Electronic Supplementary Information (ESI) for:

H_4octapa: Synthesis, Solution Equilibria and Complexes with Useful Radiopharmaceutical Metal Ions

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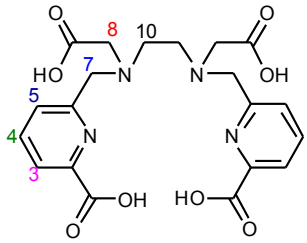
Table S1. ^{1}H NMR chemical shifts δ (ppm) and variations of chemical shifts Δδ (ppm) of a set of solutions at the same ligand concentration [H_4octapa] = 3.8 x 10^{-3} M and different acidities, at 25 °C, I = 0.16 M NaCl.



H_4octapa

H^0 or pH	H10	H8	H7	H3	H4	H5
-0.11	3.46	3.87	4.44	7.98	8.02	7.64
0.08	3.51	3.92	4.49	8.04	8.08	7.7
0.33	3.59	3.98	4.57	8.13	8.18	7.79
0.69	3.6	3.98	4.58	8.14	8.19	7.8
0.83	3.6	3.98	4.58	8.15	8.21	7.81
0.92	3.62	3.99	4.6	8.17	8.23	7.84
1.02	3.6	3.97	4.58	8.16	8.22	7.82
1.13	3.6	3.96	4.58	8.17	8.23	7.83
1.29	3.59	3.94	4.57	8.17	8.24	7.84
1.45	3.58	3.92	4.57	8.17	8.24	7.84
1.62	3.58	3.9	4.56	8.16	8.24	7.84
1.81	3.57	3.88	4.55	8.17	8.25	7.85
2.00	3.56	3.86	4.55	8.16	8.25	7.85

H^0 or pH	$\Delta\delta_{H10}$	$\Delta\delta_{H8}$	$\Delta\delta_{H7}$	$\Delta\delta_{H3}$	$\Delta\delta_{H4}$	$\Delta\delta_{H5}$
0.08	0.05	0.05	0.05	0.06	0.06	0.06
0.33	0.08	0.06	0.08	0.09	0.1	0.09
0.69	0.01	0	0.01	0.01	0.01	0.01
0.83	0	0	0	0.01	0.02	0.01
0.92	0.02	0.01	0.02	0.02	0.02	0.03
1.02	-0.02	-0.02	-0.02	-0.01	-0.01	-0.02
1.13	0	-0.01	0	0.01	0.01	0.01
1.29	-0.01	-0.02	-0.01	0	0.01	0.01
1.45	-0.01	-0.02	0	0	0	0
1.62	0	-0.02	-0.01	-0.01	0	0
1.81	-0.01	-0.02	-0.01	0.01	0.01	0.01
2.00	-0.01	-0.02	0	-0.01	0	0

Figure S1. Variation of the chemical shift δ (ppm) *vs*. Acidity of a set of solutions at the same ligand concentration [H_4octapa] = 3.8 x 10^{-3} M at 25 °C.

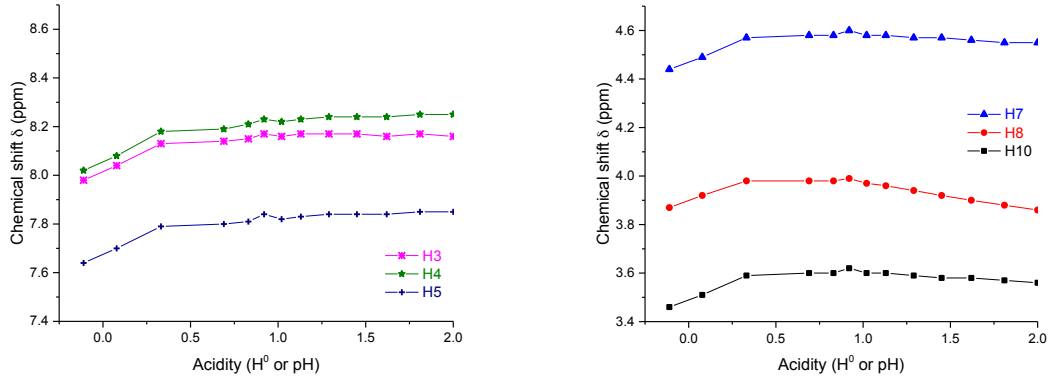


Figure S2. Representative spectra of the UV-Vis spectrophotometric titration of [H_4octapa] = 1.28 x 10^{-4} M at 25 °C, path length = 1 cm.

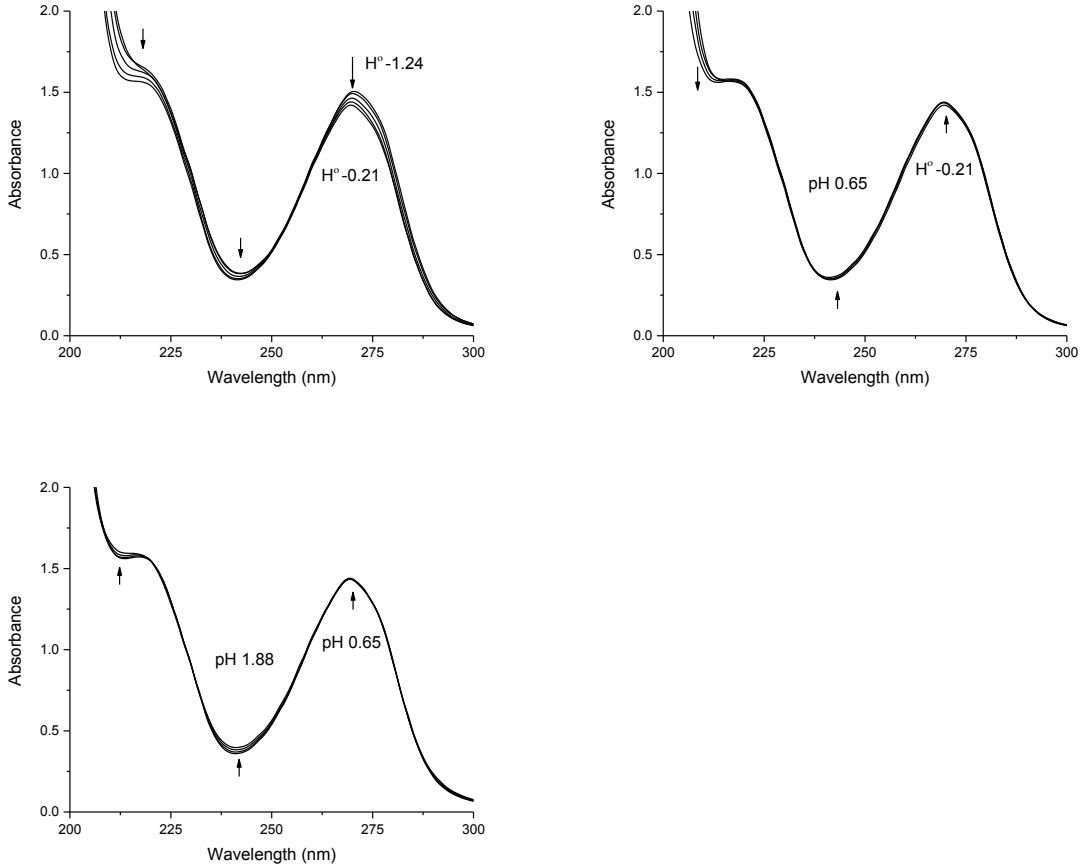


Figure S3. Representative spectra of the Sm^{3+}-H_4octapa system. a) In batch UV spectrophotometric experiments, $[H_4octapa] = [Sm]^{3+} = 1.51 \times 10^{-4}$ M, path length = 1cm; b) and c) Combined potentiometric-spectrophotometric titrations, $[H_4octapa] = 5.56 \times 10^{-4}$ M, $[Sm]^{3+} = 5.52 \times 10^{-4}$ M, path length = 0.2 cm, at 25 °C and I = 0.16 M NaCl.

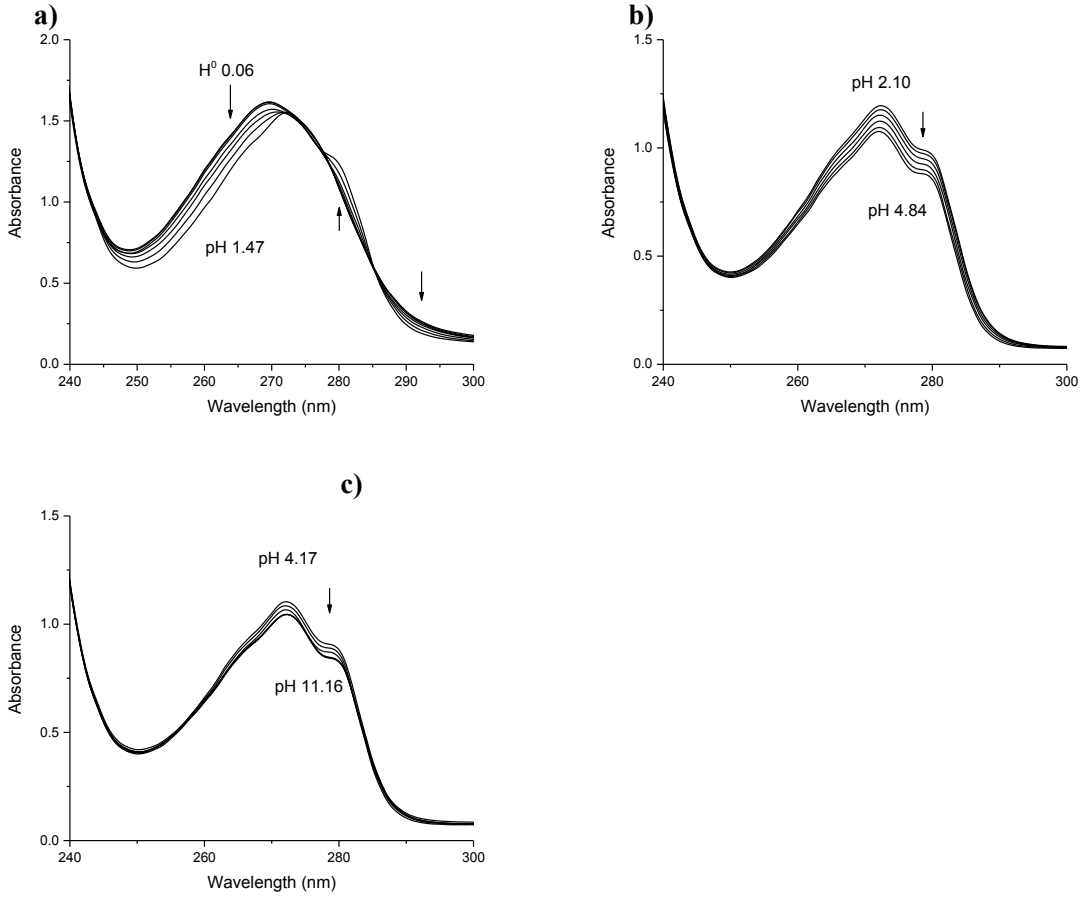


Figure S4. a) and b) Representative spectra of the in batch UV spectrophotometric experiments for the Dy^{3+}-H_4octapa system, $[H_4octapa] = 1.38 \times 10^{-4}$ M, $[Dy]^{3+} = 1.37 \times 10^{-4}$ M, path length = 1 cm, at 25 °C and I = 0.16 M NaCl.

