Supporting information for:

Dealing with supramolecular structure for ionic liquids: DOSY NMR approach

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1. Ionic liquid characterization

The BMI·Cl salts were prepared according to literature procedures.[1,2]

1-*n*-Butyl-3-methylimidazolium acetate (BMI·OAc): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.96 (t, ^3J = 7.4 Hz, 3H), 1.38 (sex, ^3J = 7.1 Hz, 2H), 1.86 (qui, ^3J = 7.4 Hz, 2H), 1.97 (s, 3H), 4.06 (s, 3H), 4.29 (t, ^3J = 7.2 Hz, 2H), 7.28 (s, 1H), 7.34 (s, 1H), 11.01 (s, 1H).

1-*n*-Butyl-3-methylimidazolium Prolinate (BMI·Pro): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.95 (t, ^3J = 7.4 Hz, 3H), 1.28-1.43 (m, 2H), 1.59-1.78 (m, 2H), 1.78-1.93 (m, 3H), 2.10 (m, 1H), 2.80 (d, ^3J = 6.7 Hz, 1H), 3.10 (d, ^3J = 6,7 Hz, 1H), 3.55 (s, 1H), 4.05 (s, 3H), 4.29 (t, ^3J = 7.3 Hz, 2H), 7.35 (s, 1H), 7.45 (s, 1H), 10.80 (s, 1H).

1-*n*-Butyl-3-methylimidazolium *o*-trifluoromehtylobenzoate (BMI·CO_2BzCF_3): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.92 (t, ^3J = 7.3 Hz, 3H), 1.26 (sex, ^3J = 7.1 Hz, 2H), 1.83 (qui, ^3J = 7.3 Hz, 2H), 4.03 (s, 3H), 4.24 (t, ^3J = 7.3 Hz, 2H), 7.19 (s, 1H), 7.26-7.32 (m, 2H), 7.45 (t, ^3J = 7.3 Hz, 1H), 7.54 (d, ^3J = 7.3 Hz, 1H), 7.61 (d, ^3J = 7.3 Hz, 1H), 10.86 (s, 1H).

1,2,3-trimethylimidazolium imidazolate (TMI·Im): yellow semisolid. ^{1}H NMR (400 MHz, D_2O): δ 2.05 (s, 3H), 3.32 (s, 6H), 6.71 (s, 2H), 6.85 (s, 2H), 7.2 (s, 1H).

1,2,3-trimethylimidazolium prolinate (TMI·Pro): yellow semisolid. ^{1}H NMR (400 MHz, D_2O): δ 2.09 (s, 3H), 3.35 (s, 6H), 1.66-1.72 (m, 2H), 1.88-1.93 (m, 1H), 2.03-2.12 (m, 1H), 2.85-2.91 (m, 1H), 3.07-3.12 (m, 1H), 3.59-3.63 (m, 1H), 6.98 (s, 2H).

Tetra-*n*-butylammonium prolinate (TBA·Pro): yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.93 (t, ^3J = 7.3 Hz, 12H), 1.36 (sex, ^3J = 7.3 Hz, 8H), 1.57 (qui, ^3J = 7.3 Hz, 8H), 1.62-1.70 (m, 2H), 1.83-1.91 (m, 1H), 1.99-2.08 (m, 1H), 2.80-2.86 (m, 1H), 3.01-3.07 (m, 1H), 3.26 – 3.28 (m, 8H), 3.54-3.58 (m, 1H), 4.41 (b, NH).

