

Supplementary Material

Simulating the ionic liquid mixing with organic-solvent clarifies the mixture's SFG spectral behavior and the specific surface region originating SFG

Leila Sakhtemanian¹, Anjeeta Duwadi², Steven Baldelli², Mohammad Hadi Ghatee^{1*}

¹*(Department of Chemistry, Shiraz University, Shiraz, 71946, Iran)*

Email: mhghatee@shirazu.ac.ir ; mhghatee2@gmail.com

Tel: +98 713 613 7174, Fax: +98 713 646 0788

²*(Department of Chemistry, University of Houston, Houston, Texas 77204-5003, USA)*

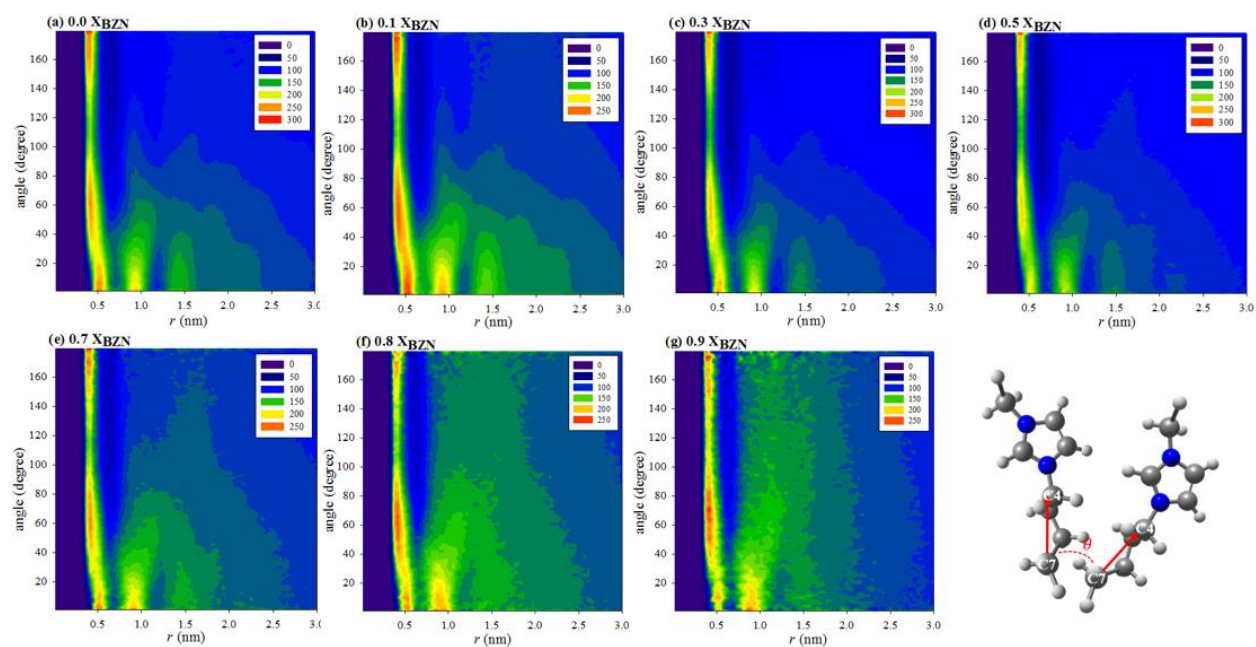


Figure S1-A. Cation-cation combined distribution functions, (a to g) at different X_{BZN} .

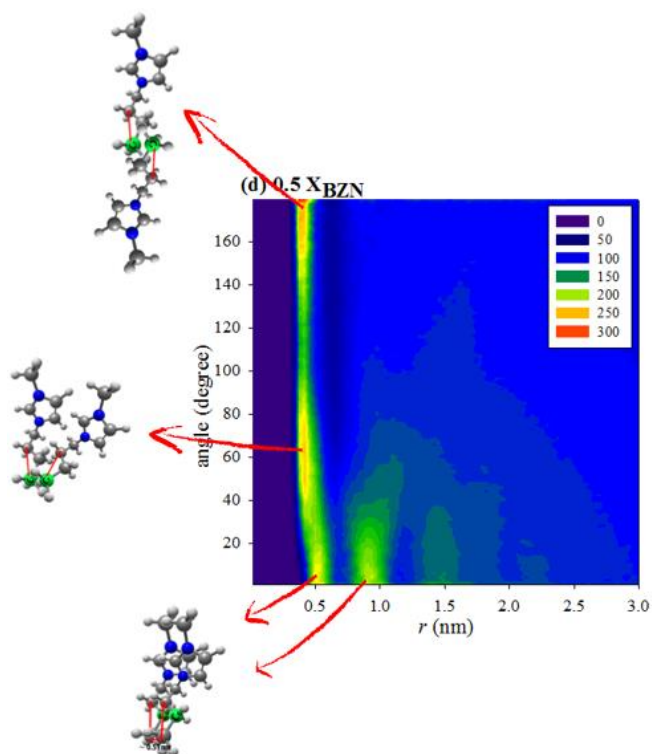


Figure S1-B. Schematic representation of cation-cation orientations with details designated.

