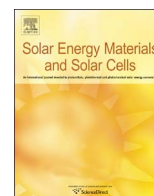




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Phase separation, crystallinity and monomer-aggregate population control in solution processed small molecule solar cells

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ABSTRACT

Small conjugated molecules are of great interest as promising alternatives to semiconducting polymers in organic photovoltaics (OPV). In this work, we introduce a more accurate assignment of the excited state of a promising squaraine (SQ) targeted for OPV application. From this assignment, we conclude that a mixed population of monomers and aggregates exists in spin-cast SQ:PC₆₁BM bulk heterojunction (BHJ) films, where monomers indicate the presence of amorphous regions that could act as traps. Since crystallinity is critically important for efficient charge transport and exciton diffusion in the BHJ, we thermally anneal the as-cast films to reduce the amorphous regions. Our analysis of annealed films demonstrates a delicate trade-off between increased crystallinity and larger domain sizes. Crystallinity improves but often at the expense of larger crystal size, as supported by XRD and TEM study. Therefore, to achieve optimal OPV efficiency, we controlled the tradeoff to improve the crystallinity while maintaining a small, highly mixed BHJ morphology. We thus highlight the importance of chemical compatibility when designing small molecules for use in high efficiency BHJ devices. Significantly, we have connected theoretically validated spectroscopic assignment with the first full study of morphology and domain size control as they affect small molecule OPV active layers.

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1. Introduction

Solution processed bulk heterojunction Organic photovoltaic devices (OPVs) have significant potential for a broadening portfolio of renewable solar technology, targeting a market that requires low cost aesthetically pleasing solutions [1]. There have been significant gains with polymeric active layer materials [2–5] with a vast amount of research having been carried out upon a disproportionately small number of polymer active layer candidates including the benchmark material, Poly(3-hexylthiophene-2,5-diyl) (P3HT) [6]. Indeed the gains in efficiency have come through an understanding of the morphology of the bulk heterojunction [7,8]. For polymers such as P3HT it is well established that, through annealing, the polymer crystallization is the driving force

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for micro/nano structure evolution in P3HT:PC₆₁BM blends, while PC₆₁BM crystallization is suppressed by miscibility of the fullerene and polymer. As a consequence, a desirable morphology is achieved with a co-existence of pure P3HT crystalline phases and P3HT:PC₆₁BM mixed phases leading to an optimal performance. During annealing, this morphology change is driven by crystallinity and chemical incompatibility, two key factors intrinsic to the molecular structure or molecular weight (polymers) of the donor and acceptor [9]. Therefore, the morphological response to processing conditions can be modified through chemical tuning.

In terms of how this morphology impacts device efficiency, a well-mixed, small-domain-size morphology with a large bulk heterojunction interface will lead to an energy landscape where charges may efficiently cascade from mixed domains towards progressively purer regions [10]. Nevertheless, a tradeoff exists between domain purity (crystallinity) and domain size (phase separation). Mixed domains are valuable for energy transfer and charge transfer cascades, but may also lead to reduced device performance due to higher probabilities for geminate or

bimolecular charge recombination. Müller et al. state that the optimization of the blend ratio and processing protocols, to dial in the perfect morphology, is a huge barrier to overcome [11]. The factors driving morphology are so dependent on molecular structure and thus polydispersity so, again, the ability to chemically tune is critical.

Incremental chemical tuning, perhaps to accommodate less toxic ink vehicles, would be expected upon scale-up for full commercialization [12,13]. At this time, the specific correlation of morphology to efficiency for polymers used in prototypes (such as P3HT) may be rendered obsolete. Associated changes in polydispersity and regioregularity upon chemical modification will also increase batch-to-batch variation [14,15]. For this reason, molecular OPV materials [16,17] are considerably attractive because the crystallinity and chemical incompatibility (with the fullerene acceptor) only depends on the molecular structure and not on the molecular weight. The intrinsic properties of a given molecule are also independent of the synthetic route, so absorbance, HOMO and LUMO levels and crystallinity can be readily modified through molecular design. In addition, small molecules can be tailored, in lock-step, to provide excellent morphology control through their ability to crystallize and phase-separate.

In recent years there has been a drive towards the synthesis of donor-acceptor (or push-pull) type molecules [18], for which absorbing wavelengths and energy levels can be easily controlled based on donor and acceptor combination. One particular family of donor-acceptor molecules of interest is the squaraines (SQs) [19]. In the morphology study presented here, we measure the amounts of crystallized and homogeneously mixed/monomeric squaraines in SQ:PC₆₁BM blends noting that there is a continuum of nanostructures ranging from (i) fully mixed to (ii) long-range interacting to (iii) crystal domains with ever increasing domain size.

