

CHARACTERIZATION AND APPLICATION OF THE SURFACE CHARGE-INDUCED
LONG-RANGE ORGANIZATION IN ROOM TEMPERATURE IONIC LIQUIDS

By

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ABSTRACT

CHARACTERIZATION AND APPLICATION OF THE SURFACE CHARGE-INDUCED LONG-RANGE ORGANIZATION IN ROOM TEMPERATURE IONIC LIQUIDS

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Room temperature ionic liquids (RTILs) are salts characterized by a melting point below room temperature. RTILs have a wide range of applications, in areas ranging from supercapacitor energy storage to sequestration of toxic gas phase species and use as reusable solvents for selected organic reactions. All these applications stem from their unique physical and chemical properties, which remain understood to a limited extent. Among the issues of greatest importance is the extent to which RTILs exist as dissociated ionic species, and the length scales over the organizations are seen to exist in them. Our group have reported previously on the existence of a surface charge-induced free charge density gradient in RTILs with a characteristic persistence length of ca. 50 μm . The existence of such a long-range organization in fluid medium is unusual. The overall goal of this work is to achieve a deeper understanding of this phenomenon, thereby providing an opportunity to better understand the local and long-range organization in RTILs and broad their potential applications which benefit from gaining such knowledge.

The induced free charge density gradient (ρ_f) is probed by measuring the fluorescence anisotropy decay of a trace-level charged chromophore in the RTIL as a function of distance from the indium-doped tin oxide (ITO) support surface. In chapter 2, we characterize the structure-dependence of this charge-induced organization as a function of the RTIL constituent identity, and use these data to evaluate the magnitude of the induced free charge density gradient. The magnitude of this gradient is found to depend on the chemical structures of the cationic and

anionic constituents of the RTIL used.

In chapter 3, we characterize ρ_f in three different pyrrolidinium RTILs and two imidazolium RTILs, which aims to expand on prior results (chapter 2) on the chemical structure-dependence of ρ_f . Our measurements demonstrate that the magnitude of ρ_f depend on the alkyl chain length of RTIL cation. ρ_f is larger in the RTIL with longer cation alkyl chain. This dependence has been revealed in both pyrrolidinium and imidazolium ionic liquids.

In chapter 4, we report on the existence of a surface charge-induced gradient in the RTIL refractive index (n) and evaluate the relationship between the gradient in n and ρ_f . Because ρ_f is uniaxial, the induced change in n is manifested as an induced birefringence. We characterize the ρ_f -dependent n of the RTIL with an apparatus that uses the RTIL as a lens. ρ_f is controlled by the surface charge density (σ_s) of the RTIL support. The far-field image of light passed through the RTIL lens as a function of σ_s is used to measure charge-induced changes in n of the RTIL. We demonstrate a significant modulation of the n with modest changes in σ_s of the RTIL support. This report places the relationship between ρ_f and RTIL dielectric response on a quantitative footing and suggests the utility of RTILs for electro-optic applications.

In chapter 5, We report on the dependence of surface charge-induced birefringence in room temperature ionic liquids (RTILs) with different cation constituents. The induced birefringence is related to ρ_f in the RTIL. We find that in all cases the induced birefringence is proportional to the σ_s and, that the change in n nearest the ITO surface can be on the order of 30%. Our findings indicate that the induced birefringence depends more sensitively on the cation aliphatic substituent length than on the identity of the charge-carrying headgroup.

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CHAPTER 1. Introduction

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Wang, Y.; Parvis, F.; Hossain, M.I.; Ma, K.; Jarošová, R.; Swain, G.M.; Blanchard, G.J., Local and Long-Range Organization in Room Temperature Ionic Liquids. *Langmuir* **2021**. 37(2), 605-615.

1. 1 Overview of Room Temperature Ionic Liquids

Room temperature ionic liquids (RTILs) are a class of materials that have proven to be of great practical utility in areas ranging from electrolytes in supercapacitors¹⁻³ and batteries⁴⁻⁵ to gas sequestration media and electrospray ion propulsion.⁶⁻⁷ Despite the utility of these materials in so many venues, there remains a great deal to be understood about ionic liquids. Ionic liquids are salts that exhibit a melting point below room temperature, where the constituent cations are typically large, organic and of low symmetry, and the anions are also usually large (examples in Figure 1. 1).

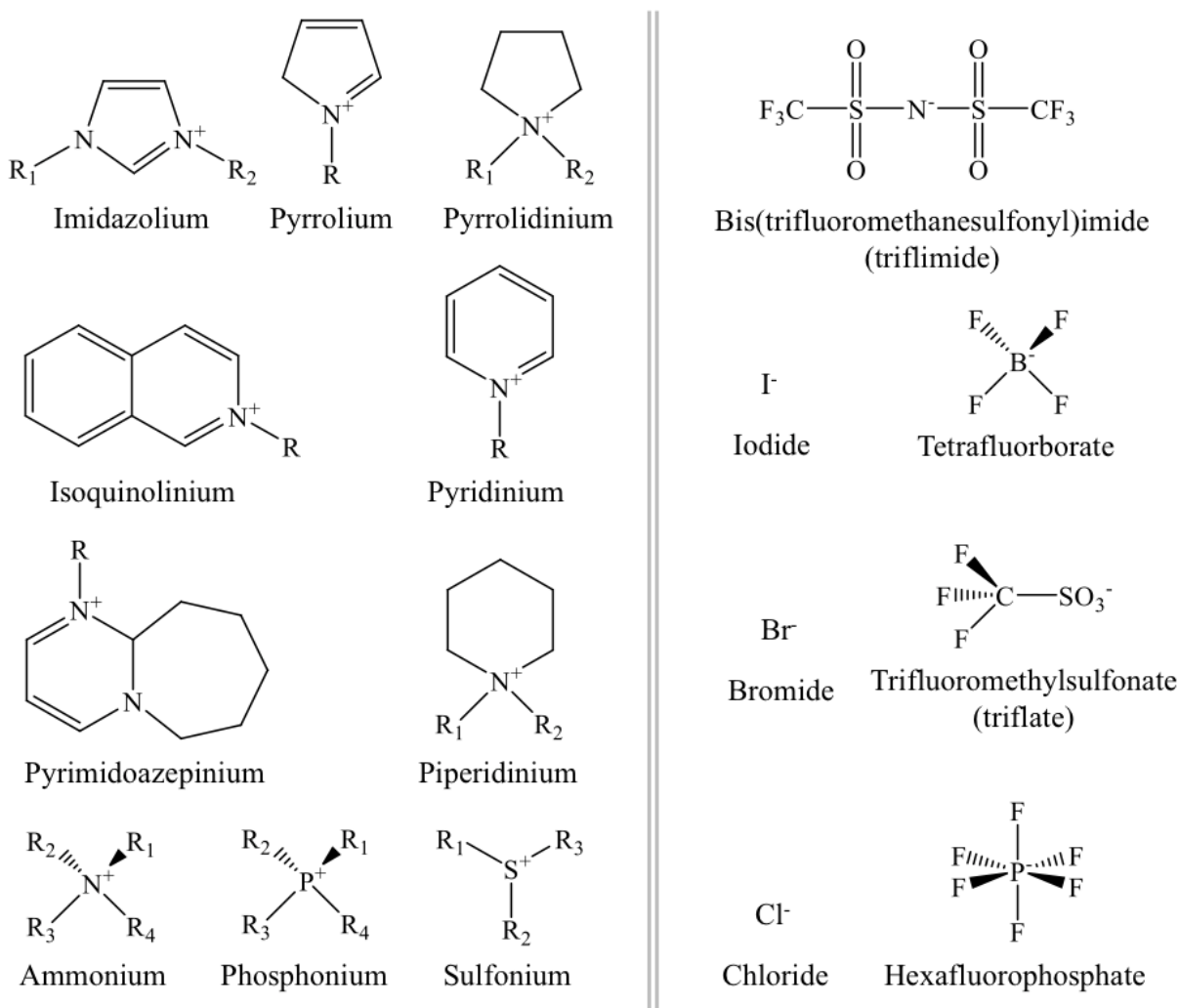


Figure 1. 1 Examples of RTIL cation and anion structures.

There has been a great deal of clever and important synthetic effort aimed at designing ionic liquids with properties optimized for specific purposes or applications.⁸⁻¹³ For example, chirality can be introduced into RTILs through the use of chiral cations⁸⁻⁹ and this may have implications on bio-related and second order nonlinear optical applications. The judicious choice of anion and cation can also be used to tailor the viscosity or the formation of local heterogeneities¹⁴⁻¹⁵ in RTILs. In many respects, ionic liquids do not behave as common liquids. Most are characterized by relatively high viscosity, essentially zero vapor pressure, and they are capable of dissolving both polar and nonpolar compounds. Ionic liquids also exhibit organization over length scales vastly in excess of that seen in (non-ionic) liquids, and it is this property that has posed a significant challenge to our understanding of these materials.

Organization in ionic liquids cannot simply mimic that of the NaCl lattice with all ions existing as discrete entities and arranged in a lattice-like structure. There is substantial evidence that ionic liquids exist primarily as ion-paired dipolar species,¹⁶⁻¹⁸ and the extent of dissociation is, in general, not well characterized because of difficulties in measuring the conductivity and free ion concentrations in the medium. It is tempting to draw parallels to ionic liquids and liquid crystals, at least to some extent. The ability to control molecular orientation by means of templating or applied potential demonstrates that organic systems can exhibit long-range organization. Indeed, some organic ionic systems go from solid to (ionic) liquid crystalline to ionic liquid phases with increasing temperature.¹⁹⁻²⁰ Such ionic liquid crystal mesophases are typically seen for alkyl imidazolium ionic liquids where one of the alkyl chains is on the order of C₁₄. This effect is thought to occur because of van der Waals interactions between the (long) aliphatic chains. Most imidazolium-based ionic liquids have a C₂-C₈ alkyl chain, with C₄ being the most widely studied. For these ionic liquids, a liquid crystalline mesophase has not been

reported, but it is possible that subtle organization may exist in these systems. There are a number of reports that indicate thin films of imidazolium-based ionic liquids exhibit ordering that is induced by the presence of an interface.²¹⁻²⁶ In addition, a recent article by the Brand group demonstrates the ability to alter the organization of an ionic liquid monolayer deposited on Au by controlling the potential of the gold surface.²⁷ They found that the orientation of the monolayer imidazolium aliphatic chains exhibited a surface potential-dependent tilt angle. This finding is not only intriguing, but also opens the door to possible control over structural organization in ILs.

Our group has found that, in addition to the ability to induce structural order in ionic liquids, free charge density gradients can also be induced over macroscopic distances.²⁸⁻³⁰ This finding not only underscores our limited current understanding of RTILs, but also raises the question of the relationship between structural order and the existence of a free charge density gradient in RTILs. There are several bodies of information, discussed below, that point to a connection.

1. 2 Organization in Room Temperature Ionic Liquids (RTILs)

Organization in RTILs has been observed experimentally and predicted by modeling, and the length scale over which the structural order is seen depends on the methodologies used for the study. There is a substantial literature on X-ray diffraction of ionic liquids that points collectively to the existence of structurally regular organization between RTIL constituent ions, with the details of the organization depending on the ion structures and temperature of the system.³¹⁻³⁵ While such data do not speak directly to the persistence length of molecular-scale structural regularity, among the interesting results that have come from this work is the notion of extended networks of RTIL constituents, ranging from polymeric supramolecular structures, through aggregates to triple-ion and contact ion pair structures.³⁵ Such organization provides a rational basis for the existence of longer length-scale order in these materials.

The Israelachvili group used temperature-dependent surface force measurements to examine the (exponential) Debye decay length of the diffuse double layer forces.¹⁶⁻¹⁷ Their results support the notion of long-range electrostatic screening in ionic liquids, a finding that is important in understanding the ability of RTILs to support the existence of a measurable free charge density gradient. Specifically, Gebbie *et al.* used equilibrium force-distance measurements to measure the effective Debye length as a function of temperature and they found a significant temperature-dependence. The Debye length was seen to vary from 6.7 nm at 22 °C to 3.4 nm at 60 °C for 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM⁺TFSI⁻) and was measured to be *ca.* 12 nm for 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM⁺TFSI⁻).¹⁶⁻¹⁷ Such a result is consistent with very low effective free ion concentrations or highly efficient screening of free charge. From their force-distance data, they determine the charge carrier activation energy to be *ca.* $9.5 k_B T$, suggesting that the dissociation of RTILs is very limited. Using the assumption that the chemical potential of RTIL dissociation is given by E_d/ϵ , where E_d is the dissociation energy and ϵ is the dielectric constant (relative permittivity) of the RTIL, they estimate the equilibrium concentration of dissociated ions to be on the order of 10^{-4} M, corresponding to a pK_d of 9.14 for BMIM⁺TFSI⁻.¹⁷ This result stands in sharp contrast to other estimates of effective ion concentration in RTILs, that estimate the effective fraction of ions that are able to participate in charge conduction based on the concept of “ionicity”.^{18, 36} The likely difference between these estimates of the free ion concentrations in RTILs lies in the fact that the ionicity measurements rely on ion exchange dynamics and diffusion (*i.e.* kinetic phenomena) while the force-distance measurements derive values based on equilibrium (thermodynamic) quantities. It is useful to consider that RTIL properties such as temperature-dependent conductivity and viscosity differ from those of simple ionic solutions such as KCl(*aq*).³⁷ The force-distance

measurements sense order in the diffuse double layer that is much longer range than would be expected if RTILs could be understood in the context of the Gouy-Chapman-Stern or other similar models.

Beyond the organization associated with a *ca.* 10 nm Debye length, structural order has been reported in a host of RTILs on length scales ranging from 1 nm to 60 nm.³⁸⁻⁴⁰ Much of this structural order is seen within the first several nm of (charged) surfaces, where “herringbone” order and charged layers have been reported. RTIL organization on this length scale has also been seen to evolve over time.⁴¹ While the details of this organization differ substantially from traditional Gouy-Chapman-Stern or Helmholtz behavior, what is observed is in much closer proximity to the interface than have been reported by several other groups. Very recently, the Brand group has reported that a surface RTIL ($C_{18}Im^+$) monolayer formed by Langmuir-Blodgett deposition gives rise to significant modification of the electric double layer at a charged electrode.²⁷

The Shaw group has found compelling evidence for long-range structural organization in ionic liquids. They formed thin RTIL films using a dynamic wetting technique and acquired FTIR, optical ellipsometry and second harmonic generation measurements.²¹⁻²³ The Shaw group monitored the (polarized) IRRAS spectra of $BMIM^+TFSI^-$ thin films as a function of time (minutes to days) and observed the gradual changes of band positions and intensities for several bands in the 1000 cm^{-1} to 1400 cm^{-1} region. While several of the bands did not change over time, there were four bands that were seen to exhibit changes in intensity and/or frequency. These bands were assigned to the S-N-S stretch (1069 cm^{-1}), the SO_2 symmetric stretch (1149 cm^{-1}), the CF_3 symmetric stretch (1244 cm^{-1}), and the SO_2 asymmetric stretch (1366 cm^{-1}) of the TFSI anion. These bands disappeared from the polarized IRRAS spectra, with the implication being that the anion was reorienting to place these vibrational modes predominantly in the film plane parallel to

the support (and film) surface. The spectral evolution required *ca.* one hour, and this finding is consistent with the time-dependent second harmonic generation response of the same thin film. For the thin films used, the organization that evolved in time was found to be present through the entire thickness of the film. The Shaw group also investigated thin film RTILs with anions containing cyano groups. Interestingly, RTILs with a B(CN)_4^- anion demonstrated ordering that appeared to template from the support surface while RTILs with a N(CN)_2^- anion demonstrated ordering that was templated from organization of the air-IL interface.²³

The Fayer group has used surface charge density as a means of controlling the properties of RTIL thin films^{24-26, 42-43} and confined environments.⁴⁴ In thin films of RTILs (50 nm to 250 nm thick), they time-resolved the band position and shape of the CN stretch of SCN^- and SeCN^- and CO_2 reorientation to assess the evolution of local environment as a function of surface charge density and RTIL imidazolium aliphatic chain length.^{24-26, 42-43} They found that dynamics within the RTIL thin were slowed by the presence of surface charge for films up to *ca.* 250 nm, and that the characteristic length scale of the influence of interfaces on RTIL dynamics was *ca.* 30 nm.²⁴ The Fayer group's work is complementary to that of the Shaw group in the sense that it points to changes in dynamics of the RTIL local environment(s) while the Shaw group's results indicate structural organization. It is likely that structural organization of thin RTIL films has a direct influence on the dynamics that characterize local environments within them. The role of surface charge in mediating these dynamics is consistent with and complementary to the ability to create long-range charge density gradients in RTILs (*vide infra*).

Long-range organization is seen in RTILs by a number of methods, both experimental and theoretical. Such organization is not consistent with models that are appropriate for dilute solutions, despite data that suggests very limited dissociation in RTILs.¹⁶⁻¹⁷ Another body of data

that is not consistent with the treatment of RTILs as “normal” liquid phase solvents is evidence, both experimental and theoretical, for nanoscale heterogeneities in RTILs.^{14-15, 45-46} The rationale for the existence of such domains stems from the amphiphilic nature of the cationic RTIL constituents when nonpolar moieties, typically on the cation, are sufficiently large to form nano-domains. Such compositional heterogeneity has been suggested as the basis for the ability of RTILs to solubilize nonpolar species.¹⁵

1. 3 Charge Density Gradients in RTILs

As noted above, there is abundant evidence for structural organization and for the influence of charged surfaces on dynamics in RTILs. Most of these reports place such organization up to multiple tens of nm,^{16-17, 24-26, 42-44} and in some instances the organization is limited by the thickness of the RTIL films examined.²¹⁻²³ Our group has found evidence for induced charge density gradients (ρ_f) in RTILs with a spatial extent of tens of μm .²⁸⁻³⁰ We discuss our findings and their implications below, with an eye toward understanding how the free charge density gradients we find may be influenced by structural organization in RTILs. One important consideration is that the structural order reported for thin RTIL films may exhibit longer-range effects in thicker samples, bringing structural organization and free charge density gradients into closer agreement.

1. 3. 1 Measuring the Charge Density Gradient

Our group have reported on a free charge density gradient in the RTIL $\text{BMIM}^+\text{BF}_4^-$, which is characterized by the rotational diffusion dynamics of charged and neutral chromophores as a function of distance from a charged support.²⁸ It is useful to consider briefly how ρ_f is measured. We sense ρ_f in RTILs through the fluorescence anisotropy decay of trace amounts of charged chromophores as a function of distance from the (charged) support.⁴⁷ We achieve depth resolution with an inverted confocal microscope through mechanical control over the microscope stage

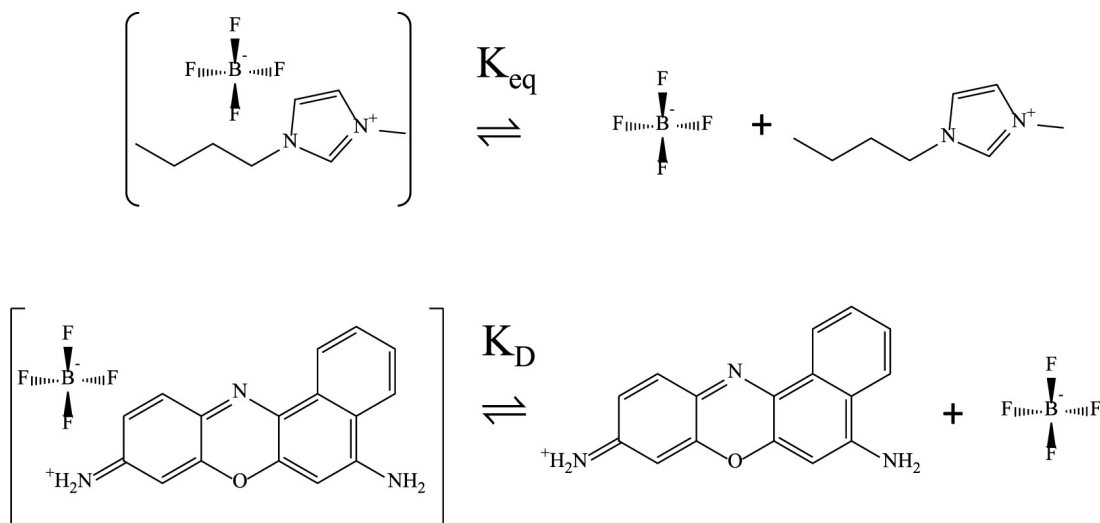
position. Charged chromophores exhibit depth-dependent rotational diffusion dynamics in RTILs in contact with a charged support.²⁸ The chromophore we use in the work reported here is cresyl violet. It is a cationic phenoxazine dye with an absorption maximum at *ca.* 600 nm and an emission maximum at *ca.* 630 nm. The quantity we measure is the induced orientational anisotropy decay, $R(t)$, of an ensemble of chromophores. $R(t)$ (Eq. 1. 1) is the normalized difference between polarized time-resolved emission intensity decays acquired using time-correlated single photon counting (TCSPC) instrumentation.

$$R(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} = R(0) \exp(-t/\tau_{OR}) \quad [1. 1]$$

$$\tau_{OR} = (6D_{ROT})^{-1} = \frac{\eta Vf}{k_B TS} \quad [1. 2]$$

The information content of $R(t)$ has been established.⁴⁸⁻⁵⁴ The modified Debye-Stokes-Einstein model (Eq. 1. 2) relates τ_{OR} , the orientational relaxation time constant extracted from $R(t)$, to the rotational diffusion constant, D_{ROT} , rotor shape, S ,⁵⁵⁻⁵⁶ RTIL viscosity, η , the volume of the rotating species, V ,⁵⁰ and the frictional boundary condition term f .^{49, 52-53}

The identities of the RTIL cation and anion influence ρ_f by virtue of RTIL dissociation (K_{eq} , Scheme 1. 1). Characterizing the spatial extent of ρ_f by rotational diffusion measurements relies on the equilibrium described by the dissociation constant K_D for the chromophore-RTIL counter-ion pair (Scheme 1. 1). Structure-dependent changes in RTIL K_{eq} affect the free ion concentrations. Mobility (as gauged by η , Eq. 1. 2) is also influenced by RTIL structure. The quantity in Eq. 1. 2 responsible for the observed charge- and depth-dependent behavior in RTILs is V , the hydrodynamic volume of the rotating entity.⁵⁰ The gradient in V is due to the charged chromophore forming a complex with the oppositely charged dissociated RTIL constituent.



Scheme 1. 1 Schematic of dissociation equilibria of BMIM⁺BF₄⁻(top) and CV⁺BF₄⁻ (bottom).

The trace chromophore (*ca.* 10⁻⁵ M) forms a complex (Scheme 1. 1), with the amount of free and complexed species determined according to Le Chatelier's principle by [BF₄⁻]. The (negatively charged) silica surface induces an excess of dissociated BMIM⁺ near the surface, resulting in a gradient in the amount of free and complexed chromophore, which is manifested as a gradient in τ_{OR} . $\nabla \cdot \tau_{OR}$ (Eq. 1. 4) is a consequence of $\nabla \cdot V$ (Eq. 1. 3).

$$\nabla \cdot V = V_{free} \nabla \cdot X_{free} + V_{complex} \nabla \cdot X_{complex} \quad [1. 3]$$

$$\nabla \cdot \tau_{OR} = \frac{\eta f}{k_B T S} \nabla \cdot V \quad [1. 4]$$

where the quantities X are mole fractions ($X_{free} + X_{complex} = 1$). V_{free} and $V_{complex}$ are calculated using the method of van der Waals increments.^{28, 50} The relationship between the measured reorientation time gradient, $\nabla \cdot \tau_{OR}$, and the free charge density gradient, ρ_f , is shown as Eq. 1. 5.

$$\nabla \cdot \tau_{OR} = \frac{\eta f}{k_B T S} \nabla \cdot V = k' \nabla \cdot \mathcal{D} = k' \varepsilon \nabla \cdot E = -k' \varepsilon \nabla^2 \phi = k' \rho_f \quad [1. 5]$$

The gradient $\nabla \cdot X_{free}$ (Eq. 1. 3) is the (normalized) free charge gradient, $\nabla \cdot \mathcal{D}$ (Eq. 1. 5), where k' is a collection of constants. In the RTIL, $\nabla \cdot \mathcal{D}$ is related to the surface potential of the silica support

through Poisson's equation (Eq. 1. 5), where ε is the dielectric constant of the RTIL, ϕ is the scalar electric potential field arising from the surface charge (σ_s). Controlling σ_s thus provides control over ρ_f in the RTIL, which is seen through $\nabla \cdot \tau_{OR}$.

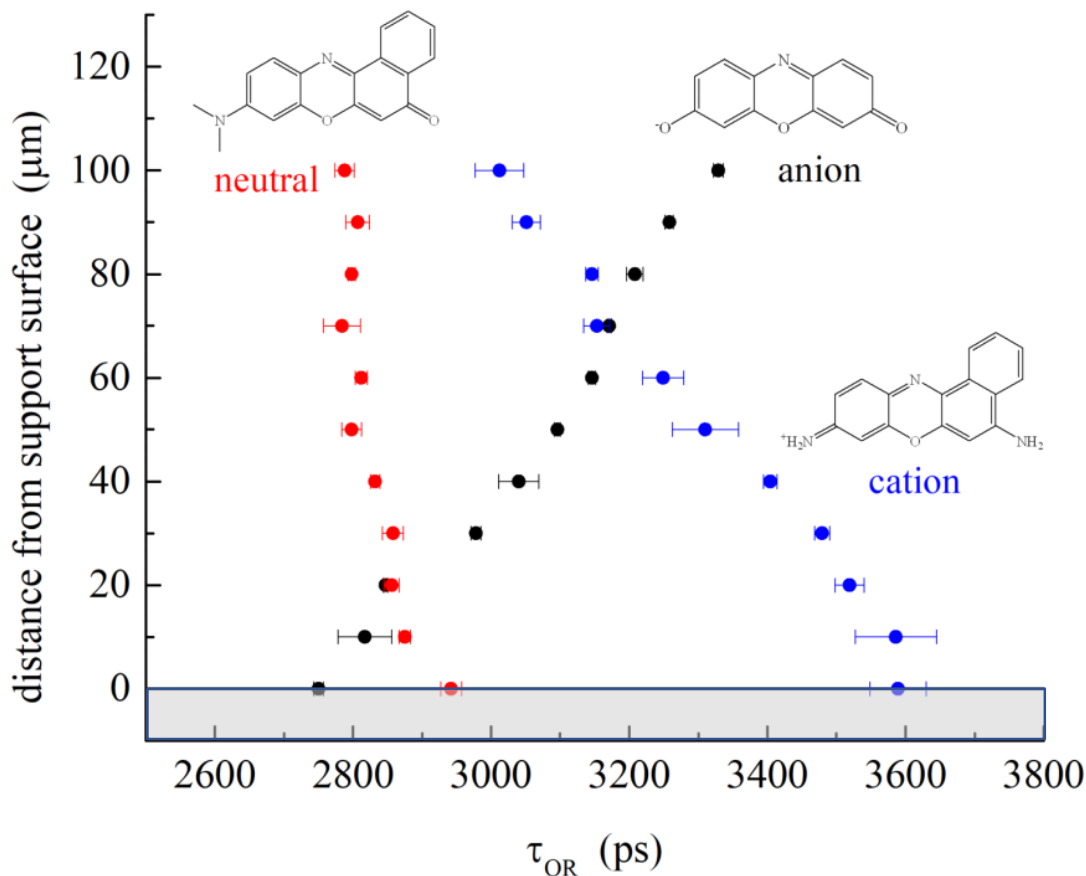


Figure 1. 2 Depth-dependent τ_{OR} in $\text{BMIM}^+\text{BF}_4^-$ supported on a silica surface for anionic (Resorufin), cationic (Cresyl Violet) and neutral (Nile Red) chromophores.

Given the existence of induced structural organization in RTILs, it is tempting to relate such order to the ρ_f we observe. There are several factors that serve to differentiate the ρ_f we report from induced structural order. The first is that the slope of the gradient depends on the charge of the chromophore and the surface charge density of the support (Figure 1. 2). The rotational diffusion dynamics of a neutral chromophore (nile red) demonstrate no depth-dependence in the same RTILs that exhibit depth-dependent reorientation for charged chromophores. The ρ_f data we

report can thus not be explained in the context of a depth-dependent effective viscosity of the RTIL, a quantity that will depend sensitively on structural organization. We note that the change in relaxation dynamics seen by the Fayer group^{24-26, 42-44} must have some effect on the rotational diffusion dynamics of larger chromophores, such as the ones we use, but the spatial extent of the slowed dynamics they report is less than the depth of focus of the optics we use for the rotational diffusion measurements and we would not expect to be sensitive to the effect they report.

1. 3. 2 Gauging the Magnitude of the Charge Density Gradient

We consider next the magnitude of ρ_f , how it depends on the chemical identity of the RTIL constituents and the sign and magnitude of the surface charge density (σ_s). Several points are relevant to this matter. First, the RTIL will maintain macroscopic neutrality because no charges are injected into or withdrawn from the system. Second, the perturbation to the RTIL that produces the observed ρ_f is determined by σ_s on the RTIL support. It is not a simple matter to quantitate σ_s for structurally complex surfaces such as silica or ITO, but we can estimate it. We use a surface silanol group density of 5 $\mu\text{mol}/\text{m}^2$ (3×10^{14} O⁻/cm²).⁵⁷ The silica surface has been studied extensively and the silanol groups are characterized by two distinct populations, with $\text{p}K_a$ values of *ca.* 4.5 (20%) and *ca.* 8.5 (80%). For the silica surface in contact with an RTIL, it is not feasible to estimate the surface pH, but assuming the silanol groups characterized by a $\text{p}K_a$ of 4.5 are deprotonated while those with a $\text{p}K_a$ of 8.5 are fully protonated, the silica surface charge density is 6×10^{13} O⁻/cm².

Evaluating the magnitude of ρ_f requires multiple assumptions. Among them are estimates of the equilibrium constants for RTIL dissociation (K_{eq} in Scheme 1. 1) and for the chromophore-RTIL counter-ion complex (K_D in Scheme 1. 1). It is also important to present the reorientation time gradients for different RTIL systems in a manner that allows for comparison. We use the

normalized change in reorientation time, $\Delta\tau_{OR}/\tau_{OR}$, where the denominator term is the value of τ_{OR} well into the bulk RTIL, where it becomes invariant with depth. Because ρ_f exists only normal to the support surface, the gradient in τ_{OR} can be expressed as a one-dimensional change, $\Delta\tau_{OR}$. From Eq. 1. 5, the term of interest is $\nabla \cdot V$ and thus the gradient in the relative concentration of the RTIL counter ion, $\nabla \cdot X_{free}$. Casting this discussion in terms of a cationic chromophore, we have defined a term, ξ (Eq. 1. 6), to relate the concentrations of the free and complexed RTIL counterion (A^-) as a function of distance from the charged support.³⁰

$$\xi = \left| K_{eq}^{-1} \left([A^-]_{surface} - [A^-]_{bulk} \right) \right| = \left| \frac{1 - X_{free}^{surface}}{X_{free}^{surface}} - \frac{1 - X_{free}^{bulk}}{X_{free}^{bulk}} \right| = \left| \frac{X_{free}^{bulk} - X_{free}^{surface}}{X_{free}^{surface} \cdot X_{free}^{bulk}} \right| \quad [1. 6]$$

Under conditions of no gradient, $\xi = 0$, and for a large gradient, where the relative amounts of X_{free} at the surface and bulk can be different by as much as a factor of ~ 10 , ξ would take on an effective maximum value of ~ 10 . Values of ξ larger than this would not be either chemically or physically realistic. For the value of τ_{OR} in the bulk, we use the value at which there is no longer a depth-dependence. Among the issues that require consideration for evaluating the observed gradient, we need to account for the difference in volume of the free and complexed chromophore. We calculate the volumes of these species by the method of van der Waals increments to determine the hydrodynamic volume for the chromophore (CV^+) and for the RTIL counter-ions we have used, BF_4^- and $TFSI^-$.⁵⁰ Using these quantities ($V(CV^+) = 217 \text{ \AA}^3$, $V(BF_4^-) = 50 \text{ \AA}^3$, $V(TFSI^-) = 169 \text{ \AA}^3$) and the concentrations of the RTILs, which will vary according to their molecular weights and densities, $\Delta\tau_{OR}/\tau_{OR}$ will be related to ξ and the specific RTIL system under examination. As the value of ξ ranges from 10 to 0, the corresponding values of X_{free} will be between 0.91 to 0.09. The normalized change in rotor hydrodynamic volume, $\Delta V/V$, is proportional to ξ according to Eq. 1.7,

$$\frac{\Delta\tau_{OR}}{\tau_{OR}} = \frac{\Delta V}{V} = \xi \left(\frac{X_{free}^{surface} \cdot X_{free}^{bulk} \cdot V_{A^-}}{V_{complex} - X_{free}^{bulk} \cdot V_{A^-}} \right) \quad [1. 7]$$

V_{A^-} is the hydrodynamic volume of the RTIL counter-ion that complexes with the chromophore. The experimentally-measured τ_{OR} gradient is thus related to the RTIL counterion concentration gradient in a manner that accounts for the molecular structure of the RTIL counterion. For the imidazolium RTILs, ρ_f ranges from *ca.* 15 ($\mu\text{C}/\text{cm}^3$)/ μm for BF_4^- anions to values up to *ca.* 110 ($\mu\text{C}/\text{cm}^3$)/ μm for TFSI^- and HMIM^+ .³⁰ To provide some perspective on this magnitude, a charge density gradient of 110 ($\mu\text{C}/\text{cm}^3$)/ μm corresponds to a concentration gradient of *ca.* 0.5 ppm/ μm . To put this gradient in perspective, the K^+ gradient across a plasma membrane is on the order of 3.5×10^5 ppm/ μm , based on $[\text{K}^+] = 10$ mM outside the cell, 100 mM inside the cell, and a plasma membrane thickness of 10 nm.

1. 3. 3 Controlling the Charge Density Gradient

The induced ρ_f can be controlled by the surface charge σ_s on the support (Figure 1. 3). As noted above, σ_s for silica is on the order of $6 \times 10^{13}/\text{cm}^2$. We have reported on the ability to control the sign and magnitude of ρ_f in RTILs.²⁹ In that work, we found that the configuration of the RTIL sample mounts between two ITO-coated or FTO-coated plates with a spacing between plates (sample thickness) of *ca.* 1 mm could be made to achieve control over the sign and magnitude of ρ_f . The ITO surface carries a net positive charge below pH 6.⁵⁸ When configured as a capacitor, the capacitance of the sample holder with a spacing between plates of 1 mm was not capable of modulating the σ_s beyond a few ppm of the ambient surface charge density, insufficient to change ρ_f measurably. Rather than configuring the sample holder as a capacitor, using one of the support surfaces as a resistor allowed for the modulation of σ_s in a charge carrier density range

commensurate with the ambient surface charge density of the ITO-coated support.³⁰ This achievement is feasible due to the small drift velocity of the carriers in the (microcrystalline) thin film conductor.