2. DOSY experiments

2.1 Effects of Cation Structures on Diffusion Coefficients

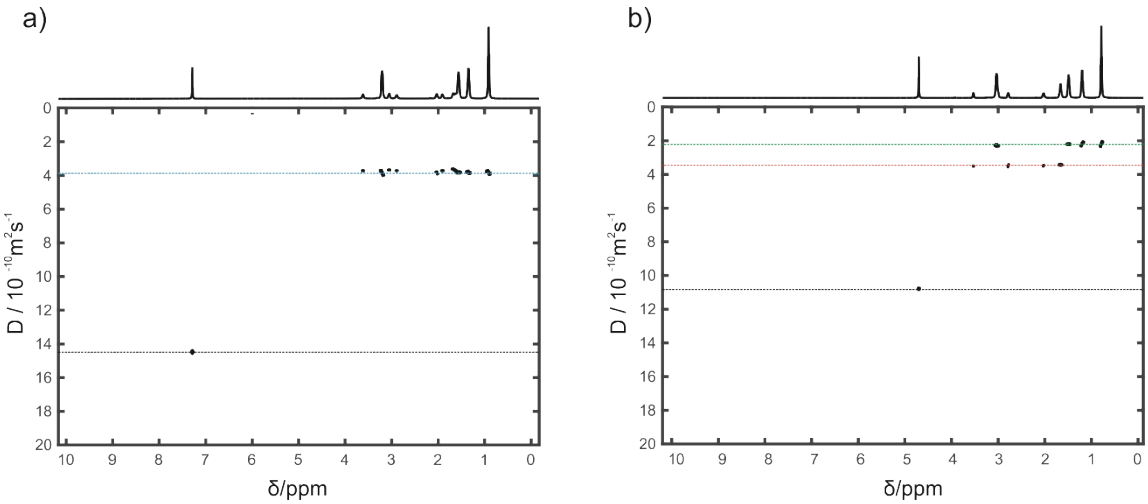


Figure S1. ^{1}H DOSY (600.17 MHz, 293 K), with [top] the least attenuated 1D spectrum of the 0.1 mol L^{-1} TBA·Pro a) in $CDCl_3$ and b) in D_2O. The signal for ionic pair, solvent, cation and anion are labelled in blue, black, green and red, respectively.

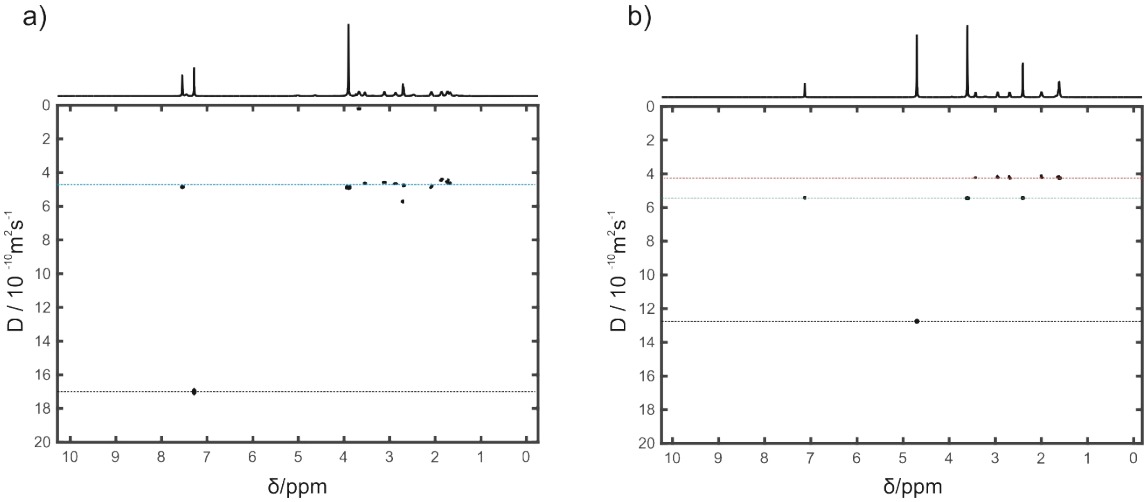


Figure S2. ^{1}H DOSY (600.17 MHz, 293 K), with [top] the least attenuated 1D spectrum of the 0.1 mol L^{-1} TMI·Pro a) in $CDCl_3$ and b) in D_2O. The signal for ionic pair, solvent, cation and anion are labelled in blue, black, green and red, respectively.

