

SUPPLEMENTARY INFORMATION

Nonpolar Solvation Dynamics for a Nonpolar Solute in Room Temperature Ionic Liquid: A Nonequilibrium Molecular Dynamics Simulation Study

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S1. Inter-atom and center of mass (COM) $g(r)$ for [Bmim][PF₆] RTIL.

Figure S1 presents the $g(r)$ s between various atoms in the RTIL. These are in very good agreement with the previous reports, indicating proper equilibration of the system.

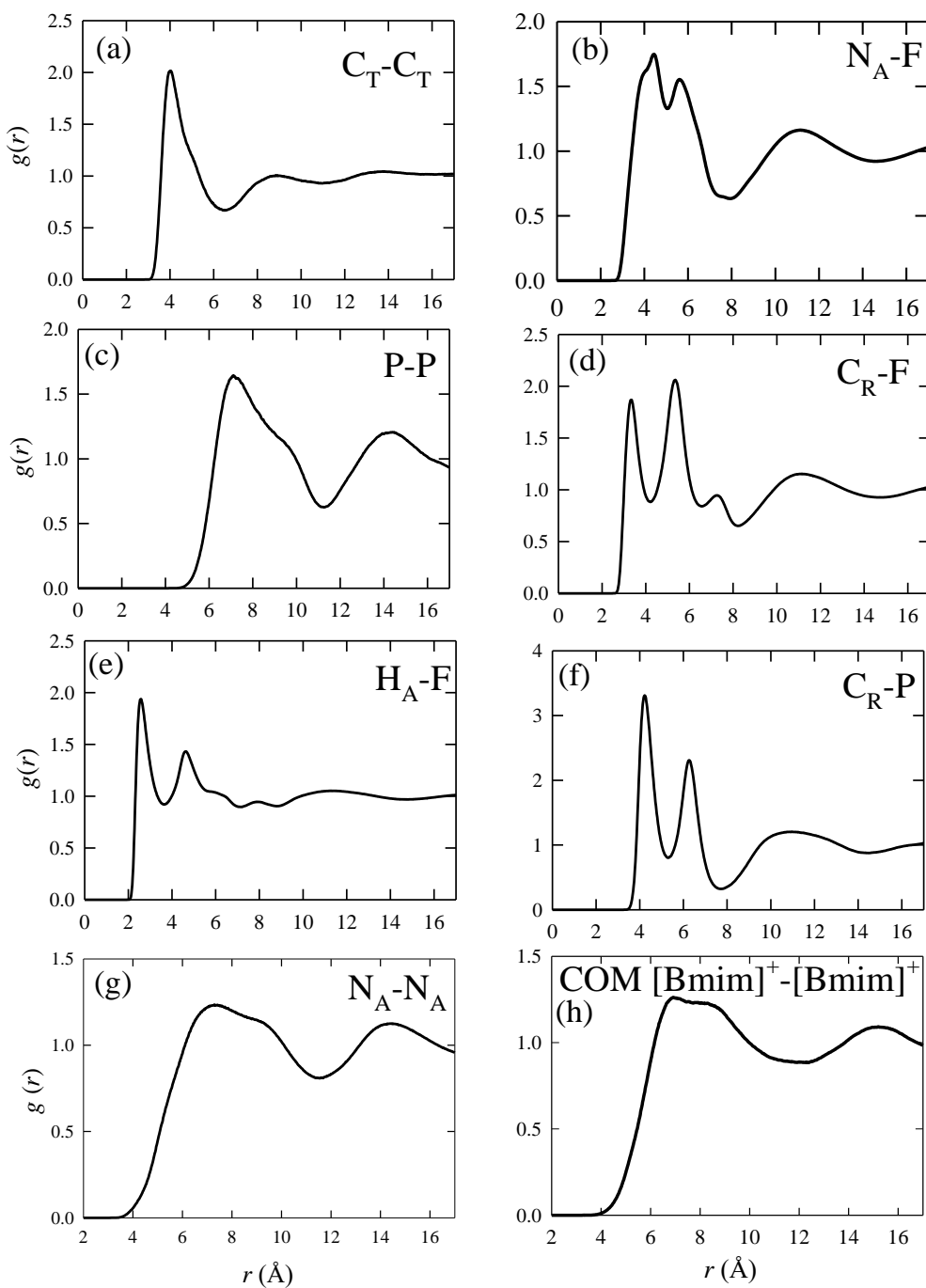


Figure S1. (a)-(g): $g(r)$ for various atoms of [Bmim][PF6] RTIL at 298 K temperature. (h) cation-cation COM $g(r)$. See Scheme 1 of the MS for atom labels.

S2. Convergence of nonequilibrium and equilibrium solvation response functions.

