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Electronic Supplementary Information (ESI)

A new bisglycolamide substituted calix[4]arene-benzo-crown-6 for the selective removal of Cesium ion: Combined experimental and density functional theoretical investigation

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Figure S1: ^{1}H NMR of 1,3-dipropenyloxy calix-benzo-crown (4):

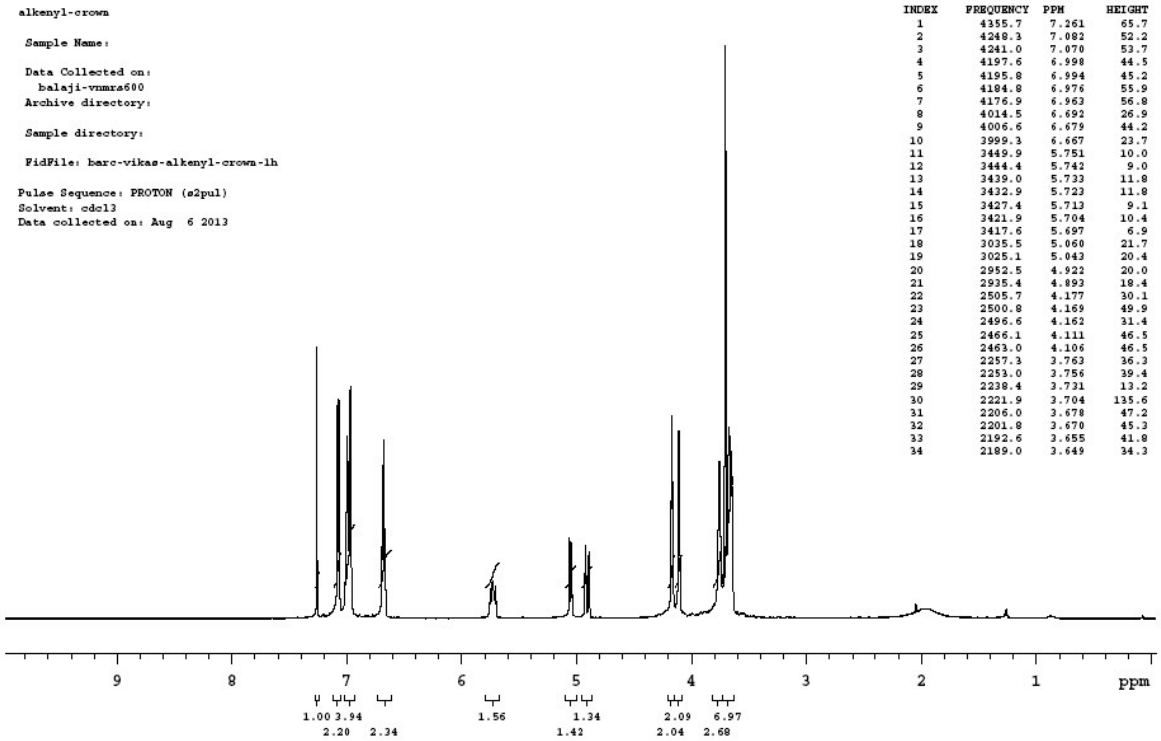


Figure S2: ^{13}C NMR of 1,3-dipropenyloxy calix-benzo-crown (4):

