Supporting Information

Quantification of Zwitterion Betaine in Betaine Bis(trifluoromethylsulfonyl)imide and its Influence on Liquid-Liquid Equilibrium with Water

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Experimental Information

[HBet][TFSI] Synthesis

Three different samples of [HBet][TFSI] (see **Fig. S1**) were synthesized, with the main difference being HTFSI being added after synthesis for samples 2 and 3. Betaine hydrochloride (HBetCl, ≥ 99 %) was purchased from Sigma-Aldrich, lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, Battery Electrolyte HQ-115) was obtained from 3M Fluorad™, and trifluoromethanesulfonimide (HTFSI ≥ 95.0 %, stored in cabinet desiccator from Scienceware) was purchased from Sigma-Aldrich.

For sample **1**, LiTFSI (26.30 g, 91.61 mmol) and HBetCl (14.06 g, 91.53 mmol) were dissolved in 100 mL water (18.2 MΩ) at 25°C. The solution was stirred for two hours. After it formed two phases, some amount of water was removed with the use of a rotary evaporator (Heidolph). Then, the bottom (product) phase was separated and washed several times with water until the aqueous extract did not test positive for chloride ion, as determined by silver nitrate tests. For the sample **2**, 50 wt % aqueous HTFSI solution (0.874 g, 3.11 mmol) was added to a portion of the first sample (5.946 g) and was put on a hot plate set at 70 °C for a day in the hood. After the reaction, the sample was placed on a Schlenk line for two days to remove extra water and HTFSI. The sample was placed in an oil bath, and the temperature set at 100 °C. For sample **3**, additional HTFSI (0.287 g, 1.02 mmol) and water (0.160 g, 18.2 MΩ) were added to a portion of sample **2** (3.1247g) at room temperature. It was stirred and heated on a hot plate for 11 hours at 70 °C. After reaction, it was put on the Schlenk line at 70 °C for 19 hours. Note that elevated temperature is required for removal of volatiles because [HBet][TFSI] has a melting point above 50 °C.[1] δ_H 3.17 (s,9H, N(CH$_3$)$_3$) 4.27 (s, 2H, N(CH$_2$)). δ_F -78.83 (s, 6F, (CF$_3$)$_2$).
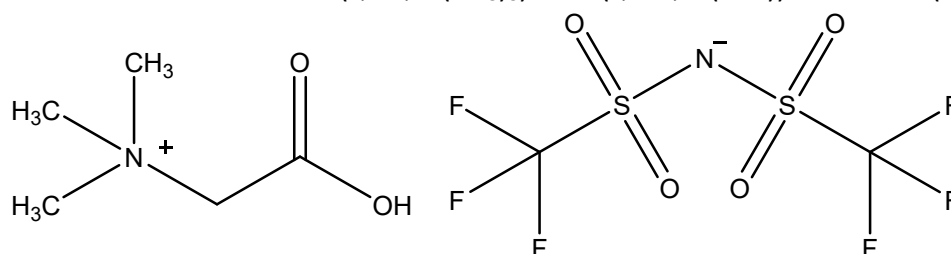

Fig. S1 Protonated betaine bis(trifluoromethylsulfonyl)imide ([HBet][TFSI])

Attempts to quantify neutral betaine by Raman Spectroscopy and ^{1}H-NMR

In addition to the use of ion chromatography, q[19]F-NMR and mass and charge balances (described below), we also investigated Raman and ^{1}H NMR spectroscopy as potential methods to quantify the amount of neutral betaine in the [HBet][TFSI] samples. Raman spectra were obtained from commercially purchased (ThermoScientific) betaine (98 %) and betaine hydrochloride (99 %). Both [HBet][TFSI] samples were synthesized via a metathesis reaction with no additional HTFSI to promote protonation of the zwitterion (**Fig. S2**). All spectra were collected using a Thermo Scientific DXRxi Raman Imaging Microscope spectrometer with a 532

nm excitation laser. The spectral region collected was 53 – 6000 cm^{-1} with exposure times ranging from 0.5 – 1 seconds. Laser powers for all of the solids ranged from 1.5 - 3.2 mW while the H_2O saturated [Hbet][TFSI] was collected with 10 mW of laser power. All samples were collected using a 10x objective and 25 μm aperture with an accumulation of 1000 scans. **Fig. S2** shows the representative spectra obtained from these measurements. Focusing on the region containing the -COO stretch, the spectra obtained from H_2O saturated [Hbet][TFSI] has a broad stretch at 1741 cm^{-1} with a small shoulder at 1765 cm^{-1}. This aligns well with protonated HBet.[2] When the solution is dried to a solid containing 0.15 wt % H_2O, a second peak appears at approximately 1652 cm^{-1}. Stretches in this region have been associated with both HBetCl when dissolved in H_2O and betaine zwitterion dissolved in H_2O. This suggests Raman spectroscopy may be used to detect both the protonated betaine and the betaine zwitterion, but significant method development is needed to use this technique for quantitative analysis.
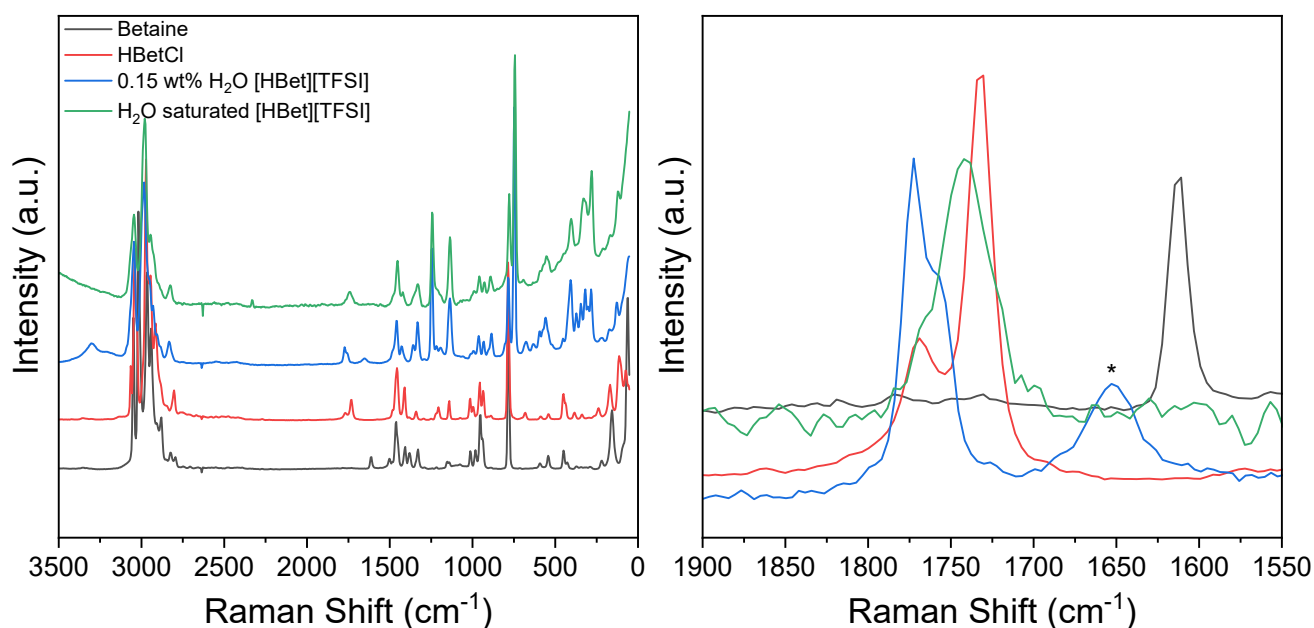
Fig. S2 Raman spectra obtained from betaine, HbetCl, 0.15 wt % H_2O [Hbet][TFSI], and H_2O saturated [HBet][TFSI] (left). The spectral region housing the –COO$^-$ and –COOH stretching displays multiple stretches in the dried down [HBet][TFSI]. The star indicates a stretch in the region of the betaine zwitterion or HBetCl when dissolved in H_2O (right).

