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Formation of charge transfer complexes significantly improves the electron transfer process of polymer solar cells

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ABSTRACT

A fluorescent inhibitor, 1-Bromo-4-Nitrobenzene (1-Br-4-NB, $C_6H_4BrNO_2$), is introduced to poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) active layer of polymer solar cells (PSCs). When the amount of 1-Br-4-NB added is 25 wt%, the device performance of PSCs is optimal. To investigate the means by which the power conversion efficiency (PCE) is improved, external quantum efficiency (EQE), fluorescence spectrum, transient absorption spectroscopy and dynamics photoresponse, X-ray diffraction (XRD) patterns are measured and density functional theory (DFT) calculations are carried out. The results indicate that excitonic recombination to the ground state is reduced and excitonic dissociation at the donor–acceptor interface is enhanced, which explains the inhibitory effect on the generation of fluorescence. Moreover, the electron transfer complexes (P3HT–$C_6H_4BrNO_2$) is demonstrated to be formed after the addition of 1-Br-4-NB. The PCE of PSCs achieves an improvement of more than 57% compared to the reference solar cell without 1-Br-4-NB.

1. Introduction

The environmental and supply problems associated with the worldwide energy demand are becoming some of the most important problems facing the world today. With the aim of addressing these problems, interest in PSCs has increased due to their numerous advantages, such as low fabrication cost, light weight, good flexibility, and ability to be printed on plastic substrates [1–6]. Organic PSCs have undergone rapid development due to their good performance. In particular, P3HT and PCBM have received widespread attention due to high hole and electron mobilities and good environmental stability. Numerous efforts have been made by many researchers to further improve the PCE of PSCs. For example, LiF, ZnO, poly(ethylene oxide) (PEO) or graphene oxide derivatives have been used to modify the electrodes to improve the PCE [7–10]. Metallic nanoparticles have been used to enhance light harvesting in PSC devices [11,12]. The use of processing additives was demonstrated to be a good method to improve the PCE of PSCs [13–16]. The synthesis and the use of the new materials can also improve the efficiency of the PSCs, such as polysilole(2,6-diyl-alt-5-octylthieno[3,4-c]pyrrole-4,6-dione) (PDTSTPD), poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT), poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), and poly{[4,8-bis-(2-ethylhexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl]-*alt*-[2-(2′-ethyl-hexanoyl)-thieno[3,4-b]thiophen-4,

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6-diyl]} (PBDTTT-C-T) [17–19]. In addition, the groups performing research on organic polymer fluorescent sensors found that the addition of nitrobenzene derivatives has an inhibitory effect on the generation of fluorescence, and researchers hold that a type of electron transfer complexes can be formed between the polymers and these nitrobenzene derivative additives and that the level structure of the electron transfer complexes contributes to the photoelectric conversion efficiency [20–22]. Inspired by the above findings, a nitrobenzene derivative, 1-Br-4-NB, was introduced to the active layer of PSCs. Here, we studied the effect of 1-Br-4-NB on the performance of PSCs.

2. Experimental details

The materials used for the active layer of PSCs are P3HT and PCBM (purchased from Luminescence Technology Corp). 1-Bromo-4-Nitrobenzene (1-Br-4-NB, $C_6H_4BrNO_2$, TCI, purity > 99%) is chosen as the fluorescent inhibitor. The chemical structures of P3HT, PCBM and 1-Br-4-NB are shown in Fig. 1. The architecture of the PSCs is ITO/PEDOT: PSS/P3HT:PCBM/LiF/Al, which is also shown in Fig. 1. The active area of the PSCs is 16 mm^2 (4 mm × 4 mm).

