SYSTEM	X^-	temp (K)	time (ns)	SYSTEM	X^-	temp (K)	time (ns)
Dry IL				***Humid IL***			
1 18C6 D_{3d}→D_{3d}	*none*	300	1.2	12 *diluted* 18C6	*none*	300	1.5
1 *18C6 D_{3d}→D_{3d}* [a]	*none*	300	2.0	12 *diluted* 18C6	*none*	400	2.0
1 18C6 C_i→D_{3d}	*none*	300	1.8	12 18C6 (“*crystal*”)	*none*	400	3.7
1 *18C6 C_i→D_{3d}* [a]	*none*	300	1.4	12 *diluted* 18C6 C_i [b]	*none*	300	4.0
1 18C6 C_i [b]	*none*	300	1.6	12 *diluted* 18C6 C_i [b]	*none*	400	4.0
12 *diluted* 18C6	*none*	300	1.0	1 Sr^{2+}⊂18C6	2 Cl^-	300	5.4
12 18C6 (“*crystal*”)	*none*	300	3	1 Sr^{2+}⊂18C6	2 Cl^-	400	5.4
12 18C6 (“*crystal*”)	*none*	400	*+7.5*	1 Sr^{2+}⊂18C6(PF_6^-)$_4$ [c]	*none*	300	–
1 Sr^{2+}⊂18C6	*none*	300	2.0	1 Sr^{2+}⊂18C6(PF_6^-)$_4$ [c]	*none*	400	6.4
1 Sr^{2+}⊂18C6 [c]	*none*	300	4.0	1 K^+⊂18C6	Cl^-	300	1.6
1 Sr^{2+}⊂18C6 [c]	*none*	400	4.2	1 K^+⊂18C6	Cl^-	400	1.2
1 Sr^{2+}⊂18C6(PF_6^-)$_4$ [c]	*none*	300	1.2	1 K^+⊂18C6 [b]	Cl^-	400	1.6
1 Sr^{2+}⊂18C6	2 Cl^-	300	0.8	1 Cs^+⊂18C6	Cl^-	300	4.0
1 Sr^{2+}⊂18C6 [a]	*none*	300	0.8	1 Cs^+⊂18C6	Cl^-	400	1.6
1 K^+⊂18C6	*none*	300	1.2	1 Sr⊂18C6($Cl)_2$	*none*	300	2.0
1 K^+⊂18C6	*none*	400	2.0	1 Sr⊂18C6($Cl)_2$	*none*	400	2.0
1 K^+⊂18C6	Cl^-	300	2.6	1 Sr⊂18C6($NO_3)_2$	*none*	300	3.4
1 Cs^+⊂18C6	*none*	300	1.6	1 Sr⊂18C6($NO_3)_2$	*none*	400	2.2
1 Cs^+⊂18C6	*none*	400	1.2	1 Sr⊂18C6($NO_3)_2$ [d]	*none*	300	4.0
1 Cs^+⊂18C6	Cl^-	300	1.8	1 Sr^{2+}⊂18C6($H_2O)_2$ [e]	*none*	300	2.0
1 Cs^+⊂18C6 [a]	Cl^-	300	0.8	1 Sr^{2+}⊂18C6($H_2O)_2$ [e]	*none*	400	2.0
1 Sr⊂18C6($Cl)_2$	*none*	300	1.2	1 K⊂18C6(NO_3) [f]	*none*	300	2.4
1 Sr⊂18C6($NO_3)_2$	*none*	300	1.2	1 K⊂18C6(NO_3) [f]	*none*	400	2.4
1 Sr^{2+}⊂18C6($H_2O)_2$ [d]	*none*	300	1.2	1 Sr^{2+}	2 Cl^-	300	4.0
1 K⊂18C6(Cl)	*none*	300	1.4	1 Sr^{2+}	2 Cl^-	400	4.0
1 K⊂18C6(NO_3)	NO_3^-	300	1.2	1 K^+	NO_3^-	300	4.0
1 Cs⊂18C6(Cl)	*none*	300	2.0	1 K^+	NO_3^-	400	4.0
1 Cs⊂18C6(Cl)	*none*	400	0.9	1 Cs^+	NO_3^-	300	1.6
1 Cs⊂18C6(NO_3)	NO_3^-	300	1.2	1 Cs^+	NO_3^-	400	1.2
1 Sr^{2+}	2 NO_3^-	400	1.0				
1 K^+	NO_3^-	300	1.5				
1 Cs^+	NO_3^-	400	1.0				
1 $Sr^{2+}(H_2O)_{8+1}$	*none*	300	1.9				

