Effect of Incorporation of Squaraine Dye on the Photovoltaic Response of Bulk Heterojunction Solar Cells Based on P3HT:PC$_{70}$BM Blend

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ABSTRACT: We report the improvement of the light-harvesting property in the bulk heterojunction organic polymer solar cell based on poly(3-hexylthiophene) (P3HT) and PC$_{70}$BM, with the incorporation of a near-infrared absorbing squaraine (SQ) dye, bis[4-(2,6-di-*tert*-butyl)vinyl-pyrylium] squaraine (TBU-SQ). With the incorporation of TBU-SQ dye (2.5% by wt) in a P3HT:PC$_{70}$BM (1:1 wt ratio) blend, the power conversion efficiency (PCE) has been enhanced up to 4.55% as compared to 3.47% for the device based on the P3HT:PC$_{70}$BM binary blend. The improvement in the photovoltaic performance with the incorporation of TBU-SQ attributed to the improvement in the light-harvesting efficiency in the near-infrared region of solar spectrum and increased exciton dissociation into free charge carriers in the ternary blended film. The PCE has been further enhanced to 5.15% when the thermally annealed P3HT:TBU-SQ:PC$_{70}$BM blend was used as the photoactive layer. It was observed that the absorption profile of the active layer was broadened upon thermal treatment as a result of the red shift as well as widening of the P3HT absorption band and the slight red shift of the TBU-SQ absorption peak in the blended film. The improved light-harvesting property of the thermally annealed film and balanced charge transport in the device were attributed to the improvement in the PCE. These results show that TBU-SQ is a promising molecular sensitizer for increasing the PCE of P3HT:PC$_{70}$BM-based polymer solar cells.

KEYWORDS: *Organic bulk heterojunction solar cells, Squaraine dye, Light harvesting, Near-infrared absorption*
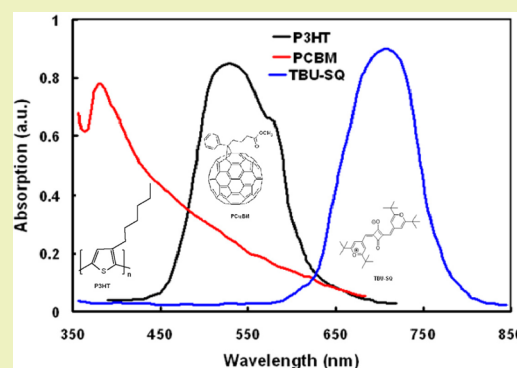
■ INTRODUCTION

The polymer/fullerene bulk heterojunction (BHJ) solar cells represent one of the most promising technologies for next generation solar energy conversion due to their low cost and large scale production.[1−8] The fundamental concept of BHJ organic solar cells involves the formation of self-assembly of a nanoscale interpenetrating network by spontaneous phase separation of an electron donor polymer and an electron acceptor fullerene throughout the whole volume of the active layer.[9−11] In binary BHJ solar cells based on a polymer−fullerene blend, the short circuit current (J_{sc}) is related to the absorption profile of the photoactive layer, which is generally limited by the band gap (E_g) of the donor polymer.[12] In general, a smaller E_g material such as D−A small molecules and polymers with a wider absorption profile absorbs the light in a broader wavelength region and consequently results in a high J_{sc}. However, the open circuit voltage (V_{oc}) is related to the energetic difference between the highest occupied molecular orbital (HOMO) energy of the donor and the lowest unoccupied molecular orbital (LUMO) energy of the acceptor.[13] It is well known that the energetic driving force (depends upon the energy difference between the LUMO level of donor

and acceptor) is needed for efficient photoinduced charge transfer in the BHJ active layer.[14] To achieve both high J_{sc} and V_{oc} in the BHJ organic solar cells, a donor with a broader absorption profile and a deep HOMO level of donor, respectively, is needed. It was found that after optimizing the HOMO and LUMO energy levels of donor and acceptor components employed in the BHJ active layer, organic solar cells with power conversion efficiencies from 2.5% to 7−9% have been reported.[15−21] However, the overall PCE of organic solar cells is limited to 10−12%.[7]

