# Bulk heterojunction solar cells based on a low band gap soluble bisazopyrrole and the corresponding $BF_2$ -azopyrrole complex

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The diazonium salt derived from 4-(hexyloxy)benzamine reacted with half an equivalent of pyrrole to afford 2,5-bis(4-hexyloxyphenylazo)-1*H*-pyrrole (**A**). The reaction of the latter with  $BF_3 \cdot Et_2O$  gave the corresponding  $BF_2$ -azopyrrole complex (**B**). The thin film absorption spectra of **A** and **B** were broad and extended into the near infrared region with optical band gaps of 1.54 and 1.49 eV, respectively. The photovoltaic properties have been investigated using blends of **A** or **B** with PCBM, and it was found that the device based on **B**:PCBM showed higher power conversion efficiency (PCE) in comparison to that for the device with **A**:PCBM blend. This has been attributed to the higher hole mobility and lower band gap of **B** relative to **A**. The effect of different thermal annealing on the photovoltaic response of the devices has been investigated and it was found that the contact annealed device displayed PCE of approximately 2.7% and 3.15% for **A**:PCBM and **B**:PCBM blends, respectively. The increase in the PCE for the contact annealed device has been interpreted in terms of more balanced charge transport.

# Introduction

Polymer solar cells have evolved as a promising cost-effective alternative to inorganic-based solar cells<sup>1,2</sup> due to their potential to be low-cost, light-weight and flexible. Since the discovery of ultrafast photoinduced charge transfer from a conjugated polymer to fullerene molecules, followed by the introduction of the bulk heterojunction (BHJ) concept,3 intensive research with potential materials has been carried out for future photovoltaic (PV) technology.<sup>4-8</sup> Two organic materials with distinct donor and acceptor properties are required to form a heterojunction in the bulk film, which is often achieved by solution processing. In such a case, the BHJ not only provides abundant donor/acceptor interfaces for charge separation, but also forms an interpenetrating network for charge transport.<sup>8,9</sup> Highly efficient polymer solar cells based on poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester (PC61BM) have been reported with PCEs of 4-5%<sup>6,10-12</sup> So far, besides the P3HT system, there are very few polymer solar cell systems reported which exceed 5% in PCE.13 Recent developments concerning processes for the production of flexible large area polymer and generally organic solar cells have been reported.<sup>14</sup> Finally, some recent reviews on organic solar cells have been reported.15

The two most decisive parameters regarding polymer solar cell efficiencies are the open circuit voltage ( $V_{oc}$ ) and the short circuit current ( $J_{sc}$ ).  $J_{sc}$  is mostly determined by the light absorption

<sup>c</sup>Jaipur Engineering College, Kukas, Jaipur (Raj.), India <sup>d</sup>Molecular Electronics Laboratory, JNCASR, Bangalore, India ability of the material, the charge-separation efficiency, and the high and balanced carrier mobilities. On the other hand,  $V_{\rm oc}$  is limited by the difference in the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor, where a small  $V_{\rm oc}$  represents a smaller driving force for the PV process. An effective method to improve the  $V_{\rm oc}$  of polymer solar cells is to manipulate the HOMO level of the donor and/or LUMO level of the acceptor.<sup>16</sup>

The photoconductive properties of azo compounds were reported as early as 1968 by Rau who observed photocurrents from thin layers of 1-(phenylazo)naphthol.<sup>17</sup> Several years later, Champ and Shattuck reported the use of a bisazo pigment derived from 3,3'-dichlorobenzidine as a photogenerating pigment in xerographic devices.<sup>18</sup> Then, azo pigments were widely studied as charge generation materials because of their technological advantages such as high sensitivity, wide spectral range (450–800 nm) and excellent stability.<sup>19</sup>

