Supporting Information

Mechanism of Charge Transfer and Recombination Dynamics in Organo Metal Halide Perovskites and Organic Electrodes, PCBM and Spiro-OMeTAD: Role of Dark Carriers

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EXPERIMENTAL SECTION

Sample preparation

The perovskite precursor solution was obtained by dissolving 0.395 g of CH_3NH_3I (MAI) and 1.157 g PbI_2 in 2 mL γ-butyrolactone, followed by heating to 60°C. Thin polycrystalline films of $MAPbI_3$ were prepared by spin-coating the precursor solution (30 s, 2000 rpm) at plasma-cleaned quartz substrates in a nitrogen-filled glovebox and annealing (1h, 100 °C). Bilayer samples were made by spin coating PCBMC60 (2 wt% in chlorobenzene, 30 s, 1000 rpm) or Spiro-OMeTAD (0.17 M in chlorobenzene, 30 s, 4000 rpm) on top of $MAPbI_3$. All samples have not been exposed to ambient conditions at any time before and during the electrical measurements.

Time-Resolved Microwave Conductivity Measurements

The Time-Resolved Microwave Conductivity (TRMC) set-up was used to determine the time-resolved change in photo-conductance $\Delta G(t)$ in the $MAPbI_3$ and bilayer films upon photo-excitation (λ = 600 nm). In the bilayer configuration, the perovskites were excited through the organic layer, which does not absorb at 600 nm. Each sample was placed inside a resonance cavity and continuously exposed to microwaves (8-9 GHz) during pulsed photo-excitation (10 Hz). The change in microwave power $\Delta P(t)$ is related to $\Delta G(t)$ by a sensitivity factor k:

$$\frac{\Delta P(t)}{P} = -K\Delta G(t)$$

ΔG_{max} is proportional to the product of yield φ and mobility $(\mu_e + \mu_h)$ by:

$$\varphi\sum\mu = \frac{\Delta G_{max}}{I_0 \beta e F_A}$$

Where I_0 is the number of photons per unit area per pulse, β is the ratio of the inner dimensions of the microwave cell, e the elementary charge and F_A the fraction of light absorbed by the sample at the excitation wavelength (600 nm).

Long Time Scale Time Resolved THz Spectroscopy set-up

The terahertz measurements at long time scales (up to 7 ns) were done using chirped pulse amplification (CPA) setup. The output (30 fs, 470 mW at 86 MHz) centered at 800 nm of a Ti:sapphire oscillator (TISSA 50, CDP Systems) pumped by a 5 W diode laser (Verdi 5, Coherent) is directed to a regenerative amplifier (Legend-USP, Coherent). The amplified fundamental beam centered at 800 nm (50 fs, 1W, 1 kHz) is split into three parts. The first one (~700 mW) is directed through an optical parametric amplifier (OPA) for wavelength conversion and the output from OPA is frequency-doubled in 1 mm BBO crystal to give 590 nm. The resulting beam is sent through a long delay line (H2W Technologies) to give a range of 7 ns and is used to photoexcite the sample in the time-resolved terahertz (THz) experiment. The second part of the fundamental beam (~200 mW) generates the THz probe in a ZnTe crystal by optical rectification. The third part (~1 mW) is used for electro-optic detection of THz in another ZnTe crystal. During the measurements the set up is continuously purge to with dry nitrogen to avoid absorption of THz radiation by water vapor.

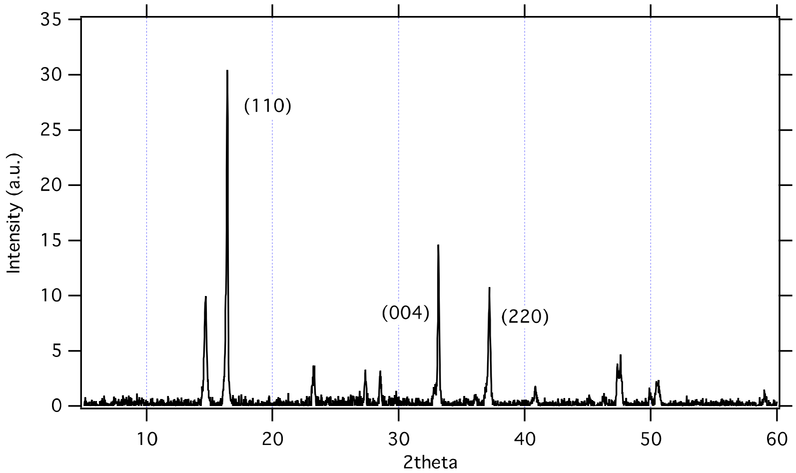

Figure S1: XRD pattern of the neat $MAPbI_3$ layer. Indicated peaks at 16°, 33° and 37° correspond to the major peaks of the tetragonal perovskite structure. Traces of lead iodide are visible at 14° (Ref. 18).

