Study of a ternary blend system for bulk heterojunction thin film solar cells*

Zubair Ahmad[1,†], Farid Touati[1], Shakoor R A[2], and Al-Thani N J[2]

[1] Department of Electrical Engineering, College of Engineering, Qatar University, Doha 2713, Qatar
[2] Center for Advanced Materials, Qatar University, Doha 2713, Qatar

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In this research, we report a bulk heterojunction (BHJ) solar cell consisting of a ternary blend system. Poly(3-hexylthiophene) P3HT is used as a donor and [6,6]-phenyl C61-butyric acid methylester (PCBM) plays the role of acceptor whereas vanadyl 2,9,16,23-tetraphenoxy-29H, 31H-phthalocyanine (VOPcPhO) is selected as an ambipolar transport material. The materials are selected and assembled in such a fashion that the generated charge carriers could efficiently be transported rightwards within the blend. The organic BHJ solar cells consist of ITO/PEDOT:PSS/ternary BHJ blend/Al structure. The power conversion efficiencies of the ITO/ PEDOT:PSS/P3HT:PCBM/Al and ITO/PEDOT:PSS/ P3HT:PCBM:VOPcPhO/Al solar cells are found to be 2.3% and 3.4%, respectively.

Keywords: organic semiconductor, charge transport, bulk heterojunction, ternary blend

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1. Introduction

Organic materials have been investigated for the fabrication of solar cells in last few decades due to their flexibilities and solution processable natures. However, the efficiency of the organic solar cells is still low due to the limited absorption of the solar spectrum and relatively poor charge mobility. The bulk heterojuction (BHJ) of a p-type organic materials and a fullerene derivative are a possible way to be developed into efficient organic photovoltaic devices. The BHJ concept has been well thought out as a leading design for organic solar cells due to better efficiency, tunable properties and processing costs.[1–4] By this approach, the splitting of the photo-induced excitons is significantly improved and the exciton diffusion length issue has been resolved to some extent. However, in BHJ solar cells the optimum value of the active layer is very crucial. Although the thicker active layer can increase the optical absorption, the efficiency starts to decline after its certain critical value due to series resistance and charge recombination effects. This difficulty might be resolved by introducing the third component, resulting in optical absorption enhancement and charge transport improvement.[5,6]

A number of binary composite-based photovoltaic schemes have been proposed so far. P3HT and PCBM proved to be the best performing combination that has been regarded as being prominent for a decade.[7] P3HT exhibits a wide-ranging absorption in the visible region of the solar band, yet, there is a fraction of sunlight which must be involved to increase the efficiency of the organic solar cells. In our previous study, we reported a collection of BHJ blend systems for the potential applications in organic photovoltaic devices.[8–11] The efficiency of up to 9.32% has been stated for a bulk heterojunction solar cell of PCDTBT:PCBM,[12] which is very close to 10%, the minimum value required for real-world applications.[13]

Ternary blend based BHJ offers a diverse platform to improve the absorption. BHJ blend with the selectively localized organic dye component between BHJ boundaries has shown improved light harvesting due to both constituents i.e. dye and polymer donor material.[14] The organic dyes from phthalocyanine group exhibits strong absorption in the visible solar spectral regime.[15] For instance, vanadyl 2, 9, 16, 23-tetraphenoxy-29H, 31H-phthalocyanine (VOPcPhO) shows the main absorption band in a range of 600 nm–800 nm, where the P3HT captivates very little. Due to the interesting properties of VOPcPhO, the BHJ of P3HT and PCBM are doped by VOPcPhO, in this study, in order to prepare a ternary blend system for BHJ solar cells. It is expected that this combination will broaden the absorption range of P3HT:PCBM blend and could increase the charge generation in the ternary-blend-based solar cell.

