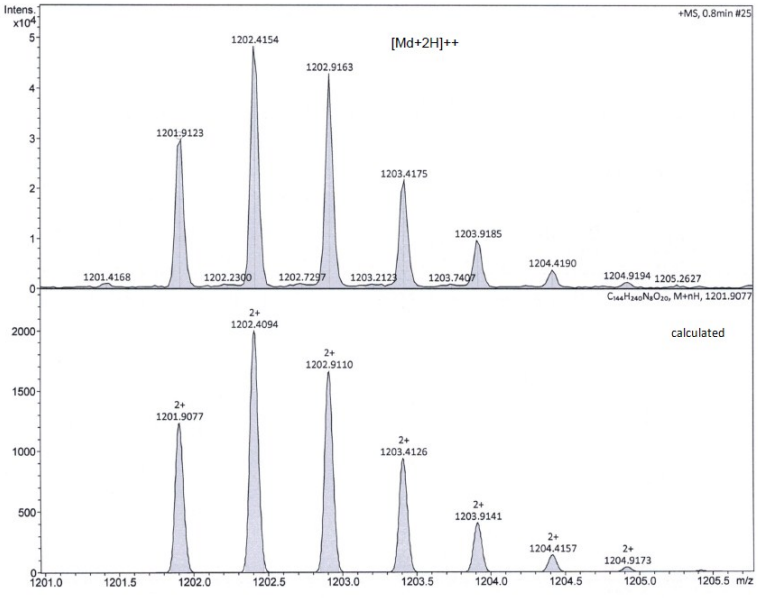
Fig. S3

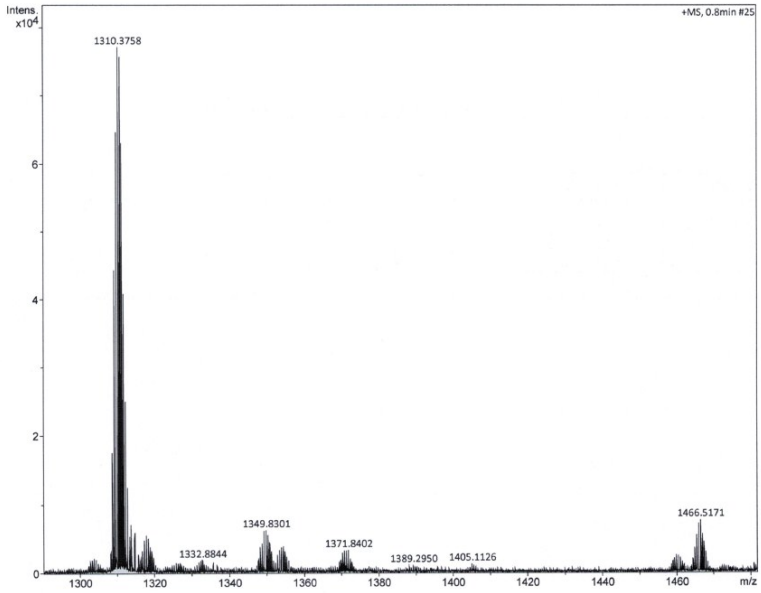
Experimental and calculated isotopic pattern for $Yb(NO_3)_3$: CR4-DODGA 2:1 complexes






Intens.
x10^4
+MS, 0.8min #25
[Md+2H]++
1202.4
11.0
11.0
[Md+H+Na]++
1213.4
[Md+2Na]++
1224.4
[Md+H+K]++
1221.4
1206.9
1210.4
1218.4
1228.9
m/z


Intens.
x10^4
+MS, 0.8min #25
[Md+2H]++
1202.4154
1202.9163
1201.9123
1203.4175
1203.9185
1204.4190
1201.4168
1202.2300
1202.7297
1203.2123
1203.7407
1204.9194
1205.2627
C144H240N4O20, M+nH, 1201.9077
calculated
2+
1202.4094
2+
1202.9110
2+
1201.9077
2+
1203.4126
2+
1203.9141
2+
1204.4157
2+
1204.9173
m/z


