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

Supporting information for:

Atomistic Simulations of Ammonium-based Protic Ionic Liquids: Steric Effects on Structure, Low Frequency Vibrational Modes and Electrical Conductivity

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Table S1: Non-bonding force field parameters.

Atom	q (e)	ϵ (kcal/mol)[a]	σ (Å)[a]
For cation			
N	0.0230	0.1500	3.2960
C_1	-0.1326	0.1094	3.4750
C_2	0.0078	0.1094	3.4750
C_3	-0.1404	0.1094	3.4750
H_1	0.1014	0.1570	1.9600
H_2	0.0468	0.1570	2.6500
H_3	0.0468	0.1570	2.6500
H_N	0.2418	0.1570	1.1050
For anion			
C	0.2730	0.0894	3.5640
F	-0.1248	0.0450	3.3500
S	0.7956	0.3400	3.8310
O	-0.4914	0.0960	3.3140

[a]Ref.,[S1] C_1=methyl/methylene carbon, C_2=ethyl/ethylene carbon, C_3=propyl chain terminal carbon, H_1=methyl/methylene Hydrogen, H_2=ethyl/ethylene Hydrogen, and H_3=propyl chain terminal Hydrogen.

Table S2: Self-diffusion coefficients ($\times$ 10^{-7} cm^2 s^{-1}) of PILs from MD simulations at 300 K.

System	Full charge model		Scaled charge model		Experiment[S2]	
	D^+	D^-	D^+	D^-	D^+	D^-
[N122][TfO]	0.09	0.08	2.12	1.25	4.16	2.18
[N133][TfO]	0.04	0.03	0.43	0.28	-	-

Table S3: Time window for calculation of self-diffusion coefficients from MSD plots at 393 K.

ILs	[N112][TFO]	[N122][TFO]	[N222][TFO]	[N133][TFO]
Time (ns)	1.5 – 6.4	1.6 – 7.9	1.2 – 2.5	11.2 – 17.7

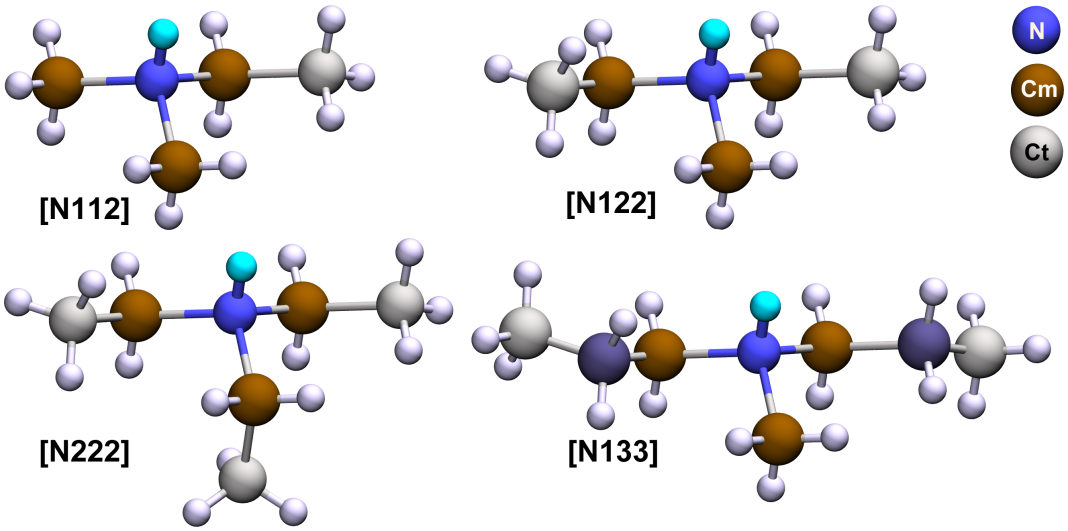

Figure S1: Atom types used in simulations for PILs a) C_m=methyl/methylene carbon, and b) C_t=ethyl or propyl chain terminal carbon [color scheme: N-blue, H_N-cyan, C_m-Ochre, C_t-gray].

