Electronic Supplementary Information

Organic electrochemical transistors monitoring micelle formation

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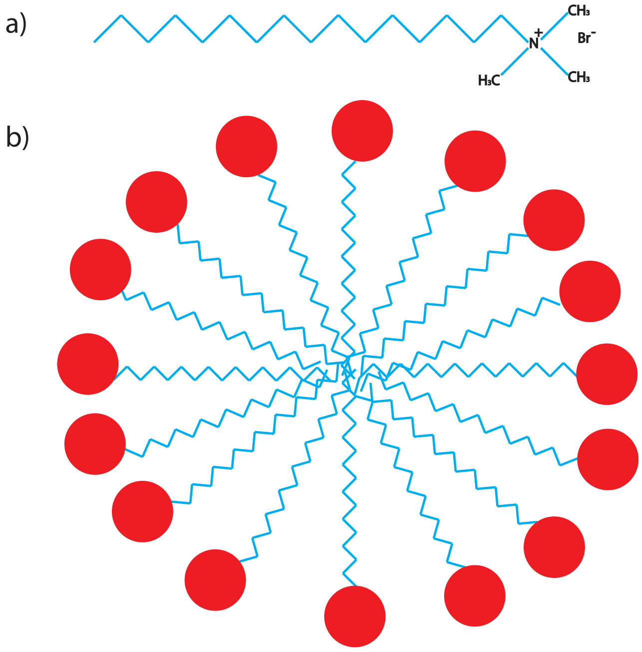

Figure S1. a) Chemical structure of CTAB and b) two-dimensional representation of a CTA$^+$ spherical micelle in water. The red, filled circles represent the positive charged hydrophilic alkylammonium groups. The typical aggregation number for CTAB is 50-60.

Device fabrication and experimental details

Device fabrication

Planar organic electrochemical transistors (OECTs) entirely made of PEDOT:PSS were fabricated on glass slides. The devices were patterned using a parylene lift-off technique. [1] First, a 2mm parlyene-C film was deposited on the glass substrate by chemical vapor deposition (CVD). Then the positive tone photoresist SPR220_3.0 (Microchem) was spun on the parylene-C film (with a first spinner ramp at 500 RPM for 6 s and a second one of 4500 RPM for 45 s), and was pre-baked on a hotplate at 115 °C for 5 min. The patterns were defined by UV-exposure for 20 s using a mask aligner. Exposure was followed by a post-bake at 115 °C for 5 min and by development in a MF26 developer solution (Microposit) for 75 s. After photoresist development the unprotected parylene was etched by oxygen reactive ion etching (RIE) to transfer the pattern to the glass substrate. Subsequently an aliquot of a mixture of 20 mL of PEDOT:PSS aqueous microdispersion (Clevios PH500, Starck GMBH), 5mL of ethylene glycol, and 100 mL of dodecyl benzene sulfonic acid (DBSA) surfactant was spun onto the substrate (1500 RPM for 45 s), to yield a 70-80 nm-thick film. The addition to the PEDOT:PSS microdispersions of compounds presenting two or more polar groups yields films with high electrical conductivity**.** After spin coating, the parylene-C was peeled off the substrate using adhesive tape, leaving the PEDOT:PSS patterns. The devices were then baked on a hot plate at 120 °C for 60 min. To complete the OECT fabrication, polydimethilsiloxane (PDMS) wells were placed on the PEDOT:PSS patterns do define the channels.

Preparation of CTAB Solutions.

CTAB solutions were prepared by serial dilution of a 10^{-2} M solution prepared by dissolving the CTAB salt (Aldrich) in deionized water.

Electrical characterization of OECTs

The transistor characteristics were evaluated using anAgilent B2902A Source/Measure precision units, controlled by LabView software. Our setup allowed simultaneous measurement of the drain/source and gate/source currents. The devices were typically operated with a maximum gate voltage of 1 V to avoid water electrolysis. The source/drain current of our devices ranged between ≈ 10^{-4} A (on state, $V_g = 0$ V) and ≈ 10^{-5} A (off state, $V_g = 1$ V).

OECTs were characterized by measuring source/drain current (I_d) versus time at a constant drain voltage (V_d) while pulsing the gate voltage from 0 V to 1 V in steps of 0.2 V, keeping V_d constant at -0.4 V. The OECT response (or current modulation) was evaluated from the plot of I_d versus time, as $|(I-I_0)/I_0|$, where I is the *off* current (for gate voltages, $V_g \neq 0$ V) and I_0 is the *on* current (for $V_g = 0$ V). [2, 3] Each gate voltage was applied for 60 s in order to reach steady state conditions.

