Exciton Delocalization Incorporated Drift-Diffusion Model for Bulk-Heterojunction Organic Solar Cells

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Supporting Information

This supplementary material offers the computational method used in solving the exciton delocalization incorporated drift-diffusion model.

In this model, we used the following equations:

$$\nabla \cdot (\varepsilon \nabla \varphi) = -q(p - n) \tag{S1}$$

$$\frac{\partial n}{\partial t} = \eta_d G + \frac{1}{q}\nabla \cdot (q\mu_n n E_n + qD_n \nabla n) + k_d X_l - R(n,p) \tag{S2}$$

$$\frac{\partial p}{\partial t} = \eta_d G - \frac{1}{q}\nabla \cdot (q\mu_p p E_p - qD_p \nabla p) + k_d X_l - R(n,p) \tag{S3}$$

$$\frac{\partial X_l}{\partial t} = (1-\eta_d)G + \nabla \cdot (D_X \nabla X_l) - k_d X_l - \frac{X_l}{\tau_f} + \eta_s R(n,p) \tag{S4}$$

where the physical explanations of all the parameters are described in the manuscript. Here, we will present the numerical method to discretize the above partial differential equation set. We used the Scharfetter-Gummel scheme in the spatial domain and the semi-implicit strategy in the temporal domain [1, 2]. The one-dimensional discretized forms of Eqs. (S1) - (S4) are respectively given by:

$$\begin{aligned}\frac{1}{\Delta y^2}\varepsilon_{i+1/2}\varphi_{i+1}^{m+1} - \left[\frac{2}{\Delta y^2}\left(\varepsilon_{i+1/2} + \varepsilon_{i-1/2}\right) + \frac{n_i^m + p_i^m}{U_t}\right]\varphi_i^{m+1} + \\ \frac{1}{\Delta y^2}\varepsilon_{i-1/2}\varphi_{i-1}^{m+1} = -q\left(p_i^m - n_i^m\right) - \frac{n_i^m + p_i^m}{U_t}\varphi_i^m\end{aligned} \tag{S5}$$

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$$\left[\frac{1}{\Delta t}+D_{n,i+1/2}B\left(\frac{\varphi_{n,i}^{m+1}-\varphi_{n,i+1}^{m+1}}{U_t}\right)+D_{n,i-1/2}B\left(\frac{\varphi_{n,i}^{m+1}-\varphi_{n,i-1}^{m+1}}{U_t}\right)\right]n_i^{m+1}$$
$$-D_{n,i+1/2}B\left(\frac{\varphi_{n,i+1}^{m+1}-\varphi_{n,i}^{m+1}}{U_t}\right)n_{i+1}^{m+1}-D_{n,i-1/2}B\left(\frac{\varphi_{n,i-1}^{m+1}-\varphi_{n,i}^{m+1}}{U_t}\right)n_{i-1}^{m+1}$$
$$=\frac{1}{\Delta t}n_i^m+\eta_d G-R\left(n_i^m,p_i^m\right)+k_{d,i}X_{l,i}^m \tag{S6}$$

$$\left[\frac{1}{\Delta t}+D_{p,i+1/2}B\left(-\frac{\varphi_{p,i}^{m+1}-\varphi_{p,i+1}^{m+1}}{U_t}\right)+D_{p,i-1/2}B\left(-\frac{\varphi_{p,i}^{m+1}-\varphi_{p,i-1}^{m+1}}{U_t}\right)\right]p_i^{m+1}$$
$$-D_{p,i+1/2}B\left(-\frac{\varphi_{p,i+1}^{m+1}-\varphi_{p,i}^{m+1}}{U_t}\right)p_{i+1}^{m+1}-D_{p,i-1/2}B\left(-\frac{\varphi_{p,i-1}^{m+1}-\varphi_{p,i}^{m+1}}{U_t}\right)p_{i-1}^{m+1}$$
$$=\frac{1}{\Delta t}p_i^m+\eta_d G-R\left(n_i^m,p_i^m\right)+k_{d,i}X_{l,i}^m \tag{S7}$$

$$\left[\frac{1}{\Delta t}+\frac{D_{X,i+1/2}+D_{X,i-1/2}}{\Delta y^2}+k_{d,i}+\frac{1}{\tau_f}\right]X_{l,i}^{m+1}-\frac{D_{X,i+1/2}}{\Delta y^2}X_{l,i+1}^{m+1}-$$
$$\frac{D_{X,i-1/2}}{\Delta y^2}X_{l,i-1}^{m+1}=\frac{1}{\Delta t}X_{l,i}^m+\left(1-\eta_d\right)G+\eta_s R\left(n_i^m,p_i^m\right) \tag{S8}$$

where the superscript m and subscript i indicate the discretized temporal and spatial steps, respectively. Meanwhile, in these equations, $U_t=\frac{k_BT}{q}$, $B(x)=\frac{x}{e^x-1}$, and the electron potential and hole potential are of the forms

$$\varphi_n=\varphi+\frac{X_i}{q}+\frac{k_BT}{q}\ln(N_c) \tag{S9}$$

$$\varphi_p=\varphi+\frac{X_i}{q}+\frac{E_g}{q}-\frac{k_BT}{q}\ln(N_v) \tag{S10}$$

where X_i is the electron affinity, E_g is the bandgap, and $N_{c,v}$ indicates the effective density of states.

For every iteration in the time domain, the Poisson's equation will be solved first, and then the exciton diffusion-dissociation equation, electron and hole drift-diffusion equations will be solved in turn. The iteration will continue until a steady solution is obtained. The convergence condition for the steady solution calculation is given by $\left|\frac{J^{m+1}-J^m}{J^m}\right|<10^{-4}$.

As shown in Fig. S1, using this numerical method, our theoretical result has a good agreement with the result extracted from the literature [L. J. A. Koster et al., Phys. Rev. B 72: 085205, 2005] by using the same exciton model in the literature. Thus, the numerical method adopted is convincing to obtain the steady solution of polymer solar cells including current density-voltage characteristics. Additionally, by setting a time-dependent generation rate, the numerical method also can be utilized to simulate transient photovoltage (TPV) or transient photocurrent (TPC) of polymer solar cells, where the excitation is not sunlight but a short laser pulse.

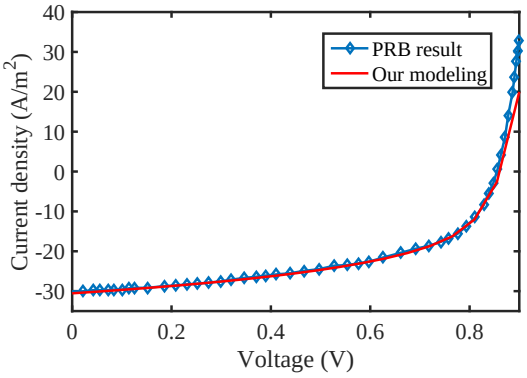

Figure S1: The current density-voltage characteristics of a polymer bulk-heterojunction solar cell. The simulation parameter can be found in [Phys. Rev. B 72: 085205, 2005.]

References

[1] S. Selberherr, Analysis and Simulation of Semiconductor Devices (Springer, 1984).

[2] W. E. I. Sha, W. C. H. Choy, Y. M. Wu and W. C. Chew, Opt. Express **20**, 2572 (2012).