

SUPPLEMENTARY MATERIAL

The microheterogeneity in ionic liquid mixtures: hydrogen bonding, dispersed ions and dispersed ion clusters

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$^1\text{H-NMR}$ spectra of neat ionic liquids.

Figure S1. $^1\text{H-NMR}$ of $[\text{C}_4\text{C}_1\text{IM}]\text{Cl}$.

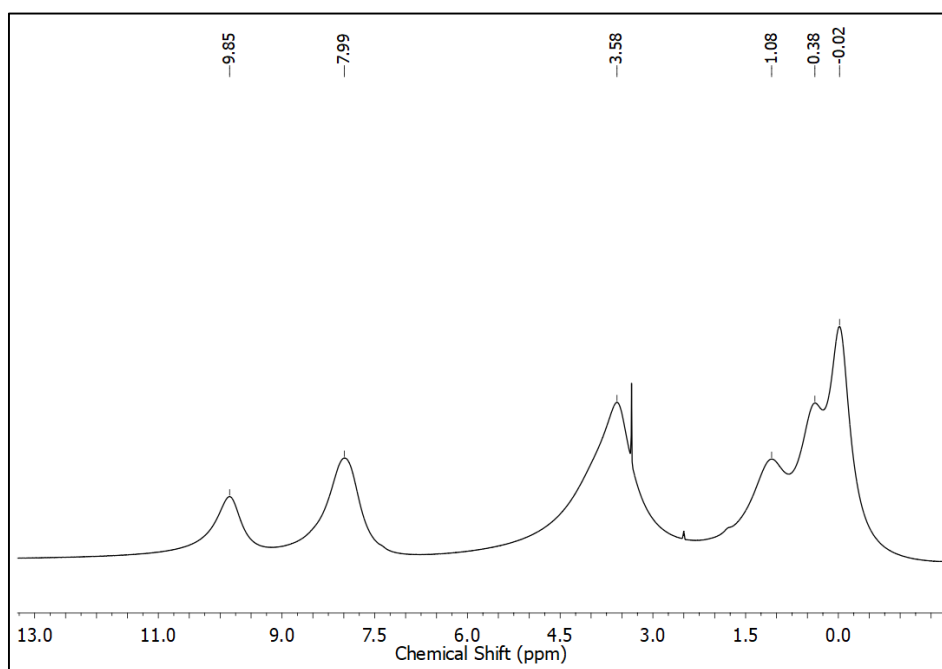


Figure S2. $^1\text{H-NMR}$ of $[\text{C}_4\text{C}_1\text{IM}]\text{Br}$.

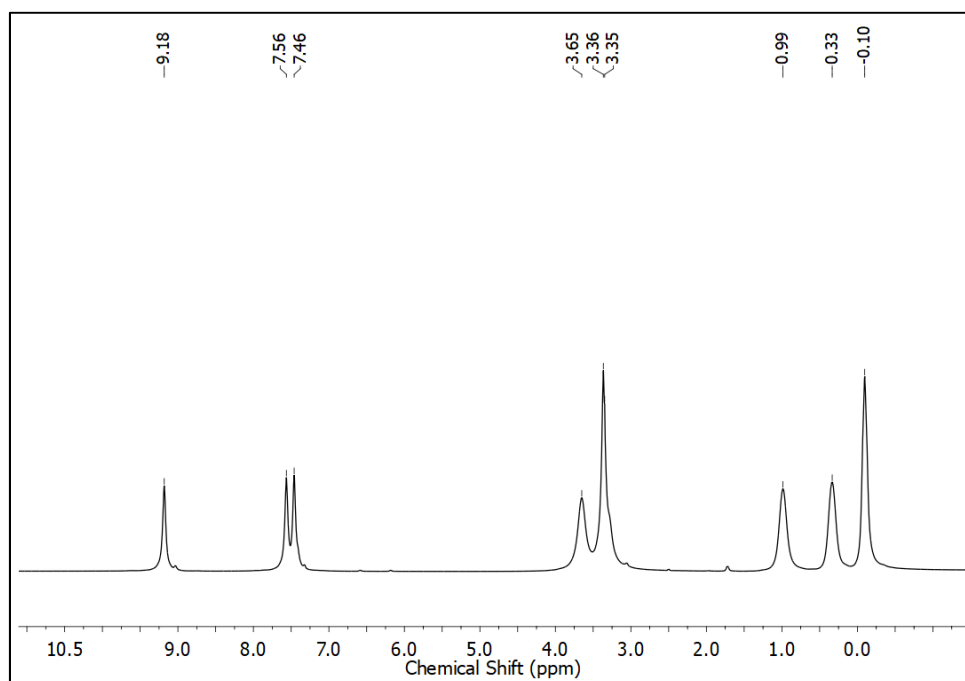


Figure S3. $^1\text{H-NMR}$ of $[\text{C}_8\text{C}_1\text{IM}]\text{Cl}$.

