

Supporting Information For: High Performance Perovskite-Polymer Hybrid Solar Cells via Electronic Coupling with Fullerene Monolayers

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1. Materials and Methods

i. Solar Cell Assembly and Characterization

Fluorine doped tin oxide (FTO) coated glass sheets (7 Ω/\square Pilkington) were etched with zinc powder and HCl (2 M) to obtain the required electrode pattern. The sheets were then washed with soap (2% Hellmanex in water), de-ionized water, acetone, methanol and finally treated under oxygen plasma for 10 minutes to remove the last traces of organic residues. The compact layer solution was prepared by adding 369 μL of Titanium isopropoxide (99.99% Sigma-Aldrich) into 2.53 mL of ethanol. Separately, 35 μL of a 2M HCl solution were added into 2.53 mL of ethanol. The second solution was then added dropwise to the first one under stirring, and the mixture filtered with a PFTE hydrophobic 0.45 μm filter. The FTO sheets were subsequently

coated with a compact layer of TiO_2 (100 nm) by spincoating this mixture at 2000 rpm for 45 sec.

The standard Dyesol TiO_2 paste 18NR-T (~20 nm in diameter, 60 % porosity) was previously diluted down in a 1:1 paste:terpineol weight ratio, shaken overnight and ultrasonicated. The paste was then screen-printed to get a TiO_2 average thickness of 600 nm. The sheets were slowly heated to 500 °C (ramped over 1 ½ hours) and baked at this temperature for 30 minutes in air. After cooling, slides were cut down to size.

The C_{60} -substituted benzoic acid self-assembled monolayer (C_{60}SAM) material was synthesized as described elsewhere^{1, 2}. The soaking solution was prepared by dissolving C_{60}SAM (0.1mM) in a 1:1 volume ratio of THF:ethanol and passing the solution through a 0.2µm PTFE filter. The functionalization was achieved by immersing the TiO_2 substrates in the C_{60}SAM solution for 24 hrs, followed by rinsing with a THF:ethanol (1:1 by volume) mixture and drying for 10 min at 100 °C.

The perovskite precursor solution was synthesized and dissolved at 40 wt% in dimethylformamide (DMF) as described previously³. The solution was spun-cast at 2000 rpm for 45 sec in air, and the substrates were subsequently heated at 100 °C for 45 min in air to allow perovskite crystal formation. The polymeric hole transporters P3HT (Rieke Metals) or PCPDTBT (One-Material) were dissolved at 1.5 wt% in chlorobenzene and spun-cast at 2000 rpm for 45 sec. Spiro-OMeTAD was dissolved at 7 wt% in chlorobenzene with tert-butylpyridine (tBP, 55 mM) and lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI, 9mM) additives and spun-cast at 1000 rpm. Finally, the films were placed in a thermal evaporator where 150 nm thick silver electrodes were deposited through a shadow mask under high vacuum (10^{-6} mbar).

Current-voltage (J-V) characteristics were measured with a Keithley 2400 SourceMeter under AM 1.5 simulated sunlight (ABET Technologies Sun 2000 Solar Simulator) at an irradiance of $100 \text{ mW}\cdot\text{cm}^{-2}$ with the intensity set using an NREC-calibrated KG5-filtered Si reference cell. External quantum efficiency (EQE) measurements were acquired by applying chopped monochromatic light while biasing with white light-emitting diodes at an equivalent solar irradiance of $10 \text{ mW}\cdot\text{cm}^{-2}$. The active areas of the devices were defined by metal optical masks with a square aperture of 3 mm, giving an area of 0.09 cm^2 .

ii. **Optical Spectroscopy**

Spectroscopic measurements were carried out on samples identical to the photovoltaic devices but prepared on glass without FTO or metal electrodes. Steady-state absorption data were acquired using a Perkin-Elmer Lambda 1050 UV/Vis/NIR Spectrometer. Films for cw-photoinduced absorption (PIA) were placed under vacuum ($<10^{-5}$ mbar) and excited with an Ar-ion laser tuned to 496.5 nm (maximal intensity of $50 \text{ mW}/\text{cm}^2$) and chopped at 23 Hz. A continuous white light probe produced by a halogen bulb (~ 1 sun intensity) was passed through the sample and detected using a monochromator (Spectra Pro 2300i, Acton Research Corp.) coupled to diodes for detection in the visible (PDA10A, Thorlabs) and in the NIR (ID-441-C, Acton Research Corp.). Data were acquired using a lock-in amplifier (SR830, Stanford Research Systems) locked to the light modulation frequency and a NI USB-6008 (National Instruments) acquisition card. A customized Labview (National Instruments) program provided an automated interface to control hardware and record spectra.