Table S1: Characteristics of the simulated ionic liquid solutions.

a) Mixing – demixing simulation (mixing performed at 500 K with the frozen solute and charges scaled down by 100).
b) The solute was kept frozen during the whole dynamics.
c) The solute was kept frozen during the minimization stage.
d) The NO_3^- anions were constrained to be bidentate during the simulation.
e) The neutrality is achieved by diluting a -2 charge onto all atoms of the box, instead of adding or deleting ions.
f) The K^+ cation was initially surrounded by 1 BMI^+ + 1PF_6^-, as found in the dry liquid, in order to restrict the $K^+\cdots H_2O$ interactions.

		BMI^+	PF_6^-	H_2O	Solvent [c]
Dry IL					
1 18C6 $C_i \rightarrow D_{3d}$ 300 K [a]	vdW	-30	-10		-40
	El	-5	-15		-20
	Total	-35	-25		-60
1 18C6 $D_{3d} \rightarrow D_{3d}$ 300 K	vdW	-34	-11		-45
	El	-7	-17		-24
	Total	-41	-28		-69
1 18C6 $C_i \rightarrow C_i$ 300 K [b]	vdW	-32	-10		-42
	El	1	-9		-8
	Total	-31	-19		-50
12 18C6 diluted [a]	vdW	-30	-9		-39
	El	-3	-16		-19
	Total	-33	-25		-58
Humid IL					
12 18C6 diluted $C_i \rightarrow D_{3d}$ 300 K [a]	vdW	-30	-9	-2	-41
	El	-6	-13	-3	-22
	Total	-36	-22	-5	-63
12 18C6 diluted $C_i \rightarrow D_{3d}$ 400 K [a]	vdW	-26	-8	-2	-36
	El	-3	-12	0	-16
	Total	-30	-21	-2	-53
12 18C6 diluted $C_i \rightarrow C_i$ 300 K [b]	vdW	-29	-10	-2	-41
	El	-1	-5	-1	-7
	Total	-30	-15	-3	-48
12 18C6 diluted $C_i \rightarrow C_i$ 400 K [b]	vdW	-28	-8	-2	-38
	El	0	-7	0	-7
	Total	-28	-15	-2	-45

Table S2: 18C6 uncomplexed. Average interaction energies (kcal/mol) between one 18C6 crown and the van der Waals and electrostatic solvent components.

a) The crown(s), initially in the C_i conformation, became D_{3d} during the dynamics.

b) Simulations performed with frozen C_i solute(s).

c) Fluctuations are ≈ ±3 kcal/mol in all cases, excepted in the case of (b), where they are ±8 kcal/mol.

