Investigating the Influence of Charge Transport on the Performance of PTB7:$PC_{71}BM$ based Organic Solar Cell

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Figure S1: Ideality Factor: The ideality factor n is determined from the slope of the open circuit voltage (V_{OC}) versus ln (IPL) graph as

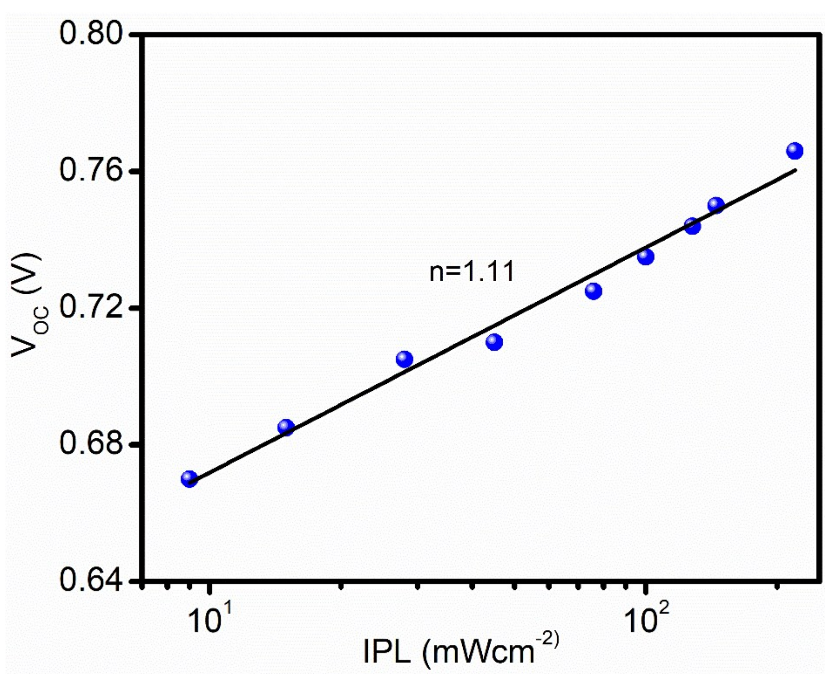


Figure S2: Shockley model; fit (solid lines) of the experimental data from Fig. 2a (symbols) by an Shockley diode model (For the comparison with charge transport model fitting plotted as in Fig 2a)

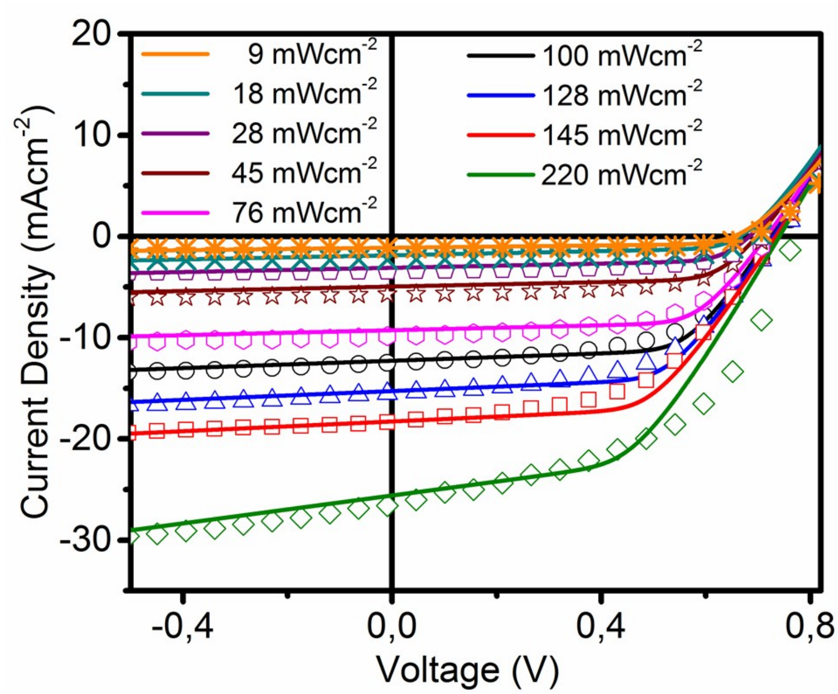


Table S1: Comparison between derived performance parameters by Shockley model and Charge transport model with experimental data at IPL 100 mWcm^{-2}

	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
Experimental	12.52	0.725	56.7	5.14
Shockley Model	12.27	0.72	64.7	5.72
Charge Transport Model	12.61	0.728	56.4	5.18

Figure S3: Plot of internal voltage versus external voltage calculated using Eq. (S4) this plot explains the variation of conductivity plotted in Figure 3b.