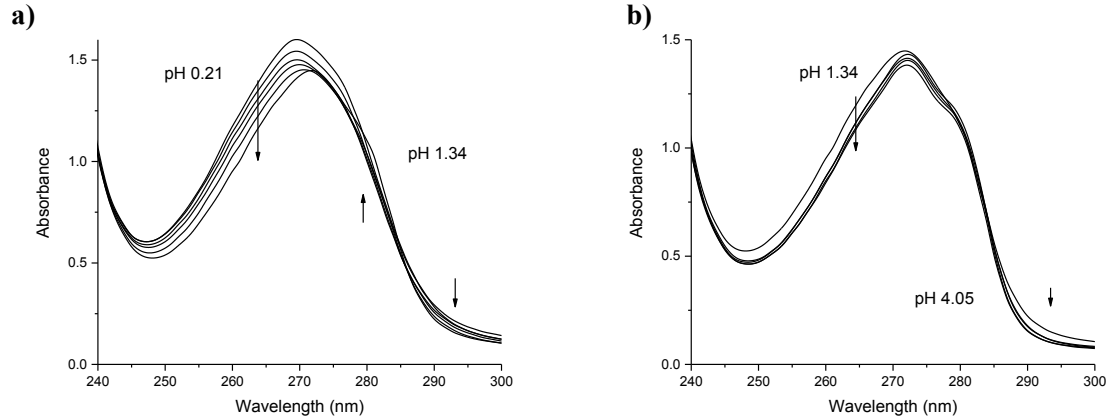
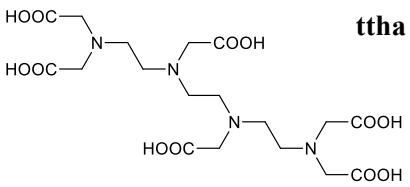


Table S2. Protonation constants and stability constants of ttha^{6-} ligand and its complexes with Sm^{3+}, Dy^{3+} and Yb^{3+} metal ions at 25 °C and I = 0.16 M NaCl.

equilibrium reaction	ttha^{6-}
$L + H+ \leftrightarrows HL$	9.98(4)
$HL + H+ \leftrightarrows H_2L$	9.21(3)
$H_2L + H+ \leftrightarrows H_3L$	6.14(3)
$H_3L + H+ \leftrightarrows H_4L$	4.04(4)
$H_4L + H+ \leftrightarrows H_5L$	2.94(5)
$H_5L + H+ \leftrightarrows H_6L$	2.10(3)



ttha ligand

$\log K_{M_pH_pL_r}$	Sm^{3+}	Dy^{3+}	Yb^{3+}
$\log K_{ML}$	23.36(3)	23.37(2)	22.71(4)
$\log K_{MHL}$	4.44(3)	4.45(2)	4.70(3)
$\log K_{MH2L}$	2.45(4)	2.55(2)	2.76(3)
$\log K_{M2L}$	2.94(2)	3.21(1)	2.85(2)

Scheme S1. Previously reported synthetic schemes for the H_4octapa ligand. Route 1, from reference[1]; route 2, from reference[2].

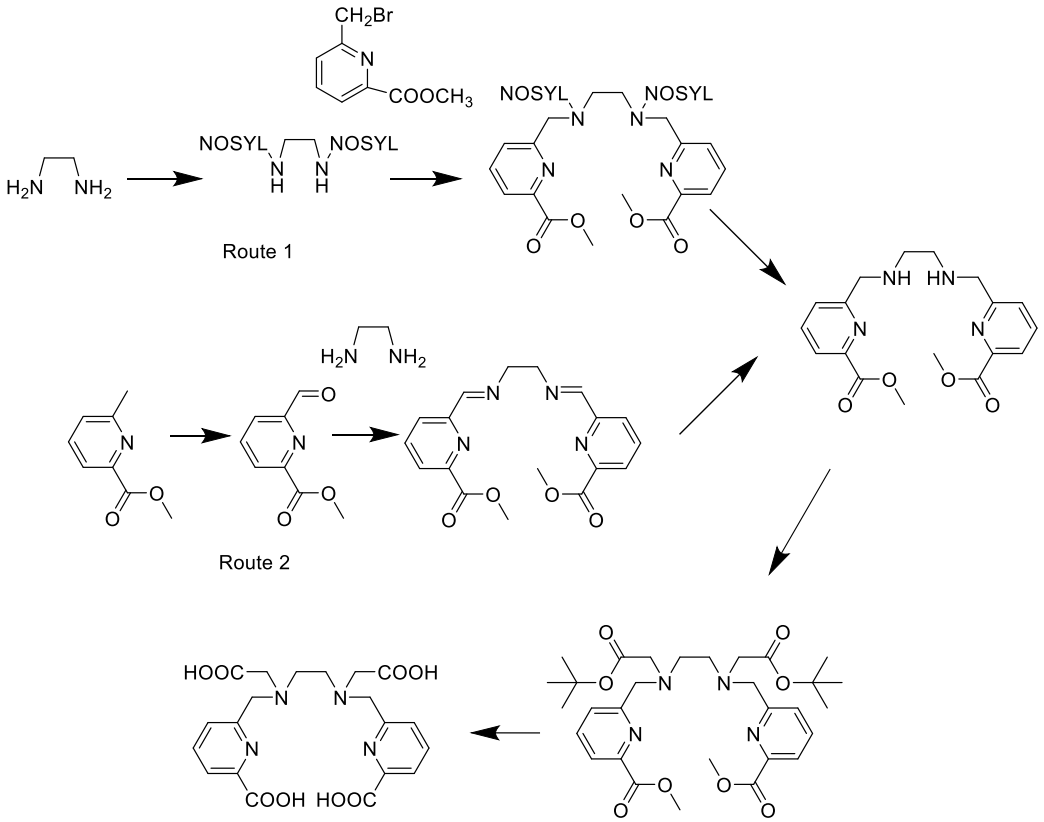


Figure S5. ^{1}H NMR (300 MHz, D_2O, 25 °C) spectrum of dimethyl-2,2'-(ethane-1,2-diylbis(azanediyl))-diacetate (**1**)

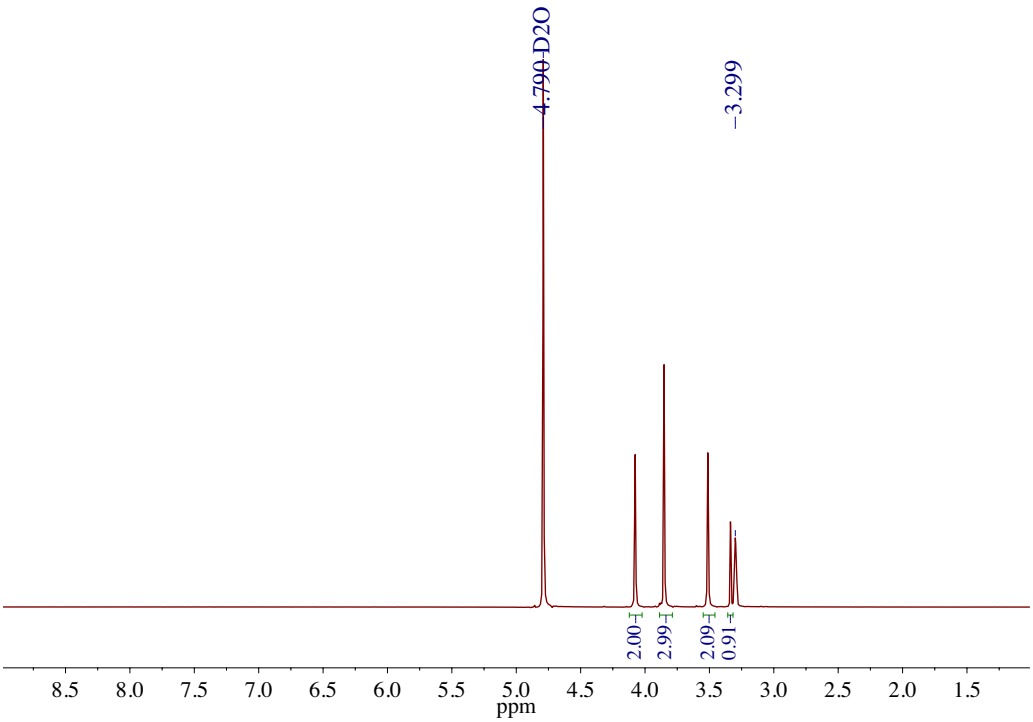


Figure S6. ^{13}C NMR (100 MHz, D_2O, 25 °C) spectrum of dimethyl-2,2'-(ethane-1,2-diylbis(azanediyl))-diacetate (**1**)

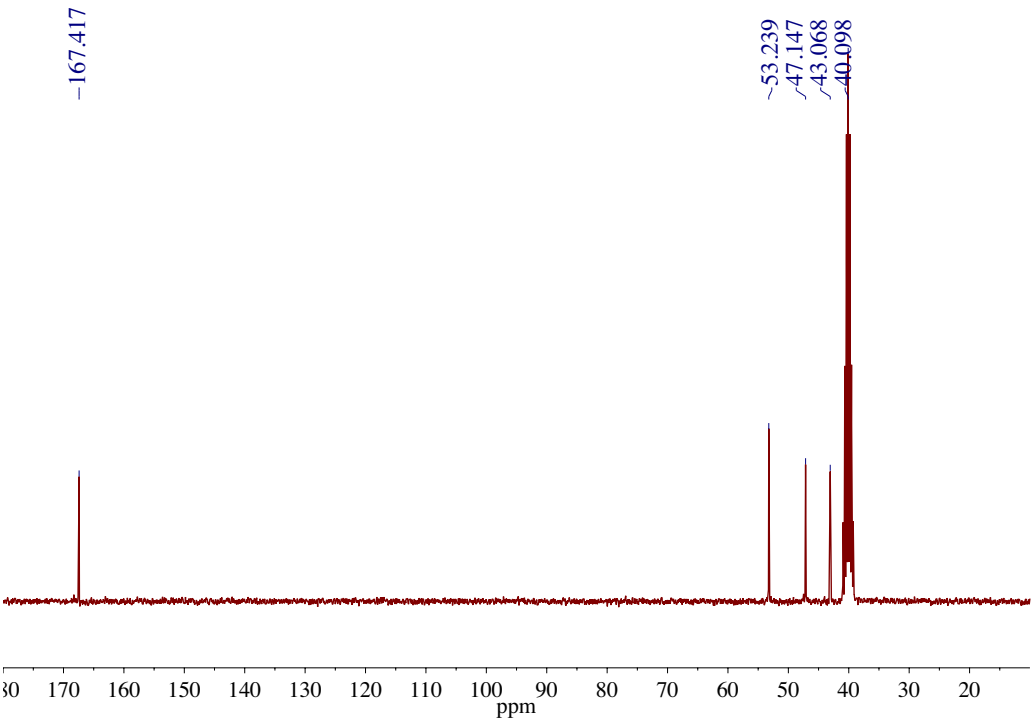


Figure S7. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) spectrum of methyl 6-(hydroxymethyl)picolinate (**2**)