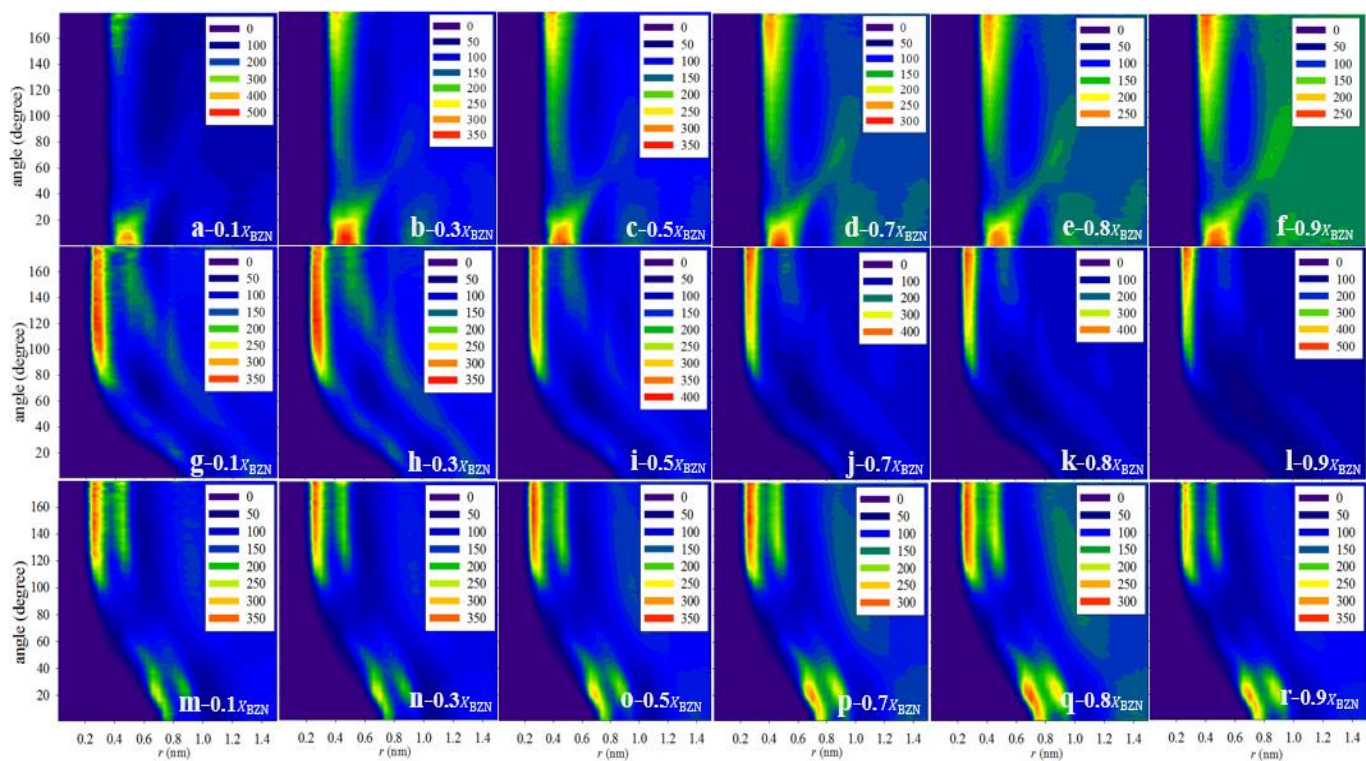


Figure S2-A. CDFs at different X_{BZN} for, (a to f) cation...BZN molecule (in stacking mode), (g to l) cation...BZN molecule (by H-bond interaction), and (m to r) anion...BZN molecule.