Recently, much effort has been spent in the synthesis of novel fluorine–boron complexes (FBC) and their application in PV devices; it is found that the modification of the FBC can not only adjust their optical characteristics but also improve their capabilities of electron-accepting and transportation.<sup>20–22</sup> Although several FBCs were reported to be used in organic light emitting diodes and field effect transistors, the exploration of FBCs as charge transport materials in organic solar cells is still inadequate. Finally, a strategy has been developed for functionalizing and solubilizing boron dipyrromethene (Bodipy) dyes at the central boron atom and changing the color by increasing delocalization on the central core. This approach leads to the formation of stable B–C and pyrrole–C linkages suitable for use in TiO<sub>2</sub>-sensitized devices.<sup>23</sup>

A series of symmetrical 2,5-bisazopyrroles and a BF<sub>2</sub>-azopyrrole complex which showed near infrared absorption has been synthesized.<sup>24</sup> Very recently, we have synthesized an alternating

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phenylenevinylene copolymer with 2,5-bisazopyrrole segments along the backbone and the corresponding  $BF_2$ -azopyrrole complex. The latter has been used for BHJ solar cells.<sup>25</sup> In addition, we have synthesized a series of low band gap dyes containing the  $BF_2$ -azopyrrole complex and carboxy or hydroxy anchoring groups which has been used for dye-sensitized solar cells.<sup>26</sup> In continuation of this research line, herein we synthesized a novel symmetrical bisazopyrrole (**A**) bearing hexyloxyphenyl terminal moieties and the corresponding  $BF_2$ -azopyrrole complex (**B**). Their simple and convenient synthesis started from inexpensive starting materials and gave products in relatively high yields. The presence of the hexyloxy chains enhanced the solubility of **A** and **B**. The latter showed a broader absorption band and a lower optical band gap relative to **A**, a feature which is attractive for PV applications.

We have also investigated the PV response of the A:PCBM and B:PCBM blend sandwiched between PEDOT:PSS-coated ITO and Al electrode. The effect of different annealing conditions on the overall PCE of the device has been studied and it was found that the contact annealed devices had relatively higher PCE in comparison to other devices. This has been attributed to the more balanced charge transport in the contact annealed device, resulting in the high value of incident photon to current efficiency (IPCE) and  $J_{sc}$ .

## Experimental

## **Reagents and solvents**

1-(Hexyloxy)nitrobenzene  $(1)^{27}$  and 4-(hexyloxy)benzamine  $(2)^{28}$  were synthesized according to reported methods. Tetrahydrofuran (THF) was dried by distillation over CaH<sub>2</sub>. Triethylamine was purified by distillation over KOH. All other reagents and solvents were commercially purchased and were used as supplied.

### Synthesis of compounds A and B

**2,5-Bis(4-hexyloxyphenylazo)-1***H*-**pyrrole (A).** A flask was charged with a suspension of 4-(hexyloxy)benzamine (2) (1.00 g, 5.18 mmol) in water (10 mL). Hydrochloric acid (2 mL) was added to the suspension. The mixture was cooled and kept at 0-5 °C in an ice bath and diazotized by adding a solution of NaNO<sub>2</sub> (0.37 g, 5.18 mmol) in water (5 ml) followed by stirring for 0.5 h at 0-5 °C. The solution of the diazonium salt (3) thus prepared was immediately used for the next coupling reaction.

The solution of **3** was slowly added to a solution of pyrrole (0.17 g, 2.59 mmol) and pyridine (2 mL) in methanol (30 mL) at 0-5 °C. The resulting mixture was stirred for 10 h and then concentrated under reduced pressure. The precipitate was filtered, washed with water and dried to afford **A**. It was purified by column chromatography, eluting with a mixture of dichloromethane and hexane (1 : 1). Yield 78% (1.92 g).

FT-IR (KBr,  $cm^{-1}$ ): 3454 (NH stretching); 2934, 2858 (C–H stretching of hexyloxy groups); 1246, 1146 (ether bond); 1598, 1496 (aromatic).

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ /ppm: 9.75 (s, 1H, NH); 7.78 (m, 4H, aromatic *ortho* to azo); 6.88 (s, 2H, pyrrole); 6.80 (m, 4H, aromatic *ortho* to oxygen); 3.97 (t, J = 6.3 Hz, 4H, OCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>); 1.81 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>); 1.35

(m, 12H, O(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>); 0.91 (t, J = 6.8 Hz, 6H, O(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>).

