Inverted P3HT:PC61BM organic solar cells incorporating a pi-extended squaraine dye with H- and/or J-aggregation.
Inverted P3HT:PC$_{61}$BM organic solar cells incorporating a \(\pi\)-extended squaraine dye with H- and/or J-aggregation.

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Abstract

In this report, we investigated the impact of adding a large $\pi$-extended squaraine dye to the classic bulk heterojunction P3HT:PC$_{61}$BM system. The compound, SQIQ-A, is a bis-indole squaraine dye appended with acetylene-indoloquinoxaline end-capping units that exhibits strong optical absorption in thin-film from 650-750 nm, beyond the absorption wavelength cut-off for P3HT:PC$_{61}$BM films (ca. ~650 nm). The dye SQIQ-A can form H or J-aggregates (blue or red shifting the optical absorption profiles) via solvent vapour annealing with CHCl$_3$ or THF, respectively, thus providing a simple method to control the morphology and optical properties of the molecule. Ternary blended films comprised of a P3HT:PC$_{61}$BM:SQIQ-A (1:1:0.3 mass ratio) were investigated as-cast, after solvent vapour annealing and after thermal annealing. Films were characterized using optical absorption spectroscopy, X-ray diffraction, atomic force microscopy, and polarized light microscopy. Solar cells were fabricated using an inverted architecture in air and analysed using current-voltage and external quantum efficiency measurements. It was found that solar cells thermally annealed at 130°C for 10 minutes gave good power conversion efficiencies of 3%, similar to the control P3HT:PC$_{61}$BM, but with improved fill factors and noticeable photocurrent generation from 650-760 nm where the SQIQ-A molecule absorbs. Exposure to solvent vapour (CHCl$_3$ or THF) results in aggregation of all components, but specifically leads to the formation of micron sized domains, lowering the overall photovoltaic performance.
Key words

**Introduction**

Organic solar cells (OSCs) are a versatile and potentially low-cost photovoltaic technology. Devices can be rendered light-weight, flexible, transparent, colored, and disposable.\(^1\)–\(^5\) Binary bulk heterojunction (BHJ) devices based on regio-regular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PC\(_{61}\)BM) have been the most studied in the past decades, with power conversion efficiencies (PCEs) of 3–5% being obtained.\(^6\)–\(^8\) However, P3HT has an optical bandgap of 1.9 eV (~650 nm) and thus only has the ability to harvest ~22% of the photons reaching the device from incident solar irradiation giving a maximum theoretical current density of ~14 mA cm\(^{-2}\).\(^9\) Furthermore, binary BHJ OSCs have typically suffered from insufficient coverage of the solar spectrum, even though many low bandgap polymers, oligomers, discrete molecules and non-fullerene acceptors have been designed to expand light absorption.\(^10\)–\(^16\) Ternary systems, which involve the addition of a third component to the BHJ, are a simple solution for creating OSCs with maximum light absorption and improved PCE. Usually, a polymer, oligomer or discrete molecule is used as the third compound.\(^17\) Ternary OSCs consisting of two ‘donor’ polymers and one ‘acceptor’ (PCBM) with high PCEs of ~9% have been reported by Yang *et al.*\(^18\) and Yu *et al.*\(^19\) demonstrating the potential of such systems. Importantly, the addition of molecular systems to polymer/PCBM BHJ blends has been shown to not only broaden and extend optical absorption into the red, but also to improve the crystallinity of the polymer and tune the active layer morphology.\(^20\)–\(^22\)