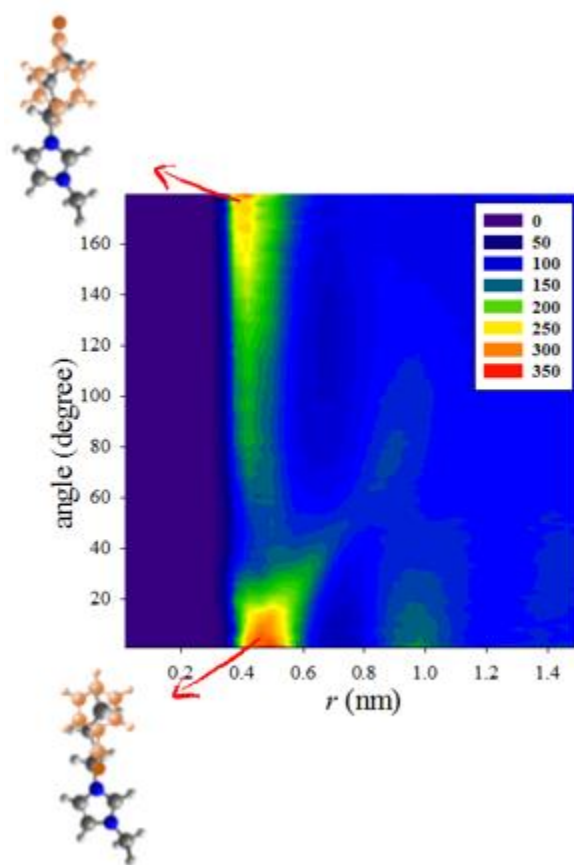


Figure S2-B. Scheme and contour diagrams of CDF, illustrating the cation's butyl chain with BZN's ring orientations.

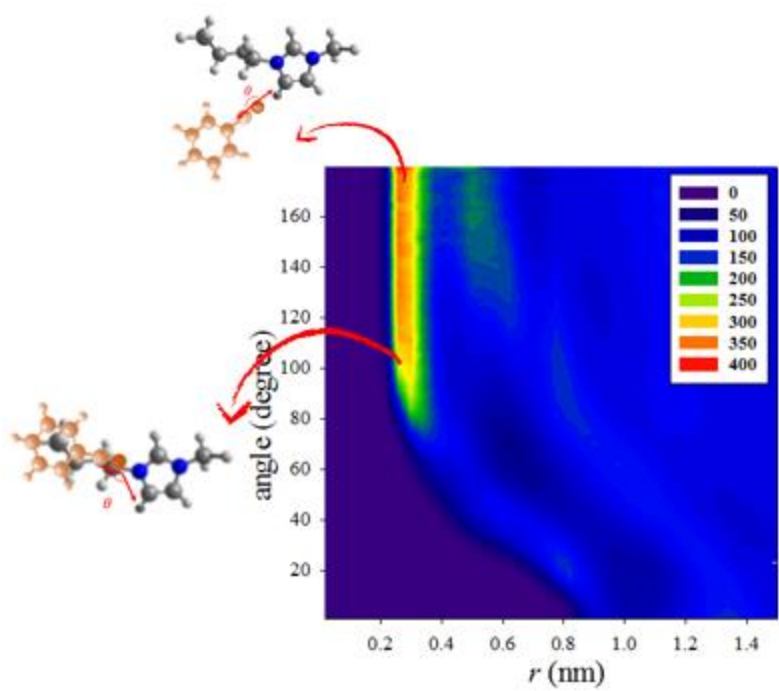


Figure S2-C. The schematic orientational distribution of CN group of BZN molecule with respect to H-atom of the imidazole ring at $0.5X_{\text{ZBN}}$.

