



Research paper

Unsymmetrical donor–acceptor–donor–acceptor type indoline based organic semiconductors with benzothiadiazole cores for solution-processed bulk heterojunction solar cells

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Abstract

Bulk heterojunction (BHJ) solar cells based on small molecules have attracted potential attention due to their promise of conveniently defined structures, high absorption coefficients, solution process-ability and easy fabrication. Three D–A–D–A type organic semiconductors (**WS-31**, **WS-32** and **WS-52**) are synthesized, based on the indoline donor and benzotriazole auxiliary acceptor core, along with either bare thiophene or rigid cyclopentadithiophene as π bridge, rhodanine or carbonocyanidate as end-group. Their HOMO orbitals are delocalized throughout the whole molecules. Whereas the LUMOs are mainly localized on the acceptor part of structure, which reach up to benzothiadiazole, but no distribution on indoline donor. The first excitations for **WS-31** and **WS-32** are mainly originated by electron transition from HOMO to LUMO level, while for **WS-52**, partly related to transition between HOMO and LUMO+1 level. The small organic molecules are applied as donor components in bulk heterojunction (BHJ) organic solar cells, using PC₆₁BM as acceptor material to check their photovoltaic performances. The BHJ solar cells based on blended layer of **WS-31**:PC₆₁BM and **WS-32**:PC₆₁BM processed with chloroform show overall photoelectric conversion efficiency (PCE) of 0.56% and 1.02%, respectively. **WS-32** based BHJ solar cells show a higher current density originated by its relatively larger driving force of photo-induced carrier in photo-active layer to LUMO of PC₆₁BM.

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Keywords: Indoline donor; Unsymmetrical organic semiconductors; BHJ solar cells; Photovoltaic performances

1. Introduction

Bulk heterojunction (BHJ) solar cells, especially those based on small molecules, have attracted world-wide attention due to their promise of conveniently defined structures, high absorption coefficients, solution process-ability and easy

fabrication [1–5]. For an efficient BHJ solar cell, the electron donor and acceptor parts always interpenetrate and entangle each other to deduce diffusion length, which can be realized through solution processing procedure during device fabrication [6]. Generally, P-type fullerene derivatives, such as PC₆₁BM or PC₇₁BM are ideal acceptors in BHJ organic solar cell due to their good solubility and lower LUMO energy level [7–10]. Comparably, small molecular semiconductor, acted as electron donor in BHJ solar cells, is a main factor influencing photovoltaic performance. An ideal small molecule should possess a broad absorption profile, large absorption coefficient, low band gap, suitable highest occupied molecular

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orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels as well as good solubility in organic solvent [6]. Molecules containing D–A or D– π –A segment have been proved desirable architecture. Up to now, the PCE of BHJ based on small molecular heterojunction organic solar cells has reached more than 9%, but there remains much upside potential with respect to polymer counterparts through molecular modification [11–14].

Triphenylamine has been widely used in organic semiconductors due to its good hole-transporting and electronic donating capacity [15–18]. With respect to triphenylamine, indoline shows better electron donating ability and widely used in dye sensitized solar cells with gratifying results [19–22]. Accordingly, a series of indoline bridged benzothiadiazole-based D–A–D–A small molecules were reported based on the following consideration: (i) Electron-rich indoline moiety was incorporated as donor unit, taking advantage of its three dimensional propeller structure to depress molecular aggregation as well as its excellent electron-donating ability; (ii) Benzothiadiazole, which has a strong co-planar, high oxidation potential, high electron affinity and super stability, is introduced to modify HOMO–LUMO gap [23,24]; and (iii) the solubility and film-formation ability can be optimized through introducing long alkyl chains to cyclopentadithiophene. Herein, unsymmetrical small organic molecules **WS-31**, **WS-32**, and **WS-52** (Fig. 1) using indoline as electron donor, benzotriazole as auxiliary acceptor, bare thiophene or cyclopentadithiophene as π bridge, rhodanine or carbonocyanide as electron acceptor were designed. BHJ solar cells were fabricated using the small molecules as donor materials, along with PC₆₁BM as acceptor, with overall PCE of 0.56, 1.02 and 0.62% for **WS-31**, **WS-32**, and **WS-52**, respectively.

