# Supporting Information of:

## Molecular Dynamics Simulations of Structure and Transport Properties of tetra-butylphosphonium Amino Acid Ionic Liquids

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**The Force Field.**   The internal structure of the anions and cations were considered fully flexible and the potential energy of the system was modeled using the standard functional form,

$$V_{\text{tot}} = \sum_{\text{bonds}} k_b (r - r_{\text{eq}})^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_{\text{eq}})^2 + \sum_{\text{dihedrals}} \frac{K_\varphi}{2} [1 + \cos(n\varphi - \gamma)]$$
$$+ \sum_{i=1}^{N-1} \sum_{j>1}^{N} \left\{ 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right\} \quad (1)$$

The first three terms represent intramolecular bond, angle, and torsional interactions. Harmonic functions with force constants $k_b$ and $k_\theta$ describe the intramolecular bond stretching and angle bending motions, respectively, and a cosine series describes the torsional motions. Intermolecular interactions are described by the last term of Eq. (1), including the pairwise additive atom-atom 12-6 Lennard-Jones (LJ) potential for the van der Waals interactions and the Coulombic term for the electrostatic interactions between point charges centered on the atoms.  The $\varepsilon_{ij}$ is the energy minima for the interaction for atoms $i$ and $j$ and $\sigma_{ij}$ gives the interatomic separation for these atoms at zero potential. The charges on atoms $i$ and $j$ are $q_i$ and $q_j$ and $\varepsilon_0$ is the dielectric permittivity constant for vacuum. The cross term LJ parameters for $i \neq j$ interactions are obtained from the conventional combination rules, $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$ and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$. Partial atomic charges of the ions were determined by fitting the electrostatic potential of the optimized structure using the B3LYP/6-311+G** method as described in Ref. [1]. The values of all force field parameters and a figure showing partial charges of the $[\text{TBP}]^+$ and $[\text{AA}]^-$ ions are given in the Supporting Information of Ref. [1].

**Table S1.** Computed diffusion coefficient (in $10^{-11}$ $m^2s^{-1}$) for the cations and anions from the slope of MSD plots (with the $\beta$ values in parentheses), the cationic transference number, $t_+$, and Nernst–Einstein electrical conductivity, $\sigma_{NE}$ (in $Scm^{-1}$), at relatively low temperatures for six [TBP][AA] ionic liquids.

| [AA]$^-$ | $T\,/\,K$ | $D_+(\beta)$ | $D_-(\beta)$ | $t_+$ | $\sigma_{NE}$ |
|---|---|---|---|---|---|
| GLY | 302 | 0.258 (0.82) | 0.324 (0.79) | 0.44 | $6.3 \times 10^{-4}$ |
| ALA | 310 | 0.162 (0.76) | 0.198 (0.78) | 0.45 | $3.6 \times 10^{-4}$ |
| LEU | 310 | 0.103 (0.48) | 0.094 (0.39) | 0.52 | $1.7 \times 10^{-4}$ |
| ASP | 320 | 0.089 (0.54) | 0.174 (0.68) | 0.34 | $2.4 \times 10^{-4}$ |
| GLU | 310 | 0.041 (0.47) | 0.054 (0.54) | 0.43 | $8.8 \times 10^{-5}$ |
| GLN | 303 | 0.028 (0.45) | 0.024 (0.38) | 0.54 | $5.0 \times 10^{-5}$ |