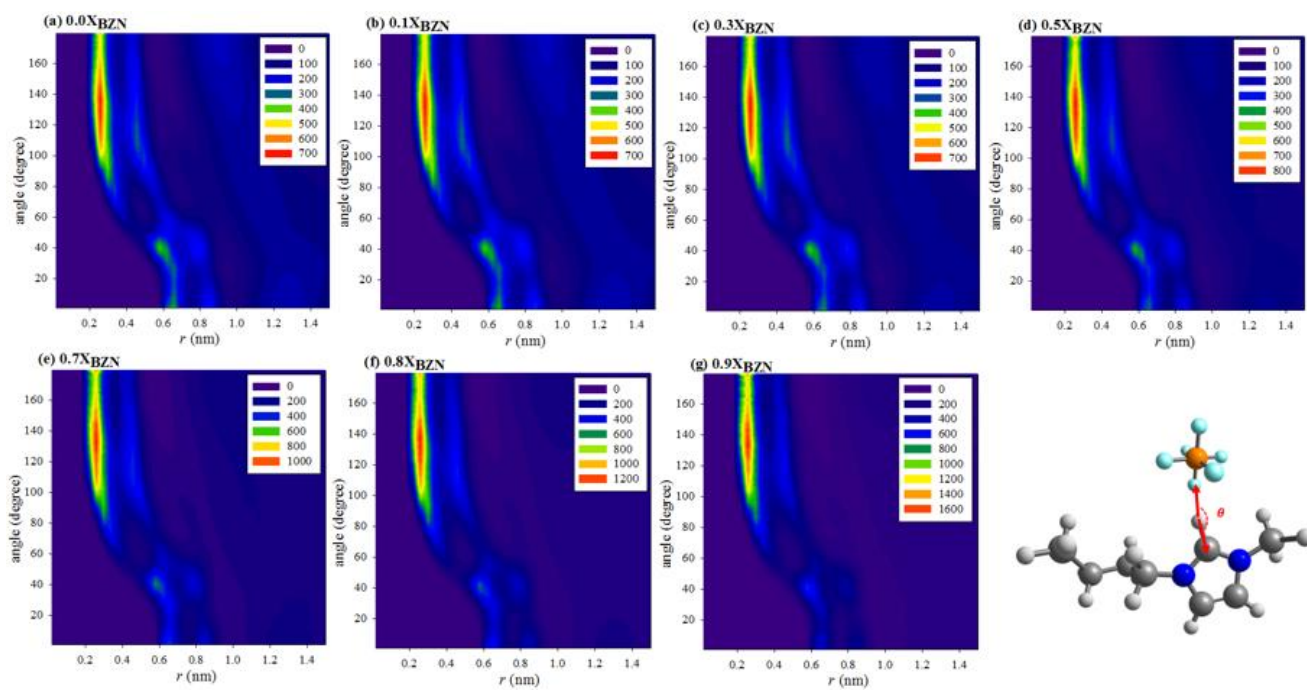


Figure S3. Combined distribution functions between anion and cation of IL, (a to g) at different X_{BZN} .

Density profile

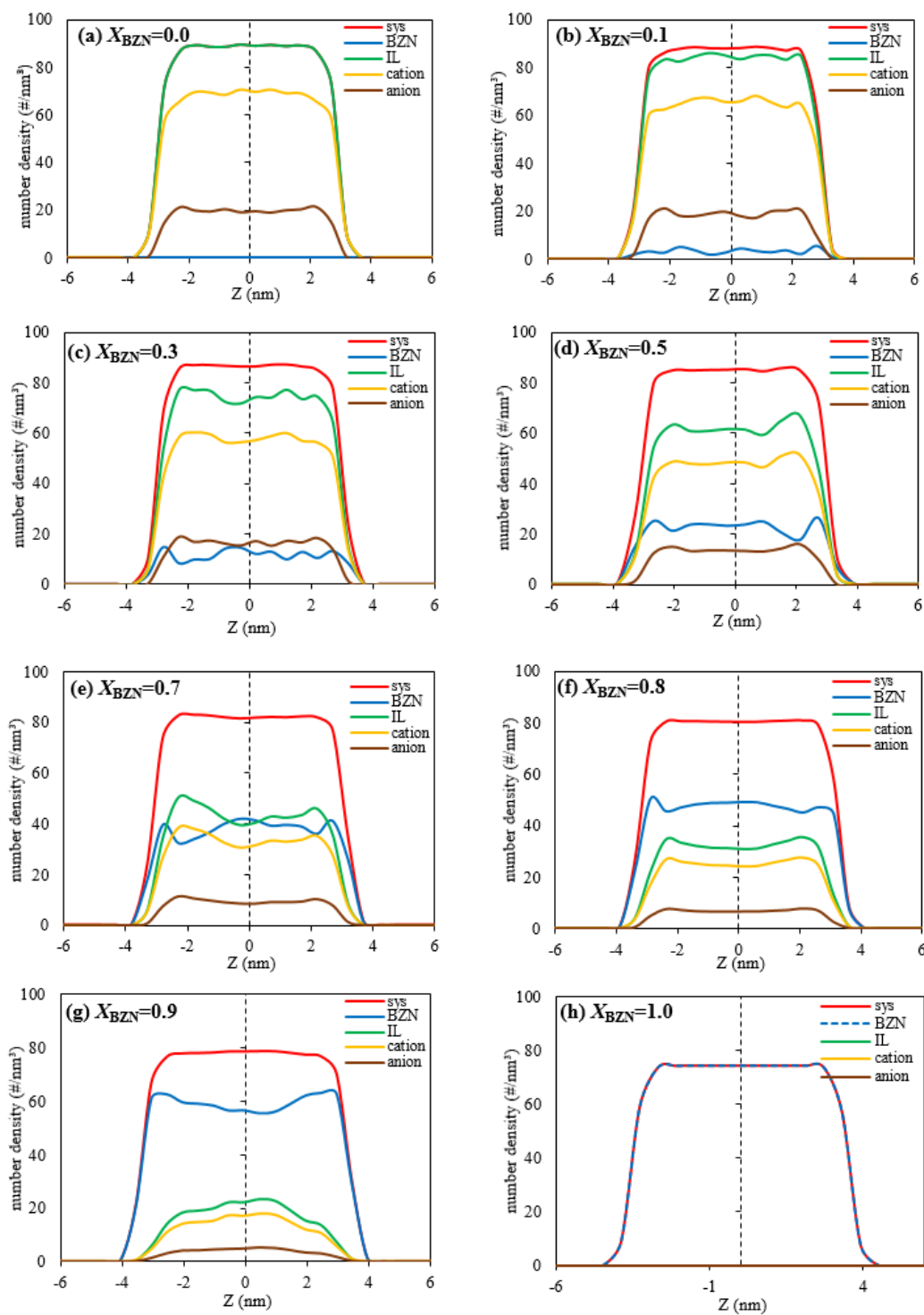


Figure S4. Local number densities of BZN and IL fragments for the mixture at different X_{BZN} .

