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.

KEYWORDS Squaraine; Aggregation; Phase separation; Organic photovoltaics

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 dis-proportionately 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 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.

Experiment

DHSQ(OH)₂: R= n-hexyl

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

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 figure 1. The corresponding amine was purchased and condensed at reflux with 1,3,5-trihydroxybenzene in a toluene / n-butanol (3:1, v/v) mixed 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.

Solutions and thin films (for absorption). All solutions were prepared in chloroform (Sigma-Aldrich, $\geq 99.5\%$, 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.

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 ($\lambda = 1.542 \text{ \AA}$) 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.

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 film. The water was allowed to evaporate under ambient conditions.

Differential scanning calorimetry (DSC). Spin-cast samples were prepared by spin coating composite DHSQ(OH)₂:PC₆₁BM solutions in chloroform (16 g/L total solutes) onto glass petri dishes, and then scraping the solid off with a razor blade. The yielded solids (1-2.5 mg) were then taken to a Shimadzu DSC-60 or a DTG-60 instrument for differential scanning calorimetry (DSC) and differential thermal analysis / Thermogravimetric analysis (DTA/TGA)

measurements. Samples for DSC were massed in a pre-tared aluminum tin on a precision digital balance (standard error < 50 μ g); a lid was gently crimped on with a TA Instruments press. Samples for DTA/TGA were loaded using similar aluminum boats, which lacked lids so that volatiles could escape; they were massed using the integrated balance in the Shimadzu DTG-60. The heating and cooling rate used for DSC was $\pm 20^{\circ}\text{C}$ per minute, while the rate used for DTA/TGA was $\pm 10^{\circ}\text{C}$ per minute.

Organic Photovoltaic devices. ITO coated glass substrates were consecutively cleaned in acetone, isopropanol and water baths under sonication. PEDOT:PSS (Al 4083, Ossila) was diluted with an equivalent volume of deionized water and was spin coated onto the pre-cleaned ITO substrates at a spin speed of 4000 rpm. The substrates were then heated at 165°C for 60 min under vacuum before being immediately transferred to a N_2 -filled glovebox. Solutions of fixed concentration $\text{DHSQ}(\text{OH})_2$ (4 mg/mL) and varying concentration PC_{61}BM (corresponding to blend ratios) were prepared in chloroform. The active layer solutions were spin coated at 1500 rpm in the glovebox, and were placed in a dark vacuum chamber to allow further evaporation of residue solvents. Then half of the films in one batch were annealed at 137°C or 175°C for 1 min in the glovebox before aluminum deposition under low pressure ($< 10^{-6}$ torr). The devices were tested immediately after completion of fabrication under an ambient condition. J-V characterization was performed on a Newport 91192 solar simulator set at a power density of $100 \text{ mW}/\text{cm}^{-2}$ (AM 1.5 G, 1-sun illumination) and by using a Keithley 2400 sourcemeter.

Results

Figure 2. The normalized absorption spectra of DHSQ(OH)₂ in dilute chloroform solution (10⁻⁵ M) and as spin cast thin films. The thin film was prepared by spin casting chloroform solution (4mg/mL) onto a glass substrate.

1. DHSQ(OH)₂ Aggregate. The absorption spectra of DHSQ(OH)₂ in chloroform solution and as a neat spin-cast film are shown in figure 2. The absorption of DHSQ(OH)₂ in chloroform is sharp and narrow, with an extinction coefficient of $1.5 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$ at the λ_{max} of 650 nm and a full width half maximum (FWHM) of 0.073 eV. The thin film absorbance has two broader peaks at 556 nm and 656 nm. This substantial broadening is typical of analino squaraines (SQs) with linear side chains [22,27,30,31], and has often been attributed to the upper and lower Davydov components in SQ aggregates under the assumption of an oblique transition dipole alignment as part of a herringbone packing geometry [27,31,32]. However, such an interpretation is inconsistent with the single crystal structure of DHSQ(OH)₂ which exhibits a single molecule per unit cell with the conjugated backbones (and transition dipole moments) parallel to one another throughout the crystal [27]. Rather, in a previous study concerning a series of similar SQs with linear side chains, we demonstrated through a validated computational approach that the origin