Steady-state photoluminescence (PL) measurements were taken using an automated spectrofluorometer (Fluorolog, Horiba Jobin-Yvon), with a 450 W xenon lamp excitation source

and a photomultiplier tube (PMT) detector. All spectra were corrected for instrumental response using a calibration lamp of known emissivity.

Time-resolved PL measurements were acquired using a time-correlated single photon counting (TCSPC) setup (FluoTime 300, PicoQuant GmbH). Film samples were photoexcited using a 507nm laser head (LDH-P-C-510, PicoQuant GmbH) pulsed at 25MHz, with a pulse duration of 117ps and fluence of $\sim 0.1 \mu\text{J}/\text{cm}^2$. The PL was collected using a high resolution monochromator and hybrid photomultiplier detector assembly (PMA Hybrid 40, PicoQuant GmbH).

iii. Transient Photocurrent and Photovoltage Decay Technique

The photovoltage and photocurrent decay measurements were performed using a similar method to O'Regan et al.⁴ and Bisquert et al.⁵. A steady-state background white illumination from an array of diodes (Lumiled Model LXHL-NWE8 Whitestar) was first applied to the cell, generating a background charge that is proportional to the light intensity applied. A short pulse between 10-100 μs , generated from red light diodes (LXHLND98 Redstar, 200), was then applied. This enabled the charge recombination and transport rate constants to be obtained directly from the exponential decays measured with a 1GHz Agilent oscilloscope.

Measurements were performed at fixed potential conditions, i.e. potentiostatic mode in order to extract the generated charge (ΔQ) by the pulse, and at fixed current conditions, i.e. galvanostatic mode in order to extract the perturbation voltage (ΔV). The differential capacitance as a function of voltage for the system can then be directly measured as $C(V) = \Delta Q / \Delta V$.

iv. Conduction and valence bands

The conduction and valence band values presented in Figure 1(a) were determined as follows. P3HT and C60-SAM values were taken from the literature in conjunction with known optical band gaps^{6, 7}. As discussed in our previous work, there is some uncertainty in the C60-SAM energy levels⁶. The perovskite and TiO₂ valence bands, with respect to the Fermi levels, were computed from x-ray photo-electron spectroscopy (XPS) valence measurements, which will be presented elsewhere⁸. TiO₂ values, with respect to vacuum, were also taken from the literature⁶ and used to shift the perovskite values to those with respect to vacuum. Conduction bands were then calculated using optical band gaps.

2. Additional Data

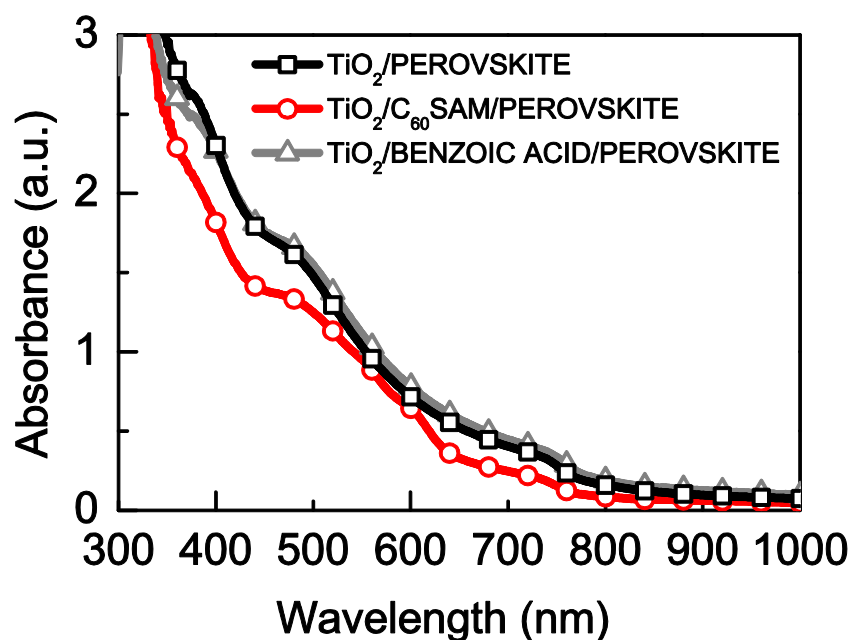


Figure S1. Absorption spectra of perovskite film on 600 nm thick mesoporous titania glass substrates with no interlayer, benzoic acid and C₆₀SAM fullerene functionalization.