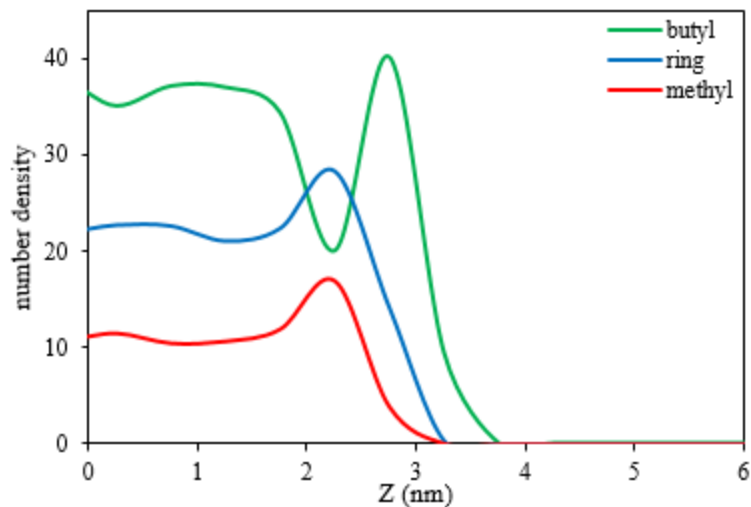


Figure S5. Local number densities for COM of different moiety of pure IL $[\text{C}_4\text{mim}][\text{PF}_6]$.

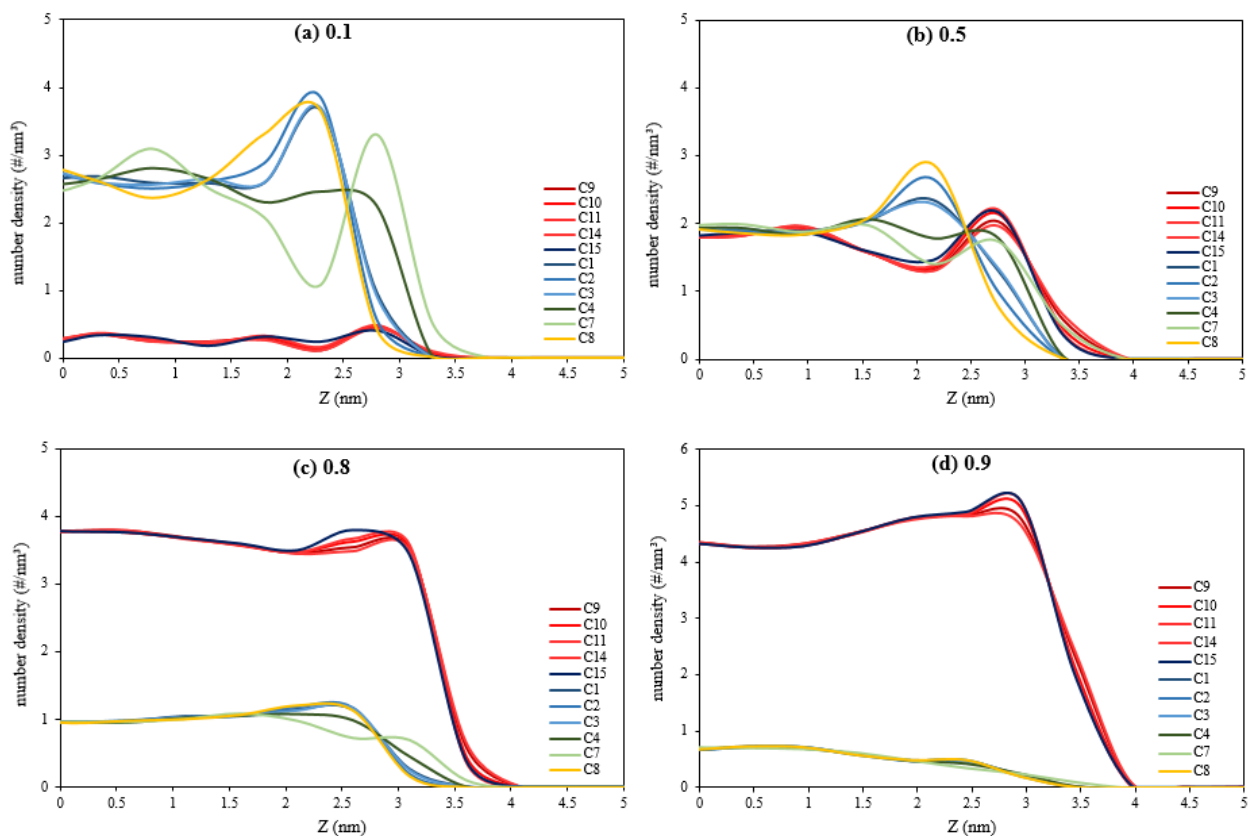
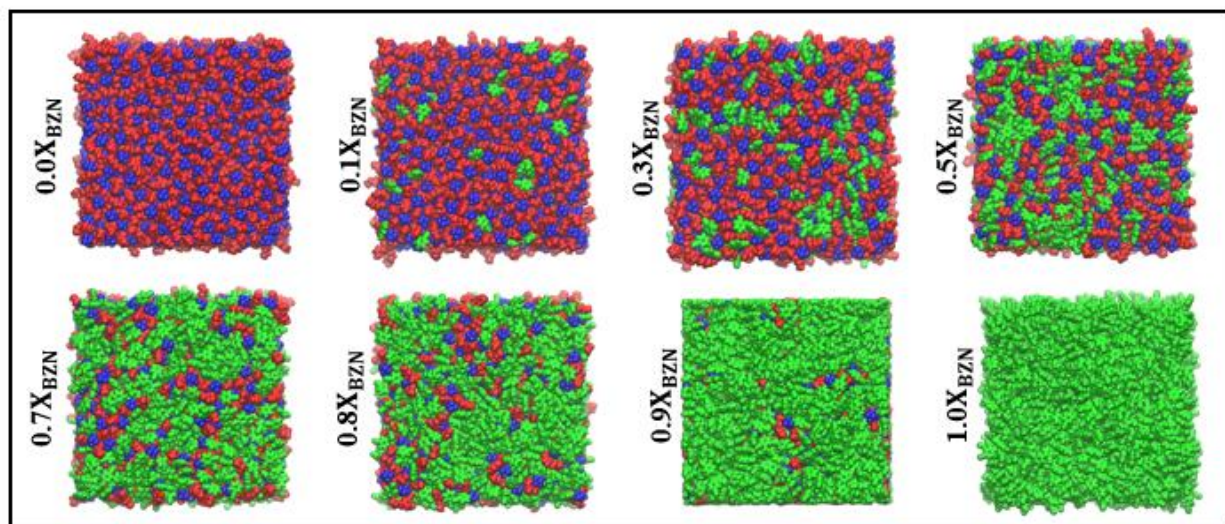


