Supplementary Information

Interfacial Structure of Non-halogenated Ionic Liquids at Charged Surfaces: Effect of Alkyl Chain Length

Seiya Watanabe[a,‡] and Georgia A. Pilkington[a], Anna Oleshkevych[a], Patricia Pedraz[a], Milad Radiom[a], Rebecca Welbourn[b], Sergei Glavatskih[c,d], Mark W. Rutland[a,e,*]

[a.] Division of Surface and Corrosion Science, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden. [b.] ISIS Facility, Rutherford Appleton Laboratory, STFC, Chilton, Didcot, OXON OX11 0QX, UK. [c.] System and Component Design, Department of Machine Design, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden. [d.] Department of Electrical Energy, Metals, Mechanical Constructions and Systems, Ghent University, B-9052 Ghent, Belgium. [e.] Surfaces, Processes and Formulation, RISE Research Institutes of Sweden, SE-100 44 Stockholm, Sweden. [f.]Laboratoire de Tribologie Dynamique des Systèmes ,36 Avenue Guy de Collongue, Ecole Centrale de Lyon, 69134 Écully, France.

‡ Current address: Tokyo University of Science, Department of Mechanical Engineering, 6-3-1 Niijuku, Katsushika-ku, Tokyo 125-8585, Japan

* Correspondence: mark@kth.se

Cyclic voltammetry of $[C_{10}C_1Im][BOB]$

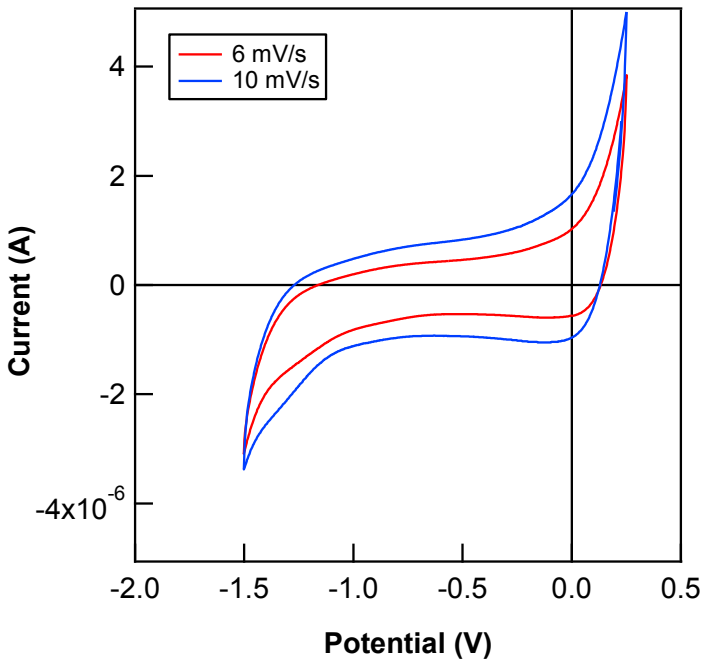

Figure S1. Representative cyclic voltammograms (CV) measured for the ionic liquid $[C_{10}C_1Im][BOB]$ after neutron reflectivity (NR) measurements at a scan rate of 6 and 10 mV/s. Both curves were stable over multiple scans and show no evidence of Faradaic events within the potential window studied.

Theoretical calculation results: Relationship between orientation angles and SFG intensity

The molecular orientation angle is defined as follows. A tilt angle θ of 0° is defined as the surface normal and that of 90° as parallel to the surface plane. A twist angle ϕ of 0° is defined as parallel to the surface and that of 90° as perpendicular to the surface.

