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Reversible photoinduced bi-state polymer solar cells based on fullerene derivatives with azobenzene groups



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1. Introduction

Polymer solar cells (PSCs) have attracted considerable attention due to their flexible nature, low weight, low cost, ease of preparation, and potential applications in building integrated photovoltaic (BIPV) devices [1–3]. Recently, the power conversion efficiency (PCE) of PSCs was demonstrated to exceed 10% based on considerable effort by several research groups [4,5]. However, new materials are still required for the development of PSCs because practical applications require further improvement of the photovoltaic properties. For example, PSCs used on the windows of buildings or agricultural greenhouses may require a self-regulation function in response to the different characteristics of the solar spectrum during different times of a day, which is similar to the "smart glass" changing its transmittance according to the sunlight intensity [6,7]. Such functionality requires new photovoltaic materials combined with photo-sensitized groups.

Azobenzene derivatives are well-known photochromic materials due to their reversible transformation between two photo-isomers [8]. The photo-isomerization of azobenzene derivatives occurs when treated with ultraviolet (UV) or visible (VIS) light. The conversion between the states is usually accompanied by

ABSTRACT

[6,6]-Phenyl-C61-butyric acid-4'-hydroxyl-azobenzene ester (PCBAb) was synthesized and used as the acceptor in the fabrication of reversible UV–VIS response bi-state polymer solar cells (PSCs) based on the photoinduced *cis–trans* isomerization of PCBAb. The device can be switched between "active" and "sleep" by the irradiation of UV and visible light, respectively. The active device has a PCE of 2.0%. With UV irradiation, the device goes to "sleep" with a lowered PCE (0.4%), and simultaneously decreased J_{sc} , V_{oc} and FF, while after visible light treatment, the device is made "active" again. The mechanism of the bi-state process involves the different electron mobilities of the isomers.

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changes in the physical properties. As a result, azobenzene derivatives are widely researched in fields that require strong optical responses, such as photovoltaics [9–11], photoswitches [12], optical data storage [13] and organic field-effect transistors (OFETs) [14]. These applications often require good electron acceptors with high electron mobilities, which promote exciton dissociation, such as fullerene derivatives. Fullerene derivatives are widely used electron acceptors with high electron mobilities of 10^{-3} cm² V⁻¹ s⁻¹. high LUMO levels of 4.3 eV (able to accept up to 6 electrons), and deep HOMO levels of 6.1 eV, responsible for efficient photoinduced hole transfer to the donor [15]. Therefore, in this work, combining the fullerene derivatives with azobenzene groups, a new material PCBAb is synthesized and applied in PSCs. PCBAb, as the electron acceptor in PSCs, has a notable electron mobility response to UV and VIS light, which can be used to control the PCE of PSCs, thereby switching the solar cell between "active" and "sleep" states.

2. Experiment

After synthesizing PCBA as reported in [16], PCBAb was synthesized through esterification of PCBA and 4-hydroxyazobenzene in dry CH₂Cl₂ in the presence of EDC and DMAP (Fig. 1a).

The bulk heterojunction solar cells of ITO/PEDOT:PSS/ P3HT:PCBAb/LiF/Al were fabricated. The PEDOT:PSS used for hole collection was spin-coated onto an ITO-coated glass substrate. The P3HT:PCBAb solvent was dissolved 1:1 w/w in dichlorobenzene with a total concentration of 26 mg/ml. Next, the active layer



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Fig. 1. (a) Synthesis of PCBAb. (b) Diagram of PCBAb photo-isomerization.

was spin-coated to a thickness of approximately 150 nm and then annealed at 150 °C for 1 h. Finally, an Al electrode with a LiF buffer layer for electron collection was thermally deposited through a 2mm diameter mask.

Current density-voltage (*J*-*V*) curves were obtained using a Keithley 2611 power source meter under AM 1.5G illumination (100 mW/cm²) using a 300-W Newport-Oriel AM 1.5G light source. The UV treatment involves irradiation of the thin films under a UV light source (2.5 W/cm²) and the VIS treatment involves the use an AM 1.5G light source (100 mW/cm²). All measurements were performed in air without encapsulation.

3. Results and discussion

3.1. UV–VIS absorption spectroscopy

PCBAb can be switched between its *trans* and *cis* forms by irradiation of UV and visible light, as shown in Fig. 1b. The structural isomerization exhibits different optical absorption. The absorption spectra of a PCBAb film were measured before and after irradiation of UV light, as shown in Fig. 2 (the insert shows the



Fig. 2. Absorption spectra of PCBAb thin films before and after UV irradiation. (Insert) Absorption differences between the PCBAb thin film before and after UV irradiation. The arrows show the remarkable peaks of the absorption differentials.

absorption difference). The peak at 350 nm is the absorption peak of the C_{60} groups [17]. The photo-isomerization leads to the differences in the absorption of the thin films.

