Supporting Information

Tuning the Miscibility of Water in Imide-Based Ionic Liquids

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1. Materials Characterization

NMR spectra were recorded on AMX-400 or AMX-300 spectrometers (Bruker) at 298 K in the indicated deuterated solvents and are listed in ppm. The signal corresponding to the residual protons or carbons of the deuterated solvent was used as an internal standard for ^{1}H and ^{13}C NMR, respectively. C_6F_6 was utilized as external standard for ^{19}F NMR. IR spectra were acquired on a Nicolet Magna-750 Fourier IR-spectrometer using KBr pellets and Spectragryph optical spectroscopy software.[1] The obtained NMR and IR spectra obtained for [C_2mim][TFSAM] and [C_2mim][TSAC] are given in Figures S1 to S6. The nomenclature of the ILs used in this work and the amount of water in the ILs after purification is provided in Table S1.

***1-Ethyl-3-methyl imidazolium 2,2,2-trifluoromethylsulfonyl-N-cyanoamide (*[C_2mim][TFSAM])**

[C_2mim][TFSAM] was prepared by ion exchange reaction between [C_2mim][Br] and KTFSAM in an aqueous medium in accordance with the procedure published by our group previously.[2,3]

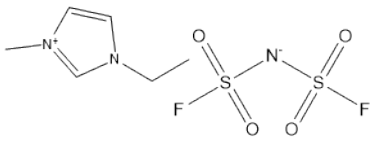
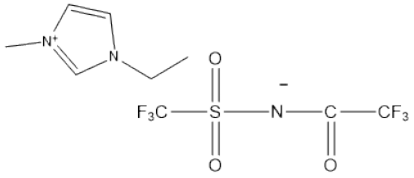
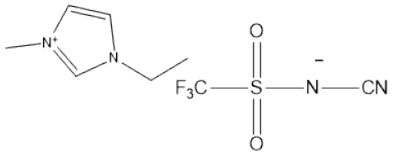
Yield: 85%; Anal. Calcd. for $C_8H_{11}N_4F_3SO_2$ (284.26), %: N, 19.71%; C, 33.80%; H, 3.90%; Found, %: N, 19.59%; C, 33.75%; H, 4.09%; ^{1}H NMR (300.2 MHz, DMSO-d_6): 9.08 (s, 1H, H2 (Im)), 7.72 (s, 1H, H4 (Im)), 7.64 (s, 1H, H5 (Im)), 4.18 (m, 2H, $\underline{CH_2}CH_3$), 3.84 (s, 3H, CH_3), 1.41 (t, 3H, $CH_2\underline{CH_3}$, J_{HH} = 7.5 Hz); ^{13}C NMR (100.6 MHz, DMSO-d_6): 136.2, 125.1-115.5 (q, $^{1}J_{CF}$ = 325 Hz), 123.5, 121.9, 114.5 (CN), 44.2, 35.6, 14.9; ^{19}F NMR (282.4 MHz, DMSO-d_6): -77.8 (s, CF_3); IR (KBr pellet): 3158 (m, ν_{C-H}), 3117 (m, ν_{C-H}), 2991 (w), 2192 (vs, $\nu_{C\equiv N}$), 1574 (s, ν_{-C-N}), 1468 (w), 1430 (w), 1391 (w), 1334 (vs, ν_{asSO2}), 1236 (vs), 1217 (vs, ν_{CF}), 1171 (vs, ν_{sSO2}), 1120 (s, ν_{CF}), 1031 (w), 960 (w), 832 (s), 752 (m), 702 (w), 640 (s), 596 (s), 545 (w), 479 (m), 449 (w), 406 (w) cm^{-1}.

***1-Ethyl-3-methyl imidazolium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide* ([C_2mim][TSAC])**

[C_2mim][TSAC] was synthesized from [C_2mim][Br] and KTSAC by using the procedure suggested by H. Matsumoto.[3-5]