Intens.
x10^4
+MS, 0.8min #25
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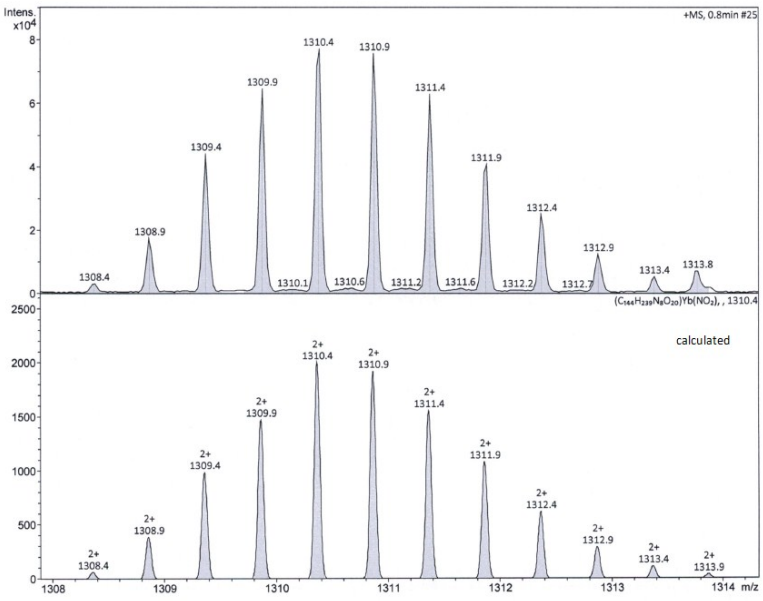
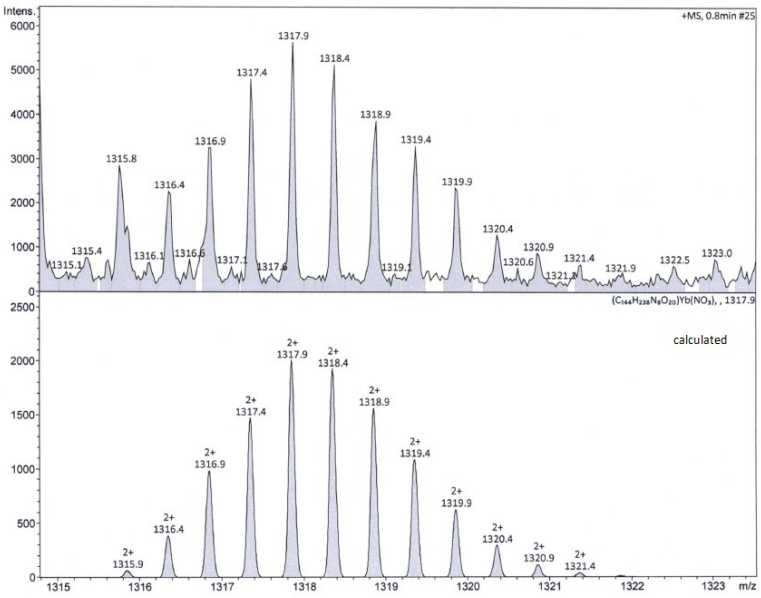
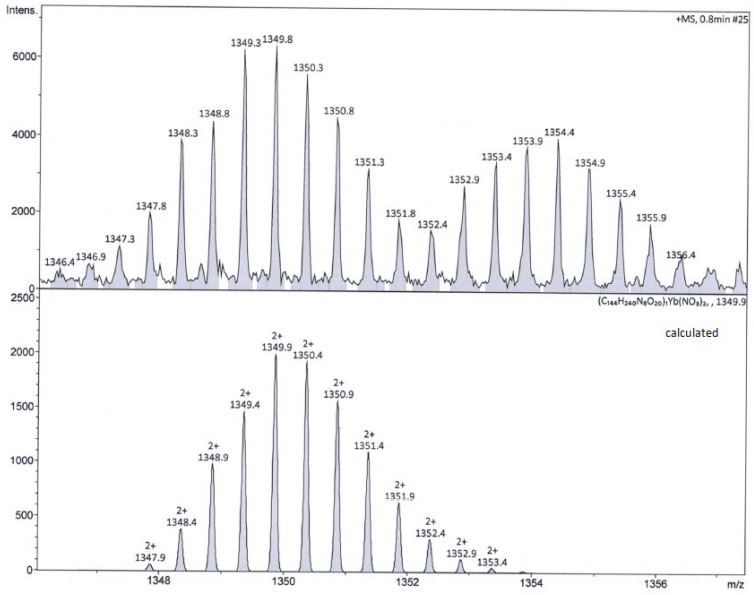
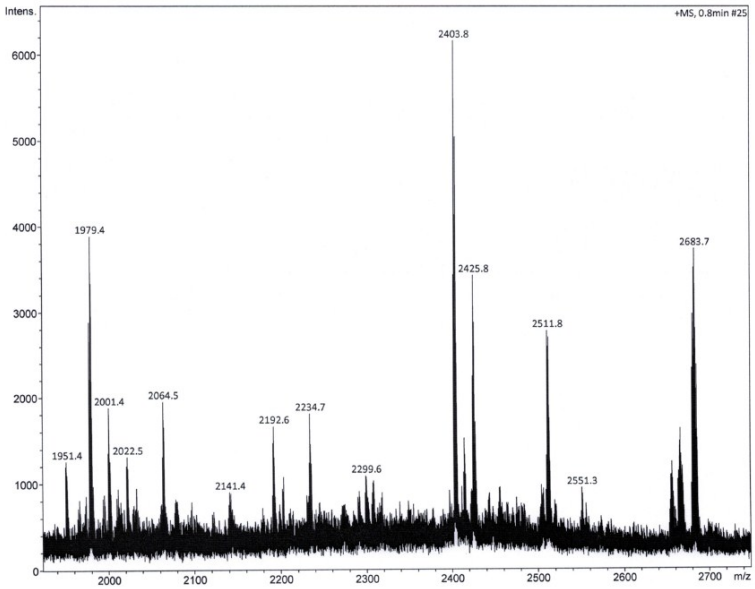
1349.8301
1371.8402
1332.8844
1389.2950
1405.1126
1466.5171
m/z


