Supplementary Information

Unique Orientations and Rotational Dynamics of 1-Butyl-3-methyl-imidazolium Hexafluorophosphate Ionic Liquid at the gas-liquid interface: The effects of Hydrogen Bond and Hydrophobic Interactions

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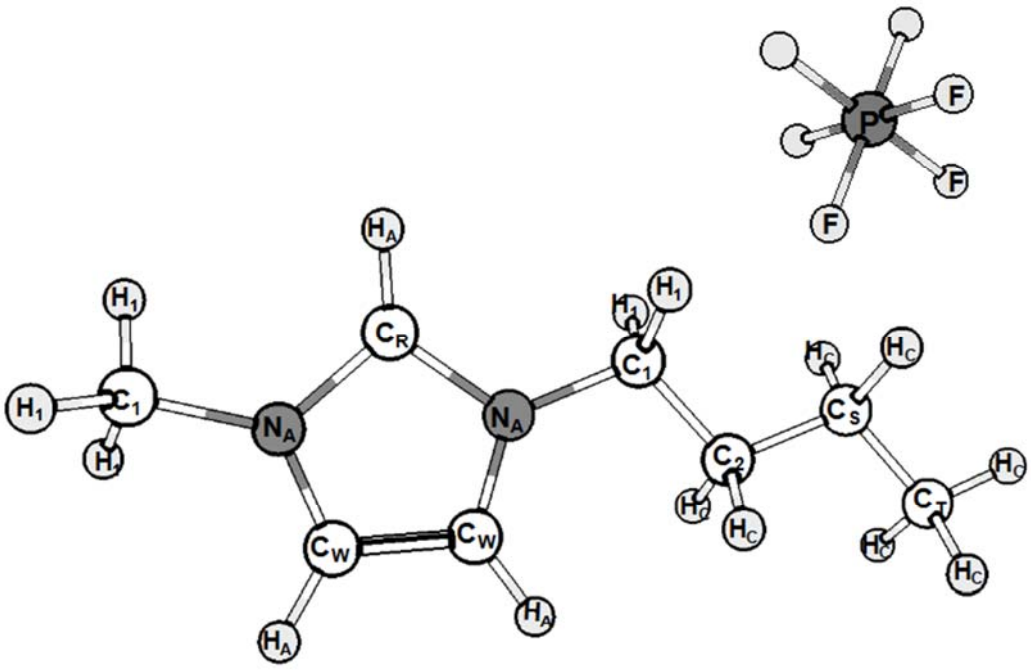
Table S1. The Lennard-Jones parameters and partial atomic charges used in this work. The atomic labels are shown in the following schematic illustration for the [BMIM][PF_6] IL.

	Atom	σ (Å)	ε (kcal/mol）	q (e)
Cation	C_R	3.55	0.07007	0.060
	C_W	3.55	0.07007	-0.020
	C_1	3.50	0.06606	-0.089
	C_2	3.50	0.06606	-0.038
	C_S	3.50	0.06606	-0.038
	C_T	3.50	0.06606	-0.065
	N_A	3.25	0.17016	0.052
	H_A	2.42	0.03003	0.096
	H_C	2.50	0.03003	0.026
	H_1	2.50	0.03003	0.105
Anion	P	3.94	0.20019	0.580
	F	3.12	0.06105	-0.230
	F	3.12	0.06105	-0.230
	F	3.12	0.06105	-0.230