Yield: 82%; Anal. calcd. for $C_9H_{11}N_3F_6SO_3$ (355.3), %: C 30.43; H 3.12; F 32.09; found, %: C 30.15; H 3.07; F 32.49; ^{1}H NMR (400.2 MHz, DMSO-d_6): 9.09 (s, 1H, H2 (Im)), 7.75 (s, 1H, H4 (Im)), 7.66 (s, 1H, H5 (Im)), 4.19 (m, 2H, $\underline{CH_2}CH_3$), 3.84 (s, 3H, CH_3), 1.41 (t, 3H, $CH_2\underline{CH_3}$, J_{HH} = 7.6 Hz); ^{13}C NMR (100.6 MHz, D_2O): 161.1-160.0 (q, $^1J_{CF}$ = 36.4 Hz, $CF_3\underline{C}O$), 136.7, 123.9, 122.4, 124.9-115.3 (q, $^1J_{CF}$ = 323 Hz, $\underline{C}F_3SO_2$), 121.2-112.6 (q, $^1J_{CF}$ = 290 Hz, $\underline{C}F_3CO$), 44.6, 36.0, 15.4; ^{19}F NMR (376.5 MHz, D_2O): -74.9 ($C\underline{F_3}CO$), -78.6 ($C\underline{F_3}SO_2$); IR (KBr pellet): 3157 (s, ν_{C-H}), 3120 (s, ν_{C-H}), 2993 (w), 1675 (vs, $\nu_{C=O}$), 1574 (s, ν_{-C-N}), 1471 (m), 1432 (w), 1384 (s), 1322 (vs, ν_{asSO2}), 1239 (s, ν_{CF}), 1189 (vs, ν_{sSO2}), 1144 (vs), 1124 (vs, ν_{CF}), 1032 (w), 959 (w), 918 (m), 827 (s), 778 (m), 754 (w), 734 (m), 702 (w), 649 (m), 620 (s), 592 (s), 561 (m), 511 (m), 453 (w) cm^{-1}.

Table S1 Chemical structure and respective nomenclature of the ILs used in this work; wt % represents the amount of water in the ILs after purification.

Ionic Liquid	**Nomenclature**	**Chemical Structure**	**wt % H_2O**
1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide	[C_2mim][FSI]		0.08
1-ethyl-3-methylimidazolium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide	[C_2mim][TSAC]		0.04
1-ethyl-3-methylimidazolium 2,2,2-(trifluoromethyl)sulfonyl-N-cyanoamide	[C_2mim][TFSAM]		1.70