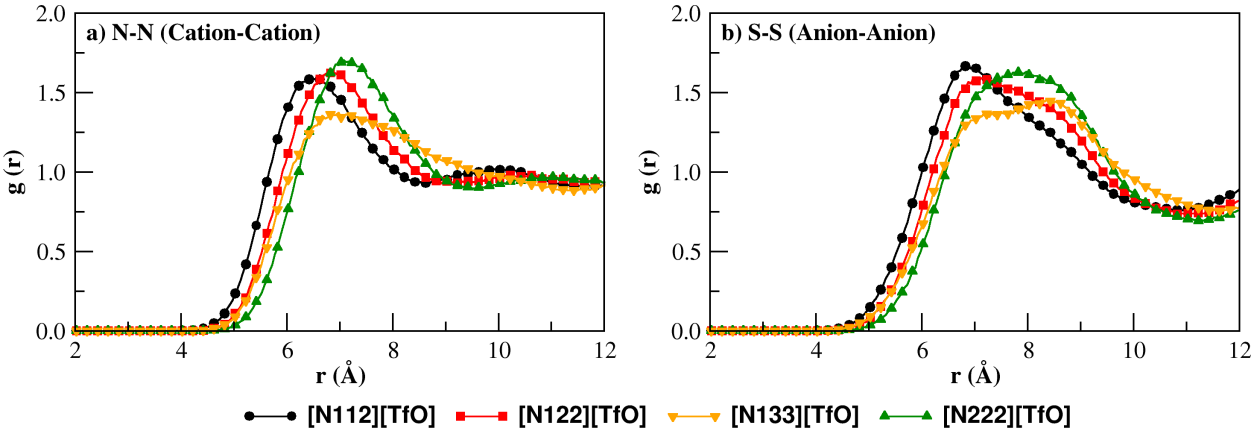

Figure S2: RDFs for a) N-N (cation–cation), and b) S–S (anion–anion interactions) at 393 K.

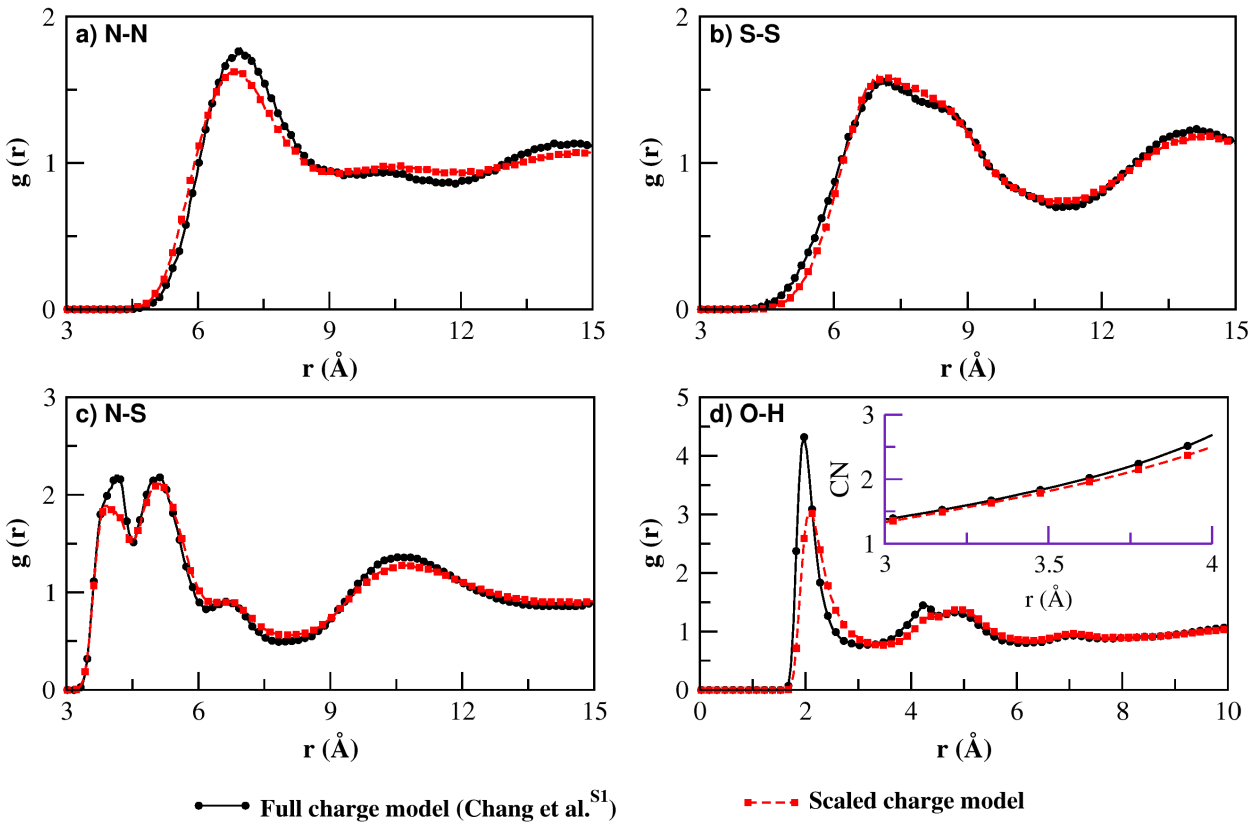

Figure S3: RDFs calculated for [N122][TfO] PIL using full charge model of Chang et al.[S1] and scaled charge model at 393 K: a) N–N (cation–cation), b) S–S (anion–anion), c) N–S (cation–anion), and d) O–H (between anion oxygen atoms and acidic hydrogen attached to nitrogen of cation; inset shows coordination numbers).

