

Supporting Information

Characterizing the Structure-Dependence of the Induced Free Charge Density Gradient in Imidazolium and Pyrrolidinium Ionic Liquids

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NMR spectra of RTILs used in this work.

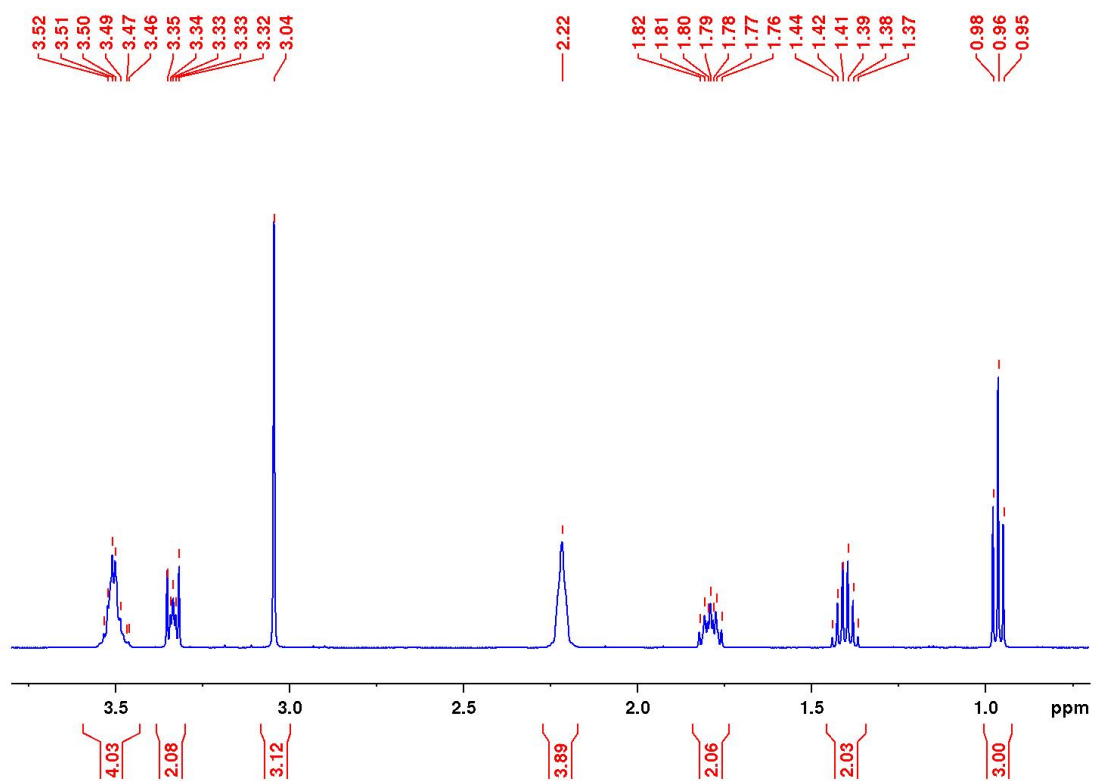


Fig S1. ¹H NMR spectrum (500 MHz, D₂O) of **BMPyrr⁺Br⁻**: δ 3.57–3.44 (m, 4H), 3.36–3.30 (m, 2H), 3.04 (s, 3H), 2.22 (tt, $J = 5.5, 1.9$ Hz, 4H), 1.84–1.74 (m, 2H), 1.40 (h, $J = 7.4$ Hz, 2H), 1.01–0.93 (m, 3H).