Discrete molecules based on squaraine dyes are attractive materials for use as third components in OSCs as they exhibit red and near-infrared (NIR) optical absorption with high extinction coefficients, they are typically photochemically and thermally stable, and are readily synthesized using low-cost precursor building blocks.\(^23\)–\(^26\) The strong low energy absorption of
squaraine dyes has certainly made them attractive for use as third components in P3HT:PCBM based blends. Recently, the group of G. Sharma showed that the PCE of P3HT:PC71BM based solar cells could be improved from ~2 to ~5% upon addition of small fractions of the bis[4-(2,6-di-tert-butyl)vinyl-pyrilyum] squaraine dye (TBU-SQ).\textsuperscript{27,28} Similarly, Fei Wu \textit{et al.} reported an increase in short circuit ($J_{sc}$) and subsequent PCE with the addition of only 2.4 wt. % of the squaraine dye TPE-SQ.\textsuperscript{29} In 2013, the group of Andre D. Taylor demonstrated the effective use of Forster resonance energy transfer (FRET) in OSCs by incorporating 2,4-bis[4-(N,N-diisobutylamino)-2,6-dihydroxyphenyl] squaraine into P3HT:PC61BM blends.\textsuperscript{30} Subsequently, the same group showed that the addition of squaraine dyes could be used to ‘color tune’ the organic solar cells in addition to affecting the performance.\textsuperscript{30}

It is important to note that all reported ternary OSCs incorporating squaraine dyes have used those with a very simple, low molecular weight structure, however oligomer systems with larger π-extended backbones have typically exhibited the best performance when compared to smaller analogues used in binary BHJ systems.\textsuperscript{31–36} Indeed, the highest performing squaraine based BHJ solar cell, reported by Kido \textit{et al.} exhibiting a PCE of 7.4%, relied on a large π-extended squaraine dye as the donor component.\textsuperscript{37}

In this article, we demonstrate for the first time, the use of a large π-extended squaraine dye as a third component in P3HT:PC61BM BHJ OSCs. The squaraine dye selected is based on \textit{bis}-indolesquaraine terminated with indoloquinoxaline end-capping units (SQIQ-A, Figure 1). Unlike related squaraine dyes, the aggregation of SQIQ-A can be controlled to form either H and/or J-aggregates using solvent vapour annealing (SVA) and/or thermal annealing (TA). Furthermore, by changing the absorption spectrum of the SQIQ-A, it is possible to vary the degree of overlap between the P3HT luminescence and SQIQ-A absorption and thus affecting
the FRET processes in P3HT:PC₆₁BM:SQIQ-A OSCs. In addition, we show that by changing the
nanomorphology of the P3HT:PC₆₁BM:SQIQ-A OSCs using SVA and/or TA, one can obtain the
same PCE improvements regardless of H- and/or J aggregation.

Optical characterization of P3HT and SQIQ-A.

The molecular structures and optical properties of the materials used in this study are
shown in Figure 1. The squaraine based molecule (Figure 1a), previously reported,³⁸ is easily
synthesized in high yield, is green in color, and exhibits excellent solubility in most organic
solvents allowing for uniform film formation from solution. The energy level diagram of the
BHJ is presented on Figure 1b. P3HT and SQIQ-A have the same highest occupied molecular
orbital (HOMO) energy level (~4.8 eV) as determined by cyclic voltammetry (CV) in our lab.³⁹
The similar energy levels may prevent the separation of charges through the HOMOs at their
boundary when an exciton is formed in the squaraine.³⁸,³⁹ The lowest unoccupied molecular
orbitals (LUMOs), determined by CV in our lab, decrease in energy from P3HT (ca. 2.6 eV) to
SQIQ (ca. 3.3 eV) to PC₆₁BM (ca. 3.7 eV) creating an energy cascade which may facilitate
electron transfer. The optical absorption spectrum of the P3HT:PC₆₁BM blend shows a broad
band from 300 to 650 nm with two peaks at 320 and 500 nm and two shoulders at 550 and 600
nm. The appearance of the red shoulder at 600 nm (~2 eV) is usually associated with ordering of
P3HT domains with improved intra- and inter-plane stacking (Figure 1c).⁷,⁴⁰ The addition of
SQIQ-A to P3HT:PC₆₁BM blends leads to the appearance of a peak at 700 nm and a shoulder at
370 nm with no observable change in the P3HT:PC₆₁BM absorption spectrum. Importantly, the
preservation of the vibronic feature at ~600 nm indicates that the SQIQ-A does not affect the
high degree of P3HT lamellar packing. Moreover, the P3HT and SQIQ-A are a good FRET pair
due to the strong overlap in the absorption of SQIQ-A and the photoluminescence of P3HT (Figure 1c).

