



A novel small molecule based on dithienophosphole oxide for bulk heterojunction solar cells without pre- or post-treatments



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ABSTRACT

A novel small molecule (PDTP-WR) with a dithieno[3,2- b:2',3'- d]phosphole oxide (DTP) core unit was designed and synthesized for use in BHJ solar cells. This small molecule had an optical band gap of 1.65 eV, appropriate for a donor material, and HOMO and LUMO energy levels of -5.10 , and -3.45 eV, respectively, which provided a broad absorption and superior charge transfer properties. The solar cell devices prepared using PDTP-WR and PC₇₁BM gave a promising power conversion efficiency of 5.04%, a J_{sc} of 12.98 mA cm^{-2} , a V_{oc} of 0.79 V, and a fill factor of 49%, without pre- or post-treatments. Morphological and structural studies revealed that PDTP-WR formed a favorable BHJ morphology. An appropriate domain size of less than 20 nm and bi-continuous interpenetrating paths with an ordered structure obtained as a result of strong intermolecular interactions can support the device performances. This is the first reported use of DTP in small molecule donor, and the results of these studies indicated that DTP-based small molecule can be a promising candidate for the photovoltaic applications.

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1. Introduction

Organic electronic materials have received widespread attention as the active materials in plastic electronics, such as organic light-emitting diodes (OLEDs), organic photovoltaic cells (OPVs), organic photodetectors (OPDs), and organic field-effect transistors (OFETs) because of their attractive features: designability, low cost, easy manipulation, and mechanical flexibility [1–4]. Of the many electronic devices that employ organic active materials, OPVs have shown promise for use as renewable energy sources in recent years because the chemical structures and functionalities of their organic active layers can be diversified through molecular design [1,5].

In an effort to realize more efficient OPV devices, a variety of

organic semiconductor materials have been developed, and their electrochemical properties have been investigated [6–10]. Solution-processable small molecule photovoltaic donor materials have attracted considerable attention for use in preparing bulk heterojunction (BHJ)-OPVs due to their unique advantages over their polymer counterparts: their synthesis, purification, and structural modifications are relatively easy, and they provide low batch-to-batch variability [9,11]. Current efforts are focused on the synthesis of high-performance donor small molecules that feature a broad absorption, suitable energy levels, and efficient charge carrier transport [12–15]. A particularly successful approach to designing new donor small molecules with higher efficiencies is the donor–acceptor approach, in which electron-rich donor units and are electron-deficient acceptor units are alternated [9,11–15].

These design strategies may be implemented using photovoltaic small molecules having an acceptor unit with a relatively strong electron affinity or a strong electron-withdrawing capacity, which lowers the band gap of the resulting active materials [16,17]. Our group recently reported the development of certain donor polymers containing a strong acceptor, the dithieno[3,2- b:2',3'- d]

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phosphole oxide (DTP) moiety, for use in OPVs and OFET applications [18–20]. The DTP moiety forms an unusual hyperconjugation ring and a rigid pyramidal geometry induced by $\sigma^*-\pi^*$ interactions between the π -conjugated scaffold and the exocyclic substituents [21,22]. This unusual structure decreases the energy level of the lowest unoccupied molecular orbital (LUMO) of the DTP blocks, making them strong electron acceptors [18–22]. The highly polarizable nature of the phosphole oxide moiety provides a highly polarized excited state, which significantly improves charge transfer to a fullerene acceptor and yields a high short-circuit current (J_{sc}) [18]. Unfortunately, however, small molecule donors comprising the DTP moiety have not been investigated, and many challenges remain toward improving the photovoltaic performances of DTP-based OPV devices.

In this study, a new small molecule donor, (5E, 5'E)-5,5'-((4-oxido-4-phenylphospholo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-dioctyl-[2,2':5',2''-terthiophene]-5'',5-diy))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one) (PDTP-WR), with a DTP moiety as a core unit, alkyl terthiophene as a linker with electron-donating abilities, and 3-ethylrhodanine as a terminal acceptor group, was synthesized and used in OPV devices. The electron-withdrawing unit, rhodanine, was widely reported to provide broad light absorption and a strong electron affinity. As such, many research groups have used rhodanine in small molecules, particularly at the end positions of compounds, due to its superior small molecule properties and potential applications to photovoltaic diodes. As a result, a novel small molecule donor, PDTP-WR, displayed a broad absorption spectrum, and superior exciton dissociation and charge carrier transport properties. The photovoltaic properties of PDTP-WR-based OPVs were investigated by fabricating devices composed of PDTP-WR:[6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM) blends. The solution-processed OPV devices displayed promising power conversion efficiencies (PCEs) exceeding 5% without the use of pre- or post-treatments, such as thermal annealing or solvent vapor annealing. The correlation between the photovoltaic performances and the active layer morphologies was examined by characterizing the morphological and microstructural properties of PDTP-WR:PC₇₁BM blend films using atomic force microscopy (AFM), transmission electron microscopy (TEM), UV-visible spectroscopy, and grazing-incidence wide-angle X-ray scattering (GIWAXS) studies.

2. Experimental section

2.1. Materials

The PC₇₁BM, used as an acceptor material was purchased from Nano-C, Inc. Poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS; Clevis P VP AI 4083) was supplied by Bayer AG. All other chemicals and reagents were purchased from Sigma-Aldrich and were used as received, except for the solvents purified prior to use.

