Supplementary information

The relative importance of domain size, domain purity and interfaces between domains to the performance of organic photovoltaic devices: How best to optimize the morphology.

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Additional details regarding Cahn-Hilliard morphology generation

We use the Cahn-Hilliard theory to model the spatio-temporal evolution of the blend composition. The equation of motion for the local volume fraction of donor, ϕ, can be written in the dimensionless form as,

$$\frac{\partial \phi(\mathbf{x}, \tau)}{\partial \tau} = \nabla_x^2 \left[\frac{1}{N_D(\chi - \chi_S)} \ln \phi - \frac{1}{N_A(\chi - \chi_S)} \ln(1 - \phi) - \frac{2\chi\phi}{(\chi - \chi_S)} \right.$$

$$\left. + \frac{2\phi - 1}{36\phi^2(1 - \phi)^2} (\nabla\phi)^2 - \frac{1}{18\phi(1 - \phi)} \nabla^2\phi \right]$$

where N_A and N_D are the degrees of polymerization of the donor and acceptor phases, χ is the Flory – Huggins interaction parameter, with χ_S its value on the spinodal curve. When $\chi > \chi_S$ the blend will undergo phase separation with diffusive dynamics described by the above equation. The first 3 terms arise from assuming that the free energy of the blend is described by the Flory – Huggins theory[1, 2]. The 4th and 5th terms on the right hand side arise from the energetic cost of gradients in composition. When $N_A = N_D = N$, which for simplicity will be the case in this work, the dimensionless time and the space variables, τ and $\mathbf{x}$, are related to real time, t, and space, $\mathbf{r}$, through $\mathbf{x} = (|\chi - \chi_S|)^{1/2} \mathbf{r}/l$ and $\boldsymbol{\tau} = ND(\chi - \chi_S)^2 t/l^2$. Hence the blend is characterized by the additional parameters, D, the mutual diffusion coefficient and l, the length of a statistical segment.

We solve the Cahn-Hilliard equation with periodic boundary conditions on a 128 x 128 x 127 cubic lattice using a finite difference scheme with reduced time and space steps of $\Delta\tau = 1.25 \times 10^{-4}$ and $\Delta x = 0.5$. We use $\chi = 0.0654$ and $N = 50$, unless otherwise specified, such that $\chi_S = 0.04$. Initially the composition of the blend is uniform throughout the lattice, such that at $\tau = 0$, $\phi(\mathbf{x}, 0) = 0.5 + \delta$, where δ is a uniformly distributed random variable in the range $-0.01 < \delta < 0.01$. These parameters are chosen to ensure we mimic a deep quench into the two-phase region, which is expected to give rise to nanoscale morphologies typically observed in photovoltaic polymer blends.

Additional details regarding Monte Carlo charge transport simulations

Each polymer site is randomly assigned a value of energetic disorder from a Gaussian-distributed density of states of width σ. Photoinjection is simulated by creating excitons at random sites within the device at a rate which corresponds to monochromatic light with a wavelength of 500nm at an incident flux of 100mW/cm^2, therefore approximating AM1.5 conditions. Excitons may hop between sites of the same polymer type via Förster transfer with a rate:

$$k_{ij}^F = \frac{1}{\tau_{PL}} \left(\frac{r_F}{r_{ij}} \right)^6.$$

Where r_{ij} is the separation between the two sites, r_F is the Förster radius and τ_{PL} is the photoluminescence lifetime. Excitons may decay with a rate τ_{PL} or dissociate into an electron-hole pair on reaching an interface between neighboring donor and acceptor sites. Electrons and holes may hop to nearest neighbor sites of the appropriate type at a rate given by a Marcus expression,

$$k_{ij} = v_o \exp \left[-\frac{\left(\Delta E_{ij} + E_r \right)^2}{4 E_r k_B T} \right].$$

Where v_0 is the hop prefactor, ΔE_{ij} is the difference in energy between the two sites, and E_r is the reorganization energy. Here, ΔE_{ij} includes the potential at each site due to all other charges and the applied electric field applied in the z direction. Contacts are selective for the corresponding carrier type. Holes and electrons on adjacent sites may recombine at a constant rate $k_{recombination}$. When deciding the next behavior for a carrier or exciton, the time to each possible event is calculated by,

$$\tau = \frac{1}{k} \ln(X).$$

Where κ is the rate of the process. Of the possible events that may occur, the one with the shortest time is chosen. We use the First Reaction Method to order the events within the simulation and to manage computational burden[3]. Simulation parameters are listed in table S1 below.

