Supplementary Information for

Molecular Mechanism of Anion Size Regulating the Nanostructure and Charging Process at Ionic Liquids-Electrode Interfaces

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Supplementary Tables:

Table S1. Estimated ion size of anion, the interaction energy between cation and anion in the bulk case, and total IL-graphite interaction. The anion size and the energy is calculated from the MD simulations.

Ionic liquid	Anion Size (Å^3)	E_{vdW} (kcal/mol)	E_{coul} (kcal/mol)	E_{total} (kcal/mol)	$E_{IL\text{-}Gra}$ (kcal/mol)
$BmimBF_4$	79	-5.66	-608.37	-614.03	-24.69
$BmimPF_6$	111	-8.52	-558.79	-567.31	-26.32
BmimOTf	126	-11.34	-531.71	-543.05	-30.50
BmimTFSI	233	-15.75	-397.56	-413.31	-39.50

Table S2. The maximum electric field within EDL of different anion system against different potential, units (V/Å)

	BF_4		PF_6		OTf		TFSI	
U(V)	-*U*/2	*U*/2	-*U*/2	*U*/2	-*U*/2	*U*/2	-*U*/2	*U*/2
0	0.65		0.62		1.22		1.54	
0.4	0.61	0.81	0.73	0.68	1.04	1.42	1.36	1.76
0.8	0.52	0.84	0.70	0.70	0.95	1.52	1.40	1.92
1.0	0.50	0.91	0.66	0.70	0.85	1.80	1.65	1.96
2.0	0.70	1.10	0.55	0.74	0.53	1.83	1.41	1.92
3.0	0.76	1.25	0.80	0.69	0.46	2.08	0.93	2.38
4.0	0.72	1.31	0.72	0.73	0.65	2.06	0.39	2.70

Table S3. The stretching factor (α) of modified exponential function for different ILs at the different electrical potential.

U (V)	BF_4	PF_6	OTf	TFSI
2.0	0.343	0.370	0.399	0.454
1.5	0.198	0.422	0.429	0.448
1.0	0.279	0.380	0.722	0.536
0.5	0.217	0.374	0.399	0.32
-0.5	0.202	0.370	0.387	0.28
-1.0	0.264	0.356	0.705	0.525
-1.5	0.219	0.428	0.376	0.442
-2.0	0.333	0.369	0.364	0.416

Table S4. The number of anions and cations in different ionic liquid simulation systems.

Ionic liquid	Cation number (#)	Anion number (#)
$BmimBF_4$	350	350
$BmimPF_6$	350	350
BmimOTf	350	350
BmimTFSI	350	350

Supplementary figures and captions:

