Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Difference in chemical bonding between lithium and sodium salts: influence of covalency on their solubility

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SUPPLEMENTARY INFORMATION

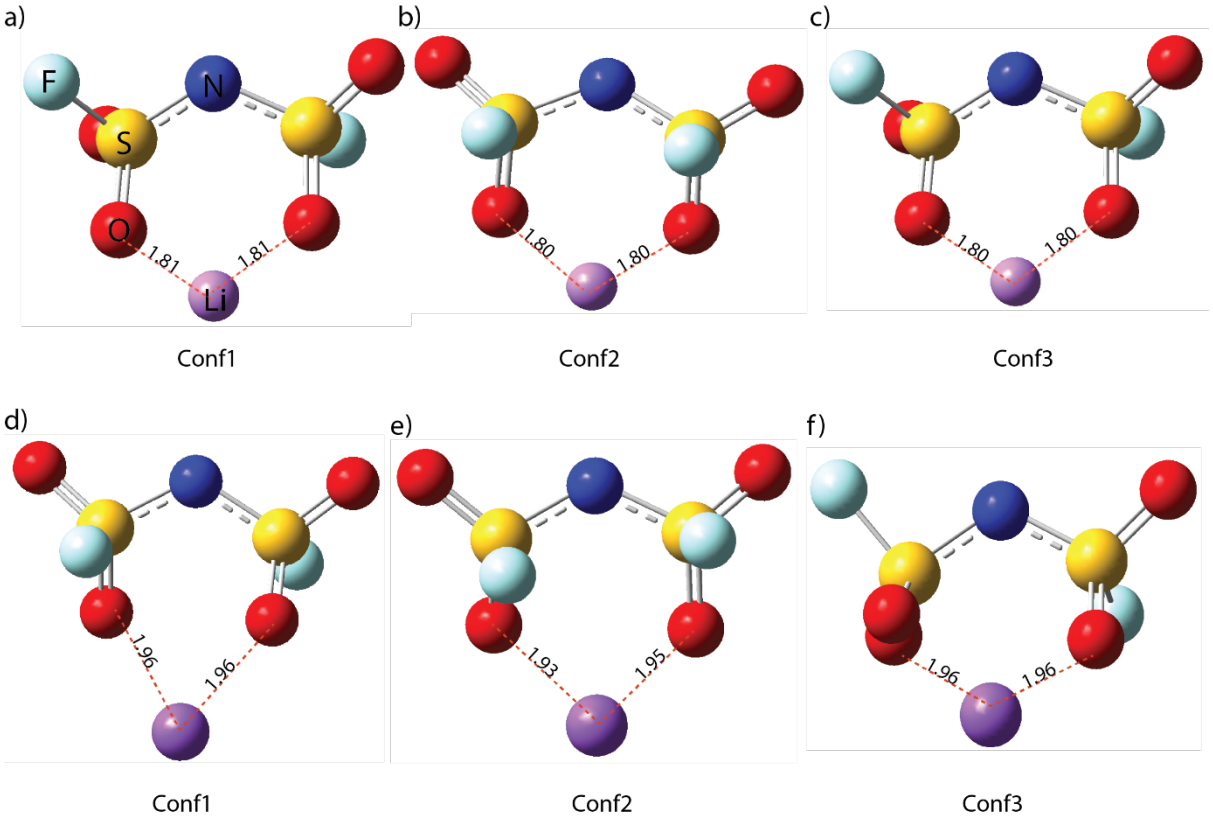

Figure S1. Optimized structures of LiFSI in gas phase (a-c) and in $CHCl_3$ (d-f)

