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

Supporting Information for

Molecular Simulation of Imidazolium-Based Tricyanomethanide Ionic Liquids using an Optimized Classical Force Field

Niki Vergadou, Eleni Androulaki, Jörg-Rüdiger Hill and Ioannis G. Economou

Table S1: Charge distributions for [$C_n$mim$^+$] cations as calculated from RI-MP2 method on isolated ions (atom labels and corresponding numbering are given to Figure S1).

Atom	**[C_2mim$^+$]**	**Atom**	**[C_4mim$^+$]**	**[C_6mim$^+$]**	**[C_8mim$^+$]**
NR2	0.1131	NR2	0.1110	0.1019	0.0969
CPH2	0.0116	CPH2	0.0054	0.0116	0.0190
NR1	0.1142	NR1	0.1124	0.1109	0.1092
CPH1	0.0075	CPH1	0.0025	0.0085	0.0097
CPH1	0.0258	CPH1	0.0353	0.0402	0.0447
HR1	0.1047	HR1	0.1030	0.0995	0.0945
HR3	0.0844	HR3	0.0808	0.0752	0.0731
HR3	0.0698	HR3	0.0604	0.0540	0.0488
CN7B	0.4203	CN7B	0.4505	0.4801	0.4968

HA	-0.0761	HA	-0.0896	-0.1019	-0.1096
HA	-0.0565	HA	-0.0686	-0.0780	-0.0839
HA	-0.0661	HA	-0.0781	-0.0895	-0.0956
CN7B	0.3356	CN7B	0.3270	0.3305	0.3323
HA	-0.0700	HA	-0.0656	-0.0703	-0.0517
HA	-0.0481	HA	-0.0448	-0.0503	-0.0727
CT1	0.1945	CT2	0.0903	0.0821	0.0913
HA	-0.0473	HA	-0.0382	-0.0658	-0.0689
HA	-0.0760	HA	-0.0667	-0.0375	-0.0413
HA	-0.0414	CT2		0.2373	0.2300
		HA		-0.0839	-0.0850
		HA		-0.0827	-0.0837
		CT2		0.1708	0.1625
		HA		-0.0740	-0.0714
		HA		-0.0772	-0.0752
		CT2			0.1989
		HA			-0.0848
		HA			-0.0835
		CT2			0.1901
		HA			-0.0873

	HA			-0.0879
	CT2	0.2489	0.2118	0.2235
	HA	-0.0927	-0.0975	-0.1068
	HA	-0.0933	-0.0956	-0.1048
	CT3	0.3018	0.3441	0.3566
	HA	-0.0997	-0.1223	-0.1343
	HA	-0.0973	-0.1158	-0.1238
	HA	-0.0947	-0.1162	-0.1257

Table S2: Charges for the [TCM^-] anion calculated from an isolated ion and averaged over multiple ion pair conformations (atom labels are given to Figure S2).

Atom	**Charge for isolated ion**	**Average charge**	**Standard deviation**
CCM	-0.5110	-0.4903	0.0095
CN	0.5653	0.4690	0.0100
CN	0.5668	0.4872	0.0046
CN	0.5654	0.4845	0.0166
NC	-0.7292	-0.5625	0.0176
NC	-0.7287	-0.5507	0.0129
NC	-0.7286	-0.5727	0.0110
Total	**-1.0000**	**-0.7355**	

Table S3: Charges for the [C_4mim^+] cation calculated as isolated ion and averaged over multiple ion pair conformations