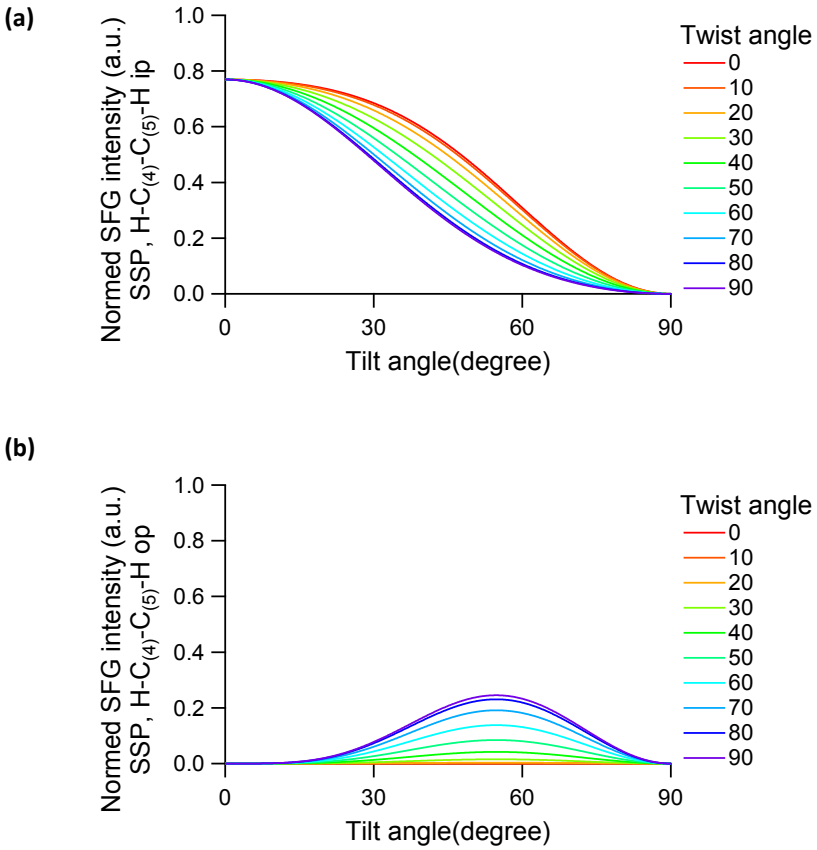

Figure S2. Relationship between orientation angles and SFG intensity of **(a)** H-$C_{(4)}$-$C_{(5)}$-H-ip and **(b)** H-$C_{(4)}$-$C_{(5)}$-H-op for SSP.

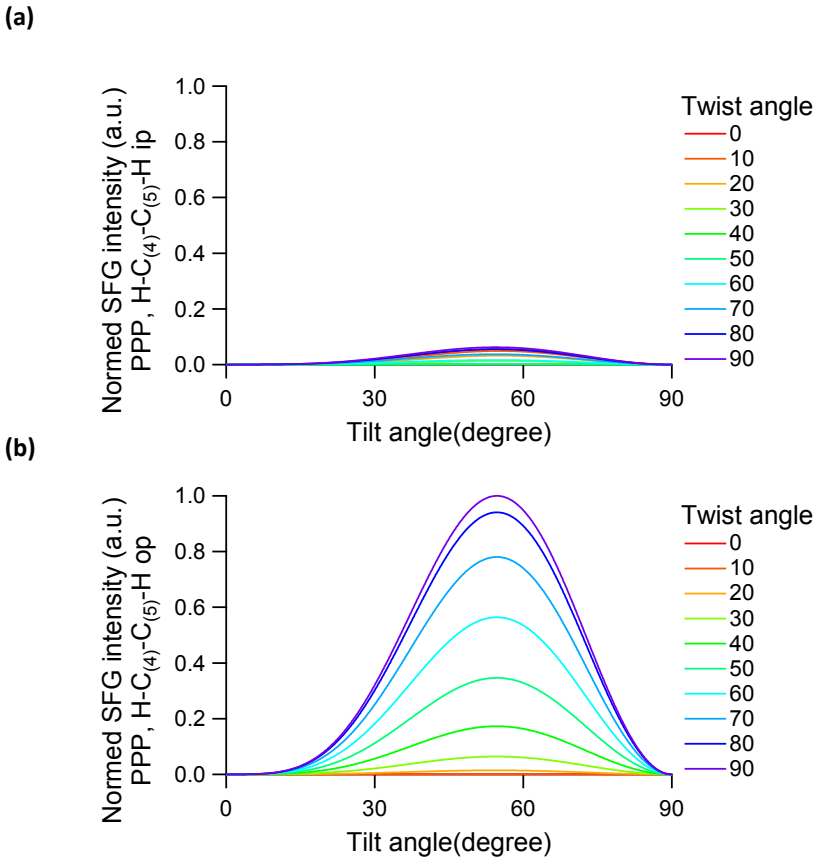

Figure S3. Relationship between orientation angles and SFG intensity of **(a)** H-$C_{(4)}$-$C_{(5)}$-H-ip and **(b)** H-$C_{(4)}$-$C_{(5)}$-H-op for PPP.