For ^{1}H NMR, this was done by adding betaine to a H_2O saturated [HBet][TFSI] sample and looking for changes in the spectra (**Fig. S3**). Betaine was commercially purchased from Acros Organics (98 %). NMR data was collected using a 400 MHz Bruker Ascend at room temperature. Betaine was added to [HBet][TFSI] in a 1bet:1HBet molar ratio assuming the synthesized [HBet][TFSI] started with no betaine zwitterion. Since no additional HTFSI was added to the [HBet][TFSI], it is likely the sample has significantly more betaine zwitterion. The IL samples were loaded into a Teflon liner with D_2O as an external solvent. Each spectrum is

referenced to D_2O (4.79 ppm). The peaks at 3.30 and 4.17 ppm are assigned to the three CH_3 and N-CH_2 groups, respectively, agreeing with the previously reported ^1H NMR.[3] We hypothesize the peak at 5.36 ppm is associated with bulk H_2O. Nockemann et al. reported a spectrum of [HBet][TFSI] with equal amounts of H_2O while ours is of H_2O saturated [HBet][TFSI] (IL rich phase) suggesting bulk H_2O would be visible in the ^1H NMR. We found that the ^1H NMR spectrum of [HBet][TFSI] is insensitive to added betaine, as shown in **Fig. S3** for water saturated samples. Even for a roughly equimolar mixture of [HBet][TFSI] and neutral betaine (1.02 moles [HBet][TFSI] per mole of betaine) there is little change in the ^1H NMR spectrum.
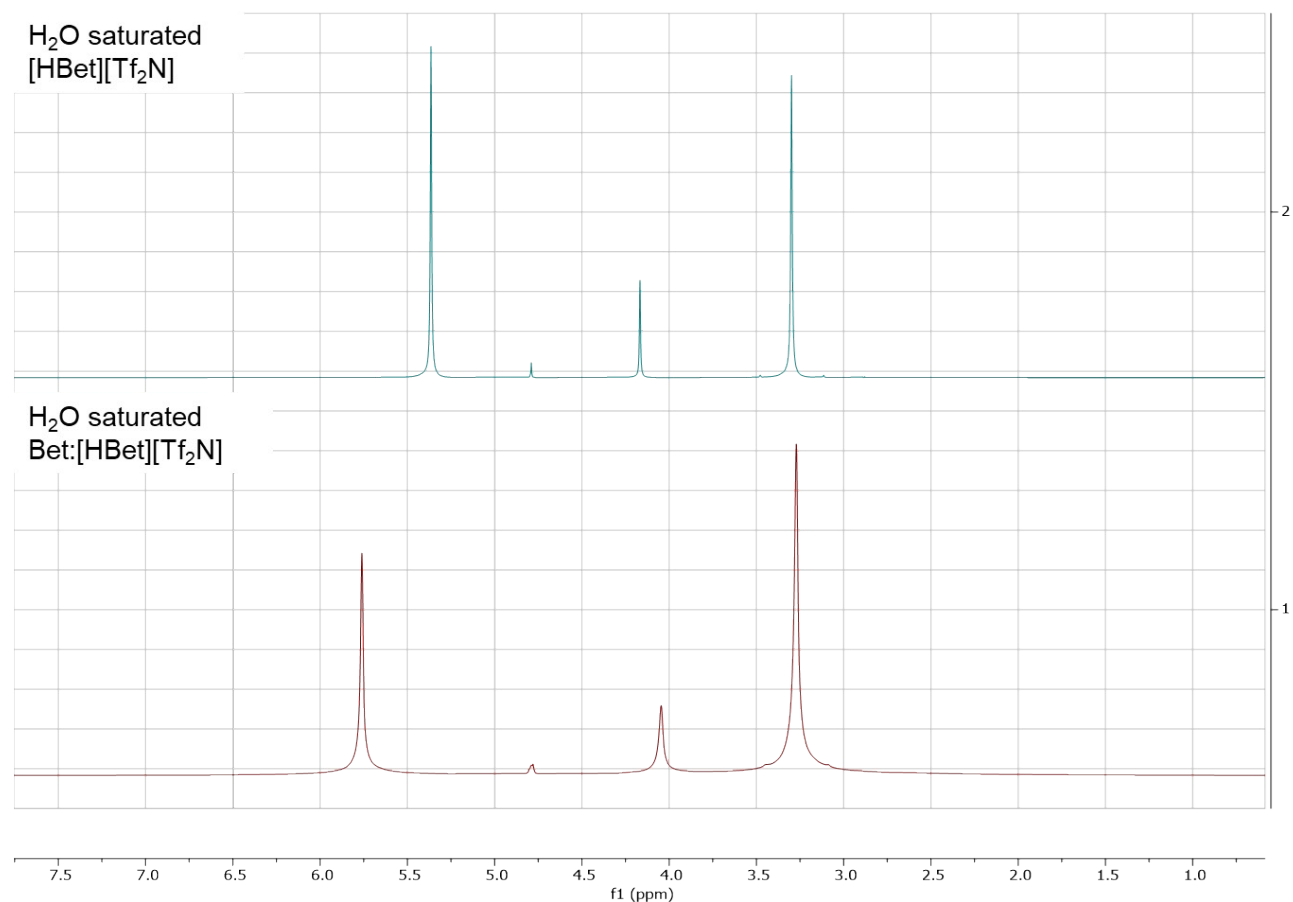
Fig. S3 ^1H-NMR spectra of H_2O saturated [HBet][TFSI] and H_2O saturated Bet:
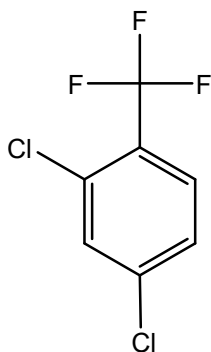[HBet][TFSI].