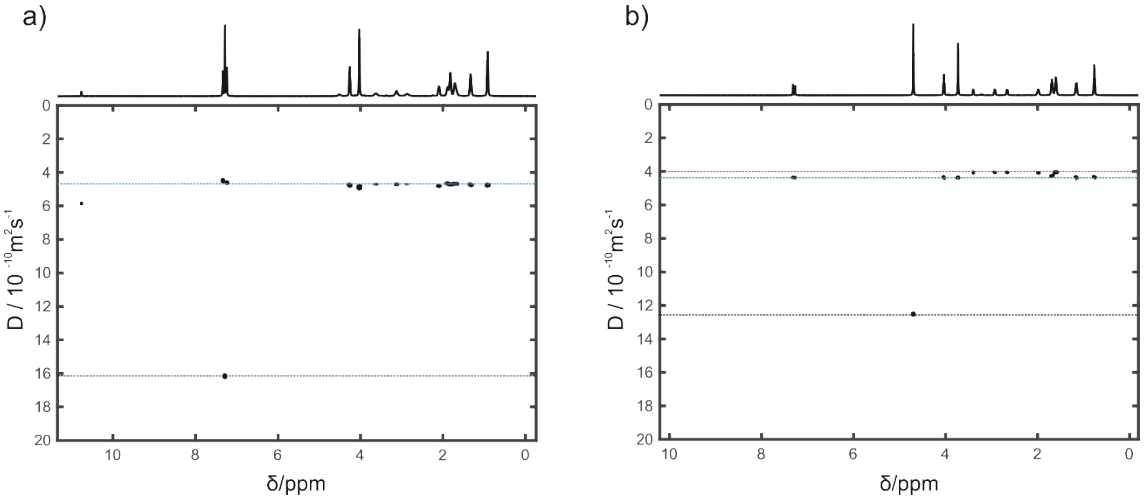
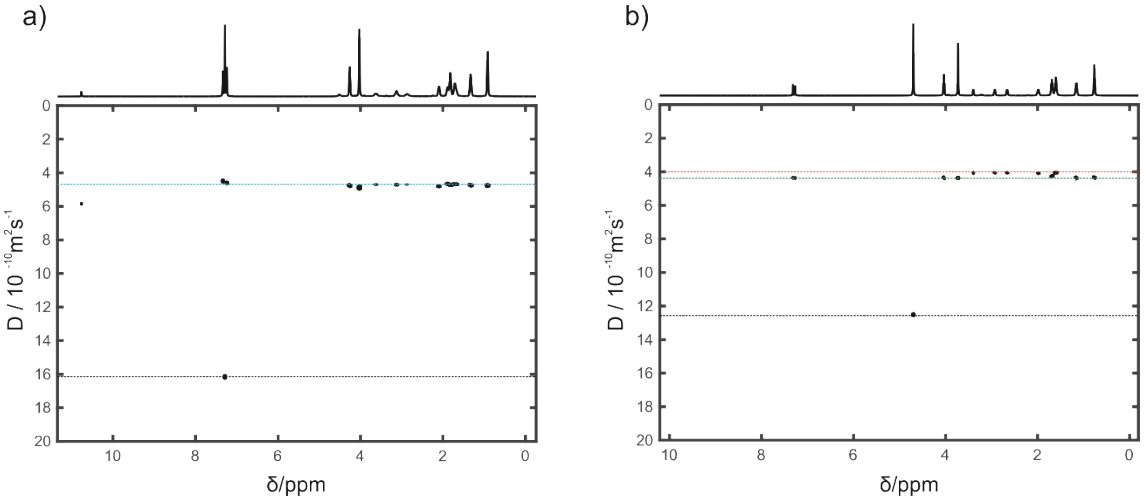


Figure S3. ^{1}H DOSY (600.17 MHz, 293 K), with [top] the least attenuated 1D spectrum of the 0.1 mol L^{-1} BMI·Pro a) in $CDCl_3$ and b) in D_2O. The signal for ionic pair, solvent, cation and anion are labelled in blue, black, green and red, respectively.

2.2 Effects of Anion Species on Diffusion Coefficients

BMI·Pro in D_2O and $CDCl_3$ are represented in Figure **S3**, respectively.