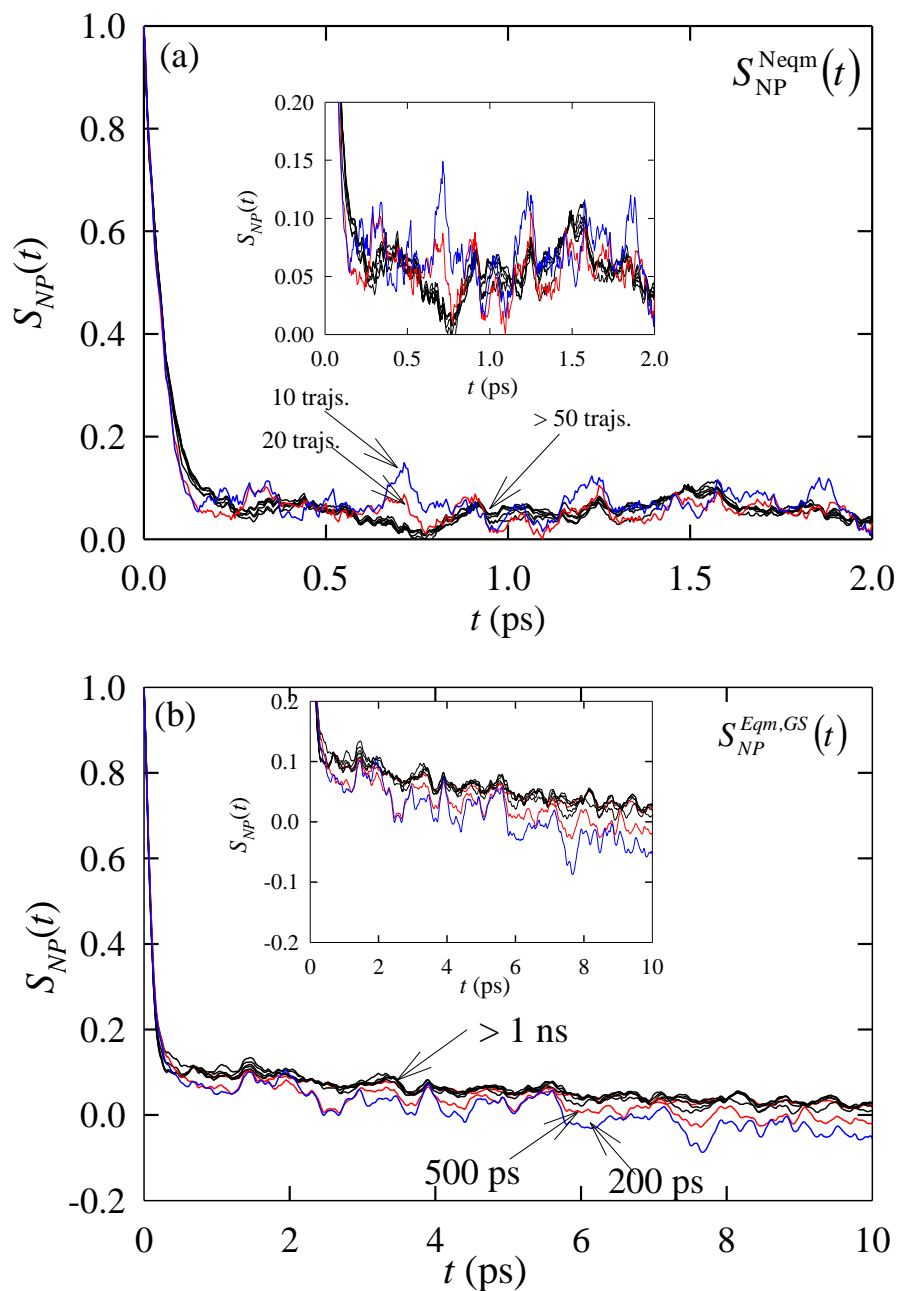


Figure S2. (a) Nonequilibrium solvation response functions calculated after averaging over different number of nonequilibrium trajectories. The response function converges after averaging over more than

50 nonequilibrium trajectories. (b) Equilibrium solvation energy correlation