Supporting Information: Molecular Dynamics Simulations of Ether-Modified Phosphonium Ionic Liquid Confined in between Planar and Porous Graphene Electrode Models

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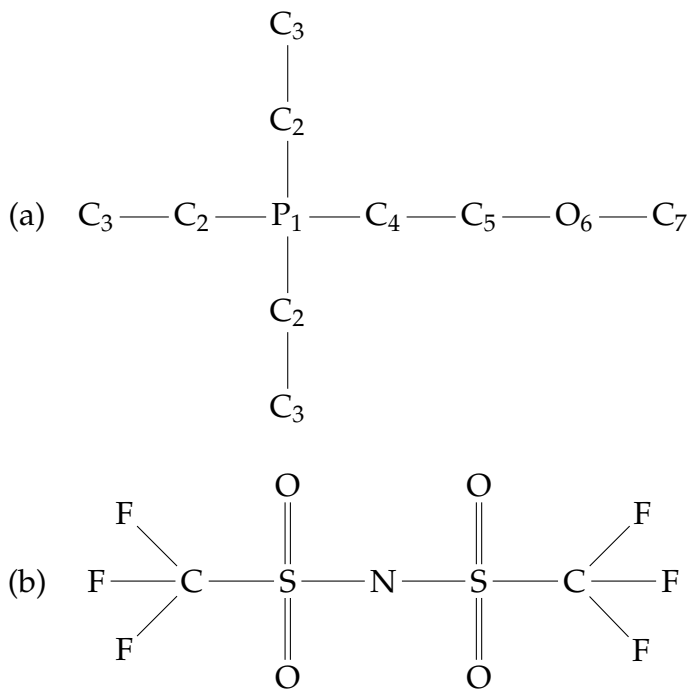

Figure S1: Chemical structure of the molecules forming the electrolyte (a) 2-(methoxy)-ethyl-triethylphosphonium [$P_{222,2O1}$] and (b) bis(trifluoro-methanesulfonyl)amide [NTf_2].

Bulk simulations

The phosphonium-based ionic liquid was simulated with GROMACS software. A non-polarizable force field with scaled-charges (scaling factor 0.8) was employed. The intermolecular interactions were dealt by Lennard-Jones and Coulomb potentials. Intramolecular interactions between atom pair apart by more than three bonds were treated by the non-bonded potential, whereas a scale factor of 0.5 was applied for intramolecular interactions between pair separated exactly by three bonds. Lennard-Jones and real space coulombic interactions were cut off at 1.5 nm. Coulomb long-range interactions were dealt with Particle Mesh Ewald (PME) method with an interpolation order of 6 and 0,08 nm grid spacing. The leapfrog algorithm was used to integrate the motion equation with time step of 2 fs.

Bonds

$$E^b = \frac{1}{2}K_b(r - r_0)^2 \tag{1}$$

Table S1: Bonds Parameter for Bulk Simulations

Bonds	K_b (kJ mol^{-1} nm^{-2})	r (nm)
P_1−C_2	87864	0.1836
P_1−C_4	87864	0.1836
C_2−C_3	129704	0.1538
C_4−C_5	129704	0.1538
C_5−O_6	133888	0.1416
O_6−C_7	133888	0.1416
N−S	311300	0.1570
S=O	533100	0.1442
S−C	197000	0.1818
C−F	369700	0.1323

Angles

$$E^a = \frac{1}{2}K_a(\theta - \theta_0)^2 \tag{2}$$

Table S2: Angles Parameter for Bulk Simulations

Angles	K_a (kJ mol^{-1} rad^{-2})	θ (deg)
P_1−C_2−C_3	313.80	115.92
P_1−C_4−C_5	313.80	115.92
C_2−P_1−C_2	209.20	109.46
C_2−P_1−C_4	209.20	109.46
C_4−C_5−O_6	209.20	105.42
C_5−O_6−C_7	251.04	113.59
S−N−S	671.00	125.60
N−S=O	789.00	113.60
N−S−C	816.00	100.20
O=S=O	870.00	102.60
O=S−C	870.00	102.60
S−C−F	694.00	111.80
F−C−F	694.00	111.80

Dihedrals

$$E^d = K_d[1 + \cos(n\phi - \phi_0)] \tag{3}$$

Table S3: Dihedrals Parameter for Bulk Simulations

Dihedrals	K_d (kJ mol^{-1})	ϕ_0 (deg)	n
C_2−P_1−C_2−C_3	0.6900000	0	3
C_2−P_1−C_4−C_5	0.6900000	0	3
C_4−P_1−C_2−C_3	0.6900000	0	3
P_1−C_4−C_5−O_6	0.6500000	0	3
C_4−C_5−O_6−C_7	2.0200000	0	3
F−C−S−N	0.6624200	0	3
C−S−N−S	16.3798400	0	1
C−S−N−S	-5.2090300	180	2
C−S−N−S	-1.5958300	0	3
F−C−S=O	0.7226400	0	3
S−N−S=O	-0.0075275	180	3