IR spectra of ILs

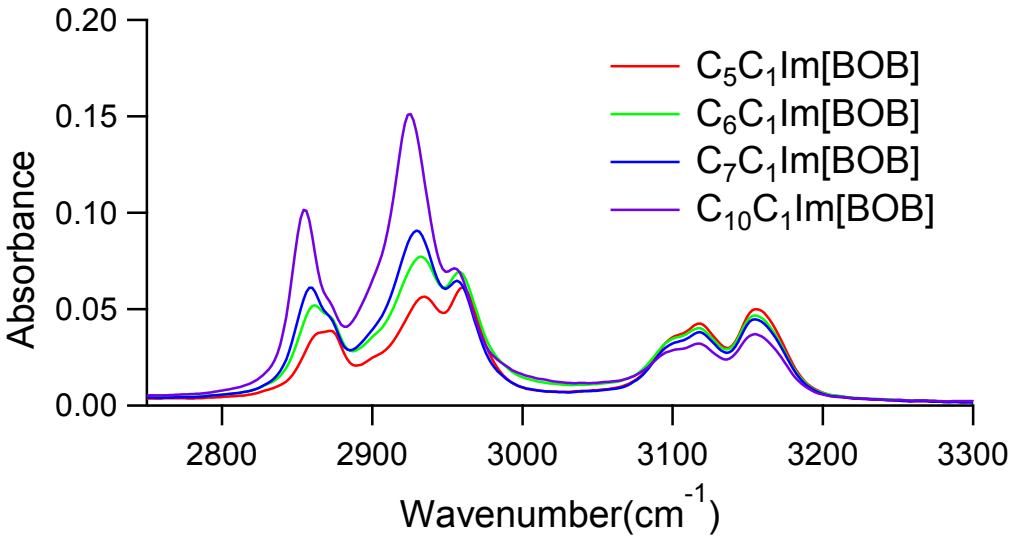

Figure S4. IR spectra of [C_5C_1Im][BOB], [C_6C_1Im][BOB], [C_7C_1Im][BOB] and [$C_{10}C_1$Im][BOB] over the wavenumber range of 2750 – 3300 cm^{-1}.

Current decays measured for [$C_{10}C_1$Im][BOB] after potential changes in neutron reflectivity experiments

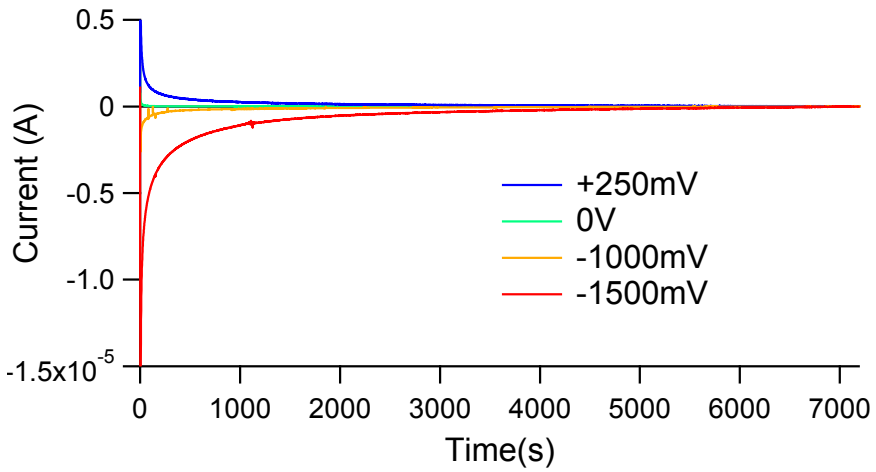

Figure S5. Current as a function of time after application of different applied potentials during NR measurements of [$C_{10}C_1$Im][BOB] at a gold electrode interface. Corresponding surface charge densities calculated from the current-time profiles are listed in the main manuscript text.

