Electronic supplementary information

Dual mode of extraction for Cs$^+$ and Na$^+$ ions with di-cyclohexano-18-crown-6 and bis-(2-propyloxy)-calix[4]-crown-6 in ionic liquids: Density Functional Theoretical investigation

Sk. M. Ali[*#], J.M. Joshi, A. Singha Deb, A. Boda, K.T. Shenoy and S.K. Ghosh

Chemical Engineering Division,
Bhabha Atomic Research Centre, Mumbai, 400 085, India.
[#]Homi Bhabha National Institute, Mumbai, 400 085, India.

*corresponding author

Table.S1 : Calculated structural parameters of DCH18C6 at different level of DFT functional and basis

Method	C-C(Å)	C-O(Å)	O-O(Å)
BP86/SVP	1.521, 1.521, 1.517, 1.517	1.412, 1.420, 1.421, 1.416, 1.412, 1.413, 1.412, 1.412, 1.415, 1.412, 1.410, 1.410	5.461, 6.062, 5.805
B3LYP/SVP	1.518, 1.517, 1.514, 1.514	1.412, 1.416, 1.413, 1.408, 1.405, 1.402, 1.402, 1.405, 1.408, 1.405, 1.405, 1.406	5.432, 6.070, 5.811
TPSSH/SVP	1.517, 1.517, 1.513, 1.513	1.419, 1.416, 1.412, 1.417, 1.408, 1.407, 1.406, 1.409, 1.412, 1.408, 1.409, 1.417	5.468, 6.017, 5.770
BP86/TZVP	1.516, 1.517, 1.513, 1.513	1.428, 1.423, 1.427, 1.430, 1.422, 1.421, 1.421, 1.423, 1.420, 1.419, 1.419, 1.420	5.503, 6.033, 5.787
B3LYP/TZVP	1.514, 1.523, 1.510, 1.510	1.418, 1.422, 1.419, 1.415, 1.414, 1.413, 1.413, 1.414, 1.412, 1.410, 1.411, 1.411	5.548,6.065, 5.814
TPSSH/TZVP	1.514, 1.514, 1.510, 1.510	1.423, 1.426, 1.422, 1.418, 1.415, 1.414, 1.414, 1.415, 1.419, 1.416, 1.417, 1.417	5.514, 6.015, 5.743

set.

Table.S2: Calculated structural parameters of Cs$^+$ ion -DCH18C6 complex at different level of DFT and basis set.

Method	C-C(Å)	C-O(Å)	O-O(Å)	M-O(Å)
BP86/SVP	1.516, 1.517, 1.518, 1.518	1.439, 1.438, 1.428, 1.430, 1.423, 1.422, 1.422, 1.424, 1.423, 1.422, 1.423, 1.422	4.704, 5.886, 5.937	3.138, 3.138, 3.126, 3.287, 3.218, 3.120
B3LYP/SVP	1.513, 1.514, 1.514, 1.514	1.431, 1.420, 1.430, 1.422, 1.415, 1.414, 1.414, 1.414, 1.416, 1.415, 1.415, 1.414,	4.724, 5.874, 5.929	3.139, 3.139, 3.125, 3.295, 3.221, 3.123
TPSSH/SVP	1.513, 1.513, 1.514, 1.514	1.434, 1.426, 1.434, 1.423, 1.420, 1.418, 1.418, 1.419, 1.419, 1.419, 1.418, 1.419	4.701, 5.851, 5.906	3.132, 3.132, 3.282, 3.111, 3.116, 3.215
BP86/TZVP	1.511, 1.511, 1.512, 1.512	1.438, 1.445, 1.445, 1.433, 1.429, 1.431, 1.433, 1.430, 1.432, 1.431, 1.430, 1.430	4.666, 5.865, 5.922	3.110, 3.094, 3.261, 3.100, 3.095, 3.188
B3LYP/TZVP	1.509, 1.509, 1.509,1.509	1.436, 1.429, 1.436, 1.426, 1.421, 1.423, 1.422, 1.422, 1.423, 1.422, 1.422, 1.422	4.688, 5.863, 5.921	3.126, 3.126, 3.287, 3.114, 3.116, 3.210
TPSSH/TZVP	1.509, 1.509, 1.509,1.509	1.439, 1.439, 1.430, 1.434, 1.424, 1.426, 1.425, 1.425, 1.427, 1.426, 1.426, 1.425	4.670, 5.905, 5.808	3.109, 3.088, 3.079, 3.262, 3.092, 3.169

Table.S3: Calculated structural parameters of Na$^+$ ion -DCH18C6 complex at different level of DFT and basis set.

Method	C-C(Å)	C-O(Å)	O-O(Å)	
BP86/SVP	1.512, 1.508, 1.513, 1.523	1.444, 1.439, 1.430, 1.438, 1.424, 1.427, 1.425, 1.430, 1.427, 1.423, 1.423, 1.425	4.872, 5.023, 4.796	2.510, 2.581, 2.710, 2.420, 2.608, 2.411
B3LYP/SVP	1.508, 1.515, 1.509, 1.519	1.421, 1.430, 1.434, 1.430, 1.416, 1.419, 1.417, 1.422, 1.419, 1.415, 1.415, 1.418	4.855, 5.014, 4.774	2.50, 2.571, 2.706, 2.597, 2.410, 2.396
TPSSH/SVP	1.508, 1.519, 1.509, 1.519	1.434, 1.438, 1.426, 1.434, 1.420, 1.423, 1.421, 1.426, 1.422, 1.419, 1.419, 1.421	4.843, 5.010, 4.766	2.495, 2.564, 2.396, 2.595, 2.410, 2.609
BP86/TZVP	1.507, 1.512, 1.512, 1.508	1.450, 1.444, 1.444, 1.436, 1.430, 1.434, 1.433, 1.435, 1.433, 1.430, 1.432, 1.436	4.939, 5.122, 5.254	2.535, 2.601, 2.663, 2.467, 2.444, 2.734
B3LYP/TZVP	1.505, 1.510, 1.505, 1.515	1.439, 1.435, 1.435, 1.427, 1.421, 1.426, 1.424, 1.427, 1.424, 1.421, 1.421, 1.423	4.913, 5.097, 4.827	2.520, 2.597, 2.740, 2.633, 2.432, 2.417
TPSSH/TZVP	1.505, 1.510, 1.505, 1.515	1.444. 1.439, 1.431, 1.439, 1.425, 1.429, 1.428, 1.431, 1.428, 1.426, 1.425, 1.426	4.890, 5.084, 4.821	2.514, 2.577, 2.643, 2.421, 2.437, 2.715

Table.S4: Calculated structural parameters of BPC6 at different level of DFT functional and basis set.

Method		C-C (Å)	C-O(Å)	O-O(Å)
Basis	Functional			
SVP	BP86	1.523, 1.521, 1.530, 1.521, 1.519	1.378, 1.387, 1.425, 1.423, 1.411, 1.412, 1.413, 1.412, 1.415, 1.416, 1.413, 1.415	6.998, 6.422, 6.729
	B3LYP	1.516, 1.518, 1.518, 1.526, 1.520	1.381, 1.374, 1.417, 1.406, 1.407, 1.409, 1.407, 1.405, 1.406, 1.404, 1.404, 1.416	6.451, 6.866, 6.816
	TPSSH	1.518, 1.517, 1.526, 1.517, 1.515	1.376, 1.383, 1.419, 1.408, 1.409, 1.410, 1.409, 1.411, 1.413, 1.411, 1.409, 1.421	6.827, 6.492, 6.922
TZVP	BP-86	1.513, 1.516, 1.525, 1.525, 1.516	1.392, 1.382, 1.434, 1.433, 1.418, 1.419, 1.420, 1.420, 1.420, 1.423, 1.423, 1.421	6.473, 7.038, 6.541
	B3LYP	1.513, 1.5111, 1.521, 1.512, 1.514	1.384, 1.377, 1.425, 1.413, 1.415, 1.416, 1.412, 1.412, 1.412, 1.411, 1.410, 1.424	6.465, 6.970, 6.656
	TPSSH	1.510, 1.513, 1.521, 1.512, 1.513	1.387, 1.37, 1.430, 1.416, 1.418, 1.419, 1.415, 1.416, 1.416, 1.414, 1.414, 1.428	6.473, 6.953, 6.591

Table.S5: Calculated structural parameters of Cs^+ ion-BPC6 complex at different level of DFT and basis set.