![Chemical structures and energy level diagram]

**Figure 1.** a) Chemical structures of SQIQ-A, PC_{61}BM and P3HT. b) Energy level diagram of bulk heterojunction active layer highlighting potential for charge generation. c) Absorption (Abs) spectra of P3HT:PC_{61}BM and P3HT:PC_{61}BM:SQIQ-A solar cells, with 1:1 and 1:1:0.3 ratios, respectively, and photoluminescence (PL) spectrum of P3HT film (λ_{ex} = 500 nm). d) Absorption spectra of SQIQ-A films as-cast (CHCl_{3}), and SVA (3 min.) from CHCl_{3} and THF, respectively. CF = CHCl_{3} and THF = C_{4}H_{8}O.

Previously, we have shown that SQIQ-A has a thin-film optical absorption spectra that is redshifted and broadened relative to that of the solution absorption, which is commonly observed for π-conjugated organic molecules. The use of post-film deposition SVA (chloroform (CHCl_{3}) or tetrahydrofuran (THF)) on SQIQ-A thin-films resulted in dramatic changes in the optical absorption profiles. As shown in Figure 1d, use of CHCl_{3}-SVA leads to a blue shift and broadening of the low energy absorption band (λ_{max} changed from ~707 to ~648 nm), resulting in a so called ‘H-aggregation’. In the case of the use of THF-SVA, a blue shift and broadening of the low energy absorption band is also observed, but a new red shifted band appears with λ_{max} at ~771 nm, resulting in a so called ‘J-aggregation’. In all cases the onset of absorption (ca. λ_{onset}}
The photoluminescence spectrum of SQIQ-A as-cast film has two maxima at 739 and 825 nm, respectively, under excitation at \( \lambda = \sim 650 \text{ nm} \) (Figure 2). The photoluminescence of SQIQ-A film after CHCl\(_3\)-SVA remains largely unchanged. However, use of THF-SVA leads to a considerable change of the photoluminescence spectrum of SQIQ-A film as shown in Figure 2. A new pronounced maximum appears at \( \sim 776 \text{ nm} \), which is a result of J-aggregation of SQIQ-A within the film.\(^{41}\) The very low Stokes-shift (ca. 0.01 eV) suggests a very rigid structure after THF-SVA.

**Figure 2.** Photoluminescence spectra of SQIQ-A films as-cast, SVA (3 min.) from CHCl\(_3\) and THF respectively (\( \lambda_{ex} = 650 \text{ nm} \)). CF = CHCl\(_3\) and THF = C\(_4\)H\(_8\)O.