Squaraines have drawn significant attention because of their enhanced panchromaticity in the solid state, such that photons can be absorbed from a broad range of the solar spectrum. It is the packing and morphology of the squaraines that leads to this broadening but, with multiple excited states accessible through crystallization, some aggregates may actually inhibit device performance because of energy level mismatch [20]. In fact, in recent work there has been significant confusion regarding the assignment of the excited states [21–27], with low energy absorption features typically being assigned to J-aggregates despite no observable fluorescence nor a crystal structure that would support Davydov splitting [28]. Despite an excellent description of the structure-property relationship in anilinic squaraines by Brück et al. [27], we consider the excited states assignment to restrict future progress and we seek to fully correct that assignment herein. We choose DHSQ(OH)₂ as a representative squaraine because of the work completed to date on this material, introduced by Brück et al. [27]. Therefore, in this work we confirm how the excited states are affected by packing geometry, we characterize the domain purity, blend ratio and domain size in thin films, we measure the impact of annealing based on thermal studies of the thin film materials and we combine all our data to explain the associated changes in device efficiencies.

2. Experiment

2.1. Synthesis

DHSQ(OH)₂ (2,4-bis[4-(N,N-dihexylamino)-2,6-dihydroxyphenyl]squaraine) was synthesized according to a one-pot two-step procedure [29]. Its molecular structure is shown in Fig. 1. The corresponding amine was purchased and condensed as reflux with 1,3,5-trihydroxybenzene in a toluene/n-butanol (3:1, v/v) mixed

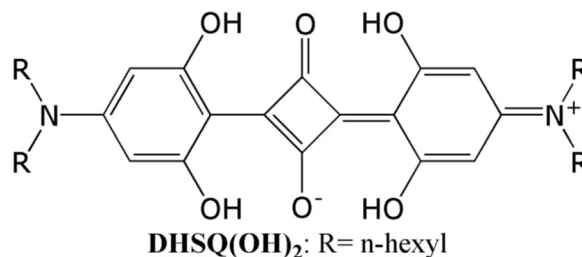


Fig. 1. Molecular structure of DHSQ(OH)₂.

solution. The yielded aniline intermediates were directly mixed with half equivalent squaric acid for the second condensation. The final products were green solids.

PC₆₁BM ([6,6]-phenyl C₆₁ butyric acid methyl ester, > 99.5%) was purchased from Solenne BV and Al 4083 PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) was purchased from Ossila. These materials were stored in a nitrogen-filled glovebox and were used as received.

2.2. Solutions and thin films (for absorption)

All solutions were prepared in chloroform (Sigma-Aldrich, ≥ 99.5%, used as received). DHSQ(OH)₂ films (neat and blends with PC₆₁BM) were prepared by spin coating in a N₂-filled glovebox at a spin speed of 800 RPM. The DHSQ(OH)₂ concentration was fixed at 3 g/L and the PC₆₁BM concentration was varied to achieve appropriate blend ratios. Thermal treatment was performed by placing the film on a hot plate at the measured temperature under a nitrogen environment. The hot plate was calibrated against an infrared thermometer and a ± 5 °C deviation from the displayed value is assumed. The cooling process occurred by simply removing the films from the hot plate and placing them onto a cold metal surface. The UV-vis spectra of as-cast and annealed films were measured using a Shimadzu-2401PC spectrophotometer.

2.3. X-ray diffraction (XRD)

X-ray diffraction patterns were measured for neat DHSQ(OH)₂ and DHSQ(OH)₂:PC₆₁BM blend films with 3:1 (75 PC₆₁BM wt%), 1:1 (50 PC₆₁BM wt%) and 1:3 (25 PC₆₁BM wt%) blend ratios. The films were prepared by spin coating chloroform solutions onto glass substrates with a total solute concentration of 16 mg/mL (except for 75 wt% films, in which case a total 32 mg/mL solute concentration was used to make a thick enough film). Monochromated Cu K α radiation ($\lambda=1.542$ Å) generated from an analytical sealed tube X-ray source was employed to make the measurements under ambient conditions (293 K). The blank glass substrate was measured on the identical set up to account for the scattering and diffraction of the X-ray beam by the substrate. The final X-ray pattern was obtained by subtracting the measured results of the blank substrate.

2.4. Transmission electron microscopy (TEM)

TEM micrographs of the SQ:PC₆₁BM films were obtained using a JEOL JEM-2010 operating at 200 kV with a 210 LaB6 filament and an AMT image capture system. The average domain size was quantified using ImageJ software. The DHSQ(OH)₂:PC₆₁BM blend films were prepared by the same method as described in the XRD section. Three films were prepared for each blend ratio; un-annealed, annealed at 137 °C or 175 °C respectively. Films were prepared by dipping spin-cast films into water, and then placing them onto copper TEM grids covered with an amorphous carbon

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