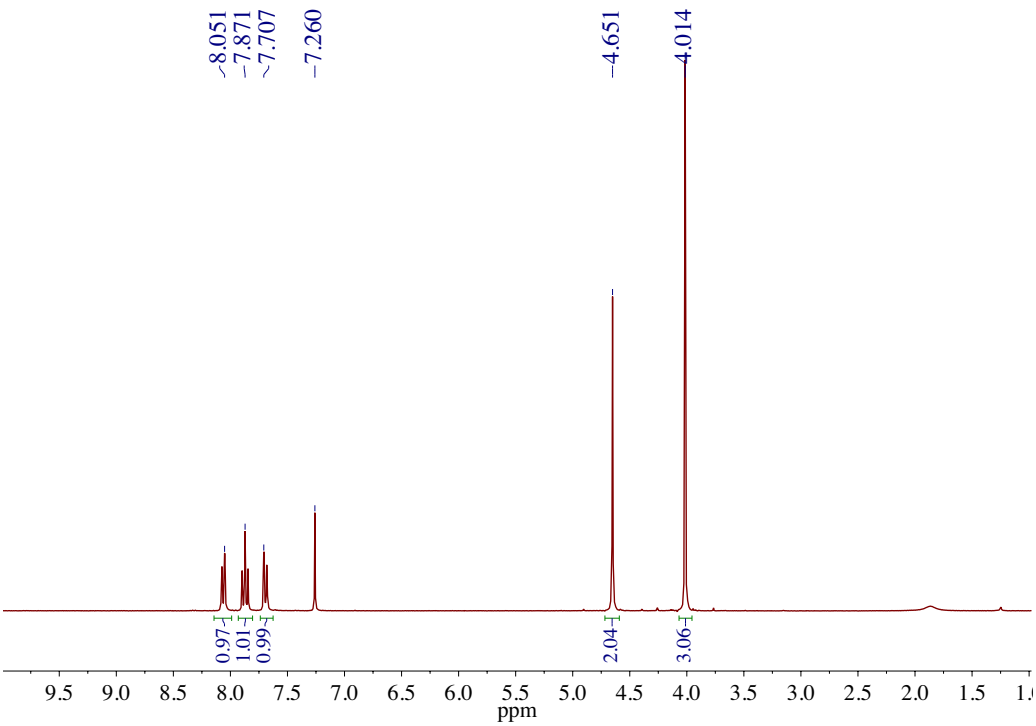


Figure S8. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) spectrum of dimethyl 6,6'-((3,10-dioxo-2,11-dioxa-5,8-diazadodecane-5,8-diyl)bis(methylene))dipicolinate (**3**).

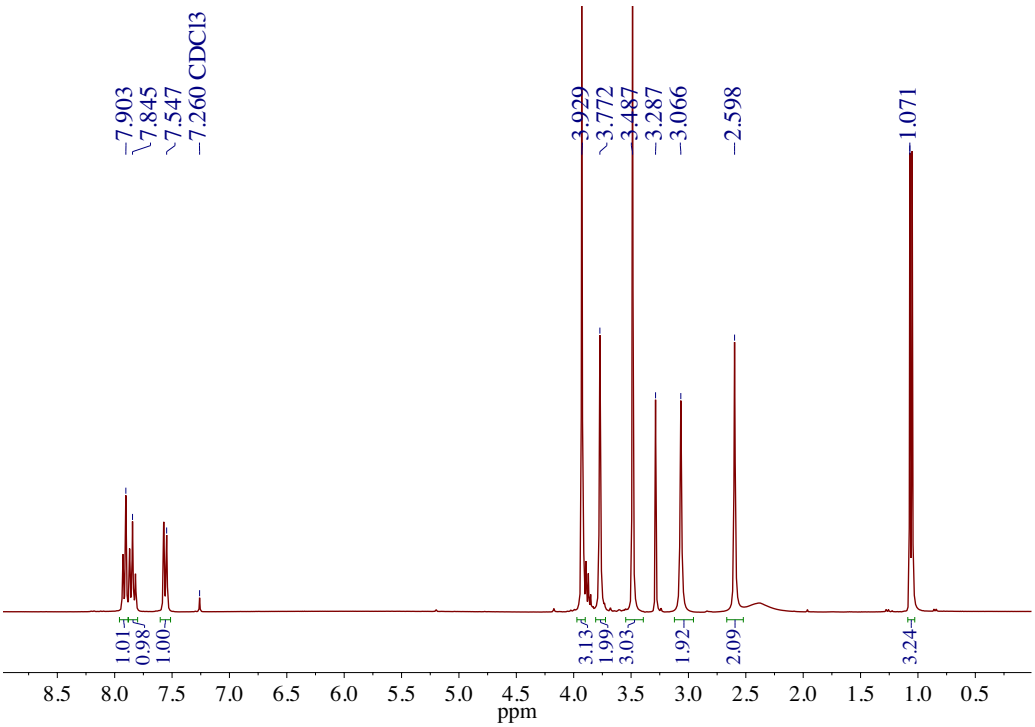


Figure S9. ^{1}H NMR (400 MHz, D2O, 25 °C) spectrum of H_4octapa, N,N′-bis(6-carboxy-2-pyridylmethyl)ethylenediamine-N,N′-diacetic acid (**4**).

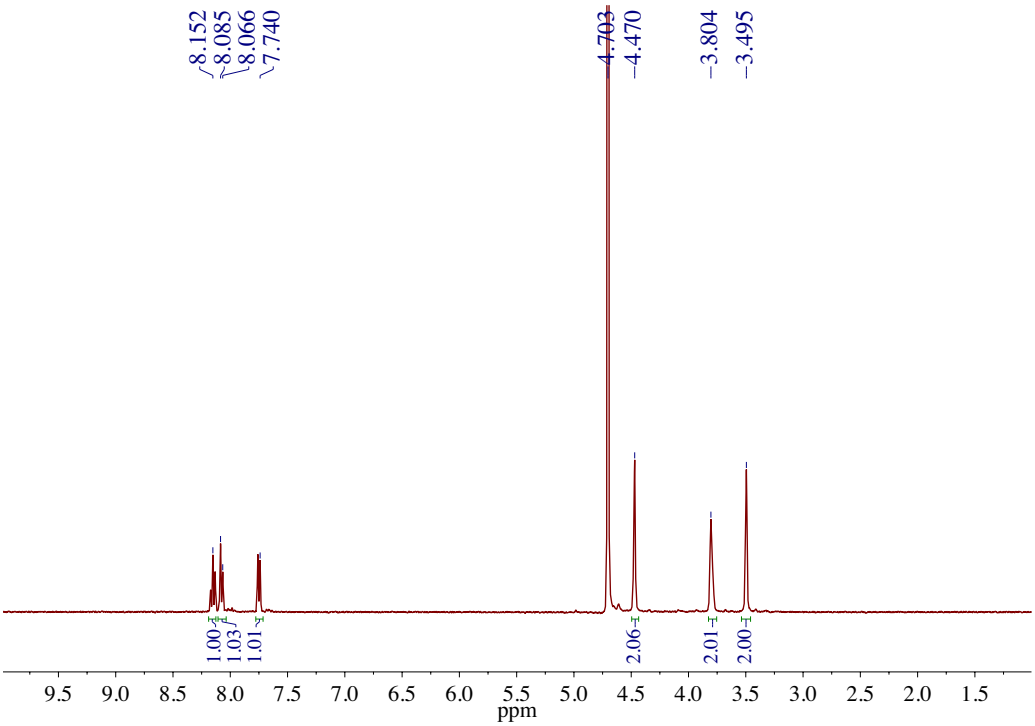


Figure S10. ^{13}C NMR (100 MHz, D2O, 25 °C) spectrum of H_4octapa, N,N′-bis(6-carboxy-2-pyridylmethyl)ethylenediamine-N,N′-diacetic acid, (**4**)

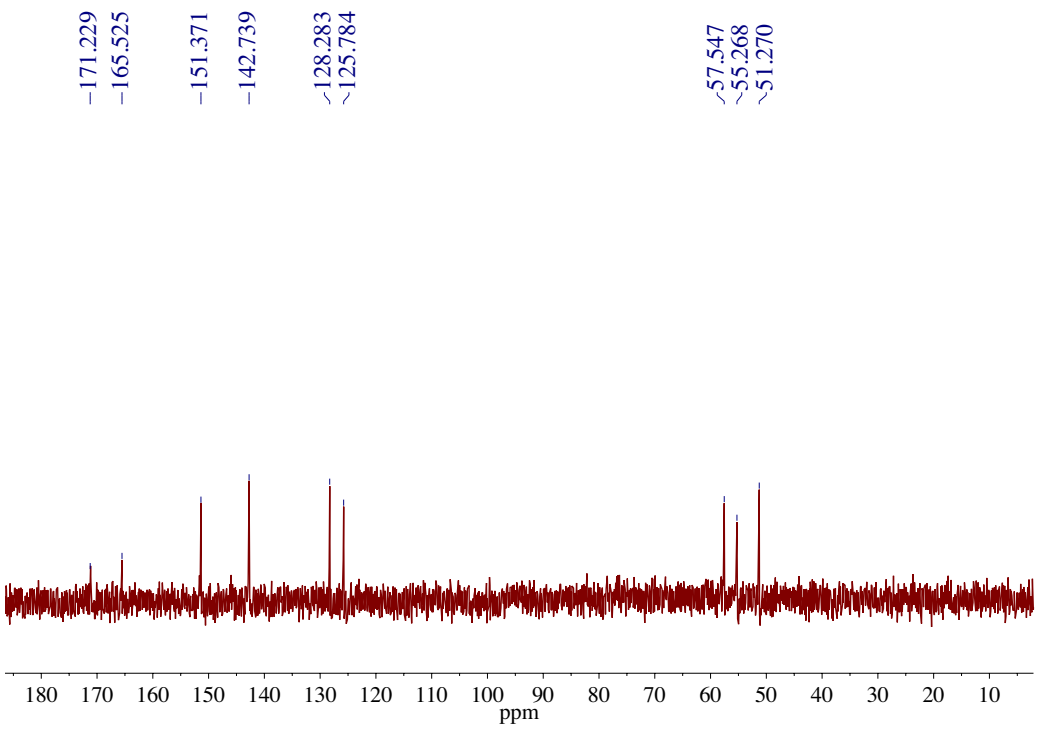


Figure S11. HR-ESI-MS spectrum of H_4octapa, N,N′-bis(6-carboxy-2-pyridylmethyl)ethylenediamine-N,N′-diacetic acid, (**4**)