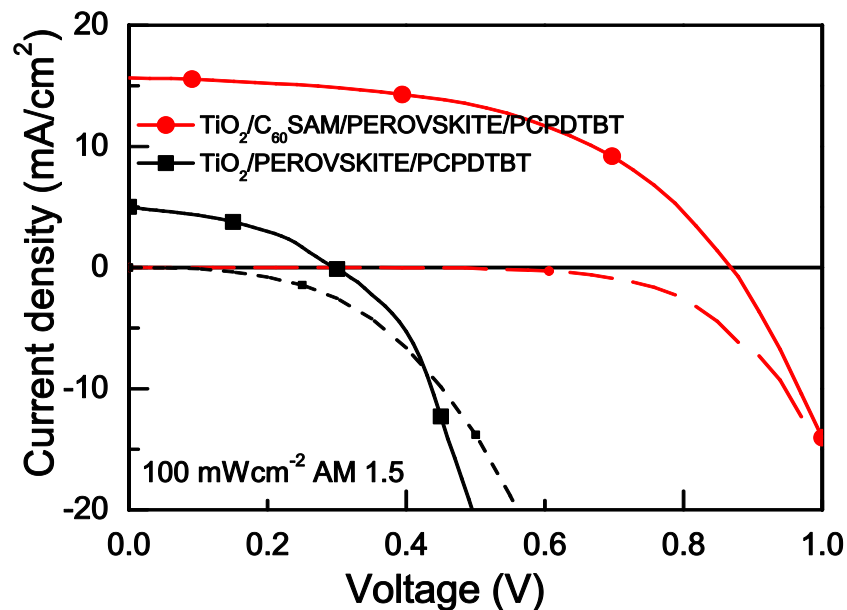


Figure S2. J-V characteristics taken under AM1.5 simulated sunlight ($100 \text{ mW}\cdot\text{cm}^{-2}$ irradiance) and in the dark for devices with and without C_{60}SAM fullerene functionalization with PCPDTBT as the hole transporter. Device parameters were $J_{\text{SC}} = 5.02 \text{ mA}\cdot\text{cm}^{-2}$, $V_{\text{OC}} = 0.3 \text{ V}$, $\text{FF} = 0.40$, $\eta = 0.58\%$ for $\text{TiO}_2/\text{Perovskite}/\text{PCPDTBT}$ devices, and $J_{\text{SC}} = 15.6 \text{ mA}\cdot\text{cm}^{-2}$, $V_{\text{OC}} = 0.88 \text{ V}$, $\text{FF} = 0.51$, $\eta = 6.84\%$ for $\text{TiO}_2/\text{C}_{60}\text{SAM}/\text{Perovskite}/\text{PCPDTBT}$ devices.

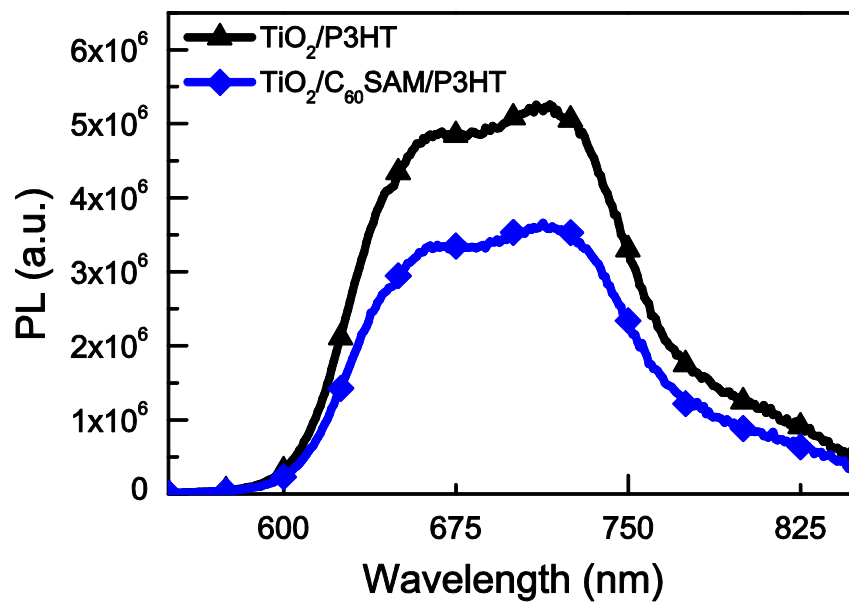


Figure S3. Photoluminescence spectra of P3HT films on 600 nm mesoporous titania glass substrates when photoexcited at 525nm, showing PL quenching due to C₆₀SAM fullerene functionalization.

