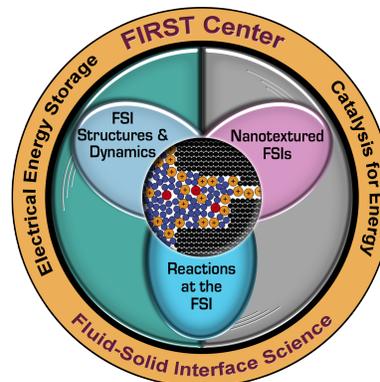


FIRST Center Research Perspective:

Nanoscale Heterogeneity and Dynamics of Room Temperature Ionic Liquids

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Research Summary: An increase of the alkyl chain length of the cation of room temperature ionic liquids (RTILs) influences the nanoscale structure and dynamics of RTILs, which in turn affect the behavior of RTILs at solid-liquid interfaces central to energy storage devices. We integrate classical molecular dynamics (CMD) simulation, fluorescence correlation spectroscopy (FCS), time resolved fluorescence anisotropy decay (TRFAD,) small angle X-ray scattering (SAXS) and nuclear magnetic resonance (NMR) to investigate the fundamental properties including structure, dynamics and interfacial behavior of RTIL electrolytes. We found that the elongation of the alkyl chain in the cation gives rise to an enhanced spatial and dynamical heterogeneity, which have been observed in CMD, FCS, TRFAD and SAXS; CMD combined with NMR has revealed the weak temperature dependence of the dynamics of RTILs at a silica surface due to the surface roughness and strong interaction between the ions and silica walls.

Technical Details: CMD is one of the most powerful tools to investigate the complex structure, dynamic processes and thermodynamic properties for many-body systems at microscopic levels. Thus, when guided and validated by integrated experimental observations, CMD is a powerful technique for exploring the behaviors of RTILs at solid-liquid interfaces. The dynamical and structural properties of RTILs extracted from CMD were analyzed in comparison with those measured in FCS, TRFAD, SAXS and NMR. We probed the translational diffusivity of trace levels of fluorescent dye species in imidazolium- and pyrrolidinium-based RTILs, and the dynamic heterogeneity in long-chain RTILs by FCS [1]. We further verified that the increased spatial heterogeneity is directly correlated with the elongation of cation alkyl chain, as evidenced by the increased low-Q peak in the structure factors (**Figure 1a, b**) obtained from CMD and SAXS [2].

It was also found that the spatial heterogeneity was attenuated at high temperature (**Figure 1a, b**), due to the local rearrangements of polar cation heads, anions and nonpolar alkyl chains. We observed spatially-controlled diffusive domains in pyrrolidinium-[3,4] and piperidinium-based [5] RTILs by integrating FCS with NMR. To understand charged solute behavior within RTILs,

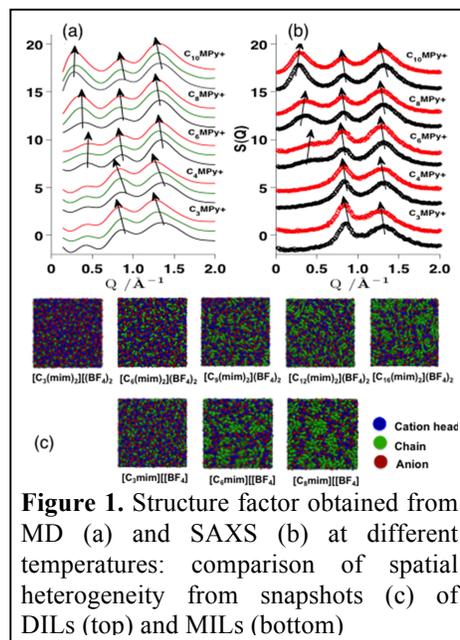


Figure 1. Structure factor obtained from MD (a) and SAXS (b) at different temperatures: comparison of spatial heterogeneity from snapshots (c) of DILs (top) and MILs (bottom)