Atom	Charge for isolated ion	Average charge	Standard deviation
NR2	0.1110	0.1664	0.0320
CPH2	0.0054	-0.0849	0.0383
NR1	0.1124	0.1632	0.0557
CPH1	0.0025	0.0032	0.0575
CPH1	0.0353	0.0069	0.0382
HR1	0.1030	0.1326	0.0110
HR3	0.0808	0.0423	0.0402
HR3	0.0604	0.0348	0.0205
CN7B	0.4505	0.4601	0.0368
HA	-0.0896	-0.1643	0.0414
HA	-0.0686	-0.1301	0.0734
HA	-0.0781	-0.0270	0.0035
CN7B	0.3270	0.2498	0.1307
HA	-0.0656	0.0170	0.0364
HA	-0.0448	-0.0796	0.0957
CT2	0.0903	0.1861	0.0721
HA	-0.0382	-0.0802	0.0504
HA	-0.0667	-0.1106	0.0251
CT2	0.2489	0.2262	0.1532
HA	-0.0933	-0.0988	0.0758
HA	-0.0927	-0.1239	0.0482

CT3	0.3018	0.4702	0.1075
HA	-0.0973	-0.1566	0.0368
HA	-0.0947	-0.1748	0.0317
HA	-0.0997	-0.1925	0.0198
Total	**1.0000**	**0.7355**	

Table S4. Force field parameters for [TCM$^-$]

Optimized Lennard-Jones parameters for [TCM$^-$] anion (Note that: $R_{mim} = \sigma\sqrt[6]{2}$).

Atom	ε (kcal/mol)	$R_{min}/2$ (Å)
CCM	0.024	1.99
CN	0.130	1.75
NC	0.390	1.72

Partial Atomic Charges (e$^-$) for [TCM$^-$] from isolated ions uniformly scaled to ±0.75e$^-$.

CCM	-0.3832275
CN	0.42438075
NC	-0.54663825

Force constants - [TCM$^-$] (Parameters from Ref. 58)

Bonds

Atom 1	Atom 2	K_b (kcal mol^{-1} Å^{-2})	b_o (Å)
CCM	CN	430.00	1.408
CN	NC	1210.0	1.167

Angles

Atom 1	Atom 2	Atom 3	K_θ (kcal mol^{-1} rad^{-2})	θ_o (deg)
NC	CN	CCM	30.0	179.99
CN	CCM	CN	44.0	120.00

Dihedral Angles

Atom 1	Atom 2	Atom 3	Atom 4	k_χ (kcal mol^{-1})	n	δ (deg)
NC	CN	CCM	CN	0.00	2	180

Improper Angles

Atom 1	Atom 2	Atom 3	Atom 4	k_ψ (kcal mol^{-1} rad^{-2})	Ψ_o (deg)
CCM	CN	CN	NC	26.7	0

Table S5. Force field parameters for [C_2mim$^+$], [C_4mim$^+$]

Bonds

Atom 1	Atom 2	K_b (kcal mol^{-1} Å^{-2})	b_o (Å)
CN7B	NR1	220.00	1.4762
CN7B	NR2	220.00	1.4762
CPH1	NR1	400.00	1.3819
CPH1	NR2	400.00	1.3819
CPH2	NR1	400.00	1.3366
CPH2	NR2	400.00	1.3366
CPH1	CPH1	410.00	1.3610
CPH2	HR1	340.00	1.0779

CPH1	HR3	365.00	1.0775
CN7B	HA	309.00	1.0889
CT2	HA	309.00	1.0954
CT3	HA	322.00	1.0935
CN7B	CT2	200.00	1.5308
CT2	CT2	222.50	1.5373
CT2	CT3	222.50	1.5314
CT1	CN7B	200.00	1.5240
CT1	HA	322.00	1.0893

Angles

Atom 1	**Atom 2**	**Atom 3**	**K_θ (kcal mol^{-1} rad^{-2})**	**θ_o (deg)**
CT2	CN7B	NR1	140.00	112.34
CPH1	NR1	CPH2	130.00	108.25
CPH1	NR2	CPH2	130.00	108.25
HA	CN7B	NR1	30.00	109.41
HA	CN7B	NR2	30.00	109.41
HR1	CPH2	NR1	25.00	125.44
HR1	CPH2	NR2	25.00	125.44
NR1	CPH1	CPH1	130.00	107.28
NR2	CPH1	CPH1	130.00	107.28
NR1	CPH2	NR2	130.00	109.11
HR3	CPH1	CPH1	25.00	130.74
NR2	CPH1	HR3	25.00	122.04
NR1	CPH1	HR3	25.00	122.04
HA	CN7B	HA	35.50	108.44
HA	CN7B	CT2	33.40	111.68
HA	CT2	CN7B	33.40	109.13
CN7B	CT2	CT2	58.35	111.50