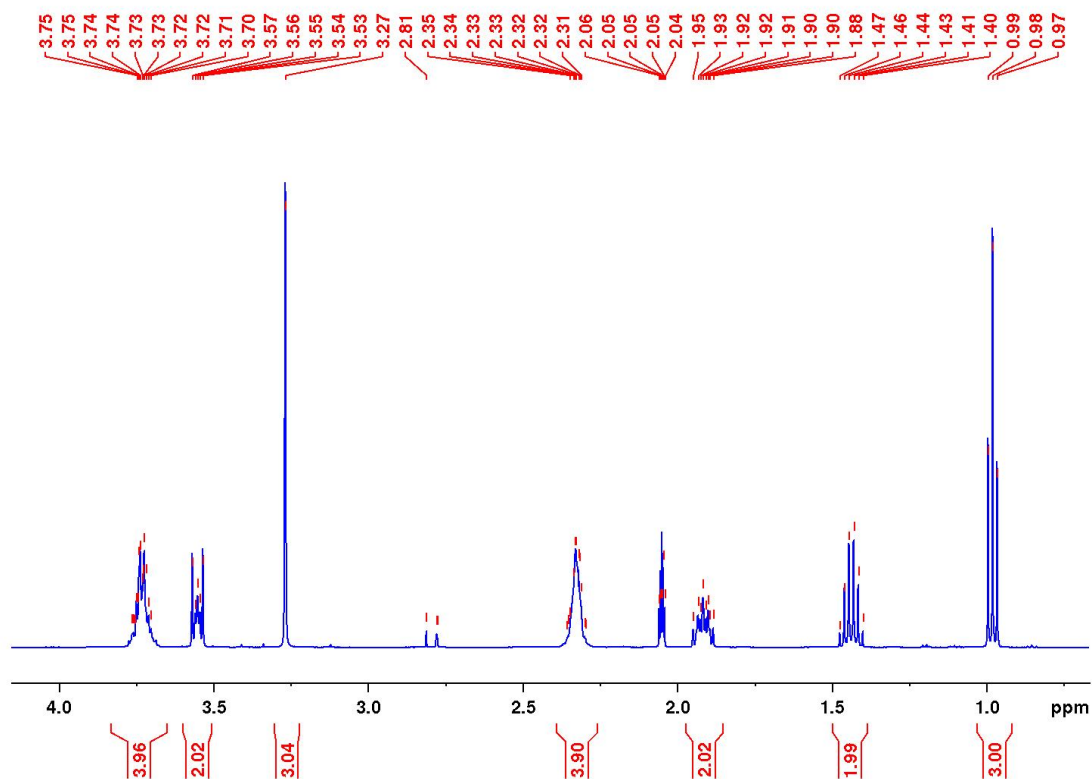


Fig S2. ^1H NMR spectrum (500 MHz, acetone- d_6) of **BMPyrr $^+$ TFSI $^-$** : δ 3.80–3.67 (m, 4H), 3.64–3.51 (m, 2H), 3.27 (s, 3H), 2.33 (dddq, $J = 7.2, 6.1, 3.2, 1.5$ Hz, 4H), 1.96–1.85 (m, 2H), 1.44 (h, $J = 7.4$ Hz, 2H), 0.98 (t, $J = 7.4$ Hz, 3H). The residual $(\text{CH}_3)_2\text{CO}$ peak from acetone- d_6 can be seen at 2.05 ppm. Peaks arising from H_2O and HDO (near 2.84 and 2.81 ppm, respectively) are evident. Control experiments validated that these arose from moisture present in the acetone- d_6 solvent itself.

