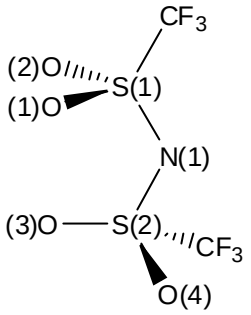
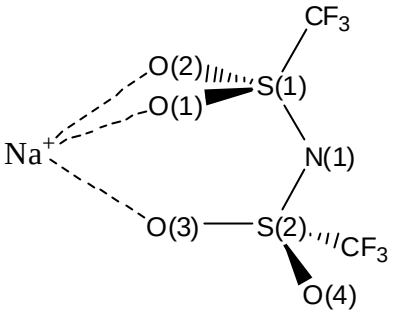


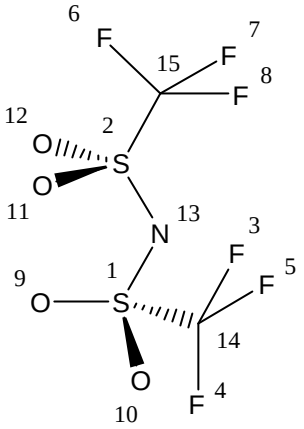
	6-31G*	6-31+G*	6-311G*	cc-pVTZ	lanL2DZ
S1-O1	1.470	1.470	1.462	1.453	1.630
S1-O2	1.467	1.468	1.460	1.453	1.626
S2-O3	1.471	1.470	1.464	1.454	1.628
S2-O4	1.470	1.471	1.462	1.454	1.626
S1-N-S2	123.3	123.9	125.6	126.1	115.9
C1-S1-N-S2	92.2	95.9	93.3	86.8	108.6
S1-N-S2-C2	-152.4	-162.175	-152.3	-130.2	178.9
CF_3..CF_3	4.600	4.769	4.594	4.241	5.315

Table S1: DFT optimized structures of Tf_2N^- with different basis sets. Main distances (Å) angles (°) and dihedrals (°).



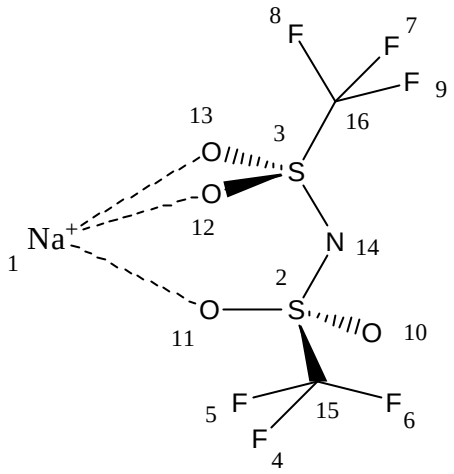
	6-31G*	6-31+G*	6-311G*	cc-pVTZ	lanL2DZ[(a)]
Na-O1	2.431	2.461	2.469	2.455	2.525
Na -O2	2.397	2.426	2.431	2.425	2.482
Na -O3	2.240	2.254	2.260	2.254	2.277
Na -O4	4.568	4.584	4.574	4.553	4.769
Na -N	3.569	3.589	3.579	3.556	3.941
S1-O1	1.489	1.488	1.482	1.472	1.648
S1-O2	1.489	1.488	1.482	1.472	1.650
S2-O3	1.494	1.494	1.487	1.478	1.647
S2-O4	1.455	1.454	1.446	1.440	1.612
S1-N-S2	117.7	118.2	119.3	119.1	109.2
C1-S1-N-S2	174.8	176.8	176.9	176.5	-173.7
S1-N-S2-C2	-104.4	-106.7	-106.9	-106.2	-120.6
CF_3..CF_3	4.994	5.042	5.025	5.016	5.558

Table S2: DFT optimized structures of $Na^+Tf_2N^-$ with different basis sets. Main distances (Å) angles (°) and dihedrals (°). (a) Optimization performed without BSSE correction.



