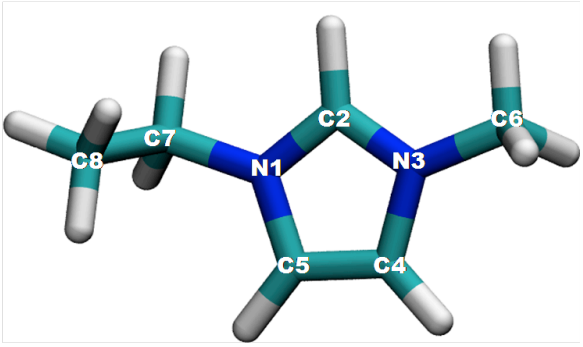
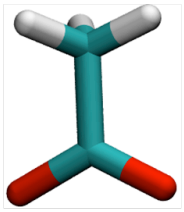
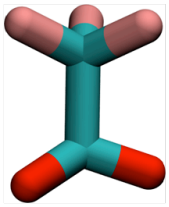
Electronic Supplementary Material (ESI) for Soft Matter.



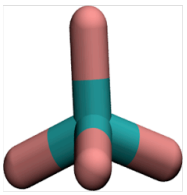
1-ethyl-3-methylimidazoliu ([emim])



Acetate [Ac]



Trifluoroacetate [Tfa]



Tetrafluoroborate [BF_4]

Figure S1: Atom notations and molecular structures of the studied IL cation and anions. Colour scheme: C, cyan; N, blue; O, red; F, pink; H, white.

