Influence of Water on Carbon Dioxide and Room Temperature Ionic Liquid Dynamics: Supported Ionic Liquid Membrane vs the Bulk Liquid

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Supporting Information

ABSTRACT: The influence of water on the dynamics of a room temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EmimNTf2), and CO2 in the RTIL was studied in the bulk liquid and a supported ionic liquid membrane (SILM) using two-dimensional infrared (IR) and IR polarization selective pump–probe spectroscopies. In the water-saturated bulk EmimNTf2, the complete orientational randomization and structural spectral diffusion (SSD) of CO2 became faster than in the dry EmimNTf2. In the poly(ether sulfone) SILM, only the longer time components of the SSD became faster in the water-saturated RTIL; the complete orientational randomization remained similar to the dry RTIL in the SILM. The implication is that the presence of water in EmimNTf2 contained in the SILM facilitates the fluctuation of globally modified RTIL structure in the pores, but the local RTIL environments are relatively unaffected.

I. INTRODUCTION

Supported ionic liquid membranes (SILMs) are promising materials for CO2 capture.1–4 SILMs consist of organic or inorganic porous membranes impregnated with room temperature ionic liquids (RTILs) in the pores. Because of the large surface area per unit volume and their mechanical structure, SILMs can efficiently capture CO2. Because CO2 does not react with the RTIL, costly chemical regeneration is not necessary. CO2 diffuses through the RTIL/membrane from the high CO2 concentration side to exit on the low concentration side.1–4

There have been many efforts to improve the SILM design and performance1–4 since the first SILM study was reported in 2002.5 Recently, we carried out polarization selective pump–probe (PSPP) and two-dimensional infrared (2D IR) experiments on poly(ether sulfone) (PES) SILMs prepared with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EmimNTf2) under dry conditions.6,7 In these studies, the orientational relaxation of SeCN− and CO2 and the structural dynamics of the RTIL significantly slowed down in two SILMs compared to the bulk RTIL. This result was surprising, given the fact that the SILMs had large averaged pore sizes of ~100 and ~350 nm, indicating long-range modification of RTIL structures by interaction with the pore interfaces.6,7 Time-dependent fluorescence Stokes shift measurements studying the effect of the RTIL cation alkyl chain length on the dynamics supported the results of the earlier work.6

In the postcombustion CO2 capture, SILMs will be exposed to humid conditions where the gas can contain 10% water.7 Therefore, the RTIL in the membrane pores will be saturated with water. Even though EmimNTf2 is not highly hygroscopic, it picks up a non-negligible amount of water at saturation, up to a mole fraction of 0.278.10 The presence of water can change the CO2 and RTIL dynamics in SILMs, but the effects of water on SILMs’ properties are not well understood.11,12 For example, the viscosity of bulk RTILs generally decreases with the presence of water,10,13 which can enhance CO2 diffusivity. However, the water effect on the CO2 diffusivity in SILMs may differ from that in the bulk RTIL because the mesoscopic RTIL structure and dynamics in SILMs are different from those in the bulk.6–8 To this end, the current study examined the influence of water on the CO2 and RTIL dynamics by comparing the PSPP and 2D IR experimental results for bulk and PES200 membrane samples with an average pore size of ~350 nm6 prepared with dry and water-saturated EmimNTf2.

II. EXPERIMENTAL METHODS

II. Sample Preparation. EmimNTf2 was purchased from Iolitec and stored in a nitrogen glovebox after drying under vacuum (~100 mTorr) at ~65 °C. Isotopically labeled 13CO2 (<99% isotopic purity) and poly(ether sulfone) membrane (Sutor 200) were purchased from Icon Isotopes and Pall corporation, respectively. The water-saturated EmimNTf2 was prepared by extracting EmimNTf2 from the phase-separated water–EmimNTf2 mixture that was stirred overnight after the

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addition of water. The SILM samples containing $^{13}$CO$_2$ were prepared according to previously described procedure, except that the water-saturated EmimNTf$_2$ was used for making the wet SILM samples. Water absorption bands in Fourier transform infrared (FT-IR) spectrum confirmed that the water content in the RTIL of the wet bulk and SILM samples were nearly the same.