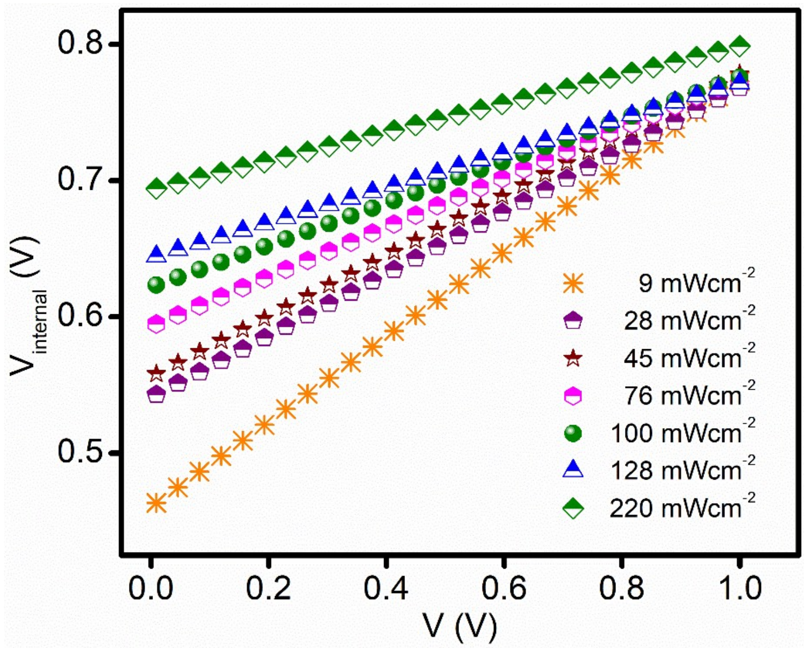


Figure S4: Behavior of α with mobility variation for different induced recombination factors

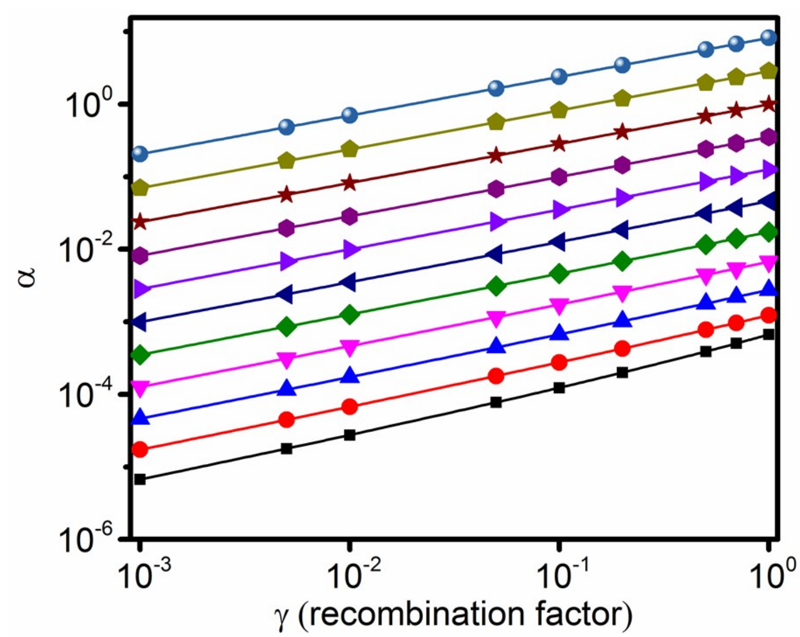


Figure S5: FF and (b) PCE in a wide range of variation effective mobility for different induced recombination factors

