Solubility of Alkali Metal Halides in the Ionic Liquid [C_4C_1im][OTf] - SI

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Supplementary information

1. Synthetic Methods. General

Syntheses of the ionic liquid used the accepted technique of first preparing the halide salt of the appropriate cation followed by anion metathesis.

The synthesis of ionic liquid was conducted in an atmosphere of dry nitrogen. Solvents were distilled from the relevant drying agents prior to use. Chloride content of the ionic liquids was determined by an $AgNO_3$ test. AgCl has a solubility of 1.4 mgl^{-1} in water, hence all of the ionic liquids synthesised will have a chloride content below this value.

1-butyl-3-methylimidazolium chloride, [C_4C_1im]Cl

1-methylimidazole (200 ml, 2.53 mol) was added dropwise to 1-chlorobutane (288 ml, 2.87 mol) in ethyl acetate (200 ml). The mixture was stirred at 55 °C for 24 days. The two-phase mixture was cooled to -14 °C until the product crystallised. The liquid was removed, the crystals were washed with ethyl acetate and recrystallised from acetonitrile. [C_4C_1im]Cl was recovered as a white crystalline solid and dried under vacuum (82.1% yield).

1-butyl-3-methylimidazolium trifluoromethanesulfonate, [C4C1im][OTf]

To a flask containing a stirred solution of [C_4C_1im]Cl (55.7 g, 0.319 mol) in CH_2Cl_2 (60 cm^3) was added lithium trifluoromethanesulfonate (33.5 g, 0.329 mmol) under N_2. The mixture was stirred for 24 h and the white precipitate was allowed to settle. Cannula filtration and subsequent washing of the LiCl residue with water (7 × 5 cm^3) until halide free, as indicated by the $AgNO_3$ test of the water washings. The liquid was dried in vacuo overnight at 50 °C to afford [C_4C_1im][OTf] (75.5% yield) as a free-flowing colourless liquid.

2. Solubility Data Modelling

a. Ideal mixture model

The simplest mixing model is the ideal model. A universal equation for solid−liquid equilibrium, which is based on thermodynamic principles is shown in equation S1 (Walas, 1985):

$$\ln x_1\gamma_1 = \frac{\Delta H_1}{R}\left(\frac{1}{T_{tp,1}} - \frac{1}{T}\right) - \frac{\Delta C_{p,1}}{R}\left(\ln\frac{T_{tp,1}}{T} - \frac{T_{tp,1}}{T} + 1\right) - \frac{\Delta V}{RT}(P - P_{tp,1}) \quad \text{Eq. S1}$$

where ΔH_1, $T_{tp,1}$, $\Delta C_{p,1}$, $P_{tp,1}$, and γ_1 are the molar enthalpy of fusion, triple-point temperature, difference of heat capacities between subcooled liquid and solid, triple-point pressure, and activity coefficient for the solid component, respectively; x_1 is the solid solubility of the component at the system temperature T and pressure p, and R is the universal gas constant. The above equation is generally simplified by replacing the triple-point temperature $T_{tp,1}$ with the normal melting temperature T_{m1}. The last two terms on the right-hand side of the equation often cancel out such that pressure correction would become negligible. The contribution of the heat-capacity difference is often minor, and no solid-to-solid conversion ranging from T to T_{tp} exists. Equation S1 therefore may be rewritten as equation S2:

$$\ln x_1\gamma_1 = \frac{\Delta H_1}{R}\left(\frac{1}{T_{m1}} - \frac{1}{T}\right) \quad \text{Eq. S2}$$

Assuming the solution is an ideal solution ($\gamma_1 = 1$), then eq. S2 can be expressed as follows (Eq. S3):

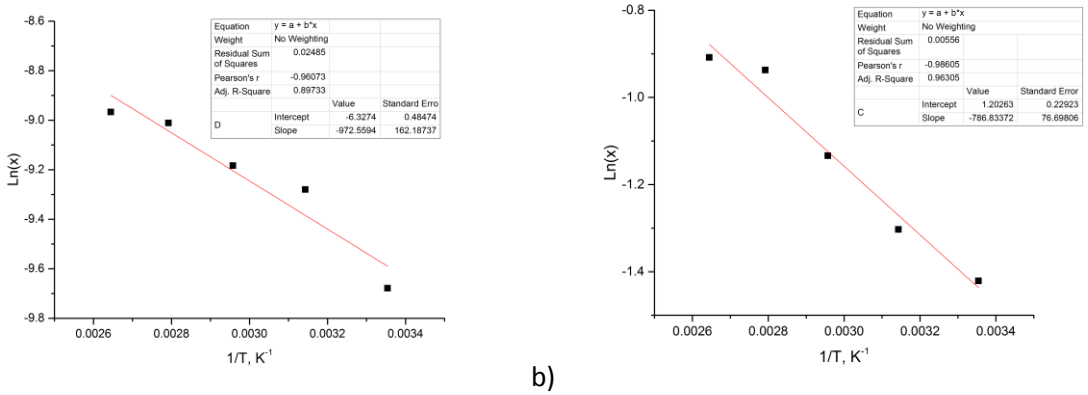
$$\ln x_1 = \frac{a}{T} + b \qquad \text{Eq. S3}$$

where a and b are the model parameters, and x_1 is the mole fraction of solubility at system temperature T.

b. The *van't Hoff equation* reflects the relationship between the mole fraction solubility of a solute and the temperature in a real solution, which is expressed as (Eq. S4) (Long, Li, Song, & Du, 2011; Tao, Wang, Gong, Hao, & Wang, 2013):

$$\ln x_1 = -\frac{\Delta H_{sol}}{RT} + \frac{\Delta S_{sol}}{R} \quad \text{Eq. S4}$$

where *R* is the gas constant, and ΔH_{sol} and ΔS_{sol} are the dissolution enthalpy and entropy respectively.



a) b)

Fig. S1. van't Hoff plots for determination of ΔH_{sol} and ΔS_{sol}. *Examples are given for the least soluble salt NaF (a) and the most soluble salt CsI (b).*

c. *Modified Apelblat equation*

The following modified Apelblat equation was used to correlate the solubility data (Eq. S5) (Apelblat, Manzurola, & She, 1999; Tao et al., 2013):

$$\ln x_1 = A + \frac{B}{T} + C \ln T \quad \text{Eq. S5}$$

where x_1 is the mole fraction solubility of the solute, *T* is the absolute temperature, and *A*, *B*, and *C* are the model parameters. The values of *A* and *B* reflect the variation in solution activity coefficients, and *C* denotes the effect of temperature on the enthalpy of fusion.

d. *The non-random two liquid (NRTL) model* has previously been applied to describe solubility properties of sodium salts in some deep eutectic solvents (S. F. G. Bagh, Mjalli, Hashim, Hadj-kali, & AlNashef, 2013). The NRTL model can be expressed in the following binary form (Eq. S6) (Kontogeorgis & Folas, 2010):

$$\ln \gamma_1 = x_2^2 \left[\frac{\tau_{21} G_{21}^2}{(x_1 + G_{21} x_2)^2} + \frac{\tau_{12} G_{12}^2}{(x_2 + G_{12} x_1)^2} \right] \quad \text{Eq. S6}$$

Where

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \text{ and } G_{21} = \exp(-\alpha_{12}\tau_{21}) \quad \text{Eq. S7}$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} = \frac{\Delta g_{12}}{RT} \text{ and } \tau_{21} = \frac{g_{21} - g_{11}}{RT} = \frac{\Delta g_{21}}{RT} \quad \text{Eq. S8}$$

Here, Δg_{12} and Δg_{21} are the cross interaction energy parameters, and α_{12} is a measure of the non-randomness of the mixture.

This model has three parameters, τ_{12}, τ_{21}, and α_{12}, for each pair of components in the multicomponent mixture. Despite some authors' hypothesis that $\tau_{12} = \tau_{21}$ (F. S. G. Bagh, Hadj-Kali, Mjalli, Hashim, & AlNashef, 2014; S. F. G. Bagh et al., 2013), we have found the best fitting correlation was with all three parameters being treated independently. The non-randomness parameter, α_{12}, was adjusted between 0.17 and 0.33 (Kontogeorgis & Folas, 2010). According to literature (Kontogeorgis & Folas, 2010) a value of 0.2 should be used for hydrocarbon–polar non-associated compounds mixtures; and 0.3 for non-polar compound-polar compound mixtures with slight negative deviations from Raoult's law or moderate positive deviations, water–polar compound mixtures.

e. The *Buchowski (λh) Equation* describes the behaviour of solid solubility in liquids with only two parameters (λ and *h*). This equation S9 gives an excellent description of experimental data without considering the activity coefficients of the components (Buchowski, Ksiazczak, & S., 1980; Tao et al., 2013):

$$\ln\left[1+\frac{\lambda(1-x_1)}{x_1}\right]=\lambda h\left[\frac{1}{T}-\frac{1}{T_m}\right] \quad \text{Eq. S9}$$

where λ and h are two equation constants, T_m is the melting temperature of the solute, and x_1 and T are mole fraction of solute and absolute temperature of the system, respectively. The value of λ reflects the nonideality of the solution system, whereas h estimates the enthalpy of solution.

The average relative deviations (ARD) were used to identify the differences between the measured and calculated data, and these are is given as follows (Eq. S10):

$$ARD=\frac{1}{N}\sum_{i=1}^{N}\frac{\left|x_{1,i}^{exptl}-x_{1,i}^{calcd}\right|}{x_{1,i}^{exptl}} \quad \text{(Eq. S10)}$$

where N is the number of experimental points; $x_{1,i}^{exptl}$ and $x_{1,i}^{calcd}$ are the experimental solubility and the calculated solubility.

Table S1. Determined model parameters of the studied salts in $[C_4C_1im][OTf]$

	Apelblat			Buchowski		NRTL			Ideal		van Hoff	
salt	a	b	c	λ	h	Δg12	Δg21	α	a	b	ΔH	ΔS
LiF	-17.19	141.67	1.42	$-0.75*10^{-4}$	$30*10^{5}$	32181.46	16054.55	0.17	-337.54	-7.47	2786.48	-62.14
LiCl	202.79	-11970.84	-29.20	3.69	541.86	-1578.72	7127.56	0.30	-1873.95	2.84	16940.21	27.49
LiBr	335.30	-18342.66	-48.55	10.30	194.09	-3668.38	12195.46	0.29	-1636.44	3.04	16621.75	33.85
LiI	-88.93	3534.24	13.27	5.33	239.15	900.36	-2336.69	0.33	-964.17	1.70	7565.78	12.77
LiOTf	118.37	- 6927.39	-17.17	$9695.59*10^{-4}$	1111.69	6906.61	-2339.30	0.17	-1073.11	1.02	9428.76	9.89
NaF	11.35	-6932.27	-17.86	$1.61*10^{-4}$	$30*10^{5}$	35977.17	18608.60	0.17	-876.64	-6.61	8085.86	-52.61
NaCl	114.31	-6932.05	-17.17	$106.25*10^{-4}$	87950.00	34566.15	9508.03	0.17	-1103.65	-2.96	10902.03	-19.67
NaBr	60.56	-3594.86	-9.58	0.92	3500.00	33420.11	8442.72	0.17	-371.36	-4.81	3269.73	-39.49
NaI	53.06	-3458.81	-8.01	$322.56*10^{-4}$	14268.06	53106.49	5092.63	0.17	-752.56	1.62	6744.65	-12.04
NaOTf	-79.04	2240.53	12.12	21.18	112.34	-3408.90	9850.12	0.31	-1953.30	3.94	14039.96	26.28
KF	-171.56	7445.87	24.28	$91.51*10^{-4}$	128350.00	32563.63	11007.64	0.17	-845.11	-4.37	6192.76	-38.82
KCl	80.04	-5332.81	-11.84	$810.74*10^{-4}$	14382.55	65035.31	8368.04	0.17	-1286.85	-0.91	11238.88	-6.04
KBr	-38.00	1333.42	5.16	$-60.14*10^{-4}$	32835.32	32835.01	2775.86	0.17	-404.34	-2.80	3263.45	-23.57
KI	35.49	-2426.84	-5.09	1.14	642.37	4225.06	-3186.83	0.33	-704.14	0.73	5973.44	6.44
KOTf	-56.65	2344.92	8.25	$251.91*10^{-4}$	2057.28	14270.02	-5953.70	0.17	-431.69	-0.38	3444.44	-3.61
RbCl	76.80	-4479.57	-12.23	$0.04*10^{-4}$	$112.8*10^{4}$	34097.46	14007.29	0.17	-365.59	-6.63	3247.23	-54.47
CsCl	-65.41	1627.33	9.61	$2341.21*10^{-4}$	6867.10	33271.80	8903.82	0.33	-1668.16	0.34	13335.36	1.23
CsI	26.82	-2053.12	-3.75	3.06	328.80	480.52	-1769.93	0.29	-781.07	1.19	6541.74	10.00

Table S2. Standard parameters for the studied salts.

