

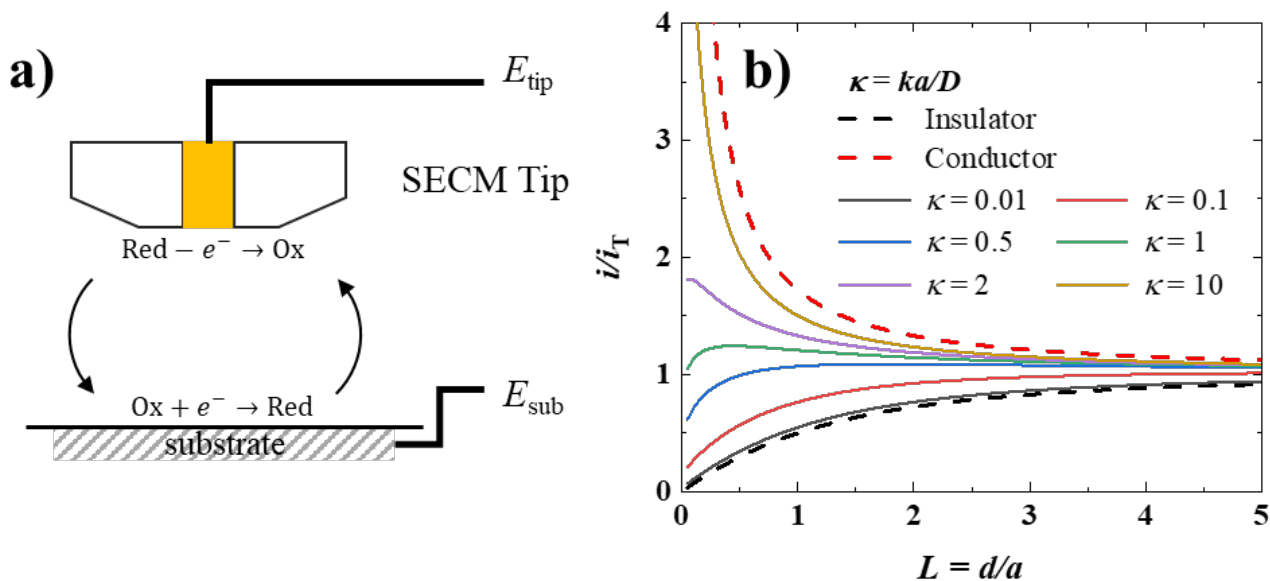
# ChemElectroChem

Supporting Information

## **Electron Transfer Kinetics at Single-Layer Graphene/Ionic Liquid Interfaces**

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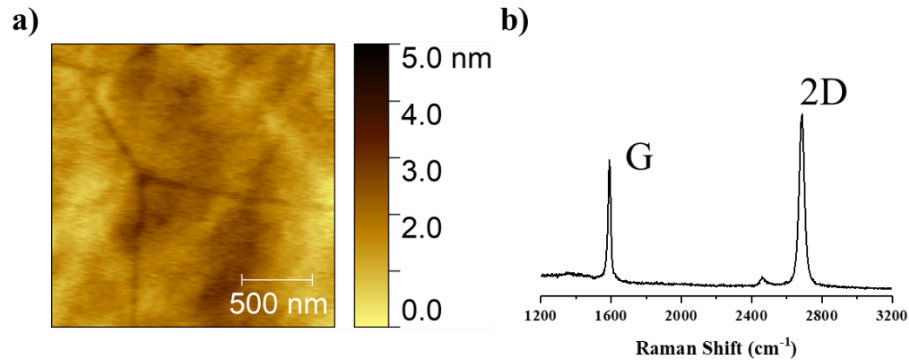
**SECM approach curves and simulations according to Lefrou *et al.* approximation (from reference 21 Lefrou *et al.* in the text)**



**Figure S1.** a) Scheme of the scanning electrochemical microscope setup. B) Calculated approach curve according to Lefrou' approximation for finite charge transfer kinetics.

The molecule is oxidized at the SECM tip and then reduced at the substrate by applying different potentials on the corresponding electrode. The probe approaching curves were altered by applying different substrate potentials where the electron transfer kinetics at the interface were changed. **b)** probe approaching curves on a substrate of insulator (black dash), conductor (red dash), and finite kinetics situation (line in colors) with different uniformed kinetics parameters  $\kappa$  where  $\kappa = k_{el}a/D$ .  $D$  represents the diffusion coefficient, and  $a$  refers to the radii of the SECM probe. In different uniformed kinetics parameter, the corresponding probe approach curve switches from a conductor-like ( $\kappa=0.01$ ) shape to an insulator-like one ( $\kappa=10$ ).