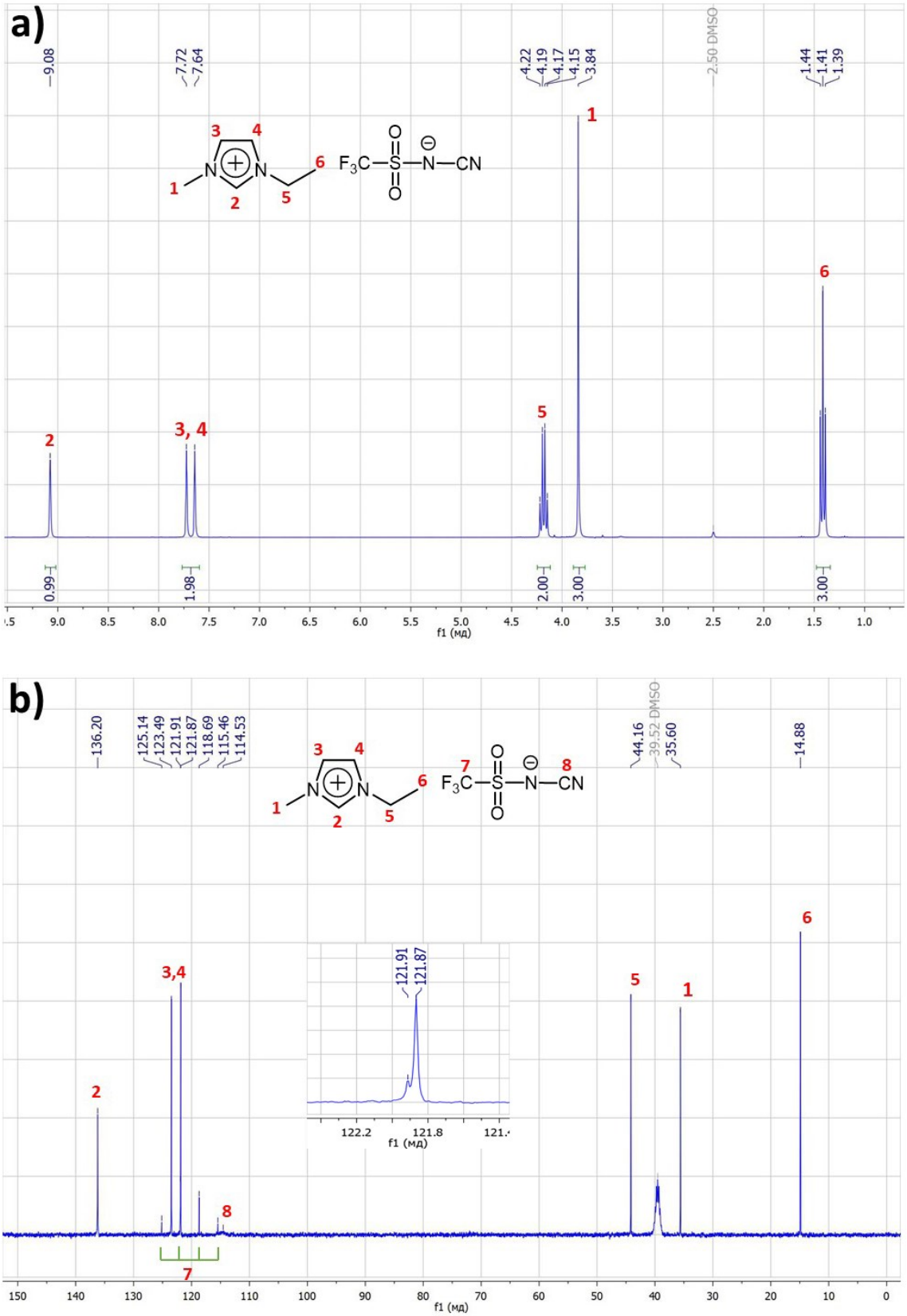


Figure S1. ^{1}H and ^{13}C NMR of [C_2mim][TFSAM].

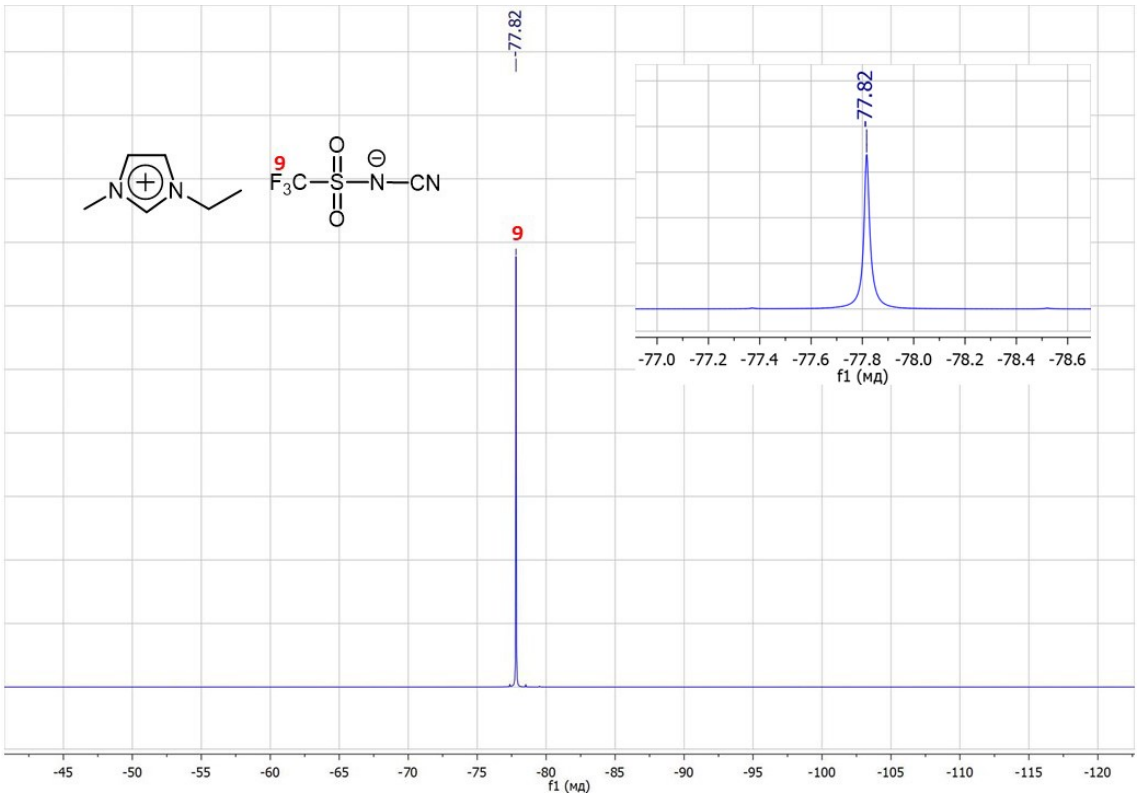


Figure S2. ^{19}F NMR of [C_2mim][TFSAM].

