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

Ab initio molecular dynamics study of proton transport in imidazolium-based ionic liquids with added imidazole

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Supplementary Information

System Density

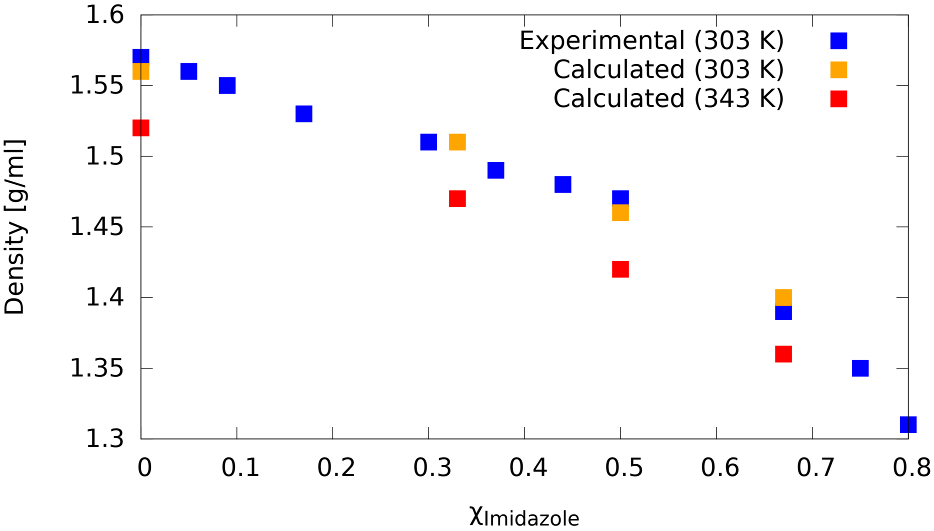

Figure S1: Comparison of calculated density with experimental densities taken from Ref. S1. While the simulations in this study were run at 343 K, the similarity of calculated and experimental densities at 303 K indicates our calculated densities at 343 K are reliable.

