

# Supporting Information

## Modulation of Molecular Orientation Enabling High Photovoltaic Performance of Block Copolymer Nanostructures

*Zhanwen Xu, Jiaping Lin,\* Liangshun Zhang, Xiaohui Tian and Liquan Wang\**

*Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrafine Materials of Ministry of Education, State Key Laboratory of Bioreactor Engineering, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China*

## Contents

<b>1. DPD Method for Determining the Self-Assembled Morphologies</b> .....	S3
<b>2. Theoretical Methods for Determining the Photovoltaic Properties</b> .....	S5
2.1 Governing Equations.....	S5
2.2 Boundary Conditions .....	S6
2.3 Parameters .....	S7
<b>3. Effect of Variations in Structural Parameters on Performance Enhancement</b> .....	S9

## 1. DPD Method for Determining the Self-Assembled Morphologies

The dissipative particle dynamics (DPD) method proposed by Hoogerbrugge and Koelman in 1992, was performed to investigate the self-assembled morphologies.<sup>S1</sup> In DPD method, a bead represents the center of mass of a group of monomers.<sup>S2-3</sup> The force acting on each bead includes non-bonded and bonded forces. The non-bonded force acting on a particle,  $\mathbf{f}_\alpha$ , is a pairwise additive force, consisting of the conservative force ( $\mathbf{F}_{\alpha\beta}^C$ ), dissipative force ( $\mathbf{F}_{\alpha\beta}^D$ ), and random force ( $\mathbf{F}_{\alpha\beta}^R$ ). The conservative force is a soft repulsion taking the form as

$$\mathbf{F}_{\alpha\beta}^C = a_{\alpha\beta} \sqrt{\omega(r_{\alpha\beta})} \hat{\mathbf{r}}_{\alpha\beta} \quad (\text{S-1})$$

where  $a_{\alpha\beta}$  is the maximum repulsive interaction between particles  $\alpha$  and  $\beta$ ,  $\mathbf{r}_{\alpha\beta} = \mathbf{r}_\alpha - \mathbf{r}_\beta$ ,  $r_{\alpha\beta} = |\mathbf{r}_{\alpha\beta}|$ ,  $\hat{\mathbf{r}}_{\alpha\beta} = \mathbf{r}_{\alpha\beta}/r_{\alpha\beta}$  and  $\omega(r_{\alpha\beta})$  is the weight function, given by

$$\omega(r_{\alpha\beta}) = \begin{cases} (1 - r_{\alpha\beta}/r_c)^2 & (r_{\alpha\beta} < r_c) \\ 0 & (r_{\alpha\beta} \geq r_c) \end{cases} \quad (\text{S-2})$$

where  $r_c$  ( $r_c=1.0$ ) is the cut-off radius. The dissipative force is a friction force that acts on the relative velocities of particles, defined as

$$\mathbf{F}_{\alpha\beta}^D = -\gamma \omega^D(r_{\alpha\beta}) (\hat{\mathbf{r}}_{\alpha\beta} \cdot \mathbf{v}_{\alpha\beta}) \hat{\mathbf{r}}_{\alpha\beta} \quad (\text{S-3})$$

and the random force, compensating the loss of kinetic energy due to the dissipative force, is defined as

$$\mathbf{F}_{\alpha\beta}^R = \sigma \omega^R(r_{\alpha\beta}) \theta_{\alpha\beta} \Delta t^{1/2} \hat{\mathbf{r}}_{\alpha\beta} \quad (\text{S-4})$$

where  $\mathbf{v}_{\alpha\beta} = \mathbf{v}_\alpha - \mathbf{v}_\beta$ ,  $\gamma$  is the friction coefficient,  $\sigma$  is the noise amplitude,  $\omega^D(r_{\alpha\beta})$  and  $\omega^R(r_{\alpha\beta})$  are weight functions vanishing for  $r > r_c$  that describe the range of the dissipative and random forces, and  $\theta_{\alpha\beta}$  is a randomly fluctuating variable with Gaussian statistics

$$\langle \theta_{\alpha\beta} \rangle = 0, \quad \langle \theta_{\alpha\beta}(t) \theta_{kl}(t') \rangle = (\delta_{\alpha k} \delta_{\beta l} + \delta_{\alpha l} \delta_{\beta k}) \delta(t - t') \quad (\text{S-5})$$