II.II. Time-Resolved Ultrafast Infrared Experiments. The details of the experimental setup are described in the Supporting Information, and only a brief outline is presented here. A Ti:sapphire regenerative amplifier pumped a home-built optical parametric amplifier creating mid-IR pulses centered at 2277 cm$^{-1}$ with $\sim 6 \mu$J pulse energy. The mid-IR beam was split into two beams, a stronger pump pulse and a weaker probe pulse. The pump pulse was passed through an acousto-optic mid-IR Fourier-domain pulse shaper. In the PSPP experiments, the pulse shaper chopped the pump pulse to obtain transient absorption signals, whereas in the 2D IR experiments the pulse shaper generated two excitation pulses and controlled the delay time ($\tau$) between them. In addition, the pulse shaper controlled the phase of the pulses and was used to overcome light scattering, which was the major difficulty in performing the laser experiments on the membranes. A mechanical delay stage in the probe pulse path controlled the time delay between the pump and probe pulses in the PSPP experiments or the time delay (waiting time, $T_w$) between the second excitation pulse and the third excitation pulse (probe pulse) in the 2D IR experiments. The pump and probe pulses are focused into the sample with a small crossing angle for both experiments.

After passing through the sample, the probe pulse was directed into a spectrograph. The spectrograph dispersed the probe pulse, which was then detected in the frequency domain by a 32 pixel HgCdTe (MCT) IR array detector. The 2D IR signal was collinear with the third pulse (probe pulse), which also acted as the local oscillator used for heterodyne detection of the signal. In the PSPP measurements, the probe polarization was horizontal (in the plane of the optical table) and the pump polarization was at 45° with respect to the probe pulse. After the sample, a polarizer mounted on a computer controlled rotation stage alternately resolved the probe pulse at $+45^\circ$ (parallel to the pump) and $-45^\circ$ (perpendicular to the pump) relative to the incident polarization (horizontal). Because the response of the spectrograph grating depended on polarization, another horizontal polarizer was placed in front of the spectrometer’s entrance slit to ensure that there was no bias in the detection of the polarizations. To carry out the polarization selective 2D IR measurements, the polarization of both excitation pulses was set to 0 or 90° relative to the probe polarization (horizontal) in the (XXXX) (parallel) and (XYYY) (perpendicular) configurations, respectively, using a half-wave-plate followed by a polarizer. The resolving polarizer after the sample was fixed to horizontal and not changed for either polarization configurations.

III. RESULTS AND DISCUSSION

III.I. Linear IR Absorption Spectra. Figure 1 displays the FT-IR absorption spectra of $^{13}$CO$_2$ in the bulk RTIL and the SILM under both dry and water-saturated conditions. As shown in Figure 1A, the asymmetric stretch band of $^{13}$CO$_2$ in the bulk RTIL appears at 2276 cm$^{-1}$. The water saturated bulk RTIL has an identical $^{13}$CO$_2$ absorption spectrum within the experimental error (Figure 1A).

The absorption spectrum of $^{13}$CO$_2$ in the SILM (Figure 1B) has an additional peak along with the 2276 cm$^{-1}$ bulk peak. In the SILM, the CO$_2$ resides in the RTIL/pores and in the PES membrane material. The band at 2271 cm$^{-1}$ was previously assigned to the asymmetric stretch of CO$_2$ in the polymer. $^{13}$CO$_2$ in the polymer is isolated from the RTIL/pores and, thus, behaves differently; CO$_2$’s orientational relaxation and spectral diffusion in the polymer are much slower than they are in the RTIL/pores. Water in the RTIL/pores does not affect CO$_2$ in the polymer; the results presented here focus on CO$_2$ in the RTIL/pores.