CT2	CT2	CT3	58.00	112.34
CT2	CT2	CT2	58.00	112.34
HA	CT2	HA	35.50	106.13
HA	CT3	HA	35.50	107.24
CT2	CT2	HA	26.50	108.43
CT2	CT3	HA	34.60	111.62
CT3	CT2	HA	34.60	109.47
CN7B	NR2	CPH2	130.00	125.75
CN7B	NR1	CPH2	130.00	125.75
CN7B	NR2	CPH1	130.00	125.67
CN7B	NR1	CPH1	130.00	125.67
HA	CT1	HA	35.50	108.27
HA	CT1	CN7B	33.40	110.64
HA	CN7B	CT1	33.40	111.58
NR1	CN7B	CT1	140.00	112.31

Dihedral Angles

Atom 1	**Atom 2**	**Atom 3**	**Atom 4**	**K_χ (kcal mol^{-1})**	**n**	**δ (deg)**
CPH2	NR1	CPH1	CPH1	14.000	2	180
CPH2	NR2	CPH1	CPH1	14.000	2	180
NR1	CPH1	CPH1	NR2	14.000	2	180
NR1	CPH2	NR2	CPH1	14.000	2	180
NR2	CPH2	NR1	CPH1	14.000	2	180
HR1	CPH2	NR1	CPH1	3.000	2	180
HR1	CPH2	NR2	CPH1	3.000	2	180
HR3	CPH1	CPH1	HR3	2.000	2	180
CPH1	CPH1	NR1	CN7B	0.000	1	0
CPH1	CPH1	NR2	CN7B	0.000	1	0
HR3	CPH1	NR2	CPH2	3.000	2	180

HR3	CPH1	NR1	CPH2	3.000	2	180
NR1	CPH1	CPH1	HR3	3.000	2	180
NR2	CPH1	CPH1	HR3	3.000	2	180
NR1	CPH2	NR2	CN7B	0.000	2	180
NR2	CPH2	NR1	CN7B	0.000	2	180
HR1	CPH2	NR1	CN7B	0.000	2	180
HR1	CPH2	NR2	CN7B	0.000	2	180
HR3	CPH1	NR1	CN7B	0.000	2	180
HR3	CPH1	NR2	CN7B	0.000	2	180
CPH2	NR1	CN7B	HA	0.195	2	180
CPH2	NR2	CN7B	HA	0.195	2	180
CPH1	NR2	CN7B	HA	0.000	3	0
CPH1	NR1	CN7B	HA	0.000	3	0
CPH2	NR1	CN7B	CT2	0.100	3	180
CPH1	NR1	CN7B	CT2	0.200	4	0
NR1	CN7B	CT2	CT2	0.000	3	0
HA	CT2	CT3	HA	0.160	3	0
CT2	CT2	CT3	HA	0.160	3	0
NR1	CN7B	CT2	HA	0.000	3	0
CN7B	CT2	CT2	CT3	0.150	1	0
HA	CN7B	CT2	HA	0.195	3	0
CT2	CT2	CN7B	HA	0.195	3	0
HA	CT2	CT2	CN7B	0.195	3	0
HA	CT2	CT2	HA	0.195	3	0
HA	CT2	CT2	CT3	0.195	3	0
HA	CT1	CN7B	HA	0.195	3	0
HA	CT1	CN7B	NR1	0.000	3	0
CT1	CN7B	NR1	CPH2	0.100	3	180
CT1	CN7B	NR1	CPH1	0.200	4	0

Improper Angles

Atom 1	Atom 2	Atom 3	Atom 4	k_ψ (kcal mol^{-1} rad^{-2})	ψ (deg)
CPH2	NR1	NR2	HR1	0.5	0
NR1	CPH1	CPH2	CN7B	0.6	0
NR2	CPH1	CPH2	CN7B	0.6	0
CPH1	CPH1	NR2	HR3	0.5	0
CPH1	CPH1	NR1	HR3	0.5	0

Lennard-Jones parameters (Note that: $R_{mim} = \sigma\sqrt[6]{2}$).

