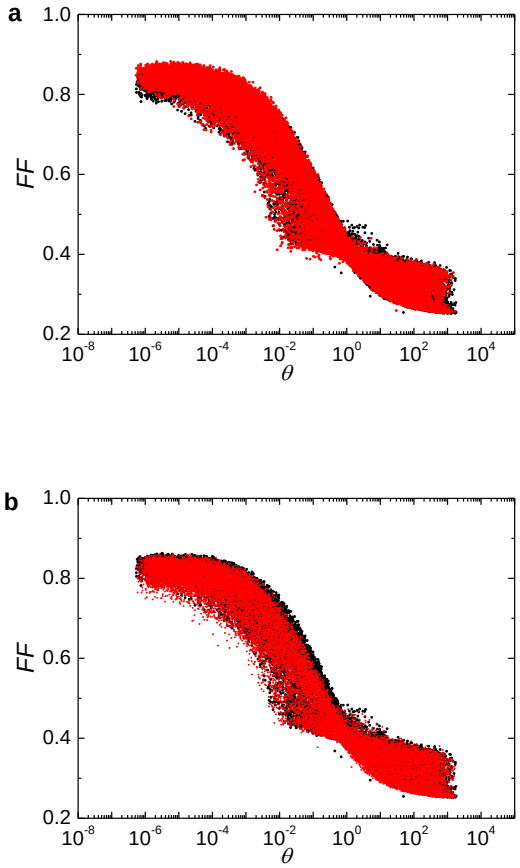
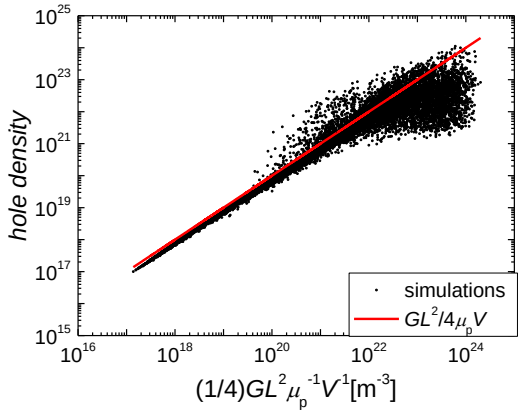
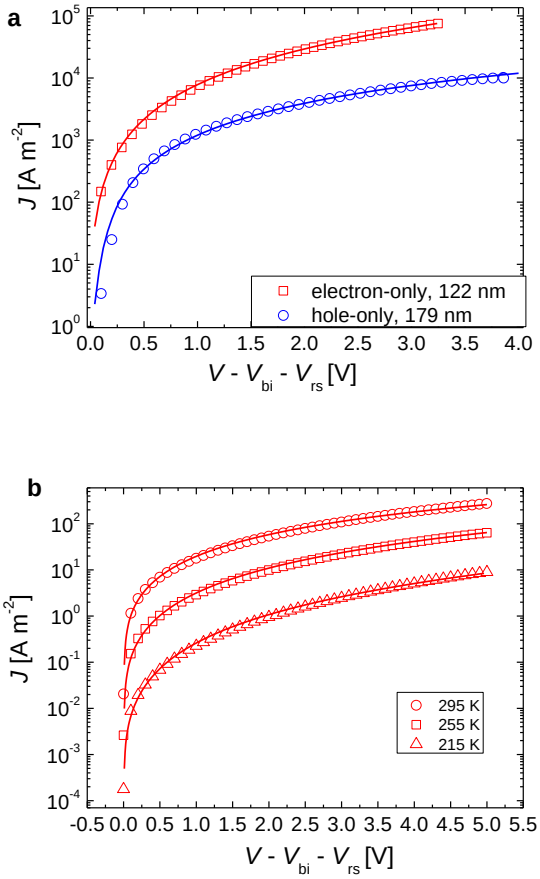


