

Supplementary Information

XPS enables visualization of electrode potential screening in an ionic liquid medium with temporal- and lateral- resolution

M. T. Camci,¹ P. Aydoğan,¹ B. Ulgut,¹ C. Kocabas,^{2,*} S. Süzer^{1,*}

¹Department of Chemistry, ²Department of Physics, Bilkent University, Ankara 06800, Turkey

Chemical Composition of the PEM+IL Medium

A survey XP spectrum of the PEM+IL is given in Figure S1, which indicates that no major surface impurities exist. Detailed spectra of the N1s and F1s regions are also given to reveal the integrity and the stoichiometry of the IL (see also Figure S2). However, the C1s signal consists of peaks from both IL and the PEM.

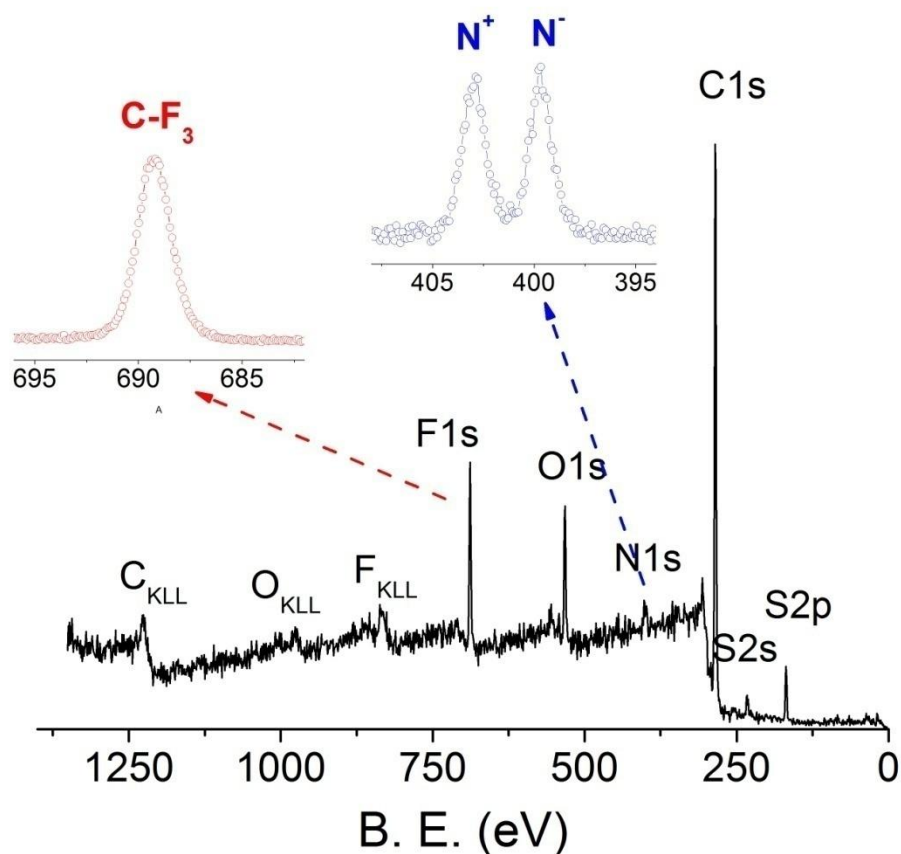
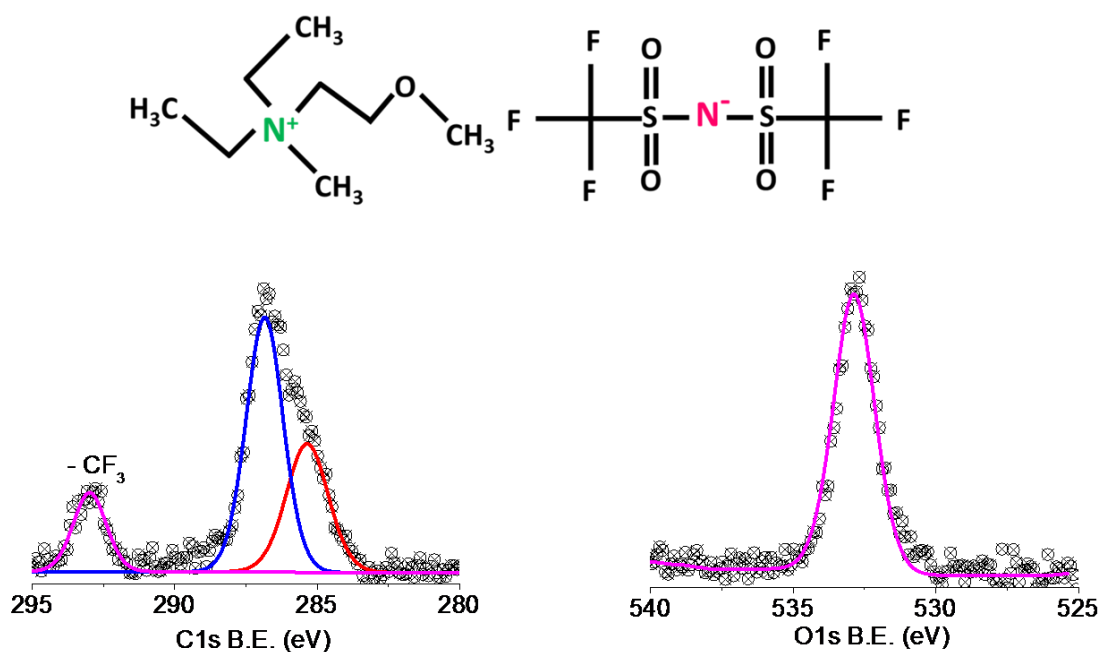