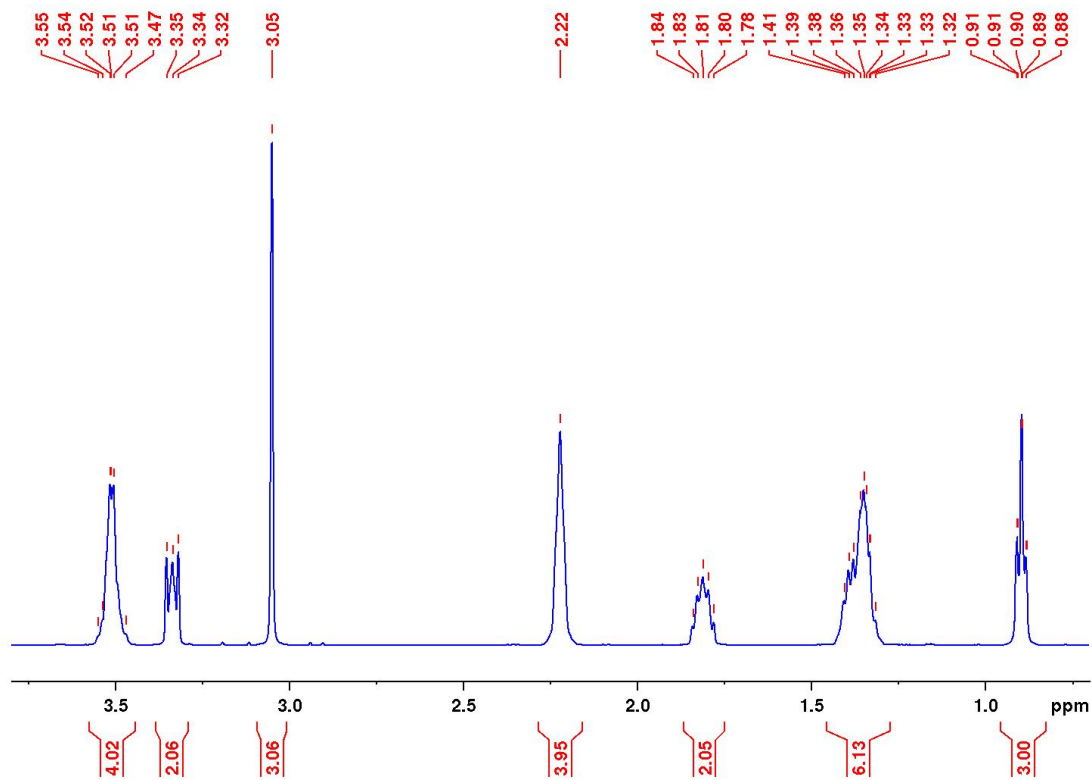


Fig S3. ¹H NMR spectrum (500 MHz, D₂O) of **HMPyrr⁺Br⁻**: δ 3.57–3.45 (m, 4H), 3.38–3.28 (m, 2H), 3.10–3.01 (m, 3H), 2.27–2.18 (m, 4H), 1.81 (ddt, $J = 12.6, 8.7, 4.6$ Hz, 2H), 1.43–1.28 (m, 6H), 0.94–0.84 (m, 3H).