Anal. Calcd. for C<sub>28</sub>H<sub>37</sub>N<sub>5</sub>O<sub>2</sub>: C, 70.71; H, 7.84; N, 14.72. Found: C, 70.24; H, 7.92; N, 14.58.

**2,5-Bis(4-hexyloxyphenylazo)-1-boron difluoride (B).** To a solution of **A** (0.30 g) and triethylamine (2 mL) in dry chloroform (20 mL) was slowly added boron trifluoride diethyl etherate (1 mL) under N<sub>2</sub>. The resulting solution was refluxed for 2 h and then evaporated to dryness. The residue was triturated with ether, filtered and dried to afford **B** as a dark purple product (0.27 g, 83%).

FT-IR (KBr, cm<sup>-1</sup>): 3198, 1068 (BF<sub>2</sub>-azopyrrole complex), 2930, 2859 (C–H stretching of hexyloxy groups); 1248, 1160 (ether bond); 1600, 1508, 1458 (aromatic).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ/ppm: 7.90 (m, 4H, aromatic *ortho* to azo); 6.93 (s, 2H, pyrrole); 6.83 (m, 4H, aromatic *ortho* to oxygen); 3.98 (t, J = 6.2 Hz, 4H, OCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>); 1.80 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>); 1.37 (m, 12H, O(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>); 0.90 (t, J = 6.7 Hz, 6H, O(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>).

Anal. Calcd. for C<sub>28</sub>H<sub>36</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>2</sub>: C, 64.25; H, 6.93; N, 13.38. Found: C, 63.86; H, 6.85; N, 13.12.

#### **Characterization methods**

IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. <sup>1</sup>H NMR (400 MHz) spectra were obtained using a Bruker spectrometer. Chemical shifts ( $\delta$  values) are given in parts per million with tetramethylsilane as an internal standard. UV-vis spectra were recorded on a Beckman DU-640 spectrometer with spectrograde THF. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer.

Electrochemical properties of both polymers were examined using cyclic voltammetry (CV) (HCH instrument). In particular, the compounds were coated on a platinum disk and immersed in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution. CV was recorded using a platinum disk as working electrode and Ag/Ag<sup>+</sup> as the reference electrode at a scan rate of 20 mV s<sup>-1</sup>.

#### Fabrication and characterisation of organic solar cells

Organic solar cells based on compound A or B were fabricated in the traditional sandwich structure through several steps. Indium tin oxide (ITO) coated glass substrates were cleaned by ultrasonication sequentially in detergent, de-ionized water, acetone and 2-propanol. After drying the substrate, PEDOT:PSS (Baytron) was spin coated (3000 rpm for 30 s) onto the ITO substrate. The film was dried at 100 °C for 10 min. After cooling the substrate, a THF solution of the compound A or B and PCBM mixture was spin coated onto the top of the PEDOT:PSS. After drying the solvent, the substrate was transferred into a thermal evaporator chamber. An Al electrode ( $\sim$ 70 nm) was evaporated onto the top of the compound A or B:PCBM layer under high vacuum ( $10^{-5}$  Pa). For the blend annealed device, the blend layer was thermally annealed in vacuum (120 °C) for 10 min, before the top Al electrode deposition. For the contact annealed device, the as cast device (*i.e.* Al top contact on the un-annealed blend layer) was annealed at 120 °C for 10 min. The current-voltage (J-V) characteristics of the devices in dark and under illumination were measured by semiconductor parameter analyzer (Keithley 4200-SCS). A xenon light source (Oriel, USA) was used to give an irradiance of 100 mW cm<sup>-2</sup> (the equivalent of one sun at AM1.5) at the surface of the device. The photoaction spectrum of the devices was measured using a monochromator (Spex 500 M, USA) and the resulted photocurrent was measured with a Keithley electrometer (model 6514), which is interfaced to the computer by LABVIEW software. The device fabrication procedure for the analysis carrier transport is identical to that of PV device fabrication, except a Au electrode was used as the top electrode instead of an Al electrode.

