Supporting Information

Effect of Interfacial Dipoles on Charge Traps in Organic-Inorganic Hybrid Solar Cells

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1. Material synthesis

1.1. Polymer

General Considerations. All chemicals were purchased from Aldrich, Alfa Aesar, or Fisher, and were used as received. 2,5-dibromo-3-hexylthiophene¹ was prepared according to literature procedures. THF was distilled over Na/benzophenone ketyl prior to use. ¹H NMR spectra were recorded using a Varian 400 MHz spectrometer. Gel permeation chromatography (GPC) was performed using THF as the eluent on a Viscotek GPCmax Solvent/Sample Module, two fluorinated polystyrene columns (IMBHW-3078 and I-MBLMW-3078) thermostatted at 24 °C arranged in series, and a Viscotek VE 3580 Refractive Index Detector or a Viscotek 2600 Photodiode Array Detector (tuned at 460 nm). Molecular weight and polydispersity data are reported relative to polystyrene standards in THF. MALDI mass spectra were obtained on a 12T Varian ProMALDI FT-ICR system equipped with a Nd:YAG laser (355 nm) using 2,5-dihydroxybenzoic acid (DHB) as the matrix.

Synthesis of P3HT-COOH. Regioregular P3HT² and P3HT-COOH³ were synthesized according to previously reported procedures. For comparative purposes, the P3HT and P3HT-

COOH samples used for device fabrication originated from the same batch of P3HT. The obtained polymers were characterized by ¹H NMR, FT-IR, GPC, and MALDI and had the following characteristics:

P3HT: ¹H NMR (CDCl₃, 400 MHz): δ 6.97 (s, 1H), 2.79 (t, 2H), 1.69 (m, 2H), 1.41 (br, 2H), 1.33 (m, 4H), 0.90 (t, 3H). GPC: $M_n = 12.6$ kDa, $M_w/M_n = 1.3$. **P3HT-COOH**: ¹H NMR (CDCl₃, 400 MHz): δ 6.97 (s, 1H), 3.00 (t, α-CH₂ of end unit attached to COOH), 2.79 (t, 2H), 1.69 (m, 2H), 1.41 (br, 2H), 1.33 (m, 4H), 0.90 (t, 3H). GPC: $M_n = 12.0$ kDa, $M_w/M_n = 1.3$. FT-IR v_{C=0} (neat): 1663 cm⁻¹.

Figure S1. MALDI mass spectra of (A) P3HT (blue circles: H/Br terminated polymers; red squares: H/H terminated polymers), and (B) P3HT-COOH (red squares: H/H terminated polymers; green triangles: H/COOH terminated polymers).



Figure S2. FT-IR spectra of (A) P3HT and (B) P3HT-COOH.



Tetrabutyl titanate (TBT) $[Ti(OC_4H_9)_4]$ and 2,4-pentanedione raw materials used to synthesize the TiO₂ sol-gel were purchased from Alfa Aesar. A previously reported sol-gel method was adopted.⁴ 10 mL of TBT was dissolved in 100 mL of anhydrous ethanol under continuous stirring. After 30 min, 10 mL of glacial acetic acid (CH₃COOH) was added to stabilize the gel, followed by 10 mL of 2,4-pentanedione for promoting uniform particle size distribution. Finally, 10 mL of de-ionized water was added to hydrolyze the gel. The mixture was stirred vigorously at room temperature for 30 min before each solvent was added. The final sol was pale yellow in color and was aged for a week prior to use.

2. Fabrication of hybrid solar cell devices

Indium-doped tin oxide (ITO)-coated glass substrates of 10 Ω/\Box sheet resistance were purchased from Nanocs (New York, NY) and cut into 1 inch by 1 inch square pieces with a diamond pen. High purity (99.999%) gold (Au) wires used for thermal evaporation were purchased from Alfa Aesar. Tungsten wire baskets for thermal evaporation were purchased from Spi supplies. ITO-coated glass substrates were first patterned by taping with polyimide tape and then slow etching (15-20 min) in a mixture of 7.5 mL of de-ionized water, 0.8 mL of HNO₃, and 2.2 mL of HCl, at 60 °C. The substrates were then rinsed with copious amounts of de-ionized water and cleaned by successive sonication (10 min each) in aqueous detergent (alconox), de-ionized water, acetone, and isopropanol. The cleaned substrates were dried in flowing nitrogen. The aged TiO₂ sol-gel was then coated onto these cleaned substrates by spincoating at 3000 rpm for 20 s on a Chemat KW4A spincoater. In order to form the electron-transporting transparent thin film of anatase TiO₂, these spincoated substrates were sintered in an air furnace at 450 °C for 120 min and cooled slowly to room temperature. The sintered TiO₂ films were transparent with a thickness of around 100 nm, as measured by a Quanta 650 scanning electron microscope (SEM).

The sintered TiO₂-coated substrates were transferred into an argon-filled glovebox immediately after removing from the furnace. 6 mg of the polymer (P3HT or P3HT-COOH) were dissolved in 1 mL of chlorobenzene by stirring at 50 °C for 2 h inside the glovebox. The resulting solution was then filtered through 0.20 μ m pore size PTFE membrane syringe filter (Pall Life sciences). Hole transporting layers were obtained by coating the P3HT solution onto the TiO₂ coated substrates at a speed of 1500 rpm for 60 s. The polymer films were ~ 50 nm thick for both P3HT and P3HT-COOH, as confirmed by Dektak 3 surface profilometer and atomic force microscope (AFM) measurements. Thicker (~ 100 nm) polymer films were obtained by doubling the polymer concentration to 12 mg/mL. The polymer-TiO₂ composites were created by heating at a temperature of 185 °C for 8 min and cooling slowly overnight. The hybrid solar cell devices were completed by depositing a 2×3 matrix of 150 nm thick Au electrodes. The evaporation was carried out at vacuum levels better than 10⁻⁷ Torr and a deposition rate of 1-2 Å/s inside a JEOL thermal evaporator, using Au wires hung on W wire

baskets. The active area of the hybrid solar cells was 3 mm x 3 mm, as defined by a metal mask. Prior to testing the devices were annealed at 135 °C for 60 min and allowed to cool for several hours.