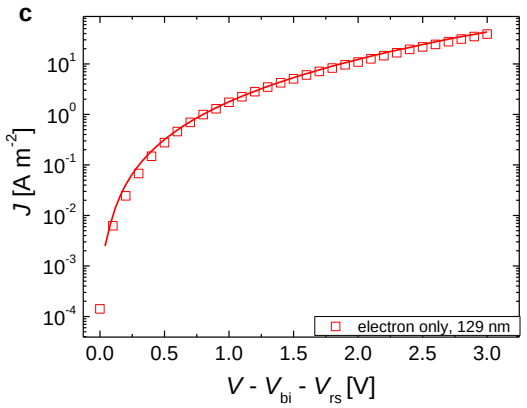
Supplementary Figure 1 (a) The effect of finite surface recombination (red symbols, $S_{n,p}$ = 10^{-4} m s^{-1}) and infinite surface recombination (black symbols). **(b)** Resulting fill-factors for $N_{cv} = 2.5 \times 10^{25}$ m^{-3} (black) and $N_{cv} = 3 \times 10^{26}$ m^{-3} (red).

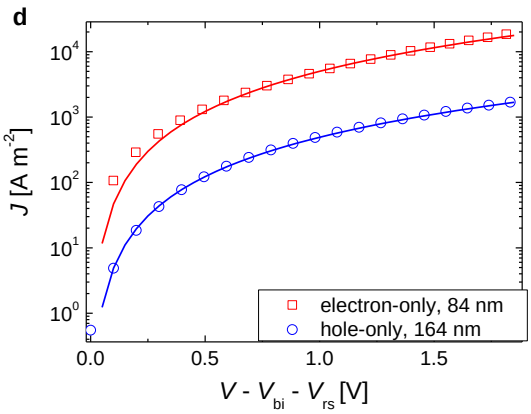


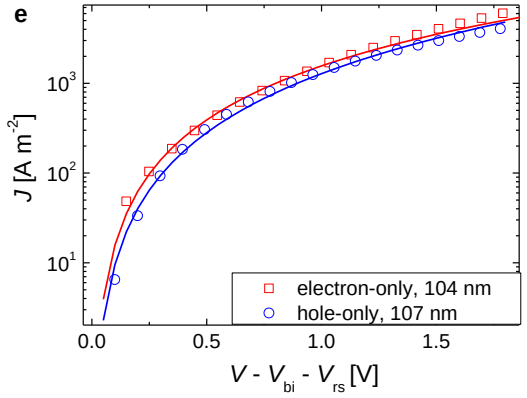
Supplementary Figure 2. Simulated density of holes at the cathode-side of the active layer as a function of $GL^2/\mu_p V_{int}$. The solid lines is calculated with the equation $p_{av} = \frac{GL^2}{4\mu_p V_{int}}$.

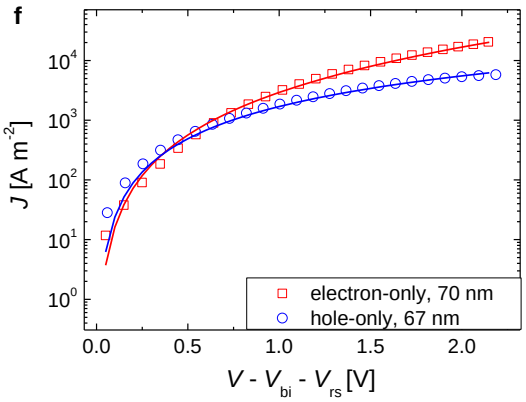
Supplementary Figure 3:



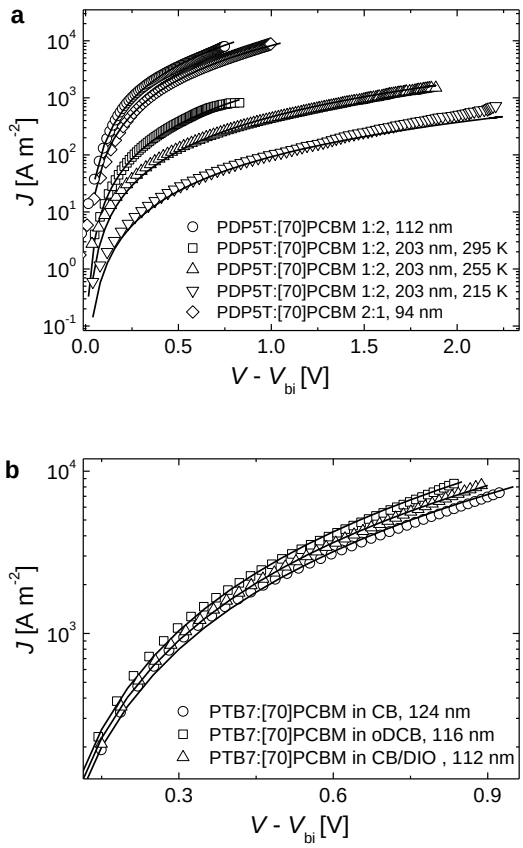

c
J [A m-2]
V - Vbi - Vrs [V]
electron only, 129 nm


d
J [A m-2]
V - Vbi - Vrs [V]
electron-only, 84 nm
hole-only, 164 nm

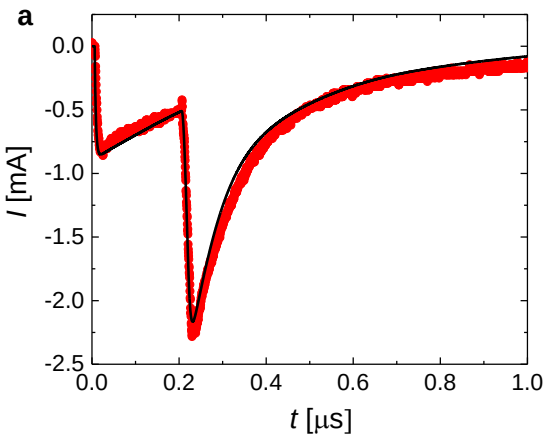

e
J [A m-2]
V - Vbi - Vrs [V]
electron-only, 104 nm
hole-only, 107 nm

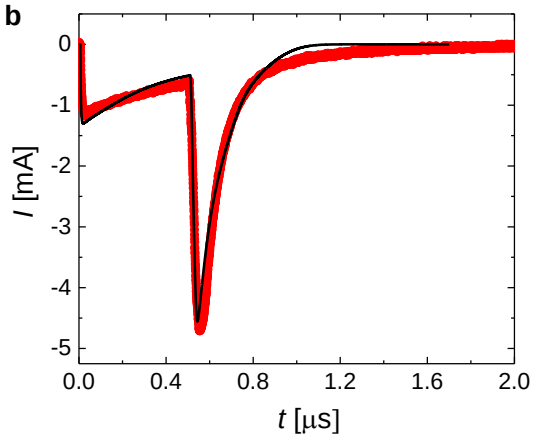


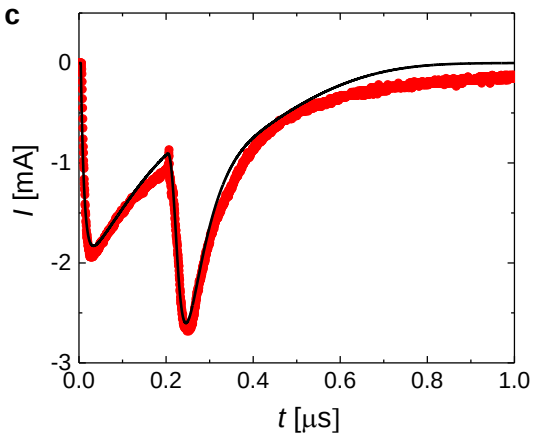
Supplementary Figure 3: *J-V* curves of PDPP5T:[70]PCBM and PTB7:[70]PCBM hole-only and electron-only devices. **(a)** PDPP5T:[70]PCBM 1:2 wt. ratio; **(b)** PDPP5T:[70]PCBM 1:1 wt. ratio; **(c)** PDPP5T:[70]PCBM 2:1 wt. ratio; **(d)** PTB7:[70]PCBM 1:1.5 wt. ratio from CB solution; **(e)** PTB7:[70]PCBM 1:1.5 wt. ratio from oDCB solution; **(f)** PTB7:[70]PCBM 1:1.5 wt. ratio from CB/DIO solution. Symbols represent experimental data, corrected for the series resistance of the substrates (10 Ω/square for the electron-only devices, 14 Ω/square for the hole-only devices) and for the built-in voltage. Solid lines represent fit of the experimental data, performed for space charge limited current with a Poole-Frenkel dependency for the mobility on the electric field[1]. The mobilities of holes and electrons are thus extracted as fit parameters from the *J-V* curves. For PDPP5T:[70]PCBM blends, the hole only was not measured for all the compositions; when the hole-only device was not fabricated, we got the hole mobility from a previous publication[2].