The OECT gate/source current was constantly measured to monitor the occurrence of Faradaic processes at the gate electrode/electrolyte interface. Figure S2 shows the gate currents *versus* time of an OECT characterized in aqueous solutions with different concentrations of CTAB. The gate current remains below 10^{-7} A, i.e. two order of magnitude lower than the typical values of the drain current. Based on a previous study, we know that the gate current is the fingerprint of the regime of

OECT operation. [3] A small gate-source current means that the OECT is working in a capacitive mode (non-Faradaic), in which the application of V_g induces a transient current in the electrolyte and no redox reaction occur at the gate electrode.

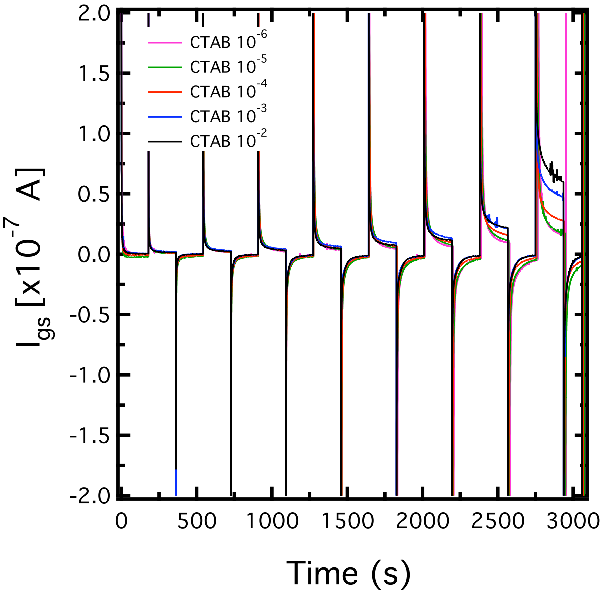

Figure S2. Gate-source current (I_{gs}) versus time for an OECT with a CTAB aqueous electrolyte (CTAB concentrations ranging from 10^{-6} M to 10^{-2} M).

Figure S3 show the OECT drain current modulation as a function of the gate voltage ($|I-I_0|/I_0=\Delta I/I_0$ vs. V_g), for aqueous solutions with CTAB concentrations of 10^{-5} M and 10^{-2} M and with NaCl concentration of 10^{-2} M (i.e. in presence and in absence of micelles). A clear gate voltage shift towards less positive values (about ~ 200 mV) is induced by the presence of micelles for a fixed $\Delta I/I_0$ (in this case 0.3), as indicated by the harrow in the plot. We found that, for the same $\Delta I/I_0$ (for instance at $\Delta I/I_0 = 0.3$ and $V_d = -0.4$V), the presence of micelles induces a gate voltage shift of about 0.22 V with respect to dissociated ions and of about 0.28 V with respect to NaCl.

The capacitance of our PEDOT:PSS gate cannot be measured using the experimental configuration employed in this work. However, making the assumption that the gate capacitance does not depend on the electrolyte, the gate voltage shift can be used to estimate the relative change in the amount of charge entering the PEDOT:PSS film in presence and in absence of micelles.

Charge, capacitance and voltage are related by the following equation:

$$Q = C\Delta V$$

Where Q is the charge, ΔV the voltage difference (gate voltage shift, in this case) and C the capacitance. Assuming a constant gate capacitance and using the measured gate voltage shift, we can estimate that the presence of the CTAB micelles determines an increase of 20-30% of the charge entering the polymer.