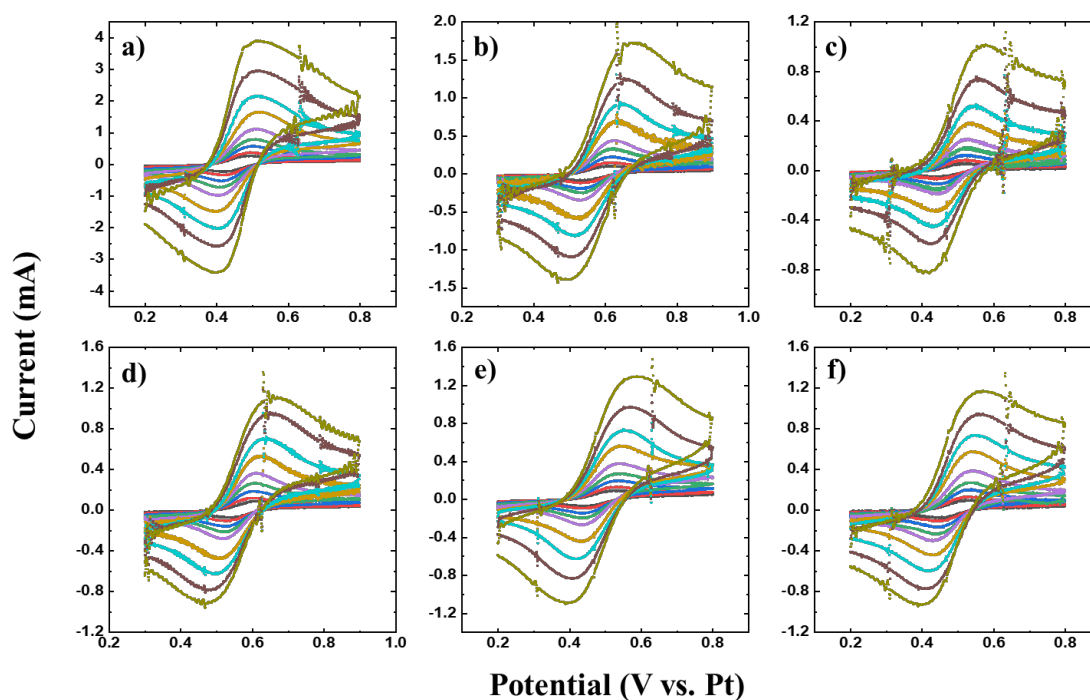
## Characterization of graphene monolayer by Raman and AFM spectroscopies.



**Figure S2** Initial control experiments. **a)** Atomic force microscopy topography of the graphene used in the experiments. The surface was found to be flat with roughness of 0.109 nm. **b)** Raman spectroscopy of the graphene. The presence of only sharp 2D peak at  $2700 \text{ cm}^{-1}$  and G peak at  $1589 \text{ cm}^{-1}$  indicates that the substrate is covered by a high-quality single-layer graphene.

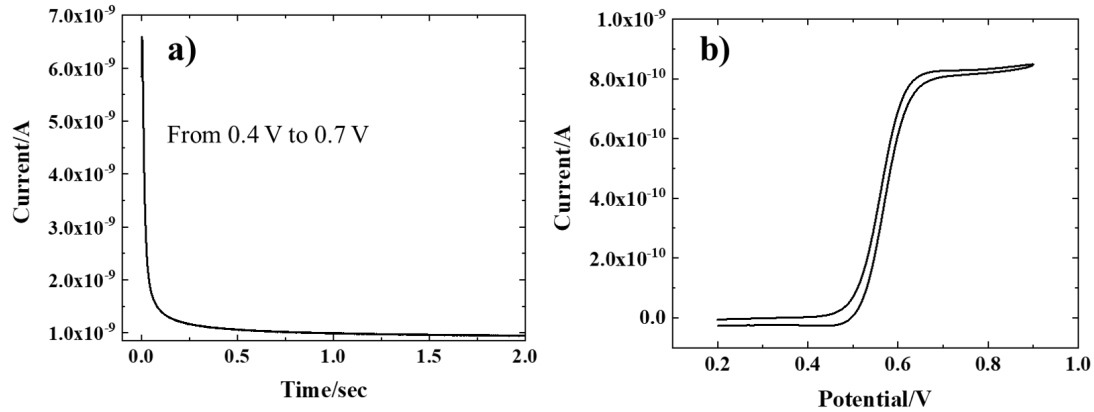
Raman measurements were performed on an XploRA confocal microprobe Raman system (HORIBA JobinYvon) equipped with a  $50\times$  (NA 0.45) objective with an excitation line of 638 nm from a He-Ne laser. The Raman frequencies were calibrated using a Si wafer. To remove the interference of fluorescence, the Raman spectra were background-corrected based on a fifth-order polynomial function.

