

Determination of Kamlet-Taft parameters for selected solvate ionic liquids.

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SUPPLEMENTARY INFORMATION

S1 Additional Methodology: Molecular Dynamics simulations

Figure S1: Typical configuration predicted for the dye—Li⁺ complex taken from the **G3TFSI** liquid simulation.

Figure S2: Radial distribution functions for molecule(O)-Li⁺ separations, taken from the **G3TFSI** and **G4TFSI** liquid simulations, with and without the presence of dye.

Figure S3: Average coordination numbers for molecule(O)-Li⁺ separations, taken from the **G3TFSI** and **G4TFSI** liquid simulations, with and without the presence of dye.

Figure S4: Histogram of oxygen-lithium distances for coordinated TFSI and glyme molecules taken from the **G3TFSI** and **G4TFSI** liquid simulations, in the absence of dye.

Figure S5: Histogram of oxygen-lithium distances for coordinated TFSI and glyme molecules taken from the **G3TFSI** and **G4TFSI** liquid simulations, in the presence of dye.

Figure S6: Radial distribution functions calculated for the **G4TFSI** liquid simulations, in the absence of dye.

S10 General and Worked Procedures for determination of α and β

S1: Additional Methodology

Simulation Details

We modeled all atoms explicitly using the OPLS force field [1-3]. The Nosé-Hoover thermostat [4,5] and barostat [4,6] were used to control the temperature and pressure, respectively. The cut-off distance for the contribution of the long range interactions was set as 12 Å. Newton's equation of motions were integrated using a timestep of 1 fs. All simulations were carried out using the freely available LAMMPS [7] software package (lammps.sandia.gov)

Preparation of the Initial Structures

The initial structures for triglyme (3G), or tetraglyme (4G), TFSI⁻ and dye molecules were generated using the freely-available AVOGADRO software package [8] and geometry-optimised until the energy difference between two successive steps dropped to below 10⁻⁸ kJ/mol. The optimised structures were packed together in a relatively low-density simulation cell using the PACKMOL software package [9], where 125 3G or 4G molecules, 125 Li⁺, and 125 TFSI⁻ were randomly distributed in the simulation cell. These comprised out G3TFSI and G4TFSI liquid samples.

Generation of the initial structures of G3TFSI and G4TFSI liquid

The contents of the simulation cell were then geometry-optimised using the LAMMPS-implemented FIRE algorithm [10], with a maximum of 10000 optimization steps, limiting the maximum displacement to 0.1 Å to prevent unrealistically large atomic displacements.

After this relaxation step, the system temperature was increased to 1000 K via MD simulations in the Canonical (NVT) ensemble for 50 ps and maintained at this temperature for 50 ps, followed by cooling back to 296 K for 50 ps. The system was then compressed under high pressure to get rid of the voids forming in the simulation cell. To do this, the system was compressed from 1 to 5000 atm at 296 K for 1 ns and kept at this pressure for 0.5 ns. Following this, the system was relaxed via decreasing the pressure from 5000 to 1 atm over a simulation period of 0.5 ns. After this decompression step, the system was equilibrated at 1 bar for an additional 0.8 ns.

Calculation of the Equilibrium Density Values of the G3TFSI and G4TFSI liquids

The resulting structure from the previous step (see above) was used in MD simulations in the isothermal-isobaric (NPT) ensemble to enable calculation of the equilibrium density of these liquids. Both liquid samples were simulated at 1 atm and 296 K for 30 ns to ensure the system reached structural equilibrium. The final density values at 296 K and 1 atm obtained after this step were 1.481 and 1.443 g.cm⁻³ for **G3TFSI** and **G4TFSI** respectively.

Once the density of the samples were calculated via NPT-MD simulations, to ensure the adequate mixing of the molecules in our sample, we applied a simulated annealing (SA) procedure, where the system temperature was increased up to a high temperature (1000 K) and then cooled back to the target temperature (296 K) via NVT MD simulations. In our annealing schedule, the sample was heated up to 1000 K for 0.2 ns and kept at 1000 K for 1 ns and then cooled back to 296 K for 0.5 ns.

We calculated radial distribution functions (RDFs) between Li^+ and the oxygen atoms of the TFSI^- and G3/G4 molecules at 296 K to characterise the liquid structuring in our samples. To do this, the RDFs between $\text{Li}^+\text{-O(G3/G4)}$ and $\text{Li}^+\text{-O(TFSA)}$ were calculated at the beginning of each SA cycle. We saved frames from the trajectories every 1 ps during the last 200 ps section (at 296 K) of each SA cycle, such that each RDF was averaged over 200 frames for each SA cycle. We terminated the SA procedure when the difference between two successive RDFs became negligible, this resulted in a total eight annealing cycles for each sample. These RDFs are shown in Figure S2 of the ESI. In addition, we calculated coordination number distributions for each system, by integrating the finalized RDFs calculated at the end of the SA procedure (see Figure S3 of the ESI).

After the SA procedure we simulated our systems further for 1 ns using NVT MD simulations at 296 K to calculate the distance histograms (see Figures S4 and S5), distances between specific atoms etc.