of the “double-hump” film absorption results from intermolecular charge transfer (ICT) between neighboring molecules in slip stacked SQ aggregates [28]. In a simplified picture, the double hump arises due to coupling between a charge separated state, which carries little oscillator strength, and the optically allowed local excitation, which carries the bulk of oscillator strength. The resulting mixed states split energetically and both retain significant oscillator strength due to the local component, leading to the observed double hump absorption. This interpretation is consistent with both the crystal structures of the studied SQ materials and the solution to aggregate transformation experiments which show that both absorption peaks arise from a single species as evidenced by a clear isosbestic point in the absorption spectra at different stages of the transformation [28]. DHSQ(OH)₂ shares the same molecular core as previously studied SQs, DPrSQ(OH)₂ and DBSQ(OH)₂, along with a similar crystal packing and absorption profile, thus allowing for successful application of the same theoretical model. The model, originally pioneered by Painelli and coworkers, is only briefly introduced here; the reader is referred to other literature [28,33,34], for greater details and depth.

In the essential states model, which accounts for both the quadrupolar character (i.e. donor-acceptor-donor conjugation) and the charge resonance in SQ molecules, the electronic structure of each chromophore is represented in a basis of three diabatic states: one neutral state, D-A-D, and two degenerate zwitterionic states, D⁺-A⁻-D and D-A⁻-D⁺. The difference in energy between the zwitterionic and neutral states is defined by η_z . Furthermore, the neutral state couples to the zwitterionic states through the transfer integral, $-t_z$, which describes electron transfer from donor (i.e. nitrogen atom) to acceptor (i.e. squarylium ring) moieties within the molecule. Linear vibronic coupling is also taken into account by introducing a vibrational mode with energy $\hbar\omega_{vib}$ for each molecular arm. The nuclear potentials of these modes are

approximated as harmonic wells with identical curvature. When the system is in a zwitterionic state, the equilibrium geometry of the corresponding arm is shifted relative to the neutral state by an amount characterized by the neutral Huang-Rhys factor, λ_Z^2 .

Squaraine aggregation is considered by extending the essential state model to account for both through space Coulombic coupling and intermolecular charge transfer (ICT) between SQ molecules. The ICT, occurring when an electron is transferred from the donor of one molecule to the acceptor of its neighbor and described by the transfer integral $-t_{CT}$, is justified by the close proximity between a donor group of one molecule and an acceptor group of its neighbor in a slip stacked packing scheme. For instance, in a DHSQ(OH)₂ crystal, the distance from the closest nitrogen atom of one molecule to the squarylium of its neighbor (5.21 Å) is closer in space than to the squarylium in its own molecule (6.68 Å). ICT enables the SQ molecules to exist in ionic states; in the anionic state the central squarylium is negatively charged, D-A⁻-D, while in the cationic state the left or right nitrogen is positively charged, D⁺-A-D and D-A-D⁺. It is also possible for the system to assume a cationic state when all three subunits are charged, D⁺-A⁻-D⁺. Thus, including ICT in the essential states model necessitates introducing these four additional diabatic states. When two molecules exist as a charge separated pair, the energy of the system increases by η_{CT} relative to when both molecules are in their neutral states. Vibronic coupling within the ionic states is also taken into account and characterized by the ionic Huang-Rhys parameter λ_{CT}^2 . Finally, through space Coulombic interactions are considered by accounting for electrostatic interactions between molecules positioned according to measured single crystal data [27]. The electron distributions within the Zwitterionic and ionic states are approximated by positive and negative point charges that reside on nitrogen atoms and the central squarylium ring respectively.

Figure 3. Simulated absorption spectra of DHSQ(OH)_2 in CHCl_3 solution (top) and as a thin film (bottom), with comparison to experimental results. The spectra were simulated using the SQ dimer as an effective aggregate model.

Table 1. The critical parameters for modeling both DHSQ(OH)_2 solution and thin film absorption spectra.