## Fast cyclic voltammetry of the redox probes in RTILs



**Figure S3.** Cyclic voltammograms of the three mediators, ferrocene(a,d), ferrocene-methanol(b,e), ferrocene-dimethanol (c,f), in two ionic liquids, EMITFSI(a-c) and BMITFSI(d-f). The scan rates in each figure are, from black to green, 1, 2, 5, 10, 20, 50, 100, 200, and 400 V/s which is the highest available in our device. All the experiments were performed on gold electrode and maintained 45 °C through water bath.

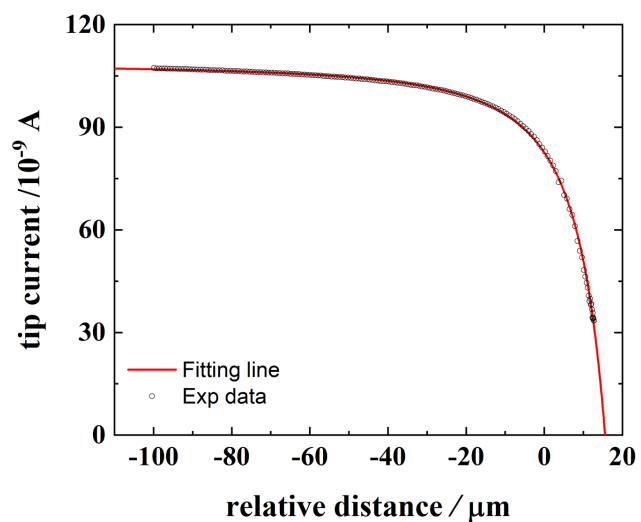
**Steady state chronoamperometry and cyclic voltammetry in ionic liquid in our experimental conditions.**



**Figure S4.** a) Double steps chronoamperometry of the ferrocene-dimethanol in EMITFSI at the temperature of around 45 Celsius. The SECM tip and all experimental conditions are the same as mentioned in the main text. And b) steady-stat cyclic voltammogram on the gold SECM tip at the same concentration of 10 mM and the scan rate of 0.01 V/s.

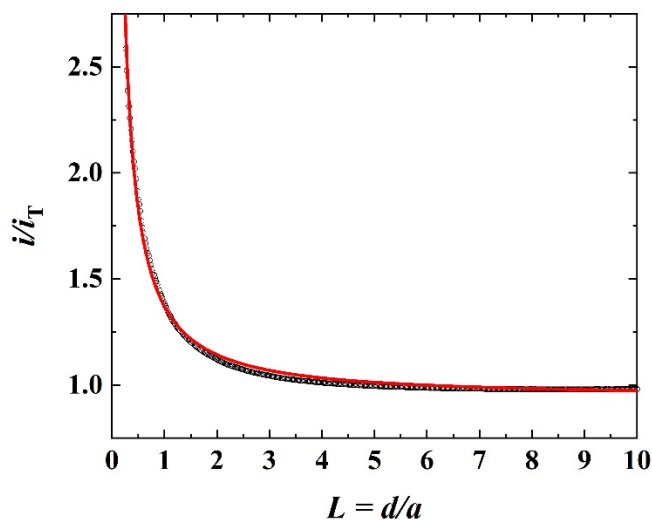
Curves presented on Figure S4 are typical experimental characterization of the tip that were performed prior the SECM experiments. The S-Shape and the stabilized current of the chronoamperometry are indicative of a steady behavior.

## Procedure for origin probe calibration using the irreversible anthracene oxidation



**Figure S5.** Probe approach curve of irreversible oxidation of 10 mM anthracene in acetonitrile (circle) and adjustment of the origin considering a totally feedback approach curve (line). The geometry of SECM probe was determined by comparing the experimental data and the fitting line.

### Approach SECM curve in an ionic liquid using a classical carbon substrate (PPF).



**Figure S5.** Example of SECM approach curve (black dots) and corresponding fitting result (red line) of 10 mM ferrocene in EMITFSI on a PPF substrate a 5 $\mu$ m radius gold tip at the temperature around 45 $^{\circ}$  C. The SECM tip and all experimental conditions are the same as mentioned in the main text. The maximum approaching rate of the tip was set to 0.1  $\mu$ m/s. (PPF : Pyrolyzed Photoresist Film).

The shape of the experimental variation (black dots) could be fitted against the theoretical curve for full diffusing-controlled behavior. It indicates that the system is under diffusion control and thus that the charge transfer rate constant is too high to be measured with our conditions.