SYSTEM		N_{BMI}	P_{PF6}	F_{PF6}	O_{H2O}
1 18C6 C_i frozen	dry	1.0 *4.2; 4.7*	4.0 *6.6; 7.3*	15.6 *6.1; 7.0*	
1 18C6 D_{3d}	dry	1.0 *3.3; 4.4*	7.2 *7.6; 8.6*	18.7 *6.5; 7.3*	
12 diluted 18C6	humid	1.7 *5.0; 6.0*	6.9 *7.7; 8.7*	55.6 *6.9; 9.9*	0.24 *1.5; 3.0*
12 18C6 ("crystal") 400 K	humid	1.4 *5.0; 6.1*	7.7 *7.6; 9.7*	52.8 *7.1; 10.3*	0.1 *2.5; 4.2*
Sr^{2+}⊂18C6	dry	9.6 *7.6; 9.3*	4.0 *4.2; 4.8*	4.0 *2.6; 3.1*	
Sr^{2+}⊂18C6,2Cl^-	dry	13.9 *8.4; 10.5*	3.0 *4.2; 4.7*	3.7 *2.6; 3.2*	
K^+⊂18C6	dry	17.6 *9.0; 11.7*	1.9 *3.9; 4.8*	3.8 *2.7; 3.7*	
K^+⊂18C6,Cl^-	dry	5.8 *6.3; 8.0*	2.0 *3.8; 5.0*	*11.4* *2.9; 5.5*	
Cs^+⊂18C6	dry	*2.5* *6.4; 7.4*	*2.9* *4.3; 6.0*	17.8 *3.3; 6.5*	
Sr⊂18C6$(Cl)_2$	dry	3.4 *6.7; 7.1*	1.7 *6.5; 6.9*	25.1 *6.9; 7.8*	
Sr⊂18C6$(NO_3)_2$	dry	5.9 *7.4; 8.4*	1.0 *4.2; 4.5*	1.0 *2.5; 3.1*	
Sr^{2+}⊂18C6$(H_2O)_2$	dry	10.8 *7.8; 10.5*	2.0 *4.2; 4.8*	2.1 *2.6; 3.3*	
K⊂18C6(Cl)	dry	4.3 *6.7; 7.8*	1.0 *4.3; 5.0*	1.3 *2.7; 3.4*	
K⊂18C6(NO_3)	dry	4.9 *7.0; 8.0*	1.0 *3.9; 4.7*	5.8 *2.9; 5.6*	
Cs⊂18C6(Cl)	dry	2.6 *6.8; 7.4*	1.9 *4.1; 5.3*	10.5 *3.0; 5.8*	
Cs⊂18C6(NO_3)	dry	1.0 *4.7; 5.7*	1.3 *4.6; 5.7*	7.7 *5.2; 5.8*	
Sr^{2+}⊂18C6	humid		1.0 *4.1; 4.5*	11.7 *2.5; 5.5*	3.1 *2.6; 3.1*
Sr^{2+}⊂18C6$(PF_6^-)_4$	humid		2.9 *5.8; 6.9*	6.4 *4.9; 5.8*	4.5 *2.6; 3.1*
Sr⊂18C6$(Cl)_2$	humid		1.1 *6.4; 7.0*	2.5 *5.4; 6.0*	2.0 *2.6; 3.1*
Sr⊂18C6$(NO_3)_2$	humid	4.3 *6.9; 8.2*	1.8 *6.3; 7.2*	62.8 *7.4; 10.3*	2.7 *2.6; 3.1*
Sr⊂18C6$(NO_3)_2$ bidentate	humid	11.9 *8.5; 10.6*	4.8 *7.5; 8.3*	15.0 *6.7; 7.5*	1.0 *2.6; 3.2*
Cs^+⊂18C6	humid		2.0 *4.1; 5.1*	5.6 *3.3; 4.5*	1.0 *3.1; 3.7*
K^+⊂18C6	humid		2.0 *3.7; 4.7*	12.4 *2.8; 5.7*	20.7 *7.2; 10.6*
K⊂18C6(NO_3)	humid	4.9 *6.5; 8.3*	9.2 *8.0; 10.1*	51.5 *8.7; 9.9*	1.1 *5.4; 6.1*

Table S3: 18C6 and its Sr^{2+}, K^+, Cs^+ complexes in [BMI][PF_6] solution with dissociated *vs* coordinated counterions. Characteristics of the first peak of the radial distribution function around the center of the crown or the M atom. First line: coordination number. *Second line*: distances (Å) of the first maximum and minimum. Averages over the last 0.2 ns of MD. Unless otherwise specified, the simulations were performed at 300 K.

DRY SYSTEM	M^{n+}			18C6			total (a)	n X^-			total (b)
	BMI^+	PF_6^-	solvent	BMI^+	PF_6^-	solvent		BMI^+	PF_6^-	solvent	
Sr^{2+}⊂18C6	860	-1211	-351	-8	7	-1	-352				
Sr^{2+}⊂18C6 (c)	838	-1143	-305	-8	1	-7	-312				
Sr^{2+}⊂18C6$(PF_6^-)_4$	823	-1156	-333	-2	1	-1	-334				
Sr^{2+}⊂18C6,2Cl^-	917	-1224	-307	-10	-1	-11	-318				
Sr^{2+}⊂18C6,2Cl^- (d)	884	-1194	-310	-2	-4	-6	-316				
Sr⊂18C6$(Cl)_2$	934	-917	17	-18	-34	-52	-35	-991	932	-59	-94
Sr⊂18C6$(NO_3)_2$	867	-897	-30	-16	-18	-34	-64	-946	903	-43	-107
Sr^{2+}⊂18C6$(H_2O)_2$	817	-1090	-273	-9	-4	-14	-287	11	-11	0	-287
K^+⊂18C6	426	-510	-83	-12	-13	-25	-108				
K^+⊂18C6,Cl^-	457	-537	-80	-18	-15	-33	-113				
K⊂18C6(Cl)	444	-455	-11	-19	-20	-39	-50	-482	443	-39	-89
K⊂18C6(NO_3)	444	-464	-20	-18	-24	-42	-62	-498	450	-48	-110
Cs^+⊂ 18C6	432	-514	-82	-10	-22	-32	-114				
Cs^+⊂ 18C6,Cl^-	445	-524	-79	-16	-23	-39	-118				
Cs^+⊂ 18C6,Cl^- (d)	446	-519	-73	-14	-22	-36	-109				
Cs⊂18C6(Cl)	455	-483	-28	-27	-25	-52	-80	-495	465	-30	-110
Cs⊂18C6(NO_3)	461	-473	-12	-15	-24	-39	-51	-526	470	-56	-107

