

Supporting Information

Charge Transfer Dynamics from Organometal Halide Perovskite to Polymeric Hole Transport Materials in Hybrid Solar Cells

Jan C. Brauer¹, Yong Hui Lee,² Mohammad Khaja Nazeeruddin,² Natalie Banerji^{1}*

¹Departement of Chemsitry, University of Fribourg, Chemin du Musée 9, CH-1700
Fribourg, Switzerland

²Group for Molecular Engineering of Functional Materials, Institute of Chemical
Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015
Lausanne, Switzerland

AUTHOR INFORMATION

Corresponding Author

Departement of Chemsitry, University of Fribourg, Chemin du Musée 9, CH-1700
Fribourg, Switzerland

Sample Preparation. The 200 nm-thick mesoporous-TiO₂ layer was formed on cleaned FTO glass substrates (Pilkington, TEC 15) by spin-coating a commercially available TiO₂ paste (Dyesol 30NRD). The substrates were baked at 500°C for 30 min, and cooled down to room temperature before the deposition of the perovskite layer by the two-step deposition method. For the deposition of the perovskite layer, 0.6 M PbI₂ solution in DMF was spin-coated on the substrate at 6,500 rpm for 20 sec. The film was dried at 90°C for 15 min, cooled down to room temperature, and dipped in methylammonium iodide (MAI) solution (8 mg of MAI in 1 mL of IPA) for 15 sec, rinsed with IPA and dried at 70°C for 5 min again. For the deposition of HTMs, PTAA (Emindex), P3HT (Merck) or PCPDTBT (1-Material) solution was spin-coated on the perovskite films at 3,000 rpm for 30 sec. Polymeric HTM solutions were prepared by dissolving 15 mg of HTMs in 1 mL of chlorobenzene. For the thicker P3HT layer, 30 mg of P3HT was dissolved in 1 mL of chlorobenzene and spin-coated at 2,000 rpm for 1 min. All the preparative work to deposit PbI₂, perovskite and HTMs was done inside the drybox to minimize the influence of moisture.

Transient Absorption Spectroscopy. Transient absorption spectra were recorded using femtosecond pulsed pump-probe spectroscopy. The samples were placed into a sealed chamber under nitrogen to prevent degradation by oxygen and humidity. The probe beam consisted of a white light continuum (400-1000 nm), generated by passing part of the 800 nm amplified 1 kHz Ti:sapphire output (Clark-MXR, CPA-2001 or Coherent, Astrella) through a moving 5 mm CaF₂ plate or 5 mm sapphire plate. The remaining intensity of the fundamental was removed by a 750 nm low pass filter or a 850 nm high pass filter (visible and nIR parts of the spectrum were recorded separately). Excitation pump pulses at 400 nm were generated by frequency doubling

the fundamental of the laser. Excitation pulses at 580 nm or 600 nm were generated in a custom-built NOPA (Clark-MXR) or OPA (OperaSolo, Coherent). The probe intensity was always less than the pump intensity, and the probe spot size was chosen to be much smaller than the pump spot size to allow for a homogeneous excitation over the probed area. The pump/probe pulses were delayed with respect to each other using a computerized translation stage.

The probe pulses were split before the sample by means of a beamsplitter into a signal (transmitted through the sample and crossed with the pump) and a reference beam. The probe signal and reference beams were then detected separately using a pair of spectrographs (SpectraPro 2500i, Princeton Instruments, or home-built prism spectrometers), equipped with 512 x 58 pixel back-thinned CCDs (Hamamatsu S07030-0906) and assembled by Entwicklungsbüro Stresing, Berlin. The pump beam was chopped at half the amplifier frequency to improve the sensitivity of the set-up. The transmitted intensity of the probe beam was recorded shot by shot and corrected for laser intensity fluctuations using the reference beam. The transient spectra were averaged at each delay until the desired signal-to-noise ratio was achieved. To avoid polarization effects, the relative polarization of the probe and pump pulses was set to magic angle. All spectra were corrected for the chirp of the white-light probe.