Mean Squared Displacements

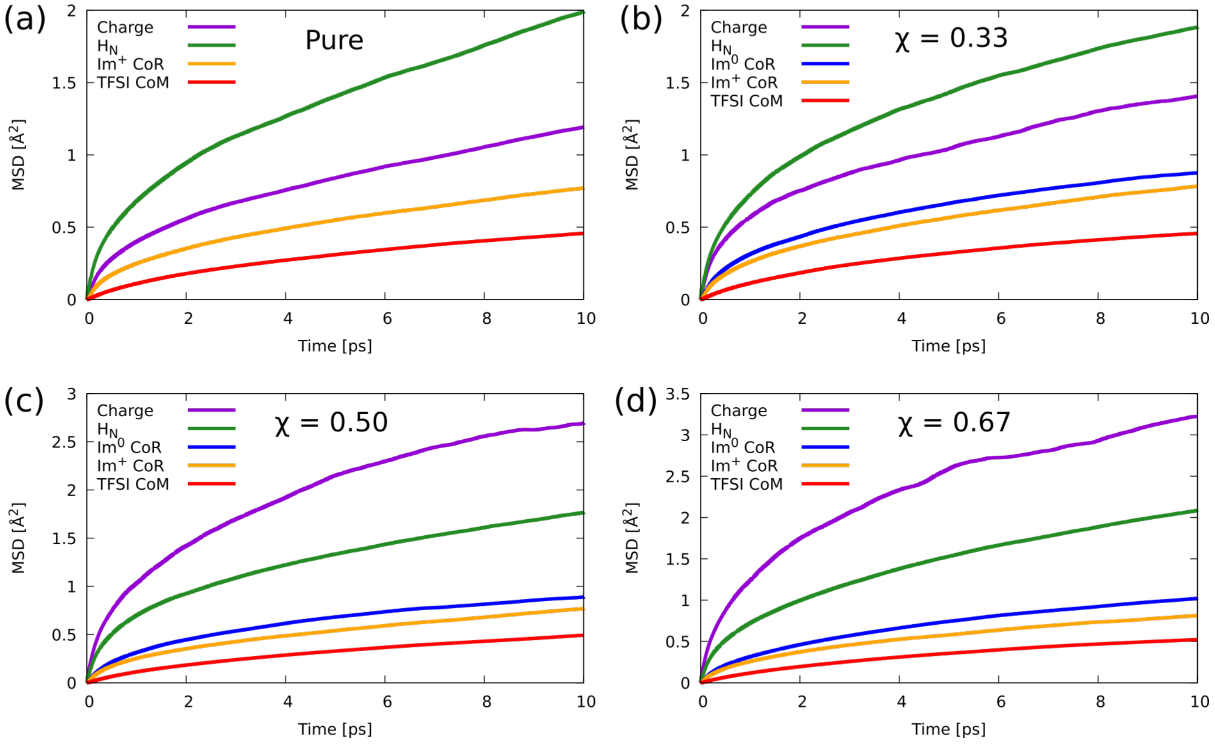

Figure S2: Mean squared displacement (MSD) of several constituent species in the four systems studied here, averaged over two independent runs. The MSD of the acidic protons, H_N, pertains to those on imidazolium and imidazole. Lastly, the MSDs for the molecular and ionic species are defined in terms of the center-of-ring (CoR) for imidazolium and imidazole and the center-of-mass (CoM) for TFSI.

Table S1: Comparison of calculated diffusion constants with experimental values found in Ref. S1. All values of *D* are shown in units of Å^2/ps.

	Experimental (303 K)			Computational (343 K)		
χ_{Im^0}	D_{Im^+}	D_{H^+}	$D_{\mathrm{H}^+}/D_{\mathrm{Im}^+}$	D_{Im^+}	D_{H^+}	$D_{\mathrm{H}^+}/D_{\mathrm{Im}^+}$
0.30	4.43×10^{-3}	5.48×10^{-3}	1.24			
0.33				6.81×10^{-3}	1.16×10^{-2}	1.70
0.37	4.67×10^{-3}	5.64×10^{-3}	1.21			
0.50	4.95×10^{-3}	5.65×10^{-3}	1.14	7.52×10^{-3}	2.55×10^{-2}	3.39
0.67	5.70×10^{-3}	6.32×10^{-3}	1.11	8.71×10^{-3}	3.85×10^{-2}	4.42

Radial Distribution Functions

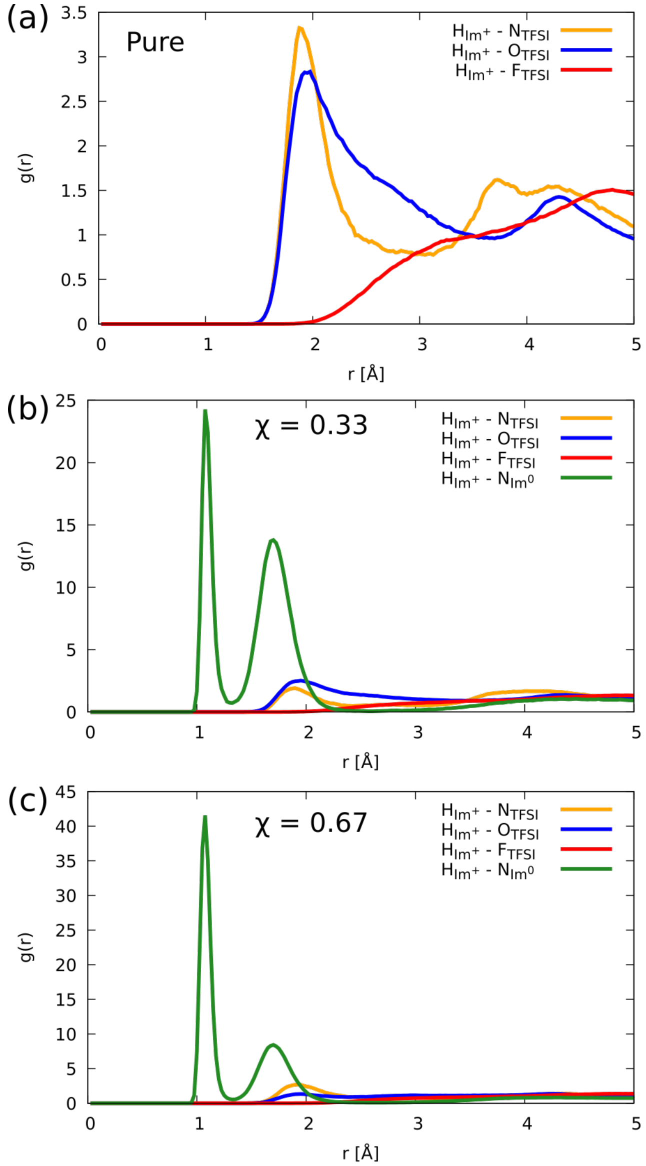

Figure S3: Radial distribution functions and coordination numbers between H_{Im^+} and species capabale of accepting H-bonds for (a) $\chi = 0.00$, (b) $\chi = 0.33$, and (c) $\chi = 0.67$.

