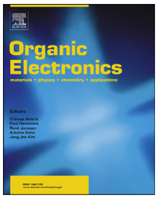
Organic Electronics 33 (2016) 142–149

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Copolymers based on thiazolothiazole-dithienosilole as hole-transporting materials for high efficient perovskite solar cells

Zhaowei Wang, Qingqing Dong, Yijun Xia, Hao Yu, Kaicheng Zhang, Xiaodong Liu, Xia Guo, Yi Zhou*, Maojie Zhang*, Bo Song*

Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, China

ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form
11 March 2016
Accepted 16 March 2016
Available online 24 March 2016

Keywords:
Perovskite solar cells
Copolymers
Hole transporting layer
Electron transporting layer
Pristine C_{60}

ABSTRACT

The interlayers, including hole transporting layer (HTL) and electron transporting layer (ETL), segregating photoactive layer and the electrodes play an important role in charge extraction and transportation in perovskite solar cells (pero-SCs). Two novel copolymers, PDTSTTz and PDTSTTz-4, for the first time were applied as HTL in the *n-i-p* type pero-SCs, with the device structure of ITO/compact TiO_2/$CH_3NH_3PbI_{3-x}Cl_x$/HTL/MoO_3/Ag. The highest occupied molecular orbitals (HOMO) levels of PDTSTTz and PDTSTTz-4 exhibit a suitable band alignment with the valence band edge of the perovskite. Both of them lead to improved device performances compared with reference pero-SCs based on P3HT as HTL. To further balance the charge extraction and the diffusion length of charge carriers, pristine C_{60} was introduced at the cathode side of the pero-SCs, working together with TiO_2 as ETL. With insertion of both the HTL and ETL, the performance of pero-SCs was greatly enhanced. The optimized devices exhibited impressive PCEs of 14.4% and 15.8% for devices based on PDTSTTz and PDTSTTz-4. The improved performance is attributed to better light harvest ability, decreased interface resistance and faster decay time due to the introduction of the interlayers.

1. Introduction

Organic-inorganic hybrid perovskite solar cells (pero-SCs) have shown very promising prospect due to the competitive power conversion efficiencies (PCEs) [1–3]. The features, such as large absorption coefficient [4–7], small exciton binding energy [8,9], high ambipolar charge mobility [10–12], long carrier diffusion length and life time [13–15] make perovskite a fantastic candidate for thin film solar cells. Bearing these advantages, the charge separation and transfer in the perovskite thin film can be easily realized by proper crystalline engineering [16–19]. However, the performance of pero-SCs also relies on efficient charge extraction and transportation to the electrodes. Therefore, the interlayers between the photo-absorber and electrodes are also crucial factors.

The interlayers reside at the anode side, used for efficient hole extraction and transport, are named as hole transporting layer (HTL) [20]. Organic small molecule (OSM), 2,2′,7,7’-tetrakis(N,N-di-pmethoxyphenylamine)-9,9’-spirobifluorene (Spiro-OMeTAD), was applied as HTL material in dye-sensitized solar cells, and is now widely employed as HTL in pero-SCs [5,21–23]. In addition to OSM, conjugated polymers are as well potential candidate of HTLs in pero-SCs. So far, commercially available polymer materials, such as poly(3-hexylthiophene-2,5-diyl) (P3HT) [24,25], poly(triarylamine) [26,27], poly-TPD [28], polyfluorene [29] were proven to be suitable for HTLs. However, the above HTLs, no matter OSMs or polymers, are all wide band gap materials, having weak or no absorption band at the wavelength over 550 nm. So far, several newly designed hole conducting OSMs and polymers [30–35], with light harvest ability, were successfully employed as HTLs in pero-SCs. It is speculated that developing new materials with absorption band covering visible and near infrared region can very likely enhance the utilization of sunlight, and improve the performances of pero-SCs in terms of the photocurrent.