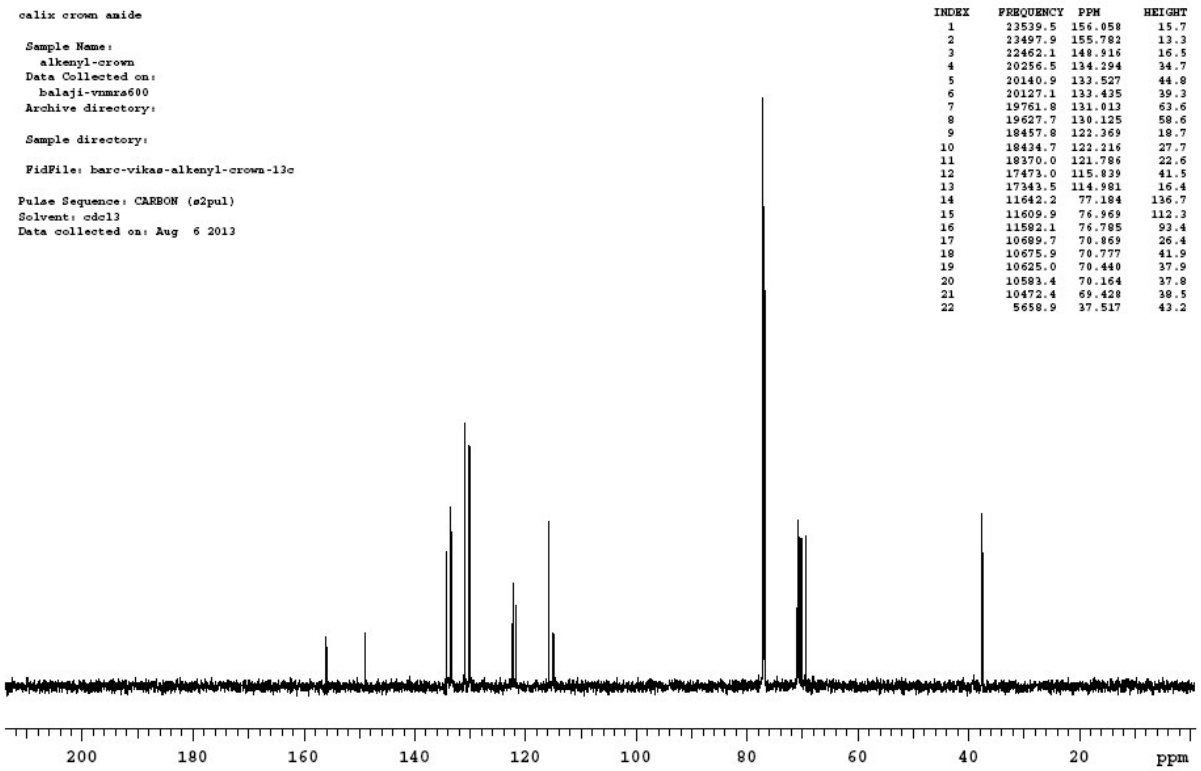


Figure S3: ESI-MS spectra of 1,3-dipropenyloxy calix-benzo-crown (4):

Spectrum Plot - 1/3/2014 3:23 PM

1 A, Scan 22 from ...ata\external\barc-vikas\new\atbenzyl cc-755.xms

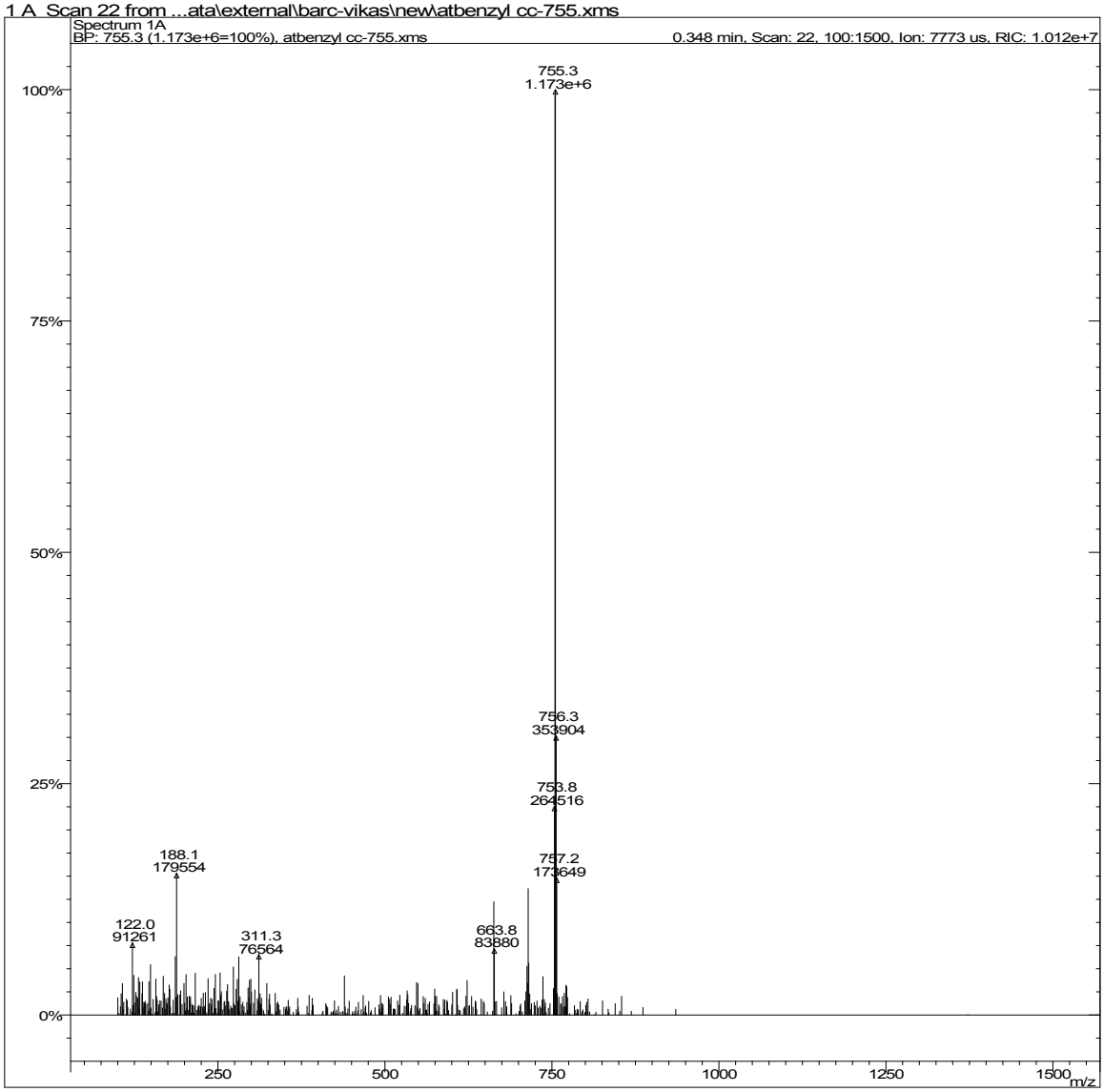
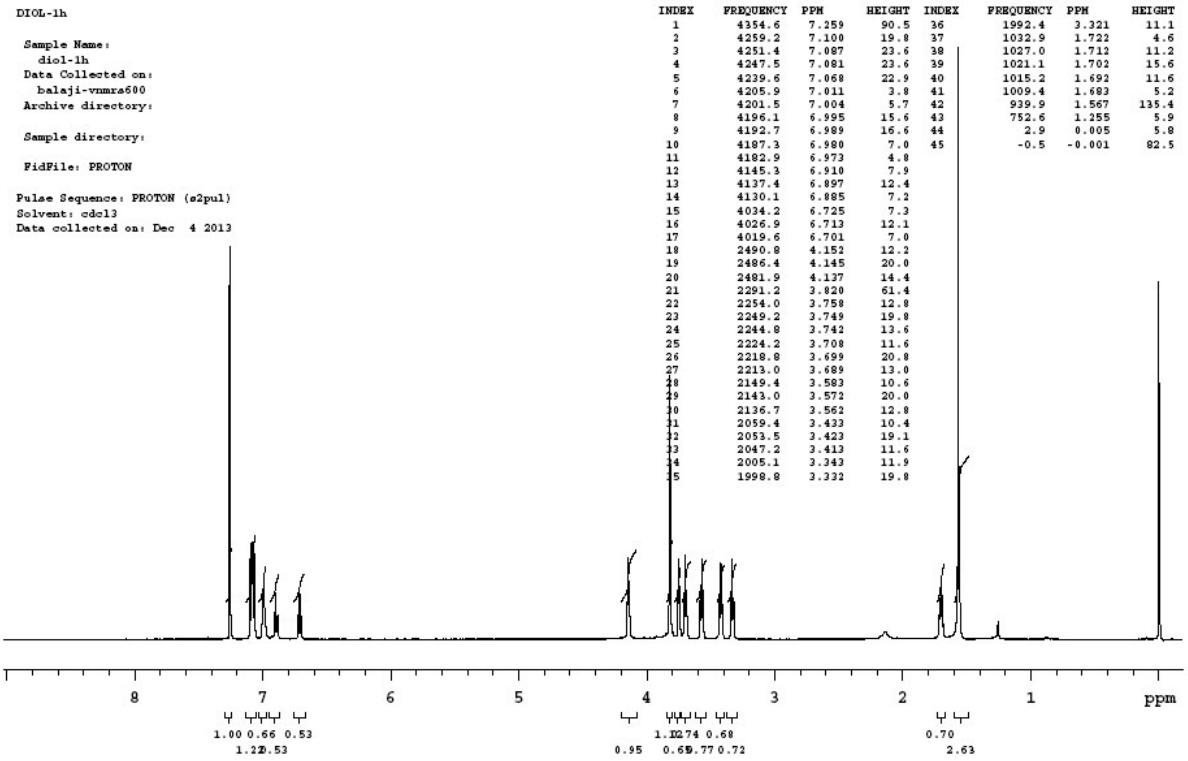