Intermolecular

$$E_{inter} = \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \left(\frac{q_i q_j}{r_{ij}} \right) + 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \tag{4}$$

Table S4: Intermolecular Parameter for Bulk Simulations

Atom	ε (kJ mol^{-1})	σ (nm)
P_1	0.83680	0.37418
$C_{2,4,5}$	0.49404	0.39050
$C_{3,7}$	0.86666	0.37750
O_6	0.71130	0.30000
C	0.20478	0.35660
S	0.80708	0.34200
N	0.63844	0.30660
O	0.37945	0.30820
F	0.22285	0.29100

Charges

Table S5: Charges Parameter for Bulk Simulations

Atom	q(e)
P_1	0.19600
C_2	0.08720
C_3	0.06560
C_4	0.10880
C_5	0.14240
O_6	-0.30560
C_7	0.20000
C	0.23905
S	0.38760
N	-0.34064
O	-0.28704
F	-0.09408

Interface simulations

Bonds

$$E^b = K_b(r - r_0)^2 \tag{5}$$

Table S6: Bonds Parameter for Interface Simulations

Bonds	K_b (kcal mol^{-1} Å^{-2})	r_0 (Å)
P_1−C_2	210.00	1.836
P_1−C_4	210.00	1.836
C_2−C_3	310.00	1.538
C_4−C_5	310.00	1.538
C_5−O_6	320.00	1.416
O_6−C_7	320.00	1.416
N−S	744.02	1.570
S=O	1274.14	1.442
S−C	470.84	1.818
C−F	883.60	1.323

Angles

$$E^a = K_a(\theta - \theta_0)^2 \tag{6}$$

Table S7: Angles Parameter for Interface Simulations

Angles	K_a (kcal mol^{-1} rad^{-2})	θ_0 (deg)
P_1−C_2−C_3	75.00	115.92
P_1−C_4−C_5	75.00	115.92
C_2−P_1−C_2	50.00	109.46
C_2−P_1−C_4	50.00	109.46
C_4−C_5−O_6	50.00	105.42
C_5−O_6−C_7	60.00	113.59
S−N−S	160.37	125.60
N−S=O	188.58	113.60
N−S−C	195.03	100.20
O=S=O	207.93	102.60
O=S−C	207.93	102.60
S−C−F	165.87	111.80
F−C−F	165.87	111.80

Dihedrals

$$E^d = \frac{1}{2}K_1[1+\cos(\phi)] + \frac{1}{2}K_2[1-\cos(\phi)] + \frac{1}{2}K_3[1+\cos(\phi)] + \frac{1}{2}K_4[1-\cos(\phi)] \quad (7)$$

Table S8: Dihedrals Parameter fo Interface Simulations

Dihedrals	K_1 (kcal mol^{-1})	K_2 (Kcal mol^{-1})	K_3 (Kcal mol^{-1})	K_4 (Kcal mol^{-1})
C_2−P_1−C_2−C_3	0.0000	0.0000	0.2708	0.0000
C_2−P_1−C_4−C_5	0.0000	0.0000	0.2708	0.0000
C_4−P_1−C_2−C_3	0.0000	0.0000	0.2708	0.0000
P_1−C_4−C_5−O_6	-0.7763	0.2361	-0.1709	0.0000
C_4−C_5−O_6−C_7	0.6500	-0.2500	0.6700	0.0000
F−C−S−N	0.0000	0.0000	0.3160	0.0000
C−S−N−S	7.8329	-2.4904	-0.7636	0.0000
F−C−S=O	0.0000	0.0000	0.3468	0.0000
S−N−S=O	0.0000	0.0000	-0.0036	0.0000

Intermolecular

$$E_{inter} = \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \left(\frac{q_i q_j}{r_{ij}} \right) + 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \tag{8}$$

Table S9: Intermolecular Parameter for Interface Simulations

Atom	ε (kcal mol^{-1})	σ (Å)
P_1	0.2000	3.7418
$C_{2,4,5}$	0.1181	3.9050
$C_{3,7}$	0.2071	3.7750
O_6	0.1700	3.0000
C	0.0489	3.5660
S	0.1929	3.4200
N	0.1526	3.0660
O	0.0907	3.0820
F	0.0533	2.9100
$C_{electrode}$	0.0699	3.5500

Charges

Table S10: Charges Parameter for Interface Simulations

Atom	q(e)
P_1	0.19600
C_2	0.08720
C_3	0.06560
C_4	0.10880
C_5	0.14240
O_6	-0.30560
C_7	0.20000
C	0.23905
S	0.38760
N	-0.34064
O	-0.28704
F	-0.09408