In relatively low temperatures (~310 K) reported in Table S1, the calculated exponent $\beta$ values for 2−4 ns time scales are in the range of 0.38−0.82 for [TBP][AA] ILs. The large [LEU]$^-$, [GLU]$^-$, and [GLN]$^-$ ILs have small $\beta$ values, which indicates slow glassy dynamics and sub-diffusive motion regimes, even over times between 2 – 4 ns.
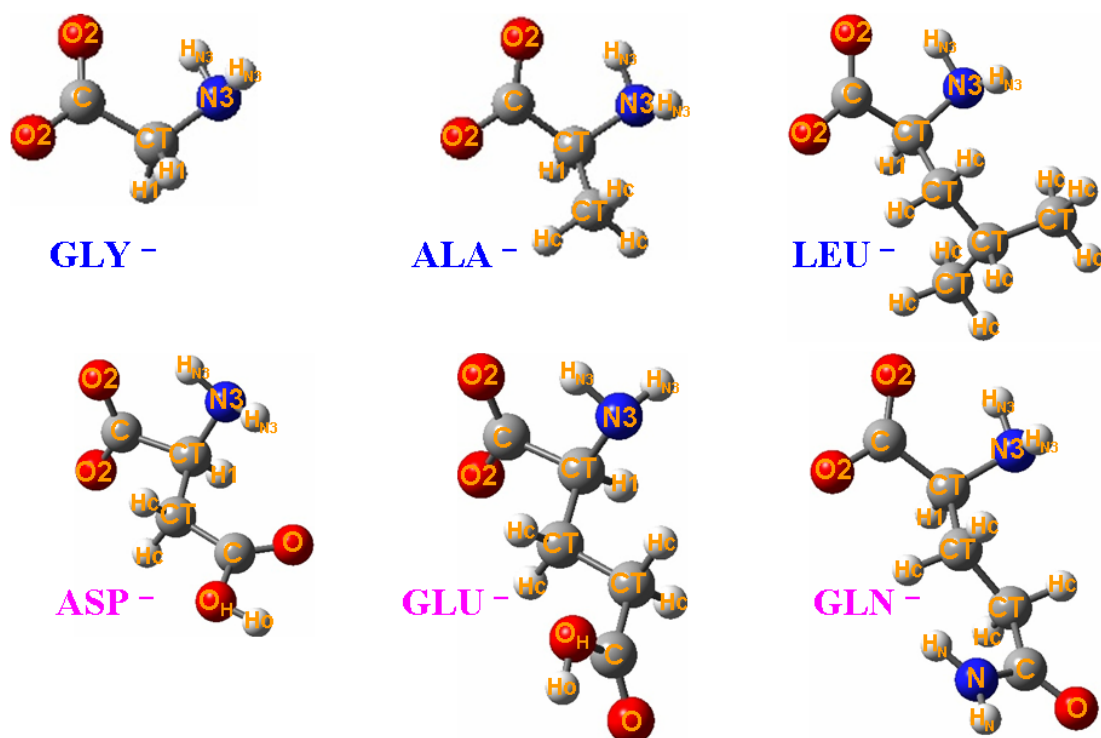
**Figure S1.** The amino acid [AA]$^-$ anions and [TBP]$^+$ cation used in this study. Some atom labels are indicated on the structures.

**The RDFs.** For clearer detailed role of the functional groups of amino acid anions in the liquid structure of AAILs, we show the site – site RDFs for the O2−$H_{N3}$ in Fig. S2, and illustrate the O2−HP pairs in Fig. S3. O2 is the oxygen atom in −COO⁻ group of the anions, $H_{N3}$ is the hydrogen atom connected to nitrogen atom (N3) of –NH$_2$ group, and HP is the hydrogen atom linked to the first carbon atom of n-butyl chains which is directly connected to the P atom in the [TBP]⁺ cations. As be shown in Fig. S2, the $g_{O2–HN3}(r)$ shows two clear peaks around 1.6 (with very huge intensity) and 2.9 Å (with moderate intensity) for each system. In good agreement with the Fig. 3 of Ref. [1], the $g_{O2–HP}(r)$ shows three clear peaks and the locations of the maxima and minima in this partial RDF are similar for all of six studied AAILs. For example, the strong first maxima are appear around 2.35 Å for all [TBP][AA] ILs and show strong interaction (hydrogen bonds) between O2 atoms of carboxylate head of [AA]⁻ with the hydrogen atoms (HP) of [TBP]⁺ cations. Similar structures were observed for [TBP][GLY] and [TBP][ALA] pairs in *ab initio* quantum chemical calculations.[2]