The system should satisfy the fluctuation-dissipation theorem and evolve to an equilibrium state corresponding to the canonical ensemble. Therefore, only one of  $\omega^D(r_{\alpha\beta})$  and  $\omega^R(r_{\alpha\beta})$  can be chosen arbitrarily and the other one is then fixed by the relation

$$\omega^D(r_{\alpha\beta}) = [\omega^R(r_{\alpha\beta})]^2 = \omega(r_{\alpha\beta}) \quad (\text{S-6})$$

And the values of parameters  $\gamma$  and  $\sigma$  are coupled by

$$\sigma^2 = 2\gamma k_B T \Delta t \quad (\text{S-7})$$

where  $k_B$  and  $T$  are the Boltzmann constant and temperature, respectively.

To modulate the molecular orientation of the block copolymers, an external electric field is applied during the self-assembly process. A dipole was set along the axis of the donor blocks, and thus the interaction between the electric field and dipoles can rotate the block copolymers.

## 2. Theoretical Methods for Determining the Photovoltaic Properties

### 2.1 Governing Equations

The drift-diffusion methodology used in our work consists of four self-consistent equations involving the electric potential  $\psi$ [V] and the charge carrier number densities  $e$ ,  $h$ ,  $X$  [ $\text{m}^{-3}$ ] of electrons, holes and excitons, respectively. These equations in steady state formula are as following, S4-6

$$\nabla \cdot [\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})] = -q[e(\mathbf{r}) - h(\mathbf{r})] \quad (\text{S-8})$$

$$\nabla \cdot [-\mu_e(\mathbf{r})e(\mathbf{r})\nabla\psi(\mathbf{r}) - \mathbf{D}_e(\mathbf{r})\nabla e(\mathbf{r})] = G_{eh}(\mathbf{r}) - R_{eh}(\mathbf{r}) \quad (\text{S-9})$$

$$\nabla \cdot [\mu_h(\mathbf{r})h(\mathbf{r})\nabla\psi(\mathbf{r}) - \mathbf{D}_h(\mathbf{r})\nabla h(\mathbf{r})] = G_{eh}(\mathbf{r}) - R_{eh}(\mathbf{r}) \quad (\text{S-10})$$

$$\nabla \cdot [\mathbf{D}_X(\mathbf{r})\nabla X(\mathbf{r})] = G_X(\mathbf{r}) + \frac{1}{4}R_{eh}(\mathbf{r}) - G_{eh}(\mathbf{r}) - R_d(\mathbf{r}) \quad (\text{S-11})$$

Equation (S8) is Poisson's equation relating the electrostatic potential to concentrations of charge carriers. In equation (S8),  $\psi(\mathbf{r})$  is the electrical penitential,  $\varepsilon(\mathbf{r})$  is the relative dielectric constant depending on the organic material at  $\mathbf{r}$ ,  $e(\mathbf{r})$  and  $h(\mathbf{r})$  are electron and hole density respectively. In equation (S9) and (S10),  $\mu_e(\mathbf{r})$  and  $\mu_h(\mathbf{r})$  are mobilities for electrons and holes, respectively. Charge carrier mobility is dependent on electrical field in Poole-Frenkel form  $\mu_i = \mu_{i0} \exp(\gamma\sqrt{|\mathbf{E}|})$  ( $i = e, h$ ).  $\mathbf{D}_e(\mathbf{r})$  and  $\mathbf{D}_h(\mathbf{r})$  are diffusion coefficients for electrons and holes respectively. The mobility  $\mu$  is approximately in Einstein relation with the diffusion coefficient  $D$ ,  $\mu_i = D_i/k_B T$  ( $i = e, h$ ), where  $k_B$  is the Boltzmann constant and  $T$  is the temperature. The exciton dissociation rate  $G_{eh}(\mathbf{r})$  is given by Onsager's theory for electrolyte dissociation,<sup>S7</sup>

$$G_{eh}(\mathbf{r}) = X(\mathbf{r}) \int_0^\infty k_D(\mathbf{E}(\mathbf{r}), a) F(a) da \quad (\text{S-12})$$