The water in the RTIL in the SILM changes the relative amplitudes of the asymmetric stretch band of CO$_2$ in the RTIL/pores and in the polymer, whereas the band positions do not change (see Figure 1B). CO$_2$ is added to the wet and dry samples in an identical manner. The membranes containing RTIL or RTIL/water in the pores are placed in 2 mL vials under CO$_2$ pressure of $\sim 0.123$ atm, which is 200 times the quantity of CO$_2$ necessary to saturate the RTIL in the SILM with CO$_2$ based on the bulk solubility. (The CO$_2$ solubility in the bulk EmimNTf$_2$ has been reported to be 0.1 mol·L$^{-1}$·atm$^{-1}$ and the same with and without water in EmimNTf$_2$.) Typically, the samples are kept in the CO$_2$ atmosphere for 20 min, but tests at 1 and 10 h do not change the band ratios. Because of the difficulty of measuring the absolute absorbance of the samples due to the extreme light scattering through the membranes, only the ratio of the two peak amplitudes can be reliably determined. Preparation of many different dry and wet samples shows that the band ratios are reproducible. The increase in the relative size of the CO$_2$ band in the RTIL/pores

![Figure 1](image-url)
with water compared to the CO₂ in the polymer suggests that CO₂ is more soluble when the RTIL is saturated with water than when it is dry. As discussed later, the time-dependent measurements show that the dynamics are different in the wet and dry membrane samples, which in turn differ from the bulk wet and dry RTILs.

The linear absorption spectra are sensitive to the structures and interactions of CO₂ with the local surrounding environment. The absence of change in the absorption spectrum of CO₂ in the RTIL with water indicates that the environment surrounding CO₂ is little changed by the addition of water. Water and CO₂ do not have strong attractive interactions as evidenced by the low CO₂ solubility in water; the CO₂ in the wet RTIL samples apparently avoids direct interactions with water and will mostly interact with the anions of the RTIL.

III.II. PSPP Measurements: Population and Rotational Dynamics. Vibrational relaxation is affected by interactions of the vibrational chromophore with the surrounding solvent molecules. In general, the vibrational energy in the initially excited mode flows into the combinations of intramolecular lower frequency modes and the continuum of low frequency intermolecular bath modes during relaxation. Therefore, the vibrational lifetime is sensitive to the environment of a vibrational oscillator. The vibrational lifetime of the ¹³CO₂ asymmetric stretch band in dry EmimNTf₂ is measured to be 64 ± 2 ps. The decay constant in the dry SILM sample is 61 ± 2 ps. These values are the same within experimental error. The vibrational lifetimes of the same band for the wet RTIL samples are obtained in this study as previously described in the dry RTIL studies. The time constant is 59 ± 1 ps for both wet bulk and SILM samples. The wet samples give almost the same lifetimes as those in the dry samples. The results indicate a small change in lifetimes in the wet samples compared to the corresponding dry samples, but the error bars overlap. The absorption spectra (Figure 2) show no significant effects with the addition of water, indicating little change in the interactions of CO₂ with its surroundings. The lifetime measurements show at most a small influence of water on the local interactions of CO₂ with the RTIL/water mixture.

Anisotropy decays (orientational relaxation) change substantially in the wet samples. Figure 2 presents the anisotropy decays of CO₂ in the RTIL bulk and SILM samples. The anisotropy consistently decays faster when the RTIL contains water in both the bulk and SILM samples. For the bulk, the anisotropy decay curves are fit well with triexponentials. The triexponential decays arise from short time restricted angular sampling of CO₂ followed by the complete randomization on the longest time scale. The data can be interpreted with the wobbling-in-a-cone model.

The anisotropy decays in the SILM also can be fit with triexponentials. The PES membrane has a large pore size distribution that ranges from 100 to 500 nm (see inset Figure 2). A previous study of two PES membranes with different average pore sizes showed that the dynamics are strongly dependent on the pore sizes, slowing for smaller pores. Therefore, CO₂ in the different pore sizes of PES200 will have different dynamics. The results for the SILMs are averages over a distribution of orientational relaxation times. For an initial comparison, we will use the correlation time, $r_{out}$, which is the integral of the curves. The correlation times are obtained by integrating the triexponential fits to normalized anisotropy decay data. The normalized orientational relaxation correlation function (second Legendre correlation function) fit parameters are given in the Supporting Information (Table S1). For the bulk samples, the correlation times are 22 ps (dry) and 11 ps (wet). In the SILMs, the correlation times are 38 ps (dry) and 30 ps (wet). As can be seen in Figure 2 and from the correlation times, saturating the RTIL with water causes the orientational relaxation to become faster. For both dry and wet samples, the orientational relaxation in the SILMs is slower than that in the bulk liquid. The change in going from dry to wet is greater in the bulk liquid than in the SILM.