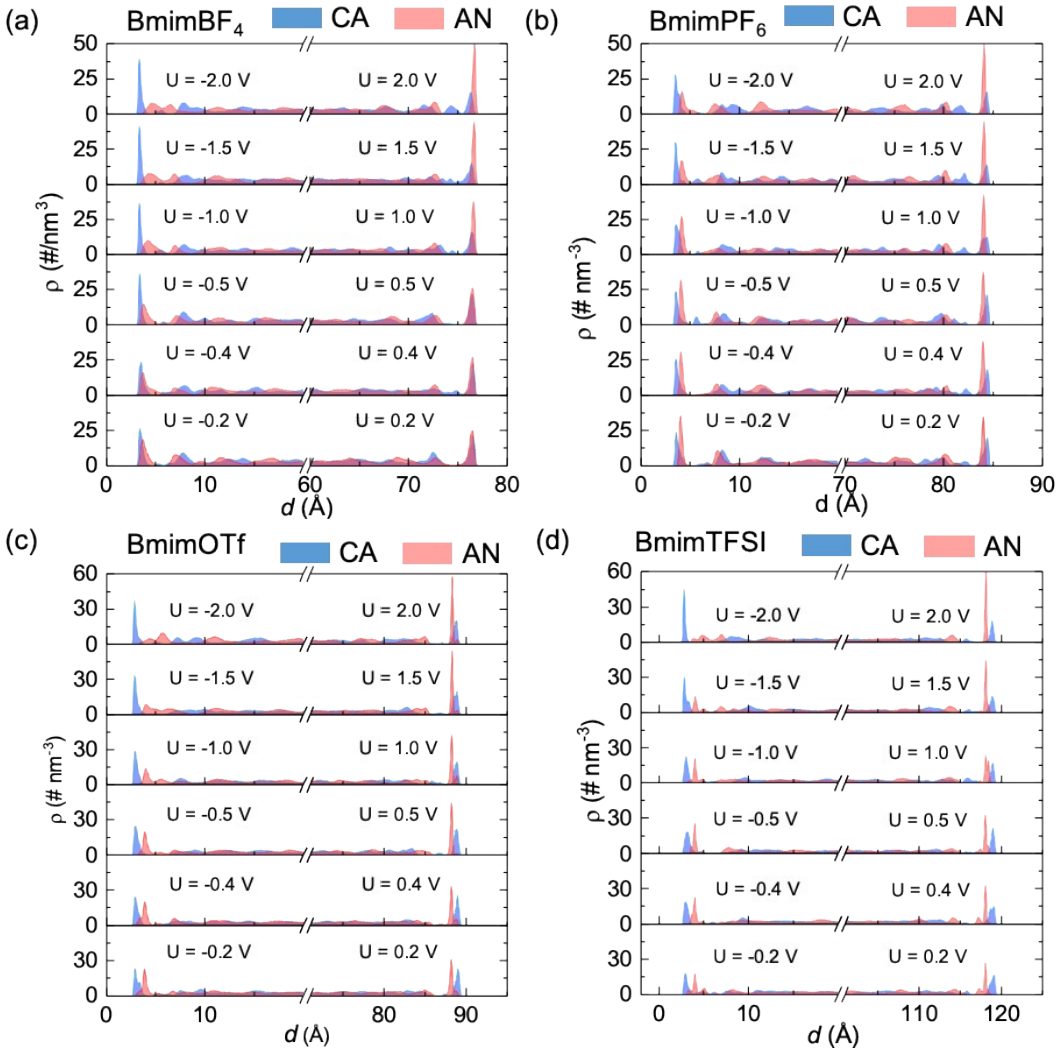

Figure S1. Centroid density distribution of different anions systems under different electrostatic potential: (a) BF_4; (b) PF_6; (c) OTf; (d) TFSI.