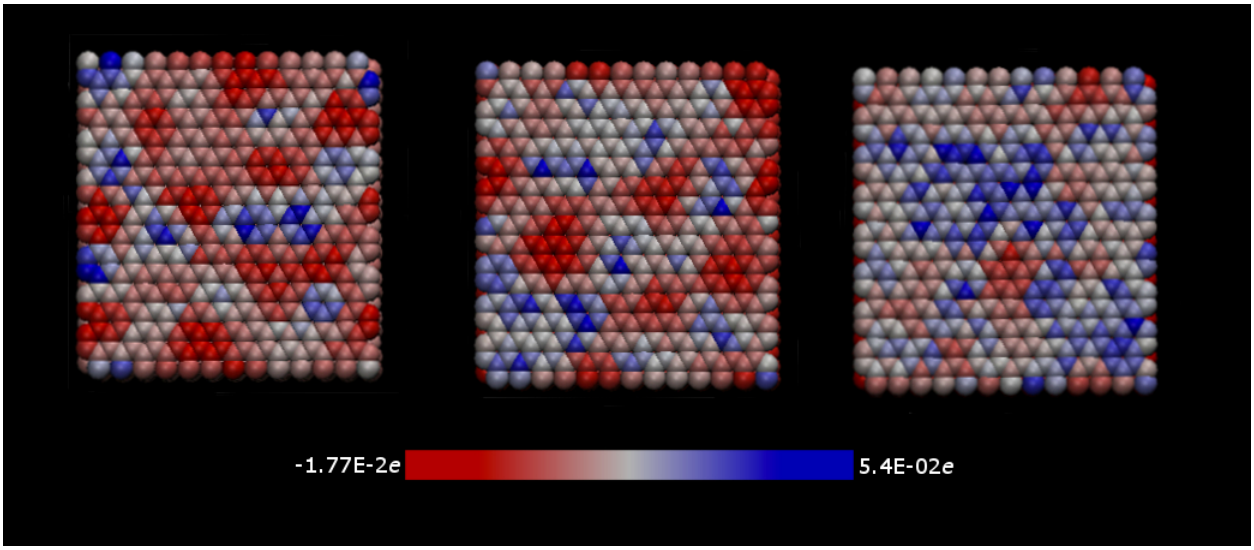

Figure S2: Charges distribution on the planar electrode $\Delta\Psi$=0, 2, and 6V. Red, gray and blue spots represent, respectively, negative, neutral , and positive charges.

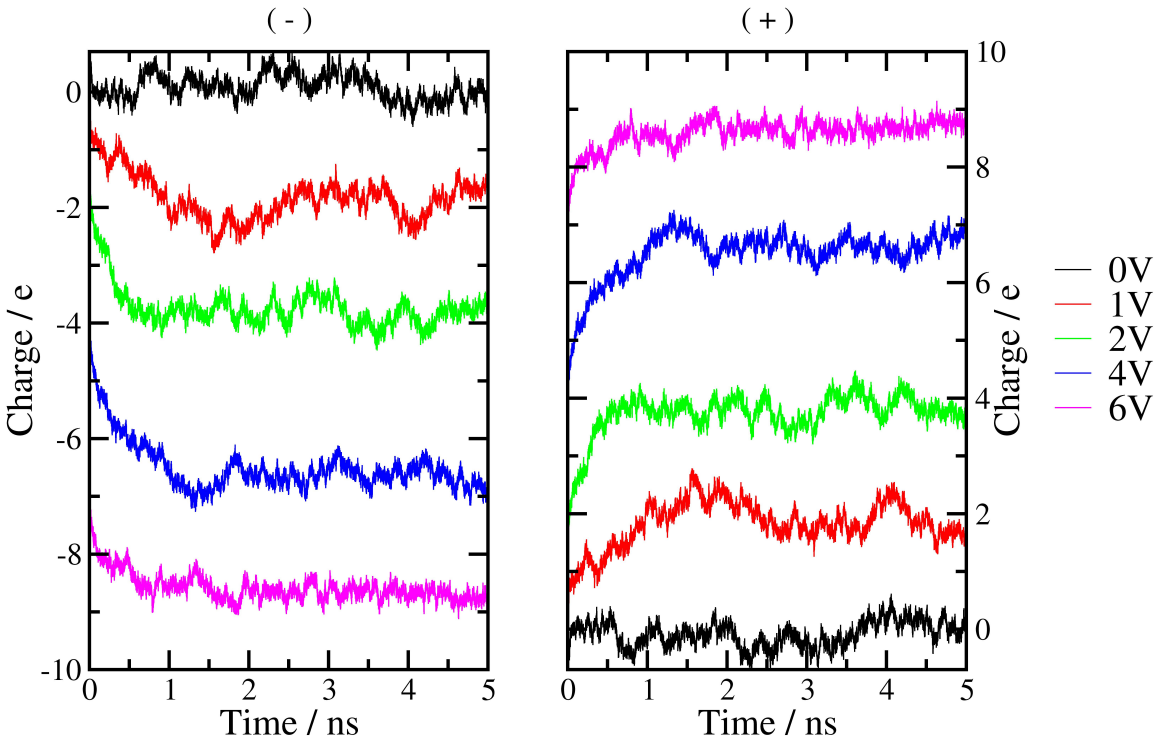

Figure S3: Total charge on the planar electrodes as function of $\Delta\Psi$.