Neutron reflectivity of gold substrate in air

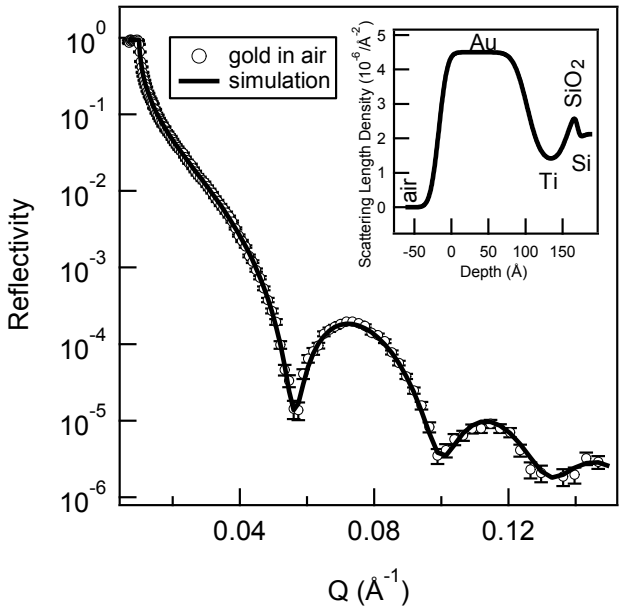

Figure S6. Neutron reflectivity of the gold electrode in air. The symbols represent experimental data, while the solid lines represent a fitted scattering length density (SLD) model fit to the data. The inset shows the corresponding SLD profile.

Table S1. Fitted parameters for the gold electrode in air corresponding to the model fit (solid line) presented in Figure S6.

Layer	Thickness (Å)	Roughness (Å)	SLD (×10^{-6}Å^{-2})
Au	119.0	9.1	4.50
Ti	55.7	14.4	1.35
SiO_2	12.2	11.3	3.06
Si	Inf	3.0	2.13

NR SLD model fit parameters

Table S2. Neutron reflectivity fitted parameters for IL on gold electrode at a potential of 0 V.

Layer	Thickness (Å)	Roughness (Å)	SLD (10^{-6}Å^{-2})
1	7.5	5.3	-0.62
2	4.2	0.6	1.92
3	6.3	1.5	2.94
4	11.2	1.9	1.14
Bulk	Inf	1.0	1.55

Table S3. Neutron reflectivity fitted parameters for IL on gold electrode at a potential of -1 V.

Layer	Thickness (Å)	Roughness (Å)	SLD (10^{-6}Å^{-2})
1	2.5	2.5	1.00
2	7.0	7.0	-0.62
3	2.0	1.0	1.91
4	11.7	1.8	3.02
5	9.6	1.1	0.39
6	12.3	1.5	1.95
Bulk	Inf	5.7	1.55

Table S4. Neutron reflectivity fitted parameters for IL on gold electrode at a potential of +0.25 V.

Layer	Thickness (Å)	Roughness (Å)	SLD (10^{-6}Å^{-2})
1	6.2	6.2	0.50
2	5.1	5.0	-0.61
3	2.0	0.3	1.90
4	6.1	1.9	2.91
5	4.0	1.3	1.97
6	8.2	1.6	0.55
7	14.0	10.9	2.22
Bulk	Inf	12.7	1.55

Table S5. Neutron reflectivity fitted parameters for IL on gold electrode at a potential of -1.5 V.