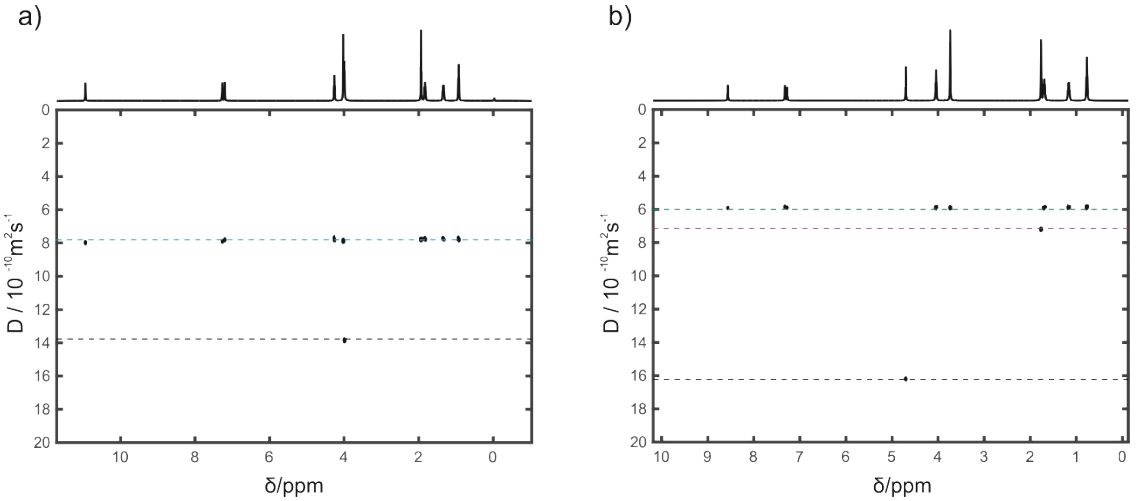


Figure S4. ^{1}H DOSY (600.17 MHz, 293 K), with [top] the least attenuated 1D spectrum of the 0.1 mol L^{-1} BMI·OAc a) in $CDCl_3$ and b) in D_2O. The signal for ionic pair, solvent, cation and anion are labelled in blue, black, green and red, respectively.

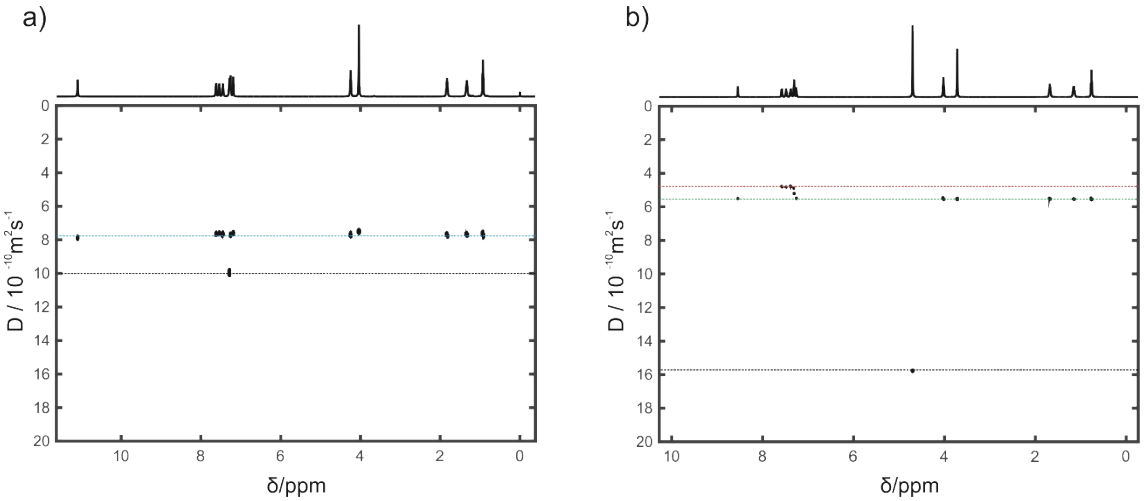


Figure S5. ^{1}H DOSY (600.17 MHz, 293 K), with [top] the least attenuated 1D spectrum of the 0.1 mol L^{-1} BMI·CO_2BzCF_3 a) in $CDCl_3$ and b) in D_2O. The signal for ionic pair, solvent, cation and anion are labelled in blue, black, green and red, respectively.