Multi-exponential global analysis. Multi-exponential global analysis serves to simultaneously analyze the set of dynamics recorded during a white light transient absorption spectroscopy experiment. Dynamics corresponding to many different probe wavelengths were obtained by taking cross sections through the chirp-corrected TA spectra recorded at about 350 different time delays in the -1 ps to 2 ns range. The interpretation of such dynamics is not trivial, given the complexity of processes

occurring in the samples. First, there are often overlapping broad spectral signatures, making assignment of the dynamics at a particular probe wavelength to a unique species or process difficult. Then, the time evolution of the TA signals can be influenced by multiple processes, for example the pure charge transfer dynamics might be entangled with spectral shifts due to relaxation. For all the above reasons, the analysis of a single-wavelength TA dynamics is typically not very meaningful. Therefore, we have opted for global analysis, i.e. for simultaneous analysis of the TA dynamics taken every 5 nm throughout the spectrum. Apart from being more robust to noise-related artifacts encountered at a single wavelength, this method allows for correlating the evolution of different signatures in the TA spectrum, greatly facilitating the interpretation.

Given the complexity of the TA dynamics, it is challenging to devise a kinetic model that accurately and comprehensively describes all the dynamics. Therefore, we have performed data analysis without imposing any specific model to the results, but instead by globally fitting a convolution of a Gaussian and a sum of exponential functions to the dynamics. There is not always a direct physical meaning to using such exponential functions. We also note that a Gaussian distribution of time constants for highly multiphasic processes can crystallize into only a few average exponential time constants. Nevertheless, the multi-exponential analysis allows an excellent overview of the data and allows estimating the time scale on which processes are occurring. Most useful are also the pre-exponential factors associated with the exponential time constants and obtained at different wavelengths throughout the TA spectrum. The sign of the pre-exponential factor indicates whether the process associated with the time constant leads to a rise or a decay of the TA signal at a given probe wavelength. By plotting the pre-exponential factors as a function of probe

wavelength (yielding decay associated amplitude spectra), concerted changes in different parts of the transient spectrum can be identified at one glimpse. This global appreciation of the evolution of several bands consolidates the assignment of the observed dynamics to physical processes.

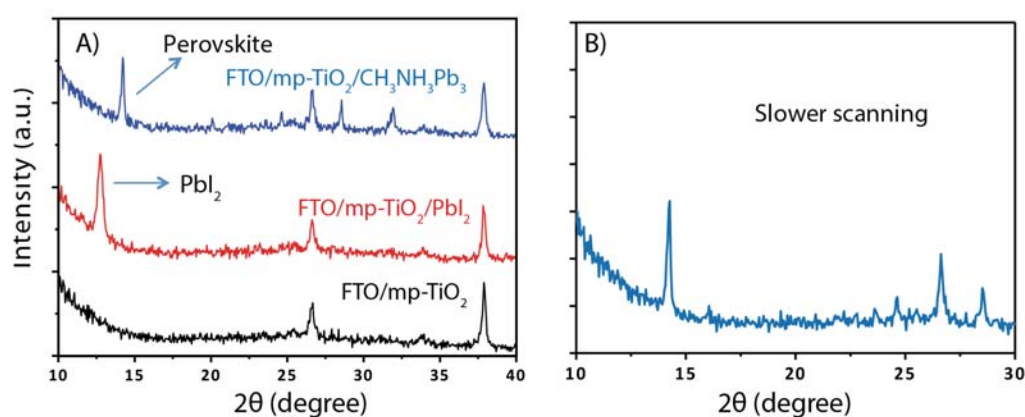


Figure S1 A) XRD spectra of films of FTO/mp-TiO₂ (black), FTO/mp-TiO₂/PbI₂ (red) and FTO/mp-TiO₂/CH₃NH₃PbI₃ (blue). B) XRD spectrum of FTO/mp-TiO₂/perovskite recorded at lower scan rate. Within the sensitivity of the experiment, we find complete conversion, and no PbI₂ is detectable in the final sample.