Figure S4: ^{1}H NMR of 1,3-dipropyloxy calix[4]arene-benzocrown diol(5):



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	4354.6	7.259	90.5	36	1992.4	3.321	11.1
2	4259.2	7.100	19.8	37	1032.9	1.722	4.6
3	4251.4	7.087	23.6	38	1027.0	1.712	11.2
4	4247.5	7.081	22.6	39	1021.1	1.702	15.6
5	4239.6	7.068	22.9	40	1015.2	1.692	11.6
6	4205.9	7.011	3.8	41	1009.4	1.683	5.2
7	4201.5	7.004	5.7	42	939.9	1.567	135.4
8	4196.1	6.995	15.6	43	752.6	1.255	5.9
9	4192.7	6.989	16.6	44	2.9	0.005	5.8
10	4187.3	6.980	7.0	45	-0.5	-0.001	82.5
11	4182.9	6.973	4.8				
12	4145.3	6.910	7.9				
13	4137.4	6.897	12.4				
14	4130.1	6.885	7.2				
15	4034.2	6.725	7.3				
16	4026.9	6.713	12.1				
17	4019.6	6.701	7.0				
18	2490.8	4.152	12.2				
19	2486.4	4.145	20.0				
20	2481.9	4.137	14.4				
21	2291.2	3.820	61.4				
22	2254.0	3.758	12.8				
23	2249.2	3.749	19.8				
24	2244.8	3.742	13.6				
25	2224.2	3.708	11.6				
26	2218.8	3.699	20.8				
27	2213.0	3.689	13.0				
28	2149.4	3.583	10.6				
29	2143.0	3.572	20.0				
30	2136.7	3.562	12.8				
31	2059.4	3.433	10.4				
32	2053.5	3.423	19.1				
33	2047.2	3.413	11.6				
34	2005.1	3.343	11.9				
35	1998.8	3.332	19.8				

Figure S5: ^{13}C NMR of 1,3-dipropyloxy calix[4]arene-benzocrown diol(5):