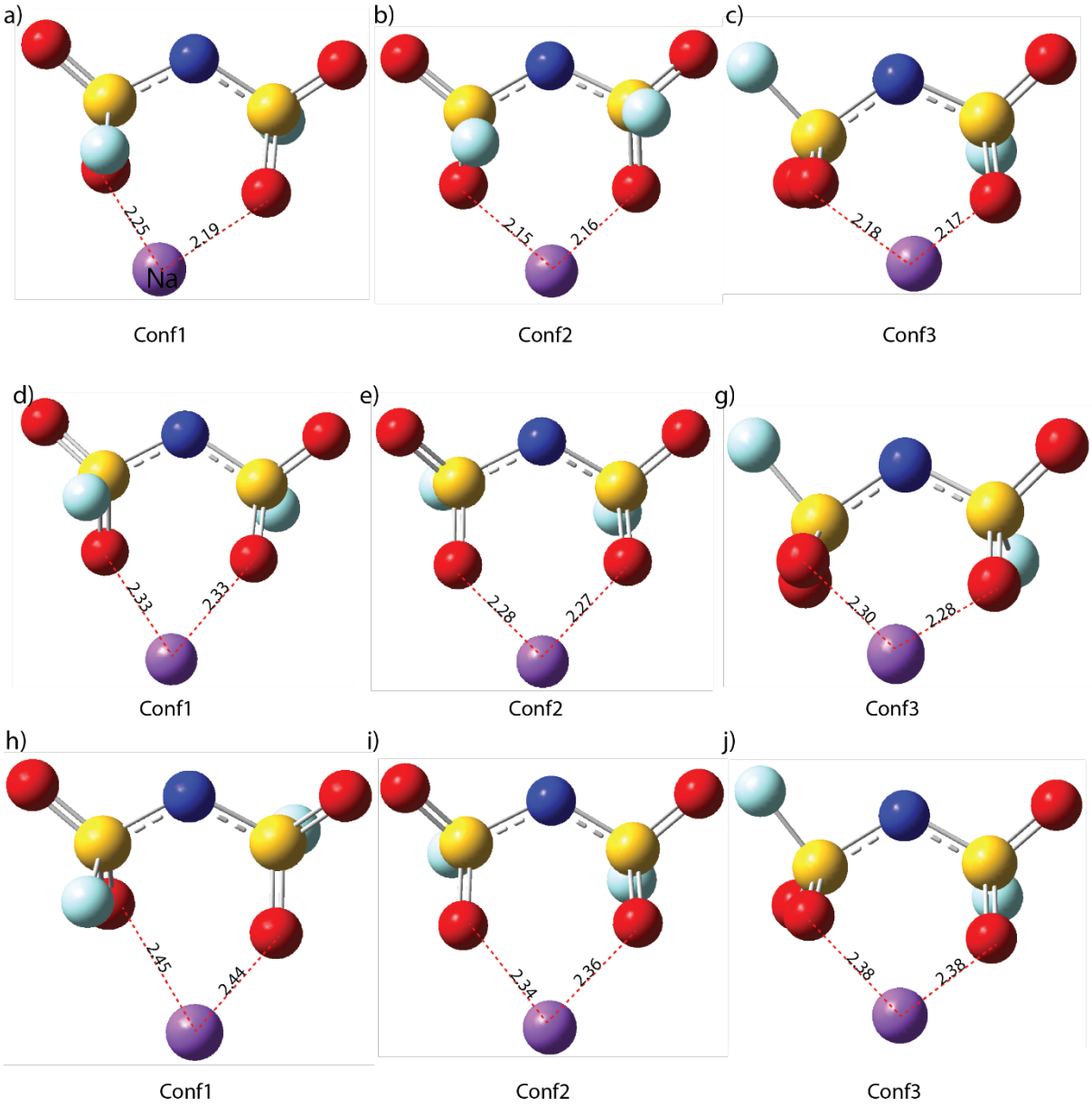

Figure S2. Optimized structures of LiFSI in a-c) gas phase, d-f) $CHCl_3$ and h-j) DMSO.