Note that the configuration of energetic disorder is different for each of the simulation nodes, which in all cases was greater than 10 nodes and in most cases was 15 nodes. Simulations proceed until at least 5000 charge carriers have been collected.

Quantity	Simulation value
Photoabsorption coefficient	1.3×10^4 cm^{-1}
Photoinjection rate	6.27×10^6 s^{-1}
Dielectric constant	3
Photoluminescence lifetime τ_{PL}	500 ps
Forster radius R_F	4.3 nm
Carrier hop prefactor v_o	1×10^{11} s^{-1}
Reorganization energy E_r	0.25eV
Width of Gaussian density of states σ	100 meV
Carrier recombination rate $k_{recombination}$	1×10^7 s^{-1}

Table S1 – Parameters used in the Monte Carlo simulations.

Note that these parameters are similar to those used elsewhere[3], as these give realistic EQEs and mobilities in polymer-polymer devices.
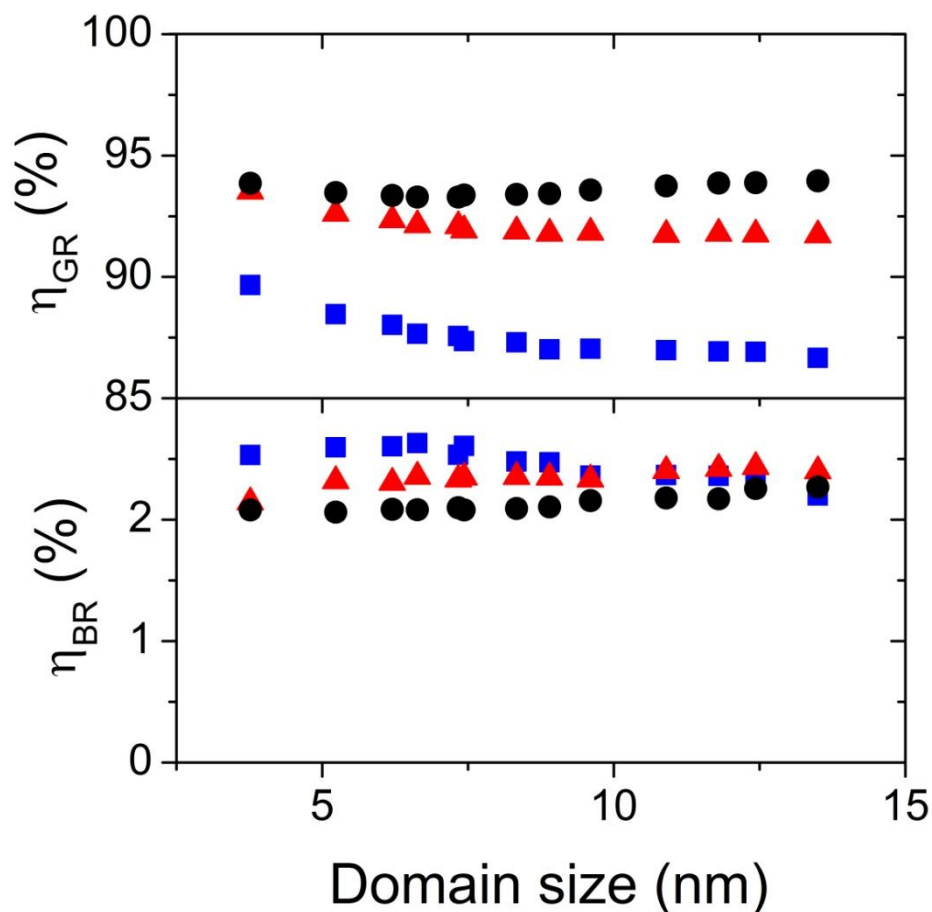
Figure S2: Simulated geminate recombination efficiency (top) and bimolecular recombination efficiency (bottom) as a function of domain size for morphologies as interpreted by the CI (black circles), DII (red triangles) and SII (blue squares) algorithms. These data correspond to those in Figure 3 of the main text.

References

1.   Flory, P. J., *J. Chem. Phys.* **1941,** *9*, 660.
2.   Huggins, M. L., *J. Am. Chem. Soc.* **1942,** *64*, 1712.
3.   Groves, C.; Kimber, R. G. E.; Walker, A. B., *J. Chem Phys,* **2010,** *133*, 144110.