3.2. J-V characteristics

Considering the cis-trans photo-isomerization of the azobenzene groups, the device characteristics under UV and VIS treat were compared. The current density vs. voltage (I-V) plot of the solar cells is shown in Fig. 3. The device characteristics, such as the short circuit current (I_{sc}) , open circuit voltage (V_{oc}) , fill factor (FF), PCE, and series and shunt resistances (R_s and R_{sh} , respectively) are summarized in Table 1. Under the illumination of 100 mW/cm² (AM 1.5G), the original PCBAb device, without any irradiation treatment, had a PCE of 2.0%, and the V_{oc} , J_{sc} and FF of the original device were 0.58 V, 7.0 mA/cm² and 0.49, respectively, which stayed in the "active" state. When irradiated under UV light with different treatment times of 1, 2, 3 and 6 min, the values of $V_{\rm oc}$, $J_{\rm sc}$, PCE, and FF all decreased simultaneously. For the 6-min UV device, the J_{sc} , V_{oc} , PCE and FF were 2.3 mA/cm², 0.45 V, 0.42% and 0.40, respectively. The J_{sc} and PCE were notably reduced to 1/3 and 1/5 of their original values, respectively. The decreased parameters indicated that the device entered the "sleep" state gradually under UV treatment. Next, the "sleeping" device was irradiated with visible light for 1, 2 and 5 min, which made it "active" again, with the parameters regained gradually. Because the VIS source had a lower intensity than the UV source, the VIS response process was considerably slower than that of the UV response process. Because the trans conformation of azobenzene is more stable than that of the cis isomer, in the dark at equilibrium, trans is the dominant isomer (99.99%) [14]. Therefore, the device was kept in the dark for 12 h to allow the trans isomer to re-establish the equilibrium. The process is reversible.

3.3. SCLC modeling

The J_{sc} exhibits an obvious decrease when treated with UV light (Table 1), as is also shown in the incident photon to converted current efficiency spectra (IPCE, Fig. 4a) of the devices. J_{sc} is greatly influenced by the absorption of the active layer and the charge transport properties of the device. The absorption spectra revealed no significant difference before and after UV treatment. To



Fig. 3. The "active" and "sleep" processes of a solar cell under UV and VIS treatments in sequence. (a) sleep process under 0–6 min of UV treatment; (b) active process under 0–5 min VIS and dark treatments.

measure the mobility change of PCBAb as an acceptor, an electrononly device was fabricated with the structure of Al/P3HT:PCBAb/ LiF/Al. The electron mobility can be calculated by fitting the *J*–*V* characteristics of the electron-only device to the model of spacecharges-limited current (SCLC) [18]. The SCLC model is given by $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where *J* is the current density, *L* is the thickness of the active layer, μ is the electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space, and *V* is the internal voltage in the device. In addition, *V* is corrected as follows: $V = V_{app} - V_{sr} - V_{bi}$, where V_{app} is the applied voltage to the device, V_{sr} is the voltage drop due to the contact resistance and the series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes. Fig. 4b shows the *J*–*V*² curves of the

Table 1

The photovoltaic performances of the device following UV and VIS treatments.

Treatment (min)	J _{sc} (mA/ cm ²)	V _{oc} (V)	PCE (%)	FF	$R_{\rm s}$ (Ω cm ²)	$R_{\rm sh}$ ($\Omega {\rm cm}^2$)
Before treat	7.0	0.58	1.99	0.49	24	743
UV 1	5.6	0.51	1.11	0.39	35	154
UV 2	4.8	0.50	0.89	0.37	42	478
UV 3	3.9	0.48	0.72	0.38	45	435
UV 6 (VIS 0)	2.3	0.45	0.42	0.40	60	329
VIS 1	2.4	0.46	0.44	0.41	60	433
VIS 2	2.5	0.47	0.48	0.41	60	612
VIS 6	2.6	0.47	0.50	0.42	50	551
Overnight (dark)	3.3	0.51	0.72	0.43	39	456



Fig. 4. (a) IPCE spectra of a device without any treatment, and with 1 min, 2 min, and 3 min of UV treatment; (b) $J-V^2$ characteristics and the fitting results of an electron-only device with no treatment, 2 min of UV treatment and 8 min of visible light treatment in sequence.



Fig. 5. $R_{\rm s}$ and $R_{\rm sh}$ dependence on the UV and VIS treatments.

electron-only device with both the original data and the linear fittings under different treatments of no treatment, 2-min UV treatment, and 8-min VIS treatment. The electron mobility of the device is related to the slopes of the fitting lines at high voltage [19]; therefore, the data with V^2 in the range of 5.0–8.5 is chosen to be fitted. The slope of original device is much higher than that of the UV treated device, and the VIS treated device has a slightly restored slope compared to the UV treated device. This result implies that UV treatment leads to an electron mobility decrease of the device and that VIS treatment restores the electron mobility. Fig. 5 shows how R_s and R_{sh} change under different times of UV and VIS treatment, which is calculated from the *J*–*V* characteristics. In UV region R_s increases from 24 to 60 Ω cm² under UV treatment, and R_{sh} also exhibits a decreasing trend from 743 to 329 Ω cm². An opposite trend is shown in VIS region. According to the equivalent circuit model, a high R_s does not affect V_{oc} but reduces J_{sc} and FF and a low R_{sh} does not affect J_{sc} but reduces V_{oc} and FF [20,21], Based on the model, both V_{oc} and J_{sc} will decrease after UV treatment, which fits the data in Table 1 very well. In addition, lower charge mobility after UV treatment leads to a higher rate of recombination of charge carriers and a lower electron collection rate, resulting in an increased R_s and a decreased R_{sh} which agree with the results in Fig. 5.

4. Conclusions

A UV–VIS response switchable polymer solar cell was fabricated based on the photo-isomeric material PCBAb. The electron mobility of the device is dependent on UV and VIS treatments, which leads to the change of device performance between "active" and "sleep" states. The results of this work indicate a future usage for smart solar cells, whose PCE responds to the variation of the solar spectrum at different times of a day.

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