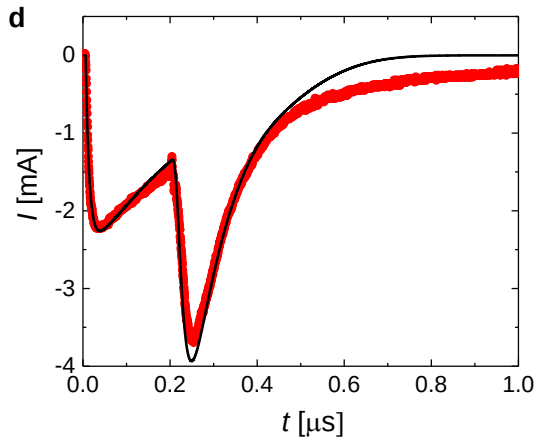


Supplementary Figure 4: *J-V* curves in dark for PDPP5T:[70]PCBM **(a)** and PTB7:[70]PCBM **(b)** solar cells. Symbols represent experimental data, solid lines represent fit of the experimental data.

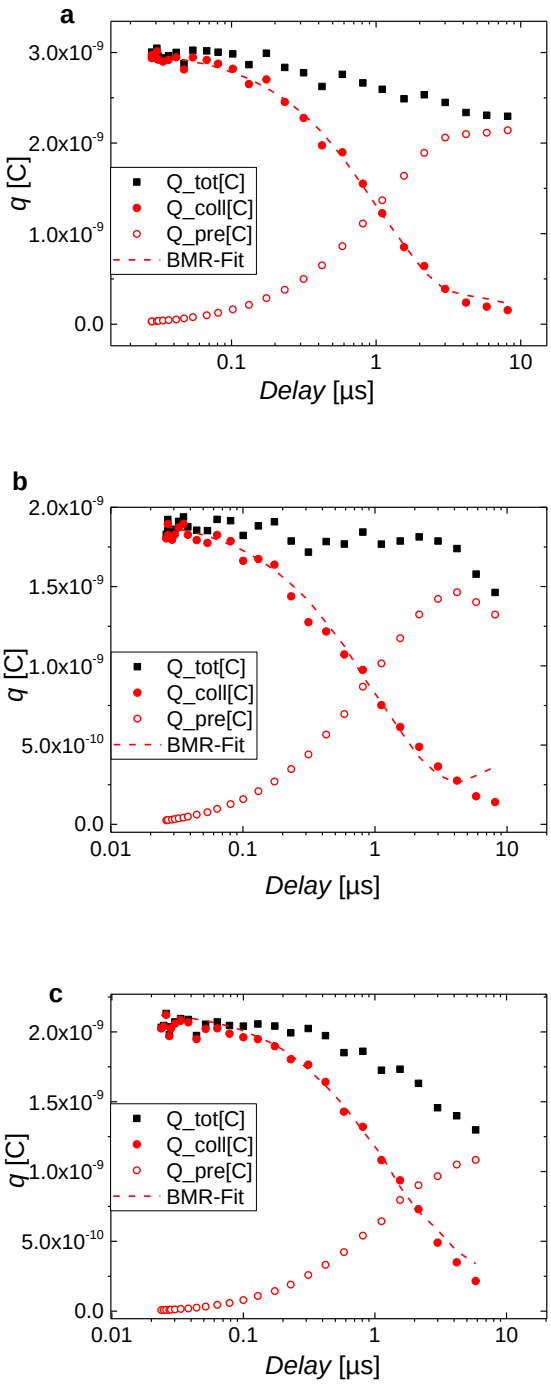

a
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
I [mA]
0.0
0.2
0.4
0.6
0.8
1.0
t [µs]