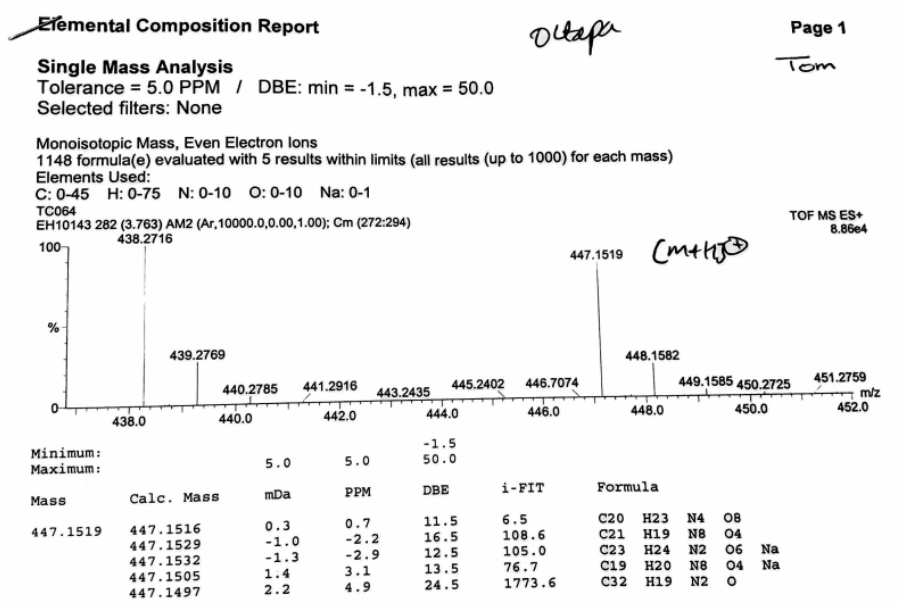


Figure S12. IR (neat) spectrum of H_4octapa, N,N′-bis(6-carboxy-2-pyridylmethyl)ethylenediamine-N,N′-diacetic acid, (**4**)

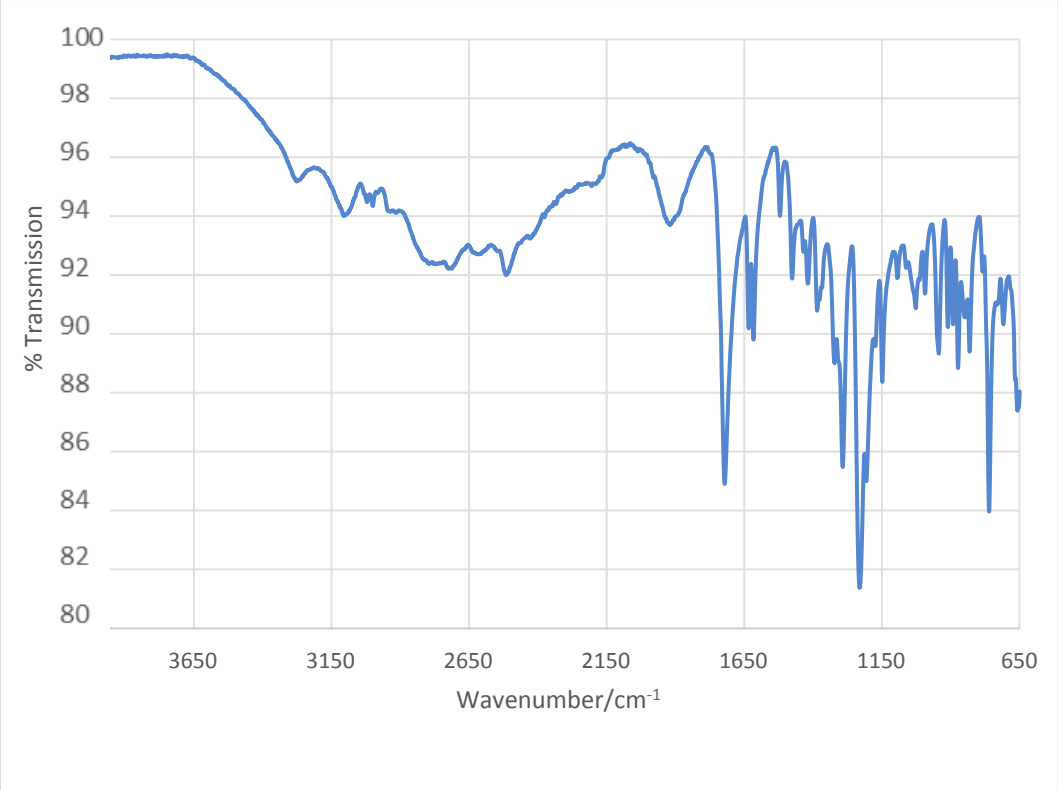


Figure S13. IR (neat) spectrum of Na[La(octapa)], (**5**)

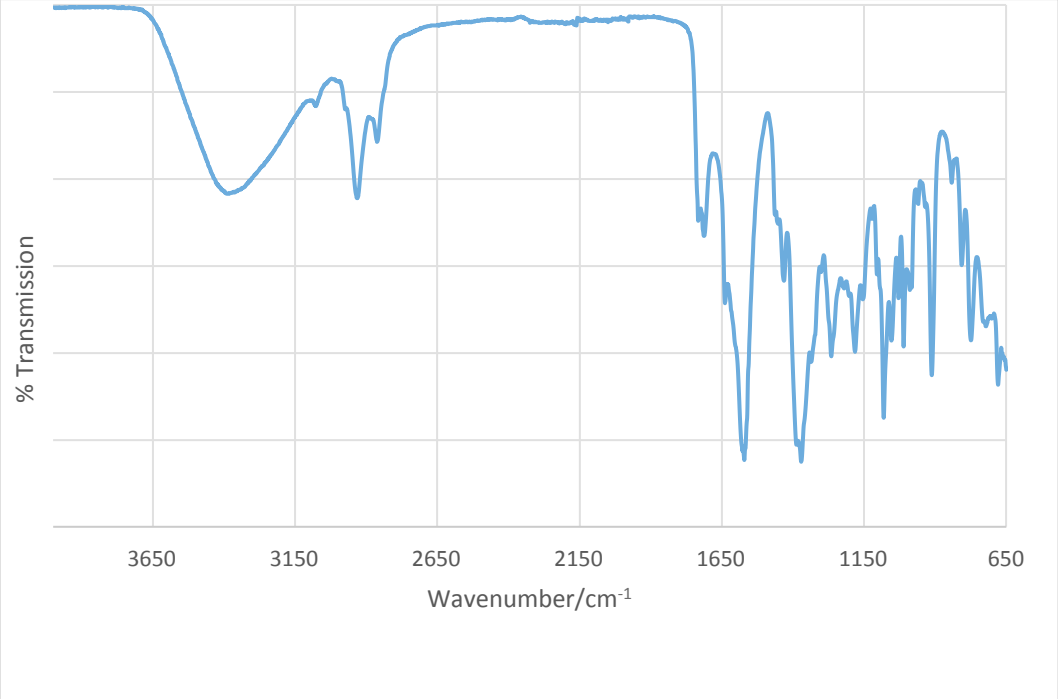


Figure S14. ^{1}H NMR (300 MHz, D_2O, 25 °C) spectrum of Na[La(octapa)], (**5**)

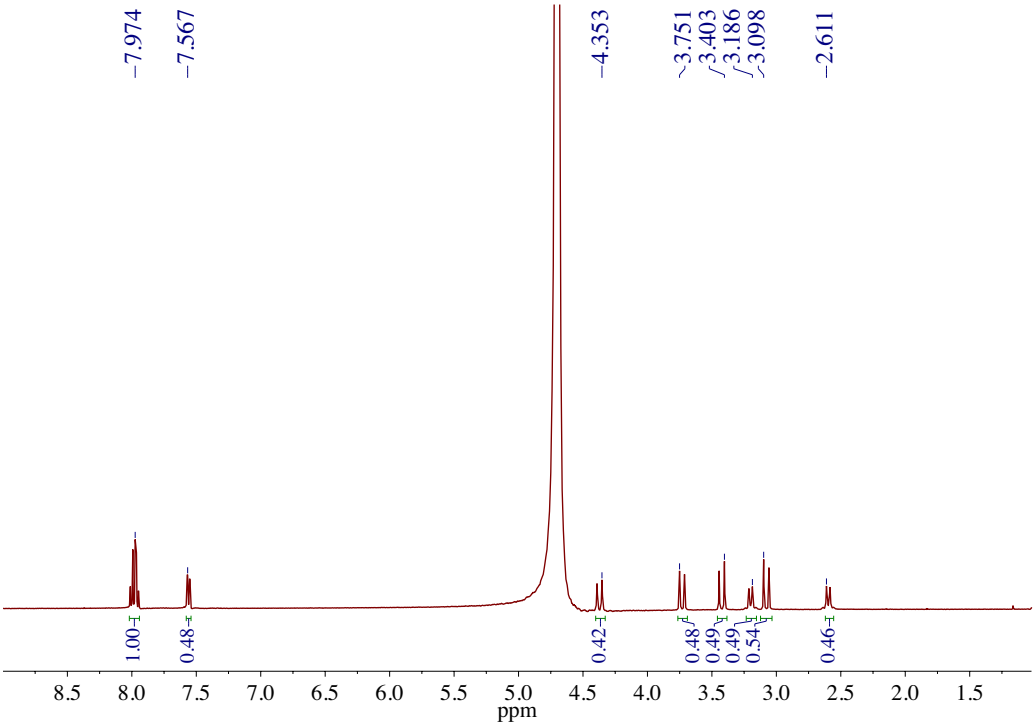


Figure 15. ^{13}C NMR (100 MHz, D_2O, 25°C) spectrum of Na[La(octapa)], (**5**)

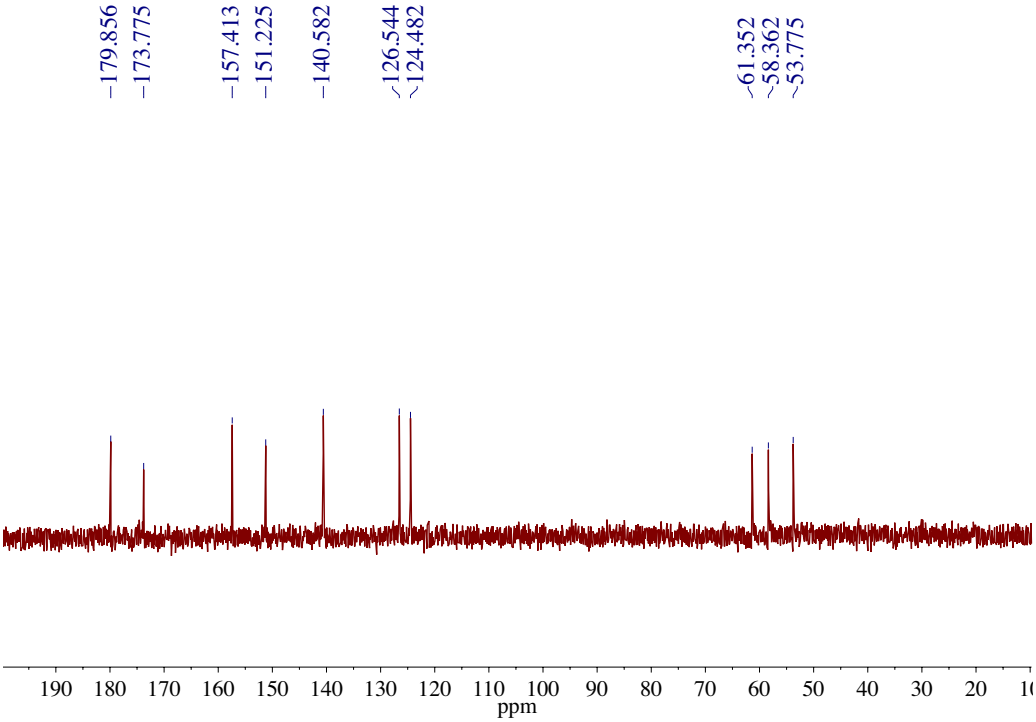


Figure S16. a) HR-ESI-MS spectrum of Na[La(octapa)], (**5**). b) Experimental data for the peak m/z = 581.0189 is shown at the top of the panel and compared with the data calculated for the $[C_{20}H_{18}N_4O_8{}^{139}La]^-$: 581.0188 (lower panel).