Salt	dH_{form}°, kJ/mol	dH_{fus}, J/g	dH_{fus}, kJ/mol	delta fG°, kJ/mol	S°, J/deg*mol	Cp°, J/deg*mol	Lattice E, kJ/mol	Lattice constant	Electroneg dif	Dissociation E, kJ/mol	Bond length	MP, K
LiF	-616	1044.4	27.05	-587.7	35.66	41.6	-1036	403.51	3	577	202	1118
LiCl	-408.6	469.4	19.8979	-384.4	59.3	48.03	-853	514	2	468	257	878
LiBr	-351.2	202.7	17.6025	-342	74.27	48.91	-807	550	1.8	423	275	825
LiI	-270.4	109.1	14.603	-270.3	86.8	51	-757	601	1.5	352	301	742
Li[OTf]	--	--	--	--	--	--	--	--	--	--	--	696
NaF	-576.6	794.3	33.3527	-546.3	51.11	46.85	-923	463	3.1	481	323	1266
NaCl	-411.2	481.8	28.1564	-384.1	72.1	50.51	-787	564	2.1	410	282	1074
NaBr	-361.08	253.8	26.1135	-349	86.82	51.38	-747	597	1.9	370	299	1020
NaI	-287.9	157.4	23.5927	-286.1	98.5	52.1	-704	647	1.6	301	324	934
Na[OTf]	--	--	--	--	--	--	--	--	--	--	--	528
KF	-567.2	468.2	27.2024	-537.8	66.5	48.98	-821	534	3.2	497.5	267	1131
KCl	-436.5	355.9	26.5323	-408.5	82.55	51.29	-715	629	2.2	427	315	1040
KBr	-393.8	214.3	25.5017	-380.7	95.9	52.3	-682	660	2	383	330	1007
KI	-327.9	144.6	24.0036	-324.9	106.3	52.9	-649	707	1.7	331	354	954
K[OTf]	--	225.54	42.44	--	--	--	--	--	--	--	--	509
RbCl	-435.35	152.2	18.404	-407.81	95.9	52.41	-689	659	2.2	448	330	991
CsCl	-442.8	94.4	15.8932	-414.4	101.18	52.44	-659	412	2.3	439	206	918
CsI	-346.6	--	--	-340.6	123.1	52.8	-604	457	1.8	339	229	894

-- data is unknown

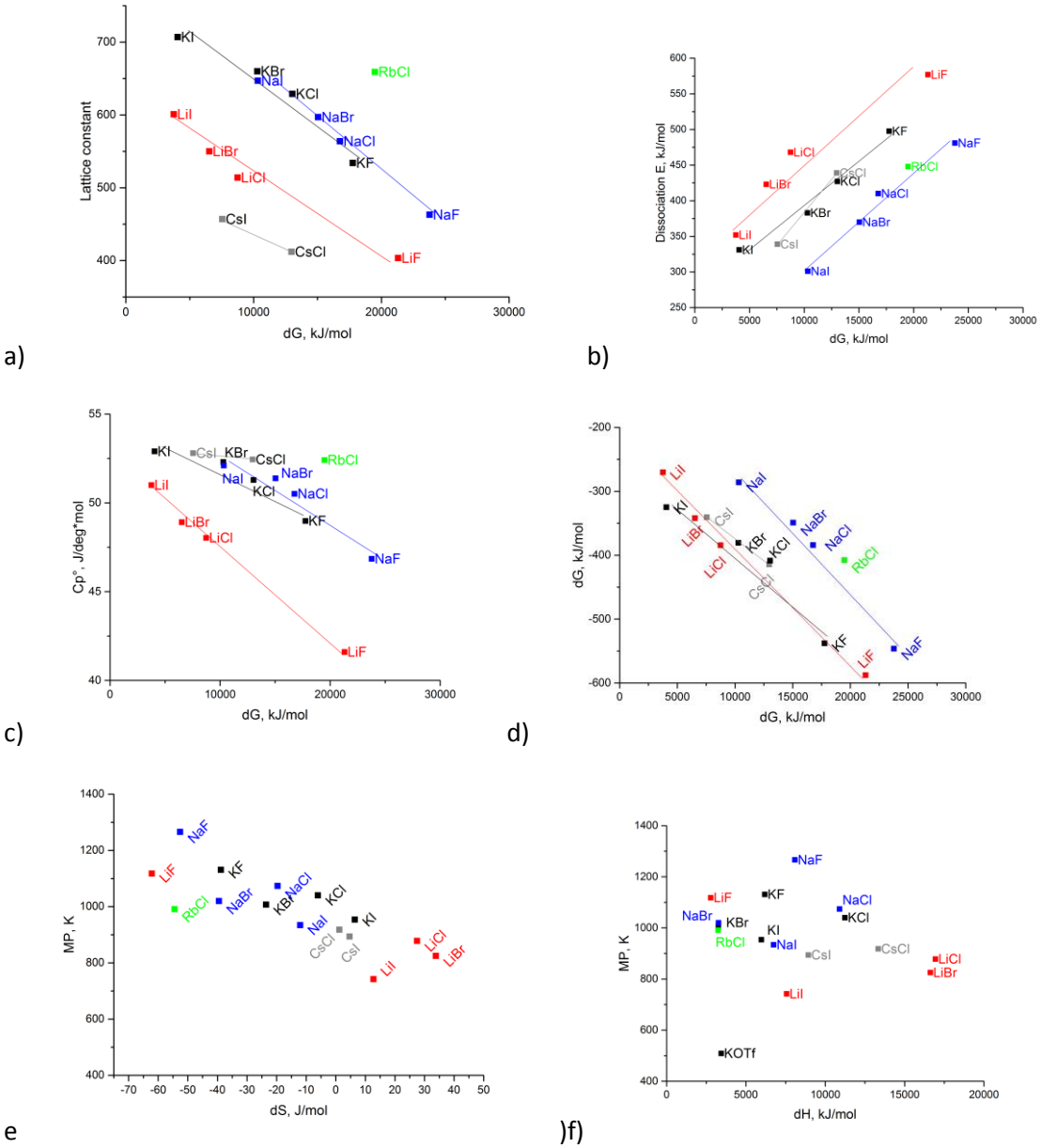


Fig. S2. Linear correlation between calculated ΔG of dissolution and standard parameters of salts dissolved in IL (a-d); representation of an absent of linear dependence of between calculated ΔS of dissolution (e) and ΔH of dissolution (f) and standard parameter (MP) of salts dissolved in IL

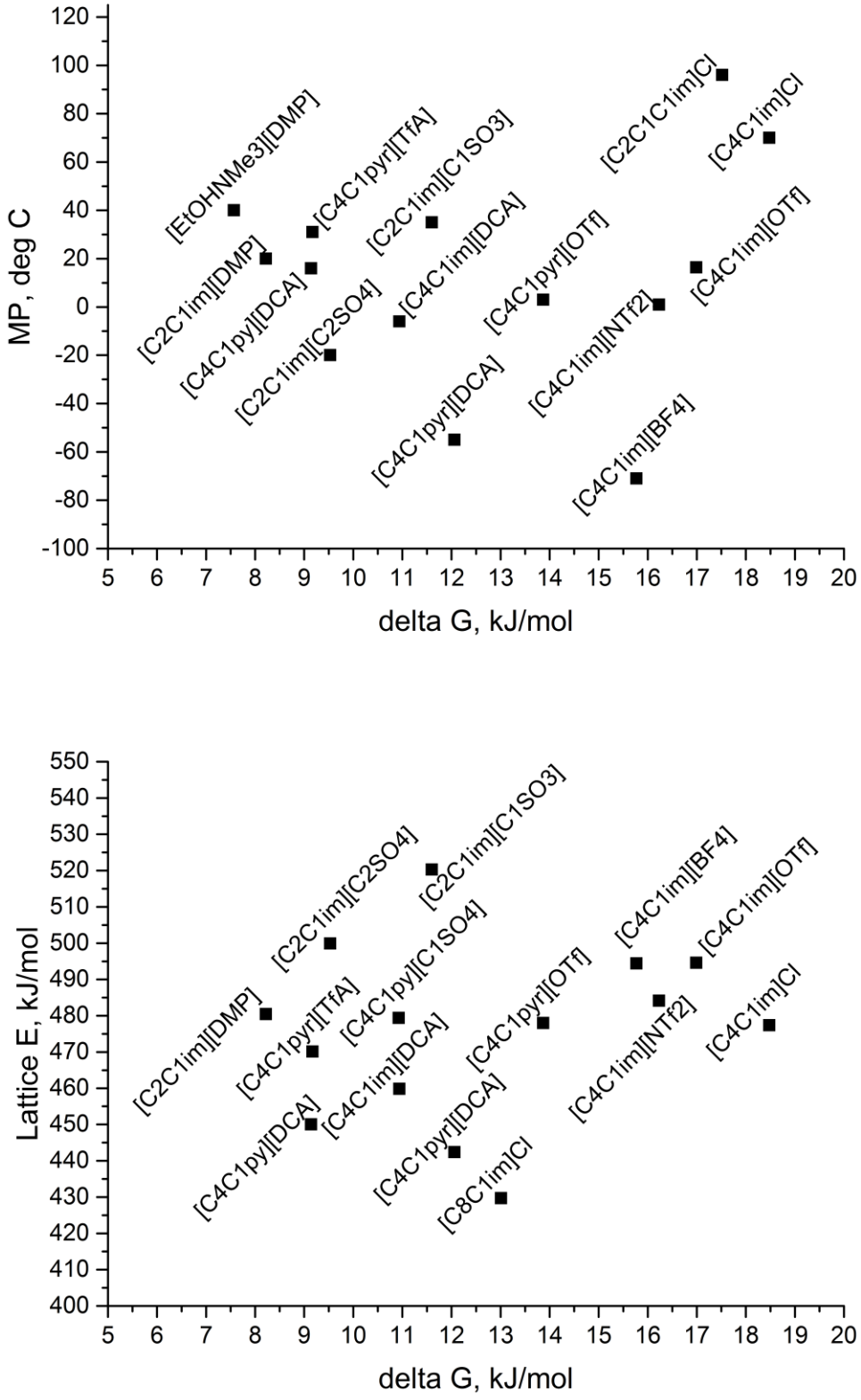
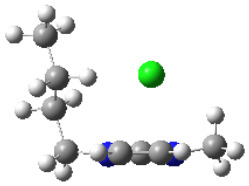


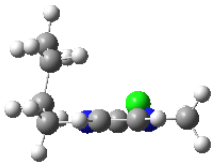
Fig. S3. Correlation of ΔG of NaCl dissolution with melting point and lattice energy of a number of ILs.