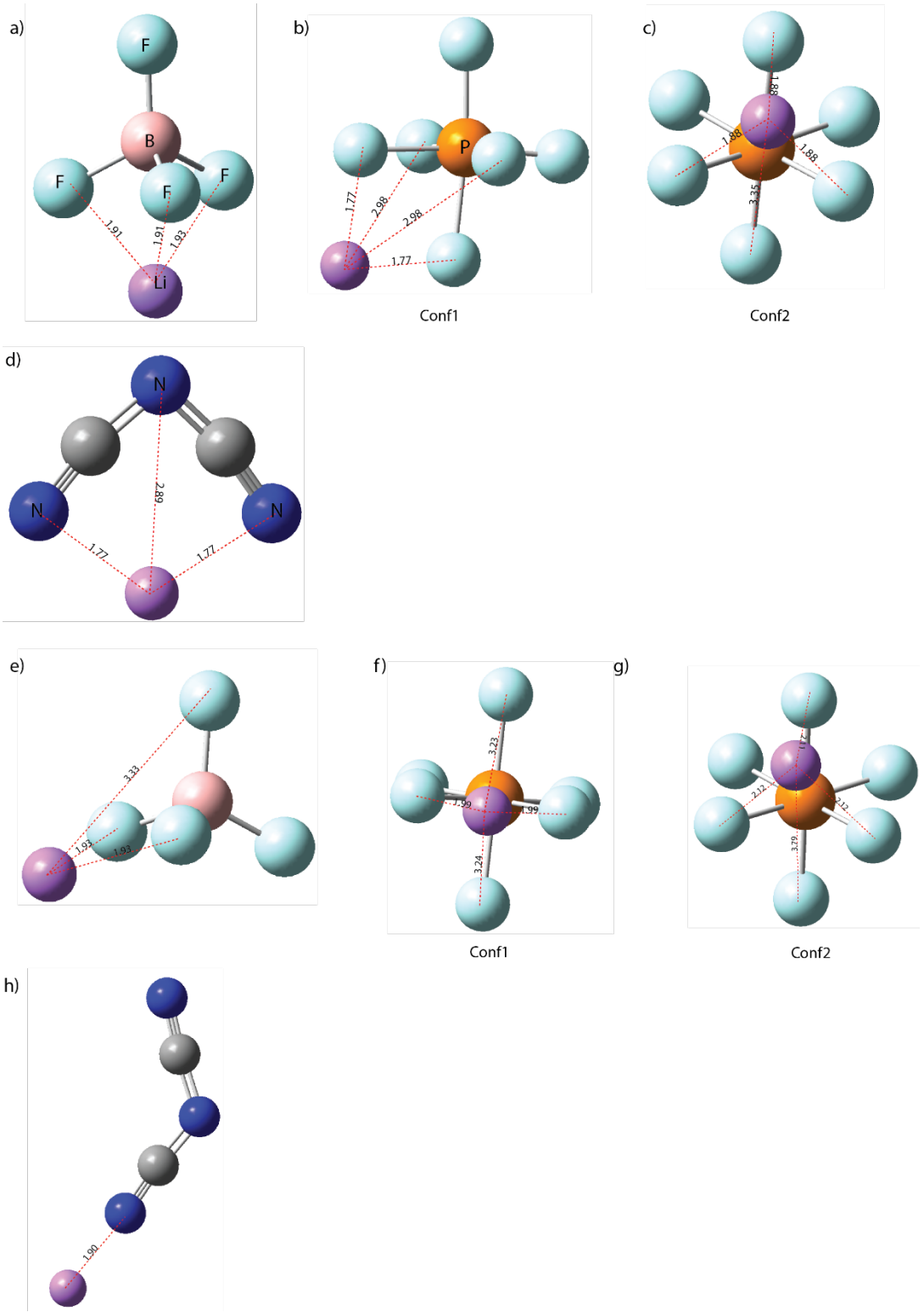

Figure S3. Optimized structures of a) $LiBF_4$ in gas phase, b-c) $LiPF_6$ in gas phase, d) LiDCA in gas phase, f) $LiBF_4$ in gas phase, e) $LiPF_6$ in gas phase and g) LiDCA in gas phase.