Impurity quantification by Ion Chromatography, q^{19}F-NMR and mass and charge balances
        The remaining lithium and chloride ions in the ionic liquids were measured by Ion Chromatography (Dionex^{TM} ICS-5000$^+$). The concentration of [TFSI$^-$] was measured by q^{19}F-NMR using a Bruker 500 MHz NMR. The inverse gated decoupling for ^1H pulse sequence was used. The acquisition time was 7.4 s, the pulse width (15 μs, 90^0) was used, and the spectral width

was about 14000 Hz (30 ppm). The delay time was 60 s and the number of scans was 32. 2,4-dichlorobenzotrifluoride (98 % purchased from Sigma-Aldrich) was used as an internal reference (see **Fig. S4**). δ_F -61.45 (s, 3F, C(CF$_3$)).

$$P_x = \frac{I_x \; N_{ref} \; M_x \; m_{ref}}{I_{ref} \; N_x \; M_{Ref} \; m_x} P_{ref} \tag{S1}$$

The above equation was used to determine the concentration of [TFSI⁻] in [Hbet][TFSI]. I, N, M, m, and P represent the integration value of the specie, the number of atoms belonging to the respective molecular unit, the molecular weight, the mass, and the purity of the species, respectively.[4]

Fig. S4 2,4-dichlorobenzotrifluoride, the reference compound used for the q^{19}F-NMR experiments

A typical ^{1}H NMR scan for [HBet][TFSI] is shown in **Fig. S5**. This particular scan is for sample (**1**). The large peak at 3.17 ppm corresponds to the nine protons of the three methyl groups on the ammonium. The peak at 4.27 ppm is the two protons on the carbon between the carboxylic acid and the ammonium. The peak at ~2.5 ppm is from DMSO (the solvent) and the broad peak centered at ~3.3 ppm is residual water. The proton on the carboxylic acid is sufficiently labile that it does not appear in the ^{1}H NMR. **Fig. S6** shows the q^{19}F-NMR of sample (**1**).   From integration of the two peaks in this spectrum we find that I_x = 262491 and I_{ref} = 326055. For [TFSI-], N_x, M_x and m_x are 6, 280.134 g/mol and 86.6 mg, respectively. Likewise, for the 2,4-dichlorobenzotrifluoride reference, N_{ref}, M_{ref} and m_{ref} are 3, 215 g/mol and 115.6 mg, respectively. P_{ref} is the purity of the 2,4-dichlorobenzotrifluoride reference material, which is 0.98. Therefore, from equation (**S1**), the concentration of [TFSI⁻] in [Hbet][TFSI] is P_x = 0.686 g [TFSI⁻] per g [Hbet][TFSI]. The equivalent q^{19}F-NMR spectra for samples (**2**) and (**3**) are shown in **Fig. S7** and **S8**, respectively, where I_x = 278356, I_{ref} = 293880, m_{ref} = 111.3 mg, and m_x = 97.5 mg for sample (**2**) and I_x = 289346 and I_{ref} = 315012, m_{ref} = 114.4 mg, and m_x = 96.5 mg for sample (**3**). Two solutions were made for sample (**1**), and three solutions were made for samples (**2**) and (**3**). Measurements were conducted two times for each solution. The weight fractions were determined as averages of the replicate measurements. The average weight fraction of [TFSI⁻] in sample (**1**) is 0.683.

A cation ion chromatogram and an anion ion chromatogram for sample (**1**) are shown in **Fig. S9** and **Fig. S10**, as examples. To obtain the weight fractions of lithium and chloride ions, two different solutions were prepared for each sample, and measurements were conducted four times for each solution using ion chromatography. Although bromide and chloride ion peaks were detected in the blank sample shown in **Fig. S11** due to column contamination, these peaks were disregarded in the calculations because their concentrations were negligible compared to the concentrations of other species in the samples. By utilizing calibration curves, the corresponding concentrations of lithium and chloride ions for **Fig. S9** and **Fig. S10** were determined as 4.0×10^{-3} ppm and 0.374 ppm, respectively. The overall concentration of the sample analysed by ion chromatography was 1946 ppm. Consequently, the weight fractions of lithium ion and chloride ion were calculated 2.1×10^{-6} and 1.9×10^{-4}, respectively. The weight fractions of lithium and chloride ions were also determined as averages of the replicate measurements. For sample (**1**), the average weight fractions of lithium and chloride ions were 3.3×10^{-6} and 1.9×10^{-4}, respectively.