Parameter	DHSQ(OH)_2
η_z	0.69 eV
t_z	1.05 eV
λ_z^2	1
η_{CT}	1.53 eV
t_{CT}	0.30 eV
λ_{CT}^2	0.25
$h\omega_{vib}$	0.16 eV

The simulated absorption spectra of DHSQ(OH)_2 in chloroform solution and in the thin films are shown in figure 3, and the fitting parameters are listed in table 1. Each spectrum is broadened with a Gaussian function having a standard deviation of 0.14 eV and the aggregate spectrum is shifted by -0.02 eV to align the most intense peak with experiment. Both spectra

show excellent agreement with experiment, validating the model for DHSQ(OH)₂ monomers and aggregates. The *monomer* parameters for DHSQ(OH)₂ are the same as those for DPrSQ(OH)₂ and DBSQ(OH)₂ molecules [28], confirming that the linear alkyl chains have little influence on the optical properties of the single SQ chromophore. For the DHSQ(OH)₂ aggregate simulation, most parameters are similar to the previously studied SQs, except for the ICT integral, $-t_{CT}$, in which case DHSQ(OH)₂ has a smaller $-t_{CT}$ than DPrSQ(OH)₂ (0.55eV) and DBSQ(OH)₂ (0.34eV). This is consistent with the larger distance between nitrogen and squarylium on neighboring molecules for DHSQ(OH)₂ (5.21 Å) compared with DBSQ(OH)₂ (5.02 Å) and DPrSQ(OH)₂ (4.98 Å). We note that, as in our previous study, DHSQ(OH)₂ aggregates are approximated using a dimer model due to computational limitations and therefore the aggregate parameters should be understood as effective values that will converge to their true values as the size of this system is increased.

In review, both peaks in the thin film absorption spectrum are assigned to the DHSQ(OH)₂ aggregate. In the crystal, DHSQ(OH)₂ molecules are arranged such that the Coulombic coupling between local excitations on nearest neighbors is positive, as in an H-aggregate. While the conventional H-aggregate model only allows transitions to the blue-shifted H-band (a transition to a lower-energy band is not optically allowed), in DHSQ(OH)₂ the CS states enabled by intermolecular charge transfer couple to the excitonic H-band, resulting in a distribution of oscillator strength over the eigenstates. The eigenstates retain oscillator strength due to the excitonic component of the wavefunction and therefore a unique “double-hump” absorption is observed in the spectrum (figure 4).

Figure 4. Illustration of the origin of DHSQ(OH)₂ aggregates absorption line shape. Through space Coulombic interactions cause the monomer excited states to split into higher- and lower-energy states [32]. In the case of an H-aggregate, the transition to the upper state (H-state) is optically allowed while that to the lower dark state (D-state) is forbidden. Due to the ability of intermolecular charge transfer (ICT) in the DHSQ(OH)₂ aggregate, there exists a charge-separated (CS) electronic state with energy close to the H-state. Although the transition dipole moment from the ground state directly to the CS state is small, the CS state is able to couple with the H-state through charge transfer, and leads to a further split in the H-state. The resulting states each have some H-state components and thus acquire some oscillator strength. The resulting mixed states, H+CS and H-CS, are responsible for the “double-hump” absorption spectra observed in the DHSQ(OH)₂ thin film. It is noted here that the “+” and “-” signs denote the relative energy of the states.

This interpretation has a fundamental significance since the OPV device efficiency depends on the properties of individual excited states. If the excited state population is shared between states that enhance charge transfer at the BHJ interface and those that inhibit charge transfer at the BHJ interface we can better recognize the importance of a correct spectral assignment and note that a poorer understanding may have inhibited progress [31,35–37]. Our model implies that the excited states of the aggregate relevant to optical absorption and emission are described by one of three electronic configurations; a dark-state, D, or the bright H+CS and

H-CS states as illustrated in figure 4. Special attention should be addressed to the D-state. It exists as a part of the DHSQ(OH)₂ aggregate and will likely act as the lowest excited state. Indeed, the non-fluorescent nature of the DHSQ(OH)₂ aggregate implies that a dark state lies below the bright H+CS and H-CS states according to Kasha's Rule [32]. By comparing the absorption onset of the low energy peak of the SQ aggregate and the absorption onset of the monomer in solution from figure 2, we conclude that the energy of lower H-CS state lies below the monomeric excited state, as shown in figure 4. Given that no fluorescence is observed for DHSQ(OH)₂ in the thin film, we consider that the energy of the dark state is lower than the H-CS state. If the excitons in both H+CS and H-CS states relax to the D-state before charge transfer, exciton dissociation at the heterojunction interface will be less energetically favorable due to the associated low energy. The presence, relative energy level and population of the dark state will be explored further in future work from our group.