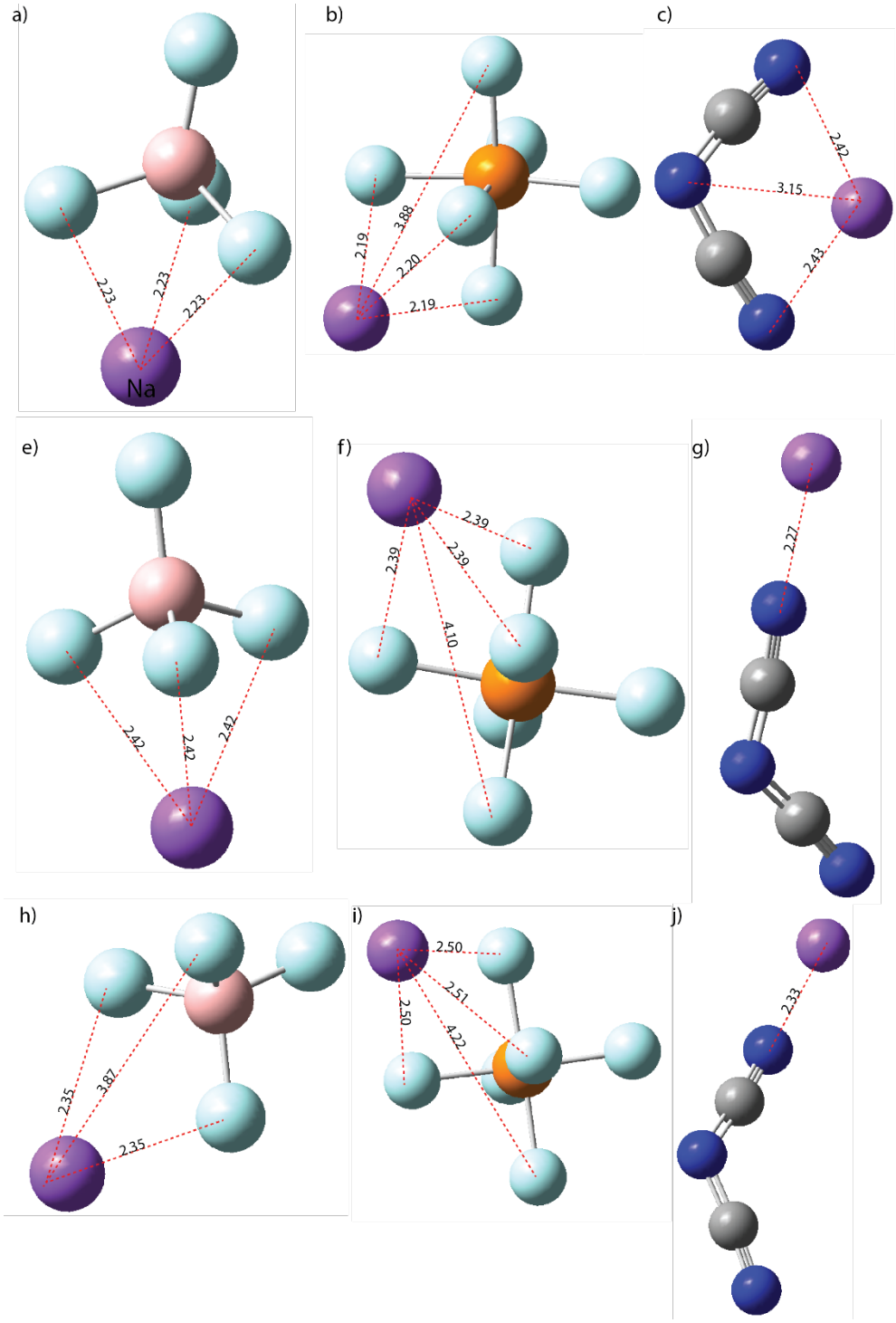

Figure S4. Optimized structures in gas phase a) $NaBF_4$, b) $NaPF_6$, c) NaDCA, in $CHCl_3$ e) $NaBF_4$, f) $NaPF_6$, g) NaDCA, , in DMSO h) $NaBF_4$, j) $NaPF_6$, k) NaDCA,

Table S1 inter-ionic distances (in Å) and CCSD(T) interaction energy of MX salts (where M=Li and Na, X=FSI, BF_4, PF_6 and DCA).

