

Supplementary materials

NMR protocol

From the possible nucleus (^{13}C , ^1H , ^{15}N , ^{33}S and ^{19}F) available in the moieties under study, ^1H and ^{19}F have the best response in NMR^{1, 2} and were thus selected. All spectra were recorded on a Bruker 300MHz located at the Institut de Chimie, Strasbourg University, France, with a probe 5 mm QNP 1H/13C/31P/19F Z-GRD. For $\text{C}_1\text{C}_4\text{im}^+$ and $\text{C}_1\text{C}_{10}\text{im}^+$ determination, we chose sodium citrate as the internal standard^{2, 3} because its protons are well separated from those of the IL cation under investigation. For Me_3BuN^+ we chose sodium-potassium tartrate² as internal standard. Sodium trifluoroacetate⁴ was used as standard for Tf_2N^- determination. The standards were introduced together with the sample in the NMR tube.

In order to perform a reliable quantitative determination of concentrations, it is very important that all spins have relaxed in between two excitation pulses. The longitudinal relaxation times, T_1 , for ^1H and ^{19}F samples and standards should thus be carefully determined as a function of the chemical conditions that may influence their values. However, no NMR signal could be obtained above $[\text{D}^+][\text{NO}_3^-] = 3 \text{ M}$ so that we performed the T_1 determinations in pure D_2O (no $[\text{D}^+][\text{NO}_3^-]$ added) and in $3\text{M } [\text{D}^+][\text{NO}_3^-]/\text{D}_2\text{O}$ only. The values displayed in table S1 show that T_1 values depend on the nature of the sample, as is well-known. The effect of the varying ionic strength of the samples onto the NMR characteristics is twofold: i) for ^1H , the chemical shifts are markedly displaced downwards as $[\text{D}^+][\text{NO}_3^-]_{\text{init}}$ is increased (from 7.3 ppm to 6.4 ppm), while this effect is almost negligible for ^{19}F . ii) the relaxation times T_1 are a decreasing function of $[\text{D}^+][\text{NO}_3^-]_{\text{init}}$. Considering these values, in order to avoid artificial distortions of the signal intensities⁵ and to limit the acquisition time, the NMR spectra were recorded with a 30° excitation pulse. All acquisition parameters are indicated in table S2. For ^1H NMR, the spectral window was 0 to 15 ppm, while for ^{19}F it was centred at -80 ppm, with a width of 80 ppm, to limit background acquisition. Data processing included apodization with an exponential broadening of 1 Hz, phase and baseline corrections. Linearity was checked (correlation coefficient above 0.99) for both ^1H and ^{19}F by adding known amounts of $[\text{Me}_3\text{BuN}^+][\text{Br}^-]$, $[\text{C}_1\text{C}_4\text{im}^+][\text{Cl}^-]$, $[\text{C}_1\text{C}_{10}\text{im}^+][\text{Cl}^-]$ and $[\text{Li}^+][\text{Tf}_2\text{N}^-]$ in pure D_2O and $\text{D}_2\text{O}/[\text{D}^+][\text{NO}_3^-]$ (3M).

Concentrations were calculated using the analyte peak integration, including the peaks due to the ^{13}C - ^1H or ^{13}C - ^{19}F couplings ($\text{C}_1\text{C}_4\text{im}^+$: B protons, $\delta = 7.4$ to 6.4 ppm; $\text{C}_1\text{C}_{10}\text{im}^+$: same B protons, $\delta = 7.0$ to 7.9 ppm; Me_3BuN^+ : C protons, $\delta = 1.7$ to 0.7 ppm; Tf_2N^- : $\delta = -79$ ppm,⁶ see scheme 1 for proton attribution) and the internal standard peak integration, each corrected from the number of contributing nuclei, taking advantage of the formula given in ⁷. Purity of the standards was taken into account in the calculations. With this protocol, the uncertainty on the cation concentrations is equal to 10% and to 5% for anions, with detection limits equal to 1 mM for each compound.

Cations/anions	T ₁ in pure D ₂ O (s)	T ₁ in 3M DNO ₃ /D ₂ O (s)
C ₁ C ₄ mim ⁺ protons B	6.06 ± 0.28 (δ = 7.37 ppm)	3.81 ± 0.30 (δ = 6.44 ppm)
Doublet of doublet	7.20 ± 0.37 (δ = 7.33 ppm)	4.09 ± 0.30 (δ = 6.40 ppm)
C ₁ C ₁₀ mim ⁺ protons B	3.13 ± 0.13 (δ = 7.38 ppm)	2.34 ± 0.15 (δ = 6.38 ppm)
Doublet of doublet	2.88 ± 0.11 (δ = 7.38 ppm)	1.80 ± 0.11 (δ = 6.32 ppm)
Me ₃ BuN ⁺ protons C	2.06 ± 0.15 (δ = 1.67 ppm)	1.82 ± 0.16 (δ = 0.75 ppm)
sodium citrate 4 protons	0.653 ± 0.074 (δ = 2.53 ppm)	0.508 ± 0.062 (δ = 2.06 ppm)
Doublet of doublet	0.627 ± 0.077 (δ = 2.44 ppm)	0.498 ± 0.059 (δ = 1.94 ppm)
sodium-potassium tartrate 2 protons	5.63 ± 0.13 (δ = 4.22 ppm)	3.41 ± 0.13 (δ = 3.83 ppm)
Tf ₂ N ⁻	2.01 ± 0.61 (δ = -80.1 ppm)	2.33 ± 0.23 (δ = -81.7 ppm)
sodium trifluoroacetate	2.13 ± 0.19 (δ = -76.5 ppm)	2.55 ± 0.17 (δ = -78.6 ppm)