Intens.
x10^4
+MS, 0.8min #25
1310.4
1310.9
1309.9
1311.4
1309.4
1311.9
1312.4
1308.9
1312.9
1313.4
1313.8
1308.4
(C166H239N8O20)Yb(NO3), , 1310.4
calculated
2+ 1310.4
2+ 1310.9
2+ 1309.9
2+ 1311.4
2+ 1309.4
2+ 1311.9
2+ 1312.4
2+ 1308.9
2+ 1312.9
2+ 1313.4
2+ 1308.4
2+ 1313.9
m/z


Intens.
+MS, 0.8min #25
1317.9
1318.4
1317.4
1318.9
1319.4
1316.9
1315.8
1319.9
1316.4
1320.4
1320.9
1315.4
1321.4
1323.0
1322.5
1321.9
1315.1
1316.1
1316.6
1317.1
1317.6
1319.1
1320.6
1321.2
(C144H228N8O20)Yb(NO3)3 , 1317.9
calculated
2+ 1317.9
2+ 1318.4
2+ 1317.4
2+ 1318.9
2+ 1316.9
2+ 1319.4
2+ 1319.9
2+ 1316.4
2+ 1320.4
2+ 1320.9
2+ 1321.4
2+ 1315.9
m/z


Intens.
+MS, 0.8min #25
1349.3
1349.8
1350.3
1348.8
1350.8
1348.3
1353.9
1354.4
1353.4
1351.3
1354.9
1352.9
1347.8
1355.4
1351.8
1355.9
1347.3
1352.4
1346.4
1346.9
1356.4
(C144H240N8O20)2Yb(NO3)3 , 1349.9
calculated
2+ 1349.9
2+ 1350.4
2+ 1349.4
2+ 1350.9
2+ 1348.9
2+ 1351.4
2+ 1351.9
2+ 1348.4
2+ 1352.4
2+ 1352.9
2+ 1347.9
2+ 1353.4
m/z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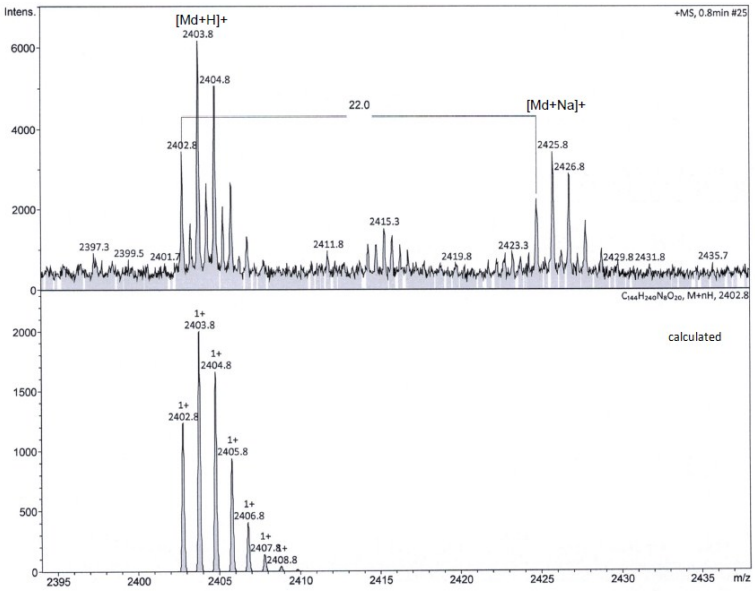
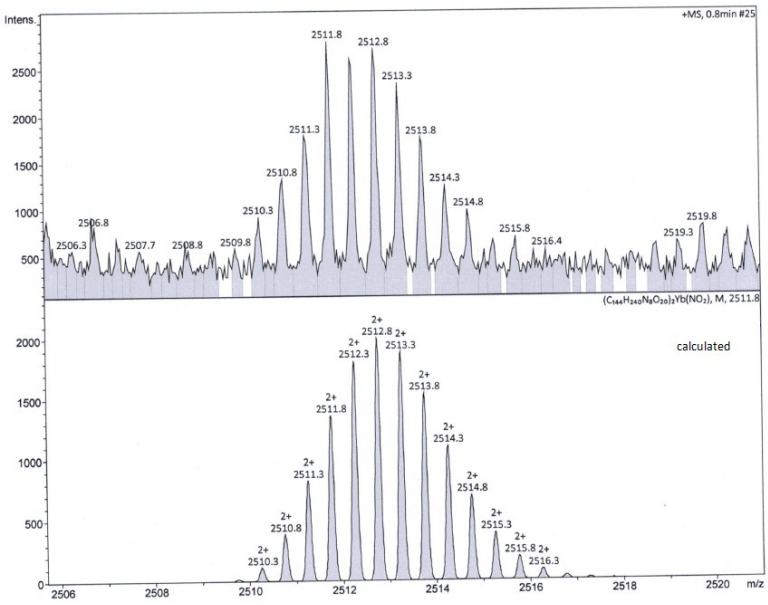
2403.8
1979.4
2425.8
2683.7
2511.8
2001.4
2064.5
2234.7
2192.6
1951.4
2022.5
2299.6
2141.4
2551.3
m/z