2. Experiment

In our experiment, regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT), vanadyl 2,9,16,23-tetraphenoxy-29H, 31H-phthalocyanine (VOPcPhO), and [6,6]-phenyl C61 butyric acid methyl ester (PCBM) were purchased from Sigma-Aldrich, whereas the aqueous solution of the poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)

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†Corresponding author. E-mail: zubairtarar@qu.edu.qa

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(PEDOT:PSS) PH 1000 was purchased from H. C. Starck. Molecular structures of VOPcPhO, P3HT, and PCBM are shown in Fig. 1(a). Chloroform was used as a solvent to prepare the solutions of the P3HT, VOPcPhO, and PCBM. The concentration of each solution was 2 wt%. In order to fabricate the solar cells, first, the PEDOT:PSS was deposited on the cleaned ITO substrates followed by depositing the composite films. The thickness of the PEDOT:PSS layer was ~ 40 nm while the thickness of the active layer was ~ 100 nm. Then the samples were annealed at 120 °C for 30 min. The top Al electrodes were deposited by thermal evaporation. A schematic diagram and the energy level diagram of the ternary-blend-based devices are shown in Fig. 1(b).

The absorption spectra were taken using Shimadzu UV-3101PC spectrophotometer. The photoluminescence (PL) spectroscopy was performed using RENISHAW Microscope instrument. The *I*–*V* measurements were done under the AM1.5G-filtered irradiation by using Keithley-2400 source measuring unit (SMU). Atomic force microscopy (AFM) has been used to evaluate the morphology composite films. Figure 2 shows the AFM images of the P3HT:PCBM and P3HT:VOPcPhO:PCBM thin films. The morphology of the P3HT:PCBM thin film exhibits a rather smooth and uniform surface. However, blending the three compounds together increases the surface roughness of the composite. The increase in the roughness can be ascribed to an effective reduction in the charge transport distance and enhancement in the current density.[16] The rougher surface morphology suggests that the interpenetrating molecular network is formed in the ternary blend film.[17]

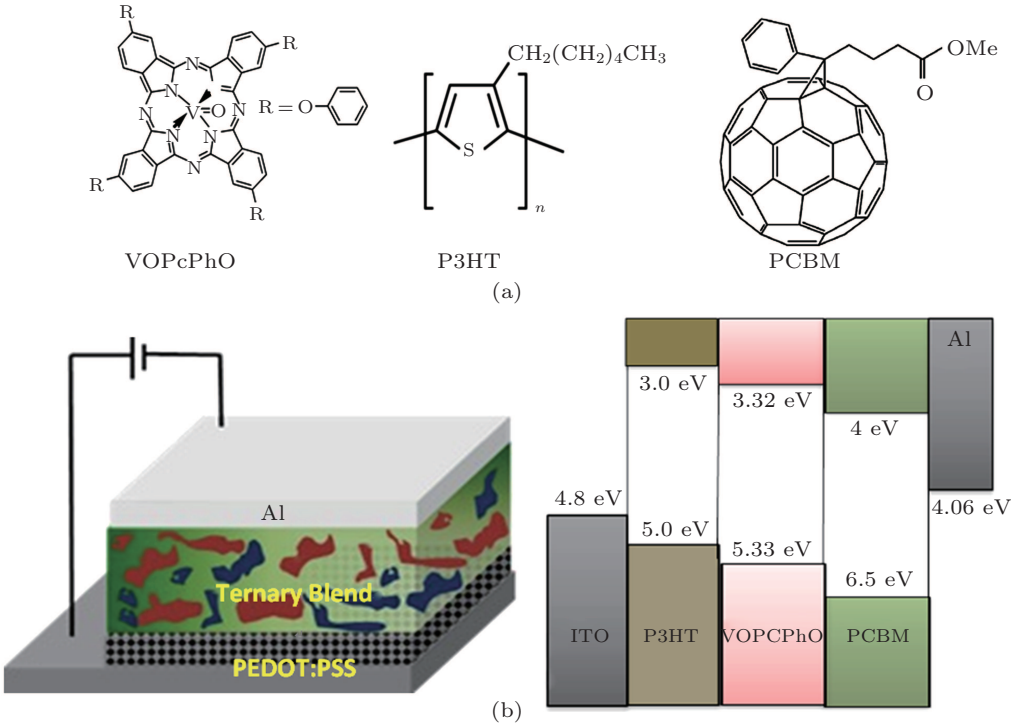


Fig. 1. (color online) (a) Molecular structures of VOPcPhO, P3HT, and PCBM, and (b) schematic diagram and an energy level diagram of the P3HT:VOPcPhO:PCBM-based solar cell.