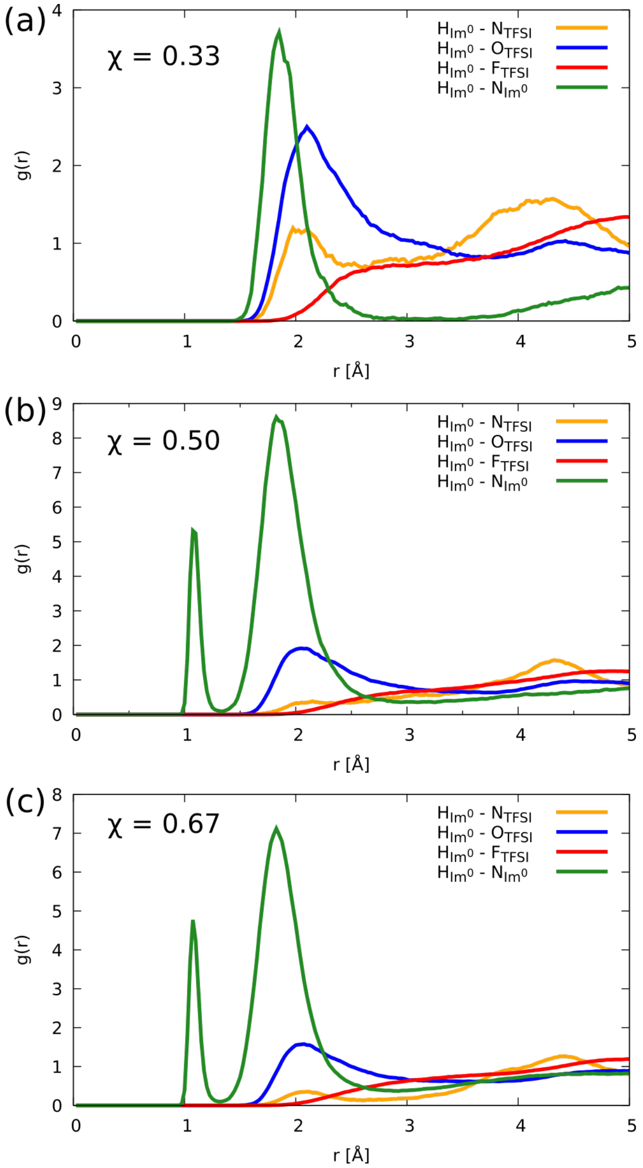

Figure S4: RDF for (a) $\chi = 0.33$, (b) $\chi = 0.50$ and (c) $\chi = 0.50$ between the proton on imidazole (H_{Im^0}) and other relevant atom types in system.

Fig. S5 shows the RDF and CN between H_{Im^0} and N_{Im^0} for all systems with added Im^0 (where the calculated RDF and CN exclude N_{Im^0} and H_{Im^0} pairs that begin the simulation on the same molecule). For both $\chi = 0.50$ and $\chi = 0.67$, there is a peak centered at 1.08 Å corresponding to instances in which the proton initially on Im^0 has transferred to another Im^0. This occurs when there are multiple sequential forward hopping events: a proton hops from C_2HIm^+ to Im^0, and then subsequently to another Im^0, as in the example shown in Fig. 4. (Over all of our simulations, we encountered one instance of autoionization, where a proton is transferred from one neutral Im^0 to another, yielding Im^- and HIm^+, lasting 34 fs. Interestingly, the neutral Im^0 which gave up its proton was solvating a HIm^+ species, resulting in $HIm^+ + Im^0 + Im^0 \rightarrow HIm^+ + Im^- + HIm^+$, where the anion formed is in direct contact with two cations.) For $\chi = 0.33$ there are no instances of multiple forward hopping events. While the RDF shows that there is clearly some solvation of H_{Im^0} by N_{Im^0}, as we show below these are isolated molecules not associated with C_2HIm^+. Comparing the CNs, we can determine the fraction of H_{Im^0} atoms which have hopped to a neighboring Im^0; using a distance cutoff of 1.33 Å, the coordination number is 0.017 for the $\chi = 0.50$ system and 0.025 for the $\chi = 0.67$ system. While these are relatively modest numbers, they do indicate a clear trend that increasing the amount of solvent increases the likelihood of extended forward hopping beyond the Im^0 immediately solvating a C_2HIm^+ ion. Integrating to a distance of 2.5 Å, the CN is 0.062 for $\chi = 0.33$; 0.356 for $\chi = 0.50$; and 0.486 for $\chi = 0.67$. Thus, roughly 36% and 49% of the potentially transferrable protons on Im^0 are solvated in the $\chi = 0.50$ and $\chi = 0.67$ systems, respectively, defined by either covalent or H-bonding, by a nitrogen on another Im^0, whereas in the $\chi = 0.33$ system, there is very little interaction between Im^0 species.