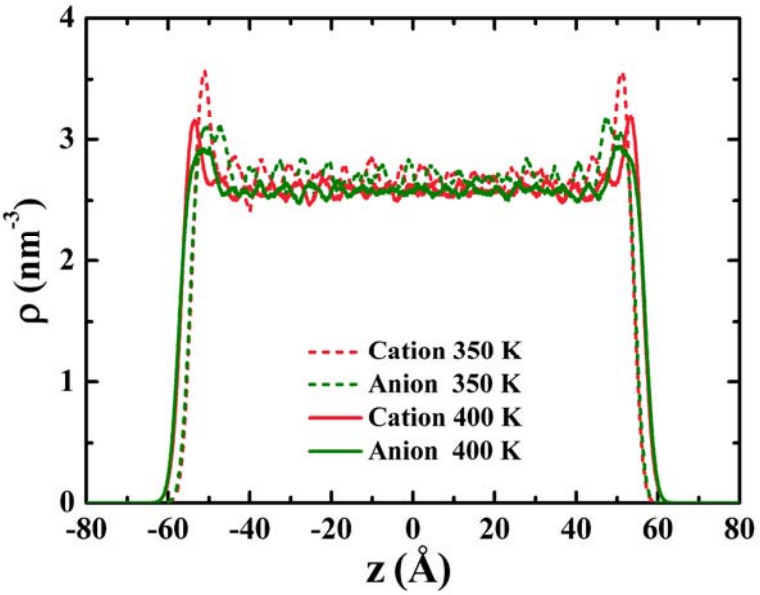


Fig. S1. The whole number density profiles (with the interval unit δz of 0.1 Å) of the $[BMIM]^+$ cations and the $[PF_6]^-$ anions along the *z* direction perpendicular to the gas-liquid interface plane.

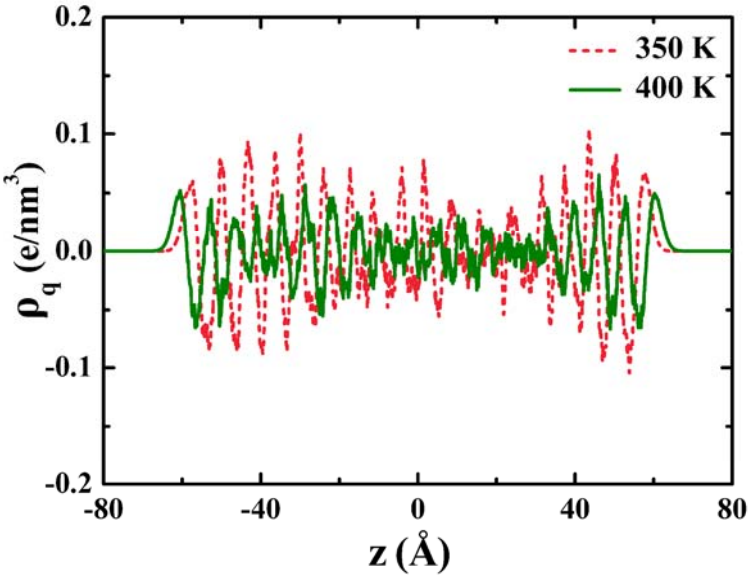


Fig. S2. The whole charge density profiles (with the interval unit δz of 0.1 Å) of the [BMIM][PF_6] IL along the *z* direction perpendicular to the gas-liquid interface plane.

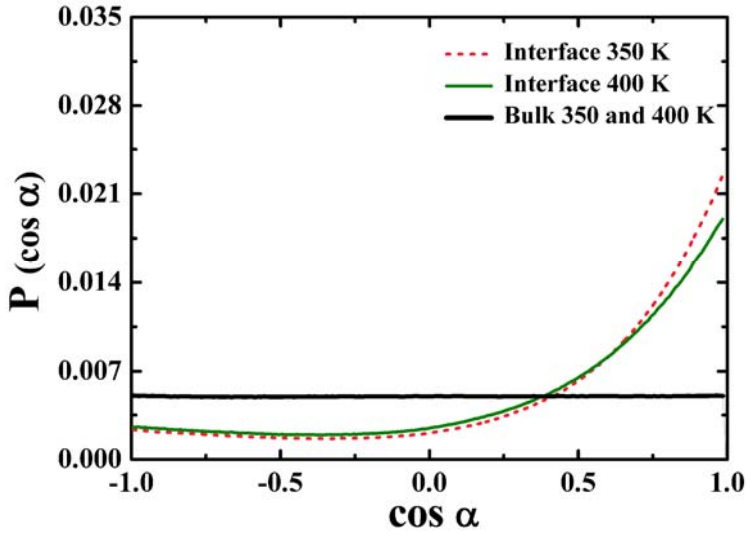


Fig. S3. The angle distribution as a function of cosα for the $[BMIM]^+$ cations at the gas-liquid interface at 350 and 400 K. For comparison, the bulk curve is also shown.