Atom		6-31G*	6-31+G*		6-311G*		cc-pVTZ		lanL2DZ	
		Sp = opt	*sp*	*opt*	*sp*	*opt*	*sp*	*opt*	*sp*	*opt*
1	**S**	1.112	1.188	1.181	1.013	1.018	0.832	0.830	1.122	1.055
2	**S**	1.117	1.094	1.113	1.020	1.024	0.854	0.838	1.092	1.035
3	**F**	-0.238	-0.266	-0.267	-0.183	-0.184	-0.152	-0.159	-0.133	-0.162
4	**F**	-0.260	-0.309	-0.310	-0.206	-0.207	-0.177	-0.177	-0.157	-0.181
5	**F**	-0.254	-0.292	-0.294	-0.200	-0.200	-0.173	-0.174	-0.145	-0.171
6	**F**	-0.264	-0.315	-0.316	-0.207	-0.208	-0.174	-0.176	-0.156	-0.182
7	**F**	-0.248	-0.275	-0.275	-0.193	-0.192	-0.166	-0.168	-0.139	-0.162
8	**F**	-0.251	-0.284	-0.283	-0.197	-0.196	-0.167	-0.168	-0.143	-0.165
9	**O**	-0.544	-0.557	-0.553	-0.510	-0.509	-0.481	-0.470	-0.588	-0.573
10	**O**	-0.537	-0.580	-0.568	-0.501	-0.499	-0.486	-0.480	-0.592	-0.566
11	**O**	-0.529	-0.567	-0.568	-0.500	-0.498	-0.485	-0.478	-0.577	-0.559
12	**O**	-0.544	-0.554	-0.555	-0.512	-0.510	-0.484	-0.471	-0.587	-0.561
13	**N**	-0.722	-0.848	-0.872	-0.719	-0.724	-0.569	-0.560	-0.671	-0.591
14	**C**	0.577	0.738	0.739	0.447	0.441	0.408	0.402	0.327	0.388
15	**C**	0.585	0.827	0.826	0.448	0.444	0.418	0.411	0.348	0.395

Table S3: Mulliken atomic charges on Tf_2N^- obtained from single point (*sp; 6-31G* optimized structures*) and fully optimized (*opt*) structures with different basis sets at the DFT level of theory.



Atom		6-31G*	6-31+G*		6-311G*		cc-pVTZ		lanL2DZ	
		sp = opt	*sp*	*opt*	*sp*	*opt*	*sp*	*opt*	*sp*	*opt*
1	**Na**	0.618	0.889	0.892	0.762	0.766	0.468	0.473	0.810	0.823
2	**S**	1.186	1.143	1.148	1.042	1.048	0.881	0.881	1.127	1.047
3	**S**	1.181	0.727	0.730	1.024	1.029	0.986	0.986	0.964	0.917
4	**F**	-0.229	-0.271	-0.272	-0.171	-0.171	-0.145	-0.146	-0.124	-0.141
5	**F**	-0.227	-0.246	-0.249	-0.168	-0.168	-0.141	-0.143	-0.121	-0.137
6	**F**	-0.222	-0.256	-0.257	-0.162	-0.161	-0.137	-0.138	-0.111	-0.134
7	**F**	-0.212	-0.233	-0.234	-0.148	-0.147	-0.128	-0.129	-0.101	-0.120
8	**F**	-0.228	-0.266	-0.267	-0.168	-0.167	-0.139	-0.140	-0.121	-0.136
9	**F**	-0.215	-0.235	-0.236	-0.151	-0.150	-0.131	-0.132	-0.106	-0.123
10	**O**	-0.464	-0.483	-0.478	-0.426	-0.425	-0.407	-0.404	-0.511	-0.491
11	**O**	-0.614	-0.644	-0.642	-0.607	-0.608	-0.500	-0.497	-0.678	-0.664
12	**O**	-0.562	-0.556	-0.547	-0.533	-0.530	-0.477	-0.474	-0.596	-0.579
13	**O**	-0.562	-0.540	-0.541	-0.538	-0.539	-0.482	-0.479	-0.592	-0.585
14	**N**	-0.683	-0.728	-0.727	-0.658	-0.668	-0.535	-0.535	-0.601	-0.529
15	**C**	0.611	0.845	0.836	0.470	0.465	0.444	0.438	0.359	0.416
16	**C**	0.621	0.854	0.844	0.430	0.424	0.444	0.440	0.401	0.438

Table S4: Mulliken atomic charges on $Na^+Tf_2N^-$ obtained from single point (*sp; 6-31G* optimized structure*) and fully optimized (*opt*) structures with different basis sets at the DFT/ level of theory.