Table S4: 18C6 and its Sr^{2+}, K^+ and Cs^+ complexes in dry [BMI][PF_6] solution. Average interaction energies ΔE (kcal/mol) between M^{n+}, 18C6, X^- and the solvent and its components. All the simulations were performed at 300 K.

a) Total for the complex (without counterions).

b) Total for the M⊂18C6$(X)_n$ complex (with Cl^- or NO_3^- counterions).

c) The solute was kept frozen during the minimization stage and free to move during dynamics.

d) Mixing - demixing simulation (mixing performed at 500 K with the frozen solute and charges scaled down by 100).

HUMID SYSTEM	M^{n+}				18C6				total [a]	nX^-				total [b]
	BMI^+	PF_6^-	H_2O	solvent	BMI^+	PF_6^-	H_2O	solvent		BMI^+	PF_6^-	H_2O	solvent	
$Sr^{2+}\subset 18C6$	762	-993	-152	-383	-2	-10	15	3	-380					
$Sr^{2+}\subset 18C6(PF_6^-)_4$	784	-1001	-177	-394	-6	-15	25	4	-390					
$Sr^{2+}\subset 18C6(PF_6^-)_4$ *400K*	736	-980	-131	-375	-1	-11	17	5	-370					
$Sr\subset 18C6(Cl)_2$	789	-770	-81	-62	-10	-30	9	-31	-93	-843	786	4	-53	-146
$Sr\subset 18C6(NO_3)_2$	793	-792	-119	-118	-7	-29	10	-26	-144	-870	816	-26	-80	-224
$Sr\subset 18C6(NO_3)_2$ [c]	759	-764	-26	-31	-4	-28	-4	-36	-67	-817	791	-41	-67	-134
$Sr^{2+}\subset 18C6(H_2O)_2$	750	-916	-241	-407	-1	-22	30	7	-400					
$K^+\subset 18C6$	382	-469	1	-86	-13	-7	-5	-25	-111					
$K\subset 18C6(NO_3)$	417	-429	0	-12	-18	-22	-3	-42	-54	-469	419	-12	-62	-116

Table S5: 18C6 and its Sr^{2+}, K^+ and Cs^+ complexes in humid [BMI][PF_6][H_2O] solution. Average interaction energies ΔE (kcal/mol) between M^{n+}, 18C6, X^- and the solvent and its components. Unless otherwise specified, the simulations were performed at 300 K.

a) Total for the complex (without counterions).

b) Total for the $M\subset 18C6(X)_n$ complex (with Cl^- or NO_3^- counterions).

c) The NO_3^- anions were constrained to be bidentate during the simulation.