Figure S1. XP survey spectrum of the polymer + IL surface in the scanning mode and with higher resolution of the regions.

Assuming the probed surface composition to be uniform, we can estimate the probed top 10 nm of the surface to contain one Ion-Pair of the IL for ~60 Carbon atoms of the polymer membrane, which means that the final IL medium within the device is not very thick. This is obtained by using the relative intensity ratio of the two strong peaks observed, i.e. F1s/C1s, and working backwards.



experiment

$$\underline{F} : \underline{O} : \underline{N} : \underline{S} : \underline{CF_3} = 1 : 0.88 : 0.39 : 0.38 : 0.32$$

theoretical

$$\underline{F} : \underline{O} : \underline{N} : \underline{S} : \underline{CF_3} = 1 : 0.83 : 0.33 : 0.33 : 0.33$$

Figure S2. High resolution XP spectra of C1s and O1s regions of IL-only, together with experimentally determined and theoretical atomic ratios.

Current Measurements

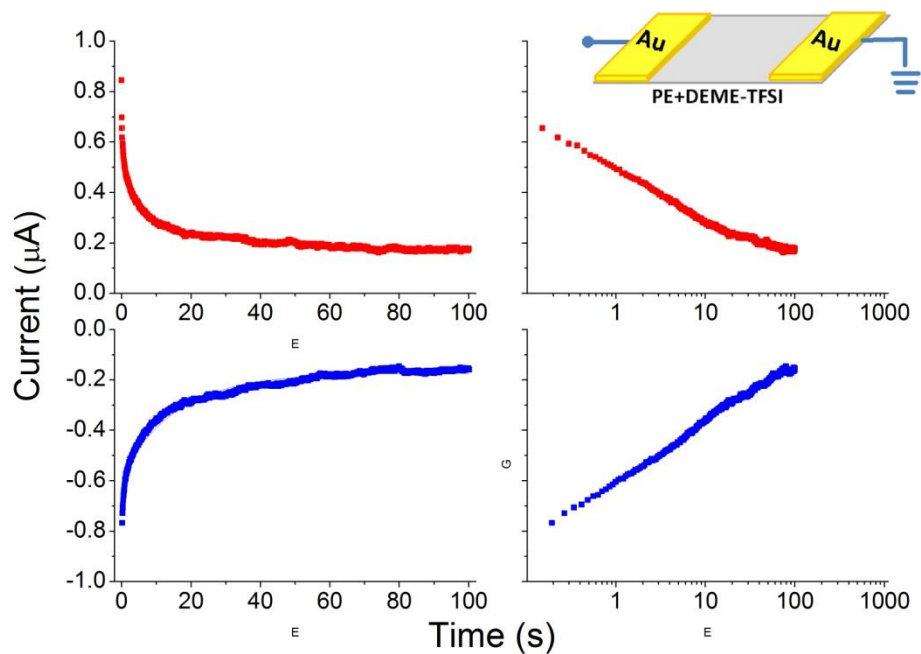


Figure S3. Current measurements.