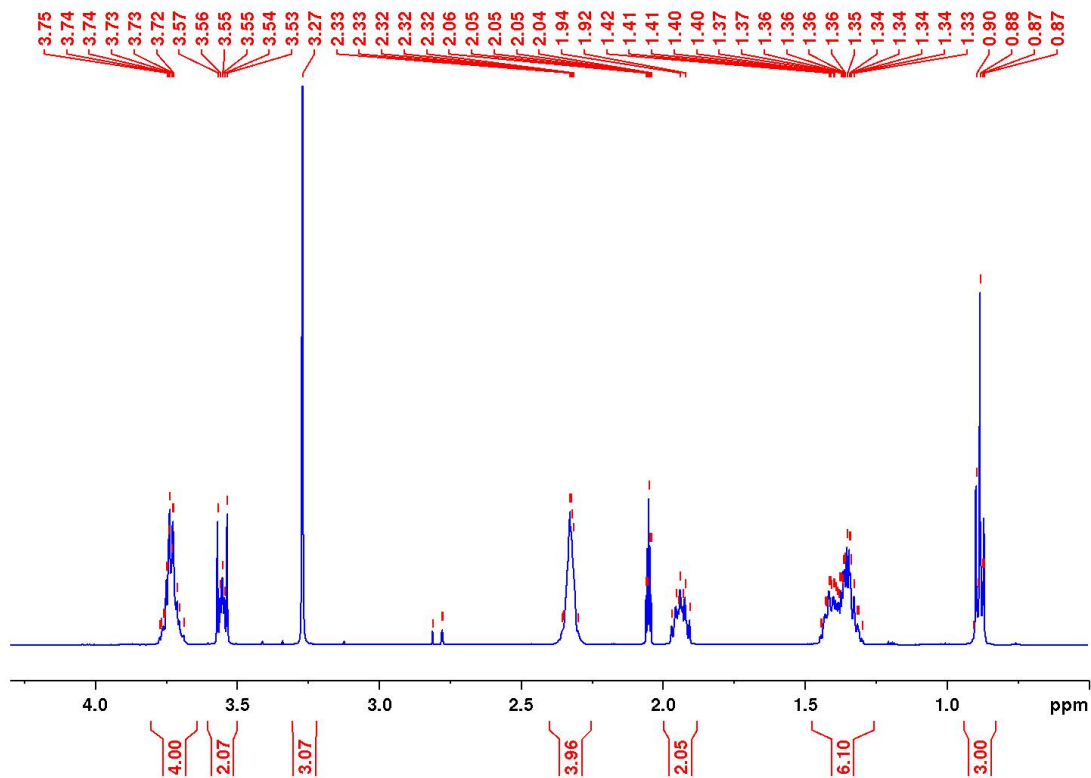


Fig S4. ¹H NMR spectrum (500 MHz, acetone-d₆) of **HMPyrr⁺TFSI⁻**: δ 3.81–3.67 (m, 1H), 3.61–3.50 (m, 1H), 3.27 (s, 1H), 2.33 (tdd, $J = 5.8, 2.9, 1.5$ Hz, 1H), 1.94 (dq, $J = 12.2, 8.2, 7.7$ Hz, 1H), 1.49–1.27 (m, 1H), 0.88 (t, $J = 7.1$ Hz, 1H).