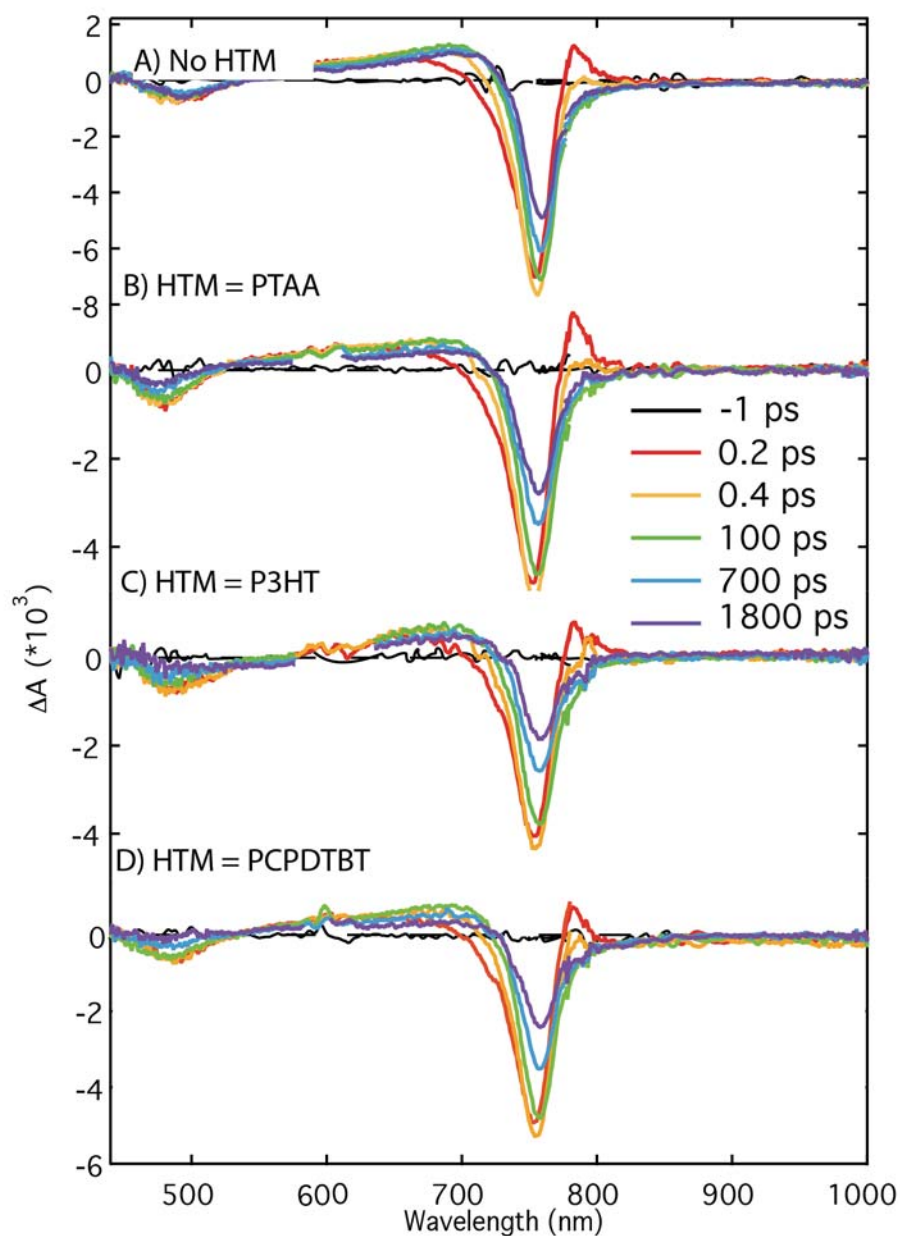


Figure S2 Transient absorption spectra following 600 nm excitation of A) $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$, B) $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PTAA}$, C) $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{P3HT}$ and D) $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCPDTBT}$. The HTM thickness was always 5-10 nm. Sometimes, the region around 600 nm was removed due to scattering by the pump excitation.

