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**Quadrant I semicircle**

During an IMPS measurement, we apply a harmonically-perturbed illumination on a solar cell and measure the resultant photocurrent. At low perturbation frequency, the photocurrent profile has zero phase shift and a certain amplitude. Typically in dye solar cells and most bulk heterojunction organic solar cells, as the frequency increases, the photocurrent profile acquires a negative phase shift and a reduced amplitude because of the finite rate of charge carrier generation or extraction. However, in some bulk heterojunction devices, the photocurrent profile acquires a positive phase shift and an increased (relative to that at low frequency) amplitude with increasing perturbation frequency. These three types of profile are given in Fig. S1(a). The positive phase shift of the 1 kHz photocurrent profile, together with an increased amplitude (relative to that at 10 Hz), constitutes a point on the quadrant I semicircle [Fig. S1(b)]. The photocurrent profile at 50 kHz, which has a negative phase shift and a reduced amplitude, yields a point on the quadrant IV semicircle.

![Figure S1: (a) Typical IMPS measurements and (b) typical Nyquist plots of the IMPS spectra of bulk heterojunction organic solar cells: photocurrent profiles at the perturbation frequency of 10 Hz (×), 1 kHz (●) and 50 kHz (+), light intensity profiles (—) at all perturbation frequencies, steady-state levels for the photocurrent and the light intensity (— —), an IMPS spectrum featuring both the quadrant I and IV semicircles (▽), and an IMPS spectrum featuring solely the quadrant IV semicircle (□). The time is normalized against the period, \( \frac{1}{f} \) to allow for a comparison of sinusoidal profiles across a range of frequencies. The inset (c) magnifies the profiles about 0.5, showing that at 1 kHz, the photocurrent has a positive phase shift.](image)
Mathematical formulation

We consider the conservation of particles, defined in the form of continuity equations as

$$\frac{\partial n_k}{\partial t} + \nabla \cdot \mathbf{J}_k = S_k,$$  \hspace{1cm} (1)

where $n_k$ is the density of species $k$, $\mathbf{J}_k$ is the particle flux density, and $S_k$ is the source/sink term.

The density of charged species, $\rho$, is related to the electric potential, $\phi$, by the Poisson’s equation

$$\nabla^2 \phi = \frac{e \rho}{\varepsilon_0 \varepsilon_r},$$  \hspace{1cm} (2)

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative permittivity of the blend, and $e$ is the elementary charge. The flux density of the electrons and holes are given by

$$\mathbf{J}_k = \begin{cases} \mu_e n_e \nabla \phi - D_e \nabla n_e, & \text{free electrons} \\ -\mu_h n_h \nabla \phi - D_h \nabla n_h, & \text{free holes} \end{cases}$$  \hspace{1cm} (3)

where $\mu_{e(h)}$ and $D_{e(h)}$ are the mobility and diffusion coefficients of electrons (holes) respectively.

The relations portrayed in Fig. 2 are captured with the following source/sink terms:

$$S_k = \begin{cases} k_d n_{ct} - k_{rb}(n_e n_h - n_i^2) - k_t(N_{trap} - n_{te})n_e + k_{dt}n_{te}, & \text{free electrons} \\ k_d n_{ct} - k_{rb}(n_e n_h - n_i^2) - k_{rt}n_{te}n_h, & \text{free holes} \\ G - k_d n_{ct} - k_{rg}n_{ct}, & \text{CT}_1 \text{ quasiparticles} \\ k_t(N_{trap} - n_{te})n_e - k_{dt}n_{te} - k_{rt}n_{te}n_h, & \text{trapped electrons} \end{cases}$$  \hspace{1cm} (4)

where $k_d$ is the CT$_1$ quasiparticle dissociation rate constant, $k_{rb}$ is the bimolecular recombination rate constant, $G$ is the CT$_1$ quasiparticle generation rate, $k_{rg}$ is the CT$_1$ quasiparticle (geminate) recombination rate constant, $k_t$ is the electron trapping rate constant, $k_{dt}$ is the electron de-trapping rate constant, $N_{trap}$ is the density of trap states, $n_i$ is the intrinsic carrier density, and $k_{rt}$ is the trap-
assisted recombination rate constant. We assume that both the bimolecular recombination and the trap-assisted recombination take the form of a Langevin recombination\textsuperscript{1–3} such that their constants can be given as

$$k_{rb} = \frac{e}{\varepsilon_0 \varepsilon_r} \mu_h, \quad k_{rt} = \alpha_t \frac{e}{\varepsilon_0 \varepsilon_r} \mu_h,$$

