

Electronic Supplementary Information:

$\pi^+-\pi^+$ Stacking of Imidazolium Cations Enhances Molecular Layering of Room Temperature Ionic Liquid at Their Interfaces

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NP-FFMD Simulation for Generating Initial Conformations of *Ab Initio* MD simulation

For generating the initial conformation for the ab initio MD (AIMD) simulations, we conducted another NP-FFMD simulation of [d-MMIM⁺][Cl⁻]/air interface and [d-MMIM⁺][Cl⁻]/graphene interface. Since all the bonds are flexible in the AIMD simulation, here we used the flexible force field for these C-H (C-D) bonds, where the force constant was set to 367 kcal/mol, based on the Amber force field.¹ Note that the original force field model of Ref. 2 employs the fixed C-H (C-D) bonds. For the Lennard-Jones potential of the carbon atoms composing the graphene, we used $\sigma = 3.5 \text{ \AA}$, $\varepsilon = 0.27614 \text{ kJ/mol}$. The intramolecular potential of carbon atom-carbon atom of graphene is given by Ref. 3. The other RTIL force field is the same as Ref. 2.

The cell size for the RTIL/graphene interface simulation was set to $25.56 \text{ \AA} \times 24.595 \text{ \AA} \times 65 \text{ \AA}$, which contained 120 [d-MMIM⁺][Cl⁻] pairs, while the cell size and number of ion pairs were the same as in the Amber NP-FFMD simulation. Periodic boundary condition was used. The simulation was run in the *NVT* ensemble. We used the canonical sampling through velocity rescaling (CSVR) thermostat⁴ to control the temperature and set the target temperatures to 450 K and 550 K. The time step for integrating the equation of motion was set to 0.5 fs. We ran 5ns to equilibrate the systems, and obtained subsequently over 20 ns MD trajectories for both RTIL/air and RTIL/graphene interfaces. The simulation was performed by using the CP2K code.⁵

For the RTIL/air interface, we obtained four initial conformations at 450 K and one initial conformation at 550 K from the 20 ns MD trajectories. For the RTIL/graphene interface, we obtained one initial conformation at 450 K. These conformations were used for AIMD simulations.

***Ab Initio* Molecular Dynamics (AIMD) Simulation (CP2K)**

We employed the Becke-Lee-Yang-Parr (BLYP)^{6,7} and Perdew–Burke–Ernzerhof (PBE)⁸ exchange-correlation functional for the AIMD simulation at the [d-MMIM⁺][Cl⁻]/air interface and the BLYP exchange-correlation functional for the AIMD simulation at the [d-MMIM⁺][Cl⁻]/graphene interface. We used the triple-zeta valence plus two polarization (TZV2P) basis sets and the real-space density cutoff of 400 Ry. The core electrons were described by the Goedecker-Teter-Hutter pseudopotential.⁹ The van der Waals correction was included via the Grimme’s D3 method.¹⁰ We used the same size of the simulation cell and the same number of ion pairs in the CP2K-NP-FFMD run. Periodic boundary conditions were used.

We started BLYP-AIMD simulations at 450 K using four different initial conformations and AIMD simulation at 550 K with one initial conformation for the RTIL/air interface, while we ran BLYP-AIMD simulation at 450 K with one initial conformation for the RTIL/graphene interface. For these initial configurations, we conducted 5 ps AIMD simulations in the *NVT* ensemble for equilibrating the systems. We used the CSVR thermostat⁴ to control the temperature. Sequential 25 ps AIMD runs were

performed for sampling the AIMD trajectories, which were used for analyzing the data. As such, we obtained total 123.4 ps (30.0 ps, 29.7 ps, 26.7 ps, 37.0 ps AIMD runs) AIMD trajectory at 450 K and, 36.5 ps AIMD trajectory at 550 K for RTIL/air and 28.6 ps AIMD trajectory for RTIL/graphene at 450 K. The time step for integrating the equation of motion was set to 0.6 fs. We used the self-consistent field convergence criteria of 3.0×10^{-7} for RTIL/air and 2.0×10^{-7} for RTIL/graphene. AIMD simulation with the QUICKSTEP¹¹ method were performed by using the CP2K code.⁵

For the PBE-AIMD simulation at the RTIL/air interface, we used the same MD simulation conditions, and the same initial configurations as the BLYP-AIMD simulations. We used the four different initial configurations for the PBE-AIMD simulation at 450 K and one configuration for the simulation at 550 K. These initial configurations were the same as used in the BLYP-AIMD simulation. For the simulation at 450 K, we performed 5 ps PBE-AIMD runs for equilibrating the systems and then performed over 27 ps AIMD runs for obtaining the MD trajectories. The total 109 ps AIMD trajectories were used for analyzing the data. For the simulation at 550 K, we performed 5 ps PBE-AIMD runs for equilibrating the systems and then performed over 14 ps AIMD runs for obtaining the MD trajectories. This 14 ps AIMD trajectory was used for analyzing the data.

