

## **Supplementary Information**

### **Extra NMR Theory**

In the case of intramolecular dipolar relaxation between protons, C is defined by:

$$C = \frac{3}{10} \gamma_H^4 \hbar^2 \sum \frac{1}{r^6}$$

where  $\gamma_H$  is the gyromagnetic ratio of protons,  $\hbar$  is the reduced Planck's constant and  $r$  the distance between interacting dipoles summed over all interacting dipoles.

For isotropic, intramolecular, dipolar relaxation of  $^{19}\text{F}$ , C is defined as:

$$C = \frac{9}{20} \gamma_F^4 \hbar^2 \sum \frac{1}{r^6}$$

where  $\gamma_F$  is the gyromagnetic ratio of fluorine and  $r$ , being the distance between the dipoles, is the distance between F atoms in the  $\text{CF}_3$  group of the  $\text{NTf}_2^-$  anion.

		$C [10^9]$	$\tau_{\infty} [s].10^{-13}$	$E_a [kJ.mol^{-1}]$	$R^2$
<b>[C<sub>3</sub>mpyr][NTf<sub>2</sub>]</b>	<b>1</b>	3.7 ± 0.2	1 ± 0.1	18.1 ± 0.5	0.998
	<b>2</b>	4.3 ± 0.1	0.9 ± 0.1	19 ± 0.3	0.999
	<b>3</b>	4.8 ± 0.4	1.3 ± 0.2	16.9 ± 0.5	0.998
	<b>4</b>	3.5 ± 0.2	1.1 ± 0.2	17.7 ± 0.5	0.997
	<b>5</b>	3.9 ± 0.1	0.7 ± 0.1	19.6 ± 0.7	0.996
	<b>6</b>	3 ± 0.1	1.5 ± 0.2	17.5 ± 0.5	0.998
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<b>[C<sub>3</sub>mpyr][NTf<sub>2</sub>] + Li NTf<sub>2</sub></b>	<b>1</b>	3.44 ± 0.04	1.24 ± 0.09	18.25 ± 0.24	0.999
	<b>2</b>	3.92 ± 0.04	1.06 ± 0.11	19.22 ± 0.31	0.999
	<b>3</b>	4.42 ± 0.12	1.75 ± 0.13	16.69 ± 0.27	0.999
	<b>4</b>	3.14 ± 0.04	1.12 ± 0.08	18.45 ± 0.23	0.999
	<b>5</b>	3.58 ± 0.07	1.35 ± 0.24	18.41 ± 0.53	0.996
	<b>6</b>	2.8 ± 0.06	2.03 ± 0.31	17.16 ± 0.48	0.997
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<b>[C<sub>3</sub>mpyr][NTf<sub>2</sub>] + Li NTf<sub>2</sub> + THF</b>	<b>1</b>	3.33 ± 0.07	0.78 ± 0.07	19.04 ± 0.3	0.999
	<b>2</b>	3.93 ± 0.04	0.68 ± 0.05	19.94 ± 0.23	0.999
	<b>3</b>	4.66 ± 0.1	1.26 ± 0.04	16.99 ± 0.13	0.999
	<b>4</b>	3.01 ± 0.05	0.73 ± 0.05	19.07 ± 0.21	0.999
	<b>5</b>	3.67 ± 0.36	0.84 ± 0.24	18.55 ± 0.99	0.992
	<b>6</b>	2.66 ± 0.06	1.25 ± 0.14	17.98 ± 0.36	0.999
	<b>THF</b>	2.11 ± 0.14	3.34 ± 0.36	14.7 ± 0.45	0.998
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<b>[C<sub>3</sub>mpyr][NTf<sub>2</sub>] + Li NTf<sub>2</sub> + Toluene</b>	<b>1</b>	3.47 ± 0.06	1.03 ± 0.07	18.37 ± 0.24	0.999
	<b>2</b>	3.97 ± 0.04	0.97 ± 0.07	19.07 ± 0.23	0.999
	<b>3</b>	4.74 ± 0.3	1.37 ± 0.13	16.83 ± 0.4	0.999
	<b>4</b>	3.27 ± 0.11	1.03 ± 0.12	18.17 ± 0.38	0.999
	<b>5</b>	3.62 ± 0.07	1.14 ± 0.14	18.51 ± 0.39	0.998
	<b>6</b>	2.87 ± 0.07	1.67 ± 0.17	17.19 ± 0.34	0.999
	<b>Toluene ring</b>	1.64 ± 0.17	4.15 ± 0.38	13.73 ± 0.47	0.998
	<b>Toluene methyl</b>	1.78 ± 0.1	5.31 ± 0.61	13.73 ± 0.46	0.998

**Table 1** Best-fit parameters of Equation 1 to the experimental  $T_1$  data for all samples; the neat IL [C<sub>3</sub>mpyr][NTf<sub>2</sub>], IL with Li NTf<sub>2</sub> and the two diluents (Toluene and THF).

