Supplementary Information to "Quantifying organic solar cell morphology: A computational study of three-dimensional maps"

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1 Morphology measurement methods

Tilt series of the films were acquired by a JEOL 2100F microscope 200 kV using DigitalMicrographTM (Gatan) with a tomography plugin capable of dynamic focusing (keeping the film in focus when tilted). Images were taken at one degree intervals using a high-tilt tomography holder (Fischione) from a minimum of +65 to -65 degrees. The images were then aligned manually using IMOD.¹

3D reconstructions were done using custom code in MATLAB implementing the DART algorithm. This algorithm uses discrete gray levels in the reconstruction volume to represent different materials. This is a physically relevant representation if the materials contain a consistent composition and density. The reconstruction process consists of finding the number and value of gray levels which results in a reconstruction which minimizes projection error (minimize the difference between the forward-projected reconstruction and the original tilt-series). The thresholds and gray levels are manipulated until the best possible fit to the data is found. In this way, a reconstruction is thresholded into separate materials (the three phases, P3HT, mixed, and fullerene-rich) which accurately matches the original images. No subjective segmentation is necessary, thus ensuring that the reconstructed morphology is not dependent on an assumed threshold.

2 Graph-based morphology quantification for three phase morphology

Details of the method can be found elsewhere^{3,4}. Here, we give a brief overview of the method for completeness. In our approach, we use an equivalence between digitized morphology and graph, as shown in the Figure 1. Specifically, all imperative information in a digitized morphology can be represented using an appropriately defined weighted, undirected graph. In such a graph, each pixel (or voxel) becomes a graph vertex with a label denoting its phase (white represents acceptor material, black represents donor material, and gray represents the mixed phase). Each vertex is connected to its neighboring vertices through edges whose weight depend on the distance between the vertices. Five meta vertices are added to the graph and represent anode, cathode, and three types of interface (between black/white, black/gray and white/gray). We use green, dark green and light green colors to label interfaces between donor/acceptor phases, donor/mixed phases and acceptor/mixed phases, respectively.

Due to such a representation, we gain the ability to use standard and efficient algorithms from graph theory to extensively characterize morphology. Specifically, many questions on morphology characterization can be recast as questions on the structural properties of an appropriately defined graph. In particular, the

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Fig. 1 Equivalent between morphology sandwiched between electrodes and weighted, undirected, labelled graph.

following fundamental graph questions occur repeatedly in the context of polymer blends for organic solar cells:

- Identifying distinct components in a graph: These correspond to the number of distinct donor, acceptor or mixed domains, and their connectivity to the electrodes. This information is important for charge transport, because only these domains with direct connection to the relevant electrode can contribute to current generation. We use basic algorithm from graph theory to find connected components in the graph⁵.
- Computing shortest distances between a pair of vertices in a graph. This is the core feature of our approach. Since we are mostly interested in transport properties, distances are the basic quantities of our interest. For example, in order to asses exciton diffusion characteristics, we find the shortest distances between any black vertices (corresponds to donor phase) to the donor/mixed phase interface (dark green vertex). To identify shortest distances between source vertex (dark green vertex representing respective interface) and all black vertices in the graph allowing, we use Dijkstra algorithm^{5,6}. When identifying shortest distances, only edges that connects black-black vertices and black-dark green vertices are considered. This assumption mimics the path exciton takes to reach the interface and reflects the energetic favorable path.

Based on the distances and connectivity data we construct physics-based morphology descriptors. For example having identified the shortest distances from any black voxel to the nearest interface (dark green vertex) as described above, we are able to build the exciton diffusion descriptors, as explained in the next section.