2.3 **Effects of Concentration on Diffusion Coefficients**

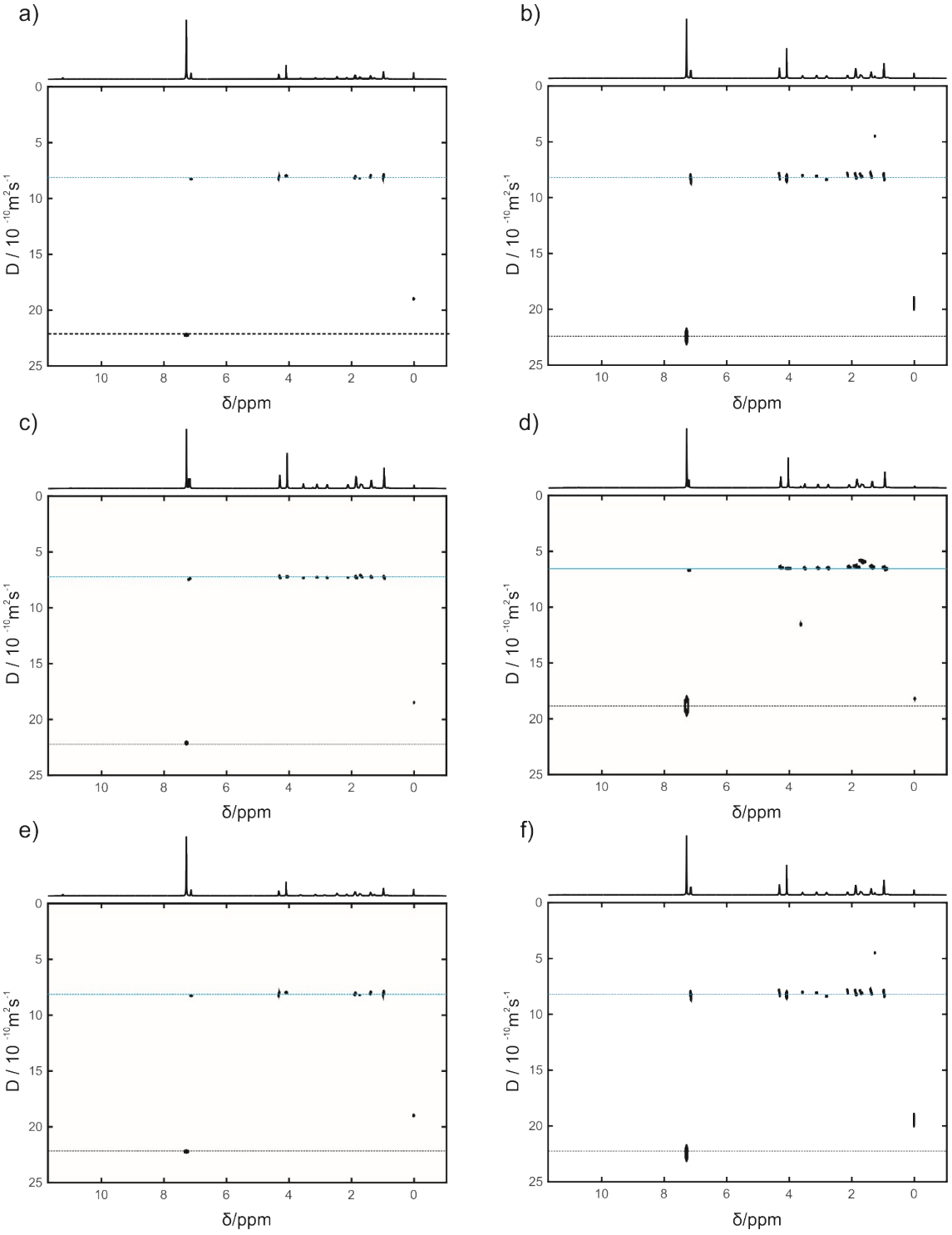


Figure S6. ^{1}H DOSY (600.17 MHz, 293 K), with [top] the least attenuated 1D spectrum of the a) 0.010 mol L^{-1}, b) 0.025 mol L^{-1}, c) 0.050 mol L^{-1}, d) 0.100 mol L^{-1}, e) 0.200 mol L^{-1} and f) 0.500 mol L^{-1} BMI·Pro in $CDCl_3$. The signal for ionic pair and solvent are labelled in blue and black, respectively.