M^+ =	Æ	Na^+	K^+	Rb^+	Cs^+
M^+	-	0.591	0.740	0.871	0.901
P	1.366	1.516	1.501	1.463	1.452
$<F_{coord}>$	-0.396	-0.380	-0.412	-0.432	-0.433
$<F_{free}>$	-0.396	-0.323	-0.335	-0.346	-0.352

Table S5: Mulliken charges of the PF_6^- anion and of the $M^+PF_6^-$ ions pairs pairs obtained from DFT/6-31G* calculations.

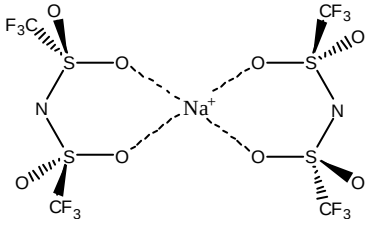
Atom	Æ	Na^+	K^+	Rb^+	Cs^+
M^+	-	0.614	0.747	0.863	0.889
$O1_{coord}$	-0.529	-0.565	-0.577	-0.582	-0.579
$O2_{coord}$	-0.544	-0.563	-0.590	-0.587	-0.586
$O3_{coord}$	-0.544	-0.615	-0.623	-0.635	-0.632
O4	-0.537	-0.465	-0.475	-0.489	-0.493
S1	1.117	1.179	1.157	1.118	1.113
S2	1.112	1.185	1.167	1.161	1.157
N	-0.722	-0.685	-0.689	-0.694	-0.696
C1	0.585	0.623	0.618	0.614	0.611
C2	0.577	0.613	0.612	0.608	0.605
<F1,2,3>	-0.254	-0.216	-0.222	-0.227	0.230
<F4,5,6>	-0.251	-0.224	-0.227	-0.232	0.234

Table S6: Mulliken charges of the Tf_2N^- anion and of the $M^+Tf_2N^-$ ions pairs pairs obtained from DFT/6-31G* calculations.

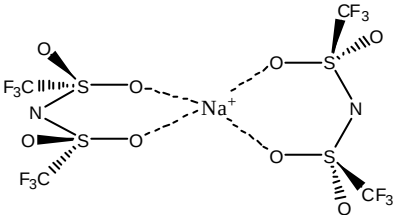
$Na^+(PF_6^-)_n$	E(HF)	E(B3LYP)	E(AMBER)
1	-118.5 *(tri)*	-123.3 *(tri)*	-100.8 *(tri)*
2	-163.2 *(tri)*	-169.1 *(tri)*	-145.8 *(tri)*
3	-126.5 *(bi)*	-131.1 *(bi)*	-116.6 *(bi)*

Table S7: Interaction energies (kcal/mol) of the $M^+(PF_6^-)_n$ aggregates and anion binding modes (in parentheses) obtained from HF, DFT and AMBER calculations.

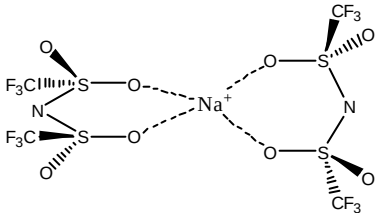
$Na^+(Tf_2N^-)_n$	E(HF)	E(B3LYP)	E(AMBER)
1	-117.9 *(2+1)*	-122.2 *(2+1)*	-103.0 *(2+1)*
		-121.4 *(1+1')*	
		-121.5 *(1+1)*	
2	-162.4 *(1+1')*	-166.1 *(1+1' perp)*	-135.6 *(2+1)*
		-164.9 *(1+1 perp)*	
		-164.3 *(1+1' planar)*	
3	-	-131.2 *(1+1')*	-114.6 *(1+1')*