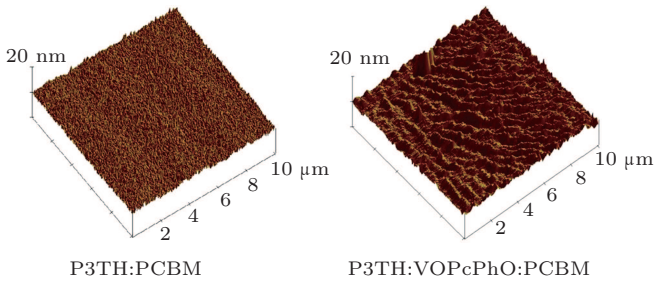


Fig. 2. (color online) Atomic force microscopy images of P3HT:PCBM and P3HT:VOPcPhO:PCBM composite thin films.

3. Results and discussion

Photoluminescence (PL) spectra of P3HT, PCBM, VOPcPhO blend films are shown in Fig. 3. The spectra are recorded in a range from 400 nm to 1000 nm by using an excitation wavelength of 325 nm. This study is to observe the quenching level to estimate the photo-induced charge transfer efficiency in the blend film. In the composite of the P3HT, PCBM, and VOPcPhO, a strong emission peak is found in a range of 700 nm–750 nm, whereas a shoulder lies in a range of 500 nm–600 nm with a peak value at ~ 580 nm. This strong peak may appear due to the first vibronic band, however the shoulder arises due to the electronic transitions. The shoulder peak in P3HT:PCBM composite is quenched after it has been doped with VOPcPhO. After the addition of the VOPcPhO, the peak at 580 nm shows a red shift which suggests that the photo-induced charge transfer in the blended film is enhanced.

The peak at 750 nm in (P3HT:PCBM blend):VOPcPhO (1:1.5) is due to VOPcPhO. The PL spectrum of the pure VOPcPhO exhibits a broad emission in a range of 530 nm–600 nm (green region) with a peak value of 555 nm. It is found that once the VOPcPhO is added in the matrix of P3HT:PCBM, the intensity of the PL spectrum is considerably reduced and a red shift is observed. This reduction of the intensity of the PL spectrum is due to a photo-induced charge transfer in the ternary composite because excitons produced have a restricted lifetime and can decay or separate through the charge transference.

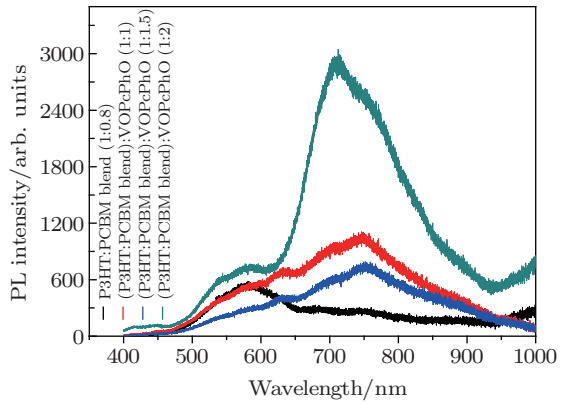


Fig. 3. (color online) Photoluminescence (PL) spectra of the composite films.