We also calculated RDFs for $\text{Li}^+\cdots\text{Li}^+$, $\text{Li}^+\cdots\text{S}$ and $\text{Li}^+\cdots\text{N}$ atom pairs in the **G4TFSI** liquid for comparison with the neutron scattering data recently reported by Murphy et al. [11]. These RDFs are provided in Figure S6.

Generation of the initial Glyme+IL+Dye structures

To create the initial structures for glyme+IL+Dye system we followed the same procedure described for the generation of dye-free systems. For the systems that included dye, the same number of glyme and IL molecules were used. One Dye molecule, 125 glyme, 125 Li^+ , and 125 TFSA^- were randomly distributed in a simulation cell. After applying the same density calculation procedure reported for the dye-free samples, the calculated final density values at 296 K and 1 atm were 1.492 and 1.448 $\text{g}\cdot\text{cm}^{-3}$ for 3G+IL+Dye and 4G+IL+Dye, respectively. RDFs were calculated using the procedure described for the dye-free samples. Additionally, the step after the SA procedure was followed for the dye-containing samples.

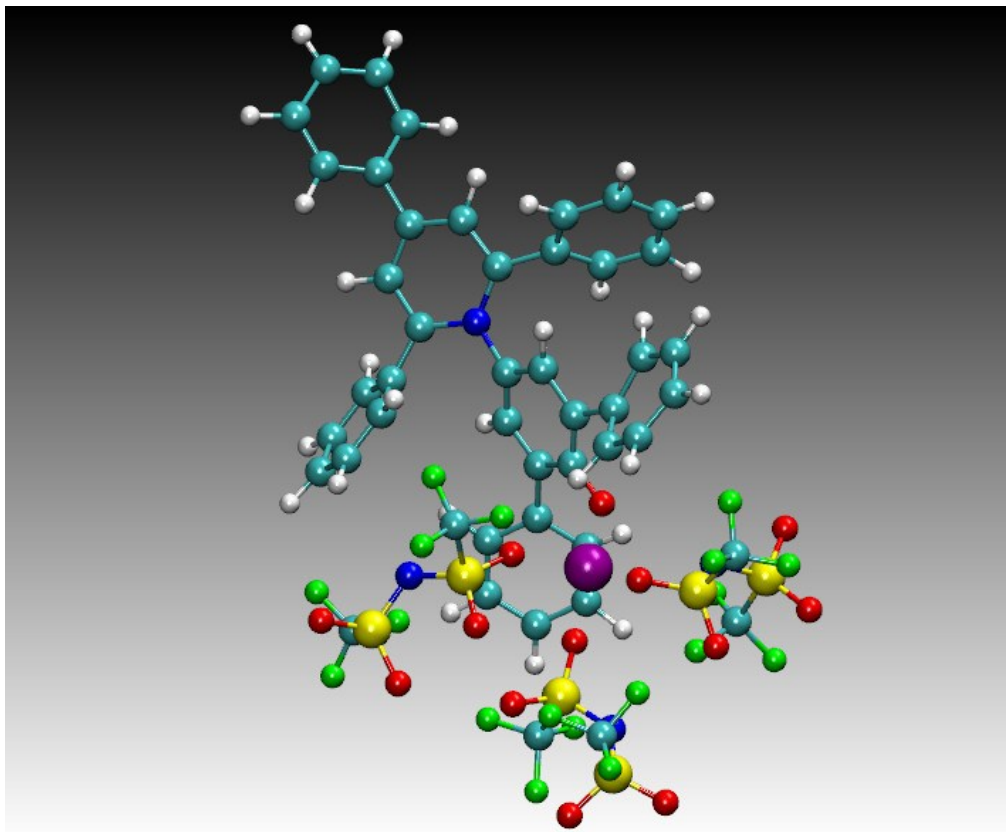


Figure S1: Typical configuration predicted for the dye—Li⁺ complex, showing additional coordination of three oxygen atoms provided by three TFSI⁻ molecules, taken from the **G3TFSI** liquid simulation. Remainder of the liquid not shown for clarity. Cyan=carbon, white=hydrogen, blue=nitrogen, red=oxygen, green=fluorine and purple=Li⁺