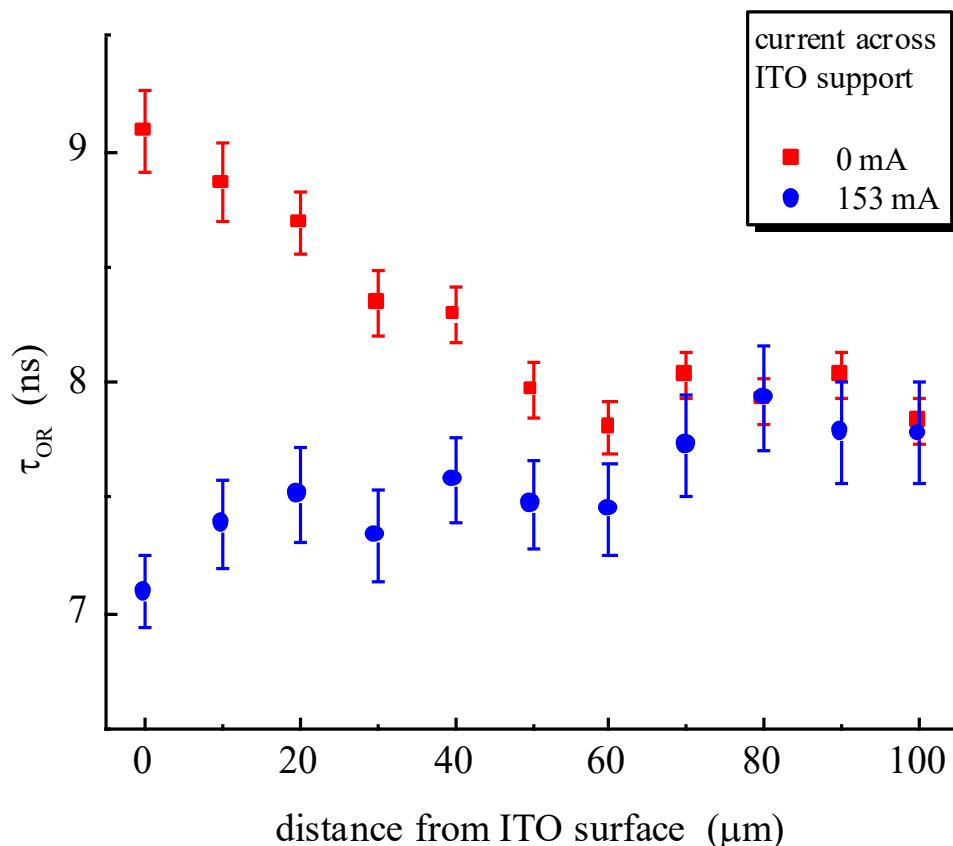


Figure 1.3 Current-dependence of ρ_f measured using CV^+ .

Using the surface thin film of the sample holder as a resistor produces Joule heating of the RTIL, and this effect must be taken into account. The rotational diffusion of the chromophore used to detect ρ_f is sensitive to the viscosity and temperature of the medium in which it is immersed (Eq. 1. 2). We characterized Joule heating by replacing the RTIL with ethylene glycol in the sample holder and measuring the rotational diffusion time constant of CV^+ in that medium as a function of current passed across the ITO support surface.⁵⁹⁻⁶⁰ The dependence of ethylene glycol viscosity on temperature has been reported before and serves as a temperature calibration.⁶¹ The anisotropy decay time constant for CV^+ changes with current applied and, importantly, no depth-

dependence is seen, ruling out a temperature gradient within the sample cell. The current required to change the sign of ρ_f produces $\Delta T \sim 6^\circ \text{C}$ in the sample. This means of modulating σ_s results in thermal and free charge density contributions that are readily separable.

1. 4 Induced birefringence

Most attempts to understand the range and nature of organization and screening in RTILs start from the assumption that this family of materials can be treated as fluid dielectric media. Such a starting point cannot be rigorously correct because of the dissociated ions that function as carriers. The extent to which ionic liquids exist as ion-paired dipolar species, (Bjerrum pairs)⁶²⁻⁶³ and as dissociated ions, is not clearly established because of the characteristically high viscosity of RTILs, and vastly different estimates of the extent of dissociation have been reported.¹⁷⁻¹⁸ Because dissociation is not complete, RTILs cannot be treated as typical conductors either. The essential questions of free ion density, the effective dielectric response of the Bjerrum pairs, and the consequent screening effect(s) in RTIL media, remain to be understood fully.⁶⁴⁻⁶⁵ For these reasons, the relationship between ρ_f and the refractive index, n , is not clear.

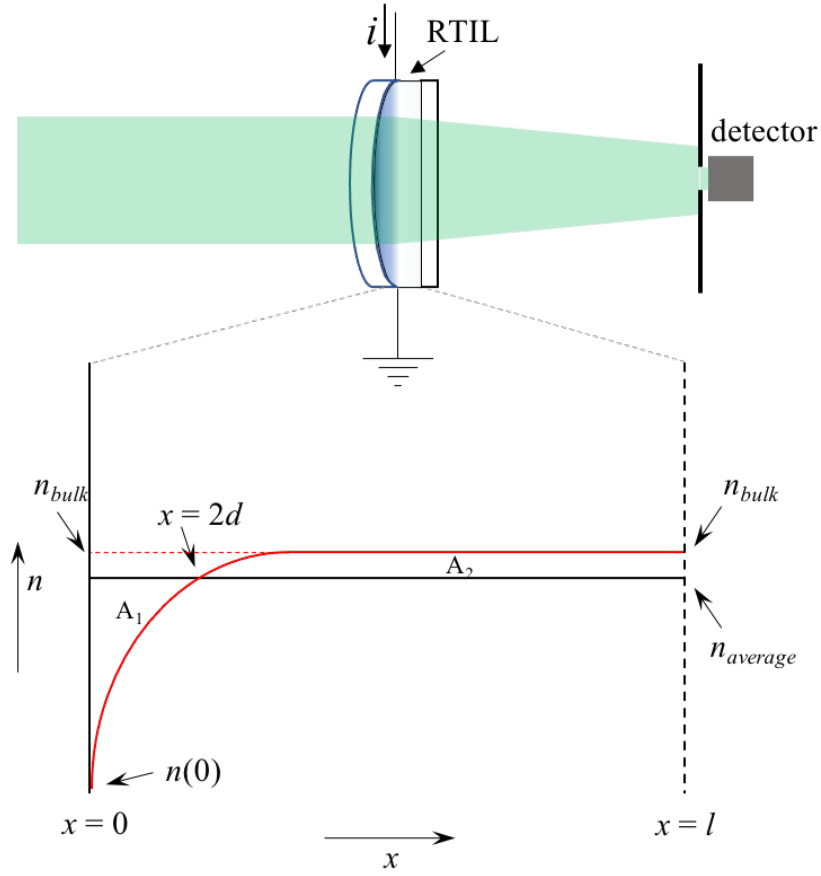
The free charge density gradient, ρ_f , is related to the charge displacement, $\mathbf{D}$, and thus the electric field imposed by the presence of a charged support, E ,

$$\begin{aligned} \mathbf{D} &= \epsilon E \\ \nabla \cdot \mathbf{D} &= \nabla \cdot (\epsilon E) = \rho_f \end{aligned} \quad [1. 8]$$

The quantity in Eq. 1. 8 related to the molecular properties of the RTIL is the dielectric response, ϵ . The dielectric response is frequency-dependent, organization-dependent, and related to the molecular polarizability through the Clausius-Mossotti relation.⁶⁶ Polarizability depends on the structure and orientation of a molecule (the Bjerrum pair for RTILs), and when considered as a bulk property, the optical susceptibility is known to depend on organization within the material.

The gradient ρ_f should thus be measurable as a refractive index gradient because $\varepsilon = \mathbf{n}^2 = (n + ik)^2$.

Measurement of the dielectric response of a material can be challenging, especially when it varies over micrometer length scales. For non-absorbing materials ($k=0$), we can evaluate n , the refractive index, in a straightforward manner. The central question is whether n varies measurably in RTILs as a function of ρ_f , which is controlled by the surface charge density, σ_s , on the solid support (Scheme 1. 2). The RTIL sample holder has the shape of a lens. The inner surface of the lens, in contact with the RTIL, is ITO and the current passed through the ITO film controls σ_s , thereby controlling ρ_f .²⁹ As ρ_f is changed, the refractive index of the RTIL is expected to change (Eq. 1. 8), and thus the focal length of the lens changes. The intensity of light at the detector aperture will change with the focal length of the lens, providing a means of measuring the dependence of n on ρ_f (Scheme 1. 2). The dependence of detector signal on n can be determined using several different liquids in the same sample cell. Thermal effects need to be accounted for because we use current to control σ_s on the lens surface, and the temperature-dependence of the refractive index of imidazolium RTILs has been reported.⁶⁷ The thermal contribution to the experimental signal (Figure 1. 4) is small and accounted for in the data. The dependence of n on ρ_f for RTILs is measurably large.⁶⁸



Scheme 1. 2 Schematic of the refractive index gradient measurement (top) and the functional form of the gradient (bottom).

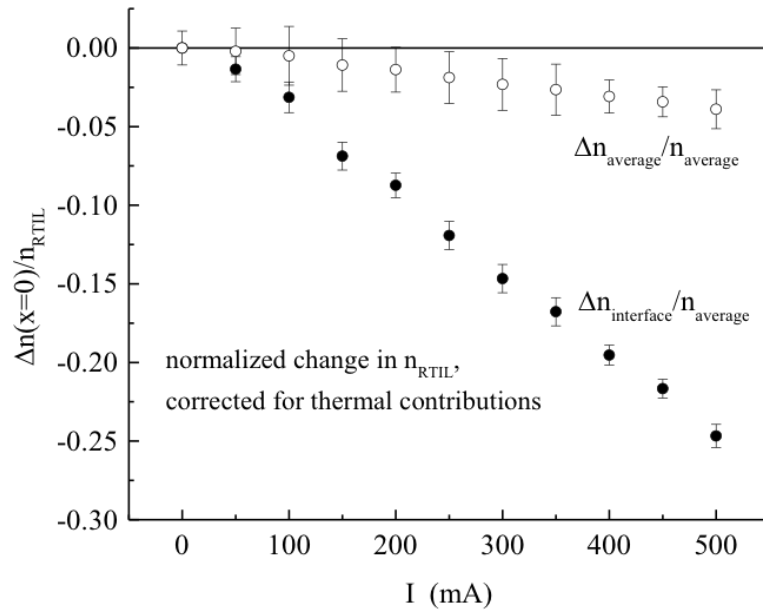


Figure 1. 4 Normalized change in $n_{average}$ and $n_{interface}$ as a function of the current applied.

The imposition of ρ_f produces a gradient in the refractive index only along the optical axis. The characteristic decay length (e^{-1}) of ρ_f in OMIM⁺TFSI⁻ is *ca.* 50 μm and the total cell thickness is 500 μm . Based on these dimensions, we can determine the change in n at the ITO support as a function of current passed through the ITO film (Scheme 1. 2). At the ITO surface, the change in n is very large, on the order of 20%. The dependence of n on ρ_f occurs along the beam axis, perpendicular to the support surface. Because there is no corresponding charge density gradient parallel to the support surface, the change in n along the beam axis we report in Figure 1. 4 must necessarily represent an induced birefringence in RTILs. This is an important point because induced birefringence (Pockels effect) is related to materials properties that depend on molecular-scale organization.

1. 5 Summary

Room temperature ionic liquids have found wide application, in large part because of properties that are anomalous when compared to “normal” solvents. Understanding the molecular-scale dynamics and interactions that are responsible for these properties is central to utilizing this family of materials to their fullest extent. Among the manifestations of the unusual effects is the existence of organization in RTILs on length scales ranging from nm to μm . To date, both structural organization and induced charge density gradients have been reported in RTILs, with the characteristic length scale of each effect depending significantly on the design of the experiment and the means by which the effect was measured. Our focus has been on understanding free charge density gradients and we continue to work to identify commonality and connection between these various long-range phenomena seen in RTILs. Making such connections will lead to novel applications for these materials.

REFERENCES

REFERENCES

1. Arbizzani, C.; Biso, M.; Cericola, D.; Lazzari, M.; Soavi, F.; Mastragostino, M. Safe, High-Energy Supercapacitors Based on Solvent-Free Ionic Liquid Electrolytes. *J. Pwr. Sources* **2008**, *185*, 1575 - 1579.
2. Newell, R.; Faure-Vincent, J.; Iliev, B.; Schubert, T.; Aradilla, D. A New High Performance Ionic Liquid Mixture Electrolyte for Large Temperature Range Supercapacitor Applications (–70° C to 80° C) Operating at 3.5 V Cell Voltage. *Electrochim. Acta*. **2018**, *267*, 15 - 19.
3. Van Aken, K. L.; Beidaghi, M.; Gogotsi, Y. Formulation of Ionic Liquid Electrolyte to Expand the Voltage Window of Supercapacitors. *Angew. Chem.* **2015**, *127*, 4888 - 4891.
4. MacFarlane, D. R.; Tachikawa, N.; Forsyth, M.; Pringle, J. M.; Howlett, P. C.; Elliott, G. D.; Davis, J. H.; Watanabe, M.; Simon, P.; Angell, C. A. Energy Applications of Ionic Liquids. *Energ. Env. Sci.* **2014**, *7*, 232 - 250.
5. Sakaebe, H.; Matsumoto, H. N-Methyl-N-Propylpiperidinium Bis(Trifluoromethane Sulfonyl)Imide (Pp13–Tfsi)–Novel Electrolyte Base for Li Battery. *Electrochem. Commun.* **2003**, *5*, 594 - 598.
6. Nabity, J. A.; Daily, J. W. Effect of Ionic Liquid Composition on Colloid Thruster Emission and Thrust Performance. *Journal of Propulsion and Power* **2017**, *34* (1), 260-266.
7. Prince, B. D.; Fritz, B. A.; Chiu, Y.-H., Ionic Liquids in Electrospray Propulsion Systems. In *Ionic Liquids: Science and Applications*, American Chemical Society: 2012; Vol. 1117, pp 27-49.
8. Rizzo, S.; Arnaboldi, S.; Cirilli, R.; Gennaro, A.; Isse, A. A.; Sannicolò, F.; Mussini, P. R. An “Inherently Chiral” 1,1'-Bibenzimidazolium Additive for Enantioselective Voltammetry in Ionic Liquid Media. *Electrochemistry Communications* **2018**, *89*, 57-61.
9. Rizzo, S.; Arnaboldi, S.; Mihali, V.; Cirilli, R.; Forni, A.; Gennaro, A.; Isse, A. A.; Pierini, M.; Mussini, P. R.; Sannicolò, F. “Inherently Chiral” Ionic-Liquid Media: Effective Chiral Electroanalysis on Achiral Electrodes. *Angewandte Chemie International Edition* **2017**, *56* (8), 2079-2082.
10. Zhao, H.; Afriyie, L. O.; Larm, N. E.; Baker, G. A. Glycol-Functionalized Ionic Liquids for High-Temperature Enzymatic Ring-Opening Polymerization. *RSC Adv.* **2018**, *8*, 36025 - 36033.
11. Trivedi, S.; Ravula, S.; Baker, G. A.; Pandey, S.; Bright, F. V. Controlling Microarray Feature Spreading and Response Stability on Porous Silicon Platforms by Using Alkene-Terminal Ionic Liquids and Uv Hydrosilylation. *Langmuir* **2020**, *36* (19), 5474-5482.
12. Ravula, S.; Larm, N. E.; Liu, Y.; Atwood, J. L.; Baker, S. N.; Baker, G. A. Ionothermal Synthesis of Magnetically-Retrieveable Mesoporous Carbons from Alkyne-Appended Ionic

Liquids and Demonstration of Their Use in Selective Dye Removal. *New Journal of Chemistry* **2018**, 42 (3), 1979-1986.

13. Tang, S.; Baker, G. A.; Zhao, H. Ether- and Alcohol-Functionalized Task-Specific Ionic Liquids: Attractive Properties and Applications. *Chemical Society Reviews* **2012**, 41 (10), 4030-4066.
14. Clark, R.; Nawawi, M. A.; Dobre, A.; Pugh, D.; Liu, Q.; Ivanov, A. P.; White, A. J. P.; Edel, J. B.; Kuimova, M. K.; McIntosh, A. J. S.; Welton, T. The Effect of Structural Heterogeneity Upon the Microviscosity of Ionic Liquids. *Chem. Sci.* **2020**, 11, 6121-6133.
15. Russina, O.; Triolo, A.; Gontrani, L.; Caminiti, R. Mesoscopic Structural Heterogeneities in Room Temperature Ionic Liquids. *J. Phys. Chem. Lett.* **2012**, 3, 27-33.
16. Gebbie, M. A.; Dobbs, H. A.; Valtiner, M.; Israelachvili, J. N. Long-Range Electrostatic Screening in Ionic Liquids. *Proc. Nat. Acad. Sci. USA* **2015**, 112 (24), 7432-7437.
17. Gebbie, M. A.; Valtiner, M.; Banquy, X.; Fox, E. T.; Henderson, W. A.; Israelachvili, J. N. Ionic Liquids Behave as Dilute Electrolyte Solutions. *Proc. Nat. Acad. Sci. USA* **2013**, 110 (24), 9674-9679.
18. MacFarlane, D. R.; Forsyth, M.; Izgorodina, E. I.; Abbott, A. P.; Annat, G.; Fraser, K. On the Concept of Ionicity in Ionic Liquids. *Phys. Chem. Chem. Phys.* **2009**, 11, 4962-4967.
19. Nelyubina, Y. V.; Shaplov, A. S.; Lozinskaya, E. I.; Buzin, M. I.; Vygodskii, Y. S. A Volume-Based Approach for Predicting Thermophysical Behavior of Ionic Liquids and Ionic Liquid Crystals. *J. Am. Chem. Soc.* **2016**, 138, 10076-10079.
20. Binnemans, K. Ionic Liquid Crystals. *Chem. Rev.* **2005**, 105, 4148-4204.
21. Anareddy, R. S.; Shaw, S. K. Long-Range Ordering of Ionic Liquid Fluid Films. *Langmuir* **2016**, 32, 5147-5154.
22. Anareddy, R. S.; Shaw, S. K. Developing Distinct Chemical Environments in Ionic Liquid Films. *J. Phys. Chem. C* **2018**, 122, 19731-19737.
23. Anareddy, R. S.; Shaw, S. K. Directing Long-Range Molecular Ordering in Ionic Liquid Films: A Tale of Two Interfaces. *J. Phys. Chem. C* **2019**, 123, 8975-8982.
24. Nishida, J.; Breen, J. P.; Wu, B.; Fayer, M. D. Extraordinary Slowing of Structural Dynamics in Thin Films of a Room Temperature Ionic Liquid. *ACS Cent. Sci.* **2018**, 4, 1065-1073.
25. Shin, J. Y.; Yamada, S. A.; Fayer, M. D. Dynamics of a Room Temperature Ionic Liquid in Supported Ionic Liquid Membranes Vs the Bulk Liquid: 2d Ir and Polarized Ir Pump-Probe Experiments. *J. Am. Chem. Soc.* **2017**, 139, 311-323.

26. Shin, J. Y.; Yamada, S. A.; Fayer, M. D. Carbon Dioxide in a Supported Ionic Liquid Membrane: Structural and Rotational Dynamics Measured with 2d Ir and Pump-Probe Experiments. *J. Am. Chem. Soc.* **2017**, *139*, 11222-11232.
27. Sieling, T.; Brand, I. In Situ Spectroelectrochemical Investigation of Potential-Dependent Changes in an Amphiphilic Imidazolium-Based Ionic Liquid Film on the Au(111) Electrode Surface. *ChemElectroChem* **2020**, *7*, 3233-3243.
28. Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G. J. Charge-Induced Long-Range Order in a Room-Temperature Ionic Liquid. *Langmuir* **2016**, *32* (37), 9507-9512.
29. Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G. J. Modulation of an Induced Charge Density Gradient in the Room Temperature Ionic Liquid Bmim⁺Bf₄⁻. *J. Phys. Chem. C* **2018**, *122*, 7361-7367.
30. Wang, Y.; Jarosova, R.; Swain, G. M.; Blanchard, G. J. Characterizing the Magnitude and Structure-Dependence of Free Charge Density Gradients in Room-Temperature Ionic Liquids. *Langmuir* **2020**, *36*, 3038-3045.
31. Sloutskin, E.; Ocko, B. M.; Tamam, L.; Kuzmenko, I.; Gog, T.; Deutsch, M. Surface Layering in Ionic Liquids: An X-Ray Reflectivity Study. *J. Am. Chem. Soc.* **2005**, *127*, 7796-7804.
32. Santos, C. S.; Murthy, S.; Baker, G. A.; Castner, E. W. Communication: X-Ray Scattering from Ionic Liquids with Pyrrolidinium Cations. *J. Chem. Phys.* **2011**, *134*, 121101 (1-4).
33. Annapureddy, H. V. R.; Kashyap, H. K.; De Biase, P. M.; Margulis, C. J. What Is the Origin of the Prepeak in the X-Ray Scattering of Imidazolium-Based Room-Temperature Ionic Liquids? *J. Phys. Chem. B* **2010**, *114*, 16838-16846.
34. Imai, Y.; Abe, H.; Yoshimura, Y. X-Ray Diffraction Study of Ionic Liquid Based Mixtures. *J. Phys. Chem. B* **2009**, *113*, 2013-2018.
35. Dupont, J. On the Solid, Liquid and Solution Structural Organization in Imidazolium Ionic Liquids. *J. Braz. Chem. Soc.* **2004**, *3*, 341-350.
36. Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. How Ionic Are Room Temperature Ionic Liquids? An Indicator of the Physicochemical Properties. *J. Phys. Chem. B* **2006**, *110*, 19593-19600.
37. Schreiner, C.; Zugmann, S.; Hartl, R.; Gores, H. J. Fractional Walden Rule for Ionic Liquids: Examples from Recent Measurements and a Critique of the So-Called Ideal Kcl Line for the Walden Plot. *J. Chem. Eng. Data* **2010**, *55*, 1784-1788.
38. Baldelli, S. Interfacial Structure of Room-Temperature Ionic Liquids at the Solid-Liquid Interface as Probed by Sum Frequency Generation Spectroscopy. *J. Phys. Chem. Lett.* **2013**, *4*, 244-252.

39. Bovio, S.; Podesta, A.; Lenardi, C.; Milani, P. Evidence of Extended Solidlike Layering in [Bmim][Ntf2] Ionic Liquid Thin Films at Room Temperature. *J. Phys. Chem. B* **2009**, *113*, 6600-6603.
40. Atkin, R.; Borisenko, N.; Druschler, M.; El Abedin, S. Z.; Endres, F.; Hayes, R.; Huber, B.; Roling, B. An in Situ Stm/Afm and Impedance Spectroscopy Study of the Extremely Pure 1-Butyl-1-Methylpyrrolidinium Tris(Pentafluoroethyl)Trifluorophosphate/Au(111) Interface: Potential Dependent Solvation Layers and the Herringbone Reconstruction. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6849-6857.
41. Han, M.; Kim, H.; Leal, C.; Negrito, M.; Batteas, J. D.; Espinosa-Marzal, R. M. Insight into the Electric Double Layer of Ionic Liquids Revealed through Its Temporal Evolution. *Adv. Mater. Interfaces* **2020**, *7*, 2001313 (1-10).
42. Wu, B.; Breen, J. P.; Fayer, M. D. Structural Dynamics in Ionic Liquid Thin Films: The Effect of Cation Chain Length. *J. Phys. Chem. C* **2020**, *124*, 4179-4189.
43. Wu, B.; Breen, J. P.; Xing, X.; Fayer, M. D. Controlling the Dynamics of Ionic Liquid Thin Films Via Multilayer Surface Functionalization. *J. Am. Chem. Soc.* **2020**, *142*, 9482-9492.
44. Thomaz, J. E.; Bailey, H. E.; Fayer, M. D. The Influence of Mesoscopic Confinement on the Dynamics of Imidazolium-Based Room Temperature Ionic Liquids in Polyether Sulfone Membranes. *J. Chem. Phys.* **2017**, *147*, 194502 1-11.
45. Triolo, A.; Russina, O.; Bleif, H.-J.; DiCola, E. Nanoscale Segregation in Room Temperature Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 4641-4644.
46. Wu, F.; Karunaratne, W. V.; Margulis, C. J. Ionic Liquid Mixture at the Vacuum Interface and the Peaks and Antipeaks Analysis of X-Ray Reflectivity. *J. Phys. Chem. C* **2019**, *1233*, 4914-4925.
47. Hay, C. E.; Marken, F.; Blanchard, G. J. Detection and Characterization of Liquid|Solid and Liquid|Liquid|Solid Interfacial Gradients of Water Nano-Droplets in Wet N-Octyl-2-Pyrrolidone. *Langmuir* **2014**, *30*, 9951-9961.
48. Chuang, T. J.; Eisinger, K. B. Theory of Fluorescence Depolarization by Anisotropic Rotational Diffusion. *J. Chem. Phys.* **1972**, *57* (12), 5094-5097.
49. Debye, P., *Polar Molecules* Chemical Catalog Co.: New York 1929; p 84.
50. Edward, J. T. Molecular Volumes and the Stokes-Einstein Equation. *J. Chem. Ed.* **1970**, *47* (4), 261-270.
51. Favro, D. L. Theory of the Rotational Brownian Motion of a Free Rigid Body. *Phys. Rev.* **1960**, *119* (1), 53-62.
52. Hu, C.-M.; Zwanzig, R. Rotational Friction Coefficients for Spheroids with the Slipping Boundary Condition. *J. Chem. Phys.* **1974**, *60* (11), 4354-4357.

53. Perrin, F. Mouvement Brownien D'un Ellipsoïde - I. Dispersion Diélectrique Pour Des Molécules Ellipsoïdales. *J. Phys. Radium* **1934**, *5*, 497.
54. Tao, T. Time-Dependent Fluorescence Depolarization and Brownian Rotational Diffusion Coefficients of Macromolecules. *Biopol.* **1969**, *8*, 609-632.
55. Blanchard, G. J. Picosecond Spectroscopic Measurement of a Solvent Dependent Change of Rotational Diffusion Rotor Shape. *J. Chem. Phys.* **1987**, *87* (12), 6802-6808.
56. Blanchard, G. J.; Cihai, C. A. Orientational Relaxation Dynamics of Oxazine 118 and Resorufin in the Butanols - Valence-Dependent and State-Dependent Solvation Effects *J. Phys. Chem.* **1988**, *92* (21), 5950-5954.
57. Mueller, R.; Kammler, H. K.; Wegner, K.; Pratsinis, S. E. Oh Surface Density of SiO₂ and TiO₂ by Thermogravimetric Analysis. *Langmuir* **2003**, *19*, 160-165.
58. Peiris, T. A. N.; Senthilarasu, S.; Wijayantha, K. G. U. Enhanced Performance of Flexible-Dye-Sensitized Solar Cells: Electrodeposition of Mg(OH)₂ in a Nanocrystalline TiO₂ Electrode. *J. Phys. Chem. C* **2011**, *116*, 1211-1218.
59. Ashida, T.; Miyamura, A.; Oka, N.; Sato, Y.; Yagi, T.; Taketoshi, N.; Baba, T.; Shigesato, Y. Thermal Transport Properties of Polycrystalline Tin-Doped Indium Oxide Films. *J. Appl. Phys.* **2009**, *105*, 073709-1-4.
60. Abb, M.; Albella, P.; Aizpurua, J.; Muskens, O. L. All-Optical Control of a Single Plasmonic Nanoantenna-Ito Hybrid. *Nano Lett.* **2011**, *11* (6), 2457-2463.
61. Bohne, D.; Fischer, S.; Obermeier, E. Thermal Conductivity, Density, Viscosity, and Prandtl-Numbers of Ethylene Glycol-Water Mixtures. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 739-744.
62. Adar, R. M.; Markovich, T.; Andelman, D. Bjerrum Pairs in Ionic Solutions: A Poisson-Boltzmann Approach. *J. Chem. Phys.* **2017**, *146*, 194904 1-8.
63. Stillinger, F. H.; Lovett, R. Ion-Pair Theory of Concentrated Electrolytes. I. Basic Concepts. *J. Chem. Phys.* **1968**, *48* (9), 3858-3868.
64. Gavish, N.; Promislow, K. Dependence of the Dielectric Constant of Electrolyte Solutions on Ionic Concentration: A Microfield Approach. *Phys. Rev. E* **2016**, *94*, 012611 1-7.
65. Zarubin, G.; Bier, M. Static Dielectric Properties of Dense Ionic Fluids. *J. Chem. Phys.* **2015**, *142*, 184502 1-6.
66. Van Rysselberghe, P. Remarks Concerning the Clausius-Mossotti Law. *J. Phys. Chem.* **1932**, *36* (4), 1152-1155.

67. Seki, S.; Tsuzuki, S.; Hayamizu, K.; Umebayashi, Y.; Serizawa, N.; Takei, K.; Miyashiro, H. Comprehensive Refractive Index Property for Room-Temperature Ionic Liquids. *J. Chem. Eng. Data* **2012**, *57*, 2211-2216.
68. Wang, Y.; Swain, G. M.; Blanchard, G. J. Charge-Induced Birefringence in a Room Temperature Ionic Liquid. *J. Phys. Chem. B* **2021**, *125*, 950-955.

CHAPTER 2. Characterizing the Magnitude and Structure-Dependence of Free Charge Density Gradients in Room-Temperature Ionic Liquids

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2. 1 Introduction

Room temperature ionic liquids (RTILs) are, in the simplest sense, salts characterized by a melting point below room temperature. This family of materials typically consists of relatively large organic cations and inorganic anions.¹ The size and shape of the ions and the absence of a dielectric solvent prevents organized ion packing, with both factors contributing to the materials existing in the liquid phase under ambient conditions. There is a substantial body of work extant focusing on the bulk physical properties of RTILs, including efforts aimed at understanding the role of hydrogen bonding in mediating mobility,² characterizing mass and charge transport,³⁻⁵ determining dissociation,⁶⁻⁸ dielectric response⁹⁻¹¹ and issues associated with local and long range electrostatic interactions.¹²⁻¹⁵ RTILs hold promise for a variety of practical applications, including use as solvents for chemical separations¹⁶⁻¹⁷ and syntheses,¹⁸⁻¹⁹ as electrolytes for supercapacitors²⁰⁻²² and fuel cells,²³⁻²⁴ and potentially as novel electro-optic materials.²⁵ Despite the wide range of applications for RTILs, there remain many fundamental issues to be resolved, especially with regard to fluidity and ion dynamics, and with understanding the organization and response of these materials when subjected to external forces.

Our group has reported on the existence of a charge density gradient in RTILs in contact with a charged support.²⁵⁻²⁷ The spatial extent of this gradient is on the order of 100 μm and its sign and magnitude depend on the surface charge resident on the (solid) support. RTILs possess many properties that are not consistent with non-ionic or dilute ionic liquid phase systems. Among the key issues with understanding RTIL properties is the extent of dissociation in these materials. Ionic liquids exist as Bjerrum pairs^{13, 28} and as dissociated ions, but the equilibrium constant for this dissociation is not known, generally, and is difficult to determine because of the characteristically high viscosity of RTILs.²⁹ Israelachvili *et al.* have worked to understand the role

of electrostatic screening in RTILs using surface force measurements³⁰ to infer information on the force applied on a charged surface by a RTIL.^{12, 31} Organization in a RTIL with a spatial extent on the order of *ca.* 10 nm was detected by measuring the force of interactions between a RTIL layer and a charged (mica) plate. This organization was attributed to the dominant form of the RTIL being ion-paired dipolar species with a relatively small fraction of free ions.⁶ Surface organization in a series of RTILs as measured by high resolution X-ray methods has also revealed order on a similar length scale.³² The Shaw group has reported the formation of highly ordered RTIL layers where the order is seen to extend over *ca.* 1 μm .³³⁻³⁵ In that work the ordering of RTIL films as a function of thickness and time was elucidated through the use of infrared reflection absorption spectroscopy (IRRAS) and second-harmonic generation (SHG) measurements. They attributed the μm length-scale organization to dipole-dipole interactions. We note that this finding is in conceptual agreement with the report of Israelachvili *et al.*, where they concluded that the dominant species present in RTILs is (dipolar) contact ion pairs, and not discrete ions.^{6, 33} Nonetheless, the spatial extent of the long-range organization of RTILs was not explored fully by these methods. Our group found that exposing 1-butyl-3-methylimidazolium tetrafluoroborate ($\text{BMIM}^+\text{BF}_4^-$) to a negatively charged planar silica surface induced a free charge density gradient (ρ_f) with a spatial extent of *ca.* 100 μm .²⁶ The presence of any organization in a fluid medium over such a range of length scales is highly unusual and without precedent. Therefore, it is important to have a deeper understanding of this charge-induced long-range organization in RTILs.

To this point, our investigations of the induced charge density gradient have focused on the ionic liquid $\text{BMIM}^+\text{BF}_4^-$. This is a widely-used RTIL, one of a large number of known ionic liquids. Changes in the molecular structure of the anionic and cationic constituents can alter physical properties, such as hygroscopicity or viscosity, for example. Related to these bulk

material variations, we expect that the anion and cation structures of RTILs will play an important role in determining the extent of dissociation and thus the magnitude and spatial extent of ρ_f . We examine the spatially-resolved chromophore rotational diffusion dynamics of low concentration dyes in selected RTILs to characterize the magnitude and spatial extent of ρ_f as a function of RTIL constituent structure. We use five RTILs for this purpose, with three alkyl imidazolium cations and two anions. These are 1-ethyl-3-methylimidazolium tetrafluoroborate ($\text{EMIM}^+\text{BF}_4^-$), 1-butyl-3-methylimidazolium tetrafluoroborate ($\text{BMIM}^+\text{BF}_4^-$), 1-hexyl-3-methylimidazolium tetrafluoroborate ($\text{HMIM}^+\text{BF}_4^-$), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($\text{BMIM}^+\text{TFSI}^-$) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($\text{HMIM}^+\text{TFSI}^-$) (Figure 2. 1). We use cresyl violet (CV^+) as the trace ionic chromophore in these RTILs. We can control ρ_f in these RTILs by changing the current passed across the ITO-coated support surface.²⁷ We also use the neutral chromophore nile red (NR) to characterize variations in the physical properties of these systems (*e.g.* viscosity, temperature) that are not related to ρ_f . In addition to demonstrating the dependence of ρ_f on RTIL structural identity, comparison between data sets for these RTILs allows for evaluation of the magnitude of ρ_f .

2. 2 Experimental Section

2. 2. 1 Materials

1-Ethyl-3-methylimidazolium tetrafluoroborate ($\text{EMIM}^+\text{BF}_4^-$, $\geq 99.0\%$, Sigma-Aldrich), 1-butyl-3-methylimidazolium tetrafluoroborate ($\text{BMIM}^+\text{BF}_4^-$, $\geq 97\%$, Sigma-Aldrich), 1-hexyl-3-methylimidazolium tetrafluoroborate ($\text{HMIM}^+\text{BF}_4^-$, $\geq 97\%$, Sigma-Aldrich), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($\text{BMIM}^+\text{TFSI}^-$, $\geq 98\%$, Sigma-Aldrich), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($\text{HMIM}^+\text{TFSI}^-$, $\geq 98\%$, Sigma-Aldrich) were purified as described below before use. The purified RTILs were stored in a

glovebox (MB 200B, Mbraun) with water level <0.5 ppm. The stock solutions (*ca.* 5×10^{-4} M) of chromophores cresyl violet perchlorate (Eastman) and nile red (Sigma-Aldrich) were prepared by dissolving the dye in ethanol ($\geq 99.5\%$, Sigma-Aldrich). Ethylene glycol (EG, $\geq 99\%$, Fisher Scientific), isopropyl alcohol (99.50%, Macron Fine Chemicals) and activated charcoal (powder, -100 particle size, Sigma-Aldrich) were used as received. Water was purified with a Mili-Q filtration system (Millipore). ITO coated glass slides (Nanocs, 10 Ohm/sq) and silicone rubber sheet (MSC Direct) were cut to size and cleaned as detailed below.