MX	Configuration	Solvent	R_{Centre} [a]	$R_{Closest}$ [b]	E_{int} [c]	MX	Configuration	Solvent	R_{Centre}	$R_{Closest}$	E_{int}
LiFSI	Conf1	Gas	3.28	1.81	-599.6	NaFSI	Conf1	Gas	3.56	2.19	-488.7
		$CHCl_3$	3.49	1.96	-579.1			$CHCl_3$	3.88	2.33	-475.3
		DMSO	3.58	2.04	-563.2			DMSO	4.01	2.44	-462.9
	Conf2	Gas	3.22	1.80	-606.8		Conf2	Gas	3.64	2.16	-491.8
		$CHCl_3$	3.43	1.93	-585.9			$CHCl_3$	3.85	2.27	-481.5
		DMSO	3.49	1.97	-575.4			DMSO	3.95	2.34	-473.5
	Conf3	Gas	3.19	1.80	-609.9		Conf3	Gas	3.58	2.17	-495.3
		$CHCl_3$	3.49	1.96	-579.0			$CHCl_3$	3.80	2.28	-484.5
		DMSO	3.58	2.04	-563.2			DMSO	3.90	2.38	-474.8
$LiBF_4$	Conf1	Gas	2.05	1.91	-621.6	$NaBF_4$	Conf1	Gas	2.39	2.23	-525.5
		$CHCl_3$	2.46	1.93	-593.6			$CHCl_3$	2.57	2.42	-508.3
		DMSO	2.57	2.04	-572.1			DMSO	2.91	2.35	-487.3
$LiPF_6$	Conf1	Gas	2.63	1.77	-591.3	$NaPF_6$	Conf1	Gas	2.79	2.19	-501.7
		$CHCl_3$	2.85	1.99	-543.8			$CHCl_3$	2.99	2.39	-479.5
		DMSO	2.91	2.06	-526.3			DMSO	3.10	2.50	-463.4
	Conf2	Gas	2.42	1.88	-604.1						
		$CHCl_3$	2.67	2.11	-557.7						
		DMSO									
LiDCA	Conf1	Gas	2.89	2.07	-600.4	NaDCA	Conf1	Gas	3.15	2.42	-501.2
		$CHCl_3$	4.35	1.90	-538.3			$CHCl_3$	4.72	2.27	-446.3
		DMSO	4.43	1.98	-528.0			DMSO	4.79	2.33	-440.1

[a] R_{Centre} – distance between the metal ion and the centre of the anion; [b] $R_{Closest}$ – distance between the metal ion and the closest atom on the anion (O on FSI, F on BF_4 and PF_6 and N on DCA); [c] E_{int} = is the total interaction energy (full-core CCSD(T)/VTZ for NaFSI/LiFSI and full-core CCSD(T)/AVTZ for the rest of salts).

Table S2. Orbital Energies (in eV) of MX (where M= Li and Na, X = FSI, BF_4, DCA and PF_6)[a]

	$1s^2$ Li^+	LiFSI	$1s^2$	$2s^2$ Na^+	$2p^6$ Na^+	NaFSI	$2s^2$	$2p^6$
Gasphase	-2.79	Conf1	-2.49	-3.08	-1.80	Conf1	-2.84	-1.56
		Conf2	-2.48			Conf2	-2.83	-1.56
		Conf3	-2.48			Conf3	-2.83	-1.56
CHCl3	-2.48	Conf1	-2.51	-2.82	-1.54	Conf1	-2.86	-1.58
		Conf2	-2.51			Conf2	-2.85	-1.57
		Conf3	-2.51			Conf3	-2.85	-1.57
DMSO	-2.41	Conf1	-2.53	-2.76	-1.48	Conf1	-2.87	-1.59
		Conf2	-2.52			Conf2	-2.86	-1.58
		Conf3	-2.53			Conf3	-2.86	-1.59
Gasphase	-2.79	LiBF4	-2.50	-3.08	-1.80	NaBF4	-2.83	-1.56
		LiPF6(Conf1)	-2.51			NaPF6	-2.86	-1.56
		LiPF6 (Conf2)	-2.50			NaDCA	-2.88	-1.56
		LiDCA	-2.49	-				
CHCl3	-2.48	LiBF4	-2.53	2.82	-1.54	NaBF4	-2.84	-1.58
		LiPF6Conf1	-2.55			NaPF6	-2.87	-1.59
		LiPF6Conf2	-2.55			NaDCA	-2.88	-1.59
		LiDCA	-2.53					
DMSO	-2.41	LiBF4	-2.54	-2.76	-1.48	NaBF4	-2.84	-1.59
		LiPF6	-2.56			NaPF6	-2.86	-1.60
		LiDCA	-2.54			NaDCA	-2.88	-1.60

[a] For $2p^6$ electrons an average of the three degenerate orbitals is given.

Table S3. Correlation interaction energies (E_{int}^{corr} kJ mol^{-1}) of MX salts in gas phase based on CCSD(T) and MP2 and Dunning's basis sets.

