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Planar inverted perovskite solar cells based on the electron transport layer of $PC_{61}BM$:ITIC

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ABSTRACT

A small molecule 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-*d*:2′,3′-*d*′]-*s*-indaceno[1,2-*b*:5,6-*b*′]-dithiophene (ITIC) was used as the additive for the electron transport layer (ETL) of phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) in planar inverted perovskite solar cells (PSCs) fabricated by the flash method. Due to the proper LUMO level and decent electrical conductivity of ITIC, the photovoltaic properties of planar inverted PSCs based on the smooth $PC_{61}BM$:ITIC (2 wt%) ETL were promoted, and the power conversion efficiency (PCE) and the short-circuit current density (J_{sc}) of the devices were increased to 12.41% and 18.53 mA cm^{-2}, respectively, which were 13.3% and 13.5% enhancements relative to those of the undoped control devices. Therefore, ITIC was a promising additive for $PC_{61}BM$ ETL in inverted PSCs and the photovoltaic properties of devices could be improved accordingly.

1. Introduction

In order to prevent energy depletion and environmental pollution, renewable energy which could take the place of fossil fuels was widely studied in the past decades. Especially, perovskite solar cells (PSCs) have been paid more attention because of the acceptable power conversion efficiency, low cost of fabrication process and the feasibility of flexible applications. [1–6] The milestone work for PSCs was reported in 2009 and the PCE was 3.8% [7]. From then on, broad attention has been paid to the study of PSCs and the PCE of PSCs has been increased to 22.1% in recent years [8].PSCs were considered to be a promising candidate for photovoltaic applications.

Fullerene and its derivatives were widely used in PSCs, [9–11] among which phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) was commonly used as the electron transport layer (ETL) in planar inverted PSCs, and photovoltaic properties of PSCs could be effectively improved. [12–14] However, there were still some drawbacks for $PC_{61}BM$ ETL, such as uneven morphology, interface traps, low coverage and so on. [15] To solve these problems, doping technology, considered as a simple and effective method, was commonly used for ETL [16–19]. Fang's group doped graphdiyne (GD) into PCBM layer, which could reduce charge recombination, improve charge extraction and benefit carrier balance [17]. PCBM:GD-based devices showed an average PCE of 13.9%, which was higher than that of the pristine PCBM-based devices (10.8%). And an enhancement of short-circuit current density (J_{sc}) and fill factor (FF) were realized simultaneously. Yan's group added polystyrene (PS) into PCBM layer (1.5 wt%) to obtain a smooth and uniform PCBM ETL [19], which benefited the photovoltaic properties of inverted PSCs. And the open-circuit voltage (V_{oc}) was increased from 0.97 V to 1.07 V with the dopant of PS in PCBM layer. Recently, bathocuproine (BCP) was adopted as an additive for ETL and PCE was increased to 13.11%. [18]

A small molecule 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-*d*:2′,3′-*d*′]-*s*-indaceno[1,2-*b*:5,6-*b*′]-dithiophene (ITIC) (Fig. 1 a)) with a bulky seven-ring fused core was used as an electron acceptor for fullerene-free polymer solar cells [20–25] due to its high electron mobility and low bandgap. Besides, ITIC was also used to optimize the ETL of PSCs. Liu's group inserted an ultrathin ITIC layer between TiO_2 ETL and perovskite active layer [26], which smoothed the TiO_2 film and benefited the quality of perovskite crystals. The efficiency of the optimized devices exceeded 20%. In this work, ITIC was doped into the $PC_{61}BM$ ETL of planar inverted PSCs for the first time. According to scanning electron microscope (SEM), uniform and smooth ETL film ($PC_{61}BM$:ITIC) was

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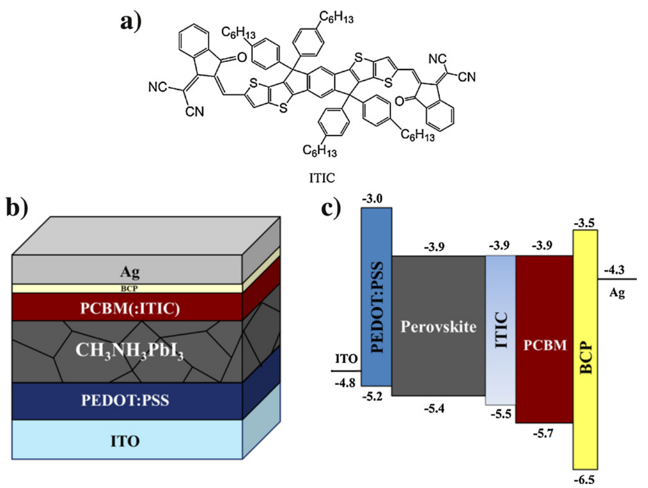

Fig. 1. a) The molecular structure of ITIC. b) The schematic structure of PSCs. c) The energy levels of the layers in PSCs.

achieved. When the doping ratio of ITIC in ETL reached 2%, the PCE and J_{sc} of the optimized device were 12.41% and 18.53 mA cm^{-2}, which were 13.3% and 13.5% enhancements relative to those of the undoped control device. Therefore, ITIC was an effective additive for $PC_{61}BM$ ETL for PSCs.