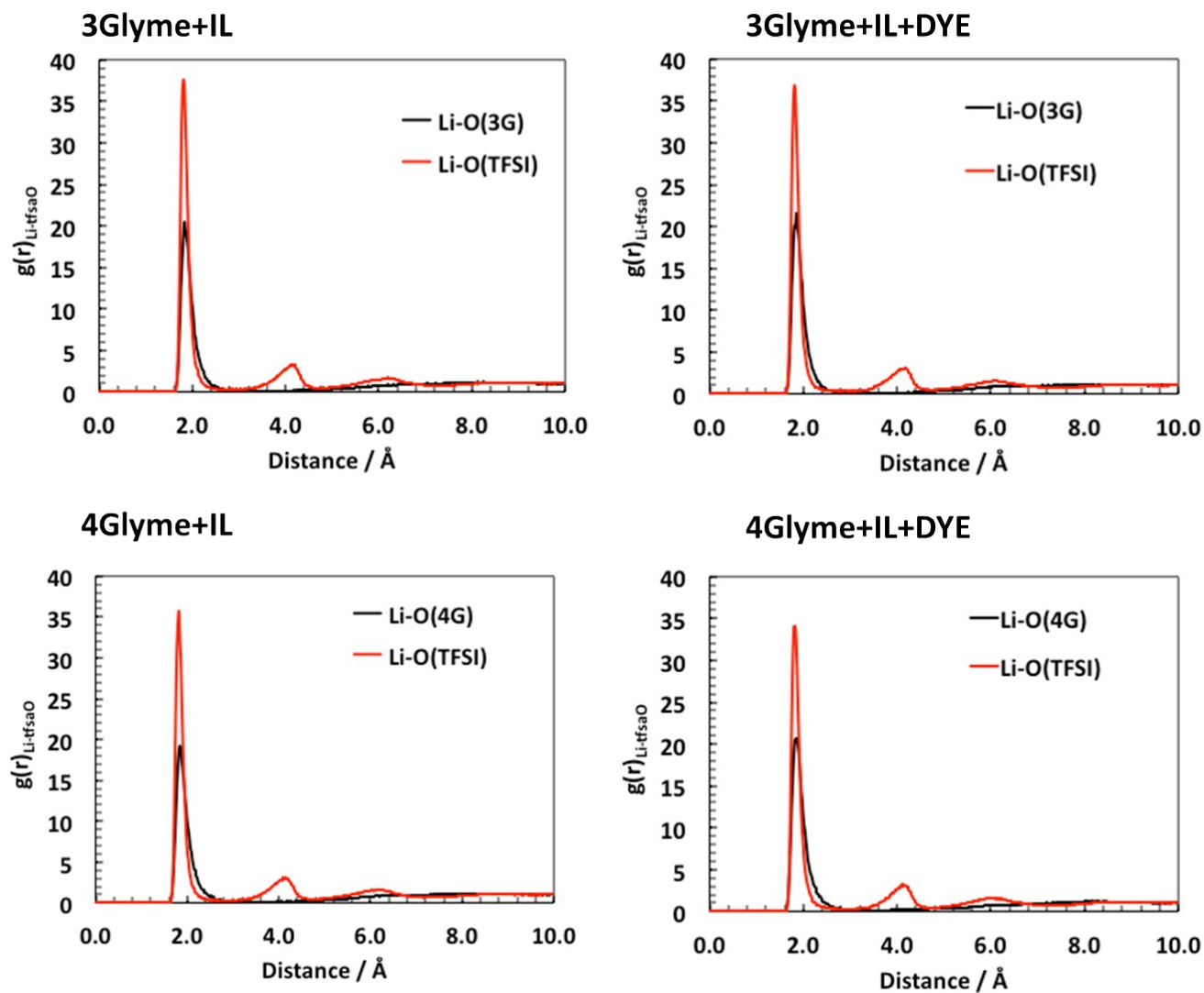


Figure S2: Radial distribution functions for 3G/4G(O)-Li⁺ separations and TFSI-(O)-Li⁺ separations, calculated from the **G3TFSI** and **G4TFSI** liquid simulations, with and without the presence of dye.