Atom	ε (kcal mol^{-1})	R_{mim}/2(Å)
CPH1	0.0500	1.800
NR1	0.2000	1.850
CPH2	0.0500	1.800
NR2	0.2000	1.850
HR3	0.0078	1.468
HR1	0.0460	0.900
CN7B	0.0200	2.275
HA	0.0220	1.320
CT3	0.0550	2.175
CT2	0.0550	2.175
CT1	0.0550	2.175

Table S6. Force field parameters for [C_6mim^+], [C_8mim^+]

Bonds

Atom 1	**Atom 2**	**K_b (kcal mol^{-1} Å^{-2})**	**b_o (Å)**
CN7B	NR1	220.00	1.4762
CN7B	NR2	220.00	1.4762
CPH1	NR1	400.00	1.3819
CPH1	NR2	400.00	1.3819
CPH2	NR1	400.00	1.3366
CPH2	NR2	400.00	1.3366
CPH1	CPH1	410.00	1.3610
CPH2	HR1	340.00	1.0779
CPH1	HR3	365.00	1.0775
CN7B	HA	309.00	1.0889
CT2	HA	309.00	1.0954
CT3	HA	322.00	1.0935
CN7B	CT2	200.00	1.5308
CT2	CT2	222.50	1.5373
CT2	CT3	222.50	1.5314

Angles

Atom 1	**Atom 2**	**Atom 3**	**K_θ (kcal mol^{-1} rad^{-2})**	**θ_o (deg)**
CT2	CN7B	NR1	140.00	112.34
CPH1	NR1	CPH2	130.00	108.25
CPH1	NR2	CPH2	130.00	108.25
HA	CN7B	NR1	30.00	109.41
HA	CN7B	NR2	30.00	109.41

HR1	CPH2	NR1	25.00	125.44
HR1	CPH2	NR2	25.00	125.44
NR1	CPH1	CPH1	130.00	107.28
NR2	CPH1	CPH1	130.00	107.28
NR1	CPH2	NR2	130.00	109.11
HR3	CPH1	CPH1	25.00	130.74
NR2	CPH1	HR3	25.00	122.04
NR1	CPH1	HR3	25.00	122.04
HA	CN7B	HA	35.50	108.44
HA	CN7B	CT2	33.40	111.68
HA	CT2	CN7B	33.40	109.13
CN7B	CT2	CT2	58.35	111.50
CT2	CT2	CT3	58.00	114.54
CT2	CT2	CT2	58.00	115.56
HA	CT2	HA	35.50	105.18
HA	CT3	HA	35.50	107.29
CT2	CT2	HA	26.50	109.09
CT2	CT3	HA	34.60	111.57
CT3	CT2	HA	34.60	109.29
CN7B	NR2	CPH2	130.00	125.75
CN7B	NR1	CPH2	130.00	125.75
CN7B	NR2	CPH1	130.00	125.67
CN7B	NR1	CPH1	130.00	125.67

Dihedral Angles

Atom 1	**Atom 2**	**Atom 3**	**Atom 4**	**K_χ (kcal mol^{-1})**	**n**	**δ (deg)**
CPH2	NR1	CPH1	CPH1	14.000	2	180
CPH2	NR2	CPH1	CPH1	14.000	2	180
NR1	CPH1	CPH1	NR2	14.000	2	180