Poly(3-hexythiophene) (P3HT) as donor and [6,6]-phenyl C$_{60}$ or C$_{70}$ butyric acid methyl ester (PC$_{60}$BM or PC$_{70}$BM) as acceptor are the most promising materials for high PCE polymer solar cells.[22−28] Apart from controlling the nanostructure of the BHJ active layer,[29,30] one major limitation of most semiconducting conjugated polymers is their high band gap, and therefore, photon absorption beyond the wavelength of 620 nm in the solar spectrum is almost negligible. The large

difference between LUMO levels of P3HT and fullerene derivatives, P3HT:PC$_{60}$BM or PC$_{70}$BM blended solar cells, also produce an unnecessary dissociation energy loss.[24,31−33] To overcome this limitation, extensive research work has been directed toward the development of new low band gap polymers with broad absorption bands[11,18,20,34−47] by using a donor−acceptor (D−A) approach, i.e., manipulating the HOMO and LUMO energy levels of the D−A copolymers. The processing of BHJ active layers based on these low band gap polymers generally require processing solvent additives, and it is difficult to control precisely both the crystalline and phase separation in the BHJ active layer. The PCE of the BHJ organic solar cells can be enhanced by extending the absorption profile of the active layer from the visible to near-infrared region.[48−50] This can be achieved by using a tandem structure[51−55] with two or more stacked subcells, each of which has a complementary absorption spectrum. However, in tandem solar cells, control and modification of the respective layer thickness and designing a full functional intermediate layer are big challenges.[55]

An alternative approach to improve the PCE of the polymer BHJ solar cells is to employ a ternary active layer consisting of either two polymer donors and a fullerene acceptor; one polymer donor and two fullerene acceptors; a polymer donor, a fullerene acceptor, and a small molecule; or a polymer donor with a nanoparticle and a fullerene acceptor that together provide complementary absorption spectra and full coverage of the solar spectrum.[56−69] In the ternary system, the energy band offsets of two donor materials must be matched with the third material. The performance of the polymer:small molecule:-fullerene ternary solar cells can theoretically be better than the performance of polymer:polymer blended solar cells.[56,67] In addition to complementary absorption spectrum and appropriate energy levels, conjugated small molecules must show good miscibility with electron donor and electron acceptor materials in order to control the domain size of the ternary BHJ active layer for efficient photoinduced charge transfer at the D−A interfaces.

Squaraine (SQ) dyes have been effectively used for small molecule organic solar cells. SQ dye-based molecules showed a broad band absorption from 550 to 900 nm in thin film, a high absorption coefficient (over 1×10^5 M^{-1} cm^{-1}), and good photochemical and thermal stability.[70−78] Recently, Thompson et.al have reported a SQ-based small molecule donor for an organic photovoltaic device, and after optimizing the morphology and molecular ordering of the SQ:PC$_{70}$BM active layer, they achieved a PCE of 5.5%[75] because the SQ-based small molecules have strong absorption bands in the near-infrared region of the solar spectrum where the P3HT has no absorption. Therefore, SQ-based small molecules can be employed as additional donors in the ternary BHJ active layer to improve the PCE of the organic solar cells through enhancing the absorption profile of the active layer in the wider wavelength range covering from the visible to near-infrared region. Recently, Forrest et al. have shown that incorporation of a small quantity of SQ dye into the P3HT:PCBM blend enhnaces the PCE up to 3.4% from 2.75% for P3HT:PCBM-based solar cells.[79]

Recently, we have used bis[4-(2,6-di-*tert*-butyl)vinyl-pyrylium] squaraine dye (TBU-SQ) as the donor material for solution-processed small molecule solar cells. However, the PCE of the TBU-SQ-based BHJ solar cell showed a relatively low PCE of 1.76% and is primarily limited by the relative FF of

the device, which can be described by the low charge carrier mobility of TBU-SQ.[80]

In this paper, we report a significant improvement in the PCE of the P3HT:PC$_{70}$BM BHJ solar cell due to an increase in the near IR harvesting capability using TBU-SQ as the third component in a ternary blend. The overall PCE of the solar cell based on P3HT:PC$_{70}$BM was improved up to 4.55% with incorporation of TBU-SQ (2.5% wt) and was further improved up to 5.15% with the thermally annealed ternary blend.

■ EXPERIMENTAL DETAILS

BHJ films of P3HT and PC$_{70}$BM (1:1 wt ratio) were prepared from a THF solution via the spin-coating method. For the ternary active layer, TBU-SQ (2.5% wt) was incorporated into the P3HT:PC$_{70}$BM blend. The synthesis and characterization of TBU-SQ has also been reported in our earlier report.[80]