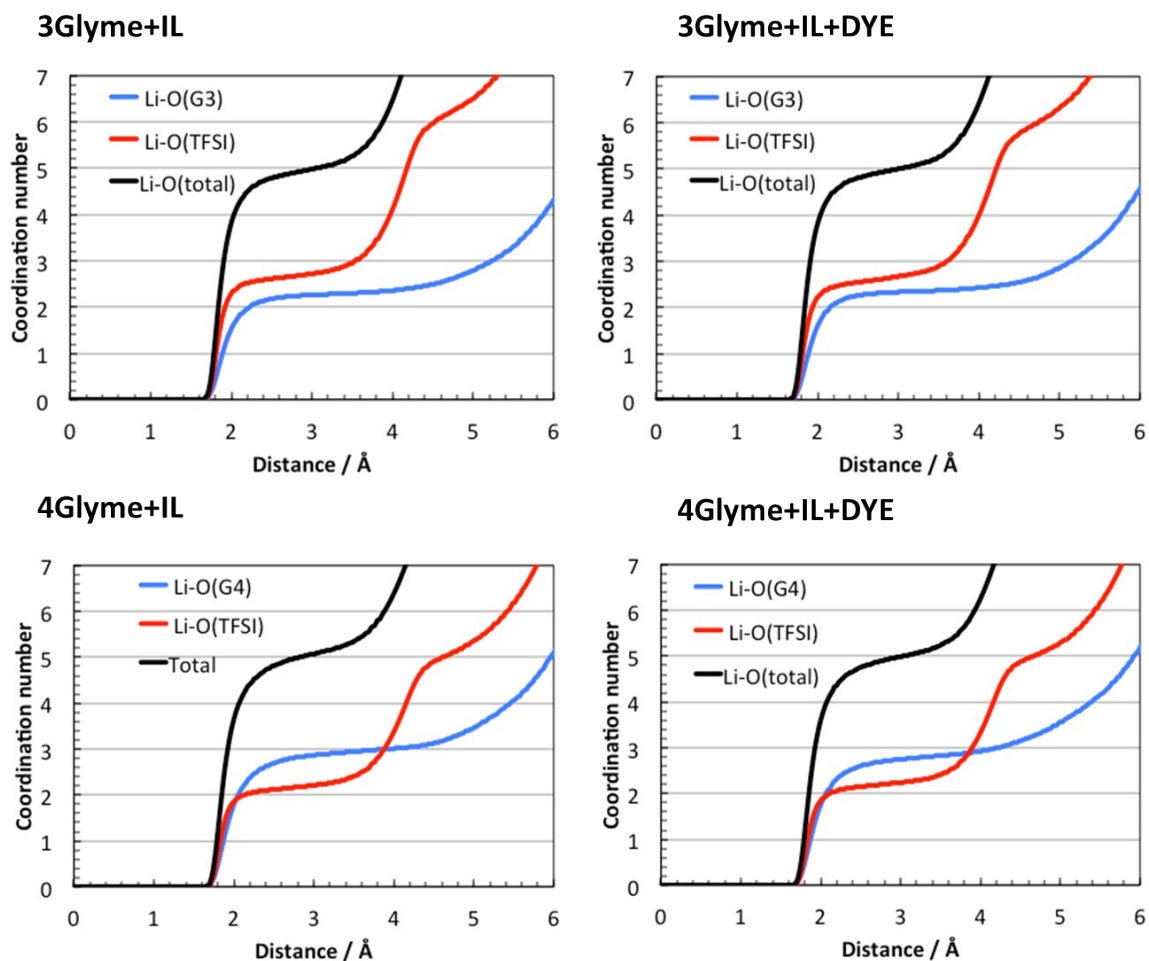
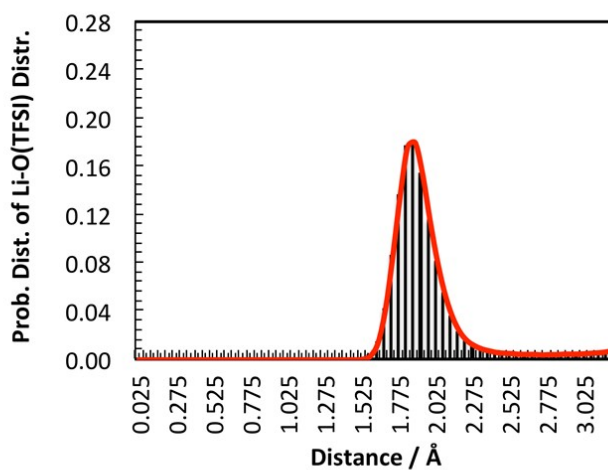
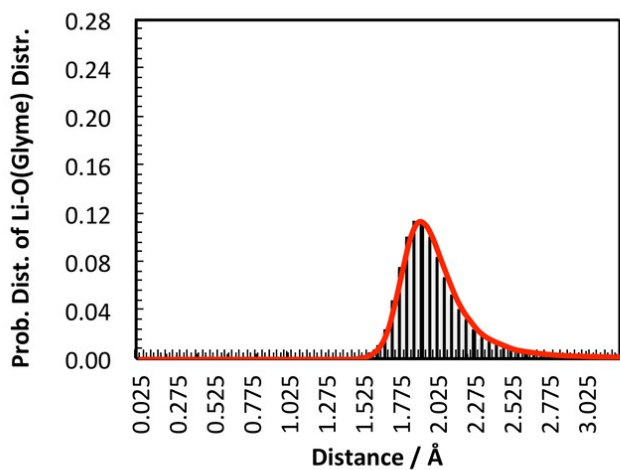


Figure S3: Coordination number distributions for 3G/4G(O)-Li⁺ and TFSI-(O)-Li⁺, calculated from the **G3TFSI** and **G4TFSI** liquid simulations, with and without the presence of dye.