Table S1: Values of the relaxation times T₁. In brackets: chemical shift of the ¹H or ¹⁹F nuclei.

ion	Number of scans	Delay (s)	Record time (s)	Signal recovery (%)
Tf ₂ N ⁻	150	0.45	3	96.5
C ₁ C ₄ mim ⁺	32	22	2.7	99.6
C ₁ C ₁₀ mim ⁺	32	15	2.7	99.9
Me ₃ BuN ⁺	32	15	2.7	99.9

Table S2: NMR acquisition parameters with a 30° excitation pulse

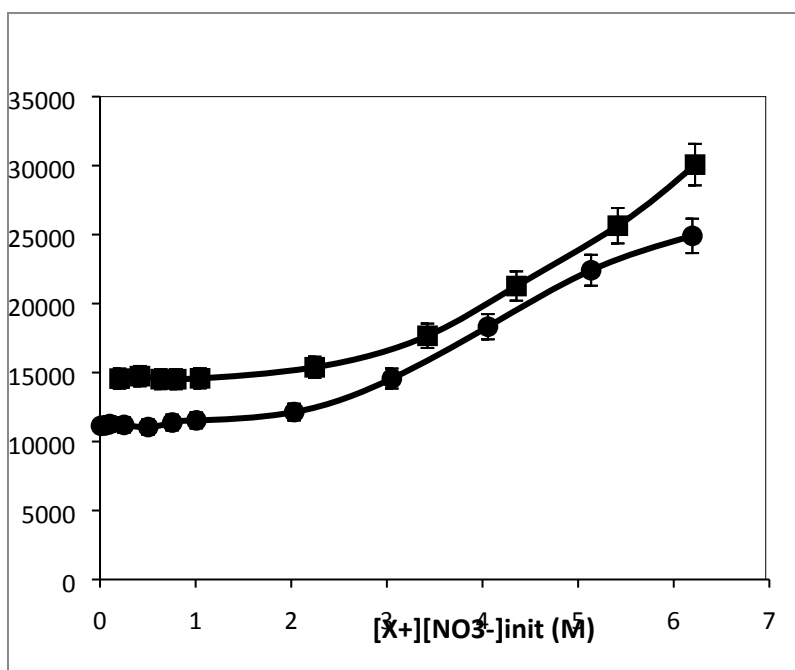


Fig. S1: Water amount for (■): $\text{H}_2\text{O}/[\text{H}^+][\text{NO}_3^-]/[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]$; (●): $\text{D}_2\text{O}/[\text{D}^+][\text{NO}_3^-]/[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]$. Solid lines are guide for the eye only.