Method		C-C(Å)	C-O(Å)	O-O(Å)	M-O(Å)
Basis	Functional				
SVP	BP86	1.514, 1.514, 1.523, 1.518, 1.518	1.400, 1.394, 1.438, 1.420, 1.422, 1.420, 1.420, 1.421, 1.421, 1.419, 1.419, 1.437	6.459, 6.597, 6.291	3.256, 3.261, 3.327, 3.445, 3.497, 3.264
	B3LYP	1.511, 1.511, 1.519, 1.515, 1.515	1.395, 1.389, 1.429, 1.430, 1.413, 1.414, 1.412, 1.412, 1.413, 1.412, 1.412. 1.412	6.452, 6.552, 6.295	3.269, 3.258, 3.268, 3.324, 3.431, 3.446
	TPSSH	1.515, 1.514, 1.519, 1.511, 1.511	1.391, 1.396, 1.433, 1.416, 1.416, 1.416, 1.417, 1.416, 1.416, 1.418, 1.417, 1.434	6.549, 6.430, 6.271	3.235, 3.251, 3.261, 3.316, 3.446, 3.463
TZVP	BP86	1.508, 1.509, 1.519, 1.513, 1.513	1.405, 1.398, 1.446, 1.427, 1.429, 1.428, 1.427, 1.427, 1.426, 1.426, 1.426, 1.444	6.430, 6.599, 6.278	3.253, 3.248, 3.257, 3.323, 3.426, 3.507
	B3LYP	1.511, 1.510, 1.516, 1.506, 1.506	1.392, 1.398, 1.436, 1.419, 1.418, 1.418, 1.419, 1.419, 1.420, 1.421, 1.420, 1.437	6.587, 6.436, 6.288	3.255, 3.281, 3.257, 3.323, 3.416, 3.467
	TPSSH	1.507, 1.507, 1.516, 1.510, 1.511	1.400, 1.394, 1.441, 1.423, 1.425, 1.423, 1.423, 1.423, 1.422, 1.422, 1.422, 1.440,	6.42, 6.502, 6.278	3.246, 3.254, 3.322, 3.257, 3.421, 3.472

Table.S6: Calculated structural parameters of Na$^+$ ion -BPC6 complex at different level of DFT and basis set.

Method	C-C (Å)	C-O (Å)	O-O (Å)	M-O (Å)
BP86/SVP	1.515, 1.517, 1.525, 1.516, 1.518	1.404, 1.408, 1.446, 1.428, 1.434, 1.415, 1.424, 1.414, 1.415, 1.423, 1.448, 1.414	5.798. 6.967, 5.123	2.382, 2.424, 2.468, 3.980, 5.013, 4.265
B3LYP/SVP	1.513, 1.514, 1.521, 1.513, 1.513	1.399, 1.403, 1.433, 1.422, 1.427, 1.407, 1.416, 1.406, 1.407, 1.416, 1.406, 1.440	5.676, 6.973, 5.079	2.362, 2.394, 2.424, 3.979. 5.014, 4.193
TPSSH/SVP	1.515, 1.512, 1.521, 1.514, 1.512	1.404, 1.400, 1.444, 1.410, 1.419, 1.411, 1.410, 1.419, 1.411, 1.430, 1.424, 1.436	6.937, 5.687, 5.080	2.398, 2.362, 3.963, 2.438, 4.980, 4.189
BP86/TZVP	1.514, 1.511, 1.520, 1.512, 1.510	1.409, 1.407, 1.453, 1.420, 1.429, 1.423, 1.420, 1.430, 1.420, 1.439, 1.433, 1.447	5.780, 6.971, 5.152	2.401, 2.439, 2.489, 3.946, 4.186, 4.941
B3LYP/TZVP	1.511, 1.509, 1.517, 1.509, 1.508	1.404, 1.401, 1.446, 1.412, 1.421, 1.414, 1.412, 1.422, 1.412, 1.431, 1.426, 1.438	6.97, 5.712, 5.146	2.428, 2.387, 3.964, 2.474, 4.959, 4.156
TPSSH/TZVP	1.507, 1.509, 1.517, 1.509, 1.511	1.402, 1.405, 1.442, 1.428, 1.434, 1.415, 1.425, 1.416, 1.418, 1.424, 1.416, 1.449	5.728, 6.944, 5.118	2.427, 2.387, 2.478, 4.155, 4.922, 3.940

Table.S7: Calculated values of binding energy of Cs^+ and Na^+ ion with DCH18C6 and BPC6 at different M06 suite of density functionals using TZ2P basis set.

System	BE (kcal/mol)					
	DCH18C6			BPC6		
	M06-L	M06	M06-2X	M06-L	M06	M06-2X
Cs	-65.89	-70.88	-63.97	-79.86	-83.89	-75.34
Na	-88.19	-91.91	-95.05	-90.84	-92.74	-96.00

Table.S8: Calculated values of HOMO-LUMO energy of Cs^+ and Na^+ ion with DCH18C6 at different DFT functional and basis set.

System	HOMO-LUMO (eV)					
	SVP			TZVP		
	BP86	B3LYP	TPSSH	BP86	B3LYP	TPSSH
DCH18C6	5.99	7.70	7.18	5.71	7.28	6.77
Cs- DCH18C6	5.56	6.85	6.32	5.72	7.02	6.50
Na- DCH18C6	6.03	7.63	7.08	5.83	7.35	6.78
BPC	3.88	5.44	4.85	3.95	5.48	4.89
Cs-BPC	4.00	5.61	4.96	3.98	5.56	4.92
Na-BPC	4.01	5.64	4.97	3.98	5.61	4.93

Table.S9: Calculated values of second order stabilization energies $E_{ij}^{(2)}$ using NBO analysis as implemented in ADF Package at B3LYP/TZ2P level of theory.

System	Donor NBO	Acceptor NBO	E2(kcal/mol)
DCH18C6-Cs$^+$	LP (1) O21	LP*(1)Cs63	0.78
	LP (1) O22	LP*(1)Cs63	0.85
	LP (1) O23	LP*(1)Cs63	0.60
	LP (1) O24	LP*(1)Cs63	0.68
	LP (1) O25	LP*(1)Cs63	0.62
	LP (1) O26	LP*(1)Cs63	0.65
DCH18C6-Na$^+$			
	LP (1) O21	LP*(1)Na27	3.11
	LP (1) O22	LP*(1)Na27	3.54
	LP (1) O23	LP*(1)Na27	3.79
	LP (1) O24	LP*(1)Na27	3.25
	LP (1) O25	LP*(1)Na27	3.72
	LP (1) O26	LP*(1)Na27	3.99

Table.S10.: Calculated values of electron density and Laplacian of electron density at BP86/TZ2P level of theory using Bader's AIM calculation as implemented in ADF package.

Complex	BCP	$\lambda 1$	$\lambda 2$	$\lambda 3$	ρ	$\nabla^2 \rho$	$\varepsilon = (\lambda 1/ \lambda 2) -1$
DCH18C6-Cs$^+$	Cs-O1	-0.0112	-0.0103	0.0712	0.0132	0.048	0.087
	Cs-O2	-0.011	-0.010	0.0693	0.0127	0.048	0.100
	Cs-O3	-0.011	-0.010	0.072	0.0133	0.050	0.100
	Cs-O4	-0.0086	-0.0077	0.0574	0.0106	0.040	0.116
	Cs-O5	-0.0112	-0.0106	0.0702	0.0103	0.048	0.056
	Cs-O6	-0.0073	-0.0067	0.0497	0.0093	0.032	0.089
DCH18C6- Na$^+$	Na-O1	-0.011	-0.0099	0.082	0.0095	0.0612	0.111
	Na-O2	-0.011	-0.011	0.087	0.0099	0.0644	0.000
	Na-O3	-0.0218	-0.0203	0.146	0.016	0.104	0.073
	Na-O4	-0.008	-0.0065	0.0612	0.0073	0.0464	0.230
	Na-O5	-0.0152	-0.0144	0.108	0.0119	0.0784	0.055
	Na-O6	-0.0199	-0.0185	0.139	0.015	0.100	0.075
BPC6- Cs$^+$	Cs-O1	-0.0078	-0.0068	0.052	0.0094	0.0368	0.147
	Cs-O2	-0.0078	-0.0068	0.0521	0.0095	0.0368	0.147
	Cs-O3	-0.0079	-0.0070	0.052	0.0095	0.0368	0.128
	Cs-O4	-0.005	-0.0048	0.035	0.0067	0.0256	0.041
	Cs-O5	-0.007	-0.0066	0.046	0.0088	0.032	0.166
	Cs-O6	-0.0020	-0.0015	0.0157	0.0031	0.0112	0.333
BPC6- Na$^+$	Na-O1	-0.020	-0.017	0.135	0.0144	0.096	0.176
	Na-O2	-0.0169	-0.0160	0.118	0.0129	0.080	0.056
	Na-O3	-0.022	-0.020	0.152	0.016	0.096	0.100

Table.S11: Calculated values of free energy of extraction for Cs^+ and Na^+ ion using implicit and explicit solvation model in BMIM ionic liquid and octanol using optimized geometry in COSMO solvent of dielectric constant 10.3.