3G+IL



4G+IL

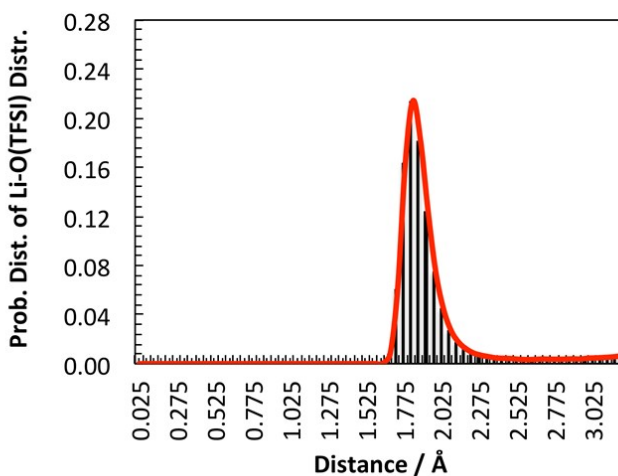
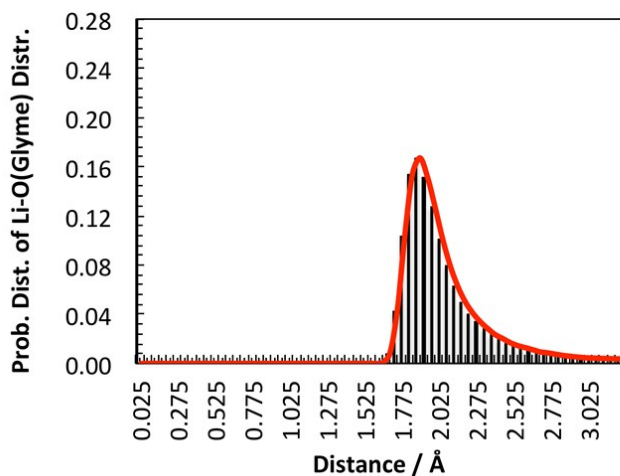
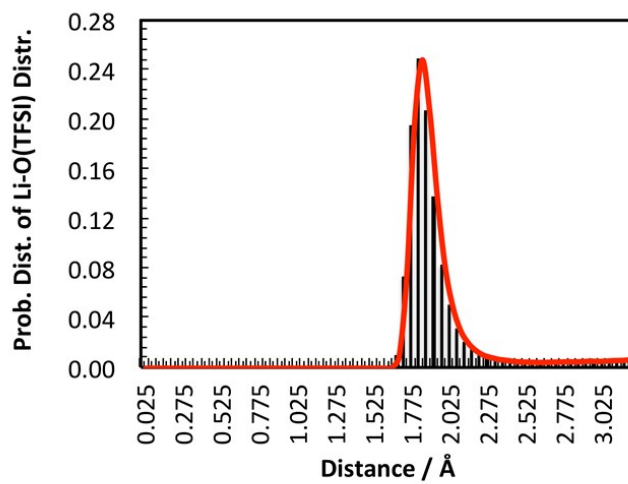
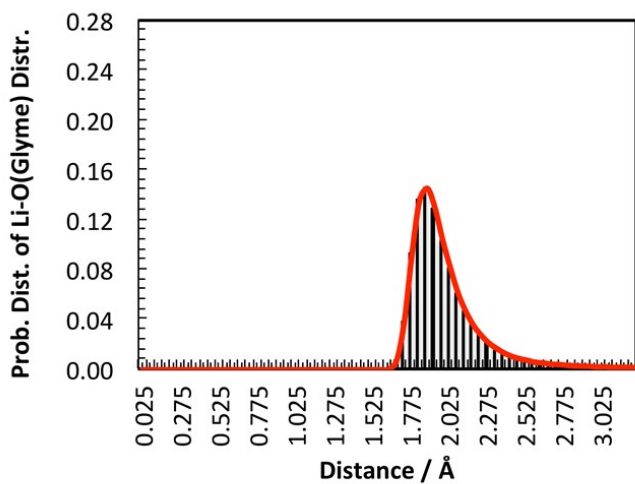


Figure S4: Histograms of oxygen-lithium “coordinated” distances for coordinated TFSI and G3/G4 molecules taken from the **G3TFSI** and **G4TFSI** liquid simulations, in samples that did not contain dye.

3G+IL+Dye



4G+IL+Dye

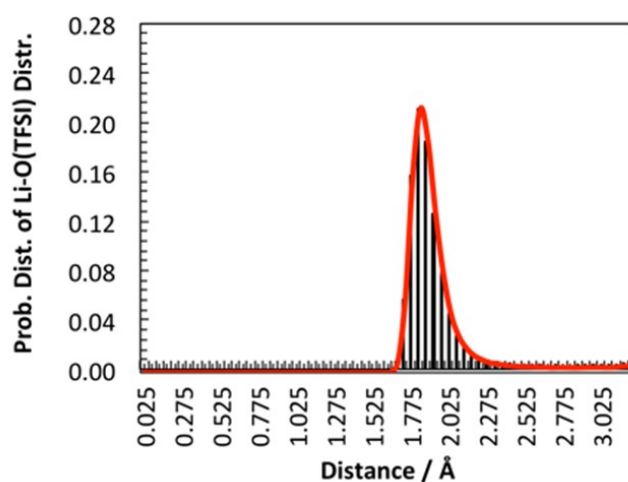
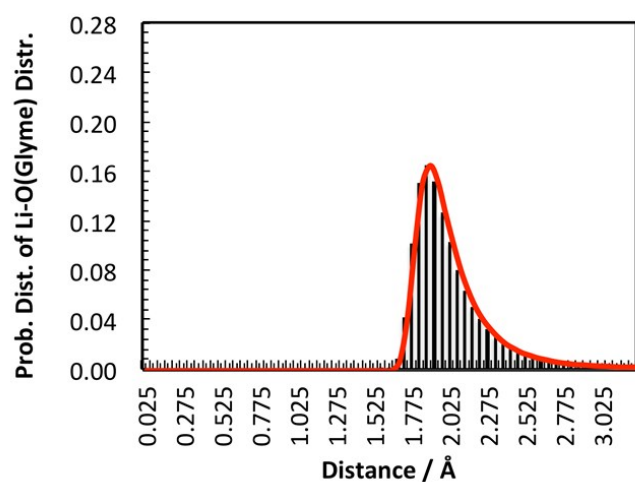


Figure S5: Histograms of oxygen-lithium “coordinated” distances for coordinated TFSI⁻ and G3/G4 molecules taken from the **G3TFSI** and **G4TFSI** liquid simulations, in samples that contained dye.