Layer	Thickness (Å)	Roughness (Å)	SLD (10^{-6}Å^{-2})
1	2.5	2.5	1.73
2	8.2	7.0	-0.62
3	4.4	1.0	2.60
4	7.0	1.6	3.02
5	3.0	1.0	1.84
6	9.1	1.0	0.81
7	13.0	1.8	2.06
Bulk	Inf	14.2	1.55

Interfacial model schematic for 0 V

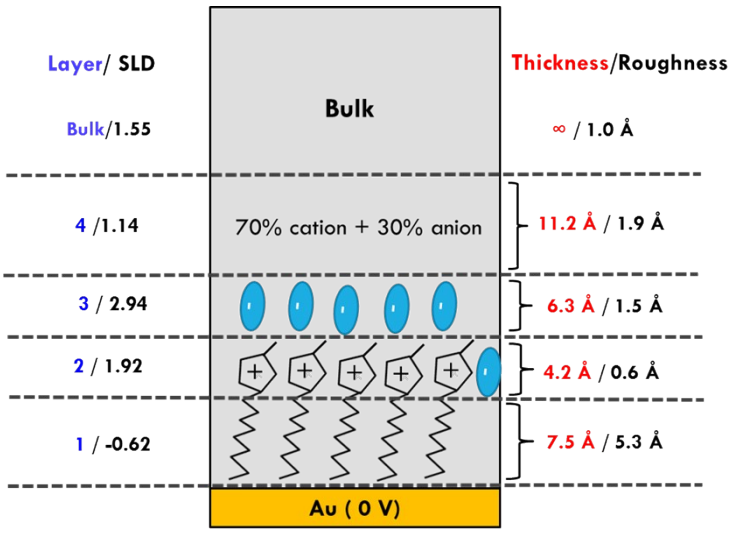

Figure S7. Schematic illustration of the interfacial structures of the ionic liquid [$C_{10}C_1$Im][BOB] at 0 V obtained from SLD model fits to the reflectivity curve at this potential.

Neutron reflectivity measurement: Kinetic results and analysis

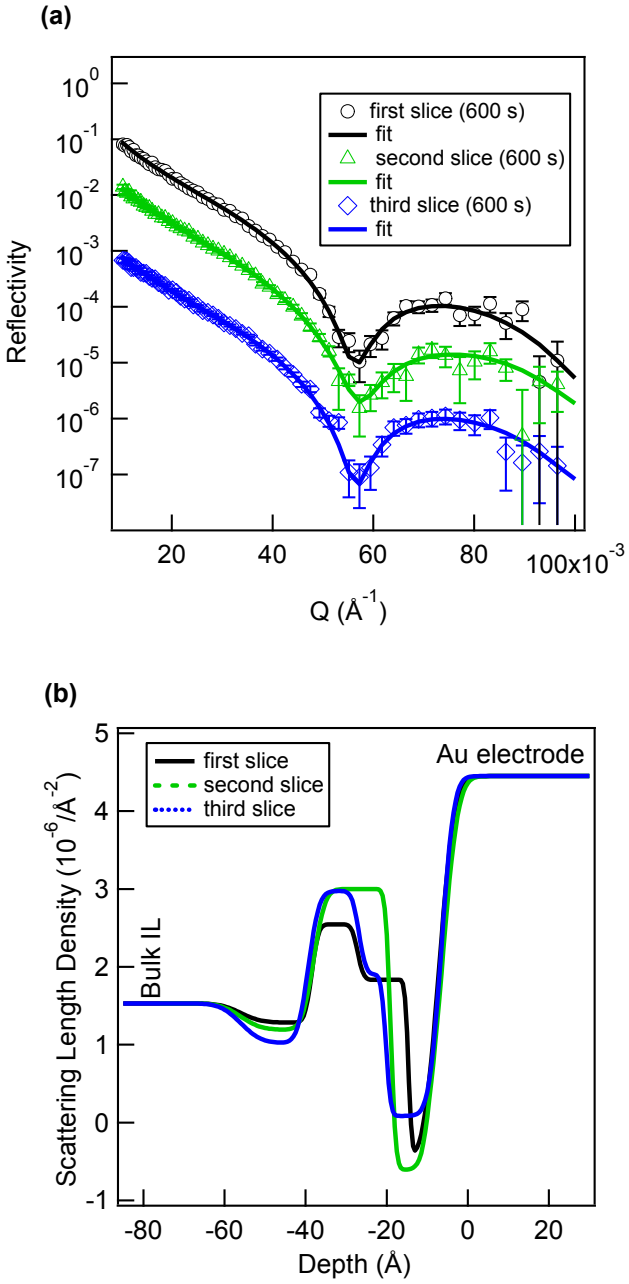

Figure S8. **(a)** Neutron reflectivity curves measured during 600 s intervals for [$C_{10}C_1$Im][BOB] at a gold electrode during equilibration at an applied potential of -1 V. The symbols represent experimental data, while the solid lines represent fitted scattering length density (SLD) model fits to the data. **(b)** shows the corresponding SLD profiles.