2. Experimental

2.1. Characterization

¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III HD 400 spectrometer using tetramethylsilane

(TMS) as the internal standard. HRMS were recorded on a Waters LCT Premier XE instrument. The UV–Vis spectra were measured with a Varian Cary 100 spectrophotometer, while the fluorescence spectra were obtained with a Varian Cary Eclipse spectrometer. The cyclic voltammograms were obtained with a Versastat II electrochemical workstation (Princeton Applied Research). Three-electrode cell was applied using a Pt working electrode, a Pt wire auxiliary electrode, and a saturated calomel electrode (SCE) reference electrode, 0.1 mol L⁻¹ tetrabutylammoniumhexafluorophosphate (TBAPF₆) in CH₂Cl₂ was used as the supporting electrolyte. The scan rate was 100 mV s⁻¹. Photovoltaic measurements employed an AM 1.5 solar simulator equipped with a 300 W xenon lamp (model NO. 91160, Oriel). *J*–*V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with Keithley2400 source meter. The voltage step and delay time of the photocurrent were 10 mV and 40 m, respectively.

2.2. Synthesis

All reagents and materials were commercial obtained unless otherwise specially stated. THF applied in Suzuki reaction was thoroughly dried with sodium and benzophenone. Dimethylformamide, dichloromethane and chloroform was pretreated with calcium hydride.

2.2.1. Synthesis of intermediate **M1**

2-Thenaldehyde was protected according to the following procedure. 2-Thenaldehyde (2.00 g, 17.8 mmol), anhydrous *p*-toluene sulfonic acid (614 mg, 3.57 mmol), toluene (60 mL) and ethylene glycol (8 mL) were added to a round-bottom flask to reflux for 10 h. The obtained mixture was poured into 40 mL of dichloromethane, followed by thoroughly washed with brine. The organic phase was separated, dried over anhydrous potassium carbonate and evaporated in *vacuo* to afford green solid 1.8 g. The aforementioned product and dry tetrahydrofuran (60 mL) was added to 250 mL of schlenk tube to cool to -78 °C under N₂ atmosphere, B(OCH₃)₃ (1.6 mL, 14.1 mmol) was added dropwise. After 2 h, the

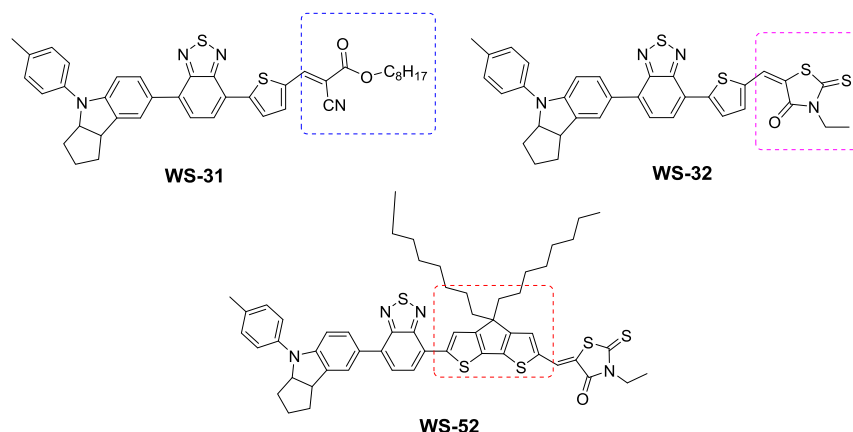


Fig. 1. Molecular structures of **WS-31**, **WS-32** and **WS-52**.

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