Density Profile Data

We calculated the axial profile of the [d-MMIM⁺][Cl⁻] at the [d-MMIM⁺][Cl⁻]/air interface for both AIMD and NP-FFMD simulations, where the origin points are set to the center of

mass for the whole system. The data are plotted in Figure S1. Note that the simulations were conducted with [d-MMIM⁺], while the density was calculated by replacing all the deuterium atoms in the simulation with the hydrogen atoms. Figure S1 shows the symmetric density profiles at the two interfaces, manifesting that the systems are properly equilibrated.

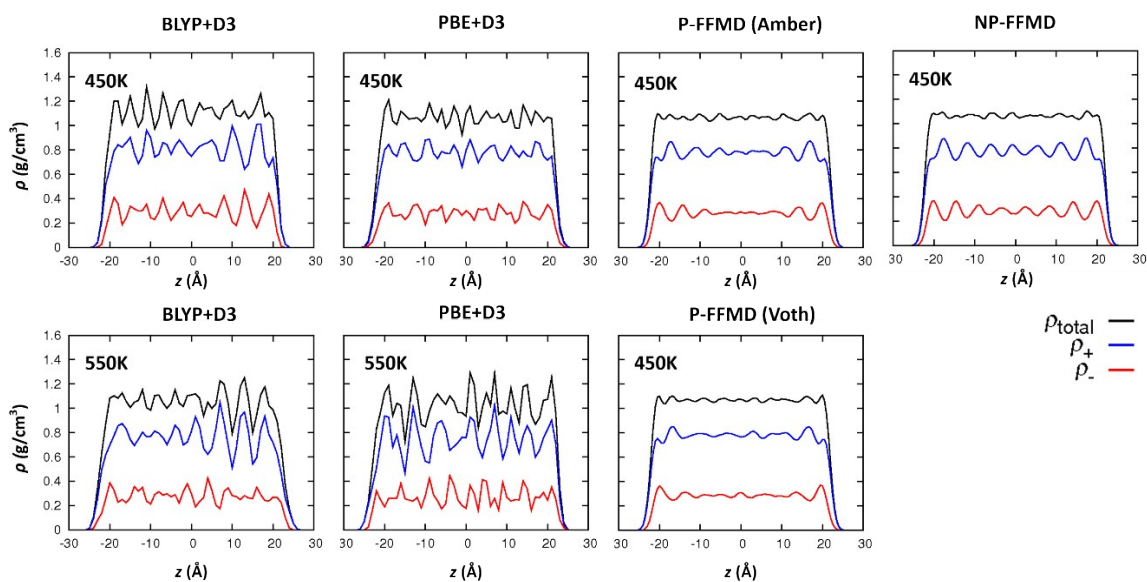


Figure S1. Axial profiles of the RTIL density calculated from the BLYP+D3/TZV2P and PBE+D3/TZV2P AIMD trajectories together with the NP-FFMD and P-FFMD trajectories. We used the resolution of 1 Å in AIMD, 0.5Å in NP-FFMD and P-FFMD, respectively.

We then fit the total density of the RTIL with the function of

$$\rho(z) = a(1 - \tanh(-\frac{|z| - z_G}{\delta})) \quad (1)$$

where δ denotes the thickness parameter, a the half of the bulk RTIL density, and z_G the position of the Gibbs dividing surface. The fit parameters are listed in Table S1. From the parameter of a , we obtained the bulk RTIL density and compared the simulated bulk density with the experimental data. The comparison of bulk density is summarized in Figure S2. The RTIL density simulated with AIMD with van der Waals corrections is in excellent agreement with the experimental data, while the NP-FFMD underestimates the RTIL density. The trend of NP-FFMD simulation agrees with the previous report.²

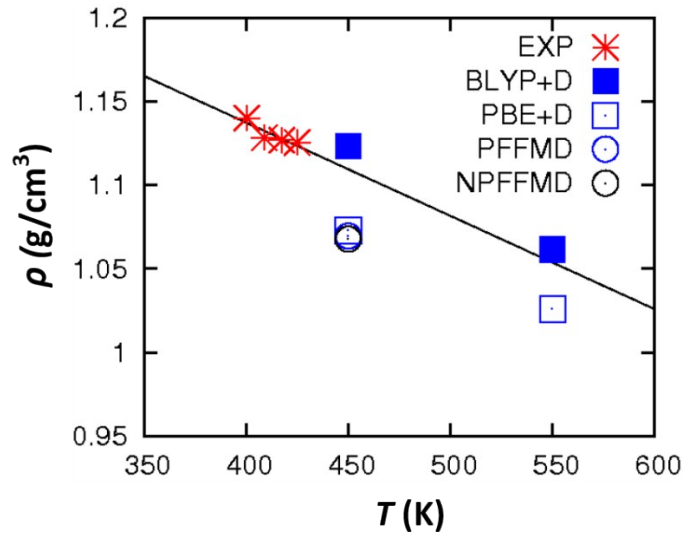


Figure S2. Simulated density of bulk [d-MMIM⁺][Cl⁻] RTIL. The experimental data and the fit curve of $\rho = 1.1745 - 5.5647 \times 10^{-4}(T - 333.15)$ are obtained from Ref. 6, where the unit of T is K.

