

Supporting Information

Structural Order: the Dominant Factor for Non-Geminate Recombination in Organic Photovoltaic Devices

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Table S1. Device parameters for the different polymer OPV devices as well as the P3HT devices with different P3HT concentrations and annealing temperatures. More than 4 devices for each condition were averaged in J - V results to calculate standard deviation. The reaction order (λ) was determined from the power law dependence between τ and n ($\tau = \tau_0 n^{-\lambda}$, Fig. S4), the relative interfacial area ([D-A]) was extracted from low-energy EQE measurements (Fig. 3(c)), the

geometric capacitance (C_g) was obtain from the impedance spectroscopy measurements performed in dark at 0V bias, and the hole mobility (μ_h) and field-dependent parameter (γ) were determined using the space-charge limited current-voltage (SCLC) model (Fig. 3(d))

Polymer	V_{oc} [mV]	J_{sc} [mA/cm ²]	FF	PCE [%]	λ	[D-A]	C_g [nF]	μ_h [cm ² V ⁻¹ s ⁻¹]	γ [cm ^{0.5} V ^{-0.5}]
P3HT ^a	602 ± 4	7.80 ± 0.07	0.64 ± 0.01	2.99 ± 0.03	1.49	5.0E-3	4.5	1.4E-4	/
PBDT-TPD	915 ± 6	8.45 ± 0.19	0.62 ± 0.01	4.78 ± 0.17	2.31	/	5.0	/	/
PCDTBT	903 ± 5	9.69 ± 0.09	0.63 ± 0.02	5.49 ± 0.07	2.27	/	5.6	/	/
P3HT ^b	650 ± 1	5.96 ± 0.09	0.61 ± 0.01	2.37 ± 0.03	2.13	8.3E-3	4.2	3.2E-4	3.7E-4
P3HT ^c	890 ± 1	4.91 ± 0.10	0.44 ± 0.01	1.92 ± 0.04	3.37	2.6E-3	5.1	2.6E-5	3.1E-3

^a P3HT:PC₇₁BM with 1:1 ratio annealed at 170 °C, Device A

^b P3HT:PC₇₁BM with 1:1 ratio annealed at 70 °C, Device B

^c P3HT:PC₇₁BM with 1:4 ratio annealed at 70 °C, Device C

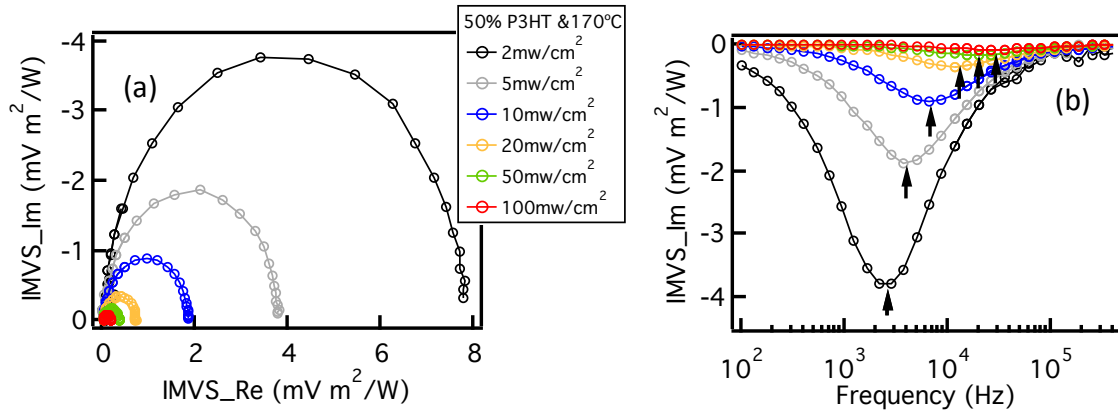


Figure S1. (a) Typical IMVS response in the complex plane for the 50% P3HT device annealed at 170 °C under different illumination intensities: 2 mW/cm² (black), 5 mW/cm² (grey), 10 mW/cm² (blue), 20 mW/cm² (orange), 50 mW/cm² (green), and 100 mW/cm² (red). (b) IMVS imaginary component vs. frequency for the same device. The carrier non-geminate recombination (NRG) time constant (τ) is calculated from $\tau = 1/2\pi f_m$, where f_m is the

characteristic frequency minimum of the IMVS imaginary component, as indicated by the arrows in (b).¹

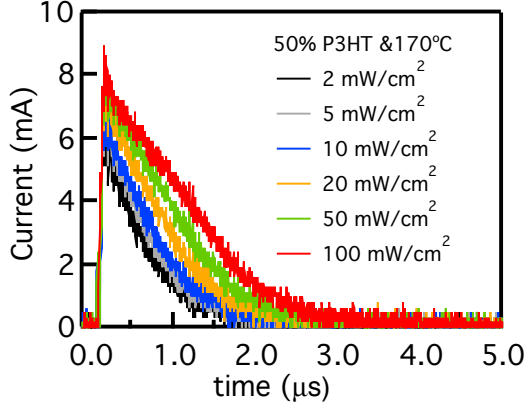


Figure S2. The current transient collected in the charge extraction (CE) experiments for the 50% P3HT and 170 °C annealed device (Device A) under different illumination intensities. To get the carrier density, each curve is integrated and then the charge accumulated at the electrodes, i.e., $C_g \times V_{oc}$, is subtracted. All colors used here are the same as in Figure S1.