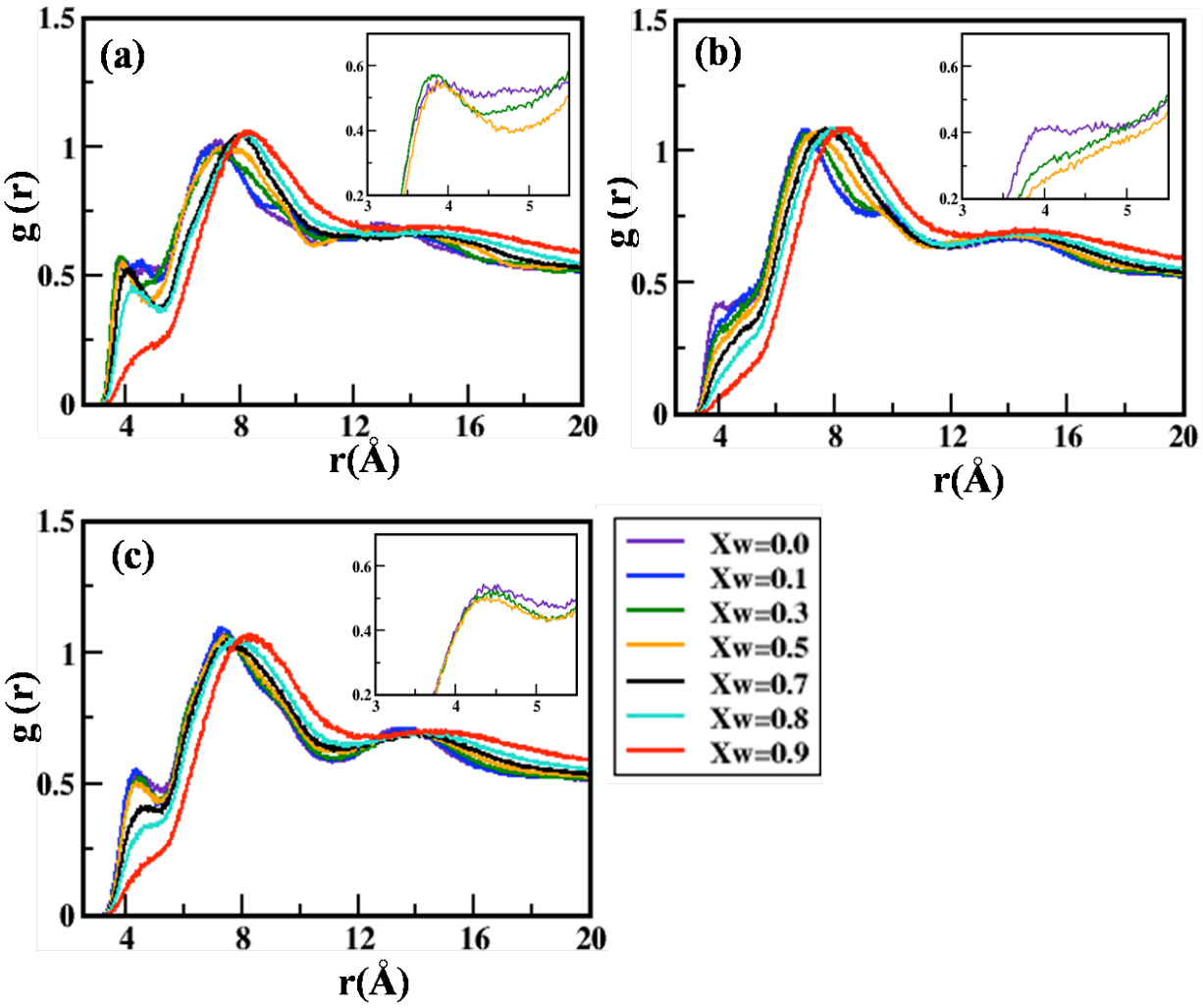


Figure S2: Center-of-mass distribution of the cation imidazolium rings around a central cation in (a) [emim][Ac]- (b) [emim][Tfa]- and (c) [emim][BF_4]/water binary mixtures at different mole fractions of water (X_w). Insets highlight the effect of water addition on the pre-peak at 4 Å, which is an indicator of the ring stacking behavior of the cation headgroups in the three binary mixtures.

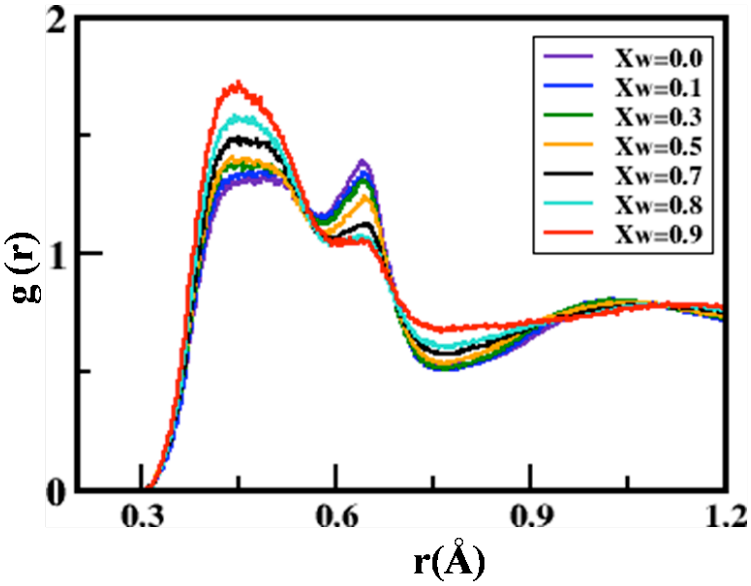


Figure S3: Center-of-mass distribution of the $-CF_3$ moeity of [Tfa] anion around the cation imidazolium head group in [emim][Tfa]/water binary mixtures at different X_w.

