Can polymer bulk heterojunctions be pre-formed in solution?

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The interaction between a semiconducting polymer and an organic acceptor in solution pre-forms the active-layer structure in plastic solar cells.

The combination of semiconducting (conjugated) polymer and acceptor molecules, e.g., polymer-fullerene blends, is the heart of state-of-the-art organic solar cells. To function efficiently, such blends, called bulk heterojunctions (BHJs), must contain two interpenetrating networks of the polymer (donor) and acceptor materials (see Figure 1). The polymer-acceptor interface area in BHJs should be as broad as possible because charges in organic solar cells are generated mainly at the interface. The optimal characteristic scale of polymer-acceptor phase separation is expected to be in the range of 10–100 nm, and developing methods that allow formation of blends with controlled 3D morphology for efficient BHJs is a key challenge in organic photovoltaics.

Optimal BHJ morphology (structure) in plastic solar cells can be realized in a number of ways, such as processing additives in the donor-acceptor solution, slow film drying, and post-deposition thermal annealing of films. All these approaches suggest that a BHJ starts to develop as a film forms from solution, i.e., during solvent evaporation. Our approach is to initiate BHJ formation in solution, i.e., as early as possible.

BHJ morphology is determined by a balance between polymer-polymer, acceptor-acceptor, and polymer-acceptor interactions. Although the first two interactions occur naturally through aggregation, the latter requires a little help. We exploit the peculiarities of polymer-acceptor interaction in the blend to enhance it in solution. Conjugated polymers form a weak intermolecular ground-state charge-transfer complex (CTC) with organic acceptors. We use blends with weak CTCs that strongly influence polymer conformation. Because the conformation should be inherited from solution into the film, we expect the CTC would influence BHJ morphology.

We have investigated how CTC formation changes the polymer conformation in donor-acceptor blends using dynamic light scattering (DLS). We have found that the polymer conformation in solution is considerably changed on addition of the acceptor (trinitrofluorenone). These changes are induced by formation of CTCs between the conjugated polymer MEH-PPV—poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]—and organic acceptor. Our DLS data shows that two conjugated segments, e.g., belonging to different macromolecules, can be glued into the CTCs with acceptor molecules sandwiched between them. The CTCs act as links between the polymer chains, and so they can change the polymer conformation from entangled to clusters of planar chains (see Figure 2). Results from Raman and optical absorption show evidence of similar polymer conformations in solution and films. Moreover, x-ray diffraction data suggests that polymer order is strongly enhanced in the blend. Domains of planar chains should improve charge transport in BHJs and hence performance of BHJ solar cells.

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Figure 2. Illustration of the structural changes induced by charge-transfer complex formation in semidilute blends.

Fundamentally, the donor-acceptor charge-transfer interaction in solution could be used to influence and perhaps even to control the BHJ morphology. However, thus far we have only been able to demonstrate the possibility of BHJ pre-formation in solution using a polymer-acceptor pair with subpar efficiency because other important parameters, such as charge mobilities and lifetime, are far from optimal. Our next step will be to extend this approach to polymer blends that can work as efficient BHJs in organic solar cells.

This work was supported by the Ministry of Education and Science of the Russian Federation (contract 16.740.11.0064). We thank V. V. Bruevich for help in preparing the figures.

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