2. Computational Data

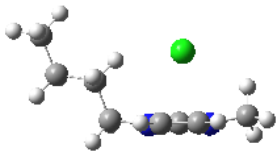
[C_4C_1Im]Cl



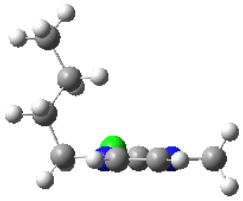
a) [C_4C_1Im]Cl_T_95_m60_180



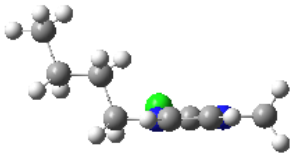
b) [C_4C_1Im]Cl_FM_150_m60_180



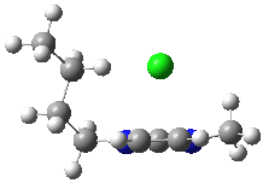
c) [C_4C_1Im]Cl_T_64_180_180



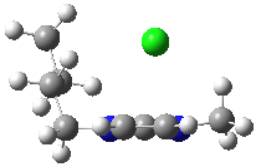
d) [C_4C_1Im]Cl_FB_70_60_180



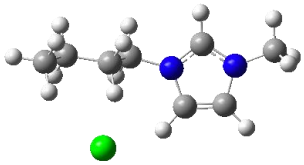
e) [C_4C_1Im]Cl_FB_90_180_180



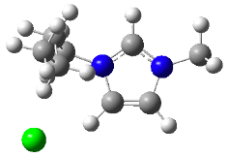
f) [C_4C_1Im]Cl_T_34_60_180



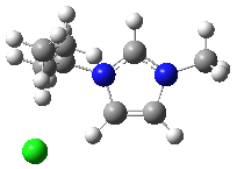
g) [C_4C_1Im]Cl_T_105_90_m180



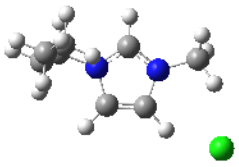
h) [C_4C_1Im]Cl_BS_80_m180_180



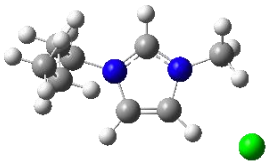
i) [C_4C_1Im]Cl_BS_100_m60_m180



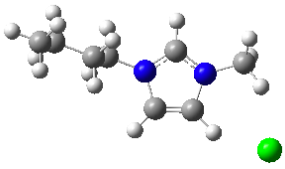
j) [C_4C_1Im]Cl_BS_80_60_180



k) [C_4C_1Im]Cl_MS_70_60_180



l) [C_4C_1Im]Cl_MS_100_m60_m180



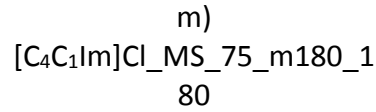
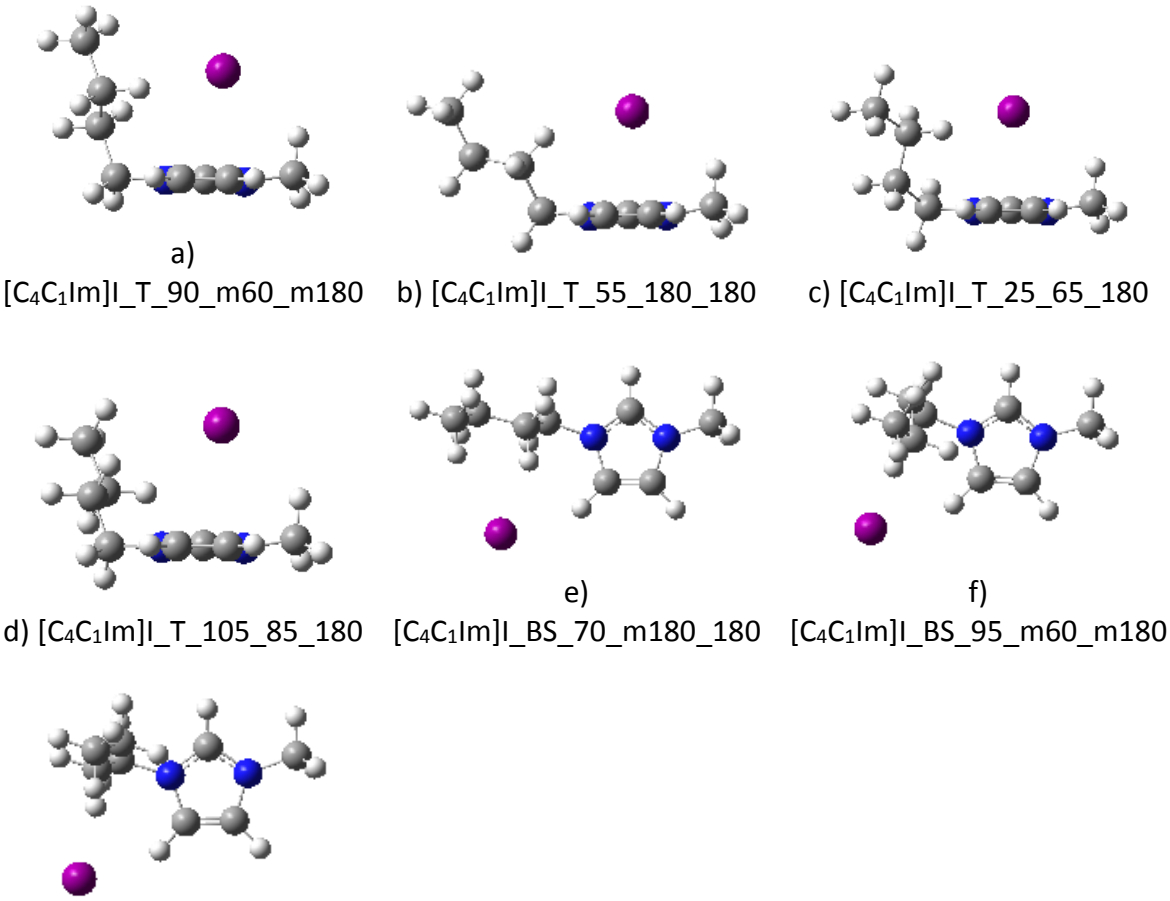


Figure S4. $[C_4C_1Im]Cl$ conformers.

Table S3. $[C_4C_1Im]Cl$ conformers, dihedral angles $\boldsymbol{\tau_1}$, $\boldsymbol{\tau_2}$ and $\boldsymbol{\tau_3}$ and relative energies Δ*E* (kJ/mol).

No.	**conformer**	$\boldsymbol{\tau_1}[°]$	$\boldsymbol{\tau_2}[°]$	$\boldsymbol{\tau_3}[°]$	**Δ*E* [kJ mol^{-1}]**
a	[C4C1Im]Cl_T_95_m60_180	94.6	-60.1	179.0	0.00
b	[C4C1Im]Cl_FM_150_m60_180	150.9	-64.1	177.6	0.42
c	[C4C1Im]Cl_T_64_180_180	63.5	173.6	179.2	3.81
d	[C4C1Im]Cl_FB_70_60_180	70.8	58.7	173.0	4.35
e	[C4C1Im]Cl_FB_90_180_180	88.4	174.7	-179.1	6.82
f	[C4C1Im]Cl_T_34_60_180	34.0	61.9	178.5	7.53
g	[C4C1Im]Cl_T_105_90_m180	105.1	89.3	-177.5	10.59
h	[C4C1Im]Cl_BS_80_m180_180	79.9	-173.1	179.1	36.28
i	[C4C1Im]Cl_BS_100_m60_m180	102.0	-58.4	-173.0	36.74
j	[C4C1Im]Cl_BS_80_60_180	77.3	59.1	177.4	38.53
k	[C4C1Im]Cl_MS_70_60_180	67.7	60.0	178.1	41.38
l	[C4C1Im]Cl_MS_100_m60_m180	102.0	-58.4	-173.0	43.18
m	[C4C1Im]Cl_MS_75_m180_180	74.6	-179.8	179.9	44.77

[C_4C_1Im]I



a) [C_4C_1Im]I_T_90_m60_m180 b) [C_4C_1Im]I_T_55_180_180 c) [C_4C_1Im]I_T_25_65_180

d) [C_4C_1Im]I_T_105_85_180 e) [C_4C_1Im]I_BS_70_m180_180 f) [C_4C_1Im]I_BS_95_m60_m180

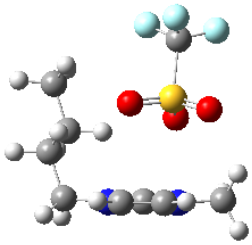
g) [C_4C_1Im]I_BS_70_60_180

Figure S5. $[C_4C_1Im]I$ conformers.

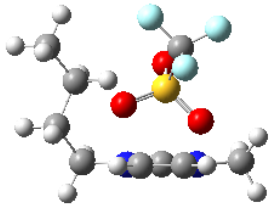
Table S4. $[C_4C_1Im]I$ conformers, dihedral angles $\boldsymbol{\tau_1}$, $\boldsymbol{\tau_2}$ and $\boldsymbol{\tau_3}$ and relative energies Δ*E* (kJ/mol).

No	Conformer	$\boldsymbol{\tau_1}[°]$	$\boldsymbol{\tau_2}[°]$	$\boldsymbol{\tau_3}[°]$	**Δ*E* [kJ mol^{-1}]**
a	[C_4C_1Im]I_T_90_m60_m180	92.1	-59.8	-179.3	0.00
b	[C_4C_1Im]I_T_55_180_180	55.4	171.8	179.4	3.70
c	[C_4C_1Im]I_T_25_65_180	24.3	64.4	180.0	6.20
d	[C_4C_1Im]I_T_105_85_180	107.1	85.1	178.9	10.24
e	[C_4C_1Im]I_BS_70_m180_180	72.7	-175.3	177.7	40.15
f	[C_4C_1Im]I_BS_95_m60_m180	97.1	-58.8	-174.5	42.83
g	[C_4C_1Im]I_BS_70_60_180	70.1	59.9	178.1	43.02

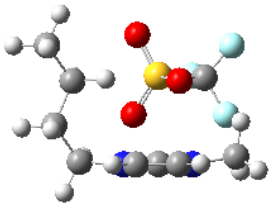
[C_4C_1Im][OTf]



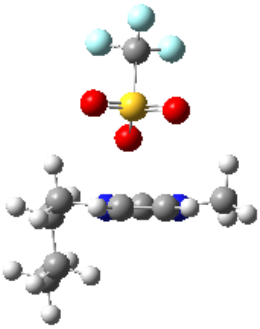
a) [C_4C_1Im]OTf_T_90_75_m180



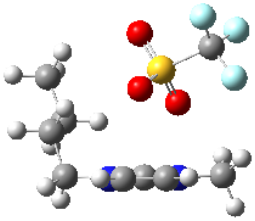
b) [C_4C_1Im]OTf_T_50_60_180



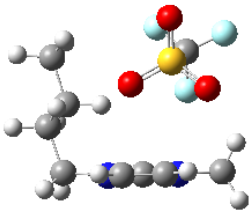
c) [C_4C_1Im]OTf_T_50_60_m180



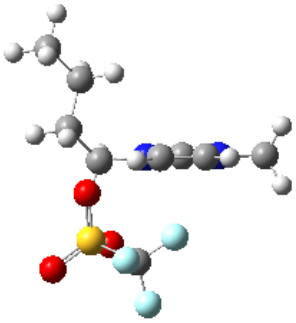
d) [C_4C_1Im]OTf_T_m160_60_180



e) [C_4C_1Im]OTf_T_100_80_180



f) [C_4C_1Im]OTf_T_90_70_m180



g) [C_4C_1Im]OTf_B_50_60_180

Figure S6. $[C_4C_1Im][OTf]$ conformers.

Table S5. $[C_4C_1Im][OTf]$ conformers, dihedral angles $\boldsymbol{\tau_1}$, $\boldsymbol{\tau_2}$ and $\boldsymbol{\tau_3}$ and relative energies Δ*E* (kJ/mol).

No.	Conformer	$\boldsymbol{\tau_1}[°]$	$\boldsymbol{\tau_2}[°]$	$\boldsymbol{\tau_3}[°]$	**Δ*E*** **[kJ mol^{-1}]**
a	[C4C1Im]OTf_T_90_75_m180	89.4	75.9	-177.4	0.00
b	[C4C1Im]OTf_T_50_60_180	47.7	59.7	176.7	0.52
c	[C4C1Im]OTf_T_50_60_m180	50.0	63.6	-178.6	2.08
d	[C4C1Im]OTf_T_m160_60_180	-161.8	64.1	179.0	5.25
e	[C4C1Im]OTf_T_100_80_180	100.5	82.1	177.1	6.36
f	[C4C1Im]OTf_T_90_70_m180	88.0	73.6	-176.8	11.13
g	[C4C1Im]OTf_B_50_60_180	49.5	60.3	178.8	36.71

Simple Salts

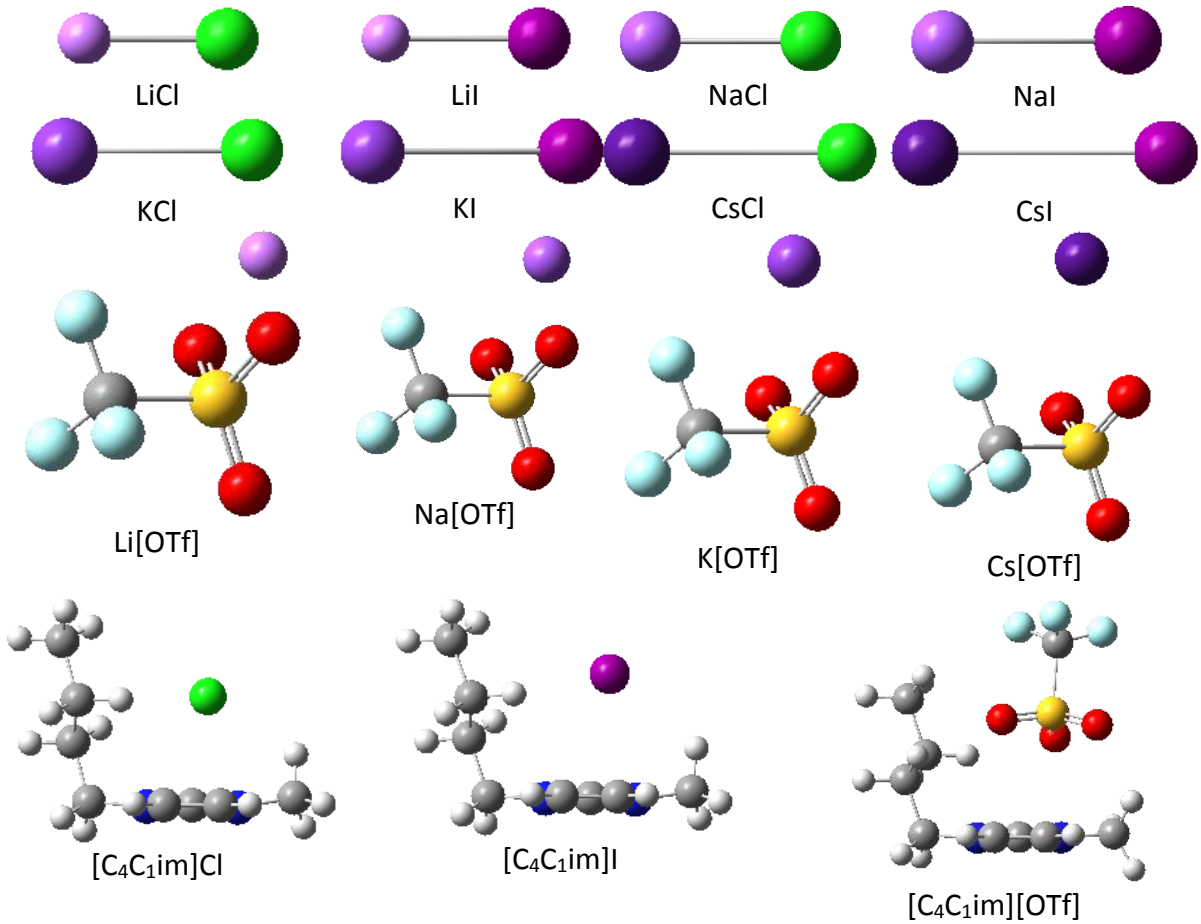


Figure S7. Structures of the simple salts, and most stable $[C_4C_1im][X]$ X=Cl-, I-, [OTf]- ion-pairs