Figure S6. Atom number density of C atoms for the (a) 0.1, (b) 0.5, (c) 0.8 and, (d) 0.9 BZN mole fractions at 298 K. (for more clarity in the density profile, only the butyl carbons, the methyl carbon, and the imidazole ring carbons for the IL molecule and only the ring carbons, and the CN group carbon for the BZN molecule are displayed).

Morphology of IL + BZN mixtures

The simulation ensembles at various mole fractions contain molecular-level information about how the two solvents are mixed and correlated. The role of BZN is considered a co-solvent for modifying the IL properties such as density, polarity, electrical conductivity, and viscosity. **Figure S7** shows snapshots of the systems at the final stage of simulation (color coding identifies the cation, anion, and BZN molecule). In pure IL, anions and cations are completely and uniformly distributed. For $0.1X_{\text{BZN}}$ and $0.3X_{\text{BZN}}$ mixtures, the BZN molecules are uniformly distributed among anions and cations, and the presence of a significant number of small-size aggregates of BZN is evident.

At $0.5X_{\text{BZN}}$, although BZN clusters are formed, their rather uniform distribution between anions and cations is phenomenal. It can be considered as the starting mole fraction for BZN domain formation with appreciable sizes. As a result of the lower surface tension of BZN compared to the IL,^{1,2} ion pairs avoid placing at the mixture surface but migrate and concentrate in the middle of the box.³



