



A new alcohol-soluble electron-transporting molecule for efficient inverted polymer solar cells



Jing Li ^{a,b}, Xiaodong Huang ^{a,b}, Jianyu Yuan ^{a,b}, Kunyuan Lu ^{a,b}, Wei Yue ^b, Wanli Ma ^{a,*}

^a Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, 199 Ren-Ai Road, Suzhou Industrial Park, Suzhou, Jiangsu 215123, PR China

^b Department of Biotechnology, Chemistry, and Environmental Engineering, Aalborg University, Sohngaardsholmsvej 57, DK-9000 Aalborg, Denmark

ARTICLE INFO

Article history:

Received 19 March 2013

Received in revised form 7 May 2013

Accepted 8 May 2013

Available online 28 May 2013

Keywords:

Inverted polymer solar cells

Electron transporting layer

Solution-processed

Small molecules

Self-assembled monolayer

ABSTRACT

A new electron-transporting material 4,7-diphenyl-1,10-phenanthroline-2,9-dicarboxylic acid (DPPA) was synthesized by modifying a *n*-type small molecule bathocuproine (BCP). The introduced carboxyl groups make DPPA soluble in polar solvent and compatible with large-scale solution-processing techniques. The anchoring of carboxyl on ZnO (or ITO) substrates helps to form a DPPA electron transporting layer, building an improved interfacial contact between the substrate and active layer. Furthermore, the highest occupied molecular orbital level of DPPA shifts to -6.45 eV, which is 0.38 eV deeper than that of BCP, suggesting enhanced hole-blocking. Inverted polymer solar cells using P3HT:PCBM blend as the active layer and DPPA modified ZnO as the electron transporting layer were fabricated. A power conversion efficiency (PCE) of 3.55% was obtained, which is about 10% higher than that of the conventional ZnO buffered devices (3.25%). The DPPA was also used to replace ZnO as the sole electron-extracting layer, resulting in an improved PCE of 3.46%, which indicates that DPPA-ETL/ITO forms a better cathode than conventional ZnO/ITO.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Polymer solar cells (PSCs) have gathered considerable attention as an inexpensive renewable energy technique due to their unique advantages, such as light weight, high flexibility and potential of roll to roll fabrication [1,2]. Up to date, the most popular PSCs configuration is bulk hetero-junction, with an active layer sandwiched between two electrodes [3]. The light-absorbing active layer is the essential part of the cells. Therefore most research focus on designing and synthesizing novel polymer donors [4–6] and fullerene acceptors [7], and optimizing the film morphology [8]. However, the interfaces between the active layer and electrodes are also critical. By judicious molecular engineering and continuous exploration of new interface materials, improved interface electronic properties have been achieved, and the photovoltaic

performance of the PSCs has been remarkably elevated to over 9% [9].

PSCs have two main types of device geometries, the conventional and inverted structures. In a conventional structure, indium tin oxide (ITO) is used as the anode and a low work function metal (Al is commonly used) acts as the cathode. A big drawback of this structure is that the low-work-function metal can be easily oxidized, leading to degradation of the device performance. In contrast, the inverted structure uses ITO as cathode and more air stable high-work-function metals as anode, leading to improved device stability and manufacturing compatibility [10]. In inverted PSCs, an ohmic contact between the ITO and active layer is required to achieve both efficient electron-extraction and high open-circuit voltage (V_{oc}). Introducing an interfacial layer [11,12] between ITO/organic is believed to be an effective method to satisfy the requirement. Inorganic *n*-type materials such as CsCO_3 , ZnO and TiO_2 have been demonstrated effective in PSCs as interface layer for electron-extracting and hole-blocking [13]. However, the

* Corresponding author. Tel.: +86 051265884280.

E-mail address: wлма@suda.edu.cn (W. Ma).

terminated hydroxyl and the oxygen absorbed on the surface of these materials can act as electron traps [14]. Therefore, organic molecules have been developed on one hand to isolate the oxygen from such *n*-type electron transporting layer (ETL) and passivate surface charge traps, on the other hand, they can also tune the energy level offset between the organic active layer and the *n*-type semiconducting ETL [11f,12c]. These functional molecules are usually tethered to the anode or cathode interfaces of PSCs and form a self-assembled monolayer (SAM) by anchoring groups such as phosphonic acid [12c,15], carboxylic acid [12b,16] and trichlorosilane groups [17].

