Supporting Information for
“Analysis of the Heterogeneous Dynamics of Imidazolium-Based [Tf₂N⁻]
Ionic Liquids using Molecular Simulation”

Eleni Androulaki, Niki Vergadou and Ioannis G. Economou

Table S1: Bond force constants (k_b) and equilibrium bond distances (b_0)

$$V_{bond} = \sum_{bonds} k_b (b - b_0)^2$$

[C₄mim⁺], [C₈mim⁺], [C₁₂mim⁺] [All parameters from C. Cadena and E. J. Maginn, J. Phys. Chem. B **110**, 18026 (2006)]

Atom 1	Atom 2	k_b (kcal mol ⁻¹ Å ⁻²)	b_0 (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

[Tf₂N⁻] [All parameters from J. N. Canongia Lopes and A. A. H. Pádua, J. Phys. Chem. B **108**, 16893 (2004)]

Atom 1	Atom 2	k _b (kcal mol ⁻¹ Å ⁻²)	b ₀ (Å)
CTF2	FTF2	441.80	1.3230
CTF2	STF2	235.42	1.8180
STF2	OTF2	637.07	1.4420
NTF2	STF2	372.01	1.5700

Table S2: Bond angle bending parameters (k_θ) and equilibrium angles (θ₀)

$$V_{angle} = \sum_{angles} k_{\theta} (\theta - \theta_0)^2$$

[C₄mim⁺], [C₈mim⁺], [C₁₂mim⁺] [All parameters from C. Cadena and E. J. Maginn, J. Phys. Chem. B **110**, 18026 (2006)]

Atom 1	Atom 2	Atom 3	k _θ (kcal mol ⁻¹ rad ⁻²)	θ ₀ (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

[Tf₂N⁻] [All parameters from J. N. Canongia Lopes and A. A. H. Pádua, J. Phys. Chem. B **108**, 16893 (2004)]

Atom 1	Atom 2	Atom 3	k _θ (kcal mol ⁻¹ rad ⁻²)	θ ₀ (deg)
FTF2	CTF2	FTF2	93.33	107.10
STF2	CTF2	FTF2	82.93	111.80
CTF2	STF2	OTF2	103.97	102.60
OTF2	STF2	OTF2	115.80	118.50
OTF2	STF2	NTF2	94.51	113.60
CTF2	STF2	NTF2	97.51	100.20
STF2	NTF2	STF2	80.19	125.60

Table S3: Dihedral angle parameters

$$V_{dihedral} = \sum_{dihedrals} \sum_{n=1}^4 k_{\chi} [1 + \cos(n\chi - \delta)]$$

[C₄mim⁺], [C₈mim⁺], [C₁₂mim⁺] [All parameters from C. Cadena and E. J. Maginn, J. Phys. Chem. B **110**, 18026 (2006) and C. Cadena, Q. Zhao, R. Q. Snurr and E. J. Maginn, J. Phys. Chem. B **110**, 2821 (2006)]

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
CN7B	CT2	CT2	CT2	0.150	1	0
HA	CT2	CT2	CT2	0.190	3	0
CT2	CT2	CT2	CT2	0.150	1	0
CT2	CT2	CT2	CT3	0.150	1	0

[Tf₂N⁻] [All parameters from J. N. Canongia Lopes and A. A. H. Pádua, J. Phys. Chem. B **108**, 16893 (2004)]

Atom 1	Atom 2	Atom 3	Atom 4	k_x (kcal mol ⁻¹)	n	δ (deg)
FTF2	CTF2	STF2	OTF2	0.1734	3	0
STF2	NTF2	STF2	OTF2	-0.0018	3	0
FTF2	CTF2	STF2	NTF2	0.1580	3	0
STF2	NTF2	STF2	CTF2	7.8329	1	0
				-2.4904	2	180
				-0.7636	3	0

Table S4: Improper dihedral angle parameters

$$V_{improper} = \sum_{improper} k_{\psi} (\psi - \psi_0)^2$$

[C₄mim⁺], [C₈mim⁺], [C₁₂mim⁺] [All parameters from C. Cadena and E. J. Maginn, J. Phys. Chem. B **110**, 18026 (2006)]

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

Table S5: Lennard-Jones parameters. Note that $\sigma = R_{\min}/\sqrt[6]{2}$

$$V_{vdW} = \sum_{i=1}^{n-1} \sum_{j>i}^n 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

[All parameters from C. Cadena and E. J. Maginn, J. Phys. Chem. B **110**, 18026 (2006)] and J. N. Canongia Lopes and A. A. H. Pádua, J. Phys. Chem. B **108**, 16893 (2004)]

Atom	ε (kcal mol ⁻¹)	R _{min} /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

NTF2	0.1700	1.824
STF2	0.2500	1.992
OTF2	0.2100	1.661
FTF2	0.0530	1.656
CTF2	0.0660	1.964

Table S6: Partial Atomic Charges q_i (e⁻)

$$V_{electrostatic} = \sum_{i=1}^{n-1} \sum_{j>i}^n \frac{q_i q_j}{4\epsilon_0 r_{ij}}$$

*For the atomic numbering see Figure S4.