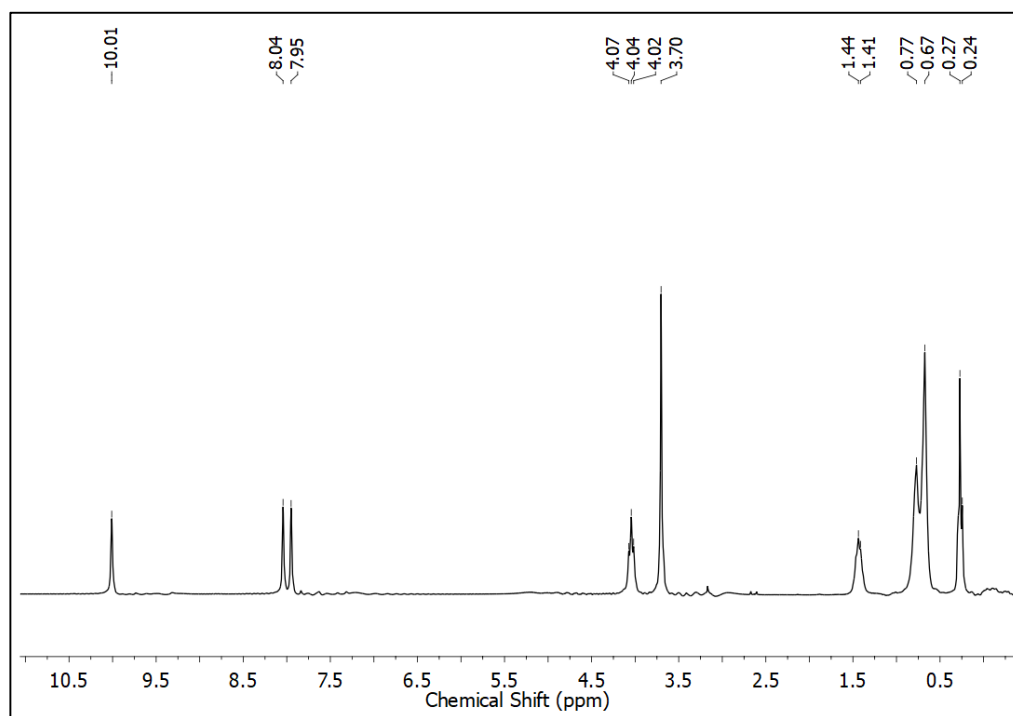


Figure S4. $^1\text{H-NMR}$ of $[\text{C}_4\text{C}_1\text{IM}]\text{Tf}_2\text{N}$.

