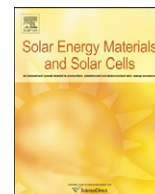




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Dibenzo[*f,h*]thieno[3,4-*b*] quinoxaline–fullerene heterojunction bilayer solar cells with complementary spectrum coverage

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ABSTRACT

In the present article, potential of a bilayer organic solar cell has been investigated. We utilize newly synthesized small molecules, namely dibenzo[*f,h*]thieno[3,4-*b*]quinoxaline as electron donors for solar cells in heterojunction bilayer configuration. These small molecules with a narrow absorption band in the range 400–450 nm provide a complementary spectrum for the fullerene C₇₀, thereby leading to an overall power conversion efficiency of $2.6 \pm 0.2\%$ under 100 mW/cm² incident radiation. Thermal annealing seems to impact the charge separation at the donor–acceptor interface, which eventually affects device performance. This work demonstrates that carefully optimized bilayer devices are comparable to the bulk heterojunction counterparts.

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1. Introduction

A steady increase in power conversion efficiencies in organic photovoltaics (OPV) has occurred over the past few decades through different device configurations which include bulk heterojunction (BHJ) [1,2], planar heterojunction [3–6], cascade structures [7], tandem architecture [8–10], etc. The basic cell component in most of the high efficiency cells is of BHJ type, wherein increased charge separation is believed to be due to the uniform mixing of the active layer components at the microscopic level, thereby leading to continuous pathway for the extracted carriers [11,12]. Alternatively, the first breakthrough in planar heterojunction solar cells was achieved by Tang et al. with a combination of copper phthalocyanine and perylenetetracarboxylic acid bis-benzimidazole to form a p–n heterojunction [13]. Stability issues and roll to roll processing of the devices were also addressed by several researchers in recent years [14,15]. Nature of the donor–acceptor interface in single heterojunction is proved to be critical to the photovoltaic properties. Furthermore, limited efficiency of the planar stacked bilayer heterojunction solar cells could be mainly attributed to the limited absorption range and the energy losses procured because of the thermal relaxation of the excitons. Among these, the absorption losses can be minimized by stacking layers of different band gaps. Compared to polymers, small molecules are easier to be synthesized in pure

form and to tune the band gap via structural modification. Though small molecules have narrower absorption band, maximization of solar spectra is still possible by judicious choice of the counterpart with complementary spectra. One such effort was made in our current article by combining dibenzo[*f,h*]thieno[3,4-*b*]quinoxaline as p-type semiconductor and fullerene C₇₀ as n-type semiconductor. The second issue of thermal relaxation of the excitons can be minimized by proper choice of heat treatments for the devices, which help in the formation of intermixing layers at the interface between the two active layers [16]. Hence, recent efforts were made to enhance the interface area through formation of intermixing layers, thermal annealing processes, or through the formation of nanostructures, etc [16,17]. Relatively new techniques such as oblique angle deposition (OAD) also have been developed to enhance the interface area [18]. However, such physical evaporation techniques require high vacuum and are time consuming. It would be ideal if the conventional spin coating process with adequate thermal treatments can be utilized for such enhancement of the interfacial area. Such an effort is made in the present work and we construct OPVs with a bilayer device structure, indium tin oxide/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)/dibenzo[*f,h*]thieno[3,4-*b*]quinoxaline/C₇₀/Al and their performance is discussed.

2. Experimental details

The synthesis scheme for the dibenzo[*f,h*]thieno[3,4-*b*]quinoxaline was reported elsewhere [19]. After purification, these

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small molecules were dissolved in 1,2,4 trichlorobenzene (2 wt%). Device fabrication process involved cleaning the ITO glass in detergent. After drying the substrates in a furnace overnight, they were subjected to UV ozone treatment for 15 min. A hole transporting layer, PEDOT:PSS was then spun on the substrates at 4000 rpm for 60 s, followed by a thermal annealing at 120 °C for 30 min. Small molecule thin films (~40 nm thick) were then prepared through spin coating in a nitrogen filled glove box. The spin speed was varied to get the desired thickness and the duration was kept constant at 60 s. By using a suitable mechanical mask, substrates were transferred to a vacuum chamber, where fullerene C₇₀ was deposited by thermal evaporation. The thickness was varied from 30 to 90 nm and the deposition rate was kept at 0.5 Å/s. Finally, 1000 Å thick Al cathodes were deposited onto these bilayer active layers to complete the device. Cathode area decides the active area of the devices and the active area of the devices was 0.1 cm². For the fabrication of TFTs, the active layers were first spun at 2000 rpm for 60 s on SiO₂ gate oxide. For comparison, 1 batch of films was allowed to dry at room temperature and the other set of films was annealed at 150 °C for 30 min. Both sets of films were masked through a suitable mask to fabricate a TFT device. A thin gold layer (~20 nm) was used as source–drain electrode. Typical channel length and width of the TFTs were 100 μm and 2 mm, respectively. All devices were tested using HP 4156 semiconductor parameter analyzer for their current–voltage characteristics. External quantum efficiency of the solar cells was measured using a lock-in detector under a monochromatic light illuminated from a xenon lamp. Calibration of the incident light was performed with a monocrystalline silicon diode. The optical absorption spectra of the films were recorded at room temperature using UV–vis spectrophotometer (V-650, Jasco).