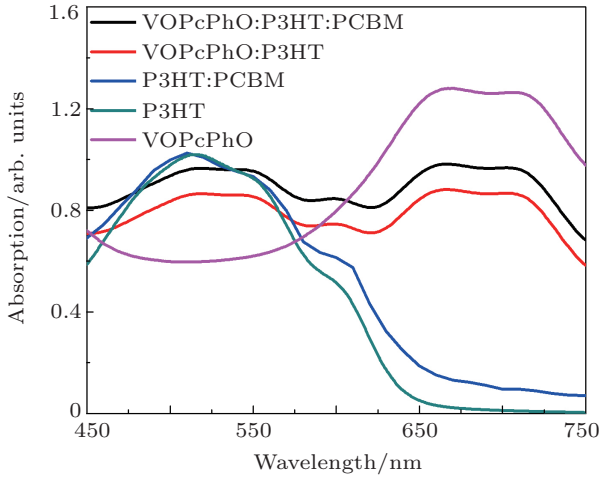


Fig. 4. (color online) UV-Vis spectra for the VOPcPhO, P3HT, P3HT:PCBM, VOPcPhO:P3HT, and VOPcPhO:P3HT:PCBM composite films.

The photo absorption spectra of the blend thin films are shown in Fig. 4. In the P3HT spectrum, a peak and two shoulders occur at 518 nm, 550 nm, and 600 nm, respectively, and there is no absorption after 650 nm whereas the VOPcPhO exhibits two bands.[18] The Q-band (630 nm–750 nm) lies in the visible region of the solar spectrum in addition to the Soret bands in a range of 300 nm–500 nm. The VOPcPhO is suitable to the extension of the absorption spectrum to a longer wavelength. Hence, it looks genuine to add VOPcPhO in the matrix of P3HT and PCBM in order to extend the photo absorption of the active layer towards the higher wavelength region. It is expected that the broader absorption of the composite could help to harvest a wider range of visible spectrum, hence, permitting high photo-current output. The external quantum efficiency (EQE) for the P3HT:VOPcPhO blend has been studied in Ref. [8]. The P3HT:VOPcPhO composite film can harvest the light over the whole visible range and EQE in ITO/PEDOT:PSS/P3HT:VOPcPhO/Al structure is found to be 20 %–25%.

In our previous studies,[15,19] we found that the VOPcPhO show the ambipolar charge transport. In order to discuss the detailed charge transport behavior of the VOPcPhO, first we describe the current–voltage (J–V) characteristics for the P3HT:VOPcPhO solar cells. The device exhibits nonlinear, asymmetric and rectification behavior. The reverse saturation current, ideality factor and shunt and series resistances for the P3HT:VOPcPhO solar cell are indicated in the inset of Fig. 5. To examine the mobility of the blend and conduction mechanism possibility in the device, the J–V characteristics are plotted in a log$J$–log$V$ scale as shown in Fig. 5. The power law behavior of the current ($I\alpha V^m$) varying with value of exponent (m) is observed. The values of "m" are 4 and 5 in regions I and II, respectively, in which the current is named the trapped-charge-limited current (TCLC). However, when the concentration of injected carriers is greater than that of the thermally caused free carriers, then the space-charge-limited current (SCLC) conduction becomes dominant. In fact, when the number of injected carriers increases rapidly, the traps are filled and the current has an exponential dependence on the applied potential instead of the square law dependence (SCLC). With further increase in applied potential the traps become filled and the current follows the trap-filled conduction model and tends into the square law dependence. With the rise in applied voltage, the number of injected carriers increases and gives rise to the space charge near the electrode, which is responsible for limiting the current and giving rise to SCLC conduction. The value is calculated in the trapped filled SCLC region by the formula given in Ref. [20]. The value of mobility of the blend film is found to be 4 cm^2/V·s–7$\times$10^{-4} cm^2/V·s. This value is consistent with the results described in the literature for P3HT (1×10^{-4} cm^2/V·s–2×10^{-4} cm^2/V·s).[21] and VOPcPhO (15.5×10^{-3} cm^2/V·s).[22] The efficiency of the VOPcPhO:P3HT-based solar cells is expected to be lower (1.09% in Ref. [8]) due to the fact that the both VOPcPhO and P3HT have low electron mobilities which may be enhanced by introducing the electron acceptor component with this binary donor blend. Therefore, a ternary blend with the inclusion of an electron acceptor component will be investigated below.