The concentration of the neutral betaine impurity in sample (**1**) was determined using the average weight fractions of each species and the charge and mass balances shown in Equations (1) and (2) in the main article. The moles per gram can be expressed by following equations.

$$[HBet^{+}] = [TFSI^{-}] + [Cl^{-}] - [Li^{+}]$$

$$[HBet^{+}] = \omega_{TFSI^{-}}/M_{TFSI^{-}} + \omega_{Cl^{-}}/M_{Cl^{-}} - \omega_{Li^{+}}/M_{Li^{+}}$$

$$P_{TFSI^{-}} = 0.683, \omega_{Cl^{-}} = 1.9 \times 10^{-4}, \omega_{Li^{+}} = 3.3 \times 10^{-6}$$
$$M_{TFSI^{-}} = 280.134, M_{Cl^{-}} = 35.453, M_{Li^{+}} = 6.941$$

$$[HBet^{+}] = 2.44 \times 10^{-3} \, mol/g, \omega_{HBet^{+}} = M_{HBet^{+}} \cdot [HBet^{+}] = 0.288$$

$$\omega_{Bet} = 1 - \omega_{Cl^{-}} - P_{TFSI^{-}} - \omega_{Li^{+}} - \omega_{HBet^{+}} = 2.87 \times 10^{-2}$$

Therefore, the overall concentration (mol/g) in sample is shown below.

$$\frac{\omega_{Cl^{-}}}{M_{Cl^{-}}} + \frac{\omega_{Li^{+}}}{M_{Li^{+}}} + \frac{P_{TFSI^{-}}}{M_{TFSI^{-}}} + [HBet^{+}] + [Bet] = 5.13 \times 10^{-2} (mol/g) = C$$

The mole fractions shown in **Table 1** for sample (**1**) were obtained by dividing the concentrations of each species (g/mol) by the overall concentration (g/mol).

The 95% confidence intervals for each species were statistically calculated, and the resulting uncertainties for each species are displayed in **Table S2**. The uncertainties of the lithium and chloride ion concentrations are relatively high; however, these uncertainties have a

negligible impact on the uncertainty in the weight fractions of [TFSI⁻], [HBet⁺] and Bet since the concentrations of lithium and chloride ions are significantly low.

Table S1. The weight fractions in the measurements for the [HBet][TFSI]

	Cl^-	Li^+	$TFSI^-$	$HBet^+$	Bet
1	1.9×10^{-4}	3.3×10^{-6}	0.683	0.288	2.88×10^{-2}
2	1.3×10^{-4}	2.5×10^{-6}	0.691	0.292	1.70×10^{-2}
3	2.7×10^{-4}	2.9×10^{-4}	0.695	0.294	1.14×10^{-2}