Diluents	Ligand	ΔGext (kcal/mol)		ΔΔGext (kcal/mol)	ΔΔΔGext (kcal/mol)
BMIMTF2N					
		Cs^+	Na^+		
Implicit	DCH18C6	2.28	-3.89	6.17	-10.14
	BPC6	-0.081	3.88	-3.97	
Explicit	DCH18C6	-56.32(-10.62)	-48.36(-2.65)	-7.96	-10.14
	BPC6	-58.69(-12.98)	-40.58(5.12)	-18.10	
octanol					
Implicit	DCH18C6	8.05	1.81	6.23	-10.21
	BPC6	5.47	9.45	-3.98	
Explicit	DCH18C6	-50.55(-4.85)	-42.65(3.05)	-7.90	-10.21
	BPC6	-53.13(-7.42)	-35.01(10.69)	-18.11	

Values in the parentheses are calculated using cluster of water molecules.
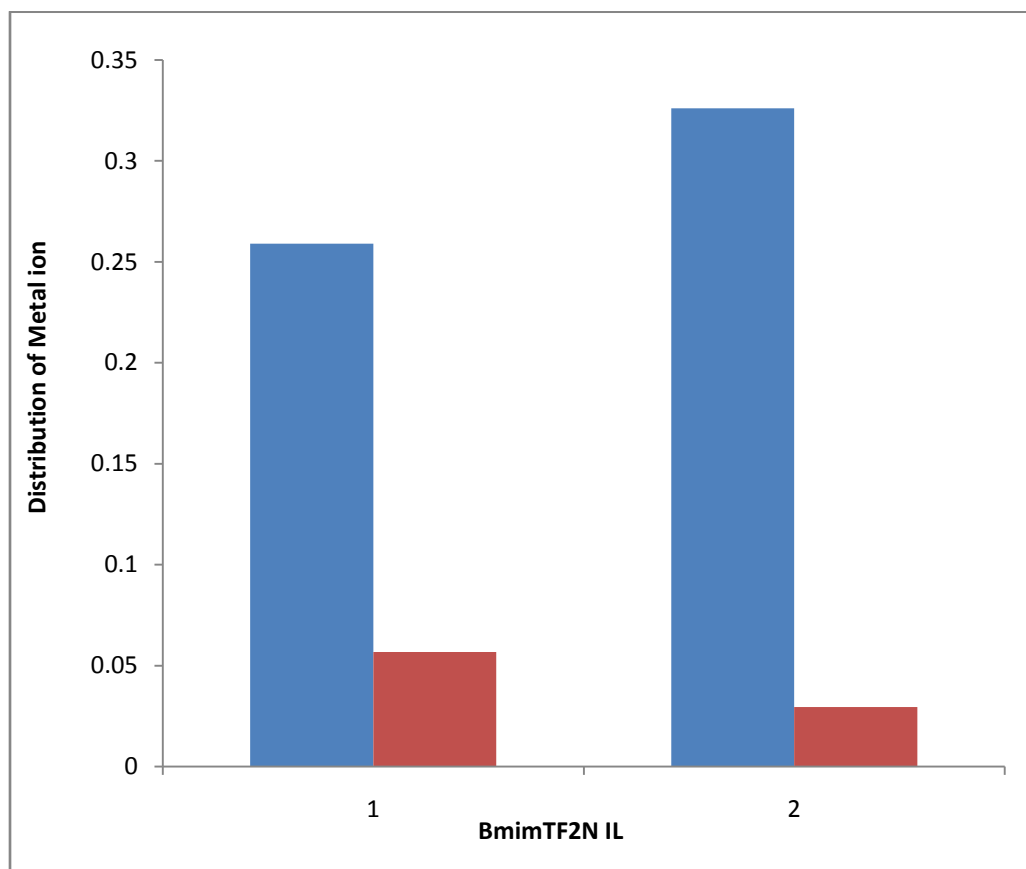
Fig.S1.: Extraction of Cs^+, Na^+ ions from neutral chloride and nitrate solution with BMIMTF2N IL. Feed of Cs: 100 ppm; Na: 100 ppm; O/A 1:1, Stirring time: 0.5 hrs; Bath:1:1 water ethanol (1) Dcs and D_{Na} in chloride salts; (2) Dcs and D_{Na} in nitrate salts.