b
0
-1
-2
-3
-4
-5
I [mA]
0.0
0.4
0.8
1.2
1.6
2.0
t [µs]


c
0
-1
-2
-3
I [mA]
0.0
0.2
0.4
0.6
0.8
1.0
t [µs]



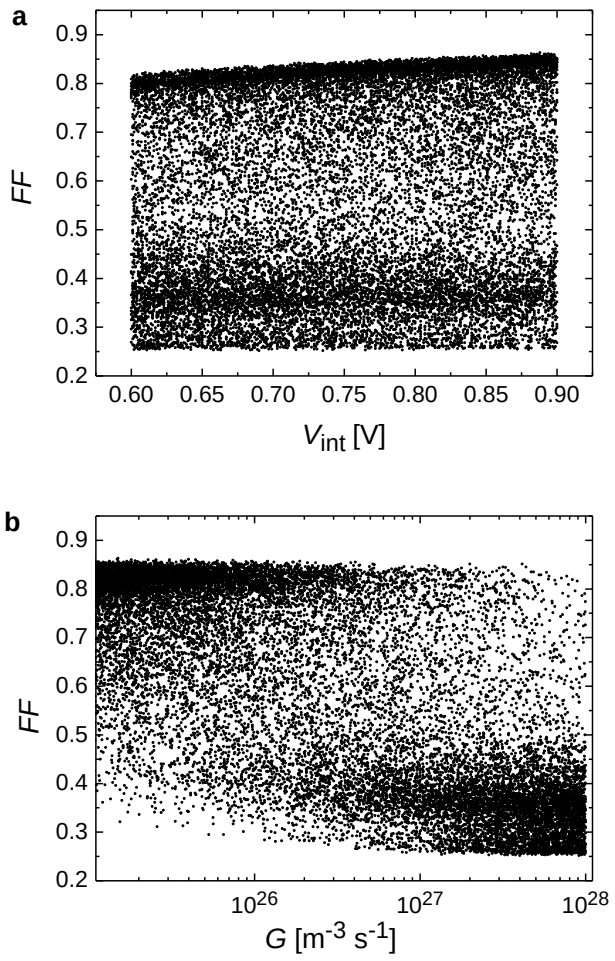
Supplementary Figure 5: TDCF transients of the polymer:polymer devices: P3HT:P(NDI2OD-T2) **(a)**, P3HT:P(PDI2OD-T2) **(b)**, POPT:P(NDI2OD-T2) **(c)**, POPT:P(PDI2OD-T2) **(d)**. The symbols represent experimental data, the solid lines represent fits with a numerical transient drift-diffusion simulation[3-5].

