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A small molecule with selenophene as the central block for high performance solution-processed organic solar cells

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ABSTRACT

A solution-processable A–D–A structure small molecule donor material called DRCN7T-Se with selenophene as the central block was synthesized. Conventional bulk-heterojunction solar cell devices based on DRCN7T-Se and $PC_{71}BM$ were optimized by thermal annealing and an excellent power conversion efficiency of 8.30% was achieved under AM 1.5G irradiation (100 mW cm^{-2}).

1. Introduction

Organic photovoltaics (OPVs) have been considered a promising alternative solution for energy and environmental problems because of their attractive advantages such as low-cost, light weight, solution-processing and potential use in flexible devices [1–6]. With the rapid progress over the last few years, polymer-based photovoltaics (P-OPVs) have achieved power conversion efficiency (PCE) around 10% in single layer bulk-heterojunction (BHJ) solar cells [7–12]. Compared to the widely studied P-OPVs, while small molecule-based OPVs (SM-OPVs) have a late start, they have recently shown tremendous development [13,14]. This is based on several significant advantages such as relatively simple synthesis and purification, defined structures without batch-to-batch variations and easy control of energy levels by chemical structure design [15–18]. With these developments, the PCE of single layer SM BHJ devices has made strides to over 9% [19–21].

We recently reported a small molecule donor material named DRCN7T for solution-processable BHJ solar cells [21]. Simply by changing the terminal groups from 3-ethyl-2-thioxothiazolidin-4-one to 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile, a PCE performance of 9.30%, at an open circuit voltage (V_{oc}) of 0.91 V, a short circuit current (J_{sc}) of 14.87 mA/cm^2 and a fill factor (FF) of 68.7% was achieved for a DRCN7T-based device, which is attributed to the better structure with an optimized interpenetrating network and optimum crystalline fibrils. The results demonstrated that a delicate balance is needed for molecule design for high performance and some minor changes significantly affect device performance. Thus, based on previous work [22–25], it was considered that if Se was to replace S in the molecule DRCN7T, a better current might be expected for a higher overall performance since the unchanged overall molecular backbone structure would not have much effect on other factors such as V_{oc} or FF. Here, we report such a molecule, named DRCN7T-Se (Scheme 1), designed from DRCN7T by replacing the

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central thiophene unit with selenophene. Though, regrettably, no higher performance was obtained, an excellent PCE of 8.30% was achieved under AM 1.5G irradiation (100 mW cm^{-2}) for solution-processed devices with $PC_{71}BM$ as the acceptor.

2. Experimental

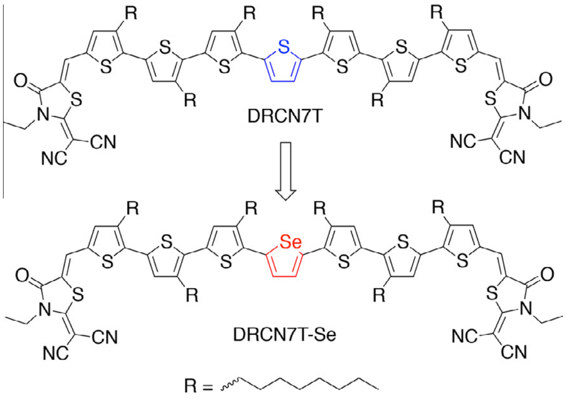
2.1. Materials and synthesis

All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. The synthesis of DRCN7T-Se is outlined in Scheme 2. 5′-Bromo-3,4′-dioctyl-[2,2′-bithiophene]-5-carbaldehyde (compound 3) and 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile (compound 4) were prepared according to the literature [21,26]. [6,6]-Phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) was purchased from American Dye Source, Inc. Other starting materials were all purchased from commercial suppliers and used without further purification.

2.1.1. 2,5-Bis(3-octylthiophen-2-yl)selenophene (compound 1)

A solution of Grignard reagent prepared from 2-bromo-3-octylthiophene (5.00 g, 18.2 mmol) in Et_2O (20 mL) and Mg (2.60 g, 108.3 mmol) in Et_2O (5 mL) under heating to reflux for 4 h with 1,2-dibromoethane as the entrainer was added using a dropping funnel to a stirred suspension of 2,5-dibromoselenophene (2.00 g, 6.9 mmol) and $NiCl_2$ (dppp) (70 mg, 0.13 mmol) in Et_2O (30 mL) under argon atmosphere. The reaction mixture was refluxed for 17 h. The resulting reddish brown solution was poured into aq 2 N HCl (25 mL)/ice (50 g), and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried with Na_2SO_4. The solvent filtered and then removed to give a red oil, which was chromatographed on silica gel with hexane as eluent to yield 2,5-bis(3-octylthiophen-2-yl)selenophene as a red oil (2.2 g, 61%.).

