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Supporting information

Investigating charge dynamics in halide perovskite-sensitized mesostructured solar cells

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Material preparation

Methylamine (CH_3NH_2) solution 33 wt% in absolute ethanol was reacted with hydroiodic acid (HI) 57 wt % in water with excess methylamine under nitrogen atmosphere in ethanol at room temperature. Typical quantities were 24 mL methylamine, 10 mL hydroiodic acid and 100 mL ethanol. Crystallization of methylammonium iodide (CH_3NH_3I) was achieved using a rotary evaporator; a white colored powder was formed indicating successful crystallization. Methylammonium iodide (CH_3NH_3I) and lead (II) chloride ($PbCl_2$) was dissolved in anhydrous N,N-Dimethylformamide at a 3:1 molar ratio of CH_3NH_3I to $PbCl_2$, to produce a mixed halide perovskite precursor solution.

Device fabrication and characterization

FTO glasses (Pilkington, TEC15, 15 Ohm/sq) etched with metallic Zn and HCl 2M. They were washes with water and cleaned in an ultrasonic bath in acetone and isopropanol for 10 min each. Then they were immersed into a TL1 washing solution (H2O2/NH3/H2O 5:1:1, v/v) and heated to 80 °C for 10 min to remove organic contamination. To make a compact TiO2 blocking layer of ~60nm, the cleaned FTO glasses were coated with 0.15 M titanium diisopropoxide bis(acetylacetonate) (75% Aldrich) in 1-butanol (Aldrich) solution by the spin-coating (2000rpm), which was heated at 125 ^{o}C for 5 min. After the coated film was cooled down to the room temperature, the same process was repeated twice with 0.3 M titanium diisopropoxide bis(acetylacetonate) solution in 1-butanol. The coated FTO glasses with TiO2 precursor solutions were heated at 450 °C for 15 min. 0.4 µm thick mesoporous TiO2 layer was deposited by spincoating TiO_2 paste (Dyesol 18NR-T) diluted further in terpineol at 1:3 by weight at 2000 RPM. 0.9 µm thick mesoporous Al_2O_3 layer was deposited by doctor blading an Al_2O_3 paste prepared according to a procedure described elsewhere.[1] Briefly, Al_2O_3 dispersion 20 wt% in water was washed by centrifuging at 6000 rpm for 3 hours and redispersing in absolute ethanol.

The washing process was repeated for three cycles. Then 3.33 g of α-terpineol and 5 g of ethyl-cellulose (5^{-15} mPa*s) previously dissolved in ethanol (10% w/w) were added to 1 g of Al_2O_3 and stirred overnight at 50°C. Finally ethanol was removed by a rotary evaporator and the Al_2O_3 paste was further diluted in terpineol at 1:2 by weight. The layers were then sintered in air at 450 °C for 1 hour.

For the D149 device, TiO_2 electrodes were immersed into the D149 (Aldrich) solutions (0.5 mM in a mixture of acetonitrile and tert-butyl alcohol (v/v, 1:1)) containing chenodeoxy cholic acid Aldrich) 1.0 mM, and kept at room temperature for 4 h.

For the **PERO** device, 20 wt% perovskite precursor solution was infiltrated into the mesoporous electrode film by spin-coating at 2000 RPM for 30 seconds in N2 atmosphere. The coated films were then placed on a hot plate set at 100 °C for 45 minutes. A chlorobenzene solution containing 131 mM Spiro-OMeTAD, 216 mM tert-butylpyridine and 58 mM lithium bis(trifluoromethylsyfonyl)imide salt was cast onto the perovskite coated substrate and spun at a rate of 2500 RPM for 45 seconds. Cells were completed by thermal evaporation of 150 nm Ag electrodes. The active area was comprised between 0.05 and 0.07 cm^2 for all the devices, which were characterized under Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 100 $mW \cdot cm^{-2}$. The IV curves and the PV parameters discussed for both **D149** and **PERO** correspond to the best of the fabricated devices, also used for the spectroscopic characterization. The efficiencies for the series of fabricated devices ranged from 2.5 to 3.2% for **D149** and from 3.5 to 7.9% for **PERO**. Absorption spectra were measured by means of a Varian Cary 5000 UV/Vis NIR spectrophotometer.