I

II

III
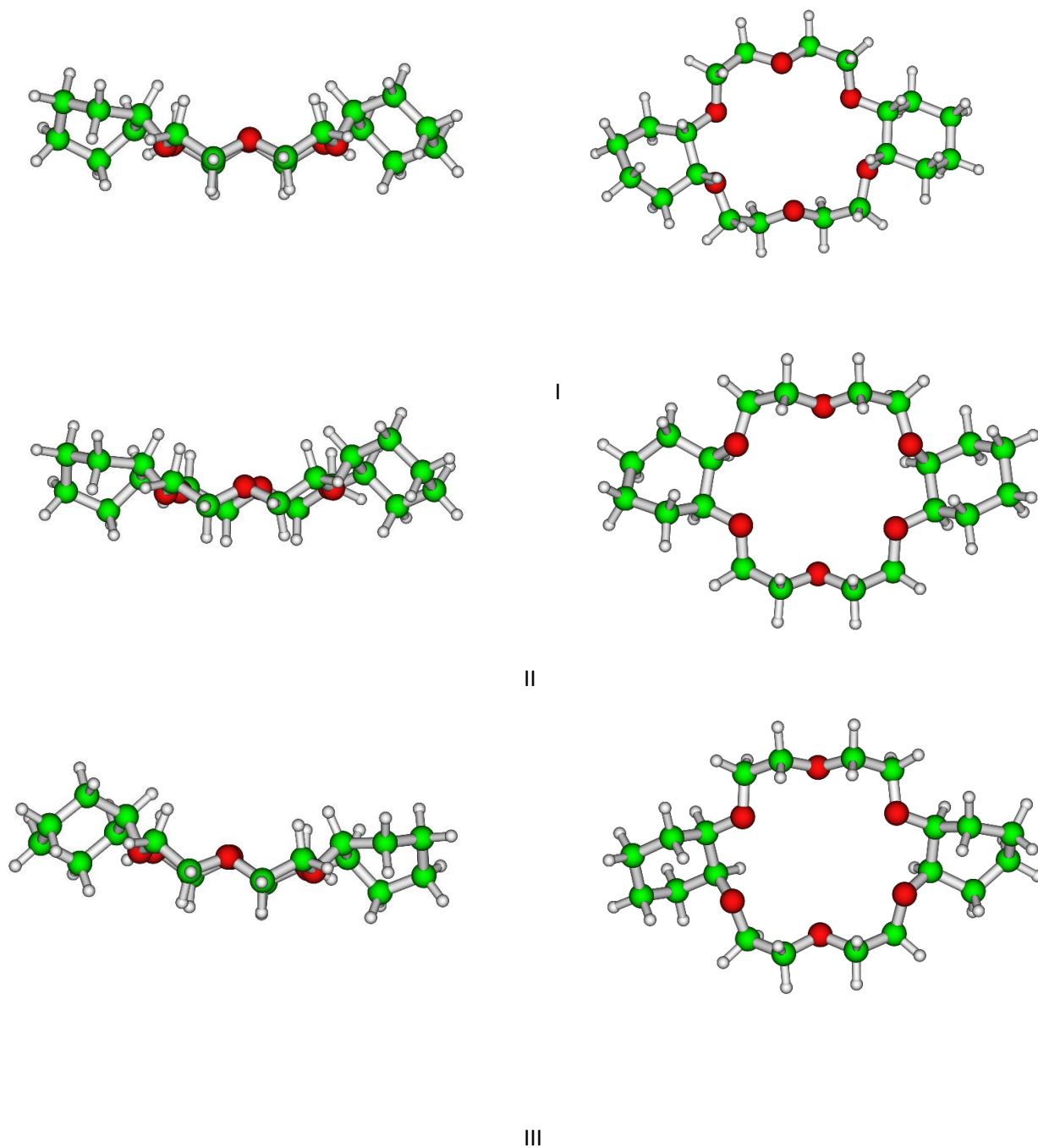
Fig.S2: Optimized minimum energy structure of free (a) DCH18C6 and (b) BPC at (I) BP86/SVP, (II) BP86/TZVP and (III) B3LYP/TZVP level of theories. Green, red and grey sphere represent the C, O and H atom respectively.
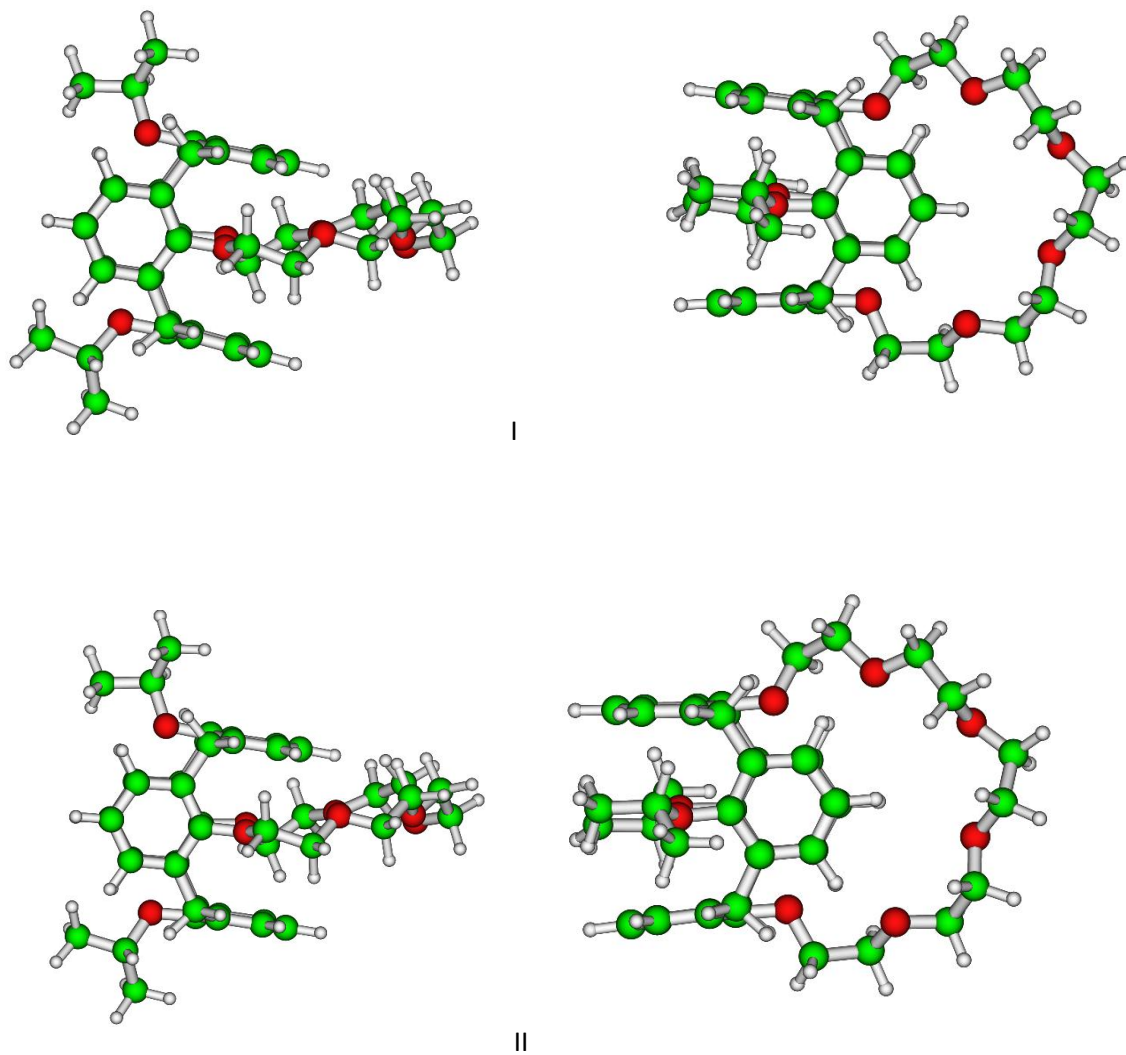
Figure.S3: Optimized minimum energy structure of free BPC6 using TZVP basis set at different level of DFT (I) BP86 and (II) B3LYP. Key is same as in Fig.S2
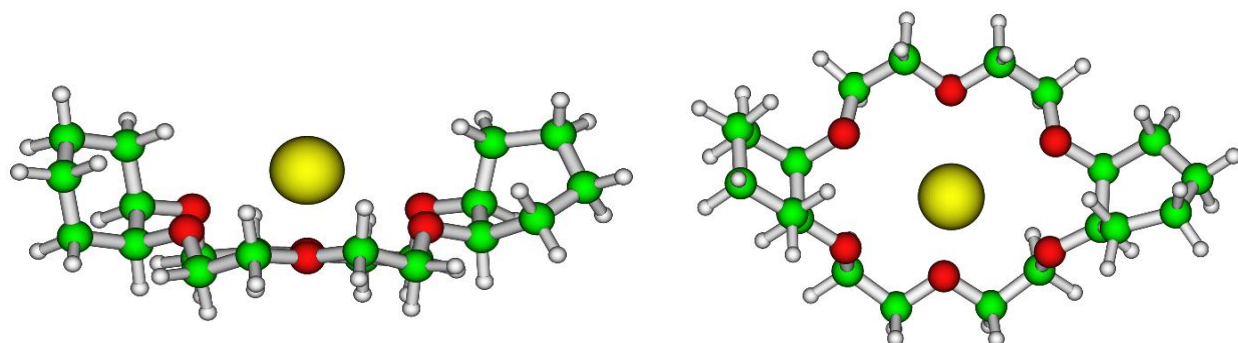
DCH18C6-Cs$^+$-BP/SVP
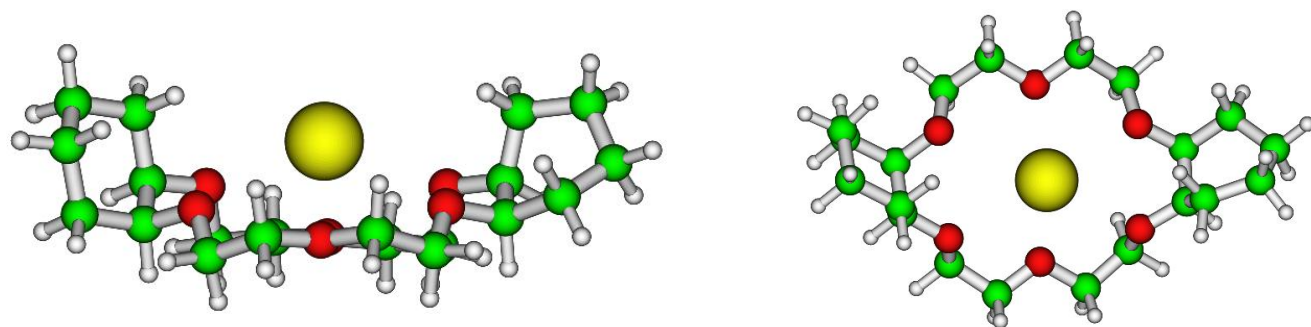
DCH18C6-Cs$^+$-B3LYP/TZVP
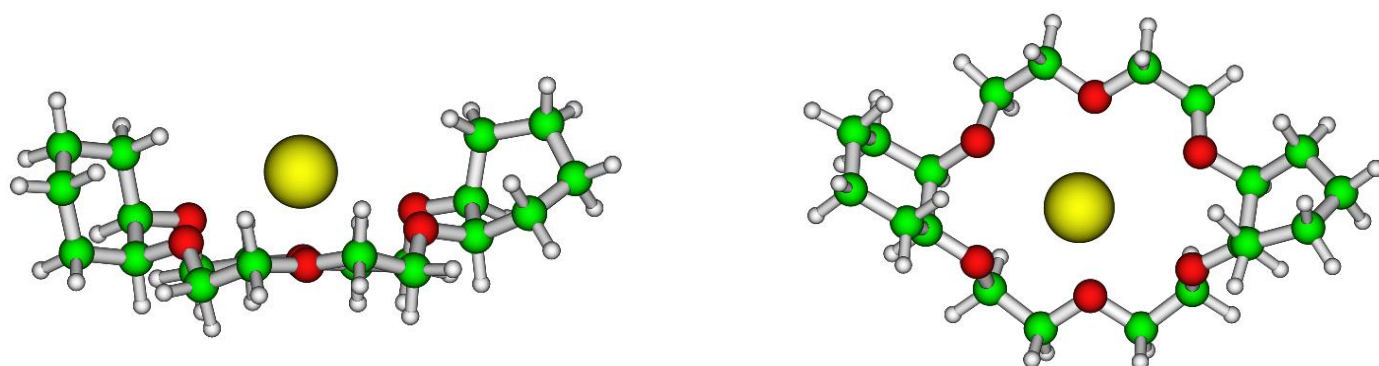
DCH18C6-Cs$^+$-B3LYP/SVP