1+1' planar

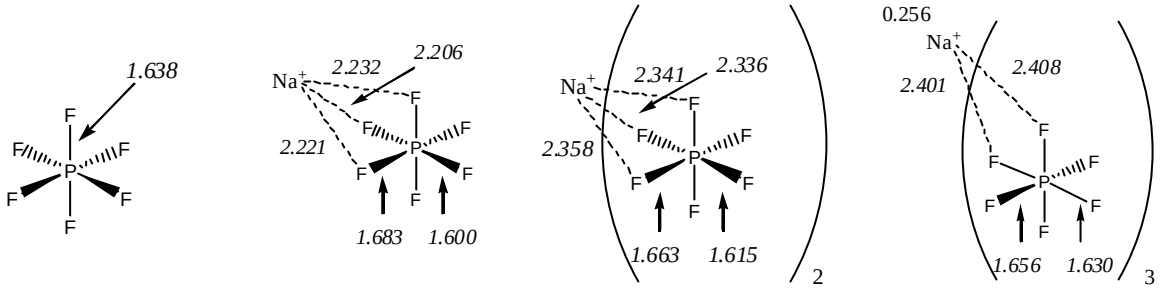


1+1 perp



1+1' perp

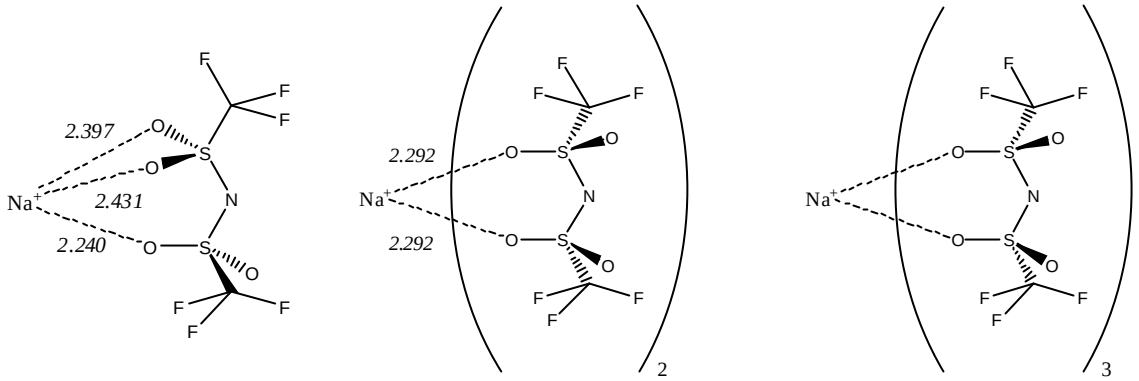
Table S8: Interaction energies (kcal/mol) of the $M^+(Tf_2N^-)_n$ aggregates and anion binding modes (in parentheses) (see figure 3 for definition) obtained by QM calculations at the HF and DFT levels of theory with the 6-31G* basis set and by AMBER.



PF_6^- **$Na^+ (PF_6^-)$** **$Na^+ (PF_6^-)_2$** **$Na^+ (PF_6^-)_3$**

	PF_6^-	$Na^+ (PF_6^-)$	$Na^+ (PF_6^-)_2$	$Na^+ (PF_6^-)_3$
Na^+		0.591	0.296	0.256
P	1.366	1.516	1.513	1.500
$<F_{coord}>$	-0.396	-0.380	-0.373	-0.376
$<F_{free}>$	-0.396	-0.323	-0.347	-0.374
$PF_6^-{}_{total}$	**-1.010**	**-0.593**	**-0.647**	**-0.750**
P			1.513	1.499
$<F_{coord}>$			-0.373	-0.376
$<F_{free}>$			-0.348	-0.374
$PF_6^-{}_{total}$			**-0.650**	**-0.751**
P				1.500
$<F_{coord}>$				-0.376
$<F_{free}>$				-0.375
$PF_6^-{}_{total}$				**-0.756**

Table S9 : Coordination modes and distances (Å) and Mulliken atomic charges *(bottom)* of the PF_6^- anion and of the $Na^+(PF_6^-)_n$ complexes (n = 1 to 3) obtained by DFT/6-31G* calculations.