2. DHSQ(OH)₂ Aggregate in SQ:PC₆₁BM blend. As described above, there are two relevant forms of DHSQ(OH)₂ in nature: the monomer and the ICT-coupled aggregate. The monomer, in chloroform solution, has a narrow and intense absorption peak at 650 nm; while the ICT-coupled aggregate, in spin cast films, has two broad peaks at 565 nm and 656 nm (figure 2). We performed annealing on neat SQ films at 175 °C and found little change in absorption spectra, indicating that the population of monomers in such films is negligible compared to that of aggregates. However, when DHSQ(OH)₂:PC₆₁BM blend solutions are spin cast, the absorption spectra of the films exhibit a drastic change as shown in figure 5a.

Figure 5. The absorption spectra of DHSQ(OH)₂:PC₆₁BM blend films prepared by spin coating chloroform solutions. a): change in thin film absorption (normalized to the low energy absorption peak of DHSQ(OH)₂) as a function of PC₆₁BM weight percent in the chloroform solution, from which the film was cast. The black arrow marks the red shifting of this peak as the amount of PC₆₁BM is increased. b): the spectral changes of 75 wt% PC₆₁BM film as a function of annealing temperature; each film was annealed at different temperatures for one minute, the spectra are normalized to the PC₆₁BM absorption peak at 336 nm.

As the PC₆₁BM wt% is increased, the relative peak height at 560 nm diminishes, with a concomitant red shift in the low energy peak. When the PC₆₁BM content is increased to 93.75 wt%, the peak at 560 nm is almost buried in the PC₆₁BM absorption line and the low energy absorption peak is red shifted to 678 nm. This is consistent with a disruption of aggregation and the dilution of DHSQ(OH)₂ by the fullerene. Thus, we assign the absorption peak at ~680 nm to the DHSQ(OH)₂ monomer absorption (note that it is different from the assignment by Brück *et al.* [27], where this peak is assigned to the DHSQ(OH)₂ J-aggregate). Yet we note that the feature assigned to the thin film monomer in blended films is substantially red-shifted when compared to the monomer feature in chloroform solution (figure 2). We attribute this red shift to

the different dielectric constant of the fullerene environment. Due to the substantial spectral overlap of the monomer and the low energy absorption peak of aggregate, a composite peak is therefore observed in the 650-700 nm range. It is important to recognize that the resulting peak shifts depend on the relative amounts of the two species present, in accordance with the apparent peak shift observed with the addition of two Gaussian peaks with different peak positions and representing states with exchanging populations.

We consider that upon spin casting from a low boiling point solvent at a fast spin speed, the homogeneous mixture of the solution is transferred to the film such that the blends are well mixed. In accordance with Ostwald's rule [10], we would expect the as-cast film to be made up of kinetically stable blended amorphous regions; a mix of DHSQ(OH)₂ monomers and PC₆₁BM. When thermally activated, squaraine molecules become mobile and start to crystallize. The absorption spectra of 75 wt% PC₆₁BM films as a function of annealing temperature are shown in figure 5b. Upon annealing for one minute, the blend films show a “recovery” of aggregate formation, indicated by the increase in absorption at 560 nm. This occurs with a simultaneous blue-shift of the low energy features from 670 nm (at 20 °C) to 655 nm (at 175 °C). Finally, the double-hump peaks are located at 560 nm and 655 nm in 175 °C-annealed films, which correspond well with the peaks in the neat SQ film (figure 2). This again strongly supports that the absorption feature at 650-700 nm results from both SQ monomer and aggregate contributions, and that the changes in peak position and peak ratio are caused by the interconversion of these two species.

Figure 6. The peak ratio between high energy absorption peak, “H”, and low energy absorption peak, “L”, in DHSQ(OH)₂:PC₆₁BM pristine (black cube) and annealed (red circle) films. The values of both peaks are obtained by properly subtracting the PC₆₁BM contribution. The ratio value, “H/L”, represents the relative population of aggregates to monomers; i.e. when there is 100% aggregate, the “H/L” is expected to be 1.57, equal to the neat SQ film. Smaller “H/L” values represent more monomer populations present in the blend films.