**Photophysical properties of P3HT:PC\(_{61}\)BM:SQIQ-A films.**
The performance of OSCs can be improved by post-deposition film treatment such as SVA and/or TA, which leads to a local rearrangement of molecules, driving the system towards the most thermodynamically stable state.\textsuperscript{39,42,43} Well known in the literature, the standard P3HT:PC\textsubscript{61}BM solar cell shows the greatest PCEs after TA treatment.\textsuperscript{6,44,45} For this study we used a standard ink formulation: a 1:1 P3HT:PC\textsubscript{61}BM blend ratio, 40 mg mL\textsuperscript{-1} solution in o-dichlorobenzene (ODCB) with SQIQ-A added at 0.1, 0.2, and 0.3 weight equivalents. P3HT:PC\textsubscript{61}BM and P3HT:PC\textsubscript{61}BM:SQIQ-A blend films were analyzed as-cast (Figure 3a) and after a standard 130°C TA post-deposition treatment (Figure 3b). TA has a strong effect on the optical absorption of P3HT:PC\textsubscript{61}BM blend with an increase in intensity and the three vibronic absorption shoulders becoming more pronounced (peaks, $\lambda = \sim 500, \sim 550$ and $\sim 600$ nm) which is associated with increasing $\pi-\pi$ interchain interactions and subsequent ordering of the film. The addition of SQIQ-A to the P3HT:PC\textsubscript{61}BM blends leads to the appearance of the low energy absorption band ($\lambda_{\text{max}} \sim 700$ nm) which increases with an increase in the concentration of the SQIQ-A added to the ink solution. The intensity of the absorption bands for P3HT ($\lambda_{\text{max}} \sim 500$ nm) and SQIQ-A ($\lambda_{\text{max}} \sim 700$ nm) are approximately the same for the 1:1:0.3 blends (Figure 3a). It should be noted that ternary systems with a low squaraine concentration usually have best performance, as high concentration is detrimental to the BHJ nanomorphology resulting in a subsequent loss in device efficiency.\textsuperscript{46}
Next, we probed the influence of SQIQ-A incorporation and how the formation of aggregates (H or J) induced by SVA affected the BHJ films. Each P3HT:PC$_{61}$BM:SQIQ-A blended film was subjected to SVA treatment with either CHCl$_3$ (H-aggregate formation) or THF (J-aggregate formation), followed by the standard TA at 130 °C used to induce aggregation of the P3HT. First it should be noted that P3HT:PC$_{61}$BM blends can be impacted by SVA treatment. Michael F. Toney et al. showed that use of SVA with CHCl$_3$ leads to molecular rearrangements of P3HT and that SVA with THF leads to an enhancement of both the P3HT and PC$_{61}$BM crystallinity. The SVA treatment using CHCl$_3$ was somewhat detrimental to the film morphology with phase segregation of P3HT and PC$_{61}$BM and PCE values only reached 1.3 %, a further TA step was required to improve the PCE to ~3%. The same was observed for P3HT:PC$_{61}$BM OSCs upon SVA treatment with THF where no improvement in PCE was observed. Thus, after SVA, the devices must be subjected to TA treatment to achieve a higher efficiency.

**SVA with CHCl$_3$:** Blended films of P3HT:PC$_{61}$BM:SQIQ-A were subjected to SVA using CHCl$_3$ and showed a dramatic change in optical absorption spectra, as shown in Figure 4b. More detailed changes in the absorption spectra as a function of CHCl$_3$ vapor exposure time (0.5 to 10
(minutes) are shown in Supplementary Figure S1(a-b). Changes in the absorption profile start to appear immediately with most pronounced changes appearing after 1.5 minutes of exposure to CHCl$_3$ vapour. The CHCl$_3$-SVA (1.5 min) of film leads to structural rearrangement of the SQIQ-A molecule within the P3HT:PC$_{61}$BM matrix resulting in a blue shift (from ca. ~700 to ~645 nm) and an intensity decrease of the low energy band, suggesting H-aggregation of SQIQ-A in the blend. Additionally, there is a red-shift of absorption spectra corresponding to P3HT:PC$_{61}$BM blends with the three vibronic absorption shoulders (peaks, $\lambda = 515, 560, 600$ nm) becoming more pronounced.$^{50}$ The vibronic peak ($\lambda = 600$ nm) has a stronger intensity after CHCl$_3$-SVA (3 min), which indicates a highly crystalline P3HT in this ternary system. Further TA leads only to an increase in the absorption of two peaks ($\lambda = 515$ and 560 nm), attributed to further P3HT aggregation. Consequently, SVA (CHCl$_3$) and TA have a strong effect on the nanomorphology of the P3HT:PC$_{61}$BM:SQIQ-A film, which are largely related to the reorganization of P3HT and SQIQ-A in the BHJ film.

