

# A Planar Small Molecule with Dithienosilole Core for High Efficiency Solution-Processed Organic Photovoltaic Cells

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Supporting Information

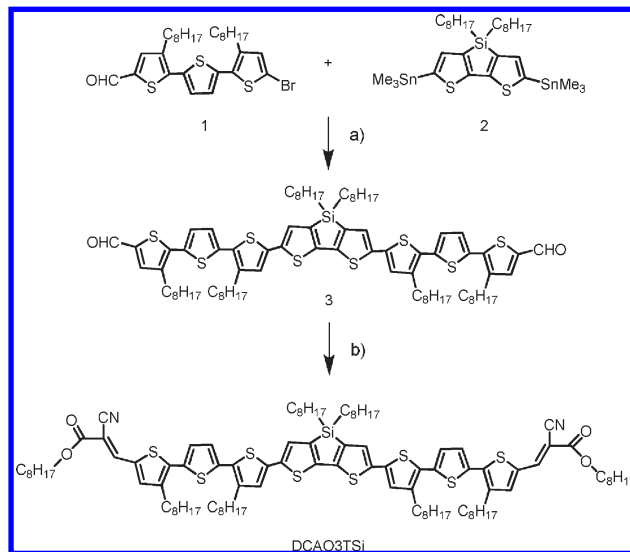
**KEYWORDS:** small molecule, organic photovoltaic, solution process, bulk heterojunction

Solution-processed organic photovoltaic (OPV) cells have drawn tremendous interest in the past decade<sup>1</sup> for the prospect of a renewable energy source, as a result of their eminent advantages such as low cost, light weight, and high mechanical flexibility. The performance of OPV has recently increased dramatically in the past few years, and power conversion efficiency (PCE) over 7% has been achieved by using low band gap polymers in the bulk heterojunction (BHJ) structure solar cells.<sup>2</sup> Meanwhile, small molecule based OPV has also stimulated great attention, owing to its well-defined structures, easier purification, and less batch to batch variation, as compared to the polymer based OPVs.<sup>2d–f</sup> Prominent results were reported on some typical small molecule materials including oligothiophenes,<sup>3</sup> fused acenes,<sup>4</sup> push–pull oligomers,<sup>5</sup> and other organic dyes.<sup>6</sup> Although PCE over 5%<sup>5g,7</sup> has been achieved, it is still significantly lower compared with that of polymers. It is thought that the undesirable performance of small molecule based OPV devices using solution process is due to the fact that both the band/energy structure and the morphology requirement of these small molecules need to be considered equally and balanced, because one of the major problems for small molecules is their generally poor film quality using the simple solution spinning process.<sup>1d,e,8</sup>

We have reported a linear oligothiophene derivative with alkyl cyanoacetate as the electron-withdrawing terminal. An encouraging PCE of 5.08% was achieved.<sup>5g</sup> Such an acceptor–donor–acceptor (A–D–A) molecule structure with a conjugated donor backbone and electron-withdrawing terminal has several advantages for BHJ devices: (1) high mobility with the planar structure and efficient  $\pi$ – $\pi$  interaction; (2) low band gap resulting from the intramolecular charge transfer; and (3) good film quality owing to a long enough conjugated backbone with dispersed alkyl chains similar to polymers.<sup>5,5f,g,8</sup> It is thus expected that great improvement could be made to the performance for small molecule OPVs through delicate chemical structure design and modification.

Considering the enlarged coplanar skeleton, strong electron donating capabilities<sup>9</sup> of the dithienosilole unit, and the excellent performances of OPVs based on the conjugated donor polymers incorporating dithienosilole unit,<sup>2c,d,10</sup> we herein report the design and synthesis of a small molecule based on the above strategy with a dithienosilole (DCAO3TSi) unit as the central

**Scheme 1.** Synthesis of DCAO3TSi (a)  $\text{Pd}(\text{PPh}_3)_4$ , Toluene and (b)  $\text{NET}_3$ ,  $\text{CHCl}_3$ , Octyl Cyanoacetate



building block. Outstanding photovoltaic property was observed when using it as the electron donor material in the BHJ cells, with a PCE of 5.84%, which is so far the best for all solution-processed small molecule OPV reported.