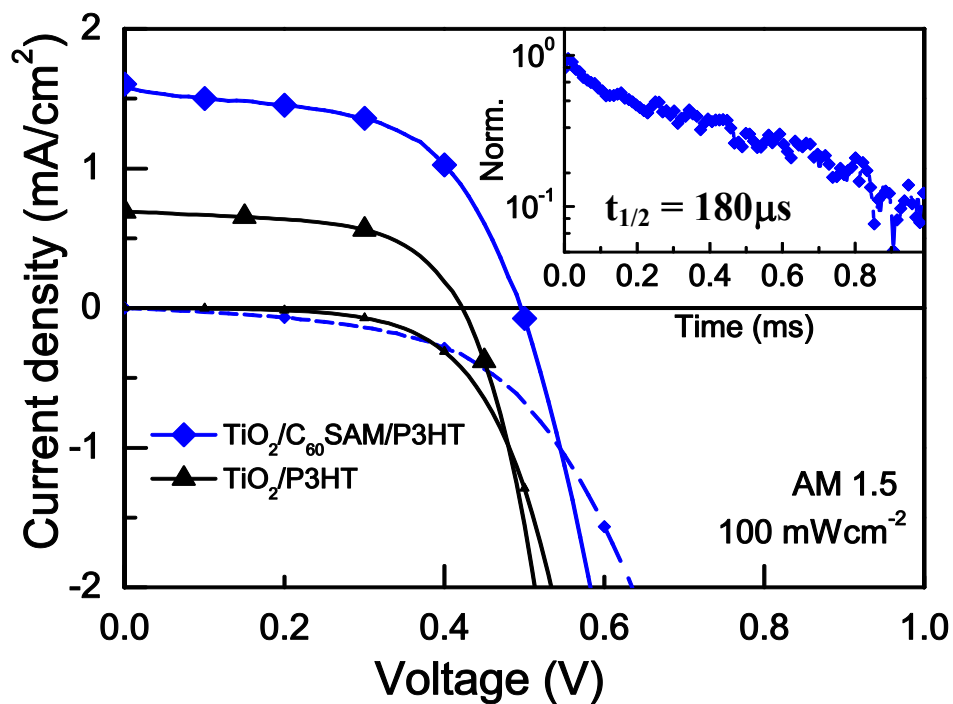


Figure S4. J-V characteristics taken under simulated AM1.5 100 mW·cm⁻² irradiance and in the dark for no-perovskite devices with and without C₆₀SAM fullerene functionalization. Device parameters were $J_{SC} = 0.69 \text{ mA}\cdot\text{cm}^{-2}$, $V_{OC} = 0.42 \text{ V}$, $FF = 0.58$, $\eta = 0.17\%$ for TiO₂/P3HT devices, and $J_{SC} = 1.6 \text{ mA}\cdot\text{cm}^{-2}$, $V_{OC} = 0.5 \text{ V}$, $FF = 0.55$, $\eta = 0.43\%$ for TiO₂/C₆₀SAM/P3HT devices. *Inset:* Transient photocurrent decay trace for a TiO₂/C₆₀SAM/P3HT device with $t_{1/2} = 180\mu\text{s}$, which is similar to that seen for “bare” TiO₂ devices⁹.

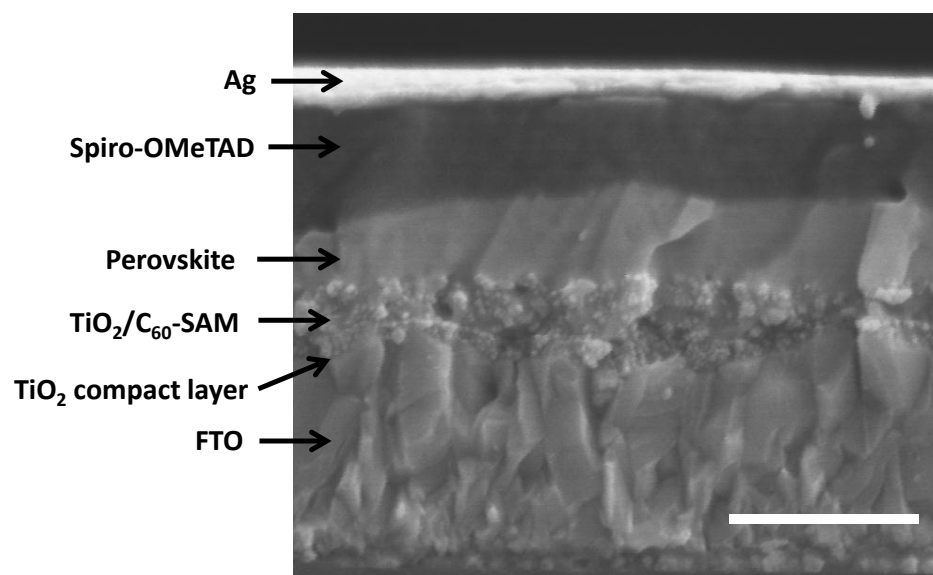


Figure S5. Cross-sectional scanning electron microscope (SEM) image of an optimized $\text{TiO}_2/\text{C}_{60}$ -SAM/Perovskite/Spiro solar cell acquired using an Hitachi S-4300. The white scale bar represents 500nm. The mesoporous TiO_2 layer and the perovskite capping layer are both ~200nm thick.

References

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