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In-situ Probing Electronic Dynamics at Organic Bulk Heterojunction/Aqueous Electrolyte Interfaces by Charge Modulation Spectroscopy

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1. Device fabrication:

A transparent quartz glass substrate was firstly ultrasonically immersed in acetone and isopropyl for 10 minutes to clean the organic impurity, and then soaked in a blend of H_2SO_4/H_2O_2 (1:1) for 5 minutes, and then modified by oxygen plasma surface treatment equipment for 5 min. The Au/Cr gate and source/drain electrodes were firstly patterned together by photolithography and on a transparent quartz glass substrate and deposited by evaporation in high vacuum of 10^{-5} mbar. The source/drain electrode was designed as an interdigital channel structure with channel width and length of 15 mm and 10 μm. The gap between the gate electrode and the source/drain electrode was ~1 mm to avoid the gate electrode from contacting with the OSC layer and ensure the aqE solution cover the source/drain channel and gate electrode. The surfaces of the electrodes were treated by 10 mM 1-octanethiol for 2 minutes in ambient air after the cleaning process to reduce the contact resistance and improve the surface morphology. And then, to construct aqEGOT and aqEGHT devices, a 40-nm-thick pOSC or OBHJ active layer was deposited on the substrate by spin-coating 5 mg/mL solution of electron donor P3HT (Sigma-Aldrich Co. LLC) or blend solution of P3HT and electron acceptor $PC_{71}BM$ (Sigma-Aldrich Co. LLC) (mass ratio 1:1) followed by annealing at 145 ^oC for 20 minutes in a glovebox. Finally, a 2-mm-thick poly(dimethylsiloxane) (PDMS, Sigma-Aldrich Co. LLC) square well with width and length of ~1 mm and ~3 mm was attached on the substrate to reserve 0.1 M NaCl aqE solution.

To carry out the CMS experiment, a semitransparent top-gate field-effect transistor with a polymer dielectric PMMA was constructed. The source-drain electrodes and active layer were defined in similar with those in aqEGOT and aqEGHT devices. Next, the A 630 nm-thick dielectric layer of PMMA spin-coated on the pOSC and OBHJ films and dried at 80 ^oC for 30 minutes. Finally, a semitransparent aluminum gate electrode was evaporated.

2. CIMS measurements:

In the CIMS experiment, the aqEGOT device is placed on a transparent floating holder. The source/drain electrodes were grounded and a variable gating voltage was applied by Keithley 2612B Sourcemeter. A wide-spectrum light emitted from a halogen lamp (Avantes AvaLight-HAL-S-MIN) was coupled to the interdigital part of the device through a fiber. Then, the transmission light through a beam splitter was collected by a UV-visible (Avantes AvaSpec-ULS 2048x64TEC) or a NIR (Ocean Optics NIRQuest256-2.5) fiber-optic spectrometer. In the TR-CIMS experiment, in case that the gating voltage is switched on, the spectra curves are immediately and automatically recorded at a time interval of one second.

3. Capacitance characteristics:

Capacitance characteristics of the samples are carried out by impedance spectroscopy with a Hewlett Packard 4284A LCR meter in a probe station. The source/drain electrodes were grounded and a gating voltage of a variable value and ac small signal 100 mV was applied onto the gate termination of the pOSC and OBHJ samples.