Organic photovoltaic devices were fabricated on an indium tin oxide (ITO)-coated glass substrate with sheet resistance of 10 Ω/square. Before coating with organic layers, the ITO-coated glass substrate was cleaned by sonification in isopropropyl alcohol and acetone and was then rinsed in deionized water and then dried. The polymer photovoltaic devices were fabricated by spin-coating blends of P3HT:PC$_{70}$BM and P3HT:TBU-SQ:PC$_{70}$BM onto poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). First, PEDOT:PSS is spin coated onto the ITO-coated glass substrate at 2000 rpm for 30 s, followed by annealing at 80 °C for 20 min in air. Then, an active layer, i.e., P3HT:PC$_{70}$BM (1:1) or P3HT:TBU-SQ:PC$_{70}$BM (1:1 with different concentration of TBU-SQ), was spin coated on the PEDOT:PSS layer at 1500 rpm for 30s and was dried in ambient conditions. The average thickness of the PEDOT:PSS layer was 60 nm, and the active layer thickness was about 90 nm. The aluminum (Al) electrode was deposited with the thermal evaporation method. The prethermal annealing of the active layer was carried out at 110 °C for 2 min on a hot plate before deposition of the Al electrode.

The current−voltage (J−V) characteristics of the fabricated devices were measured using a computer-controlled Keithley source meter in dark and under an illumination intensity of 100 mW/cm^2. A xenon light source was used to give a simulated irradiance of 100 mW/cm^2 (equivalent to an AM 1.5 irradiation) at the surface of the device. The J−V characteristic measurements under illumination were carried out in a dark chamber with a window slit of 10 mm^2 area for illumination.

■ RESULTS AND DISCUSSION

The chemical structures of P3HT, PC$_{70}$BM, and TBQ-SQ are shown Figure 1. Figure 2 shows the optical absorption spectra of PC$_{70}$BM, P3HT, and TBU-SQ dye thin films. It is shown in this figure that the PC$_{70}$BM absorbs mainly below the wavelength region 500 nm with a peak around 380 nm. The P3HT spectrum shows an absorption peak at 520 nm and absorption edge extending up to 630 nm, and TBU-SQ shows an absorption band in the longer wavelength region extending
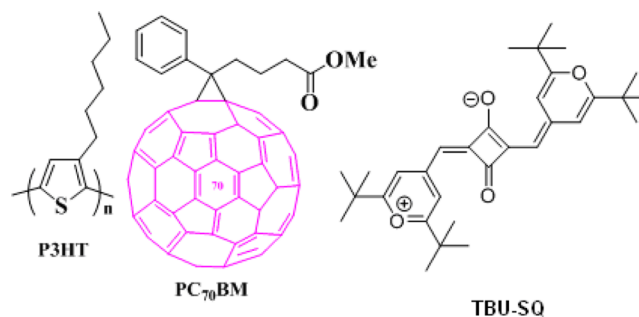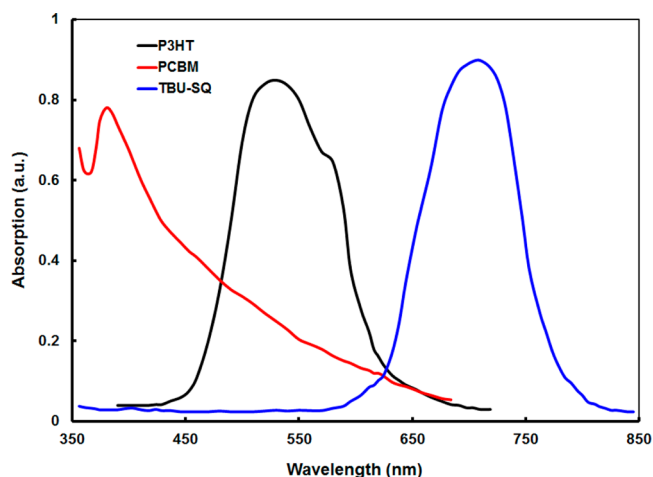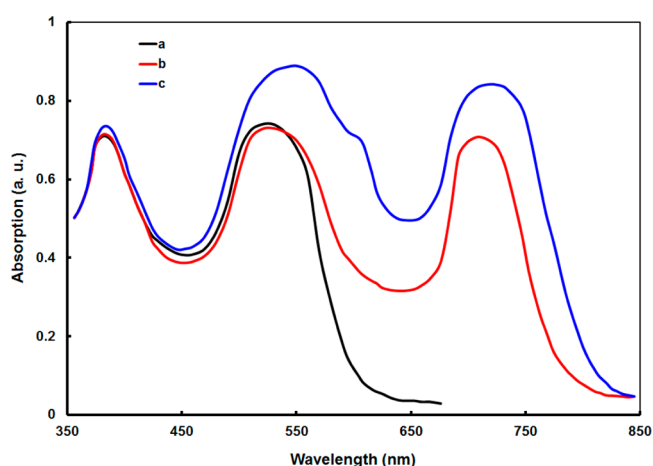

Figure 1. Chemical structure of P3HT, PC$_{70}$BM, and TBU-SQ.