Intens.
+MS, 0.8min #25
[Md+H]+
2403.8
2404.8
22.0
[Md+Na]+
2402.8
2425.8
2426.8
2415.3
2397.3
2399.5
2401.7
2411.8
2419.8
2423.3
2429.8
2431.8
2435.7
C144H240N6O20, M+nH, 2402.8
calculated
1+
2403.8
1+
2404.8
1+
2402.8
1+
2405.8
1+
2406.8
1+
2407.8
1+
2408.8
m/z


Intens.
+MS, 0.8min #25
2511.8
2512.8
2513.3
2511.3
2513.8
2510.8
2514.3
2514.8
2510.3
2506.8
2515.8
2519.8
2506.3
2507.7
2508.8
2509.8
2516.4
2519.3
(C144H142N8O20)2Yb(NO2), M, 2511.8
calculated
2+
2512.8
2+
2512.3
2+
2513.3
2+
2513.8
2+
2511.8
2+
2514.3
2+
2511.3
2+
2514.8
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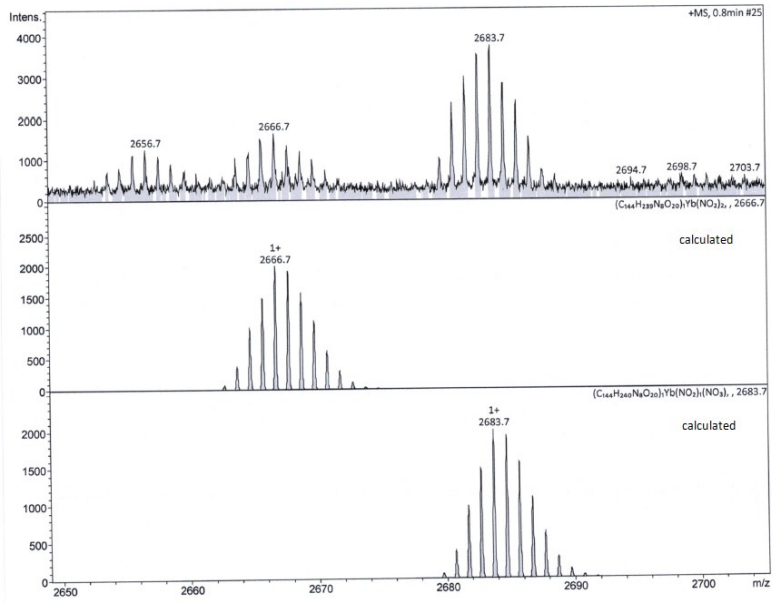
2+
2515.8
2+
2510.3
2+
2516.3
m/z


Intens.
+MS, 0.8min #25
2683.7
2666.7
2656.7
2694.7
2698.7
2703.7
(C144H239N8O20)3Yb(NO2)3, , 2666.7
calculated
1+
2666.7
(C144H240N8O20)3Yb(NO2)3(NO3), , 2683.7
calculated
1+
2683.7
m/z