Figure.S4: Optimized minimum energy structure of Cs$^+$-DCH18C6 complex at different level of DFT and basis set.
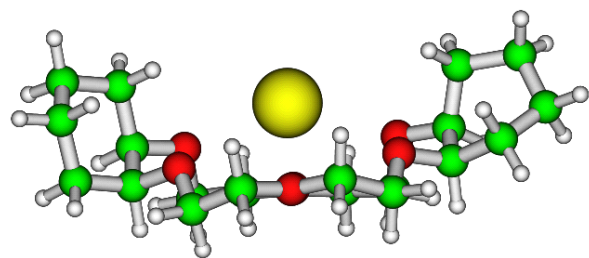
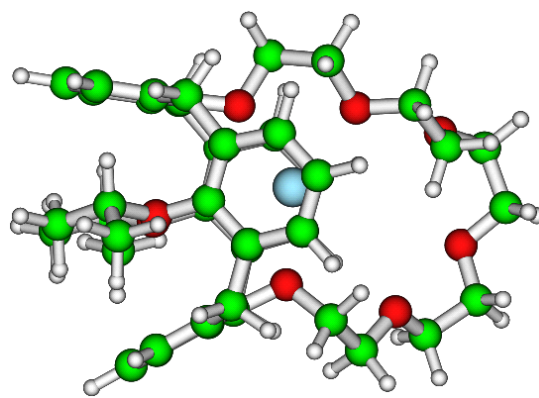DCH18C6-Cs$^+$-TPSSH/TZVP
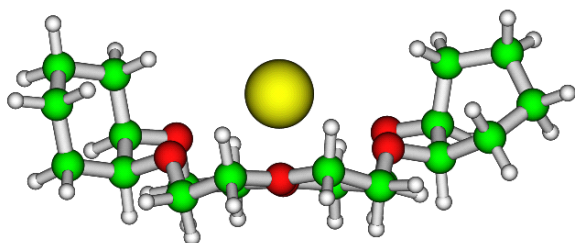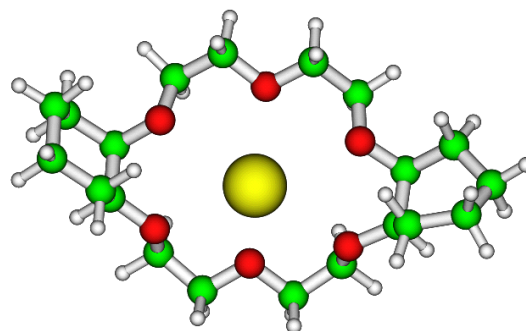
DCH18C6-Cs$^+$-TPSSH/SVP
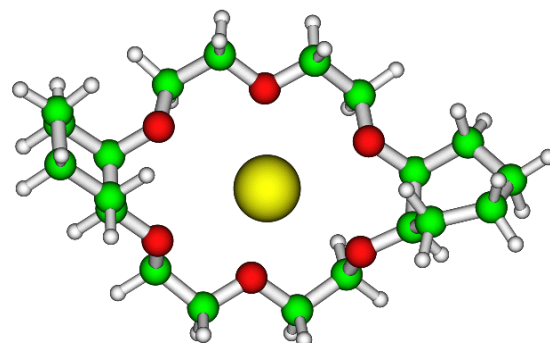
Figure.S5: Optimized minimum energy structure of Cs$^+$-DCH18C6 complex at TPSSH level of theory with different basis set.

DCH18C6-Na$^+$-B3LYP /TZVP

DCH18C6-Na$^+$-B3LYP /SVP
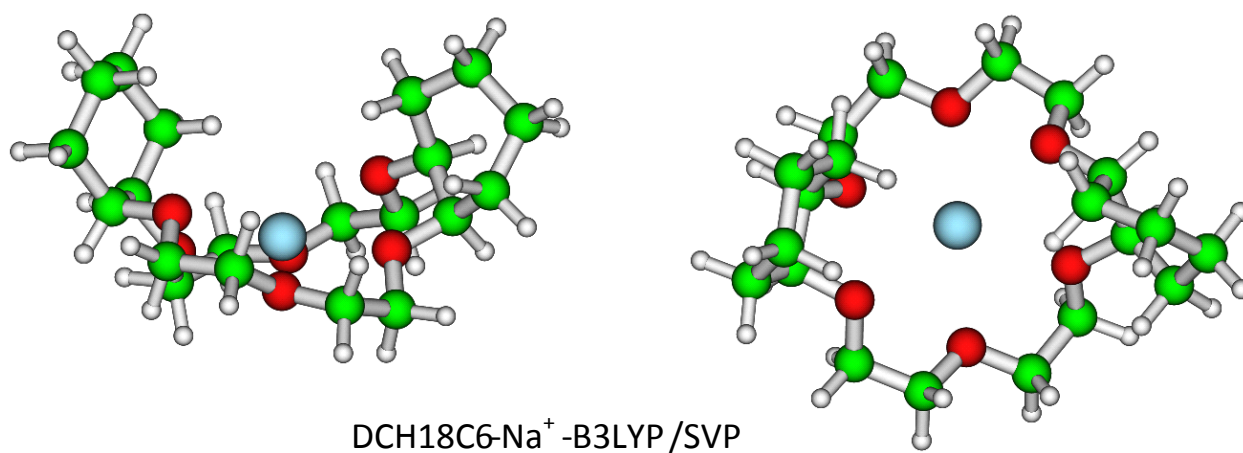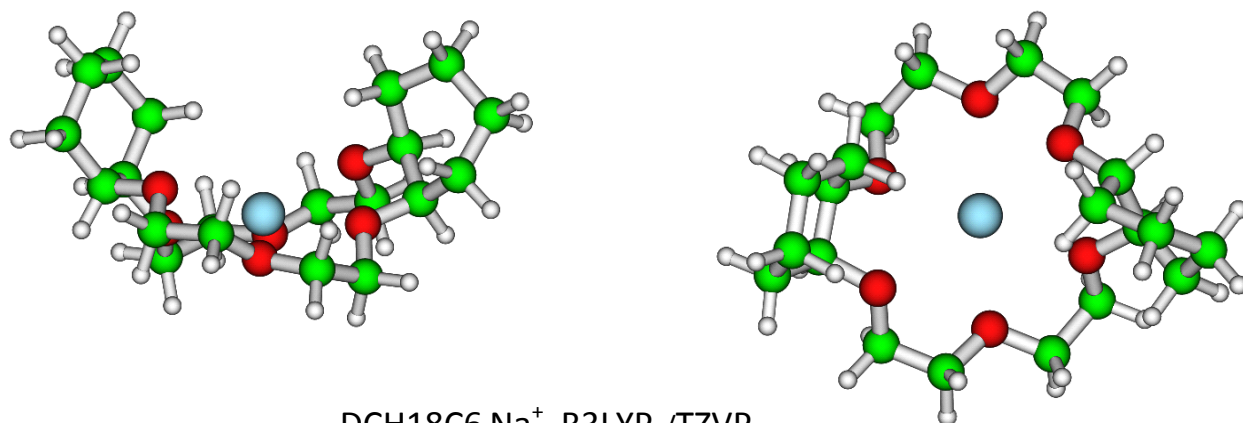
Figure.S6: Optimized minimum energy structure of Na$^+$-DCH18C6 complex at B3LYP level of theory with different basis set.
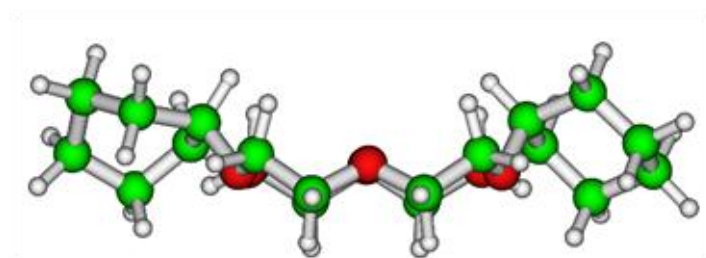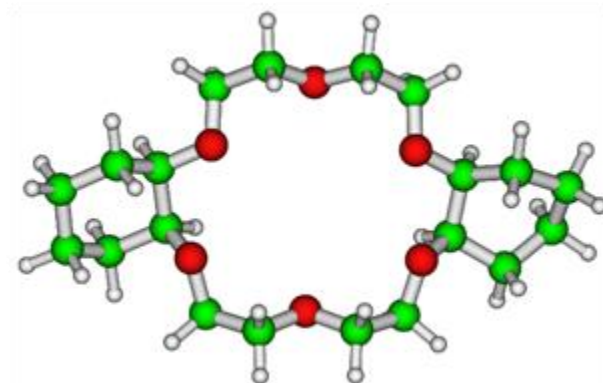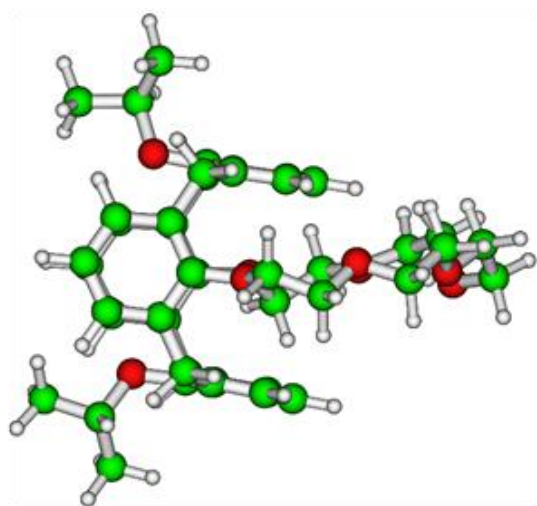
DCH18C6-Na$^+$-TPSSH/TZVP