## **Results and discussion**

#### Synthesis and characterization

Scheme 1 outlines the general synthetic strategy for the intermediate compounds 1-3, as well as the target compounds A and **B**. In particular, 4-nitrophenol reacted with 1-bromohexane in the presence of  $K_2CO_3$  to afford the ether derivative 1.<sup>27</sup> The catalytic hydrogenation of the latter in a Parr apparatus afforded the diamine 2.<sup>28</sup> Compound 2 reacted subsequently with NaNO<sub>2</sub>/ aqueous HCl at temperature 0-5 °C to yield the diazonium salt 3. Then, it reacted with half an equivalent of pyrrole in methanol neutralized with pyridine to give the symmetrical bisazopyrrole A. Finally, A reacted with boron trifluoride etherate in the presence of triethylamine to afford the corresponding BF<sub>2</sub>-azopyrrole complex  $\mathbf{B}^{24}$  It has been reported that such complexes are stable in nonprotic solvents like THF, chloroform, acetone, acetonitrile etc., but unstable in protic solvents like ethanol.24 Consequently, they are also humidity sensitive, a drawback for these complexes. Both A and B were readily soluble in common organic solvents owing to the hexyloxy chains.

The chemical structures of **A** and **B** were confirmed by FT-IR and <sup>1</sup>H NMR spectroscopy. Both these compounds displayed common absorption bands at approximately 2934, 2858 (C–H stretching of aliphatic moieties) and 1246, 1146 (ether bond). Moreover, **A** showed a sharp band at 3454 cm<sup>-1</sup>, assigned to the NH stretching of pyrrole, while this absorption was absent in **B** due to complexation of the pyrrole nitrogen. It has been well established that the N=N frequency of aromatic azo compounds is difficult to identify by IR. The N=N frequencies are not only weak but are overlaid by the other aromatic bands as well.<sup>29</sup> The IR spectrum of **B**, as compared to **A**, was broader and showed new intense absorption bands at 3198 and 1068 cm<sup>-1</sup> associated with the BF<sub>2</sub>-azopyrrole complex. The <sup>1</sup>H NMR spectra of **A** and **B** were similar, but **A** displayed an additional signal at  $\delta$  9.75 assigned to the NH proton of pyrrole.

A significant change in the colour of the reaction solution was observed during the complexation. In particular, the colour of the chloroform solution of **A** in the presence of Et<sub>3</sub>N changed from red to dark purple when BF<sub>3</sub>·Et<sub>2</sub>O was added to this solution. This indicates a bathochromic shift of the absorption spectrum during the complexation reaction. It has been reported that the BF<sub>2</sub>-azopyrrole complexes show a near infrared absorption which presumably results from considerable  $\pi$ -electron delocalization by extending the conjugation around the N=N bond.<sup>24</sup>

### Photophysical properties

Fig. 1 shows the UV-vis absorption spectra of A and B in THF solution  $(10^{-5} \text{ M})$  and thin film. Their photophysical characteristics are summarized in Table 1. A and B displayed in solution an absorption maximum ( $\lambda_{a,max}$ ) at ~420 nm and a shoulder at 550 nm. This shoulder was more pronounced in B. The absorption spectra in thin films were broader relative to solution and covered the visible and near infrared region. This feature was attributed to intramolecular interactions in solid state. The thin films showed  $\lambda_{a,max}$  at 494 nm for  $\boldsymbol{A}$  and 515 nm for  $\boldsymbol{B}.$  In addition, B showed a shoulder at 615 nm, which widened its absorption curve. Apparently, the complexation reaction broadened the absorption curve and extended it into to the near infrared region. This is attributable to the formation of rigid azo configuration which extended the  $\pi$ -conjugation.<sup>24</sup> The thin film absorption onset of A and B is located at 808 and 829 nm corresponding to an optical band gap  $(E_g^{opt})$  of 1.54 and 1.49 eV, respectively. These values of  $E_{e}^{opt}$  are comparable to those of other related materials which have been synthesized in our laboratory.25,26

#### **Electrochemical properties**

We have carried out the electrochemical cyclic voltammetry for both **A** and **B** films on glassy carbon electrodes to get information about the positions of the highest occupied molecular orbital



Scheme 1 Synthesis of compounds A and B.



