Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Materials for

"A Scanning Tunneling Microscope Break Junction Method with Continuous Bias Modulation"

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Current Response of the Solvents on the Bias Applied with Various Modulation Frequencies

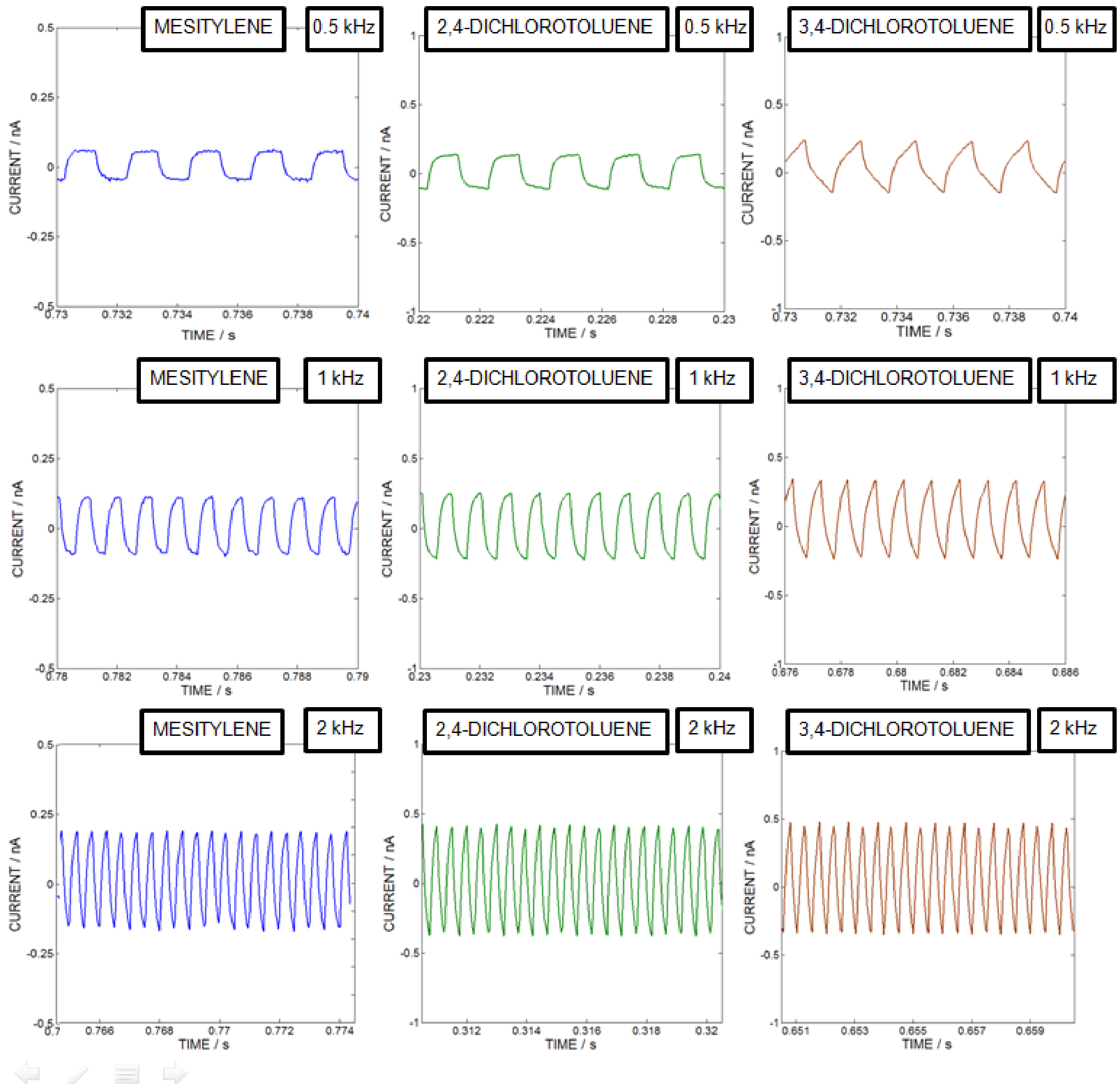

Figure S1. Current-time traces in the solvent regime recorded for mesitylene, 2,4-dichlorotoluene, and 3,4-dichlorotoluene at 0.5, 1, and 2 kHz frequency of the 0.3 ± 0.3 V bias modulation.