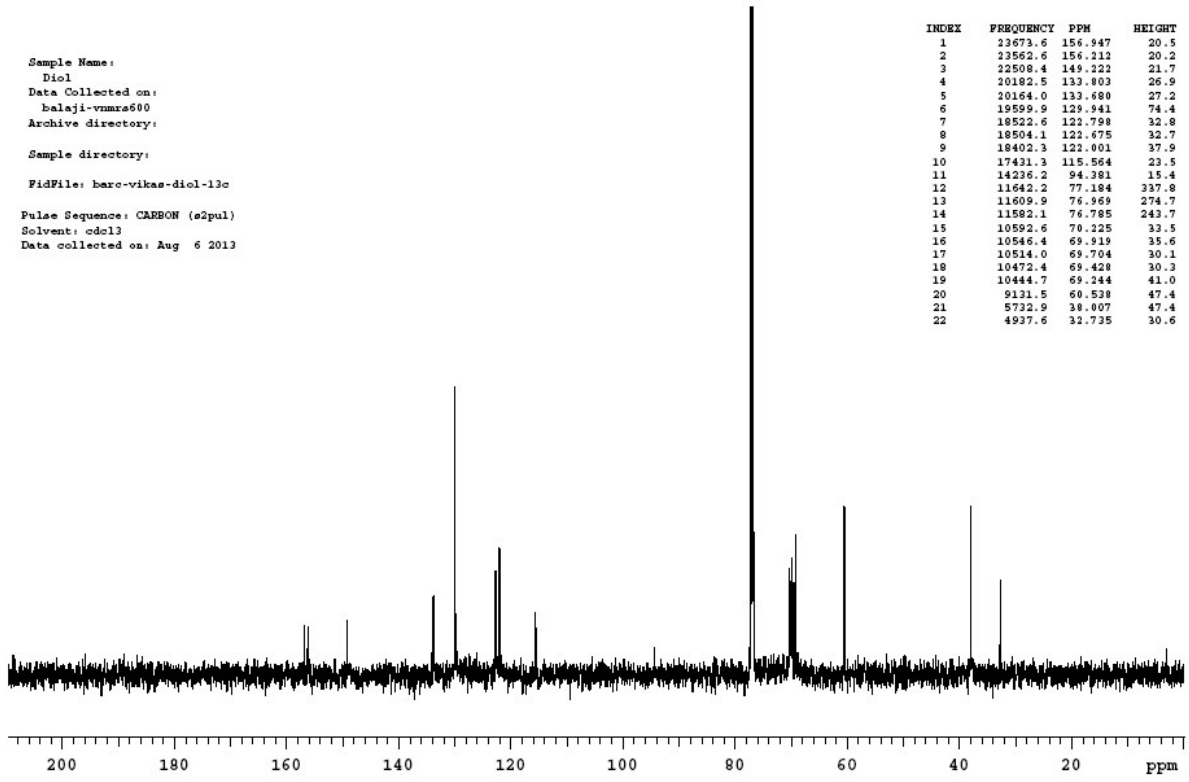


Figure S6: ESI-MS spectra of 1,3-dipropyloxy calix[4]arene-benzocrown diol(5):