Fig. 1 Normalized absorption spectra of compounds A and B in THF solution (top) and thin film (bottom).

Table 1 Optical and electrochemical properties of A and B

Compound	Α	В
$\lambda_{a,\max}$ in solution/nm <sup>a</sup>	418, $550^d$	420, $550^d$
$\lambda_{a \max}$ in thin film/nm <sup>a</sup>	494	515, 615 <sup>d</sup>
Thin film absorption onset/nm	808	829
$E_{\circ}^{\mathrm{opt}}/\mathrm{eV}^{b}$	1.54	1.49
$\tilde{E_{onset}}/N$	-1.10	-1.25
$E_{\text{onset}}^{\text{red}}/N$	0.50	0.40
HOMO/eV	-5.20	-5.10
LUMO/eV	-3.60	-3.55
$E_{\rm g}^{\rm el}/{ m eV}^c$	1.60	1.55

 ${}^{a}\lambda_{a,\max}$ : The absorption maxima from the UV-vis spectra in THF solution or in thin film.  ${}^{b}E_{g}^{opt}$ : Optical band gap determined from the absorption onset in thin film.  ${}^{c}E_{g}^{el}$ : Electrochemical band gap determined from cyclic voltammetry.  ${}^{d}$  Shoulder of the absorption curve.

(HOMO) and lowest unoccupied molecular orbital (LUMO) of these compounds. The onset reduction potential ( $E_{red}^{onset}$ ) and oxidation potential ( $E_{ox}^{onset}$ ) have been measured with respect to a Ag/Ag+ electrode. HOMO and LUMO levels were estimated from the following equations:<sup>30</sup>

$$E_{HOMO} = -e(E_{ox}^{onset} - 4.7)$$

$$E_{LUMO} = -e(E_{red}^{onset} - 4.7)$$
(1)

where the unit of potential is V vs. Ag/Ag.+

The reduction potential, oxidation potential, HOMO and LUMO levels, and electrochemical band gap of compounds **A** and **B** are collected in Table 1. The band gaps of **A** and **B**, which were estimated from the electrochemical method, are similar to the optical band gaps from the UV-Vis absorption onset. The values of the HOMO and LUMO levels of PCBM were also estimated from CV and were found to be -6.3 and -4.0 eV, respectively. It can be seen from Table 1 that the difference between the LUMO of PCBM and compound **A** or **B** is greater than the binding energy of excitons in the organic semiconductor (0.35 eV).<sup>31</sup> Consequently, the blend of **A** or **B** as donor with PCBM as acceptor can be used as a photoactive layer for BHJ PV devices.

## Electrical and photovoltaic properties

We have measured the J-V characteristics of the devices based on pure A or B sandwiched between the PEDOT:PSS and Al electrodes, under dark and under illumination intensity of 100 mW cm<sup>-2</sup> at room temperature, and they are shown in Fig. 2(a) and 2(b). The J-V characteristics of both devices in the dark show a rectification effect, when positive potential is applied to the PEDOT:PSS-coated ITO electrode with respect to the Al electrode. The work function of PEDOT:PSS-coated ITO (5.2 eV) is very close to the HOMO level of A (5.2 eV) or B (5.1 eV) and forms a nearly Ohmic contact for hole injection from PEDOT:PSS to the HOMO of the organic materials. However, the LUMO level of both A and B compounds is very far from the work function of Al (4.2 eV) and forms the Schottky barrier for the electron injection from Al into the LUMO level of A or **B**. Therefore, the rectification effect is due to the formation of the Schottky barrier at the Al-A or Al-B interfaces for the respective devices.