Table S1. Fit parameters obtained for the axial profiles of RTIL at the [d-MMIM⁺][Cl⁻]/air interface from AIMD (BLYP+D3 and PBE+D3) and FFMD (P-FFMD and NP-FFMD). The standard deviations of a and z_G are at most 2 %, while the standard deviation of δ is at most 17 % in the AIMD simulation at the BLYP+D3/TZV2P and PBE+D3/TZV2P levels of theory.

	BLYP+D3		PBE+D3		NP-FFMD	P-FFMD
	450K	550K	450K	550K	450K	450K
a (g/cm ³)	0.5616	0.5308	0.5363	0.5132	0.5339	0.5348
z_G (Å)	21.176	22.417	22.154	23.142	22.265	22.225
δ (Å)	1.0586	1.6189	1.0823	1.2168	1.0276	1.0089

Dependence of Cell Size on RTIL Interfacial Structure

Since we used the limited number of the ion pairs, we checked the size dependency of the simulation cell on the RTIL structure. In the slab model, the cell is composed of the two components; the surface area and the length along the surface normal. The dependency of the length along the surface normal on the RTIL structure has been checked carefully in the previous simulation work;⁷ Bhargava and Balasubramanian simulated the RTIL/air interface using 256 and 512 ion pairs in the cell with the surface area of the $44.83 \text{ \AA} \times$

44.83 Å surface area and confirmed that the size effects is negligible, even for 256 ion pairs. Note that 256 ion pairs for the 44.83 Å × 44.83 Å surface area provides less RTIL layers than the current simulation of 70 ion pairs for the 18 Å × 18 Å surface area, suggesting that the limited number of RTIL layers has negligible effects on the RTIL interfacial structure.

Next, we examine the effect of the surface area of the cell on the RTIL interfacial structure, by computing the number of the RTIL ion pairs on the axial profiles of RTIL density and π^+ conformations of the cations by using the NP-FFMD simulation. Here, we prepared the simulation cells with their surface areas of 24 Å × 24 Å and 30 Å × 30 Å. Note that we did not change the cell length along the surface normal. These simulation boxes contain 120 ion pairs and 200 ion pairs, respectively. After 1 ns MD runs for equilibration, we obtained 4.7ns MD trajectory for the system with the largest cell (surface area of 30 Å × 30 Å), while we obtained over 10 ns for the other systems. Subsequently, we calculated the number of π^+ -interaction cations from these trajectories. We used the CP2K package in this NP-FFMD simulation.

The data are shown in Figure S3. One can see a slight increase in the π^+ -interaction number when the cell with the 24 Å × 24 Å surface area is used instead of the smallest cell with the 18 Å × 18 Å surface area, while the distributions of the π^+ -interaction number are nearly identical between the cells with the 24 Å × 24 Å surface area and the 30 Å × 30 Å surface area. More importantly, the relative ratios between the stacked conformations, displaced conformations, and T-shaped conformations are unchanged. This manifests that

the limited size of the cell used in this study does not affect the conclusion obtained in the NP-FFMD, P-FFMD, and AIMD simulations.

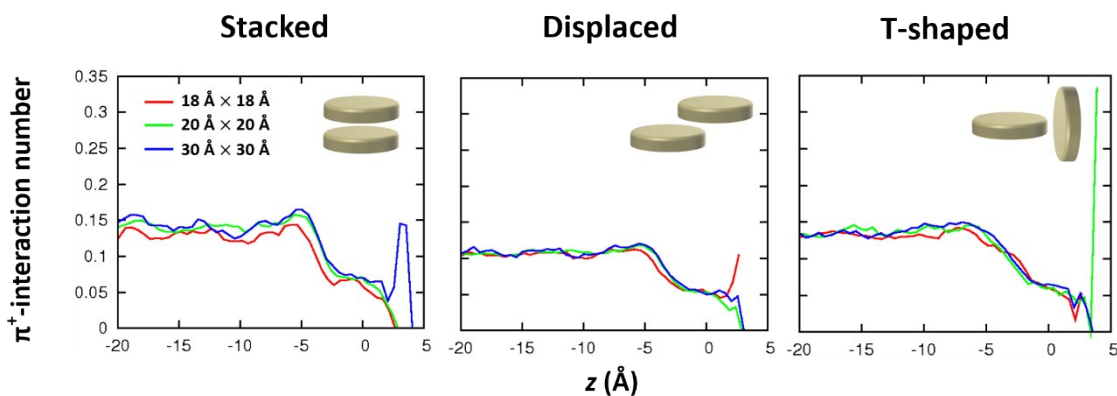


Figure S3. Axial profile of the number of the three $\pi^+ - \pi^+$ conformations obtained from NP-FFMD simulation with different cell sizes.

Reference

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