3. Results and discussion

The chemical structure of the synthesized molecule and fullerene C₇₀ is shown in Fig. 1. Details of the synthesis scheme

and chemical structure can be found elsewhere [19]. The figure also displays the device structure used in the present investigation. Different from the commonly used bulk heterojunction structures, the authors utilized a bilayer concept. Normalized UV–vis absorption spectrum of the individual small molecule, C₇₀ and the stacked bilayer films is displayed in Fig. 2. The spectra for the pristine small molecule films show that the absorption range is narrow with a peak exhibited at 416 nm, which could be attributed to the π – π^* transition for thienoquinoxaline unit. And the absorption of C₇₀ originates at 700 nm and tends to increase with decrease in wavelength and reaches a maximum value around 500 nm. Apart from this maximum visible absorption, C₇₀ also possesses a high absorption in the near UV regime (~397 nm). Overall, a narrow absorption of the small molecule is complementary to the C₇₀ absorption as shown in the figure. Hence, bilayer of such a

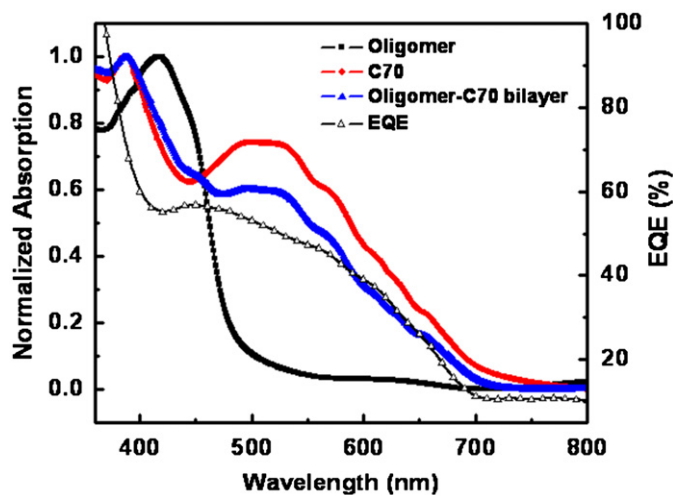


Fig. 2. Optical absorption spectra of the newly synthesized small molecule, fullerene and bilayer films. EQE of the bilayer solar cell device is also shown.