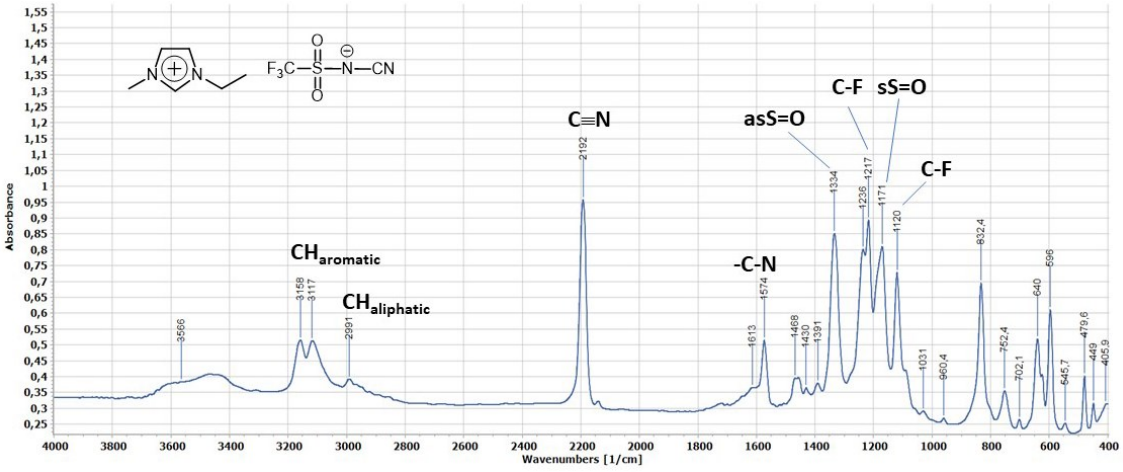


Figure S3. FT-IR spectrum of [C_2mim][TFSAM].