We also probe the effects of the polar functional groups of amino acid anions on the transport properties by computing of specific desirable RDF sites. The site – site RDFs are shown for O–$H_{N3}$ (upper panel) and O–HP (bottom panel) pairs in Fig. S4. The oxygen (O) site refers to the oxygen atom in the carboxyl segment (– COOH) of the [ASP] and [GLU] or in the amide group (– CONH$_2$) of the [GLN]. The $g_{O–HN3}(r)$ shows one clear large peak around 4.5 – 5 Å for each of the three amino acids with polar functional side chain. The $g_{O–HP}(r)$ shows three clear peaks centered around 2.4, 4, and 6 Å. The first peak in the $g_{O–HP}(r)$ maybe corresponds to hydrogen bonds between O–HP pairs of three [TBP][AA] ILs with polar functional side chains.

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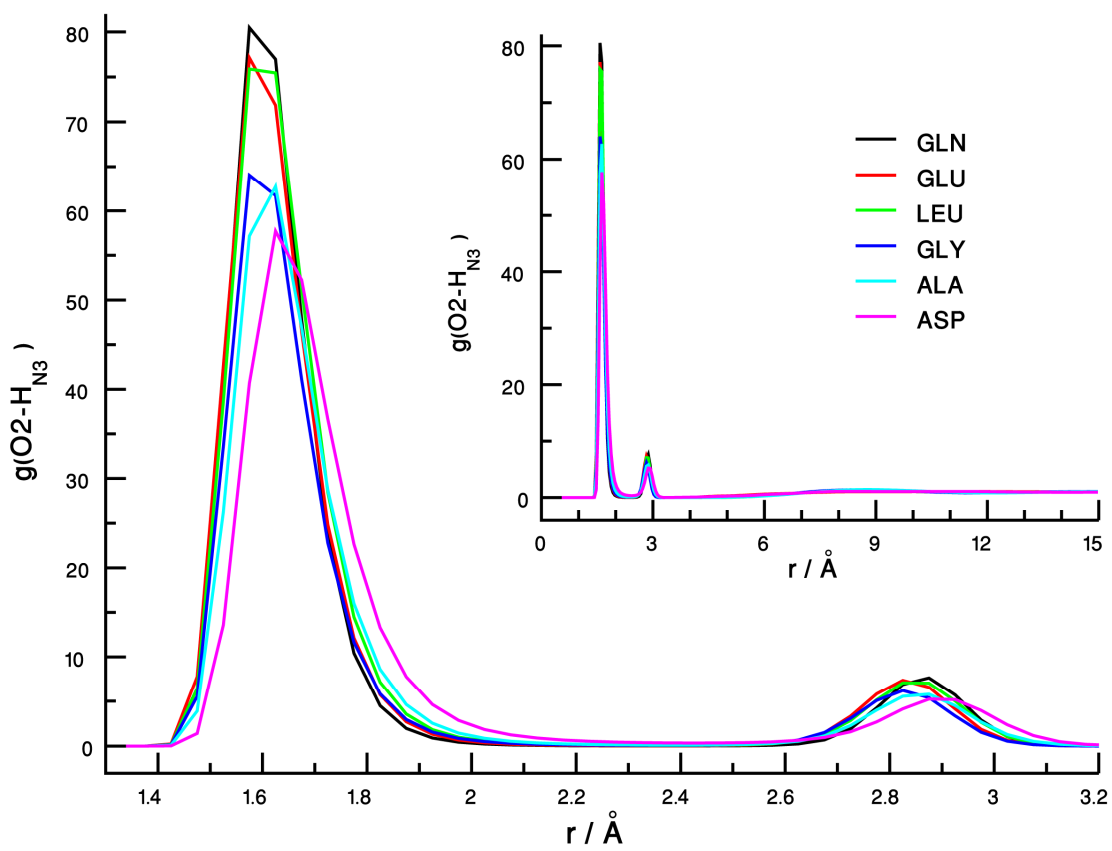
**Figure S2.** The RDFs for the O2−$H_{N3}$ pairs of AAILs. O2 is the oxygen atom in $-COO^-$ of the anions, $H_{N3}$ is the hydrogen atom connected to nitrogen atom (N3) of $-NH_2$ group.
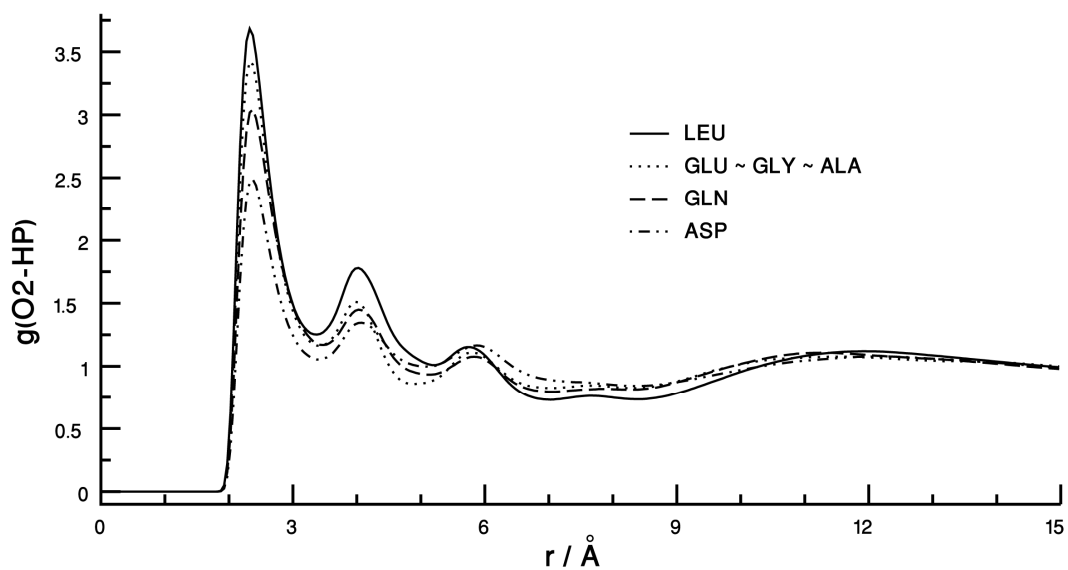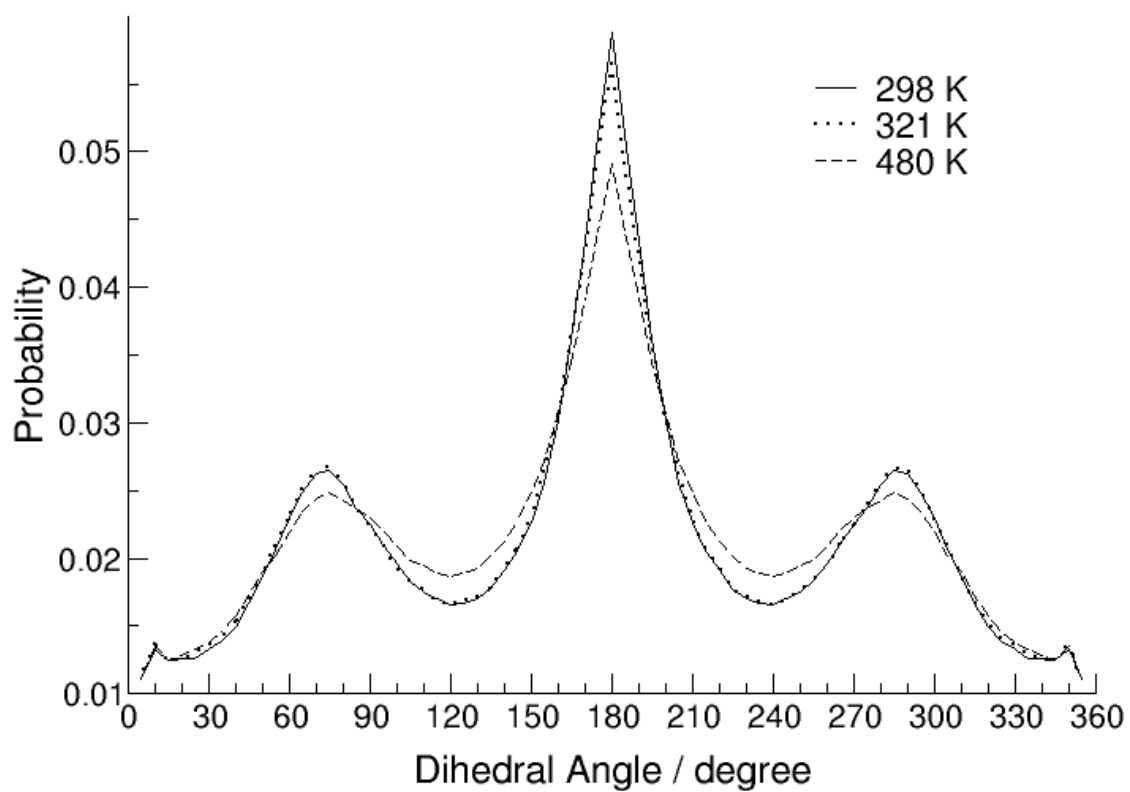