SYSTEM	N_{BMI}	P_{PF6}	F_{PF6}	N_{BMI}	P_{PF6}	F_{PF6}	O_{H2O}
	DRY			**HUMID**			
Sr^{2+} *300 K*	5.3 *6.4; 7.9*	**5.0** *3.5; 5.0*	10.1 *2.6; 3.4*	(a)	7.0 *5.8; 7.0*	42.4 *4.8; 8.1*	8.3 *2.6; 3.4*
K^+ *300 K*	3.9 *5.5; 7.2*	4.0 *3.6; 4.7*	12.2 *2.8; 4.1*	(a)	2.3 *3.9; 4.5*	20.8 *2.9; 6.2*	3.4 *2.7; 3.6*
Cs^+ *300 K*	5.0 *6.3; 7.8*	4.0 *4.1; 5.4*	11.3 *3.1; 4.4*	(a)	3.1 *4.1; 5.3*	20.4 *3.1; 6.1*	2.0 *3.0; 3.8*
Cl^- 300 K	2.0 *4.7; 5.4*	**3.1** 6.5; 7.2	N/A	3.2 *5.0; 6.5*	2.0 *6.5; 7.1*	N/A	4.5 *3.3; 3.9*
Sr^{2+} *400 K*	5.5 *6.2; 7.3*	5.0 *3.5; 5.0*	9.9 *2.6; 3.4*	(a)	5.2 *5.7; 6.9*	39.6 *4.9; 8.0*	8.2 *2.6; 3.4*
K^+ *400 K*	3.6 *5.5; 6.9*	4.0 *3.7; 4.9*	11.7 *2.8; 4.0*	(a)	2.0 *4.0; 4.9*	18.7 *2.7; 6.1*	3.9 *2.7; 3.6*
Cs^+ *400 K*	5.1 *5.7; 6.7*	4.0 *4.1; 5.5*	11.5 *3.1; 4.4*	(a)	3.7 *4.1; 5.3*	23.8 *3.1; 6.1*	1.8 *3.1; 4.0*
Cl^- *400 K*				5.6 *4.5; 2.5*	14.0 *6.4; 11.1*	89.8 *7.2; 11.4*	2.5 *3.3; 4.2*

Table S6: Sr^{2+}, K^+, Cs^+ and Cl^- "free" ions in dry versus humid IL solution. Characteristics of the ion···solvent RDFs. *First line*: coordination number. *Second line*: distances (Å) of the first maximum and minimum. Averages over the last 0.2 ns of MD.

a) Value not reported because the peak is ill-defined.

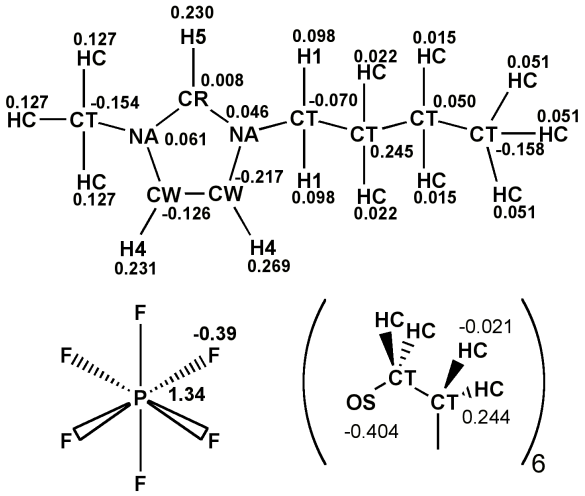

Figure S1: AMBER atom types and charges used for the simulations.