This same annealing study was conducted through a comprehensive set of different blend ratios. The peak ratio of the high energy peak absorbance to the low energy peak absorbance (i.e. “H/L”) measured after subtraction of the PC₆₁BM contribution to each spectrum, is plotted against the blend ratio before and after annealing, and is shown in figure 6. This plot is very similar in appearance to the plot of the low energy peak position as a function of blend ratio (figure S1), which reemphasizes the monomer and aggregate interconversion during annealing. For unannealed films, the “H/L” steadily decreases as fullerene wt% increases, as shown in figure 6. A predominant monomer population is present in the high PC₆₁BM content films. However, after annealing at 175 °C for one minute, the “H/L” increases to almost the same value as for the neat SQ films, as long as the weight ratio of PC₆₁BM is below 80 wt%. Above this

threshold, the aggregate formation upon annealing is hindered or retarded by the overwhelming amount of fullerenes. A large extent of monomer/aggregate population interconversion is obtained by annealing the 75 wt% PC₆₁BM films.

In summary, DHSQ(OH)₂ neat films demonstrate the effects of fast aggregation during the spin casting process but, in the presence of PC₆₁BM, transfer of an amorphous, more homogeneous mixture to the film dominates and aggregation is disrupted. Disruption of aggregation and the relative population of monomer and aggregate correlate well with the percent composition of PC₆₁BM. Upon thermal annealing, the SQ monomers start to aggregate with an observable spectral change. After annealing, the absorption spectra are almost identical for different blend films with PC₆₁BM wt% < 75%. A large interconversion between monomers and aggregates was seen in films with a range of 50 wt% to 75 wt% PC₆₁BM. This change in squaraine species population is expected to impact the spectral response of the DHSQ(OH)₂:PC₆₁BM active layer, as well as the excited states at the donor acceptor interface.

3. Film morphology upon annealing. For a comprehensive connection between aggregation and device efficiency, we investigate the morphological changes of the films during annealing. Here, we study the effect of annealing temperature on the crystallinity and phase separation of the films. Indeed, both crystallinity and phase separation contribute to the power conversion efficiency (PCE) of the solar cells [7,8,38,39]. With a large phase separation, the surface area of the donor-acceptor interface shrinks, the distance required for exciton diffusion to the interface increases and therefore the free charge generation will be reduced. On the other hand, high crystallinity is considered to be beneficial for exciton diffusion rate and charge capture. When the dipole orientation factor of donor and acceptor is large, the Förster Resonance Energy Transfer (FRET) is efficient [40]. The dipole orientation factor is large in a highly

ordered crystal material, and is small in an amorphous state with randomized dipole alignments [30]. Hence exciton diffusion rates are enhanced in ordered materials. Increased charge transfer integrals between ordered molecules would also indicate more efficient frontier orbital overlap and improved mobility. Reduced bimolecular charge recombination will result leading to improved device performance [10]. Therefore, with annealing we have demonstrated an apparent interconversion from DHSQ(OH)₂ monomers to aggregates. Since aggregates can be populated when crystals are formed, we therefore expect that annealing strongly influences the crystallinity of the film. To confirm this, we measured X-ray diffraction of the films.

Figure 7. X-ray diffraction data recorded for DHSQ(OH)₂:PC₆₁BM films at different blend ratios in pristine films (a) and as a function of thermal annealing (b). The films were prepared by spin coating DHSQ(OH)₂ or DHSQ(OH)₂:PC₆₁BM blend solutions with 0 wt% (neat SQ), 25 wt%, 50 wt% and 75 wt% PC₆₁BM onto a glass substrate. The films were then subjected to thermal annealing at 137 °C and 175 °C, respectively, for 3 min. The main diffraction peaks for various blend ratios are located at $q = 0.37$ Å⁻¹, which corresponds to the (001) plane in the single crystal structure [27]. The dwell time for data acquisition is 2 s for all films except the 75 wt% films, in which 8 s dwell time was used to resolve the peak structure.

In neat SQ films, the main diffraction peak at $q = 0.37$ Å⁻¹ is in good agreement with the 001 plane calculated from single crystal structure of DHSQ(OH)₂ [27]. For as-cast films, with increasing amount of PC₆₁BM, the diffraction peak diminishes and broadens, indicating a decrease in crystallinity in those films. The PC₆₁BM dilutes the DHSQ(OH)₂ with disruption of

the aggregation, resulting in amorphous and mixed domains. This disruption is reversed by thermal annealing, as illustrated in figure 7b, such that the crystal peak increases in relative intensity. The diffraction peak intensity of neat DHSQ(OH)₂ films is independent of annealing temperature and is not shown. However, there is a clear increase of the diffraction peak in blended films after annealing, confirming the increase in the extent of crystallinity. These results are thus consistent with higher aggregate absorption, interpreted from and observed in figures 5 and 6.