**Figure 2.** Optical absorption spectra of $PC_{70}BM$, P3HT, and TBQ-SQ thin film cast from THF solution.

up to 800 nm with an absorption peak around 708 nm. In addition, P3HT shows a shoulder at 570 nm, representing a vibronic structure due to its crystalline nature.[81] Figure 3 shows

Figure 3. Optical absorption spectra of (a) $P3HT:PC_{70}BM$, (b) $P3HT:PC_{70}BM$ (1:1):TBU-SQ (2.5 wt %) (as cast), and (c) $P3HT:PC_{70}BM$ (1:1):TBU-SQ (2.5 wt %) (thermally annealed) blended thin films.

the absorption spectra of $P3HT:PC70BM$ and P3HT:TBU-SQ:$PC_{70}BM$ blended films. The $P3HT:TBU-SQ:PC70BM$ blended film showed a broad and intense absorption band around 340−450 and 450−630 nm can be ascribed to the absorption spectrums of $PC_{70}BM$ and P3HT, respectively. The enhanced absorption in the 650−780 nm range relative to the $P3HT:PC_{70}BM$ blended film arises from the absorption of TBU-SQ, which contributes to the NIR wavelength region. Therefore, TBU-SQ is suitable for extending the absorption region of a BHJ active layer toward the longer wavelength region.

The current−voltage (J−V) characteristics of the photovoltaic devices based on $P3HT:PC_{70}BM$ (1:1) and P3HT:TBU-SQ (2.5% wt):$PC_{70}BM$ blends cast from the THF solvent are shown in Figure 4, and the photovoltaic parameters are listed in Table 1. We have fabricated a series of ternary BHJ polymer solar cells with different TBU-SQ concentrations (0.5, 1.0, 2.0, 2.5, and 3.0 wt %) as the second
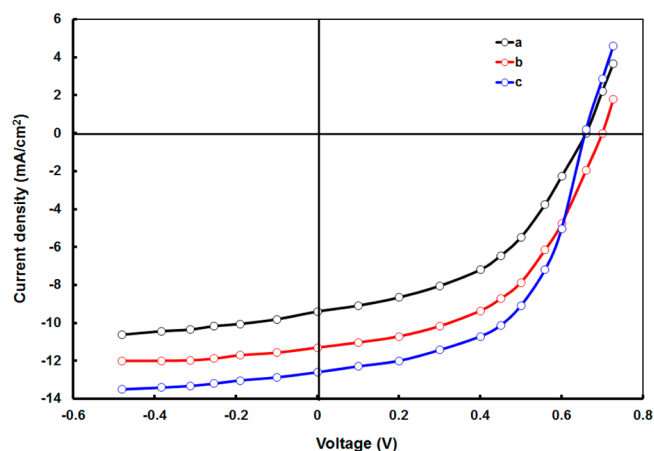

Figure 4. J−V characteristics of BHJ organic solar cells based on (a) $P3HT:PC_{70}BM$ (as cast), (b) $P3HT:PC_{70}BM:TBU-SQ$ (as cast), and (c) $P3HT:PC_{70}BM:TBU-SQ$ (thermally annealed) blends.

Table 1. Photovoltaic Parameters of BHJ Solar Cells Using Different Blends

TBU-SQ in $P3HT:PC_{70}BM$ (wt %)	J_{sc} (mA/cm²)	V_{oc} (V)	FF	PCE (%)
0^a	9.4	0.66	0.56	3.47
0.5^a	9.94	0.66	0.56	3.67
1.0^a	10.43	0.68	0.57	4.04
2.0^a	10.85	0.68	0.58	4.28
2.5^a	11.2	0.70	0.58	4.55
3.0^a	10.65	0.69	0.58	4.26
2.5^b	12.6	0.66	0.62	5.15

^{a}Cast from THF. ^{b}Thermally annealed.