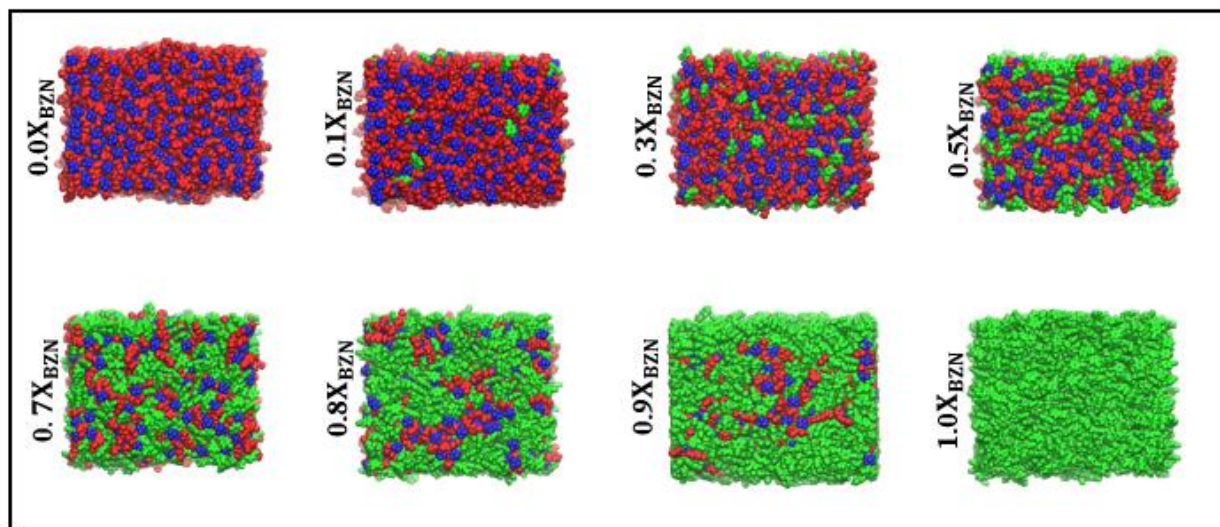


Figure S7. The top (above) and side (below) view snapshots images of the simulation ensembles at different X_{BZN} — cation, red; anion, blue; BZN molecule, green.

Inter-dynamic properties

The MSDs for mixtures were calculated from the trajectory coordinates of the particles during the simulation in the NVT ensemble:

$$MSD = \frac{1}{N} \langle \sum_{i=1}^N |r_i(t) - r_i(0)|^2 \rangle \quad (1)$$

where, $r_i(t)$ is the COM location of the particle i at time t , and N is the number of particles. Self-diffusion coefficient (D_i) represents the microscopic liquid dynamics and were obtained from the linear regime of MSDs curves at long simulation time using the Einstein relation:

$$D_i = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |r_i(t) - r_i(0)|^2 \rangle \quad (2)$$

The long-time simulation (up to 300 ns) performed at all mole fractions ensures attaining a state of uniform mixing and steady-state dynamics, especially the IL with sluggish dynamics. The MSD diagrams for the various fragments in all mixtures give a good sense of linearity, as plotted in **Figure S8**. The MSD for the whole system of a mixture is quantitatively closer to the component being in a greater amount.

MSD values for BZN, IL, and their mixture increase with increasing X_{BZN} , being the highest for BZN at all X_{BZN} . At low X_{BZN} (=0.1 and 0.3), the plots in **Figure S8** demonstrate that the dynamics of the mixture are very close to the IL and its fragments. At mid X_{BZN} (=0.5 and 0.7), the MSD graph of the mixture places almost in between BZN and IL, indicating that both IL and BZN contribute almost equally to the mixture's MSD. Also, at high X_{BZN} (=0.8 and 0.9), the MSD of the mixture is closer to BZN, and the more significant impact of BZN in the molecular transport of the mixture is evident.

