Supporting Information

Intensity-Modulated Scanning Kelvin Probe Microscopy for Probing Recombination in Organic Photovoltaics

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This file includes:

Figures S1 to S9

Equations S1 and S4

Schematics of Transient Photovoltage (TPV) and Charge Extraction (CE) setup

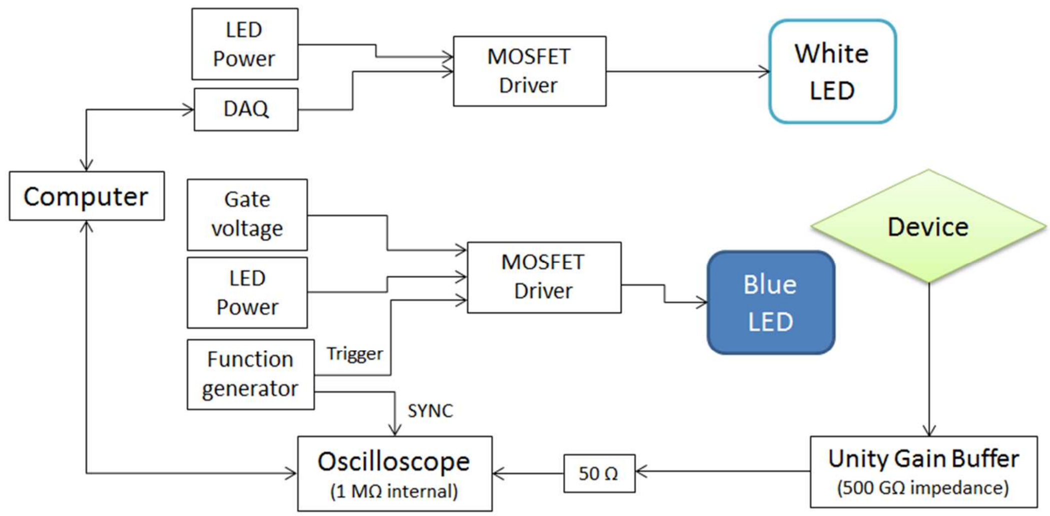

Figure S1. TPV measurement setup as used previously.[1]

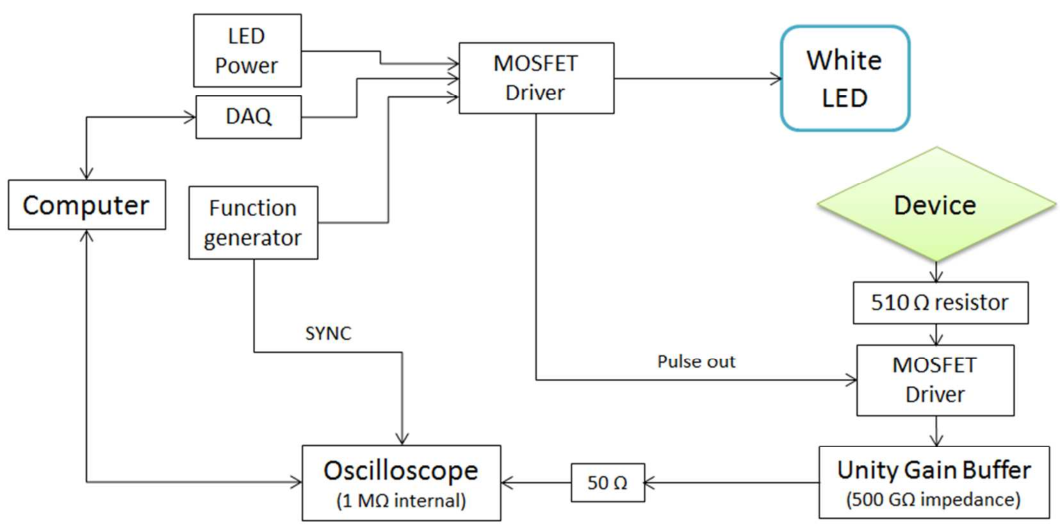

Figure S2. CE measurement setup.[1]

