**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 –CF₃ 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][BF₄]/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][BF₄]. 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][BF₄]/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 $\tau_{avg}$ values indicate 2-3 orders of magnitude slower re-organization of H-bonds in these mixtures compared to bulk water.

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