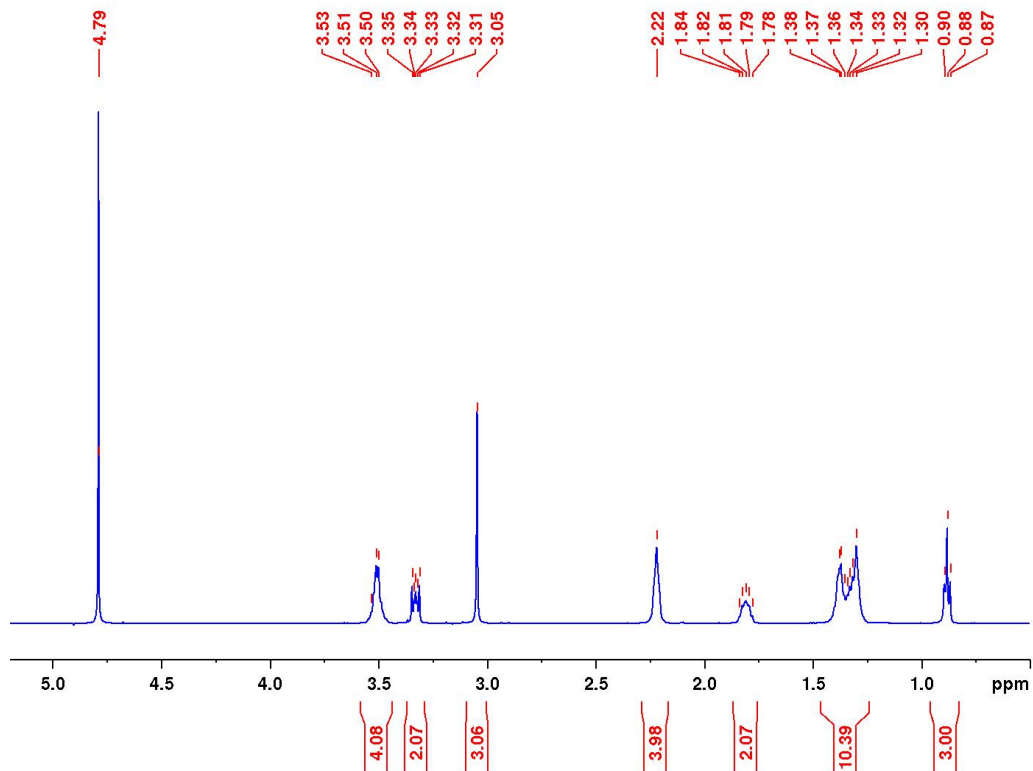


Fig S5. ^1H NMR spectrum (500 MHz, D_2O) of $\text{OMPyr}^+\text{Br}^-$: δ 3.51 (h, $J = 5.7, 4.7$ Hz, 4H), 3.35–3.31 (m, 2H), 3.05 (s, 3H), 2.22 (q, $J = 4.5, 3.7$ Hz, 4H), 1.84–1.78 (m, 2H), 1.38–1.30 (m, 10H), 0.88 (t, $J = 6.6$ Hz, 3H). A residual water peak from D_2O is seen at 4.79 ppm.

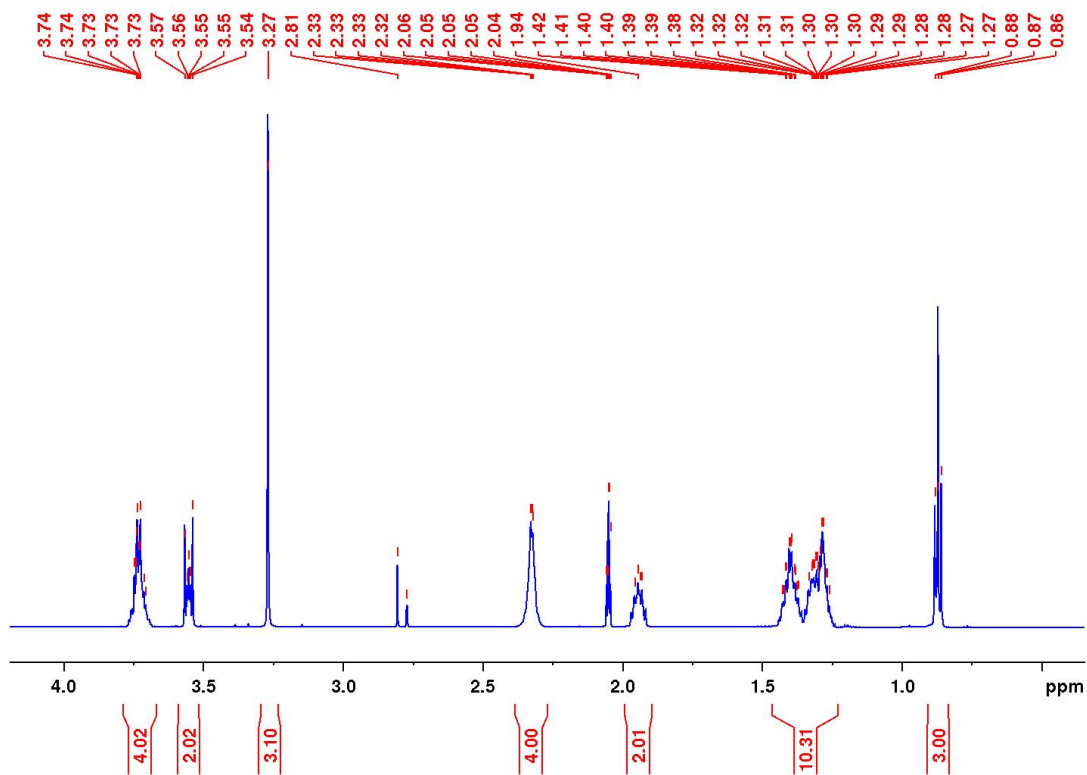


Fig S6. ^1H NMR spectrum (600 MHz, acetone- d_6) of **OMPyr $^+$ TFSI $^-$** : δ 3.74–3.73 (m, 4H), 3.57–3.54 (m, 2H), 3.27 (s, 3H), 2.33 (dt, $J = 6.2, 4.7, 3.7, 1.7$ Hz, 4H), 1.94 (dq, $J = 12.0, 8.1, 7.6$ Hz, 2H), 1.42–1.27 (m, 10H), 0.87 (t, $J = 7.0$ Hz, 3H).