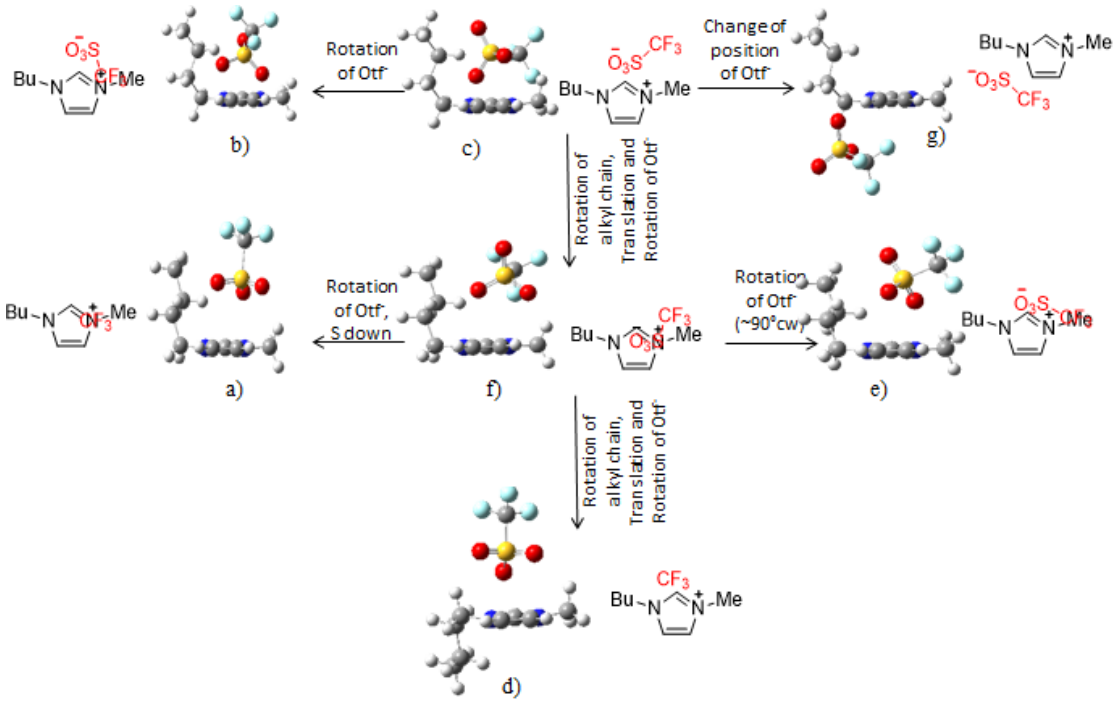
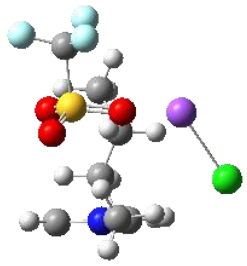


Figure S8. Structural correlation between the different conformers of $[C_4C_1Im][OTf]$.

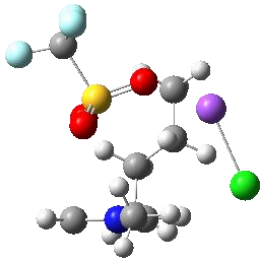
Table S6. Total energy of the simple salts and $[C_4C_1im][X]$ X=Cl-, I-, [OTf]- ion-pairs energies ΔE (Hartree).

MX	E [Hartree]	M[OTf]	E [Hartree]	$[C_4C_1im]X$	E [Hartree]
		LiOTf		$[C_4C_1im]Cl$	-883,779574301
LiCl	-467,83525435		-969,257353593		
		NaOTf	-1.124,025493530	$[C_4C_1im]I$	-434,948493582
LiI	-18,99148858				
		KOTf	-1.561,676162670	$[C_4C_1im]$ [OTf]	-1.385,20820655
NaCl	-622,60262877				
NaI	-173,76604145	CsOTf	-981,621304279		
KCl	-1.060,24956358				
KI	-611,41081551				
CsCl	-480,18804892				
CsI	-31,35037663				

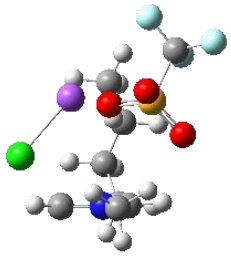
[C_4C_1Im][OTf][Na][Cl]



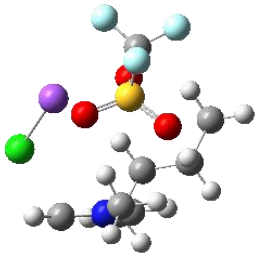
a
$[C_4C_1Im][OTf][Na][Cl]\_1\_F$



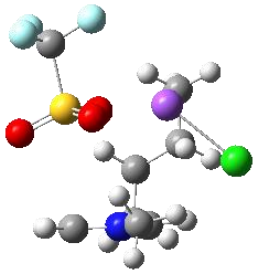
b
$[C_4C_1Im][OTf][Na][Cl]\_1\_F$



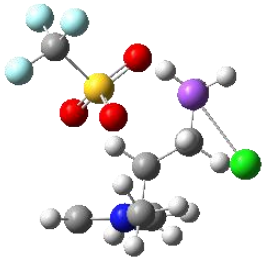
c
$[C_4C_1Im][OTf][Na][Cl]\_1\_MS$



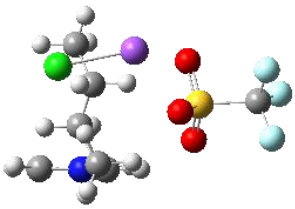
d
$[C_4C_1Im][OTf][Na][Cl]\_1\_B$



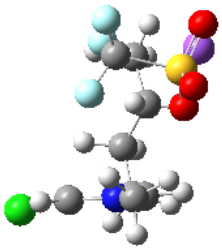
e
$[C_4C_1Im][OTf][Na][Cl]\_2\_F$



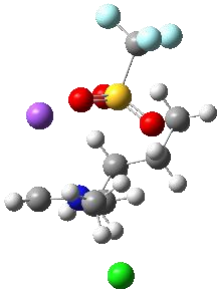
f
$[C_4C_1Im][OTf][Na][Cl]\_2\_F\_$



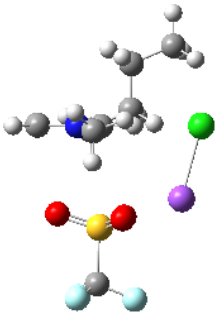
g
$[C_4C_1Im][OTf][Na][Cl]\_2\_T$
$\_1$



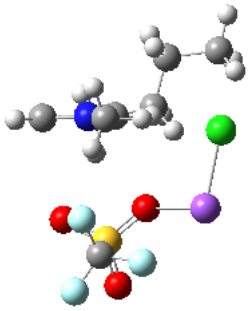
h $[C_4C_1Im][OTf][Na][Cl]$
$\_2\_BA\_1$



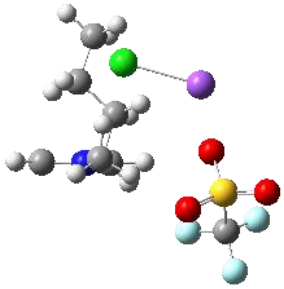
i
$[C_4C_1Im][OTf][Na][Cl]\_2\_BC$



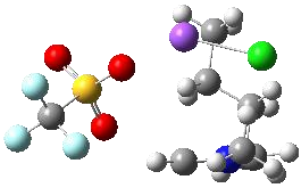
j
$[C_4C_1Im][OTf][Na][Cl]\_3\_F$



k
$[C_4C_1Im][OTf][Na][Cl]\_3\_F$

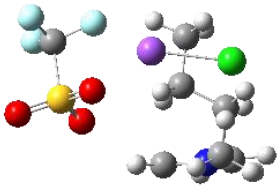


l
$[C_4C_1Im][OTf][Na][Cl]\_3\_T$
$\_1$



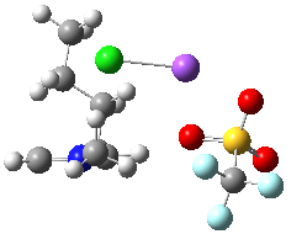
m

$[C_4C_1Im][OTf][Na][Cl]\_3\_T\_$



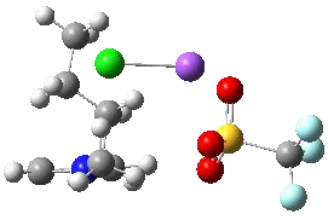
n

$[C_4C_1Im][OTf][Na][Cl]\_3\_T\_$



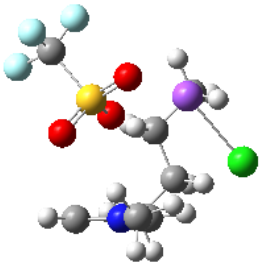
o

$[C_4C_1Im][OTf][Na][Cl]\_3\_T\_$



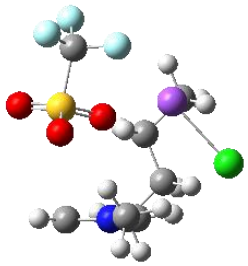
p

$[C_4C_1Im][OTf][Na][Cl]\_3\_T\_$



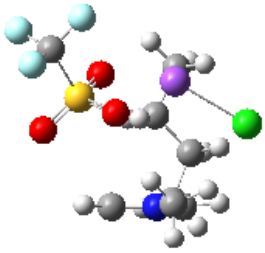
q

$[C_4C_1Im][OTf][Na][Cl]\_3\_F\_$



r

$[C_4C_1Im][OTf][Na][Cl]\_3\_F\_$



s

$[C_4C_1Im][OTf][Na][Cl]\_3\_F\_$

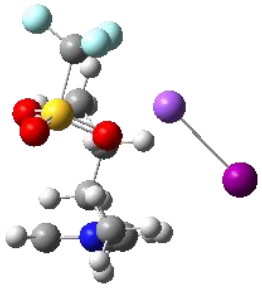
Figure S9. $[C_4C_1Im][OTf][Na][Cl]$ conformers.

Table S6. $[C_4C_1Im][OTf][Na][Cl]$ conformers, Na-Cl and Na-O(Tf) distances in Å and relative energies Δ*E* (kJ/mol).

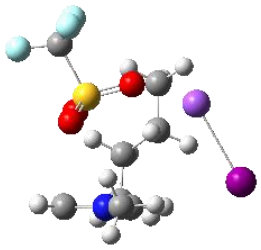
No.	Conformer	d(Cl^--Na^+) [Å]	d(Na^+-O-Tf^-) [Å]	Δ*E* [kJ/mol]
a	$[C_4C_1Im][OTf][Na][Cl]\_1\_F\_1$	2.50	2.15	9.26
b	$[C_4C_1Im][OTf][Na][Cl]\_1\_F\_2$	2.49	2.15	6.26
c	$[C_4C_1Im][OTf][Na][Cl]\_1\_MS\_1$	2.50	2.37/2.38	12.54
d	$[C_4C_1Im][OTf][Na][Cl]\_1\_BS\_1$	2.50	2.37/2.40	9.94
e*	$[C_4C_1Im][OTf][Na][Cl]\_2\_F\_1$	2.51	2.38/2.38	3.68
f	$[C_4C_1Im][OTf][Na][Cl]\_2\_F\_2$	2.51	2.34/2.39	0.00
g	$[C_4C_1Im][OTf][Na][Cl]\_2\_T\_1$	2.49	2.36/2.40	3.57
h	$[C_4C_1Im][OTf][Na][Cl]\_2\_BO\_1$	7.26	2.30/2.32	161.98
i	$[C_4C_1Im][OTf][Na][Cl]\_2\_BO\_2$	5.84	2.26/2.29	140.45
j	$[C_4C_1Im][OTf][Na][Cl]\_3\_F\_1$	2.51	2.36/2.37	2.56
k	$[C_4C_1Im][OTf][Na][Cl]\_3\_F\_2$	2.5	2.18	20.42
l	$[C_4C_1Im][OTf][Na][Cl]\_3\_T\_2$	2.48	2.16	26.39
m	$[C_4C_1Im][OTf][Na][Cl]\_3\_T\_3$	2.5	2.13	25.37
n	$[C_4C_1Im][OTf][Na][Cl]\_3\_T\_4$	2.51	2.22	25.78
o	$[C_4C_1Im][OTf][Na][Cl]\_3\_T\_5$	2.5	2.31/2.44	16.45
p	$[C_4C_1Im][OTf][Na][Cl]\_3\_T\_6$	2.5	2.34/2.40	6.10
q	$[C_4C_1Im][OTf][Na][Cl]\_3\_F\_3$	2.51	2.35/2.37	0.30
r	$[C_4C_1Im][OTf][Na][Cl]\_3\_F\_4$	2.5	2.19	12.51
s	$[C_4C_1Im][OTf][Na][Cl]\_3\_F\_5$	2.51	2.34/2.38	1.18

* imaginary frequency of 7.11 cm^{-1}

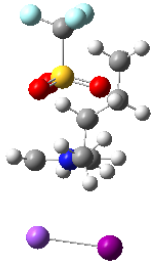
[C_4C_1Im][OTf][Na][I]