Table S2. The uncertainties in the measurements for the [HBet][TFSI] samples

	Cl^-	Li^+	$TFSI^-$	$HBet^+$	Bet
1	$\pm1.0\times10^{-5}$	$\pm8.7\times10^{-7}$	$\pm4.14\times10^{-3}$	$\pm1.75\times10^{-3}$	$\pm5.89\times10^{-3}$
2	$\pm2.3\times10^{-5}$	$\pm6.6\times10^{-7}$	$\pm1.57\times10^{-3}$	$\pm6.61\times10^{-4}$	$\pm2.23\times10^{-3}$
3	$\pm9.5\times10^{-6}$	$\pm6.9\times10^{-7}$	$\pm1.86\times10^{-3}$	$\pm7.84\times10^{-4}$	$\pm2.64\times10^{-3}$
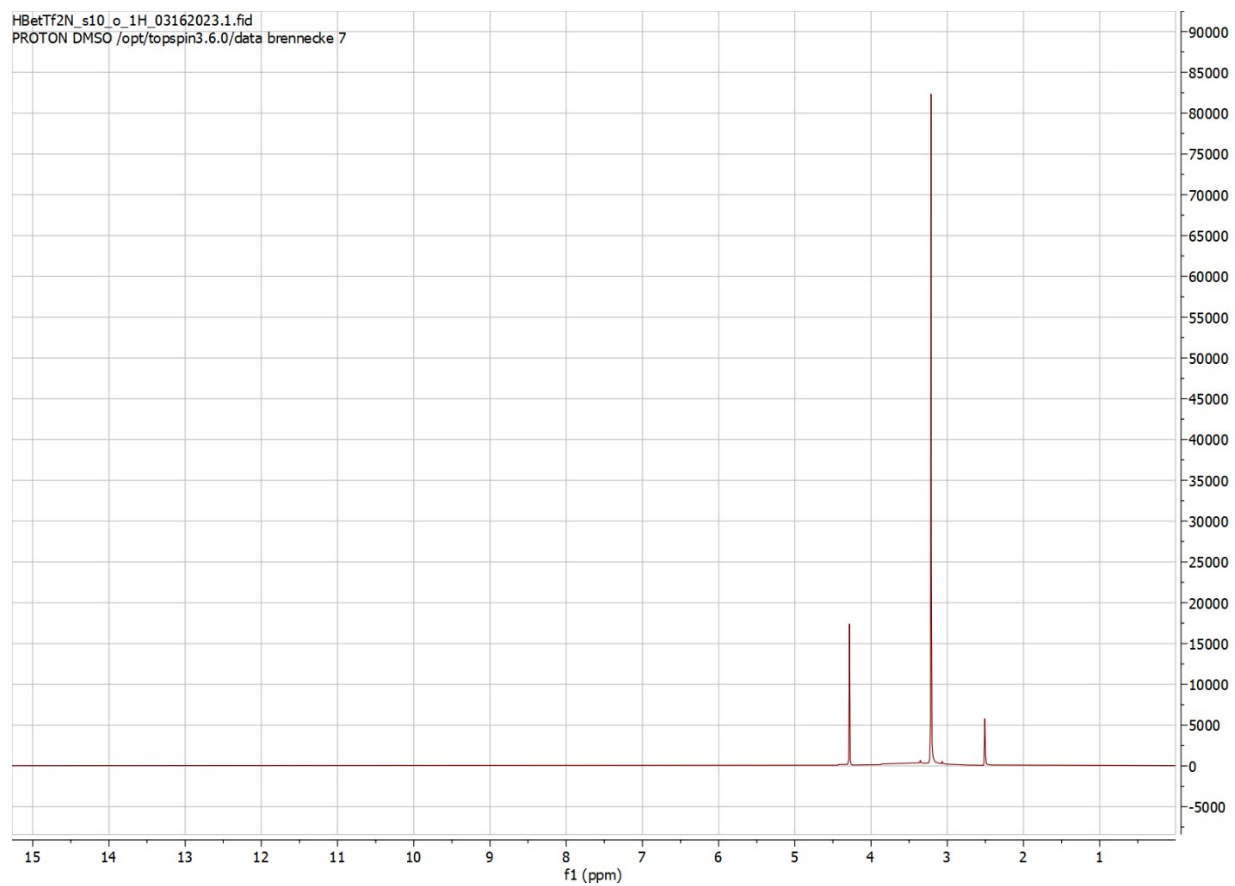
Fig. S5 ¹H-NMR for sample (**1**)
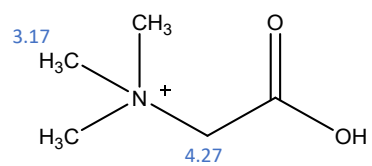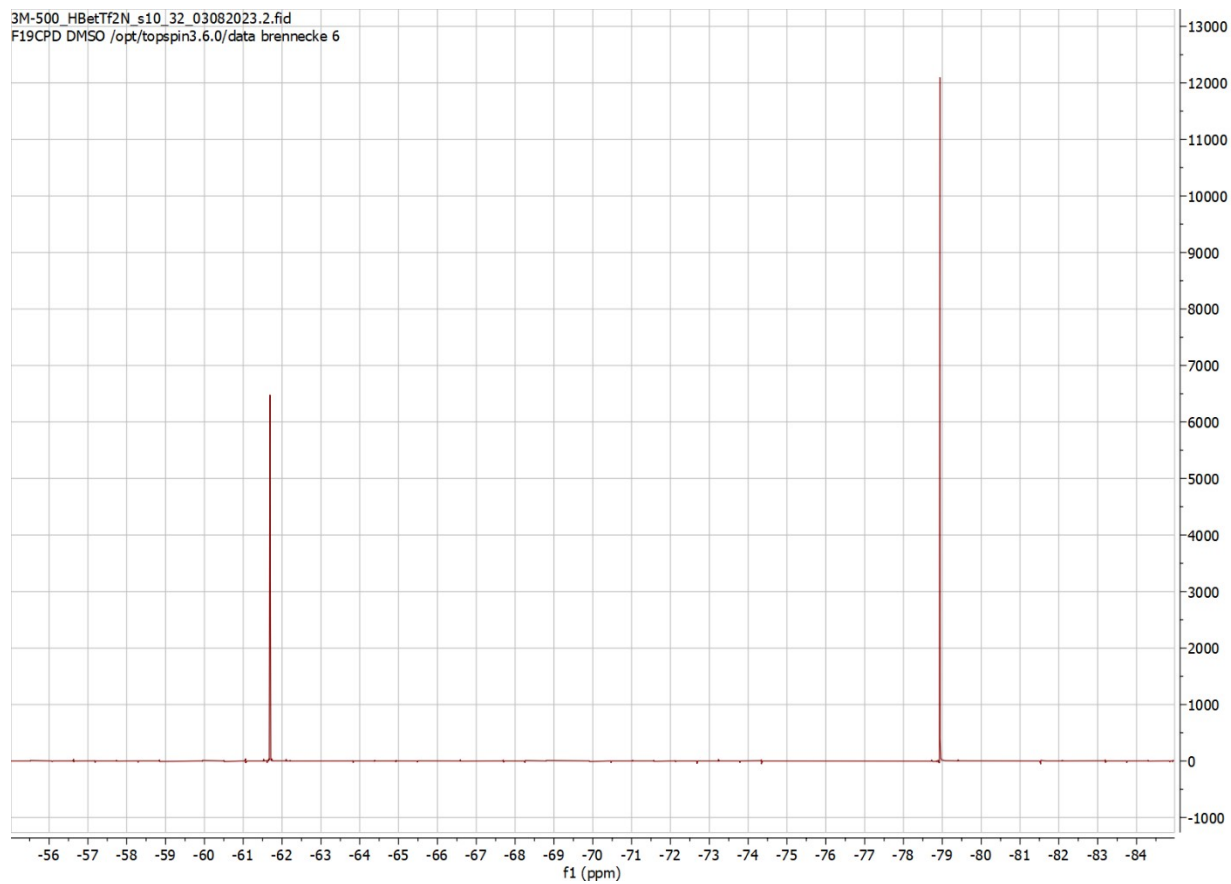
Fig. S6 q^{19}F-NMR for sample (**1**)
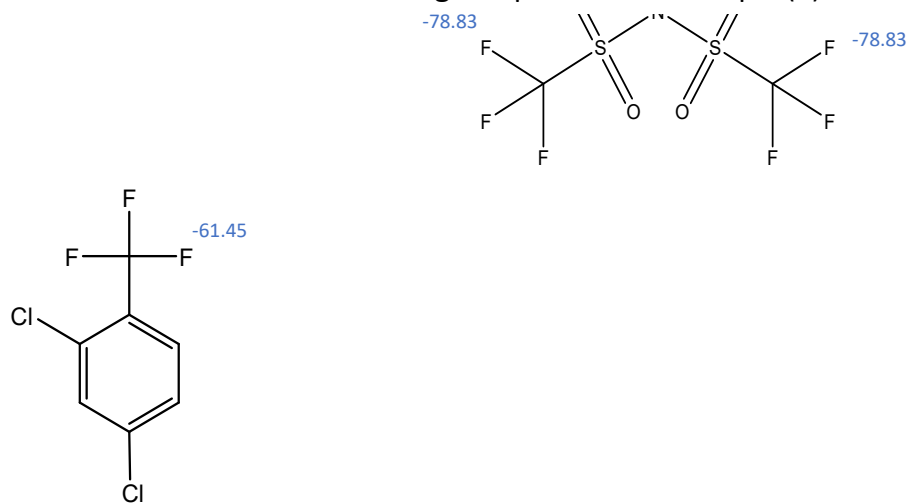
-78.83