3. Characterization techniques

Solar cell current density-voltage (J-V) characteristics were measured inside an argon filled glovebox with a Keithley 2400 source measurement unit. No UV blocking filter was used. The hybrid solar cells were illuminated from the ITO side using an Oriel 91160 300 W solar simulator as the excitation source (100 mW/cm² white light illumination under AM 1.5G conditions). Photovoltaic parameters (open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF) that determine the overall power conversion efficiency of a solar cell) were measured for a total of 20 cells (5 cells on each substrate) and the values were found to be repeatable.

ID-FVS measurements were performed on a home-built apparatus based on an inverted microscope (Zeiss, Axiovert 200) with a 5X objective lens (NA 0.12). The excitation source was the 488-nm line of an Ar-Kr ion laser (Melles Griot, model 35 LAL-030-208). For the traces shown in the main text, the excitation beam was focused onto the device and the emission was detected by an avalanche photodiode (APD) (Perkin-Elmer Optoelectronics SPCM-AQR-15). A master function generator was used to synchronize both a function generator (Wavetek, model 29) and a multichannel scalar board (MCS, Becker Hickl PMS-400). The applied bias to the device was programmed to be a triangular waveform of 0-1-0- (-1)-0 V as one cycle and each cycle was set to be 1 s (4 V/s). Acquisition time per point was 0.01 s and 4000 points were recorded for each measurement. In these experiments, the excitation intensity was minimized (~800 mW/cm²) to mimic the power range of a solar simulator and the voltage bias rate was

adjusted to match the solar cell testing conditions. Fluorescence modulation results were acquired for 40 cycles and they were synchronously averaged to increase the signal-to-noise ratio. For the movie shown in Supporting Information, the excitation source was focused on a back aperture of the objective lens to achieve a wide-field fluorescence imaging scheme and the series of images were recorded by an EMCCD (Andor, model iXon+ DU-897E). The excitation intensity in the wide-field imaging scheme was ~10 mW/cm².

4. Supporting movie

A series of wide-field fluorecence images captured while a triangle bias of 0-1-0- (-1)-0 V was applied at 0.025 Hz. The length scale of images is 700 x 700 μ m, and the excitation power was ~10 mW/cm². The movie clearly shows fluorescent (bright green) regions in the polymer film, which get less brighter as the fluorescence get quenched on applied a positive bias. The fluorescence recovers when a negative bias is applied.

We use fluorescence intensity to probe charge transfer across the hybrid polymer/TiO₂ interface. Fluorescence intensity is maximum when there is no charge transfer and decreases as more charges are transferred to polymer. Therefore, the difference in fluorescence intensity before and after fluorescence quenching is an important measure of such charge transfer processes. To compare how much polymer films are quenched, we normalized the amount of quenching by dividing the difference between fluorescence signal intensities before and after the fluorescence quenching events by the fluorescence intensity before quenching. This is defined as "quenching depth".

5. Absorption spectra

UV-Vis absorption spectra were obtained on a Agilent, model 8453

Figure S3: Absorption spectra of sol-gel derived anatase TiO₂ film on ITO coated glass substrate



Figure S4: Absorption spectra of (a) P3HT and (b) P3HT-COOH film over TiO₂



6. SiO₂-Polymer hole injection device

To verify that the fluorescence quenching is not caused by hole injection from the gold electrode into the polymer, we made capacitor-type devices in which the TiO_2 layer was replaced by an insulating SiO_2 layer. Briefly, SiO_2 was deposited by inductively coupled plasma chemical vapor deposition (ICP-CVD) at 200 °C (Oxford Instruments, Plasmalab 80+) for a film thickness of 70 nm. The SiO_2 -Polymer device when tested behaved as an open circuit. On performing FVS on these devices, we observe almost no fluorescence quenching as seen in Figure S5.

Figure S5: Fluorescence intensity variation as a function of (a) time (b) voltage bias





In devices containing thicker P3HT films (~ 100 nm), the change in fluorescence intensity due to any kind of interfacial charge transfer is small (Figure S6). For instance, the fluorescence quenching depth is smaller for devices with thicker (~ 100 nm) films compared to those containing thinner (~ 50 nm) films, as indicated in Table 2 of main manuscript. This is because in thicker films the portion of the conjugated polymer that is far from the P3HT/TiO₂ interface (referred to here as "bulk" portion) and which does not participate in interfacial charge transfer can be significantly larger than the "interfacial" portion. Hence, the effect of interfacial

modifier on charge trapping can become more visible when the film thickness was minimized and the amount of bulk portion was decreased. Accordingly, as the thickness of the P3HT film increases, the bulk portion also increases, and the observed hysteresis becomes smaller. However, the exact role of the bulk portion in devices containing thicker P3HT films is not fully understood. For example, a large number of injected charges can diffuse into the bulk portion and may behave differently compared to the case when they are confined within interfacial regions. Although the performance of devices featuring thicker P3HT films were better than those of devices with thinner films, it is not possible to conclusively say that this improvement is because of the lack of hysteresis.



COOH



8. AFM images

AFM images were collected on the Asylum MFP-3D AFM/SPM

Figure S7: AFM images of (a) P3HT and (b) P3HT-COOH film over TiO₂



References

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