Figure 8. The DSC heating and cooling thermograms of DHSQ(OH)₂:PC₆₁BM bulk heterojunction blends of different composition. The samples were heated to 260 °C (a, step 1), cooled to below 75 °C (b, step 2), and then heated to 350 °C (c, step 3). The exothermic and endothermic peaks are normalized to the mass of the solids.

Beyond the increase in extent of crystallinity throughout the films, a separate issue is the increase in crystal domain size and the phase separation, also important for OPV performance [7,8,41–43]. Here, we go on to consider phase separation through a differential scanning calorimetry (DSC) study. During the measurement, the samples are 1) heated from 50 °C to 260 °C, and then 2) cooled to below 75 °C, and again 3) heated back up to 350 °C. The DSC thermograms recorded during these three steps are shown in figure 8. During step 1 for each blend ratio, separate exothermic and endothermic features are observed respectively at 155 °C-165 °C and 194 °C-208 °C. The endotherms correspond with the melting point of DHSQ(OH)₂ and is consistent with the literature [44]. The exothermic peak is only observed in the blend films, and increases in intensity with PC₆₁BM content. It is associated with the phase separation and, as expected, is not observed in step 3 since the phase separation is assumed to be complete at the end of step 1. The phase separated state is assumed to represent the thermodynamically stable state. It should be noted that the highest temperature for step 1 is delicately set below the melting point of PC₆₁BM (at 290 °C, identified by the small endothermic peak in 100 wt% PC₆₁BM film in figure 8, step 3) to eliminate the possibility of DHSQ(OH)₂ and PC₆₁BM remixing in their liquid-liquid phase.

In the cooling step (step 2), the features at 135 °C-150 °C are assigned to the DHSQ(OH)₂ crystallization exotherms from the melt. In step 3, the re-melting temperature for DHSQ(OH)₂ is slightly decreased (< 12 °C) compared to the melting point in the first step 1 heating process and for each sample the melting point is the same, perhaps expected because the materials are assumed to be phase separated. The shift itself is not fully anticipated but is consistent with a gradual decomposition of the SQ during the process. The decomposition of squaraine was also observed in absorption spectra (figure S2) when the films were annealed at a temperature slightly

higher than the SQ melting point. This observation is consistent with the thermal decomposition temperature measured by Tian *et al.* [44]. Substantial degradation of DHSQ(OH)₂ was found at 280 °C, where the large exothermic peak was found in the step 3. The corresponding Thermogravimetric analysis (TGA) thermograms are shown in figure S3, where decreases in total solid mass also imply material degradation. The PC₆₁BM does not show any decomposition below 400°C based on an evaluation of the material mass through DTA/TGA (figure S3).

Based on these data we subsequently investigate the phase separation through transmission electron microscopy (TEM) at two key annealing temperatures, one at 137 °C at a point just upon the recrystallization endotherm but just below the phase separation exotherm, and the other at 175 °C at a point well above the phase transition exotherm but below the melting point. These data are shown in figure 9.

Figure 9. TEM micrographs of spin-cast $\text{DHSQ(OH)}_2\text{:PC}_{61}\text{BM}$ films without treatment (top) and annealed at $137\text{ }^\circ\text{C}$ (middle) and $175\text{ }^\circ\text{C}$ (bottom) for 3 min. The blend ratios under study are from left to right: 25 wt%, 50 wt% and 75 wt% of PC_{61}BM . The scale bar at the bottom of each image is 200 nm.