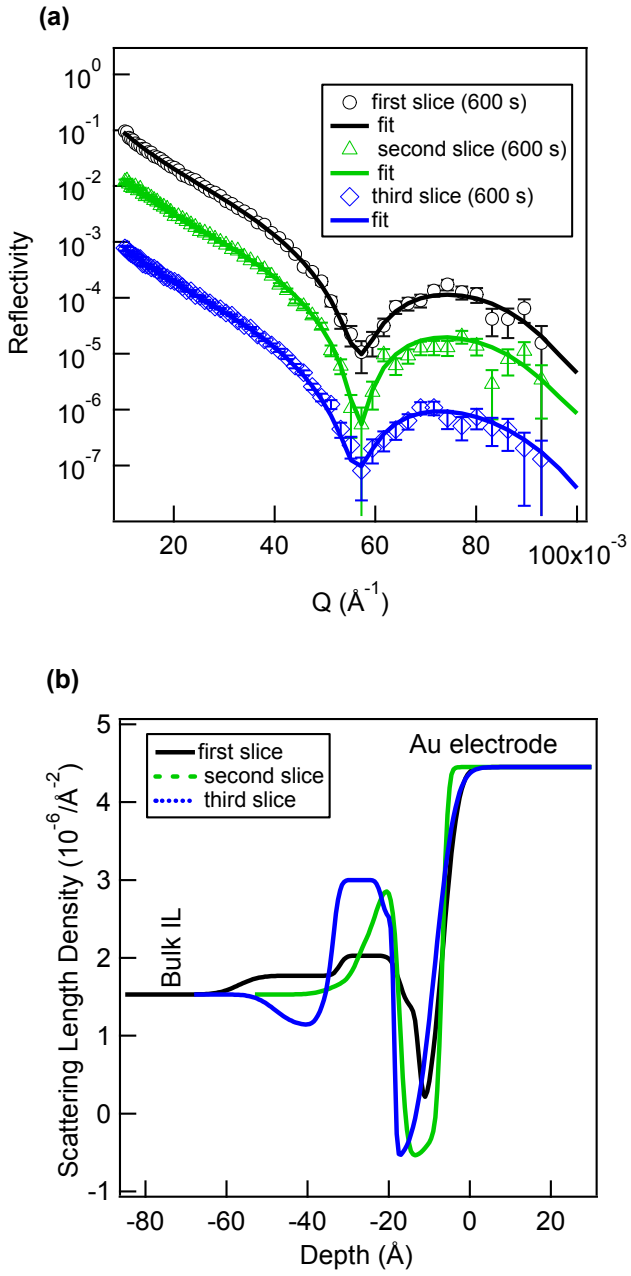

Figure S9. (a) Neutron reflectivity curves measured during 600 s intervals for [$C_{10}C_1$Im][BOB] at a gold electrode during equilibration at an applied potential of +0.25 V. The symbols represent experimental data, while the solid lines represent fitted scattering length density (SLD) model fits to the data. **(b)** shows the corresponding SLD profiles.

