



# Solution-processed star-shaped oligomers in normal and inverted organic solar cells



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## ABSTRACT

The performance of three different star-shaped oligomers (SSOs) as electron donor materials for organic solar cells is investigated. These promising donor components are blended with [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) fullerene acceptor and solution-processed normal and inverted organic solar cells are fabricated. These SSOs are based on a triphenylamine core and differ in the solubilizing groups and the oligothiophene arm length. We have found that the power conversion efficiency (PCE) is by 10–60% higher in the normal structure, mainly due to an enhanced open-circuit voltage and fill factor. The observed difference in device performance can be assigned partly to the lower leakage currents. By using contact angle measurements and atomic-force microscopy studies, we estimate the degree of vertical phase separation in bulk heterojunctions. The latter has a good correlation to the corresponding photocurrent differences obtained in the normal and inverted structure devices.

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## 1. Introduction

Small molecule donor materials are perspective competitors of conjugated polymers in organic solar cells due to their well-defined molecular structure and molecular weight, better reproducibility and easier purification [1]. Moreover, the record power conversion efficiency (PCE) of organic solar cells was achieved with the use of small molecular donors [2]. Among them, the star-shaped oligomers (SSO) with a triphenylamine core and dicyanovinyl acceptor groups are promising donor materials for solution-processed organic photovoltaics [3]. For a recent few years, a number of SSO with various solubilizing groups and different lengths of the oligothiophene arms have been synthesized and studied in organic solar cells [4–6]. Some SSO can form various columnar mesophases [7], which can be used to control the bulk heterojunctions morphology. A PCE higher than 5% was reported for SSO in the normal structure of organic solar cells, where high and low work-function electrodes are at the bottom and the top of the active layer, respectively [8]. On the other hand, the inverted

structure, in which the high work-function electrode is on the top and the low work-function electrode is at the bottom of the active layer, usually provides higher air stability, which is crucial for practical applications [9–12]. However, the photovoltaic performance can differ from normal to inverted structure due to several reasons. For example, the vertical separation of the donor and acceptor phases may occur in the active layer upon film formation [13]. If the donor phase is concentrated at the bottom (top) of the active layer, the normal (inverted) structure is more (less) preferential for efficient collection of the photogenerated charges. Moreover, the different electrode and interface materials used in the normal and inverted structures can affect the cell performance. Therefore, both structures deserve comparing when studying novel materials for bulk heterojunction solar cells.

Among the SSO-based organic solar cells, the SSO N(Ph-2T-DCV-Et)<sub>3</sub> (Fig. 1, referenced below as SSO1) was compared in a previous work in normal and inverted structures. The photovoltaic performance was virtually the same for both architectures with a PCE of around 3–4% [14]. Interestingly, the different chemical moieties within the SSO1 molecule allowed using green solvents for its processing, leading to comparable photovoltaic performances as with halogenated solvents [15]. It was also found that small solubilizing groups at the SSO branch endings are beneficial

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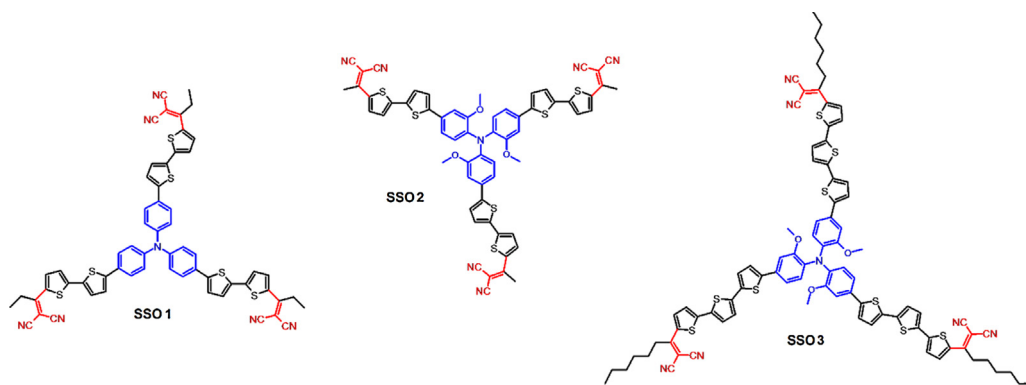


Fig. 1. Structural formulas of studied star-shaped oligothiophenes SSO1–3.