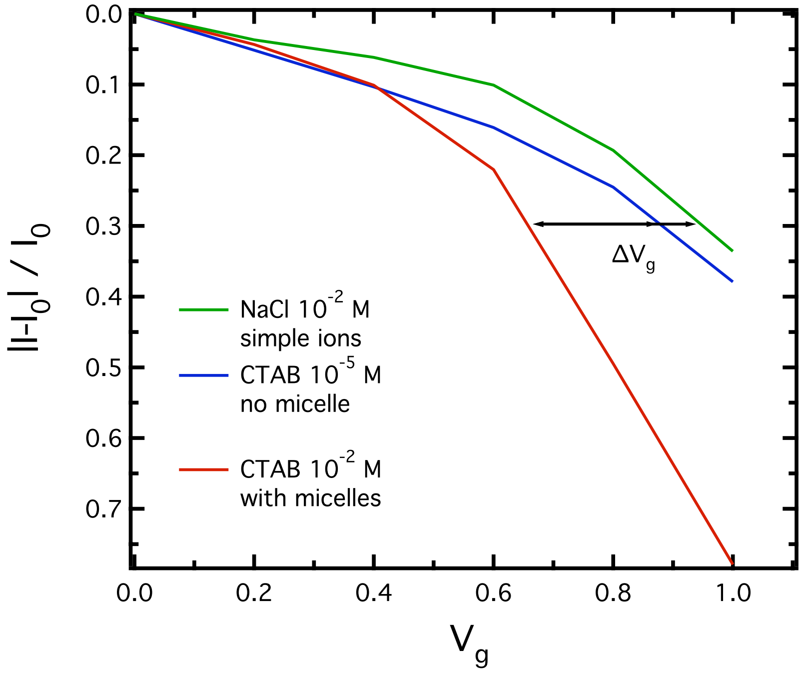

Figure S3. OECT drain current modulation as a function of the gate voltage (($|I-I_0|/I_0 = \Delta I/I_0$ vs. V_g), for aqueous solutions with CTAB concentrations of 10^{-5} M and 10^{-2} M and with NaCl concentration of 10^{-2} M (i.e. in presence and in absence of micelles).

Simultaneous electrical and optical OECT characterization

Absorption spectra were measured using a JASCO V-530 Ultra Violet-Visible Spectrophotometer (UV-Vis), with 1 nm wavelength step.

To perform the experiment, we fabricated a dedicated OECT device, sealing the OECT slide with another glass slide separated by mica spacers of about 2 mm (Figure S3). The space between the two slides was filled with a CTAB 10^{-2} M aqueous solution. The contacts to the drain and source electrodes were fabricated at the edges of the PEDOT:PSS stripes and were not exposed to the electrolyte. A Pt wire immersed in the electrolyte before sealing, served as the gate electrode. The source, drain and gate electrodes were connected to the Source-Measure Unit via copper wires. The device was placed into the spectrophotometer cuvette space. The light source was first calibrated outside the PEDOT:PSS stripe in order to acquire a reference baseline through the glass-electrolyte-glass sandwich. UV-Vis spectra were acquired during operation of the OECT, at $V_g = 0$ V and $V_g =$ 1V, with a fixed $V_d = -0.4$ V

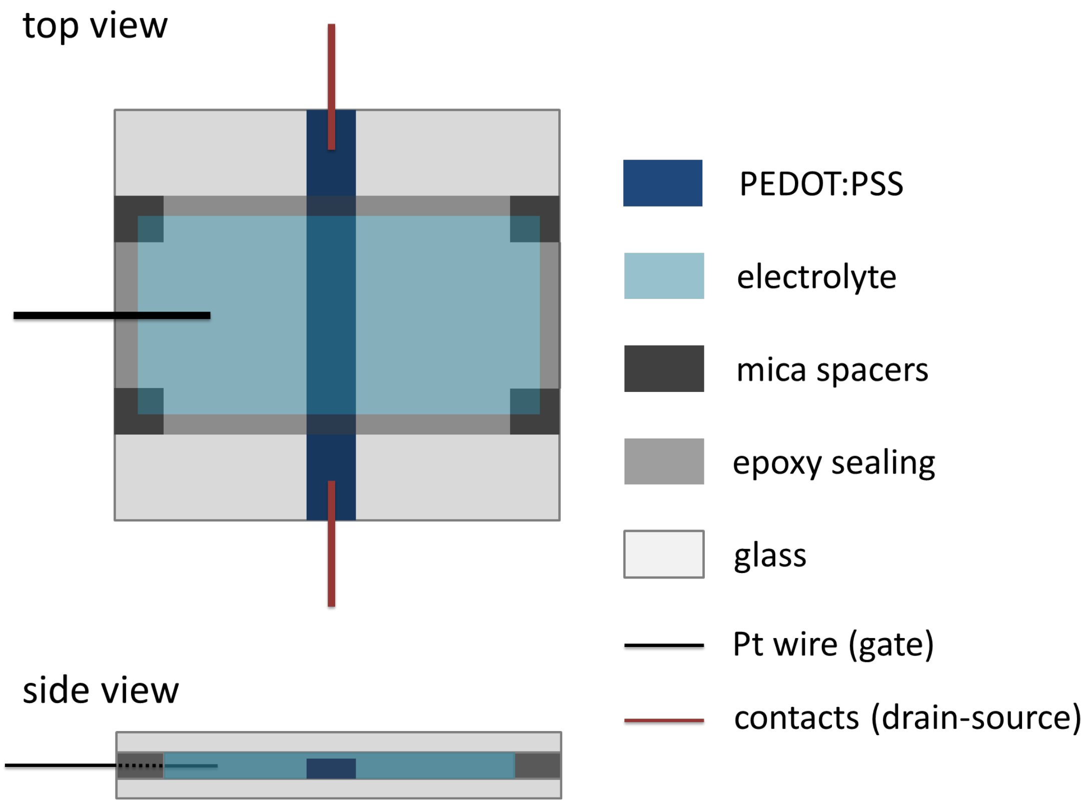

Figure S4. OECT device specifically fabricated to be placed within the location of the spectrophotometer cuvette.