Herein, we introduced two donor-acceptor copolymers based on dithienosilole (DTS) and thiazolothiazole (TTz), denoted by PDTSTTz and PDTSTTz-4, as HTL materials in pero-SCs. These two copolymers showed strong absorption in visible region and were applied as light-absorber in polymer solar cells (PSC) in our

---

* Corresponding authors.
E-mail addresses: yizhou@suda.edu.cn (Y. Zhou), mjzhang@suda.edu.cn (M. Zhang), songbo@suda.edu.cn (B. Song).

http://dx.doi.org/10.1016/j.orgel.2016.03.020

previous work [36,37]. Compared to another widely used electron donor materials P3HT in PSC, the absorption band of PDTSTTz and PDTSTTz-4 are more broader from 400 nm to 700 nm. As HTL materials in pero-SCs, the hole mobility and energy levels are inevitably considered for efficient charge extraction and transporation. In comparison with the relatively low hole mobility of Spiro-OMeTAD (~10^{-4} – 10^{-5} cm^2 V^{-1} s^{-1}), and even P3HT (~10^{-3} cm^2 V^{-1} s^{-1}) [38–40], both PDTSTTz (3.6×10^{-3} cm^2 V^{-1} s^{-1}) [36] and PDTSTTz-4 (7.8×10^{-2} cm^2 V^{-1} s^{-1}) [37] show higher hole mobilities due to enhanced backbone planarity and strong π-stacking properties contributed from rigid and coplanar fused ring of DTS and TTz unit. Moreover, the highest occupied molecular orbitals (HOMO) energy level of PDTSTTz and PDTSTTz-4 are −5.1 and −5.0 eV respectively, which are energetically favorable for hole transfer from perovskite to HTL. The devices based on PDTSTTz and PDTSTTz-4 show comparable performances with that based on P3HT, and slightly improvement in short current density (J_{sc}).

Furthermore, to solve the unbalanced diffusion length problems of charge carriers in pero-SCs using only TiO_2 as electron transporting layer (ETL) [41,42], a layer of C_{60} was sandwiched between TiO_2 and perovskite. This strategy worked in facilitating the charge extraction and transportation [24,43–51]. Impressive improved PCE of 14.4% and 15.8% for pero-SCs based on PDTSTTz and PDTSTTz-4 were achieved, respectively. The insight investigation was addressed by alternating current impedance spectrometry (ACIS) and fluorescence spectra. This work demonstrated that the appropriate engineering of interlayers in pero-SCs would help in improving the performance.

2. Experimental section

2.1. Materials

The $PbCl_2$ (99.999%) was purchased from Alfa. Anhydrous N, N-dimethylformamide (DMF, 99.8%) was bought from Acros. Titanium (IV) isopropoxide (99.999%), lithium salt (Li-TFSI) and acetonitrile were acquired from Sigma-Aldrich. 4-tert-butylpyridine (tBP) was from TCI. P3HT was purchased from Rieke Metals, lnc. Spiro-OMeTAD was purchased from Xi'an polymer light technology Co., Ltd, China. Pristine C_{60} was purchased from Suzhou Dade Carbon Nanotechnology Co., Ltd, China. The synthesis of PDTSTTz and PDTSTTz-4 refer to our previous publication [36,37].

2.2. Preparation of perovskite precursor

MAI was synthesized according to literature [52]. The perovskite precursor was prepared by mixing MAI with $PbCl_2$ [molar ratio of 3:1] in anhydrous DMF, and the mixture was kept stirring overnight at 60 °C. The final concentration was controlled to 40 wt%. The precursor solution was stored in glovebox filled nitrogen, and filtrated with 0.45 μm PTFE filters every time right before use.