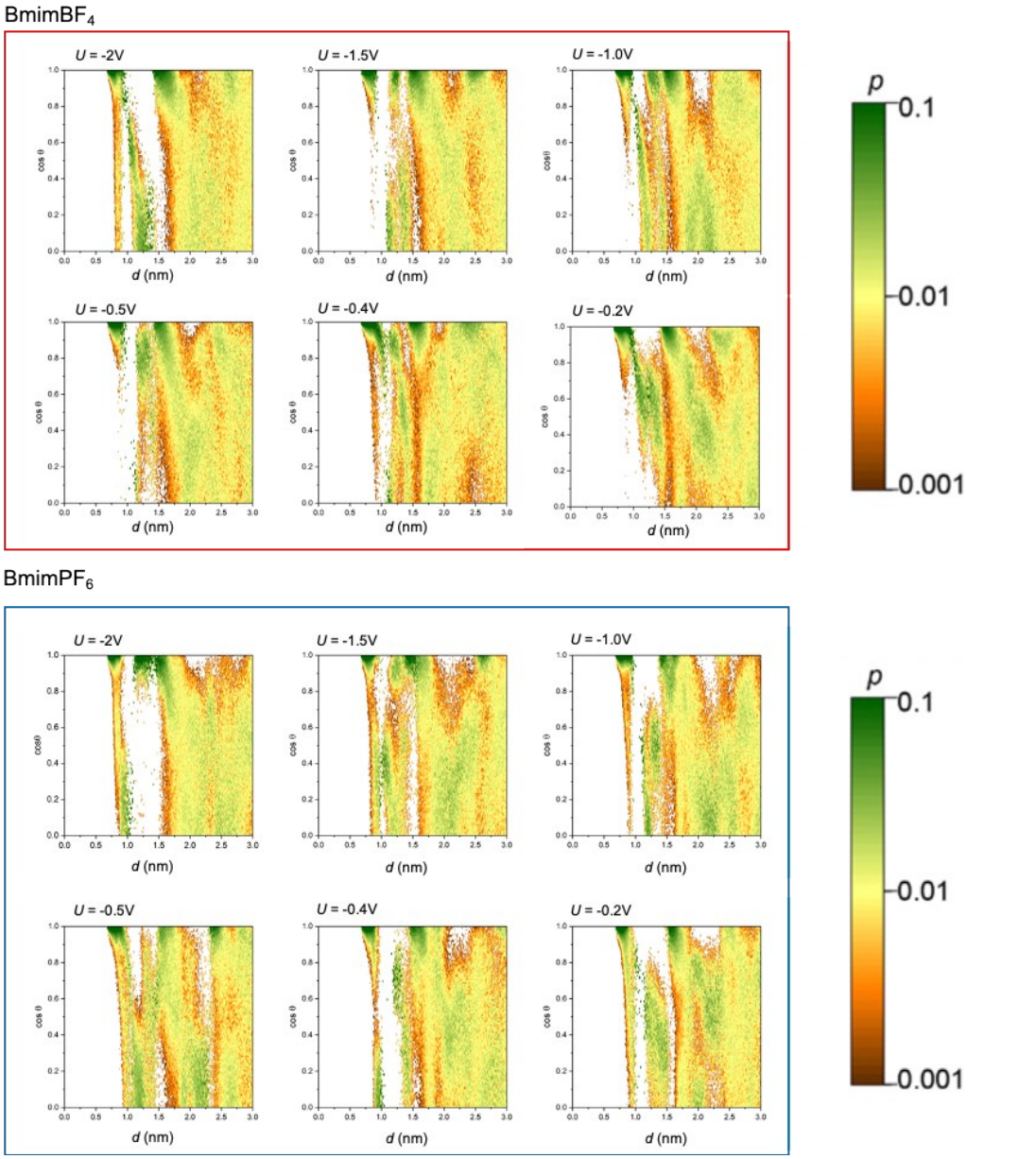

Figure S2. The 2D orientation plot for $BmimBF_4$ and $BmimPF_6$ near the electrode surface with potential from -2V to -0.2V, respectively.