Interaction between micelles and PEDOT:PSS

Figure S5 reports the proposed mechanism of interaction between CTA^+ micelles and PEDOT:PSS.

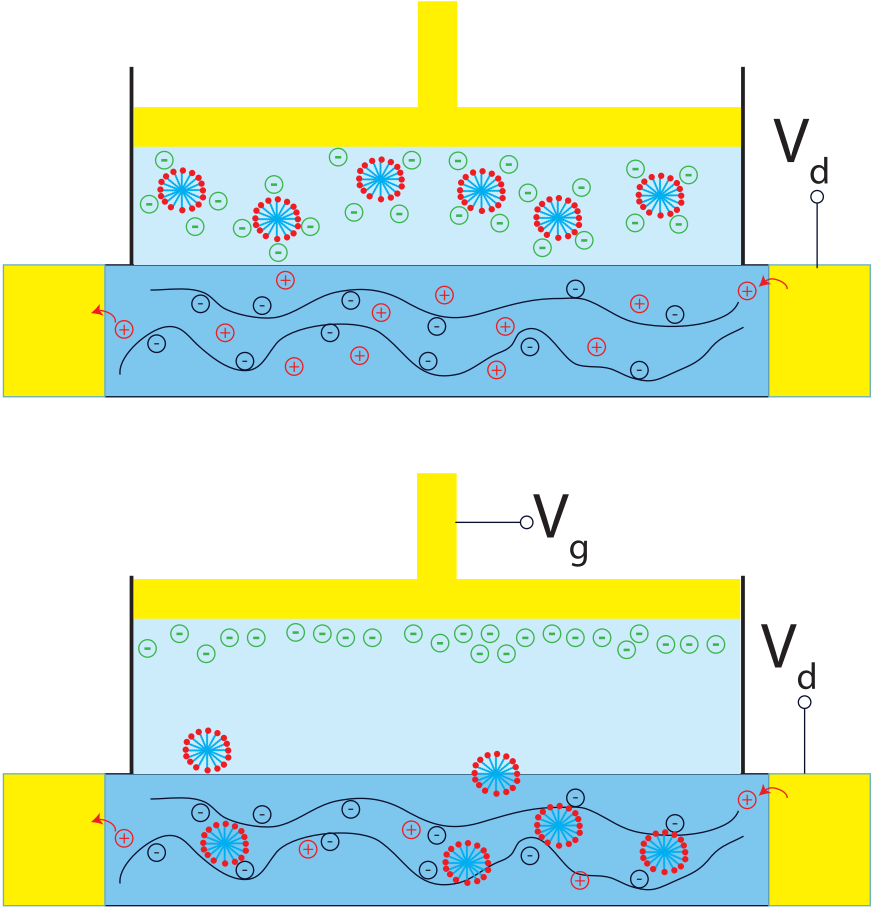

Figure S5: Tentative description of the interaction between CTA$^+$ micelles (sketched in Figure S1) and PEDOT:PSS in OECTs. Green circles filled with the sign – indicate negative ions (i.e. Br$^-$) in the electrolyte, black circles filled with the sign – indicate negative PSS$^-$ sites within the polymer, circles filled with sign + indicate mobile holes in the polymer. Being PEDOT:PSS a hole conductor, the application of a negative V_d bias generates a drain-source hole current. Upon application of a positive V_{gs}, the CTA+ micelles redistribute in solution. Part of the micelle ions enter the PEDOT:PSS channel and dedope it, thus decreasing the source-drain current. Due to their large size and high surface charge, we expect micelles to neutralize several PSS$^-$ sites per micelle entering the PEDOT:PSS bulk, while an 'individual' entering cation only neutralize a single PSS$^-$ site.

[1] DeFranco, J.A., Schmidt, B.S., Lipson, M., Malliaras, G.G. Photolithographic patterning of organic electronic materials. Organic Electronics **2006** 7, 22.

[2] Cicoira, F.; Sessolo, M.; Yaghmazadeh, O.; DeFranco, J. A.; Yang, S. Y.; Malliaras, G. G. *Adv. Mater.* **2010**, *22*, 1012.

[3] Tarabella, G.; Santato, C.; Yang, S. Y.; Iannotta, S.; Malliaras, G. G.; Cicoira, F. *Appl. Phys. Lett.* **2010**, *97,* 123304.