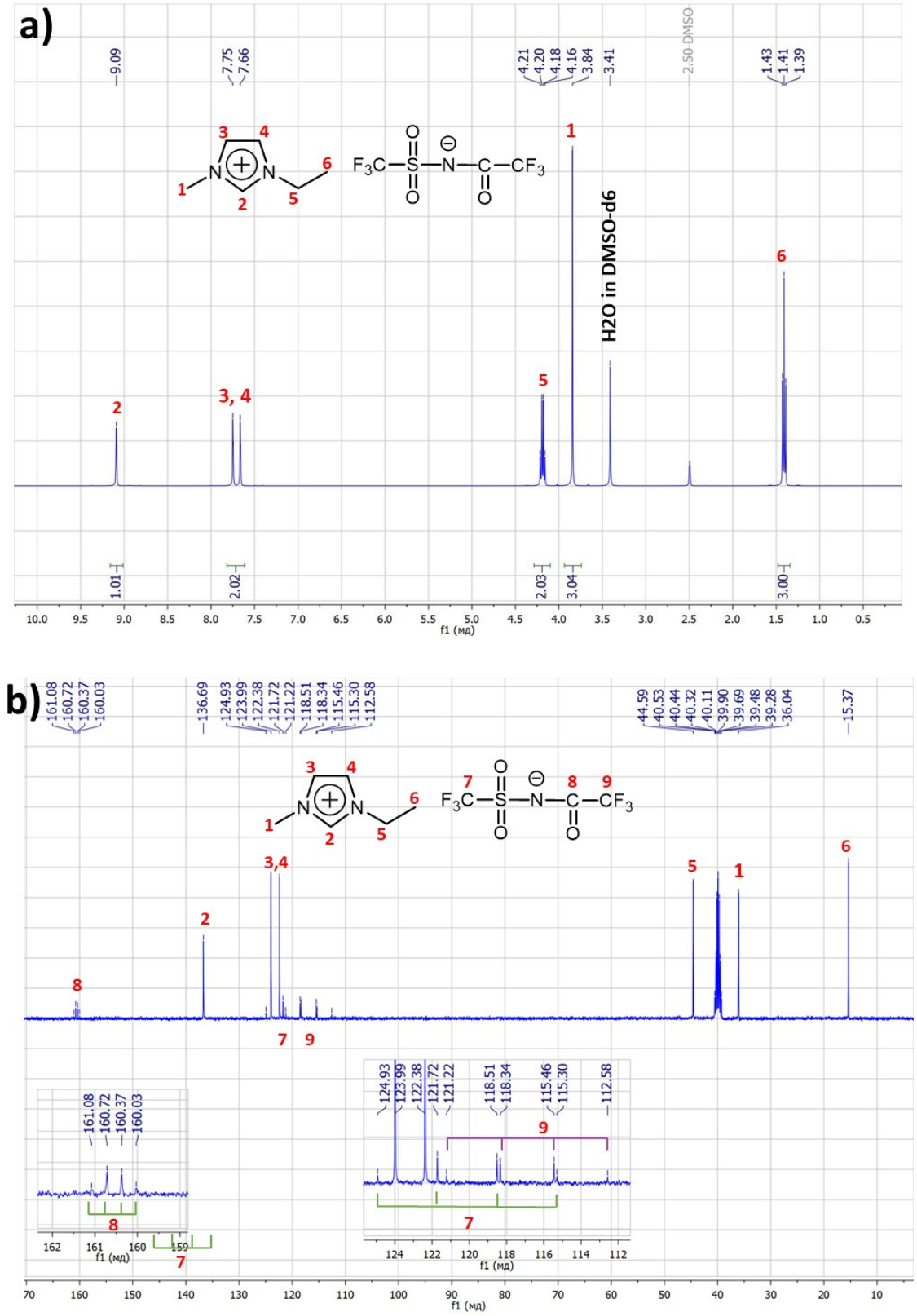


Figure S4. ^{1}H and ^{13}C NMR of [C_2mim][TSAC].

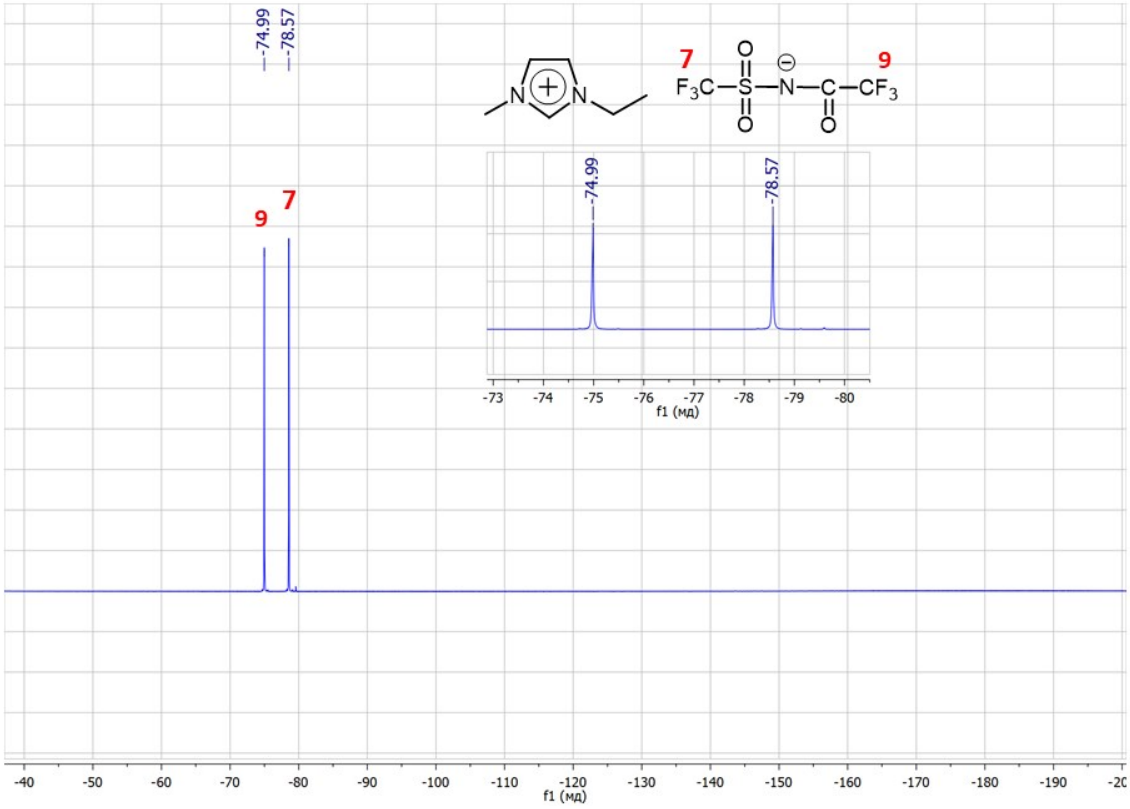


Figure S5. ^{19}F NMR of [C_2mim][TSAC].