Method	Gas Phase	Full core	Frozen core	Gas phase	Full core	Frozen core
CCSD(T)/AVTZ	LiFSI(Conf1)	-	13.6	NaFSI(Conf1)	-	2.3
	LiFSI(Conf2)	-	15.6	NaFSI(Conf2)	-	7.4
	LiFSI(Conf3)	-	15.5	NaFSI(Conf3)	-	6.5
CCSD(T)/VTZ	LiFSI(Conf1)	3.6	7.8	NaFSI(Conf1)	-0.4	-0.6
	LiFSI(Conf2)	5.3	9.6	NaFSI(Conf2)	4.8	4.5
	LiFSI(Conf3)	5.1	9.4	NaFSI(Conf3)	3.9	3.5
MP2/AVTZ	LiFSI(Conf1)	11.7	16.9	NaFSI(Conf1)	4.6	4.6
	LiFSI(Conf2)	13.8	19.1	NaFSI(Conf2)	10.5	10.4
	LiFSI(Conf3)	13.6	18.9	NaFSI(Conf3)	9.5	9.4
MP2/VTZ	LiFSI(Conf1)	6.9	10.7	NaFSI(Conf1)	1.0	0.8
	LiFSI(Conf2)	8.9	5.2	NaFSI(Conf2)	7.1	6.8
	LiFSI(Conf3)	8.6	12.5	NaFSI(Conf3)	6.0	5.7
CCSD(T)/AVTZ	$LiBF_4$	-2.2	3.0	$NaBF_4$	0.7	0.6
	$LiPF_6$(Conf1)	2.5	7.4	$NaPF_6$	1.6	1.4
	$LiPF_6$ (Conf2)	-1.0	4.6	NaDCA	-0.6	-0.7
	LiDCA	2.4	6.9			
CCSD(T)/VTZ	$LiBF_4$	-5.7	-1.7	$NaBF_4$	-1.5	-1.8
	$LiPF_6$ (Conf1)	-1.7	1.8	$NaPF_6$	-1.5	-1.8
	$LiPF_6$ (Conf2)	-5.4	-1.4	NaDCA	-1.0	-1.2
	LiDCA	1.5	4.9			
MP2/AVTZ	$LiBF_4$	-0.4	4.1	$NaBF_4$	2.3	2.3
	$LiPF_6$ (Conf1)	4.0	8.3	$NaPF_6$	2.9	2.8
	$LiPF_6$ (Conf2)	0.5	5.4	NaDCA	1.2	1.0
	LiDCA	5.3	9.5			
MP2/VTZ	$LiBF_4$	-4.8	-1.3	$NaBF_4$	-0.8	-1.0
	$LiPF_6$ (Conf1)	-0.8	2.3	$NaPF_6$	-1.1	-1.3
	$LiPF_6$ (Conf2)	-4.7	-1.2	NaDCA	0.2	0.0
	LiDCA	9.2	7.0			

Table S4. Correlation interaction energies (E_{int}^{corr} kJ mol^{-1}) of MX salts in solvents on CCSD(T) and MP2 and Dunning's basis sets.