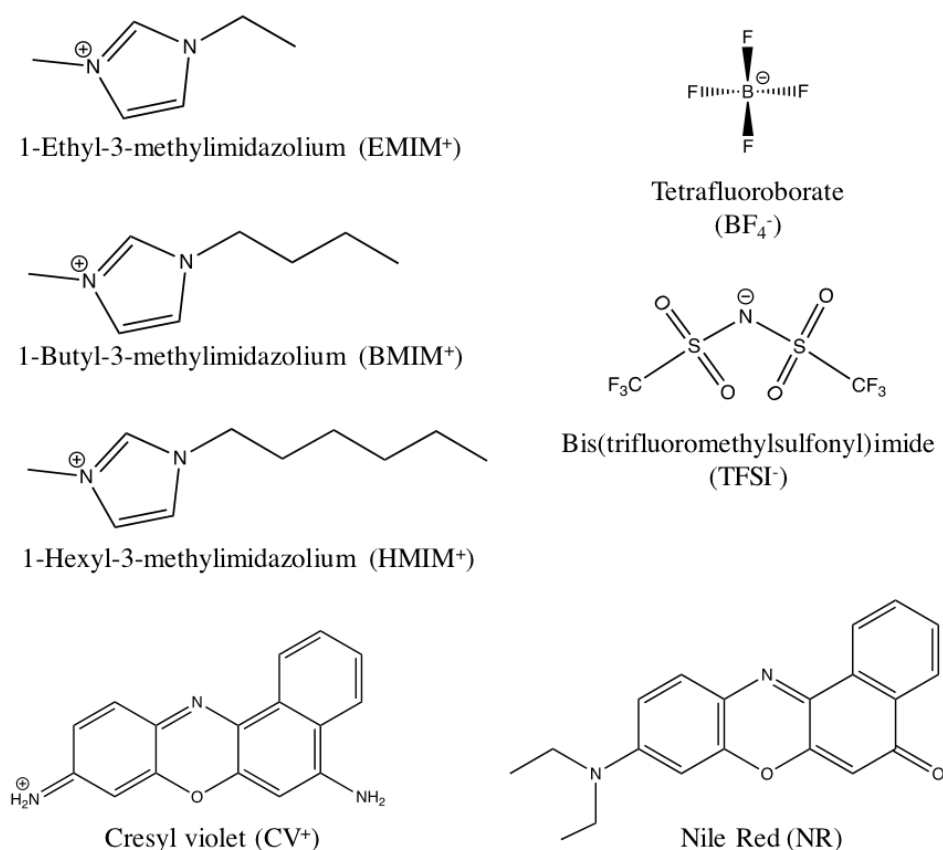


Figure 2. 1 Structures of the RTIL constituents and chromophores used in this work.

2. 2. 2 RTILs Purification and Preparation of Chromophore-RTIL Solutions

The RTIL purification method has been described previously.^{26, 36} Briefly, the RTIL, as received, is stored over activated carbon for three days. The RTIL is then removed by syringe

filter with a Durapore[®] membrane (0.22 μm sterile filtration, Millex). The RTIL is then heated to 90 °C for 3 h while purging with ultrapure Ar (99.9995%, Linde) to remove water in the RTIL. The purified RTILs are stored in an anhydrous glovebox. The chromophore-RTIL solution is prepared by transferring 100 μL of the chromophore stock solution (*ca.* 5×10^{-4} M) into a vial and placing the vial in an oven at 150 °C for 3 h to evaporate the ethanol. Following removal from the oven and cooling in a desiccator. Purified RTIL (1000 μL) is then added into the vial inside the glovebox. The resulting chromophore-RTIL solution (*ca.* 5×10^{-5} M) was stirred for 12 h before use. To minimize water contamination, all glassware was dried at 150 °C for at least 24 h before use.

2. 2. 3 Electrode and Sample Cell Preparation

We construct a closed sample cell that confines the RTIL between two transparent conductive ITO electrodes. The sample cell preparation has been described before.³⁶ ITO coated glass slides are cleaned by sonication in detergent (Sparkleen 1, Fisher) solution, Milli-Q water, then isopropanol for 15 min at each step. The cleaned ITO-coated glass electrodes are removed from isopropanol, rinsed with ethanol (100%), and dried at 200 °C for 30 min. The cooled electrodes are then placed into a UV/ozone cleaner for 20 min. Copper wires are connected to the ITO surface using silver epoxy. The epoxy is cured at 120 °C for 30 min. The cell spacer (O-ring) is cut from a silicone rubber sheet, which is cleaned by sonication in detergent solution and Milli-Q water for 15 min each, then rinsed with ethanol and dried by N_2 flow.

2. 2. 4 Time-resolved Fluorescence Anisotropy Decay Measurements

The fluorescence anisotropy decay of the chromophore in the RTILs is measured as a function of distance from the ITO electrode into the bulk. Depth resolution is achieved with an inverted confocal microscope through mechanical control over the distance between microscope

stage and objective. The time-resolved data are acquired using a time-correlated single photon counting (TCSPC) instrument that has been described in detail elsewhere.^{26,37} The time resolution of the instrument is < 100 ps.³⁷ The light source is a synchronously pumped, cavity dumped dye laser system that produces *ca.* 5 ps pulses at the excitation wavelength of the dyes (575 nm), with inter-pulse spacing of at least 240 ns. This period is more than $5\times$ the fluorescence lifetime of either CV⁺ or NR. The confocal scanning head (Becker & Hickl DCS-120) for the microscope (Nikon Eclipse Ti-U) allows for the acquisition of the anisotropy decay time constant (τ_{OR}) data over a small depth of focus (*ca.* 2 μm for acquisition with a $10\times$ objective). Mechanical resolution and reproducibility of the microscope stage are both under 1 μm .

2.3 Results and Discussion

The central goals of this work are to determine how ρ_f varies with the molecular structure of the RTIL constituents, and to provide a useful estimate of the magnitude of ρ_f . Connecting ρ_f to bulk material and RTIL molecular properties is of fundamental interest and is a prerequisite to controlling ρ_f for a variety of potential applications. We briefly recap the information content of the measurements and how it can be used in the characterization of ρ_f . To characterize this gradient in RTILs, we measure the fluorescence anisotropy decay of selected chromophores in the RTILs as a function of the distance from support (ITO) surface. The study of diffusion, solvation dynamics and energy transfer in RTILs has proven to be an important means of understanding local organization and longer-range diffusional behavior in these systems.³⁸⁻⁴⁹ In our work, the experimental signals acquired are the time-resolved emission transients polarized parallel ($I_{\parallel}(t)$) and perpendicular ($I_{\perp}(t)$) to the incident excitation light pulse. The induced orientational anisotropy decay function, $R(t)$, is the normalized difference between $I_{\parallel}(t)$ and $I_{\perp}(t)$. Example $I_{\parallel}(t)$, $I_{\perp}(t)$ and $R(t)$ data are provided in the appendix (Figures A. 1-A. 10). The chemical information

of interest is contained in the functional form of the decay of $R(t)$, which has been considered in detail previously.^{25-26, 50-56} The modified Debye-Stokes-Einstein (DSE) model (Eq. 2. 1)⁵¹

$$\tau_{OR} = 6D^{-1} = \frac{\eta Vf}{k_B TS} \quad [2. 2]$$

provides a connection between the observed anisotropy decay time constants, the properties of the reorienting chromophore and those of its immediate surroundings. In Eq. 2. 1, f is a frictional boundary condition term ($f = 1$ here), $k_B T$ is the thermal energy and S is the shape factor of the chromophore to account for its (ellipsoidal) shape ($S = 0.75$ for CV^+).⁵⁷⁻⁵⁸ The time constant for chromophore reorientation is also related to the viscosity of the medium (η) and hydrodynamic volume (V)⁵² of the rotating entity. The reorientation time constant gradient ($\nabla \cdot \tau_{OR}$ in Eq. 2. 2) is a consequence of the gradient in the hydrodynamic volume ($\nabla \cdot V$) of the reorienting entity, which is the weighted average of the free and complexed forms of the (charged) chromophore (Eq. 2. 3). The charged chromophores will complex with the dissociated RTIL constituents of opposite charge.²⁵⁻²⁶

$$\nabla \cdot \tau_{OR} = \left(\frac{\eta f}{k_B TS} \right) \nabla \cdot V = k \nabla \cdot V \quad [2. 2]$$

$$\nabla \cdot V = V_{free} \nabla \cdot X_{free} + V_{complex} \nabla \cdot X_{complex} \quad [2. 3]$$

$$\nabla \cdot V = k' \nabla \cdot D = k' \rho_f \quad [2. 4]$$

The terms X in Eq. 2. 3 are the mole fractions of the free and complexed forms of the chromophore, $X_{free} + X_{complex} = 1$. The term D in Eq. 2. 4 is the displaced excess charge and k' is a

proportionality constant. The quantity $\nabla \cdot V$ is directly related to the gradient in RTIL free ion density (X_{free} , Eq. 2. 3) and thus to ρ_f , the free charge density gradient (Eq. 2. 4). In the work reported here, we use the cationic chromophore cresyl violet (CV^+) in the RTILs to probe the concentration gradient of dissociated RTIL anions induced by the surface charge density resident on the ITO support surface. The initial systems were chosen to demonstrate the dependence of ρ_f on the aliphatic chain length of the RTIL imidazolium cation ($EMIM^+BF_4^-$, $BMIM^+BF_4^-$, and $HMIM^+BF_4^-$). The identity of the RTIL cation can influence the magnitude of ρ_f in a number of ways, including the extent to which the RTIL ion pair dissociates and the viscosity of the RTIL. For the series of RTILs with a common anion, the chromophore complexation process should be the same in all RTILs because the same chromophore-anion complex is being formed. These data are shown in Figure 2. 2a. It is clear from these data that ρ_f is seen in all RTILs studied and that the magnitude of the observed effect does indeed vary with imidazolium aliphatic chain length. This finding is reinforced by data showing ρ_f in $BMIM^+TFSI^-$ and $HMIM^+TFSI^-$ (Figure 2. 2b).

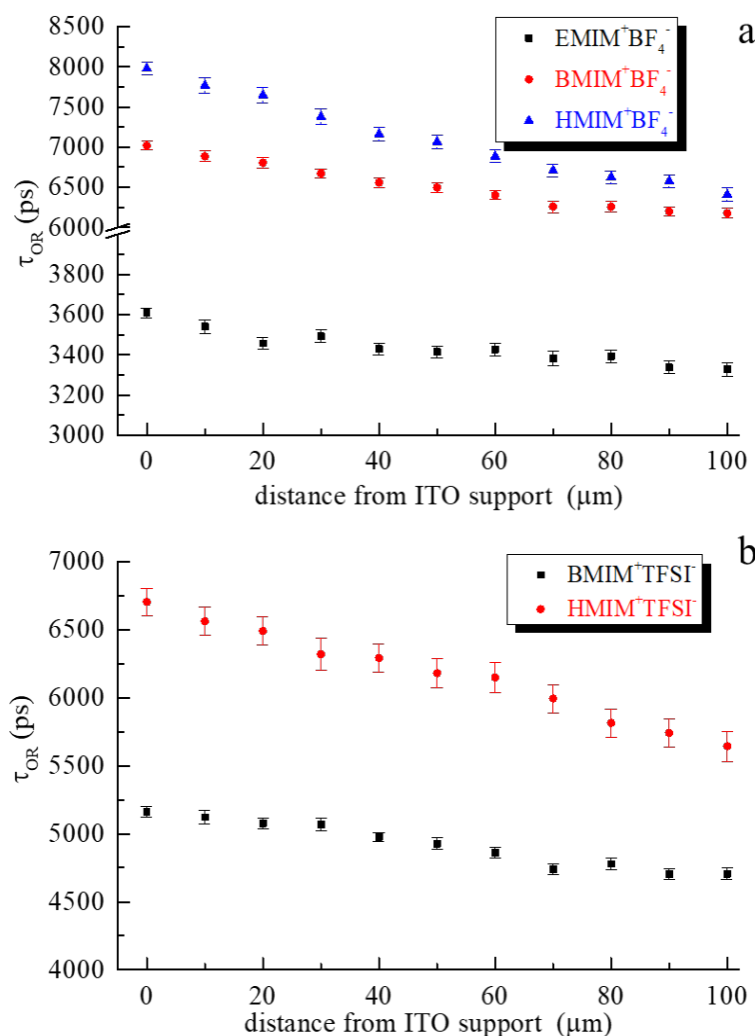


Figure 2. 2 Cresyl violet anisotropy decay time constants as a function of the RTIL cation aliphatic chain length, with same anion. (a) Blue triangles are HMIM $^+\text{BF}_4^-$, red circles are BMIM $^+\text{BF}_4^-$, and black squares are EMIM $^+\text{BF}_4^-$. (b) Blue triangles are HMIM $^+\text{TFSI}^-$ and red circles are BMIM $^+\text{TFSI}^-$. For all data points, the error bars represent $\pm 1\sigma$ for three individual measurements.

For the cationic chromophore CV^+ , there is an equilibrium between free ionic species and the CV-BF_4 complex for the BF_4^- RTILs.²⁶ The presence of the (positive) ambient surface charge on ITO induces a gradient in dissociated RTIL constituents, which is sensed by complexation with CV^+ . For the positively charged ITO surface, excess BF_4^- near the surface yields a higher concentration of complexed chromophore, X_{complex} , and longer τ_{OR} . As X_{complex} decreases and X_{free} increases with increasing distance from the surface, τ_{OR} becomes shorter. The sign of the gradient

is reversed when a negatively-charged support (SiO_x) is used.²⁶ The extent of RTIL dissociation varies with imidazolium aliphatic chain length, as does the RTIL viscosity. Consequently, both the magnitude and spatial extent of ρ_f depends on RTIL constituent structure. Before considering this matter in detail, we report on the variation of ρ_f with RTIL anion identity (Figure 2. 3). These data are shown for the cation BMIM^+ and the anions BF_4^- and TFSI^- in Figure 2. 3a, and for the cation HMIM^+ with the same two anions in Figure 2. 3b.

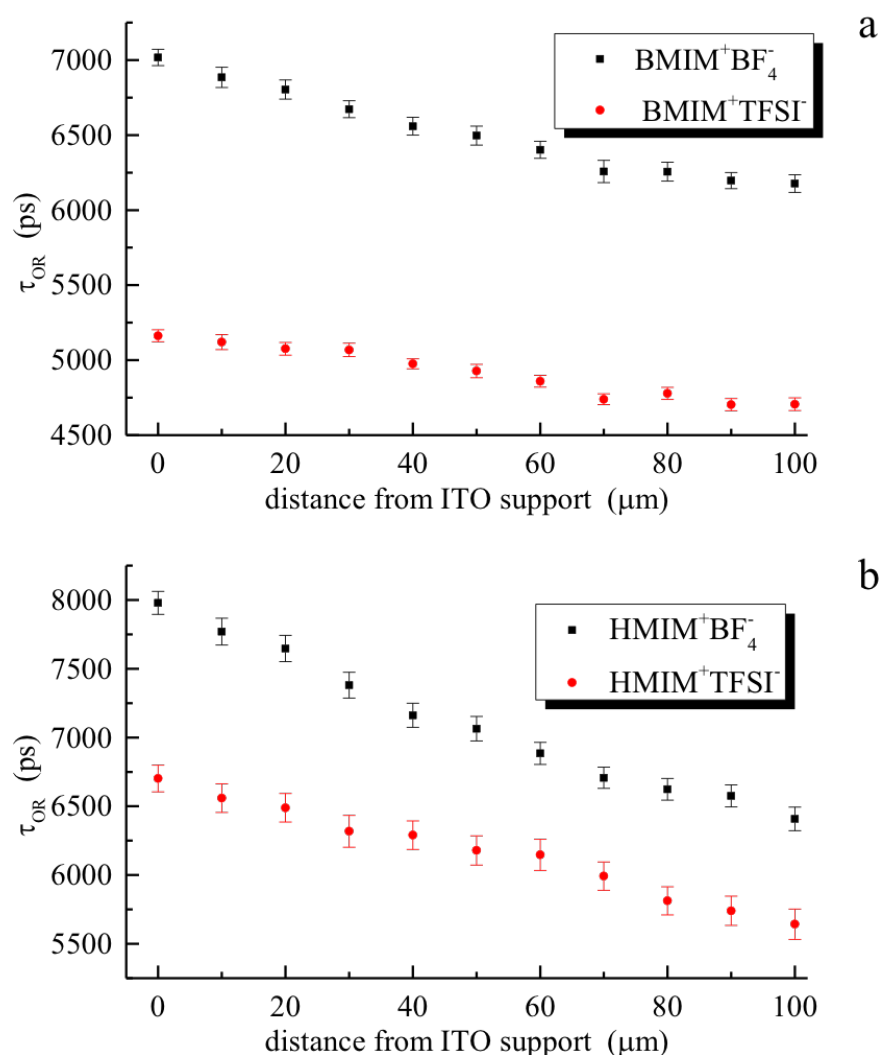


Figure 2. 3 Cresyl violet anisotropy decay time constants as a function of RTIL anion identity with a common cation aliphatic chain length. (a) Black squares are $\text{BMIM}^+\text{BF}_4^-$ and red circles are $\text{BMIM}^+\text{TFSI}^-$. (b) Black squares are $\text{HMIM}^+\text{BF}_4^-$ and red circles are $\text{HMIM}^+\text{TFSI}^-$. For all data points, the error bars represent $\pm 1\sigma$ for three individual measurements.

The data shown in Figures 2. 2 and 2. 3 demonstrate that ρ_f depends on the identities of the RTIL constituent ions. This is a qualitative assessment, however, and we need to be able to quantitate ρ_f in order to evaluate the structural dependence in a meaningful way. The discussion that follows is, of necessity, semi-quantitative because some of the quantities required in the evaluation of ρ_f are not known for the systems we report on here. With that caveat in mind, we consider the equilibrium condition experienced by the probe at any given point in the system,

$$\begin{aligned}
 CV - A &\xrightleftharpoons{K_{eq}} CV^+ + A^- \\
 K_{eq} &= \frac{[CV^+][A^-]}{[CV - A]} = \frac{X_{free}}{(1 - X_{free})} [A^-]
 \end{aligned}
 \tag{2. 5}$$

where A^- is the dissociated RTIL anion and CV-A is the complex between CV^+ and A^- . As discussed above, the relative amount of free and complexed CV will vary with the concentration of A^- at any given point in the system according to Le Chatelier's principle and it is this gradient in A^- that we desire to quantitate. Determination of the change in $[A^-]$ over the spatial extent of ρ_f will allow evaluation of its magnitude. Experimental data on X_{free} are available from the rotational diffusion measurements (Eqs. 2. 2 and 2. 3) and the central point of uncertainty is thus the value of K_{eq} for chromophore complexation. We are not aware of any determinations of K_{eq} for the systems we report here. Somewhat more information is known, however, about the chromophore resorufin. The equilibrium constant for resorufin-sodium dissociation in butanol has been reported previously to be 4×10^{-5} M.⁵⁹ Clearly, this value for K_{eq} will not be quantitatively correct for the systems we report here, but we expect that it will be within an order of magnitude. There are data for the interaction of resorufin with BMIM⁺ in the RTIL BMIM⁺BF₄⁻ as a function of distance from a silica surface. These data show that at the silica surface $X_{free} = 0.54$ and at a distance of 100 μm from the surface $X_{free} = 0.79$.²⁶ For this range of mole fractions and with the value of K_{eq}

$= 4 \times 10^{-5}$ M, we calculate a change in concentration of the dissociated RTIL ion of 2.4×10^{-5} M over a 100 μm distance. While this is an intrinsically useful value, it would be of more significance to know what fraction of all (dissociated) RTIL ions this gradient represents.

Determining the extent of dissociation in a RTIL is more complex than intuition may suggest. The simplest way to make this determination would be through measurement of the conductivity of the RTIL. Performing such measurements is challenging, however, because of the high viscosity of the RTIL and the unknown nature of the interactions between dissociated ions and Bjerrum pairs, and both factors affect ion mobility. The Grätzel group has performed some conductivity measurements on RTILs and they found that $\text{BMIM}^+\text{TFSI}^-$ is *ca.* 25% dissociated at room temperature.⁶⁰ That extent of dissociation corresponds to *ca.* 1.3 M, indicating that the concentration gradient in RTIL dissociated ion is *ca.* 18 ppm over the 100 μm spatial extent of the gradient, or $\rho_f \sim 0.2$ ppm/ μm .

To re-emphasize, the value of $\rho_f \sim 0.2$ ppm/ μm is not quantitatively accurate for our systems because of the absence of information available about the specific RTILs we have studied. The calculated value of ρ_f , however, is useful in the sense that it will allow the experimental data reported in Figures 2. 2 and 2. 3 to be evaluated under an identical set of assumptions, affording a means of gauging the RTIL constituent-dependence of ρ_f . Of equal significance is understanding the magnitude of ρ_f . The observation of ρ_f in RTILs must intrinsically carry limits owing to the ability to separate charge over macroscopic distances, but the exact extent to which charge separation proceeds in these systems, *i.e.* the magnitude of ρ_f , has been unknown to this point. The magnitude of ρ_f being in the 0.2 ppm/ μm range is consistent with a highly screening medium that allows for limited ion mobility.

The detection of ρ_f requires a probe chromophore that complexes with counterions to only a limited extent. If the chromophore does not complex with free ions, no gradient is observed, as is seen for the neutral chromophore nile red (Figure 2. 4). If the chromophore complexes efficiently with free ions, then essentially all chromophores will be complexed for all relevant ion concentrations, resulting in a loss of sensitivity to the existence of ρ_f .

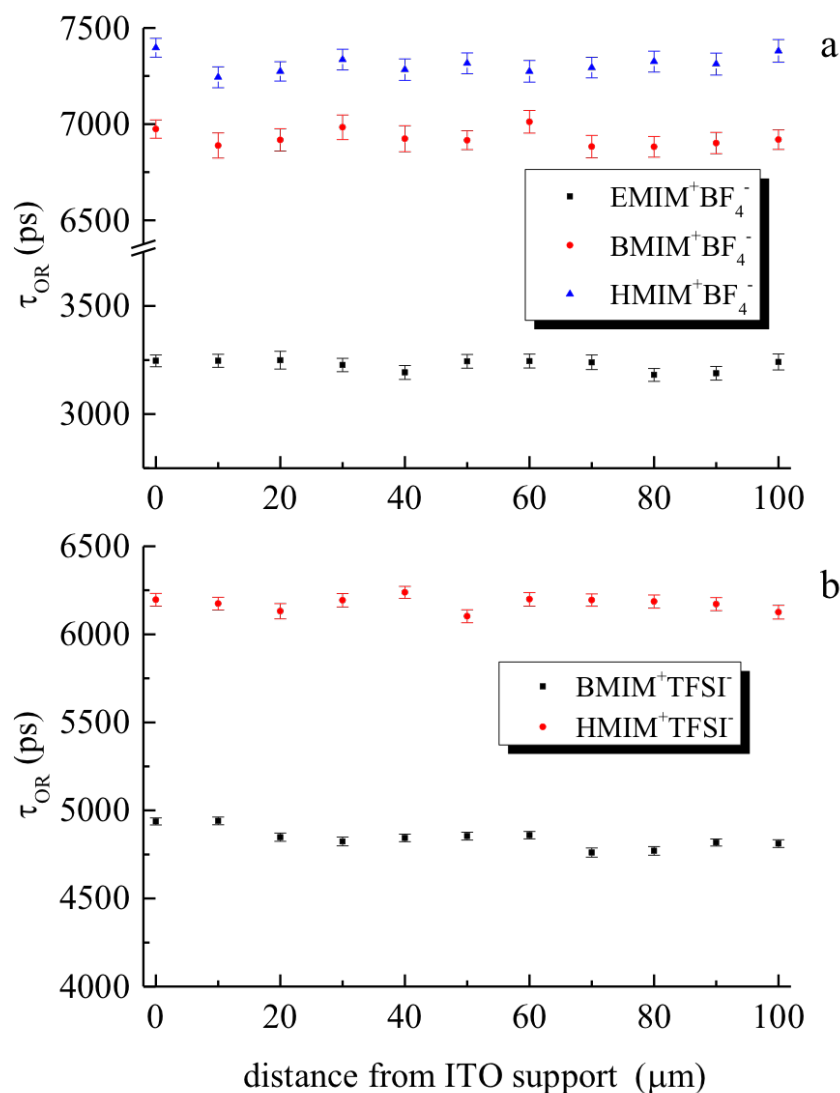


Figure 2. 4 Nile Red anisotropy decay time constants as a function of RTIL cation aliphatic chain length, with same anion. (a) Black squares are EMIM $^+$ BF $_4^-$, red circles are BMIM $^+$ BF $_4^-$ and blue triangles are HMIM $^+$ BF $_4^-$. (b) Black squares are BMIM $^+$ TFSI $^-$ and red circles are HMIM $^+$ TFSI $^-$. For all data points, the error bars represent $\pm 1\sigma$ for three individual measurements.

With this information and perspective in mind, we turn to how RTIL constituent structure influences the magnitude of ρ_f . In order to make this comparison, it is useful to consider the fractional change in τ_{OR} over the spatial extent of the gradient and how the identity of the RTIL counterion affects the measured magnitude. We thus need to evaluate $\Delta\tau_{OR}/\tau_{OR}$ over the spatial extent of ρ_f , where the denominator is taken as τ_{OR} at $x=100\text{ }\mu\text{m}$. We use the terminology $\Delta\tau_{OR}$ because we measure the gradient along one axis. For any system that follows Eq. 2. 5, the relevant quantity is the change in extent of complexation, which is given by $\nabla \cdot X_{free}$. For the purposes of this evaluation, we define the term ξ ,

$$\xi = \left| K_{eq}^{-1} \left([A^-]_{0\mu\text{m}} - [A^-]_{100\mu\text{m}} \right) \right| = \left| \frac{1 - X_{free}^{0\mu\text{m}}}{X_{free}^{0\mu\text{m}}} - \frac{1 - X_{free}^{100\mu\text{m}}}{X_{free}^{100\mu\text{m}}} \right| = \left| \frac{X_{free}^{100\mu\text{m}} - X_{free}^{0\mu\text{m}}}{X_{free}^{0\mu\text{m}} \cdot X_{free}^{100\mu\text{m}}} \right| \quad [2. 6]$$

Which would take on a value of $\xi=0$ for no gradient, and a practical upper limit of $\xi=10$. Any value beyond 10 would not only be physically unrealistic but would also not be quantifiable (*vide infra*). The changes in ξ reflect changes in X_{free} , which can be used to assess $\nabla \cdot V$ and thus $\nabla \cdot \tau_{OR}$. In the discussion that follows, we report ρ_f as $\Delta\tau_{OR}/\tau_{OR}^{100\mu\text{m}}$ to provide a facile means of relating the experimental data to the quantities relevant to the gradient. Because τ_{OR} depends on η for each RTIL, the volumes of the RTIL anions differ, ($V(\text{BF}_4^-) = 50\text{ }\text{\AA}^3$, $V(\text{TFSI}^-) = 169\text{ }\text{\AA}^3$) and the neat concentrations of the RTILs differ according to molecular weight and density, a given value of $\Delta\tau_{OR}/\tau_{OR}$ will correspond to a value of ξ that depends on the specific RTIL system. From Eq. 2. 6, for ξ varying from 10 to 0, X_{free} will vary from 0.909 to 0.091. With this range of values, the quantity $\Delta V/V = \Delta\tau_{OR}/\tau_{OR}$ can be calculated using Eqs. 2. 2 and 2. 3 (Figure 2. 5). The quantity $\Delta V/V$ is related to ξ by (Eq. 2. 7)

$$\frac{\Delta\tau_{OR}}{\tau_{OR}} = \frac{\Delta V}{V} = \xi \left(\frac{X_{free}^{0\mu m} \cdot X_{free}^{100\mu m} \cdot V_{RI}}{V_{complex} - X_{free}^{100\mu m} \cdot V_{RI}} \right) \quad [2. 7]$$

where V_{RI} is the hydrodynamic volume of the RTIL ion that complexes with the chromophore (A^- in Eq. 2. 5, $V_{RI} = V_{complex} - V_{free}$). It is clear from Figure 2. 5 that $\Delta\tau_{OR}/\tau_{OR}$ depends sensitively on both the ratio of the complexed chromophore to free chromophore and on the volume of the complexing RTIL ion relative to the volume of the chromophore. The detailed relationship between the RTIL, chromophore and extent of RTIL dissociation will depend on the specific properties of the system, and the quantity $\Delta\tau_{OR}/\tau_{OR}$ can be related to ρ_f . To establish the relationship between $\Delta\tau_{OR}/\tau_{OR}$ and ρ_f , we must be able to estimate both the change in concentration of the anionic RTIL constituent, A^- , over the gradient range and the average concentration of A^- in the bulk RTIL medium. The former quantity requires we use the same K_{eq} as was used earlier ($K_{eq} = 4 \times 10^{-5}$ M) and the latter quantity requires we estimate the extent of RTIL dissociation. In the

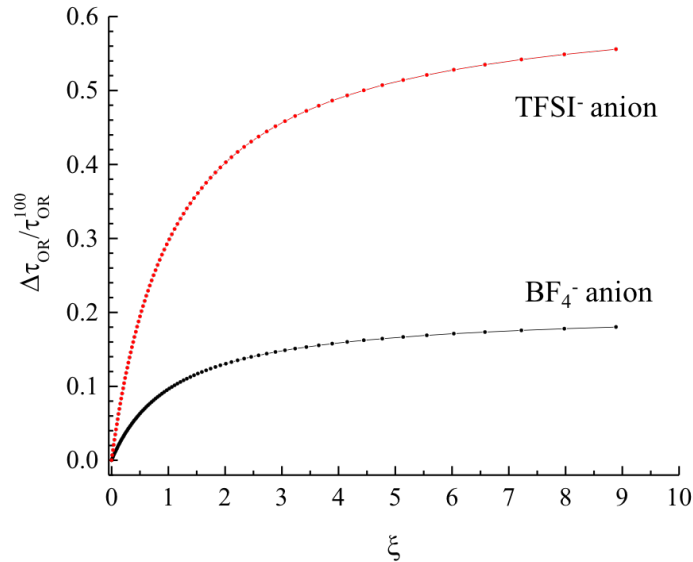


Figure 2. 5 Normalized anisotropy decay time gradient, $\Delta\tau_{OR}/\tau_{OR}$, as a function of the change in ratio of the complexed to free chromophore, ξ . The relationship between $\Delta\tau_{OR}/\tau_{OR}$ and ρ_f depends on RTIL density, molecular weight and constituent anion hydrodynamic volume. See text for a discussion.

absence of quantitative experimental data, we assume that the dissociation of all RTILs studies is the same, at 25%. We recognize these are significant, but constant, approximations in this estimate. With that caveat, and the experimental $\Delta\tau_{OR}/\tau_{OR}$ data, we show the variation in ρ_f with changes in RTIL constituent structure (Table 2. 1). Even with the assumption that the extent of RTIL dissociation is the same, the gradient is seen to vary because of the density of the RTILs and the variations in hydrodynamic volume of the constituent species.

Table 2. 1 Dependence of the induced free charge density gradient (ρ_f) on RTIL structure. The gradient is reported in units of change in charge carrier concentration per distance (ppm/ μm) and change in charge density per distance ($(\mu\text{C}/\text{cm}^3)/\mu\text{m}$). The relationship between concentration and charge density depends on RTIL density and molecular weight.

RTIL	η (cP)	$\Delta\tau_{OR}/\tau_{OR}$	ξ	ρ_f (ppm/ μm)	ρ_f ($(\mu\text{C}/\text{cm}^3)/\mu\text{m}$)
EMIM ⁺ BF ₄ ⁻	41 ⁶¹	0.08 $\pm$ 0.01	0.8	0.03 $\pm$ 0.01	15 $\pm$ 5
BMIM ⁺ BF ₄ ⁻	112 ⁶¹	0.14 $\pm$ 0.01	2.5	0.04 $\pm$ 0.01	17 $\pm$ 4
HMIM ⁺ BF ₄ ⁻	174 ⁶¹⁻⁶²	0.25 $\pm$ 0.01	>10	0.08 $\pm$ 0.01	30 $\pm$ 3
BMIM ⁺ TFSI ⁻	45 ⁶¹	0.10 $\pm$ 0.01	0.2	0.18 $\pm$ 0.09	41 $\pm$ 20
HMIM ⁺ TFSI ⁻	81 ⁶²	0.19 $\pm$ 0.02	0.5	0.52 $\pm$ 0.14	112 $\pm$ 30

Two points emerge from these findings. The first is that, in all cases, the magnitude of ρ_f is small, and this finding is consistent with intuition. Even in viscous media, it is not possible to separate charge substantially on electrostatic grounds, and also that the magnitude of the ambient charge on an ITO support must be relatively modest, and it is this charge that is the driving force for the formation of the gradient in the first place. The second point is that the magnitude of the gradient increases with increasing imidazolium aliphatic chain length and is greater for the TFSI⁻ anion than for the BF₄⁻ anion. Both of these RTIL structural dependencies are consistent with the structure-dependent changes in charge density for these RTIL systems. It is important to note that,

despite the structural dependence we observe, Eq. 2. 6 indicates that there is no explicit viscosity-dependence in our gradient measurements because the term $\Delta\tau_{OR}/\tau_{OR}$ normalizes for structure-dependent variations in RTIL viscosity.

It is also important to consider that there is significant uncertainty in the above estimates of ρ_f because we do not know quantitatively either K_{eq} for the chromophore-counterion equilibrium or the extent of RTIL dissociation, and both these quantities may vary with RTIL identity. That said, the trends we observe in these data are in agreement with chemical intuition in terms of charge density of the RTIL constituents. Further work to elucidate more accurately the relationship between RTIL constituent structure and ρ_f is in progress. A promising area in the arena of RTIL constituent structure lie in the use of structurally regular series of both anions and cations to elucidate the fundamental chemical factors involved in the ability to support a charge density gradient over macroscopic distances.⁶³⁻⁶⁵ Recent advances in the design and characterization of chiral RTILs indicates that structural control over second order nonlinear optical response is readily achievable, opening the door to facile control over RTIL optical properties.⁶⁶⁻⁶⁹

The magnitude of ρ_f achievable, especially as a function of applied support surface charge,²⁷ will play an central role in determining the potential applications for which these materials are appropriate. It is our hope that experimental determination of ρ_f in these systems will also be of use in establishing how best to model this class of materials.

2. 4 Conclusions

We report on the dependence of the free charge density gradient, ρ_f , that is formed in RTILs when interfaced with a charged support. The gradient ρ_f is found to depend sensitively on the identities of the RTIL constituents. The magnitude of ρ_f as a function of the RTIL constituent identities lies in the range of 0.03 ppm/ μm to 0.5 ppm/ μm for the systems studied, and this

information points the way toward RTIL design parameters to optimize ρ_f . The magnitude of ρ_f is in all cases less than 1 ppm/ μm , consistent with chemical intuition and the magnitude of the support surface charge. It is clear from Eq. 2. 6 that the volume of the dissociated RTIL ion relative to the volume of the chromophore plays an important role in our observations. The gradient is greater for TFSI⁻ salts than for BF₄⁻ salts, provided the assumptions made about chromophore complexation equilibrium constant and extent of RTIL dissociation hold. We continue to evaluate both of these quantities in order to provide more quantitative information on the magnitude of ρ_f in different RTIL systems.

APPENDIX

APPENDIX

The experimental signals acquired are the time-resolved emission transients polarized parallel ($I_{\parallel}(t)$) and perpendicular ($I_{\perp}(t)$) to the incident excitation light pulse. The induced orientational anisotropy decay function, $R(t)$, is the normalized difference between polarized emission transients, $I_{\parallel}(t)$ and $I_{\perp}(t)$. τ_{OR} is the decay time constant of $R(t)$.

$$R(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} = R(0) \exp(-t/\tau_{OR})$$

The anisotropy decay time constants (τ_{OR}) are obtained from fitting the raw data of $R(t)$ by using ExpDecay1 fitting model in Microcal Origin v9.0. The equation used for fitting is $y = y_0 + A_1 \exp(-(x - x_0)/t_1)$, and y offset is set to be 0 ($y_0 = 0$). We show several sets of raw data and of $R(t)$ for a series of distances from the ITO support, for cresyl violet in EMIM⁺BF₄⁻ (Figures A. 1-A. 5) and BMIM⁺TFSI⁻ (Figures A. 6-A. 10). For all data, the slight perturbation in signal at *ca.* 12 ns after $t=0$ is pulse leakage from the cavity dumper on the dye laser. We have verified experimentally that its presence does not affect the regressed decay times significantly.