for the photovoltaic performance but result in limited solubility, whereas the bulky solubilizing groups increase solubility but limit the PCE [7]. To achieve a proper balance between an acceptable solubility and high photovoltaic performance, it was suggested to attach solubilizing groups to the SSO interior, specifically methoxy groups at the triphenylamine core [16]. A SSO with methoxy groups,  $N(\text{Ph}(\text{OMe})\text{-}2\text{T-DCV-Me})_3$  (Fig. 1, further designated as SSO2), was synthesized and tested in the normal structure of bulk heterojunction solar cells [16], but its PCE did not outperform that of SSO1. One of the possible reasons for the lower SSO2 performance could be an unsuitable vertical separation of the SSO and PCBM phases in the active layer. To investigate this, normal and inverted architectures should be compared. Moreover, methoxy-substitution at the triphenylamine core resulted in acceptable solubility for the SSO with longer oligothiophene arms and lead to a columnar mesophase [7] in films of  $N(\text{Ph}(\text{OMe})\text{-}3\text{T-DCV-Hex})_3$  (Fig. 1, referenced below as SSO3) [17]. All in all, the recent advances in the SSO-based solution-processed photovoltaics together with the mentioned morphological uncertainties motivate us to compare the normal and inverted structures of SSO-PCBM organic solar cells.

In this work, we compare the photovoltaic performance of organic solar cells based on the three SSO depicted in Fig. 1 in normal and inverted structures. We have found that the PCE is higher in the normal structure and analyzed possible reasons of the lower performance of the inverted solar cells.

## 2. Experimental

Fig. 1 shows the chemical structures of the studied SSO, which were synthesized using the recently developed approach presented in Refs. [5,7]. The solubilities of SSO1, SSO2 and SSO3 in *o*-

dichlorobenzene are 8 g/l, 14 g/l and 15 g/l, respectively [7,16,17]. PC<sub>71</sub>BM of 99% purity was purchased from Solenne.

Fig. 2 presents the schematic structures of normal and inverted organic solar cells. The set of organic solar cell devices were fabricated in the following way. First, glass substrates coated with a patterned indium-tin oxide (ITO) layer were cleaned in an ultrasonic bath and treated in an ultraviolet photoreactor. Then, for normal structure devices, a 50-nm-thick layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was deposited on the ITO and annealed at 140 °C for 15 min. For inverted structure devices, a 40-nm thick ZnO layer was deposited on the ITO using a sol-gel method [18]. Solutions of the SSO:PC<sub>71</sub>BM blend (mass ratio 1:2) in *o*-dichlorobenzene with a total concentration of 27 g/l were prepared and stirred overnight at 75 °C prior to deposition. The active layer was deposited in air conditions by doctor-blading, yielding a thickness of 50–60 nm in all the cases. On top of the active layer, a top electrode consisting of Ca/Al (MoO<sub>3</sub>/Ag) for the normal (inverted) structure was evaporated in a vacuum chamber. The active area (*S*) of each device, defined through a shadow mask, was 9 mm<sup>2</sup>. Current-voltage characteristics of the devices were measured using a source-meter (Keithley SourceMeter 2400) in dark and under AM1.5G irradiation with an intensity of 100 mW/cm<sup>2</sup>. Contact angle measurements (DataPhysics OCA 15EC) were performed on the films without top electrodes using a 1–2 mm-diameter drop of deionized water on top of the film.

## 3. Results and discussion

Fig. 3 shows current-voltage (*J*-*V*) characteristics under simulated solar light and in dark conditions for the best normal and inverted solar cells of each SSO. Fig. 4 compares maximum and

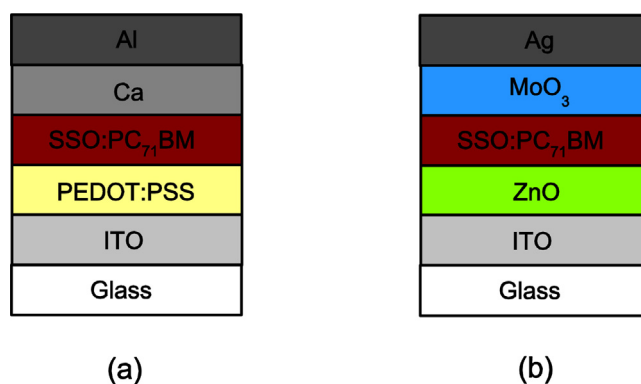


Fig. 2. Normal (a) and inverted (b) device structures of SSO-based organic solar cells.

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