Atom type	[C ₄ mim ⁺]	Atom type	[C ₈ mim ⁺]	Atom type	[C ₁₂ mim ⁺]	numbering*
NR2	0.114066	NR1	0.024070	NR2	0.113661	1
CPH2	-0.005023	CPH1	-0.146402	CPH2	0.003943	2
NR1	0.072051	CPH1	-0.138310	NR1	0.038418	3
CPH1	-0.150818	HR1	0.169833	CPH1	-0.133520	4
CPH1	-0.119084	HR3	0.171085	CPH1	-0.120058	5
HR1	0.162674	HR3	0.158893	HR1	0.157867	6
HR3	0.160531	CN7B	-0.160790	HR3	0.151642	7
HR3	0.143848	HA	0.106563	HR3	0.138461	8
CN7B	-0.134237	HA	0.131649	CN7B	-0.138837	9
HA	0.093148	HA	0.077515	HA	0.091942	10
HA	0.115758	CN7B	0.133611	HA	0.116908	11
HA	0.068199	HA	0.019223	HA	0.068197	12
CN7B	0.004610	HA	0.003134	CN7B	0.072413	13
HA	0.042303	CT2	0.051998	HA	0.026374	14
HA	0.035583	HA	-0.028160	HA	0.015200	15
CT2	0.060092	HA	-0.003037	CT2	0.074603	16
HA	-0.022770	CT2	0.053619	HA	-0.032802	17

HA	0.000509	HA	-0.000357	HA	-0.005889	18
CT2	0.177646	HA	-0.023661	CT2	0.057542	19
HA	-0.019075	CT2	0.051979	HA	-0.005830	20
HA	-0.040461	HA	-0.012184	HA	-0.023939	21
CT3	-0.204311	HA	-0.019140	CT2	0.001878	22
HA	0.048036	CT2	-0.010809	HA	-0.003555	23
HA	0.040404	HA	-0.011111	HA	-0.010047	24
HA	0.106323	HA	-0.006227	CT2	0.058475	25
		CT2	0.027512	HA	-0.021918	26
		HA	-0.017818	HA	-0.017501	27
		HA	-0.010696	CT2	0.028428	28
		CT2	0.226885	HA	-0.020041	29
		HA	-0.058635	HA	-0.012959	30
		HA	-0.063263	CT2	0.091083	31
		CT3	-0.175720	HA	-0.035033	32
		HA	0.197174	HA	-0.037697	33
		HA	-0.049603	CT2	0.080397	34
		HA	-0.062110	HA	0.107481	35
				HA	-0.104288	36
				CT2	-0.012216	37
				HA	-0.010875	38
				HA	-0.012262	39
				CT2	0.022457	40
				HA	-0.014745	41
				HA	-0.014013	42
				CT2	0.175919	43
				HA	-0.040949	44
				HA	-0.040971	45
				CT3	-0.166469	46
				HA	0.029911	47

		HA 0.033622	48
		HA 0.029590	49

Partial charges for [Tf ₂ N ⁻] (e ⁻)		
[C ₄ mim ⁺][Tf ₂ N ⁻]	[C ₈ mim ⁺][Tf ₂ N ⁻]	[C ₁₂ mim ⁺][Tf ₂ N ⁻]
CTF2 0.272407	CTF2 0.246756	CTF2 0.217797
FTF2 -0.102320	FTF2 -0.121077	FTF2 -0.106293
STF2 0.670558	STF2 0.866655	STF2 0.677125
OTF2 -0.417747	OTF2 -0.418029	OTF2 -0.347396
NTF2 -0.351024	NTF2 -0.578520	NTF2 -0.512500

Table S7. Mass density calculations for the three ILs at different temperatures and 1 bar. In all cases, the statistical uncertainty is less than 0.001.

T (K)	Mass Density (gr/cm ³)		
	[C ₄ mim ⁺][Tf ₂ N ⁻]	[C ₈ mim ⁺][Tf ₂ N ⁻]	[C ₁₂ mim ⁺][Tf ₂ N ⁻]
298.15	1.4357	1.322	1.236
348.15	1.3791	1.270	1.1886
398.15	1.3213	1.220	1.140

Table S8. Anions' and cations' self-diffusion coefficients of the center of mass for the three ILs at different temperatures and 1 bar.

T (K)	Self Diffusion Coefficients (10 ⁻⁷ cm ² /s)					
	[C ₄ mim ⁺][Tf ₂ N ⁻]		[C ₈ mim ⁺][Tf ₂ N ⁻]		[C ₁₂ mim ⁺][Tf ₂ N ⁻]	
	Anion	Cation	Anion	Cation	Anion	Cation
298.15	1.0	1.9	0.6	0.5	0.4	0.4
348.15	3.8	6.9	3.3	3.2	2.5	2.2
398.15	10.2	16.2	8.6	7.6	7.5	7.0

Table S9. Viscosity calculations for the three ILs at different temperatures and 1 bar.

T (K)	Viscosity (Pa*s)		
	[C ₄ mim ⁺][Tf ₂ N ⁻]	[C ₈ mim ⁺][Tf ₂ N ⁻]	[C ₁₂ mim ⁺][Tf ₂ N ⁻]
298.15	0.075	0.12	0.17
348.15	0.025	0.04	0.035
398.15	0.007	0.007	0.008

(a)

(b)

Figure S1: Mean square displacement (MSD) at 398.15 K analyzed in specific axes on the ions for (a) cation and (b) anion of $[\text{C}_4\text{mim}^+][\text{Tf}_2\text{N}^-]$.

Figure S2: Mean square displacement (MSD) of the center of mass of the anion (full lines) and the cation (dotted lines) of $[\text{C}_{12}\text{mim}^+][\text{Tf}_2\text{N}^-]$ calculated at 298.15 K (black), 348.15 K (red) and 398.15 K (blue) plotted in a log-log scale. The slope of the dotted green lines is equal to unity and indicates the Fickian regime of the MSD.

Figure S3: Self-part of the Van Hove function $G_s(r,t)$ at 398.15 K compared to the expected Gaussian distribution for the cation of $[\text{C}_4\text{mim}^+][\text{Tf}_2\text{N}^-]$.

Figure S4: Atomic labeling for (a) $[C_n\text{mim}^+]$, $n > 2$ and (b) $[\text{Tf}_2\text{N}^-]$.