electron donor, and the photovoltaic data are summarized in Table 1. The inclusion of TBU-SQ (2.5 wt %) into the $P3HT:PC_{70}BM$ blend yields both increased J_{sc} and FF (J_{sc} increased from 9.4 to 11.2 mA/cm² and FF from 0.56 to 0.58) relative to the $P3HT:PC_{70}BM$ blend. The enhancement in the J_{sc} with TBU-SQ is attributed to the increase in the photogenerated excitons as a result of a broader absorption profile (Figure 3). The IPCE spectrum of the device is shown in Figure 5. The IPCE spectra of the device based on the $P3HT:PC_{70}BM:TBU-SQ$ ternary blend is closely resembled to
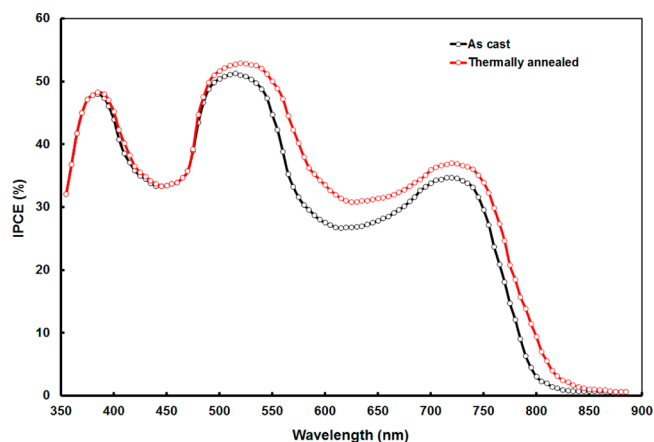

Figure 5. Incident photon to current conversion efficiency (IPCE) of organic BHJ solar cells based on cast and thermally annealed P3HT:PC70BM:TBU-SQ active layers.

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dx.doi.org/10.1021/sc500276u | ACS Sustainable Chem. Eng. 2014, 2, 1743−1751

the absorption spectra of the ternary blend. The IPCE spectrum show three clear bands, which correspond to $PC_{70}BM$ (around 385 nm), P3HT (around 520 nm), and TBU-SQ (around 710 nm), indicating that each component in the ternary blend contributes to the exciton generation. With the incorporation of TBU-SQ into the P3HT:$PC_{70}BM$ blend, the overall PCE of the polymer BHJ solar cell improved up to 4.55%. Similar results have been reported by Ota et.al with the incorporation of boron dibenzopyrromethene (BODIPY) dye into the P3HT:$IC_{70}BA$ blend-based organic solar cells.[82] They found that with the addition of BODIPY, the carrier mobility has been improved due to the controlled nanoscale crystallinity of P3HT in the polymer solar cells. It is shown in Table 1 that the PCE of the ternary BHJ device decreases when the concentration of TBU-SQ was more than 2.5 wt %, which is mainly due to the decreased value of J_{sc}. The decreased value of J_{sc} may be attributed to the disturbed interpenetrating network between P3HT and $PC_{70}BM$ with the relative decrease in P3HT:$PC_{70}BM$ content with the high concentration of TBU-SQ, which hinders the charge transportation.[69,83]

To explain these results, we have used schematic energy level diagrams of charge generation and transfer in the solar cells with P3HT:TBU-SQ:$PC_{70}BM$ as shown in Figure 6. We
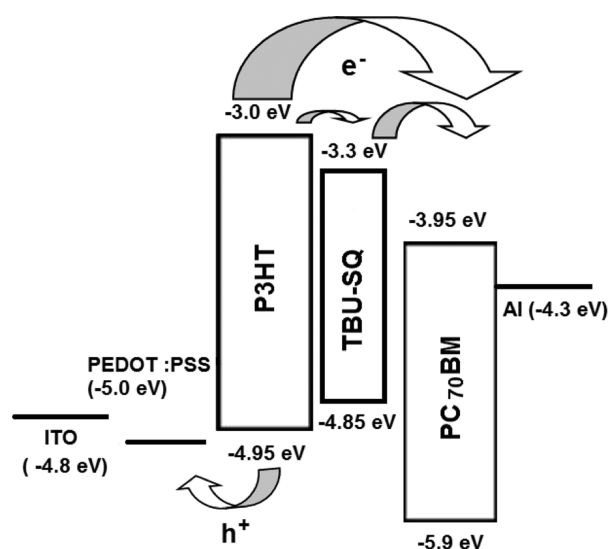
Figure 6. Energy level diagrams of P3HT, TBU-SQ, and $PC_{70}BM$ in the organic solar cell employing a ternary BHJ active layer.