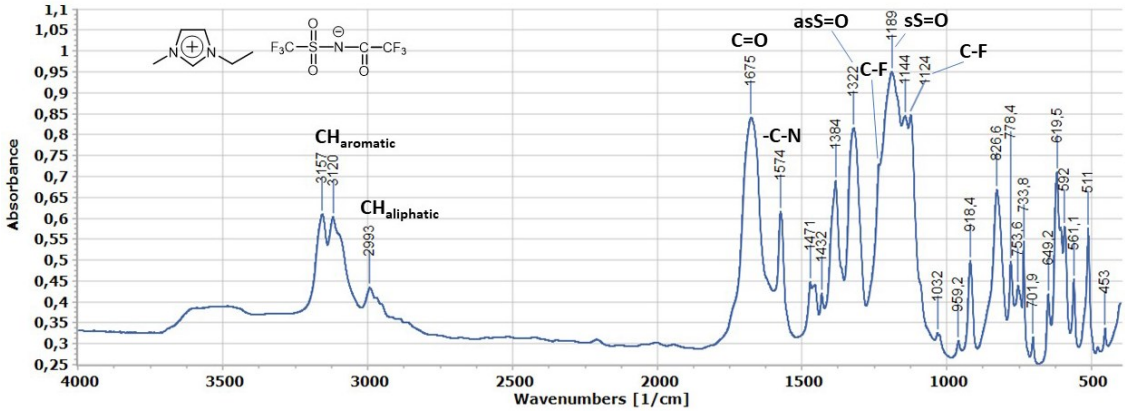


Figure S6. FT-IR spectrum of [C_2mim][TSAC].

2. Solubility Data

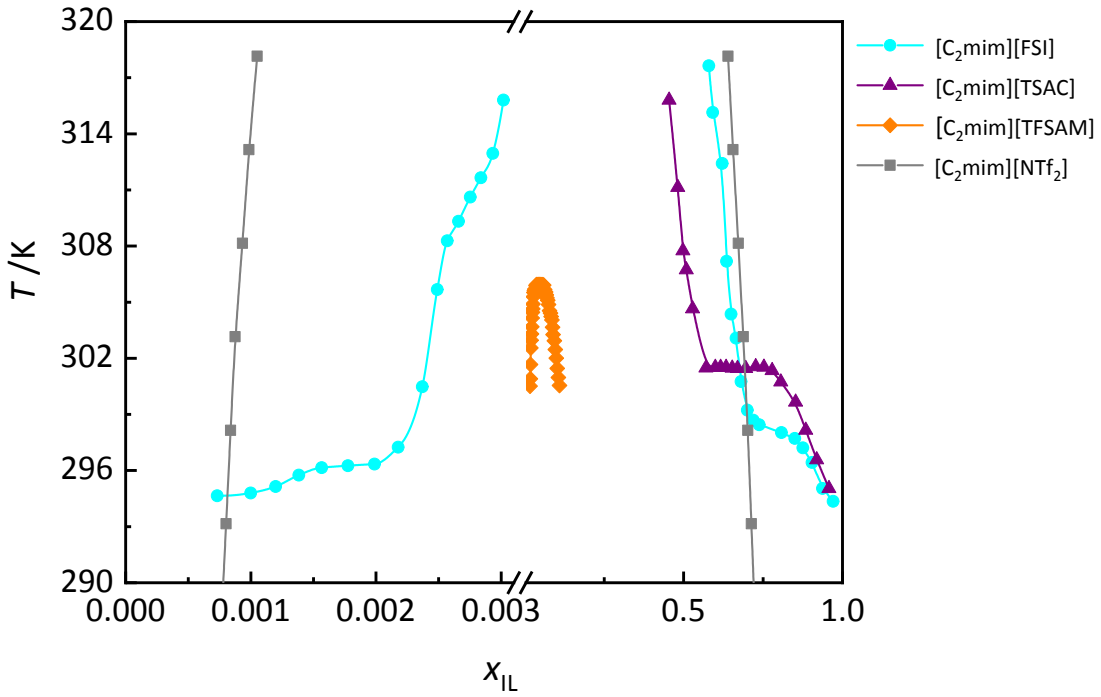


Figure S7. Temperature-composition phase diagram for water and ILs as a function of ILs mole fraction, highlighting the high dilution region of Figure 2 of the main text: (■) [C2mim][NTf2][23], (●) [C2mim][FSI], (▲) [C2mim][TSAC], and (♦) [C2mim][TFSAM]. The lines are just guide to the eye.