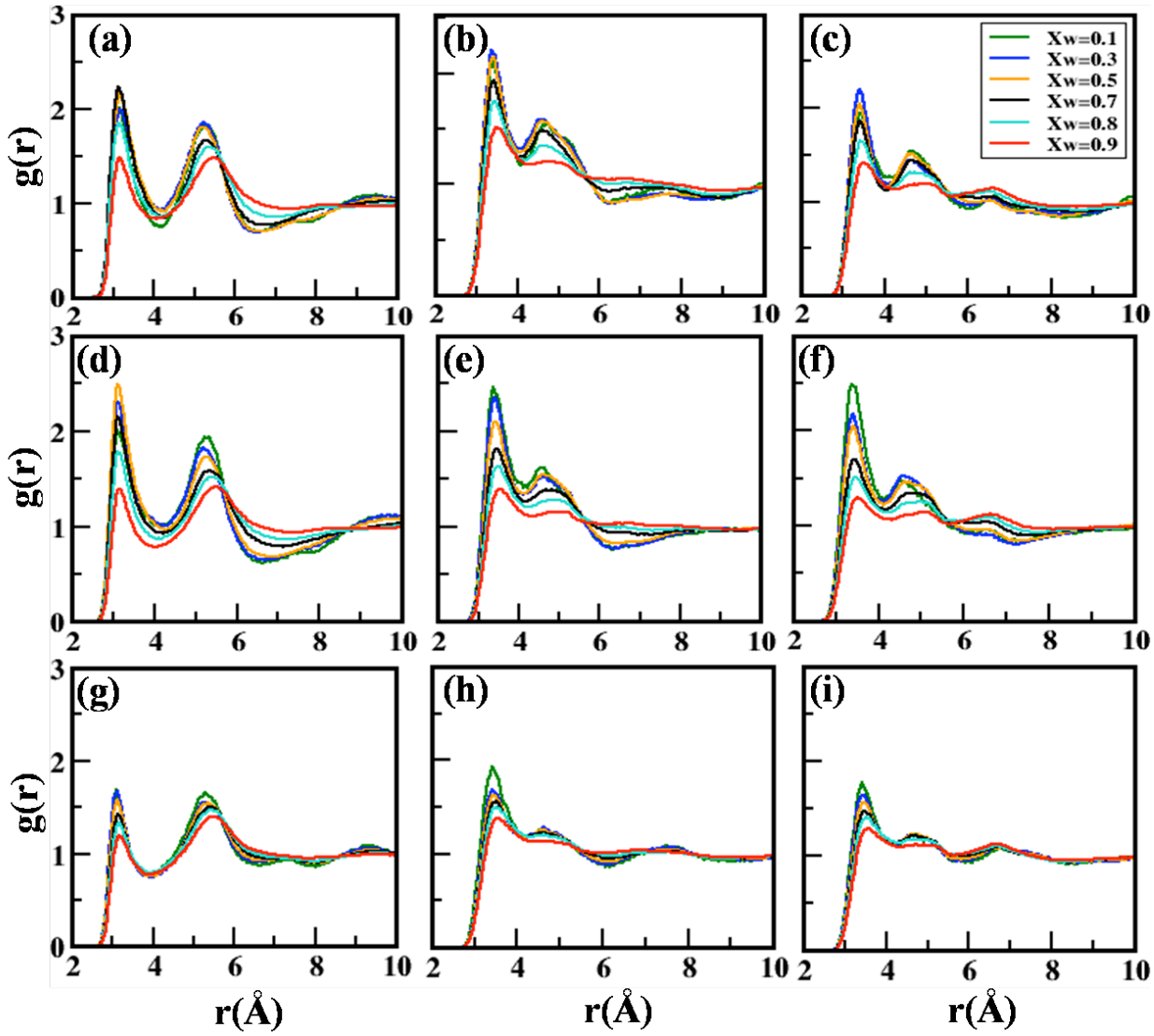


Figure S4: Site-site RDFs of water around cation imidazolium ring carbons C2, C4 and C5, respectively in the binary mixtures of (a-c) [emim][Ac], (d-f) [emim][Tfa] and (g-i) [emim][BF_4] at different X_w. For atom notations see Figure S1.