NR1	CPH2	NR2	CPH1	14.000	2	180
NR2	CPH2	NR1	CPH1	14.000	2	180
HR1	CPH2	NR1	CPH1	3.000	2	180
HR1	CPH2	NR2	CPH1	3.000	2	180
HR3	CPH1	CPH1	HR3	2.000	2	180
CPH1	CPH1	NR1	CN7B	0.000	1	0
CPH1	CPH1	NR2	CN7B	0.000	1	0
HR3	CPH1	NR2	CPH2	3.000	2	180
HR3	CPH1	NR1	CPH2	3.000	2	180
NR1	CPH1	CPH1	HR3	3.000	2	180
NR2	CPH1	CPH1	HR3	3.000	2	180
NR1	CPH2	NR2	CN7B	0.000	2	180
NR2	CPH2	NR1	CN7B	0.000	2	180
HR1	CPH2	NR1	CN7B	0.000	2	180
HR1	CPH2	NR2	CN7B	0.000	2	180
HR3	CPH1	NR1	CN7B	0.000	2	180
HR3	CPH1	NR2	CN7B	0.000	2	180
CPH2	NR1	CN7B	HA	0.195	2	180
CPH2	NR2	CN7B	HA	0.195	2	180
CPH1	NR2	CN7B	HA	0.000	3	0
CPH1	NR1	CN7B	HA	0.000	3	0
CPH2	NR1	CN7B	CT2	0.100	3	180
CPH1	NR1	CN7B	CT2	0.200	4	0
NR1	CN7B	CT2	CT2	0.000	3	0
HA	CT2	CT3	HA	0.160	3	0
CT2	CT2	CT3	HA	0.160	3	0
NR1	CN7B	CT2	HA	0.000	3	0
CN7B	CT2	CT2	CT2	0.150	1	0
HA	CN7B	CT2	HA	0.195	3	0

CT2	CT2	CN7B	HA	0.195	3	0
HA	CT2	CT2	CN7B	0.195	3	0
HA	CT2	CT2	CT2	0.195	3	0
HA	CT2	CT2	HA	0.195	3	0
HA	CT2	CT2	CT3	0.195	3	0
CT2	CT2	CT2	CT2	0.195	3	0
CT2	CT2	CT2	CT3	0.195	3	0

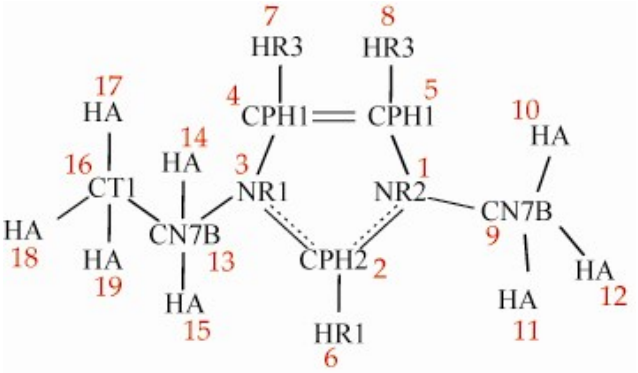
Improper Angles

Atom 1	**Atom 2**	**Atom 3**	**Atom 4**	**k_ψ (kcal mol^{-1} rad^{-2})**	**ψ (deg)**
CPH2	NR1	NR2	HR1	0.5	0
NR1	CPH1	CPH2	CN7B	0.6	0
NR2	CPH1	CPH2	CN7B	0.6	0
CPH1	CPH1	NR2	HR3	0.5	0
CPH1	CPH1	NR1	HR3	0.5	0

Lennard-Jones parameters (Note that: $R_{mim} = \sigma\sqrt[6]{2}$).