*SA with THF*: In the case of THF-SVA, vapour exposure time was found to be very important in ‘locking-in’ aggregated morphologies. Blended films of P3HT:PC$_{61}$BM:SQIQ-A were exposed to THF vapor from 0.5 to 10 minutes as shown in the Supplementary Figure S1(c-d). Large changes in the optical absorption spectrum appear after 1 minute of exposure to THF vapour and are most pronounced from 1.5-3 minutes exposure. This treatment results in the appearance of a new red shifted band at ~770 nm accompanied by a strong decrease in intensity of the band at 700 nm (Figure 4c-d), indicative of J-aggregation of SQIQ-A in the blend. Strong changes in the absorption spectrum from 300 to 650 nm are also observed and are attributed to the reorganization of P3HT:PC$_{61}$BM in the ternary system (Figure 4c-d).$^{51}$ Prolonged exposure to THF vapor (10 minutes) results in a loss of the low energy peak at ~770 nm and the
emergence of strong, well-defined absorption bands from 600-700 nm, similar to that after CHCl$_3$-SVA treatment. This indicates a shift from J- to H-aggregation with longer exposure times, thus the formation of J-aggregates is likely not thermodynamically stable. In contrast to CHCl$_3$-SVA, the absorption profiles after subsequent TA are drastically different depending on the THF-SVA exposure time (Figure 4c-d). Sequential TA of the P3HT:PC$_{61}$BM:SQIQ-A film after 1.5 minute THF exposure results in the loss of the SQIQ-A peak at ~770 nm accompanied by the reemergence of the absorption band at ~700 nm. On the other hand, TA of the P3HT:PC$_{61}$BM:SQIQ-A film after 3 minutes exposure to THF vapor shows no loss of the low energy band at ~770 nm and only a partial reemergence of the band at ~700 nm. In both cases the band from 400-600 nm attributed to P3HT become more well defined with vibronic character emerging. The detailed changes in the absorption spectra as a function of THF vapor exposure time and thermal annealing are shown in Supplementary Figure S1(c-d).

Based on these observations, it is clear that the formation of SQIQ-A J-aggregates is not stable, but can be ‘locked-in’ to a certain degree by carefully selecting the THF solvent exposure time (2-5 minutes). Such precise control over the aggregation behavior of a ternary blend is quite unprecedented and points to the π-extended squaraine structure as a unique system to study.
Figure 4. Selected optical absorption spectra of P3HT:PC$_{61}$BM:SQIQ-A (1:1:0.3 weight ratio) BHJ OSCs:

a) films as-cast and TA at 130°C for 10 minutes.

b) films as-cast, SVA using CHCl$_3$ for 3 minutes, and SVA using CHCl$_3$ for 3 minutes + TA at 130°C for 10 minutes.

c) films as-cast, SVA using THF for 1.5 minutes, and SVA using THF for 1.5 minutes + TA at 130°C for 10 minutes.

d) films as-cast, SVA using THF for 3 minutes, and SVA using THF for 3 minutes + TA at 130°C for 10 minutes.

CF = CHCl$_3$ and THF = C$_4$H$_8$O.

Photovoltaic Properties.

Solar cells were fabricated with the inverted structure: indium tin oxide (ITO) / ZnO (30nm) / P3HT:PC$_{61}$BM:SQIQ-A (~200-220 nm film thickness) / MoOx (10nm) / Ag (100nm). The active layers were spin-cast at 1500 rpm from ODCB solutions with 40 mg ml$^{-1}$ total concentration. For complete fabrication details, see the supplementary information. All solar cells were measured under one sun illumination (simulated AM 1.5G irradiation at 100 mW cm$^{-2}$). Solar cells based on P3HT:PC$_{61}$BM:SQIQ-A active layers with varying SQIQ-A
concentration were investigated first. Current-Voltage (J-V) curves, EQE spectra, and tabulated solar cell data are presented in Figure S2 and Table S1. Solar cells with no SQIQ-A reached ~3% which is expected. The addition of the SQIQ-A dye from 0.1-0.3 weight equivalents resulted in a slight decrease of the PCE to ~2%, but photocurrent generation from 650-750 nm, where the SQIQ-A absorbs, was observed. We choose to investigate blends with a 1:1:0.3 weight ratio as a function of SVA as more dye loading should lead to more photocurrent generation.

