

Engineered exciton diffusion enhances device efficiency in organic solar cells

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Organic photovoltaics (OPVs) are a promising solar technology because of their potential to give lightweight, flexible and low-cost solar cells. Whilst good progress has been made, giving devices with power conversion efficiency (PCE) of more than 10%¹⁻³, the entire field is shaped by the exciton diffusion length being much shorter than the absorption length. This means that efficient exciton harvesting (leading to charge generation) generally requires the use of a bulk heterojunction. Charge generation occurs at the interface between the electron donor and acceptor, and for efficient exciton harvesting the donor and acceptor domain sizes should be smaller than the exciton diffusion length (L_D) which is typically rather short, about 5 nm.^{4,5} Delicate control of morphology is needed both to achieve charge separation and charge extraction. These considerations make exciton diffusion an important process to explore and improve in OPV materials. We have approached this by developing measurements of exciton diffusion, using them to start to develop structure-property relations and exploring the influence of processing on exciton diffusion with the aim of increasing it.

In order to establish structure-property relations for exciton diffusion in organic semiconductors, it is instructive to control intermolecular interactions, film morphology and crystallinity. Several processing methods including annealing (thermal or solvent)⁶, addition of solvent additive⁷ and crystal nucleating agents⁸ etc. have been suggested for controlling the structural order and crystallinity within the film. We explored the influence of crystallinity by studying the two anthracene containing donor materials poly(*p*-phenylene-ethynylene)-alt-poly(*p*-phenylene-vinylene) (PPE-PPV) copolymers (AnE-PPV) that have the same conjugated backbone but differ in the number and position of branched side-chains, which leads them to be either semi-crystalline or amorphous⁹. The ability to modify the overall crystallinity of the film, by changing the blend ratio of amorphous to semi-crystalline polymer, makes blends of these polymers an ideal model system to investigate some important unanswered questions in OPV research— how does the crystallinity influence exciton diffusion? what influence does this have on exciton harvesting? How does the

polymer's ability to crystallize influence the distribution of acceptor in the blend? We studied exciton diffusion and fluorescence quenching by dispersing fullerene molecules in these blends of amorphous and semi-crystalline copolymers, and found that fullerene preferentially mixes into disordered regions of the polymer film. We also found that the diffusion length is more than two times higher in a semi-crystalline copolymer compared to an amorphous copolymer. This is due to lower energetic disorder in the semi-crystalline polymer. On the other hand the amorphous polymer has a distribution of energy states on the order of 5 times kT and exciton transport can be described with time-dependent diffusion i.e. dispersive diffusion.¹⁰

We then explored the effect of the structural order and the degree of crystallinity of the film by polymer processing (thermal and solvent vapour annealing). For this study, we first used a random copolymer of polyalkylthiophenes, polyhexylthiophenes and polydodecylthiophenes, P3HT-co-P3DDT, and found an enhancement in the relative degree of crystallinity and exciton diffusion in processed films. The exciton diffusion coefficient was increased by more than a factor of 3 when thin films were annealed with CS_2 solvent vapour and doubled upon melt annealing at 200 °C. The corresponding films show about 50% enhancement in the degree of crystallinity.¹¹

In our recent work, we controlled morphology, structural order and crystallinity of the active layer of two-dimensional small molecules named SMPV1 and DR3TBDT by solvent vapor annealing. We found an enhancement in both the exciton diffusion length and also in the domain size. This engineered increase of the exciton diffusion length in combination with the larger domain size leads to efficient light harvesting and charge extraction, and hence a substantial (20%) increase in device efficiency. In both molecules, carbon disulfide (CS_2) shows the most promising results, with more than three-fold enhancement in exciton diffusion coefficient (D) and nearly two-fold enhancement in exciton diffusion length. The optimized CS_2 annealed devices consistently show a PCE between 7.0 and 7.7%, and a charge extraction efficiency above 80% at short circuit conditions which is enabled by a large average domain size of about 30 nm. Large domain size would normally reduce exciton harvesting but in our case higher device efficiency is obtained because of the increase in exciton diffusion length. Our results show that control of processing conditions to enhance both exciton diffusion length and domain size in organic semiconductor blends can improve solar cell efficiency.

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