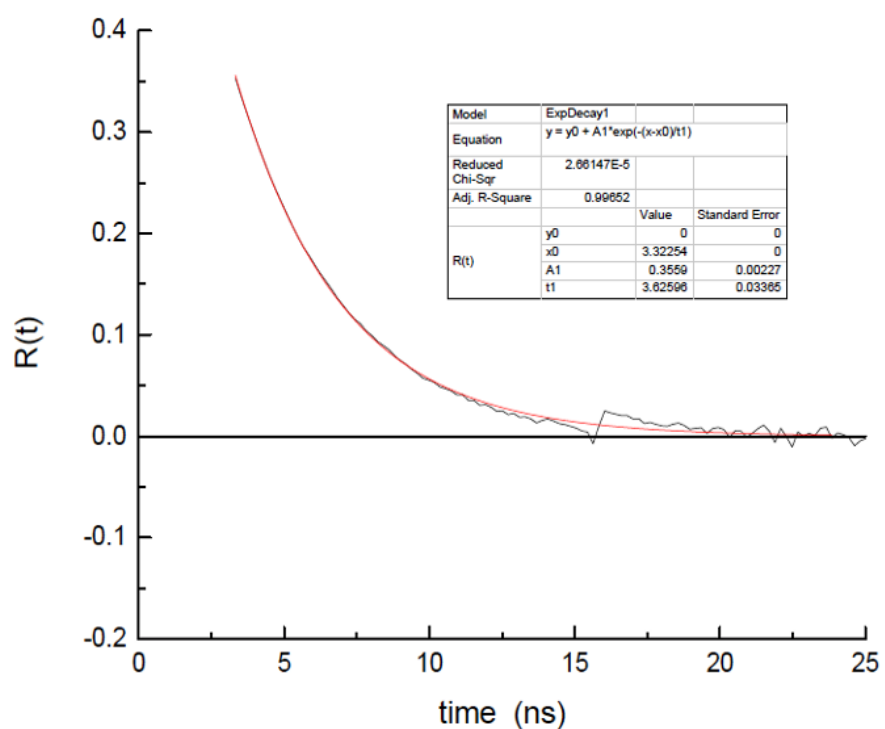
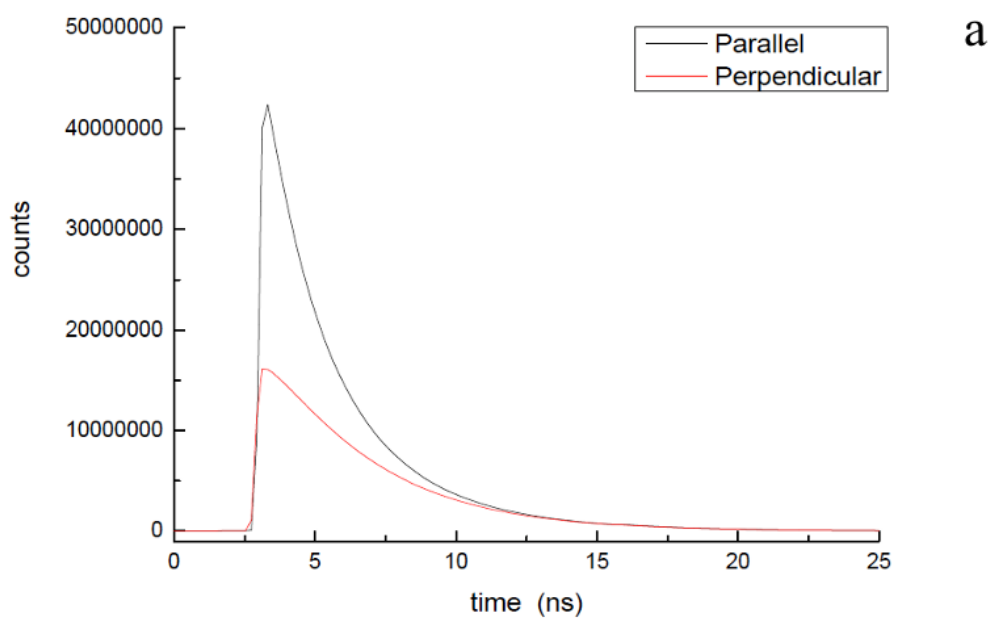


Figure A. 1 Cresyl violet anisotropy decay in EMIM⁺BF₄⁻ measured at 0 μm from ITO support.
 (a) Experimental signals $I_{\parallel}(t)$ and $I_{\perp}(t)$. (b) Orientational anisotropy decay function $R(t)$.

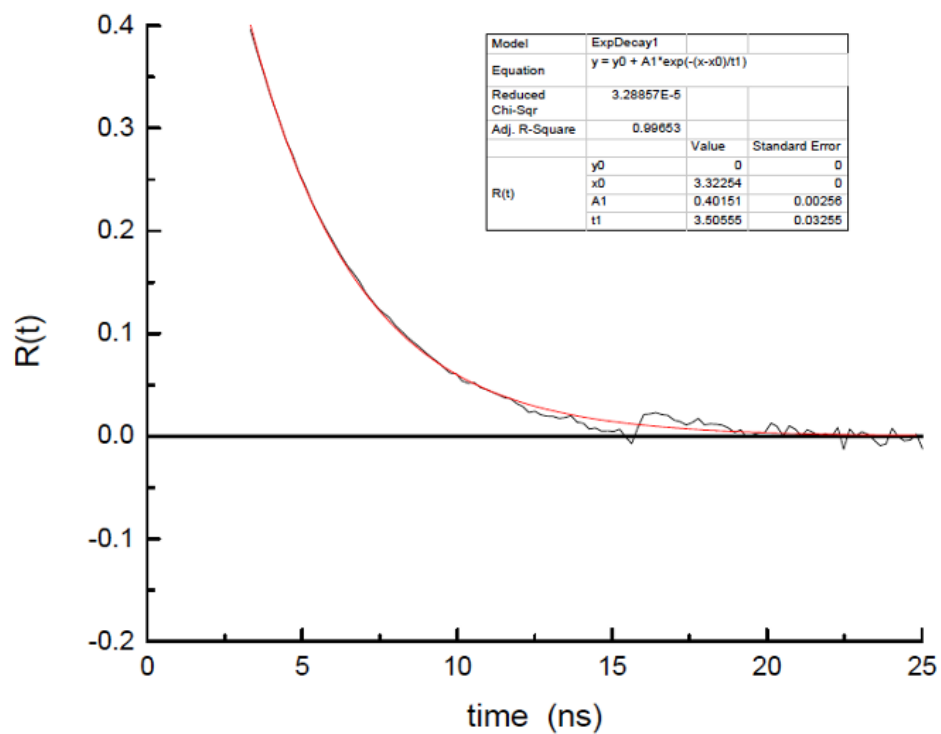
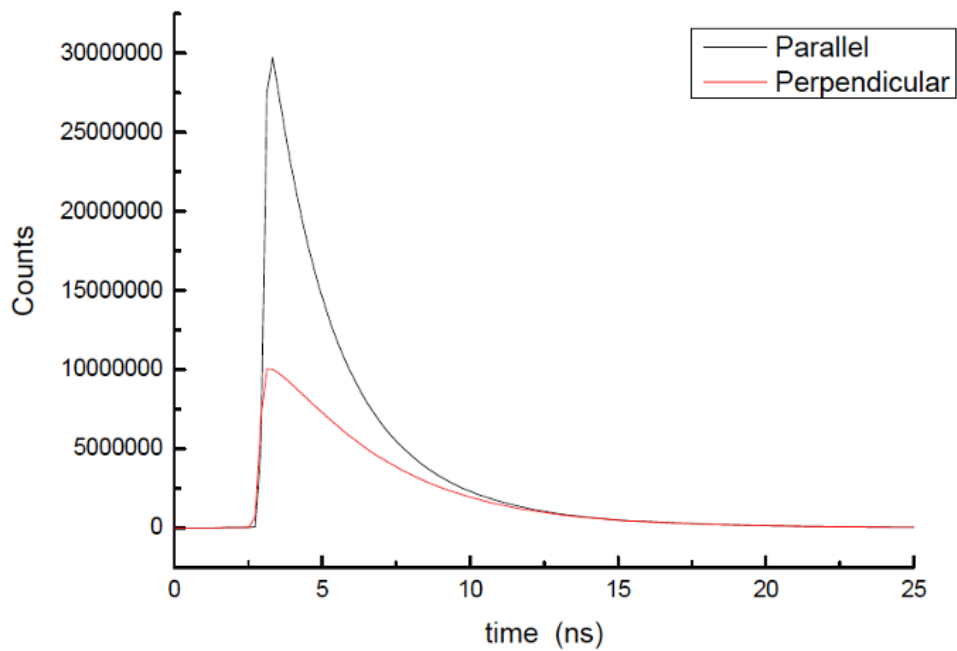


Figure A. 2 Cresyl violet anisotropy decay in $\text{EMIM}^+\text{BF}_4^-$ measured at $20\ \mu\text{m}$ from ITO support. (a) Experimental signals $I_{\parallel}(t)$ and $I_{\perp}(t)$. (b) Orientational anisotropy decay function $R(t)$.

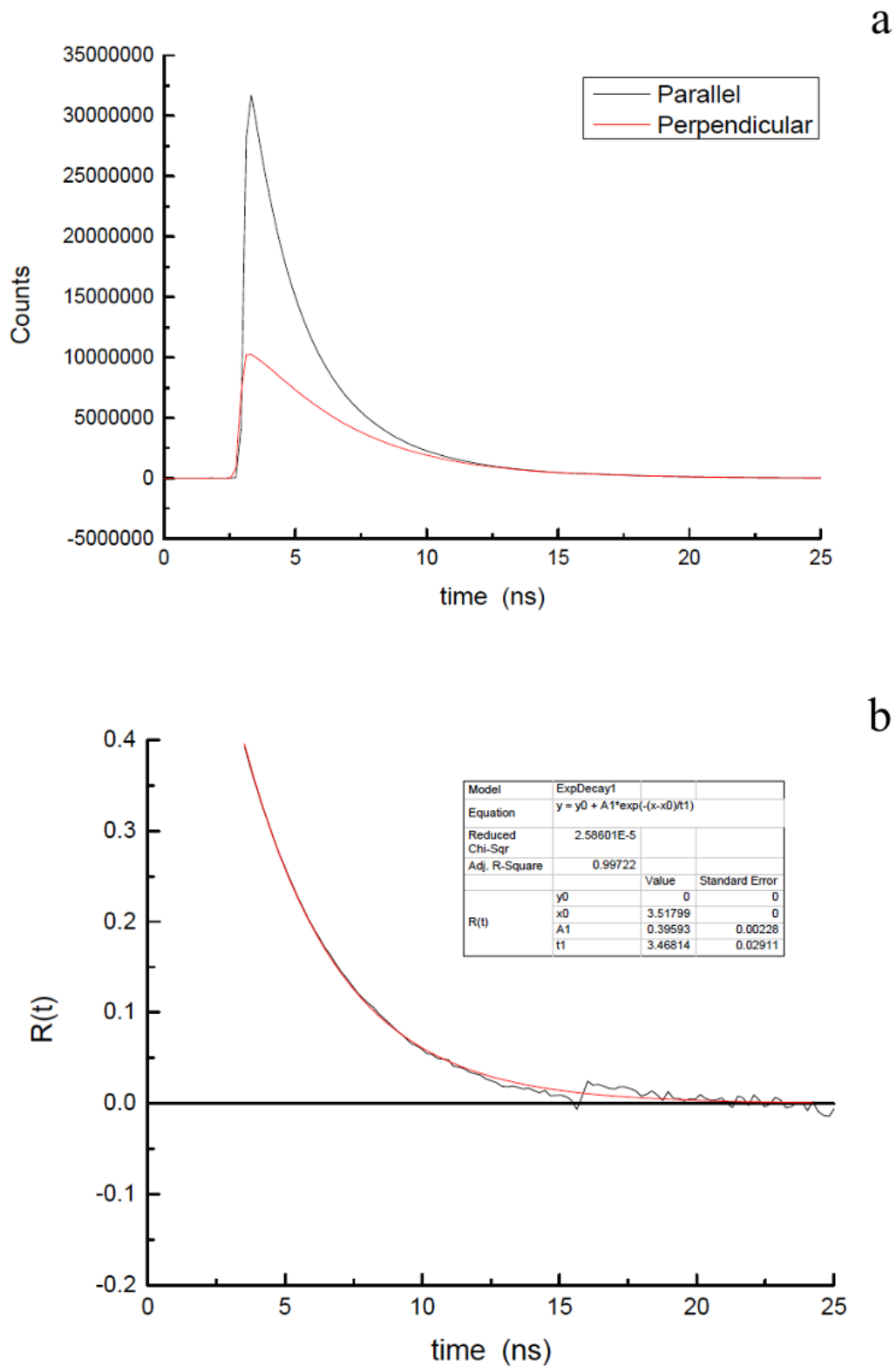


Figure A. 3 Cresyl violet anisotropy decay in $\text{EMIM}^+\text{BF}_4^-$ measured at $50\ \mu\text{m}$ from ITO support. (a) Experimental signals $I_{\parallel}(t)$ and $I_{\perp}(t)$. (b) Orientational anisotropy decay function $R(t)$.

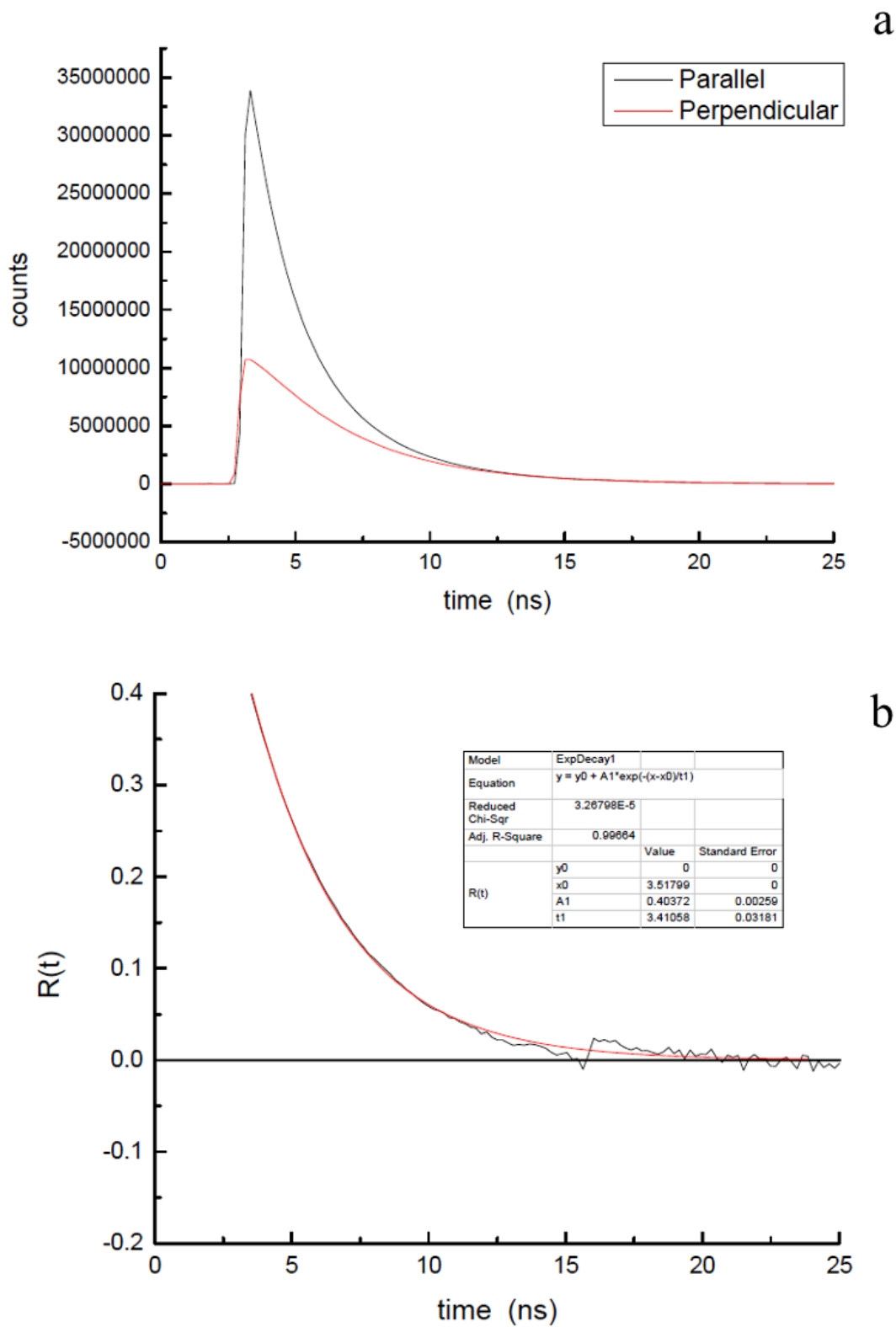


Figure A. 4 Cresyl violet anisotropy decay in $\text{EMIM}^+\text{BF}_4^-$ measured at 70 μm from ITO support. (a) Experimental signals $I_{\parallel}(t)$ and $I_{\perp}(t)$. (b) Orientational anisotropy decay function $R(t)$.

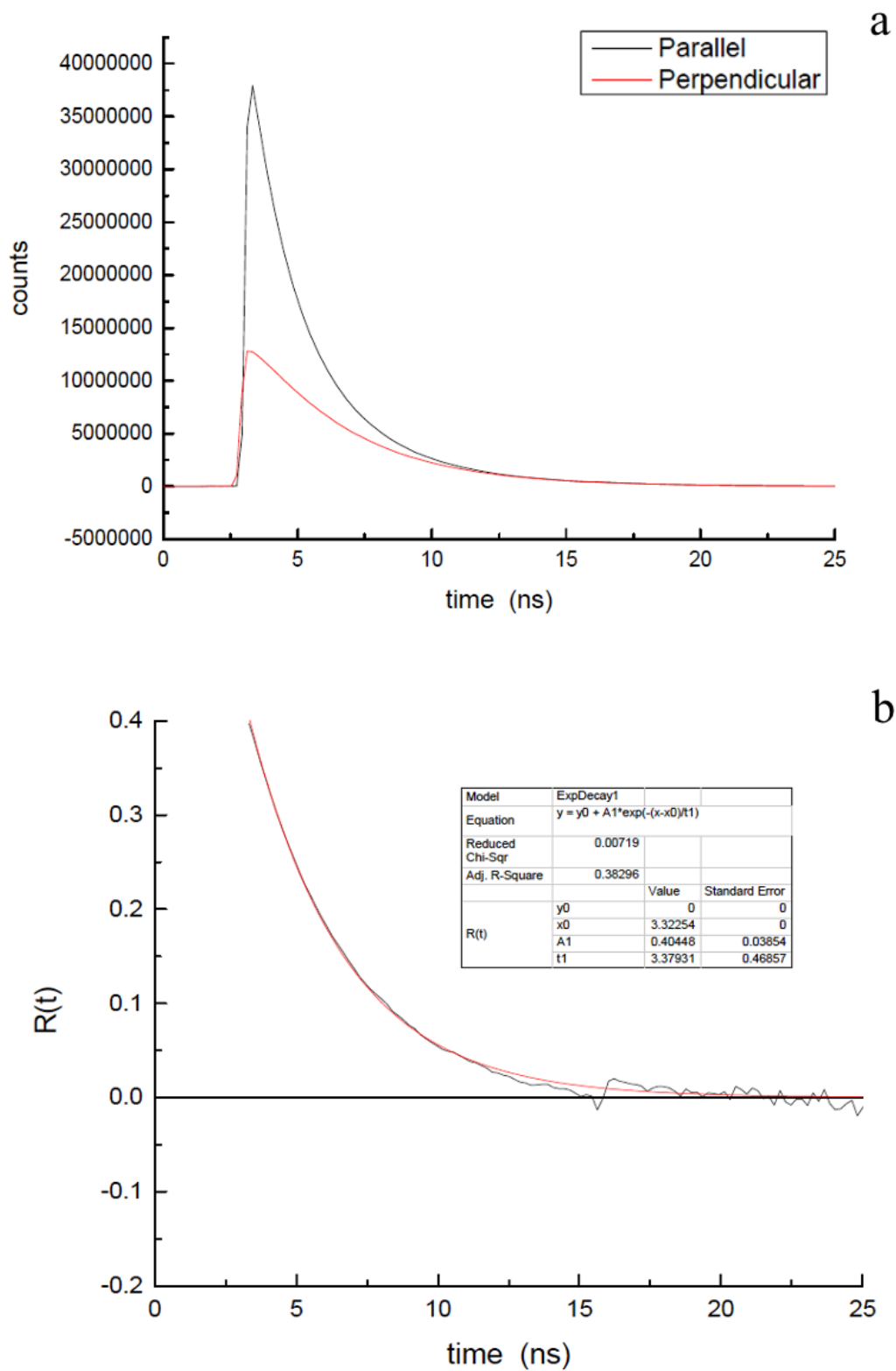


Figure A. 5 Cresyl violet anisotropy decay in EMIM⁺BF₄⁻ measured at 100 μ m from ITO support. (a) Experimental signals $I_{||}(t)$ and $I_{\perp}(t)$. (b) Orientational anisotropy decay function $R(t)$.

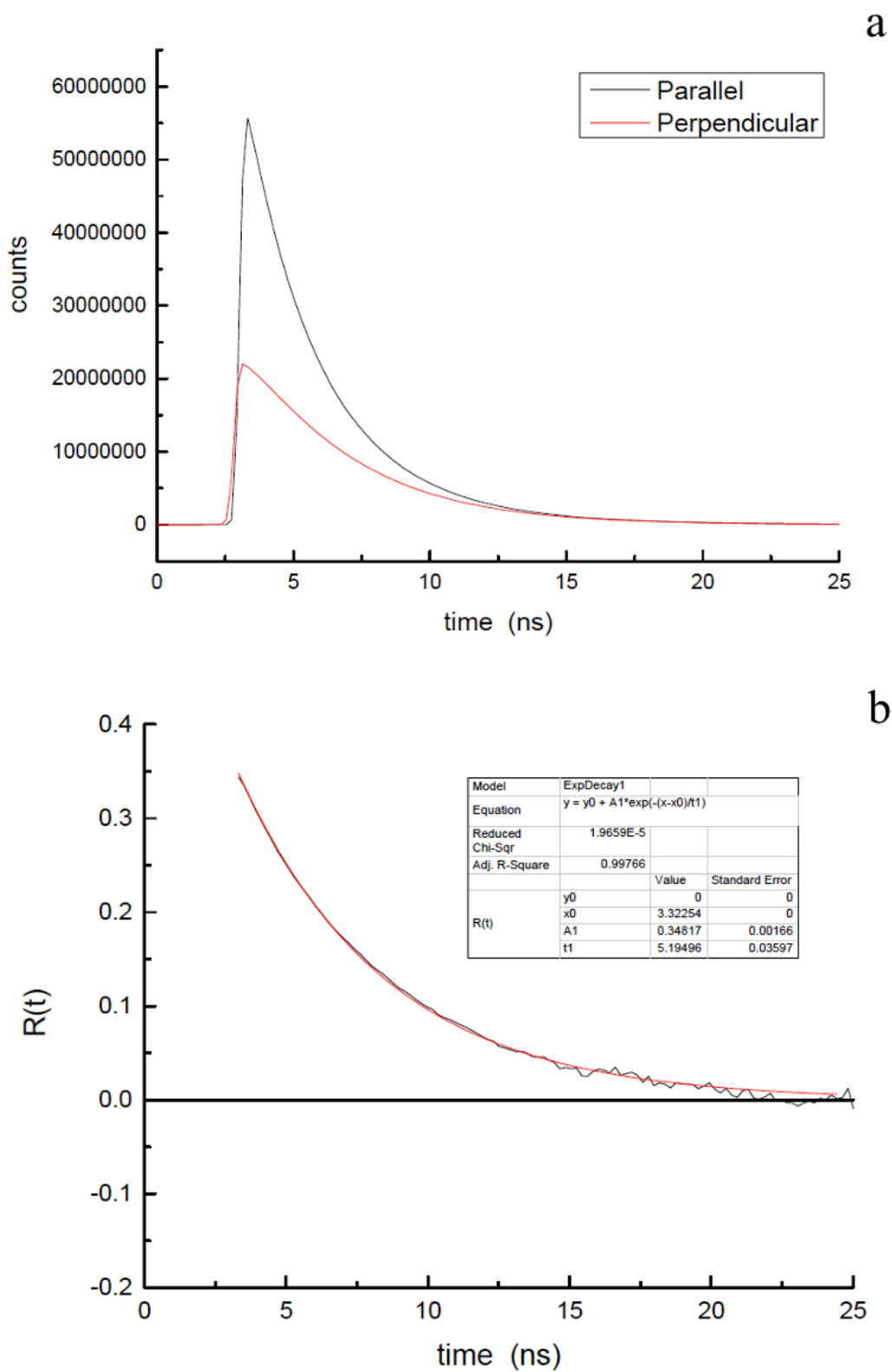


Figure A. 6 Cresyl violet anisotropy decay in BMIM⁺TFSI⁻ measured at 0 μm from ITO support. (a) Experimental signals $I_{\parallel}(t)$ and $I_{\perp}(t)$. (b) Orientational anisotropy decay function $R(t)$.

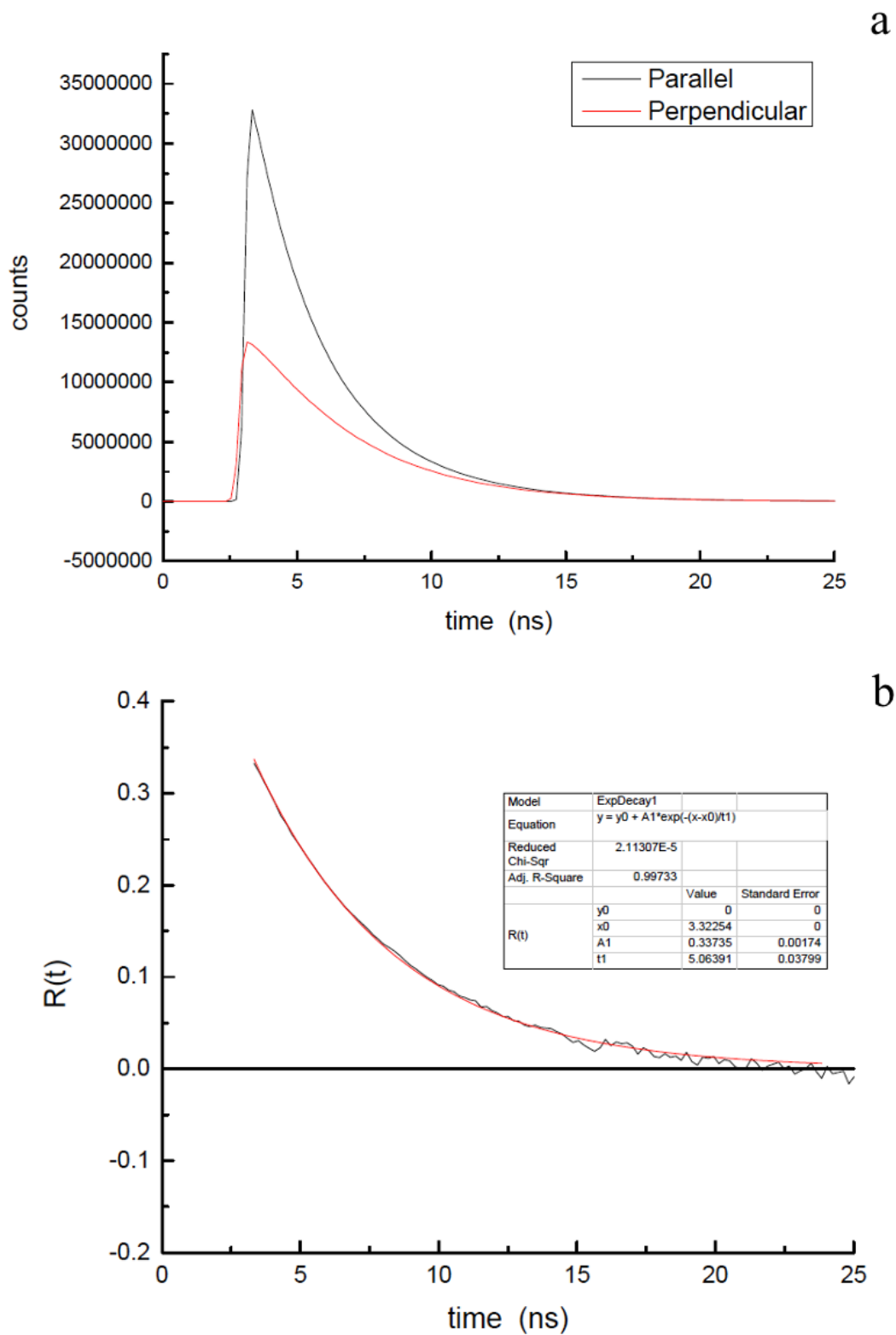


Figure A. 7 Cresyl violet anisotropy decay in BMIM⁺TFSI⁻ measured at 20 μ m from ITO support. (a) Experimental signals $I_{\parallel}(t)$ and $I_{\perp}(t)$. (b) Orientational anisotropy decay function $R(t)$.

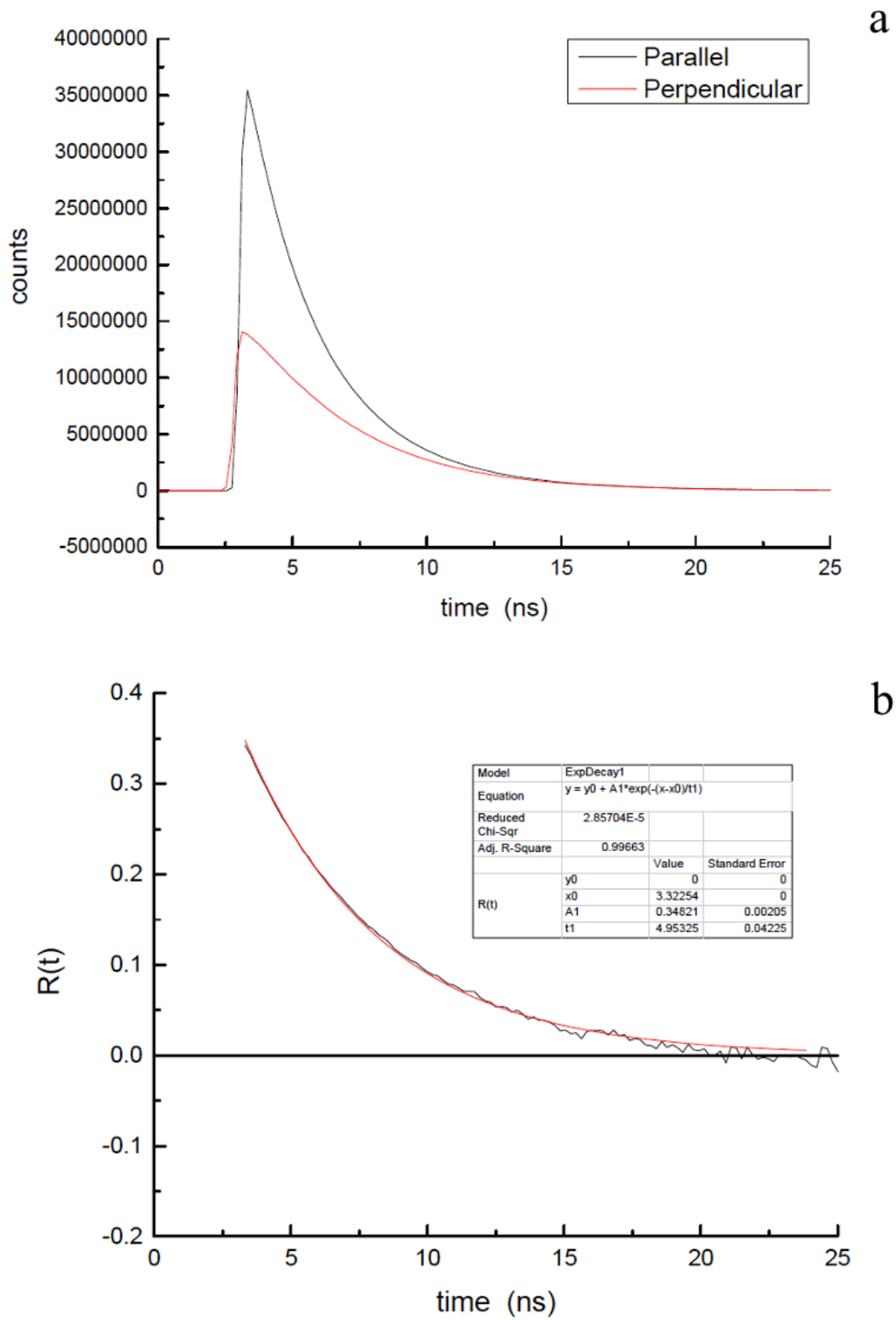


Figure A. 8 Cresyl violet anisotropy decay in BMIM⁺TFSI⁻ measured at 50 μm from ITO support. (a) Experimental signals $I_{\parallel}(t)$ and $I_{\perp}(t)$. (b) Orientational anisotropy decay function $R(t)$.

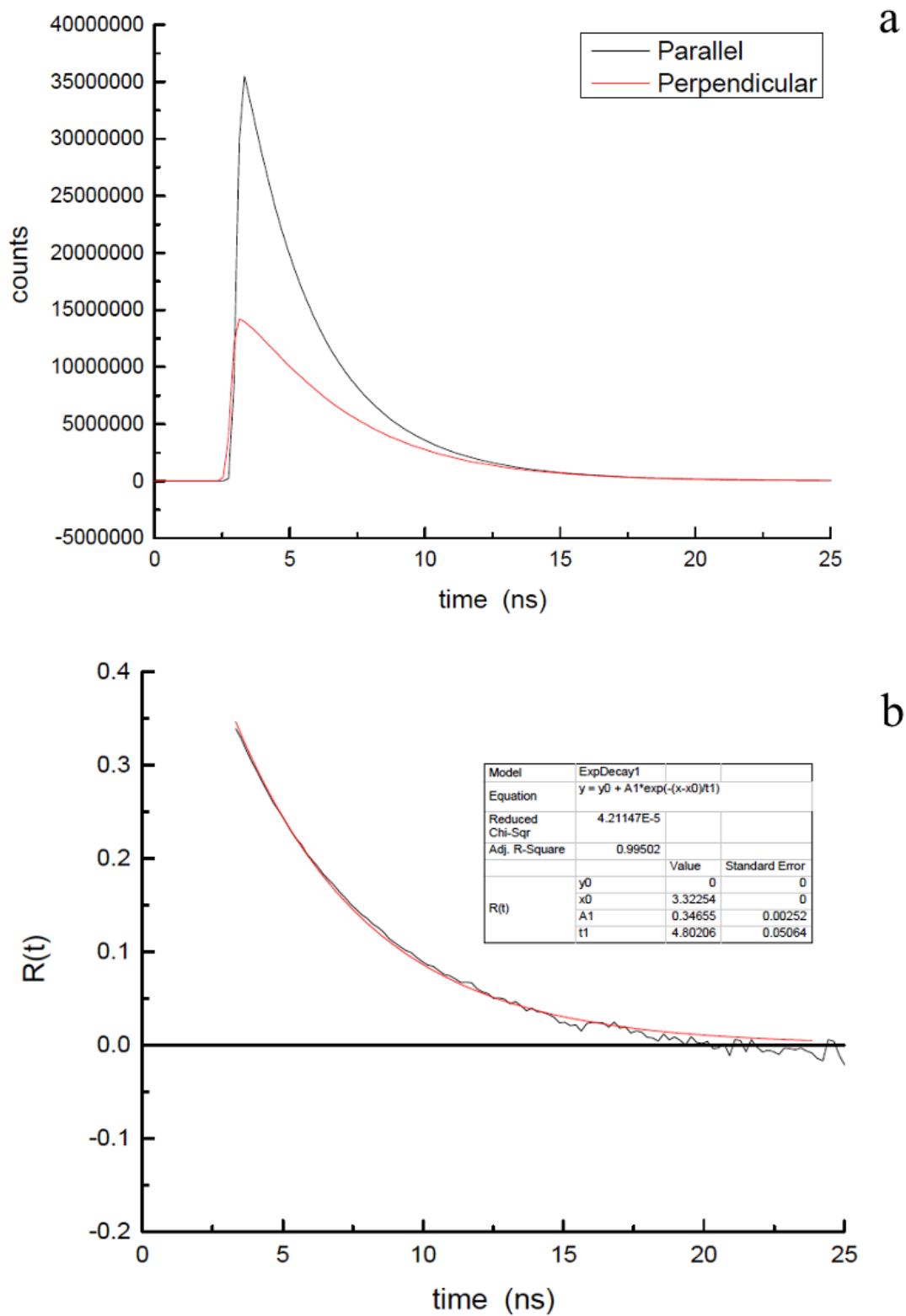


Figure A. 9 Cresyl violet anisotropy decay in BMIM⁺TFSI⁻ measured at 70 μ m from ITO support. (a) Experimental signals $I_{\parallel}(t)$ and $I_{\perp}(t)$. (b) Orientational anisotropy decay function $R(t)$.