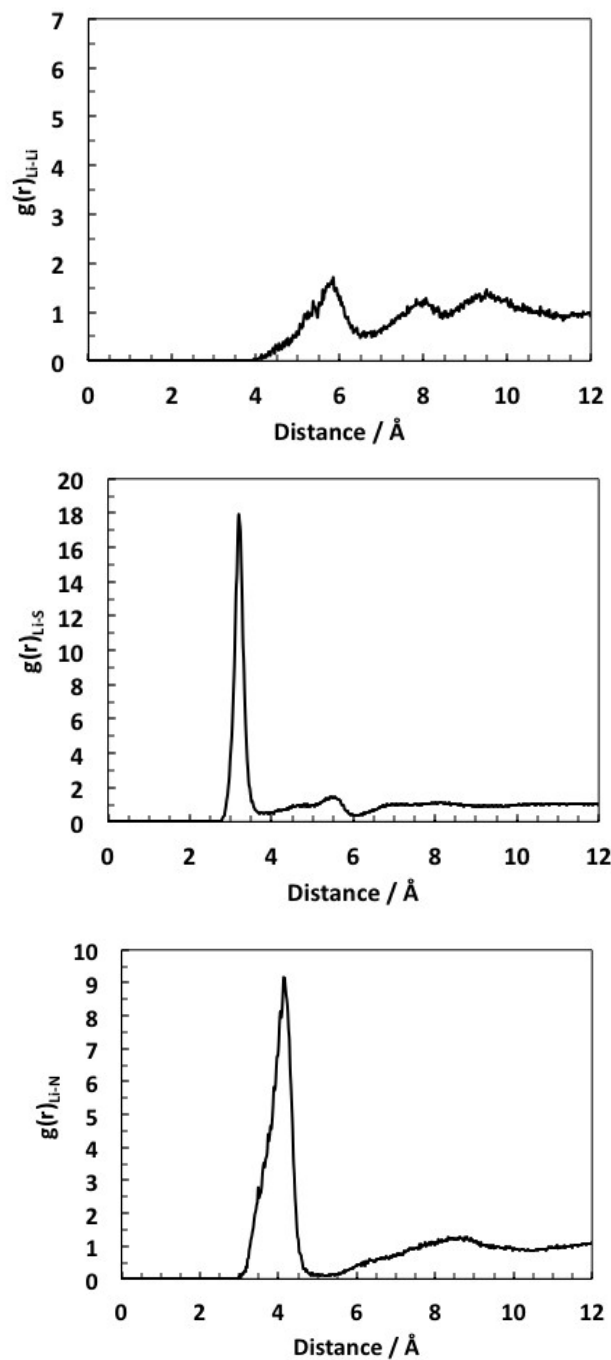


Figure S6: Radial distribution functions calculated from simulations of liquid **G4TFSI** in the absence of dye. a) $Li^+ \cdots Li^+$ b) $Li^+ \cdots S$ and c) $Li^+ \cdots N$.

General procedure for determination of α

Procedure for the determination of α (hydrogen bond donating)

Using Reichardt's Dye **1** and *p*-nitroanisole **2** (other dyes can be used but they have to have different abilities to hydrogen bond accept)

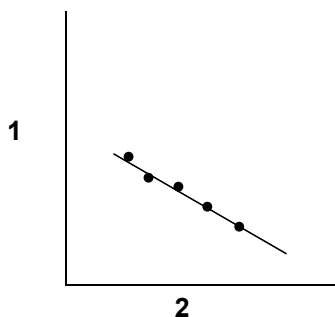
Step 1: Use a dilution of each dye so that the absorbance is suitable, typically in the sub mM region.

Step 2: Measure the maximum absorbance (ν_{\max}) of each dye in a range of **non-hydrogen donating** solvents. The more the better but a good guide may be 5 (e.g. hexane, diethyl ether, DMSO, 1,2-dichloroethane, Ethyl acetate).

Step 3: All of the ν_{\max} values in wavelength must be converted to kilokeiser (kK).

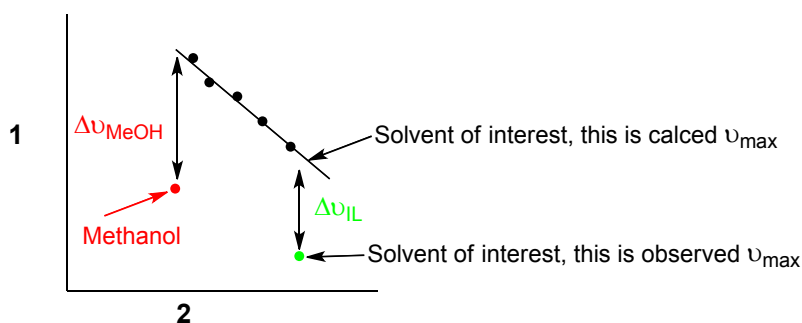
1 kK = 1000 cm^{-1} , therefore a ν_{\max} of 400 nm is converted as such: invert the wavelength ($1/400 \times 10^{-9} = 2\,500\,000\, \text{m}^{-1}$) to get this into wavenumbers, divide by 100 (100 cm in 1 m), giving 25 000 cm^{-1} . Now, with 1 kK = 1000 cm^{-1} , a ν_{\max} of 400 nm = 25 kK.