Table S2. Experimental mole and mass fraction solubilities of [C_2mim][TFSAM] in water as a function of temperature.[a]

$T \pm 2\sigma$ (K) (n=2)	$x_{[C2mim][TFSAM]}$	$w_{[C2mim][TFSAM]}$
300.55 ± 0.02	0.1092	0.6593
300.97 ± 0.03	0.1055	0.6507
301.46 ± 0.02	0.1019	0.6417
302.01 ± 0.01	0.0990	0.6344
302.47 ± 0.03	0.0960	0.6264
302.94 ± 0.02	0.0928	0.6178
303.27 ± 0.02	0.0892	0.6072
303.66 ± 0.03	0.0873	0.6016
304.05 ± 0.01	0.0852	0.5954
304.23 ± 0.03	0.0828	0.5877
304.41 ± 0.02	0.0805	0.5804
304.54 ± 0.02	0.0775	0.5704
304.87 ± 0.04	0.0748	0.5609
305.10 ± 0.03	0.0722	0.5515
305.23 ± 0.03	0.0698	0.5425
305.59 ± 0.03	0.0675	0.5335
305.54 ± 0.02	0.0655	0.5252
305.67 ± 0.02	0.0627	0.5136
305.91 ± 0.02	0.0595	0.4997
305.93 ± 0.01	0.0564	0.4857
305.93 ± 0.01	0.0518	0.4632
305.93 ± 0.02	0.0489	0.4482
305.93 ± 0.01	0.0472	0.4388
305.93 ± 0.02	0.0453	0.4282
305.93 ± 0.02	0.0439	0.4204
305.93 ± 0.03	0.0416	0.4068
305.93 ± 0.03	0.0387	0.3888
305.93 ± 0.02	0.0369	0.3771
305.88 ± 0.02	0.0350	0.3639
305.70 ± 0.02	0.0314	0.3389
305.62 ± 0.03	0.0303	0.3306
305.52 ± 0.03	0.0287	0.3185
305.29 ± 0.02	0.0270	0.3046
304.90 ± 0.01	0.0255	0.2928
304.64 ± 0.01	0.0252	0.2897
304.46 ± 0.02	0.0241	0.2808
304.15 ± 0.02	0.0230	0.2710
303.68 ± 0.02	0.0219	0.2612
303.30 ± 0.03	0.0210	0.2526
302.96 ± 0.02	0.0199	0.2431
302.55 ± 0.02	0.0191	0.2349
301.67 ± 0.02	0.0182	0.2263
300.90 ± 0.01	0.0172	0.2169
300.51 ± 0.02	0.0166	0.2102

[a] σ (T) is the standard error of the mean; standard uncertainty u is $u_r(x) = 0.0001$; n is the number of replicates.

Table S3. Experimental mole and mass fraction solubilities of [C_2mim][FSI] in water as a function of temperature.[a]

$T \pm 2\sigma$ (K) (n=2)	$x_{[C2mim][FSI]}$	$w_{[C2mim][FSI]}$
295.65 ± 0.03	0.0007	0.0117
294.80 ± 0.04	0.0010	0.0159
295.14 ± 0.03	0.0012	0.0190
295.75 ± 0.05	0.0014	0.0219
296.15 ± 0.03	0.0016	0.0248
296.26 ± 0.03	0.0018	0.0280
296.34 ± 0.02	0.0020	0.0312
297.24 ± 0.03	0.0022	0.0341
300.48 ± 0.05	0.0024	0.0370
305.67 ± 0.05	0.0025	0.0388
308.28 ± 0.02	0.0026	0.0400
309.32 ± 0.02	0.0027	0.0414
310.62 ± 0.02	0.0028	0.0428
311.65 ± 0.04	0.0028	0.0440
312.95 ± 0.03	0.0029	0.0454
315.80 ± 0.04	0.0030	0.0467
318.66 ± 0.03	0.0031	0.0480

[a] σ (T) is the standard error of the mean; standard uncertainty u is $u_r(x) = 0.0001$; n is the number of replicates.