Na^+ (Tf_2N^-) **Na^+ (Tf_2N^-)$_2$** **Na^+ (Tf_2N^-)$_3$**

	Tf_2N^-	Na^+ (Tf_2N^-)	Na^+ (Tf_2N^-)$_2$	Na^+ (Tf_2N^-)$_3$
Na^+		0.614	0.461	0.360
$<O_{coord}>$	-0.539	-0.581	-0.574	-0.540
$<O_{free}>$	-0.537	-0.465	-0.501	-0.528
$Tf_2N^-_{total}$	**-1.000**	**-0.613**	**-0.730**	**-0.780**
$<O_{coord}>$			-0.574	-0.540
$<O_{free}>$			-0.501	-0.523
$Tf_2N^-_{total}$			**-0.731**	**-0.792**
$<O_{coord}>$				-0.543
$<O_{free}>$				-0.522
$Tf_2N^-_{total}$				**-0.788**

Table S10 : Coordination modes and distances and Mulliken atomic charges of the Tf_2N^- anion and of the $Na^+(Tf_2N^-)_n$ (n = 1 to 3) complexes obtained by DFT/6-31G* calculations.

	Tf_2N^-	$Na^+(Tf_2N^-)$		$Cs^+(Tf_2N^-)$		$Na^+(Tf_2N^-)_2$	$Cs^+(Tf_2N^-)_2$
Starting coord. modes		***1+1' or 2+2***	***Mono or 1+1' or 2+1***	***2+1 or 2+2***	***Mono***	***2+1***	***2+1***
Final coord. mode		***1+1'***	***2+1***	***2+1***	***1+1+1***	***1+1***	***2+1***
M-O1		2.164	2.431	3.029	4.939	2.291	3.336
M-O2		4.347	2.397	4.144	3.224	4.775	3.351
M-O3		2.187	2.240	3.744	4.670	2.291	3.162
M-O4		4.560	4.568	6.066	3.243	4.776	5.586
M-N		3.674	3.569	4.723	3.011	3.975	4.626
S1-O1	1.470	1.495	1.489	1.440	1.460	1.481	1.477
S1-O2	1.467	1.457	1.489	1.453	1.479	1.460	1.478
S2-O3	1.471	1.492	1.494	1.447	1.461	1.481	1.479
S2-O4	1.470	1.454	1.455	1.445	1.478	1.460	1.462
S1-N-S2	123.3	126.6	117.7	130.5	127.8	125.0	120.0
C1-S1-N-S2	92.2	119.8	174.8	137.7	119.0	98.6	170.2
S1-N-S2-C2	-152.4	-80.8	-104.4	108.1	-100.9	98.8	-99.6
C1..C2	4.600	4.088	4.994	5.175	4.235	5.249	4.883

Table S11: Main distances (Å) angles (°) and dihedrals (°) of QM optimized Tf_2N^- and $M^+(Tf_2N^-)_n$ complexes. See Figure 3 for definitions of the binding modes. DFT/6-31G* optimizations.

	[BMI][PF_6]-dry			
	P	**F**	**BMI**	**H_2O**
Na^+	4.0 (0.0)	9.7 (1.1)	10.6 (0.8)	-
	3.40 / 5.50	*2.45 / 3.60*	*6.35 / 10.0*	-
Cs^+	4.0 (0.0)	11.7 (0.7)	12.5 (0.6)	-
	4.00 / 5.60	*3.15 / 4.35*	*7.15 / 10.0*	-
LNa^+	1.0 (0.0)	2.3 (0.5)	8.3 (1.2)	-
	3.35 / 4.50	*2.45 / 3.25*	*5.65 / 10.0*	-
LCs^+	1.0 (0.0)	2.5 (0.6)	8.9 (1.1)	-
	4.00 / 5.30	*3.05 / 4.00*	*7.25 / 10.00*	-
	[BMI][PF_6]-humid			
	P	**F**	**BMI**	**H_2O**
Na^+	1.3 (0.6)	1.5 (1.0)	10.9 (1.4)	4.3 (0.7)
	3.95 / 4.70	*2.50 / 3.15*	*5.40 / 10.00*	*2.45 / 3.40*
Cs^+	3.0 (0.4)	5.8 (1.5)	10.4 (1.0)	4.4 (1.2)
	4.20 / 5.85	*3.15 / 4.10*	*7.35 / 10.00*	*3.10 / 4.35*
LNa^+	1.0 (0.1)	1.4 (0.7)	6.4 (1.1)	1.0 (0.0)
	1.14 / 6.80	*4.65 / 5.25*	*8.10 / 10.00*	*2.35 / 3.20*
LCs^+	0.9 (0.4)	(a)	6.8 (1.0)	1.0 (0.2)
	6.60 / 7.00	*(a)*	*6.50 / 10.00*	*3.05 / 4.05*
	[BMI][Tf_2N]-dry			
	N	**O**	**BMI**	**H_2O**
Na^+	4.0 (0.1)	5.7 (0.5)	9.7 (0.8)	-
	4.05 / 7.25	*2.45 / 3.25*	*7.10 / 10.00*	-
Cs^+	5.0 (0.2)	6.2 (1.0)	9.4 (0.9)	-
	5.40 / 6.45	*3.10 / 4.05*	*6.10 / 10.00*	-
LNa^+	1.0 (0.3)	0.8 (0.4)	3.4 (0.9)	-
	4.60 / 6.90	*2.25 / 3.65*	*8.05 / 10.00*	-
LCs^+	1.0 (0.0)	1.1 (0.4)	6.5 (0.8)	-
	5.30 / 6.30	*3.00 / 3.95*	*8.00 / 10.00*	-