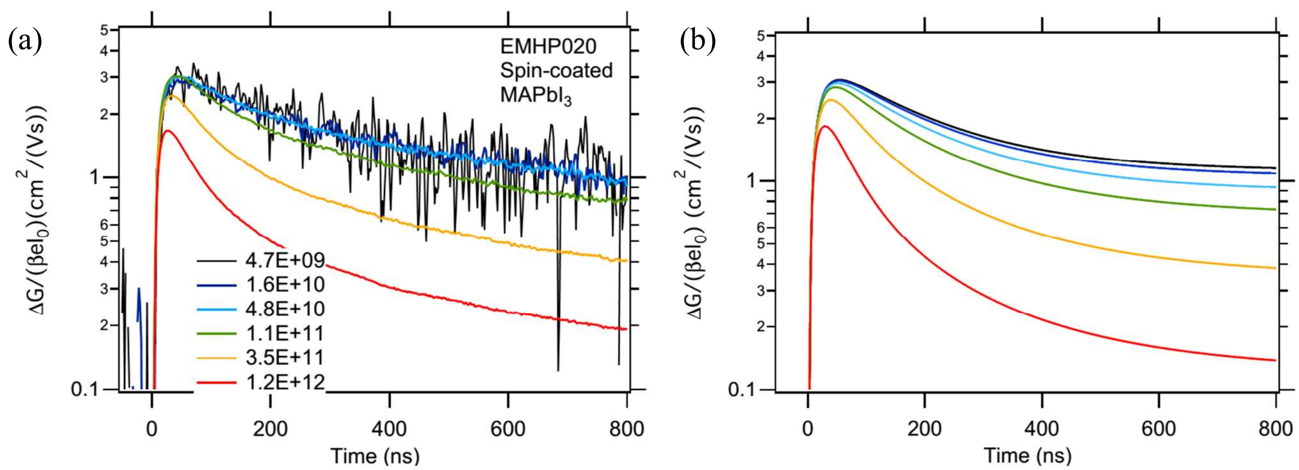

Figure S2: (a) TRMC traces for $MAPbI_3$ at indicated intensities expressed in ph/cm^2 per pulse (λ_{pump} = 600 nm). (b) TRMC traces using the model described below.

Kinetic Model

The following set of coupled differential equations was used to model the concentrations of electrons in the conduction band (n_e), holes in the valence band (n_h) and trapped electrons (N_T) as function of time after photoexcitation of the perovskite single crystal. For a full description of this kinetic model, see Ref. [1].

$$\frac{dn_e}{dt} = G_C - k_2 n_e(n_h + p_0) - k_T n_e(N_T - n_t) \tag{1}$$

$$\frac{dn_h}{dt} = G_C - k_2 n_e(n_h + p_0) - k_R n_t(n_h + p_0) \tag{2}$$

$$\frac{dn_t}{dt} = k_T n_e (N_T - n_t) - k_R n_t (n_h + p_0) \quad (3)$$

Table S1. Kinetic parameters used to model the TRMC measurements . Here, k_2, k_T and k_R are the rate constants for band-to-band electron-hole recombination, trap filling and trap emptying, respectively. N_T denotes the concentration of trap states, p_0 is the background hole concentration at thermal equilibrium. Finally, μ_e and μ_h are the mobilities of electrons (e) and holes (h).

k_2 (cm^3s^{-1})	4.5×10^{-10}
k_T (cm^3s^{-1})	6×10^{-10}
k_R (cm^3s^{-1})	1×10^{-11}
N_T (cm^{-3})	9×10^{15}
p_0 (cm^{-3})	1×10^{15}
$\Sigma\mu_h$ *(cm^2/Vs)	4
$\Sigma\mu_e$ *(cm^2/Vs)	2