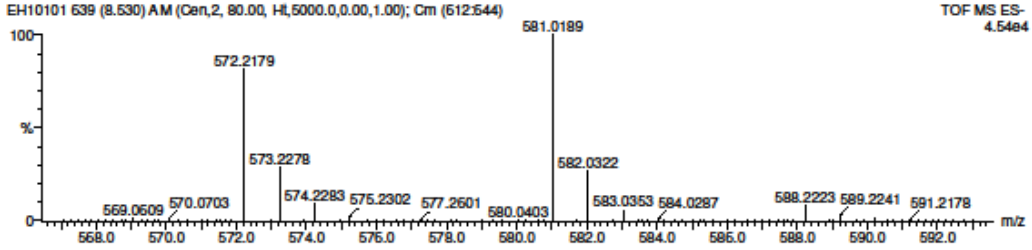
a)

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 80.0
Selected filters: None

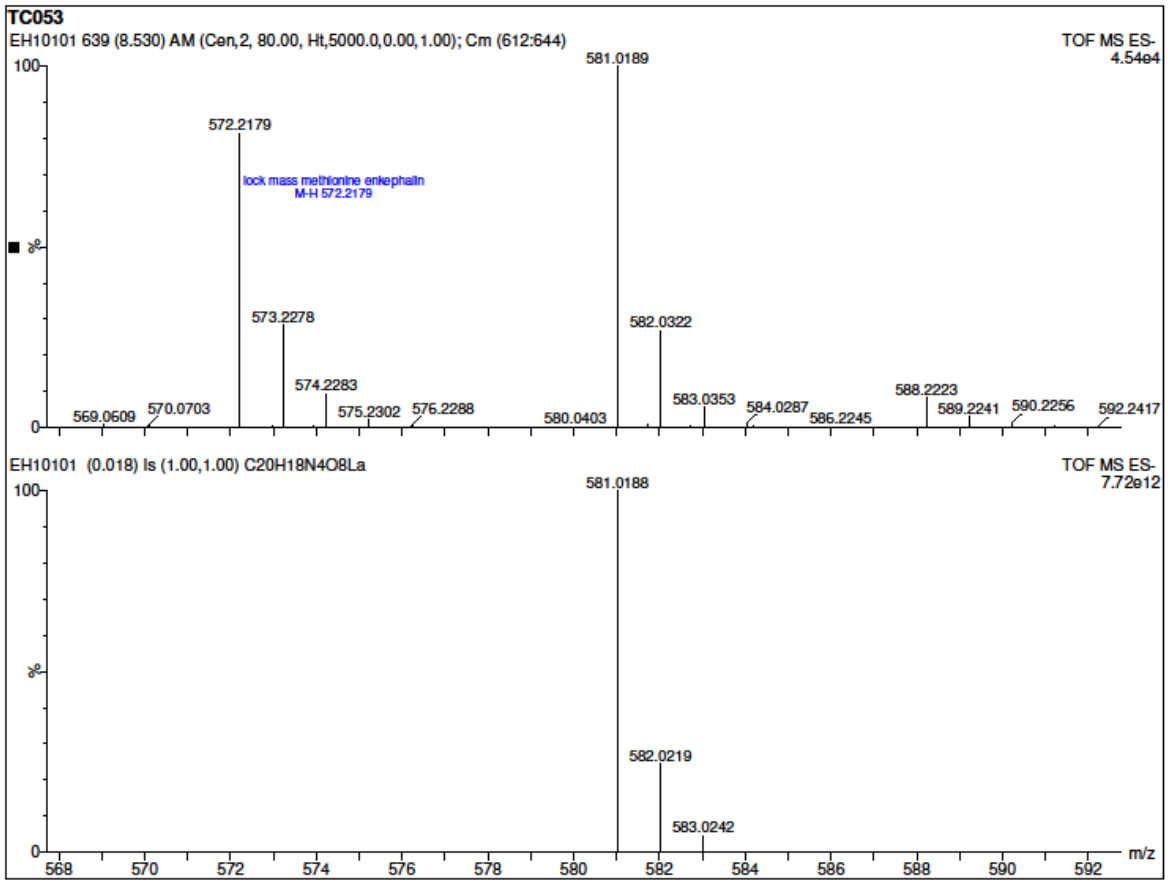
Monoisotopic Mass, Even Electron Ions
569 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-40 H: 0-60 N: 0-10 O: 0-10 139La: 1-1

TC053
EH10101 639 (8.530) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Cm (612:644) TOF MS ES-
4.54e4



Minimum:				-1.5		
Maximum:		5.0	5.0	80.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
581.0189	581.0188	0.1	0.2	14.5	94.6	C20 H18 N4 O8 139La
	581.0202	-1.3	-2.2	19.5	77.2	C21 H14 N8 O4 139La
	581.0170	1.9	3.3	27.5	578.2	C32 H14 N2 O 139La
	581.0161	2.8	4.8	15.5	339.0	C16 H14 N10 O6 139La

b)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%
0
581.0189
572.2179
lock mass methionine enkephalin
M-H 572.2179
573.2278
582.0322
574.2283
583.0353
584.0287
588.2223
589.2241
590.2256
592.2417
569.0609
570.0703
575.2302
576.2288
580.0403
586.2245
EH10101 (0.018) Is (1.00,1.00) C20H18N4O8La
TOF MS ES-
7.72e12
581.0188
582.0219
583.0242
m/z
568
570
572
574
576
578
580
582
584
586
588
590
592

Figure S17. a) HR-ESI-MS spectrum of Na[Sm(octapa)], (**6**). b) Experimental data for the peak m/z = 589.0271 is shown at the top of the panel and compared with the data calculated for the $[C_{20}H_{18}N_4O_8{}^{147}Sm]^-$: 589.0274 (lower panel).

a)

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 80.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
2526 formula(e) evaluated with 16 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-45 H: 0-75 N: 0-15 O: 0-15 147Sm: 0-1

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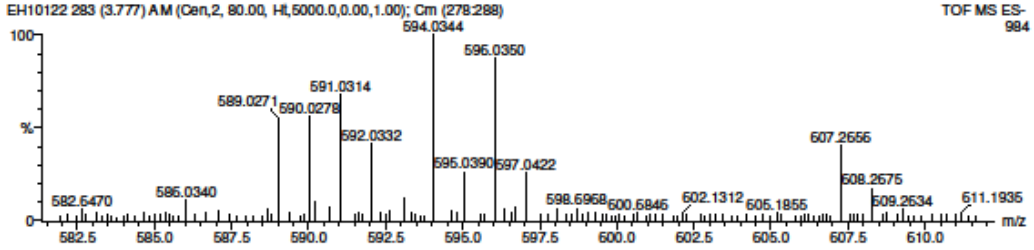
984



Minimum:				-1.5		
Maximum:		5.0	5.0	80.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
589.0271	589.0274	-0.3	-0.5	14.5	0.8	C20 H18 N4 O8 147Sm
	589.0268	0.3	0.5	27.5	391.4	C29 H9 N4 O11
	589.0265	0.6	1.0	2.5	6.6	C4 H18 N12 O13 147Sm
	589.0263	0.8	1.4	45.5	319.1	C42 H N6
	589.0281	-1.0	-1.7	32.5	382.1	C30 H5 N8 O7
	589.0260	1.1	1.9	9.5	1.1	C19 H22 O12 147Sm
	589.0260	1.1	1.9	20.5	1.1	C17 H10 N14 O2 147Sm
	589.0255	1.6	2.7	27.5	1.5	C32 H14 N2 O 147Sm
	589.0287	-1.6	-2.7	19.5	0.7	C21 H14 N8 O4 147Sm
	589.0254	1.7	2.9	33.5	399.0	C26 H N14 O5
	589.0254	1.7	2.9	22.5	400.8	C28 H13 O15
	589.0292	-2.1	-3.6	1.5	4.8	C8 H22 N6 O15 147Sm
	589.0249	2.2	3.7	40.5	327.6	C41 H5 N2 O4
	589.0247	2.4	4.1	15.5	1.5	C16 H14 N10 O6 147Sm
	589.0295	-2.4	-4.1	37.5	373.0	C31 H N12 O3
	589.0300	-2.9	-4.9	19.5	448.7	C18 H9 N10 O14

b)

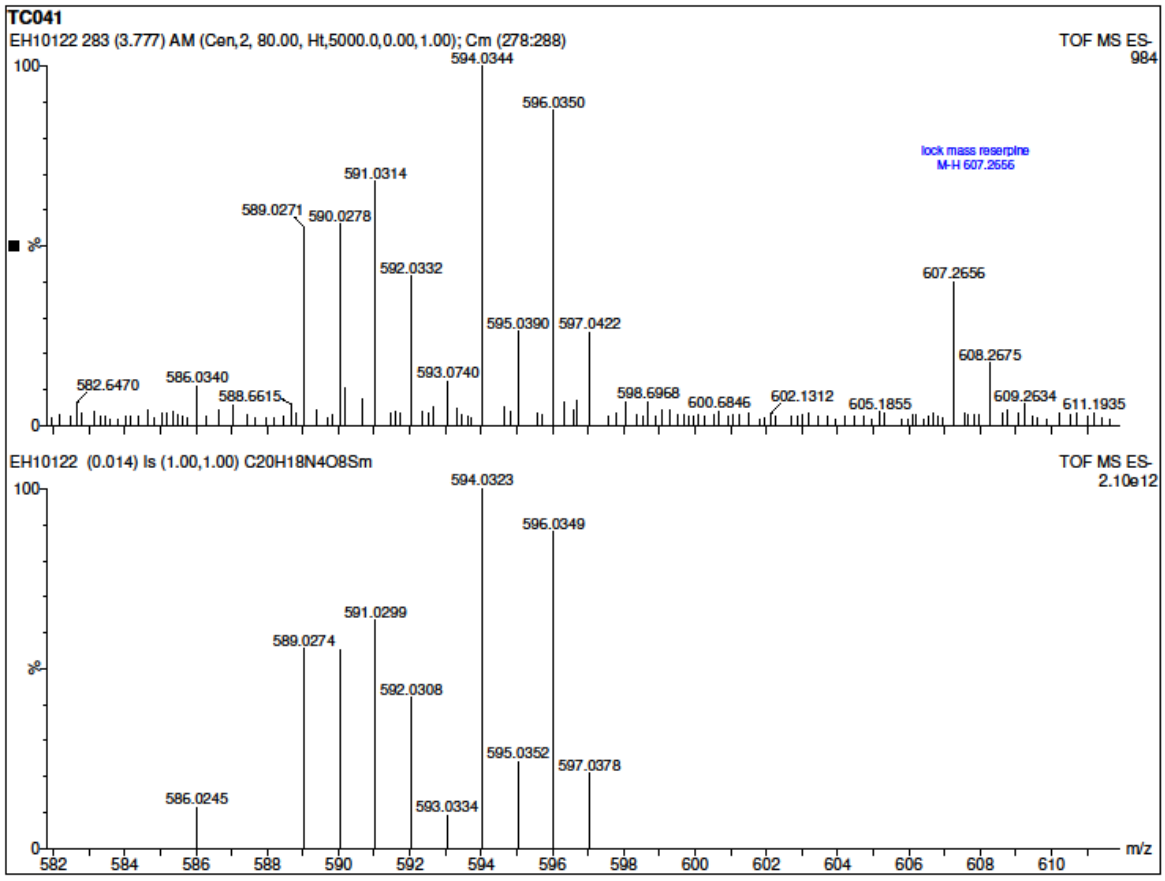

TC041
EH10122 283 (3.777) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Cm (278:288)
TOF MS ES-
984
100
%
0
594.0344
596.0350
lock mass reserpine
M-H 607.2656
591.0314
589.0271
590.0278
592.0332
607.2656
595.0390
597.0422
608.2675
582.6470
586.0340
588.6615
593.0740
598.5968
600.6846
602.1312
605.1855
609.2634
611.1935
EH10122 (0.014) Is (1.00,1.00) C20H18N4O8Sm
TOF MS ES-
2.10e12
100
%
0
594.0323
596.0349
591.0299
589.0274
592.0308
595.0352
597.0378
586.0245
593.0334
m/z
582
584
586
588
590
592
594
596
598
600
602
604
606
608
610

Figure S18. a) HR-ESI-MS spectrum of Na[Dy(octapa)], (**7**). b) Experimental data for the peak m/z = 603.0396 is shown at the top of the panel and compared with the data calculated for the $[C_{20}H_{18}N_4O_8{}^{161}Dy]^-$: 603.0394 (lower panel).