Charge carrier mobility is an important parameter for materials used in organic solar cells. Hole mobility in pure **A** or **B** was determined by the space charge limited current (SCLC) method,<sup>32,33</sup> with a device structure ITO/PEDOT:PSS/**A** or **B**/Au. As shown in Fig. 3, the results were plotted as

$$\ln \left[ Jd^3 / (V_{app} - V_{bi})^2 \right] vs. \sqrt{(V_{app} V_{bi})}.$$
 The analysis of the SCLC

results gives hole mobility of  $2.15 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and  $7.18 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for **A** and **B**, respectively. The PV parameters were estimated from the *J*–*V* characteristics under illumination (Fig. 2b) and are summarized in Table 2. It can be seen that the *J*<sub>sc</sub> and PCE of the devices using **B** is higher than that for **A**, under the same conditions. The lower band gap and higher hole mobility of **B** as compared to **A** leads to the relatively higher PV performance of the device based on **B**.

Fig. 4(a) and 4(b) show the J-V characteristics of the devices using A:PCBM and B:PCBM blends under different conditions and illumination of AM 1.5 (100 mW cm<sup>-2</sup>). The corresponding open circuit voltage ( $V_{oc}$ ),  $J_{sc}$ , fill factor (FF) and PCE of the devices are summarized in Tables 3 and 4. It can be seen from Table 3 that the PCE of the contact annealed device is higher than that for both the as cast and blend annealed devices. Two important changes in J-V characteristics are responsible for the observed improvement in the PCE of the contact annealed



Fig. 2 Current–voltage (J-V) characteristics of the devices based on compounds (a) in dark (b) under illumination intensity of 100 mW cm<sup>-2</sup>.

device. The enhancement in the  $J_{sc}$  originates from the changes in the internal material properties other than the blend morphology, because we observed only a slight increase in the  $J_{sc}$ in the devices similarly annealed prior to contact deposition (*i.e.* blend annealed). The increase in both  $V_{oc}$  and FF can also be correlated with the decrease in current leakage for the contact annealed device. Both the as cast and blend annealed devices show more dark current in comparison with the contact annealed device, as shown in the J-V characteristics in the dark for the device using **B**:PCBM blend (Fig. 5).

The incident photon to current efficiency (IPCE) spectra of the BHJ PV devices using the as cast blends under monochromatic light are shown in Fig. 6. The shape of the IPCE spectra of the



**Fig. 3** Current–voltage curves for ITO/PEDOT:PSS/A or B/Au devices in the form of  $\ln[Jd^{p}/(V_{appl} - V_{bi})^{2}]$  vs.  $[(V_{appl} - V_{bi})/d]^{1/2}$ .

 Table 2
 Photovoltaic parameters for devices based on pristine A and B using ITO/PEDOT:PSS and Al electrodes

Compound	Short circuit current $(J_{sc})/mA \text{ cm}^{-2}$	Open circuit voltage (V <sub>oc</sub> )/V	Fill factor (FF)	Power conversion efficiency $(\eta)$ (%)
A	0.12	0.74	0.38	0.034
B	0.24	0.78	0.40	0.074

devices is very similar to the absorption spectra of the respective blends, indicating that all the absorption of compound **A** or **B** contributed to the PV conversion. The IPCE spectrum of the device based on the **B**:PCBM blend has been extended up to 820 nm. The improved IPCE for the device based on the **B**:PCBM blend as compared to the device based on the **A**:PCBM may be due to the higher hole mobility and lower band gap of **B** relative to **A**. The driving force for the dissociation of excitons into free carriers in the BHJ device is the difference between the LUMO levels of the donor and acceptor used in the blend. This difference in the **B**:PCBM blend is higher than that for the **A**:PCBM blend, and may also be responsible for the higher value of  $J_{sc}$  and IPCE in the PV devices based on the **B**:PCBM blend.

