Nano-size thin films comprising poly (3-hexylthiophene) (P3HT) and a fullerene derivative [6, 6] phenyl-C$_{61}$-butyric acid methyl ester (PCBM) incorporating squarylium dye III (SQ3) are reported. The materials prepared were evaluated for their optical, electrical and photo-conversion efficiency. Active layer materials comprising a blend of P3HT:SQ3:PCBM were deposited by spin-coating to produce thin films measuring 100 nm and subsequently annealed at 140°C for 10 min. The films were characterized by UV-Vis-NIR spectroscopy for their optical properties, atomic force microscopy for surface morphology and film thickness, and electrical properties. Optical measurements for blends incorporating different amounts of dye showed increased photo-absorbance with increasing dye concentration. The combined contribution of SQ3 and thermal annealing resulted in increased power conversion efficiency ($\eta$) of pristine P3HT:PCBM solar cells from 1.9 to 3.9 %. The dye in the active layer improved photo-absorption by enhanced light harvesting while thermal treatment improved the nanoscale morphology leading to better metal-film interface contact and broadening of the absorption wavelength range.

Key words: Polymer solar cell (PSC), squarylium dye III (SQ3), bulk hetero-junction (BHJ), power conversion efficiency (PCE), poly (3-hexylthiophene (P3HT), [6, 6]-phenyl C$_{60}$ butyric acid methyl ester (PCBM).

INTRODUCTION

Energy is essential to modern society. Its global demand has continued to increase due to increasing population and rapid economic development in Africa. Depletion in fossil fuel resources together with the demand for more environmentally friendly energy sources has given impetus to research on ‘green’ energy alternatives.
Conversion of solar energy via photo-voltaic systems has emerged as one of the most promising of the green energy alternatives that can be deployed on a large scale. The cost of generating power using the current solar cells is more expensive than commercial power generation (Miyake et al., 2010). Conventional solar cells currently are made of silicon which is associated with high manufacturing cost due to processes that requires high temperature and vacuum. Additionally, dissemination has been hampered by high installation costs. Polymer solar cells offer a tantalizing possibility of lower cost devices. One of the most promising polymer solar cell (PSCs) in terms of efficiency and long term stability, is the system based on regio-regular poly(3-hexylthiophene) (rrP3HT) as the electron donor and the fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as the electron acceptor material. To attain high efficiencies in PSCs, there is need to understand the fundamental electronic interactions between the polymeric donors and the fullerene acceptors as well as the complex interplay of device architecture, morphology and processing. Additionally, a sound understanding of the fundamental electronic processes involved is important.

The state of the art in the field of PSCs is currently represented by bulk hetero-junction (BJH) solar cells based on P3HT and PCBM (Yu et al., 1995; Hoppe, 2006; Kim et al., 2006; Ma et al., 2005; Padinger et al., 2003; Reyes-Reyes et al., 2005). Low photo-conversion efficiencies of polymer solar cells compared to their inorganic counter-parts have remained a major drawback towards commercialization. Photo-conversion is typically below 9%. The limitation towards achieving high efficiencies can in-part be attributed to their narrow absorption band which lies in the 450 to 750 nm region. P3HT has a large band gap of about 1.9 eV with a limiting wavelength of harvested light of 650 nm. Almost half of the sun's power spectrum lies outside the absorption range of many organic systems (Bird et al., 1986; Diffey, 1991). Hence, thicker layers in the order of 300 nm would be required to enhance photo-absorption. However, use of layers of this thickness would lead to recombination of charges. As a compromise, polymer layers are typically 200 nm (Stratakis and Kymakis, 2013).