Samples for PIA spectroscopy were fabricated with identical device configuration. The **D149**/perovskite layer was covered with an insulating poly(methyl methacrylate) (PMMA, MW 120000, Aldrich) film, spin-coated from a 30 mg/mL solution in chloroform at 2000 rpm (400 nm average thickness).

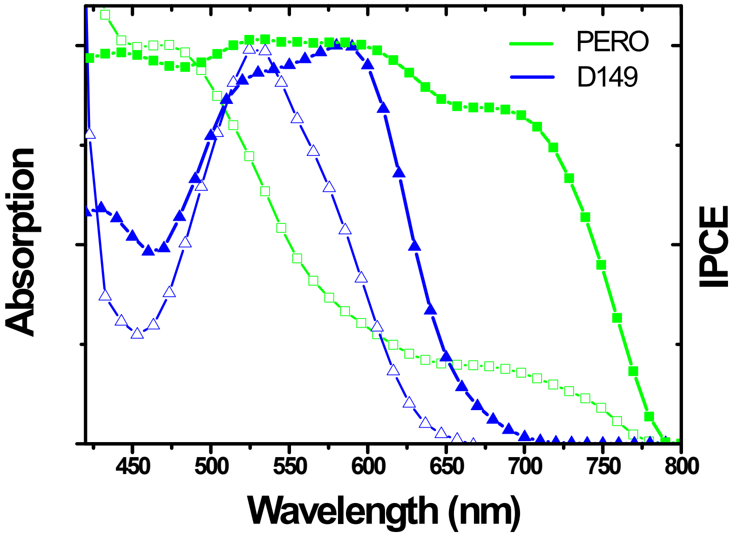

Figure S1: Normalized Absorption (open symbols) and Incident Photon to Current Efficiency (IPCE) (full symbols) for devices based on **PERO** and **D149** organic dye, realized as described above.

Photo induced absorption spectroscopy

Photo-induced absorption (PIA) spectra were recorded using a white probe light generated by a 250 W tungsten-halogen lamp which was superimposed to a square-wave modulated laser (spectra physics, 50 mW nominal power, λ = 488 nm) used for excitation. The white probe light passed through a first monochromator (Princeton Acton Spectra Pro) before being focused on the sample in a spot of 0,5 cm^2. The light transmitted through the sample was focused onto a second monochromator and, for the visible spectra (600-1100 nm), detected by a silicon photodiode connected to a current amplifier (femto DLPCA200) and lock-in amplifier (Stanford Research System model SR 830). For the IR region (1000-1600 nm) a PbS photodiode was coupled and connected to the same lock-in, without further amplification. An intensity of approximately 15 mW/cm^2 and a modulation frequency of 230 Hz were used for the excitation laser.