Different from the bottom-up synthesis scheme of our previous work about compound DCAO7T, the diformyl precursor of DCAO3TSi was simply obtained by the part-sum Stille coupling method. This strategy is much easier and could be applied for other efficient building blocks easily. The synthesis route of DCAO3TSi is depicted in Scheme 1 (see the Supporting Information for details). The targeted molecule was prepared by Knoevenagel condensation of compound 3 with octyl cyanoacetate in a yield as high as 90%. Thermogravimetric analysis (TGA) suggests that DCAO3TSi exhibits good stability with a

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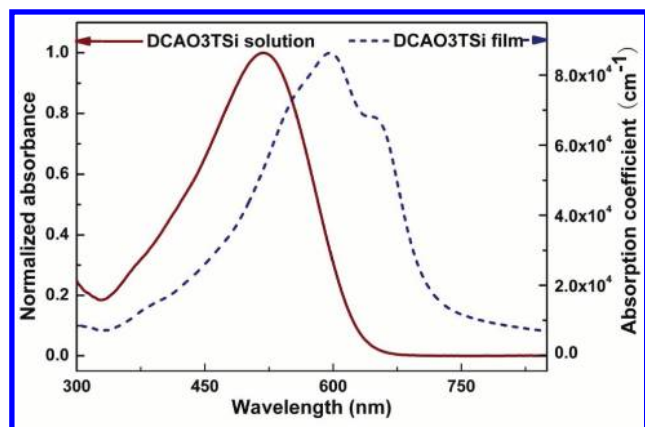


Figure 1. Absorption spectra of DCAO3TSi in  $\text{CHCl}_3$  and in film.

decomposition temperature ( $T_d$ ) greater than  $370^\circ\text{C}$  under a  $\text{N}_2$  atmosphere (see Figure S1 in the Supporting Information).

As shown in Figure 1, the DCAO3TSi optical spectrum in chloroform presents an absorption peak at 518 nm. The DCAO3TSi film spin-coated from  $\text{CHCl}_3$  ( $8\text{ mg}\cdot\text{ml}^{-1}$ ) exhibits an obvious red-shifted  $\lambda_{\text{max}} = 596\text{ nm}$ , with a very high maximum absorption coefficient of  $8.6 \times 10^4\text{ cm}^{-1}$  (with a film thickness of 80 nm), and a vibronic shoulder at 650 nm, indicating a strong  $\pi$ - $\pi$  packing between the molecule backbones.<sup>11</sup> The optical gap of DCAO3TSi is estimated to be 1.73 eV by extrapolation of the absorption onset at 715 nm in the film state. The HOMO and LUMO levels of DCAO3TSi were measured by electrochemical cyclic voltammetry (CV).<sup>12</sup> As displayed in Figure S2 the Supporting Information, the HOMO and LUMO levels were estimated to be at  $-4.95$  and  $-3.26$  eV, respectively, giving an electrochemical band gap of 1.69 eV.

X-ray diffraction (XRD) analysis was used to investigate the structural ordering of DCAO3TSi at the solid state. In Figure S3 in the Supporting Information, the (100), (200), and (300) diffraction peaks for DCAO3TSi are at  $4.3^\circ$ ,  $8.6^\circ$ , and  $13.0^\circ$ , respectively. The strong (100) peak indicates a highly ordered structure along with a  $d(100)$ -spacing of 21 Å as a result of the interchain distance separated by the octyl side chains.<sup>5b</sup> The obvious second-order diffraction peak (200) and the third-order diffraction peak (300) for DCAO3TSi also prove a well organized assembly of the  $\pi$ -conjugated molecule in thin film.<sup>5e,g,11b</sup> Moreover, the planar structure was supported by the calculation result using density functional theory (DFT) with the B3LYP/6-31G(d) model (Figure S4 in the Supporting Information).<sup>13</sup> As plotted in Figure S5 in the Supporting Information, the hole mobility through the hole-only device measured by using the space charge limited current (SCLC) method is  $1.8 \times 10^{-4}\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ , which is similar to that of the commonly used donor polymer P3HT ( $1.4 \times 10^{-4}\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ).<sup>14</sup> The high absorption coefficient, low band gap, well organized assembly, and relatively large hole mobility prospect DCAO3TSi a bright performance in BHJ blends as an electron donor material.

We explored the photovoltaic properties of DCAO3TSi based BHJ devices with the standard sandwich structure ITO/PEDOT:PSS/DCAO3TSi:PC61BM/LiF/Al using the simple solution process from a  $\text{CHCl}_3$  solution. Device optimizations were presented in the Supporting Information. Figure 2 presents a typical  $J$ - $V$  curve of the 130 nm thick DCAO3TSi:PC<sub>61</sub>BM (1:0.8 w/w) BHJ films processed from chloroform under AM 1.5G

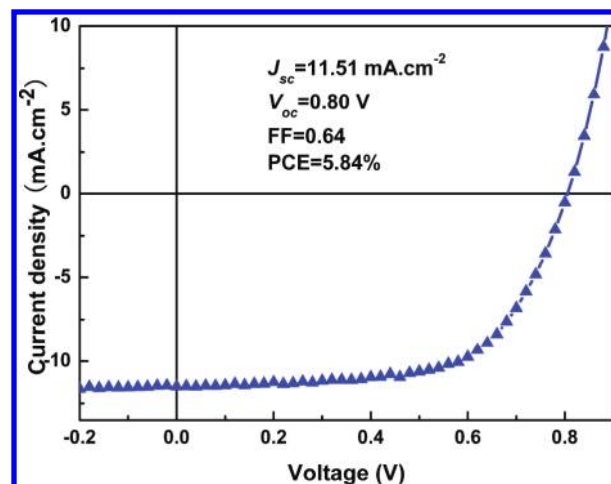


Figure 2.  $J$ - $V$  curve of the DCAO3TSi:PC<sub>61</sub>BM (1:0.8) BHJ films processed from chloroform under AM 1.5G illumination.