3 Quantifying exciton diffusion

The current practice in the OPV community (in the context of exciton diffusion/dissociation) is simply to compare average domain sizes with the exciton diffusion length, L_d . The domain size is usually extracted from the power spectral density of morphology. The argument then is that if the average domain



Fig. 2 Comparison between two shapes with identical characteristic sizes: (top) circle and (bottom) stripe. Both domains have the same characteristic length scale: 10nm (radius of circle and half-width of stripe). In both cases, 100% of domain is distributed within a distance of 10nm from the interface. However, when histogram of shortest distances to the interface (middle column) are plotted, differences between shapes are apparent.

size is smaller than L_d , a majority of the excitons generated have a high probability of reaching the interface. When the domain size is larger than L_d , on an average, the excitons have a smaller probability of reaching the interface. Such bulk 'binary' comparison, although insightful, is only coarse and does not account for topological aspects of morphology. For example it will give comparable answers for striped and round domains with the same characteristic domain size (see figure 2, both stripe and circle have the same characteristic length, in this case: R=10nm).

Therefore, to improve upon this coarse quantification, we look at distributions of shortest distances to nearest interface. For each point of the photoactive material, we find the shortest distance to the nearest interface and construct the histogram of the distances. We choose to use the shortest distance to the nearest interface as characteristic length scale. The motivation to do this is because a distribution of distances to the interface encodes details of the topological features of the morphology. Moreover, this descriptor provides a rich variety of additional information in addition to differentiation between topologies. For instance, the first value of the histogram gives the number of pixels that are adjacent to the interface and thus provides a measure of the interfacial area. Additionally, we can easily estimate the fraction of D phase that have a low probability of reaching the interface, simply by reading off the last few points in the histogram.

Thus, this simple formulation allows to distinguish between topologically different shapes. For instance, in Fig. 2, the round shape has a higher fraction of pixels close to the interface. In contrast, the striped-morphology has more pixels distributed further from the interface. Both however have the same characteristic distance, which the distribution of the distances clearly distinguishes.

Using physics-based intuition, we then assigned a weight ($w = \exp(-d/L_d)$) that penalized longer distances. Weighting is done for each voxels based on the shortest distance to nearest interface, d. We choose an exponential distribution since it reflects a diffusion process. This approach does not account for intricate aspects of the physics as done by full scale models such as Monte Carlo, excitonic-drift-diffusion models, yet it encodes basic local topological features of the morphology in the context of exciton transport pro-



Fig. 3 (Left) Correlation between exciton dissociation morphology descriptors (P_{ex} and wf) and performance indicator from full scale analysis (η_{diss}). (Right) example morphologies used in the correlation study.

cess. Finally, to asses the morphology-scale feature with respect to exciton diffusion we average weighted distances for all voxels of interest.

In practice, the procedure consist of three steps: In the first step the shortest distances from the interface to any voxel is graph are found. This is executed efficiently by calling Dijkstra algorithm once for entire sample with low computational cost (Nlog(N)), where N is number of voxels). In the second step, each distance is weighted by $w = \exp(-d/L_d)$. Finally, average weighted distances for all voxels of interest: $wf = \sum_{i}^{nD} w(d_i)/n_D$, where n_D is total number of D voxels (or A voxels if acceptor absorbs light efficiently).

We note, however, that this approach, although more detailed than other descriptors commonly used, does not account for all aspects of the exciton transport process. In particular, we choose only one characteristic distance (the shortest distance to the interface), while exciton may not necessary find the closest segment of the interface during a random walk. One of the reviewers suggested using a more detailed descriptor that represents the random walk dynamics more accurately. This morphology descriptor searches all directions and visits all interfacial segments.

