On the Relationship of the Effective Mobility and Photoconductance Mobility in Organic Solar Cells -
Supplementary Information

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S1 Experimental Details

S1.1 Materials

In this study we consider systems with three donor polymers:
- Poly-(3-hexylthiophen-2,5-diyl) (P3HT);
- Poly[[4,8-bis[5-(2-ethylhexyl)-4-fluoro-2-thienyl]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl]-2,5-thiophenediyl-
[5,7-bis(2-ethylhexyl)-4,8-dioxo-4H,8H-benz0[1,2-c:4,5-c’]dithiophene-1,3-diyl]-2,5-thiophenediyl] (PM6);
- Poly[(2,5-bis(2-hexyldecoxy)phenylene)-alt-(5,6-difluoro-4,7-di(thiophen-2-yl)-benzo[c]-[1,2,5] thiadiazole)] (PPDT2FBT).

Furthermore, fullerene and non-fullerene acceptors were used:
- [6,6]-phenyl-C61-butyricacidmethylester (P3HT:PC60BM);
- 2,2’-(2Z,2’Z)-(12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno-
bis(3-oxo-2,3-dihydro-1H-indene-2,1-diyli)dimalononitrile (Y5);
- 2,2’-(2Z,2’Z)-(12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno-
bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diyli)dimalononitrile (Y6);
- 2,2’-((2Z,2’Z)-(6,12,13-tris(2-ethylhexyl)-3,9-dimdeceyl-12,13-dihydro-6H-thieno[2′,3′:4,5′]thieno-
[2″,3″:4′,5′]pyrrolo[3,2-g]thieno[2′,3′:4,5′]thieno[3,2-b][1,2,3]triazolo[4,5-e]indole-2,10-diyl)bis(methanlylidene))-
bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (Y11);
- 2,2’-((12,13-bis(4-ethyloctyl)-3,9-dimdeceyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno-
[2″,3″:4′,5′]thieno[2′,3′:4,5′]thieno[3,2-b]indole-2,10-diyl)bis(methanlylidene))-
bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (N4);
- 2,2’-((6-(2-ethylhexyl)-12,13-bis(4-ethyloctyl)-3,9-dimdeceyl-12,13-dihydro-6H-thieno-
[2″,3″:4′,5′]thieno[2′,3′:4,5′]pyrrolo[3,2-g]thieno[2′,3′:4,5′]thieno[3,2-b]indole-2,10-diyl)bis(methanlylidene))-
bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (Y11-N4).

S1.2 Device Fabrication

A variety of organic photovoltaic (OPV) solar cells employed for the study were fabricated on 
indium-tin oxide (ITO)-coated pre-etched and pre-cleaned glass substrates. In all OPV devices, a 
30-nm-thick poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) film was used 
as a hole-transporting layer (HTL). Active layer solutions were spin-coated by varying spin speeds 
and accelerations to obtain the desired thicknesses. The weight ratios of a donor to acceptor for the 
different blend systems employed in this study were as follows: P3HT:PC_{60}BM – 1:1, PM6:Y11-
1:1.2. The PM6:Y6 solar cells included a chloronaphthalene (CN) solvent additive in the amount 
of 0.5% by volume. Active layer annealing was performed at the following conditions: PM6 and 
PPDT2FBT-based NFA devices at 110°C for 10 min. For the PM6 and PPDT2FBT-based NFA 
cells, a 10-nm-thick PDINO electron-injecting layer (ETL) was spin-cast, whereas a 10-nm-thick 
PDINN ETL was spin-cast instead of PDINO for one of the PM6:Y6 devices. Finally, thermal evap-
oration was employed to deposit the Ag-electrode (45 nm in case of the PM6:N4 and PM6:Y11-N4 
devices, 100 nm for all the other devices).

S1.3 Device Characterization

Current-voltage (J-V): J-V measurements of the studied solar cells were performed using a LabVIEW-
controlled Keithley 2400 SourceMeter under the illumination of a white-light LED array.

Impedance: The impedance measurements were performed using a Keysight E5061B Vector Net-
work Analyser in the frequency range from 50 Hz to 10 MHz under the illumination of a white-light 
LED array. The 85032E Type N kit was used for the instrument calibration, and the presence of 
the test fixture was compensated for using the “Open,” “Short,” and “50 Ohm” measurements. 
Capacitance-frequency spectra of the studied solar cells were generated from the impedance mea-
surements at various light intensities and applied biases (cf. Fig. S11 - S19). The integration of the
capacitance over the voltage range yields the charge carrier density \( n \): 

\[
    n = \frac{1}{qAL} \int_{V_{\text{sat}}}^{V_{\text{OC}}} \left[ C_b - C_g \right] dV_{\text{cor}}, \tag{S1}
\]

where \( q \) is the elementary charge, \( A \) is the device area, \( L \) is the active layer thickness, \( V_{\text{sat}} \) is the saturated voltage (usually \( V_{\text{sat}} \leq 0 \) V), \( C_b \) is the frequency dependent barrier capacitance obtained via the impedance measurements, \( C_g \) is the geometric capacitance resulting from the electrodes of the device forming a plate capacitor, and \( V_{\text{cor}} \) is the voltage corrected for the series resistance \( R_{\text{series}} \). More details related to this technique can be found in Ref. [1].