Simulation of V_{OC} evolution with time based on measurements from TPV and CE

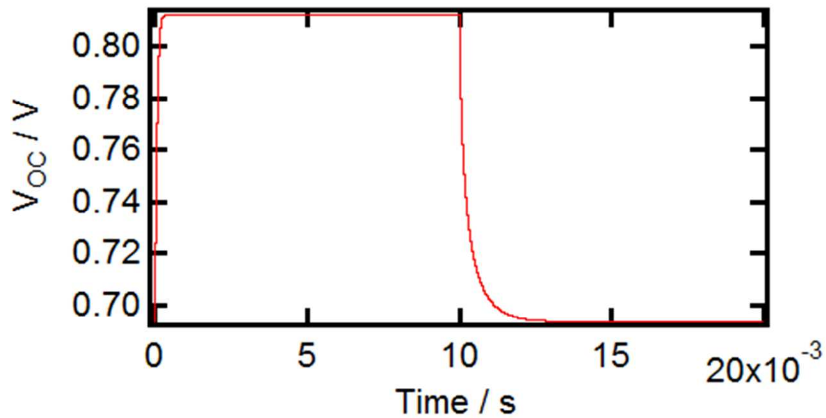

Figure S3. Simulated V_{OC} as a function of time under LED modulating frequency of 50 Hz and an equivalent white light background excitation intensity of 1 mW/cm^2 and a modulated LED peak intensity of 25 mW/cm^2.

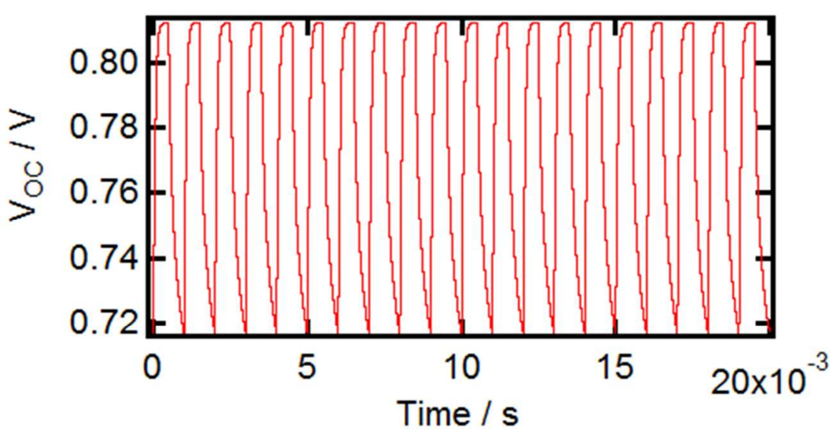

Figure S4. Simulated V_{OC} as a function of time under LED modulating frequency of 1000 Hz and an equivalent white light background excitation intensity of 1 mW/cm^2 and a modulated LED peak intensity of 25 mW/cm^2.

To compare these simulations to the experimental data, we computed the time averaged voltage over one period and plotted the result in Fig. 6 in the main text. The simulations were carried out using numerical integration of the generation and recombination (Eqn. S1) in Igor.

$$\frac{dn}{dt} = G - R \qquad \textbf{Equation S1}$$

where G is the generation rate defined as absorbed photon flux per unit area corrected for double pass of light (by multiplying by 2) then divided by the thickness of the film. The unit of G is $cm^{-3} \cdot s^{-1}$. The recombination rate, R, was determined from the experimental device TPV data as described below. First, the raw data of carrier density from charge extraction measurements were corrected for recombination during charge extraction[2] and geometric capacitance[3] to determine the net charge carrier density generated in the active layer. To determine an instantaneous recombination rate as a function of carrier density, we plotted the carrier lifetime τ, V_{OC} and corrected carrier density n, following conventions used to analyze TPV data.[4] The fitted results were then used to generate a computable functional form for the instantaneous recombination rate at an arbitrary n, as shown in Equation S2, which was then used to numerically simulate the evolution of carrier density *vs.* time.

$$R = -\frac{n^{1+\lambda}}{(1+\lambda)\tau_0 n_0^{\lambda}} \qquad \textbf{Equation S2}$$

The prefactors and exponents in Eqn. S2 were given by best fits to the experimental data in Figs. S5 and S7 below. Although there is some scatter in the data, and possible deviation from the rigorous power law forms, both the general trends (decreased pseudo first order rate constant with increasing n), and overall magnitude of the data are reasonably well parameterized by the fits.