Figure S2 shows the capacitance values associated with the solvent in the model electrical circuit (Figure 4 in manuscript) that was used for the simulation of the current responses for the data shown in Figure S1. We note that the current response of the solvent and therefore its capacitance is highly dependent on the purity of the solvent. Note that the mesitylene and 2,4-dichlorotoluene solvents were used as received, and the 3,4-dichlorotoluene was purified by fractional distillation under argon. Using unpurified 3,4-dichlorotoluene resulted in about a two fold increase in the amplitude of the current oscillations and 2.5 higher capacitance (data not shown). Similarly, the amplitude of the current response of the mesitylene saturated intentionally with deionized water (data not shown) was over fifty percent higher than that of pure (99+ %) solvent.

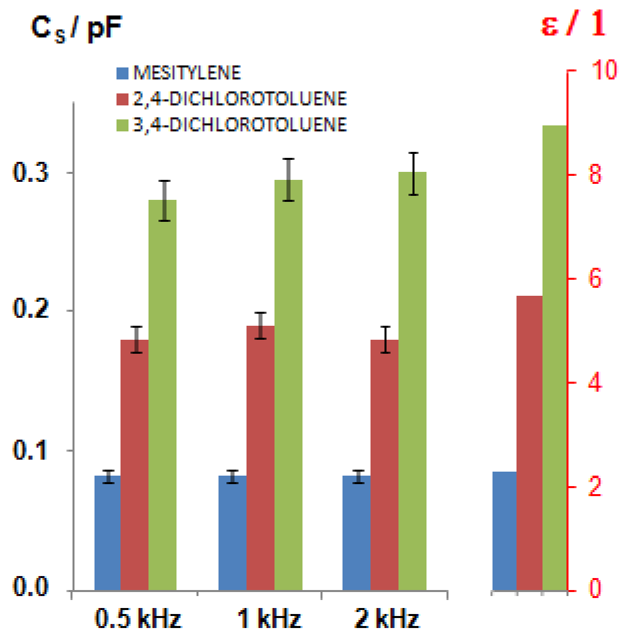

Figure S2. Dependence of the solvents capacitance simulated using the model electrical circuit (Figure 4 in manuscript) on the bias modulation frequency. The error is estimated as 5%. The data is compared to the dielectric constant values adapted from refs 1 and 2.

For our experimental setup, we determined the RC time constants of ~ 75 μs for mesitylene, 90 μs for 2,4-dichlorotoluene, and 225 μs for 3,4-dichlorotoluene. The above values correspond to frequency cutoffs of ~2.15 kHz for mesitylene, 1.75 kHz for 2,4-dichlorotoluene, and 0.7 kHz for 3,4-dichlorotolune.

Influence of Macroscopic Geometrical Factors on the Capacitive Current Waveforms

The capacitor formed between the STM tip and the substrate is macroscopic in comparison to the junction itself; therefore small changes in the tip-substrate separation in comparison to the dimensions of the electrodes have no effect on the capacitive current waveform. The influence of major geometrical factors on the capacitive current waveform is given in figures S3-S5.

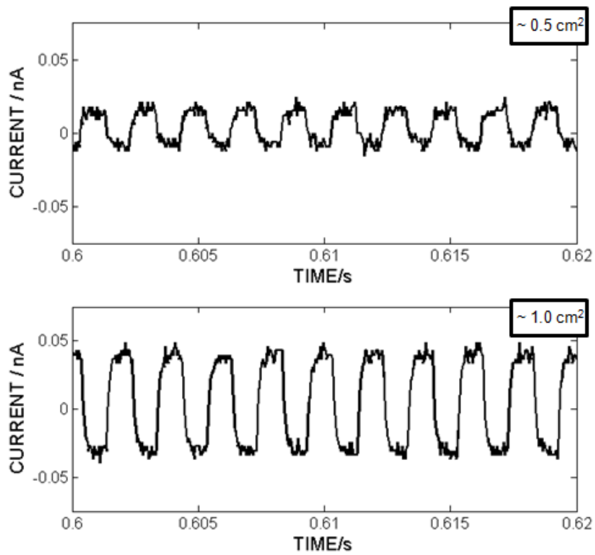

Figure S3. Current-time traces recorded in air above the gold substrates with different geometrical surface areas. The traces were recorded at 0.5 kHz frequency of the 0.3 ± 0.3 V bias modulation. The STM tip – substrate separation was of about 300 μm.