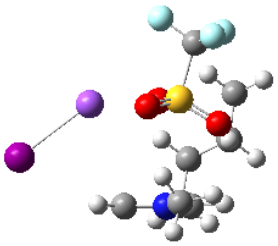
a $[C_4C_1Im][OTf][Na][I]\_1\_F\_1$



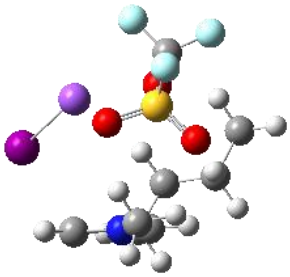
b
$[C_4C_1Im][OTf][Na][I]\_1\_F\_2$



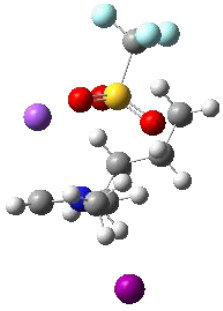
c
$[C_4C_1Im][OTf][Na][I]\_1\_BO\_1$



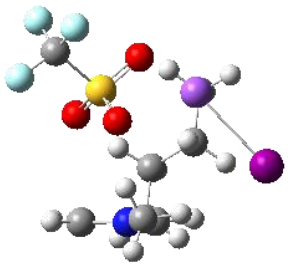
d
$[C_4C_1Im][OTf][Na][I]\_1\_BA\_1$



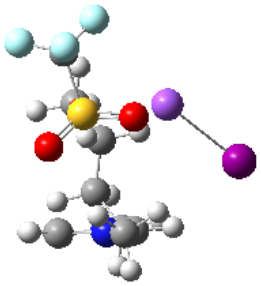
e
$[C_4C_1Im][OTf][Na][I]\_1\_BS\_1$



f
$[C_4C_1Im][OTf][Na][I]\_2\_BO\_1$



g
$[C_4C_1Im][OTf][Na][I]\_2\_F\_1\_1$



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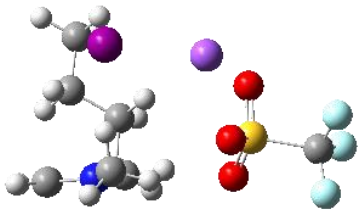
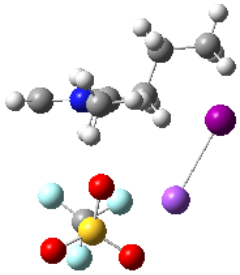
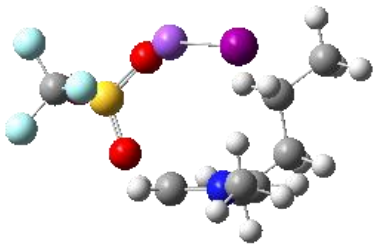
$[C_4C_1Im][OTf][Na][I]\_2\_F\_2$



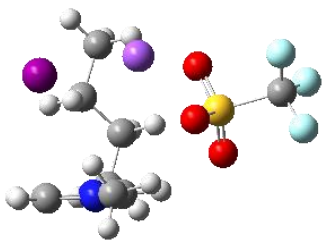
i $[C_4C_1Im][OTf][Na][I]\_3\_T\_1$



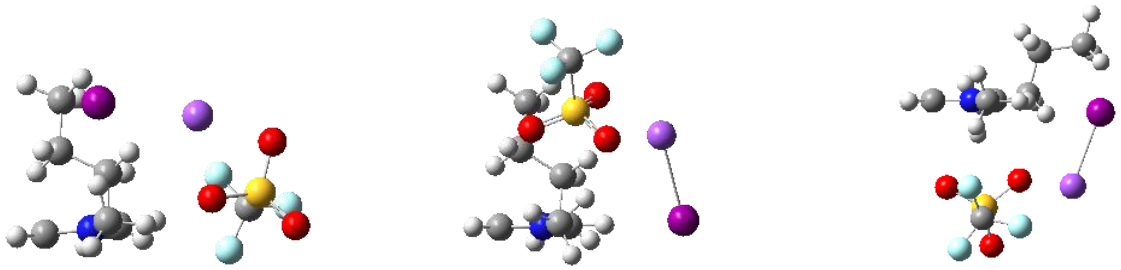
j $[C_4C_1Im][OTf][Na][I]\_3\_F\_1$



k
$[C_4C_1Im][OTf][Na][I]\_3\_T\_2$



l $[C_4C_1Im][OTf][Na][I]\_3\_T\_3$



m $[C_4C_1Im][OTf][Na][I]\_3\_T\_4$ **n** $[C_4C_1Im][OTf][Na][I]\_3\_F\_2$ **o** $[C_4C_1Im][OTf][Na][I]\_3\_F\_3$

Figure S10. $[C_4C_1Im][OTf][Na][I]$ conformers..

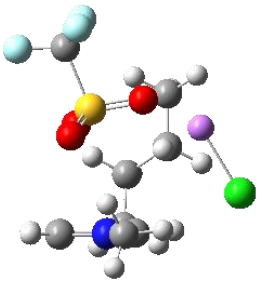
Table S7. $[C_4C_1Im][OTf][Na][I]$ conformers, Na-I and Na-O(Tf) distances in Å and relative energies Δ*E* (kJ/mol).

No.	Conformer	d(I^--Na^+) [Å]	d(Na^+-O-Tf^-) [Å]	Δ*E* [kJ/mol]
a	$[C_4C_1Im][OTf][Na][I]\_1\_F\_1$	2.87	2.17	12.12
b*	$[C_4C_1Im][OTf][Na][I]\_1\_F\_2$	2.85	2.12	11.51
c	$[C_4C_1Im][OTf][Na][I]\_1\_BO\_1$	2.78	5.93	139.59
d	$[C_4C_1Im][OTf][Na][I]\_1\_BA\_1$	2.85	2.35/2.39	11.51
e	$[C_4C_1Im][OTf][Na][I]\_1\_BS\_1$	2.86	2.35/2.37	8.45
f	$[C_4C_1Im][OTf][Na][I]\_2\_BO\_1$	6.26	2.25/2.28	126.7
g	$[C_4C_1Im][OTf][Na][I]\_2\_F\_1$	2.88	2.32/2.37	2.09
h†	$[C_4C_1Im][OTf][Na][I]\_2\_F\_2$	2.88	2.33/2.36	3.24
i	$[C_4C_1Im][OTf][Na][I]\_3\_T\_1$	2.87	2.31/2.38	2.35
j	$[C_4C_1Im][OTf][Na][I]\_3\_F\_1$	2.88	2.30/2.38	13.52
k	$[C_4C_1Im][OTf][Na][I]\_3\_T\_2$	2.86	2.19	29.15
l	$[C_4C_1Im][OTf][Na][I]\_3\_T\_3$	2.85	2.33/2.38	0.04
m	$[C_4C_1Im][OTf][Na][I]\_3\_T\_4$	2.87	2.31/2.39	8.01
n	$[C_4C_1Im][OTf][Na][I]\_3\_F\_2$	2.87	2.34/2.36	0.00
o	$[C_4C_1Im][OTf][Na][I]\_3\_F\_3$	2.86	2.18	21.32

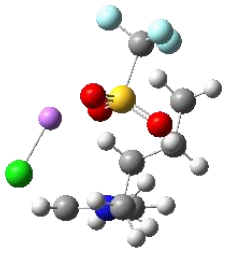
* imaginary frequency of 12.42 cm^{-1}

† imaginary frequency of 15.63 cm^{-1}

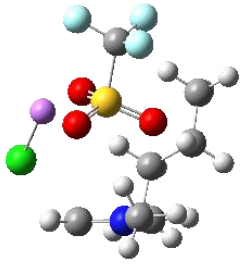
[C_4C_1Im][OTf][Li][Cl]



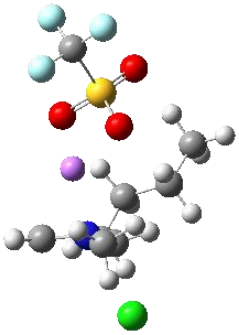
a $[C_4C_1Im][OTf][Li][Cl]$ _1_F_1



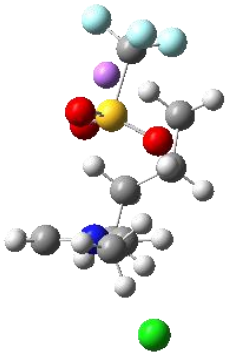
b $[C_4C_1Im][OTf][Li][Cl]$ _1_MS_1



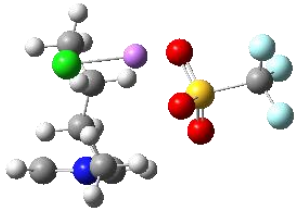
c $[C_4C_1Im][OTf][Li][Cl]$ _1_BS_1



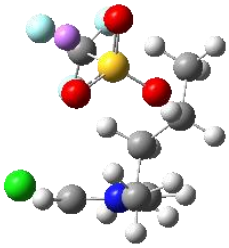
d $[C_4C_1Im][OTf][Li][Cl]$ _2_BO_1



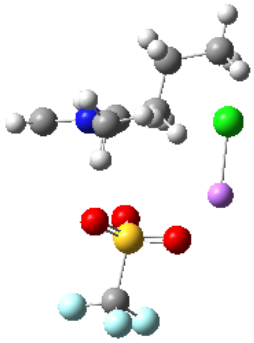
e $[C_4C_1Im][OTf][Li][Cl]$ _2_BO_2



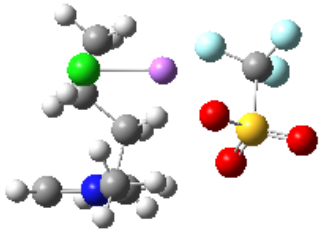
f $[C_4C_1Im][OTf][Li][Cl]$ _2_T_1



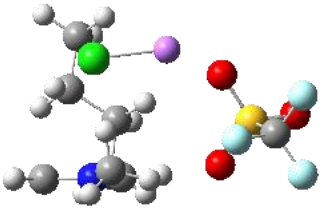
g $[C_4C_1Im][OTf][Li][Cl]$ _2_BS_1



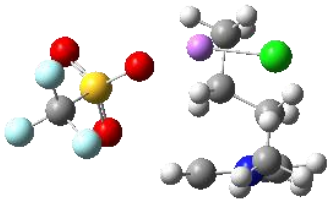
h $[C_4C_1Im][OTf][Li][Cl]$ _3_F_1



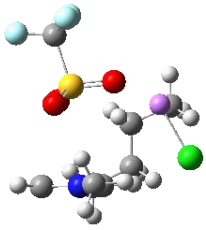
i $[C_4C_1Im][OTf][Li][Cl]$ _3_T_1



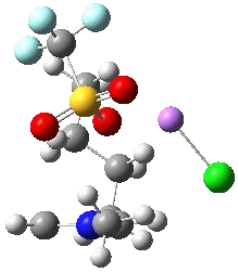
j $[C_4C_1Im][OTf][Li][Cl]$ 3_T_2



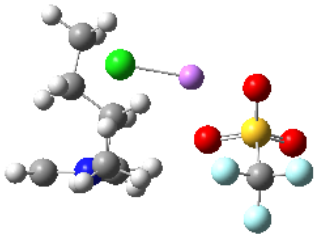
k $[C_4C_1Im][OTf][Li][Cl]$ _3_T_3



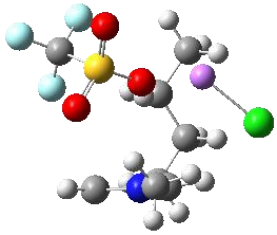
l $[C_4C_1Im][OTf][Li][Cl]$ _3_F_2



m $[C_4C_1Im][OTf][Li][Cl]$ _3_F_3



n $[C_4C_1Im][OTf][Li][Cl]$ _3_T_4



o $[C_4C_1Im][OTf][Li][Cl]$ _3_F_4

p $[C_4C_1Im][OTf][Li][Cl]$ _3_T_5

Figure S11. $[C_4C_1Im][OTf][Li][Cl]$ conformers.

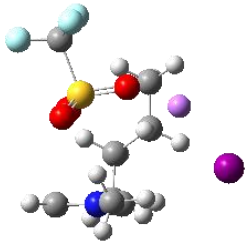
Table S8 $[C_4C_1Im][OTf][Li][Cl]$ conformers, Li-Cl and Li-O(Tf) distances in Å and relative energies Δ*E* (kJ/mol).

No.	Conformer	d(Cl^--Li^+) [Å]	d(Li^+-O-Tf^-) [Å]	Δ*E* [kJ/mol]
a	$[C_4C_1Im][OTf][Li][Cl]\_1\_F\_1$	2.13	1.79	2.48
b	$[C_4C_1Im][OTf][Li][Cl]\_1\_MS\_1$	2.12	1.79	28.85
c	$[C_4C_1Im][OTf][Li][Cl]\_1\_BS\_1$	2.13	1.8	30.53
d	$[C_4C_1Im][OTf][Li][Cl]\_2\_BO\_1$	4.67	1.93/1.94	334.72
e	$[C_4C_1Im][OTf][Li][Cl]\_2\_BO\_2$	7.97	1.78	484.26
f	$[C_4C_1Im][OTf][Li][Cl]\_2\_T\_1$	2.12	1.79	13.29
g	$[C_4C_1Im][OTf][Li][Cl]\_2\_BS$	8.24	1.89/1.91	461.20
h	$[C_4C_1Im][OTf][Li][Cl]\_3\_F\_1$	2.14	1.80	12.13
i	$[C_4C_1Im][OTf][Li][Cl]\_3\_T\_1$	2.12	1.86	39.23
j	$[C_4C_1Im][OTf][Li][Cl]\_3\_T\_2$	2.12	1.79	28.79
k	$[C_4C_1Im][OTf][Li][Cl]\_3\_T\_3$	2.14	1.77	48.92
l	$[C_4C_1Im][OTf][Li][Cl]\_3\_F$	2.14	1.78	11.14
m	$[C_4C_1Im][OTf][Li][Cl]\_3\_F\_3$	2.15	2.01/2.05	0.00
n	$[C_4C_1Im][OTf][Li][Cl]\_3\_F\_3$	2.13	1.79	21.44
o	$[C_4C_1Im][OTf][Li][Cl]\_3\_F\_4$	2.14	1.78	11.14
p	$[C_4C_1Im][OTf][Li][Cl]\_3\_T\_5$	2.16	2.00/2.03	5.72

* imaginary frequency of 21.50 cm^{-1}

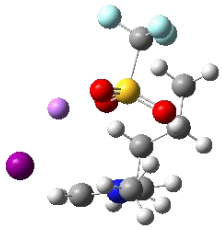
† imaginary frequency of 2.16 cm^{-1}

[C_4C_1Im][OTf][Li][I]