Although the anisotropy decays obtained for SILMs are an average over pore sizes, the fact that they are described well with triexponential functions indicates that the CO₂ orientational dynamics occur in the same manner as in bulk samples. The three time constants found for the SILM samples are the times for wobbling and complete orientational relaxation, but each process is still an averaged observable over the distribution of pore sizes. Nonetheless, it is still useful to compare the time constants and amplitudes of the exponentials and to perform the wobbling-in-a-cone analysis (Table 1). The analysis enables us to acquire the time for the complete orientational diffusion of CO₂ in the SILM. The rotational diffusion is closely related to the translational diffusion that is an important measure of SILM performance. (In addition, the parameters from the wobbling-in-a-cone analysis are used in the 2D IR data analysis as discussed later.)

All of the curves show initial anisotropy values less than 0.4 (the maximum anisotropy, see Figure 2). CO₂ undergoes inertial motions, responsible for the initial drop from 0.4, on an ultrafast time scale that cannot be resolved in the experiments. In the wobbling model, the CO₂ can sample a limited range of angles, a cone, determined by the constraints imposed by the solvation environment. Relaxation of the constraints on some time scale allows a larger range of angles to be sampled until additional constraints are released. Eventually, the CO₂ will be able to sample all of the angles, i.e., complete orientational randomization. The triexponential decays indicate that the two cones are sampled diffusively, followed by complete diffusive randomization. In addition, there is an initial inertial cone. From the wobbling-in-a-cone analysis, the triexponential decay time constants and the associated amplitudes yield the
Table 1. Parameters from Wobbling Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \theta_{c1} ) (deg)</th>
<th>( \theta_{c2} ) (deg)</th>
<th>( \theta_{m} ) (deg)</th>
<th>( \tau_{c1} ) (ps)</th>
<th>( \tau_{c2} ) (ps)</th>
<th>( \tau_{m} ) (ps)</th>
<th>( D_{c1} ) (10^{-2} ps^{-1})</th>
<th>( D_{c2} ) (10^{-2} ps^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk dry</td>
<td>22.5 ± 1.5</td>
<td>30.3 ± 0.9</td>
<td>33.3 ± 0.8</td>
<td>48.7 ± 0.5</td>
<td>0.9 ± 0.1</td>
<td>7.4 ± 0.9</td>
<td>52 ± 1</td>
<td>8.2 ± 1.4</td>
</tr>
<tr>
<td>wet</td>
<td>16.3 ± 3.4</td>
<td>36.9 ± 1.4</td>
<td>33.1 ± 0.9</td>
<td>50.5 ± 0.6</td>
<td>0.5 ± 0.1</td>
<td>5.6 ± 0.9</td>
<td>31 ± 1</td>
<td>21.6 ± 3.6</td>
</tr>
<tr>
<td>SILM dry</td>
<td>16.6 ± 2.7</td>
<td>31.5 ± 1.3</td>
<td>30.4 ± 0.7</td>
<td>45.5 ± 0.4</td>
<td>0.6 ± 0.1</td>
<td>8.2 ± 1.1</td>
<td>90 ± 2</td>
<td>12.9 ± 2.3</td>
</tr>
<tr>
<td>wet</td>
<td>17.2 ± 2.0</td>
<td>33.0 ± 0.9</td>
<td>35.1 ± 0.4</td>
<td>49.5 ± 0.3</td>
<td>0.5 ± 0.1</td>
<td>8.2 ± 0.6</td>
<td>84 ± 2</td>
<td>16.1 ± 2.0</td>
</tr>
</tbody>
</table>

"The inertial cone angle. \( \theta_{i1} \) and \( \theta_{i2} \) are the first and second diffusive cone half angles, respectively. The total cone half angle accounting for all three cones. \( \tau_{c1} \), \( \tau_{c2} \), and \( \tau_{m} \) are the decay times associated with the first and second diffusive cones and the final free diffusion, respectively. \( D_{c1} \) and \( D_{c2} \) are the first and second cone diffusion constants, respectively. Numbers are from ref 7."
Table 2. SSD Parameters from RISD Fits Based on the Second-Order Stark Effect Model