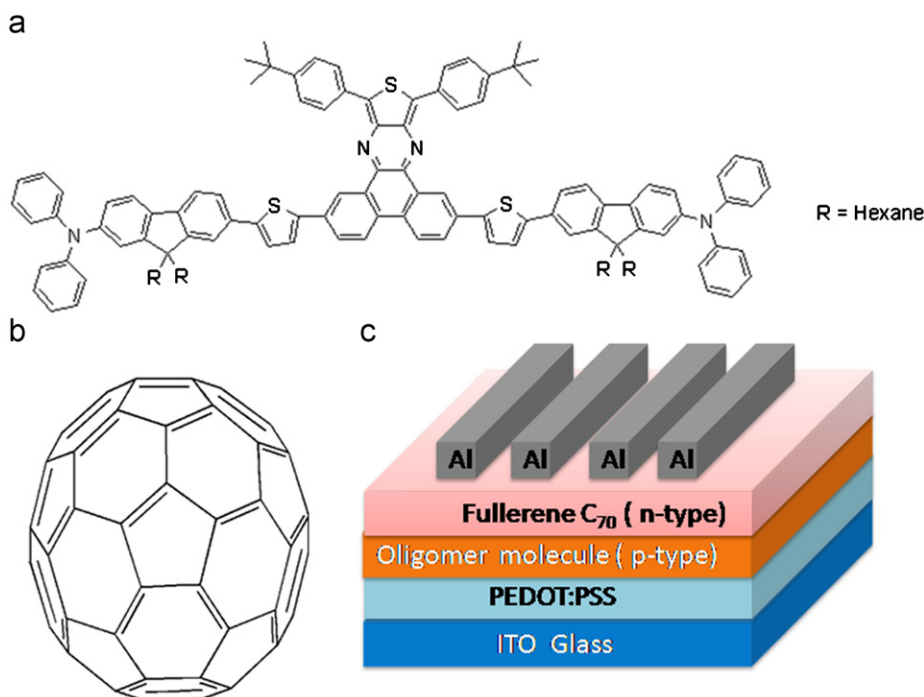


Fig. 1. Molecular structures of (a) Dibenzo[*ff,h*]thieno[3,4-*b*] quinoxaline small molecule, (b) C₇₀ Fullerene and (c) bilayer device configuration.

combination leads to an extended overall absorption in the wavelength range 380–700 nm. Such complementary spectra coverage of the active layers is related to the increased short circuit current density of the devices due to the increased photogenerated charge carriers over the extended spectral range. Cyclic voltammetry was also conducted to determine the HOMO and LUMO level of the small molecule. From the onset of the oxidation and reduction currents, we found -5.16 and -3.34 eV for the HOMO and LUMO level, respectively [19]. Energy levels are suitable for the band alignment with the C_{70} (HOMO and LUMO levels of 6.2 and 4.5 eV, respectively), so that the carriers have an easy pathway towards the respective electrodes. Fig. 2 also depicts external quantum efficiency of the bilayer devices. Correlating well with the absorption spectra, these bilayer devices exhibited a photon conversion efficiency of 45%. Obtained EQE have spectra has a broader spectra coverage compared to the BHJ devices composed of small molecule: PCBM blends [19], which is believed to be due to the asymmetric nature of the C_{70} molecules. As a result of such broader spectral response, the improved performance is obtained in bilayered devices, as explained in the subsequent sections.

In order to understand the effect of thermal annealing on the device performance, their dark current–voltage characteristics were analyzed [20]. Fig. 3a shows the dark current density versus voltage characteristics of the as deposited and annealed (150°C) small molecule– C_{70} bilayer devices, with the device structure ITO/PEDOT:PSS/small molecule/ C_{70} /Al. As can be seen from the figure, the as pristine devices exhibited a poor rectification ratio, with a large leakage associated with it. However, the rectification ratio increased by over 4 orders of magnitude due to the thermal

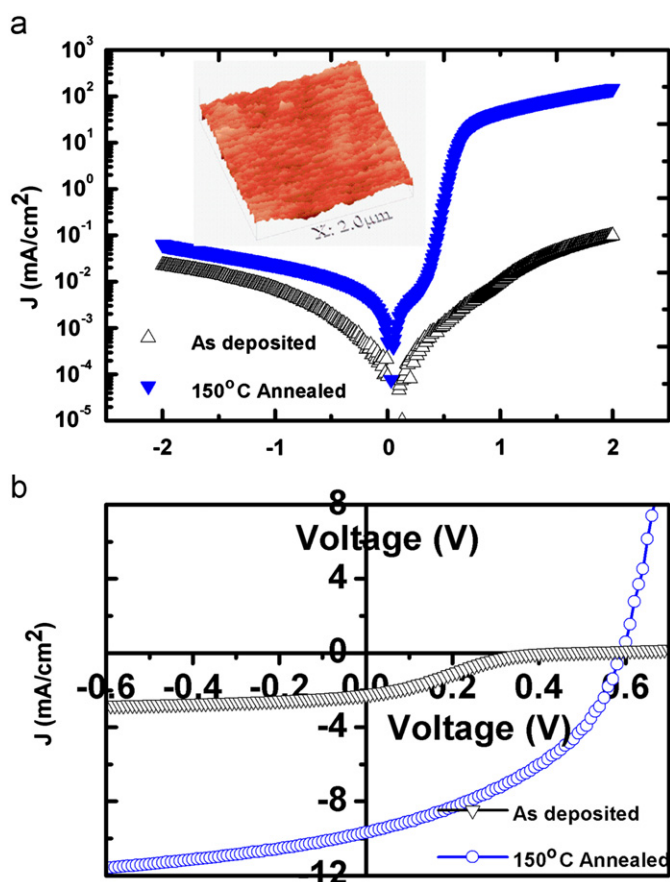


Fig. 3. (a) Dark and (b) illuminated current density–voltage (J – V) characteristics of the bilayer devices (inset (a): AFM image of the small molecule film annealed at 150°C).

