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Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

An arylene-vinylene based donor-acceptor-donor small molecule for the donor compound in high-voltage organic solar cells



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ARTICLE INFO

Article history:

Received 30 November 2014

Received in revised form

3 June 2016

Accepted 12 June 2016

Available online 24 June 2016

Keywords:

Organic solar cell

Small-molecule donor

Fullerene acceptor

Solution processing

High open-circuit voltage

Thermal stability

ABSTRACT

A donor-acceptor-donor (D-A-D) molecule has been designed and synthesized for use as the electron-donating material in solution-processed small-molecule organic solar cells (OSCs). The D-A-D molecule comprises a central electron-accepting (2Z,2'Z)-2,2'-(2,5-bis(octyloxy)-1,4-phenylene)bis(3-(thiophen-2-yl)acrylonitrile) (ZOPTAN) core, which is chemically connected to two peripheral and electron-donating triphenylamine (TPA) units. The ZOPTAN-TPA molecule features a low HOMO level of -5.2 eV and an optical energy gap of 2.1 eV. Champion OSCs based on a solution-processed and non-annealed active-material blend of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and ZOPTAN-TPA in a mass ratio of 2:1 exhibits a power conversion efficiency of 1.9% and a high open-circuit voltage of 1.0 V.

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1. Introduction

The organic solar cell (OSC) is emerging as a complementary alternative to the entrenched silicon-based solar cell, because it can deliver important and unique benefits such as flexibility, light-weight, transparency, and low-cost and high-throughput solution-based processing [1–3]. OSCs are commonly based on a donor/acceptor bulk heterojunction (BHJ) active material, with a conjugated polymer being the electron donor and a small-molecule fullerene being the electron acceptor. However, the employment of a small-molecule semiconductor also for the donor compound is an interesting alternative, particularly if it can be processed from solution. One notable advantage with small molecules over polymers is a well-defined molecular structure that facilitates purification and batch-to-batch repeatability, which are factors of relevance in the quest for a functional up-scalable OSC system [4,5]. Accordingly, significant efforts are currently aimed at the development of functional and solution-processable small-molecule donor compounds [6–12].

However, in order to turn OSCs into commercially interesting entities, their performance needs to be further enhanced. One

viable path towards this end includes the development of new small-molecule donor compounds, which feature one or several of the following characteristics: (i) a broadened absorption range to better match the solar spectrum as attained through a decreased energy gap (E_g); (ii) an improved donor/acceptor active-material morphology for the facilitation of the electron-transfer process as manifested in an improved short-circuit current density (J_{sc}); and (iii) a lowered highest occupied molecular orbital (HOMO) level in order to increase the open-circuit voltage (V_{oc}) [13]. A route to the fulfillment of these criteria includes the development of a donor compound, which is assembled from *internal* donor and acceptor groups. The functionality of this approach has been demonstrated through the realization of a decreased E_g [14], and through the attainment of a high J_{sc} [10–12,15]. The number of reports on the attainment of a high V_{oc} , ideally exceeding 1 V, are however more sparse [7,8]. This shortcoming can be rationalized by that the tuning of the HOMO level in a donor-acceptor (D-A) compound is a delicate matter, with the appropriate selection of, and interaction between, the donor and acceptor units playing a critical role [16–24].

Here, we report on the synthesis of a D-A-D type small-molecule compound termed ZOPTAN-TPA, with its central (2Z,2'Z)-2,2'-(2,5-bis(octyloxy)-1,4-phenylene)bis(3-(thiophen-2-yl)acrylonitrile) unit, denoted ZOPTAN, acting as the internal A unit. It is chemically connected through its thiophenylene end groups to two peripheral triphenylamine (TPA) groups, which act as the

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internal donor units. This compound was selected on the basis of that the incorporation of electron-withdrawing CN units was anticipated to lower the HOMO level, while the TPA capping groups were expected to provide for efficient hole transport. As desired, we find that the ZOPTAN-TPA molecule exhibits a low HOMO level of -5.2 eV, and that champion OSC devices comprising a solution-processed and non-annealed blend film of ZOPTAN-TPA and [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) as the active material display a high V_{oc} of 1.0 V.