-78.83
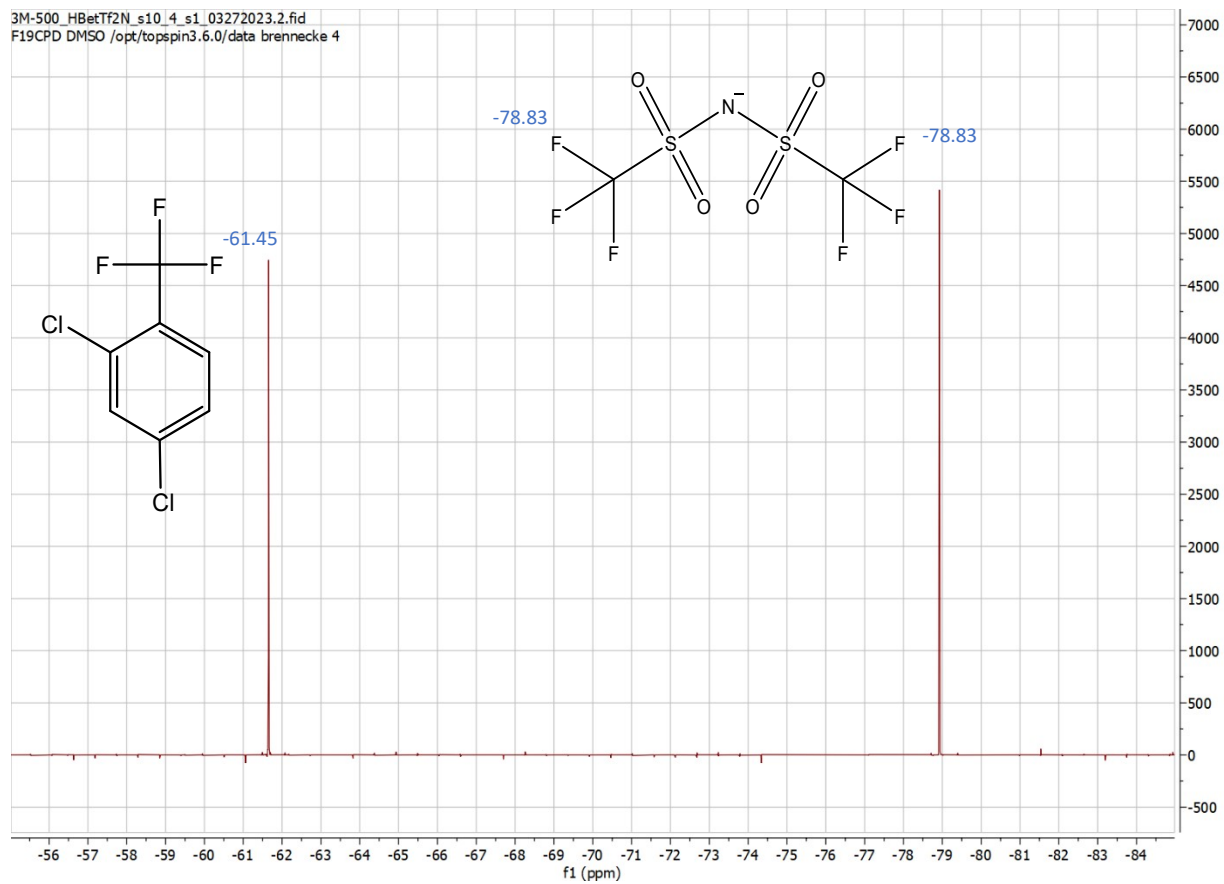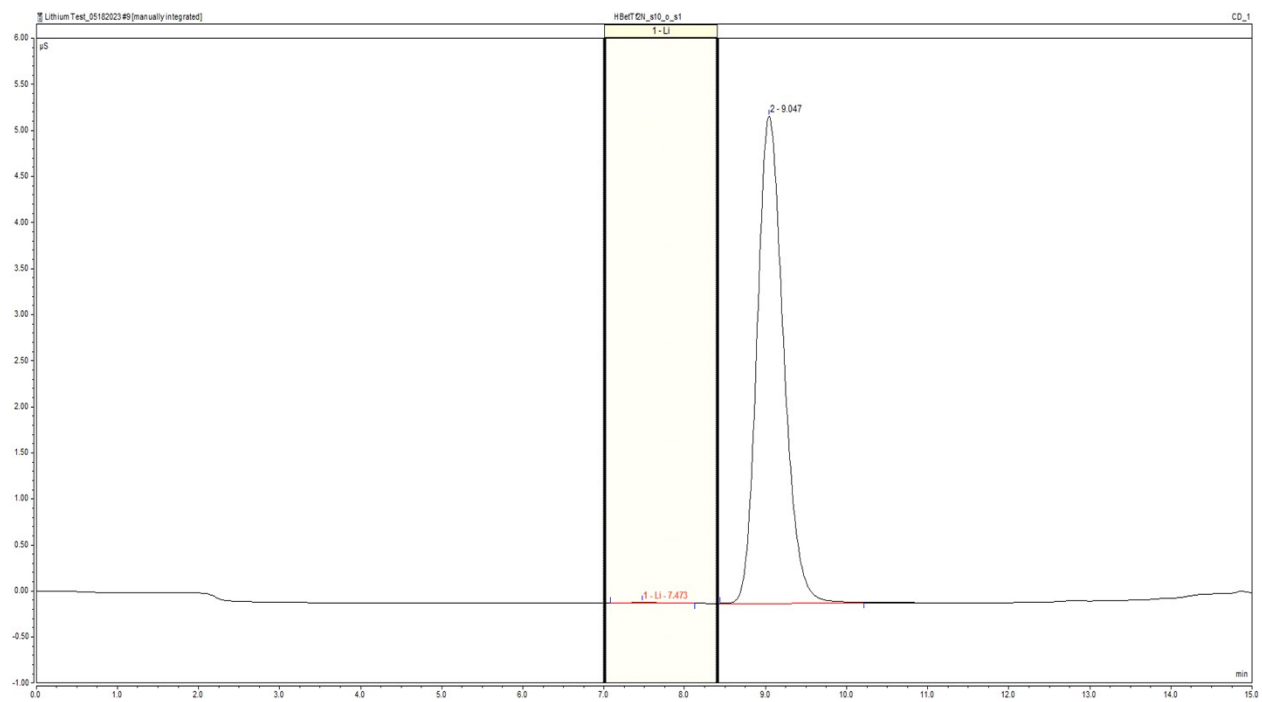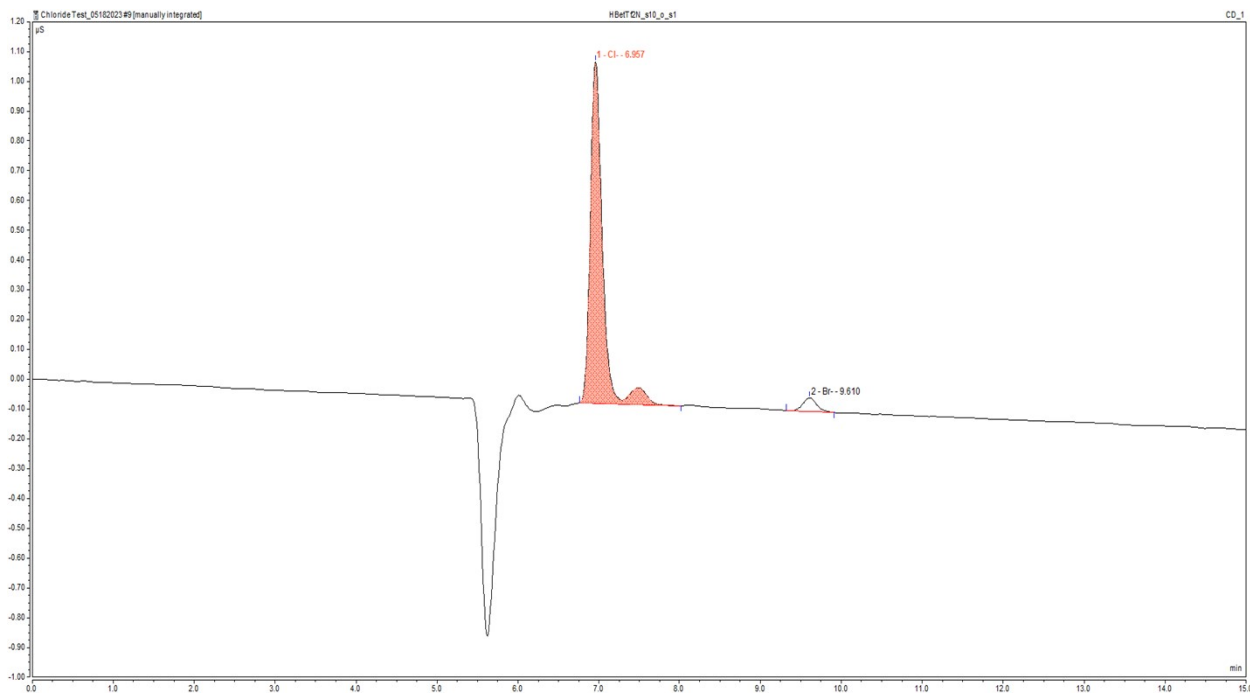