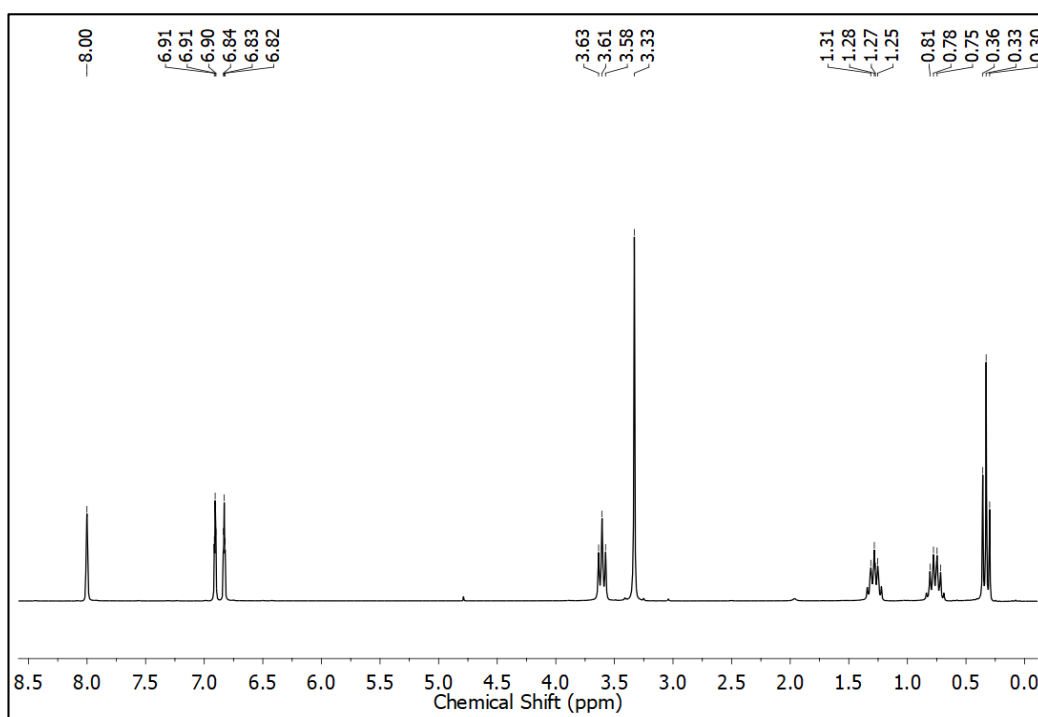


Figure S5. $^1\text{H-NMR}$ of $[\text{C}_4\text{C}_1\text{IM}]\text{PF}_6$.

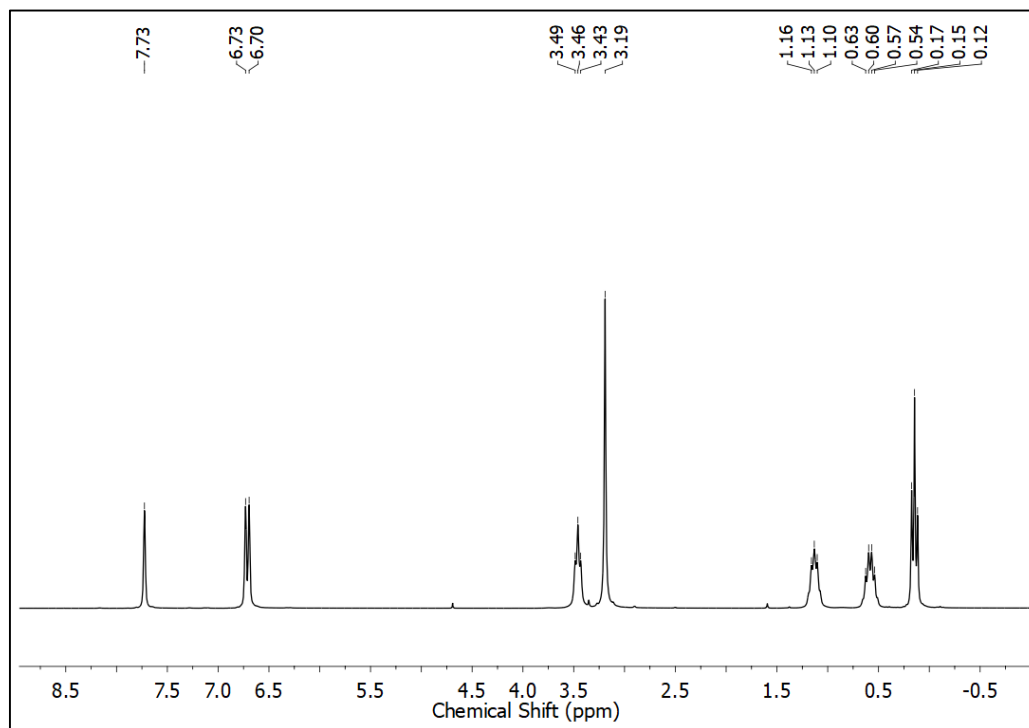
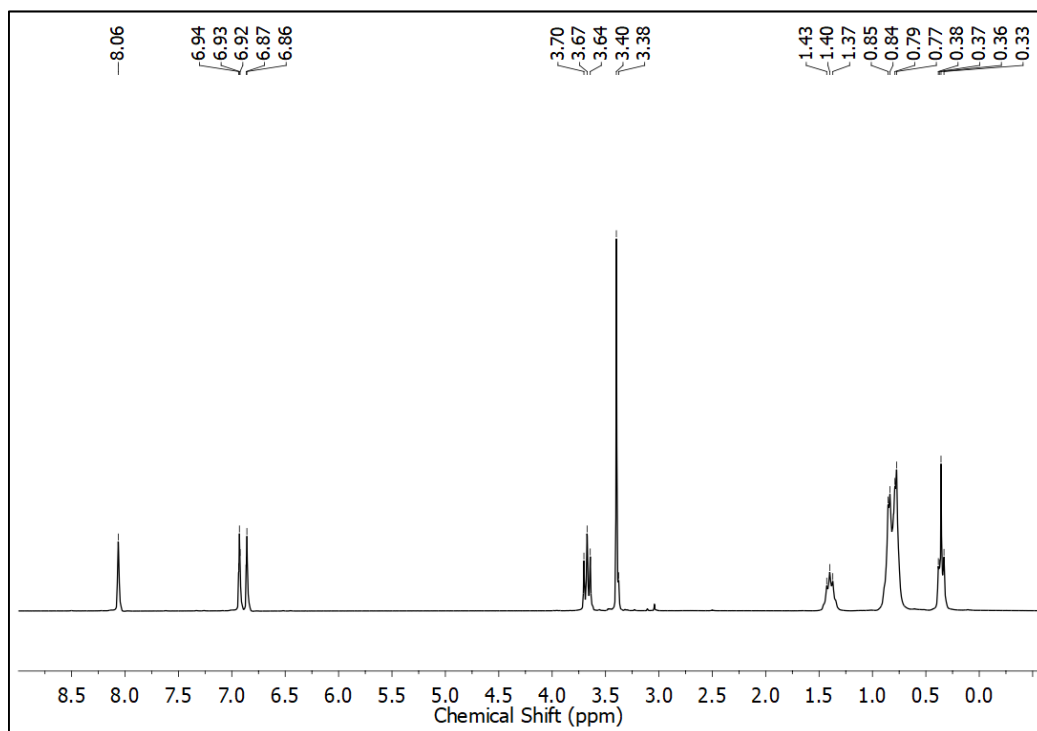