**Quasi-steady state photoconductance:** Quasi-steady state photoconductance of the devices under illumination was determined at the respective open-circuit conditions using the real part of admittance \( Y = 1/Z \) averaged across the lower-frequency range of 50 Hz to 1 kHz, in which conductance varies insignificantly.[2]

**Space-charge limited current (SCLC):** SCLC measurements were performed similar to the \( J-V \) measurements in the dark on single-carrier diodes using either an ITO/PEDOT:PSS - MoO\(_3\)/Ag electrode combination for hole-only devices, or an ITO/ZnO - PDINO/Ag electrode combination for electron-only devices. Mobilities were determined via drift-diffusion fitting using a previously reported open-source software.[3]
S2 Optoelectronic Characterization

S2.1 Overview of Mobility Results

In this study, nine different organic solar cells were investigated over a wide range of light intensities. Namely, solar cells based on P3HT:PC$_{60}$BM, PM6:Y11-N4, PM6:Y5, PPDT2FBT:Y6, PM6:Y11, PM6:N4, and PM6:Y6, the latter with varying electron transport layers and thicknesses, were fabricated (cf. Fig. S1).

Figure S1: Experimentally determined values for $\mu_{\text{ph}}$ (black squares; cf. Eq. 4 in the main manuscript) and $\mu_{\text{eff}}^{\exp}$ ($V_{\text{OC}}$) (red circles; cf. Eq. 3 in the main manuscript) for various organic solar cells. Calculation of the maximum and minimum mobilities determined via the harmonic and geometric approach ($\mu_{\text{har}}^{\text{max}}$, $\mu_{\text{har}}^{\text{min}}$: green dots, cf. Eq. 8 and Eq. 9 in the main manuscript; $\mu_{\text{geo}}^{\text{max}}$, $\mu_{\text{geo}}^{\text{min}}$: orange dash-dots, cf. Eq. 11 and Eq. 12 in the main manuscript) and for the relationship $\mu_{\text{eff}}^{\exp} = 0.5 \cdot \mu_{\text{ph}}$ (gray squares; cf. Eq. 6 in the main manuscript). The horizontal lines show the electron ($\mu_n$: blue) and hole ($\mu_p$: red) mobilities determined via the SCLC method of single carrier diodes. These mobilities are shown as horizontal lines due to the unknown charge carrier density at which they were measured.
Figure S2: Current-density-voltage characteristics of a P3HT:PC$_{60}$BM solar cell at different light intensities (black: dark; yellow: increasing light intensity).
Figure S3: Current-density-voltage characteristics of a PM6:Y11-N4 solar cell at different light intensities (black: dark; yellow: increasing light intensity).

Figure S4: Current-density-voltage characteristics of a PM6:Y5 solar cell at different light intensities (black: dark; yellow: increasing light intensity).
Figure S5: Current-density-voltage characteristics of a PPDT2FBT:Y6 solar cell at different light intensities (black: dark; yellow: increasing light intensity).

Figure S6: Current-density-voltage characteristics of a PM6:Y11 solar cell at different light intensities (black: dark; yellow: increasing light intensity).
Figure S7: Current-density-voltage characteristics of a PM6:N4 solar cell at different light intensities (black: dark; yellow: increasing light intensity).

Figure S8: Current-density-voltage characteristics of a PM6:Y6 (PDINO; \( L = 100 \text{ nm} \)) solar cell at different light intensities (black: dark; yellow: increasing light intensity).
Figure S9: Current-density-voltage characteristics of a PM6:Y6 (PDINO; $L = 90$ nm) solar cell at different light intensities (black: dark; yellow: increasing light intensity).

Figure S10: Current-density-voltage characteristics of a PM6:Y6 (PDINN; $L = 100$ nm) solar cell at different light intensities (black: dark; yellow: increasing light intensity).
S2.3 Capacitance Spectra

Figure S11: Frequency dependent barrier capacitance $C_b$ at different light intensities ($V_{LED}$) and DC-voltages ($V_{DC}$) of a P3HT:PC$_{60}$BM solar cell.
Figure S12: Frequency dependent barrier capacitance $C_b$ at different light intensities ($V_{LED}$) and DC-voltages ($V_{DC}$) of a PM6:Y11-N4 solar cell.
Figure S13: Frequency dependent barrier capacitance $C_b$ at different light intensities ($V_{\text{LED}}$) and DC-voltages ($V_{\text{DC}}$) of a PM6:Y5 solar cell.
Figure S14: Frequency dependent barrier capacitance $C_b$ at different light intensities ($V_{LED}$) and DC-voltages ($V_{DC}$) of a PPDT2FBT:Y6 solar cell.
Figure S15: Frequency dependent barrier capacitance $C_b$ at different light intensities ($V_{LED}$) and DC-voltages ($V_{DC}$) of a PM6:Y11 solar cell.
Figure S16: Frequency dependent barrier capacitance $C_b$ at different light intensities ($V_{LED}$) and DC-voltages ($V_{DC}$) of a PM6:N4 solar cell.
Figure S17: Frequency dependent barrier capacitance $C_b$ at different light intensities ($V_{LED}$) and DC-voltages ($V_{DC}$) of a PM6:Y6 (PDINO; $L = 100$ nm) solar cell.
Figure S18: Frequency dependent barrier capacitance $C_b$ at different light intensities ($V_{\text{LED}}$) and DC-voltages ($V_{\text{DC}}$) of a PM6:Y6 (PDINO; $L = 90$ nm) solar cell.
Figure S19: Frequency dependent barrier capacitance $C_b$, at different light intensities ($V_{LED}$) and DC-voltages ($V_{DC}$) of a PM6:Y6 (PDINN; $L = 100$ nm) solar cell.
S2.4 SCLC-Analysis for the Reference Mobilities

Figure S20: SCLC-plots of PM6:Y11-N4 hole and electron only diodes.

Figure S21: SCLC-plots of PM6:Y5 hole and electron only diodes. Both diodes have a 100 nm thick active layer.
Figure S22: SCLC-plots of PPDT2FBT:Y6 hole and electron only diodes. Both diodes have a 100 nm thick active layer.

Figure S23: SCLC-plots of PM6:Y11 hole and electron only diodes. Both diodes have a 100 nm thick active layer.
References