Time variations of the current to 0 to +3 and 0 to -3V voltage pulses, plotted both in linear and logarithmic time scales, are given in Figure S1. The current at the onset is exponentially decaying in time very similar to the F1s signal recorded with 1s time resolution as shown in Figures 3 and 4 in the main manuscript. As can be seen from the figures that a persistent current remains, which reaches ~ 10 nA at times longer than 1000 s, recorded during XPS measurements .

Two Electrode Device with Graphene in Between

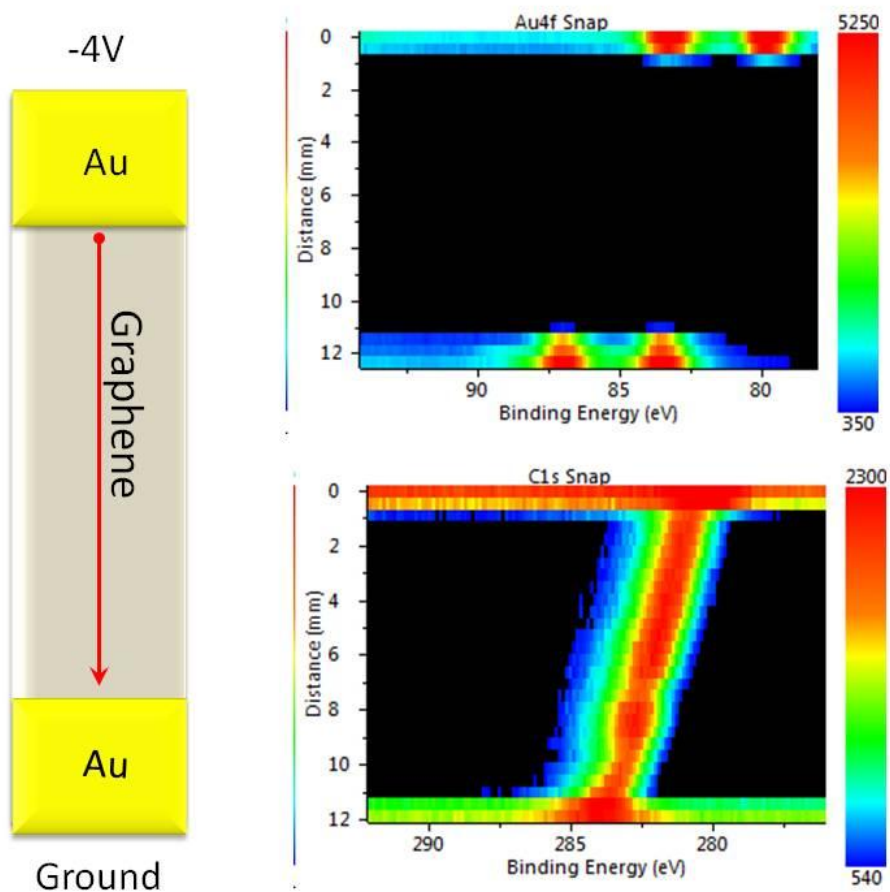


Figure S4. The Au 4f and C1s spectra recorded in the line scan mode across the two electrodes, when the top electrode is subjected to -4V d.c. bias, and the bottom electrode is grounded. Note that contrary to the F1s position depicted in Figure 2 of the main manuscript, C1s exhibits a smoothly and linearly varying position-dependent binding energy shift of 4.0 eV. In this device the graphene layer acts as a simple resistive strip.