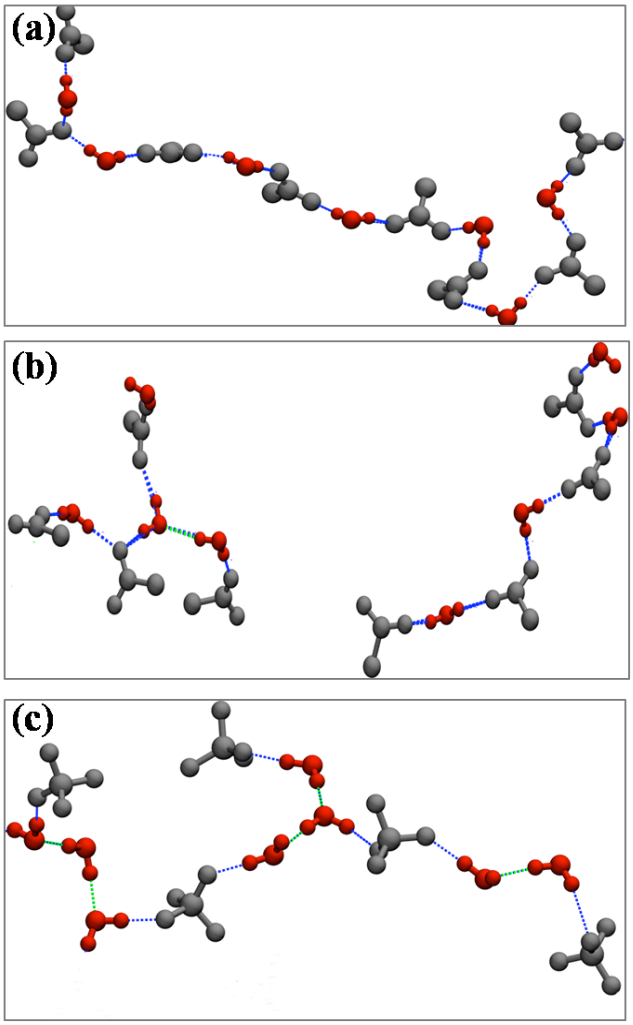


Figure S5: Magnified illustrations of anion-water wires at $X_w = 0.5$ in (a) [emim][Ac]-, (b) [emim][Tfa]- and (c) [emim][BF_4]/water mixtures depict the different hydrogen bonding patterns in the three systems. Compare the continuous, long, uninterrupted anion-water wires (blue dashes) in [emim][Ac] with shorter anion-water wires in [emim][Tfa] and anion-water wires interspersed with water-water hydrogen bonds (green dashes) in [emim][BF_4]. Color scheme for molecules: grey: anion, red: water. Anion H's are omitted for clarity. See Figure 6 in main text for complete details.

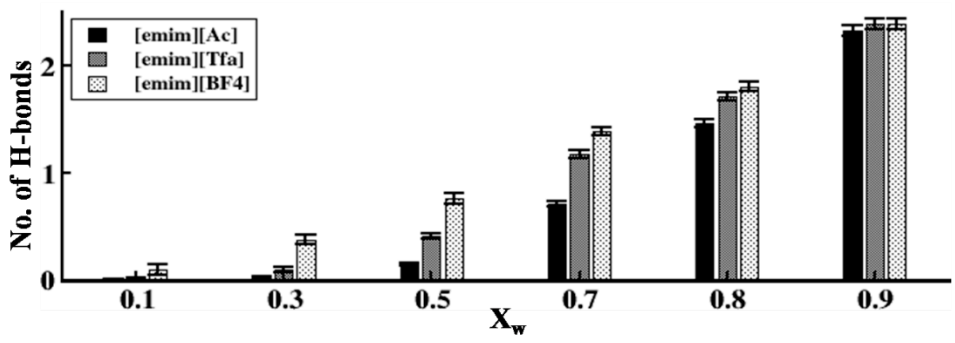


Figure S6: Number of water-water hydrogen bonds formed per molecules of water in different IL/water binary mixtures as a function of X_w.