assume that the TBU-SQ is located at the interface between $PC_{70}BM$ and P3HT as reported in the literature for ternary system-based organic solar cells.[60−64] The energy levels, i.e., HOMO and LUMO of TBU-SQ[80] and P3HT,[84] were determined by cyclic voltammetry measurement. The HOMO and LUMO levels of P3HT were estimated to be −4.8 and −2.9 eV, respectively. The energy levels of $PC_{70}BM$[85] are taken from the literature. The HOMO energy level of the TBU-SQ dye (4.85 eV) is estimated to be lower than that of P3HT by 0, and 25 eV enabled it to avoid charge trapping on the TBU-SQ dye. Therefore, P3HT acts as an electron donor, and TBU-SQ acts as an acceptor molecule at the heterojunction formed between P3HT and TBU-SQ. Therefore, it is considered that the photoinduced charge transfer in the donor−acceptor system occur at the D−A interfaces, i.e., P3HT/TBU-SQ, P3HT/$PC_{70}BM$, and TBU-SQ/$PC_{70}BM$. As discussed above, the ternary blend showing a wider absorption from 350 to 800

nm implies that the photons are absorbed by each component and generates excitons. When the excitons are generated in the P3HT phase, they are dissociated at the P3HT/TBU-SQ interface, and TBU-SQ accepts electrons from the P3HT and transfers electrons to $PC_{70}BM$. However, when the excitons are generated in TBU-SQ due to the absorption of photons by TBU-SQ, after the exciton dissociation, TBU-SQ donated holes to P3HT and transfers the remaining electrons to $PC_{70}BM$. Photoinduced charge transfer also occurs between P3HT and $PC_{70}BM$. The interfacial area between P3HT and $PC_{70}BM$ might decrease upon the addition of TBU-SQ, but the TBU-SQ works as both an electron acceptor and electron donor transport material. The TBU-SQ has a strong light-harvesting property in near IR where P3HT does not, and it also behaves as both a donor and an acceptor with respect to $PC_{70}BM$ and P3HT, respectively. Therefore, the photon absorption efficiency of the polymer solar cell in the NIR could be improved without decreasing the D−A interface area.

The V_{oc} of the device was also slightly increased by incorporation of TBU-SQ in the P3HT:$PC_{70}BM$ blend. Because V_{oc} is related to the energy difference between the donor HOMO and acceptor LUMO levels, there should be a change in V_{oc}, if the exciton separation process occurs at the TBU-SQ/$PC_{70}BM$ interface. Considering the HOMO levels of P3HT and TBU-SQ, there is a 0.2 eV energy difference between them, which is suitable for energy transfer. The difference between the LUMO level of TBU-SQ and $PC_{70}BM$ is about 0.65 eV, which provides sufficient driving force for the exciton dissociation at the TBU-SQ/$PC_{70}BM$ interface and possibly the exciton separation also occurs at this interface and increases the value of V_{oc}.

The V_{oc} of a BHJ solar cell is expressed as

$$V_{oc} = [nkT/q]\ln(J_{sc}/J_{so}) + \Delta E_{DA}/2q$$

Here, n is the diode ideality factor, k is the Boltzmann's constant, T is the Kelvin temperature, J_{sc} is the short circuit current, J_{so} is the leakage current, and ΔE_{DA} is the interfacial energy gap between the donor and acceptor. The above equation suggests a linear dependence of V_{oc} on the ΔE_{DA}. In spite of the similar HOMO levels of P3HT and TBU-SQ, the V_{oc} has been increased after incorporation of the TBU-SQ dye. For a given ΔE_{DA}, J_{so} played a role in controlling the V_{oc}.[86,87] The magnitude of J_{so} depends upon the carrier generation, recombination rate, and independent energy barrier ΔE_{DA}. As discussed above, the J_{so} is lower for the P3HT:TBU-SQ:$PC_{70}BM$ blend-based device as compared to P3HT:$PC_{70}BM$, and the increase in V_{oc} may be attributed to the lower value of J_{so}.

The electron and hole mobilities in the BHJ active layer play important roles in the PCE of the organic BHJ solar cells. To understand the increase in the PCE of the BHJ polymer solar cells after the incorporation of a small amount of TBU-SQ in the P3HT:$PC_{70}BM$, we have estimated the electron and hole mobilities of the device with and without TBU-SQ in the P3HT:$PC_{70}BM$ blend. We have fabricated a hole-only device ITO/PEDOT:PSS/blend/Au and electron-only device (Al/blend/Al), where the blend is P3HT:$PC_{70}BM$ with and without TBU-SQ and recorded the current−voltage characteristics in the dark. The space charge limited current (SCLC) hole and electron mobilities were estimated using the Mott−Gurney square law.[88]