the rotational dynamics of three illustrative xanthene fluorescent probes within a series of N-alkylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[\text{C}_n\text{mpyr}][\text{Tf}_2\text{N}]$) RTILs with different n-alkyl chain lengths were also studied using TRFAD (**Figure 2**). The rotational dynamics varied from slip to stick character, depending upon the specific solute-solvent interactions that prevailed (Coulombic vs hydrogen bonding)[3,4]. We performed SAXS and CMD simulations of dicationic RTILs, $[\text{C}_n\text{mim}_2^{2+}][\text{BF}_4]_2$, which are of great interest for capacitive energy storage, revealing that the alkyl chain length (C_n) exerts less influence on local structural organization of dicationic ionic liquids (DILs) in comparison with the common monocationic ionic liquids (MILs)[6] as shown in the snapshots from CMD (**Figure 1c**). The interfacial dynamics of RTILs $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ at silica and carbon mesopore were studied [7] by MD simulation and NMR measurement [8]. A weak temperature dependence of interfacial RTIL dynamics was observed in silica mesopores in contrast to the behavior in carbon mesopores (**Figure 3**), which resulted from the surface roughness and stronger ion-silica wall interactions in the silica. We have also found that eutectic mixtures of RTILs exhibited excellent supercapacitor performance over wide temperature ranges (-40 to 80 °C) due to the decreased melting point and enhanced conductivity, which was explored computationally [9] and experimentally[10].

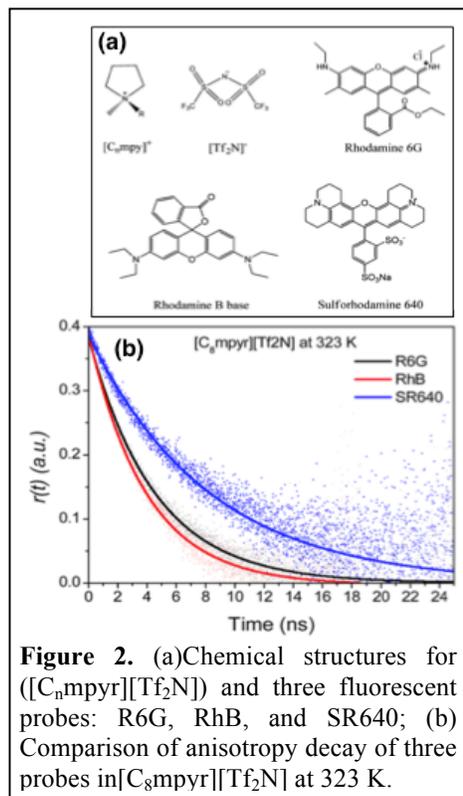


Figure 2. (a) Chemical structures for ($[\text{C}_n\text{mpyr}][\text{Tf}_2\text{N}]$) and three fluorescent probes: R6G, RhB, and SR640; (b) Comparison of anisotropy decay of three probes in $[\text{C}_8\text{mpyr}][\text{Tf}_2\text{N}]$ at 323 K.

Significant Impacts on Science and Technology: Our studies integrate a series of computational and experimental probes to elucidate the fundamental properties of RTILs and provides preliminary insights into the performance of RTIL electrolytes at the solid-liquid interfaces of energy storage devices. Based on our CMD, FCS, and SAXS studies, the biphasic diffusion regimes in RTILs with long alkyl chains was initially proposed, and this phenomenon was shown to result from the chain-length dependent self-aggregation of alkyl chains. This provides an informative picture for the local structure and dynamics of RTILs and represents a novel approach for integration of CMD, FCS and SAXS to exploit the fundamental properties for other novel RTILs. The influence of temperature on the spatial heterogeneity was for the first time illustrated by measuring the variation in the local arrangement of polar and nonpolar groups. Our study on DILs takes the first step towards the use of dicationic ionic liquids as electrolytes for energy storage devices, by comparing their structural organization with the most commonly investigated MILs. The distinctive temperature-dependent interfacial behaviors of RTILs emphasizes

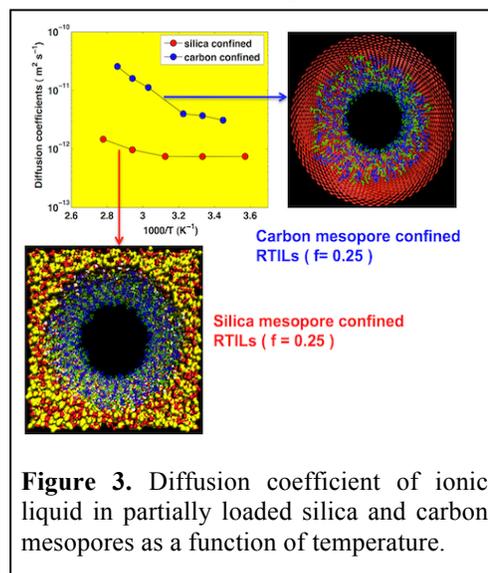


Figure 3. Diffusion coefficient of ionic liquid in partially loaded silica and carbon mesopores as a function of temperature.

the importance of investigating electrode properties, including the surface roughness and composition of electrodes, on the behavior of RTILs electrolytes, which will motivate further exploration of electrode properties with desired features. The use of eutectic mixtures of RTILs as promising electrolytes in severe cold environments was suggested based on our computational and experimental investigations, which has inspired the development of energy storage devices at extreme conditions.