In Fig. 6, we show the J–V characteristics for the ITO/PEDOT:PSS/P3HT:PCBM:VOPcPhO/Al solar cell under dark and illumination conditions. The photovoltaic properties such as open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency

(η), are given in Table 1. The J_{sc} of the P3HT:PCBM cell is 7.8×10^{-3} A·cm^{-2}. After being doped with VOPcPhO, it attains a value of 13.5×10^{-3} A·cm^{-2}. Consequently, the efficiency of the ITO/PEDOT:PSS/P3HT:PCBM/Al solar cells is enhanced from 2.3% to 3.4%. The improvement in efficiency can be credited to two features. Firstly, the wider absorption range of solar spectrum could enhance charge generation. Secondly, the excitons produced under illumination disconnected due to the ternary BHJ which might be limited in binary-blend-based solar cells.

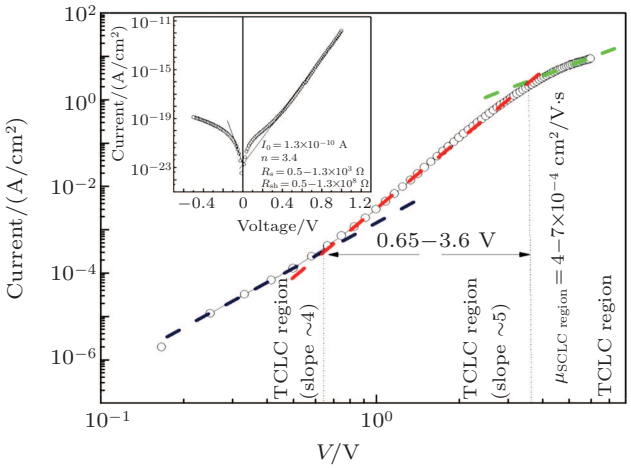


Fig. 5. (color online) The *J*–*V* characteristics of ITO/PEDOT:PSS/P3HT:VOPcPhO/Al device under dark condition, plotted on a double log scale. The inset shows the dark *J*–*V* characteristics plotted on a semi-log scale.

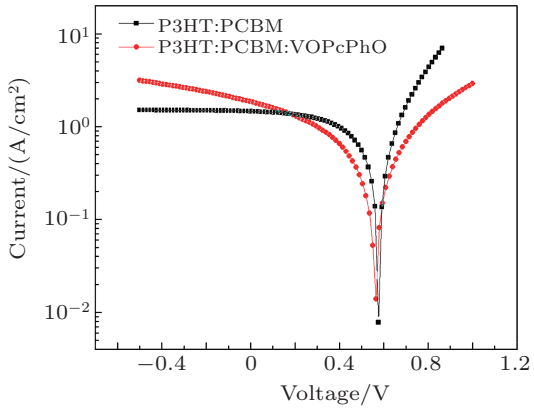


Fig. 6. (color online) The current–voltage characteristics of the ITO/PEDOT:PSS/P3HT:PCBM/Al and ITO/PEDOT:PSS/P3HT:PCBM:VOPcPhO/Al solar cells under 100-mW/cm^2 incident light intensity.

Table 1. The photovoltaic characteristics for the ITO/PEDOT:PSS/P3HT:PCBM/Al and ITO/PEDOT:PSS/P3HT: PCBM:VOPcPhO/Al photovoltaic devices.

Entity	V_{oc}/V	J_{sc}/(A/cm^2)	FF	η/%
P3HT:PCBM	0.58	7.8×10^{-3}	0.51	2.3
P3HT:PCBM:VOPcPhO	0.56	13.5×10^{-3}	0.45	3.4

4. Conclusions

A dye material VOPcPhO is added into the blend P3HT:PCBM as an ambipolar material. A significant increase in the short-circuit current is observed due to the absorption of light in the region where P3HT:PCMB blend cannot adsorb light. Finally, we conclude that the ternary blend system could be a promising fashion to be implemented in bulk heterojunction solar cells, together with electron acceptor component due to better charge transfer potential.