The J-V characteristics of the P3HT:PC_{61}BM:SQIQ-A solar cells with weight ratio 1:1:0.3 and are shown in Figure 5. Device parameters are summarized in Table 1. Our standard P3HT:PC_{61}BM devices, after thermal treatment, gave PCEs of ~3% with average $J_{sc}$ of 10.32 mA cm$^{-2}$, a $V_{oc}$ of 0.58 V, and fill factor (FF) of 48%, consistent with accepted literature results. As-cast ternary P3HT:PC_{61}BM:SQIQ-A devices had PCEs of 1.5%, but could be improved to 2-3% upon thermal treatment. Looking at the device metrics, we see that the FF increases from 48 % to 57 % upon addition of SQIQ-A to the binary P3HT:PC_{61}BM system but a decrease in $J_{sc}$ from 10.32 to 8.22 mA cm$^{-2}$ is observed. This was quite surprising as we assumed the SQIQ-A would help with photocurrent generation and increase $J_{sc}$ but instead it appears the SQIQ-A has a bigger impact on the active layer morphology, improving it, leading to much better FF values. Since the thermal treatment is necessary to give best performance, all other devices investigated were subjected to such TA. Next, we investigated the effect of SVA on the solar cell device performance. Use of CHCl$_3$-SVA resulted in PCEs of ~3%. Here a large increase in $J_{sc}$ (best ca. 13.4 mA cm$^{-2}$) was observed, but the FF decreased back to ~47%. Use of THF-SVA negatively impacted all device metrics and PCEs of only ~2% were obtained.

Investigation of the external quantum efficiency (EQE) spectra of all blends shows each to be consistent with the optical absorption spectra. All devices had spectral responses from
~300-620 nm associated with P3HT:PC$_61$BM and from ~620-800 nm attributed to SQIQ-A. Looking at Figure 6a, we can see that the addition of SQIQ-A does indeed contribute to photocurrent generation in the region from ~650-750 nm. Unfortunately, the contribution from SQIQ-A is quite small and is significantly less than that observed in the optical absorption spectrum (Figure 4a). Looking at Figure 6b, we can see that the use of CHCl$_3$-SVA has the effect of increasing photocurrent-generation from ~650-700 nm, where the H-aggregated SQIQ-A absorbs. Use of THF-SVA reduces photocurrent generation across the entire spectrum. Most notable is the decrease from ~550-650 nm, primarily where P3HT is responsible for photocurrent generation. This implies that the J-aggregated SQIQ-A may be preventing charge generation and transport within the P3HT:PC$_61$BM matrix. For both the 1.5 and 3 minute THF exposure times, the EQE spectra do not match the absorption spectra, thus indicating that the SQIQ is indeed having a big impact on the electronic properties of the active layer.

Figure 5. The J-V characteristics of P3HT:PC$_61$BM (1:1) and P3HT:PC$_61$BM:SQIQ-A (1:1:0.3) BHJ OSCs. a) as-cast and thermally annealed at 130 °C for 10 minutes. b) SVA with CHCl$_3$ (3 minutes), THF (1.5 minutes), (THF 3 minutes), all films thermally annealed at 130 °C 10 minutes. CF = CHCl$_3$ and THF = C$_4$H$_8$O.
Figure 6. The J-V characteristics of P3HT:PC₆₁BM (1:1) and P3HT:PC₆₁BM:SQIQ-A (1:1:0.3) BHJ OSCs. a) as-cast and thermally annealed at 130 °C for 10 minutes. b) SVA with CHCl₃ (3 minutes), THF (1.5 minutes), (THF 3 minutes), all films thermally annealed at 130 °C 10 minutes. CF = CHCl₃ and THF = C₄H₈O.

Table 1. Tabulated data for solar cells based on the P3HT:PC₆₁BM:SQIQ-A active layers.