Publications and Manuscripts:

1. Guo, J.; Baker, G. A.; Hillesheim, P. C.; Dai, S.; Shaw, R. W.; Mahurin S. M. Fluorescence correlation spectroscopy evidence for structural heterogeneity in ionic liquids. *Phys. Chem. Chem. Phys.* **2011a**, 13, 12395-12398, [doi: 10.1039/c1cp20929a].
2. Li, S.; Bañuelos, J. L.; Guo, J.; Anovitz, L.; Rother, G.; Shaw, R. W.; Hillesheim, P. C.; Dai, S.; Baker, G. A.; Cummings, P. T. Alkyl Chain Length and Temperature Effects on Structural Properties of Pyrrolidinium-Based Ionic Liquids: A Combined Atomistic Simulation and Small Angle X-ray Scattering Study, *J. Phys. Chem. Lett.* **2011**, 3, 125-130, [10.1021/jz2013209].
3. Guo, J.; Han, K. S.; Mahurin, S. M.; Baker, G. A.; Hillesheim, P. C.; Dai, S.; Hagaman, E. W.; Shaw, R. W. Rotational and Translational Dynamics of Rhodamine 6G in a Pyrrolidinium Ionic Liquid: A Combined Time-Resolved Fluorescence Anisotropy Decay and NMR Study, *J. Phys. Chem. B* **2012a**, 116, 7883-7890, [10.1021/jp303186v].
4. Guo, J.; Mahurin, S.; Baker, G.; Hillesheim, P.; Dai, S.; Shaw, R. Influence of Solute Charge and Pyrrolidinium Ionic Liquid Alkyl Chain Length on Probe Rotation Reorientation Dynamics, *J. Phys. Chem. B* **2013**, **Accepted**.
5. Han, K. S.; Li, S.; Hagaman, E. W.; Baker, G. A.; Cummings, P. T.; Dai, S. Rotational and Translational Dynamics of N-butyl-N-Methylpiperidinium Trifluoromethanesulfonimide Ionic Liquids Studied by NMR and MD Simulations, *J. Phys. Chem. C* **2012**, 116, 20779-20786, [10.1021/jp3069283].
6. Li, S.; Feng, G.; Bañuelos, J. L.; Rother, G.; Fulvio, P. F.; Dai, S.; Cummings, P. T. Distinctive Nanoscale Organization of Dicationic Versus Monocationic Ionic Liquids, *J. Phys. Chem C* **2013a**, 117 (35), 18251-18257, [10.1021/jp406381g].
7. Li, S.; Han, K. S.; Feng, G.; Hagaman, E. W.; Vlcek, L.; Cummings, P. T. Dynamic and Structural Properties of Room Temperature Ionic Liquids near Silica and Carbon Surfaces, *Langmuir* **2013b**, 29 (31), 974409749, [10.1021/la401172z].
8. Han, K. S.; Wang, X.; Dai, S.; Hagaman, E. W. Distribution of 1-Butyl-3-Methylimidazolium Bistrifluoromethylsulfonimide in Mesoporous Silica As a Function of Pore Filling, *J. Phys. Chem. C* **2013**, 117 (30), 15754-15762, [10.1021/jp404990q].
9. Li, S.; Feng, G.; Fulvio, P. F.; Hillesheim, P. C.; Liao, C.; Dai, S.; Cummings, P. T. Molecular Dynamics Simulation Study of the Capacitive Performance of a Binary Mixture of Ionic Liquids Near an Onion-Like Carbon Electrode, *J. Phys. Chem. Lett.* **2012**, 3, 2465-2469, [10.1021/jz3009387].
10. Tsai, W.Y.; Lin, R.; Murali, S.; Zhang, L. L.; McDonough, J. K.; Ruoff, R. S.; Taberna, P.L.; Gogotsi, Y.; Simon, P. Outstanding Performance of Activated Graphene Based Supercapacitors in Ionic Liquid Electrolyte From -50 to 80 °C., *Nano Energy* **2013**, 2 (3), 403-11, [10.1016/j.nanoen.2012.11.006].