2.2. Synthesis

2.2.1. Synthesis of 3,3''-dioctyl-5''-(tributylstannyl)-[2,2':5',2''-terthiophene]-5-carbaldehyde (1)

The anhydrous THF (700 mL) was cooled to -78°C . N-methylpiperazine (2.4 g, 2.4 mmol) was injected into the solution, followed by n-butyl lithium (8.8 mL, 2.5 M in hexane, 2.2 mmol). After the reaction had been stirred for 15 min, the compound 3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (10.0 g, 2.0 mmol) was slowly added to the solution. 3,3''-Dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde was obtained using the method reported [23]. After the mixture had been stirred for

15 min, followed by a second addition of n-butyl lithium (8.8 mL, 2.5 M in hexane, 2.2 mmol), the solution was stirred for another 1 h. Tributyltin chloride (7.8 g, 2.4 mmol) was then added to the solution, and the cooling bath was removed. After warming to room temperature, the reaction was stirred for 1 h. The organic layer was separated, and the aqueous phase was extracted with ether and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the resulting residue was purified by silica gel chromatography using ether:hexane (1:1). The crude product was used in the next reaction without further purification.

2.2.2. Synthesis of 2,6-dibromo-4-phenylphospholo[3,2-b:4,5-b']dithiophene 4-oxide (2)

The reaction reported in the literature was followed [24]. ¹H NMR (300 MHz, CDCl₃) [ppm] δ = 7.77 (m, 2H), 7.56 (m, 1H), 7.55 (m, 2H), 7.0 (s, 2H).

2.2.3. Synthesis of 4'',4''''-(4-oxido-4-phenylphospholo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (3)

2,6-Dibromo-4-phenylphospholo[3,2-b:4,5-b']dithiophene 4-oxide (0.50 g, 0.0011207 mol), 0.03 g (0.00003362 mol) Pd₂(dba)₃, 0.041 g (0.00013448 mol) tri-*o*-tolylphosphine, and 3''-dioctyl-5''-(tributylstannyl)-[2,2':5',2''-terthiophene]-5-carbaldehyde (2.2g, 0.0028017 mol) were added to the reaction in dry toluene (25 mL). The mixture was stirred at 110 °C for 24 h under N₂. After the organic layer had separated and the aqueous phase was extracted with CH₂Cl₂, the extracted layer was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the resulting residue was purified by silica gel chromatography using hexane: ethyl acetate (1:3) as the eluent. Yield: (0.3 g, 21%). ¹H NMR (300 MHz, CDCl₃, δ): 9.85 (s, 2H), 7.85–7.78 (m, 2H), 7.62–7.57 (m, 3H), 7.52–7.46 (m, 2H), 2.87–2.75 (m, 8H), 1.74–1.64 (m, 8H), 1.44–1.22 (m, 40H), 0.91–0.86 (m, 12H). ¹³C NMR (500 MHz, CDCl₃, δ): 182.54, 155.64, 146.47, 144.58, 141.26, 140.79, 140.40, 140.30, 139.02, 137.47, 135.96, 135.28, 134.98, 134.22, 130.98, 130.89, 130.45, 130.10, 129.75, 129.30, 129.15, 128.14, 127.89, 127.45, 126.95, 126.52, 121.90, 121.71, HRMS (FAB⁺): Calcd. for C₇₂H₈₅O₃PS₈: 1284.4002. Found: (M⁺) 1285.4.

Synthesis of (5E, 5'E)-5,5'-((4-oxido-4-phenylphospholo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-dioctyl-[2,2':5',2''-terthiophene]-5'',5-diy))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one) (PDTP-WR).

Compound 3 (0.20 g, 0.0001555306 mol) and 3-ethyl rhodanine (0.161 g, 0.0009331844 mol) were dissolved in dry chloroform (30 mL) under nitrogen, and five drops of piperidine were added to the mixture. The mixture was stirred at 80 °C for 48 h under N₂. After the organic layer had been separated and the aqueous phase had been extracted with CH₂Cl₂, the extracted solution was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the resulting residue was purified by silica gel chromatography using hexane: chloroform (1:3) as the eluent. The product was further purified by recrystallization from chloroform and ethyl acetate to give a black powder. Yield: (0.14 g, 58%). ¹H NMR (300 MHz, CDCl₃, δ): 7.87–7.79 (m, 2H), 7.65–7.6 (m, 3H), 7.58–7.53 (m, 2H), 7.13–7.1 (d, 4H), 7.07–7.06 (d, 2H), 6.95–6.94 (d, 2H), 6.87 (s, 2H), 4.19–4.10 (m, 4H), 2.74–2.63 (m, 8H), 1.66–1.6 (m, 8H), 1.34–1.25 (m, 46H), 0.93–0.88 (m, 12H). ¹³C NMR (500 MHz, CDCl₃, δ): 192.03, 167.30, 143.62, 141.21, 141.11, 141.00, 139.85, 139.26, 137.29, 137.13, 135.33, 135.00, 134.10, 132.77, 130.98, 130.89, 130.24, 129.15, 129.05, 127.46, 127.28, 126.44, 124.84, 122.19, 121.91, 121.80, 120.70, 39.94, 31.90, 30.45, 30.29, 29.71, 29.59, 29.46, 29.28, 22.68, 14.13, 12.30, HRMS (FAB⁺): Calcd. for C₈₂H₉₅N₂O₃PS₁₂: 1570.3729. Found: (M⁺) 1571.3.

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