In the TEM image of unannealed films (figure 9, top panel), the composites appear to be well mixed. For 25 wt% PC_{61}BM , the fullerene phase cannot be distinguished from the SQ aggregate phase. In 50 wt% PC_{61}BM films, SQ and fullerene phases can be seen with an estimated size of 50-100 nm in diameter. Such domains, if chemically pure, are considered detrimental for exciton dissociation. In 75 wt% PC_{61}BM films, small and fine phases are formed. DHSQ(OH)_2 and PC_{61}BM appear to mix well therefore when the weight percentage and volume percentage of one component is much higher than the other. We infer from the 50 wt% sample

that these two compounds are chemically incompatible and phase separate when mixed evenly. This is consistent with thermodynamically driven phase separation. UV-Vis absorption showed that even in 75 wt% PC₆₁BM films, the squaraine aggregates still exist in a high population but, given these TEM images and our XRD data, the crystalline domains formed in such films are small in size, assuring a high donor acceptor interfacial area. Annealing at 175 °C induces a dramatic phase separation for all films independent of the blend ratio. At a slightly lower annealing temperature, 137 °C, the phase separation was not as profound as for the 175 °C annealed films, as hypothesized. This is because the annealing temperature is below the critical phase separation temperature characterized by DSC. Given the increase in aggregate absorption in UV-Vis spectra (figure 5b) and the increase in X-ray diffraction peak (figure 7b) after annealing at 137 °C, the extent of crystallinity is increased while further phase separation is minimized leading towards an optimized morphology for OPV device operation.

4. Organic photovoltaic devices. The Organic bulk heterojunction solar cells are fabricated in a stacked geometry: ITO/PEDOT:PSS/ DHSQ(OH)₂:PC₆₁BM/Al. The blend ratios are varied from 3:1 (25 wt% PC₆₁BM), 1:1 (50 wt% PC₆₁BM), 1:3 (75 wt% PC₆₁BM). The active layers were annealed at 137 °C or 175 °C for 30 seconds, and the device results are compared to unannealed devices. It should be mentioned that optimizing the devices to reach the best efficiency is not a key outcome for this work; rather we seek to use device data to confirm an understanding of how the properties of these materials (based on morphology) influence device efficiency with a view for prescribing a high-potential modified structure for future OPV devices. We therefore simplify our device sandwich structures retaining only an electron blocking layer and active layer. Nevertheless, we note that the OPV cell can be optimized to achieve higher efficiency by inserting an electron transporting or exciton blocking layer, such as

bathocuproine (BCP) [31,37], by replacing the PEDOT:PSS layer with materials with better energy matching, such as MoO₃ [35,45] and by replacing PC₆₁BM with PC₇₁BM, which absorbs more efficiently in the visible spectrum [27].

Table 2. The device performance of DHSQ(OH)₂:PC₆₁BM at different blend ratios with and without thermal treatment.

Blend ratio	Thermal treatment ^a	Device parameters ^b			
		J _{SC} (mA/cm ⁻²)	V _{OC} (V)	FF	PCE (%)
3:1	None	1.95 ± 0.32	0.29 ± 0.06	0.27 ± 0.07	0.15 ± 0.05
	175 °C	0.2	0.02	0.07	0.00 (diode) ^c
1:1	None	4.15 ± 0.15	0.53 ± 0.05	0.39 ± 0.03	0.86 ± 0.12
	137 °C	3.84 ± 0.22	0.55 ± 0.04	0.43 ± 0.05	0.92 ± 0.19
	175 °C	0.54	0.15	0.26	0.02 (diode) ^c
1:3	None	4.69 ± 0.30	0.52 ± 0.06	0.40 ± 0.06	0.98 ± 0.19
	137 °C	4.64 ± 0.21	0.59 ± 0.07	0.45 ± 0.06	1.24 ± 0.26
	175 °C	1.08	0.18	0.26	0.06 (diode) ^c

^a The thermal treatment was performed in a N₂-filled glovebox before evaporation of cathode layer; ^b The device performance is characterized at AM 1.5G illumination and the results are averaged over 16 devices for each data point; ^c the devices showed diode behavior and the parameters can hardly be obtained and thus are considered imprecise.

Data from the device performance study for DHSQ(OH)₂:PC₆₁BM are shown in table 2.