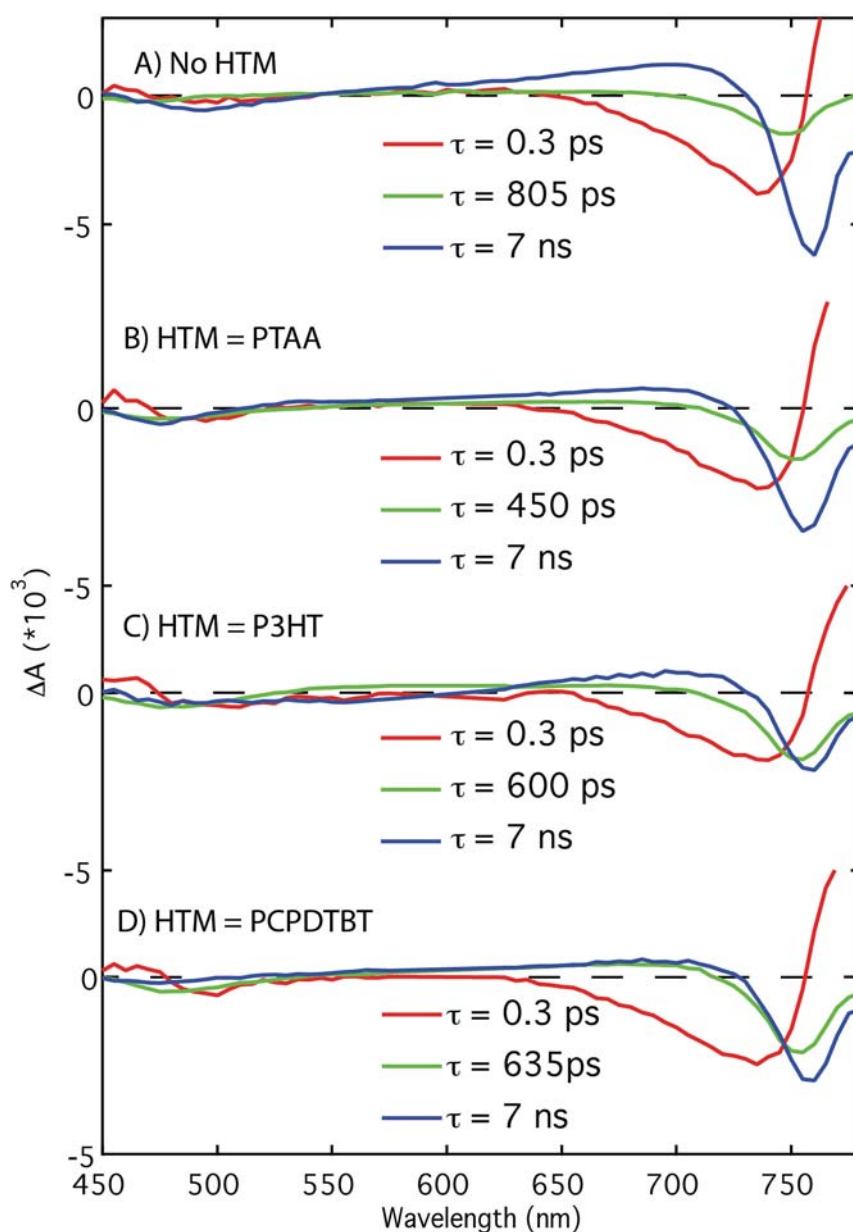


Figure S3 Amplitude spectra associated with the time constants shown in the legend, obtained by multi-exponential global analysis of the transient absorption data of A) $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$, B) $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PTAA}$, C) $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{P3HT}$ and D) $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCPDTBT}$ following excitation at 600 nm.