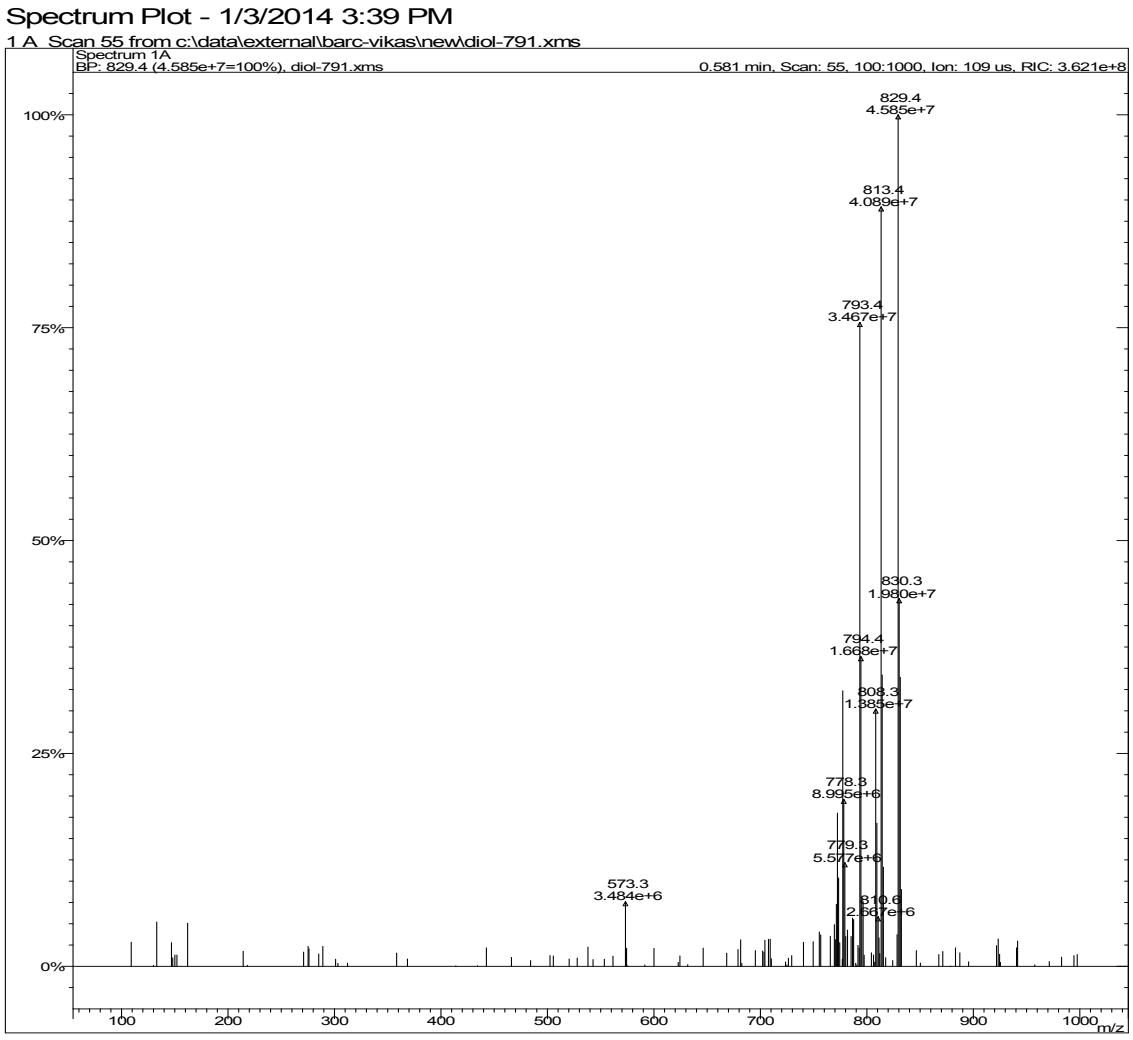


Figure S7: ^{1}H NMR of 1,3- alternate Calix[4]arene-benzocrown-bisglycolamide (6)

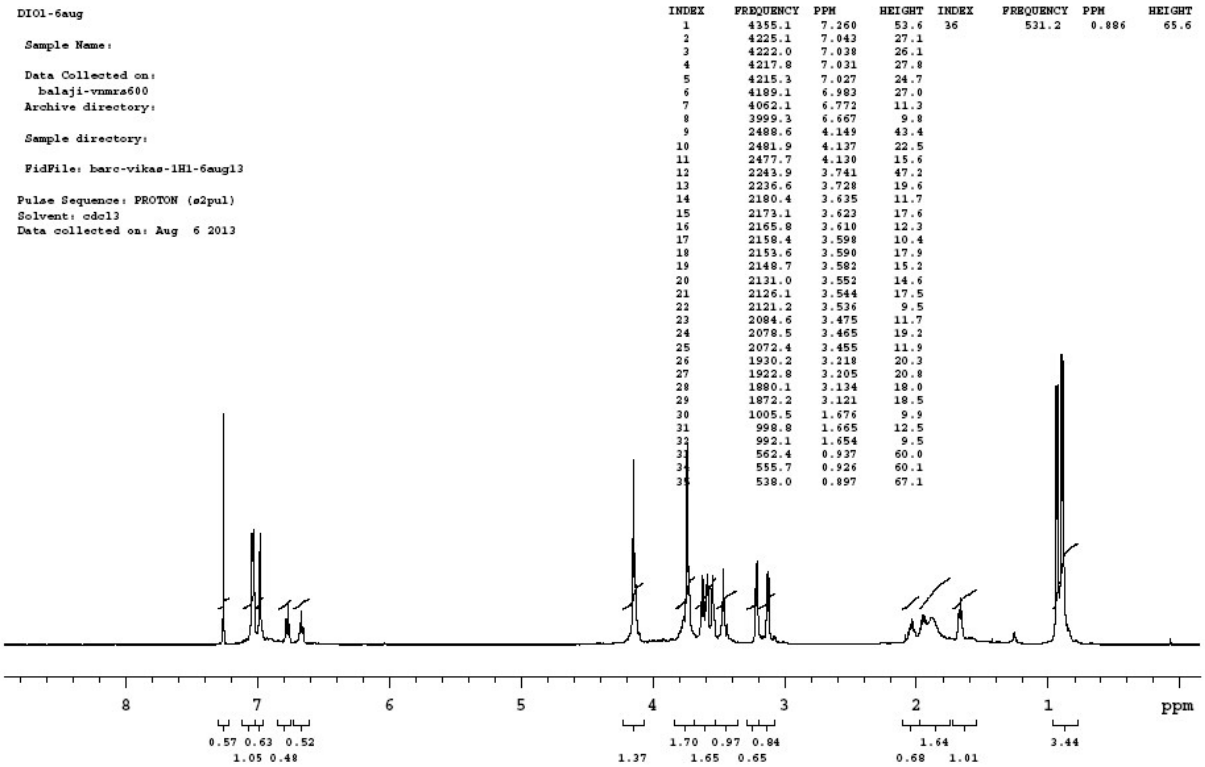


Figure S 8: ^{13} C NMR of 1,3- alternate Calix[4]arene-benzocrown-bisglycolamide (6)

CBCDA-13c

Sample Name:
CBCDA-13c
Data Collected on:
balaji-vnmrs600
Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 4 2013