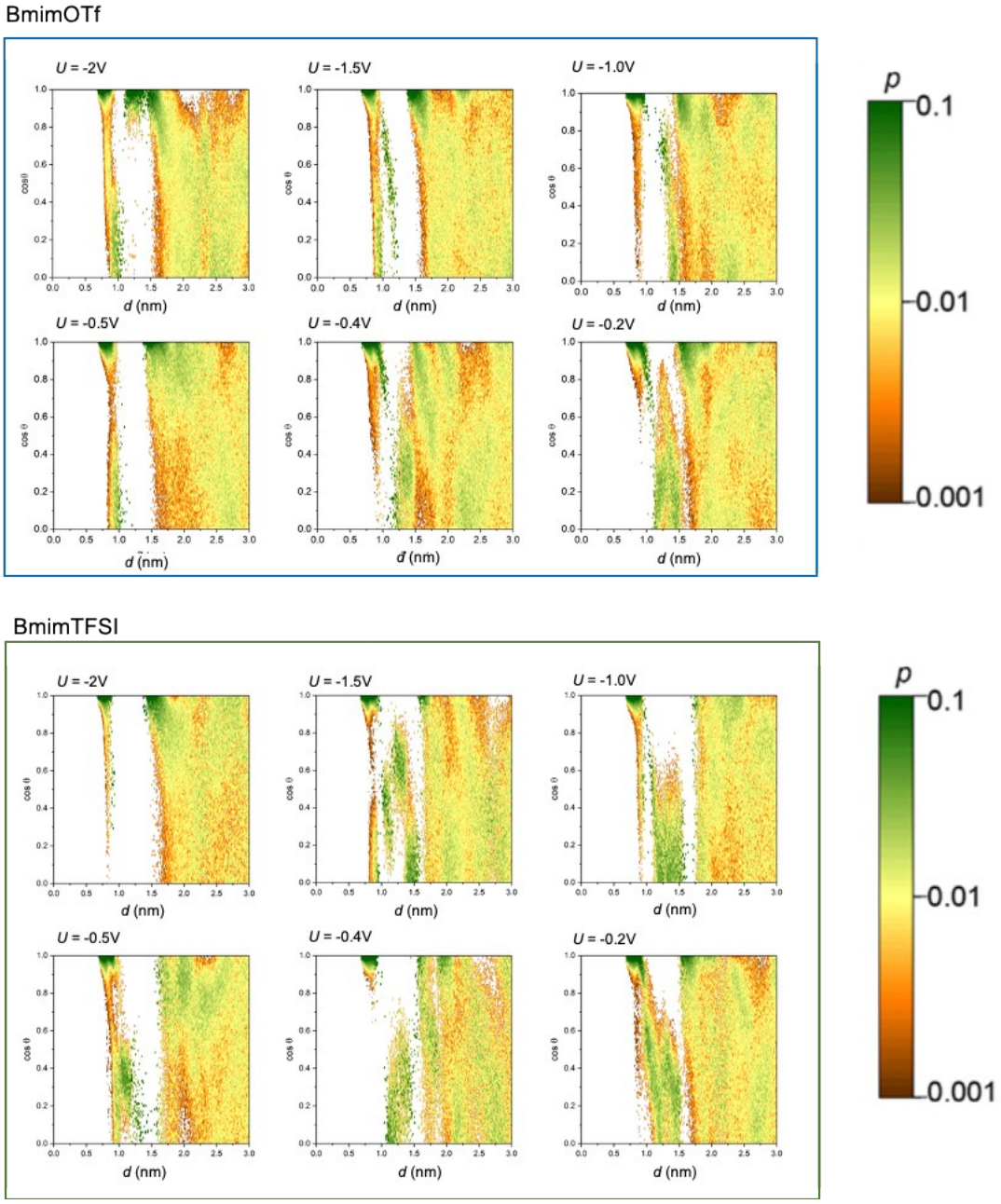

Figure S3. The 2D orientation plot for BmimOTf, and BmimTFSI near the electrode surface with potential from -2V to -0.2V, respectively.