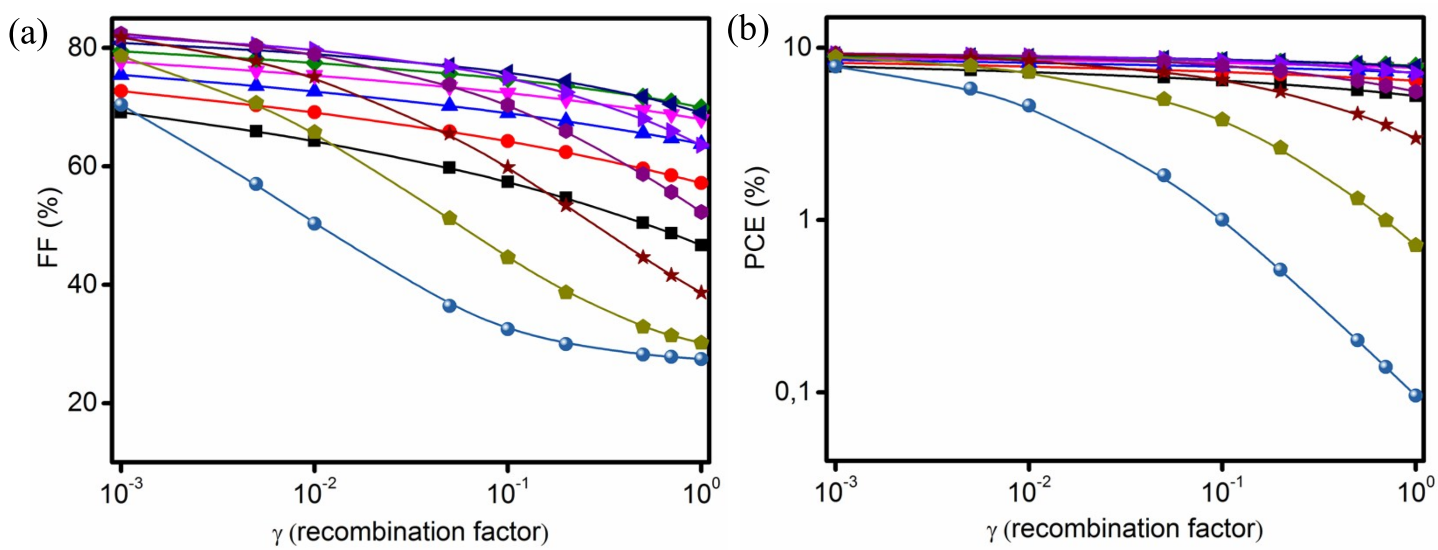


Figure S6. Plot of k_r versus mobility variation for different induced recombination factors