INDEX	FREQUENCY	PPM	HEIGHT
1	25571.7	169.531	24.8
2	23606.4	156.502	23.3
3	23565.9	156.234	23.8
4	22482.6	149.051	20.9
5	20201.4	133.928	37.7
6	20186.9	133.832	36.1
7	19597.1	129.922	47.9
8	19578.1	129.796	40.4
9	18423.7	122.143	27.8
10	18412.3	122.067	26.2
11	18377.2	121.834	33.5
12	17395.3	115.325	26.1
13	11634.3	77.132	170.8
14	11603.1	76.924	169.8
15	11571.0	76.712	171.6
16	10591.4	70.217	38.8
17	10575.4	70.111	44.1
18	10565.5	70.045	41.5
19	10499.1	69.605	31.2
20	10361.0	68.690	36.6
21	10265.6	68.057	21.8
22	10259.5	68.017	29.9
23	8155.3	54.067	36.7
24	7883.0	52.261	39.2
25	5826.1	38.625	19.6
26	5672.7	37.608	41.8
27	4480.3	29.702	33.1
28	4461.9	29.581	31.3
29	4346.7	28.817	20.0
30	4111.0	27.254	39.7
31	3937.0	26.101	43.7
32	3449.5	22.869	19.4
33	3025.3	20.057	53.2
34	3013.1	19.976	47.6

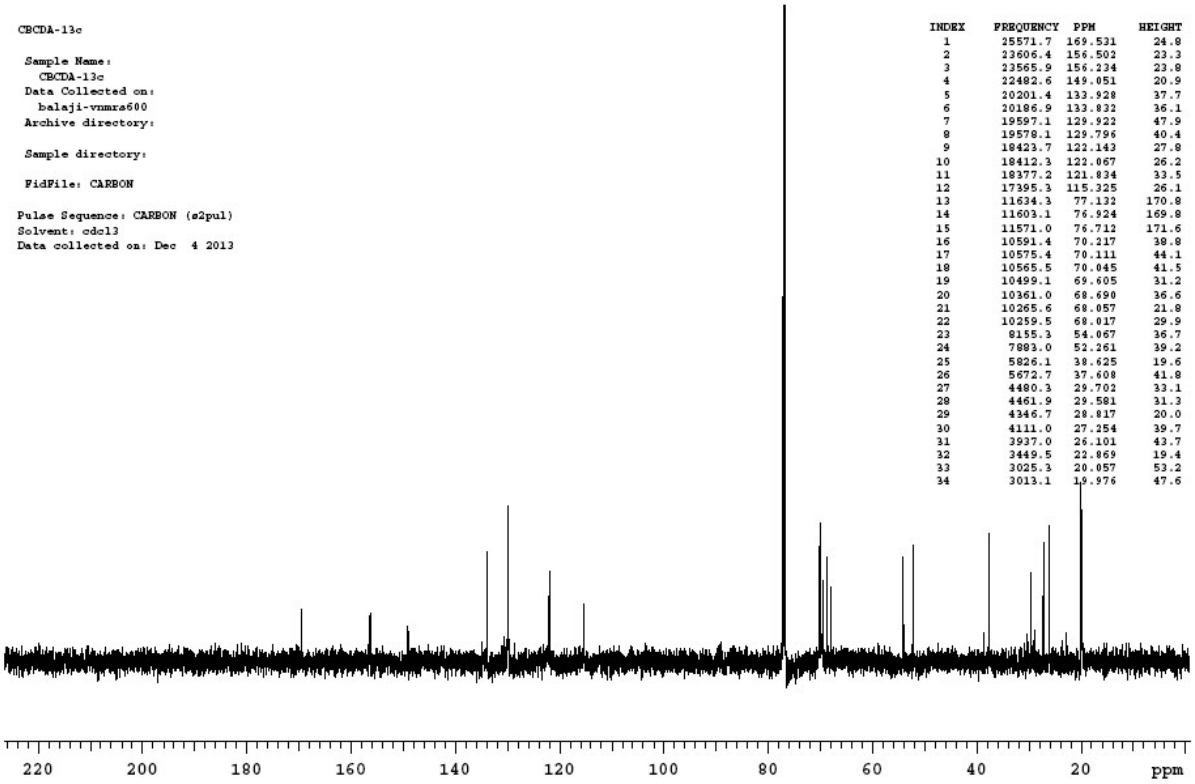


Figure S9: ESI-MS spectra of 1,3- alternate Calix[4]arene-benzocrown-bisglycolamide (6)