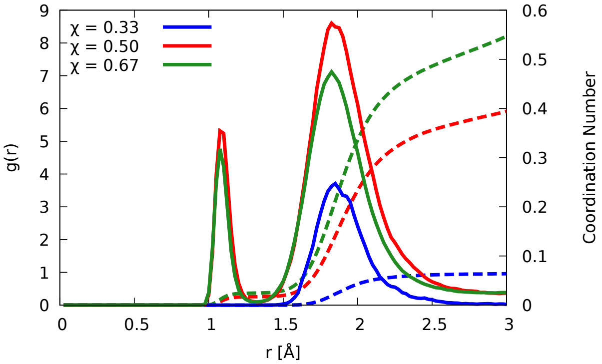

Figure S5: (a) Radial distribution functions (solid lines) and coordination numbers (dashed lines) between H_{Im^0} and the unprotonated nitrogen of imidazole N_{Im^0} for all the systems containing added Im^0. The calculated RDF and CN excludes pairs of H_{Im^0} and N_{Im^0} that begin the simulation on the same molecule.

Charge Correlation Functions

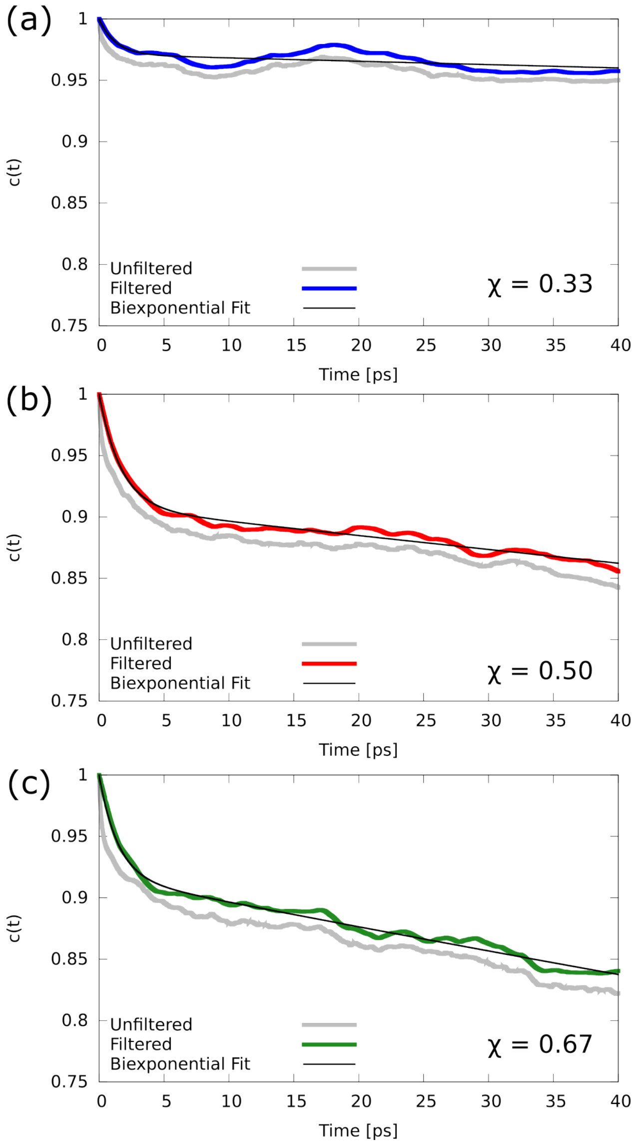

Figure S6: Filtered charge correlation functions, along with triexponential decay functions and unfiltered correlation functions for comparison.