2. Experimental

2.1. Materials

All the materials used in this work were listed as follows: Lead iodide (PbI_2, > 99.99%, Xi'an Polymer Light Technology Corp.), methylamine alcohol solution (CH_3NH_2,27.0%～32.0%, AR, Sinopharm Chemical Reagent Co., Ltd), hydroiodic acid (HI, > 45.0%, AR, Sinopharm Chemical Reagent Co., Ltd), poly (3,4-ethylenedioxythiophene)-poly (styrenesulfonate) (PEDOT:PSS, PVP Al 4083, Heraeus), phenyl-C61 -butyric acid methyl ester ($PC_{61}BM$, > 99%, CAS 160848-22-6), N,*N*-dimethylformamide (DMF, 99.8%, Aladdin), chlorobenzene (CB, 99.9%, Spectrophotometric Grade, Alfa Aesar), dimethyl sulfoxide (DMSO, HPLC, 99.5%, Kermel). Methyl ammonium iodide (CH_3NH_3I) was synthesized with methylamine alcohol solution and hydroiodic acid according to the previous literatures. [27] ITIC was synthesized according to the literature [20] in our laboratory. All of the materials were not purified further before use.

2.2. Material preparation and device fabrication

$CH_3NH_3PbI_3$ solution: 1 mmol PbI_2 powder and 1 mmol CH_3NH_3I powder were dissolved in 1 mL DMF, and 88 μL DMSO was also mixed into the solution. Then, the solution was filtered through a 0.22 μm filter before use.

ETL solution: The concentration of $PC_{61}BM$ in CB solvent was 20 mg mL^{-1}. The $PC_{61}BM$ solution was doped with ITIC and the doping ratios varied from 1 wt% to 4 wt%.

Fabrication of PSCs: The devices with the configuration of ITO/PEDOT:PSS/perovskite/$PC_{61}BM$(:ITIC)/BCP/Ag were fabricated in this work as shown in Fig. 1b). The ITO-coated glass was washed with deionized water, acetone and ethanol in ultrasonic cleaning machine for 15 min respectively. Then, the substrates were treated by plasma to remove organic contamination. PEDOT:PSS was spin coated onto ITO substrates at the speed of 4000 rpm for 30 s and then annealed at 140 ℃ for 10 min. After that, the active layer of perovskite was spin coated onto PEDOT:PSS layer (4000 rpm, 7 s) and then immediately transferred into a home-made vacuum cavity. The color of the perovskite film changed from light yellow to reddish brown under the pressure of 20 Pa for ～30 s. Then, the devices were annealed at 100 ℃ for 10 min and the perovskite films turned to dark brown. For comparison, the $PC_{61}BM$:ITIC solution and the pristine $PC_{61}BM$ solution were spin coated onto perovskite layers at the speed of 4000 rpm for 30 s, respectively. The BCP film acted as the hole blocking layer in the devices. At last, Ag cathode of 100 nm was evaporated to complete the fabrication of inverted PSCs.

2.3. Characterization

The current density–voltage (J–V) curves of the inverted PSCs were measured under the AM 1.5 G (100 mW/cm^2, Newport) standard illumination. The morphology of the perovskite films and ETLs was studied by scanning electron microscope (SEM, Hitachi S-4800) and atomic force microscope (AFM, Agilent Technology N9610 A AFM/SPM Controller, closed loop enabled-Series 5500). The energy levels of ETLs were measured with ultraviolet photoelectron spectrometer (UPS). The absorption spectra of ETLs were measured by UV-VIS-NIR spectrophotometer (UV3600PLUS, Shimadzu).The incident photon-to-current conversion efficiency (IPCE) spectra were measured with a lock-in amplifier (model SR830 DSP).

3. Results and discussion

The energy levels of the materials used in this work were shown in Fig. 1c). The lowest unoccupied molecular orbital (LUMO) energy level of ITIC was -3.91 eV [23], which was identical to that of perovskite active layers. The highest occupied molecular orbital (HOMO) level of pristine and ITIC-doped $PC_{61}BM$ layer was measured with UPS as shown in Fig. 2a) and the bandgap was calculated according to the absorption spectra (Fig. 5e)). Although the doping ratio of ITIC was rather small, the HOMO of $PC_{61}BM$:ITIC film was reduced to some extent. The LUMO of $PC_{61}BM$:ITIC film was 3.86 eV, which was almost

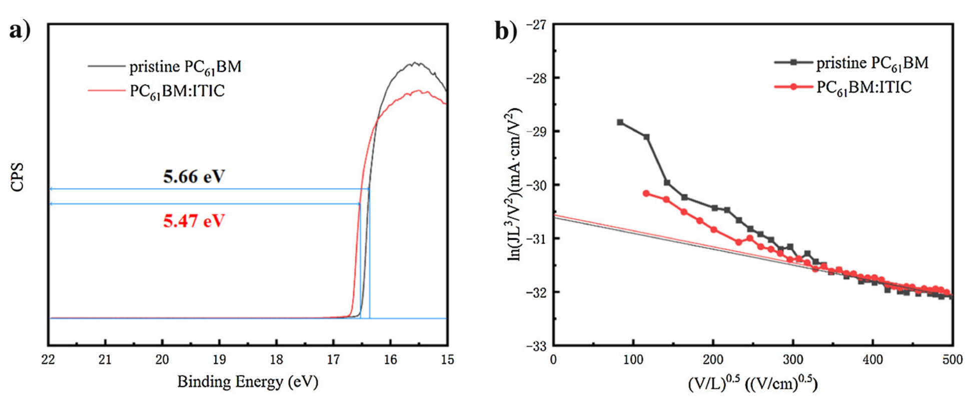

Fig. 2. a) The photoemission cutoff via UPS. b) The ln(JL^3/V^2) versus $(V/L)^{0.5}$ curves of electron-only devices.