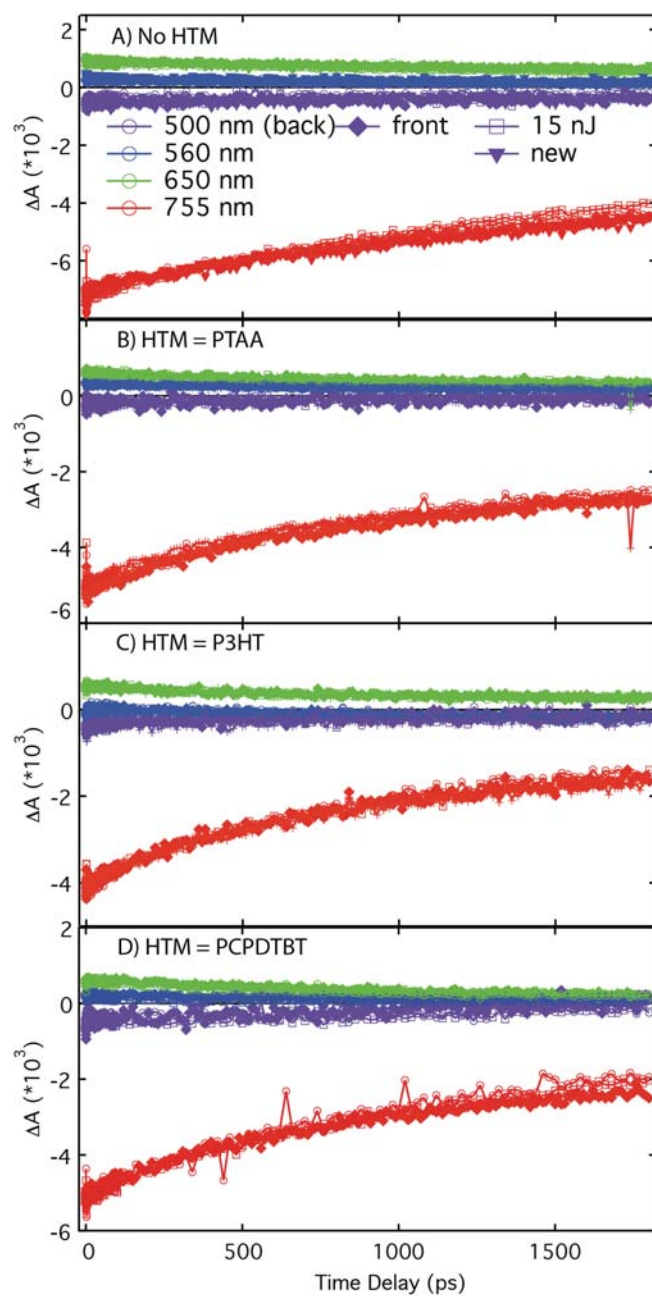


Figure S4 TAS time profiles at various probe wavelengths for the different $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{HTM}$ samples (5-10 nm HTM thickness), following 600 nm excitation. Practically identical overlaid dynamics were obtained upon irradiating from the front or backside, when using a new sample prepared in similar conditions, and when slightly increasing the excitation intensity from 10 nJ to 15 nJ (scaled) with a spot size of 0.9 mm.