We can understand the effect of processing the blend active layer by examining the details of hole and electron conduction through the blend network. We have measured the electronic transport through two independent networks in the blend layer using the appropriate choice of metallic top and bottom electrodes.<sup>34,35</sup> We have fabricated the BHJ devices using the **B**:PCBM blend with PEDOT:PSS (bottom) and Au (top) contacts (Fig. 7), to investigate the hole and electron transport in **B** and PCBM domains. Under reverse bias (Fig. 7b), where Au is positively biased with respect to PEDOT:PSS, the device permits only hole transport *via* the HOMO of **B**, because hole injection from Au to the HOMO of **B** occurs with nominal energy barrier.



**Fig. 4** Current–voltage characteristics under illumination of intensity 100 mW cm<sup>-2</sup> for three devices with compound (a) **A**:PCBM (1 : 1) and (b) **B**:PCBM blend BHJ photovoltaic devices with different annealed conditions.

 Table 3
 Photovoltaic parameters for the as cast, blend annealed and contact annealed devices based on A:PCBM (1:1) blend using ITO/PEDOT:PSS and Al electrodes

	Short circuit current $(J_{sc})/mA \text{ cm}^{-2}$	Open circuit voltage (V <sub>oc</sub> )/V	Fill factor (FF)	Power conversion efficiency $(\eta)$ (%)
As cast	5.20	0.75	0.45	1.76
annealed	6.22	0.72	0.46	2.00
Contact annealed	6.90	0.80	0.49	2.70

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 Table 4
 Photovoltaic parameters for the as cast, blend annealed and contact annealed devices based on the B:PCBM (1:1) blend using ITO/PEDOT:PSS and Al electrodes

	Short circuit current $(J_{\rm sc})/{\rm mA~cm^{-2}}$	Open circuit voltage $(V_{oc})/V$	Fill factor (FF)	Power conversion efficiency $(\eta)$ (%)
As cast	6.30	0.72	0.47	2.22
Blend annealed	7.00	0.69	0.47	2.27
Contact annealed	8.20	0.74	0.52	3.15



Fig. 5 Current–voltage characteristics in the dark for three devices with B:PCBM blend BHJ devices with different annealed conditions.



Fig. 6 IPCE spectra of BHJ photovoltaic devices with compound A or B:PCBM blends.



**Fig. 7** (a) Schematic energy diagram for a PEDOT:PSS/**B**:PCBM/Au device in an open circuit condition. Energy values are relative to the vacuum level. The difference in work function values of PEDOT:PSS (5.2 eV) and Au (5.1 eV)<sup>31</sup> results in  $V_{\rm bi}$  of 0.1 eV. (b) Energy diagram under reverse voltage bias showing hole injection from Au. (c) Energy diagram under forward voltage bias, showing hole injection from PEDOT:PSS and electron injection from Au.

Electron injection from PEDOT:PSS to the LUMO of PCBM is suppressed by the 1.2 eV Schottky barrier, as evidenced by negligible reverse bias current in the device having PEDOT:PSS as the bottom contact. In our device with a Au top electrode, the electrons can also be injected from the Au into the LUMO level of the PCBM due to the reduction in Schottky barrier height by interface dipoles (in forward bias condition). Consequently, the total current in forward bias (Fig. 7c) consists of contributions from both electron and hole currents.<sup>35,36,37</sup>

The hole transport through the **B** network in both the as cast and contact blend annealed devices at low reverse applied voltage  $V_a < 1.5$  V is well described using the SCLC model in trap filled limit, as the square root of reverse bias current  $(J_R^{1/2})$  increases nearly with bias across the blend over the entire voltage range (Fig. 8a). In the trap filled SCLC model, the *J*–*V* characteristics can be described as:

$$J = \frac{9}{8} \varepsilon_o \varepsilon_r \mu \frac{V^2}{d^3} \tag{2}$$

where  $V = V_{\rm a} - V_{\rm bi}$ ,  $V_{\rm a}$  is the applied voltage,  $V_{\rm bi}$  is the built in voltage due to the difference in the electrode work functions,  $\varepsilon_0$  is vacuum permittivity,  $\varepsilon_{\rm r}$  is the relative dielectric constant of the transport medium,  $\mu$  is the mobility of charge carriers and *d* is the thickness of the blend layer in the device. From the slope of the curves shown in Fig. 8a, we have estimated the hole mobility and found it to be  $1.15 \times 10^{-5}$  and  $6.56 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for the as cast and contact annealed devices, respectively.