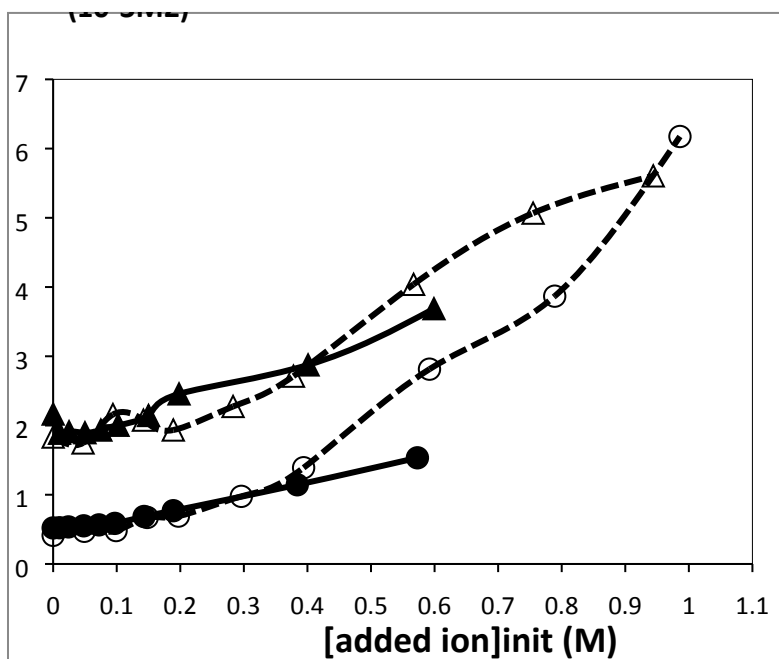


Fig. S2. Variation of the solubility product, $k_s = [\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]$ for samples S#4 – S#7 as a function of the added ion. (▲): $[\text{D}^+][\text{NO}_3^-] = 2.2 \text{ M}$, $[\text{C}_1\text{C}_4\text{im}^+][\text{Cl}^-]$ added. (Δ): $[\text{D}^+][\text{NO}_3^-] = 2.2 \text{ M}$, $[\text{Li}^+][\text{Tf}_2\text{N}^-]$ added. (●): $[\text{D}^+][\text{NO}_3^-] = 0.35 \text{ M}$, $[\text{C}_1\text{C}_4\text{im}^+][\text{Cl}^-]$ added. (○): $[\text{D}^+][\text{NO}_3^-] = 0.35 \text{ M}$, $[\text{Li}^+][\text{Tf}_2\text{N}^-]$ added. Solid and dotted lines are guide for the eye only.

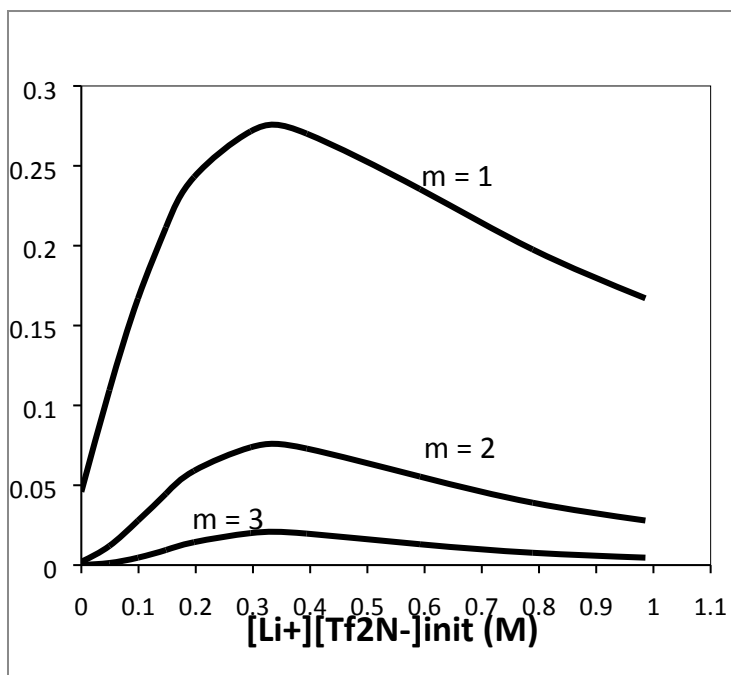


Fig. S3: Predicted variation of D as a function of added $[\text{Li}^+][\text{Tf}_2\text{N}^-]$ salt in case of cation exchange. $[\text{D}^+][\text{NO}_3^-] = 0.305$ M.

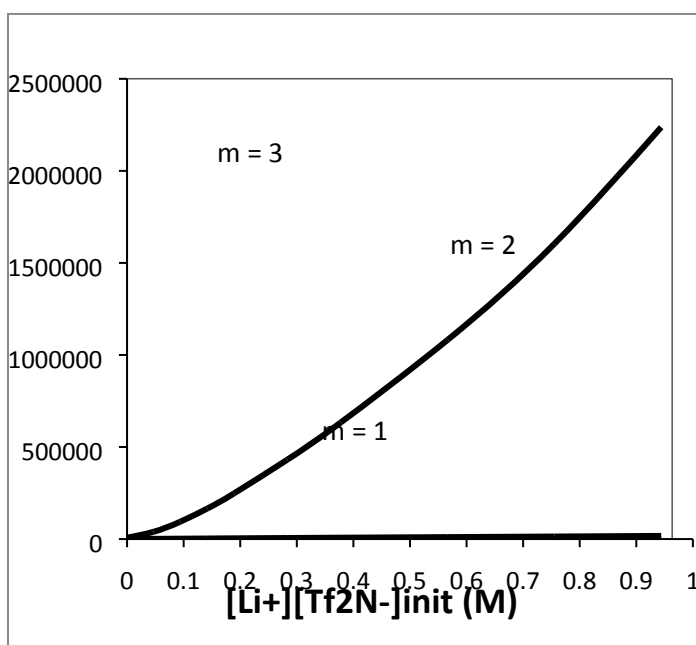


Fig. S4: Predicted variation of D as a function of added $[\text{Li}^+][\text{Tf}_2\text{N}^-]$ salt in case of cation exchange. $[\text{D}^+][\text{NO}_3^-] = 2.2$ M.

References

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