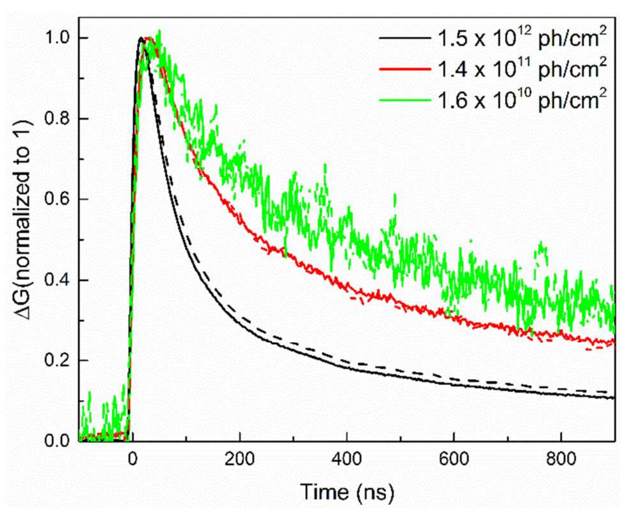

Figure S3: TRMC traces for $MAPbI_3$ (full lines) and $MAPbI_3$/Spiro-OMeTAD bilayer (dashed lines) recorded at indicated intensities expressed in photons/cm^2 per pulse (λ_{pump} = 600 nm).

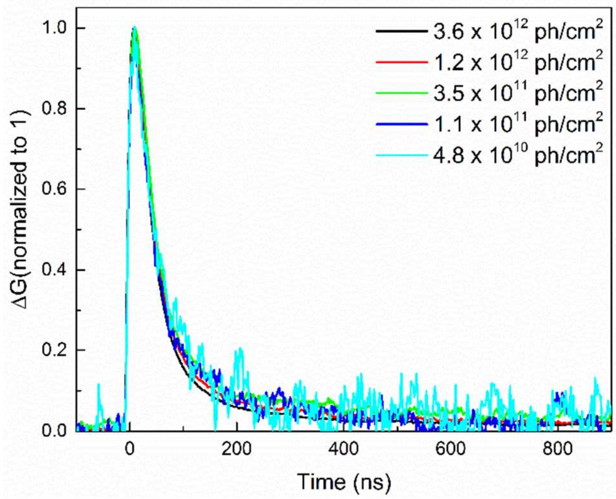

Figure S4: Normalized TRMC traces for the $MAPbI_3$/PCBM bilayer recorded at indicated intensities expressed in photons/cm^2 per pulse (λ_{pump} = 600 nm).

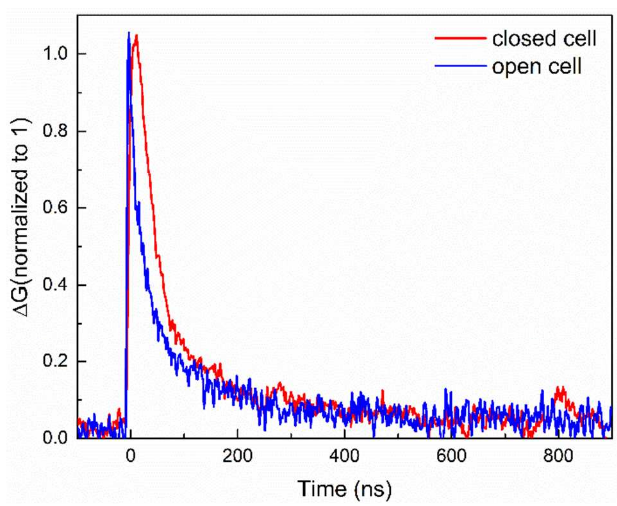

Figure S5: TRMC traces of $MAPbI_3$/PCBM pump at 1×10^{12} ph/cm^2 per pulse (λ_{pump} = 600 nm) comparing open and closed cell configuration.