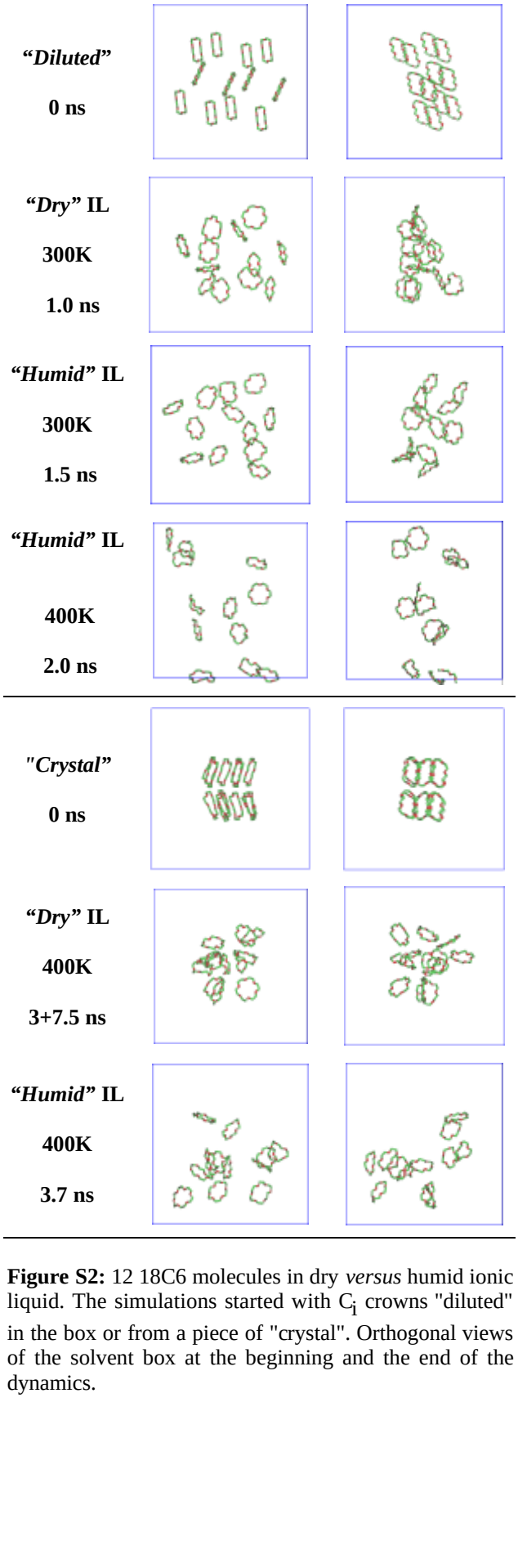

Figure S2: 12 18C6 molecules in dry *versus* humid ionic liquid. The simulations started with C_i crowns "diluted" in the box or from a piece of "crystal". Orthogonal views of the solvent box at the beginning and the end of the dynamics.

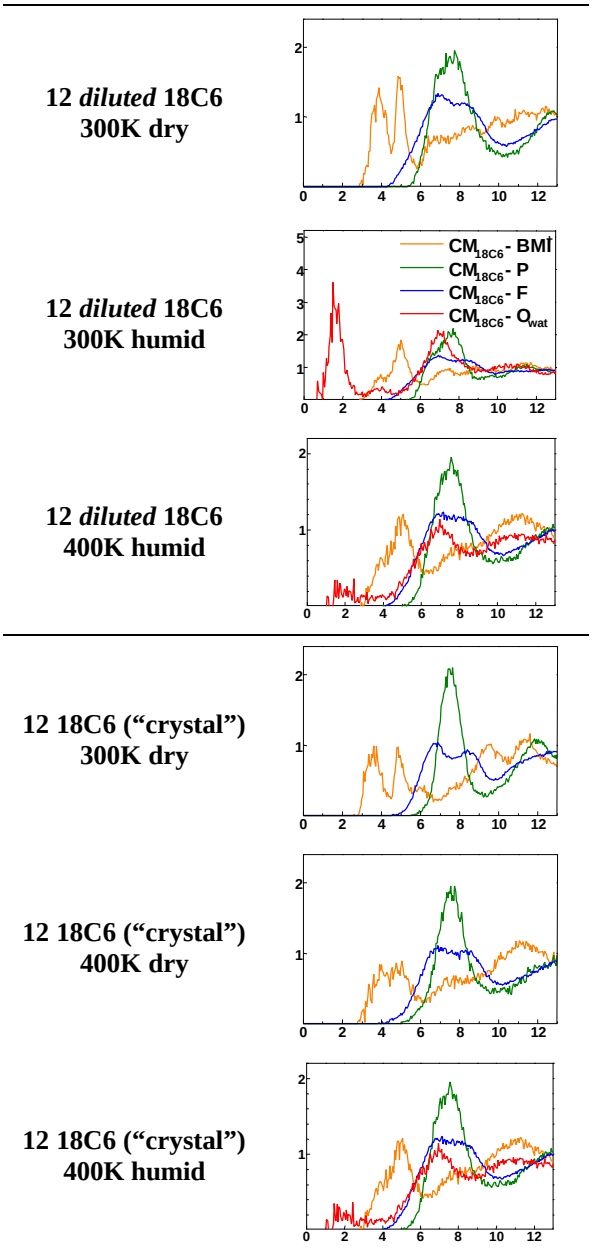

Figure S3: 12 18C6 molecules in dry *versus* humid IL solutions. Final RDF from simulations which started with 12 C_i crowns “diluted” in the box (*top*) or from a piece of “crystal” (*bottom*).