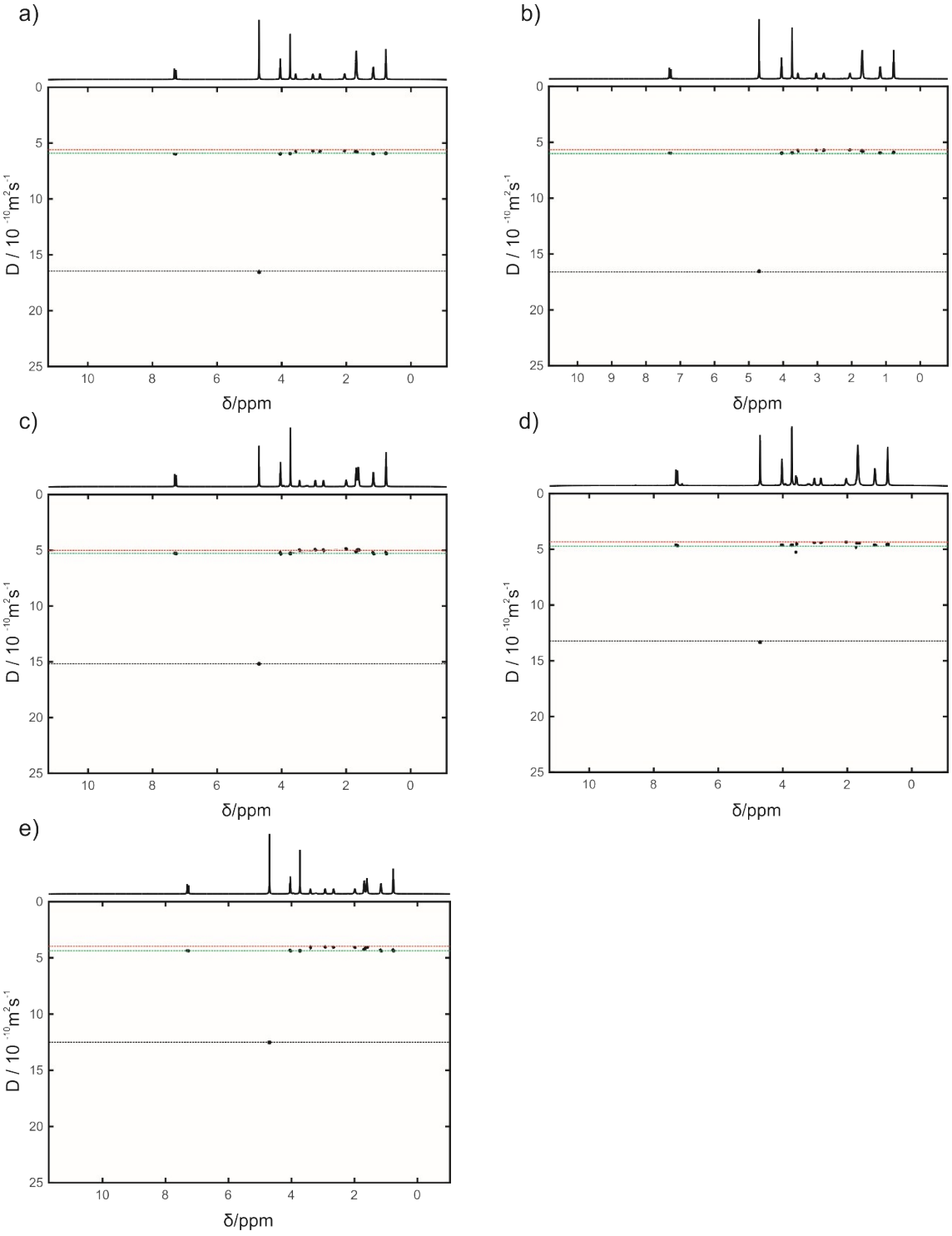


Figure S7. ^{1}H DOSY (600.17 MHz, 293 K), with [top] the least attenuated 1D spectrum of the a) 0.025 mol L^{-1}, b) 0.050 mol L^{-1}, c) 0.100 mol L^{-1}, d) 0.200 mol L^{-1} and e) 0.500 mol L^{-1} BMI·Pro in D_2O. The signal for ionic pair, solvent, cation and anion are labelled in blue, black, green and red, respectively.

2.4 Water interaction **and effect on Diffusion Coefficients**

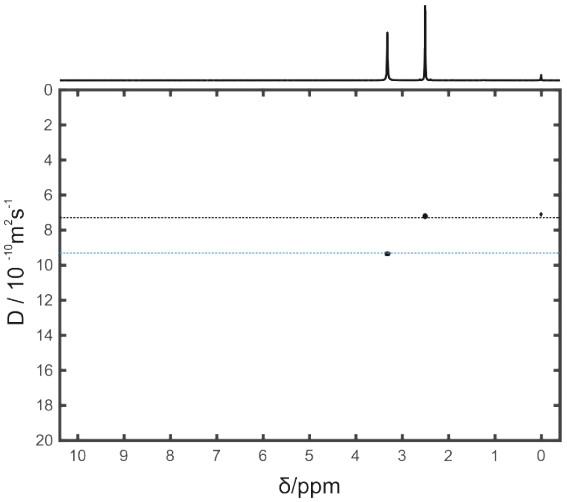


Figure S8. ^{1}H DOSY (600.17 MHz, 298 K), with [top] the least attenuated 1D spectrum of the DMSO-d_6. The signals for DMSO and residual water are labelled in black and blue, respectively.