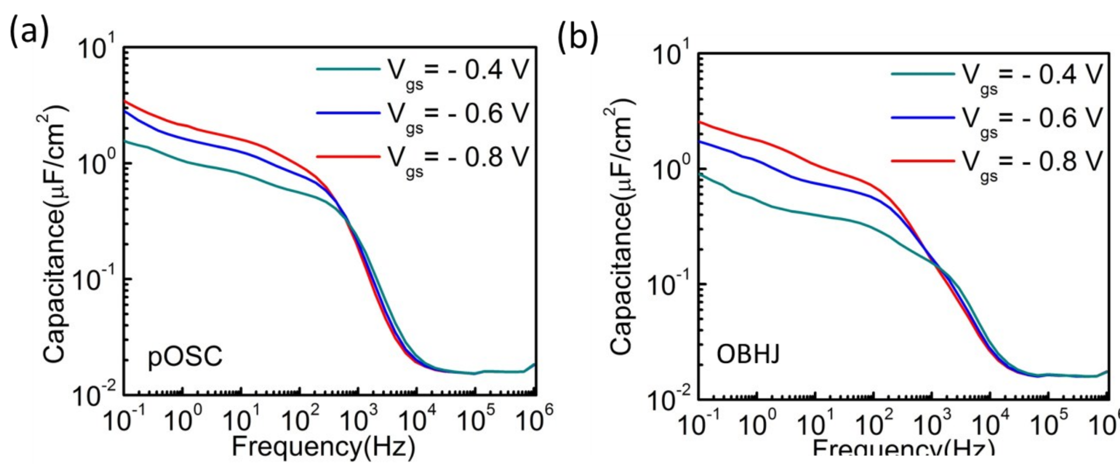

Fig. S1 The effective capacitance versus frequency of (a) aqEGOT and (b) aqEGHT samples at V_{gs}= -0.4V, -0.6V and -0.8V.

4. Transistor characteristics:

Both the aqEGOT and aqEGHT device were measured by Keithley 2612B sourcemeter in a probe station in air. The hole mobility was extracted from the following equation:

$$\mu_p = \frac{2L}{W \cdot C_i} \times \left(\frac{\partial \sqrt{|I_{ds}|}}{\partial V_{gs}}\right)^2 \quad (1)$$

Where L is the channel length (L=10 μm), W is the channel width (W=15 mm), C_i is the capacitance of the OSC/aqE interface which were obtained from the capacitance-frequency curves at f=10 Hz.