-61.45
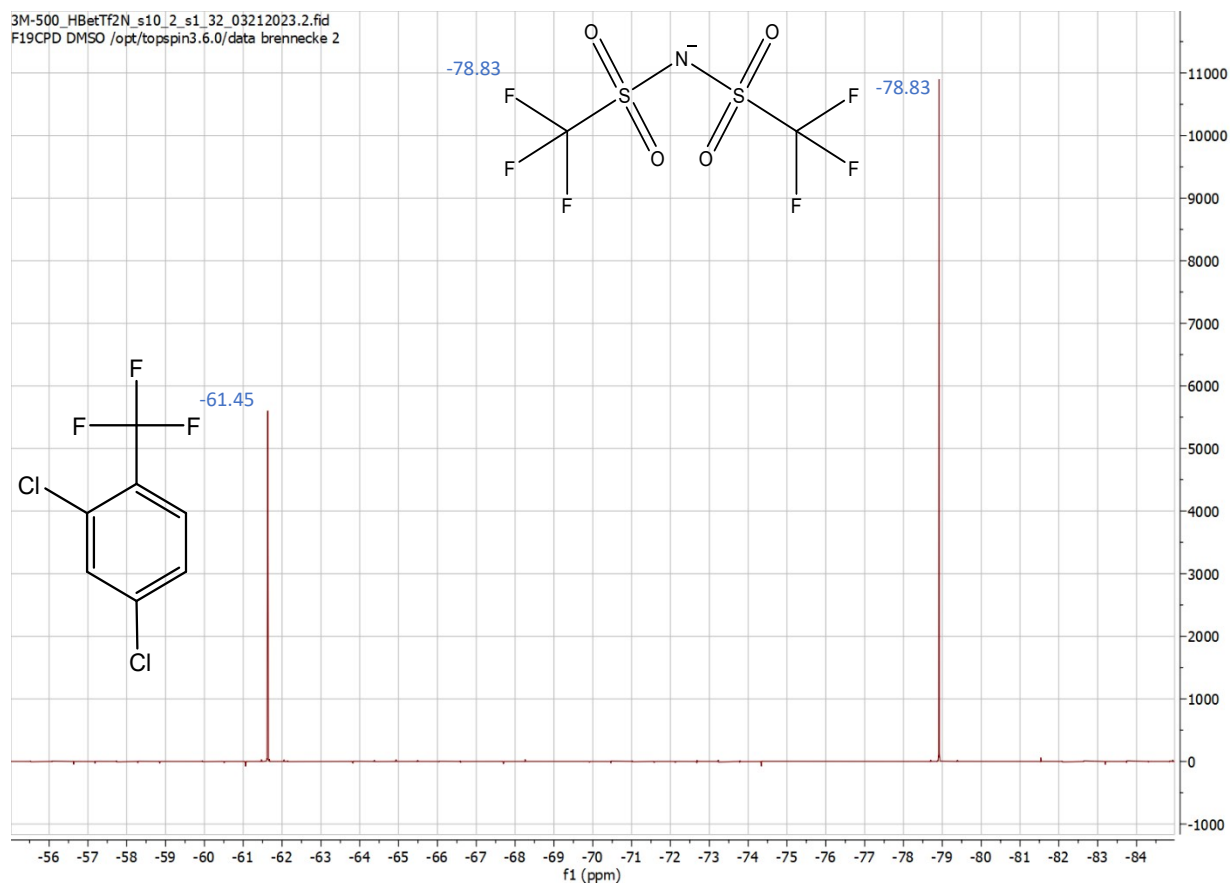
Fig. S7 q^{19}F-NMR for sample (**2**)