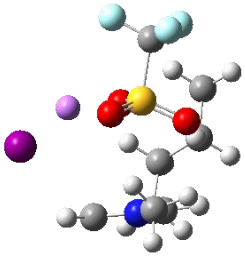
a

$[C_4C_1Im][OTf][Li][I]\_1\_F\_1$



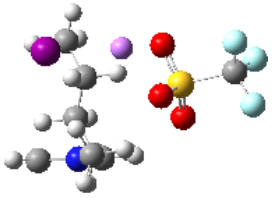
b

$[C_4C_1Im][OTf][Li][I]\_1\_MS\_1$



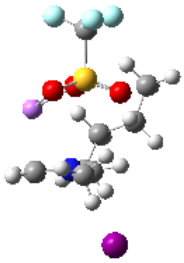
c

$[C_4C_1Im][OTf][Li][I]\_1\_BS\_1$



d

$[C_4C_1Im][OTf][Li][I]\_2\_T\_1$

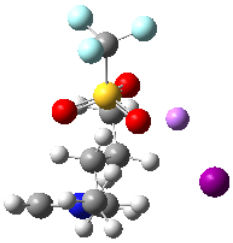


e

$[C_4C_1Im][OTf][Li][I]\_2\_BO\_1$

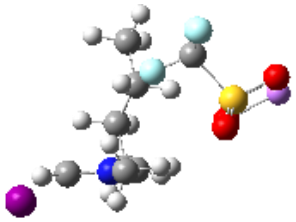
f

$[C_4C_1Im][OTf][Li][I]\_2\_F\_1$



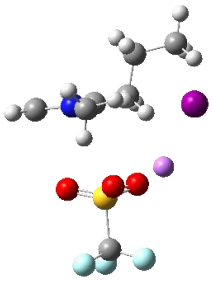
g

$[C_4C_1Im][OTf][Li][I]\_2\_F\_2$



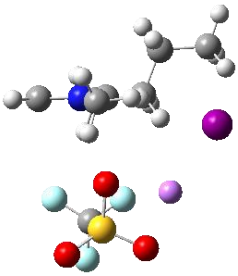
h

$[C_4C_1Im][OTf][Li][I]\_2\_BS\_1$



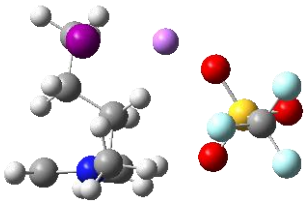
i

$[C_4C_1Im][OTf][Li][I]\_3\_F\_1$



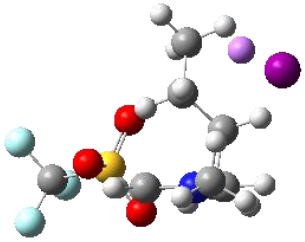
j

$[C_4C_1Im][OTf][Li][I]\_3\_F\_2$



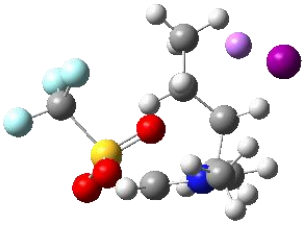
k

$[C_4C_1Im][OTf][Li][I]\_3\_T\_1$



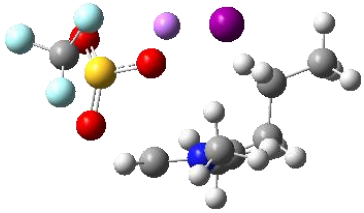
l

$[C_4C_1Im][OTf][Li][I]\_3\_T\_2$



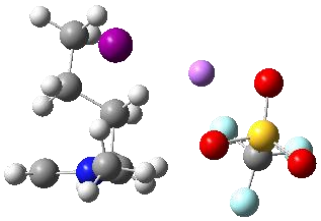
m

$[C_4C_1Im][OTf][Li][I]\_3\_T\_3$



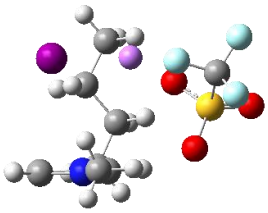
n

$[C_4C_1Im][OTf][Li][I]\_3\_T\_4$



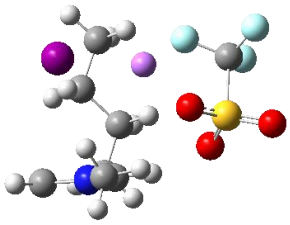
o

$[C_4C_1Im][OTf][Li][I]\_3\_T\_5$



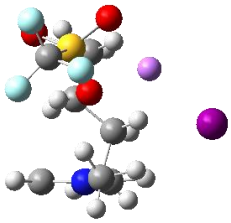
p

$[C_4C_1Im][OTf][Li][I]\_3\_T\_6$



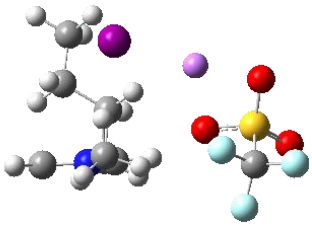
q

$[C_4C_1Im][OTf][Li][I]\_3\_T\_7$



r

$[C_4C_1Im][OTf][Li][I]\_3\_F\_3$



s

$[C_4C_1Im][OTf][Li][I]\_3\_T\_8$

Figure S12. $[C_4C_1Im][OTf][Li][I]$ conformers.

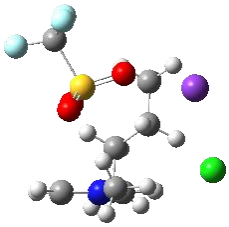
Table S9. $[C_4C_1Im][OTf][Li][I]$ conformers, Li-I and Li-O(Tf) distances in Å and relative energies Δ*E* (kJ/mol).

No.	Conformer	d(I^--Li^+) [Å]	d(Li^+-O-Tf^-) [Å]	Δ*E* [kJ/mol]
a	$[C_4C_1Im][OTf][Li][I]\_1\_F\_1$	2.51	1.77	3.35
b*	$[C_4C_1Im][OTf][Li][I]\_1\_MS\_1$	2.51	1.78	13.93
c	$[C_4C_1Im][OTf][Li][I]\_1\_BS\_1$	2.51	1.79	12.07
d	$[C_4C_1Im][OTf][Li][I]\_2\_T\_1$	2.53	2.00/2.04	0.00
e	$[C_4C_1Im][OTf][Li][I]\_2\_BO\_1$	5.93	1.90/1.93	126.21
f†	$[C_4C_1Im][OTf][Li][I]\_2\_F\_1$	2.54	2.00/2.01	4.57
g	$[C_4C_1Im][OTf][Li][I]\_2\_F\_2$	2.54	1.99/2.02	2.33
h	$[C_4C_1Im][OTf][Li][I]\_2\_BS\_1$	9.08	1.91/1.91	170.97
i	$[C_4C_1Im][OTf][Li][I]\_3\_F\_1$	2.55	1.99/2.02	0.13
j	$[C_4C_1Im][OTf][Li][I]\_3\_F\_2$	2.56	1.97/2.03	10.09
k	$[C_4C_1Im][OTf][Li][I]\_3\_T\_1$	2.5	1.78	10.31
l	$[C_4C_1Im][OTf][Li][I]\_3\_T\_2$	2.47	5.12	147.05
m	$[C_4C_1Im][OTf][Li][I]\_3\_T\_3$	2.47	5.01	147.70
n	$[C_4C_1Im][OTf][Li][I]\_3\_T\_4$	2.53	1.83	22.89
o	$[C_4C_1Im][OTf][Li][I]\_3\_T\_5$	2.55	1.97/2.05	5.21
p	$[C_4C_1Im][OTf][Li][I]\_3\_T\_6$	2.51	1.84	10.30
q	$[C_4C_1Im][OTf][Li][I]\_3\_T\_7$	2.54	1.99/2.00	3.68
r	$[C_4C_1Im][OTf][Li][I]\_3\_F\_3$	2.55	1.99/2.00	3.15
s	$[C_4C_1Im][OTf][Li][I]\_3\_T\_8$	2.55	1.96/2.06	7.78

* small imaginary frequency of 2.42 cm^{-1}

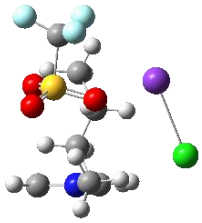
† imaginary frequency of 36.68 cm^{-1}

[C_4C_1Im][OTf][K][Cl]



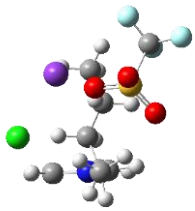
a

$[C_4C_1Im][OTf][K][Cl]\_1\_F\_1$



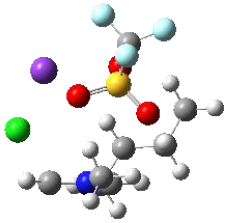
b

$[C_4C_1Im][OTf][K][Cl]\_1\_F\_$



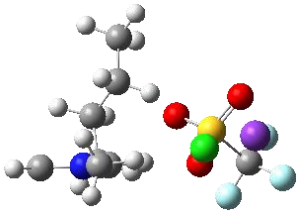
c

$[C_4C_1Im][OTf][K][Cl]\_1\_MS\_$



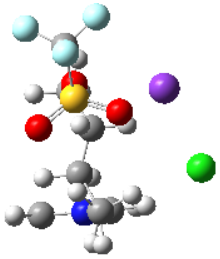
d

$[C_4C_1Im][OTf][K][Cl]\_1\_BS\_$



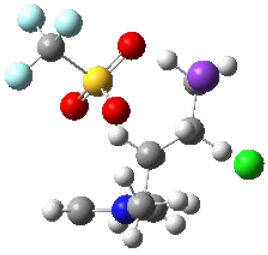
e

$[C_4C_1Im][OTf][K][Cl]\_2\_F\_$



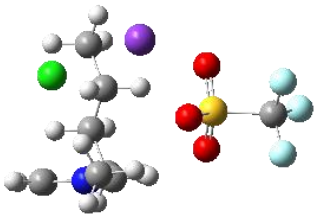
f

$[C_4C_1Im][OTf][K][Cl]\_2\_F\_2$



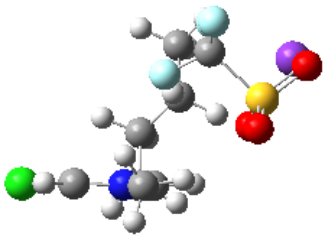
g

$[C_4C_1Im][OTf][K][Cl]\_2\_F\_3$



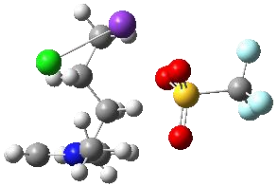
h

$[C_4C_1Im][OTf][K][Cl]\_2\_T\_$



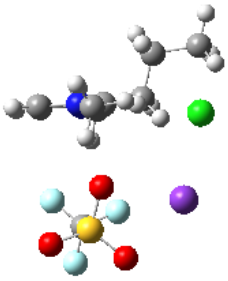
i

$[C_4C_1Im][OTf][K][Cl]\_2\_BS\_1$



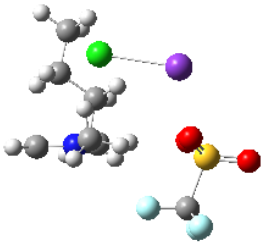
j

$[C_4C_1Im][OTf][K][Cl]\_3\_T\_1$



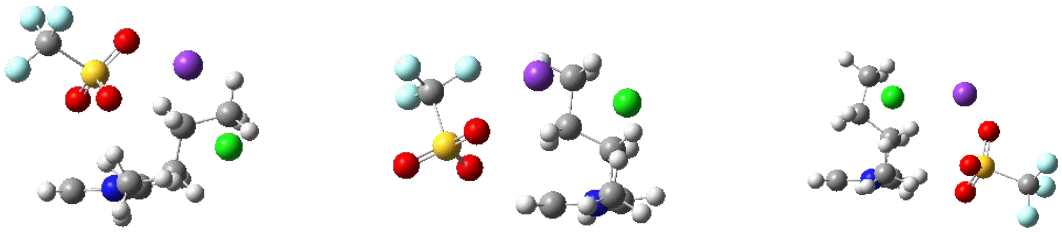
k

$[C_4C_1Im][OTf][K][Cl]\_3\_F\_$

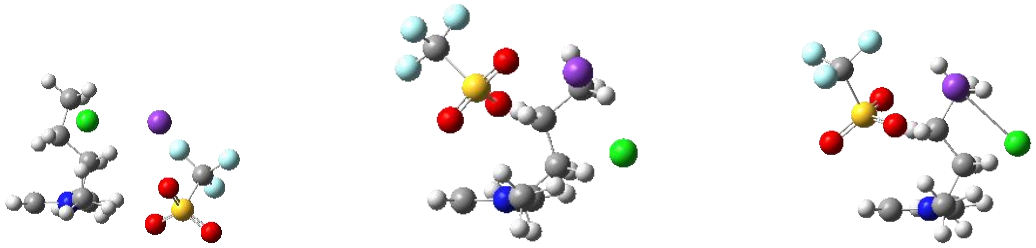


l

$[C_4C_1Im][OTf][K][Cl]\_3\_T\_2$



m $[C_4C_1Im][OTf][K][Cl]\_3\_F\_2$ **n** $[C_4C_1Im][OTf][K][Cl]\_3\_T\_$ **o** $[C_4C_1Im][OTf][K][Cl]\_3\_T\_4$



p $[C_4C_1Im][OTf][K][Cl]\_3\_T\_5$ **q** $[C_4C_1Im][OTf][K][Cl]\_3\_F\_$ **r** $[C_4C_1Im][OTf][K][Cl]\_3\_F\_4$

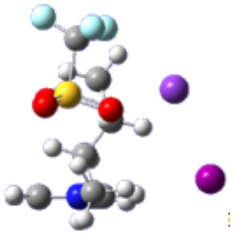
Figure S13. $[C_4C_1Im][OTf][K][Cl]$ conformers.