$$J = (9/8)\varepsilon_0\varepsilon_r\mu_{eorh}(V^2/L^3)$$

where J is the current density, L is the thickness of the active layer, μ_{eorh} is the electron or hole mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10^{-12} F/m), V is the internal voltage of the device, i.e, $V = V_{app} - V_{bi}$, V_{app} is the voltage applied to the device, and V_{bi} is the built in voltage due to the relative work function of two electrodes. V_{bi} has been determined from the transition between the Ohmic region and the SCLC region. We found that the hole mobility has been increased from 3.4×10^{-6} to 5.2×10^{-5} cm^2/(V s) with the incorporation of TBU-SQ in the P3HT:PC$_{70}$BM blend, whereas the electron mobility slightly increases from 4.67×10^{-4} to 5.34×10^{-4} cm^2/(V s). The ratio of electron mobility to hole mobility has been reduced from 137.35 to 10.27 with the incorporation of the TBU-SQ in the blend, resulting in more balance charge transport and enhancing the J_{sc} and PCE. The incorporation of TBU-SQ in the P3HT:PC$_{70}$BM blend may have influenced the absorption spectra, charge separation, and charge transport, all of which would have improved the PCE of the solar cell.

We have also compared the series resistances (R_s) and shunt resistance (R_{sh}) of the devices estimated from the slope of $J-V$ characteristics under illumination at the voltage near 0.8 and 0 V, respectively. It was found that the R_s has been decreased for the device based on the BHJ active layer with TBU-SQ as compared to that without TBU-SQ.

We have also measured the X-ray diffraction pattern of the BHJ P3HT:PC$_{70}$BM with and without TBU-SQ (Figure 7).
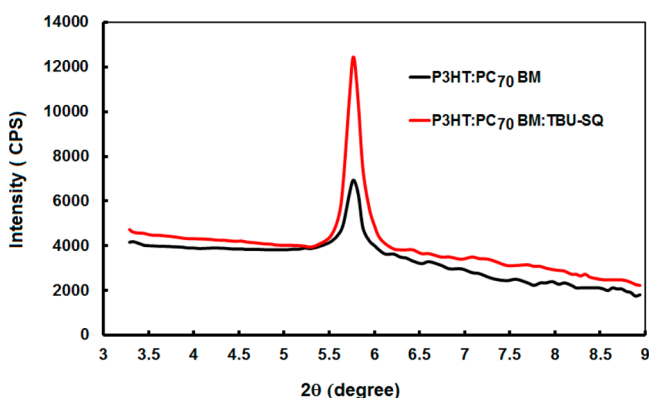
Figure 7. XRD patterns of P3HT:PC$_{70}$BM and P3HT:PC$_{70}$BM:TBU-SQ thin films.

Incorporating TBU-SQ in the P3HT:PC$_{70}$BM increases the intensity of the diffraction peak at $2\theta = 5.76°$ (corresponds to the interchain spacing of P3HT), indicating that the crystalline fibrils consisting of a more ordered packing of P3HT chains were formed by TBU-SQ. We suggest that the changes in the morphology induced by TBU-SQ leads to well-organized interpenetrating nanodomains and hence enlarge the donor/acceptor interfacial area for efficient generation of charge carriers.

The incorporation of TBU-SQ in the active layer of the polymer BHJ solar cells has significantly improved the PCE but is still low as compared to other low band gap conjugated polymer solar cells. The performances of polymer BHJ solar cells are affected by many other factors, e.g., interaction of donor polymers and acceptors, morphology of the blended films, interfacial properties, and electrodes.[89−91] All these parameters are crucial for exciton generation, charge transfer,

and collection. A larger D−A interfacial area that requires a controlled phase separation between donor and acceptor (nanoscale morphology) is necessary for efficient excitons dissociation. Several effective methods have been developed to optimize the phase separation formed by the electron donor and acceptor molecules, including thermal annealing[25,26,92,93] and solvent additives.[22,27,94] We have investigated the effect of thermal annealing on the optical absorption of the blends and photovoltaic response of the BHJ devices based on the P3HT:TBU-SQ:PC$_{70}$BM blend.

The $J-V$ characteristics of the polymer solar cell-based thermally annealed P3HT:TBU-SQ:PC$_{70}$BM blend is shown in Figure 4, and the photovoltaic parameters are complied in Table 1. The overall PCE of the devices based on thermally annealed P3HT:TBU-SQ:PC$_{70}$BM reached up to 5.15%, which is higher than that of the device based on the cast from the THF solvent. This increase may be mainly attributed to enhancement of the J_{sc} and FF. The photocurrent of the organic solar cells depends strongly on both light absorption and charge carrier transfer. We assume that the increase in the J_{sc} is attributed to the both enhancement in light absorption and charge carrier transfer ability because the absorption band of the thermally annealed blend is broadened as discussed below.