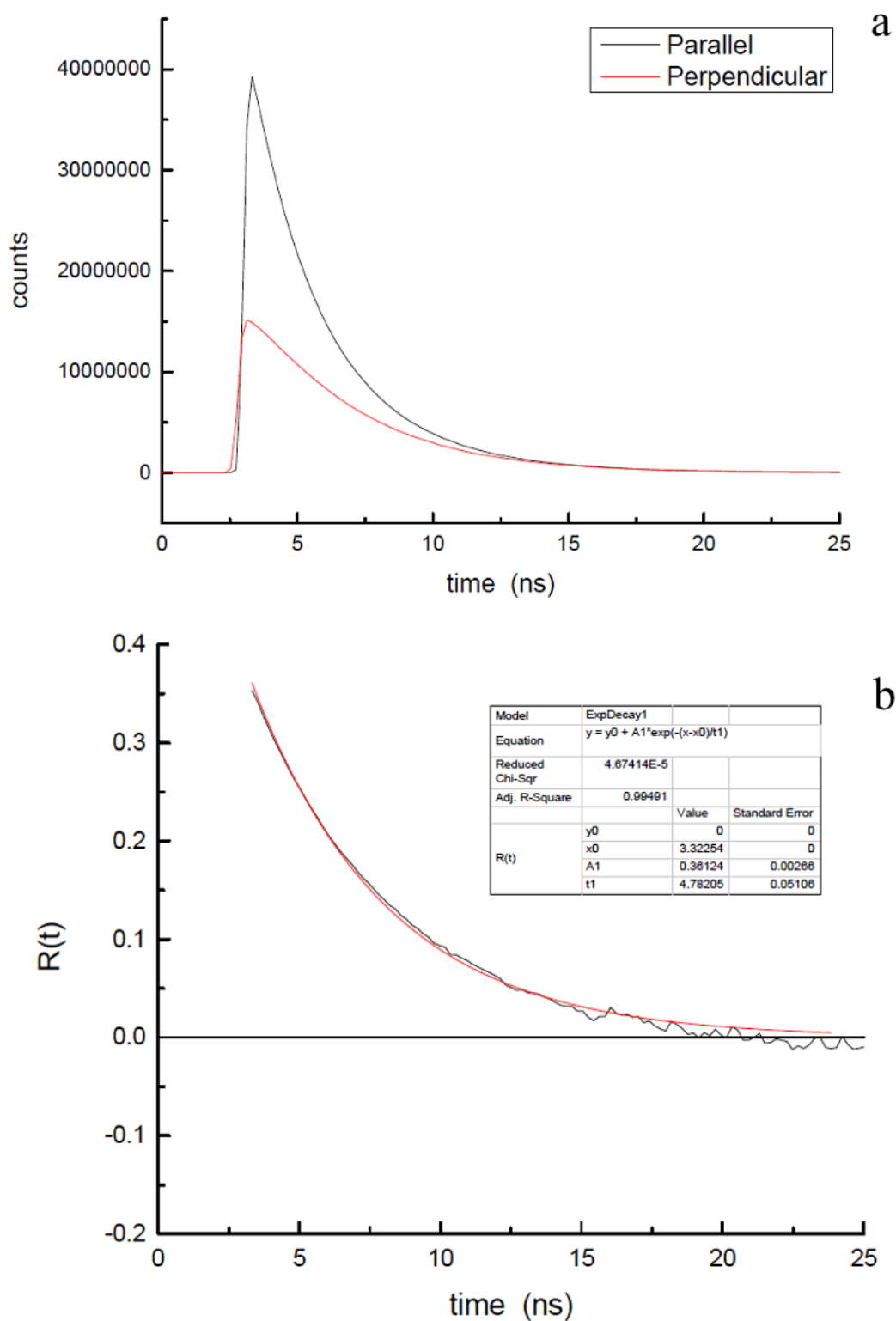


Figure A. 10 Cresyl violet anisotropy decay in BMIM⁺TFSI⁻ measured at 100 μm from ITO support. (a) Experimental signals $I_{\parallel}(t)$ and $I_{\perp}(t)$. (b) Orientational anisotropy decay function $R(t)$.

REFERENCES

REFERENCES

1. Welton, T., Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071-2084.
2. Kohagen, M.; Brehm, M.; Lingscheid, Y.; Giernoth, R.; Sangoro, J.; Kremer, F.; Naumov, S.; Iacob, C.; Karger, J.; Valiullin, R.; Kirchner, B., How hydrogen bonds influence the mobility of imidazolium-based ionic liquids. A combined theoretical and experimental study of 1-n-butyl-3-methylimidazolium bromide. *J. Phys. Chem. B* **2011**, *115*, 15280-15288.
3. Sangoro, J. R.; Serghei, A.; Naumov, S.; Galvosas, P.; Karger, J.; Wespe, C.; Bordusa, F.; Kremer, F., Charge transport and mass transport in imidazolium-based ionic liquids. *Phys. Rev. E* **2008**, *77*, 051202.
4. Iacob, C.; Sangoro, J. R.; Serghei, A.; Naumov, S.; Korth, Y.; Karger, J.; Friedrich, C.; Kremer, F., Charge transport and glassy dynamics in imidazole-based liquids. *J. Chem. Phys.* **2008**, *129*, 234511.
5. Krause, C.; Sangoro, J. R.; Iacob, C.; Kremer, F., Charge transport and dipolar relaxations in imidazolium-based ionic liquids. *J. Phys. Chem. B* **2010**, *114*, 382-386.
6. Gebbie, M. A.; Valtiner, M.; Banquy, X.; Fox, E. T.; Henderson, W. A.; Israelachvili, J. N., Ionic liquids behave as dilute electrolyte solutions. *Proc. Nat. Acad. Sci. USA* **2013**, *110* (24), 9674-9679.
7. Bhat, M. A.; Dutta, C. K.; Rather, G. M., Exploring physicochemical aspects of N-alkylimidazolium based ionic liquids. *J. Mol. Liq.* **2013**, *181*, 142-151.
8. Wiser, N., Dielectric constant with local field effects included. *Phys. Rev.* **1963**, *129*, 62-69.
9. Wakai, C.; Oleinikova, A.; Ott, M.; Weingartner, H., How polar are ionic liquids? Determination of the static dielectric constant of an imidazolium-based ionic liquid by microwave dielectric spectroscopy. *J. Phys. Chem. B Lett.* **2005**, *109*, 17028-17030.
10. Wemple, S. H.; DiDomenico, M., Jr., Behavior of the electronic dielectric constant in covalent and ionic materials. *Phys. Rev. B* **1971**, *3*, 1338-1351.
11. Zarubin, G.; Bier, M., Static dielectric properties of dense ionic fluids. *J. Chem. Phys.* **2015**, *142*, 184502.
12. Gebbie, M. A.; Dobbs, H. A.; Valtiner, M.; Israelachvili, J. N., Long-range electrostatic screening in ionic liquids. *Proc. Nat. Acad. Sci. USA* **2015**, *112* (24), 7432-7437.
13. Adar, R. M.; Markovich, T.; Andelman, D., Bjerrum pairs in ionic solutions: A Poisson-Boltzmann approach. *J. Chem. Phys.* **2017**, *146*, 194904 1-8.

14. Hein, T. M.; Dung, H. T.; Welsch, D.-G., Local-field correction in the strong coupling regime. *Phys. Rev. A* **2011**, *83*, 043820.
15. Mahan, G. D., Local-field corrections to Coulomb interactions. *Phys. Rev.* **1967**, *153*, 983-988.
16. Han, D.; Row, K.-H., Recent applications of ionic liquids in separation technology. *Molecules* **2010**, *15*, 2405-2426.
17. Yadav, J. S.; Reddy, B. V. S.; Premalatha, K., 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄) ionic liquid : A novel and recyclable reaction medium for the synthesis of *vic*-diamines. *Adv. Synth. Catal.* **2003**, *345*, 948-952.
18. Itoh, T., Ionic liquids as tool to improve enzymatic organic synthesis. *Chem. Rev.* **2017**, *117*, 10567-10607.
19. Sowmiah, S.; Cheng, C. I.; Chu, Y.-H., Ionic liquids for green organic synthesis. *Curr. Org. Synth.* **2012**, *9*, 74-95.
20. Arbizzani, C.; Biso, M.; Cericola, D.; Lazzari, M.; Soavi, F.; Mastragostino, M., Safe, high-energy supercapacitors based on solvent-free ionic liquid electrolytes. *J. Pwr. Sources* **2008**, *185* (2), 1575-1579.
21. Balducci, A.; Dugas, R.; Taberna, P. L.; Simon, P.; Plée, D.; Mastragostino, M.; Passerini, S., High temperature carbon-carbon supercapacitor using ionic liquid as electrolyte. *J. Pwr. Sources* **2007**, *165* (2), 922-927.
22. Van Aken, K. L.; Beidaghi, M.; Gogotsi, Y., Formulation of ionic-liquid electrolyte to expand the voltage window of supercapacitors. *Angew. Chem.* **2015**, *127*, 4888-4891.
23. de Souza, R. F.; Padilha, J. C.; Goncalves, R. S.; DuPont, J., Room temperature dialkylimidazolium ionic liquid-based fuel cells. *Electrochem. Comm.* **2003**, *5*, 728-731.
24. Lee, S.-Y.; Ogawa, A.; Kanno, M.; Nakamoto, H.; Yasuda, T.; Watanabe, M., Nonhumidified intermediate temperature fuel cells using protic ionic liquids. *J. Am. Chem. Soc.* **2010**, *132*, 9764-9773.
25. Ma, K.; Jarosova, R.; Wang, Y.; Swain, G. M.; Blanchard, G. J., Ionic liquids: A unique and useful class of materials. *Chem. Educ.* **2018**, *23*, 265-272.
26. Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G. J., Charge-induced long-range order in a room-temperature ionic liquid. *Langmuir* **2016**, *32* (37), 9507-9512.
27. Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G. J., Modulation of an induced charge density gradient in the room temperature ionic liquid BMIM⁺BF₄⁻. *J. Phys. Chem. C* **2018**, *122*, 7361-7367.

28. Stillinger, F. H.; Lovett, R., Ion-pair theory of concentrated electrolytes. I. Basic concepts. *J. Chem. Phys.* **1968**, *48* (9), 3858-3868.
29. Lee, A. A.; Vella, D.; Perkin, S.; Goriely, A., Are room-temperature ionic liquids dilute electrolytes? *J. Phys. Chem. Lett.* **2015**, *6*, 159-163.
30. Israelachvili, J. N.; Min, Y.; Akbulut, M.; Alig, A.; Carver, G.; Greene, W.; Kristiansen, K.; Meyer, E.; Pesika, N.; Rosenberg, K.; Zeng, H., Recent advances in the surface forces apparatus (SFA) technique. *Rep. Prog. Phys.* **2010**, *73*, 036601.
31. Gebbie, M. A.; Smith, A. M.; Dobbs, H. A.; Lee, A. A.; Warr, G. G.; Banquy, X.; Valtiner, M.; Rutland, M. W.; Israelachvili, J. N.; Perkin, S.; Atkin, R., Long range electrostatic forces in ionic liquids. *ChemComm* **2017**, *53*, 1214-1224.
32. Haddad, J.; Pontoni, D.; Murphy, B. M.; Festersen, S.; Runge, B.; Magnussen, O. M.; Steinruck, H.-G.; Reichert, H.; Ocko, B. M.; Deutsch, M., Surface structure evolution in a homologous series of ionic liquids. *Proc. Nat. Acad. Sci. USA* **2018**, *115*, E1101-E1107.
33. Anareddy, R. S.; Shaw, S. K., Long-range ordering of ionic liquid fluid films. *Langmuir* **2016**, *32*, 5147-5154.
34. Anareddy, R. S.; Shaw, S. K., Developing distinct chemical environments in ionic liquid films. *J. Phys. Chem. C* **2018**, *122*, 19731-19737.
35. Lucio, A. J.; Shaw, S. K.; Zhang, J.; Bond, A. M., Large-amplitude Fourier-transformed AC voltammetric study of the capacitive electrochemical behavior of the 1-butyl-3-methylimidazolium tetrafluoroborate-polycrystalline gold electrode interface. *J. Phys. Chem. C* **2017**, *121*, 12136-12147.
36. Jarosova, R.; Swain, G. M., Rapid preparation of room temperature ionic liquids with low water content as characterized with ta-C:N electrode. *J. Electrochem. Soc.* **2015**, *162*, H507-H511.
37. Hay, C. E.; Marken, F.; Blanchard, G. J., Detection and characterization of liquid|solid and liquid|liquid|solid interfacial gradients of water nano-droplets in wet N-octyl-2-pyrrolidone. *Langmuir* **2014**, *30*, 9951-9961.
38. Rumble, C. A.; Kaintz, A.; Yadav, S. K.; Conway, B.; Araque, J. C.; Baker, G. A.; Margulis, C.; Maroncelli, M., Rotational dynamics in ionic liquids from NMR relaxation experiments and simulations: Benzene and 1-ethyl-3-methylimidazolium. *J. Phys. Chem. B* **2016**, *120*, 9450-9467.
39. Zhang, X. X.; Liang, M.; Ernsting, N. P.; Maroncelli, M., Conductivity and solvation dynamics in ionic liquids. *J. Phys. Chem. Lett.* **2013**, *4*, 1205-1210.
40. Zhang, X. X.; Liang, M.; Ernsting, N. P.; Maroncelli, M., Complete solvation response of coumarin 153 in ionic liquids. *J. Phys. Chem. B* **2013**, *117*, 4291-4304.

41. Roy, D.; Maroncelli, M., Simulations of solvation and solvation dynamics in an idealized ionic liquid model. *J. Phys. Chem. B* **2012**, *116*, 5951-5970.
42. Wulf, A.; Ludwig, R.; Sasisanker, P.; Weingartner, H., Molecular reorientation in ionic liquids: A comparative dielectric and magnetic relaxation study. *Chem. Phys. Lett.* **2007**, *439*, 323-326.
43. Prabhu, S. R.; Dutt, G. B., Rotational diffusion of charged and nondipolar solutes in ionic liquid-organic solvent mixtures: Evidence for stronger specific solvent-solute interactions in presence of organic solvent. *J. Phys. Chem. B* **2015**, *119*, 10720-10726.
44. Guo, J.; Mahurin, S. M.; Baker, G. A.; Hillesheim, P. C.; Dai, S.; Shaw, R. W., Influence of solute charge and pyrrolidinium ionic liquid alkyl chain length on probe rotational reorientation dynamics. *J. Phys. Chem. B* **2014**, *118*, 1088-1096.
45. Khara, D. C.; Samanta, A., Rotational dynamics of positively and negatively charged solutes in ionic liquid and viscous molecular solvent studied by time-resolved fluorescence anisotropy measurements. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7671-7677.
46. Karve, L.; Dutt, G. B., Rotational diffusion of neutral and charged solutes in ionic liquids: Is solute reorientation influenced by the nature of the cation? *J. Phys. Chem. B* **2011**, *115*, 725-729.
47. Gangamallaiiah, V.; Dutt, G. B., Rotational diffusion of nonpolar and ionic solutes in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides: Is solute rotation always influenced by the length of the alkyl chain on the imidazolium cation? *J. Phys. Chem. B* **2012**, *116*, 12819-12825.
48. Patra, S.; Samanta, A., Microheterogeneity of some imidazolium ionic liquids as revealed by fluorescence correlation spectroscopy and lifetime studies. *J. Phys. Chem. B* **2012**, *116*, 12275-12283.
49. Majhi, D.; Sarkar, M., Probing the microscopic structural organization of neat ionic liquids (ILs) and ionic liquid-based gels through resonance energy transfer (RET) studies. *Phys. Chem. Chem. Phys.* **2017**, *19*, 23194-23203.
50. Chuang, T. J.; Eisinger, K. B., Theory of fluorescence depolarization by anisotropic rotational diffusion. *J. Chem. Phys.* **1972**, *57* (12), 5094-5097.
51. Debye, P., *Polar Molecules* Chemical Catalog Co.: New York 1929; p 84.
52. Edward, J. T., Molecular volumes and the Stokes-Einstein equation. *J. Chem. Ed.* **1970**, *47* (4), 261-270.
53. Favro, D. L., Theory of the rotational Brownian motion of a free rigid body. *Phys. Rev.* **1960**, *119* (1), 53-62.
54. Hu, C.-M.; Zwanzig, R., Rotational friction coefficients for spheroids with the slipping boundary condition. *J. Chem. Phys.* **1974**, *60* (11), 4354-4357.

55. Perrin, F., Mouvement brownien d'un ellipsoïde - I. Dispersion diélectrique pour des molécules ellipsoïdales. *J. Phys. Radium* **1934**, 5, 497.
56. Tao, T., Time-dependent fluorescence depolarization and Brownian rotational diffusion coefficients of macromolecules. *Biopol.* **1969**, 8, 609-632.
57. Blanchard, G. J., Picosecond spectroscopic measurement of a solvent dependent change of rotational diffusion rotor shape. *J. Chem. Phys.* **1987**, 87 (12), 6802-6808.
58. Blanchard, G. J.; Cihal, C. A., Orientational relaxation dynamics of oxazine 118 and resorufin in the butanols - valence-dependent and state-dependent solvation effects *J. Phys. Chem.* **1988**, 92 (21), 5950-5954.
59. Rasimas, J. P.; Blanchard, G. J., A time-resolved spectroscopic study of solution phase ionic exchange: Resorufin in binary butanol solutions. *J. Phys. Chem.* **1996**, 100, 11526-11533.
60. Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M., Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg. Chem.* **1996**, 35, 1168-1178.
61. Yu, G.; Zhao, D.; Wen, L.; Yang, S.; Chen, X., Viscosity of ionic liquids: Database, observation and quantitative structure-property relationship analysis. *AIChE J.* **2012**, 58, 2885-2899.
62. Diogo, J. C. F.; Caetano, F. J. P.; Fareleira, J. M. N. A.; Wakeham, W. A., Viscosity measurements on ionic liquids: A cautionary tale. *Int. J. Thermophys.* **2014**, 35, 1615-1635.
63. Penalber, C. Y.; Baker, G. A.; Baldelli, S., Sum frequency generation spectroscopy of imidazolium-based ionic liquids with cyano-functionalized anions at the solid salt-liquid interface. *J. Phys. Chem. B* **2013**, 117, 5939-5949.
64. Kaintz, A.; Baker, G.; Benesi, A.; Maroncelli, M., Solute diffusion in ionic liquids, NMR measurements and comparisons to conventional solvents. *J. Phys. Chem. B* **2013**, 117, 11697-11708.
65. Liang, M.; Kaintz, A.; Baker, G. A.; Maroncelli, M., Bimolecular electron transfer in ionic liquids: Are reaction rates anomalously high? *J. Phys. Chem. B* **2012**, 116, 1370-1384.
66. Longhi, M.; Arnaboldi, S.; Husanu, E.; Grecchi, S.; Buzzi, I. F.; Cirilli, R.; Rizzo, S.; Chiappe, C.; Mussini, P. R.; Guazzelli, L., A family of chiral ionic liquids from the natural pool: Relationships between structure and functional properties and electrochemical enantiodiscrimination tests. *Electrochim. Acta* **2019**, 298, 194-209.
67. Rizzo, S.; Arnaboldi, S.; Cirilli, R.; Gennaro, A.; Isse, A. A.; Sanniccolo, F.; Mussini, P. R., An "inherently chiral" 1,1'-bibenzimidazolium additive for enantioselective voltammetry in ionic liquid media. *Electrochem. Comm.* **2018**, 89, 57-61.

68. Rizzo, S.; Arnaboldi, S.; Mihali, V.; Cirilli, R.; Forni, A.; Gennaro, A.; Isse, A. A.; Pierini, M.; Mussini, P. R.; Sannicolo, F., "Inherently chiral" ionic liquid media: Effective chiral electroanalysis on achiral electrodes. *Angew. Chem.* **2017**, *56*, 2079-2082.
69. Arnaboldi, S.; Cirilli, R.; Forni, A.; Gennaro, A.; Isse, A. A.; Mihali, V.; Mussini, P. R.; Pierini, M.; Rizzo, S.; Sannicolo, F., Electrochemistry and chirality in bibenzimidazole systems. *Electrochim. Acta* **2015**, *179*, 250-262.

CHAPTER 3. Characterizing the Structure-Dependence of the Induced Free Charge Density Gradient in Imidazolium and Pyrrolidinium Ionic Liquids

3. 1 Introduction

Room temperature ionic liquids (RTILs) are salts that exist in liquid state at room temperature.¹ They typically consist of large organic cations of low symmetry and either organic or inorganic anions.² RTILs have a wide range of applications, including their use as substitutes for conventional solvents in some organic syntheses because of their low vapor pressure and high thermal stability.³⁻⁴ RTILs have been used to dissolve biopolymers,⁵⁻⁶ and as green reaction media for synthesis and catalysis processes.⁷⁻⁹ RTILs can also be used as lubricants, dispersing agents and antistatic agents.¹⁰⁻¹² RTILs have also found application in supercapacitors, batteries and fuel cells, improving the energy density of these devices.¹³⁻¹⁶

Despite their wide range of applications, there remain questions regarding fundamental issues such as the extent of dissociation, exchange dynamics and the existence of organization in RTILs that extends over length scales well beyond that which are characteristic of liquid solvents.¹⁷⁻²⁹ Our group has investigated the existence of a free charge density gradient (ρ_f) in RTILs induced by support surface charge.^{17, 30-33} We have demonstrated the existence of ρ_f in several 1-alkyl-3-methylimidazolium RTILs, with a characteristic persistence length of ca. 50 μm .^{30, 32} The sign of the gradient can be controlled by the polarity of the surface charge of the surface in contact with the RTIL.³¹ The magnitude and spatial extent of ρ_f depends on the identity of RTIL cation and anion as well as the support surface charge density.³² The gradient ρ_f is not known to exist over distances beyond the electric double layer in ionic solutions. In order for ρ_f to exist in RTILs, individual charged species must be screened sufficiently to prevent efficient recombination due to Coulombic forces and/or charge mobility of discrete ions must be characterized by low mobility. The work we have performed to date has focused on imidazolium-based RTILs and in that work we have evaluated the dependence of ρ_f on the identity of the anion

and on the imidazolium aliphatic chain length. We have not, however, investigated RTILs that use other cations, and that is the purpose of the work we report here.

Another widely used class of RTILs are formed using 1-alkyl-1-methylpyrrolidinium cations. While the pyrrolidinium cation bears passing resemblance to the imidazolium cation (Fig. 1), it's lack of unsaturations provides the opportunity to evaluate the role that unsaturations play in the ability to support ρ_f . This is a significant question because the quantity ρ_f is related to the polarizability of the medium, and the role of the imidazolium cation in determining the RTIL polarizability is not known. It is known that changing the alkyl chain length of the RTIL cation can alter the degree and nature of ion pairing in RTILs,³⁴ a factor that influences their physicochemical properties such as density, thermal stability, ionic conductivity, hydrophobicity and viscosity.³⁵⁻³⁸ We have found that ρ_f depends on imidazolium cation aliphatic chain length.³² We expect that the alkyl chain length will also influence the magnitude and spatial extent of ρ_f in pyrrolidinium ionic liquids.

To characterize ρ_f , we measure the fluorescence anisotropy decay of a trace cationic chromophore as a function of distance from an indium doped tin oxide (ITO) support surface to probe ρ_f in the RTIL. We do not vary the surface charge density of ITO, but have chosen this material because it is known to carry a positive surface charge for pH values below six.³⁹ We characterize ρ_f for three different pyrrolidinium ionic liquids and compare the results to those seen for imidazolium ionic liquids. The pyrrolidinium RTILs we use are 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPyr⁺TFSI⁻), 1-hexyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (HMPyr⁺TFSI⁻), and 1-octyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (OMPyr⁺TFSI⁻). The imidazolium RTILs we use are 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM⁺TFSI⁻

) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM⁺TFSI⁻) (Figure 3.

1). Understanding how ρ_f depends on RTIL constituent identity will aid in understanding the molecular properties that influence the ability to support a charge density gradient over macroscopic length scales.

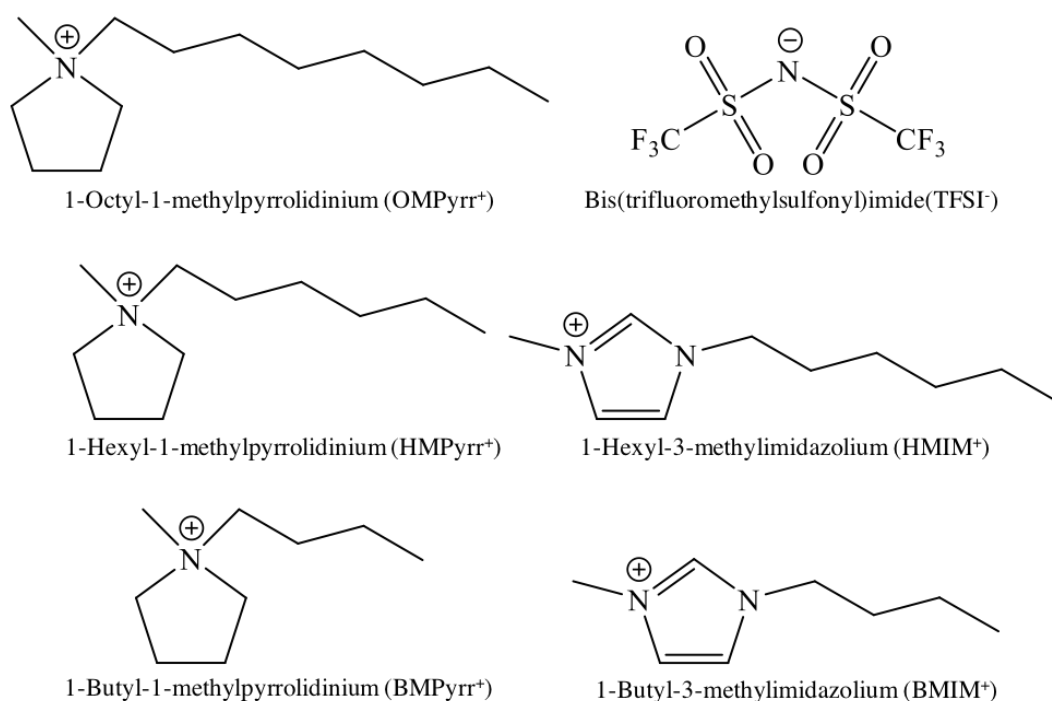


Figure 3. 1 Structures of the RTIL constituents used in this work.

3. 2 Experimental Section

3. 2. 1 Materials

The pyrrolidinium ionic liquids BMPyrr⁺TFSI⁻, HMPyrr⁺TFSI⁻ and OMPyrr⁺TFSI⁻ are synthesized following methods reported earlier,⁴⁰⁻⁴¹ with slight modifications. The preparation of BMPyrr⁺Br⁻ and its subsequent conversion to the TFSI⁻ salt are described below. The two remaining pyrrolidinium RTILs are prepared by parallel means using the appropriate bromoalkanes.

The synthesis of BMPyrr⁺Br⁻ begins by combining 50 mL of ethyl acetate with 15.93 g (0.187 mol) of 1-methylpyrrolidine in a dry 250-mL round-bottom flask. This solution is cooled

in an ice water bath and, once cooled, a small molar excess (30.76 g, 1.2 equiv., 0.225 mol) of freshly-distilled 1-bromobutane is added dropwise over the course of 30 min by addition funnel with magnetic stirring under flowing N_2 . Following addition of 1-bromobutane, the reaction mixture is removed from the ice bath and stirred overnight at room temperature followed by additional heating at 60 °C for 24 h. After cooling to room temperature, the resulting white to off-white solid product is filtered on a cooled water-jacketed medium sintered glass frit and washed several times with cold ethyl acetate (5×20 mL). Residual solvent is removed by rotary evaporation and, if the product is not pristinely white, the product is further recrystallized from acetonitrile or ethyl acetate and dried under vacuum overnight to obtain a white powder of $BMPyr^+Br^-$ in 85-90% yield.

To perform anion metathesis, 35.43 g (0.159 mol) of $BMPyr^+Br^-$ is dissolved in 70 mL water in a 250-mL round-bottom flask. Rapid addition of a solution comprising 50.36 g (1.1 eq., 0.175 mol) of Li^+TFSI^- dissolved in 70 mL of water resulted in almost immediate biphasic formation. After vigorous stirring (300-400 rpm) overnight, the stirring is discontinued. After the mixture has been quiescent for at least 1 h, the upper aqueous layer is removed and discarded and the lower RTIL layer is rinsed several times with distilled water (5×50 mL) to remove the water-soluble LiBr byproduct. The final product is dried by rotary evaporation for at least 6 h at 60 °C to obtain $BMPyr^+TFSI^-$ as a colorless liquid (yield: 85-93%). The remaining pyrrolidinium RTILs are prepared similarly.

The imidazolium ionic liquids $BMIM^+TFSI^-$ ($\geq 98\%$) and $HMIM^+TFSI^-$ ($\geq 98\%$) are purchased from Sigma-Aldrich. All RTILs are purified as detailed below before measurements. Activated charcoal (powder, -100 particle size, Sigma-Aldrich) and isopropyl alcohol (99.50%, Macron Fine Chemicals) are used as received. The stock chromophore solution (*ca.* 5×10^{-4} M) of

cresyl violet perchlorate (CV^+ , Eastman) is prepared by dissolution of the chromophore in ethanol ($\geq 99.5\%$, Sigma-Aldrich). Water is obtained from a Milli-Q filtration system (Millipore). Indium doped tin oxide (ITO) coated glass slides (10 Ohm/sq, Nanocs) and silicone rubber sheet (MSC Direct) are cleaned as described below prior to use.

3. 2. 2 RTIL Sample Cell Preparation

The sample cell preparation has been described in detail elsewhere.³⁰ The closed sample cell confines the RTIL between two glass slides coated by ITO. ITO-coated slides are cleaned by sonication in detergent (Sparkleen 1, Fisher) solution, Milli-Q water, then isopropyl alcohol for 15 min at each step. The cleaned ITO coated slides are removed from isopropyl alcohol and dried for 30 min at 200 °C. The ITO coated slides are cooled to room temperature in a desiccator and then placed in a UV/ozone cleaner for 20 min. The cell spacer (O-ring, *ca.* 1 mm thick) is cut from a silicone rubber sheet, which is cleaned by sonication in detergent solution and Milli-Q water for 15 min each, then dried by N_2 flow.

3. 3. 3 Purification of RTILs

The method of RTIL purification has been reported previously.⁴² The RTIL is stored over activated carbon for three days. Then, the RTIL is filtered by syringe filter with a Durapore® poly-(vinylidene difluoride) (PVDF) membrane (0.22 μm sterile filtration, Millex) to separate the RTIL from the activated carbon. The RTIL is then heated for 3 h at 90 °C while stirring and purging with ultrapure Ar (99.9995%, Linde) to minimize water in the RTIL. The water content in purified RTILs is *ca.* 50 ppm, measured by Karl Fischer titration (Mettler-Toledo C10S).

3. 3. 4 Preparation of CV^+ -RTIL Solutions

The CV^+ -RTIL solution is prepared by transferring 100 μL of the CV^+ stock solution (*ca.* 5×10^{-4} M) into a vial and placing it in an oven for 3 h at 150 °C to evaporate the solvent ethanol.

After removal from the oven and cooling in a desiccator, 1000 μL purified RTIL is added into the vial to dissolve CV^+ . The CV^+ -RTIL solution (*ca.* 5×10^{-5} M) is then stirred overnight before use. To minimize water contamination, all glassware is dried for at least 24 h at 150 $^{\circ}\text{C}$ before use.

3. 3. 5 Characterization of the Charge Density Gradient in RTILs

The fluorescence anisotropy decay of the cationic chromophore CV^+ is measured as a function of distance from the ITO support surface to probe the induced free charge density gradient (ρ_f) in the RTILs. A detailed description of the confocal scanning TCSPC imaging system have been reported elsewhere.^{30, 43} We mechanically control the distance between the inverted confocal microscope objective and sample stage to achieve depth resolution (<1 μm). The time-resolved emission intensity decays are acquired by time-correlated single photon counting (TCSPC) electronics (Becker & Hickl) and the laser light source is a cavity dumped synchronously pumped dye laser (Coherent 701-3, Pyrromethene 567 dye, 575 nm, 5 ps pulses, 4 MHz repetition rate, <1 mW average power at the sample) excited by the second harmonic output (532 nm, 12 ps pulse at 80 MHz repetition rate, 2.5 W average power) of a passively mode-locked Nd:YVO₄ laser (Spectra Physics Vanguard). The instrument response function of this system is <100 ps.

3. 3 Results and Discussion

The purpose of this work is to characterize the dependence of ρ_f on the molecular structure of the RTIL cation. We have reported on the dependence of ρ_f on the aliphatic chain length of the imidazolium cation and on the identity of the anion.³² We characterize ρ_f in three different pyrrolidinium ionic liquids, and compare those results to ρ_f for imidazolium ionic liquids. All of these RTILs have the same anion (TFSI⁻). We acquire polarized time-resolved emission intensity data using the TCSPC instrumentation. The emission transients polarized parallel ($I_{\parallel}(t)$) and perpendicular ($I_{\perp}(t)$) to the excitation polarization are used to construct the induced orientational

anisotropy function, $R(t)$ (Eq. 3. 1).

$$R(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} = R(0) \exp(-t/\tau_{OR}) \quad [3. 1]$$

For all of the data reported here, $R(t)$ decays as a single exponential with a time constant, τ_{OR} . The information content of $R(t)$ is well established.⁴⁴⁻⁵¹ The zero-time anisotropy, $R(0)$ is a gauge of the angle between the absorbing and emitting transition dipole moments, and the anisotropy decay time constant, τ_{OR} , is related to system properties through the modified Debye-Stokes-Einstein equation (Eq. 3. 2).⁴⁵

$$\tau_{OR} = 6D^{-1} = \frac{\eta Vf}{k_B TS} \quad [3. 2]$$

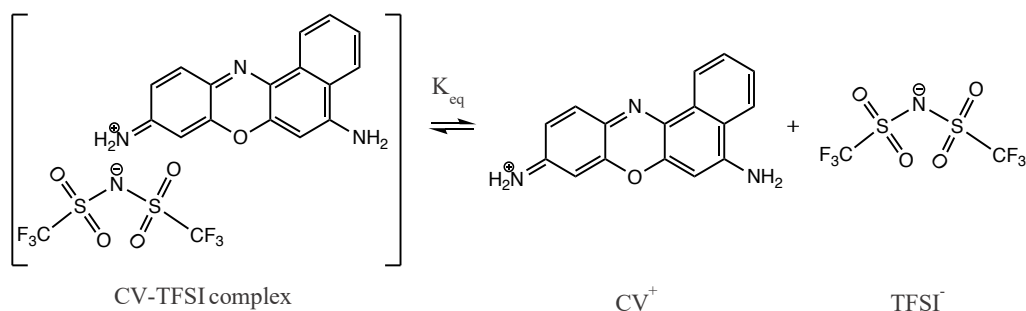
Where η is the viscosity of the medium in which the chromophore is reorienting, V is the hydrodynamic volume of the rotating entity,⁴⁶ f is the frictional boundary condition term⁴⁸ and S is the shape factor to account for the ellipsoidal shape of the rotating entity.⁵⁰ We have established that the free charge density gradient, ρ_f , is related to the spatial variation in τ_{OR} through the volume of the reorienting entity, which is the weighted average of the free and complexed chromophore (Eqs. 3. 3 and 3. 4),

$$\nabla \cdot \tau_{OR} = \left(\frac{\eta f}{k_B TS} \right) \nabla \cdot V = k \nabla \cdot V \quad [3. 3]$$

$$\nabla \cdot V = V_{free} \nabla \cdot X_{free} + V_{complex} \nabla \cdot X_{complex} \quad [3. 4]$$

In RTILs, charged chromophores form complexes with the dissociated RTIL constituents of opposite charge.^{30, 32} The position-dependent change in the measured reorientation time constant ($\nabla \cdot \tau_{OR}$) is a consequence of a concentration gradient of RTIL ionic (dissociated) species that results from the presence of the surface charge on the support. This gradient is manifested as a gradient

in hydrodynamic volume of the rotating entity ($\nabla \cdot V$). Thus, $\nabla \cdot \tau_{OR}$ reflects the induced free charge density gradient in RTILs (Scheme 3. 1).