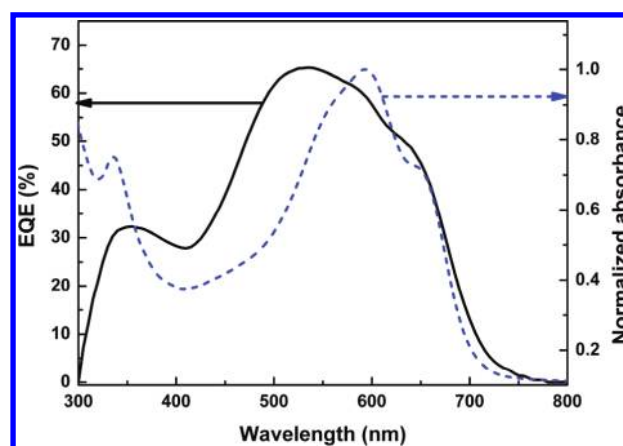


Figure 3. EQE and absorption spectrum of a 1:0.8 DCAO3TSi:PC<sub>61</sub>BM active layer OPV device.

illumination. The optimized device, with a ratio of 1:0.8 for DCAO3TSi:PC<sub>61</sub>BM, exhibits a PCE of 5.84%, with an open circuit voltage ( $V_{\text{oc}}$ ) of 0.80 V, a short-circuit current density ( $J_{\text{sc}}$ ) of  $11.51\text{ mA}\cdot\text{cm}^{-2}$ , and a high fill factor ( $FF$ ) of 0.64. Note that the fill factors varied from 0.60 to 0.68 in our device optimization. To the best of our knowledge, the PCE and the  $FF$  are, so far, the best for solution-processed OPV devices using small molecule as the donor, indicating the high efficiency for the charge carriers extracting in the device.<sup>15</sup> In general, fill factor was low for solution-processed small molecules based OPV.<sup>1e,5e</sup> One of the main reasons is their poor film quality using spin-coating.<sup>16</sup> Thus, it is hard to form an ideal nanoscale interpenetrating network for charge transport to the electrodes.<sup>2a,17</sup> Thereby, large leak current is produced, a decreased shunt resistance is exhibited in the  $J$ - $V$  curve, and the fill factors decrease accordingly.<sup>15a</sup>

Wondrously, the compound DCAO3TSi seems to overcome these drawbacks. This is supported by the atomic force microscopy (AFM) images (Figure S6 in the Supporting Information) where the blend film of DCAO3TSi:PC<sub>61</sub>BM (1:0.8, by weight) exhibits rather uniform and optimal features with the domain size of 10–20 nm. Compared with our compound DCAO7T,<sup>5g</sup> using the dithienosilole block as the central unit proved to promote the

$J_{sc}$  and  $FF$  resulting from the broad and high intensity absorption spectrum, good hole transport property, and fine film quality of DCAO3TSi.

The performance of these devices using DCAO3TSi was also supported by the results from the studies for the external quantum efficiency (EQE) as shown in Figure 3. The monochromatic spectrum presents a broad and strong response from 320 to 720 nm, with the maximum EQE value reaching 65% at 530 nm. The calculated  $J_{sc}$  integrated from EQE is  $10.36 \text{ mA} \cdot \text{cm}^{-2}$ , with around 10% mismatch compared to the  $J_{sc}$  from the  $J-V$  measurement.

In conclusion, a new low band gap small molecule with a dithienosilole core has been designed and easily synthesized. By the simple solution spin coating and rather preliminary optimization, the BHJ devices based on this small molecule demonstrated a PCE of 5.84% along with a noticeably high fill factor of 0.64, which is the best performance for solution-processed small molecule based OPVs reported so far. More importantly, this work indicates that small molecules could achieve comparable device performance with that of polymer devices through delicate design and modification. Further optimization in both the molecule and device structure on this system is underway at our group for better photovoltaic performance.

## ■ ASSOCIATED CONTENT

**S** Supporting Information. Experimental details of the synthesis of the molecule, the fabrication and characterization of the devices, measurements, and instruments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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