Table S10. $[C_4C_1Im][OTf][K][Cl]$ conformers, Na-I and Na-O(Tf) distances in Å and relative energies Δ*E* (kJ/mol).

No.	Conformer	d(Cl^--K^+) [Å]	d(K^+-O-Tf^-) [Å]	Δ*E* [kJ/mol]
a	$[C_4C_1Im][OTf][K][Cl]\_1\_F\_1$	2.85	2.48	8.27
b	$[C_4C_1Im][OTf][K][Cl]\_1\_F\_2$	2.86	2.52	9.42
c	$[C_4C_1Im][OTf][K][Cl]\_1\_MS\_1$	2.85	2.72/2.74	14.16
d	$[C_4C_1Im][OTf][K][Cl]\_1\_BS\_1$	2.86	2.72/2.77	11.33
e	$[C_4C_1Im][OTf][K][Cl]\_2\_F\_1$	2.88	2.70/2.71	16.68
f	$[C_4C_1Im][OTf][K][Cl]\_2\_F\_2$	2.88	2.69/2.75	2.16
g	$[C_4C_1Im][OTf][K][Cl]\_2\_F\_3$	2.88	2.71/2.73	0.34
h	$[C_4C_1Im][OTf][K][Cl]\_2\_T\_1$	2.85	2.73/2.74	5.29
i	$[C_4C_1Im][OTf][K][Cl]\_2\_BS\_1$	8.20	2.64/2.70	136.14
j	$[C_4C_1Im][OTf][K][Cl]\_3\_T\_1$	2.84	2.73/2.73	8.24
k	$[C_4C_1Im][OTf][K][Cl]\_3\_F\_1$	2.89	2.71/2.72	15.89
l	$[C_4C_1Im][OTf][K][Cl]\_3\_T\_2$	2.84	2.76/2.82	24.23

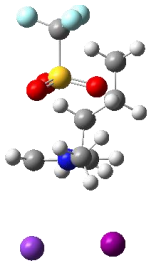
m	$[C_4C_1Im][OTf][K][Cl]\_3\_F\_2$	2.89	2.72/2.73	1.23
n	$[C_4C_1Im][OTf][K][Cl]\_3\_T\_3$	2.88	2.56	27.49
o	$[C_4C_1Im][OTf][K][Cl]\_3\_T\_4$	2.86	2.70/2.73	7.15
p	$[C_4C_1Im][OTf][K][Cl]\_3\_T\_5$	2.83	2.56	24.17
q	$[C_4C_1Im][OTf][K][Cl]\_3\_F\_3$	2.88	2.70/2.72	0.00
r	$[C_4C_1Im][OTf][K][Cl]\_3\_F\_4$	2.88	2.72/2.73	2.13

[C_4C_1Im][OTf][K][I]



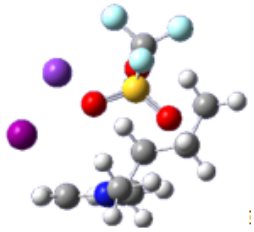
a

$[C_4C_1Im][OTf][K][I]\_1\_F\_1$



b

$[C_4C_1Im][OTf][K][I]\_1\_BO\_1$

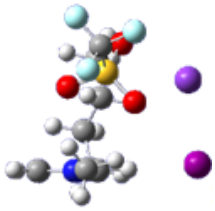


c

$[C_4C_1Im][OTf][K][I]\_1\_BS\_1$

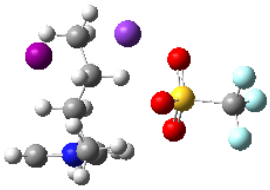
d

$[C_4C_1Im][OTf][K][I]\_2\_BO\_1$



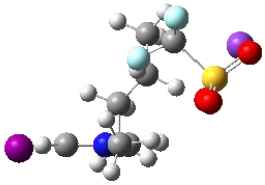
e

$[C_4C_1Im][OTf][K][I]\_2\_F\_1$



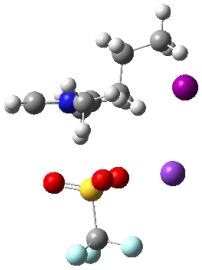
f

$[C_4C_1Im][OTf][K][I]\_2\_T\_1$



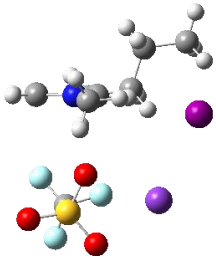
g

$[C_4C_1Im][OTf][K][I]\_2\_BS\_1$



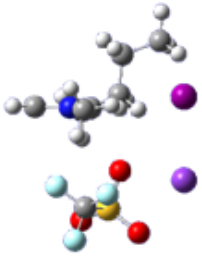
h

$[C_4C_1Im][OTf][K][I]\_3\_F\_1$



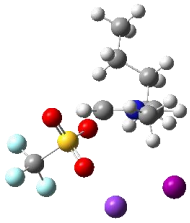
i

$[C_4C_1Im][OTf][K][I]\_3\_F\_2$



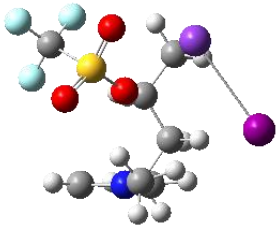
j

$[C_4C_1Im][OTf][K][I]\_3\_F\_3$



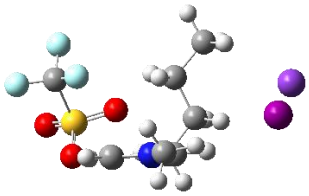
k

$[C_4C_1Im][OTf][K][I]\_3\_BO\_1$



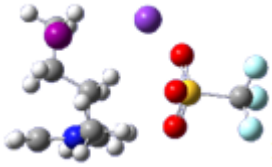
l

$[C_4C_1Im][OTf][K][I]\_3\_F\_4$



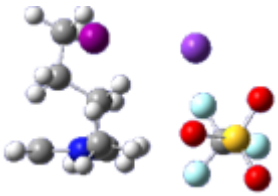
m

$[C_4C_1Im][OTf][K][I]\_3\_F\_5$



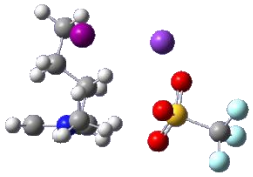
n

$[C_4C_1Im][OTf][K][I]\_3\_T\_1$



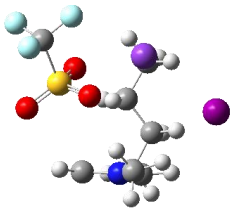
o

$[C_4C_1Im][OTf][K][I]\_3\_T\_2$



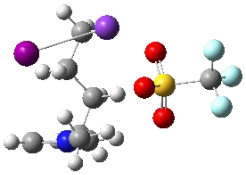
p

$[C_4C_1Im][OTf][K][I]\_3\_T\_4$



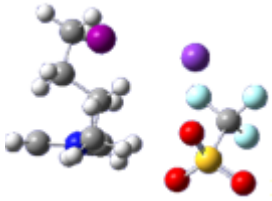
q

$[C_4C_1Im][OTf][K][I]\_3\_F\_6$



r

$[C_4C_1Im][OTf][K][I]\_3\_T\_6$



s

$[C_4C_1Im][OTf][K][I]\_3\_T\_7$

Figure S14. $[C_4C_1Im][OTf][K][I]$ conformers.

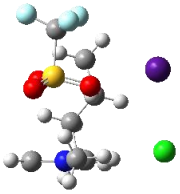
Table S11. $[C_4C_1Im][OTf][K][I]$ conformers, K-I and K-O(Tf) distances in Å and relative energies Δ*E* (kJ/mol).

No.	Conformer	d(I^--K^+) [Å]	d(K^+-O-Tf^-) [Å]	Δ*E* [kJ/mol]
a	$[C_4C_1Im][OTf][K][I]\_1\_F\_1$	3.27	2.51	9.12
b	$[C_4C_1Im][OTf][K][I]\_1\_BO\_$	3.14	6.69	128.75
c	$[C_4C_1Im][OTf][K][I]\_1\_BS\_1$	3.26	2.69/2.72	11.20
d*	$[C_4C_1Im][OTf][K][I]\_2\_BO\_1$	6.53	2.56/2.60	112.16
e	$[C_4C_1Im][OTf][K][I]\_2\_F\_1$	3.27	2.64/2.71	3.69
f	$[C_4C_1Im][OTf][K][I]\_2\_T\_1$	3.25	2.69/2.71	1.52
g	$[C_4C_1Im][OTf][K][I]\_2\_BS\_1$	8.62	2.63/2.67	124.22
h	$[C_4C_1Im][OTf][K][I]\_3\_F\_1$	3.27	2.69/2.71	3.56
i	$[C_4C_1Im][OTf][K][I]\_3\_F\_2$	3.29	2.67/2.69	17.34
j	$[C_4C_1Im][OTf][K][I]\_3\_F\_3$	3.29	2.67/2.70	13.67
k	$[C_4C_1Im][OTf][K][I]\_3\_BO\_1$	3.26	2.43	33.88
l	$[C_4C_1Im][OTf][K][I]\_3\_F\_4$	3.29	2.61/2.75	0.00
m	$[C_4C_1Im][OTf][K][I]\_3\_F\_5$	3.19	6.32	133.94
n†	$[C_4C_1Im][OTf][K][I]\_3\_T\_1$	3.24	2.67/2.70	5.96
o	$[C_4C_1Im][OTf][K][I]\_3\_T\_2$	3.27	2.67/2.72	11.17
p	$[C_4C_1Im][OTf][K][I]\_3\_T\_4$	3.26	2.66/2.70	4.53
q	$[C_4C_1Im][OTf][K][I]\_3\_F\_6$	3.29	2.69/2.69	2.06
r	$[C_4C_1Im][OTf][K][I]\_3\_T\_6$	3.24	2.69/2.71	2.41
s	$[C_4C_1Im][OTf][K][I]\_3\_T\_7$	3.24	2.54	19.46

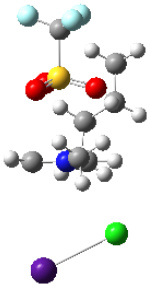
* imaginary frequency of 10.95 cm^{-1}

† imaginary frequency of 20.63 cm^{-1}

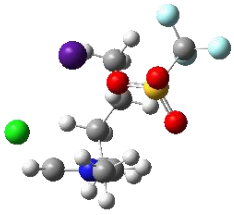
[C_4C_1Im][OTf][Cs][Cl]



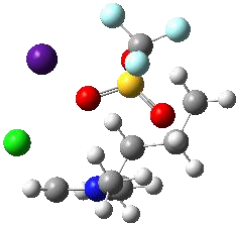
a
$[C_4C_1Im][OTf][Cs][Cl]\_1\_F\_1$



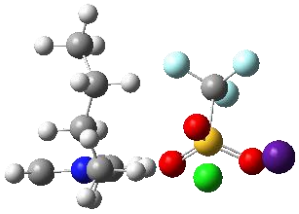
b
$[C_4C_1Im][OTf][Cs][Cl]\_1\_BO\_1$



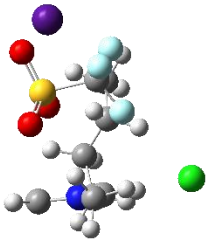
c
$[C_4C_1Im][OTf][Cs][Cl]\_1\_MS\_1$



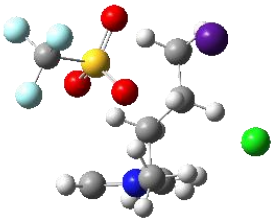
d
$[C_4C_1Im][OTf][Cs][Cl]\_1\_BS\_1$



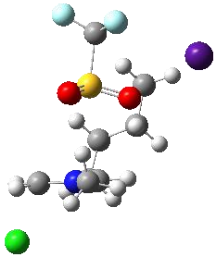
e
$[C_4C_1Im][OTf][Cs][Cl]\_2\_F\_1$



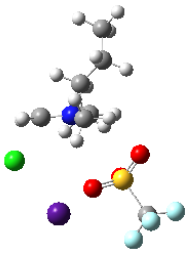
f $[C_4C_1Im][OTf][Cs][Cl]\_2\_F\_2$



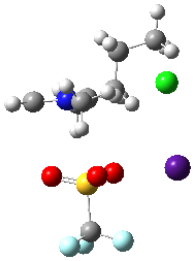
g
$[C_4C_1Im][OTf][Cs][Cl]\_2\_F\_3$



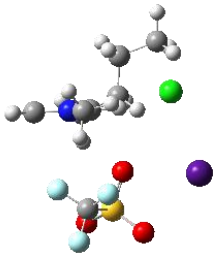
h
$[C_4C_1Im][OTf][Cs][Cl]\_2\_BO\_1$



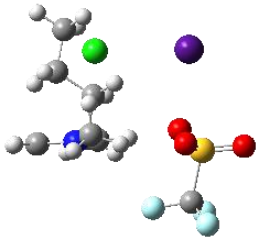
i
$[C_4C_1Im][OTf][Cs][Cl]\_2\_BO\_2$



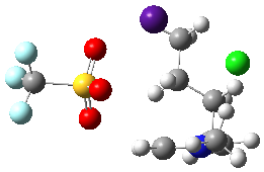
j $[C_4C_1Im][OTf][Cs][Cl]\_3\_F\_1$



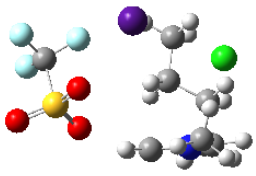
k $[C_4C_1Im][OTf][Cs][Cl]\_3\_F\_2$

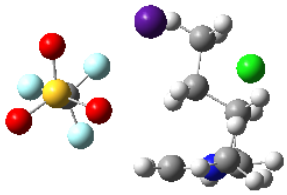


l $[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_1$



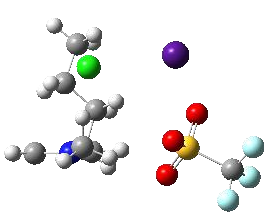
m
$[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_2$