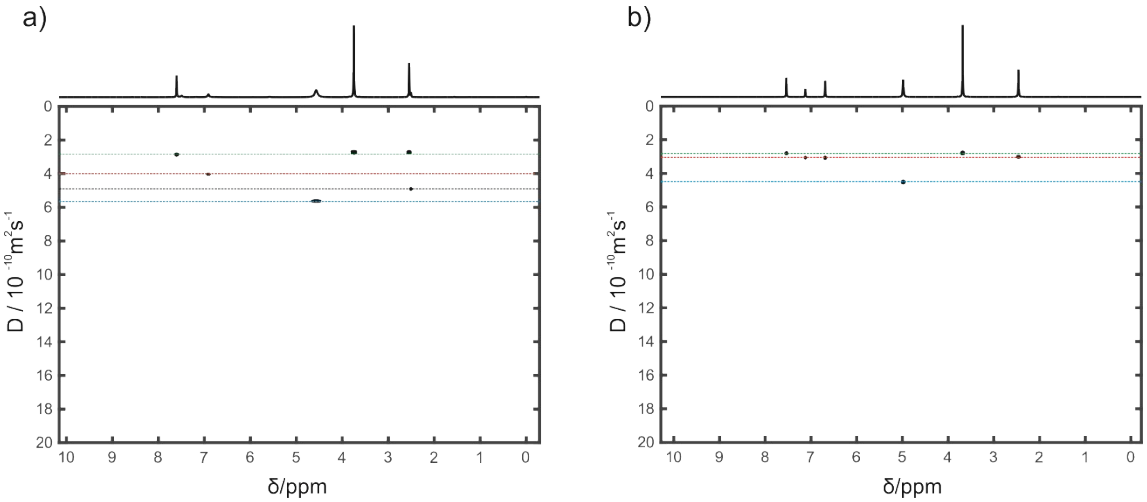


Figure S9. ^{1}H DOSY (600.17 MHz), with [top] the least attenuated 1D spectrum of the bear TMI·Im in in DMSO-d_6 a) 0.1 mol L^{-1} at 293 K and b) 1 mol L^{-1} at 298 K. The signal for DMSO, residual water, cation and anion are labelled in black, blue, green and red, respectively.

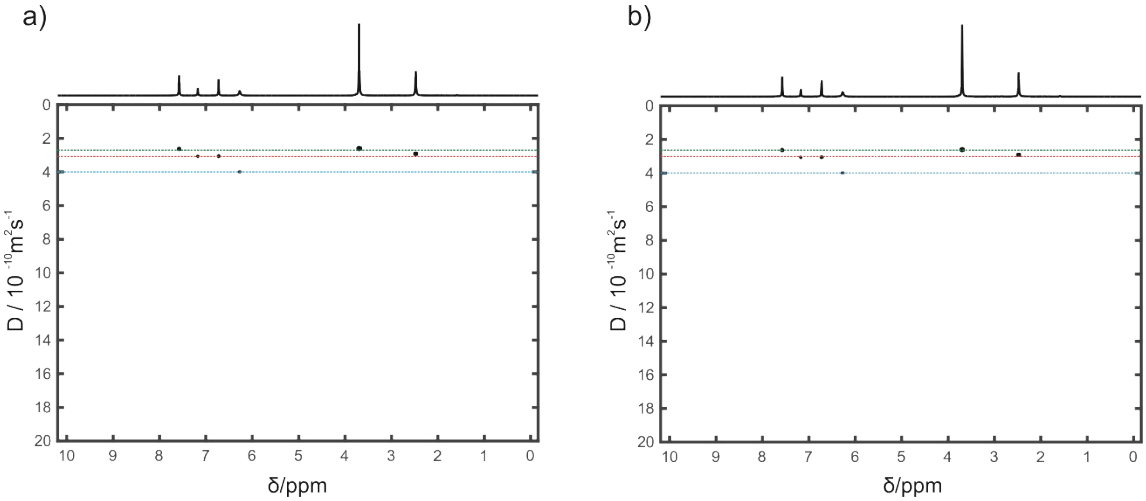


Figure S10. ^{1}H DOSY (600.17 MHz, 298 K) with [top] the least attenuated 1D spectrum of the 1 mol L^{-1} TMI·Im a) dry with molecular sieve and b) add 25 µL of water in DMSO-d_6. The signal for residual water, cation and anion are labelled in black, blue, green and red, respectively