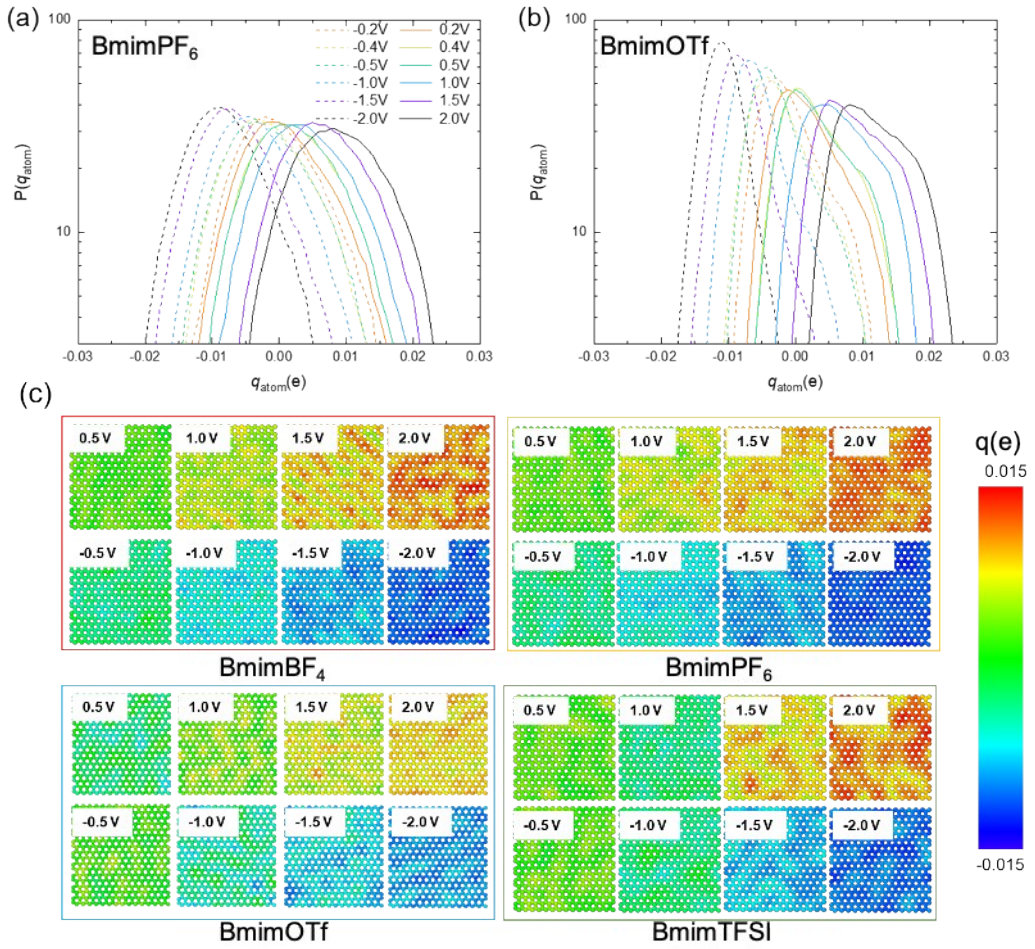

Figure S4. (a-b) The distribution of electrode atom charges at various electrostatic potential differences for $BmimPF_6$ and BmimOTf electrode interfaces. (c) The spatial distribution of charge on the electrode surface different interfaces.

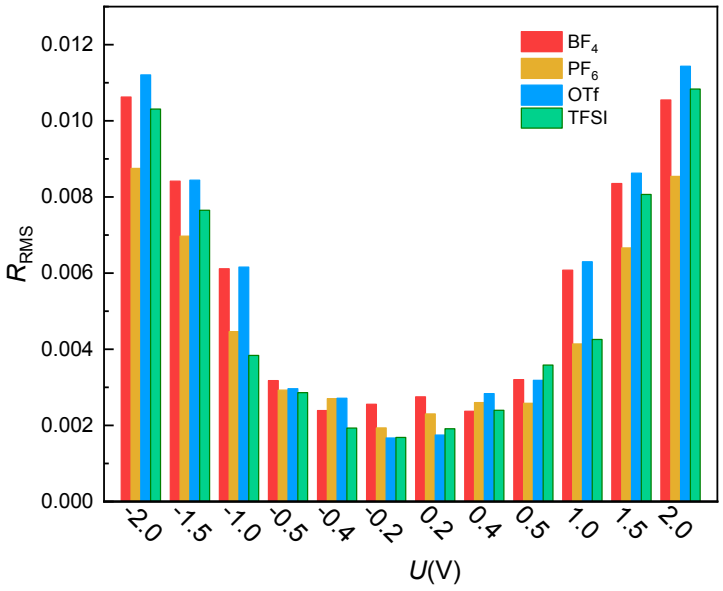

Figure S5. The roughness of the distribution R_{RMS} of the charge distribution of the first electrode layer under different surface potential for different IL systems.