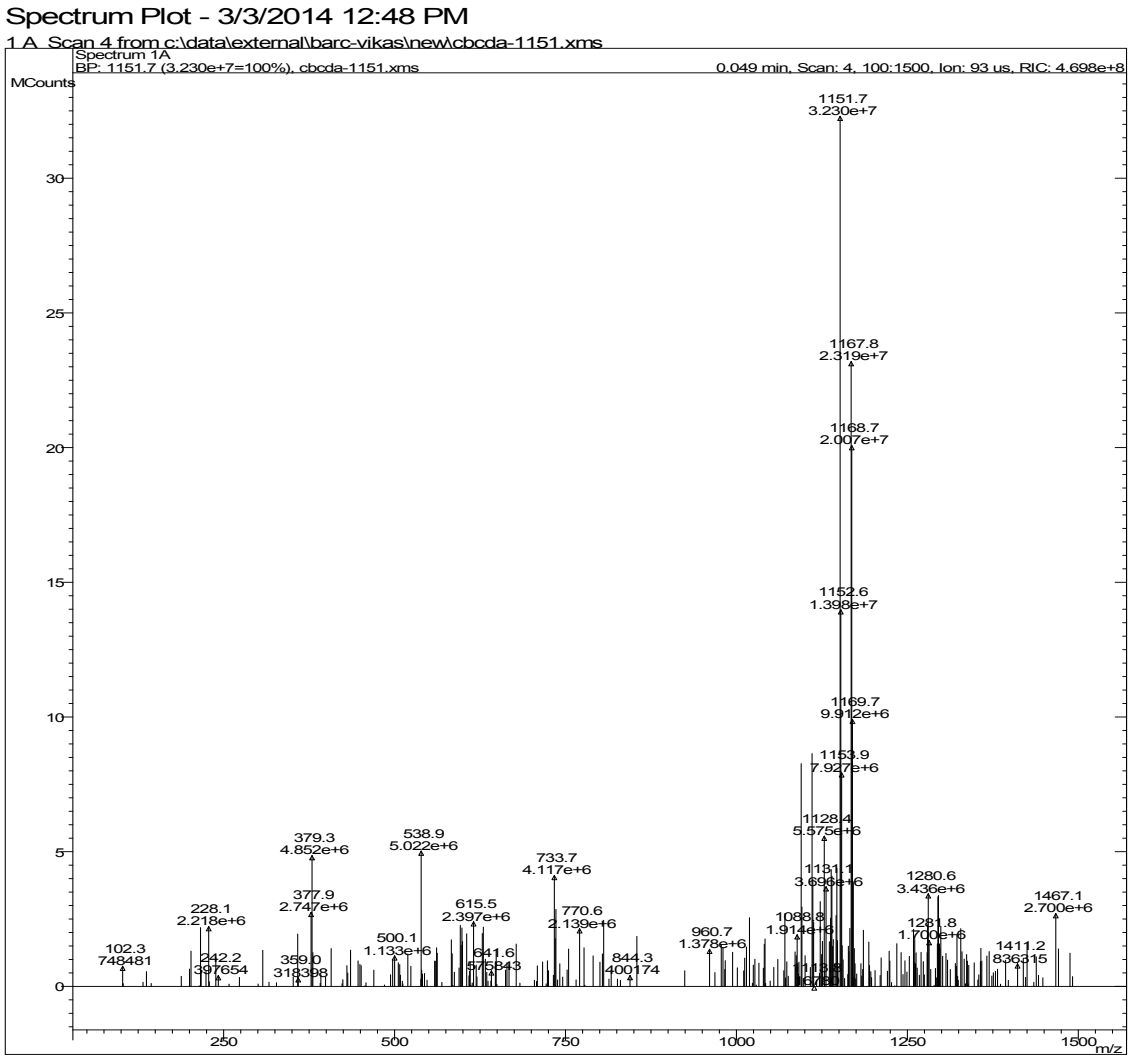


Figure S10: ESI-MS of CBCBGA complexes with Cesium

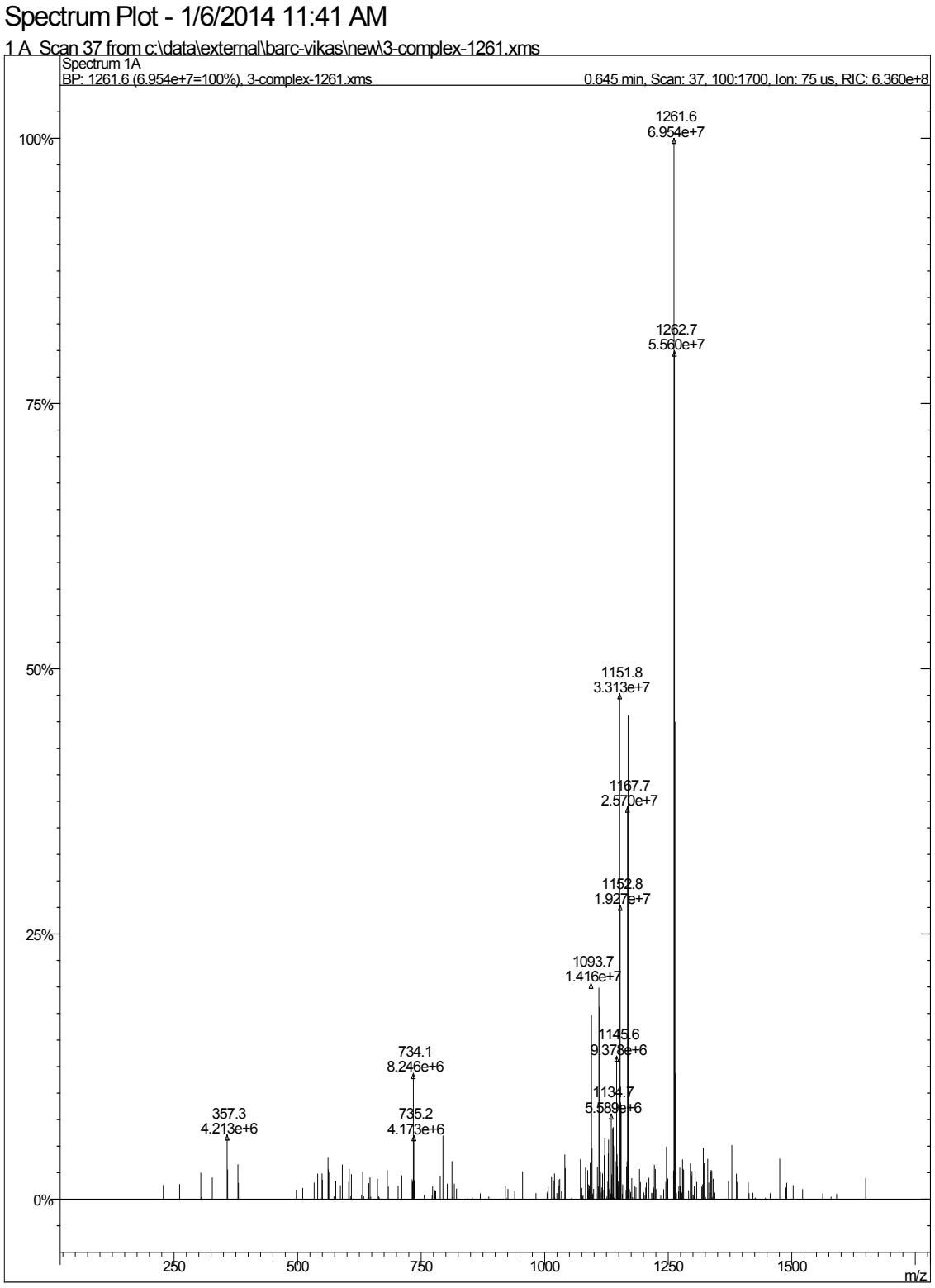


Table S1: Computed values of electron density and Laplacian of electron density and ellipsity of MNO_3-CBCBGA and metal ion-hydrated complexes at the B3LYP/DZP level using Bader's AIM calculation.

Metal-ion complex	BCP	ρ	Ave. ∇2ρ	Ave. ε
Cs^+-CBCBGA	Cs-O1	0.0105	0.039	0.069
	Cs -O2	0.0056		
	Cs -O3	0.0076		
	Cs -O4	0.0103		
	Cs -O5	0.0104		
	Cs -O6	0.0078		
	Cs -O7	0.0111		
	Cs -O8	0.0130		
Na^+-CBCBGA	Na-O1	0.0105	0.079	0.062
	Na -O2	0.0041		
	Na -O3	0.0091		
	Na -O4	0.0134		
	Na -O5	0.0276		
Cs^+-$(H_2O)_8$	Cs-O1	0.0082	0.031	0.078
	Cs -O2	0.0084		
	Cs -O3	0.0080		
	Cs -O4	0.0084		
	Cs -O5	0.0080		
	Cs -O6	0.0081		
	Cs -O7	0.0076		
	Cs -O8	0.0086		
Na^+-$(H_2O)_6$	Na-O1	0.015	0.096	0.055
	Na -O2	0.015		
	Na -O3	0.015		
	Na -O4	0.015		
	Na -O5	0.015		
	Na -O6	0.015		