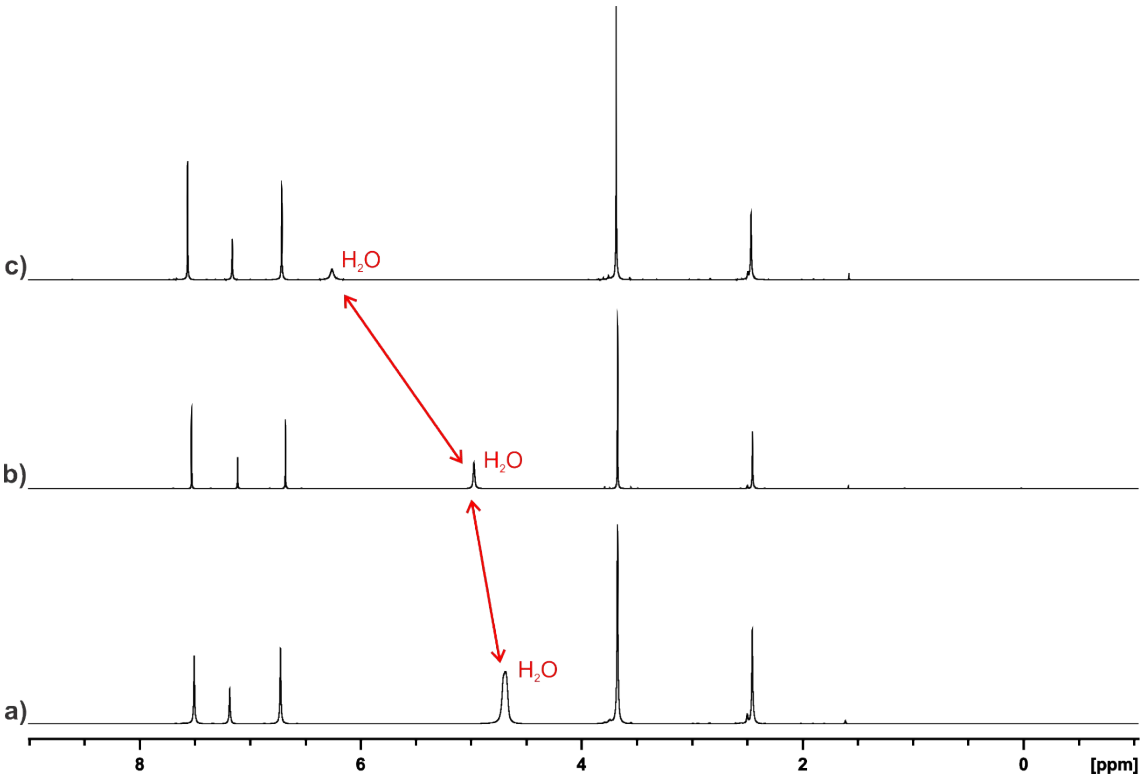


Figure S11. ^{1}H NMR spectra for sample containing 1 mol L^{-1} of TMI·IM in DMSO-d_6 with different amount of water. **a)** 25 µL of water was added to sample; **b)** sample prepared with DMSO-d_6 containing a regular/normal amount of water (bear IL); **c)** DMSO-d_6 and IL were dried over molecular sieves.

3. References

(1) Dupont, J.; Consorti, C. S.; Suarez, P. A. Z.; de Souza, R. F.; Dupont, J.; Consorti, C. S.; Suarez, P. A. Z.; de Souza, R. F. Preparation of 1-Butyl-3-Methyl Imidazolium-Based Room Temperature Ionic Liquids. In *Organic Syntheses*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2003; pp 236–236.

(2) Zanatta, M.; Girard, A.-L.; Marin, G.; Ebeling, G.; dos Santos, F. P.; Valsecchi, C.; Stassen, H.; Livotto, P. R.; Lewis, W.; Dupont, J.; et al. Confined Water in Imidazolium Based Ionic Liquids: A Supramolecular Guest@host Complex Case. *Phys. Chem. Chem. Phys.* **2016**, *18* (27), 18297–18304.