Table S12: Characteristics of the first peak of the solvent RDFs around M^+. Coordination number and RMS fluctuations (first line), distance (Å) of the first maximum and minimum (second line). Averages over the last 0.5 ns of MD. (a) Not reported because the first peak is ill defined.

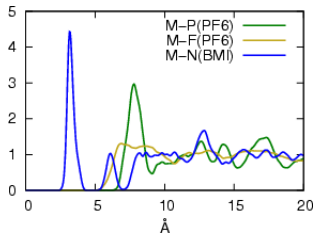
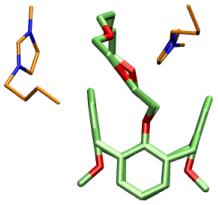
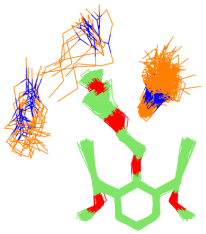
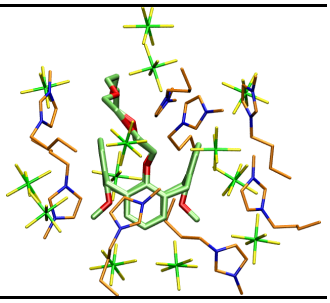
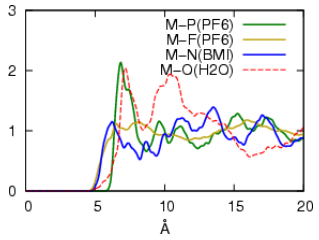
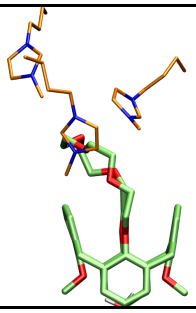
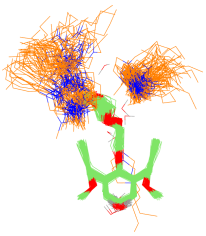
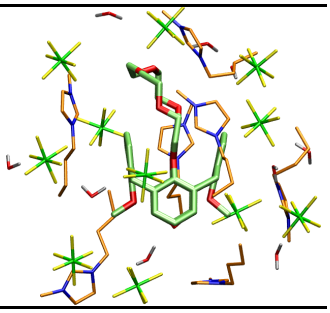
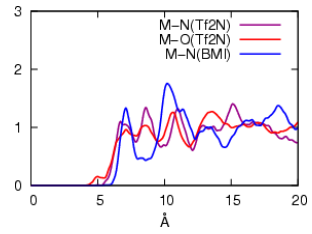
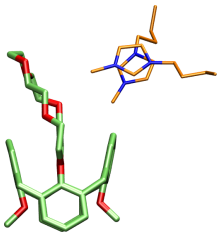
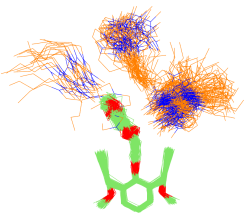
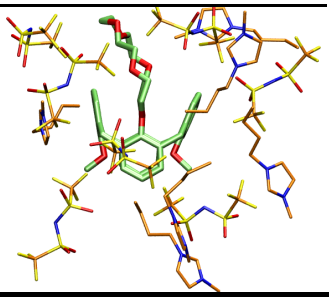
RDF	*[BMI]-crown*	*Cumulated [BMI]-crown*	*Snapshot < 10 Å*
[BMI][PF_6]-dry			
			