Atom	**ε (kcal mol^{-1})**	**R_{mim}/2(Å)**
CPH1	0.0500	1.800
NR1	0.2000	1.850
CPH2	0.0500	1.800
NR2	0.2000	1.850
HR3	0.0078	1.468
HR1	0.0460	0.900
CN7B	0.0200	2.275
HA	0.0220	1.320
CT3	0.0800	2.060
CT2	0.0550	2.175

(a)



(b)

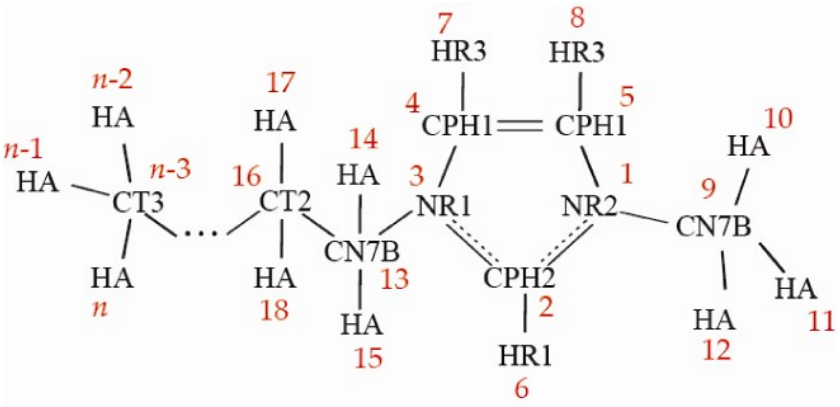


Figure S1: Atom labels for imidazolium cations: (a) [C_2mim$^+$] and (b) [$C_n$mim$^+$], $n > 2$.

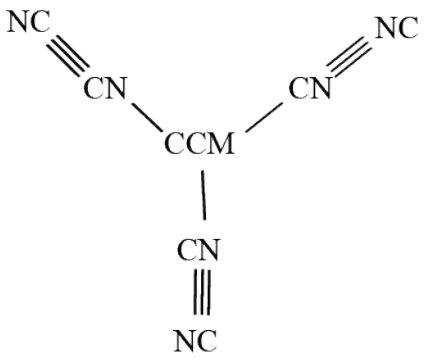


Figure S2: Atom labels for [TCM$^-$]

.