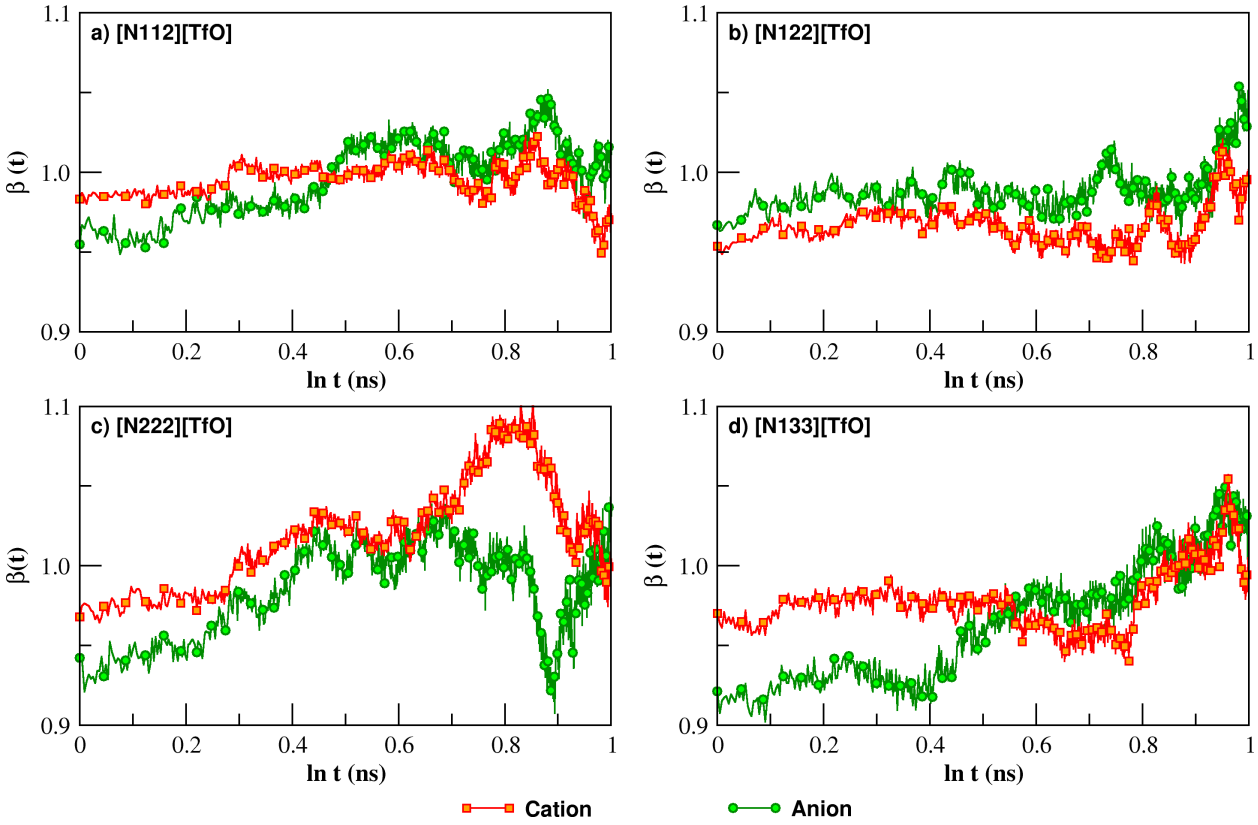

Figure S4: β plot as a function of time for cations and anions of PILs at 393 K.

References

(S1) Chang, T. M.; Dang, L. X.; Devanathan, R.; Dupuis, M. *J. Phys. Chem. A* **2010**, *114*, 12764–12774.

(S2) Lee, S.-Y.; Ogawa, A.; Kanno, M.; Nakamoto, H.; Yasuda, T.; Watanabe, M. *J. Am. Chem. Soc.* **2010**, *132*, 9764–9773.