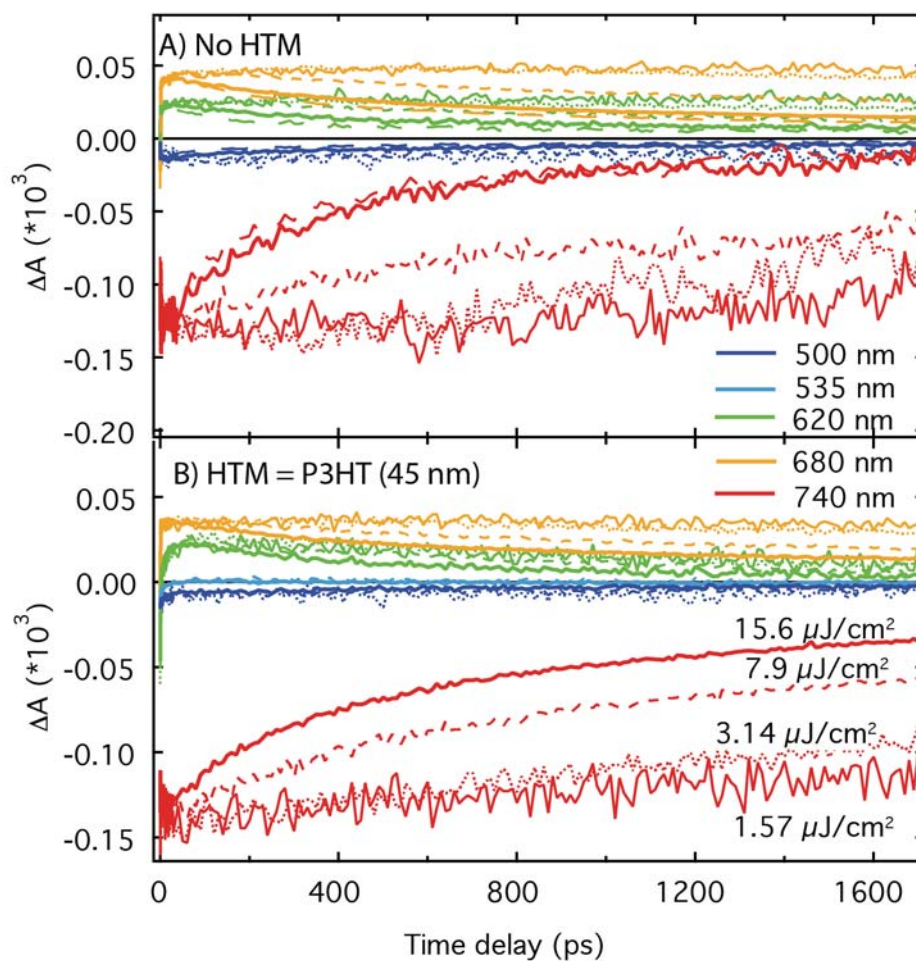


Figure S5 Strong fluence dependence of the TAS time profiles at various probe wavelengths for $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{P3HT}$ (45 nm), following 580 nm excitation. At the used pump intensity of $3.14 \mu\text{J}/\text{cm}^2$, fluence effects were negligible, since the dynamics were almost identical to the ones recorded at $1.57 \mu\text{J}/\text{cm}^2$.