DCH18C6-Na$^+$-TPSSH /SVP
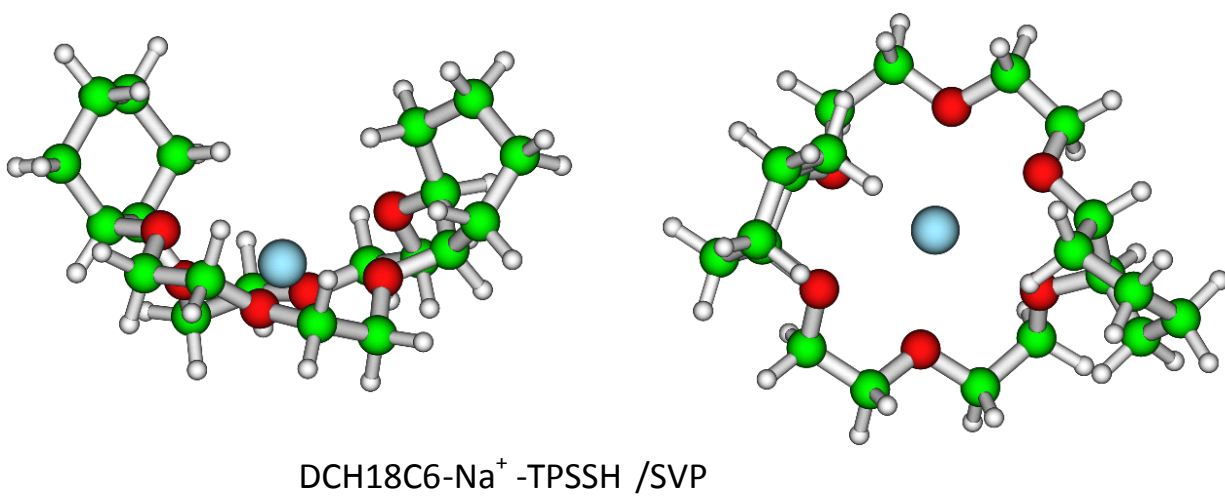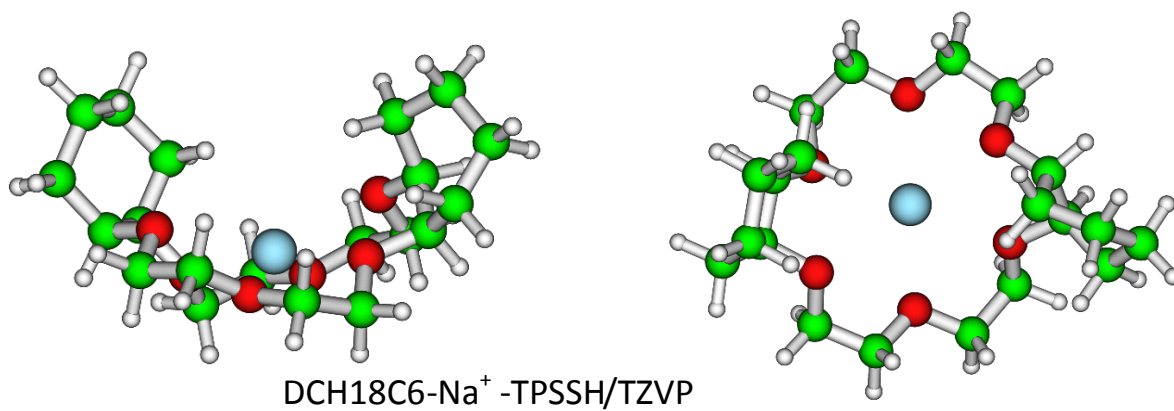
Figure.S7: Optimized minimum energy structure of Na$^+$-DCH18C6 complex at TPSSH level of theory with different basis set.