Other peaks of the IL

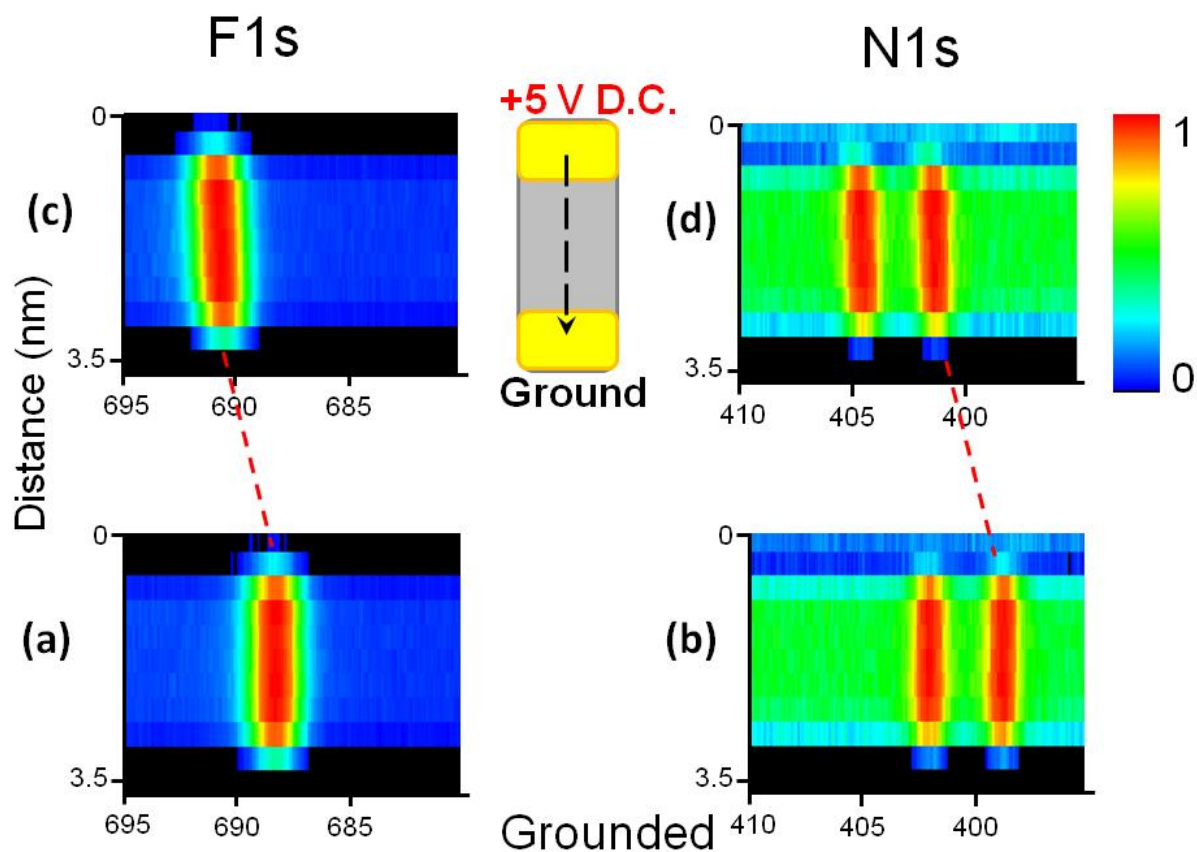


Figure S5. XP Line Scan spectra of F1s and N1s regions between the electrodes when grounded **(a)** and **(b)** and when +5 V is applied to the top electrode **(c)** and **(d)**. N1s region has two peaks corresponding to N- and N+ moieties (see Figure S1), and the color bar represents the intensities. This device is a different one than what is presented in the main manuscript and has a more uniform IL distribution. Nevertheless, similar to what is depicted in Figure 2 of the main manuscript both F1s and N1s peak positions exhibit a constant and 2.5 ± 0.15 eV shift, which is again half of the applied +5V bias.