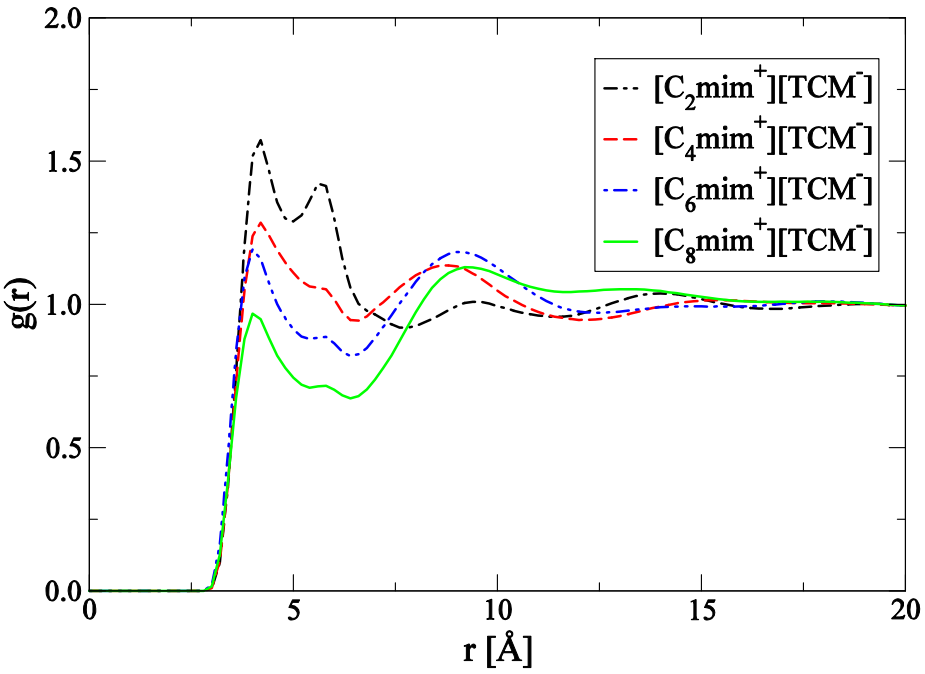


Figure S3: Radial distribution function $g(r)$ between the terminal carbon of the cation's alkyl tail and the central carbon of the anion (see Fig. S2) for $[C_2mim^+][TCM^-]$ (black), $[C_4mim^+][TCM^-]$ (red), $[C_6mim^+][TCM^-]$ (blue) and $[C_8mim^+][TCM^-]$ (green) at 298.15 K.

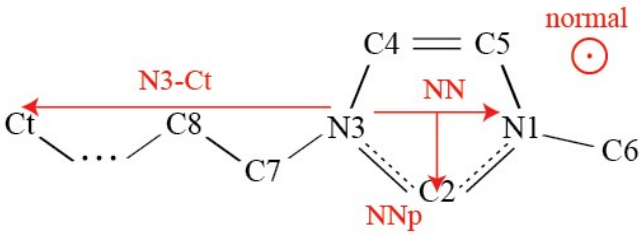


Figure S4: The vectors defined on the cation along which the translational motion of the center of mass was analyzed.

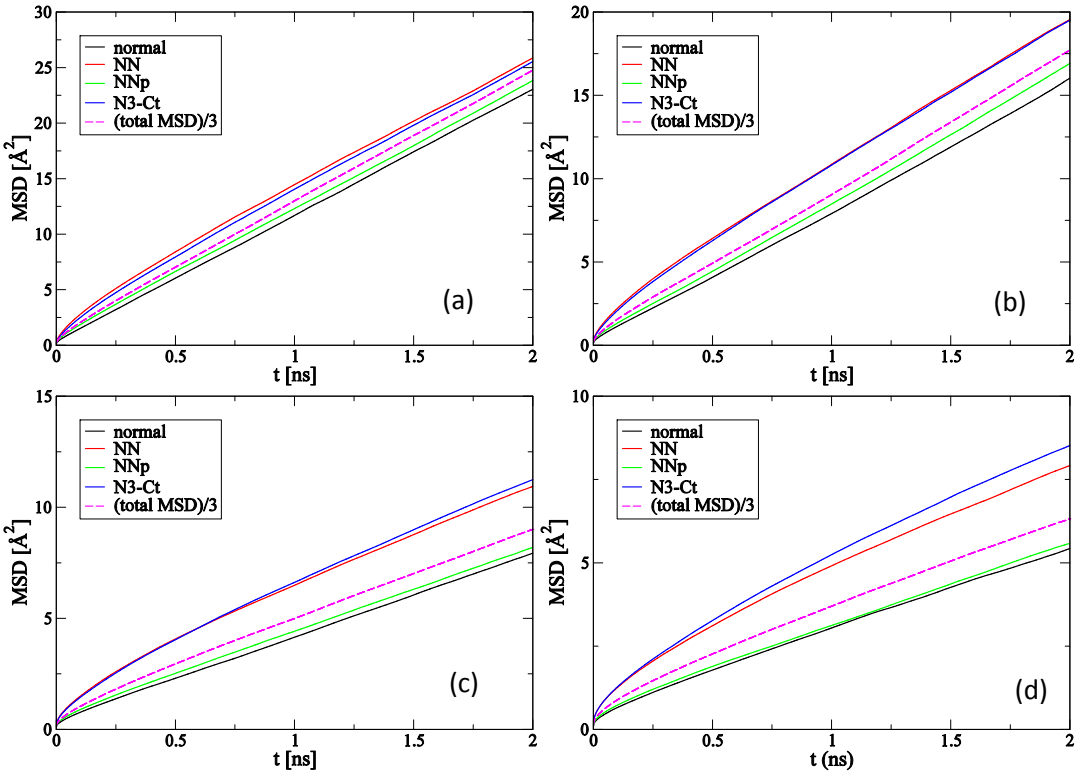


Figure S5: Mean square displacement (MSD) at 298.15 K calculated along the direction of the vector that is normal to the imidazolium plane (black), the vectors NN (red) and NNp (green), and along the the end-to-end vector N3-Ct of the alkyl tail (blue) of the cation compared to the 1/3 of the total MSD of the center of mass for (a) $[C_2mim^+][TCM^-]$, (b) $[C_4mim^+][TCM^-]$, (c) $[C_6mim^+][TCM^-]$ and (d) $[C_8mim^+][TCM^-]$.