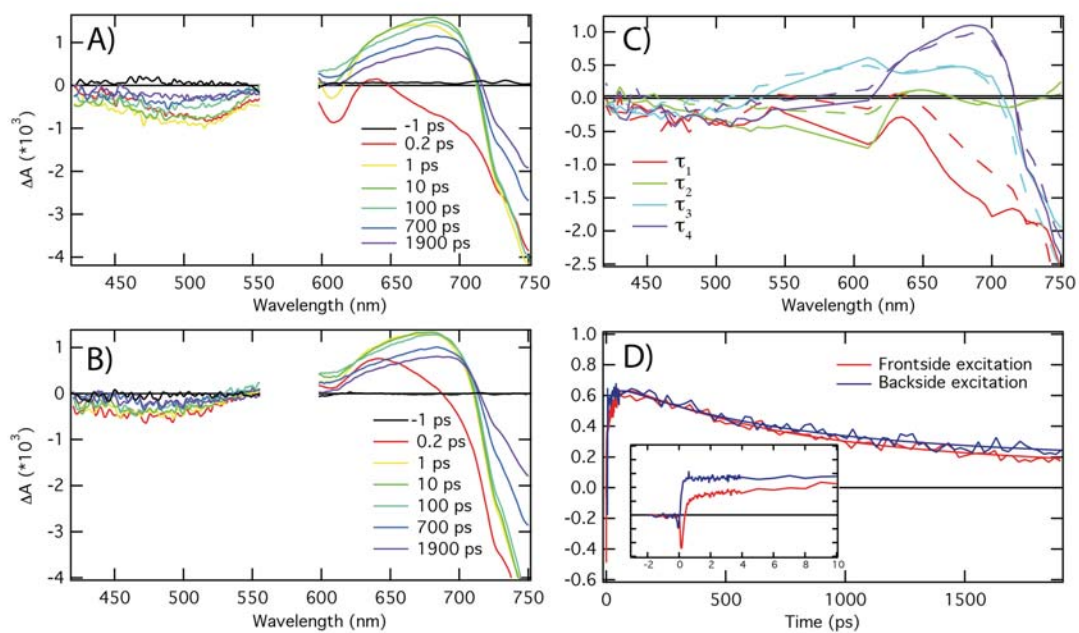


Figure S6 A) transient spectra of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{P3HT}$ following 580 nm frontside excitation, B) corresponding spectra following backside excitation, C) decay associated spectra corresponding to A) and B) (dashed lines) D) transient dynamics following 580 nm excitation at 620 nm. Inset shows a zoom at early times. The initial GSB of P3HT is more pronounced with frontside excitation. The fact that the amplitude 80 ps after excitation is similar for both excitation directions supports the proposed energy-transfer from photo-excited P3HT to the perovskite.

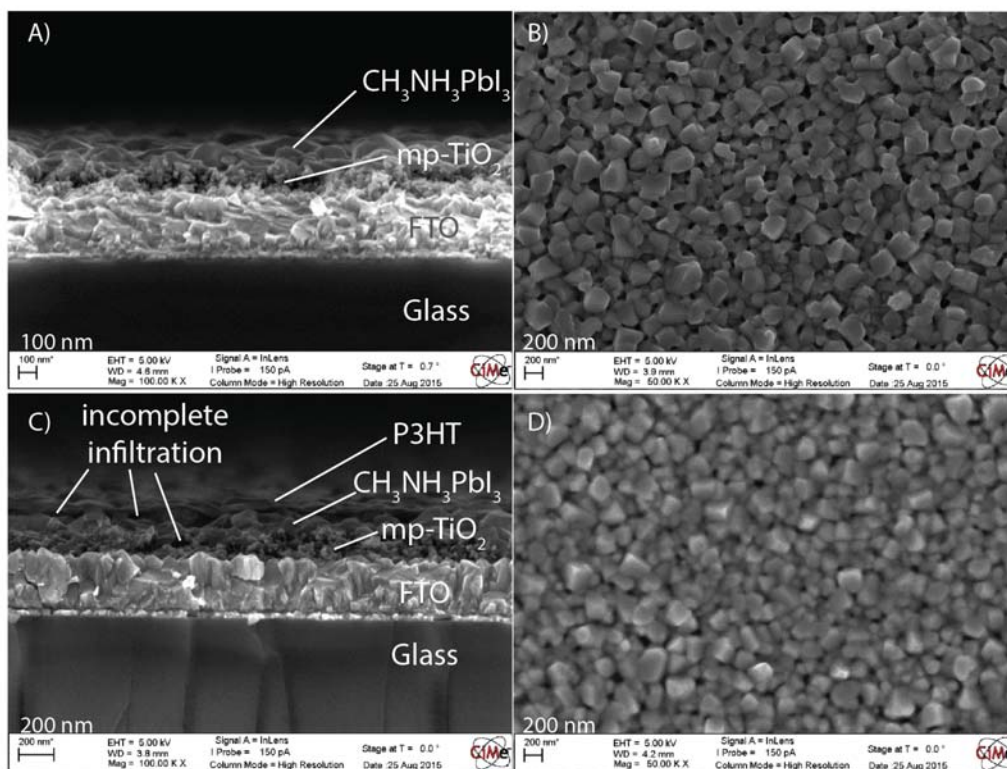


Figure S7 SEM pictures of A,B) FTO/mp-TiO₂/CH₃NH₃PbI₃ and C,D) FTO/TiO₂/CH₃NH₃PbI₃/P3HT. It is visible on picture C) that P3HT does not completely infiltrate the pores.