Table S2: Fitting parameters for biexponential decay functions for the charge correlation functions of the filtered trajectories:

Mole Fraction of Imidazole	a	τ_1 (ps)	b	τ_2 (ps)	τ_{fit} (ps)
0.33	0.029	1.25	0.971	3527	3425
0.50	0.092	1.69	0.908	775	704
0.67	0.083	1.44	0.917	441	405

Table S3: Fitting parameters for triexponential decay functions for the charge correlation functions calculated only over those charges that undergo hopping.

Mole Fraction of Imidazole	a	τ_1 (ps)	b	τ_2 (ps)	c	τ_3 (ps)	τ_{fit} (ps)
0.33	0.121	0.420	0.021	1.31	0.858	562	482
0.50	0.067	0.076	0.171	1.61	0.762	267	204
0.67	0.062	0.119	0.082	1.63	0.856	257	220

Table S4: Fitting parameters for biexponential decay functions for the charge correlation functions of the filtered trajectories calculated only over those charges that undergo hopping.

Mole Fraction of Imidazole	a	τ_1 (ps)	b	τ_2 (ps)	τ_{fit} (ps)
0.33	0.104	0.94	0.896	521	467
0.50	0.219	1.75	0.781	298	233
0.67	0.126	1.45	0.874	268	234

Hydrogen-Bond Correlation Function Fitting Parameters

Table S5: Fitting parameters for triexponential decay functions for the hydrogen-bond correlation functions shown in Fig. 13 of the main text.

Mole Fraction of Imidazole	a	τ_1 (ps)	b	τ_2 (ps)	c	τ_3 (ps)	τ_{fit} (ps)
0.00	0.354	0.088	0.244	2.83	0.402	113	46.1
0.33	0.251	0.062	0.149	1.49	0.600	185	111
0.50	0.206	0.070	0.094	2.25	0.700	485	340
0.67	0.175	0.067	0.116	2.78	0.709	473	336

Orientational Correlation Functions

We calculated the orientational correlation function, defined as

$$c(t) = \langle \mathbf{r}_i(t) \cdot \mathbf{r}_i(0) \rangle$$

where $\mathbf{r}_i$ is the unit vector in direction i, where the directions are calculated are: (1) normal to the imidazole/imidazolium ring; (2) pointing from the imidazole/imidazolium CoR to the C2 carbon; and (3) the vector perpendicular to these two, in the plane of the imidazole/imidazolium ring. These vectors and their corresponding correlation functions are shown in Fig. S6. We also show of the fitting parameters for the different systems in Table S4.

Table S6: Fitting parameters for triexponential decay functions for the orientational correlation functions, with the three axes of rotation defined according to Fig. S6.

Mole Fraction of Imidazole	Species	Axis of Rotation	a	τ_1 (ps)	b	τ_2 (ps)	c	τ_3 (ps)	τ_{fit} (ps)
0.00	C_2HIm^+	1	0.050	0.406	0.209	18.8	0.741	736	550
		2	0.044	0.497	0.107	7.48	0.849	171	146
		3	0.041	0.780	0.080	15.7	0.879	350	309
0.33	C_2HIm^+	1	0.051	0.426	0.171	15.5	0.778	913	713
		2	0.051	0.589	0.160	14.3	0.789	555	441
		3	0.041	0.731	0.100	24.7	0.859	851	734
	Im^0	1	0.067	0.396	0.113	6.21	0.820	986	809
		2	0.096	0.939	0.930	13.0	0.811	949	771
		3	0.053	0.400	0.058	2.96	0.889	858	763
0.50	C_2HIm^+	1	0.061	0.557	0.079	31.1	0.860	191	167
		2	0.058	0.667	0.172	29.4	0.770	277	218
		3	0.039	0.754	0.070	27.9	0.891	390	349
	Im^0	1	0.049	0.220	0.100	3.87	0.851	340	290
		2	0.054	0.390	0.115	5.44	0.831	582	484
		3	0.035	0.190	0.075	3.07	0.890	713	635
0.67	C_2HIm^+	1	0.026	0.111	0.065	2.58	0.909	156	142
		2	0.021	0.130	0.080	3.16	0.899	149	135
		3	0.022	0.209	0.050	6.12	0.920	720	663
	Im^0	1	0.047	0.210	0.183	6.94	0.770	212	164
		2	0.043	0.247	0.248	10.2	0.709	615	439
		3	0.035	0.190	0.085	3.88	0.880	382	336