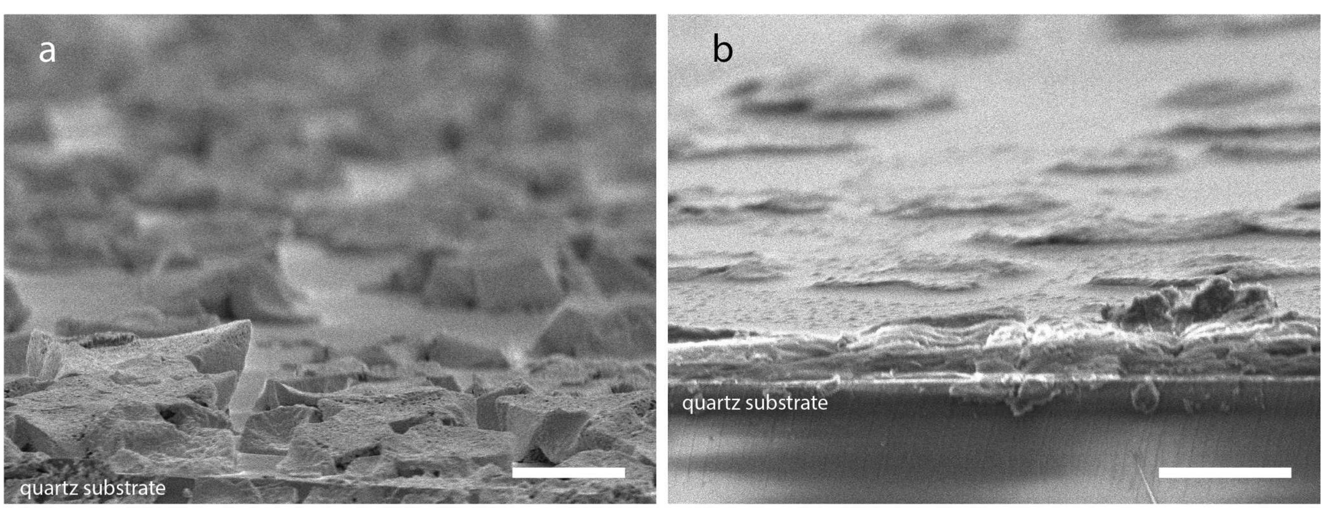

Figure S6: cross-sectional Scanning Electron Microscopy (SEM) images of (a) polycrystalline perovskite film spin-coated on a quartz substrate with thickness ~ 4 µm and (b) polycrystalline perovskite film covered with PCBM, thickness ~ 3 µm. Both samples are tilted at 10 degrees. Scale bars correspond to 20 µm and 10 µm, respectively.

Open and Closed Cell TRMC Measurements

The change in conductance as measured by TRMC, $\Delta G_m(t)$ is the convolution of the instrumental response function of the system, IRF(t) and the actual change in conductance, $\Delta G(t)$ induced by the laser pulse given by (see also ref 41)

$$\Delta G_m(t) = IRF(t) \times \Delta G(t)$$

The IRF function can be described by the exponential response of the used microwave cell. For the cavity the exponent is 18 ns, while for the so called open cell it is only about 2 ns. How this affects the rise time is illustrated below and is now also included in the SI. In the left Figure, a block like photoconductance signal with a lifetime comparable to the laserpulse (3 ns) will yield TRMC kinetics depending on the IRF of the microwave cell as shown by both dashed lines, while TRMC kinetics for a long-lived photoconductance signal are shown in the right panel. As can be clearly observed the risetime for the long-lived signal seems longer than for the short-lived signal.

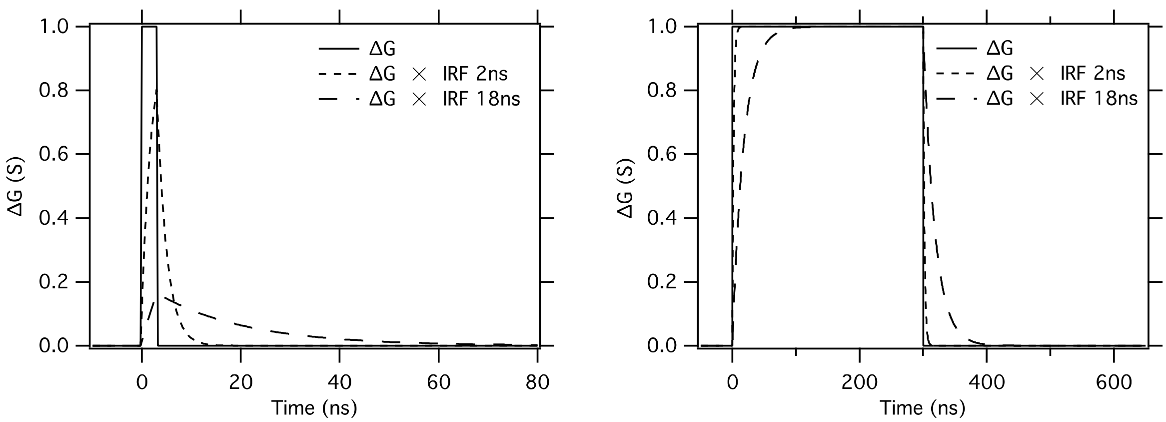

Figure S7: Comparison of the observed TRMC kinetics for a (mathematical) short (left) and long (right) photoconductance signal (full line) measured with the cavity (long-dash, IRF: 18 ns) and the open cell (short-dash, IRF: 2 ns)