Scheme 3. 1 Scheme of the dissociation equilibria of chromophore-RTIL anion complex.

Because the RTILs used here have a common anion, TFSI⁻, the same chromophore-RTIL anion complex is formed in all of the RTILs examined. The identity of the RTILs constituents determine the viscosity of the medium and K_{eq} (Scheme 3. 1), as well as the extent of RTIL dissociation.³⁴ The concentration of dissociated TFSI⁻ will determine the amount of free CV⁺ and complexed CV-TFSI in the system. The magnitude of ρ_f can be evaluated by measuring the variation of [TFSI⁻] with the distance from the charged support. The depth-dependent τ_{OR} data for CV⁺ in BMPyrr⁺TFSI⁻, HMPyrr⁺TFSI⁻ and OMPyrr⁺TFSI⁻ is presented in Figure 3. 2, and these results are compared to the same information for BMIM⁺TFSI⁻ and HMIM⁺TFSI⁻. As shown in Figure 3. 2, the observed ρ_f does depend on the aliphatic chain length of both the pyrrolidinium and imidazolium cations.

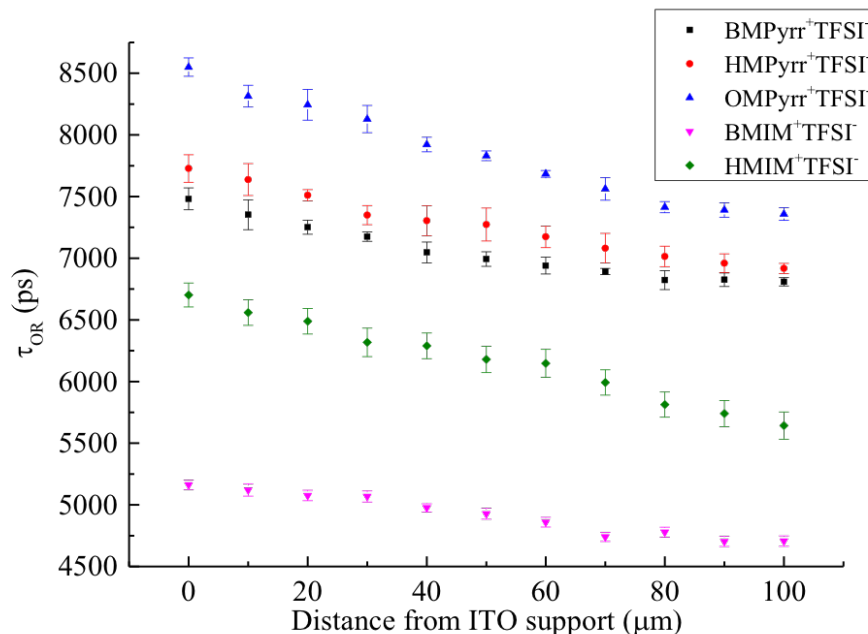


Figure 3. 2 Cresyl violet anisotropy decay time constants (τ_{OR}) as a function of RTIL cation alkyl chain length, with the same anion. Black squares represent for BMPyrr⁺TFSI⁻, red circles are HMPyrr⁺TFSI⁻, blue triangles are OMPyrr⁺TFSI⁻, purple inverted triangles are BMIM⁺TFSI⁻, and green diamonds are HMIM⁺TFSI⁻. For all data points, $n=3$.

While the data shown in Figure 3. 2 demonstrate the presence of ρ_f , direct comparison of the magnitude and persistence length of ρ_f is more facile when the data are normalized. We use the quantity $\Delta\tau_{OR}/\tau_{OR}$ to facilitate the comparison, where the denominator term is taken to be τ_{OR} in the bulk RTIL, where ρ_f has decayed fully. As shown in Figure 3. 3a, $\Delta\tau_{OR}/\tau_{OR}$ is larger in the pyrrolidinium RTILs with longer alkyl chain (OMPyrr⁺TFSI⁻ > HMPyrr⁺TFSI⁻ > BMPyrr⁺TFSI⁻). The analogous dependence is also seen in imidazolium ionic liquids (Figure 3. 3b). Comparison of the pyrrolidinium and imidazolium RTILs with same cation aliphatic chain length (Figure 3. 4) shows that $\Delta\tau_{OR}/\tau_{OR}$ is indistinguishable in magnitude and persistence length for BMPyrr⁺TFSI⁻ and BMIM⁺TFSI⁻ (Figure 3. 4a) but there appears to be a slight difference in the slope of the decay of $\Delta\tau_{OR}/\tau_{OR}$ for HMPyrr⁺TFSI⁻ and HMIM⁺TFSI⁻ (Figure 3. 4b). We note that for all data points in Figure 3. 4b, the values of $\Delta\tau_{OR}/\tau_{OR}$ for a given distance, d , are the same to within the experimental uncertainty.

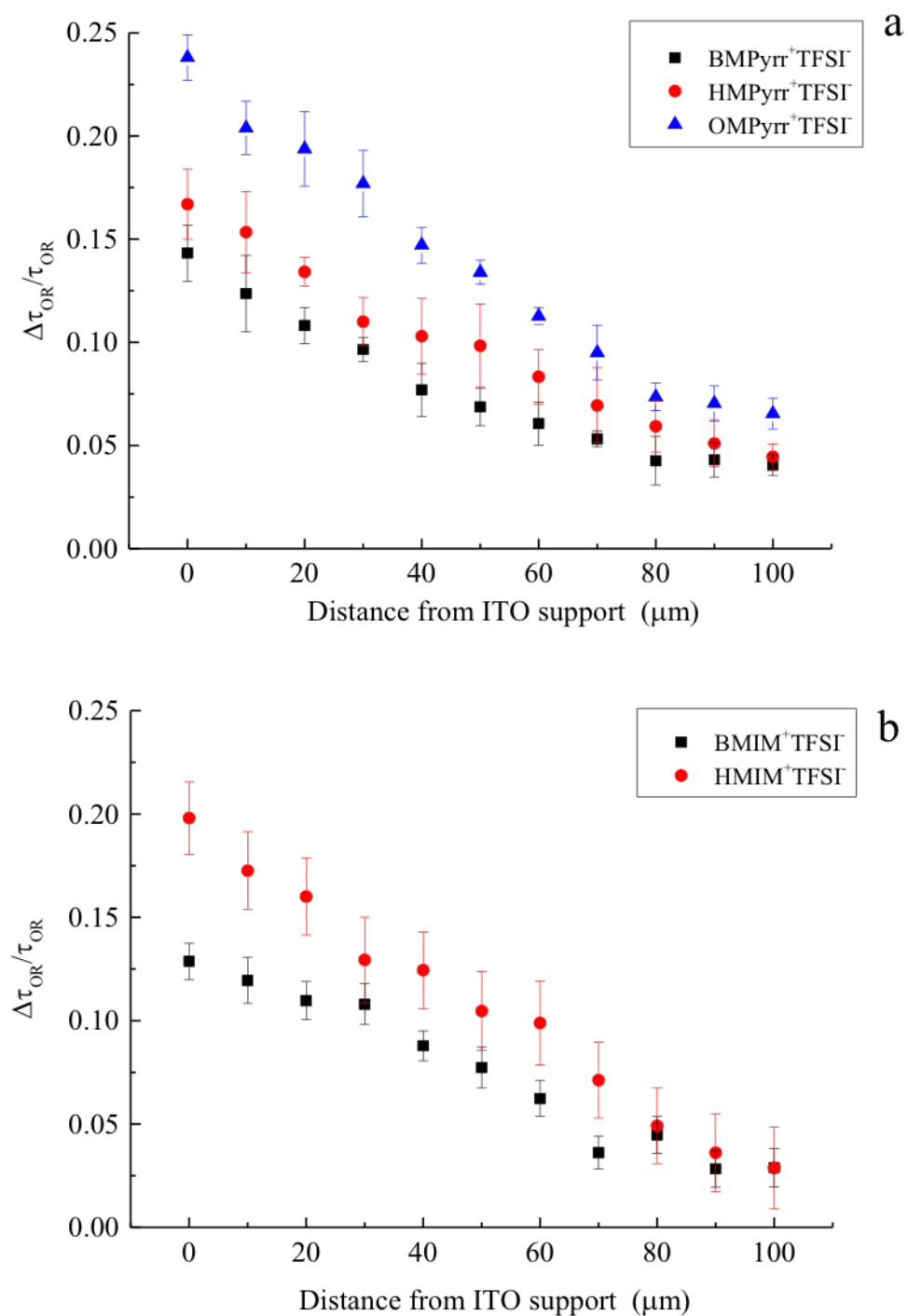


Figure 3. 3 Normalized anisotropy decay time gradient ($\Delta\tau_{OR}/\tau_{OR}$) of Cresyl violet, as a function of distance from ITO support and RTIL cation alkyl chain length. (a) Black squares represent for BMPyrr⁺TFSI⁻, red circles are HMPyrr⁺TFSI⁻ and blue triangles are OMPyrr⁺TFSI⁻. (b) Black squares are BMIM⁺TFSI⁻ and red circles are HMIM⁺TFSI⁻. For all data points, n=3.

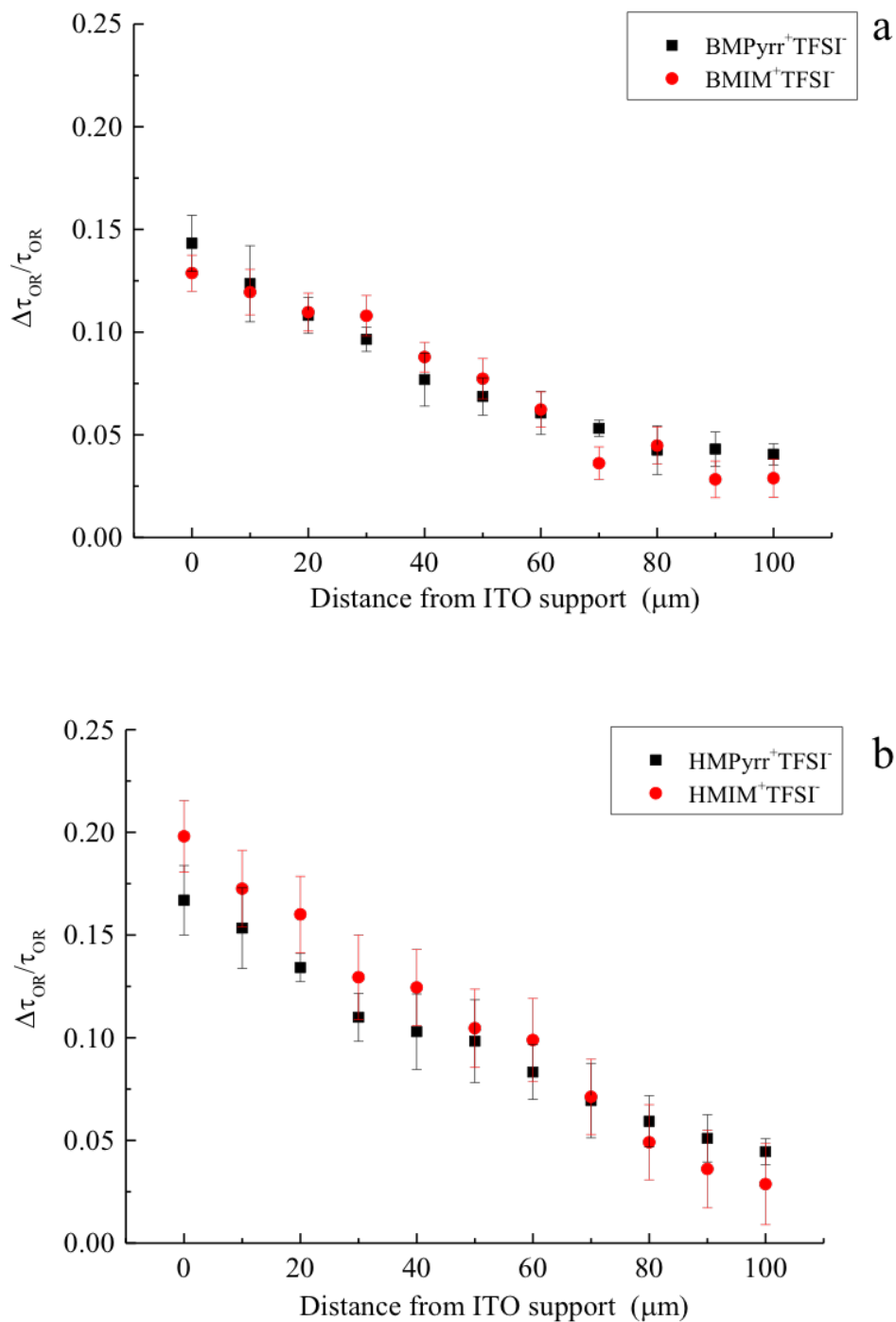


Figure 3. 4 Comparison of the normalized anisotropy decay time gradient ($\Delta\tau_{OR}/\tau_{OR}$) of Cresyl violet in pyrrolidinium and imidazolium RTILs with same cation alkyl chain length. (a) Black squares represent for BMPyr⁺TFSI⁻ and red circles are BMIM⁺TFSI⁻. (b) Black squares are HMPyr⁺TFSI⁻ and red circles are HMIM⁺TFSI⁻. For all data points, n=3.

From the data presented in Figure 3. 3 we can determine the magnitude of ρ_f .³² To characterize the gradient, we need to establish the difference in amount of CV⁺ that is complexed at $d = 0$ and the amount complexed at distances d where the $\rho_f = 0$. Measuring such quantities directly is not feasible, but they can be estimated by the change in hydrodynamic volume of the reorienting entity. The calculation of hydrodynamic volume has been demonstrated to be reliable, and from the volume change data (Eq. 3. 5) and an estimate of K_{eq} for the CV⁺-TFSI⁻ complex, we can relate the concentration gradient in the RTIL anion over the decay of ρ_f (Eq. 3. 6). We define a term ξ (Eq. 3. 5) for this purpose. V_{RI} is the hydrodynamic volume of the RTIL ion which forms complex with the chromophore. In this work, $V_{RI} = V_{(TFSI^-)} = 169 \text{ \AA}^3$.⁴⁶

$$\frac{\Delta\tau_{OR}}{\tau_{OR}} = \frac{\Delta V}{V} = \xi \left(\frac{X_{free}^{0\mu m} \cdot X_{free}^{100\mu m} \cdot V_{RI}}{V_{complex} - X_{free}^{100\mu m} \cdot V_{RI}} \right) \quad [3. 5]$$

$$\xi = \left| K_{eq}^{-1} ([A^-]_{0\mu m} - [A^-]_{100\mu m}) \right| = \left| \frac{1 - X_{free}^{0\mu m}}{X_{free}^{0\mu m}} - \frac{1 - X_{free}^{100\mu m}}{X_{free}^{100\mu m}} \right| = \left| \frac{X_{free}^{100\mu m} - X_{free}^{0\mu m}}{X_{free}^{0\mu m} \cdot X_{free}^{100\mu m}} \right| \quad [3. 6]$$

$$\rho_f(x) = \rho_f(0) \exp(-x/d) \quad [3. 7]$$

The value of ξ reflects the concentration gradient in the RTIL anion, and we report our findings in Table 3. 1. Several important points emerge from these data. The first is the point is that ρ_f is seen to depend on the RTIL cation aliphatic chain length, but not on the identity of the cationic headgroups (pyrrolidinium and imidazolium). In all cases, the gradient is modest. While the values of ρ_f do not match precisely those that were reported previously, this is not a surprising result. The magnitude of the gradient necessarily depends on the surface charge density of the support, a quantity that can vary from lot-to-lot for the ITO deposited on the support surface. The

results reported here, however, are all acquired using the same lot of ITO-coated glass and are thus comparable. The significance of these results is that ρ_f appears to be comparatively insensitive to the identity of the cation headgroup for the two species reported here, but ρ_f is seen to depend more sensitively on cation aliphatic chain length. Given that aliphatic chains are characterized by modest dielectric constants, it would appear that the molecular-scale organization for these systems, which is known to exist,⁵²⁻⁵⁶ can influence the ability to support a free charge density gradient. An important next step will be to establish an understanding of ρ_f in the context of the molecular scale and longer-range ordering seen in RTILs.

Table 3. 1 Magnitude and persistence length of the induced free charge density gradient (ρ_f) in imidazolium and pyrrolidinium RTILs.

RTIL	η (cP)	$\Delta\tau_{OR}/\tau_{OR}$	ξ	ΔC (mol/L)	ρ_f (($\mu\text{C}/\text{cm}^3$)/ μm)	d (μm)
OMPyrr ⁺ TFSI ⁻	130 ³⁷	0.24 $\pm$ 0.02	0.59	(2.34 $\pm$ 0.19) $\times 10^{-5}$	23 $\pm$ 2	76 $\pm$ 3
HMPyrr ⁺ TFSI ⁻	98 ⁵⁷	0.17 $\pm$ 0.02	0.39	(1.58 $\pm$ 0.34) $\times 10^{-5}$	15 $\pm$ 3	75 $\pm$ 1
HMIM ⁺ TFSI ⁻	81 ⁵⁸	0.20 $\pm$ 0.02	0.47	(1.82 $\pm$ 0.28) $\times 10^{-5}$	18 $\pm$ 3	66 $\pm$ 6
BMPyrr ⁺ TFSI ⁻	78 ³⁷	0.14 $\pm$ 0.02	0.31	(1.20 $\pm$ 0.16) $\times 10^{-5}$	12 $\pm$ 1	74 $\pm$ 3
BMIM ⁺ TFSI ⁻	52 ⁵⁹	0.13 $\pm$ 0.01	0.30	(1.30 $\pm$ 0.16) $\times 10^{-5}$	13 $\pm$ 1	69 $\pm$ 5

We also evaluate the spatial extent of ρ_f . The spatial dependence is given by Eq. 3. 7,³³ where d is the e^{-1} characteristic persistence length of ρ_f . By fitting the experimental ρ_f to this function, we can obtain the value of d . The data in Table 3. 1 also show that the persistence length of ρ_f is the same to within the experimental uncertainty for all the RTIL structures reported here. The apparent structural independence of d suggests a physical rather than a chemical basis for determining ρ_f . For dipolar systems the presence of an E field can serve to orient the dipoles and the interaction between the E field and the dipolar constituents is described in terms of induced

polarization. For systems that are not strictly dielectric media, but possess some density of carriers, the spatial extent of the induced polarization will be attenuated. For RTIL systems characterized by similar extents of dissociation,³⁴ one would thus expect the distance over which the induced polarization would persist to be similar, as is the case for the pyrrolidinium and imidazolium RTILs.

3.4 Conclusions

We have examined the cation structure-dependence of the induced free charge density gradient (ρ_f) for pyrrolidinium and imidazolium RTILs. We find that the magnitude of ρ_f depends primarily on the cation aliphatic chain length and differs little with the identity of the charge-carrying cation headgroup. An implication of these findings is that local organization in the RTILs that is mediated by the nonpolar constituents of the cations plays a significant role in the ability of these systems to support a charge density gradient over macroscopic distances. Conversely, we find that the characteristic persistence length of ρ_f is similar for all RTILs examined here. This finding could be accounted for by the extent of RTIL dissociation, which is similar for the RTILs studied here. Taken collectively, these data provide additional insight into the physical and structural factors that are most important in determining ρ_f in RTILs.

REFERENCES

REFERENCES

1. Dean, P. M.; Pringle, J. M.; MacFarlane, D. R., Structural Analysis of Low Melting Organic Salts: Perspectives on Ionic Liquids. *Chem. Phys. Phys. Chem.* **2010**, *12*, 9144-1953.
2. Joshi, M. D.; Anderson, J. L., Recent Advances of Ionic Liquids in Separation Science and Mass Spectrometry. *RSC Advances* **2012**, *2*, 5470-5484.
3. Durga, G.; Mishra, A., *Ionic Liquids: Industrial Applications*. Wiley: 2016.
4. Rogers, R. D.; Seddon, K. R., Ionic Liquids - Solvents of the Future. *Science* **2003**, *302*, 792-793.
5. Garcia, H.; Ferriera, R.; Petkovic, M.; Ferguson, J. L.; Leitao, M. C.; Gunaratne, H. N.; Seddon, K. R.; Rebelo, L. P. N.; Periera, C. S., Dissolution of Cork Biopolymers in Biocompatible Ionic Liquids. *Green Chem.* **2010**, *12*, 367-369.
6. Wilpiszewska, K.; Szychaj, T., Ionic Liquids: Media for Starch Dissolution, Plasticization and Modification. *Carbohydr. Polym.* **2011**, *86*, 424-428.
7. Hallett, J. P.; Welton, T., Room Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. 2. *Chem. Rev.* **2011**, *111*, 3508-3576.
8. Vekariya, R. L., A Review of Ionic Liquids: Applications Towards Catalytic Organic Transformations. *J. Mol. Liq.* **2017**, *227*, 44-60.
9. Yadav, J. S.; Reddy, B. V. S.; Premalatha, K., 1-Butyl-3-methylimidazolium Tetrafluoroborate ([BMIM]BF₄) Ionic Liquid. A Novel and Recyclable Reaction Medium for the Synthesis of *vic*-Diamines. *Adv. Synth. Catal.* **2003**, *345*, 948-952.
10. Reeves, C. J.; Siddaiah, A.; Menezes, P. L., Tribological Study of Imidazolium and Phosphonium Ionic Liquid-Based Lubricants as Additives in Carboxylic Acid-Based Natural Oil: Advancements in Environmentally Friendly Lubricants. *J. Clean. Prod.* **2018**, *176*, 241-250.
11. Weyershausen, B.; Lehmann, K., Industrial Application of Ionic Liquids as Performance Additives. *Green Chem.* **2005**, *7*, 15-19.
12. Zhao, H., Innovative Applications of Ionic Liquids as "Green" Engineering Liquids. *Chem. Eng. Commun.* **2006**, *193*, 1660-1677.
13. Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B., *Ionic Liquid Materials for the Electrochemical Challenges of the Future*. World Scientific: 2010.
14. MacFarlane, D. R.; Tachikawa, N.; Forsyth, M.; Pringle, J. M.; Howlett, P. C.; Elliott, G. D.; Davis, J. H.; Watanabe, M.; Simon, P.; Angell, C. A., Energy Applications of Ionic Liquids. *Energ. Env. Sci.* **2014**, *7*, 232-250.

15. Qiu, B.; Lin, B.; Yan, F., Ionic Liquid/Poly (Ionic Liquid)-Based Electrolytes for Energy Devices. *Polym. Int.* **2013**, *62*, 335-337.
16. van Aken, K. L.; Beidaghi, M.; Gogotsi, Y., Formulation of Ionic Liquid Electrolyte to Expand the Voltage Window of Supercapacitors. *Angew. Chem. Int. Ed. Engl.* **2015**, *127*, 4888-4891.
17. Wang, Y.; Parvis, F.; Hossain, M. I.; Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G. J., Local and Long-Range Organization in Room Temperature Ionic Liquids. *Langmuir* **2021**, *37*, 605-615.
18. Anaredy, R. S.; Shaw, S. K., Long-range ordering of ionic liquid fluid films. *Langmuir* **2016**, *32*, 5147-5154.
19. Anaredy, R. S.; Shaw, S. K., Developing distinct chemical environments in ionic liquid films. *J. Phys. Chem. C* **2018**, *122*, 19731-19737.
20. Anaredy, R. S.; Shaw, S. K., Directing long-range molecular ordering in ionic liquid films: A tale of two interfaces. *J. Phys. Chem. C* **2019**, *123*, 8975-8982.
21. Baldelli, S., Interfacial structure of room-temperature ionic liquids at the solid-liquid interface as probed by sum frequency generation spectroscopy. *J. Phys. Chem. Lett.* **2013**, *4*, 244-252.
22. Gebbie, M. A.; Dobbs, H. A.; Valtiner, M.; Israelachvili, J. N., Long-range electrostatic screening in ionic liquids. *Proc. Nat. Acad. Sci. USA* **2015**, *112* (24), 7432-7437.
23. Gebbie, M. A.; Valtiner, M.; Banquy, X.; Fox, E. T.; Henderson, W. A.; Israelachvili, J. N., Ionic liquids behave as dilute electrolyte solutions. *Proc. Nat. Acad. Sci. USA* **2013**, *110* (24), 9674-9679.
24. Nishida, J.; Breen, J. P.; Wu, B.; Fayer, M. D., Extraordinary slowing of structural dynamics in thin films of a room temperature ionic liquid. *ACS Cent. Sci.* **2018**, *4*, 1065-1073.
25. Shin, J. Y.; Yamada, S. A.; Fayer, M. D., Dynamics of a room temperature ionic liquid in supported ionic liquid membranes vs the bulk liquid: 2D IR and polarized IR pump-probe experiments. *J. Am. Chem. Soc.* **2017**, *139*, 311-323.
26. Shin, J. Y.; Yamada, S. A.; Fayer, M. D., Carbon dioxide in a supported ionic liquid membrane: Structural and rotational dynamics measured with 2D IR and pump-probe experiments. *J. Am. Chem. Soc.* **2017**, *139*, 11222-11232.
27. Thomaz, J. E.; Bailey, H. E.; Fayer, M. D., The influence of mesoscopic confinement on the dynamics of imidazolium-based room temperature ionic liquids in polyether sulfone membranes. *J. Chem. Phys.* **2017**, *147*, 194502 1-11.
28. Wu, B.; Breen, J. P.; Fayer, M. D., Structural dynamics in ionic liquid thin films: The effect of cation chain length. *J. Phys. Chem. C* **2020**, *124*, 4179-4189.

29. Wu, B.; Breen, J. P.; Xing, X.; Fayer, M. D., Controlling the dynamics of ionic liquid thin films via multilayer surface functionalization. *J. Am. Chem. Soc.* **2020**, *142*, 9482-9492.
30. Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G. J., Charge-Induced Long-Range Order in a Room-Temperature Ionic Liquid. *Langmuir* **2016**, *32*, 9507-9512.
31. Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G. J., Modulation of an Induced Charge Density Gradient in the Room Temperature Ionic Liquid BMIM⁺BF₄⁻. *J. Phys. Chem. C* **2018**, *122*, 7361-7367.
32. Wang, Y.; Jarosova, R.; Swain, G. M.; Blanchard, G. J., Characterizing the Magnitude and Structure-Dependence of Free Charge Density Gradients in Room Temperature Ionic Liquids. *Langmuir* **2020**, *36*, 1152-1155.
33. Wang, Y.; Swain, G. M.; Blanchard, G. J., Charge-Induced Birefringence in a Room Temperature Ionic Liquid. *J. Phys. Chem. B* **2021**, *125*, 950-955.
34. Nordness, O.; Brennecke, J. F., Ion Dissociation in Ionic Liquids and Ionic Liquid Solutions. *Chem. Rev.* **2020**, *120*, 12873-12902.
35. Harris, K. R.; Woolf, L. A.; Kanakubo, M.; Ruther, T., Transport Properties of N-Butyl-N-Methylpyrrolidinium Bis (Trifluoromethylsulfonyl) Amide. *J. Chem. Eng. Data* **2011**, *56*, 4672-4685.
36. Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D., Characterization and Comparison of Hydrophilic and Hydrophobic Room Temperature Ionic Liquids Incorporating the Imidazolium Cation. *Green Chem.* **2001**, *3*, 156-164.
37. Salminen, J.; Papaiconomou, N.; Kumar, R. A.; Lee, J. M.; Kerr, J.; Newman, J.; Prausnitz, J. M., Physicochemical Properties and Toxicities of Hydrophobic Piperidinium and Pyrrolidinium Ionic Liquids. *Fluid Phase Equil.* **2007**, *261*, 421-426.
38. Tokuda, H.; Ishii, K.; Susan, M. A. B. H.; Tsuzuki, S.; Hayamizu, K.; Watanabe, M., Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 3. Variation of Cationic Structures. *J. Phys. Chem. B* **2006**, *110*, 2833-2839.
39. Peiris, T. A. N.; Senthilarasu, S.; Wijayantha, K. G. U., Enhanced performance of flexible-dye-sensitized solar cells: Electrodeposition of Mg(OH)₂ in a nanocrystalline TiO₂ electrode. *J. Phys. Chem. C* **2012**, *116*, 1211-1218.
40. Burrell, A. K.; Del Sesto, R. E.; Baker, S. N.; McCleskey, T. M.; Baker, G. A., The Large Scale Synthesis of Pure Imidazolium and Pyrrolidinium Ionic Liquids. *Green Chem.* **2007**, *9*, 449-454.
41. Baker, G. A.; Pandey, S.; Pandey, S.; Baker, S. N., A New Class of Cationic Surfactants Inspired by N-alkyl-N-methyl Pyrrolidinium Ionic Liquids. *Analyst* **2004**, *129*, 890-892.

42. Jarosova, R.; Swain, G. M., Rapid Preparation of Room Temperature Ionic Liquids with Low Water Content as Characterized by Ta-C:N Electrode. *J. Electrochem. Soc.* **2015**, *162*, H507-H511.
43. Hay, C. E.; Marken, F.; Blanchard, G. J., Detection and Characterization of Liquid|Solid and Liquid|Liquid|Solid Interfacial Gradients of Water Nano-Droplets in Wet N-Octyl-2-Pyrrolidone. *Langmuir* **2014**, *30*, 9951-9961.
44. Chuang, T. J.; Eiseenthal, K. B., Theory of Fluorescence Depolarization by Anisotropic Rotational Diffusion. *J. Chem. Phys.* **1972**, *57*, 5094-5097.
45. Debye, P. M., *Polar Molecules*. Chemical Catalog Co.: New York, 1929.
46. Edward, J. T., Molecular Volumes and the Stokes-Einstein Equation. *J. Chem. Ed.* **1970**, *47*, 261-270.
47. Favro, L. D., Theory of the Rotational Brownian Motion of a Free Rigid Body. *Phys.. Rev.* **1960**, *119*, 53-62.
48. Hu, C.-M.; Zwanzig, R., Rotational Friction Coefficients for Spheroids with the Slipping Boundary Condition. *J. Chem. Phys.* **1974**, *60*, 4354-4357.
49. Lakowicz, J. R., *Fluorescence Anisotropy*. Springer: Boston, MA, 1999.
50. Perrin, F., Mouvement Brownien D'un Ellipsoide. I. Dispersion Dielectrique Pour les Molecules Ellipsoidales. *J. Phys. Radium* **1934**, *5*, 497.
51. Tao, T., Time-Dependent Fluorescence Depolarization and Brownian Rotational Diffusion Coefficients of Macromolecules. *Biopolymers* **1969**, *8*, 609-632.
52. Schaffer, J.; Alber, M.; Korth, W.; Cokoja, M.; Jess, A., Ionic Liquids as Micellar Agents for Perrhenate-catalysed Olefin Epoxidation. *Chem. Eur.* **2017**, *2*, 11891-11898.
53. Triolo, A.; Russina, O.; Blief, H.-J.; Di Cola, E., Nanoscale Segregation in Room Temperature Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 4641-4644.
54. Dupont, J., On the Solid, Liquid and Solution Structural Organization of Imidazolium Ionic Liquids. *J. Braz. Chem. Soc.* **2004**, *15*, 341-350.
55. Santos, C. S.; Murthy, N. S.; Baker, G. A.; Castner Jr., E. W., Communication: X-Ray Scattering from Ionic Liquids with Pyrrolidinium Cations. *J. Chem. Phys.* **2011**, *134*, 121101 (1-4).
56. Annapureddy, H. V. R.; Kashyap, H. K.; De Biase, P. M.; Margulis, C. J., What is the Origin of the Prepeak in the X-Ray Scattering of Imidazolium-Based Room-Temperature Ionic Liquids? *J. Phys. Chem. B* **2010**, *114*, 16838-16846.

57. Morais, A. R. C.; Alaras, L. M.; Baek, D. L.; Fox, R. V.; Shiflett, M. B.; Scurto, A. M., Viscosity of the 1-Alkyl-1-Methylpyrrolidinium Bis (Trifluoromethylsulfonyl) Imide Ionic Liquids Saturated with Compressed CO₂. *J. Chem. Eng. Data* **2019**, *64*, 4658-4667.
58. Diogo, J. C. F.; Caetano, F. J. P.; Fareleira, J. M. N. A.; Wakeham, W. A., Viscosity Measurements on Ionic Liquids: A Cautionary Tale. *Int. J. Thermophys.* **2014**, *35*, 1615-1635.
59. Harris, K. R.; Kanakubo, M., Self-Diffusion, Velocity Cross-Correlation, Distinct Diffusion and Resistance Coefficients of the Ionic Liquid [BMIM][Tf₂N] at High Pressure. *Phys. Chem. Chem. Phys.* **2015**, *17*, 23977-23993.

CHAPTER 4. Charge-Induced Birefringence in a Room Temperature Ionic Liquid

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4. 1 Introduction

Room temperature ionic liquids (RTILs) have found wide application, but gaining a fundamental understanding of the forces, dynamics and molecular-scale organization within them that are responsible for their interesting properties remains to be achieved. This family of materials is typically composed of relatively large organic cations and either organic or inorganic anions.¹ RTILs are used as substitutes for conventional organic solvents and aqueous electrolytes in a wide range of applications,²⁻³ including as solvents for chemical syntheses,⁴⁻⁶ catalysis⁷⁻⁹ and separations,¹⁰⁻¹¹ and for energy storage in supercapacitors,¹²⁻¹⁴ batteries¹⁵⁻¹⁶ and fuel cells.¹⁷⁻¹⁹

From a more fundamental perspective, several groups have reported structural organization in RTILs, with the details and characteristic persistence length of the organization depending on the technique used.²⁰⁻³⁰ To date, there is no unifying model of the driving forces responsible for such organization. Our group has reported on the existence of a surface charge-induced free charge density gradient (ρ_f) with a spatial extent of *ca.* 50 μm .³¹⁻³⁴ We have demonstrated experimental control over the sign and magnitude of ρ_f through the charge density of the surface in contact with the RTIL.³² The magnitude and spatial extent of ρ_f depends on RTIL constituent structure.³⁴ The presence of such long-range organization in a fluid medium is unusual and requires a fuller understanding.