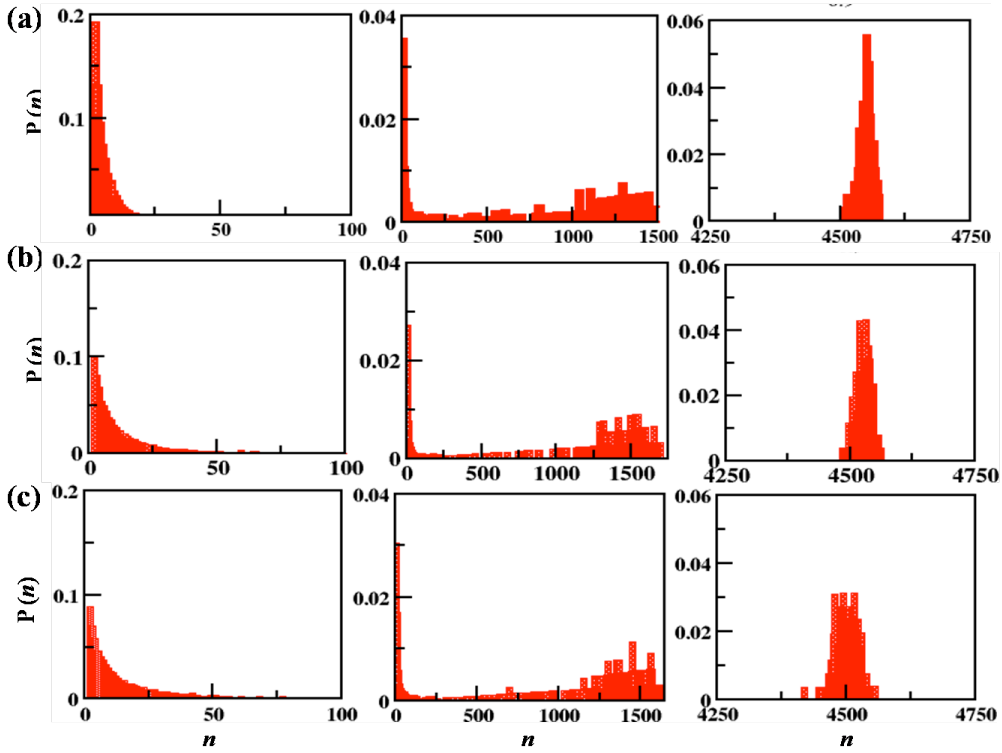


Figure S7: Size distribution of water aggregates formed in (a) [emim][Ac]-, (b) [emim][Tfa]- and [emim][BF_4]/water binary mixtures at water concentrations of X_w = 0.7 (left panel), 0.8 (middle panel) and 0.9 (right panel). At a very high dilution of X_w = 0.9, all the water molecules (4608 water, see Table 1 for composition of simulated systems) belong to a single mutually hydrogen bonded water network, resulting in a single peak in the water cluster distribution.

Table S1: Fit parameters of the water-water hydrogen bond time correlation function for representative IL/water binary mixtures. The τ_{avg} values indicate 2-3 orders of magnitude slower re-organization of H-bonds in these mixtures compared to bulk water.

IL	X_w	c_1	τ_1	c_2	τ_2	c_3	τ_3	c_4	τ_4	τ_{avg}
[Ac]	0.3	0.23	1.65	0.001	42.68	0.73	688.79	0.04	13018.05	1023.96
	0.5	0.18	2.35	0.08	75.43	0.34	821.73	0.40	12070.44	5114.02
	0.9	0.37	1.43	0.54	13.53	0.09	73.65	-	-	14.46
[Tfa]	0.3	0.11	1.13	0.11	7.91	0.39	176.11	0.39	2808.37	1164.94
	0.5	0.21	2.48	0.15	39.97	0.39	202.28	0.26	1168.85	389.31
	0.9	0.42	1.27	0.52	9.07	0.06	57.32	-	-	8.69
[BF_4]	0.3	0.16	1.11	0.25	14.74	0.41	86.77	0.17	533.32	130.10
	0.5	0.30	3.15	0.55	41.45	0.13	257.52	-	-	57.22
	0.9	0.41	1.17	0.53	6.88	0.06	39.65	-	-	6.51