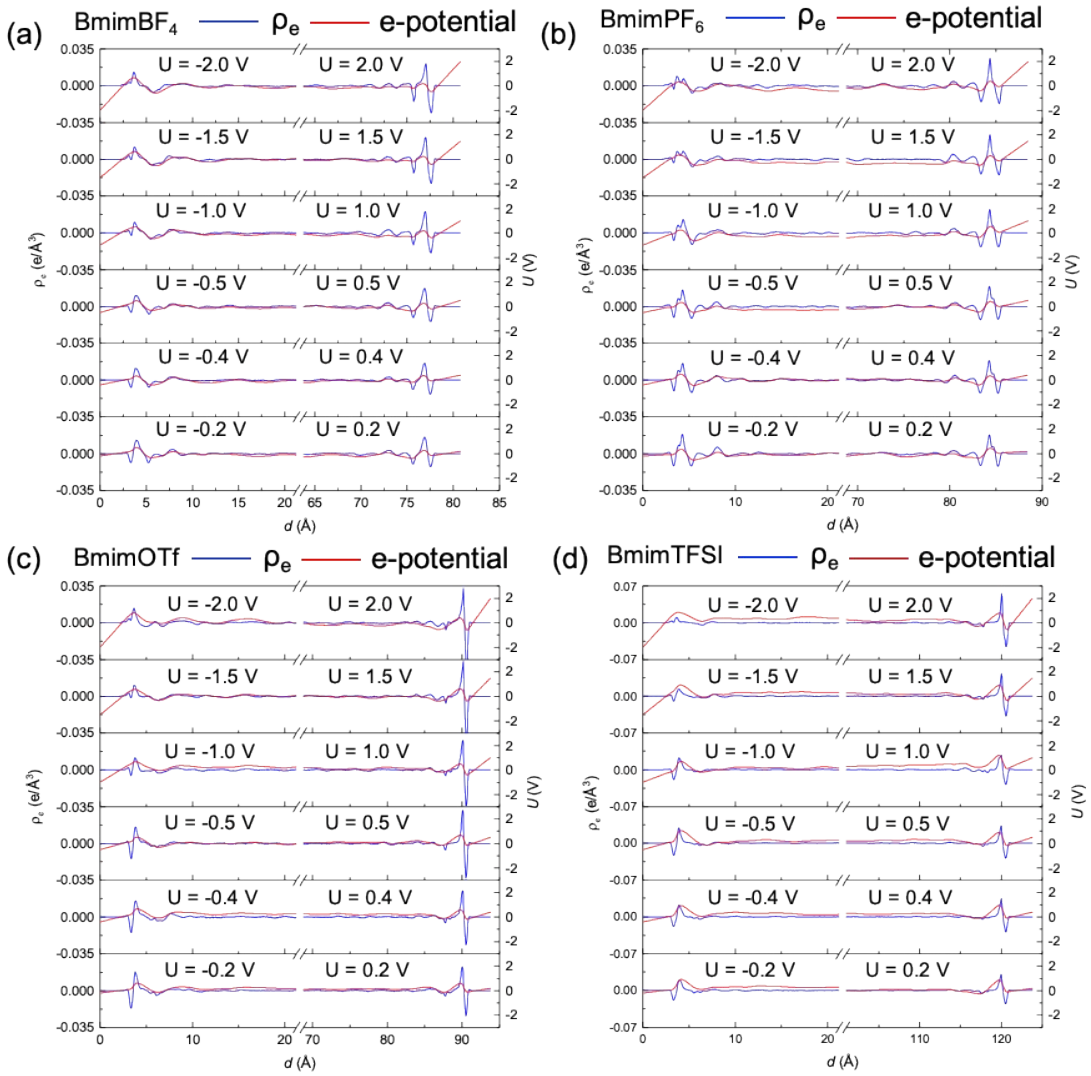

Figure S6. (a-d) The plane charge density and potential of the different anion system (BF_4, PF_6, OTf, and TFSI) along the *z*-direction at an electrostatic potential.

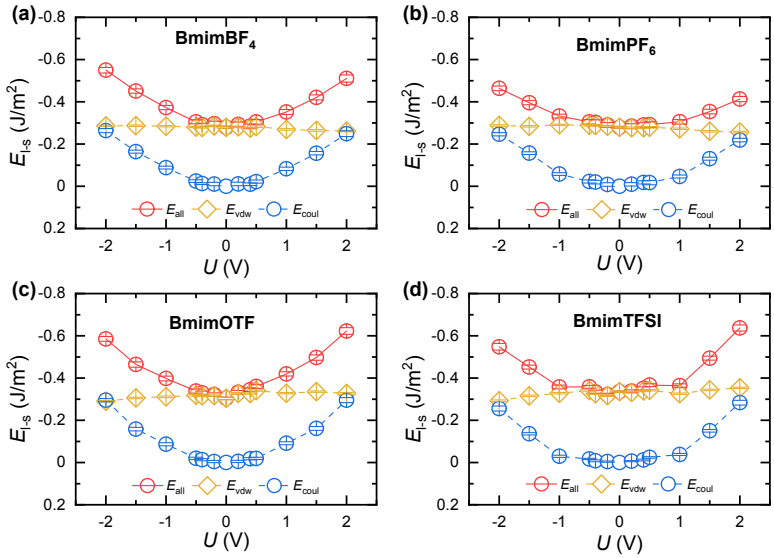

Figure S7. The interaction between electrode and ILs as a function of the external electrical potential: (a) $BmimBF_4$; (b) $BmimPF_6$; (c) BmimOTF; (d) BmimTFSI.