Figure S6. $^1\text{H-NMR}$ of $[\text{C}_8\text{C}_1\text{IM}]\text{ Tf}_2\text{N}$.



¹H-NMR table of mixtures

Table S1: ¹H NMR chemical of [C₄C₁IM][Tf₂N]_{1-x}Cl_x mixtures.

χ_{Cl}	H ² ppm	H ⁴ ppm	H ⁵ ppm
0	8.001	6.909	6.834
0.0127	8.044	6.921	6.846
0.0221	8.073	6.931	6.847
0.0736	8.242	6.986	6.909
0.104	8.345	7.031	6.943
0.146	8.463	7.068	6.985
0.227	8.697	7.158	7.071
0.377	9.018	7.314	7.207
0.509	9.288	7.469	7.371
0.705	9.576	7.712	7.597
0.847	9.721	7.867	7.751
0.955	9.808	7.858	7.858
1	9.847	7.987	7.987

Table S2: ¹H NMR chemical of [C₄C₁IM][Tf₂N]_{1-x}Br_x mixtures.

χ_{Br}	H ² ppm	H ⁴ ppm	H ⁵ ppm
0	8.001	6.907	6.829
0.0107	8.024	6.918	6.841
0.0195	8.046	6.932	6.854
0.0619	8.143	6.974	6.881
0.0942	8.224	6.997	6.918
0.133	8.303	7.028	6.941
0.193	8.416	7.092	6.998
0.321	8.613	7.172	7.073
0.452	8.800	7.264	7.174
0.658	8.998	7.389	7.296
0.818	9.110	7.483	7.391
0.945	9.177	7.541	7.442
1	9.216	7.557	7.451

Table S3: ^1H NMR chemical of $[\text{C}_4\text{C}_1\text{IM}][\text{PF}_6]_{1-x}\text{Cl}_x$ mixtures.

χ_{Cl}	H^2 ppm	H^4 ppm	H^5 ppm
0.0000	7.727	6.726	6.697
0.0094	7.760	6.737	6.704
0.0210	7.796	6.746	6.709
0.0550	7.899	6.778	6.749
0.0965	8.022	6.821	6.784
0.134	8.135	6.863	6.818
0.183	8.281	6.908	6.872
0.332	8.644	7.071	7.008
0.455	8.943	7.186	7.118
0.659	9.337	7.517	7.407
0.815	9.567	7.714	7.601
0.945	9.754	7.891	7.784
1	9.847	7.987	7.987

Table S4: ^1H NMR chemical of $[\text{C}_8\text{C}_1\text{IM}][\text{Tf}_2\text{N}]_{1-x}\text{Cl}_x$ mixtures