We have estimated the electron mobility through the PCBM domain in the blend layers through analysing the forward bias J-V characteristics of the devices. In the forward bias condition, the Au electrode is biased negatively with respect to PEDOT:PSS (Fig. 7c). The total device current consists of both an electron current,  $J_e$  (electron injection from Au electrode into the LUMO level of PCBM), and hole current,  $J_h$  (hole injection from PEDOT:PSS into the HOMO level of compound **B**). The total forwards bias current,  $J_F = (J_e + J_h)$ , which is analogous to double injection of electrons and holes into an insulator in the



**Fig. 8** (a) Low voltage J-V characteristics of reverse biased PEDOT:PSS/**B**:PCBM/Au devices for the as-cast and contact annealed conditions, displaying trap-filled SCLC behavior. (b) J-V characteristics, *i.e.*  $J_{f-r}$  vs.  $(V_a - V_{bi})$  for electron transport in the **B**:PCBM blend, the plot indicating SCLC conduction at  $V_a - V_{bi} > 1$  V.

space charge current, limit with high recombination probability.<sup>38</sup> Since the work functions of Au and PEDOT:PSS are similar, we can assume that the hole conduction through the HOMO of compound **B** is symmetric with respect to the bias voltage direction. Therefore, we can separate the forward bias electron current through the LUMO level of PCBM by subtracting the total reverse current from the forward bias current, *i.e.*  $J_e = J_f - J_h = J_f - J_r = J_{f-r}$ . The variation of  $J_{f-r}$  with  $V_a - V_{bi}$ is shown in Fig. 8b for both the as cast and contact annealed devices. It can be seen from these curves that at sufficiently high forward bias voltages, both devices show J-V behaviour consistent with space charge limited electron conduction through PCBM in trap filled limit *i.e.*  $J_{f-r} \sim (V_a - V_{bi})^2$ . The J-V characteristics can be described by a SCLC model including a field dependent mobility  $\mu(E)$ .<sup>39</sup>

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu(E) \frac{V^2}{d^3}$$
(3a)

where  $\mu(E)$  is given by

$$\mu(E) = \mu(0) \exp\left(0.891\gamma \sqrt{\frac{V}{d}}\right) \tag{3b}$$

where  $\gamma$  is the field activation factor and  $\mu(0)$  is the zero field mobility. The analysis of *J*–*V* characteristics is shown in Fig. 8b and eqn 3a and 3b. We have estimated the values of electron mobility, which are  $3.2 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and  $4.3 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for the as cast and contact annealed device, respectively.

Comparing the electron and hole mobility for the as cast and contact blend device, it is found that the difference in the electron and hole mobility is about 28 and 6.5, respectively. This decrease in the difference causes the reduction of recombination in the contact annealed device and leads to an improvement in the PCE of the PV device.

## Conclusions

A symmetrical bisazopyrrole (**A**) and the corresponding  $BF_{2^-}$ azopyrrole complex (**B**) were successfully synthesized and used for BHJ solar cells. Compounds **A** and **B** were soluble in common organic solvents, but **B** was stable only in nonprotic solvents. The thin film absorption spectrum of **B** was broader and showed lower band gap (1.49 eV) than that (1.54 eV) of **A**. The HOMO and LUMO levels of both compounds **A** and **B** are found suitable for the BHJ photoactive layer. We have shown that a suitable post-device-fabrication thermal treatment (contact annealed) results in high performance **A**:PCBM or **B**:PCBM blend BHJ solar cells. The PCE values are 2.70% and 3.15% for the devices based on the **A**:PCBM and **B**:PCBM blend, respectively. We found that the improved PCE for the contact annealed device results from the improved balanced charge transport, due to the enhanced hole mobility.

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