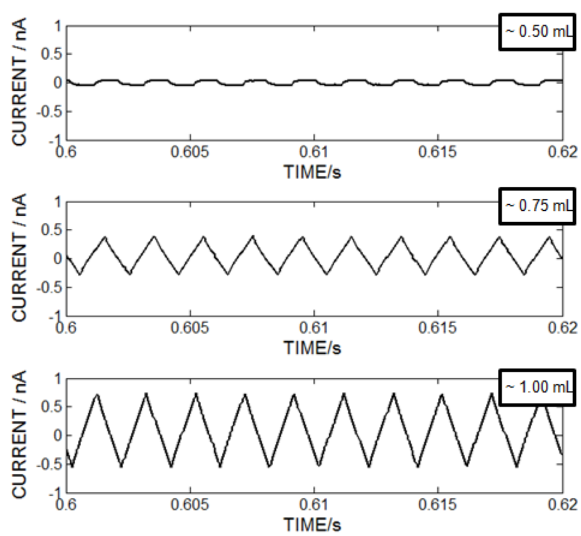

Figure S4. Current-time traces recorded in the cell filed with different volumes of the 3,4-dichlorotoluene. The traces were recorded at 0.5 kHz frequency of the 0.3 ± 0.3 V bias modulation, with the STM tip – substrate separation of about 300 μm. Subsequent additions of the 0.25 mL of the solvent were made to cell. Note that first additions with total solvent volume below 0.75 mL were not sufficient to cover the surface of the gold substrate with solvent.

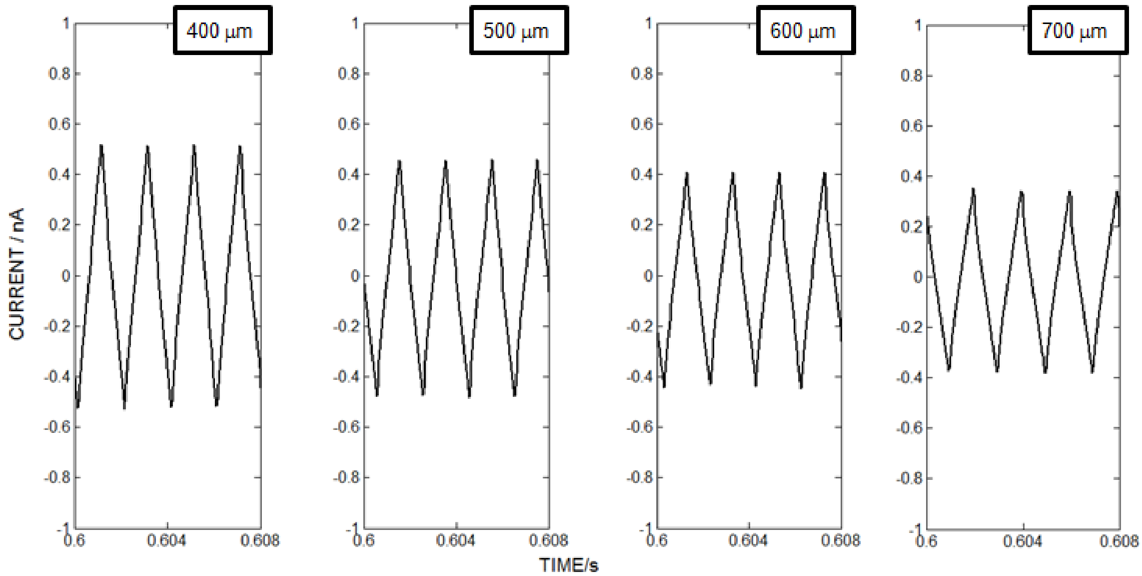

Figure S5. The current-time traces recorded at different STM tip – substrate separations. The traces were recorded at 0.5 kHz frequency of the 0.3 ± 0.3 V bias modulation, in the cell filled with 1 mL of 3,4-dichlorotoluene. Note that the separation is micrometers in length scale, thus a decrease in the current waveform amplitude originates from the decrease of the amount of the gold wire forming the tip that was immersed in the solvent.

References

1. *CRC Handbook of Chemistry and Physics 84th Ed.*, CRC Press, Boca Raton, FL, 2003.
2. R. R. Dreisbach, in *Physical Properties of Chemical Compounds*, American Chemical Society, 1961, vol. 15, ch. 1, pp. 3-523.