There are two strategies to obtain the functional organic molecules. The most adopted strategy is to design and synthesize new molecules, which, in most situations, results in time-consuming process and undesired materials. The other strategy is to modify the existing small-molecule ETL materials with proven efficiency in OPV (organic photovoltaics) and OLED (organic light emitting diode), allowing them to be solution-processible. For example, bathocuproine (BCP) has been proved to be a good electron transporting and hole-blocking material with a deep HOMO (highest occupied molecular orbital) level. Nonetheless, the BCP deposition often requires high vacuum and high temperature, which is not desired in a low-cost, large-area fabrication process. Herein, we synthesized a new alcohol-soluble electron-transporting material 4,7-diphenyl-1,10-phenanthroline-2,9-dicarboxylic acid (DPPA) based on BCP, with carboxyl groups introduced to the molecule to improve its solubility in polar solvent and to act as anchoring groups. The synthesized DPPA can be dissolved in polar solvents such as methanol, dimethylformamide (DMF) and formic acid, and form ETL on the surface of ZnO or ITO. Furthermore, the HOMO level of DPPA was measured to be 0.38 eV lower than that of BCP due to the introduction of carboxyl groups, making DPPA a possible better hole-blocking material. Inverted PSCs using Poly(3-hexylthiophene) (P3HT):PCBM blends as the active layer and DPPA modified ZnO nano-particles (ZnO-NP) as the ETL were fabricated. The DPPA-ETL was also used to replace ZnO-NP as the sole electron-extracting layer in PSCs.

2. Experimental section

2.1. Materials and instrument

All chemicals were purchased from J&K Chemicals or Sigma-Aldrich and used as received. UV-vis spectra were recorded on a Perkin Elmer model Lambda 750 instrument. Thermo-gravimetric analysis (TGA) was carried out using a Perkin Elmer TGA4000 at a heating rate of 10 °C/min in nitrogen atmosphere. Cyclic voltammetry were carried out using a Zahner IM6 electrochemical workstation in anhydrous acetonitrile (DPPA) and DMF (BCP) with Bu₄NPF₆ (0.1 M) as the electrolyte at a scan rate of 50 mV/s. Ferrocene was used as the internal standard ($E_{1/2(\text{ferrocene})} = 0.65$ mV vs Ag/AgCl). Tapping-mode AFM images were obtained by using a Veeco Multimode V instrument. The formation of the DPPA-ETL onto ZnO and ITO was evaluated by using a simple solution spin-coating method.

Solvents are then used to rinse away any unbound molecules from the ZnO or ITO surface and dried prior to measurement. The contact angles were investigated by using a DataPhysics OCA.

2.2. Device fabrication and characterization

Inverted PSCs were fabricated with a structure of ITO/ZnO-NP/X/P3HT:PCBM/MoO₃/Al or ITO/X/P3HT:PCBM/MoO₃/Al (X = BCP or DPPA-ETL). Patterned ITO glass substrates were cleaned by sequential ultrasonic treatment in detergent, acetone, deionized water, and isopropyl alcohol for 10 min, then dried by nitrogen stream. The organic residue was further removed by treating with UV-ozone for 10 min. A thin layer of ZnO-NP was spin-coated on ITO at 4000 rpm for 40 s, then baked in air at 150 °C for 5 min, as reported by Yang [18]. BCP and DPPA ETLs were prepared either by dip-coating for 2 h in 0.5 mg/ml methanol or formic acid solutions, or spin-coating at 2000 rpm for 40 s from 1 mg/ml methanol or formic acid solutions. The active layers were prepared by spin-coating a P3HT:PCBM (1:2 w/w) 1,2-dichlorobenzene solution (containing 2% (v/v) DIO) at a speed of 700 rpm for 60 s and thermal annealing at 110 °C for 10 min. 8 nm MoO₃ and 100 nm Al were thermally evaporated at a speed of 0.04 nm/s and 3 nm/s respectively at a vacuum of 1.0×10^{-6} mbar, the active area of the unit cell is 7.25 mm². The current density–voltage characteristics (*J*–*V*) of the photovoltaic cells were measured using a Keithley 2400 digital source meter under a simulated AM 1.5G solar irradiation at 100 mW cm⁻² (Newport, Class AAA solar simulator, 94023A-U). The light intensity is calibrated by a certified Oriel Reference Cell (91150 V).

3. Result and discussion

3.1. Synthesis and characterization

The structure and synthetic route of DPPA are shown in Scheme 1. DPPA was synthesized based on commercially available BCP in two steps by following the procedure reported by Evangelista et al. [19]. Firstly, BCP was reacted with N-chlorosuccinimide (NCS) using benzoyl peroxide (BDH) as initiator to obtain the chlorinated compound Cl-BCP with a yield of 95%. Then Cl-BCP reacted with concentrated sulfuric acid and sequentially hydrolyzed in water, giving DPPA in a high yield of 90%. The thermal stability of DPPA was characterized by thermo-gravimetric analysis (TGA). As shown in Fig. S1, a decomposition stage with a weight loss of 12% was observed at the temperature ~200 °C, which can be ascribed to the decomposition of the two carboxyl groups since this amount of weight loss is consistent with the theoretical result calculated from the molecule structure of DPPA. The onset decomposition temperature (*T*_D) is 187 °C, clarifying that DPPA is a thermally robust material. In general, alcohol-soluble DPPA was obtained in a high yield by applying a simple modification to BCP, apparently more time and labor-saving than the synthesis of new molecules.

Download English Version:

<https://daneshyari.com/en/article/10566461>

Download Persian Version:

<https://daneshyari.com/article/10566461>

[Daneshyari.com](https://daneshyari.com)