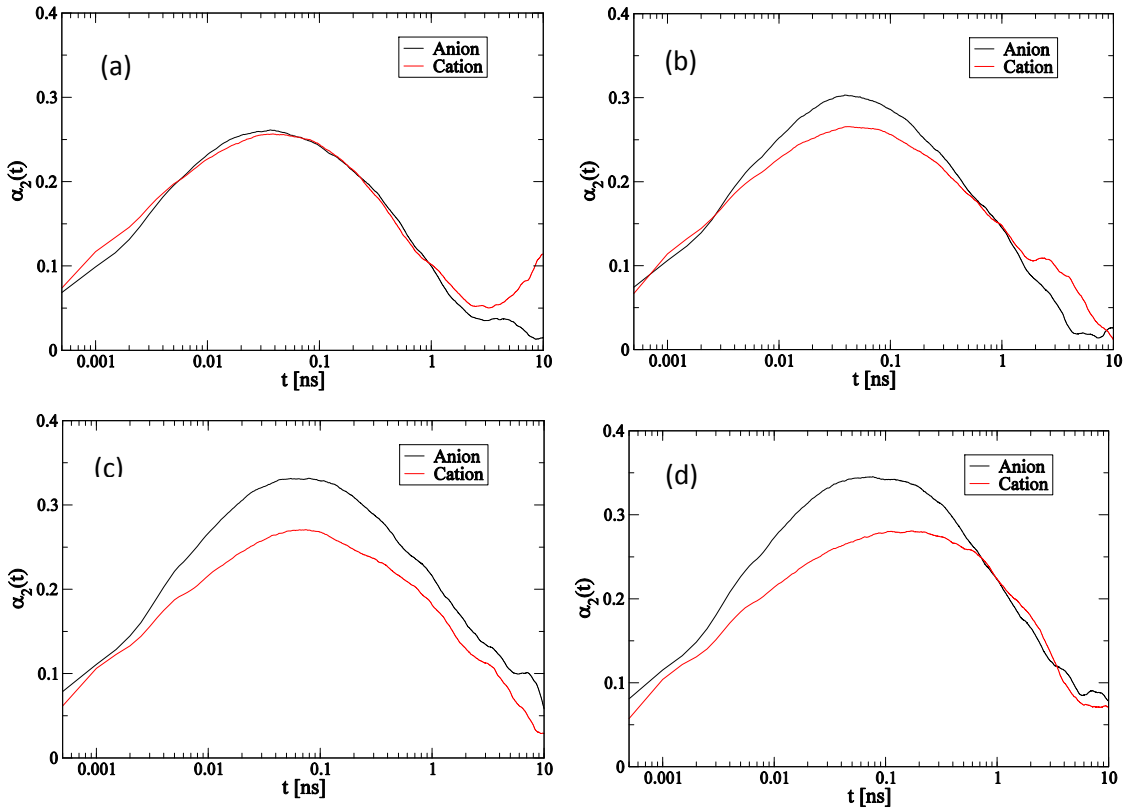


Figure S6: Non-Gaussian parameter $\alpha_2(t)$ for the anion (black) and the cation (red) of (a) $[C_2mim^+][TCM^-]$, (b) $[C_4mim^+][TCM^-]$, (c) $[C_6mim^+][TCM^-]$ and (d) $[C_8mim^+][TCM^-]$ calculated at 298.15 K.