Step 4: Plot the kK values of **1** and **2** against each other for the non-hydrogen bonding solvents examined. There should be a decent correlation between the two kK values in these non-hydrogen bonding solvents. From this a linear equation can be worked out ($y = mx + c$) or in this case $\Delta\nu_{\max} \mathbf{1} \text{ (kK)} = m (\Delta\nu_{\max} \mathbf{2}) + c$



Step 5: Measure the ν_{\max} in the solvent of interest and a strongly hydrogen donating solvent (e.g. water or methanol) should be used here as well, to confirm the data obtained is consistent with literature values. The eventual α value calculated for the solvent of interest will be relative to this solvent (e.g. water or methanol).

Step 6: The values of ν_{\max} for these solvents will, more than likely, not fall on the line calculated in **step 4**. The amount that it falls from the linear regression gives an idea on how large α will be. Now calculate the value of $\Delta\nu_{\max}$ ($\Delta\nu_{\max} = \nu_{\max} \text{ (observed)} - \nu_{\max} \text{ (calculated)}$). The calculated value of ν_{\max} is determined by using the equation found in **step 4**, express all values in kK.



Step 7: Now standardise the $\Delta\nu_{\max}$ against the largest $\Delta\nu_{\max}$ for the series of solvents here. For example, if Methanol had the largest $\Delta\nu_{\max}$ value then $\alpha = \Delta\nu_{\max} \text{ (IL)} / \Delta\nu_{\max} \text{ (Methanol)}$ which will give you a value for α which is normalised to methanol. Note for α in this case the data points were above the trend line, though this may not be the case in all instances, this is also the case for β .

Worked Example For α for G3TFSI

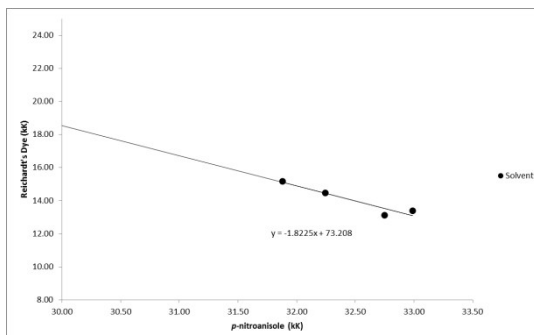
First, a series of non-hydrogen bond donating solvents must be selected, and each UV-vis spectroscopically analysed in relation to two dyes; one hydrogen bond accepting (Reichardt's Dye) and one non-hydrogen bond accepting (*p*-nitroanisole). The ν_{\max} for these solvents are converted to kiloKaisers (kK) and the results of the two dyes plotted against each other, from which a line of best fit and be generated, and an equation for that line elucidated.

For example, if the Average ν_{\max} for THF was 762.80 nm in Reichardt's Dye:

$$\frac{1}{762.80 \times 10^{-9} \text{ m}} = 1310959.622 \text{ m}^{-1}$$

$$\frac{1310959.622 \text{ m}^{-1}}{100} = 13109.60 \text{ cm}^{-1}$$

$$\frac{13109.60 \text{ cm}^{-1}}{1000} = 13.11 \text{ kK}$$



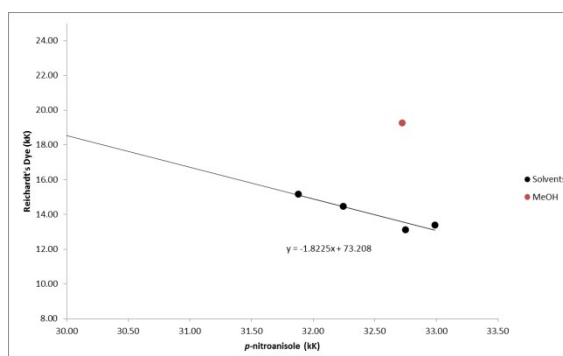
Repeat this process for a strongly hydrogen bond donating solvent (MeOH) to compare unknowns against and plot. Then calculate the distance of MeOH using the equation of the line.