P3HT and PCBM were dissolved in a mixed solvent of CB/CF (V/V = 3/1) in a weight ratio of 1:1 at a concentration of 20 mg/ml. 1-Br-4-NB was added to the solution to obtain weight percentages of 0 wt%, 15 wt%, 20 wt%, 25 wt%, and 30 wt%, and then the respective solutions were stirred for more than 8 h on the stirrer table at room temperature. Pre-patterned ITO-coated glass with a sheet resistance of 12 Ω/□ was used as the substrate and the anode electrode. The substrate was sequentially cleaned with detergent, de-ionised water, absolute ethanol, acetone and isopropanol using an ultrasonic bath, followed by UV-ozone treatment for 4.5 min. Poly(3,4-ethylenedioxythiophen-e):poly(styrenesulphonate) (PEDOT:PSS, Clevios P VP AI4083, H.C. Stark) treated by isopropanol according to the volume ratio of 5:1 was spin-coated onto the substrate at 3000 rpm for 30 s [23] and then transferred into a glove box filled with high-purity nitrogen and dried at 130 °C for 10 min. The thickness of the dried PEDOT:PSS layer was approximately 40 nm. Subsequently, the P3HT:PCBM absorber blend was spin-coated at 1500 rpm onto the PEDOT:PSS layer and then dried at 130 °C for 15 min. The resulting thickness of the absorber layer was approximately 100 nm. The cathode was formed by depositing 1 nm LiF and 130 nm Al through a shadow mask. Finally, these devices were annealed at 130 °C for 10 min.

All the thicknesses were measured using a Stylus Profiler (Dektak150). The current density–voltage (*J*–*V*) characteristics were measured using a solar simulator (AM 1.5) (100 mW/cm^2, Japan, SAN-EI, ELS 155 (XE)) and a Keithley 2400 Sourcemeter. The EQE was measured using the IPCE/QE/spectral response test system (America, CROWNTECH). The fluorescence spectrum was measured by a fluorescence spectrophotometer (HITACHI F-4500), and XRD patterns were measured by a diffractometer (Bruker D8). The dynamical data from transient absorption spectroscopy were collected using a highly sensitive femtosecond transient absorption system equipped with a pump laser of 400 nm and a pulse width and pump power of 100 fs and 70 μJ/cm^2, respectively.

3. Results and discussion

The *J*–*V* characteristics of the devices with 1-Br-4-NB at 0 wt% (the reference cell), 15 wt%, 20 wt%, 25 wt% and 30 wt% are displayed in Fig. 2(a). The trend of an initial increase followed by a decrease can be observed in the *J*–*V* curve compared to the response of the reference solar cell without 1-Br-4-NB. The specific device performance parameters are presented in Table 1. The reference cell exhibited an open-circuit voltage Voc of 0.57 V, a short-current Jsc of 10.3 mA/cm^2, and a fill factor (FF) of 56.3%, resulting in a calculated PCE of 3.3%. After the addition of 1-Br-4-NB to the active layers, the values of Voc do not exhibit obvious differences. This lack of obvious differences is because the Voc value of PSCs is directly proportional to the offset between the HOMO level of the electron donor and the LUMO level of the electron acceptor [24]. The Jsc

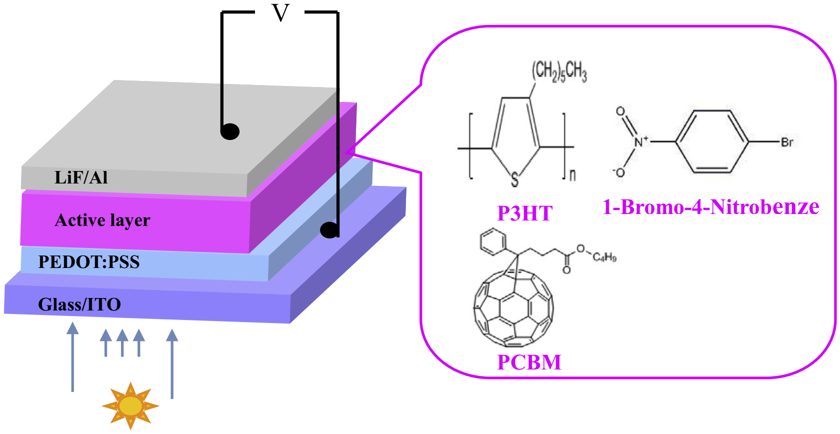

Fig. 1. The chemical structures of P3HT, PCBM, and 1-Bromo-4-Nitrobenzene (1-Br-4-NB) as well as the architecture of the PSCs.