BPC6-Cs$^+$-B3LYP/TZVP

BPC6-Cs$^+$-B3LYP/SVP
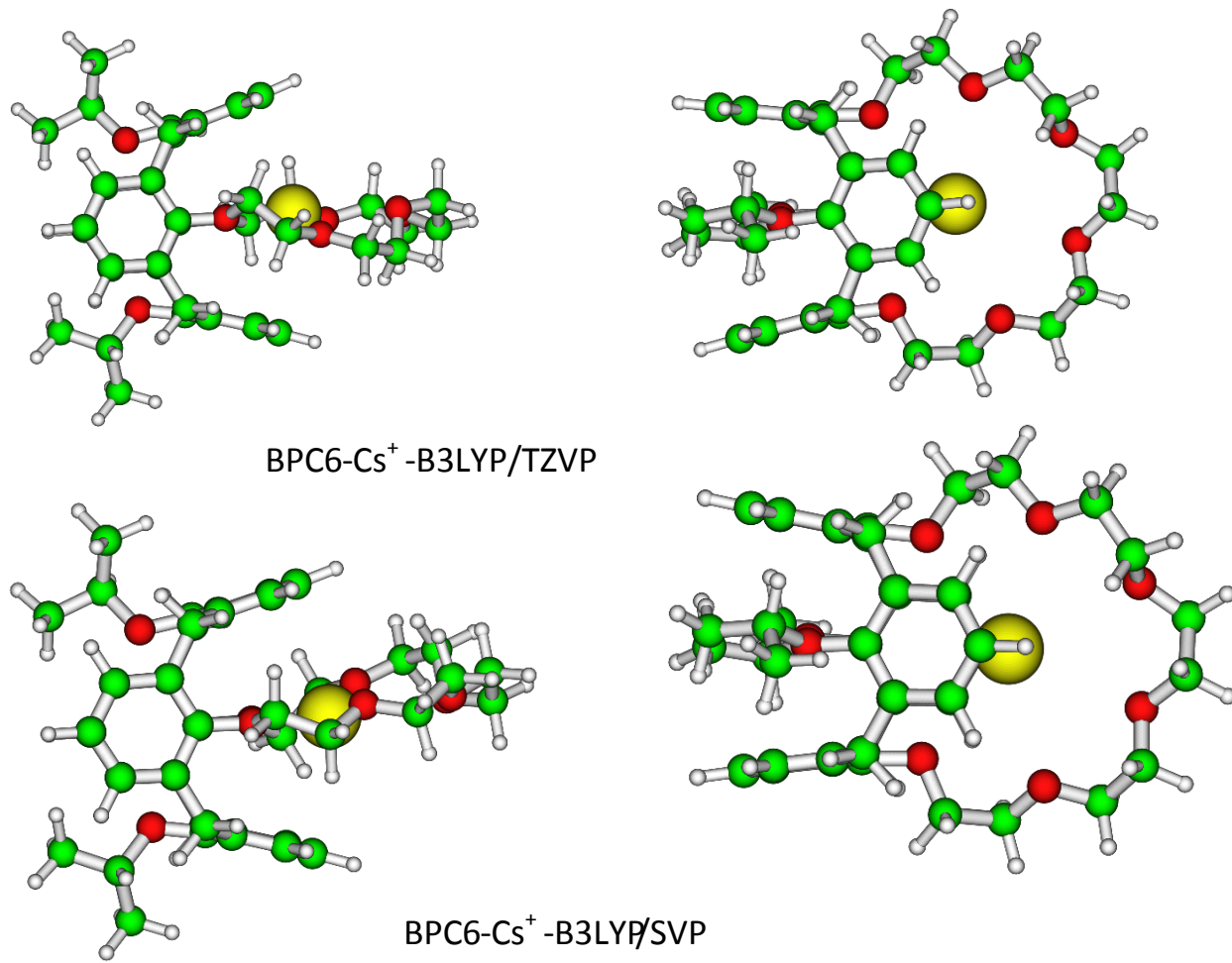
Figure.S8: Optimized minimum energy structure of Cs$^+$-DCH18C6 complex at B3LYP level of theory with different basis set.
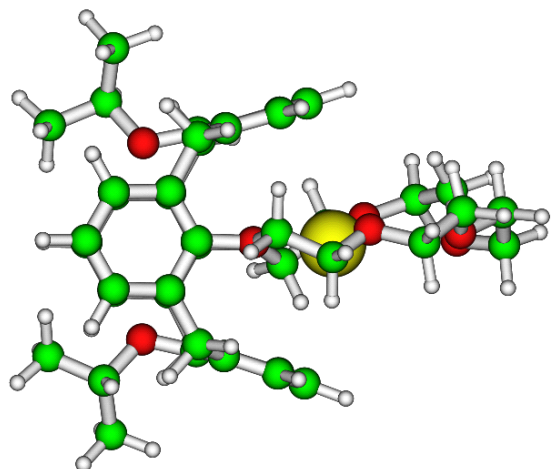
BPC6-Cs$^+$-TPSSH /TZVP
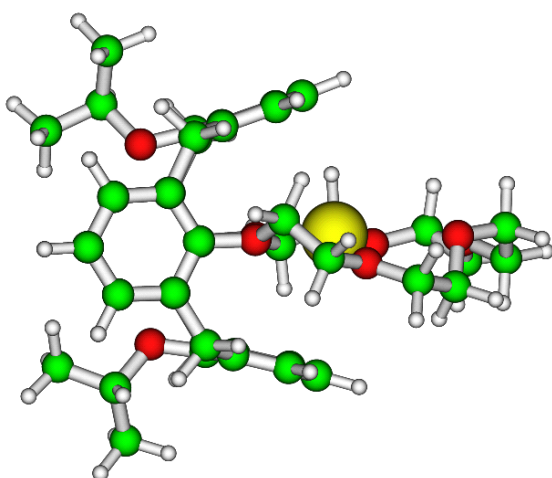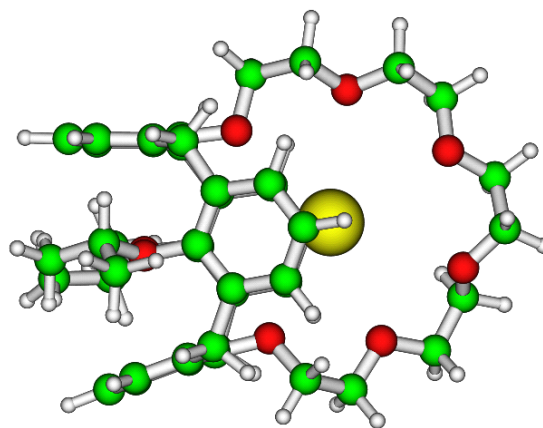
BPC6-Cs$^+$-TPSSH/SVP
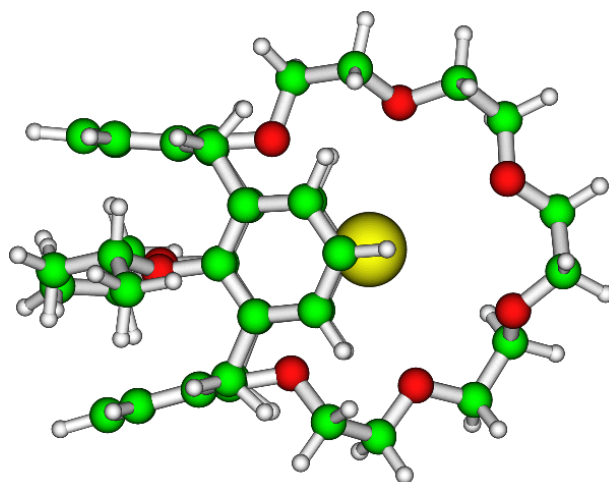
Figure.S9: Optimized minimum energy structure of Cs$^+$-DCH18C6 complex at TPSSH level of theory with different basis set.
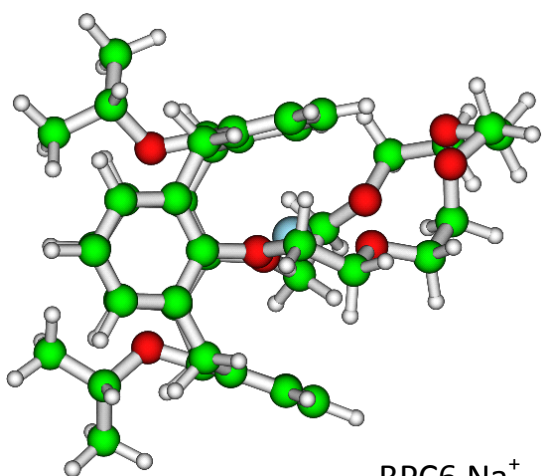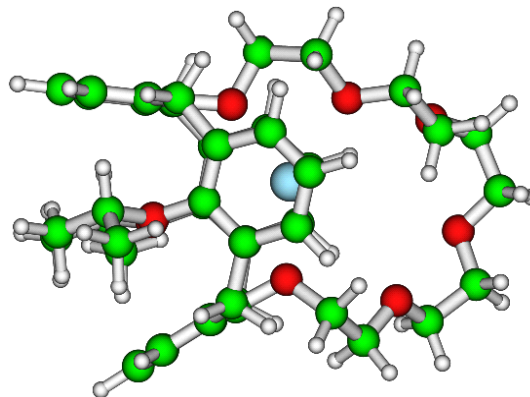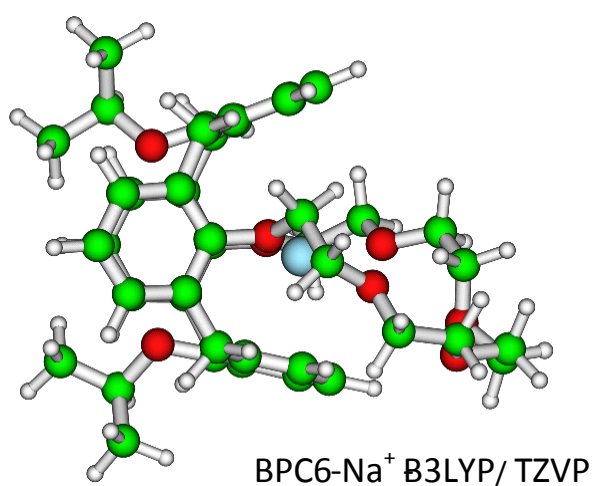
BPC6-Na$^+$ B3LYP/ TZVP

BPC6-Na$^+$ - B3LYP/ SVP
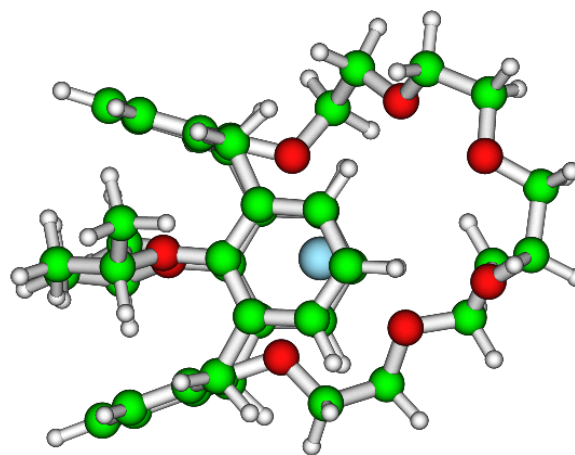
Figure.S10: Optimized minimum energy structure of Na$^+$-DCH18C6 complex at B3LYP level of theory with different basis set.
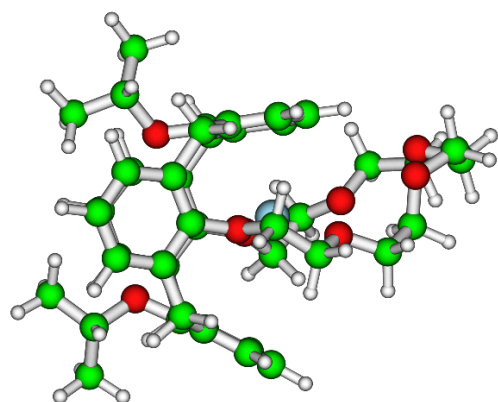
BPC6-Na$^+$ -TPSSH/TZVP
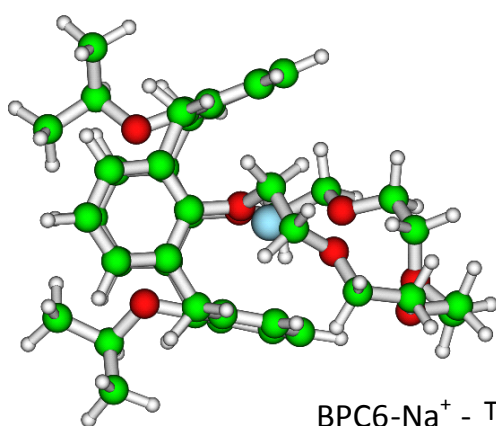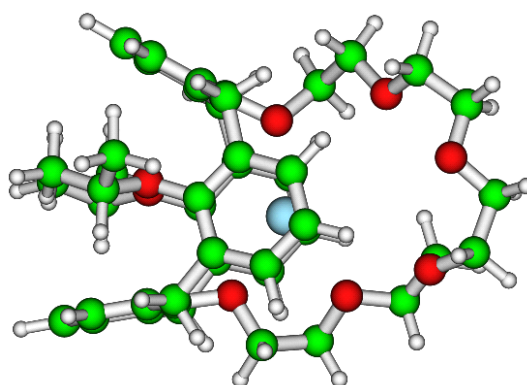
BPC6-Na$^+$ - TPSSH/SVP

Figure.S11: Optimized minimum energy structure of Na$^+$-DCH18C6 complex at TPSSH level of theory with different basis set.