Organic dyes have been used to increase light harvesting capacity in P3HT:PCBM blend (Ameri et al., 2013). Squaraine dyes have been reported as promising small molecules that can be incorporated into polymer solar cells to improve light harvesting capacity owing to their intense absorption in the long wavelength range (Chen et al., 2014). Power conversion efficiencies of 5.5% have been obtained in ternary P3HT:PCBM systems incorporating a squaraine dye following thermal annealing (Rao et al., 2014). They observed enhanced absorption in the range 650 to 780 nm relative to P3HT:PCBM blend. Huang et al. (2013) demonstrated experimentally that in addition to extending absorption in the solar spectrum, small molecules, such squaraine dyes (SQ), improved exciton harvesting via Förster resonance energy transfer (FRET). Inclusion of SQ provides two mechanisms for charge transfer following excitation. The first one involves excitation of P3HT and charge transfer to PCBM while the second is charge transfer involving FRET of the P3HT excitation to SQ and subsequent dissociation. In this paper we report the improvement in power conversion efficiency of pristine P3HT:PCBM through the combined contribution of squarylium III dye (SQ3) and thermal annealing. Ternary P3HT:SQ3:PCBM systems showed an increase in absorption maximum and a red shift in the absorption band. The combined effect of dye inclusion and thermal annealing was to increase power conversion efficiency from 1.9 to 3.9%.

**EXPERIMENTAL PROCEDURES**

**Materials and solutions**

Regio-regular P3HT, PCBM and SQ3 were used without further purification. P3HT:PCBM blends containing SQ3 concentrations of 4.76, 9.09, 13.04 and 16.67% were prepared to investigate the effect of dye loading. The blend solutions were vigorously stirred for more than 24 h at room temperature under nitrogen atmosphere in a glove box to maximize mixing.

**Film and device fabrication**

For optical absorption measurements, the P3HT:PCBM and P3HT:SQ3:PCBM blend films (with different concentrations of the dye) were prepared by spin-coating the solutions onto cleaned micro-glass substrates. Thin film preparation and thermal annealing conditions were kept the same as those of the corresponding devices for accurate comparison. For solar cell fabrication, ITO-glass (15 Ohm/sq) substrates were sequentially cleaned in an ultrasonic bath using acetone and methanol, rinsed with de-ionized water then finally dried. PEDOT:PSS was spin-coated onto the ITO layer in air and dried using a digitally controlled hot plate at 100°C for 10 minutes. The PEDOT:PSS layer increased the electrode work function and its electrical connection with the organic active layer. The P3HT:PCBM and P3HT:SQ3:PCBM blend solutions were spin-coated (1500 rpm) on top of the insoluble PEDOT:PSS layer. Thin films were then heated at 100°C for 10 min to remove any residual solvent. A 100 nm thick aluminum (Al) electrode was thermally deposited onto the active layer using a vacuum deposition system at a pressure of about 3 x 10^-5 Pa through a shadow mask to obtain cells with an active area of 1cm². Devices were thermally annealed at 140°C for 4 min. The complete organic solar cells, with a configuration shown in Figure 1, were stored in the dark under suitable pressure until measurement.

**Measurements**

Films prepared were characterized for their optical properties using a Lambda 90 UV-Vis-NIR spectrophotometer before and after annealing. Morphological characteristics were established by atomic force microscopy. The power conversion efficiency (PCE) was calculated from the Current-Voltage (I-V) characteristics under
RESULTS AND DISCUSSION

Absorption characteristics of P3HT:SQ3:PCBM blends

The chemical structures of SQ3 are shown in Figure 2. Absorption spectra of the active layer materials (P3HT, PCBM and SQ3 dye) are shown in Figure 3. It is shown in this figure that PCBM absorbs mainly below the wavelength region of 500 nm. The P3HT spectrum shows an absorption peak at 511 nm and absorption edge extending to 630 nm. P3HT also has vibronic shoulders at 547 and 607 nm and these are associated with $\pi-\pi^*$ stacking in P3HT and indicative of its crystallinity. SQ3 shows an absorption band extending in the longer wavelength region extending to 650 nm with an absorption peak at 627 nm.

The contribution of SQ3 in light harvesting was investigated by incorporating SQ3 in quantities of 4.76, 9.09, 13.04 and 16.67% in P3HT:PCBM solar cell active layer are shown in Figure 4. Inclusion of SQ3 improves the absorption profile of the P3HT:SQ3:PCBM blend with an increase in absorption intensity and widening the absorption range from the visible to near – infra red. This can be attributed to the combined effect of the P3HT absorption (400 to 700 nm) and SQ3 (550 to 575 nm) spectrum. The shape of the shoulders at about 547 and 607 nm remain relatively the same as SQ3 increased.