where  $a$  is the separation distance of hole-electron pair of excitons assumed to follow the Gaussian distribution  $F(a) = \frac{4a_0^2 a^2}{\pi^{1/2}} \exp(-a^2/a_0^2)$  ( $a_0$  is the maximum property separation distance of 1nm), and  $k_D(\mathbf{E}(\mathbf{r}), a)$  is the field-dependent dissociation rate constant derived by Braun,<sup>S8</sup>

$$k_D(\mathbf{E}(\mathbf{r}), a) = \frac{3\mu_{avg}q}{4\pi\epsilon a^3} \exp(-\Delta E/k_B T) \frac{J_1\left[2\sqrt{2}(-b)^{\frac{1}{2}}\right]}{2\sqrt{2}(-b)^{\frac{1}{2}}} \quad (\text{S-13})$$

where  $\mu_{avg}$  is the averaged mobilities of electrons and holes,  $\mathbf{E}(\mathbf{r})$  is electrical field which is calculated from negative gradient of position dependent electrical potential  $\psi(\mathbf{r})$ ,  $\Delta E$  is the binding energy of electron-hole pairs(excitons) minus the difference in electron affinity, and  $b = \frac{q^3|\mathbf{E}(\mathbf{r})|}{8\pi(\epsilon)k_B T}$ .

The carrier recombination rate  $R_{eh}(\mathbf{r})$  is described by a bimolecular recombination of the Langevin form as following,<sup>S4</sup>

$$R_{eh}(\mathbf{r}) = \frac{q(\mu_e + \mu_h)}{\epsilon} e(\mathbf{r})h(\mathbf{r}) \quad (\text{S-14})$$

In equation (S11),  $D_X(\mathbf{r})$  stands for exciton diffusion coefficient, and  $X(\mathbf{r})$  stands for exciton density. The function  $G_X(\mathbf{r})$  is for exciton generation events, which can be calculated from the formula as following,

$$G_X(\mathbf{r}) = \sum_i \phi_i(\nu_i) \alpha_i(\nu_i) \exp[\alpha_i(L_y - y)] \quad (\text{S-15})$$

Where  $\phi_i(\nu_i)$  represents incident photon flux, which is dependent on frequency ( $\nu_i$ ).<sup>S9</sup> The photon absorption coefficient is also frequency dependent, and it is assumed to have a Gaussian distribution against the frequency. The exciton decay rate  $R_d(\mathbf{r})$  is determined by the lifetime ( $\tau$ ) of exciton with the form,  $R_d(\mathbf{r}) = X(\mathbf{r})/\tau$ .  $D_X(\mathbf{r})$  is related with  $\tau$  and diffusion length  $l_d$  in the formula  $D_X(\mathbf{r}) = l_d^2/\tau$ .

To include the effect of molecular orientation on the photovoltaic performance, we extended the drift-diffusion equation by considering anisotropic characteristics in the mobility of excitons and charge carriers. In the extended formalism, the anisotropy of the mobility is determined by the order parameter and the inherent anisotropic characteristic of the donor-acceptor block copolymers. Thus, the mobilities of the charge carriers and excitons are described as anisotropic tensors.

## 2.2 Boundary Conditions

The boundary conditions in the  $x$  and  $z$  directions paralleling to electrodes are set as periodic for all

the equations above. The boundary conditions in the  $y$  direction perpendicular to electrodes are set as following equations,

$$\psi(x, L_{active}, z) - \psi(x, 0, z) = \frac{\phi_a - \phi_c}{q} - U_{appl} \quad (\text{S-16})$$

$$\begin{cases} e(x, 0, z) = N_0 \exp\left(-\frac{\phi_c - LUMO_A}{k_B T}\right) \\ J_{e, \hat{y}}(x, L_{active}, z) = 0 \end{cases} \quad (\text{S-17})$$

$$\begin{cases} J_{h, \hat{y}}(x, 0, z) = 0 \\ h(x, L_{active}, z) = P_0 \exp\left(-\frac{\phi_a - HOMO_D}{k_B T}\right) \end{cases} \quad (\text{S-18})$$

$$\begin{cases} J_{X, \hat{y}}(x, 0, z) = 0 \\ J_{X, \hat{y}}(x, L_{active}, z) = 0 \end{cases} \quad (\text{S-19})$$