Assuming a Gaussian probability distribution for random walk dynamics, the probability that an exciton will be at a location x away from its origin, x_o is $P(x;x_o) = \frac{1}{(L_d\sqrt{2\pi})^n} \exp(-|x-x_o|^2/(2L_d^2))$, with n = 3 is the dimension. Consider a donor domain Ω , with boundary Γ . The probability of the exciton reaching the boundary can be calculated as

(1 - probability of the exciton remaining in the donor domain). Now, the probability of an exciton (starting at x_o) remaining in the donor domain is simply the point-wise probability summed over the domain, i.e. the integral of the probability over the domain: $F(x_o) = \int_{\Omega} P(x;x_o) dx$. (for each voxel we focus on the radius $3L_d$, beyond this radius $P \rightarrow 0$) The probability of the exciton starting from, x_o reaching the interface is thus $1 - F(x_o)$. Summing this over the entire donor domain give a measure of the probability of an exciton (generated anywhere in the donor domain, Ω) reaching the interface:

$$P_{ex} = \int_{\Omega} (1 - F(x_o)) dx_o / \int_{\Omega} dx_o \tag{1}$$

For a discrete morphology (as considered here), the above equation can be represented as $\sim 1/N\sum_N(1 - F(x_o))$ where N is the number of voxels in the donor domain. Defined in this way, this morphology descriptor for each voxel searches all directions and visits all interfacial segments.

To further test our assertion that choice of morphology descriptor is reasonable, we performed an ex-



Fig. 4 (Left) Anisotropy of distances from Mixed phase to D/M and A/M interface. (Right) Vertical distribution of distances from the mixed phase to the D/M and A/M interfaces.

haustive correlation analysis between these two descriptors and a full-scale excitonic drift diffusion equation (based on the framework described in our paper⁷). In Figure 3, we plot the correlation between this weighted fraction and exciton dissociation efficiency ($\eta_{diss} = \int_D \frac{G-X}{G} dD$, where *G* is exciton generation rate, and *X* is the concentration of non-dissociated excitons) computed for about 100 morphologies. We made sure that the morphologies had a wide variety of characteristic lengths and shapes. Both exciton dissociation descriptors show high correlation with full scale analysis. This high correlation increased our confidence that both descriptors are in fact a good descriptors to encoding exciton diffusion. High similarity between two approaches is remarkable. Two approaches are clearly built using different level of simplification. Yet when averaged over entire morphology they give comparable values.

While the morphology descriptor based on distribution of shortest distances, and the more accurate morphology descriptor give nearly equivalent results; the latter descriptor is much more computationally expensive. For instance, evaluating the latter descriptor on 3D data for one RVE takes several hours, comparing to 3 mins for all others morphology descriptors computed in the paper. Therefore, in the main text we include only the values of weighted fractions along with histogram of shortest distances.

4 Anisotropy of distances to interface within mixed phase

We quantify mixed phase by computing distance to the nearest interface. For every voxel we find two distances, to the nearest D/M interface and A/M interface. The averaged distances in both directions are shown in Figure 4. For all the films but the As-cast and the CaCap10:19, the average distances in both directions are comparable. However, in the As-cast and CaCap10:19 films, the average distances differ significantly (by a factor of 1.5).

To further inspect these differences the vertical distributions of the distances in both directions were also plotted in the same figure. Notice that for three films with comparable distances between both directions, two curves corresponding to two directions roughly overlap, with the best balance in the CaCap film. For the As-cast and CaCap10:19 films, large discrepancies are exposed. The different distances in two opposite directions are a direct consequence of vertical segregation of the phases and the resulting availability of the interface. The CaCap film has a mostly homogeneous and volume-wise balanced vertical segregation profile (see main text) and correspondingly the distances to both interfaces are homogeneous and balanced. However, the CaCap10:19 film has the least homogeneous vertical P3HT phase profile but a relatively homogeneous fullerene-rich phase vertical profile. Correspondingly, the distance from the mixed voxels

to the A/M interface is homogeneous, but the distance from the mixed voxels to the D/M interface it is height-dependent. Moreover, it can be seen that the higher the fraction of P3HT (e.g. in the middle zone), the shorter the distance to the D/M interface (close to boundaries). These same tendencies are observed for other films. One should notice that for all five films the differences between distances in opposite directions are comparable with pixel size (1.4nm).

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