Upon increasing the PC₆₁BM ratio from 25 wt% to 75 wt%, there is a 6-fold improvement of power conversion efficiency (PCE). This is attributed to the large heterojunction interface provided by the finely mixed donor and acceptor phase at high fullerene content and the associated higher electron mobility for high volume percentage PC₆₁BM [11]. However, the well mixed phases separate into large chemically pure domains upon 175 °C annealing, as shown in the TEM images (figure 9), which leads to the diode like behavior and a tremendous deterioration of device efficiency. When annealed at 137 °C, the low temperature onset of the crystallization exotherm of DHSQ(OH)₂ obtained from DSC thermograms, the device performance improves from 0.86% to 0.92% for the 1:1 blend and from 0.98% to 1.24% for the 1:3 blend. The increased device efficiency mainly stems from the improved open circuit voltage and fill factor (table 2). The short circuit current, however, stays the same or even slightly

decreases after annealing. This is counterintuitive given that film crystallinity increases without any detrimental phase separation, as demonstrated by XRD and TEM. The reason for unimproved J_{SC} is still unclear. We consider the following explanation based on our accurate assignment of the excited states. The “dark” state lying below the two “bright” H-states will be populated through Kasha’s rule relaxation and these resulting lower energy excitons will likely dissociate with a reduced probability given their lower energy levels relative to the PC₆₁BM LUMO, described in part by Marcus Theory [20,46].

In previous studies of squaraine materials in OPV devices, the same strategies employed to optimize solar cells, such as thermal annealing, do not always lead to the same resulting device efficiency. It has been reported that improving crystallinity of the SQ films by thermal annealing [35,45] and solvent annealing [36] results in an optimized solar cell performance. Our group has found a decrease in the device efficiency after thermal annealing [20] and, in this case, we assign this to the significant SQ:PC₆₁BM phase separation at high annealing temperatures. The domain size after phase separation is estimated to be 50-200 nm in diameter according to the TEM images (figure 9), comparable to the expected thickness of the films. In addition, we found that the DHSQ(OH)₂ and PC₆₁BM completely phase separate under slow evaporation of chloroform, leaving fiber-like snowflake-shaped SQ crystals with PC₆₁BM domains filling the rest of the space (figure S4). During this slow evaporation process over a month, the system moves towards a well-established, thermally equilibrated, large-scale phase separation. Extensive phase separation will lead to loss of PCE but mixing can be controlled through rapid evaporation of spin-casting solvent and dilution by PC₆₁BM. The increase in efficiency resulting from higher PC₆₁BM blend ratios therefore has a different origin to the increase in efficiency described elsewhere [35,36,47], associated with conducting PC₆₁BM networks.

The phase separation of small squaraine molecules when mixed with fullerenes is unique when compared to polymers. It has been reported that the P3HT and PC₆₁BM are essentially miscible in the films [9,11]. In our study, we found that the phase separation happened with no limitation (figure S4). This suggests that the optimization strategy of squaraine based OPV devices should be different from that of polymer based devices. In particular, based on our work, we suggest that more attention should be paid to the phase separation during fabrication. Thermal annealing, solvent annealing and use of solvent additives remain important since these processing parameters that allow some control over intrinsic factors like crystallinity and chemical incompatibility [9].

Conclusion

In this work we introduce a more accurate assignment of the excited states of a representative functional squaraine, DHSQ(OH)₂. We correctly assign the thin film spectral features to the monomer and intermolecular charge transfer coupled aggregate, which moves beyond the preliminary qualitative assignments made by Brück *et al* [27]. From this assignment we recognize that a mixed population of aggregates and monomers exists in spin-cast thin film samples. The presence of monomers indicates amorphous structures in as-cast active layer films, when squaraine is blended with PC₆₁BM. Since crystallinity is critically important because associated high mobility and exciton diffusion rates lead to higher PCE, we enable an interconversion of monomers to aggregates through thermal annealing. Our X-ray diffraction analysis of annealed films demonstrates an increase in crystallinity, but often at the expense of larger crystal size as shown in the TEM images. The over-grown crystal domains largely explain the deterioration in device performance when SQ:PC₆₁BM films were annealed at high temperature. Thus, blend morphology is driven by chemical incompatibility with our mixtures

tending strongly towards a completely phase separated morphology. Nevertheless, our optimal device performance is achieved by 1) maintaining high fullerene content to maximize mixing during the spin casting and 2) annealing the film at sufficiently low temperatures such that crystallinity is increased without initiating phase separation. In conclusion we highlight the importance of chemical compatibility when designing small molecules for use in high efficiency bulk heterojunction devices. This work has a substantial impact in that we have connected theoretically validated spectroscopic assignment with a full study of morphology and domain size control as they affect small molecule BHJ active layers.

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Figure1

DHSQ(OH)₂: R= n-hexyl

Figure2

Figure3

Figure4

Figure5

Figure6

Figure7a

Figure 7b

Figure 8

Figure9