## Nernst-Einstein Calculation

Through the combination of diffusion, density and conductivity measurements the ionicity ratio of the samples can be examined, providing an indication of the ions available to contribute to conductivity. It must be stated that although this ratio is a valuable quantification of the ionicity, the use of 4-5 individual measurements can potentially cause large propagated errors and it must, therefore, be primarily regarded as qualitative. <sup>1</sup> Using the Nernst-Einstein equation (Equation 1), the molar conductivity of an infinitely dilute, non-interacting, ionic solution can be calculated from the diffusion coefficients of the ions ( $\Lambda_{\text{NMR}}$ ). In the case of the lithium containing samples, an effective cation diffusion coefficient is calculated based on the diffusion coefficients of the pyrrolidinium and lithium weighted to their mole fractions.

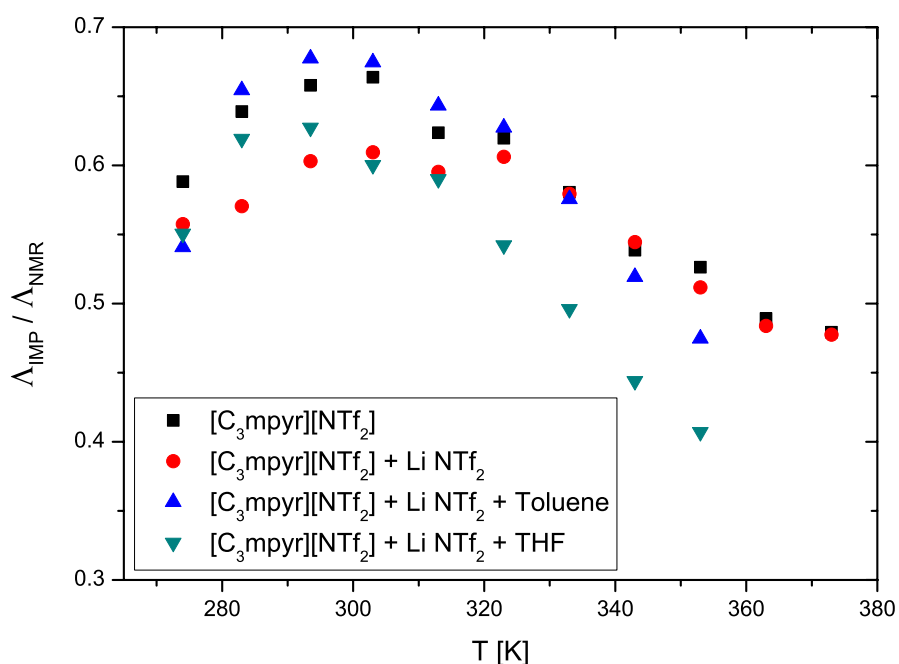
$$\Lambda_{\text{NMR}} = \frac{N_A e^2}{kT} (D_+ + D_-)$$

**Equation 1**

The molar conductivity can be directly measured through the use of electrochemical impedance spectroscopy and density measurements to give the quantity referred to as  $\Lambda_{\text{IMP}}$ . The ionicity ratio is, by definition, the ratio of these molar conductivities ( $\Lambda_{\text{IMP}} / \Lambda_{\text{NMR}}$ ). As the diffusion measurements do not distinguish between ion pairs or higher order clusters,  $\Lambda_{\text{NMR}}$  is a measure of the maximum possible molar conductivity. With the actual measured molar conductivity ( $\Lambda_{\text{IMP}}$ ) invariably less than that calculated through the Nernst-Einstein equation for ILs, the ionicity ratio is less than unity (with a value of unity implying complete ionic dissociation). The discrepancy has been attributed to the existence of neutral ion pairs or clusters that cannot contribute to ionic conductivity. <sup>2</sup>

Figure 1 presents the ionicity ratio ( $\Lambda_{\text{IMP}} / \Lambda_{\text{NMR}}$ ) of all samples as a function of temperature. To calculate the molar concentration, and obtain the molar conductivity of the additive containing samples, the variable temperature

density was calculated from the gradient of a linear fit of the density versus temperature for  $[\text{C}_3\text{mpyr}][\text{NTf}_2] + \text{Li NTf}_2$  and the single temperature measurement of the additive containing sample previously published.<sup>3</sup> Importantly, the trend of all the samples with temperature is well reproduced despite the possible errors. As convection in the diffusion measurements will be the greatest contributing factor to the error in this calculation, one can have slightly more confidence in the room temperature measurements. There appears to be a reasonable drop in the availability of ions when the  $\text{Li NTf}_2$  salt is added to the neat IL, consistent with the dramatic drop in transport properties. The difference between the additives is harder to draw any conclusions from; at 293 K it appears as if both additives have increased the availability of the ions in the system (over the IL + lithium salt sample) while at the temperature extremes there are fewer. With the subtle differences between these additives, the samples become the same within error.



**Figure 1** Ionicity as a function of temperature for the neat IL  $[\text{C}_3\text{mpyr}][\text{NTf}_2]$ , IL with  $\text{Li NTf}_2$  and the two diluents (Toluene and THF).

**References:**

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2. H. Tokuda, K. Hayamizu, K. Ishii, M. A. B. H. Susan and M. Watanabe, *J. Phys. Chem. B*, 2004, **108**, 16593-16600.
3. P. M. Bayley, G. H. Lane, N. M. Rocher, B. R. Clare, A. S. Best, D. R. MacFarlane and M. Forsyth, *PCCP*, 2009, **11**, 7207-7208.