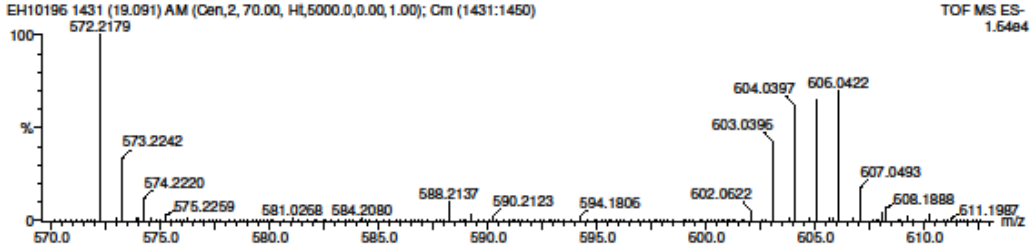
a)

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 80.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
2540 formula(e) evaluated with 18 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-45 H: 0-75 N: 0-15 O: 0-15 161Dy: 0-1

TC097
EH10196 1431 (19.091) AM (Cen,2, 70.00, Ht,5000.0,0.00,1.00); Cm (1431:1450) TOF MS ES-
1.64e4



Minimum:				-1.5		
Maximum:		5.0	5.0	80.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
603.0396	603.0397	-0.1	-0.2	28.5	7583.1	C26 H7 N10 O9
	603.0394	0.2	0.3	14.5	9.1	C20 H18 N4 O8 161Dy
	603.0386	1.0	1.7	2.5	6.9	C4 H18 N12 O13 161Dy
	603.0406	-1.0	-1.7	40.5	6315.1	C42 H7 N2 O4
	603.0407	-1.1	-1.8	19.5	13.6	C21 H14 N8 O4 161Dy
	603.0384	1.2	2.0	23.5	7731.2	C25 H11 N6 O13
	603.0411	-1.5	-2.5	22.5	7483.4	C29 H15 O15
	603.0381	1.5	2.5	9.5	6.0	C19 H22 O12 161Dy
	603.0381	1.5	2.5	20.5	8.4	C17 H10 N14 O2 161Dy
	603.0411	-1.5	-2.5	33.5	7434.7	C27 H3 N14 O5
	603.0413	-1.7	-2.8	1.5	2.9	C8 H22 N6 O15 161Dy
	603.0379	1.7	2.8	41.5	6567.0	C38 H3 N8 O2
	603.0376	2.0	3.3	27.5	49.5	C32 H14 N2 O 161Dy
	603.0419	-2.3	-3.8	45.5	6165.5	C43 H3 N6
	603.0421	-2.5	-4.1	24.5	19.9	C22 H10 N12 161Dy
	603.0424	-2.8	-4.6	27.5	7336.2	C30 H11 N4 O11
	603.0367	2.9	4.8	15.5	6.6	C16 H14 N10 O6 161Dy
	603.0426	-3.0	-5.0	6.5	2.8	C9 H18 N10 O11 161Dy

b)

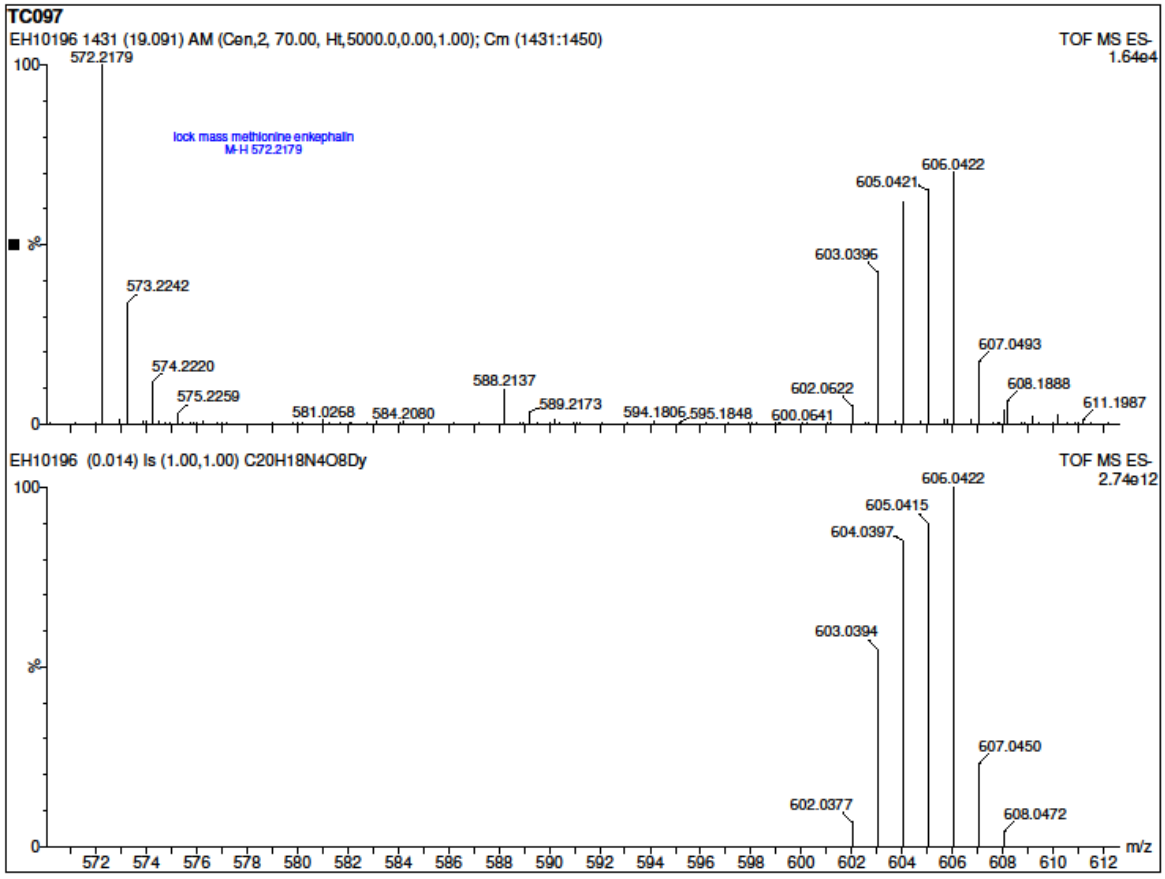

TC097
EH10196 1431 (19.091) AM (Cen,2, 70.00, Ht,5000.0,0.00,1.00); Cm (1431:1450)
TOF MS ES-
1.64e4
100
572.2179
lock mass methionine enkephalin
M-H 572.2179
606.0422
605.0421
603.0395
573.2242
607.0493
574.2220
588.2137
608.1888
575.2259
602.0622
611.1987
581.0268
584.2080
589.2173
594.1806
595.1848
600.0641
%
0
EH10196 (0.014) Is (1.00,1.00) C20H18N4O8Dy
TOF MS ES-
2.74e12
100
606.0422
605.0415
604.0397
603.0394
607.0450
602.0377
608.0472
%
0
572 574 576 578 580 582 584 586 588 590 592 594 596 598 600 602 604 606 608 610 612
m/z

Figure S19. a) HR-ESI-MS spectrum of Na[Yb(octapa)], (**8**). b) Experimental data for the peak m/z = 613.0482 is shown at the top of the panel and compared with the data calculated for the $[C_{20}H_{18}N_4O_8{}^{171}Yb]^-$: 613.0488 (lower panel).

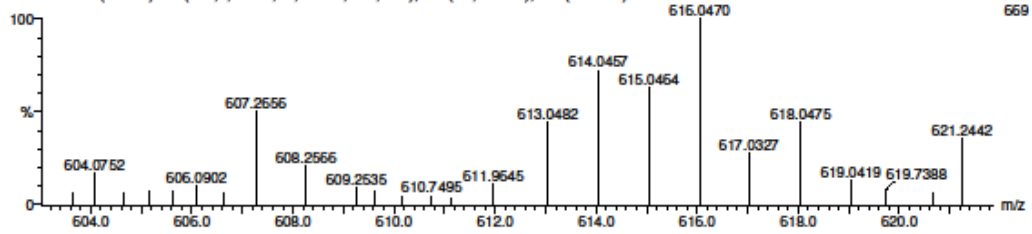
a)

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 80.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
2128 formula(e) evaluated with 11 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-40 H: 0-60 N: 0-10 O: 0-10 Na: 0-1 171Yb: 0-1

TC096
EH10198 977 (13.035) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (962:977) TOF MS ES-
669



Minimum:				-1.5		
Maximum:		5.0	5.0	80.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
613.0482	613.0477	0.5	0.8	16.5	0.2	C19 H15 N8 O4 Na 171Yb
	613.0488	-0.6	-1.0	14.5	0.2	C20 H18 N4 O8 171Yb
	613.0492	-1.0	-1.6	29.5	319.4	C29 H9 N8 O9
	613.0470	1.2	2.0	27.5	1.4	C32 H14 N2 O 171Yb
	613.0468	1.4	2.3	26.5	328.1	C27 H10 N8 O9 Na
	613.0464	1.8	2.9	11.5	0.1	C18 H19 N4 O8 Na 171Yb
	613.0501	-1.9	-3.1	19.5	0.4	C21 H14 N8 O4 171Yb
	613.0461	2.1	3.4	15.5	0.1	C16 H14 N10 O6 171Yb
	613.0461	2.1	3.4	37.5	280.8	C40 H9 N2 O6
	613.0504	-2.2	-3.6	15.5	0.4	C23 H19 N2 O6 Na 171Yb
	613.0509	-2.7	-4.4	30.5	310.8	C32 H10 N6 O7 Na

b)