2.3. Fabrication of the perovskite solar cell

ITO glass slides were cleaned by sequentially sonicating in detergent, deionized water, acetone, ethanol and isopropanol each for 15 min. After blown dry in nitrogen flow, the slides were treated with ultraviolet-ozone (UVO) for 15 min TiO_2 precursor was prepared by dissolving 350 μL titanium (IV) isopropoxide in 2.5 mL anhydrous ethanol with 35 μL of HCl (2 mol L^{-1}). The solution was spin-coated on ITO glass slides at 2000 rpm for 40 s. The slides were sintered at 500 °C for 30 min to obtain a compact TiO_2 layer. Pristine C_{60} was deposited on compact TiO_2 by vacuum evaporation. The thickness was controlled to approximately 10 nm. The perovskite precursor was spin-coated at 3000 rpm for 50 s in glovebox filled with nitrogen. The samples were annealed at 105 °C for 80 min. HTLs used in this work were P3HT, PDTSTTz and PDTSTTz-4. All the concentrations of polymer HTL materials were 15 mg mL^{-1}. To 1 mL of *ortho*-dichlorobenzene solution of the polymers, added 10.2 μL of tBP and 20.4 μL of Li-TFSI/acetonitrile (28.3 mg mL^{-1}). Polymer HTLs were prepared by spin-coating at 1500 rpm for 50 s. A Spiro-OMeTAD solution was prepared by dissolving 72.3 mg of Spiro-OMeTAD in 1 mL of chlorobenzene. To the solution, 28.8 μL of tBP and 17.5 μL of Li-TFSI/acetonitrile (520 mg mL^{-1}) was added. Spiro-OMeTAD films were deposited by spin-coating at 3500 rpm. At last, MoO_3 and Ag were sequentially deposited by vacuum evaporation. The active area (4 mm^2) was defined with a shadow mask during the thermal evaporation.

2.4. Characterization

The absorption spectra of perovskite covering different HTMs were measured on a Cary 5000 (Agilent) instrument. Atomic force microscopy (AFM) images were captured on Multimode 8 microscope (Bruker, Santa Barbara, CA) with peak force quantitative nanomechanical mode. ScanAsyst-Air probe (nominal spring constants 0.4 N m^{-1}, frequency 70 kHz, purchased from Bruker) was employed during the measurement. Scanning electron microscopy (SEM) images were taken on S-4700, Hitachi. The current density-voltage (*J-V*) curves were recorded on Keithley 2400 under illumination of a simulated Air Mass 1.5 global (AM 1.5G) solar with an intensity of 100 mW/cm^2. The measurement was carried out in the glovebox (both O_2 and H_2O < 0.1 ppm). The corresponding incident-photo-to-current conversion efficiency (IPCE) was measured by a solar cell spectral response measurement system (Enli Technology Co., Ltd., QE-R3011) in air. Both the illumination intensities of the light sources used in *J-V* curve and IPCE measurements were calibrated by standard single-crystal silicon solar cells. The alternating current impedance spectrometry curves were measured on IM6 electrochemical workstation (Zahner Zennium, Germany) in dark with a bias near the corresponding open circuit voltage (V_{oc}) condition. The oscillating voltage was 10 mV and the frequency ranged from 4 MHz to 0.5 Hz. The impedance spectra were analyzed by Z-View software. Steady-state photo-luminescence (PL) measurements were conducted on FLS980 (Edinburgh Instrument, UK). Time-resolved PL spectra were acquired on Life-spec (Edinburgh Instrument, UK) by monitoring the signal at 790 nm excited with a 477 nm laser (2 MHz).

3. Results and discussions

The contribution of the HTL materials to the light harvesting was qualitatively assessed by UV-vis absorption spectra. In doing so, $CH_3NH_3PbI_{3-x}Cl_x$ perovskite films on TiO_2 were prepared by varying the covering materials as P3HT, PDTSTTz and PDTSTTz-4. The sample without covering was applied as control. Note, to make a parallel comparison, the perovskite precursor was from the same batch of synthesis, and the thicknesses of perovskite film and covering layer were maintained to the same levels. As shown in Fig. 1, the absorption in region of 300–700 nm increases in the order of control, perovskite films with covering materials of P3HT, PDTSTTz and PDTSTTz-4. The enhanced light absorption may promise higher photocurrent when being used as HTL materials in the pero-SCs.

Herein, the *n-i-p* type device configuration was adopted for preparation of pero-SCs. As shown in Fig. 2a, from bottom to top, the device structure is indium tin oxide (ITO)/compact TiO_2 (~90 nm)/C_{60} (10 nm)/$CH_3NH_3PbI_{3-x}Cl_x$ (~350 nm)/HTL (~50 nm)/MoO_3 (6 nm)/Ag (~100 nm). PDTSTTz and PDTSTTz-4 were used as