[BMI][PF_6]-humid			
			
[BMI][Tf_2N]-dry			
			

Figure S1: Solvation of free calixarene (**L)** in the dry [BMI][PF_6], the humid [BMI][PF_6] and the dry [BMI][Tf_2N]. Cumulated views plotted over the last 0.5 ns of MD selecting anions at within 6 Å from the center of the crown.

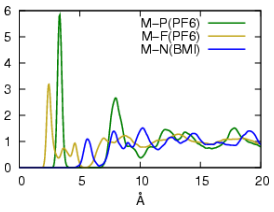
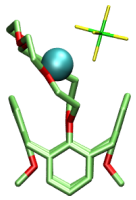
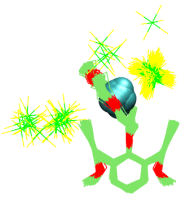
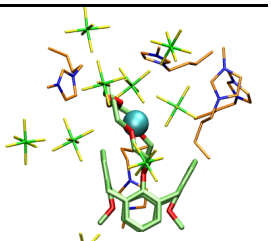
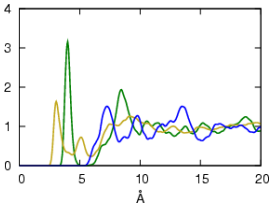
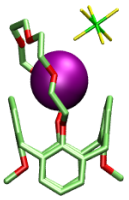
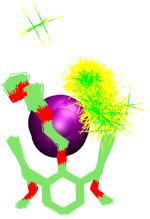
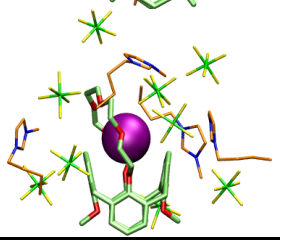
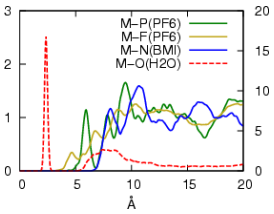
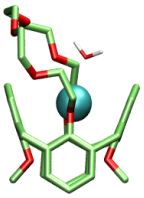
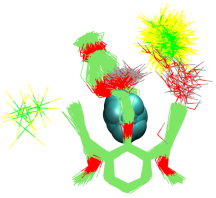
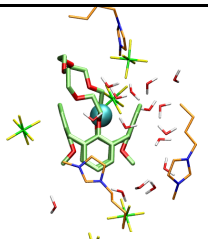
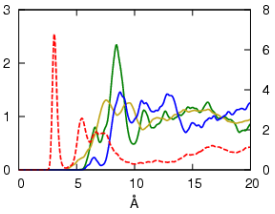
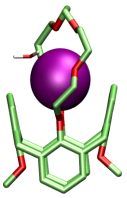
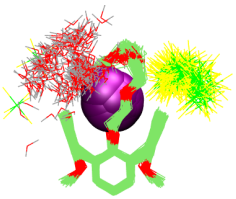
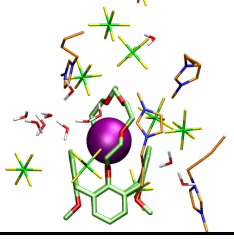
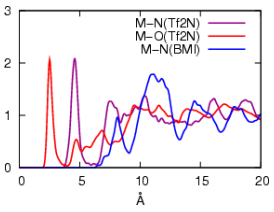
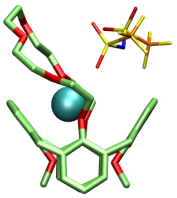
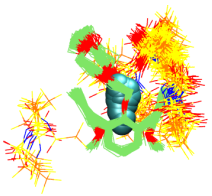
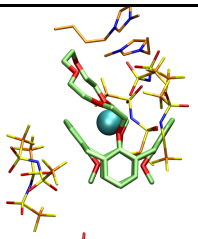
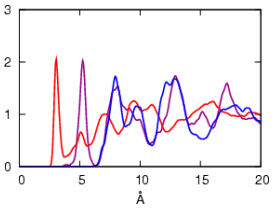
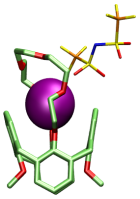
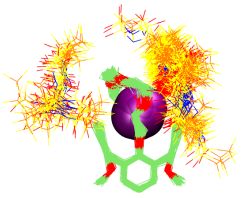
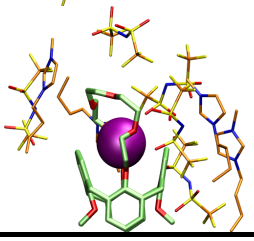
LM$^+$	*RDF*	*First shell*	*Cumulated first shell*	*First + second shells*
[BMI][PF$_6$]-dry				
LNa$^+$				
LCs$^+$				
[BMI][PF$_6$]-humid				
LNa$^+$				
LCs$^+$				
[BMI][Tf$_2$N]-dry				
LNa$^+$				
LCs$^+$				