<table>
<thead>
<tr>
<th>sample</th>
<th>scalar</th>
<th>vector</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_1$</td>
<td>$\tau_1$ (ps)</td>
</tr>
<tr>
<td>bulk</td>
<td>0.09 ± 0.02</td>
<td>20 ± 5</td>
</tr>
<tr>
<td>dry</td>
<td>0.04 ± 0.01</td>
<td>17 ± 8</td>
</tr>
<tr>
<td>wet</td>
<td>0.07 ± 0.02</td>
<td>16 ± 3</td>
</tr>
<tr>
<td>wet samples</td>
<td>0.36 ± 0.01</td>
<td>57 ± 5</td>
</tr>
</tbody>
</table>

(4) Amplitude of each exponential. (5) Values are from ref 7.

Table 3. Ratios of Fit Parameters among Dry/Wet and SILM/Bulk Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>anisotropy</th>
<th>SSD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_m$</td>
<td>$\tau_1$</td>
</tr>
<tr>
<td>dry/wet</td>
<td>1.65 ± 0.06</td>
<td>2 ± 0.54</td>
</tr>
<tr>
<td>SILM</td>
<td>1.08 ± 0.04</td>
<td>1.06 ± 0.54</td>
</tr>
<tr>
<td>SILM/bulk</td>
<td>1.76 ± 0.05</td>
<td>0.85 ± 0.45</td>
</tr>
<tr>
<td>dry</td>
<td>2.68 ± 0.11</td>
<td>1.6 ± 0.34</td>
</tr>
<tr>
<td>wet</td>
<td></td>
<td>1.23 ± 0.14</td>
</tr>
</tbody>
</table>

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The RTIL is saturated with water, the SSD is accelerated in both bulk and SILM samples; the time constants of the SSD decrease in the wet RTIL condition for both samples, with the exception of the SILM shortest time constant, $\tau_1$ (Table 2). However, the extent of change induced by water differs between the bulk and SILM. This difference is shown clearly in the correlation times, $\tau_{2D}$ given earlier in the paper.

III.IV. Water Effects on the Dynamics in the SILM. The ratios of the SSD time constants and the complete reorientational diffusion time constant, $\tau_{2D}$ are given in Table 3 and Figure 4. Figure 4A presents the ratios of the time constants of the dry sample to those from the wet sample and compares the trends for the bulk and SILM samples. It shows that all four time constants of the bulk sample are affected by water, with the dynamics accelerated upon addition of water. In contrast, for the SILM samples, water only impacts the longer time scale SSD parameters, $\tau_2$ and $\tau_3$, whereas the complete orientational diffusion, $\tau_{2D}$ and the short time SSD, $\tau_1$, remain basically unchanged. Moreover, the ratios of $\tau_2$ and $\tau_3$ for the SILM are larger than those for the bulk. When the time constant ratios are calculated for the SILM and bulk samples and compared between dry and wet conditions, as displayed in Figure 4B, the ratios of $\tau_2$ and $\tau_3$ become smaller in going from dry to wet conditions. However, the ratios of $\tau_{2D}$ and $\tau_1$ increase for the wet samples because these time constants for the SILMs are almost unaffected under wet condition but become significantly faster in the bulk RTIL.

As mentioned earlier, the longer time scale SSD parameters, $\tau_2$ and $\tau_3$, reflect the fluctuations of global RTIL structure, whereas the short time SSD and the complete orientational diffusion report on the local structural fluctuations. Therefore, the trend observed in the time constant ratios suggests that water facilitates the global fluctuations of liquid structure in the SILM more than it does in the bulk, but it does not greatly impact the local RTIL environments experienced by the CO$_2$ molecules in the SILM. In addition, the presence of water in the SILM does not seem to hamper the long-range RTIL structuring induced by the membrane interface; under wet condition, all of the ratios are larger than 1, meaning that the overall dynamics in the wet SILM are still slower than those in the wet bulk (see Figure 4B).