This indicates that there was no disruption to P3HT crystallinity (Aziz et al., 2014). Increasing the dye content in the P3HT:PCBM blend increases light harvesting through the increase in absorbance and broadening of
the absorption range. Additionally, the peak absorbance increased from 0.31 to 0.36 a.u representing about 16% increment. Since the absorption at about 600 nm is associated with P3HT crystallinity, an increase would suggest the formation of a more ordered morphology promoted by SQ3 molecules. Thus, the total number of photons absorbed by the solar cell active layer increases when SQ3 dye is added to the P3HT:PCBM blend. The increase is due to a synergistic effect in the absorption characteristics of P3HT and SQ3. However, there is a decrease in absorbance when the concentration of SQ3 was 16.67%. The decrease may be attributed to the
Figure 5. UV-Vis absorbance spectra of 100 nm P3HT:PCBM blend films spin coated at 1400 rpm treated in the following ways: as cast (green), thermally annealed at 100°C (blue), 120°C (red) and 140°C.

Effect of annealing

UV-Vis absorption spectroscopy was used to study the effect of thermal annealing on thin films of P3HT:PCBM spin coated on glass substrates. Thermal annealing optimized the morphology of P3HT:PCBM thin films and thus improved photo-absorbance as shown in Figure 5. The untreated film has peak absorbance of 0.30 a.u. and shoulders at 501, 545 and 597 nm. Thermal annealing at temperatures of 100, 120 and 140°C increased the peak absorbance to 0.31, 0.32 and 0.36 a.u respectively. The increase in absorption intensity is associated with higher crystallinity of P3HT following reordering in annealed samples. Additionally, films treated at 140°C show a red shift of peak absorption wavelength from 501 to 510 nm while the shoulders shift to 549 and 604 nm respectively. The red shift is ascribed to increased inter-chain interaction among the P3HT chains arising from annealing. This results in lowering of the band gap and increase in of the optical $\pi-\pi^*$ transition, an indication of formation of crystallites.

Atomic Force Microscope (AFM) studies

AFM was used to evaluate the effect of adding SQ3 and thermal annealing on P3HT:PCBM blends. The images are shown in Figure 6. The results show that as cast films without SQ3 had a surface roughness of 0.38 nm while samples annealed at 140°C had a roughness of 0.75 nm. A significant increase in roughness was observed on addition of SQ3 weight of 13.04%. However, annealing at 140°C of P3HT:SQ3:PCBM showed a slight decrease in roughness to 0.8 nm. An increase in roughness is associated with increased order in the P3HT phase (Aziz et al., 2014). Thus, the slight reduction suggests reduced crystallinity and disturbance in the morphology at a dye load of 6 mg and annealing temperature of 140°C. Huang et al. (2013) showed that SQ molecules was prefer to reside at the interface between P3HT and PCBM increasing phase separation in the polymer blend. Decrease in roughness maybe a result of loss of the favoured morphology following annealing at 140°C.

Electrical properties

The solar cell electrical characteristics are determined by measuring the current density to voltage (I-V) characteristics, both in dark and under illumination. The open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$), fill factor (FF) and maximum power point ($P_{max}$) were deduced from the I-V curve. The power conversion efficiency is subsequently determined using these data and is tabulated in Table 3.

Current -voltage (I-V) characterization

The polymer solar cell device structure is shown in Table 2 and their I-V curves in Figure 7. The active layer
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Figure 6. Two dimensional AFM images of P3HT:PCBM (a) and PCBM:SQ3:PCBM (b), 3 Dimension AFM images of P3HT:PCBM (c) and PCBM:SQ3:PCBM (d).

Table 1. Weight percentage of SQ3 in P3HT:PCBM.

<table>
<thead>
<tr>
<th>SQ3 mass (mg)</th>
<th>PCBM mass (mg)</th>
<th>P3HT mass (mg)</th>
<th>SQ3 weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>20</td>
<td>20</td>
<td>4.76</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>20</td>
<td>9.09</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>20</td>
<td>13.04</td>
</tr>
<tr>
<td>8</td>
<td>20</td>
<td>20</td>
<td>16.67</td>
</tr>
</tbody>
</table>

Table 2. Polymer solar cells device structure.