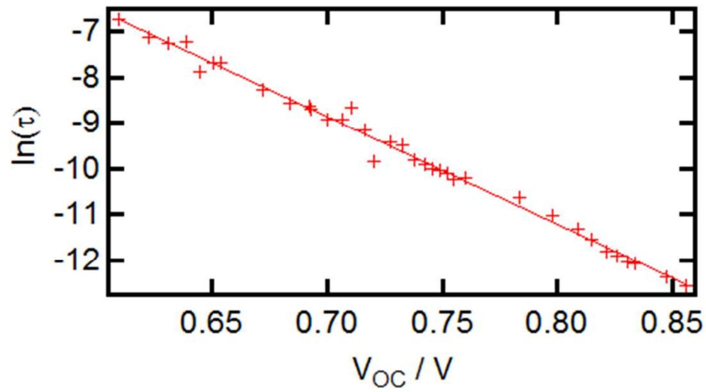

Figure S5. Natural log of the small perturbation carrier lifetime, τ, plotted as a function of Voc. The solid line is a fit to $\tau = \tau_0 \exp(-\alpha V_{OC})$,[4] where τ is carrier lifetime measured from TPV, V_{OC} is the measured open circuit voltage. τ_0 and α are fitting parameters.

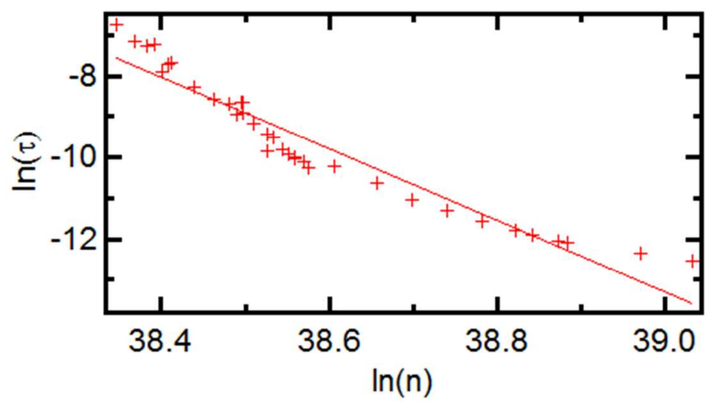

Figure S6. Natural log of the small perturbation carrier lifetime, τ, plotted as a function of Voc. The solid line is a fit to $\tau = \tau_0 (n_0/n)^{\lambda}$, after Durrant and co-workers.[4] Here λ is fitting parameter.

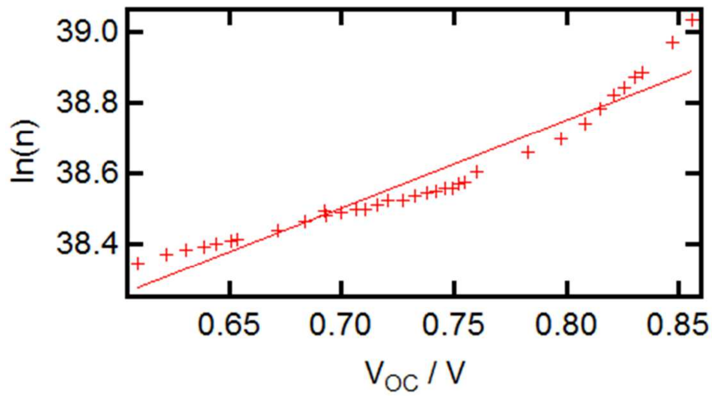

Figure S7. Carrier density, n, plotted as a function of Voc. The solid line is a fit to $n = n_0 \exp(\gamma V_{OC})$.[4] Here, n is the carrier density measured from charge extraction, corrected for recombination during extraction and device geometric capacitance. n_0 and γ are fitting parameters. The corrected n vs. Voc data show the largest deviation from the single exponential form.

Finally, the simulated carrier density was then converted back into a voltage according using the double exponential extrapolation based experimental Voc *vs.* n data shown in Fig. S8.