Derivation of Equation 5.

As noted, comparison of τ_{OR} values for the different RTILs is done most effectively when the normalized charge density gradient is compared for the different RTILs.

$$\nabla \cdot \tau_{OR} = \left(\frac{\eta f}{k_B T S} \right) \nabla \cdot V = k \nabla \cdot V \quad [S1]$$

And from our previous work,

$$\nabla \cdot \tau_{OR} = k' \nabla \cdot D = k' \rho_f \quad [S2]$$

Where D is the charge displacement and ρ_f is the free charge density gradient. Because the gradient ρ_f is normal to the plane of the support, it can be expressed simply as $\Delta\tau_{OR}$, the difference in τ_{OR} between $x=0$ and $x=\infty$, which is determined by the difference in concentration of the RTIL ion (RI) that complexes with the rotating moiety being observed. From the Debye Stokes Einstein equation (Eq. 2) and prior work showing constant viscosity in the RTIL,

$$\begin{aligned} \tau_{OR}^{x=0} &= \frac{\eta V_{eff}^{x=0} f}{k_B T S} \\ \tau_{OR}^{x=\infty} &= \frac{\eta V_{eff}^{x=\infty} f}{k_B T S} \end{aligned} \quad [S3]$$

Where

$$\begin{aligned} V_{eff}^{x=0} &= X_{free}^{x=0} V_{free} + X_{complex}^{x=0} V_{complex} = X_{free}^{x=0} V_{free} + (1 - X_{free}^{x=0}) V_{complex} \\ V_{eff}^{x=0} &= V_{complex} + X_{free}^{x=0} (V_{free} - V_{complex}) = V_{complex} - X_{free}^{x=0} V_{RI} \end{aligned} \quad [S4]$$

$$\begin{aligned} V_{eff}^{x=\infty} &= X_{free}^{x=\infty} V_{free} + X_{complex}^{x=\infty} V_{complex} = X_{free}^{x=\infty} V_{free} + (1 - X_{free}^{x=\infty}) V_{complex} \\ V_{eff}^{x=\infty} &= V_{complex} + X_{free}^{x=\infty} (V_{free} - V_{complex}) = V_{complex} - X_{free}^{x=\infty} V_{RI} \end{aligned}$$

All of the chromophore is either free or complexed; $X_{free} + X_{complex} = 1$. The quantity V_{RI} is the volume of the RTIL counterion that complexes with the chromophore: $V_{complex} = V_{free} + V_{RI}$.

The difference in τ_{OR} between $x=0$ and $x=\infty$, normalized for bulk reorientation time, $\tau_{OR}^{x=\infty}$ provides a way to characterize the fractional change in τ_{OR} and allows for comparison between different RTILs.

$$\frac{\Delta \tau_{OR}}{\tau_{OR}} = \frac{\tau_{OR}^{x=0} - \tau_{OR}^{x=\infty}}{\tau_{OR}^{x=\infty}} = \frac{\Delta V}{V} = \frac{V_{eff}^{x=0} - V_{eff}^{x=\infty}}{V_{eff}^{x=\infty}} \quad [\text{S5}]$$

$$\frac{V_{eff}^{x=0} - V_{eff}^{x=\infty}}{V_{eff}^{x=\infty}} = \frac{(V_{assoc} - X_{free}^{x=0} V_{RI} - V_{assoc} + X_{free}^{x=\infty} V_{RI})}{V_{assoc} - X_{free}^{x=\infty} V_{RI}} = \frac{(X_{free}^{x=\infty} - X_{free}^{x=0}) V_{RI}}{V_{assoc} - X_{free}^{x=\infty} V_{RI}} \quad [\text{S6}]$$