^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 2H), 7.15 (d, J = 5.1 Hz, 2H), 6.93 (d, J = 5.1 Hz, 2H), 2.79–2.72 (m, 4H), 1.69 (m, 4H), 1.24 (m, 20H), 0.92–0.81 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.30 (s), 139.40 (s), 132.91 (s), 130.16 (s), 128.12 (s), 123.70 (s), 31.92 (s), 30.79 (s), 29.46 (dd), 22.72 (s), 14.15 (s).



Scheme 1. Chemical structure of DRCN7T-Se.

2.1.2. 2,5-Bis(3-octyl-5-(tributylstannyl)thiophen-2-yl) selenophene (compound 2)

Under a N_2 atmosphere, n-BuLi (3.2 mL, 7.9 mmol) was added to a THF (30 mL) solution of compound 1 (1.40 g, 3.16 mmol) at −78 °C. After keeping it at this temperature for 30 min, this mixture was warmed to room temperature for another 30 min, and finally recooled to −78 °C for 2 h. Trimethyltin chloride (7.9 mL, 7.9 mmol, 1 M) was then added. This mixture was stirred overnight at room temperature and poured into water for extraction with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine (2 × 100 mL) and dried over $MgSO_4$. After the solvent had been removed under reduced pressure, the residue was purified by recrystallization from acetone to yield compound 3 (3.23 g, 93%).

2.1.3. Compound DCHO7T-Se

A solution of compounds 2 (1.20 g, 0.72 mmol) and 3 (0.8 g, 1.61 mmol) in toluene (30 ml) was degassed twice with argon followed by the addition of $Pd(PPh_3)_4$ (0.025 g, 0.022 mmol). After stirring at 100 °C for 48 h under argon, the reaction mixture was poured into cold water and extracted with $CHCl_3$. The organic layer was washed with water and then dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was purified by silica gel using a mixture of dichloromethane and petroleum ether (3:1) as eluent to yield compound DCHO7T-Se (0.61 g, 62.5%) as a red solid.

^1H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 2H), 7.62 (s, 2H), 7.28 (s, 2H), 7.15 (s, 2H), 7.04 (s, 2H), 2.93–2.72 (m, 12H), 1.72 (s, 12H), 1.44 (s, 10H), 1.31 (t, 60H), 0.90 (dd, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.52 (s), 151.78–141.82 (m), 141.23 (s), 141.23 (s), 140.99 (d), 141.82–140.17 (m), 141.82–133.36 (m), 133.26 (s), 133.25–132.91 (m), 132.70 (d), 130.52 (s), 128.68 (d), 31.90 (d), 30.58 (d), 30.27 (s), 29.48 (ddd), 22.70 (s), 14.13 (s). MS (MALDI-TOF): calcd for $C_{78}H_{112}O_2S_6Se$ $[M]^+$, 1352.62; found, 1352.61.

2.1.4. Compound DRCN7T-Se

Under the protection of argon, three drops of piperidine were added to a chloroform (50 ml) solution of DCHO7T-Se (0.50 g, 0.37 mmol) and compound 4 (0.70 g, 3.6 mmol). The resulting solution was stirred and refluxed for 48 h. The reaction mixture was then poured into cold water and extracted with $CHCl_3$. The organic layer was washed with water and then dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was purified by silica gel using chloroform as eluent. The crude solid was recrystallized from a mixed solvent of $CHCl_3$ and n-hexane three times to yield DRCN7T-Se as a black solid (0.51 g, 81.1%).

^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.29 (s, 4H), 7.18 (s, 2H), 7.05 (s, 2H), 4.32 (d, J = 7.2 Hz, 4H), 2.92–2.71 (m, 13H), 1.78–1.64 (m, 13H), 1.49–1.22 (m, 75H), 0.88 (t, J = 6.6 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.86 (s), 165.59 (s), 141.17 (s), 140.52 (s), 139.93 (s), 138.94 (s), 133.58 (s), 133.17 (s), 130.61 (s), 129.17 (s), 128.60 (s), 128.09 (s), 113.30 (d, J = 13.9 Hz), 112.32 (s), 55.45 (s),