2. Experimental section

2.1. Synthesis

The synthesis of the precursors, (2Z,2'Z)-2,2'-(2,5-bis(octyloxy)-1,4-phenylene)bis(3-(5-bromothiophen-2-yl)acrylonitrile) (ZOPTAN-Br) and 4-(diphenylamino)phenylboronic acid (TPA-B(OH)₂), were inspired by findings in the literature [25,26] and are described in detail in the [Supplementary material](#). ZOPTAN-TPA was synthesized as follows: ZOPTAN-Br (0.1 g, 0.13 mmol) and TPA-B(OH)₂ (0.114 g, 3.96 mmol) were dissolved in 20 ml toluene. After the addition of 5 ml of 2 M K₂CO₃, the mixture was flushed with Ar for 15 min. Subsequently, 20 mg of tetrakis-(triphenylphosphine) palladium (Pd(PPh₃)) was added, and the reaction mixture was flushed with Ar for 15 min. The solution was heated to reflux for 30 h. The reaction mixture was thereafter cooled to room temperature and extracted with CH₂Cl₂. The organic layer was dried with anhydrous MgSO₄. After filtration, the solvent was removed by vacuum evaporation. The concentrated mixture was eluted on silica gel using *n*-heptane: ethyl acetate (10:1) and recrystallized from tetrahydrofuran/methanol. The desired product was obtained as red crystals; yield: 0.080 g, 56%.

¹H NMR and ¹³C NMR spectra were recorded with Bruker AVANCE III 400 and 600 MHz spectrometers. High resolution mass spectrometry (HRMS) was conducted using a microTOF II mass spectrometer with electrospray ionization from Bruker. Elemental analysis was carried out on an EA 1108 CHNS-O elemental analyzer at Mikroanalytisches Laboratorium, Univ. of Vienna. ¹H NMR (CDCl₃, 400 MHz): δ 8.04 (s, 1 H), 7.57 (s, 1 H), 7.53 (d, 8.4 Hz, 2 H), 7.30–7.26 (m, 5 H), 7.13 (m, 5 H), 7.07 (m, 4 H), 4.10 (t, 6.3 Hz, 2 H), 1.89 (p, 6–7 Hz, 2 H), 1.50 (m, 2 H), 1.4–1.2 (m, 8 H), 0.86 (t, 6.8 Hz, 3 H); see also [Fig. S-1](#) in the [Supplementary material](#). ¹³C NMR (CDCl₃, 100 MHz): δ 150.7, 149.4, 148.4, 147.3, 138.8, 136.6, 134.0, 129.4, 127.1, 127.0, 125.0, 124.4, 123.6, 123.0, 122.7, 118.7, 114.3, 103.4, 69.9, 31.9, 29.5, 29.4, 29.3, 26.4, 22.7, and 14.1; see also [Fig. S-2](#) in the [Supplementary material](#). HRMS: *m/z* Calcd for C₇₂H₇₀N₄O₂S₂ [M]⁺: 1086.49. Found: 1086.48. Anal. Calcd for C₇₂H₇₀N₄O₂S₂: C, 79.52; H, 6.49; N, 5.15; S, 5.90. Found: C, 79.32; H, 6.71; N, 5.17; S, 5.71. The synthesized ZOPTAN-TPA compound was found to be soluble in a high concentration of > 20 g l⁻¹ in common organic solvents, such as chloroform and

dichlorobenzene. The chemical structures of ZOPTAN-Br, TPA-B(OH)₂, and ZOPTAN-TPA are presented in [Scheme 1](#).