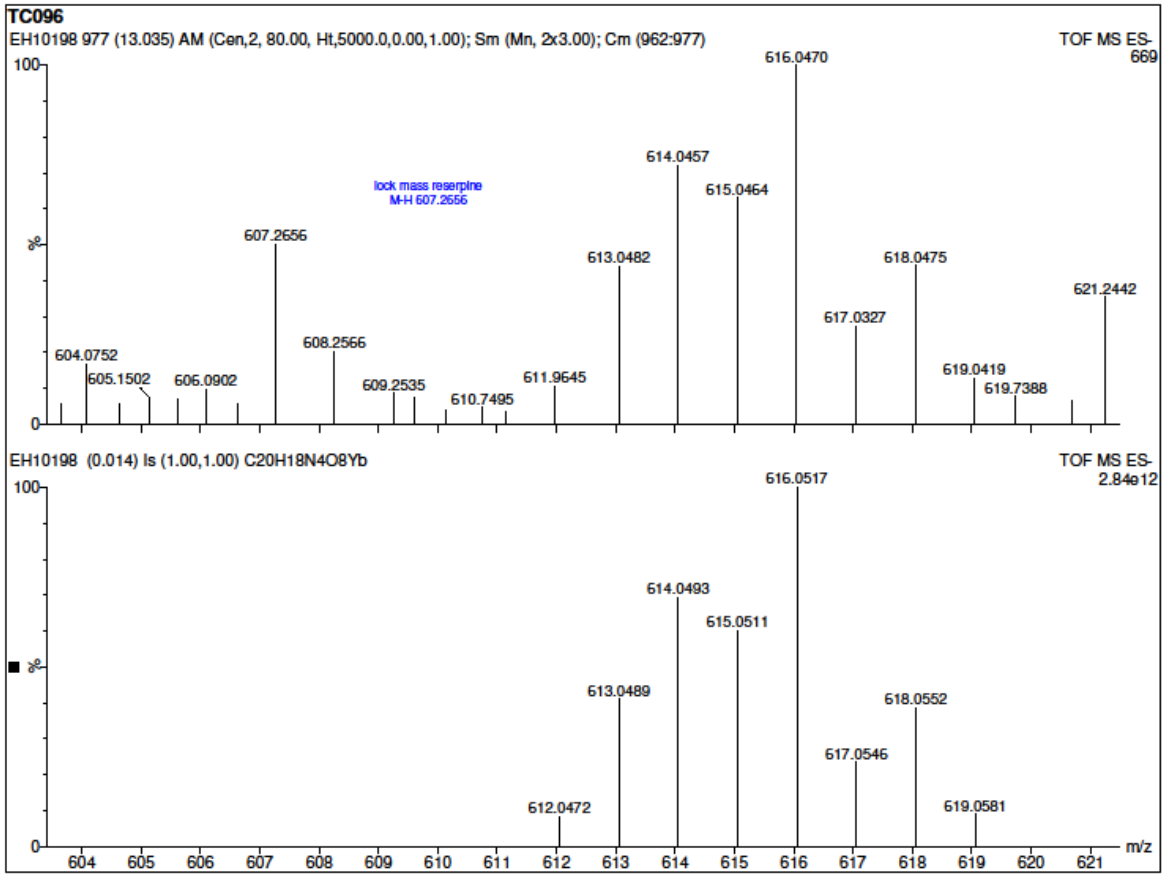
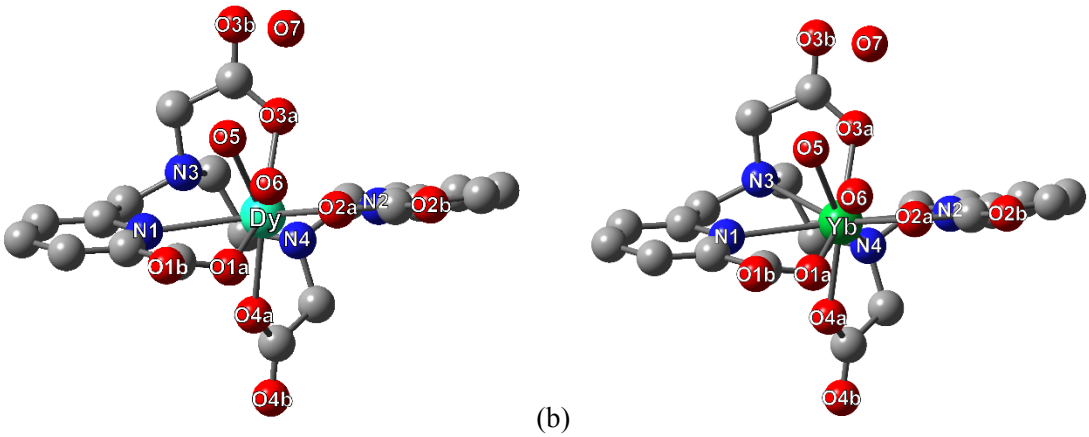
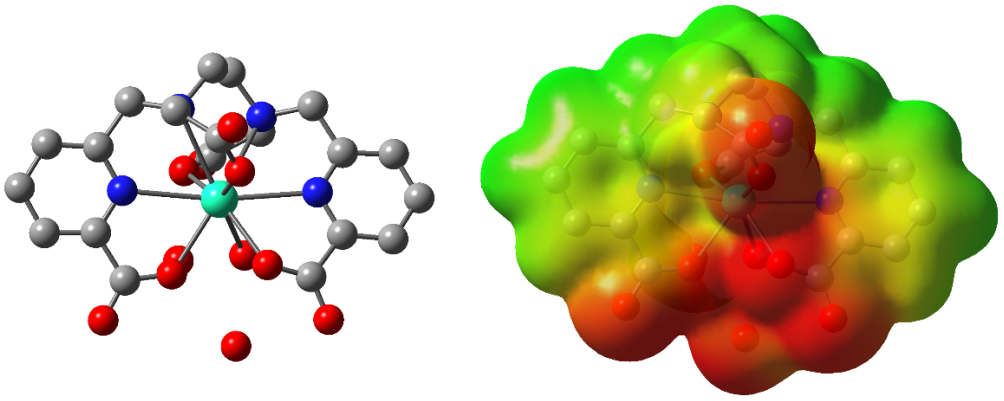

TC096
EH10198 977 (13.035) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (962:977)
TOF MS ES-
669
100
%
0
lock mass reserpine
M+H 607.2656
616.0470
614.0457
615.0464
607.2656
613.0482
618.0475
621.2442
617.0327
604.0752
608.2566
605.1502
606.0902
609.2535
611.9645
610.7495
619.0419
619.7388
EH10198 (0.014) Is (1.00,1.00) C20H18N4O8Yb
TOF MS ES-
2.84e12
100
%
0
616.0517
614.0493
615.0511
613.0489
618.0552
617.0546
612.0472
619.0581
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
m/z

Figure S20. Optimized structure of (a) the $[Dy(octapa)(H_2O)]^-\cdot 2H_2O$ anion and (b) the $[Yb(octapa)(H_2O)]^-\cdot 2H_2O$ with labels on selected atoms.

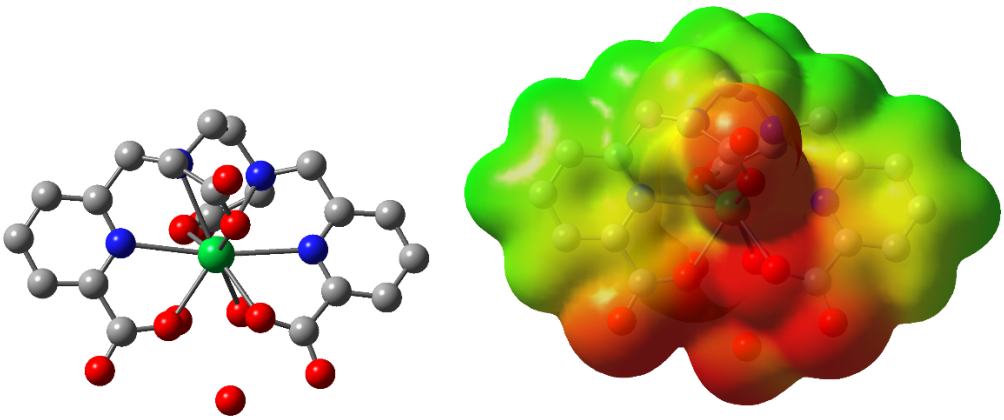


(a) (b)

Figure S21. MEP mapping of (a) $[Dy(octapa)(H_2O)]^-\cdot 2H_2O$ anion and (b) $[Yb(octapa)(H_2O)]^-\cdot 2H_2O$ anion, where red = negative, blue = positive, representing a maximum potential of 0.200 au and a minimum of -0.200 au, mapped onto electron density isosurface of 0.002 $Å^{-3}$. All hydrogen atoms have been omitted for clarity.



(a)



(b)

Table S3. DFT atomic coordinates of $[Sm(octapa)(H_2O)]^- \cdot 2H_2O$:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	62	0	-0.009587	0.142875	-0.223180
2	7	0	-2.705083	0.038663	-0.183724
3	7	0	2.674060	-0.160936	-0.301512
4	7	0	1.221872	-1.937135	1.225206
5	7	0	-1.302615	-2.304086	-0.430127
6	6	0	-5.487415	0.080224	-0.028391
7	6	0	4.751243	-1.218295	0.263020
8	6	0	3.352241	-1.200876	0.210195
9	6	0	2.517375	-2.374964	0.666826
10	6	0	0.294480	-3.091273	1.331146
11	6	0	1.418391	-1.338965	2.560321
12	6	0	4.752387	0.960817	-0.756530
13	6	0	3.359490	0.893579	-0.784192
14	6	0	2.504825	2.003833	-1.358958
15	6	0	5.459295	-0.120443	-0.227623
16	6	0	-4.778363	1.250692	-0.300581
17	6	0	-3.386678	1.185667	-0.369731
18	6	0	-2.551825	2.423890	-0.637956
19	6	0	-4.782454	-1.107750	0.168671
20	6	0	-3.385087	-1.088865	0.089497
21	6	0	-2.553995	-2.322790	0.352686
22	6	0	-0.396745	-3.394102	0.008888
23	6	0	-1.591030	-2.482403	-1.870447
24	1	0	-6.571369	0.089496	0.026443
25	1	0	5.267641	-2.074427	0.684240
26	1	0	2.315583	-3.006373	-0.205614
27	1	0	3.080037	-2.988903	1.385663
28	1	0	0.830062	-3.988483	1.676099
29	1	0	-0.446279	-2.850415	2.096459
30	1	0	2.270571	-0.651987	2.512609
31	1	0	1.650554	-2.093904	3.325459
32	1	0	5.247495	1.843520	-1.143592
33	1	0	6.544043	-0.108418	-0.192589
34	1	0	-5.267040	2.204217	-0.461145
35	1	0	-5.300378	-2.037730	0.378307
36	1	0	-2.289481	-2.326836	1.415137
37	1	0	-3.144308	-3.229482	0.151925
38	1	0	-0.947245	-4.344059	0.092687
39	1	0	0.350989	-3.527611	-0.778574
40	1	0	-2.449553	-1.854670	-2.133305
41	1	0	-1.857676	-3.522177	-2.105838
42	8	0	1.283327	1.691269	-1.584075
43	8	0	3.015719	3.130824	-1.546638
44	8	0	-1.274611	2.217908	-0.653719
45	8	0	-3.124885	3.510095	-0.808844
46	8	0	0.647448	4.163298	-0.255010