Figure S2: Solvation of complexed **L**Na$^+$ and **L**Cs$^+$ in the dry [BMI][PF$_6$], the humid [BMI][PF$_6$] and the dry [BMI][Tf$_2$N]. Cumulated views plotted over the last 0.5 ns of MD selecting anions at less then 6 Å from cations.

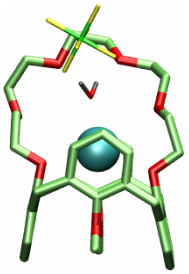
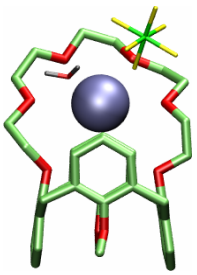
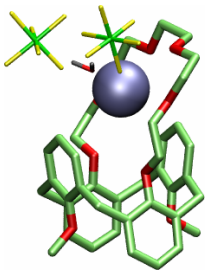
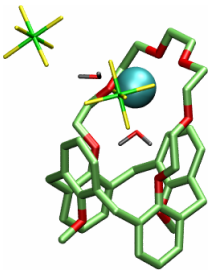
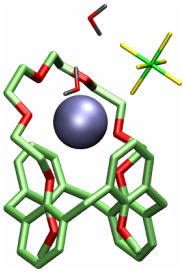
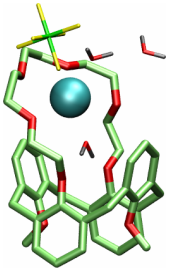
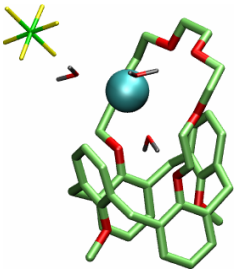
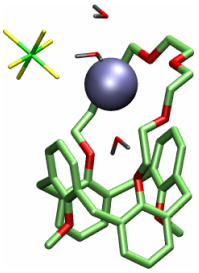
Mutation	*Starting configuration*	*Final configuration*	$DG_{4\,/\,IL}$
A Na^+ ® K^+	 *endo*	 *exo*	13.1 (1.5) 15.0 (2.5)[(a)] 12.9 (1.3)[(b)]
B K^+ ® Na^+	 *exo*	 *exo*	-11.4 (1.6)
C K^+ ® Na^+	 *exo*	 *exo*	-16.2 (1.9)
D Na^+ ® K^+	 *exo*	 *exo*	16.4 (2.2)

Figure S3: Initial and final structures (up to 5 Å from M^+) and ΔG_4 values (kcal/mol) for distinct mutations of complexed cations in humid [BMI][PF_6]. Unless specified, calculations performed at 300 K using 100+100 ps. (a) Mutation performed at 400 K using 100+100 ps. (b) Mutation performed at 300 K using 400+100 ps.