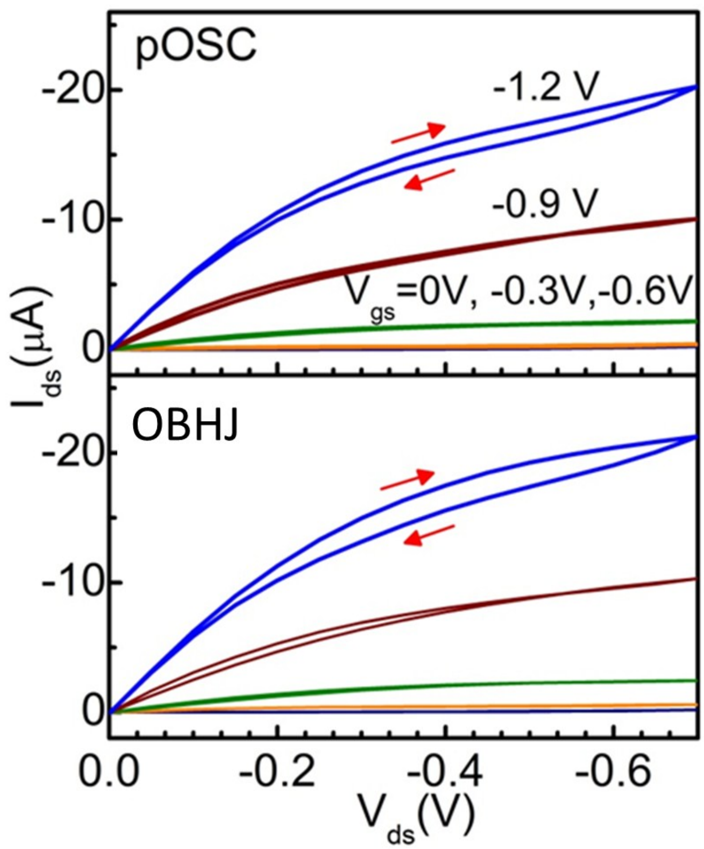

Fig. S2 Output characteristics of the aqEGOT and aqEGHT devices

5. Charge modulation spectroscopy (CMS):

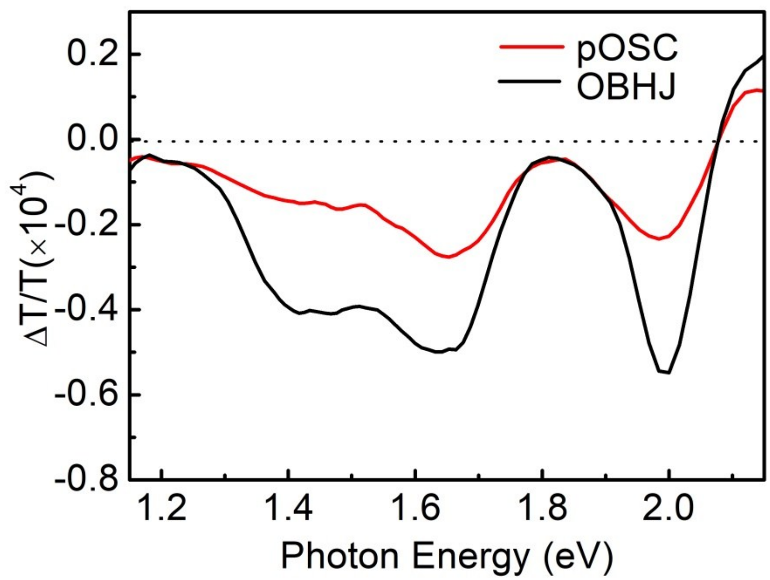

Fig S3. CMS spectra of pOSC and OBHJ FETs in the hole accumulation region (V_{gs} is set to -50V).

6. The aqEGOT sample based on pure P3HT with annealing temperature of 90 °C

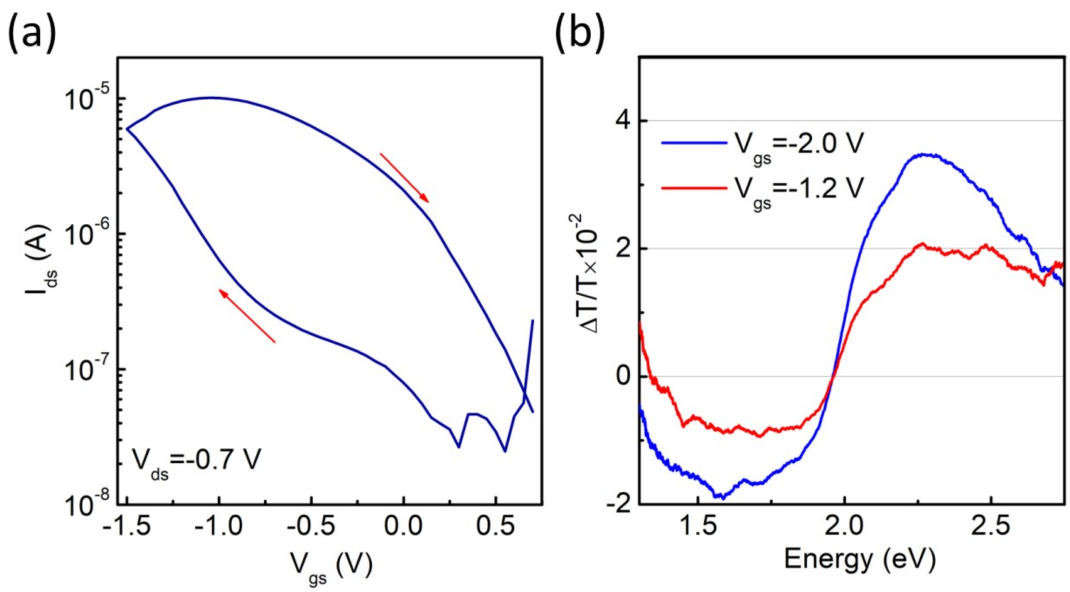

Fig S4. (a)Transfer characteristics and (b) CMS spectra of the aqEGOT based on pure P3HT with annealing temperature of 90 °C.