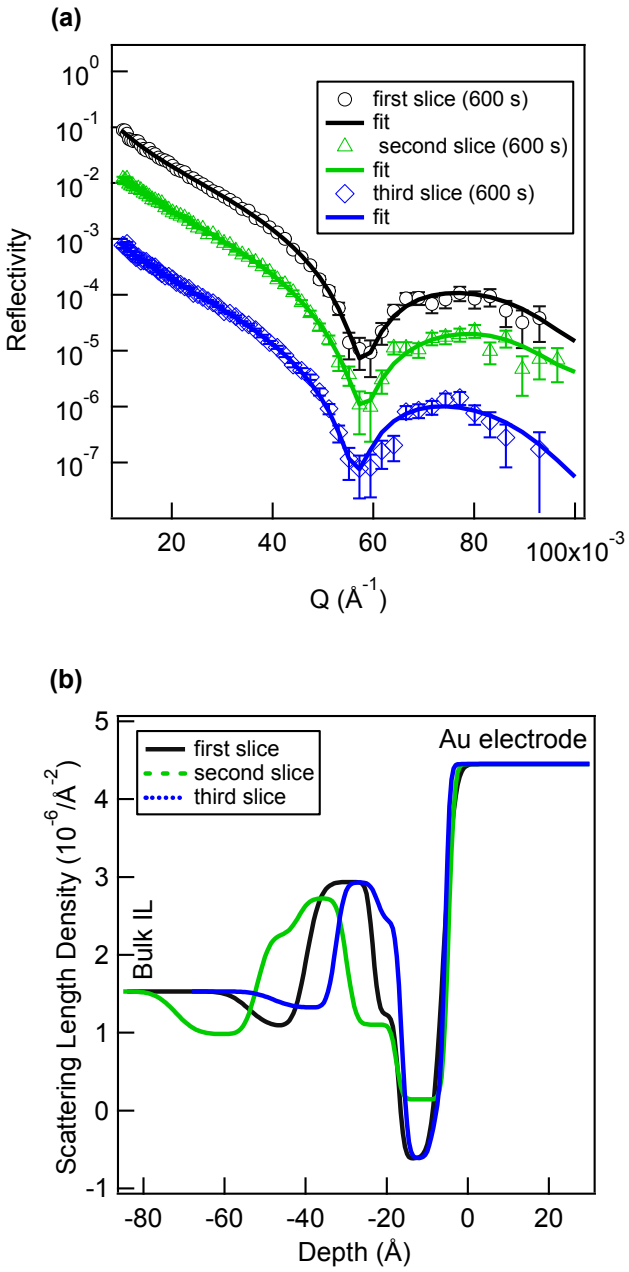

Figure S10. (a) Neutron reflectivity curves measured during 600 s intervals for [$C_{10}C_1$Im][BOB] at a gold electrode during equilibration at an applied potential of -1.5 V. The symbols represent experimental data, while the solid lines represent fitted scattering length density (SLD) model fits to the data. **(b)** shows the corresponding SLD profiles.

SFG peak intensity ratios in alkyl chain region

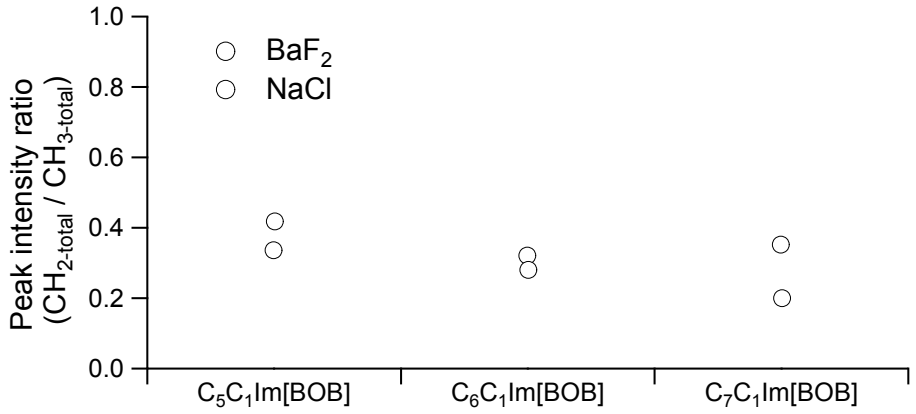

Figure S11. Peak intensity ratio of $CH_{2\text{-total}}/CH_{3\text{-total}}$ obtained from SFG spectra. C_5 - C_7 at NaCl surface showed decrease in the peak intensity ratio of $CH_{2\text{-total}}/CH_{3\text{-total}}$ with increase of chain length, while at the BaF_2 showed constant of the ratio against chain length. This indicates cation with longer alkyl chain adopts a form with less gauche defects in the alkyl chain and therefore can pack more efficiently. Conversely, C_{10} does not show any strong aliphatic C-H peaks (data not included as signal was too weak). This is believed to be due to this IL forming a bilayer structure resulting in a cancelling out effect of the alkyl peaks.