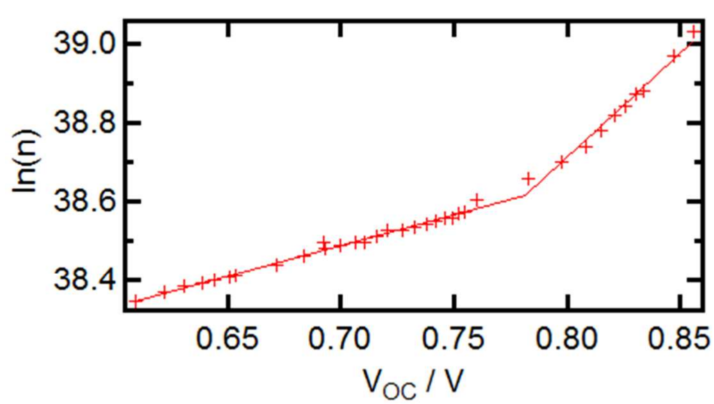

Figure S8. Natural log of carrier density plotted against V_{OC}, the raw data were fitted with by two exponentials to yield more accurate extrapolation of V_{OC}.

Fitting intensity-modulated SKPM data with Stretched exponential function

A stretched exponential function can be used to describe dispersive kinetics where the lifetime changes with time. Thus, postulating that the surface photovoltage decays with time in the form of stretched exponential, we used Equation S3 as a convenient way to parameterize fits to the experimental data and simulation.

$$SPV(t) = SPV_0 exp^{-(\frac{t}{\tau})^{\beta}}$$ **Equation S3**

Here SPV(t) is the surface photovoltage at a given time, SPV_0 is the SPV(t) at time zero, τ is the characteristic lifetime, β is the stretching exponent lying between 0 and 1, representing the multi-exponential decay process.

The experimental data we obtained from intensity-modulated SKPM is the time averaged SPV at different modulating frequencies. We used Equation S4 to fit the data

$$SPV(f) = \frac{SPV_0}{2} + \frac{SPV_0 \tau f \Gamma(\frac{1}{\beta}, (\frac{1}{2\tau f})^{\beta})}{\beta}$$ **Equation S4**

where f is the modulating frequency. Here Γ() is the Gamma function, τ is the characteristic lifetime, and β is the stretching exponent.

Comparison of intensity-modulated SKPM decay across different samples

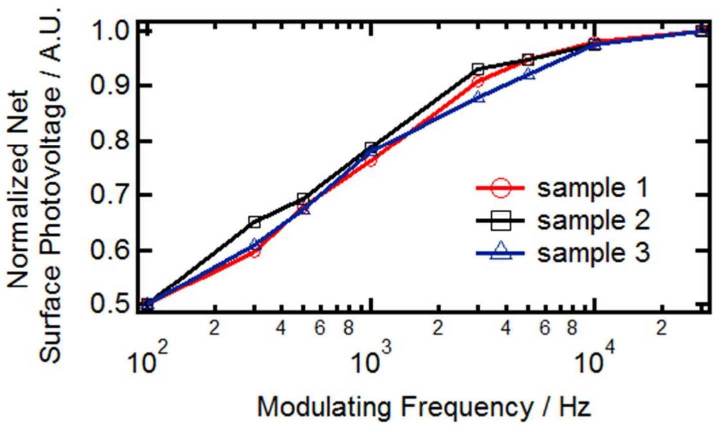

Figure S9. Intensity-modulated SKPM with probing intensity of 12.5 mW/cm^2 and no background illumination measured on three different samples prepared identically.

Shown in Fig. S9 is the intensity-modulated SKPM across three different samples of PCDTBT:PC_{71}BM blend with probing intensity of 12.5 mW/cm^2 and no background illumination. The variation is insignificant across different samples.

References:

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2. Shuttle, C. G.; Maurano, A.; Hamilton, R.; O'Regan, B.; de Mello, J. C.; Durrant, J. R. Charge Extraction Analysis of Charge Carrier Densities in a Polythiophene/Fullerene Solar Cell: Analysis of the Origin of the Device Dark Current. *Appl. Phys. Lett.* **2008**, 93.

3. Credgington, D.; Jamieson, F. C.; Walker, B.; Nguyen, T. Q.; Durrant, J. R. Quantification of Geminate and Non-Geminate Recombination Losses within a Solution-Processed Small-Molecule Bulk Heterojunction Solar Cell. *Adv. Mater.* **2012**, 24, 2135-2141.

4. Shuttle, C. G.; O'Regan, B.; Ballantyne, A. M.; Nelson, J.; Bradley, D. D. C.; de Mello, J.; Durrant, J. R. Experimental Determination of the Rate Law for Charge Carrier Decay in a Polythiophene: Fullerene Solar Cell. *Appl. Phys. Lett.* **2008**, 92, 093311-1-093311-3.