$$y = -1.8225x + 73.208; \quad x = 32.72(\text{kK})$$

$$y = -1.8225(32.72) + 73.208$$

$$y = 13.58$$

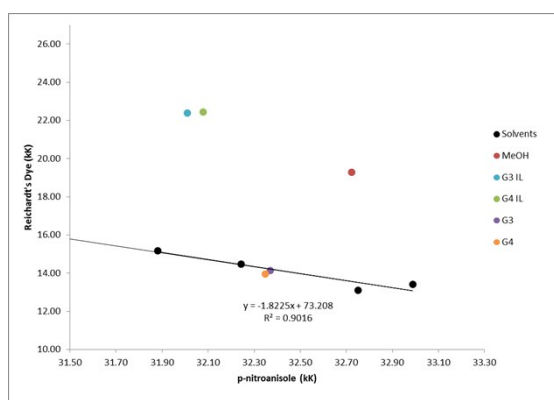
$$y_{\text{MeOH}} - y_{\text{line}} = 19.28 - 13.58 = 5.7$$



From here, the measurements of the unknown solvents can be taken and added to the graph. Using the same methodology, the distance between the data point of the solvent and the line can be calculated and the differences compared to that of MeOH.

$$y_{\text{G3 TFSI}} - y_{\text{line}} = 7.5221$$

$$\alpha = \frac{\Delta kK_{\text{G3 TFSI} - \text{line}}}{\Delta kK_{\text{MeOH} - \text{line}}} = \frac{7.5221}{5.7} = 1.32$$



Therefore, G3 TFSI is 1.32 times *more* 'hydrogen bond donating' than MeOH.

Procedure for the determination of β (hydrogen bond accepting)

Using *p*-nitroaniline **1** and *N,N*-diethyl-4-nitroaniline **2** (or 4-nitroanisole and 4-nitrophenol)

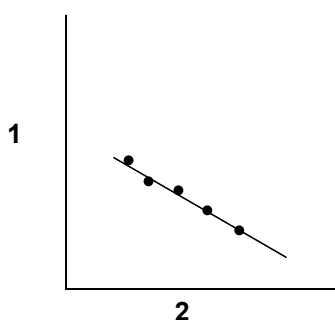
Step 1: Use a dilution of each dye so that the absorbance is suitable, typically in the sub mM region.

Step 2: Measure the maximum absorbance (ν_{\max}) of each dye in a range of **non-hydrogen accepting** solvents. The more the better but a good guide may be 4 (e.g. hexane, toluene, 1,2-dichloroethane, DCM).

Step 3: All of the ν_{\max} values in wavelength must be converted to kilokeiser (kK).

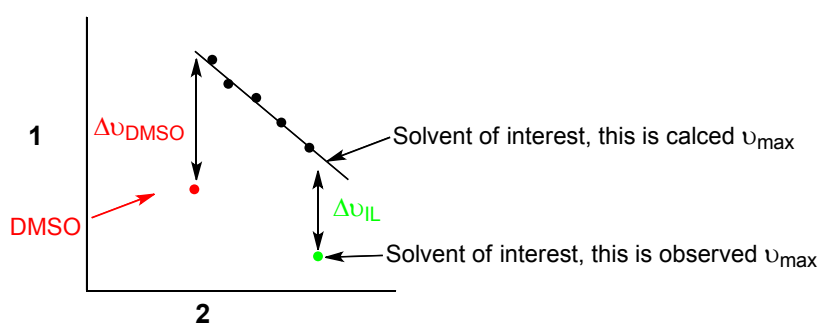
1 kK = 1000 cm^{-1} , therefore a ν_{\max} of 400 nm is converted as such: invert the wavelength ($1/400 \times 10^{-9} = 2\,500\,000\ \text{m}^{-1}$) to get this into wavenumbers, divide by 100 (100 cm in 1 m), giving 25 000 cm^{-1} . Now, with 1 kK = 1000 cm^{-1} , a ν_{\max} of 400 nm = 25 kK.

Step 4: Plot the kK values of **1** and **2** against each other for the non-hydrogen bonding solvents examined. There should be a decent correlation between the two kK values in these non-hydrogen bonding solvents. From this a linear equation can be worked out ($y = mx + c$) or in this case $\nu_{\max} \text{ 1 (kK)} = m (\nu_{\max} \text{ 2}) + c$



Step 5: Measure the ν_{\max} in the solvent of interest and a strongly hydrogen accepting solvent (DMSO/DMF) should be used here as well, to confirm the data obtained is consistent with literature values. The eventual β value calculated for the solvent of interest will be relative to this solvent (e.g. DMSO/DMF).

Step 6: The values of ν_{\max} for these solvents will, more than likely, not fall on the line calculated in **step 4**. The amount that it falls from the linear regression gives an idea on how large α will be. Now calculate the value of $\Delta\nu_{\max}$ ($\Delta\nu_{\max} = \nu_{\max} \text{ (observed)} - \nu_{\max} \text{ (calculated)}$). The calculated value of ν_{\max} is determined by using the equation found in **step 4**, express all values in kK.



Step 7: Now standardise the $\Delta\nu_{\max}$ against the largest $\Delta\nu_{\max}$ for the series of solvents here. For example, if DMSO had the largest $\Delta\nu_{\max}$ value then $\alpha = \Delta\nu_{\max} \text{ (IL)} / \Delta\nu_{\max} \text{ (DMSO)}$ which will give you a β value normalised to DMSO.

Determination of π^*

As stated in the main document the elucidation of π^* is dependent on the dye which is used to measure this value. As such we have provided the formulae and data within the main document.

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