<table>
<thead>
<tr>
<th>P3HT:PC₆₁BM:SQIQ-A</th>
<th>Treatment</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA cm⁻²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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<tr>
<td>1:1:0</td>
<td>TA</td>
<td>0.58 (0.55)</td>
<td>10.67 (12.78)</td>
<td>48.2</td>
<td>2.96 (3.44)</td>
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<tr>
<td>1:1:0.3</td>
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<td>0.61 (0.62)</td>
<td>4.61 (4.73)</td>
<td>52.3</td>
<td>1.47 (1.50)</td>
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<tr>
<td>1:1:0.3</td>
<td>TA</td>
<td>0.60 (0.57)</td>
<td>8.22 (9.39)</td>
<td>57.5</td>
<td>2.80 (2.97)</td>
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<tr>
<td>1:1:0.3</td>
<td>¹SVA CHCl₃ + TA</td>
<td>0.52 (0.50)</td>
<td>11.85 (13.46)</td>
<td>47.0</td>
<td>2.86 (2.94)</td>
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<tr>
<td>1:1:0.3</td>
<td>²SVA THF + TA</td>
<td>0.56 (0.58)</td>
<td>7.11 (7.77)</td>
<td>44.1</td>
<td>1.77 (2.15)</td>
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<tr>
<td>1:1:0.3</td>
<td>¹SVA THF + TA</td>
<td>0.58 (0.58)</td>
<td>7.42 (7.54)</td>
<td>44.8</td>
<td>1.94 (1.97)</td>
</tr>
</tbody>
</table>

Device size: 9 mm².  
Substrate Size: 15 x 15 x 0.7 mm.  
Average values presented (values from best device in parenthesis)
Morphology characterization of the active layers

X-ray diffraction: The X-ray diffraction (XRD) patterns of relevant active layer films are shown in Figure 7. Additional XRD patterns are shown in Figures S3-S10. The P3HT:PC_{61}BM blend film shows a typical diffraction peak ~5.4° attributed to crystallized P3HT (Figure 7a). Thermal annealing shifts this peak to slightly lower angles (ca. ~5.3°) as seen in Supplementary Figure S3. Subjecting these binary blended films to SVA with either THF or CHCl\textsubscript{3} had minimal impact on the crystalline nature of the films as the diffraction patterns did not change (Supplementary Figures S4-S6). The addition of the SQIQ-A dye to the P3HT:PC_{61}BM blend did not impact the P3HT ordering as no changes were observed in the XRD pattern (Figure 7a). Upon THF-SVA for 1.5 min followed by TA at 130°C for 10 minutes of the P3HT:PC_{61}BM:SQIQ-A ternary blend, minimal changes to the P3HT peak were perceived. However, the emergence of an additional sharp higher intensity peak at ~5.9°, attributed to crystallization of the SQIQ-A molecule, was observed (Figure 7b). This diffraction peak was not observed after the P3HT:PC_{61}BM:SQIQ-A films are subjected to SVA with either CHCl\textsubscript{3} or THF 3-minutes and TA (Figure 7b). This longer SVA time most likely lead to a reorganization of organic molecules, which prevented SQIQ-A crystallization. Based on these results, the SQIQ-A does not completely impede the organization of P3HT and crystallization of the SQIQ-A molecule can be induced by short SVA-THF time and TA (note that longer SVA-THF times showed less crystalline features). Since the THF vapour annealed solar cell devices showed a decrease in performance we might rationalize that the domain sizes are becoming too large which can inhibit charge separation.
Figure 7. X-ray diffraction (XRD) patterns of P3HT:PC_{61}BM and P3HT:PC_{61}BM:SQIQ-A films: a) as-cast. b) SVA with CHCl_{3} (3 minutes) and with THF (1.5 and 3 minutes) + TA at 130 °C for 10 minutes. CF = CHCl_{3} and THF = C_{4}H_{8}O.