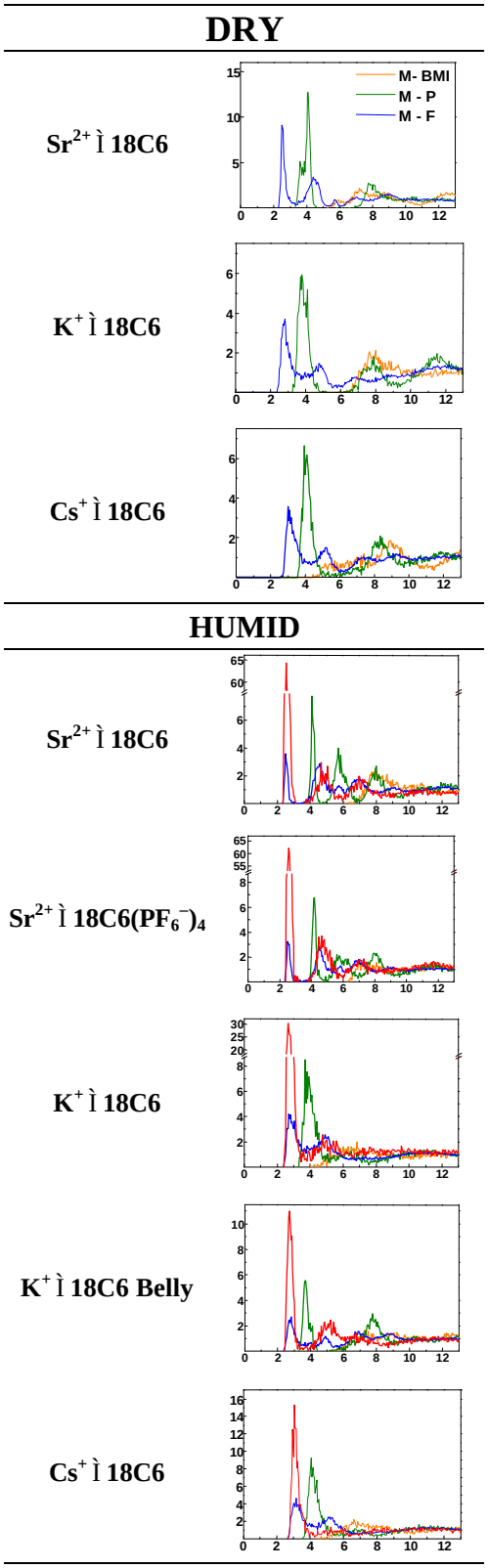

Figure S4: 18C6 complexes simulated at 400 K without counterions, or with dissociated counterions in the dry *versus* humid ionic liquid. Radial distribution functions around the Sr^{2+}, K^{+}, or Cs^{+} atom.

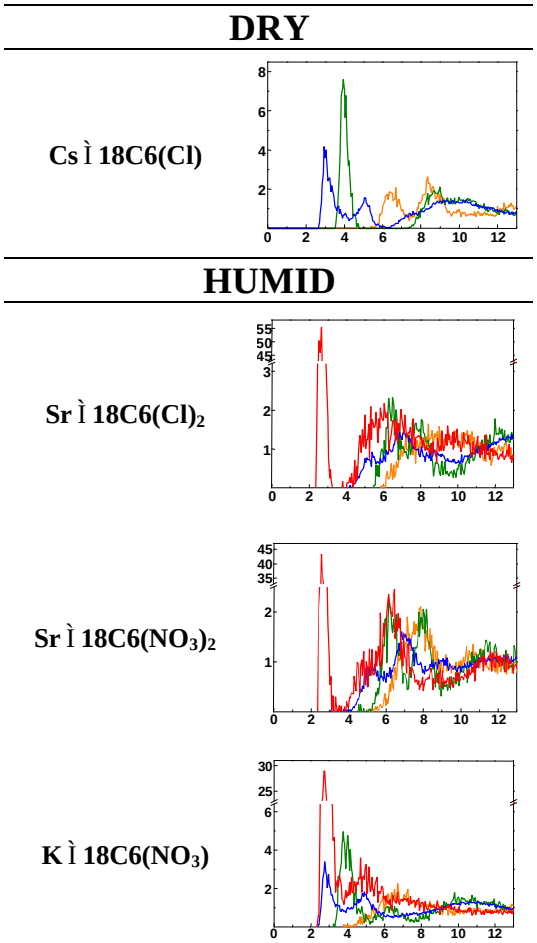

Figure S5: M⊂18C6(X)$_n$ complexes simulated at 400 K with coordinated counterions X^- in the ionic liquid. Radial distribution functions around the Sr^{2+}, K^+ and Cs^+ ions.