treatment. Moreover, the ideality factor of the annealed devices was computed to be 1.22 as against 1.9 of the pristine devices. It can be inferred that the thermal annealing leads to reduction in the recombination dominated charge transport. Moreover, the series resistance of the device was also decreased to $2.7 \Omega \text{ cm}^2$ upon annealing, which further manifest the necessity of thermal annealing. Hence, we anticipate that the thermal annealing improves the illuminated device parameters as well and Fig. 3b shows the J – V characteristics of the pristine and annealed bilayer devices. The optimized devices show an open-circuit voltage (V_{oc}) of 0.59 V. Ideally, V_{oc} is linearly correlated to the energy difference of the HOMO of the donor and the LUMO of the acceptor. Obtained V_{oc} was appreciably lower than the values obtained in BHJ devices (~ 0.87 eV) [19]. However, the current density was appreciably high in bilayer devices, with the optimized devices exhibiting a J_{sc} of 9.8 mA/cm^2 . Although J_{sc} is satisfyingly high, low fill factor of the device limits the device efficiency. Still, power conversion efficiency of the best bilayer device was 2.6%, which is about 1.5 times higher than the results obtained for the BHJ devices. In addition to the complementary nature of the active layers, we have also monitored the morphology of the small molecule thin films and its effect on the device performance was also investigated through atomic force microscopy. As cast small molecule films had a smooth surface without any ordered features (roughness ~ 1.4 nm) (data not shown). However, as the annealing temperature was raised to 150°C , molecules tend to align themselves and hence result in a periodic array, which can be considered rough surface (roughness ~ 6.9 nm) as shown in the AFM image (inset of Fig. 3(a)). In the absence of interpenetrating 3D networks, it is essential to have such morphology, which is desired for increasing the interfacial area. Hence, from the results it is evident that bilayers can also

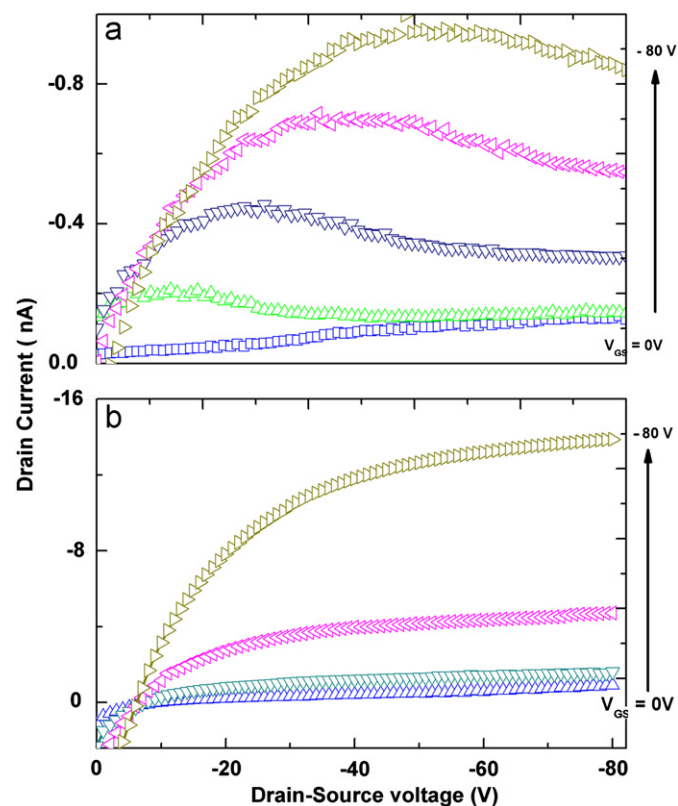


Fig. 4. Output curve of newly synthesized small molecule TFT grown on SiO_2 gate dielectric (a) as cast and (b) 150°C .

be used in device structures provided their morphology and complementary spectra coverage are carefully optimized.