The optical absorption spectra of thermally annealed P3HT:TBU-SQ:PC$_{70}$BM blended film cast from THF is also shown in Figure 3. The major effect of thermally blended films is that the shifting of absorption peak corresponds to P3HT shifting toward the longer wavelength region. The P3HT in the P3HT:PC$_{70}$BM blended film cast from the THF solvent shows an absorption peak at 520 nm, whereas for thermally annealed film, it shows an absorption peak around 540 nm. In the case of the P3HT:TBU-SQ:PC$_{70}$BM blended film, the absorption peak that resulted from the incorporation of TBU-SQ into the P3HT:PC$_{70}$BM blend not only slightly shifts toward the longer wavelength region but also gets broadened. Generally, the shift of the absorption spectrum in the thin film of SQ upon thermal annealing may be the due aggregation. The marginal shift in the absorption peak of TBU-SQ upon thermal annealing may be due to the small amount of TBU-SQ in the blend, and TBU-SQ is not aggregating in the blended film. The red shift in the absorption peak corresponds to P3HT, and the broadening of the TBU-SQ absorption band results in a broadening of the absorption wavelength range of the P3HT:TBU-SQ:PC$_{70}$BM. The intensity of the absorption band also increases for the thermally annealed blended thin film. By comparing, we can observe that the red shift in the absorption band corresponding to P3HT in the P3HT:TBU-SQ: PC$_{70}$BM blended film is higher than that of the absorption band resulting from TBU-SQ in the blend.

The absorption spectra the P3HT:TBU-SQ:PC$_{70}$BM blended thin film is red shifted (particularly the band corresponding to P3HT) and can be explained on the basis of the structural organization of the P3HT chains, which are known to crystallize upon thermal annealing.[95] After thermal annealing, a part of the absorption spectra of P3HT originates from the ordered phase and is red shifted. The thermal annealing extends the polymer chains through the crystallites and results in an increase in conjugation length. The shift in the absorption band toward the longer wavelength region is more pronounced for P3HT as compared to TBU-SQ. This means that the effect of thermal annealing on P3HT is higher due to large molecules than that of TBU-SQ as a small molecule in the

blend. The red shift in the absorption of the thermally annealed P3HT:TBU-SQ:PC$_{70}$BM film is an indication of the increase in the conjugation length in the blend. This means that the alternation of single−double bonds between carbon atoms increases and, therefore, shifts the $\pi-\pi^*$ transition toward lower energy, resulting in a decrease in the effective optical bandgap of the thermally annealed thin film. Therefore, in the thermally annealed P3HT:TBU-SQ:PC$_{70}$BM blend, the P3HT and TBU-SQ absorb a large amount of light photons, which have lower energy, and consequently, the generation of charge carriers may increase in the solar cells. Therefore, with thermally annealed film, light-harvesting efficiency was enhanced through the increase in absorption intensity in the blend and broadening of the wavelength range.

We have also measured the electron and hole mobility of the thermally annealed film, and the ratio of electron to hole mobility has been reduced to 6.23, indicating more balanced charge transport in the thermally annealed BHJ active layer due to its increased crystallinity.

CONCLUSION

In this paper, we investigated the effect of the incorporation of TBU-SQ squaraine dye on the photovoltaic performance of P3HT:PC$_{70}$BM bulk heterojunction organic solar cells. In the P3HT:TBU-SQ:PC$_{70}$BM, the light-harvesting property in the wavelength region from 620 to 800 nm was improved, and J_{sc} was enhanced from 9.4 to 11.2 mA/cm^2. As a result, the PCE was improved from 3.47% to 4.55%. Recently, similar improvement in the PCE (3.4%) of the P3HT:PC$_{60}$BM blend with the incorporation of a SQ dye has been observed by Kido et al.[96] This shows the TBU-SQ behaves as a more effective sensitizer than other SQ dyes.

The PCE has been further improved up to 5.15%, when the thermally annealed P3HT:TBU-SQ:PC$_{70}$BM blended film was used as photoactive layer. This improvement has been attributed to the broadening of the absorption wavelength range induced by thermal annealing. The thermal annealing of the photoactive layer results in an increase in conjugation length of the P3HT chain. In the P3HT:TBU-SQ-PC$_{70}$BM active layer, the TBU-SQ dye rises the light harvesting of the blend effectively and also increases the D−A interfaces for exciton dissociation in the blend. These results indicate that organic solar cells based on solution-processed ternary BHJ active layers are promising candidates for next generation solar cells.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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