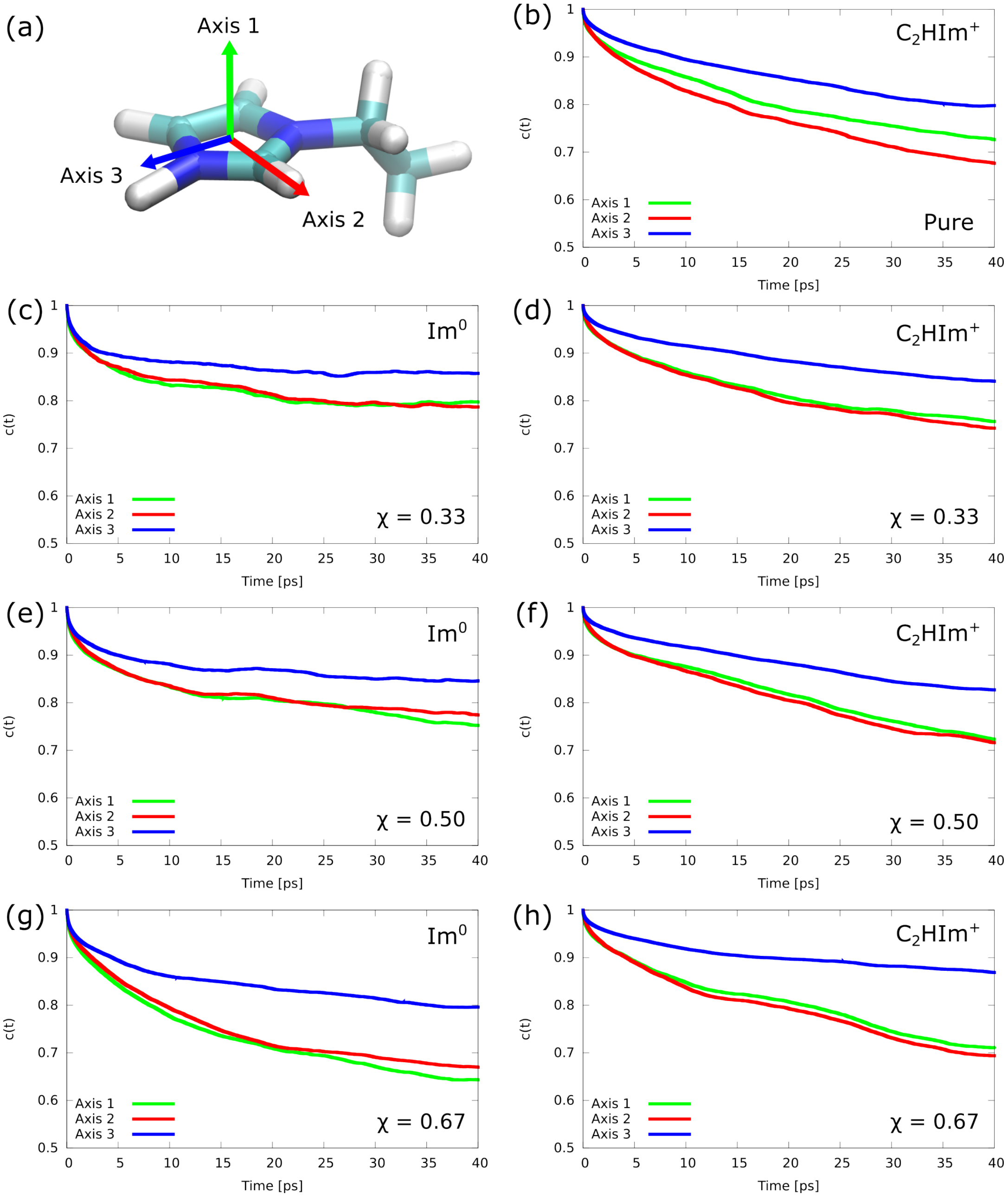

Figure S7: Orientational correlation functions for C_2HIm^+ and Im^0 for the different systems studied in this investigation.

References

S1. N. Yaghini, V. Gómez-González, L. M. Varela and A. Martinelli, *Physical Chemistry Chemical Physics*, 2016, **18**, 23195-23206