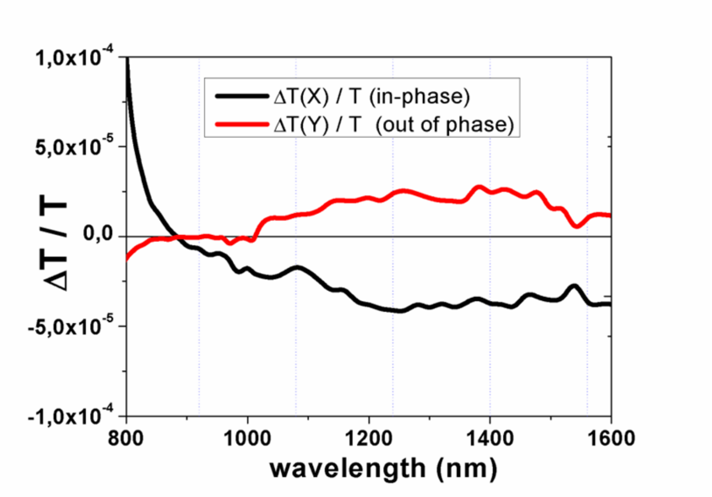

Figure S2: Photoinduced absorption spectra (PIA) for TiO_2 thin film sensitized with **PERO** covered with a film of PMMA. The two curves correspond to the in-phase (black) and out-of-phase (red) signal provided by the lock-in amplifier.

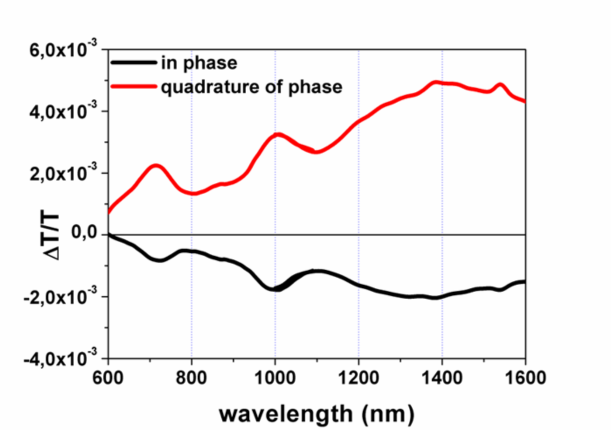

Figure S3: Photoinduced absorption spectra (PIA) for TiO_2 thin film sensitized with **PERO** covered with a film of spiro-OMeTAD. The two curves correspond to the in-phase (black) and out-of-phase (black) signal provided by the lock-in amplifier.

Transient Voltage/Current

Photocurrent and photovoltage transients were taken using a pump pulse generated by a ns tunable laser at a rate of 1 Hz (InnoLas OPO, 6 ns pulse FWHM). Excitation was provided at the absorption peak of each sample (i.e 700 nm for perovskite and 540 nm for **D149** solar cells). The pulse intensity was controlled to keep the variation of Voc due to the pulse below 10 mV.

To simulate the 1 sun working condition, illumination was provided by 9 white LEDs (Luxeon Star) whose intensity was tuned under computer control. The cells were connected to a data acquisition (DAQ) card that allowed measurement of the steady state and the transient voltage/current, and the selection of open- or short circuit condition. Voltages at open circuit and currents at short circuit were measured over a Giga Ω and 2 Ω resistor respectively.

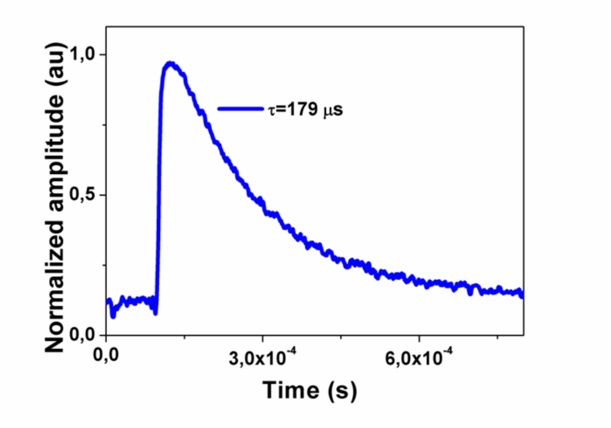

Figure S4: Transient photocurrent measurement for **PERO**-sensitized device with 1 sun bias illumination. Carrier lifetime in the inset is obtained fitting the curve with single exponential.

Time correlated single photon counting

Time resolved photoluminescence measurements were performed using time-correlated single-photon counting (TCSPC) apparatus of Hamamatsu FL980, 100 ps time resolution with deconvolution analysis.

1. M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, *Science (New York, N.Y.)*, 2012, **338**, 643–647.