χ_{Cl}	H^2 ppm	H^4 ppm	H^5 ppm
1	10.016	8.061	8.051
0.947	9.924	7.991	7.984
0.827	9.816	7.843	7.8209
0.654	9.581	7.662	7.595
0.470	9.392	7.505	7.431
0.344	9.113	7.337	7.254
0.191	8.714	7.171	7.097
0	8.087	6.954	6.873

Additivity parameters

Table S5. Additivity parameters of mixtures

C ₄ C ₁ IM PF ₆ ->Cl			C ₈ C ₁ IM Tf ₂ N->Cl			C ₄ C ₁ IM Tf ₂ N -> Br			C ₄ C ₁ IM Tf ₂ N -> Cl		
χ	725-925	2800-3200	χ	725-925	2800-3200	χ	725-925	2800-3200	χ	725-925	2800-3200
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.13	0.07	0.05	0.19	0.04	0.35	0.19	0.11	0.32	0.15	0.08	0.32
0.18	0.09	0.02	0.34	0.02	0.10	0.32	0.14	0.20	0.23	0.10	0.30
0.33	0.09	0.02	0.47	0.02	0.16	0.45	0.18	0.17	0.38	0.15	0.22
0.46	0.14	0.04	0.65	0.03	0.14	0.66	0.23	0.19	0.51	0.18	0.19
0.66	0.13	0.03	0.83	0.04	0.24	0.82	0.29	0.26	0.70	0.25	0.31
0.82	0.10	0.03	0.95	0.02	0.20	0.95	0.33	0.12	0.85	0.29	0.39
1.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00	0.96	0.31	0.14

Thermal gravimetric analysis (TGA) of mixtures

Figure S1: Temperature-ramped TGA for ionic liquids mixtures. Upper: [C₄C₁IM][Tf₂N]_{1-x}Cl_x; middle: [C₄C₁IM][Tf₂N]_{1-x}Br_x; lower: [C₈C₁IM][Tf₂N]_{1-x}Cl_x.

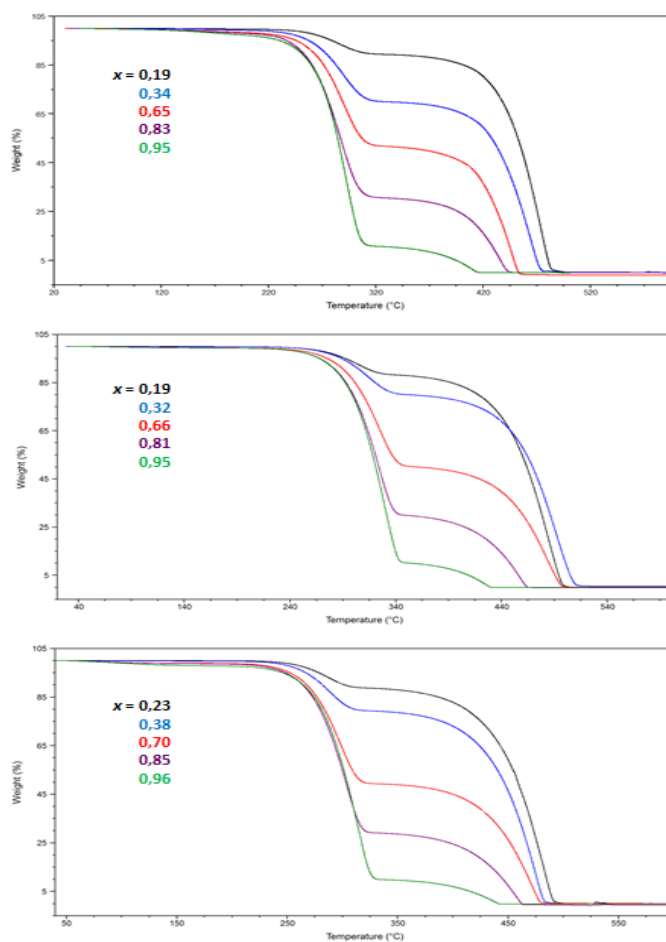


Figure S2: T_{peak} of mixtures of upper: $[\text{C}_4\text{C}_1\text{IM}][\text{Tf}_2\text{N}]_{1-x}\text{Cl}_x$; middle: $[\text{C}_4\text{C}_1\text{IM}][\text{Tf}_2\text{N}]_{1-x}\text{Br}_x$; lower: $[\text{C}_8\text{C}_1\text{IM}][\text{Tf}_2\text{N}]_{1-x}\text{Cl}_x$.