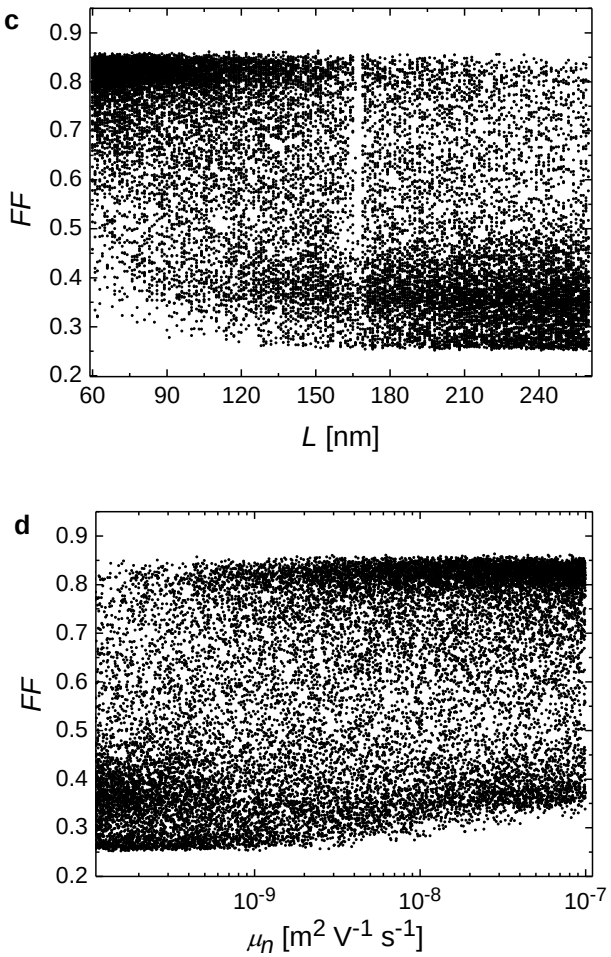


Supplementary Figure 6: Delay dependent total (Q_{tot}, black squares), collection (Q_{coll}, red full circles) and pre-charge (Q_{pre}, red empty circles) for P3HT:P(PDI2OD-T2) (a), POPT:P(NDI2OD-T2) (b) and POPT:P(PDI2OD-T2) (c). A pre-bias close to the maximum power point of each solar cell has been applied. The bimolecular recombination coefficients γ has been extracted from the fit of Q_{coll} with the equation[2]

$$Q_{coll}(t_D+\Delta t)=Q_{coll}(t_D)-[Q_{pre}(t_D+\Delta t)-Q_{pre}(t_D)]-\frac{\gamma}{eAd}[Q_{coll}^2(t_D)+2Q_{coll}(t_D)Q_{bg}]\Delta t \qquad (1)$$

Here, A and d are the device area and thickness, Q_{bg} is the background charge that arises due to dark injection from the contacts at forward bias.





Supplementary Figure 7: *FF* vs V_{int} (**a**), *G* (**b**), *L* (**c**) and μ_n (**d**) for the simulated data.

Supplementary Note 1 - Carrier densities at the contacts

In the case of thermal equilibrium at the contacts, it is assumed that the electron and hole density at the cathode (x=0) are equal to

$$n(0) = N_{cv} \tag{2}$$

$$p(0) = N_{cv} \exp\left(-\frac{E_g^{eff}}{kT}\right), \tag{3}$$

where N_{cv} is the density of available states [REFKoster2005], and E_g^{eff} is $LUMO_A$ - $HOMO_D$. At the anode the densities are given by

$$n(L) = N_{cv} \exp\left(-\frac{E_g^{eff}}{kT}\right) \tag{4}$$

$$p(L) = N_{cv} \tag{5}$$

In Ref. 6 it is assumed that $N_{cv} = 2.5 \times 10^{25}$ m^{-3}. If there is 1 hop site per 1.5 nm, then $N_{cv} = 3 \times 10^{26}$ m^{-3}.

In the case of near-zero surface recombination, the boundary conditions on $p(0)$ and $n(L)$ are replaced by the requirement that the hole, respectively, electron current densities are zero at cathode and anode. This is done by assuming

$$J_{n(p)} = qS_{np}(n(p) - n(p)_{eq}) \tag{6}$$

where S_{np} is the surface recombination velocity, where $n(p)_{eq}$ is the equilibrium electron (hole) density[5]. Near-zero recombination velocity is achieved by setting $S_{n,p} = 10^{-4}$ m/s.

Supplementary References

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5. Kniepert, J., Lange, I., van der Kaap, N. J., Koster, L. J. A. & Neher, D. A conclusive view on charge generation, recombination, and extraction in as-prepared and annealed P3HT:PCBM blends: combined experimental and simulation work. *Adv. Energy Mater.* **4,** 1301401 (2014).

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