For a free charge density gradient to exist in a fluid medium, the individual charges must be screened from one another and/or their mobility must be sufficiently limited to make recombination inefficient. For RTILs, there is some ambiguity regarding the extent of dissociation of ion-paired species. Comparatively short-range force measurements indicate that the extent of dissociation is very small, while other treatments that consider the “ionicity” of the RTILs arrive at an estimate that is orders of magnitude different than what is obtained from force

measurements.^{24, 35} This issue is important to understanding the existence of a free charge density gradient in RTILs because it bears on the polarizability of these materials. Free ions (monopoles) exhibit very different polarizabilities than ion-paired (dipolar) species. In the work we report here, the dielectric response of RTILs and how it is influenced by the magnitude of ρ_f is described. The dielectric constant, ϵ , is organization-dependent and related to the molecular polarizability through the Clausius-Mossotti relation.³⁶ For the RTIL studied here we access the real part of the (complex) dielectric constant, the refractive index $n = \epsilon^{1/2}$.³⁷ The extent to which the surface charge density, σ_s , induces ρ_f and thus a change in n is the question of interest here. We characterize the ρ_f -dependent refractive index of an imidazolium-based ionic liquid, 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (OMIM⁺TFSI⁻), with an apparatus that uses the RTIL as an optical element. We demonstrate a usefully large modulation of n with modest changes in σ_s , and describe the relationship between ρ_f and n .

4. 2 Experimental Section

4. 2. 1 Materials

1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (OMIM⁺TFSI⁻, $\geq 99\%$, Alfa Aesar) was purified as described below prior to use. Ethanol ($\geq 99.5\%$, Sigma-Aldrich), butanol ($\geq 99.9\%$, Sigma-Aldrich), isopropyl alcohol (IPA, $\geq 99.5\%$, Sigma-Aldrich), ethylene glycol ($\geq 99\%$, Fisher Scientific) and activated carbon (powder, 100 mesh particle size, decolorizing, Sigma-Aldrich) were used as received. Water was purified with a Milli-Q filtration system (Millipore). ITO-coated single depression concave glass slides (slide size: 25 mm $\times$ 75 mm $\times$ 1 mm, concave region: 16 mm diameter and 0.5 mm maximum depth, Amscope) and microscope cover glasses (22 mm $\times$ 22 mm $\times$ 0.175 mm, Globe Scientific) were cleaned as detailed

below.

4. 2. 2 RTIL Purification

OMIM⁺TFSI⁻ was purified by using the RTIL purification method described previously.³⁸ Briefly, OMIM⁺TFSI⁻ is stored over activated carbon for 3 days and removed by syringe filter with a Durapore[®] (PVDF) membrane (0.22 μ m sterile filtration, Millex). OMIM⁺TFSI⁻ is then stirred and heated at 90 °C for 3 h while purging with ultrapure Ar (99.9995%, Linde) to remove water in the RTIL. The purified OMIM⁺TFSI⁻ was stored in a glovebox (MB-200B, Mbraun). Water content in the purified OMIM⁺TFSI⁻ was measured by Karl Fischer titration (Mettler-Toledo C10S) to be 49 ± 2 ppm. All glassware was dried at 150 °C at least 24 h before use to minimize the water contamination.

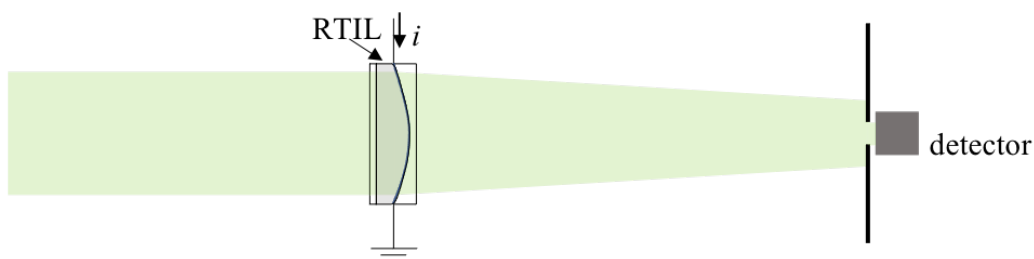
4. 2. 3 Sample Cell Preparation

We constructed a closed cell (Scheme 4. 1) to confine the sample between a transparent conductive ITO-coated concave slide and a microscope cover glass. ITO-coated concave slides and microscope cover glasses were cleaned as the same way described before.³² ITO-coated concave slides and cover glasses were sonicated in detergent (Sparkleen 1, Fisher) solution, Milli-Q water, and IPA for 15 min at each step. The cleaned ITO-coated slides and cover glasses were removed from IPA, rinsed with ethanol, and dried at 200 °C for 30 min. The cooled slides and cover glasses were then cleaned using a UV/ozone cleaner for 20 min. Copper wires were connected to the ITO surface by silver conductive epoxy (MG Chemicals). The epoxy was fixed at 120 °C for 30 min. The RTIL is added to the concave region of the slide using a syringe, then the cover glass is set in place.

4. 2. 4 Characterization of Refractive Index

The intensity of a light beam (575 nm) was detected using an optical power meter

(Newport) as a function of current passed through the ITO coating on the concave slide, described above. A schematic of the optical apparatus is shown in Scheme 4. 1. The refractive index of the medium in the lens-shaped sample holder determines the focal length of the device and thus the amount of light that passes through an aperture in front of the detector. Calibration is accomplished by using a series of solvents that do not support the establishment of a free charge density gradient (Figure 4. 1).



Scheme 4. 1 Schematic of the sample holder and optical system used to measure changes in n with σ_s .

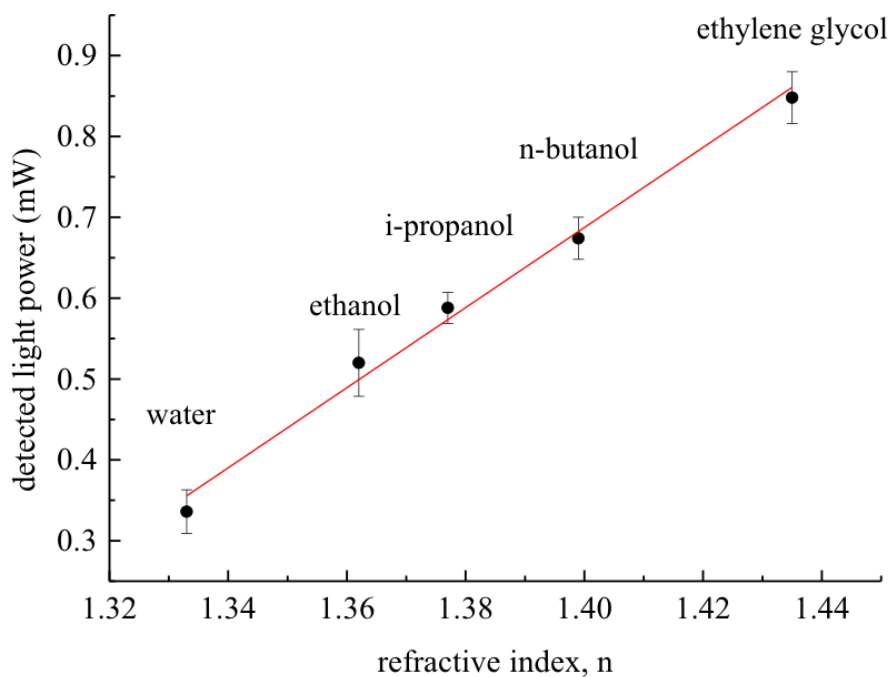


Figure 4. 1 Dependence of detected optical intensity as a function of refractive index of the medium in the sample holder. For all data points, the error bars represent standard deviations ($\pm 1\sigma$) for five individual measurements.

4. 3 Results and Discussion

The primary purpose of this work is to establish experimentally the relationship between surface charge-induced ρ_f and change in refractive index, n , in an RTIL. The experimental configuration (Scheme 4. 1) uses a sample holder for the RTIL that is in the shape of a plano-convex lens, with the curved inner surface of the lens being coated with ITO, an optically transparent conductor. In this configuration, the surface charge density, σ_s , can be controlled by the current passed through the ITO film. Because of the potential drop across the surface and the microcrystalline nature of the ITO film, the drift velocity of the carriers (e^-) in the ITO film is very small,³² making current proportional to carrier density.

Given that we control surface charge density (σ_s) on a conductive surface in contact with the RTIL, it is useful to consider whether or not electrochemical (Faradaic) processes contribute to our data. It is important to note that there is no reference electrode in our system, and that we achieve control over carrier density by using the ITO film as a resistor. As such, there is no direct relationship between surface charge density (σ_s) and surface potential (V_s). The electrochemical “window” for RTILs is characteristically large (*ca.* 5-6 V),³⁹ and previous work, where redox-active chromophores have been added to RTILs in the same experimental configuration, has shown no electrochemical changes in chromophore optical properties.³² In addition, the effect we report here is reversible and reproducible over many cycles. For these reasons, we believe that only non-Faradaic surface charging processes are operative in our system.

Any change in the refractive index of the lens material will alter the focal length of the lens, thereby changing the intensity of light that passes through the (small) aperture in front of the optical detector. We observe experimentally the dependence of light intensity at the detector as a function of current applied across the ITO surface in Figure 4. 2. These data require calibration of

the relationship between light intensity at the detector and refractive index of the medium that forms the lens. We use five different liquids to evaluate the relationship between detected light intensity and refractive index. The five liquids are water ($n = 1.333$), ethanol ($n = 1.361$), isopropyl alcohol ($n = 1.378$), *n*-butanol ($n = 1.399$) and ethylene glycol ($n = 1.432$),⁴⁰⁻⁴³ and the relationship between detected light intensity and refractive index is shown in Figure 4. 1. Using this calibration information and the data contained in Figure 4. 2, we find the dependence of OMIM⁺TFSI⁻ refractive index on current through the ITO surface (Figure 4. 3).

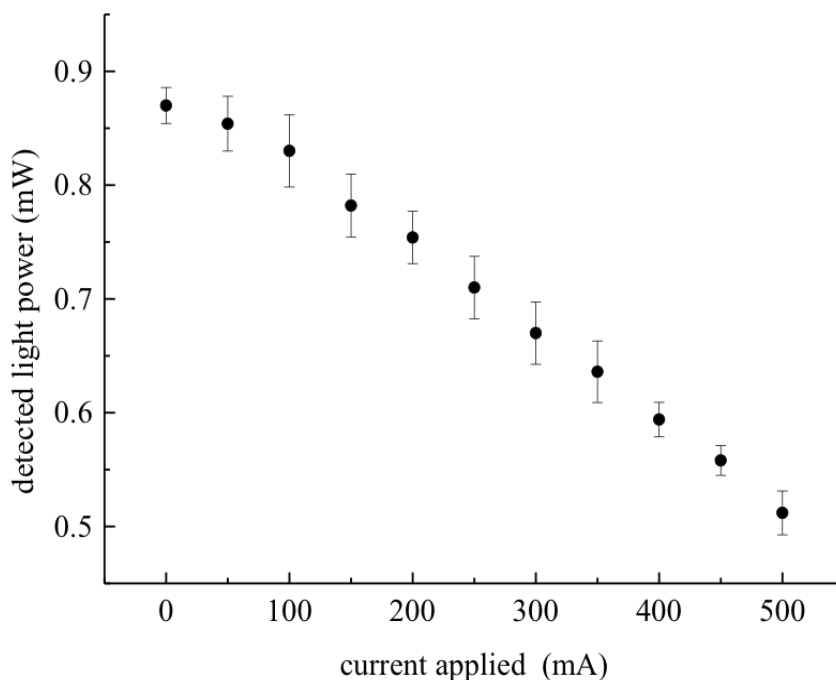


Figure 4. 2 Dependence of detected optical intensity as a function of the current passed through the ITO film on the sample support surface. The error bars represent for standard deviations ($\pm 1\sigma$) for five individual measurements.

We control σ_s by varying the current passed through the resistive ITO film, which necessarily gives rise to Joule heating. We must therefore account for thermal contributions to the change in refractive index observed for OMIM⁺TFSI⁻. We can determine the temperature of the lens and RTIL using information reported previously to gauge temperature as a function of current applied,³² and we find that the maximum increase in temperature is 60 °C. The temperature-

dependence of RTIL refractive index has been studied previously and, while it has not been reported for OMIM⁺TFSI⁻, it has been reported for two related RTILs, BMIM⁺TFSI⁻ and EMIM⁺TFSI⁻.⁴⁴ The slopes of the temperature-dependent refractive indices for these RTILs are the same, and we use this slope to estimate the temperature-dependent refractive index of OMIM⁺TFSI⁻ (dashed line in Figure 4. 3). The difference between the induced change in refractive index reported here and that associated with Joule heating of OMIM⁺TFSI⁻ is due to the dependence of ρ_f on σ_s .

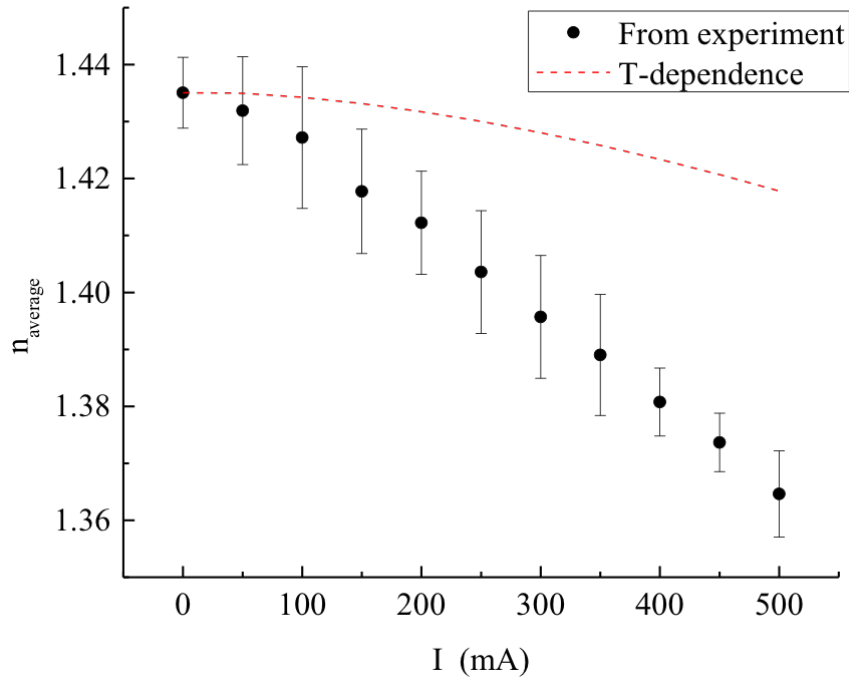


Figure 4. 3 Refractive index ($n_{average}$) as a function of the current (I) passed through the ITO film on the sample support surface. The red dashed line is the temperature-dependence of the refractive index of OMIM⁺TFSI⁻ (Ref. 44).

We now turn to elucidating the relationship between ρ_f and the refractive index gradient, ∇n . The value of n that we extract from the experimental data is averaged over the thickness of the lens. It is of interest to determine how n varies as a function of position within the RTIL and establish the relationship between the change in average n and the change in n at the RTIL-ITO

interface, $n(0)$. To make this connection, we require knowledge of the functional form of ρ_f and n . We do not utilize any chromophores in this work but, from past work using charged chromophores to characterize ρ_f , we know that the spatial dependence of the gradient is given by Eq. 4. 1,^{31-32, 34}

$$\rho_f(x) = \rho_f(0) \exp(-x/d) \quad [4. 1]$$

where d is the e^{-1} characteristic persistence length of ρ_f , which we have determined to be *ca.* 50 μm , and the thickness of the RTIL medium is *ca.* 500 μm . From Maxwell's equations,

$$\rho_f = \nabla \cdot (\epsilon E) \quad [4. 2]$$

In Eq. 4. 2, E is the electric field resulting from the support surface charge, σ_s , and ϵ is the dielectric constant of the medium. From Gauss's law for a planar surface, E is invariant with the distance from the support, on either side of the surface plane. While this is strictly true only for dielectric media, we believe this approximation to be valid for OMIM⁺TFSI⁻ based on the measured dielectric properties of RTILs,⁴⁵⁻⁴⁶ and the apparently limited extent of dissociation seen for this class of materials.²³⁻²⁴ The free charge density gradient ρ_f must thus reflect a gradient in ϵ , the (complex) dielectric constant. The dielectric constant, $\epsilon = \mathbf{n}^2$, where $\mathbf{n} = (n+ik)$. For the RTILs we consider, k , the extinction coefficient is zero (no attenuation), leaving $\epsilon = n^2$ (Eq. 4. 3).

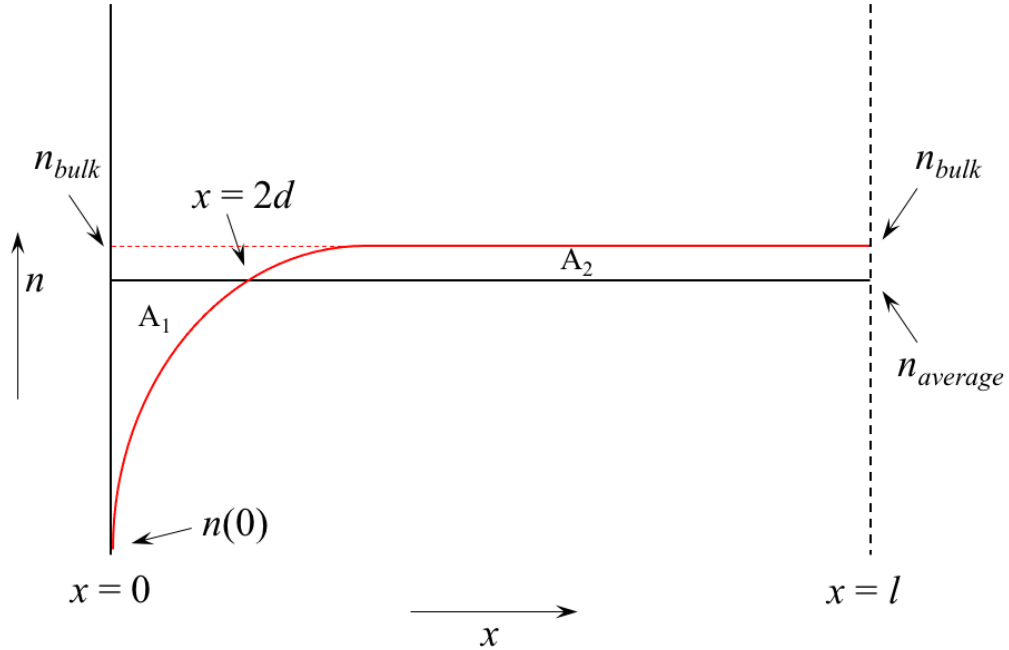
$$\rho_f = \nabla \cdot (n^2 E) = n^2 \nabla \cdot E + (\nabla n^2) \cdot E = (\nabla n^2) \cdot E \quad [4. 3]$$

The issue at hand is thus relating the quantities we determine experimentally to ∇n and for a system in which n is changing only along the x axis, perpendicular to the charged support (yz) plane. Because the refractive index change is only along the x -axis, but not along either the y or z axes, the effect we observe is, in fact, birefringence. We measure the change in n along the optical axis and not perpendicular to it, and do not expect to observe a polarization-dependence.

It is the change in n with x that is important, rather than the absolute value of n , and there is a potential sign ambiguity because of the square-law relationship between ρ_f and n (Eq. 4. 4),

$$|n(x) - n_{bulk}| = |n(0) - n_{bulk}| \exp(-x/2d) \quad [4. 4]$$

Where n_{bulk} is the value of n for the RTIL for $\sigma_s = 0$. As seen in Scheme 4. 2, we measure experimentally a change in n averaged over the thickness of the lens. The thickness of the lens is *ca.* 10 times the persistence length of ρ_f , and from this information and the functional form of $n(x)$ we can characterize the change in n at the interface between the RTIL and the charge-carrying support. We know the persistence length of ρ_f (d), the thickness of the lens (l), and the value of n_{bulk} , and from this information, we can extract the value of n at the interface, $n(0)$. The relationship between these quantities is schematized in Scheme 4. 2 and is described as follows.



Scheme 4. 2 Schematic of the refractive index gradient induced by σ_s . The axis x is the optical axis of the measurement and the vertical solid line of the left is the charged surface.

For the measured average value of n , $n_{average}$, to change from n_{bulk} , the areas A_1 and A_2 must be equal in magnitude but are of opposite sign (Eq. 4. 5).

$$\int_{x=0}^{x=2d} \exp(-x/2d) dx = - \int_{x=2d}^{x=l} \exp(-x/2d) dx \quad [4. 5]$$

normalizing area in terms of refractive index changes relative to its bulk value (Eq. 4. 6),

$$(n(0) - n_{bulk}) \int_{x=0}^{x=2d} \exp(-x/2d) dx \approx (l - 2d) (n_{average} - n_{bulk}) \quad [4. 6]$$

$$(n(0) - n_{bulk}) = \left(\frac{l - 2d}{1.264d} \right) (n_{average} - n_{bulk})$$

Using the experimentally obtained quantities we can thus determine $n(0)$, which we find to be substantially different than n_{bulk} (Figure 4. 4). The observed change in average refractive index reported in this work appears more modest because of the relative values of d , the persistence length of ρ_f , and the lens thickness, l . By optimizing the dimensions of the lens such that d becomes similar to l , the experimentally observed changes in $n_{average}$ will be more pronounced.

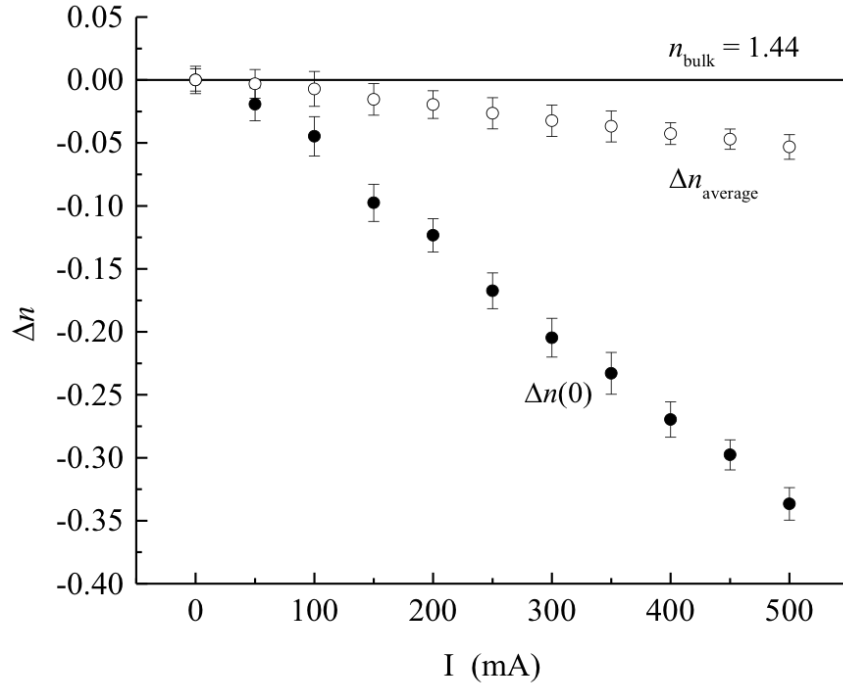


Figure 4. 4 Change in refractive index of OMIM⁺TFSI⁻ at support surface, $\Delta n(0)$ (solid black circles) and the average change in index ($\Delta n_{average}$), as a function of the current (I) passed through the ITO film on the sample support surface, after correction for thermal contributions.

The magnitude of the induced birefringence at the interface bears some discussion. The change in refractive index can range up to *ca.* 25%, which is remarkably large, suggesting a change in polarizability. From the Lorentz-Lorenz equation (Eq. 4. 7),⁴⁷⁻⁴⁸

$$\alpha = \left(\frac{3}{4\pi N} \right) \left(\frac{n^2 - 1}{n^2 + 2} \right) \quad [4. 7]$$

For $n_{bulk} = 1.44$ and $n(0) = 1.19$ (Figure 4. 4), α changes from $37.6 \text{ \AA}^3$ to $17.4 \text{ \AA}^3$. Importantly, this measure of ρ_f does not provide information more specific than the molecular polarizability volume. Given the structural complexity of the RTIL constituents, it would be of interest to understand which moieties in the RTIL are responsible for the large observed change in polarizability. Spatially-resolved Raman scattering measurement of OMIM⁺TFSI⁻ as a function of σ_s and d should provide a detailed, molecular-scale understanding of the chemical functionality primarily responsible for ρ_f . These experiments are underway.

4. 4 Conclusions

We report on the characterization of the refractive index gradient in the RTIL OMIM⁺TFSI⁻ induced by a charged surface. This induced change in refractive index of an RTIL is proportional to the current passed through the ITO film on the support surface. We also demonstrate the existence of induced birefringence in OMIM⁺TFSI⁻, which supports the potential application of RTILs as novel electro-optic materials. While the functional relationship between ρ_f and ∇n are understood, there has not been to date an experimental measurement that has related the proportionality between these two quantities. This work serves to make that connection and to demonstrate an alternative means of characterizing the effect of surface charge on RTILs.

REFERENCES

REFERENCES

1. Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071-2084.
2. Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. Ionic Liquid Materials for the Electrochemical Challenges of the Future. *Nature Materials* **2009**, *8*, 621-629.
3. Rogers, R. D.; Seddon, K. R. Ionic Liquids - Solvents of the Future? *Science* **2003**, *302* (5646), 792-793.
4. Itoh, T. Ionic Liquids as a Tool to Improve Enzymatic Organic Synthesis. *Chem. Rev.* **2017**, *117*, 10567-10607.
5. Sowmiah, S.; Cheng, C. I.; Chu, Y.-H. Ionic Liquids for Green Organic Synthesis. *Curr. Org. Synth.* **2012**, *9*, 74-95.
6. Yadav, J. S.; Reddy, B. V. S.; Premalatha, K. 1-Butyl-3-Methylimidazolium Tetrafluoroborate ([Bmim]Bf₄) Ionic Liquid. A Novel and Recyclable Reaction Medium for the Synthesis of *Vic*-Diamines. *Adv. Synth. Catal.* **2003**, *345*, 948-952.
7. Hallett, J. P.; Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. 2. *Chem. Rev.* **2011**, *111*, 3508-3576.
8. Wilkes, J. S. Properties of Ionic Liquid Solvents for Catalysis. *J. Mol. Cat. A: Chemical* **2004**, *214*, 11-17.
9. Zhao, D.; Wu, M.; Kou, Y.; Min, E. Ionic Liquids: Applications in Catalysis. *Catal. Today* **2002**, *74*, 157-189.
10. Berthod, A.; Ruiz-Angel, M. J.; Carda-Broch, S. Ionic Liquids in Separation Techniques. *J. Chromat. A* **2008**, *1184*, 6-18.
11. Han, D.; Row, K.-H. Recent Applications of Ionic Liquids in Separation Technology. *Molecules* **2010**, *15*, 2405-2426.
12. Arbizzani, C.; Bisio, M.; Cericola, D.; Lazzari, M.; Soavi, F.; Mastragostino, M. Safe, High-Energy Supercapacitors Based on Solvent-Free Ionic Liquid Electrolytes. *J. Pwr. Sources* **2008**, *185*, 1575-1579.
13. Newell, R.; Faure-Vincent, J.; Iliev, B.; Schubert, T.; Aradilla, D. A New High Performance Ionic Liquid Mixture Electrolyte for Large Temperature Range Supercapacitor Applications (–70° C to 80° C) Operating at 3.5 V Cell Voltage. *Electrochim. Acta.* **2018**, *267*, 15-19.
14. Van Aken, K. L.; Beidaghi, M.; Gogotsi, Y. Formulation of Ionic Liquid Electrolyte to Expand the Voltage Window of Supercapacitors. *Angew. Chem.* **2015**, *127*, 4888-4891.

15. MacFarlane, D. R.; Tachikawa, N.; Forsyth, M.; Pringle, J. M.; Howlett, P. C.; Elliott, G. D.; Davis, J. H.; Watanabe, M.; Simon, P.; Angell, C. A. Energy Applications of Ionic Liquids. *Energ. Env. Sci.* **2014**, 7, 232-250.
16. Sakaebe, H.; Matsumoto, H. N-Methyl-N-Propylpiperidinium Bis(Trifluoromethane Sulfonyl)Imide (Pp13-Tfsi)—Novel Electrolyte Base for Li Battery. *Electrochem. Commun.* **2003**, 5, 594-598.
17. de Souza, R. F.; Padilha, J. C.; Goncalves, R. S.; DuPont, J. Room Temperature Dialkylimidazolium Ionic Liquid-Based Fuel Cells. *Electrochem. Commun.* **2003**, 5, 728-731.
18. Lee, S.-Y.; Ogawa, A.; Kanno, M.; Nakamoto, H.; Yasuda, T.; Watanabe, M. Nonhumidified Intermediate Temperature Fuel Cells Using Protic Ionic Liquids. *J. Am. Chem. Soc.* **2010**, 132, 9764-9773.
19. Liu, S.; Zhou, L.; Wang, P.; Zhang, F.; Yu, S.; Shao, Z.; Yi, B. Ionic-Liquid-Based Proton Conducting Membranes for Anhydrous H₂/Cl₂ Fuel-Cell Applications. *ACS Appl. Mat. Int.* **2014**, 6, 3195-3200.
20. Anaredy, R. S.; Shaw, S. K. Long-Range Ordering of Ionic Liquid Fluid Films. *Langmuir* **2016**, 32, 5147-5154.
21. Anaredy, R. S.; Shaw, S. K. Developing Distinct Chemical Environments in Ionic Liquid Films. *J. Phys. Chem. C* **2018**, 122, 19731-19737.
22. Anaredy, R. S.; Shaw, S. K. Directing Long-Range Molecular Ordering in Ionic Liquid Films: A Tale of Two Interfaces. *J. Phys. Chem. C* **2019**, 123, 8975-8982.
23. Gebbie, M. A.; Dobbs, H. A.; Valtiner, M.; Israelachvili, J. N. Long-Range Electrostatic Screening in Ionic Liquids. *Proc. Nat. Acad. Sci. USA* **2015**, 112 (24), 7432-7437.
24. Gebbie, M. A.; Valtiner, M.; Banquy, X.; Fox, E. T.; Henderson, W. A.; Israelachvili, J. N. Ionic Liquids Behave as Dilute Electrolyte Solutions. *Proc. Nat. Acad. Sci. USA* **2013**, 110 (24), 9674-9679.
25. Nishida, J.; Breen, J. P.; Wu, B.; Fayer, M. D. Extraordinary Slowing of Structural Dynamics in Thin Films of a Room Temperature Ionic Liquid. *ACS Cent. Sci.* **2018**, 4, 1065-1073.
26. Shin, J. Y.; Yamada, S. A.; Fayer, M. D. Dynamics of a Room Temperature Ionic Liquid in Supported Ionic Liquid Membranes Vs the Bulk Liquid: 2d Ir and Polarized Ir Pump-Probe Experiments. *J. Am. Chem. Soc.* **2017**, 139, 311-323.
27. Shin, J. Y.; Yamada, S. A.; Fayer, M. D. Carbon Dioxide in a Supported Ionic Liquid Membrane: Structural and Rotational Dynamics Measured with 2d Ir and Pump-Probe Experiments. *J. Am. Chem. Soc.* **2017**, 139, 11222-11232.

28. Thomaz, J. E.; Bailey, H. E.; Fayer, M. D. The Influence of Mesoscopic Confinement on the Dynamics of Imidazolium-Based Room Temperature Ionic Liquids in Polyether Sulfone Membranes. *J. Chem. Phys.* **2017**, *147*, 194502 1-11.
29. Wu, B.; Breen, J. P.; Fayer, M. D. Structural Dynamics in Ionic Liquid Thin Films: The Effect of Cation Chain Length. *J. Phys. Chem. C* **2020**, *124*, 4179-4189.
30. Wu, B.; Breen, J. P.; Xing, X.; Fayer, M. D. Controlling the Dynamics of Ionic Liquid Thin Films Via Multilayer Surface Functionalization. *J. Am. Chem. Soc.* **2020**, *142*, 9482-9492.
31. Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G., J. Charge-Induced Long-Range Order in a Room-Temperature Ionic Liquid. *Langmuir* **2016**, *32*, 9507-9512.
32. Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G., J. Modulation of an Induced Charge Density Gradient in the Room Temperature Ionic Liquid Bmim⁺Bf₄⁻. *J. Phys. Chem. C* **2018**, *122*, 7361-7367.
33. Ma, K.; Jarosova, R.; Wang, Y.; Swain, G. M.; Blanchard, G., J. Ionic Liquids: A Unique and Useful Class of Materials. *Chem. Educ.* **2018**, *23*, 265-272.
34. Wang, Y.; Jarosova, R.; Swain, G. M.; Blanchard, G., J. Characterizing the Magnitude and Structure-Dependence of Free Charge Density Gradients in Room-Temperature Ionic Liquids. *Langmuir* **2020**, *36*, 1152-1155.
35. MacFarlane, D. R.; Forsyth, M.; Izgorodina, E. I.; Abbott, A. P.; Annat, G.; Fraser, K. On the Concept of Ionicity in Ionic Liquids. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4962-4967.
36. Van Rysselberghe, P. Remarks Concerning the Clausius-Mossotti Law. *J. Phys. Chem.* **1932**, *36*, 3038-3045.
37. Schubert, E. F.; Kim, J. K.; Xi, J. Q. Low-Refractive-Index Materials: A New Class of Optical Thin-Film Materials. *Phys. Stat. Sol.* **2007**, *244*, 3002-3008.
38. Jarosova, R.; Swain, G. M. Rapid Preparation of Room Temperature Ionic Liquids with Low Water Content as Characterized with Ta-C:N Electrode. *J. Electrochem. Soc.* **2015**, *162*, H507-H511.
39. Eftekhari, A. Supercapacitors Utilising Ionic Liquids. *Ener. Stor. Mat.* **2017**, *9*, 47-69.
40. El-Kashef, H. The Necessary Requirements Imposed on Polar Dielectric Laser Dye Solvents. *Physica V: Cond. Matter* **2000**, *279*, 295-301.
41. Kozma, I. Z.; Krok, P.; Riedle, E. Direct Measurement of the Group-Velocity Mismatch and Derivation of the Refractive-Index Dispersion for a Variety of Solvents in the Ultraviolet. *J. Opt. Soc. Am. B* **2005**, *22*, 1479-1485.
42. Rheims, J.; Koser, J.; Wriedt, T. Refractive-Index Measurements in the near-Ir Using an Abbe Refractometer. *Meas. Sci. Tech.* **1997**, *8*, 601.

43. Sani, E.;Dell'Oro, A. Optical Constants of Ethylene Glycol over an Extremely Wide Spectral Range. *Opt. Mat.* **2014**, *37*, 36-41.
44. Seki, S.; Tsuzuki, S.; Hayamizu, K.; Umebayashi, Y.; Serizawa, N.; Takei, K.;Miyashiro, H. Comprehensive Refractive Index Property for Room Temperature Ionic Liquids. *J. Chem. Eng. Data* **2012**, *57*, 2211-2216.
45. Singh, T.;Kumar, A. Static Dielectric Constant of Room Temperature Ionic Liquids: Internal Pressure and Cohesive Energy Density Approach. *J. Phys. Chem. B.* **2008**, *112*, 12968-12972.
46. Huang, M.-M.; Jiang, Y.; Sasisanker, P.; Driver, G. W.;Weingartner, H. Static Relative Dielectric Permittivities of Ionic Liquids at 25 C. *J. Chem. Eng. Data* **2011**, *56*, 1419-1499.
47. Lorenz, L. Ueber Die Refraktionsconstante. *Annal. der Physik* **1880**, *247* (9), 70-103.
48. Lorentz, H. A. Ueber Die Anwendung Des Satzes Vom Virial in Der Kinetischen Theorie Der Gase. *Annal. der Physik* **1881**, *248* (1), 127-136.

