Organic photovoltaics are an alternative form of solar energy that uses plastic as the light-absorbing material and a fullerene derivative as the electron acceptor. While cheap to produce, they require further research to increase their efficiency and make them economically viable. This requires an ideal degree of mixing between the two materials, which is achieved through active layer formation. Here, the electron-donating polymer mixes with an electron-accepting fullerene derivative to form an inter-penetrating network called a bulk heterojunction (BHJ). Blend-casting (BC) is the most common method for BHJ construction: the polymer and fullerene are mixed in solution and the resulting solution is spin-cast onto a substrate where the two materials de-mix to form the BHJ. However, controllable formation of the active layer is quite difficult as the morphology is hypersensitive to the processing kinetics of the active layer materials. Since efficient solar cells require optimum mixing of the electron donor and acceptor materials, achieving this ideal morphology is often the result of significant trial-and-error. One parameter required in achieving a high efficiency for the majority of polymer systems is the inclusion of co-solvents or solvent additives: by adding just a few volume percent of additive to the blend solution, the morphology improves significantly. However, despite its widespread use and efficiency-enhancing effect, the solvent additive mechanism remains unclear.

Here, we use an alternative processing technique called sequential-processing (SqP) to investigate the solvent additive mechanism for the most commonly used solvent additive, 1,8-diodooctane (DIO). SqP is useful since it converts BHJ formation into two distinct steps: in the first step, a polymer film is spin-cast from a solution of pure polymer while in the second step the fullerene is spin-cast from a fullerene solvent that will not dissolve the polymer film, but facilitates fullerene intercalation within the polymer film through polymer swelling. Thus, SqP avoids the kinetics of de-mixing as both polymer and fullerene are spin-cast in two separate steps. By casting a polymer film from a solution of polymer dissolved in the host solvent and 3% DIO, we find that DIO swells the polymer film. After depositing the fullerene on top of the swollen polymer film in the second SqP step, we find through a series of structural measurements that DIO swells the polymer films and acts as a plasticizer. This increases the fullerene mobility throughout the polymer film, thereby significantly improving the morphology and vertical phase distribution. This combined effect significantly increases the device performance and explains the solvent additive mechanism.

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