Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Relevance of ion clusters for Li transport at elevated salt concentrations in [Pyr_{12O1}][FTFSI]** ionic liquid-based electrolytes

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1. Experimental details of electrophoretic NMR

The NMR measurements are performed on a BRUKER AVANCE III HD 400-spectrometer with a permanent field strength of 9.4 T using a gradient probe head (‘Diff50’, Bruker) with selective high temperature radiofrequency inserts for 7Li, 19F and 1H. The temperature is controlled using a GMH 3710 controller with a PT100 thermocouple (Greisinger electronics, Germany).

Electrophoretic NMR (eNMR) measurements of ionic mobilities are performed using a self-built dc voltage pulse generator and a self-built electrode configuration with a sample holder fitted to commercial 5 mm NMR tubes. The latter hosts a mechanical support and capillaries to suppress convection in the sample. Details were previously described.[1] The support and the capillaries are dried under high vacuum at 100 °C for at least 3 hours. The pulse program is based on a double-stimulated-echo (DSTE) for convection compensation,[2] and contained two electric field pulses with different polarity during each observation period.[3] The absence of artefacts is proven for all experiments of this paper by comparing the overall conductivity as calculated from mobilities to that determined by impedance spectroscopy (see details in section 2 of this ESI).

The pulse program is based on a double-stimulated-echo (DSTE) for convection compensation.[2]

The gradient pulse length δ is set between 1 and 3 ms, the observation time Δ_{drift} to 300 ms and the gradient strength g is set between 100 and 400 G/cm as a compromise for sufficient phase shift as well as sufficient signal intensity. The distance of the electrodes d is 2.1 cm. The phase shift is measured as a function of the applied voltage starting at 0 V and then applying alternating negative and positive voltages up to -100 and 100 V in steps of 5 V.

2. Cross-check of total conductivity

Due to various potential artefacts such as electroosmosis or convective flow, which might occur in eNMR and yield larger than expected mobility values, an important cross-check is the calculation of the overall conductivity as the sum of the species' contributions σ_i from the electrophoretic mobilities by eq. (S1).

$$\sigma_{eNMR} = \sum_i \sigma_i = \sum_i z_i \cdot N_i \cdot \mu_i \tag{S1}$$

Here, z_i is the ion charge and N_i the number density. As shown in Figure S1, the conductivities obtained by eq. (S1) are in very good agreement with those from the impedance spectroscopy, proving the absence of systematic errors.

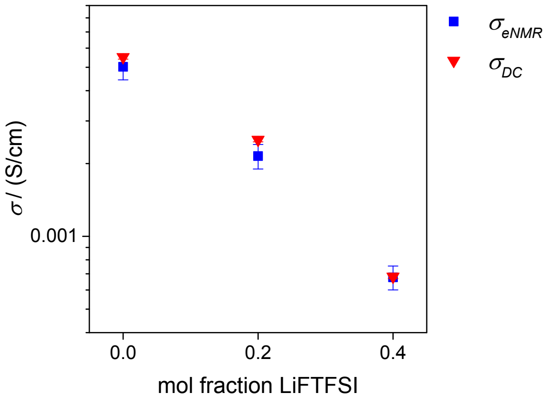

Figure S1: Conductivities σ_{DC} determined by impedance spectroscopy[4] (red triangle) compared with the conductivity σ_{eNMR} calculated from the electrophoretic mobilities (blue square) at 25 °C. Errors are calculated by error propagation.

3. Additional phase shift data

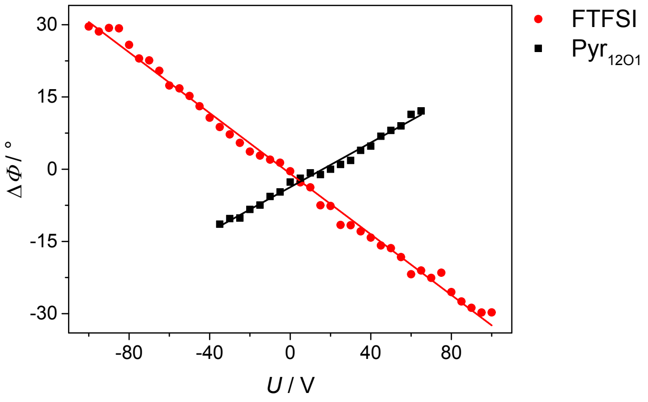

Figure S2: Phase shift as a function of the voltage U for the sample FTFSI 0.0. The lines result from a linear regression.

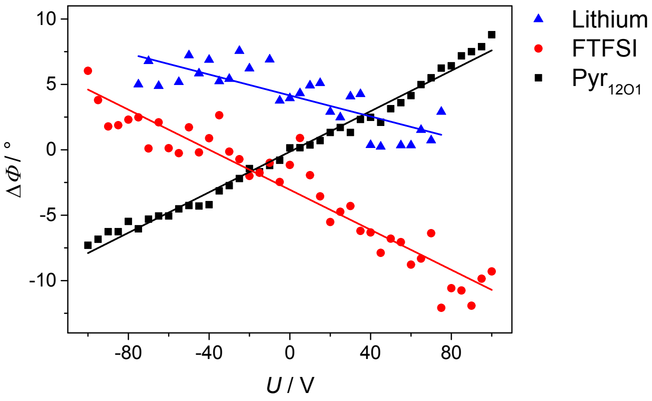

Figure S3: Phase shift as a function of the voltage U for the sample FTFSI 0.4. The lines result from a linear regression.

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4. G. A. Giffin, A. Moretti, S. Jeong and S. Passerini, *J. Power Sources*, 2017, **342**, 335-341.