CHAPTER 5. Structure-Dependence of the Charge-Induced Refractive Index Change in Room Temperature Ionic Liquids

5. 1 Introduction

Room temperature ionic liquids (RTILs) have received extensive attention, not only because of their demonstrated utility in a wide range of applications, but also because achieving a fundamental understanding of the factors that are responsible for observed bulk behavior remains to be accomplished. Among the reasons for the interest in RTILs is that this class of materials possesses a *ca.* 5 eV electrochemical window in addition to their ability to dissolve compounds with a wide range of polarities. Careful examination of RTIL properties by a number of groups has revealed the existence of long-range organization on a variety of length scales and it remains to be determined how all of these observations can be reconciled within the framework of a single model. The Shaw group has reported on structural organization in RTIL thin films that evolves subsequent to the formation of the film. In that work, they reported that the structural organization persists over distances of at least 1 μm , based on vibrational spectroscopic and second order nonlinear optical data.¹⁻³ The Fayer group has also reported variation in the order of RTILs over distances in the hundreds of nm range in thin RTIL films based on their use of small vibrational chromophores.⁴⁻⁹ Gebbie *et al.* have also identified organization in RTILs but on a much shorter length scale, using force measurements, and based on their data they asserted that the extent of RTIL dissociation was rather limited.¹⁰⁻¹¹ The Blanchard group has reported on the existence of an induced free charge density gradient (ρ_f) in RTILs that persists over distances greater than 50 μm .¹²⁻¹⁶ While all of these investigations share the conclusion that organization in RTILs can persist for distances vastly in excess of that seen in normal solution phase systems, identifying the connection(s) between these different bodies of work as well as the molecular basis for this organization, remains to be accomplished.

Among the issues that complicate the treatment of RTILs is a knowledge gap concerning

the extent of their dissociation. The measurement of conductivity is one means to evaluate extent of dissociation provided the bulk materials properties of the RTIL are known with sufficient accuracy,¹⁷ and there is an emerging body of work that suggests the extent of dissociation is on the order of 50% in many RTILs.¹⁸ This finding, which provides important insight into this class of materials, also complicates their theoretical treatment because they are neither purely dielectric materials nor conductors, and the applicability of Maxwell's equations in either limit is not fully justified.

We have reported recently on the induced birefringence in RTILs that is a direct consequence of ρ_f . What was not clear from first principles was the relationship between the magnitude of ρ_f and the magnitude of the resulting gradient in refractive index (n). In the initial report, we found that the refractive index of an imidazolium RTIL (BMIM⁺TFSI⁻) could, in fact, be substantial. This is an important finding for several reasons. It provides a probe-free means of evaluating ρ_f and demonstrates a simple way to characterize the polarizability of RTILs. In this work we consider the dependence of the induced birefringence on the molecular structure of the RTIL cation. We have examined two pyrrolidinium RTILs with pendant butyl and octyl aliphatic chains, alongside their imidazolium RTIL counterparts possessing the same aliphatic chain lengths. We find that the magnitudes of the induced birefringence are similar for the pyrrolidinium and imidazolium cations, with the primary structural-dependence being the length of the cation aliphatic chains.

5. 2 Experimental Section

5. 2. 1 Materials

1-octyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (OMPyr⁺TFSI⁻) and 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPyr⁺TFSI⁻) were prepared

followed the method reported elsewhere.¹⁹ 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (OMIM⁺TFSI⁻, ≥99%) was from Alfa Aesar. 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM⁺TFSI⁻, ≥98%) was from Sigma-Aldrich. All RTILs were purified as detailed below before use. 2-propyl alcohol (≥99.5%, Sigma-Aldrich) and activated charcoal (powder, -100 mesh particle size, decolorizing, Sigma-Aldrich) were used as received.

5. 2. 2 Purification of RTILs

RTILs were purified by the method described previously.^{12, 20} The RTIL is stored over activated charcoal for 3 days and removed by a syringe filter (Durapore® (PVDF), 0.22 μm pore size, Millex). The RTIL is then stirred and heated for 3 h at 90 °C while purging with ultrapure Ar (99.9995%, Linde) to reduce water in the RTIL. The water content in purified RTILs is *ca.* 50 ppm, determined by Karl Fischer titration. All glassware is dried at 150 °C at least 24 h before use to minimize water contamination.

5. 2. 3 Sample Cell Preparation

We have constructed a closed sample cell to confine the RTIL between a transparent conductive ITO-coated single depression concave glass slide (slide size: 25 mm×75 mm×1 mm. The concave region size is 16 mm in diameter and 0.5 mm maximum depth, Amscope) and a microscope cover glass (22×22 mm, #1.5 thickness: 0.175 mm, Globe Scientific). The details of the sample cell construction have been illustrated before.¹⁶ The ITO-coated concave slide and cover glass are sonicated in detergent (Sparkleen 1, Fisher) solution, Milli-Q water, and 2-propyl alcohol for 15 min each. The cleaned ITO-coated slide and cover glass are dried for 30 min at 200 °C and cooled in a desiccator. The cooled slide and cover glass are then placed in a UV/ozone cleaner for 20 min. Copper wires are connected to the conductive ITO surface by silver epoxy

(MG Chemicals). To cure the epoxy, the ITO-coated slide is heated for 30 min at 120 °C. The purified RTIL sample is added to the concave region of the ITO-coated slide by syringe and the cover glass is set in place.

5. 2. 4 Characterization of Charge-Induced Change in RTIL Refractive Index

The far-field image of the light beam passed through the RTIL lens is used to measure the change of RTIL refractive index.¹⁶ The intensity of light passing through an aperture is detected with an optical power meter (Newport) as a function of the current applied to the ITO film on the concave slide. The light source is a dye laser that produces light at 575 nm (< 10 mW average power). When the Gaussian laser beam passes through the RTIL sample in the cell, the shape of the far-field image varies according to the refractive index of the RTIL.

5. 3 Results and Discussion

The induced charge density gradient ρ_f is related to the refractive index gradient according to Eq. 5. 1.¹⁶

$$\rho_f = (\nabla n^2) \cdot E \quad [5. 1]$$

We have characterized the cation structure-dependence of ρ_f and found in that work that the primary factor influencing ρ_f was the cation aliphatic chain length.¹⁹ In that work, we used the rotational diffusion dynamics of a charged chromophore to evaluate ρ_f , whereas we use an entirely different means of characterizing the gradient in this work. The conclusions of the two bodies of work are the same.

The characterization of ∇n in the four RTILs examined was done using the experimental apparatus and procedure described previously.¹⁶ From our characterization of ρ_f with rotational diffusion measurements, we know that the characteristic persistence length for these RTILs is the same for all to within the experimental uncertainty, *ca.* 70 μm . It is useful to note the

complementary nature of these two measurement schemes. The persistence length of ρ_f is not measured directly with the ∇n measurements and, conversely, while the persistence length of ρ_f is readily available from the rotational diffusion measurements, evaluating the magnitude of ρ_f with this approach is more involved.

As noted above, the RTIL sample cell is in the form of a plano-convex lens. We control ρ_f in the RTIL contained within the sample cell by controlling the surface charge (σ_s) on the curved inner surface of the sample cell. σ_s is controlled by the current passed through the ITO film on the RTIL support surface. The charge-induced change in n will alter the effective focal length of the RTIL lens, thereby changing the intensity of the light beam in the far field. We detect experimentally the intensity of light reaching the detector through a fixed aperture as a function of current passed across the ITO film surface in the sample holder. To calibrate the system for intensity of light measured as a function of refractive index of the medium within the sample cell, we performed measurements for a range of solvents of different refractive index.¹⁶ This calibration provides a direct means to evaluate the dependence of the average refractive index of the RTIL in the sample cell as a function of current passed across the ITO surface. To gauge the effect of RTIL structure on ∇n , we have selected four RTILs which have a common anion but different cations (Figure 5. 1). The relationship between detected light intensity and applied current for these RTILs is shown in Figure 5. 2. With the calibration of the relationship between refractive index and light intensity,¹⁶ we can evaluate the relationship between the average RTIL refractive index within the sample cell and current passed across the ITO surface.

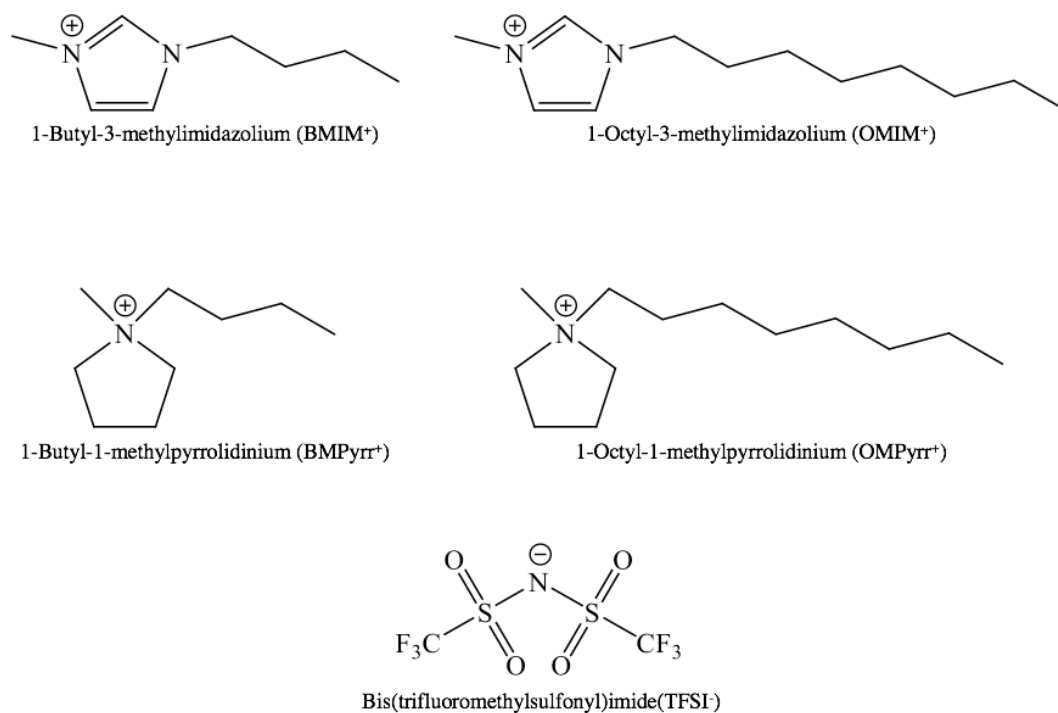


Figure 5. 1 Structure of the RTILs used.

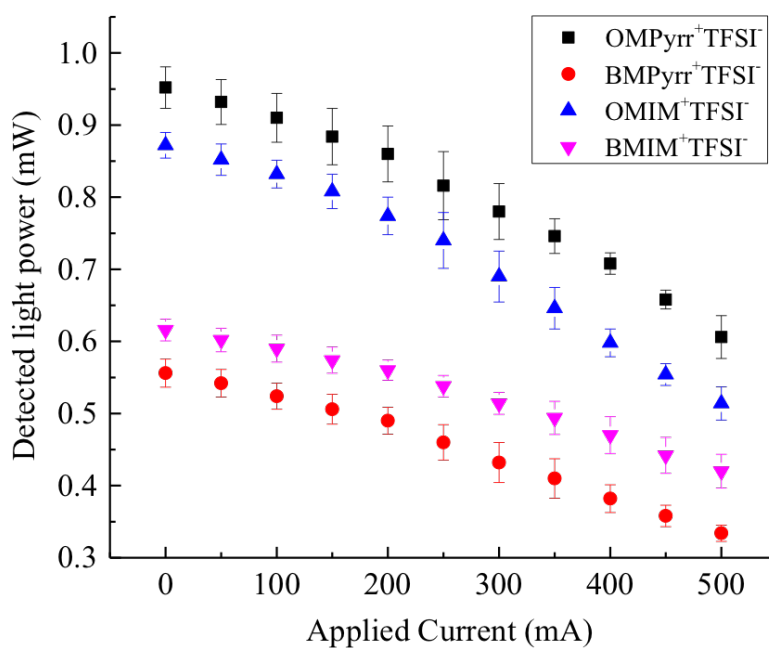


Figure 5. 2 Detected optical intensity as a function of RTIL constituent identity and the current passed through ITO. Black squares represent for OMPyr⁺TFSI⁻, red circles are BMPyr⁺TFSI⁻, blue triangles are OMIM⁺TFSI⁻ and purple inverted triangles are BMIM⁺TFSI⁻. For all data points, the error bars represent for standard deviations for five individual measurements.

In considering the data presented in Figure 5. 2, it is important to note that the manner we use to control σ_s on the ITO surface produced Joule heating. Because the refractive index of any material will exhibit a temperature-dependent refractive index, it is important to discern the contribution to our experimental signals from Joule heating and those from induced ∇n . We have previously reported on the temperature change of the RTIL BMIM⁺TFSI⁻ as a function of current applied.¹³ The temperature-dependence of RTIL refractive index has also been studied for a number of other imidazolium and pyrrolidinium RTILs.²¹ We have calibrated our sample cell in terms of Joule heating as a function of current applied.¹³ With this calibration information, we can thus determine the change of the RTIL refractive index caused by joule heating as a function of the current across the ITO film (Figure 5. 3).

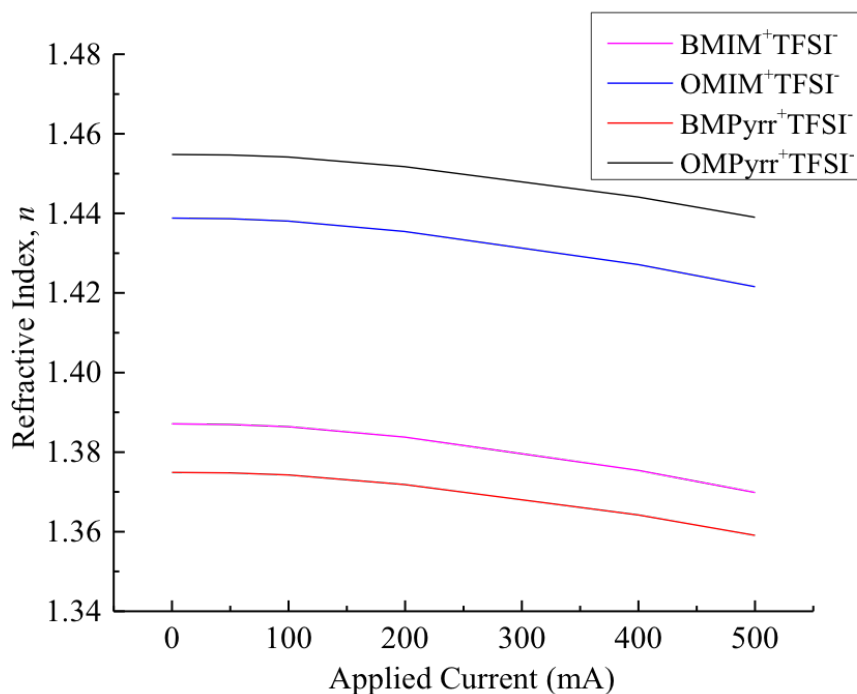


Figure 5. 3 Change in the refractive index (n) of RTILs caused by Joule heating. Black line represents for OMPyrr⁺TFSI⁻, red line is BMPyrr⁺TFSI⁻, blue line is OMIM⁺TFSI⁻ and purple line is BMIM⁺TFSI⁻.

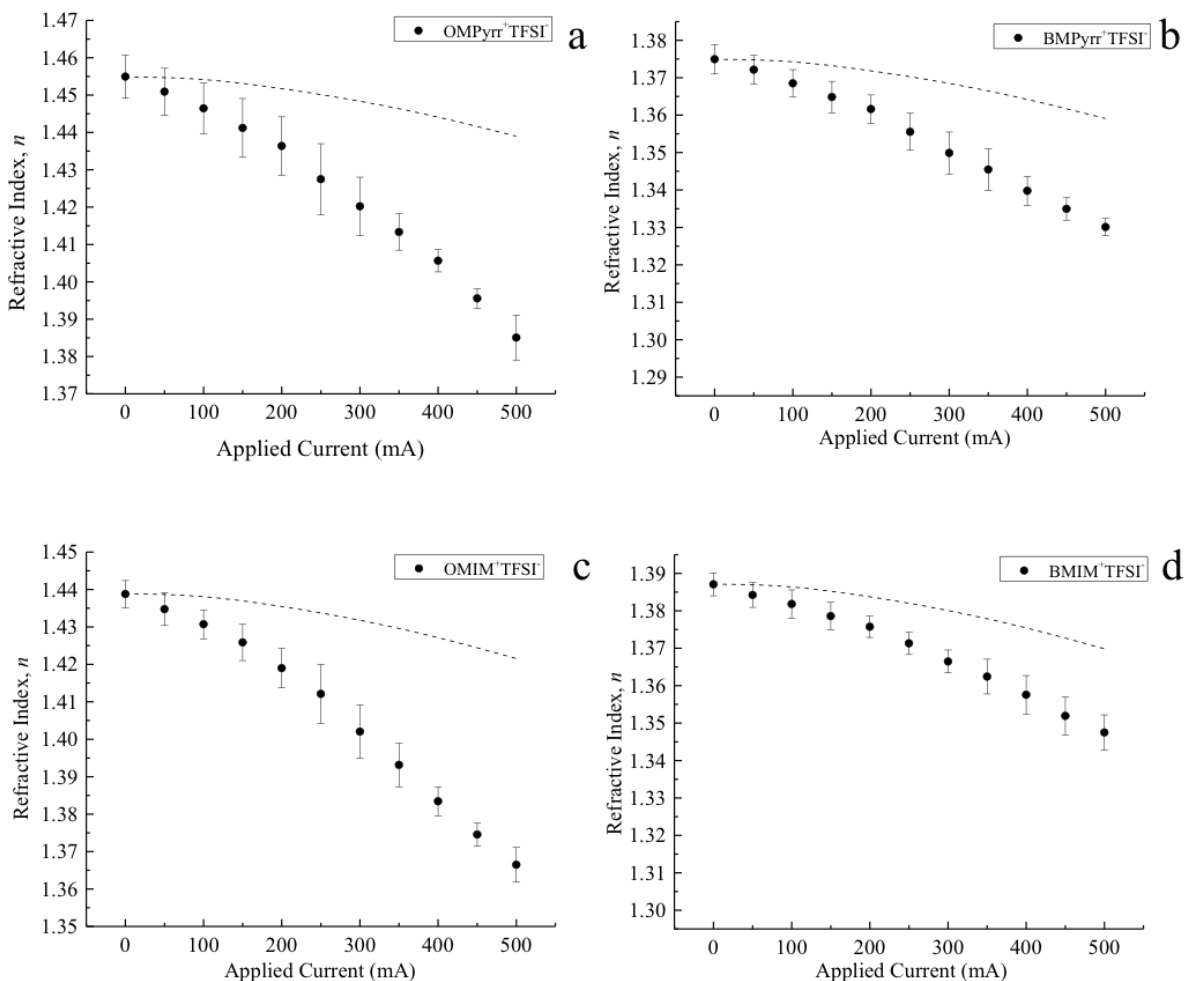


Figure 5. 4 Refractive index (n) as a function of the current applied on ITO support for different RTILs (data symbols). The dashed lines account for the temperature-dependence of the RTIL refractive index via Joule heating. (a) OMPyrr⁺TFSI⁻, (b) BMPyrr⁺TFSI⁻, (c) OMIM⁺TFSI⁻, (d) BMIM⁺TFSI⁻.

The identity of the RTIL cation plays an important role in determining the magnitude of ρ_f in RTILs.¹⁴ The charge-induced change in n of the RTIL is related to ρ_f and it follows that the change in detected light intensity is dependent on the RTIL cation structure. These data are shown in Figure 5. 4. The difference between the induced change in n of the RTIL reported here and that associated with Joule heating (dashed line) is due to the dependence of ρ_f on σ_s . For each RTIL, the induced change in n is averaged over the thickness of the sample lens. Determining the change in n at the RTIL-ITO interface is important because it provides a gauge for what could be achieved

using a thin film format. We have related the included change in average n ($n_{average}$) and the change in n at the interface ($n(0)$).¹⁶ We know the functional form of $\rho_f(x)$ ^{12, 14-15} and this can be related to the functional form of $n(x)$ (Eq. 5. 2),¹⁶

$$|n(x) - n_{bulk}| = |n(0) - n_{bulk}| \exp(-x/2d) \quad [5. 2]$$

where x is the distance from the surface, d is the e^{-1} characteristic persistence length of ρ_f , n_{bulk} is the value of n for $\sigma_s = 0$. With this information, we can extract the value of $n(0)$.¹⁶

We consider next the dependence of $n(0)$ on surface charge density for the four RTILs. The change in $n(0)$ for RTILs as a function of the current applied is found to be different from the change in $n_{average}$ (Figure 5. 5). The relatively modest change in $n_{average}$ is because of the relative values of the lens thickness (l) and the ρ_f persistence length (d). Larger change in $n_{average}$ could be observed by optimizing the thickness of the lens to be similar to d .

By comparing the Δn for the selected four RTILs, it is clear that Δn varies with the identity of the RTIL cation (Figure. 5). The magnitude of Δn for OMPyrr⁺TFSI⁻ (Figure 5. 5a) is larger than that of BMPyrr⁺TFSI⁻ (Figure 5. 5b). This finding is consistent with the analogous data for OMIM⁺TFSI⁻ (Figure 5. 5c) and BMIM⁺TFSI⁻ (Figure 5. 5d). Based on these findings, it is clear that the RTIL cation alkyl chain length plays a larger role in determining ρ_f and thus Δn than the RTIL cation charged headgroup does.

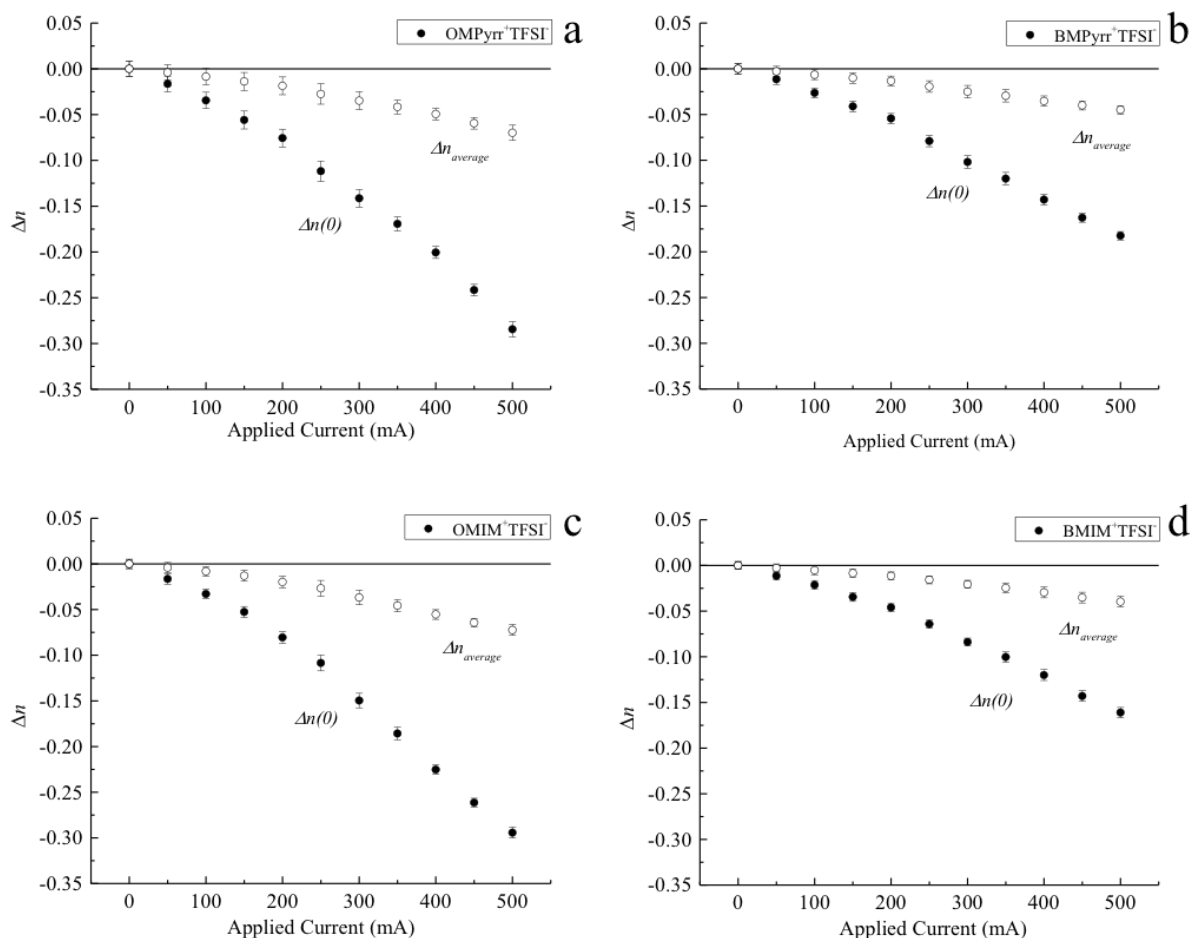


Figure 5. 5 Change in refractive index of RTILs at the support surface ($\Delta n(0)$), and the average change in refractive index ($\Delta n_{average}$), as a function of the current applied on ITO support, after correction for thermal contributions. (a) OMPyrr⁺TFSI⁻, (b) BMPyrr⁺TFSI⁻, (c) OMIM⁺TFSI⁻, (d) BMIM⁺TFSI⁻.

The polarizability of a molecule depends on structure and orientation. In this case we consider that the relevant molecule is the RTIL ion pair, not the dissociated ion(s). The optical susceptibility of a material is likewise known to depend on molecular-organization within the material. As discussed above, the induced change in n is significant for all RTILs studied here, suggesting that these systems exhibit comparatively large polarizabilities. We can utilize the Lorentz–Lorenz expression to evaluate polarizabilities and changes in polarizability for the pyrrolidinium and imidazolium RTILs (Eqs. 5. 3 and 5. 4).²²⁻²³

$$\alpha = \left(\frac{3}{4\pi N} \right) \left(\frac{n^2 - 1}{n^2 + 2} \right) \quad [5.3]$$

$$\Delta\alpha = \left(\frac{3}{4\pi N} \right) \left(\frac{n(0)^2 - 1}{n(0)^2 + 2} - \frac{n_{bulk}^2 - 1}{n_{bulk}^2 + 2} \right) \quad [5.4]$$

We evaluate the structure-dependence of the charge-induced change in refractive index and polarizability of RTILs (Table 5. 1). For both imidazolium and pyrrolidinium RTILs, the change in α is more significant for RTILs with longer cation alkyl chain lengths. This finding may appear to be counter-intuitive given the structures of the RTIL cations, but when taken in the context that it is the paired RTIL ions that are primarily responsible for the polarizability in these systems, the lack of knowledge regarding the detailed structure of the paired ions precludes a more detailed discussion of this point. Empirically, we find the RTIL cation aliphatic chains play the primary structure-dependent role in these systems.

Table 5. 1 Evaluation of the change in n and α of RTILs. The value of $n(0)$ reported here is for the data acquired at $I = 500\text{mA}$.

RTIL	FW (g/mol)	ρ (g/cm ³)	N (cm ⁻³)	$n(0)$	n_{bulk}	$\alpha(0)$ (Å ³)	α_{bulk} (Å ³)	$\Delta\alpha$ (Å ³)
OMPyr ⁺ TFSI ⁻	478.52	1.270	1.599×10^{21}	1.1705	1.4549	16.39	40.50	-24.11
BMPyr ⁺ TFSI ⁻	422.41	1.390	1.982×10^{21}	1.1924	1.3749	14.85	27.57	-12.72
OMIM ⁺ TFSI ⁻	475.48	1.320	1.672×10^{21}	1.1445	1.4388	13.37	37.54	-24.17
BMIM ⁺ TFSI ⁻	419.37	1.437	2.064×10^{21}	1.2259	1.3871	16.61	27.24	-10.63

5. 4 Conclusions

We characterize the charge-induced change in refractive index for four RTILs, as a function of the current passed across the ITO film in contact with the RTIL. The induced change in n is along the E-field propagation axis, x , and there is no change in n parallel to the support

surface (yz plane). The induced change in n is thus an induced birefringence in the RTIL, which suggests the potential of RTILs to be used as novel electro-optic materials.³ We achieve significant change in n with modest change in σ_s . The magnitude of Δn and $\Delta\alpha$ is found to depend on the RTIL cation aliphatic chain length, providing useful insight into the design of RTIL constituents for the optimization of electro-optic effects. This work also demonstrates the connection between the ρ_f and Δn in the RTIL, induced by the surface charge.

REFERENCES

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1. Anareddy, R. S.; Shaw, S. K., Long-range ordering of ionic liquid fluid films. *Langmuir* **2016**, *32*, 5147-5154.
2. Anareddy, R. S.; Shaw, S. K., Developing distinct chemical environments in ionic liquid films. *J. Phys. Chem. C* **2018**, *122*, 19731-19737.
3. Anareddy, R. S.; Shaw, S. K., Directing long-range molecular ordering in ionic liquid films: A tale of two interfaces. *J. Phys. Chem. C* **2019**, *123*, 8975-8982.
4. Nishida, J.; Breen, J. P.; Wu, B.; Fayer, M. D., Extraordinary slowing of structural dynamics in thin films of a room temperature ionic liquid. *ACS Cent. Sci.* **2018**, *4*, 1065-1073.
5. Shin, J. Y.; Yamada, S. A.; Fayer, M. D., Dynamics of a room temperature ionic liquid in supported ionic liquid membranes vs the bulk liquid: 2D IR and polarized IR pump-probe experiments. *J. Am. Chem. Soc.* **2017**, *139*, 311-323.
6. Shin, J. Y.; Yamada, S. A.; Fayer, M. D., Carbon dioxide in a supported ionic liquid membrane: Structural and rotational dynamics measured with 2D IR and pump-probe experiments. *J. Am. Chem. Soc.* **2017**, *139*, 11222-11232.
7. Thomaz, J. E.; Bailey, H. E.; Fayer, M. D., The influence of mesoscopic confinement on the dynamics of imidazolium-based room temperature ionic liquids in polyether sulfone membranes. *J. Chem. Phys.* **2017**, *147*, 194502 1-11.
8. Wu, B.; Breen, J. P.; Fayer, M. D., Structural dynamics in ionic liquid thin films: The effect of cation chain length. *J. Phys. Chem. C* **2020**, *124*, 4179-4189.
9. Wu, B.; Breen, J. P.; Xing, X.; Fayer, M. D., Controlling the dynamics of ionic liquid thin films via multilayer surface functionalization. *J. Am. Chem. Soc.* **2020**, *142*, 9482-9492.
10. Gebbie, M. A.; Dobbs, H. A.; Valtiner, M.; Israelachvili, J. N., Long-range electrostatic screening in ionic liquids. *Proc. Nat. Acad. Sci. USA* **2015**, *112* (24), 7432-7437.
11. Gebbie, M. A.; Valtiner, M.; Banquy, X.; Fox, E. T.; Henderson, W. A.; Israelachvili, J. N., Ionic liquids behave as dilute electrolyte solutions. *Proc. Nat. Acad. Sci. USA* **2013**, *110* (24), 9674-9679.
12. Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G. J., Charge-Induced Long-Range Order in a Room-Temperature Ionic Liquid. *Langmuir* **2016**, *32*, 9507-9512.
13. Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G. J., Modulation of an Induced Charge Density Gradient in the Room Temperature Ionic Liquid BMIM⁺BF₄⁻. *J. Phys. Chem. C* **2018**, *122*, 7361-7367.

14. Wang, Y.; Jarosova, R.; Swain, G. M.; Blanchard, G. J., Characterizing the Magnitude and Structure-Dependence of Free Charge Density Gradients in Room Temperature Ionic Liquids. *Langmuir* **2020**, *36*, 1152-1155.
15. Wang, Y.; Parvis, F.; Hossain, M. I.; Ma, K.; Jarosova, R.; Swain, G. M.; Blanchard, G. J., Local and Long-Range Organization in Room Temperature Ionic Liquids. *Langmuir* **2021**, *37*, 605-615.
16. Wang, Y.; Swain, G. M.; Blanchard, G. J., Charge-Induced Birefringence in a Room Temperature Ionic Liquid. *J. Phys. Chem. B* **2021**, *125*, 950-955.
17. Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M., Hydrophobic, Highly Conductive Ambient-temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168-1178
18. Nordness, O.; Brennecke, J. F., Ion Dissociation in Ionic Liquids and Ionic Liquid Solutions. *Chem. Rev.* **2020**, *120*, 12873-12902.
19. Wang, Y.; Adhikari, L.; Baker, G. A.; Blanchard, G. J., Characterizing the Structure-Dependence of the Induced Free Charge Density Gradient in Imidazolium and Pyrrolidinium Ionic Liquids. *Langmuir* **2021**, *submitted*.
20. Jarosova, R.; Swain, G. M., Rapid Preparation of Room Temperature Ionic Liquids with Low Water Content as Characterized by Ta-C:N Electrode. *J. Electrochem. Soc.* **2015**, *162*, H507-H511.
21. Seki, S.; Tsuzuki, S.; Hayamizu, K.; Umebayashi, Y.; Serizawa, N.; Takei, K.; Miyashiro, H., Comprehensive refractive index property for room temperature ionic liquids. *J. Chem. Eng. Data* **2012**, *57*, 2211-2216.
22. Lorentz, H. A., Ueber die Anwendung des Satzes vom Virial in der kinetischen Theorie der Gase. *Annal. der Physik* **1881**, *248* (1), 127-136.
23. Lorenz, L., Ueber die Refractionsconstante. *Annal. der Physik* **1880**, *247* (9), 70-103.

SUMMARY

Room temperature ionic liquids (RTILs) have found wide range of applications because of properties that are anomalous when compared to conventional solvents. Understanding the molecular-scale dynamics and interactions that are responsible for these properties is the key to utilize this family of materials most effectively.

We report on the induced free charge density gradients (ρ_f) in different RTILs. The fluorescence anisotropy decay of a trace-level charged chromophore in the RTIL is measured as a function of distance from the positively charged indium-doped tin oxide (ITO) support surface to probe ρ_f . We characterize the structure-dependence of this induced long-range organization in RTILs and evaluate the magnitude of the gradient ρ_f . This gradient is found to depend sensitively on the identities of the RTIL constituents. The magnitude of ρ_f increases with increasing imidazolium cation aliphatic chain length and is greater for the RTIL with bis(trifluoromethylsulfonyl)imide (TFSI⁻) anion than that of the RTIL with tetrafluoroborate (BF₄⁻) anion.

We also characterize ρ_f for different pyrrolidinium ionic liquids and compare the results to those seen for imidazolium ionic liquids. We find that the magnitude of ρ_f depends primarily on the cation aliphatic chain length and differs little with the identity of the charge-carrying cation headgroup. An implication of these findings is that local organization in the RTILs that is mediated by the nonpolar constituents of the cations plays a significant role in the ability of these systems to support a charge density gradient over macroscopic distances. Understanding how this gradient depends on RTIL constituent identity provides insight into which intermolecular interactions mediate the effect and help to determine the range of utility for this effect, with such knowledge, we can design the systems with specific, predetermined properties.

In order to explore the potential application of ρ_f in RTILs, we relate ρ_f to the dielectric response. We establish experimentally the relationship between surface charge-induced ρ_f and change in refractive index (n) in the RTIL. We design a RTIL sample holder that is in the shape of a plano-convex lens, with the curved inner surface of the lens being coated with ITO, an optically transparent conductor. The surface charge density (σ_s) of the RTIL support is controlled by the current passed through the ITO film. The farfield image of light passed through the RTIL lens as a function of σ_s is used to measure the charge-induced changes in n of the RTIL. We demonstrate the existence of charge-induced refractive index gradient and birefringence in RTILs, and suggest the utility of RTILs as novel electro-optic materials. This work also provides a probe-free means of evaluating ρ_f and demonstrates a simple way to characterize the polarizability of RTILs. We also examine the cation structure-dependence of the charge-induced change in n . The magnitude of Δn is found to depend on the RTIL cation aliphatic chain length, providing essential information for design of RTIL constituents for the optimization of electro-optic effects. This work also demonstrates the connection between the ρ_f and Δn in the RTIL, induced by the surface charge.

Our focus has been on understanding the surface charge-induced free charge density gradients in RTILs, and our group continue to work to identify the commonality and connection between various long-range phenomena seen in RTILs. Making such connections will improve the understanding of the long-range organization in RTILs and lead to more effective utilization of these materials.