where  $\phi_a$  and  $\phi_c$  are work functions of anode and cathode electrode,  $L_{active}$  is the thickness of active layer,  $LUMO_A$  is  $LUMO$  energy level of acceptor,  $HOMO_D$  is  $HOMO$  energy level of donor.  $N_0$  and  $P_0$  are number of energy states available for electron and holes, respectively. Equation (S-16) is the boundary condition for Poisson equation, while equations (S-17), (S-18), (S-19) are boundary conditions for continuity equations of electrons, holes and excitons, respectively. In these boundary condition equations, we have assumed there are no current of electrons across the anode and holes across the cathode, respectively. For excitons, a zero-flux boundary condition at the metal-semiconductor interfaces is assumed.

### 2.3 Parameters

The electrical parameters used in the photovoltaic calculations are listed in Table S1. Most of the parameters used here are typical for polymeric materials used in polymer photovoltaic cells.<sup>S10-12</sup>

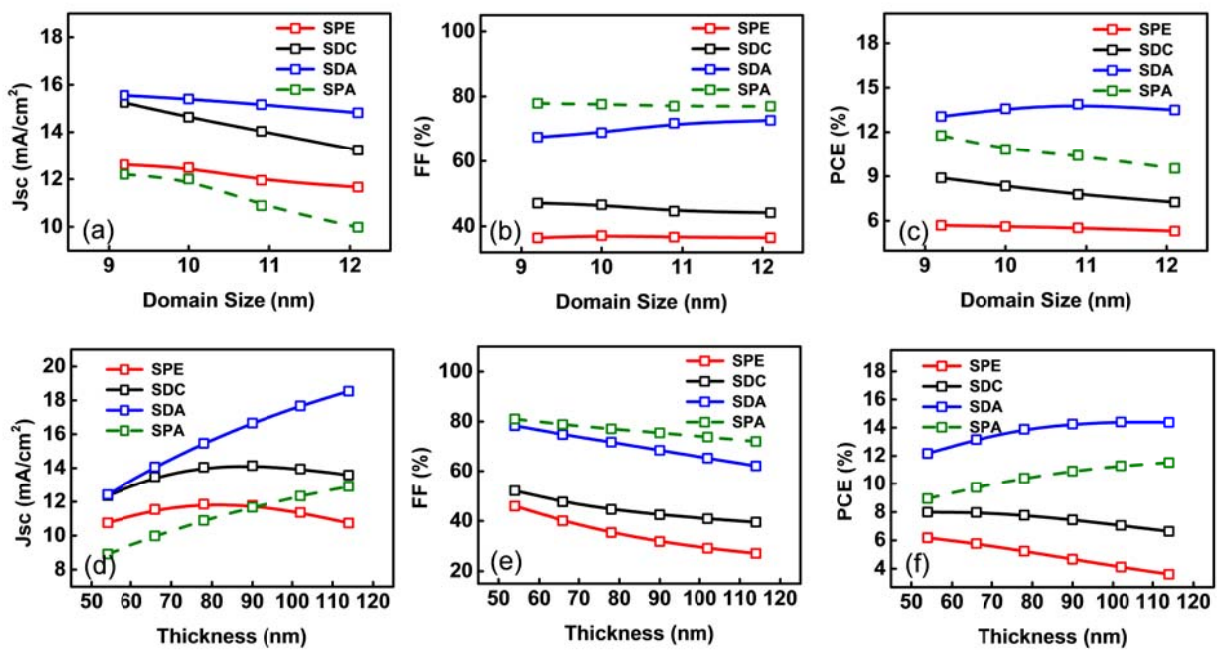
**Table S1** Parameters for drift-diffusion model.