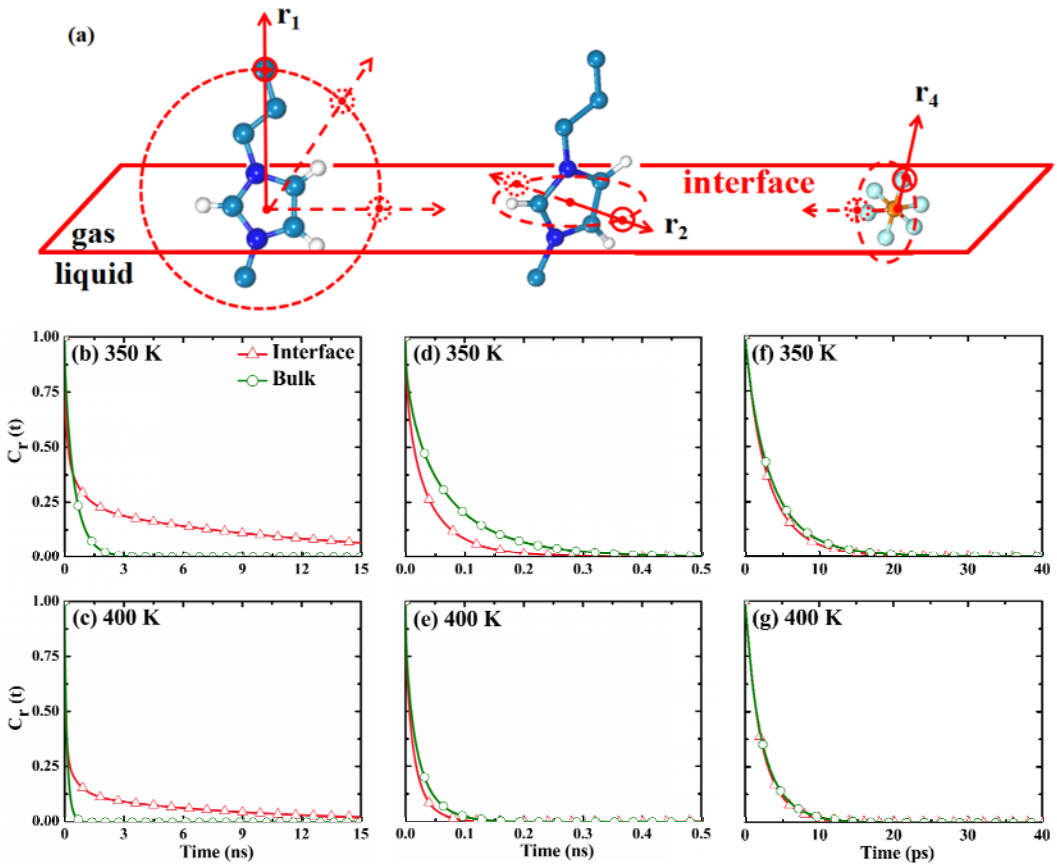


Fig. S4. (a) Schematic illustrations for the rotational motions of the butyl chains, the imidazolium rings, and the anions, respectively. Rotational TCFs of the butyl chains with longer time horizon at (b) 350 K and (c) 400 K, the imidazolium rings at (d) 350 K and (e) 400 K, and the anions at (f) 350 K and (g) 400 K.

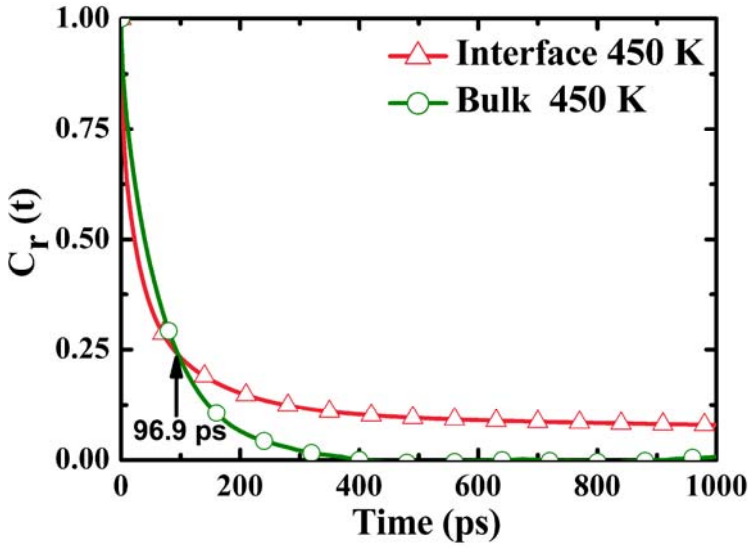


Fig. S5. Rotational TCFs of the butyl chains at 450 K in bulk phase as well as at the gas-liquid interface.