functions, calculated from different simulated trajectory length. It shows convergence at more than 1 ns trajectory length.

S3. Solute-RTIL side chain $g(r)$

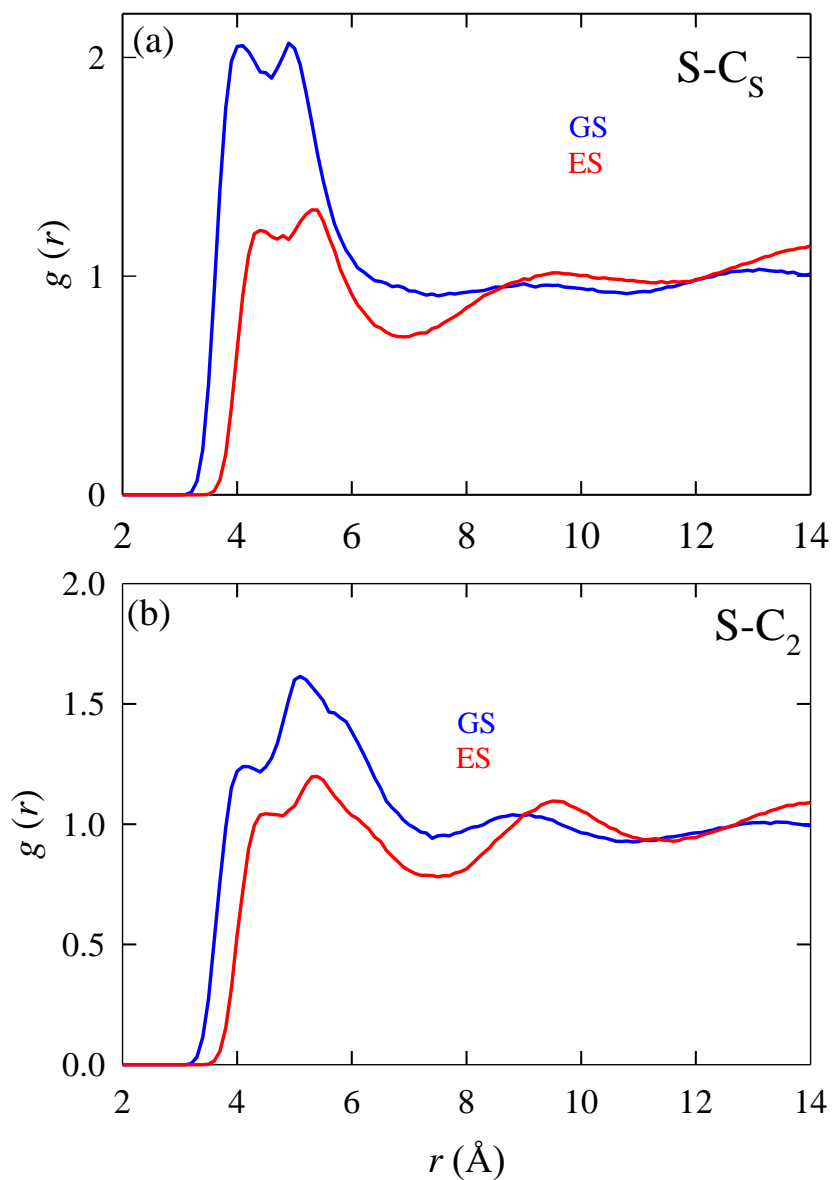


Figure S3. $g(r)$ between solute atoms and different carbon atoms of the side chain of the $[\text{Bmim}]^+$ cation.