Method			Full core	Frozen core	Gas phase	Full core	Frozen core
CCSD(T)/AVTZ	$CHCl_3$	LiFSI(Conf1)	-	8.6	NaFSI(Conf1)	-	2.5
		LiFSI(Conf2)	-	10.9	NaFSI(Conf2)	-	5.5
		LiFSI(Conf3)	-	8.6	NaFSI(Conf3)	-	4.9
	DMSO	LiFSI(Conf1)	-	6.2	NaFSI(Conf1)	-	1.3
		LiFSI(Conf2)	-	9.4	NaFSI(Conf2)	-	5.7
		LiFSI(Conf3)	-	6.2	NaFSI(Conf3)	-	4.0
CCSD(T)/VTZ	$CHCl_3$	LiFSI(Conf1)	0.4	3.3	NaFSI(Conf1)	-0.2	-0.4
		LiFSI(Conf2)	2.4	5.4	NaFSI(Conf2)	2.6	2.4
		LiFSI(Conf3)	0.4	3.3	NaFSI(Conf3)	1.9	1.7
	DMSO	LiFSI(Conf1)	-1.2	1.2	NaFSI(Conf1)	-1.5	-1.6
		LiFSI(Conf2)	1.3	4.0	NaFSI(Conf2)	1.2	1.2
		LiFSI(Conf3)	-1.2	1.2	NaFSI(Conf3)	0.9	0.8
MP2/AVTZ	$CHCl_3$	LiFSI(Conf1)	7.7	11.2	NaFSI(Conf1)	4.8	4.8
		LiFSI(Conf2)	10.3	13.9	NaFSI(Conf2)	8.2	8.2
		LiFSI(Conf3)	7.7	11.2	NaFSI(Conf3)	7.4	7.4
	DMSO	LiFSI(Conf1)	5.6	8.5	NaFSI(Conf1)	3.2	3.2
		LiFSI(Conf2)	9.0	12.2	NaFSI(Conf2)	8.8	8.0
		LiFSI(Conf3)	5.6	8.5	NaFSI(Conf3)	6.3	6.2
MP2/VTZ	$CHCl_3$	LiFSI(Conf1)	3.0	5.6	NaFSI(Conf1)	1.3	1.2
		LiFSI(Conf2)	5.4	8.1	NaFSI(Conf2)	4.7	4.5
		LiFSI(Conf3)	3.0	5.6	NaFSI(Conf3)	3.8	3.7
		LiFSI(Conf1)	1.0	3.1	NaFSI(Conf1)	-0.3	-0.3
		LiFSI(Conf2)	4.1	6.5	NaFSI(Conf2)	3.1	3.1
		LiFSI(Conf3)	1.0	3.1	NaFSI(Conf3)	2.6	2.5
CCSD(T)/AVTZ	$CHCl_3$	$LiBF_4$	-0.9	2.3	$NaBF_4$	-3.0	-3.0
		$LiPF_6$ (Conf1)	-2.9	-0.2	$NaPF_6$	-2.6	-2.6
		$LiPF_6$ (Conf2)	-5.6	-2.8	NaDCA	1.1	1.0
		LiDCA	1.9	4.8			
	DMSO	$LiBF_4$	-2.5	-2.5	$LiBF_4$	-1.0	-1.1
		$LiPF_6$	-2.9	-2.9	$LiPF_6$	-3.8	-3.8
		LiDCA	0.8	0.8	LiDCA	0.5	0.4
CCSD(T)/VTZ	$CHCl_3$	$LiBF_4$	-4.0	-1.7	$NaBF_4$	-5.6	-5.6
		$LiPF_6$ (Conf1)	-6.9	-5.1	$NaPF_6$	-5.9	-6.0
		$LiPF_6$ (Conf2)	-10.0	-8.0	NaDCA	0.2	0.0
		LiDCA	0.5	2.6			
	DMSO	$LiBF_4$	-5.7	-4.0	$NaBF_4$	-3.5	-3.6
		$LiPF_6$	-6.9	-5.1	$NaPF_6$	-7.2	-7.2
		LiDCA	-0.6	1.2	NaDCA	-0.5	-0.6
MP2/AVTZ	$CHCl_3$	$LiBF_4$	0.3	0.3	$NaBF_4$	-2.1	-2.1
		$LiPF_6$ (Conf1)	-2.2	-2.2	$NaPF_6$	-1.9	-1.9
		$LiPF_6$ (Conf2)	-5.1	-5.1	NaDCA	2.3	2.2
		LiDCA	3.1	3.1			
	DMSO	$LiBF_4$	-1.7	-1.7	$NaBF_4$	-0.3	-0.3
		$LiPF_6$	-3.6	-3.6	$NaPF_6$	-3.4	-3.4
		LiDCA	2.3	2.3	NaDCA	1.5	1.5

MP2/VTZ	$CHCl_3$	$LiBF_4$	-3.5	-3.5	$NaBF_4$	-5.4	-5.4
		$LiPF_6$ (Conf1)	-6.7	-6.7	$NaPF_6$	-5.9	-5.9
		$LiPF_6$ (Conf2)	10.0	10.0	NaDCA	1.0	0.9
		LiDCA	1.8	1.8			
	DMSO	$LiBF_4$	-5.5	-5.5	$NaBF_4$	-3.3	-3.4
		$LiPF_6$	-7.8	-7.8	$NaPF_6$	-7.2	-7.3
		LiDCA	0.5	0.5	NaDCA	1.0	0.9

Table S5. Net charge transfers of LiFSI and NaFSI

	Gas phase			$CHCl_3$			DMSO		
LiFSI	Conf1	Conf2	Conf3	Conf1	Conf2	Conf3	Conf1	Conf2	Conf3
	0.14	0.13	0.14	0.12	0.11	0.12	0.11	0.10	0.12
NaFSI	Conf1	Con2	Conf3	Conf1	Con2	Conf3	Conf1	Con2	Conf3
	0.10	0.06	0.12	0.06	0.07	0.10	0.05	0.06	0.09