Side view   (I)   Top view

(II)
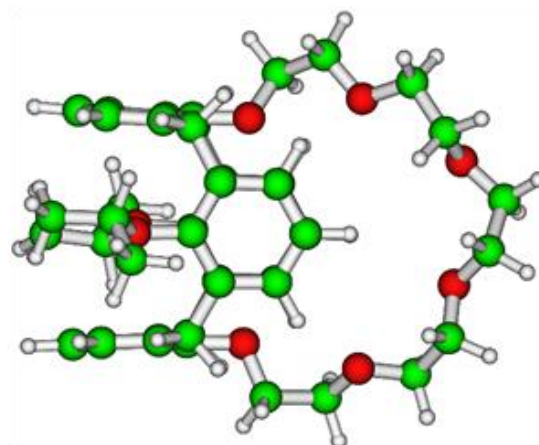
Fig.S12: Optimized minimum energy structure of free (I) DCH18C6 and (II) BPC at TPSSH/TZVP level of theory.
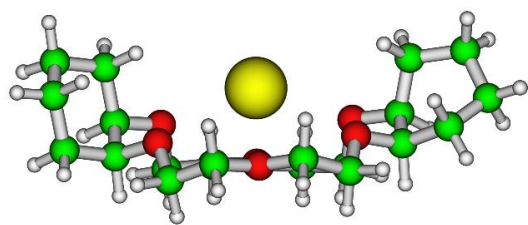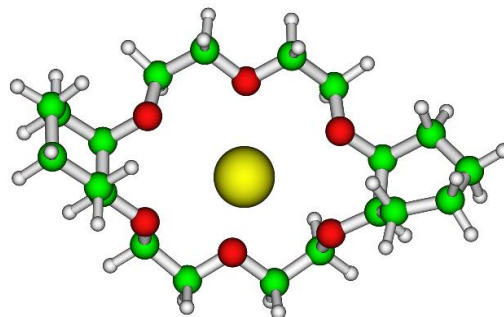
Side view   top view

I
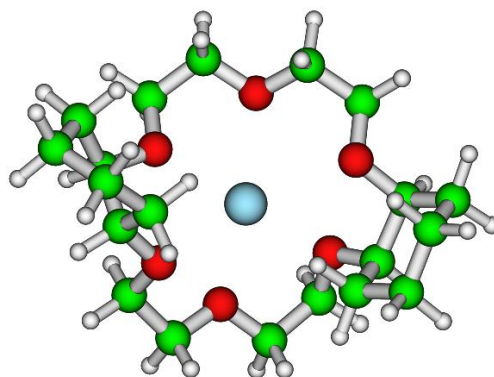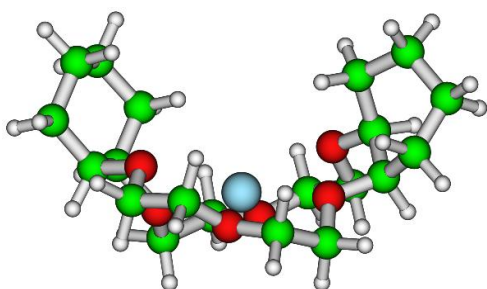
II

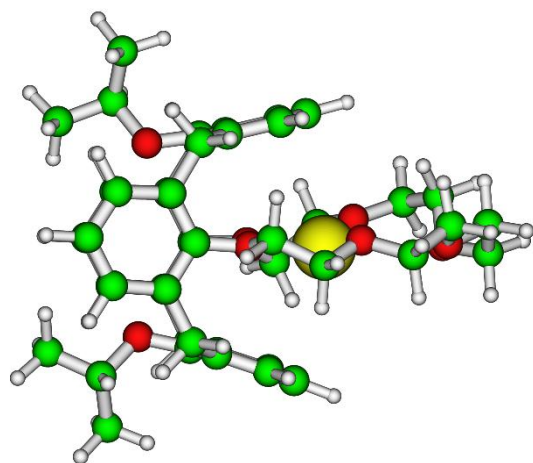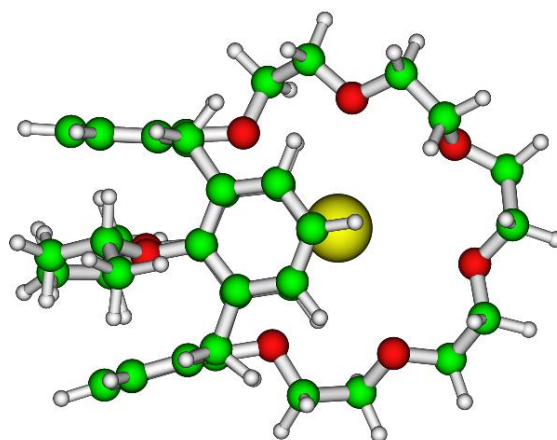**Fig.S13**: Optimized minimum energy structure of Cs^+ and Na^+ complex of DCH18C6 using TPSSH/TZVP level of theory.
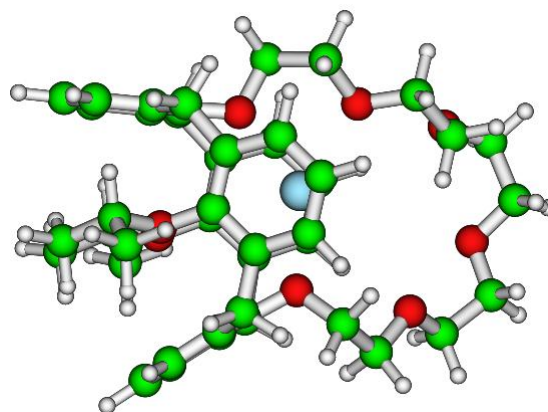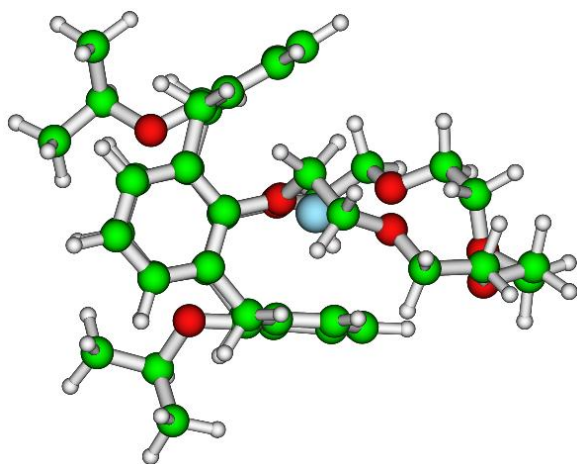
Side view

top view

I

II

Fig.S14: Optimized minimum energy structure of Cs$^+$ and Na$^+$ complex of TPSSH/TZVP level of theory.

The reason for the close values of ΔΔG and ΔΔΔG in IL and octanol can be followed using the below equations.

For e.g implicit

Octanol solvent

$$Cs^+_{(aq)} + L1_{(org)} \longrightarrow Cs^+L1_{(org)} \quad (\Delta G1_{ext}) \qquad (1)$$

$$Na^+_{(aq)} + L1_{(org)} \longrightarrow Na^+L1_{(org)} \quad (\Delta G2_{ext}) \qquad (2)$$

L1=DCH18C6

$$\Delta\Delta Gext=(\Delta G1_{ext}-\Delta G2_{ext}) \qquad (1)-(2) \text{ leads to}$$

$$L1Na^+_{(org)} + Cs^+_{(aq)} \longrightarrow L1Cs^+_{(org)} + Na^+_{(aq)}$$

IL solvent

$$Cs^+_{(aq)} + IL^+_{(org)} + L1_{(org)} \longrightarrow Cs^+L1_{(org)} + IL^+_{(aq)} \quad (\Delta G1_{ext}) \qquad (1)$$

$$Na^+_{(aq)} + IL^+_{(org)} + L1_{(org)} \longrightarrow Na^+L1_{(org)} + IL^+_{(aq)} \quad (\Delta G2_{ext}) \qquad (2)$$

L1=DCH18C6

$$\Delta\Delta Gext=(\Delta G1_{ext}-\Delta G2_{ext}) \qquad (1)-(2) \text{ leads to}$$

$$L1Na^+_{(org)} + Cs^+_{(aq)} \longrightarrow L1Cs^+_{(org)} + Na^+_{(aq)}$$
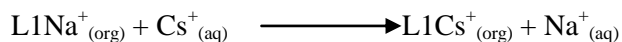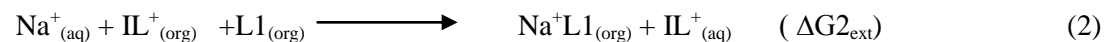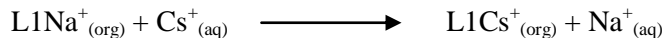
$\Delta G1_{ext}$ and $\Delta G2_{ext}$ for both octanol and IL solvent are different this is due to different equations involved. Whereas ΔΔGext is very close because of identical exchange and close dielectric constant for both octanol (10.3) and BMIMTF2N (11.6). Similarly, the ΔΔΔG (ΔΔΔG$_{ext}$= ΔΔG[L2] - ΔΔG[L1]) can be shown to be very close.