References

[1] Cai W, Gong X and Cao Y 2010 *Solar Energy Materials and Solar Cells* **94** 114

[2] Lilliu S, Böberl M, Sramek M, Tedde S F, Macdonald J E and Hayden O 2011 *Thin Solid Films* **520** 610

[3] Ichikawa M, Takeuchi T, Jeon H G, Jin Y, Lee S and Kim K S 2012 *Jpn. J. Appl. Phys.* **51** 034103

[4] Guvenc A B, Ozkan C and Ozkan M 2012 *Early-Effect like Behavior in Space Charge Regions of Organic Bulk-Heterojunction Photodiodes* (Cambridge: Cambridge University Press)

[5] Ferry V E, Verschuuren M A, Lare M C V, Schropp R E, Atwater H A and Polman A 2011 *Nano Lett.* **11** 4239

[6] Ye F, Burns M J and Naughton M J 2011 "Embedded metallic nanopatterns for enhanced optical absorption", in: *SPIE Solar Energy + Technology*: International Society for Optics and Photonics, p. 811103

[7] Mihailetchi V D, Xie H, de Boer B, Koster L J A and Blom P W 2006 *Adv. Func. Mater.* **16** 699

[8] Mah Abdullah S, Ahmad Z, Aziz F and Sulaiman K 2012 *Org. Electron.* **13** 2532

[9] Ahmad Z, Suhail M H, Muhammad I I, Al-Rawi W K, Sulaiman K, Zafar Q, Hamzah A S and Shaameri Z 2013 *Chin. Phys. B* **22** 100701

[10] Zafar Q, Ahmad Z, Sulaiman K, Hamzah A S and Rahman Z A 2014 *Sensors and Actuators A: Physical* **206** 138

[11] Ahmad Z, Abdullah S M and Sulaiman K 2013 *Measurement* **46** 2073

[12] Abdullah S M, Ahmad Z and Sulaiman K 2015 *Procedia-Social and Behavioral Sciences* **195** 2135

[13] Miyake K, Uetani Y, Seike T, Kato T, Oya K, Yoshimura K and Ohnishi T 2010 *R & D Report, "SUMITOMO KAGAKU"* **2010** 1

[14] Honda S, Yokoya S, Ohkita H, Benten H and Ito S 2011 *J. Phys. Chem. C* **115** 11306

[15] Ahmad Z, Abdullah S M, Zafar Q and Sulaiman K 2014 *J. Mod. Opt.* **61** 1730

[16] Li G, Shrotriya V, Huang J, Yao Y, Moriarty T, Emery K and Yang Y 2005 *Nat. Mater.* **4** 864

[17] Guo T F, Wen T C, L'vovich Pakhomov G, Chin X G, Liou S H, Yeh P H and Yang C H 2008 *Thin Solid Films* **516** 3138

[18] Aziz F, Sayyad M, Ahmad Z, Sulaiman K, Muhammad M and Karimov K S 2012 *Physica E: Low-dimensional Systems and Nanostructures* **44** 1815

[19] Abdullah S M, Ahmad Z, Aziz F and Sulaiman K 2012 *Org. Electron.* **13** 2532

[20] Lampert M A and Mark P 1970 *Current Injection in Solids* (New York: Academic Press)

[21] Ballantyne A M, Wilson J S, Nelson J, Bradley D D C, Durrant J R, Heeney M, Duffy W and McCulloch I 2006 *TOF mobility measurements in pristine films of P3HT: control of hole injection and influence of film thickness*, eds. Zakya H K and Paul A L, SPIE, p. 633408

[22] Khan S M, Sayyad M H and Karimov K S 2010 *Ionics* **17** 307