Parameter	Symbol	Value
Isotropic Hole mobility(zero-field)	$\mu_{h0}$	$5 \times 10^{-9} m^2 V^{-1} s^{-1}$
Isotropic Electron mobility(zero-field)	$\mu_{e0}$	$5 \times 10^{-9} m^2 V^{-1} s^{-1}$
Field-dependent constant for hole mobility	$\gamma_h$	$2.4 \times 10^{-4} m^{1/2} V^{-1/2}$
Field-dependent constant for electron mobility	$\gamma_e$	$2.4 \times 10^{-4} m^{1/2} V^{-1/2}$
Exciton diffusion length	$l_d$	10 nm
Exciton lifetime	$\tau$	$10^{-9} s$
Donor HOMO	HOMOD	4.9 eV
Acceptor LUMO	LUMOA	3.5 eV
Cathode work function	$\phi_c$	3.7 eV
Anode work function	$\phi_a$	5.0 eV



### 3. Effect of Variations in Structural Parameters on Performance Enhancement

To further confirm the generality of our findings, we calculate the photovoltaic performance of **SPE**, **SDC**, **SDA** and **SPA** nanostructures with active layer thickness varied from ~50 nm to ~110 nm and domain size varied from ~9 nm to ~12 nm, respectively. The photovoltaic properties of these structures against active layer thickness are plotted in Figure S1. As can be seen, with the variation of the structural parameters, the **SDA** nanostructure always exhibits high  $J_{sc}$  and  $FF$  and then shows much higher efficiencies than the other nanostructures.



**Figure S1** Plots of  $J_{sc}$  (a, d),  $FF$  (b, e) and  $PCE$  (c, f) against the domain size and active layer thickness respectively for **SPE**, **SDC**, **SDA** and **SPA** nanostructures.

## References

- S1. Hoogerbrugge, P. J. and Koelman, J. M. V. A. Simulating Microscopic Hydrodynamic Phenomena with Dissipative Particle Dynamics. *Europhys. Lett.*, **1992**, 19 (3), 155.
- S2. Jiang, T.; Wang, L.; Lin, S.; Lin, J. and Li, Y. Structural Evolution of Multicompartment Micelles Self-Assembled from Linear A<sub>2</sub>B<sub>3</sub>C Triblock Copolymer in Selective Solvents. *Langmuir*, **2011**, 27 (10), 6440-6448.
- S3. Jiang, T.; Wang, L. and Lin, J. Mechanical Properties of Designed Multicompartment Gels Formed by A<sub>2</sub>B<sub>3</sub>C Graft Copolymers. *Langmuir*, **2013**, 29 (39), 12298-12306.
- S4. Gavin, A. B. and Nigel, C. Computer Simulation of Polymer Solar Cells. *Modell. Simul. Mater. Sci. Eng.*, **2007**, 15 (2), 13.
- S5. Barker, J. A.; Ramsdale, C. M. and Greenham, N. C. Modeling the Current-Voltage Characteristics of Bilayer Polymer Photovoltaic Devices. *Phys. Rev. B*, **2003**, 67 (7), 075205.
- S6. Buxton, G. A. and Clarke, N. Predicting Structure and Property Relations in Polymeric Photovoltaic Devices. *Phys. Rev. B*, **2006**, 74 (8), 085207.
- S7. Onsager, L. Initial Recombination of Ions. *Phys. Rev.*, **1938**, 54 (8), 554-557.
- S8. Braun, C. L. Electric Field Assisted Dissociation of Charge Transfer States as a Mechanism of Photocarrier Production. *J. Chem. Phys.*, **1984**, 80 (9), 4157-4161.
- S9. Fahrenbruch, A. and Bube, R., *Fundamentals of Solar Cells*. Academic Press: New York, 1983.
- S10. Ray, B.; Nair, P. R. and Alam, M. A. Annealing Dependent Performance of Organic Bulk-Heterojunction Solar Cells: A Theoretical Perspective. *Sol. Energy Mater. Sol. Cells*, 2011, 95(12), 3287-3294.
- S11. Min Nam, Y.; Huh, J. and Ho Jo, W. Optimization of Thickness and Morphology of Active Layer for High Performance of Bulk-Heterojunction Organic Solar Cells. *Sol. Energy Mater. Sol. Cells*, 2010, 94 (6), 1118-1124.
- S12. Hufnagel, M.; Fischer, M.; Thurn-Albrecht, T. and Thelakkat, M. Influence of Fullerene Grafting Density on Structure, Dynamics, and Charge Transport in P3HT-b-PPC<sub>61</sub>BM Block Copolymers. *Macromolecules*, 2016, 49 (5), 1637-1647.