Study of nanomorphology – AFM/POM

Microscopy: To investigate morphology of the blend films after SVA and TA treatments, we used both atomic force microscopy (AFM) and polarized optical microscopy (POM). As shown in Figure 8, the AFM-images of binary and ternary films after TA have similar uniform surfaces with smooth root-mean-square (RMS) roughness of 1.0 and 1.2 nm, respectively. This smooth and uniform morphology reflects the good performance (ca. PCE ~3%) of both systems. Figure 9 shows AFM-images of the ternary blended films as a function of SVA and TA. The CHCl_{3}-SVA and TA leads to uneven BHJ film with a high RMS roughness of 9.9 nm (Figure 9a), but the
performance of solar cell devices remained high (ca. PCE ~3). The BHJ film subjected to THF-SVA (1.5 min) and TA exhibits long aggregates of ~2µm as seen in the AFM images (Figure 9b) which is attributed to SQIQ-A aggregation. This BHJ film is highly crystalline as shown in POM image (Figure 10b and e) which agrees well with the XRD experiments (Figure 7b). The BHJ film subjected to THF-SVA (3 minutes) and TA shows a slightly less rough/crystalline morphology. As seen in the AFM image (Figure 9c), the films are more uniform with an overall RMS roughness of ~3.5 nm. The POM images show no significant crystalline formations, but do reveal large phase separated domains. Lastly, the THF-SVA (5 min or 10 min) with or without TA leads to the complete phase separation of the organic materials as shown on Figure S12. Despite the strong difference in the morphology of the films due to SQIQ-A aggregation as a function of SVA time, the ternary systems annealed with THF have similar PCEs of ~2%. Furthermore, the SVA- CHCl₃ and TA leads to strong RMS roughness but does not affect the overall efficiency of the device.

**Figure 8.** AFM-images of a) P3HT:PC₆₁BM and b) P3HT:PC₆₁BM:SQIQ-A blended films after thermal annealing at 130 °C for 10 minutes. Both films are similar with RMS values ~1 nm and reflect the good performance of ~3% achieved for each active layer composition.
Figure 9. AFM images of P3HT:PC$_{61}$BM:SQIQ-A blended films. A) CHCl$_3$-SVA 3 minutes. B) THF-SVA 1.5 minutes. C) THF-SVA 3 minutes. All films TA at 130°C for 10 minutes. CF = CHCl$_3$ and THF = C$_4$H$_8$O.

Figure 10. Top: OM images of P3HT:PC$_{61}$BM:SQIQ-A blended films. A) CHCl$_3$-SVA 3 minutes. B) THF-SVA 1.5 minutes. C) THF-SVA 3 minutes. All films TA at 130°C for 10 minutes. Bottom: POM images of P3HT:PC$_{61}$BM:SQIQ-A blended films. D) CHCl$_3$-SVA 3 minutes. E) THF-SVA 1.5 minutes. F) THF-SVA 3 minutes. All films TA at 130°C for 10 minutes. CF = CHCl$_3$ and THF = C$_4$H$_8$O.

Conclusions

In this paper, we have explored, for the first time, the impact of adding a large π-conjugated squaraine based molecule, denoted SQIQ-A, to the classic thin-film bulk-heterojunction P3HT:PC$_{61}$BM. The SQIQ-A molecule offers strong low energy absorption and its aggregation
in the solid-state can be finely controlled through use of solvent vapour annealing and thermal annealing. The ternary blended films P3HT:PC$_{61}$BM:SQIQ-A exhibited panchromatic optical absorption with the SQIQ-A molecule primary contributing to the low energy absorption from ~650-750 nm. Importantly, the optical absorption profile of the blended film was easily modified to ‘blue’ shift or ‘red’ shift though exposure to CHCl$_3$ or THF solvent vapour, respectively. Photovoltaic devices based on this active layer showed similar power conversion efficiencies of ~3% to the standard P3HT:PC$_{61}$BM, but with improved fill factors and photocurrent generation in the red and near-IR. Unfortunately, the use of solvent vapour annealing was shown to result in crystallization of SQIQ-A molecule which resulted in the formation of large aggregated domains and a slight decrease (CHCl$_3$) and large decrease (THF) in photovoltaic performance. None-the-less, simple thermal annealing proved viable to organize all three materials into an organized structure without loss of performance. Thus, the use of large π-extended squaraine molecules as third components in P3HT:PC$_{61}$BM based solar cells is a simple strategy to change the bulk properties without significant loss in photovoltaic performance. Through structural evolution of the squaraine based molecule and rigorous device active layer optimization, we anticipate the realization of performance metrics that are superior to the binary bulk-heterojunction blend.

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Controlling the optical properties and solid state morphology of a classic bulk heterojunction blend

800x400mm (96 x 96 DPI)