Finally, the results suggest that the diffusivity of CO$_2$ through the SILM used in this study will not be significantly improved by the presence of water. The orientational diffusion of CO$_2$ in
the SILM is mainly governed by the local RTIL environment. Water only affects the global RTIL structural fluctuations in the SILM, but the local RTIL structures and, thus, the reorientation of CO$_2$ are relatively insensitive to the water content. If the orientational relaxation and the translational diffusion are consistent with hydrodynamics, then the complete orientational relaxation, $\tau_{ow}$, is given by the Debye–Stokes–Einstein equation and the translational diffusion is described by the Stokes–Einstein equation. These equations are closely related, suggesting that if the orientational diffusion is not affected by the addition of water, then the translational diffusion will also not be affected. Indeed, Scovazzo et al. observed that the CO$_2$ permeability through the same SILM as used in the current study did not change significantly with the relative humidity of the gas.$^{12}$ (The permeability is the product of solubility and diffusivity in the solution—diffusion mass-transfer model.)$^{1-4}$ The permeability only increased from 960 to 1050 barrers as the relative humidity of CO$_2$ changes from 10 to 85%.$^{12}$ Figure 1B may suggest that CO$_2$ solubility increases somewhat in the wet SILM. Therefore, our results are consistent with those from the CO$_2$ permeability experiments of Scovazzo et al. On the other hand, Zhao et al. reported a different water effect on the CO$_2$ permeability in the SILM consisting of PES membranes and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide (BmimBF$_4$). In that SILM, the CO$_2$ permeability increases when the water content in the RTIL is small, but decreases again as the water content increases.$^{11}$ They attributed their observation to the combined effects of water, that is, enhancing diffusivity and diminishing solubility of CO$_2$: the diffusivity effect is more dominant at the low water content, but the solubility effect becomes predominant at the high water content.$^{11}$ It is important to note that BmimBF$_4$ is completely miscible with water, which can result in different water effects in the SILM. Therefore, similar water effects as those observed in the current study are expected in the SILMs containing other nonwater-miscible RTILs, and significant enhancement in CO$_2$ diffusion by the addition of water in these SILMs is unlikely.

IV. CONCLUDING REMARKS

The water effects on the CO$_2$ dynamics in the bulk EmimNTf$_2$ and SILM were investigated by the PSPPP and 2D IR spectroscopies. The FT-IR spectrum of asymmetric stretch band of CO$_2$ in the water-saturated EmimNTf$_2$ did not differ from that measured in the dry condition. In the wet SILM sample, the relative size of CO$_2$ band in the RTIL/pores increased compared to the CO$_2$ band in the PES polymer without the frequency shifts or band broadening. This may indicate the change in CO$_2$ solubility in the wet SILM. The vibrational lifetimes of CO$_2$ band were very similar between wet and dry samples for both bulk and SILM samples. Unchanged absorption spectrum and vibrational lifetimes were indicative of the negligible influence of water on the local interaction of CO$_2$ with its surroundings. Anisotropy decays from the PSPPP measurements and CLS decays from the 2D IR experiments demonstrated that water effects on the CO$_2$ and RTIL dynamics were different between the bulk and SILM samples. In the bulk samples, the time constants for the complete orientational diffusion of CO$_2$, $\tau_{ow}$, and the SSD time constants decreased by a factor of 1.2–2 as EmimNTf$_2$ was saturated with water and the effective viscosity was decreased (Table 3 and Figure 4A). In contrast, only the longer time scale SSD parameters, $\tau_2$ and $\tau_3$, decreased by a factor of 2 in the wet SILM sample, whereas $\tau_1$ and the short time scale SSD, $\tau_{1s}$, remained unchanged (Table 3 and Figure 4A). These results suggested that in the SILM, water accelerated the global fluctuations of ordered RTIL structures but did not affect the local RTIL environments near CO$_2$ molecules. Because the orientational diffusion process is strongly related to the translational diffusion that is an important measure of the SILM performance for CO$_2$ capture, the results implied that the translational diffusion of CO$_2$ would not be improved by the addition of water in the SILM prepared with nonwater-miscible RTILs like EmimNTf$_2$.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.8b01163.

Detailed descriptions of experimental methods and second-order Stark effect RISD theory, triexponential fit parameters of anisotropy decays, CLS decay curves for parallel (\textit{XXXX}) polarization configuration, and isotropic FFCF parameters (PDF)

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The authors declare no competing financial interest.
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