<table>
<thead>
<tr>
<th>Solar Cell</th>
<th>Device Structure</th>
<th>Illumination</th>
<th>Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ITO/PEDOT:PSS/P3HT:SQ3:PCBM/Al</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>B</td>
<td>ITO/PEDOT:PSS/P3HT:PCBM/Al</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>C</td>
<td>ITO/PEDOT:PSS/P3HT:SQ3:PCBM/Al</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>D</td>
<td>ITO/PEDOT:PSS/P3HT:PCBM/Al</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>E</td>
<td>ITO/PEDOT:PSS/P3HT:SQ3:PCBM/Al</td>
<td>YES</td>
<td>YES</td>
</tr>
</tbody>
</table>

electrical parameters determined from Figure 7 of the devices and are summarized in Table 3. The control device comprising P3HT:PCBM without SQ3 with no

consisted of an active layer of 13.04% weight SQ3 inP3HT:PCBM. Thermal annealing was done at a temperature of 140°C as the optimum temperature. The
Figure 7. Current versus voltage (I-V) curves obtained for solar cells under AM 1.5 solar spectrum simulations (light) at irradiation intensity of 100 mW.cm⁻².

Table 3. Electrical characteristics of P3HT:SQ3:PCBM solar cells.

<table>
<thead>
<tr>
<th>Solar Cell</th>
<th>V oc (V)</th>
<th>I sc (mA)</th>
<th>I max (mA)</th>
<th>P max (W)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.53</td>
<td>5.78</td>
<td>3.39</td>
<td>1.08</td>
<td>0.35</td>
<td>1.3</td>
</tr>
<tr>
<td>C</td>
<td>0.61</td>
<td>6.88</td>
<td>4.29</td>
<td>1.59</td>
<td>0.38</td>
<td>2.5</td>
</tr>
<tr>
<td>D</td>
<td>0.62</td>
<td>7.88</td>
<td>5.04</td>
<td>1.81</td>
<td>0.37</td>
<td>2.8</td>
</tr>
<tr>
<td>E</td>
<td>0.64</td>
<td>9.68</td>
<td>6.86</td>
<td>2.41</td>
<td>0.40</td>
<td>3.9</td>
</tr>
</tbody>
</table>

thermal treatment had an I sc value of 5.7 mA, V oc of 0.32 V and FF of 0.55. The power conversion efficiency (PCE) was established to be 1.3%. The inclusion of SQ3 combined with thermal annealing resulted in a device with 3.9% PCE. The I sc increased from 5.78 mA for the control to 9.68 mA for the annealed ternary blend. The V oc and FF increased from 0.53 to 0.64 mA respectively. Increase in I sc is due to the increase in photo generated excitons arising from the broadened absorption range to the NIR. The V oc is related to the energy difference between the donor HOMO and acceptor LUMO, a change is expected if exciton separation occurs at the donor-acceptor interface. It has been reported by Huang et al. (2013) that the highest occupied molecular orbital (HOMO) of SQ is located in-between the HOMOs of P3HT and PCBM, similarly for the lowest unoccupied molecular orbital (LUMO) levels. Consequently the initial excitation leads to two possible routes for current generation: (i) photo induced charge transfer between P3HT and PCBM, (ii) FRET excitation of P3HT to SQ3 followed by charge dissociation. Thus, increase in PCE from 1.3 to 3.9% can be attributed to the synergistic effect arising from the change in absorption profile to near infra red (NIR) and establishment of an addition charge transfer route in the system. This represents a two-fold increase in PCE.

Conclusion

In this work, we have investigated the effect of adding SQ3 dye to P3HT:PCBM forming a ternary system. The light harvesting capacity was increased by broadening the absorption band to NIR. A red shift was observed with vibronic shoulders shifting from 501 and 547 nm to 510 and 600 nm respectively. The increase in absorption
intensity of these shoulders suggest an increase in P3HT crystallinity. Furthermore, inclusion of SQ3 resulted in broadening of the absorption spectrum. A similar effect was observed as a result of thermal treatment of the ternary system at 140°C. The combined contribution of SQ3 and thermal annealing resulted in increased power conversion efficiency (η) of pristine P3HT:PCBM solar cell from 1.9 to 3.9%. Increase in PCE is attributed to the extension of the absorption range thus improving light harvesting capacity and introduction of an additional charge transfer mechanism through SQ3.

Conflict of Interest
The authors have not declared any conflict of interest.

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