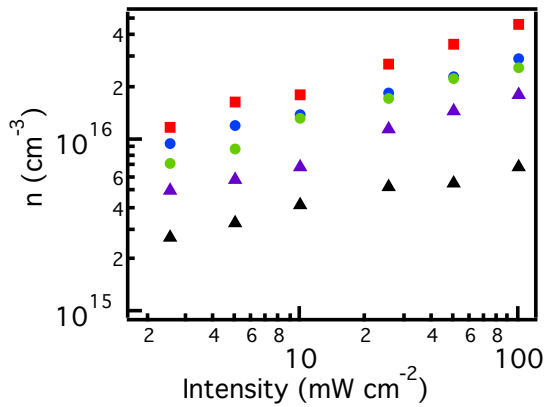


Figure S3. The carrier density at open circuit (n) obtained from the CE measurements vs. illumination intensity for all the devices studied. All colors and symbols used here are the same as in Figure 2.

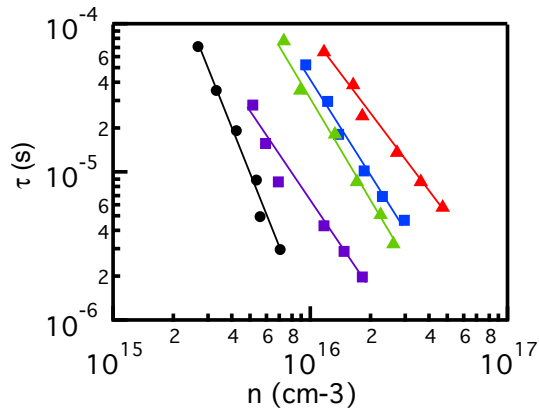


Figure S4. τ vs. n measured at open circuit condition under different illumination intensities for all the devices studied. Solid lines are fitted results with the slope of $-\lambda$. λ is the reaction order which provides information on how the carrier density affects recombination behavior.²⁻⁴ $\lambda > 1$ (Table S1) is observed in all devices investigated, indicating highly carrier-density dependent recombination ($\lambda = 1$ represents bimolecular recombination with a constant recombination coefficient).^{4,5} Moreover, λ increases from Device A to C with the highest λ (3.37) found in the Device C. All colors and symbols used here are the same as in Figure 2.

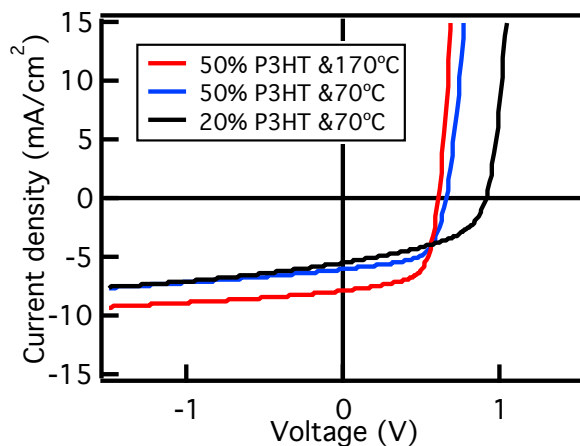


Figure S5. J - V curves taken at AM 1.5G 100 mW/cm² illumination condition of the P3HT:PC₇₁BM model system. All colors used here are the same as in Figure 2.

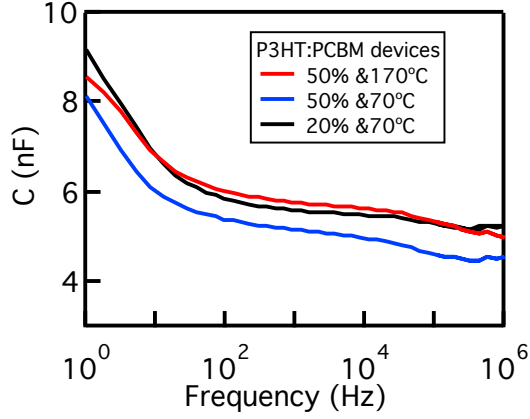


Figure S6. C vs. f in the dark at zero bias for the devices with different P3HT concentrations and annealing temperatures. All colors used here are the same as in Figure 2.

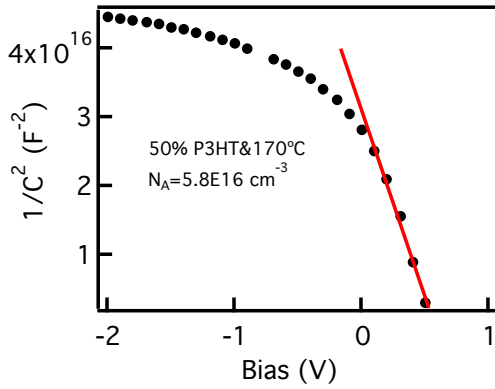


Figure S7. (a) Mott-Schottky curve showing the $1/C^2$ (measured at 10 kHz) vs. V for the 50% P3HT and 170 °C annealed device (70 nm). Lines represent the fitting according to the Mott-Schottky analysis, from which the upper limit of N_A is obtained to be $5.8 \times 10^{16} \text{ cm}^{-3}$.⁶

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