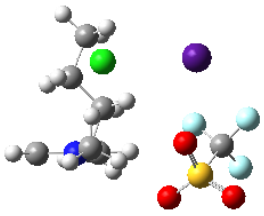


o $[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_4$

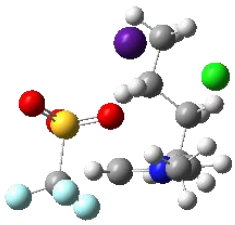
n
$[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_3$



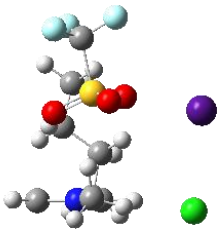
p
$[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_5$



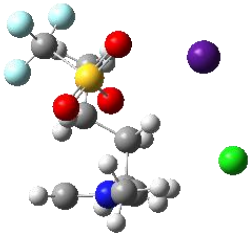
q
$[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_6$



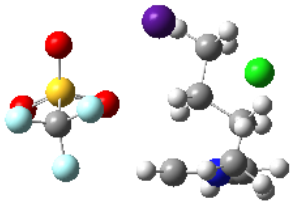
r $[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_7$



s
$[C_4C_1Im][OTf][Cs][Cl]\_3\_F\_3$



t $[C_4C_1Im][OTf][Cs][Cl]\_3\_F\_4$



u $[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_8$

Figure S15. $[C_4C_1Im][OTf][Cs][Cl]$ conformers.

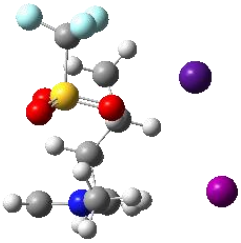
Table S12. $[C_4C_1Im][OTf][Cs][Cl]$ conformers, Cs-Cl and Cs-O(Tf) distances in Å and relative energies Δ*E* (kJ/mol).

No.	Conformer	d(Cl^--Cs^+) [Å]	d(Cs^+-O-Tf^-) [Å]	Δ*E* [kJ/mol]
a	$[C_4C_1Im][OTf][Cs][Cl]\_1\_F\_1$	3.37	2.94	6.78
b	$[C_4C_1Im][OTf][Cs][Cl]\_1\_BO\_1$	3.26	7.11	111.31
c	$[C_4C_1Im][OTf][Cs][Cl]\_1\_MS\_1$	3.36	3.14/3.16	13.69
d	$[C_4C_1Im][OTf][Cs][Cl]\_1\_BS\_1$	3.37	3.14/3.20	11.18
e[1]	$[C_4C_1Im][OTf][Cs][Cl]\_2\_F\_1$	3.37	3.09/3.16	19.18
f	$[C_4C_1Im][OTf][Cs][Cl]\_2\_F\_2$	6.97	3.08/3.12	90.65
g	$[C_4C_1Im][OTf][Cs][Cl]\_2\_F\_3$	3.39	3.09/3.22	1.52
h[2]	$[C_4C_1Im][OTf][Cs][Cl]\_2\_BO\_1$	9.54	2.89	169.42
i	$[C_4C_1Im][OTf][Cs][Cl]\_2\_BO\_2$	3.37	3.15/3.23	14.46
j	$[C_4C_1Im][OTf][Cs][Cl]\_3\_F\_1$	3.36	3.13/3.19	6.44
k	$[C_4C_1Im][OTf][Cs][Cl]\_3\_F\_2$	3.38	3.12/3.15	15.18
l	$[C_4C_1Im][OTf][Cs][Cl]\_3\_T$	3.35	3.28/3.36	23.33
m	$[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_2$	3.39	3.11/3.17	13.26
n	$[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_3$	3.38	2.97	27.70
o[3]	$[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_4$	3.41	3.15/3.16	27.49
p	$[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_5$	3.36	3.11/3.16	11.00
q[4]	$[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_6$	3.34	2.96	24.09
r	$[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_7$	3.38	3.16/3.30	28.43
s	$[C_4C_1Im][OTf][Cs][Cl]\_3\_F\_3$	3.36	3.12/3.15	1.27
t[5]	$[C_4C_1Im][OTf][Cs][Cl]\_3\_F\_4$	3.38	3.12/3.16	0.00
u	$[C_4C_1Im][OTf][Cs][Cl]\_3\_T\_8$	3.41	3.10/3.21	26.90

[1] imaginary frequency of 7.11 cm^{-1}
[2] imaginary frequency of 10.07 cm^{-1}
[3] imaginary frequency of 15.02 cm^{-1}
[4] imaginary frequency of 2.49 cm^{-1}

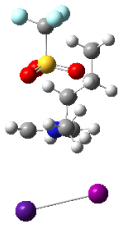
[5] imaginary frequency of 4.20 cm^{-1}

[C_4C_1Im][OTf][Cs][I]



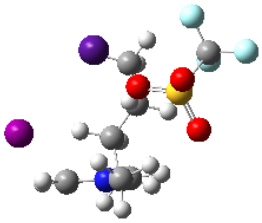
a

$[C_4C_1Im][OTf][Cs][I]\_1\_F\_1$



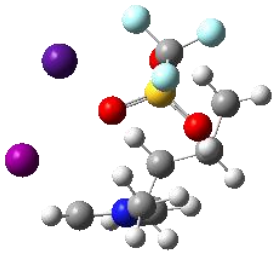
b

$[C_4C_1Im][OTf][Cs][I]\_1\_BO\_$



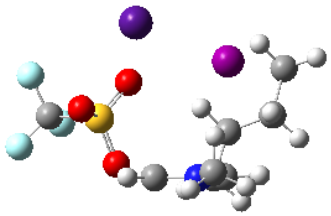
c

$[C_4C_1Im][OTf][Cs][I]\_1\_MS\_$



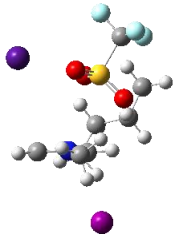
d

$[C_4C_1Im][OTf][Cs][I]\_1\_BS\_$



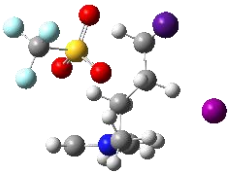
e

$[C_4C_1Im][OTf][Cs][I]\_2\_T\_1$



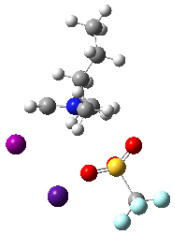
f

$[C_4C_1Im][OTf][Cs][I]\_2\_BO\_$



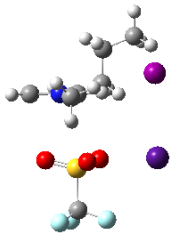
g

$[C_4C_1Im][OTf][Cs][I]\_2\_F\_1$



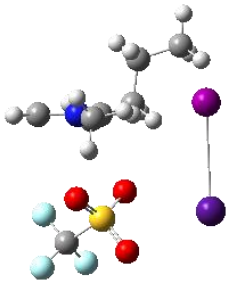
h

$[C_4C_1Im][OTf][Cs][I]\_2\_BO\_$



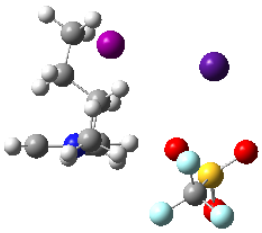
i

$[C_4C_1Im][OTf][Cs][I]\_3\_F\_1$



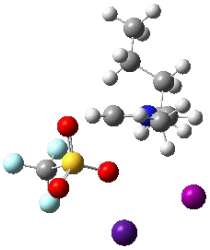
j

$[C_4C_1Im][OTf][Cs][I]\_3\_F\_2$



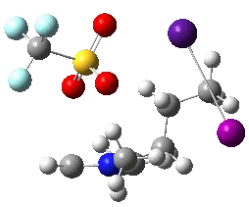
k

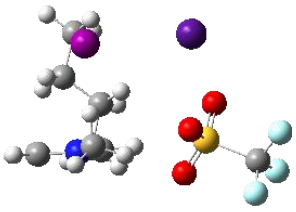
$[C_4C_1Im][OTf][Cs][I]\_3\_T\_1$

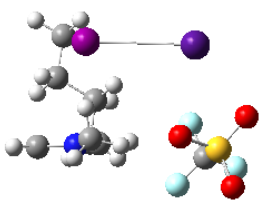


l

$[C_4C_1Im][OTf][Cs][I]\_3\_BO\_$

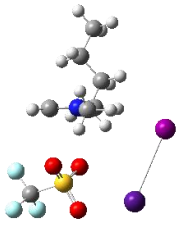






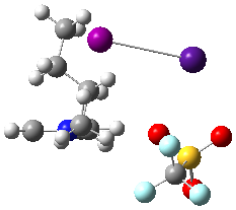
m

$[C_4C_1Im][OTf][Cs][I]\_3\_F\_3$



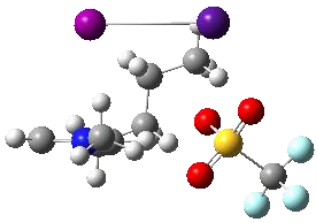
n

$[C_4C_1Im][OTf][Cs][I]\_3\_T\_2$



p

$[C_4C_1Im][OTf][Cs][I]\_3\_T\_3$



q

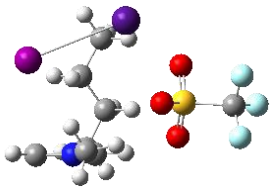
$[C_4C_1Im][OTf][Cs][I]\_3\_F\_4$

r

$[C_4C_1Im][OTf][Cs][I]\_3\_T\_4$

s

$[C_4C_1Im][OTf][Cs][I]\_3\_T\_5$



t

$[C_4C_1Im][OTf][Cs][I]\_3\_T\_6$

Figure S16. $[C_4C_1Im][OTf][Cs][I]$ conformers.

Table S13. $[C_4C_1Im][OTf][Cs][I]$ conformers, Cs-I and Cs-O(Tf) distances in Å and relative energies Δ*E* (kJ/mol).

No.	Conformer	d(I^--Cs^+) [Å]	d(Cs^+-O-Tf^-) [Å]	Δ*E* [kJ/mol]
a	$[C_4C_1Im][OTf][Cs][I]\_1\_F\_1$	3.78	2.94	6.48
b[1]	$[C_4C_1Im][OTf][Cs][I]\_1\_BO\_2$	3.67	6.69	112.68
c	$[C_4C_1Im][OTf][Cs][I]\_1\_MS\_1$	3.76	3.13/3.16	14.37
d	$[C_4C_1Im][OTf][Cs][I]\_1\_BS\_1$	3.78	3.13/3.17	9.89
e	$[C_4C_1Im][OTf][Cs][I]\_2\_T\_1$	3.78	3.11/3.13	15.98
f	$[C_4C_1Im][OTf][Cs][I]\_2\_BO\_1$	7.85	3.01/3.04	101.39
g	$[C_4C_1Im][OTf][Cs][I]\_2\_F\_1$	3.80	3.10/3.18	0.00
h[2]	$[C_4C_1Im][OTf][Cs][I]\_2\_BO\_2$	3.78	3.14/3.22	13.63
i[3]	$[C_4C_1Im][OTf][Cs][I]\_3\_F\_1$	3.77	3.14/3.17	6.39
j	$[C_4C_1Im][OTf][Cs][I]\_3\_F\_2$	3.78	3.12/3.15	7.76
k[4]	$[C_4C_1Im][OTf][Cs][I]\_3\_T\_1$	3.79	3.10/3.16	13.14
l	$[C_4C_1Im][OTf][Cs][I]\_3\_BO\_1$	3.79	3.12/3.13	14.11
m	$[C_4C_1Im][OTf][Cs][I]\_3\_F\_3$	3.82	3.12/3.16	0.37
n	$[C_4C_1Im][OTf][Cs][I]\_3\_T\_2$	3.77	3.11/3.15	4.79
o	$[C_4C_1Im][OTf][Cs][I]\_3\_T\_3$	3.77	3.09/3.18	13.79
p	$[C_4C_1Im][OTf][Cs][I]\_3\_F\_4$	3.80	3.08/3.17	14.81
q	$[C_4C_1Im][OTf][Cs][I]\_3\_T\_4$	3.79	3.10/3.16	13.14
r[5]	$[C_4C_1Im][OTf][Cs][I]\_3\_T\_5$	3.77	3.14/3.16	7.92
s	$[C_4C_1Im][OTf][Cs][I]\_3\_T\_6$	3.74	3.12/3.17	3.42

[1] imaginary frequency of 8.29 cm^{-1}
[2] imaginary frequency of 7.57 cm^{-1}
[3] imaginary frequency of 5.74 cm^{-1}
[4] imaginary frequency of 3.62 cm^{-1}
[5] imaginary frequency of 3.54 cm^{-1}

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