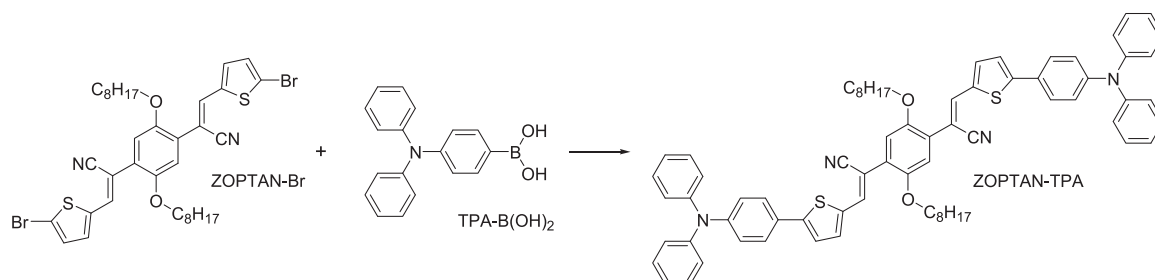
2.2. Quantum-chemical calculations and material characterization

Density functional theory (DFT) was utilized to calculate the optimized ground-state geometry, and the HOMO and lowest unoccupied molecular orbital (LUMO) energies and electron density distributions, for the ZOPTAN-TPA molecule. The DFT calculations were executed using the restricted B3LYP exchange-correlation functional [27], with the 6-31G basis set and 'd' polarization functions on non-hydrogen atoms [28]. The electronic singlet excitations for the lowest-energy conformation of ZOPTAN-TPA were calculated using the Coulomb attenuated method B3LYP functional (CAM-B3LYP) and the 6-31+G(d) basis set [29]. The Gaussian 09 software was used for the calculations [30]. To reduce the complexity of the structures in the calculations, the OC₈H₁₇ side chains were replaced by OCH₃ groups. No imaginary frequencies were found by vibrational frequency calculations for the geometry-optimized structures, reinforcing that these indeed represent energy minima.

UV-vis absorption spectra (Lambda 35 UV-vis spectrometer, PerkinElmer) were recorded on a 3×10^{-5} M solution of ZOPTAN-TPA in chloroform, using a quartz cuvette with 10 mm path length (PerkinElmer), and on thin films spin-coated onto 1 mm thick quartz substrates (Ted Pella). Differential scanning calorimetry (DSC, Q1000, TA Instruments) and thermo-gravimetric analysis (TGA, Q5000IR, TA Instruments) were conducted under N₂ atmosphere with a heating and cooling rate of 10 K min⁻¹. The cyclic voltammetry (CV) data were recorded with a potentiostat (Autolab PGSTAT302, Metrohm) using the general purpose electrochemical software (GPES). A ZOPTAN-TPA thin film was deposited onto an Au-coated glass substrate which functioned as the working electrode, a Pt rod was the counter electrode, and an Ag wire was the quasi-reference electrode. The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate (TBAPF₆, Fluka) in anhydrous CH₃CN. The measurements were carried out at room temperature under inert N₂ atmosphere using a scan rate of 50 mV s⁻¹. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the internal reference. The redox levels were established as the onset of oxidation and reduction in the anodic and cathodic scans, respectively. More details on the CV measurement can be found in Ref. [31].

2.3. Solar cell fabrication and characterization

ITO-coated substrates (Thin Film Devices Inc.) were cleaned by subsequent 10 min ultra-sonication in detergent (Extran MA01: deionized water, 1:10 volume ratio), deionized water, acetone and isopropyl alcohol. The cleaned substrates were blown dry with compressed air and stored in an oven at 120 °C. Immediately prior to device fabrication, the ITO-coated substrates were exposed to



Scheme 1. ZOPTAN-TPA was synthesized through Suzuki coupling of (2Z,2'Z)-2,2'-(2,5-bis(octyloxy)-1,4-phenylene)bis(3-(5-bromothiophene-2-yl)acrylonitrile) and 4-(diphenylamino)phenylboronic acid.

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