(5)

where $\alpha_t$ is the trap-assisted recombination rate constant prefactor. The mobility and the diffusion coefficients of each mobile charge species are related by the Einstein relation

$$D_{e(h)} = \mu_{e(h)} k_B T e.$$

(6)

We solve the differential equations throughout the one-dimensional computational domain subject to the following boundary conditions:

- It is assumed that the work functions of the charge carrier collectors are matched perfectly with the conduction band (the LUMO manifold) and the valence band (the HOMO manifold) of the effective semiconductor, such that the organic-metal interfaces form Ohmic contacts. In the one-dimensional model, this implies that

$$n_e(0, t) = N_{cv}, \quad n_h(0, t) = N_{cv} \exp\left(-\frac{E_{eg}^{\text{eff}}}{k_B T}\right), \quad \text{negative charge carrier collector}$$

(7)

$$n_h(L, t) = N_{cv}, \quad n_e(L, t) = N_{cv} \exp\left(-\frac{E_{eg}^{\text{eff}}}{k_B T}\right), \quad \text{positive charge carrier collector}$$

(8)

where $L$ is the thickness of the P3HT:PCBM blend, $N_{cv}$ is the effective density of states of both conduction and valence band, and $E_{eg}^{\text{eff}}$ is the effective band gap\textsuperscript{4} of the semiconducting blend. We assume equal effective density of states for conduction and valence bands.

- At the negative charge carrier collector, we specify a ground potential

$$\phi(0, t) = 0.$$
At the positive charge carrier collector, we apply a voltage bias, $V_a$

$$\varphi(L,t) = V_a - \frac{1}{e} E^e_{\text{eff}}.$$  \hspace{1cm} (10)

In the one-dimensional model, the externally measurable current is obtained by evaluating the following expression\textsuperscript{5,6} at the boundaries ($x = 0$ or $x = L$)

$$I = eA \left[ D_e \frac{\partial n_e}{\partial x} - D_h \frac{\partial n_h}{\partial x} - \mu_e n_e \frac{\partial \varphi}{\partial x} - \mu_h n_h \frac{\partial \varphi}{\partial x} \right] - A \varepsilon_0 \varepsilon_r \frac{\partial}{\partial t} \left( \frac{\partial \varphi}{\partial x} \right),$$  \hspace{1cm} (11)

where $A$ is the active area of the device.

### Parameters

**Table S1: Parameters for the IMPS model predictions of the aged and fresh devices.**

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<th>Par.</th>
<th>Units</th>
<th>Value</th>
<th>Source</th>
<th>Value</th>
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**Validation with the photocurrent transients**

To validate the mathematical model, we measured the short-circuit photocurrent transient responses of the aged and fresh devices. We used a green LED (525 nm) with a turn on time of around 1 ns to illuminate the solar cell with a 1 ms step-function pulse. The LED was controlled by a 30 MHz function generator. The current signals from the solar cell were recorded with a 500 MHz oscilloscope (Tektronix).

As illustrated in Figs. S2(a) and S2(b), the model-predicted photocurrent’s profile mirrors the measured photocurrent’s, indicating that the models maintain their fidelity in describing the electrical behavior of the devices across different timescales even when it was applied to the measurement data from a different instrumental setup. The photocurrent transients of the aged device have the following features: in the order of $\mu$s, a sharp rise and a sharp drop corresponding to the start and the end of the step-function pulse respectively; in the order of ms, a slower drop in photocurrent from the peak to the steady-state value, a slower decay of photocurrent towards zero, and a negative current peak. With the exception of the negative current peak, all these features have been observed experimentally\(^9\) and modeled with a trapping model\(^10\) for P3HT:F8TBT devices. These phenomena in the ms time regime, which are absent in the photocurrent transients of the fresh device, are analogous to those in the kHz regime of the IMPS spectrum, thus linking them to the trap equation.

The negative current peak [Fig. S2(c)] can be explained by the trap-assisted recombination. As the light pulse is switched off, the mobile charges are extracted at a rate faster than the trap-assisted recombination rate and the de-trapping rate. Thus, the mobile carrier densities decay at a higher rate than the trapped carrier density. As a result of the imbalanced decay rates, the trap-assisted recombination – which involves a mobile hole and a trapped electron – causes the decay in mobile hole density to overshoot its equilibrium value in the dark condition, forcing the local electric potential further from its equilibrium state. The resultant electric potential forces a current injection into the device, thus generating a negative current.
Figure S2: Measured short-circuit photocurrent responses of the (a) fresh (▲) and (b) aged (▼) devices subjected to a 100 W m$^{-2}$ illumination from 0.5 ms to 1.5 ms and model predictions (—). The negative current peak is magnified in (c), which focuses on the photocurrent dynamics of both devices in the ms regime after the light pulse is switched off.

References