**Figure S3.** The RDFs for the O2−HP pairs of ILs. O2 is the oxygen atom in $-COO^-$ part of the anions, and HP is the hydrogen atom of $[TBP]^+$ cation.
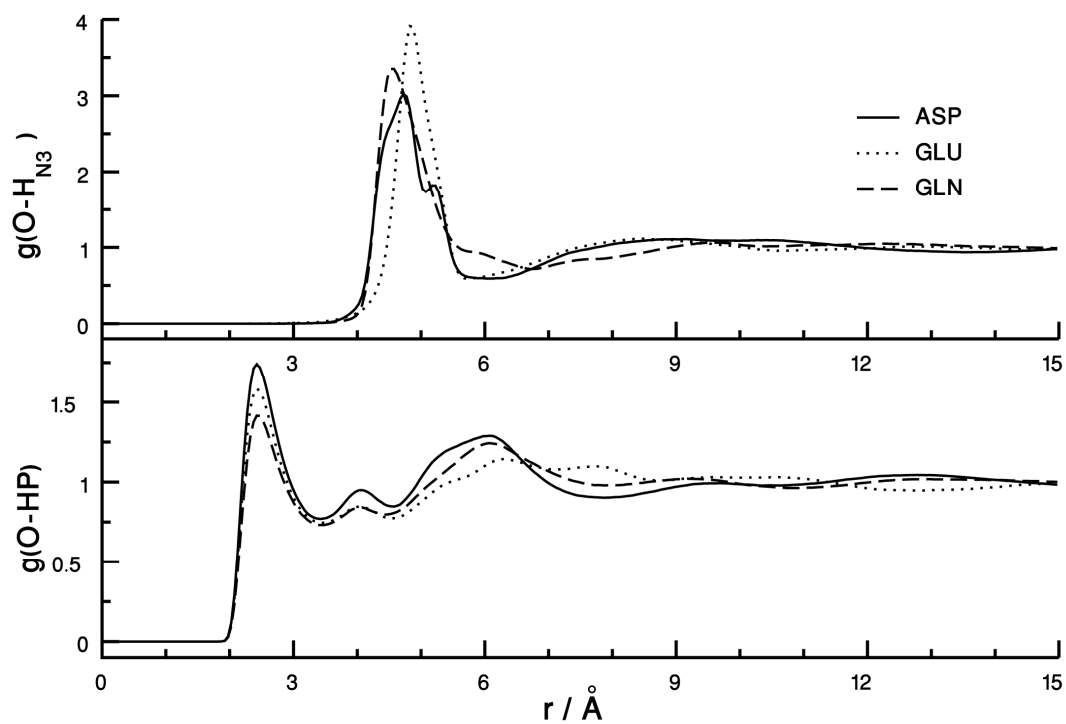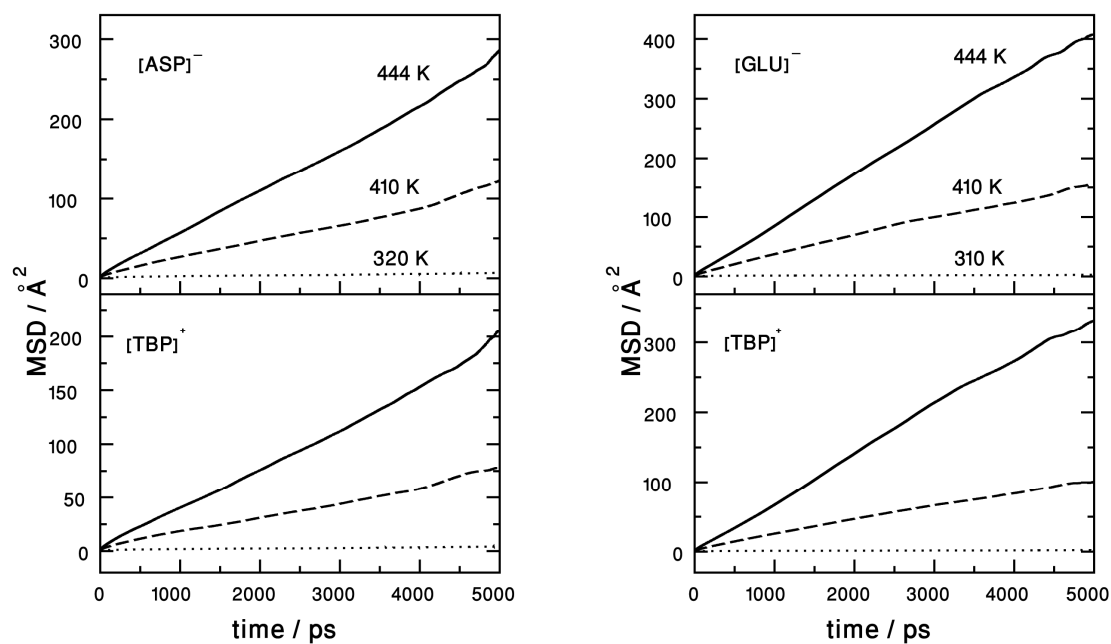
**Figure S4.** The RDFs for O–$H_{N3}$ (upper panel) and O–HP (bottom panel) pairs of AAILs. The oxygen (O) site refers to the oxygen atom in the carboxyl segment (– COOH) of the [ASP] and [GLU] or in the amide group (– $CONH_2$) of the [GLN].

**Figure S5.** Dihedral angle probability of n-butyl side chains of the $[P(C_4H_9)_4]^+$ cations of [TBP][GLY] at three different temperatures.

**Figure S6.** The temperature dependence of the MSD curves for the [TBP][ASP] and [TBP][GLU] at three selected temperatures.

**References**

[1] G. Zhou, X. Liu, S. Zhang, G. Yu, and H. He, *J. Phys. Chem. B*, 2007, **111**, 7078−7084.

[2] G. R. Yu, S. J. Zhang, X. Yao, J. Zhang, K. Dong, W. Dai, and R. Mori, *Ind. Eng. Chem. Res.*, 2006, **45**, 2875−2880.