S4. Nonpolar Solvation Response Function

The Hamiltonian of the ground and excited states are, respectively,

$$H = K_{GS} + V_{GS} + H_{IL} + U_{GS,IL} \quad (1)$$

$$H^* = K_{ES} + V_{ES} + H_{IL} + U_{ES,IL} \quad (2).$$

In eq. 1 K_{GS} and V_{GS} are respectively the kinetic and constant electronic energies of the solute at GS. H_{IL} is the solvent IL Hamiltonian including total kinetic energy and potential energy and $U_{GS,IL}$ is the interaction potential between the solute at GS and IL solvent. Due to the fact that the solute is nonpolar, $U_{GS,IL}$ is composed of the solute-IL LJ interaction only. Similarly, in eq. 2 K_{ES} and V_{ES} are respectively the kinetic energy and constant electronic energies of the solute at excited state. The interaction potential energy between the excited state solute and IL solvent is $U_{ES,IL}$.

As the current study is motivated only to study the nonpolar solvation of IL we assume that Frank-Condon type excitation of the solute changes its LJ parameter(s) without affecting the GS dipole moment. It is needless to mention that this type of excitation of the solute is unnatural although insightful for understanding the specific nonpolar part of the total process, which includes the change of dipole moment of the solute too. Frank-Condon type excitation implies that the solute and solvent IL nuclei remain fixed in a fluorescence transition. Therefore the TRFSS frequency is

$$\begin{aligned}
\hbar\langle\omega(t)\rangle &= \langle H^*(t)\rangle - \langle H(t)\rangle \\
&= \hbar\omega_0 + \left[\langle U_{ES,IL}(t)\rangle - \langle U_{GS,IL}(t)\rangle \right] \\
&= \hbar\omega_0 + \left[\langle V_{ES,IL}^{LJ}(t)\rangle - \langle V_{GS,IL}^{LJ}(t)\rangle \right] \\
&= \hbar\omega_0 + \langle\Delta E(t)\rangle
\end{aligned} \tag{3}$$

Note that “ $\langle \rangle$ ” indicates the quantity averaged over various initial conditions. In eq. 3 $\hbar\omega_0$ is the constant difference between V_{ES} and V_{GS} . Evidently the time dependent change of $\hbar\langle\omega(t)\rangle$ depends on how the RTIL solvent responds to the instantaneous change of solute-RTIL solvent LJ interaction.

The TDF red shift —averaged over initial conditions— can be written, from eq. 3, as

$$\delta\hbar\langle\omega(t)\rangle = \hbar\langle\omega(t)\rangle - \hbar\omega_0 = \langle\Delta E(t)\rangle \tag{4}$$

The normalized version of eq. 4 is called as non-equilibrium solvation response function, which is written as,

$$S_{NP}^{Neqm}(t) = \frac{\delta\hbar\langle\omega(t)\rangle - \delta\hbar\langle\omega(\infty)\rangle}{\delta\hbar\langle\omega(0)\rangle - \delta\hbar\langle\omega(\infty)\rangle} = \frac{\langle\Delta E(t)\rangle - \langle\Delta E(\infty)\rangle}{\langle\Delta E(0)\rangle - \langle\Delta E(\infty)\rangle}, \tag{5}$$

where $\langle\Delta E(t)\rangle$ relaxes from its initial value $\langle\Delta E(0)\rangle$ at $t=0$ to the final value $\langle\Delta E(\infty)\rangle$.