Table S2: Calculated values of average second order stabilization energies $E_{ij}^{(2)}$ using NBO analysis at the B3LYP/DZP level of theory.

Donar nbo (i)	Accepter nbo (j)	E(2) (kcal/mol)
LP(1)O1	LV(1)Cs179	0.68
LP(1)O3	LV(1)Cs179	2.02
LP(2)O3	LV(1)Cs179	0.32
LP(1)O5	LV(1)Cs179	1.02
LP(2)O5	LV(1)Cs179	0.10
LP(1)O6	LV(1)Cs179	2.81
LP(2)O6	LV(1)Cs179	0.22
LP(1)O7	LV(1)Cs179	0.91
LP(2)O7	LV(1)Cs179	0.48
LP(1)O8	LV(1)Cs179	0.94
LP(2)O8	LV(1)Cs179	0.07
LP(1)O13	LV(1)Cs179	1.82
LP(1)O14	LV(1)Cs179	6.49
LP(2)O14	LV(1)Cs179	0.36
LP(3)O14	LV(1)Cs179	0.30
LP(1)O15	LV(1)Cs179	6.03
LP(2)O15	LV(1)Cs179	0.47
LP(3)O15	LV(1)Cs179	0.56
Donar nbo (i)	Accepter nbo (j)	E(2) (kcal/mol)
LP(1)O69	LV(1)Na87	1.00
LP(2)O69	LV(1)Na87	0.14
LP(1)O70	LV(1)Na87	2.27
LP(1)O71	LV(1)Na87	0.67
LP(2)O71	LV(1)Na87	0.23
LP(1)O74	LV(1)Na87	1.42
LP(2)O74	LV(1)Na87	0.07
LP(1)O75	LV(1)Na87	2.00
LP(1)O76	LV(1)Na87	0.84
LP(1)O81	LV(1)Na87	3.91

LP(2)O81	LV(1)Na87	0.12
LP(1)O82	LV(1)Na87	2.93
LP(2)O82	LV(1)Na87	0.09
LP(1)O83	LV(1)Na87	1.67