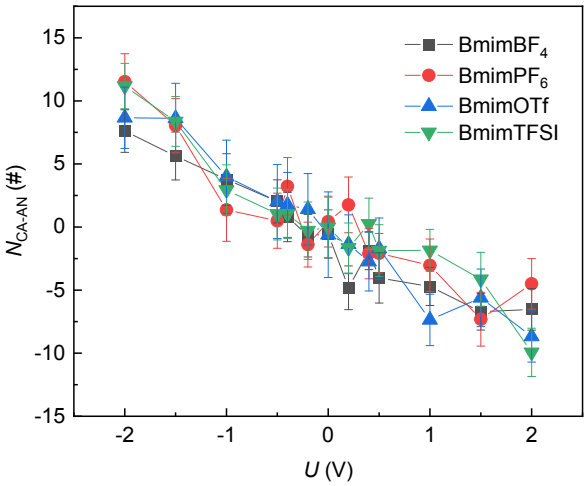

Figure S8. The number of the excess ion at the electrode interface for different ILs as a function of the electrode potential. The excess ion is defined as the difference between cation and anion (N_{CA}-N_{AN}).

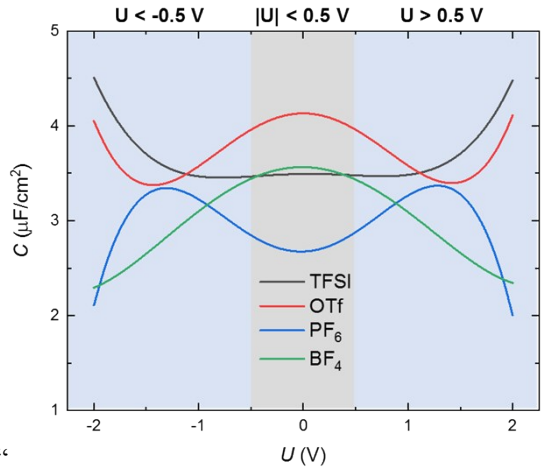

Figure S9. The differential capacitance as a function of the electrode potential for different ILs.

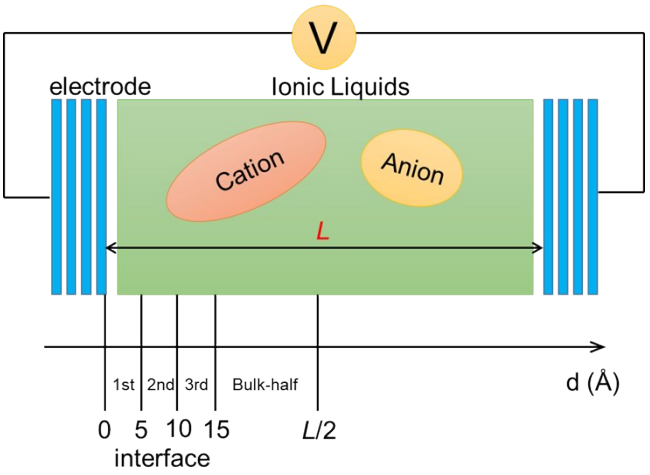

Figure S10. Schematic diagram of the division of the three-layer interface region and the bulk region.

Supplementary Force Field Parameters:

In this work, Both the -CH2-, -CH3, and -CF3 groups in $[Bmim]^+$, $[OTf]^-$ and $[TFSI]^-$ were modeled as united atoms (UAs). The UA model is a good approximation in this work since the contribution of the high-frequency intramolecular vibrations atoms can be regarded as negligible. To correctly describe the movement of the ionic liquids, the charge of the cation and anion, the total charges (absolute values) on the cation/anion are scaled to 0.8. The specific parameters of van der Waals (vdW) interactions, electrostatic interactions, and bond, angle, dihedral for [Bmim]+ , $[BF_4]^-$, $[PF_6]^-$, $[OTf]^-$, and $[TFSI]^-$ are from previous work of Liu et. al.[1]

[1] Zhong, X.; Liu, Z.; Cao, D., Improved Classical United-Atom Force Field for Imidazolium-Based Ionic Liquids: Tetrafluoroborate, Hexafluorophosphate, Methylsulfate, Trifluoromethylsulfonate, Acetate, Trifluoroacetate, and Bis(trifluoromethylsulfonyl)amide. *Journal of Physical Chemistry B* **2011,** *115* (33), 10027-10040. DOI: 10.1021/jp204148q