Table S4. Experimental mole and mass fraction solubilities of water in [C_2mim][FSI] IL as a function of temperature.[a]

$T \pm 2\sigma$ (K) (n=2)	$x_{[C2mim][FSI]}$	$w_{[C2mim][FSI]}$
294.35 ± 0.05	0.9705	0.9981
295.04 ± 0.03	0.9373	0.9959
296.43 ± 0.04	0.9041	0.9935
297.21 ± 0.04	0.8755	0.9913
297.72 ± 0.03	0.8500	0.9892
298.03 ± 0.03	0.8078	0.9855
298.44 ± 0.02	0.7378	0.9785
298.69 ± 0.04	0.7191	0.9764
299.22 ± 0.03	0.7006	0.9743
300.75 ± 0.02	0.6807	0.9718
303.08 ± 0.05	0.6650	0.9698
304.36 ± 0.07	0.6495	0.9677
307.19 ± 0.03	0.6351	0.9657
312.42 ± 0.06	0.6217	0.9638
315.14 ± 0.01	0.5915	0.9591
317.64 ± 0.01	0.5796	0.9571

[a] σ (T) is the standard error of the mean; standard uncertainty u is $u_r(x) = 0.0001$; n is the number of replicates.

Table S5. Experimental mole and mass fraction solubilities of water in [C_2mim][TSAC] IL as a function of temperature.[a]

$T \pm 2\sigma$ (K) (n=2)	$x_{[C2mim][TSAC]}$	$w_{[C2mim][TSAC]}$
295.04 ± 0.03	0.9577	0.9978
296.57 ± 0.07	0.9187	0.9955
298.16 ± 0.02	0.8844	0.9934
299.66 ± 0.02	0.8526	0.9913
300.74 ± 0.04	0.8061	0.9880
301.35 ± 0.03	0.7786	0.9858
301.53 ± 0.02	0.7527	0.9836
301.55 ± 0.02	0.7269	0.9813
301.46 ± 0.01	0.6956	0.9783
301.46 ± 0.01	0.6694	0.9756
301.48 ± 0.02	0.6527	0.9737
301.52 ± 0.01	0.6337	0.9715
301.52 ± 0.01	0.6166	0.9695
301.52 ± 0.01	0.5999	0.9673
301.48 ± 0.03	0.5702	0.9632
304.65 ± 0.02	0.5281	0.9567
306.73 ± 0.01	0.5083	0.9533
307.75 ± 0.04	0.4980	0.9514
311.13 ± 0.03	0.4816	0.9483
315.80 ± 0.04	0.4545	0.9427

[a] σ (T) is the standard error of the mean; standard uncertainty u is $u_r(x) = 0.0001$; n is the number of replicates.

3. Dynamic Light Scattering Experiments

The Dynamic Light Scattering (DLS) experiments were performed at 298.15 K on a Zetasizer Nano ZS from Malvern, model ZEN3600. This apparatus was equipped with a 4 mW He–Ne solid-state laser operating at 633 nm. The backscattered light was detected at 173° and the data processed using the Zetasizer software. For the acquisition of the autocorrelation curve, the difference between refractive index of water (found in the software database) and ILs[6] was considered. In general, the results quality was not found to be good and z-average between 6200 and 9000 nm. The three ILs present low viscosities at 298.15 K ([C_2mim][FSI] (η = 19.3 mPa s), [C_2mim][TSAC] (η = 25.3 mPa s), and [C_2mim][TFSAM] (η = 20.2 mPa s)), as previously reported by us.[7]

4. Molecular Dynamics Simulations Details

Table S6. Simulation boxes details used in the Molecular Dynamics runs.

Ionic Liquid	Number of Ion Pairs	Number of Water Molecules	x_{IL}	Box Side / Å
$[C_2mim][NTf_2]$	300	33	0.9	5.073
	300	100	0.75	5.092
$[C_2mim][FSI]$	300	33	0.9	4.669
	300	100	0.75	4.689
$[C_2mim][TSAC]$	300	33	0.9	4.942
	300	100	0.75	4.976
	300	200	0.6	5.012
$[C_2mim][TFSAM]$	300	33	0.9	4.742
	300	100	0.75	4.771
	300	200	0.6	4.812
	300	2700	0.1	5.712

5. References

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