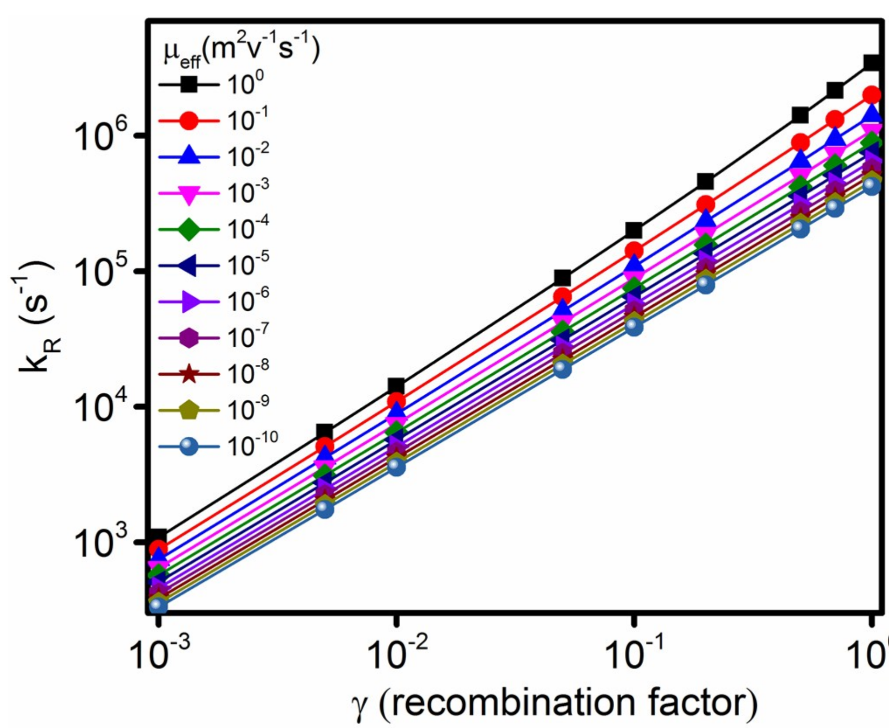
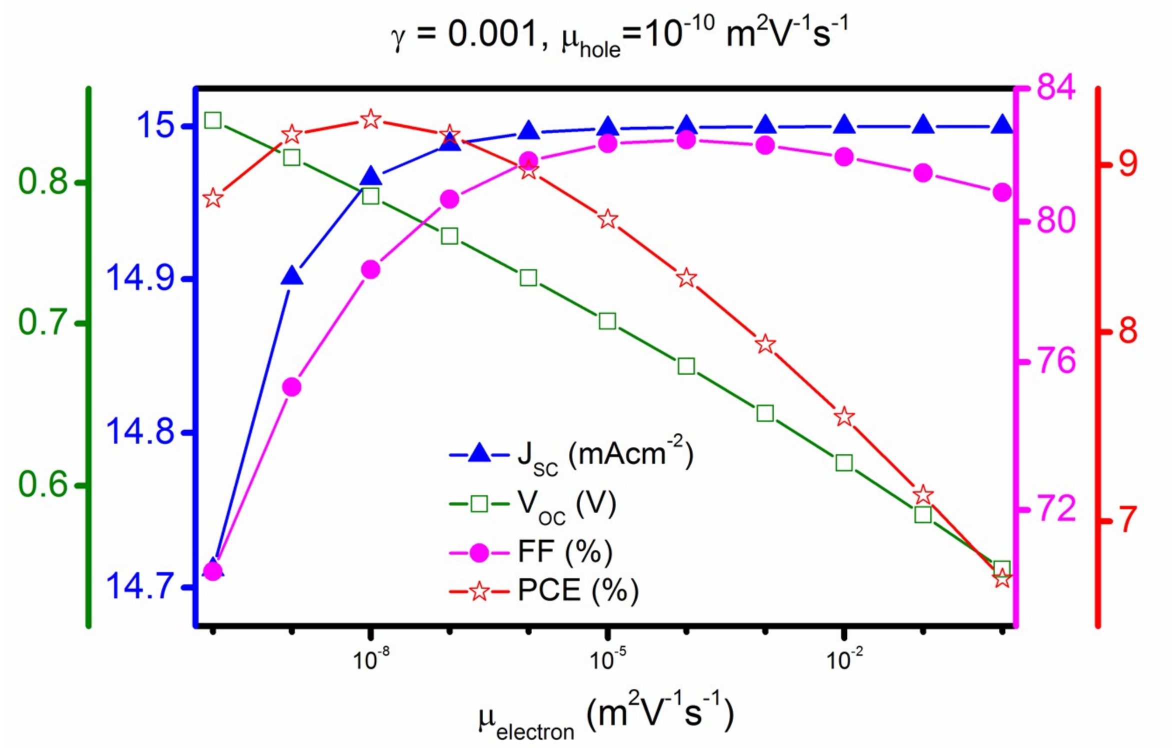


Figure S7: Plot of performance parameters versus electron mobility ($\mu_{electrone}$) variation for constant γ and hole mobility ((μ_{hole})



Note 1:

The transport limited photovoltaic response can be described in terms of the quasi - Fermi level splitting by replacing external voltage with internal voltage ($V_{internal}$) through [1],

$$V_{internal} = V - \left(\frac{LJ}{\sigma}\right) \tag{S1}$$

The electrical conductivity σ depends on the position of quasi-Fermi level which is defined by [1],

$$\sigma = 2q\mu_{eff} N_i \exp\left(\frac{qV_{internal}}{2k_B T}\right) \tag{S2}$$

Therefore, a closed form expression of the J-V curve under transport limited condition can be derived using well known relations, $V_{OC} = \frac{k_B T}{q} \ln\left(\frac{J_G + J_o}{J_o}\right)$ with the assumption $J_0 << J_G$ [2],

$$J = J_G \left\{ \exp\left[\frac{q}{k_B T} \left(V_{internal} - V_{OC} \right) \right] - 1 \right\} \tag{S3}$$