Fig. S8 q^{19}F-NMR for sample (**3**)

Fig. S9 Cation ion chromatogram for sample (**1**). Li⁺ and HBet⁺ are eluted at ≈ 7.46 min and ≈ 9.05 min, respectively.

Fig. S10 Anion ion chromatogram for sample (**1**). Cl$^-$ is eluted at ≈ 6.96 min. The peak at ≈ 9.61 min is Br$^-$ due to the contamination of the column. TFSI$^-$ was not detected because of its longer retention time than the time window.
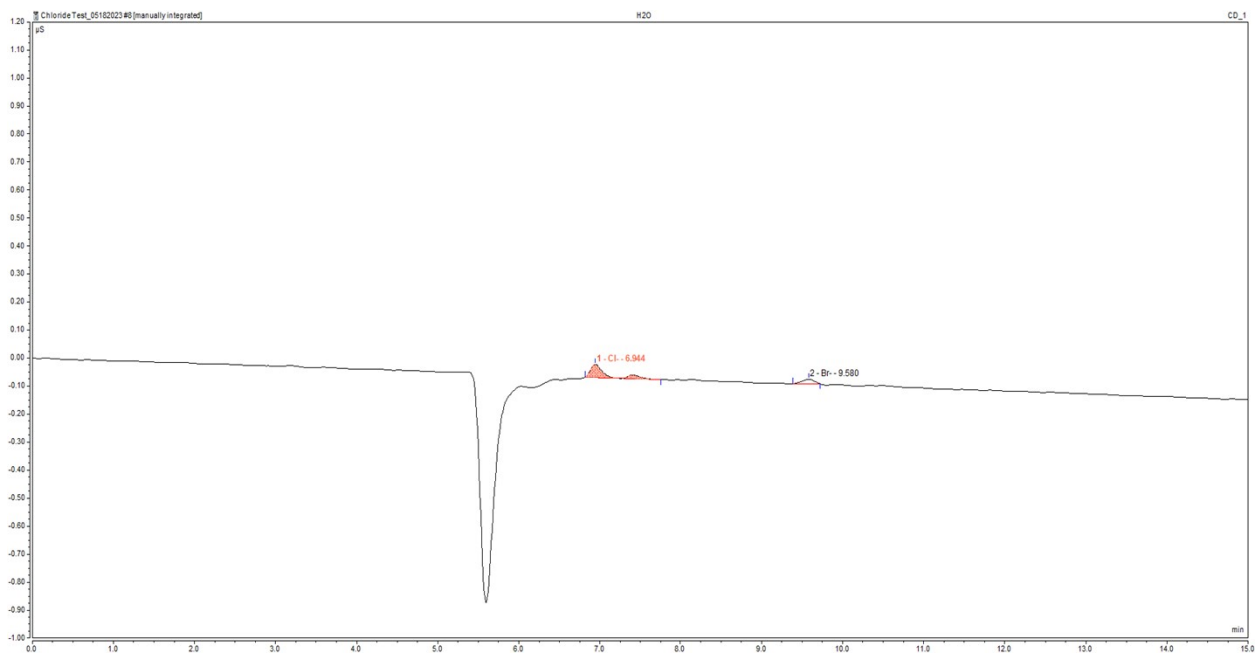

Fig. S11 Anion ion chromatogram for blank. Cl$^-$ is eluted at ≈ 6.94 min. The peak at ≈ 9.58 min is Br$^-$. The contamination happened.

Cloud point measurement

       The cloud point measurements were conducted visually. Approximately 0.3 g of a [Hbet][TFSI]/water stock solution was place in a jacketed vial with a stirring bar, and the vial was connected to a chiller to control the temperature. The water content of the stock solution was measured using Karl-Fisher Coulometer (Metrohm 917 Coulometer). The vial was placed on a stirring plate, and the temperature was measured with a platinum resistance thermometer. The solution was heated or cooled to find the approximate temperature of the cloud point. Then the temperature was slowly cycled to determine 3-5 independent measurements of the cloud point temperature (i.e., the temperature where the sample first exhibited opacity). After the measurements for one composition were complete, water was injected into the vial to study the next composition. A platinum thermometer (VWR traceable RTD platinum thermometer) was used. The uncertainty in the cloud point temperature measurements is calculated from the sum of absolute error (0.05 ^{o}C) and statistical error. In all cases the total uncertainty in the cloud point temperatures is less than 0.6 ^{o}C.

Effect of Li$^+$ concentration

       In some preliminary work, we synthesized and tested samples of [Hbet][TFSI] where we had not adequately washed the IL with water to reduce the Li$^+$ concentration to the low values shown for the samples described in the main text. Therefore, we are able to compare [Hbet][TFSI] + water cloud point curves for samples containing similar amounts of neutral zwitterionic betaine, but significantly different amounts of Li$^+$. This is shown in **Fig. S12**. The presence of more Li$^+$ lowers the entire cloud point curve, with the effect being more pronounced on the IL-rich side of the diagram.
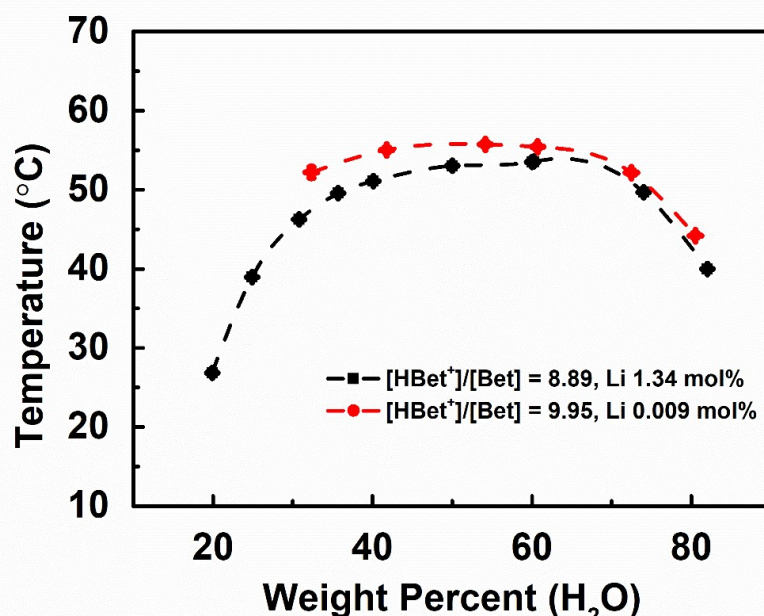
Fig. S12 Effect of Li$^+$ concentration on the cloud point curve of [HBet][TFSI] with water at similar [HBet][TFSI]/neutral betaine ratio.

Reference

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