Charge carrier mobility is the key factor for the efficient collection of the photo generated charges in photovoltaic cells. Hence they were computed by utilizing these newly synthesized small molecules as well as C_{70} as active layers in thin film transistors. The devices were constructed on SiO_2 gate dielectric and Au was used as S–D electrode. In general, mobility of the donor material is lower than that of the acceptor material [21]. Ideally, it is preferable to have a balanced charge transport, which can result in symmetric carrier extraction. Typical output and transfer curves of TFTs fabricated from the pristine and annealed small molecule active layer are displayed in Fig. 4 and Fig. 5a. In the present case, hole mobility value was calculated from the plot of (drain current, I_D)^{1/2} versus (gate–source voltage, V_{GS}) of TFT devices (Fig. 5b). Interestingly, hole mobility of the small molecule increased by about 2 orders of magnitude due to thermal treatment at 150 °C, whereas the electron mobility of C_{70} remains unchanged after thermal annealing. The mobility values for the hole and electrons for the as fabricated devices were 2.11×10^{-6} and 1.5×10^{-2} cm²/V s, respectively, and those for the annealed devices were 9.2×10^{-5} and 1×10^{-2} cm²/V s, respectively. Though the mobility values between n- and p-type moieties are unbalanced leading to asymmetric charge transport, increased hole mobility resulted in increase in the current density of the devices. Higher mobility of the small molecule could be attributed to the molecular ordering and increased crystallinity of the films. Crystallinity of the films leading to higher mobilities is

also found in other types of small molecules as found in the literature [22]. The best performance of all the devices occurred at a device annealing of 150 °C. As the annealing temperature exceeded this value, there was a drastic reduction in the open circuit voltage possibly because of complete penetration of the fullerene into the small molecule films. Overall, improvement of the device performance can be attributed to the following reasons: (1) significant changes in the series resistance and increase in hole mobility upon annealing; (2) complementary nature of the active layers.

4. Conclusion

In conclusion, we have demonstrated the necessity of creating a suitable morphology of the first layer for efficient bilayer solar cells. The device with bipolar small molecule containing dibenzo[*f,h*]thieno[3,4-*b*]quinoxaline units as donor and fullerene C_{70} as acceptor has resulted in a PCE of $2.6 \pm 0.2\%$. Thermal annealing helps to increase the mobility of the small molecules and consequently raises the current density of the devices. Thermal annealing is also beneficial for increasing the interfacial area and thus enabling the formation of intermixed layers at the interface. In addition, the complementary and non-overlapping nature of the small molecules and fullerene C_{70} is partially helpful in the effective utilization of the solar spectrum. Overall, this small molecule has a narrow absorption window suggesting that they can be potential candidates for the tandem solar cells.

Acknowledgements

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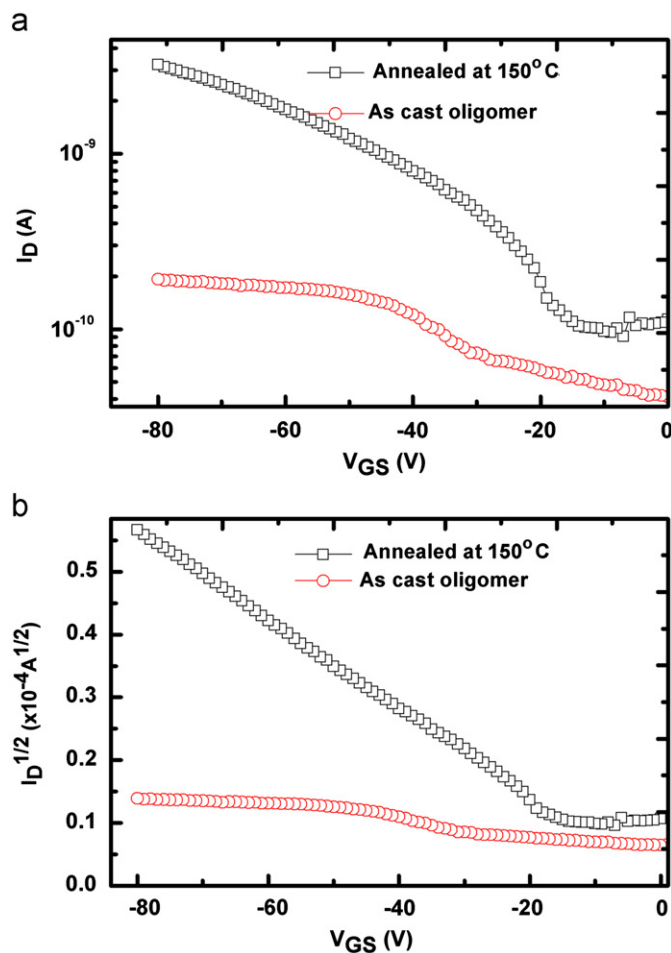


Fig. 5. (a) Transfer curve and (b) variation of $I_D^{1/2}$ versus V_{GS} of the small molecule TFTs.

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