So, we can rewrite the Eq. (S1) as,

$$V = V_{internal} + \left(\frac{LJ_G}{\sigma} \left\{ \exp\left[\frac{q}{k_B T} \left(V_{internal} - V_{OC} \right) \right] - 1 \right\} \right)$$

$$= V_{internal} + \left(\frac{LJ_G}{2q\mu_{eff} N_i} \exp\left(-\frac{qV_{internal}}{2k_B T} \right) \left\{ \exp\left(\frac{qV_{internal}}{k_B T} \right) \exp\left(-\frac{qV_{OC}}{k_B T} \right) - 1 \right\} \right)$$

$$= V_{internal} + \left(\frac{LJ_G}{2q\mu_{eff} N_i} \left\{ \exp\left(\frac{qV_{internal}}{2k_B T} \right) \exp\left(-\frac{qV_{OC}}{k_B T} \right) - \exp\left(-\frac{qV_{internal}}{2k_B T} \right) \right\} \right)$$

$$= V_{internal} + \left(\frac{LJ_G}{2q\mu_{eff} N_i} \exp\left(-\frac{qV_{OC}}{2k_B T} \right) \left\{ \exp\left(\frac{qV_{internal}}{2k_B T} \right) \exp\left(-\frac{qV_{OC}}{2k_B T} \right) - \exp\left(-\frac{qV_{internal}}{2k_B T} \right) \exp\left(\frac{qV_{OC}}{2k_B T} \right) \right\} \right)$$

$$= V_{internal} + \left\{ \frac{LJ_G}{2q\mu_{eff} N_i} \exp\left(-\frac{qV_{OC}}{2k_B T} \right) 2\sinh\left(\frac{q}{2k_B T} \left(V_{internal} - V_{OC} \right) \right) \right\}$$

$$= V_{internal} + \left\{ \frac{LJ_G}{2q\mu_{eff} N_i} \exp\left(-\frac{qV_{OC}}{2k_B T} \right) \frac{q}{k_B T} \left(V_{internal} - V_{OC} \right) \right\} \quad \text{(Using the simplification } \sinh(x) \to x \text{)}$$

$$= V_{internal} + \alpha \left(V_{internal} - V_{OC} \right) \tag{S4}$$

where,

$$\alpha = \frac{J_G L}{2k_B T \mu_{eff} N_i} \exp\left(\frac{-qV_{OC}}{2k_B T} \right) \tag{S5}$$

Inserting the value from Eq. (S4) into Eq. (2) leading finally [2],

$$J = J_G \left\{ \exp\left(\frac{q\left(V - V_{OC} \right)}{\left(1 + \alpha \right) k_B T} \right) - 1 \right\} \tag{S6}$$

As we know that at open circuit condition V = V_{int} = V_{OC}. Using this condition, Equation 2 leads to well- known expression $V_{OC} = \frac{k_B T}{q} \ln\left(\frac{J_G}{J_0}\right)$. This is reasonable because at open circuit the current density is zero and transport issues are irrelevant.

Finally, putting the value of $\exp\left(-\frac{qV_{OC}}{k_B T}\right) = \frac{J_0}{J_G}$, where $J_0 = qdk_L N_i^2$, α can be rewritten as,

$$\alpha = \frac{qL^2 \sqrt{k_L G}}{2\mu_{eff} k_B T} \tag{S7}$$

This equation relates α to the charge carrier concentration, recombination coefficient, layer thickness and mobility. If we take G to be proportional to IPL and assume all remaining parameter as a constant, Eq. (S7) can be derived as function of IPL as follow,

$$\alpha = X\sqrt{(k_L)(IPL)} \tag{S8}$$

Here, X is a physical constant taken for all remaining parameters $\left(= \frac{qL^2}{2\mu_{eff} k_B T}\right)$.

Also, Similar equation as Eq. (S7) has been derived by bartesaghi et al. by relating recombination and extraction rate at short circuit condition given as [3],

$$\theta = \frac{\gamma k_L G L^4}{\mu_{eff} V_{internal}^2} = \frac{k_R}{k_{sep}} \tag{S9}$$

Comparing Eq. (S7) and Eq. (S9), Neher et al. yields a relation between α and θ [2].

$$\theta = \left(\frac{qV_{internal}\alpha}{2k_B T}\right)^2 \tag{S10}$$

Here, we derive the relationship between the dependence of electrical performance parameter and θ to understand the recombination process using above equations. In order to qualitatively understand the *J-V* characteristics, mechanism of photo-generated charge carrier dissociation in terms of probability has derived as a function of k_r and k_{sep} which is given as [4]:

$$P = \frac{k_{sep}}{k_{sep} + k_R} \tag{S11}$$

Substituting the value of θ from Eq. S9, *P* can be rewritten as,

$$P = \frac{1}{1 + \left(\frac{qV_{internal}\alpha}{2k_B T} \right)^2} = \frac{4\left(k_B T\right)^2}{\left(1 + \left(V_{internal}\alpha\right)^2\right)q^2} \tag{S12}$$

References

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