Table S6. Net charge transfers of MX (where M = Li or Na and X = BF_4, PF_6 and DCA)

Gas phase			$CHCl_3$				DMSO			
$LiBF_4$	LiPF6 (Conf1)	$LiPF_6$ (Conf2)	LiDCA	$LiBF_4$	$LiPF_6$ (Conf1)	$LiPF_6$ (Conf2)	LiDCA	$LiBF_4$	$LiPF_6$	LiDCA
0.17	014	0.16	0.28	0.13	0.11	0.12	0.08	0.17	0.10	0.09
$NaBF_4$	$NaPF_6$	NaDCA	NaDCA	$NaBF_4$	$NaPF_6$			$NaBF_4$	$NaPF_6$	NaDCA
0.11	0.10	0.19	0.06	0.10	0.08			0.08	0.08	0.06

Table S7. Solubility (in M) of LiX and NaX salts in six ionic liquids.

Ionic liquids	$LiNTf_2$	$LiNTf_2$	$LiPF_6$	$NaPF_6$	$LiBF_4$	$NaBF_4$
$[C_3mpyr][NTf_2]$	2.16 M	0.64 M	0.94 M	< 0.1 M	1.63 M	< 0.1 M
$[C_3mpyr][FSI]$	4.75 M	0.91 M	0.89 M	< 0.1 M	0.60 M	< 0.1 M
$[C_{101}mpyr][NTf_2]$	3.05 M	0.84 M	1.37 M	< 0.1 M	0.84 M	< 0.1 M
$[C_{101}mpyr][FSI]$	5.48 M	1.74 M	1.09M	0.11 M	1.64 M	< 0.1 M
$[C_2mim][NTf_2]$	3.56 M	0.84 M	1.64 M	0.12 M	2.05 M	< 0.1 M
$[C_2mim][FSI]$	5.99 M	1.61 M	0.90 M	0.12 M	2.57 M	< 0.1 M

Table S8. Correlation interaction energy (E_{int}^{corr} in kJ/mol) of MX (where M=Li and Na, X=FSI, BF_4, PF_6 and DCA) with CCSDT and MP2 methods

Ion pair	CCSD(T)/AVTZ[a]	MP2/CBS1[b]	MP2/CBS2[c]
LiFSI	5.8	10.8	
$LiBF_4$	2.5	-4.2	-3.5
$LiPF_6$	4.0	-4.6	
LiDCA	0.8	1.0	1.0
NaFSI	4.0	5.1	
$NaBF_4$	-1.0	-1.3	-2.8
$NaPF_6$	-3.8	-4.1	
NaDCA	-0.5	0.5	-0.8

[a] Full-core the Li/Na cation and frozen core for the FSI anion.
[b] Extrapolation of cc-pVTZ and cc-VQZ basis sets
[c] Extrapolation of aug-cc-pVTZ and aug-cc—VQZ basis sets

Table S9. Correlation interaction energy (E_{int}^{corr} in kJ/mol) of MX (where M=Li and Na, X=F and C) with CCSDT and MP2 methods.[a]

Ion pair	Methods	Basis sets	E_{int}^{corr}	Methods	Basis set	E_{int}^{corr}
LiF	CCDS(T)	ATZ	0.5	MP2	ATZ	2.0
		AQZ	-5.7		AQZ	-3.2
		QZ	-7.0		QZ	-4.6
		5Z	-10.5		5Z	-8.1
LiCl	CCDS(T)	ATZ	-1.4	MP2	ATZ	-0.3
		AQZ	-3.4		AQZ	-1.9
		QZ	-5.3		QZ	-4.0
		5Z	-5.7		5Z	-4.3
NaF	CCDS(T)	ATZ	1.5	MP2	ATZ	2.5
		AQZ	-3.8		AQZ	-2.1
		QZ	-3.5		QZ	-2.0
		5Z	-11.2		5Z	-9.3
NaCl	CCDS(T)	ATZ	-1.2	MP2	ATZ	-0.4
		AQZ	-2.9		AQZ	-1.7
		QZ	-4.0		QZ	-3.0
		5Z	-7.0		5Z	-5.6

[a] ATZ = aug-cc-pVTZ, AQZ = aug-cc-pVQZ, QZ = cc-pVQZ, 5Z = cc-pV5Z.