47	1	0	-0.087762	3.596979	-0.595175
48	1	0	1.386031	3.985431	-0.876971
49	8	0	0.954137	1.951352	1.298894
50	8	0	-0.497407	2.446719	3.584285
51	1	0	-1.416564	2.481644	3.280562
52	1	0	0.426796	2.132580	2.122815
53	1	0	0.940584	2.813735	0.796534
54	1	0	-0.395893	1.519876	3.932470
55	6	0	0.200613	-0.512465	2.990843
56	6	0	-0.410183	-2.032566	-2.748733
57	8	0	0.169721	-0.096346	4.171945
58	8	0	-0.673242	-0.258176	2.087157
59	8	0	0.360312	-1.134952	-2.220533
60	8	0	-0.300533	-2.510387	-3.886195

Table S5. DFT atomic coordinates of $[Dy(octapa)(H_2O)]^- \cdot 2H_2O$:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.663686	0.059381	-0.174493
2	7	0	2.645761	-0.225422	-0.327848
3	7	0	1.191312	-1.938238	1.244882
4	7	0	-1.318170	-2.302787	-0.395254
5	6	0	-5.449081	0.158312	-0.034347
6	6	0	4.722793	-1.291339	0.229005
7	6	0	3.323247	-1.256554	0.201711
8	6	0	2.486676	-2.404919	0.711688
9	6	0	0.259308	-3.085487	1.372246
10	6	0	1.382253	-1.308122	2.565666
11	6	0	4.731526	0.852580	-0.858028
12	6	0	3.337963	0.804578	-0.853483
13	6	0	2.490164	1.914571	-1.433619
14	6	0	5.435985	-0.220719	-0.310335
15	6	0	-4.714785	1.310436	-0.316526
16	6	0	-3.324424	1.216295	-0.372623
17	6	0	-2.459606	2.433222	-0.624099
18	6	0	-4.767324	-1.039015	0.185172
19	6	0	-3.369613	-1.048866	0.111429
20	6	0	-2.564035	-2.292912	0.394619
21	6	0	-0.428746	-3.400429	0.052296
22	6	0	-1.625352	-2.494079	-1.829888
23	1	0	-6.532940	0.189179	0.013604
24	1	0	5.234856	-2.140879	0.668515
25	1	0	2.287093	-3.079125	-0.128823
26	1	0	3.045591	-2.984749	1.461056
27	1	0	0.789769	-3.978828	1.733886
28	1	0	-0.482260	-2.829223	2.131784
29	1	0	2.232920	-0.620521	2.503133
30	1	0	1.611156	-2.043866	3.349938
31	1	0	5.228092	1.717095	-1.282378
32	1	0	6.521266	-0.222502	-0.297319
33	1	0	-5.182328	2.272147	-0.490909
34	1	0	-5.303119	-1.955757	0.407805
35	1	0	-2.296564	-2.282996	1.455967
36	1	0	-3.170177	-3.192562	0.210170
37	1	0	-0.990537	-4.343010	0.145059
38	1	0	0.319302	-3.553261	-0.732225
39	1	0	-2.522258	-1.914607	-2.074268
40	1	0	-1.838364	-3.545839	-2.064330
41	8	0	1.251500	1.631264	-1.582848
42	8	0	3.023655	3.016901	-1.694295
43	8	0	-1.188198	2.200656	-0.567332
44	8	0	-2.998718	3.528110	-0.841853
45	8	0	0.768516	4.126040	-0.277056
46	1	0	0.009323	3.571434	-0.581865
47	1	0	1.472060	3.933789	-0.934104
48	8	0	1.032654	1.882654	1.257263

49	8	0	-0.414511	2.510097	3.517848
50	1	0	-1.327271	2.606864	3.208405
51	1	0	0.506380	2.100224	2.072779
52	1	0	1.051005	2.739272	0.746924
53	1	0	-0.380651	1.586363	3.884317
54	6	0	0.162980	-0.471738	2.968523
55	6	0	-0.496493	-1.969350	-2.729061
56	8	0	0.104225	-0.057487	4.148497
57	8	0	-0.683858	-0.203899	2.041745
58	8	0	0.190033	-0.989052	-2.229290
59	8	0	-0.347996	-2.458156	-3.856327
60	66	0	0.000442	0.134701	-0.208394

Table S6. DFT atomic coordinates of $[Yb(octapa)(H_2O)]^- \cdot 2H_2O$:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	70	0	0.004584	0.142695	-0.192148
2	7	0	-2.640249	0.037908	-0.179412
3	7	0	2.633695	-0.204876	-0.287670
4	7	0	1.184126	-2.000029	1.176942
5	7	0	-1.290238	-2.291070	-0.504794
6	6	0	-5.426487	0.135130	-0.009317
7	6	0	4.719634	-1.273208	0.235003
8	6	0	3.319807	-1.250226	0.200352
9	6	0	2.494079	-2.428618	0.653210
10	6	0	0.265198	-3.161776	1.231385
11	6	0	1.335288	-1.423649	2.525412
12	6	0	4.714175	0.911087	-0.764832
13	6	0	3.321336	0.849185	-0.769708
14	6	0	2.466509	1.967886	-1.316467
15	6	0	5.426564	-0.175425	-0.254889
16	6	0	-4.691517	1.298436	-0.239027
17	6	0	-3.302362	1.202953	-0.312850
18	6	0	-2.434054	2.423905	-0.510502
19	6	0	-4.744713	-1.072363	0.142241
20	6	0	-3.347507	-1.080757	0.056090
21	6	0	-2.543929	-2.339148	0.267170
22	6	0	-0.398076	-3.406304	-0.114862
23	6	0	-1.577082	-2.394925	-1.951320
24	1	0	-6.509805	0.165326	0.049877
25	1	0	5.236152	-2.136114	0.642194
26	1	0	2.319974	-3.074087	-0.215200
27	1	0	3.049439	-3.027825	1.390132
28	1	0	0.799985	-4.067985	1.552213
29	1	0	-0.490879	-2.956348	1.992294
30	1	0	2.180964	-0.727163	2.514033
31	1	0	1.547590	-2.187025	3.287666
32	1	0	5.203568	1.796234	-1.153495
33	1	0	6.511704	-0.167268	-0.234363
34	1	0	-5.157530	2.269075	-0.360088
35	1	0	-5.279695	-1.999025	0.321841
36	1	0	-2.292217	-2.399951	1.330618
37	1	0	-3.145851	-3.225730	0.016000
38	1	0	-0.950406	-4.358833	-0.090332
39	1	0	0.364581	-3.501200	-0.894534
40	1	0	-2.472303	-1.804260	-2.174163
41	1	0	-1.780288	-3.430597	-2.255942
42	8	0	1.229767	1.679359	-1.465581
43	8	0	2.990939	3.080206	-1.554022
44	8	0	-1.164453	2.177200	-0.479529
45	8	0	-2.963253	3.534081	-0.666145
46	8	0	0.751286	4.118234	-0.067662
47	1	0	-0.000032	3.572113	-0.405998
48	1	0	1.458656	3.965969	-0.731219

49	8	0	0.992113	1.788267	1.341353
50	8	0	-0.509153	2.329554	3.590944
51	1	0	-1.412332	2.450027	3.262376
52	1	0	0.444965	1.968547	2.152360
53	1	0	1.024358	2.669767	0.876106
54	1	0	-0.493723	1.390598	3.917175
55	6	0	0.097412	-0.614295	2.921794
56	6	0	-0.433517	-1.811261	-2.791115
57	8	0	-0.018879	-0.266503	4.118459
58	8	0	-0.708671	-0.296789	1.973622
59	8	0	0.240519	-0.866620	-2.211745
60	8	0	-0.256894	-2.223605	-3.944374

Table S7. DFT atomic coordinates of $[La(octapa)(H_2O)]^- \cdot 2H_2O$:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.008149	-0.035875	0.007743
2	7	0	-2.786153	-0.194670	0.147647
3	7	0	2.765025	-0.473325	-0.138442
4	7	0	1.249083	-2.178965	1.486970
5	7	0	-1.344879	-2.537776	-0.116708
6	6	0	-5.562076	-0.207765	0.419738
7	6	0	4.781321	-1.665073	0.396091
8	6	0	3.386420	-1.546822	0.383541
9	6	0	2.505451	-2.668095	0.884632
10	6	0	0.288555	-3.302563	1.626388
11	6	0	1.514784	-1.592725	2.817107
12	6	0	4.907391	0.456819	-0.721087
13	6	0	3.512464	0.503393	-0.690133
14	6	0	2.767297	1.676831	-1.300030
15	6	0	5.552631	-0.646496	-0.163598
16	6	0	-4.888514	0.973548	0.107999
17	6	0	-3.499933	0.935163	-0.024496
18	6	0	-2.716340	2.190757	-0.361380
19	6	0	-4.825476	-1.379800	0.592055
20	6	0	-3.432703	-1.332611	0.456433
21	6	0	-2.575680	-2.553524	0.698932
22	6	0	-0.429739	-3.620775	0.320527
23	6	0	-1.669984	-2.736213	-1.546634
24	1	0	-6.642605	-0.219192	0.521648
25	1	0	5.245727	-2.541626	0.835515
26	1	0	2.245860	-3.293529	0.023369
27	1	0	3.065641	-3.305060	1.585362
28	1	0	0.803865	-4.206593	1.985410
29	1	0	-0.433477	-3.021425	2.395758
30	1	0	2.411062	-0.966226	2.748812
31	1	0	1.716128	-2.362130	3.576731
32	1	0	5.446100	1.279869	-1.175003
33	1	0	6.635858	-0.714977	-0.164061
34	1	0	-5.402446	1.915856	-0.038983
35	1	0	-5.315030	-2.319065	0.827166
36	1	0	-2.283311	-2.551103	1.754185
37	1	0	-3.163408	-3.467298	0.522309
38	1	0	-0.979419	-4.568840	0.430186
39	1	0	0.300708	-3.766975	-0.480344
40	1	0	-2.525597	-2.099201	-1.796864
41	1	0	-1.962250	-3.775229	-1.754973
42	8	0	1.480661	1.569727	-1.327406
43	8	0	3.425980	2.644135	-1.718271
44	8	0	-1.441838	2.018747	-0.506608
45	8	0	-3.326123	3.265768	-0.465298
46	8	0	0.445209	3.927873	-0.349436
47	1	0	-0.416993	3.449331	-0.446020
48	1	0	1.000735	3.366630	-0.934178

49	8	0	0.891942	1.959743	1.486587
50	8	0	-0.362238	2.307850	3.901513
51	1	0	-1.309063	2.298319	3.697360
52	1	0	0.421428	2.129922	2.346165
53	1	0	0.801999	2.784767	0.938351
54	1	0	-0.178778	1.380405	4.216131
55	6	0	0.366270	-0.684367	3.282460
56	6	0	-0.513714	-2.327604	-2.480655
57	8	0	0.432505	-0.220461	4.444621
58	8	0	-0.550754	-0.421988	2.426290
59	8	0	0.326593	-1.471475	-1.994183
60	8	0	-0.494207	-2.802251	-3.625219

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