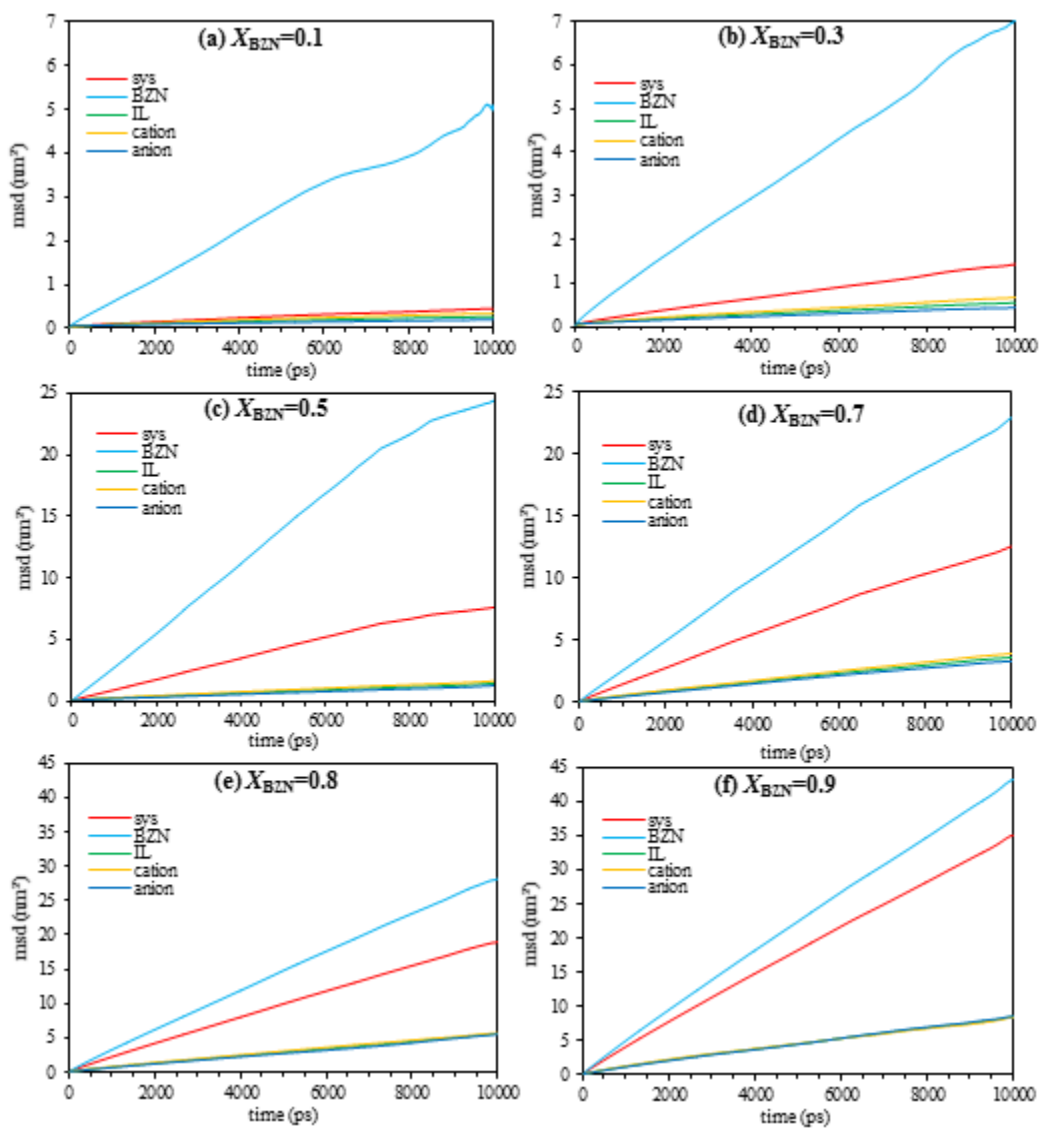


Figure S8. MSDs for the whole system, BZN, cation, and anion fragments in mixtures at different X_{BZN} .

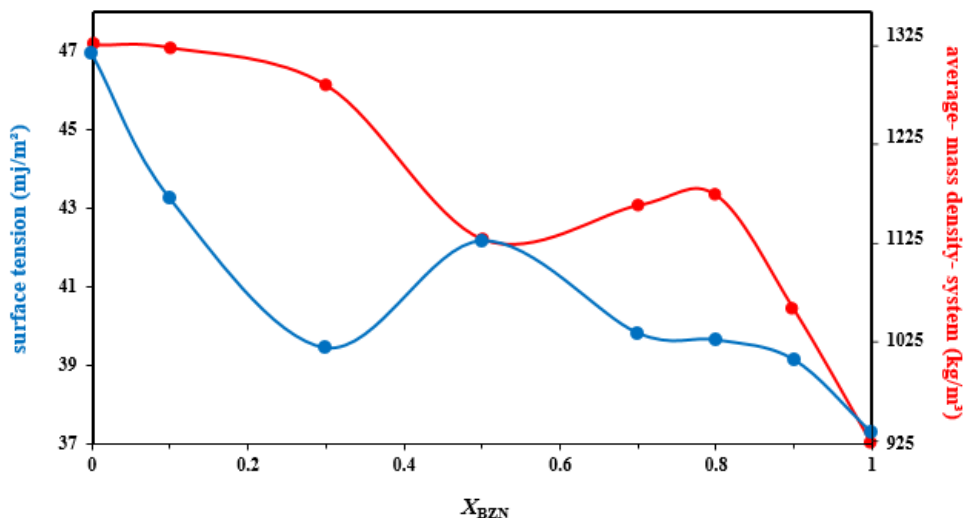


Figure S9. The simulated mass density and the surface tension for a binary mixture of BZN and [C₄mim][PF₆] at different X_{BZN} at 298 K. The lines are trend lines.

REFERENCES

- (1) M. H. Ghathe and A. R. Zolghadr, Surface Tension Measurements of Imidazolium-based Ionic Liquids at Liquid -Vapor Equilibrium. *Fluid Phase Equilibria*. **263**, 168-175 (2008).
- (2) L. Sakhtemanian and M. H. Ghathe, Simulation Investigation of Bulk and Surface Properties of Liquid Benzonitrile: Ring Stacking—Assessment and Deconvolution. *ACS Omega*. **7**, 29, 25693-25704 (2022).
- (3) M. H. Ghathe, Z. Fotouhabadi, A. R. Zolghadr, F. Ghanavati and F. Borousan, Molecular dynamics studies of binary mixtures of pyridine and alkyl derivatives in *n*-octane, *Fluid Phase Equilibria*. **393**, 101-110 (2015).