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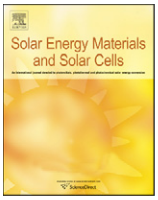

Novel solution processable small molecule containing new electron-withdrawing group and oligothiophene for photovoltaic applications

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A novel electron-withdrawing group 5-(2,6-dimethyl-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxo-dihydropyrimidine-4,6(1H,5H)-dione (PD) was designed and synthesized according to Knoevenagel condensation. On this basis, a small molecule 8TPDC8 with oligothiophene as electron-donating unit and PD as electron-accepting unit was designed and synthesized. UV–vis absorption spectrum displayed that 8TPDC8 possesses a relatively broad absorption range (from 300 to 900 nm). The cyclic voltammetry investigation displayed that the highest occupied molecular orbital (HOMO) energy level of 8TPDC8 was -5.28 eV, which promised good air stability and high open circuit voltage (V_{oc}) for photovoltaic application. The bulk heterojunction (BHJ) photovoltaic devices were fabricated with 8TPDC8 as the donor material and (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM) as the acceptor material. A power conversion efficiency of 1.28% has been obtained under the illumination of AM 1.5, 100 mW/cm^2.

1. Introduction

Photovoltaic devices based on organic polymers and small molecules are evolving into a promising cost-effective alternative to silicon-based solar cells due to their low-cost fabrication through solution processing, light weight, as well as excellent compatibility with flexible substrates [1]. In contrast with polymers [2], solution processable small molecules possess many advantages, such as high purity, well-defined molecular structures, and definite molecular weights. Until now, profound progress has been achieved in the synthesis of new solution processable small molecules and their photovoltaic applications [3–8].

In order to enlarge the absorption spectra of organic conjugated molecules, donor–acceptor (D–A) structure molecules were designed and synthesized [3,4,10–12]. As usual, in D–A small molecules, sulfonyldibenzene [9], 2-(2,6-dimethyl-4H-pyran-4-ylidene) malononitrile (PM) [8,13], malononitrile [7], benzothiadiazole [10], diketopyrrolopyrrole [11], and squaraine [5], etc. were used as the electron-withdrawing groups. However, few small molecules exhibited the extremely desirable absorption spectra matching well with the solar spectrum because of the relatively weak [7,9,10] or strong [5,11] electron-withdrawing abilities of the electron-withdrawing groups in small molecules. For example, the D–A small molecules with sulfonyldibenzene as the electron-accepting unit only covered the absorption range from 300 to 500 nm [9] Molecules based on malononitrile or PM showed the main absorption range from 300 to 650 nm [7,13]. Molecules containing benzothiadiazole also displayed the main absorption range from 300 to 650 nm [10]. Meanwhile the small molecules based on diketopyrrolopyrrole and oligothiophene exhibited its absorption range mainly from 500 to 800 nm [11], And the small molecules based on squaraine demonstrated its absorption range of 550–900 nm [5]. As for the absorption spectra of D–A molecules, the wavelength of the absorption peaks of the electron-donating unit, electron-accepting unit and π–π^* interactions between molecules is usually less than *ca.* 400 nm, while that of the absorption peak of ICT generally is longer than *ca.* 480 nm. Therefore, the narrow absorption spectra (300–650 nm) could mainly be caused by the relatively weak ICT, because of the weak electron-withdrawing ability of electron-accepting groups. In the molecules containing diketopyrrolopyrrole or squaraine group, the ICT is so strong that there is an absorption valley (400–500 nm) appearing between the absorption of π–π^* interaction and the ICT in the absorption spectrum. So, electron-withdrawing groups with too weak or strong electron-withdrawing

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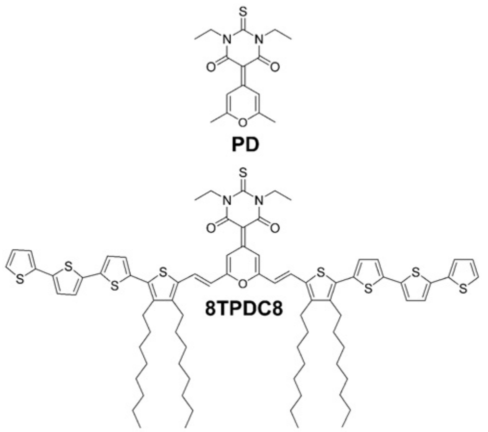

Fig. 1. The chemical structure of PD and 8TPDC8.

ability are not very suitable for achieving D–A molecules with a desirable absorption spectra.

In this article, we designed and synthesized a new electron-withdrawing group PD, incorporating 1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione with 2,6-dimethyl-4H-pyran-4-one by a knoevenagel reaction (Fig. 1). We also synthesized 8TPDC8 by using PD as electron-accepting group and oligothiophenes as electron-donating group (Fig. 1). We chose oligothiophene as the electron-donating unit due to its excellent coplanarity, high carrier mobility, good air stability, and strong electron-donating ability [8,11]. The symmetrical combination of a PD unit with alkylated thiophenevinyl assured longer conjugated length and better coplanarity, which could enhance the intermolecular interactions and further reduce the band gap of the molecules. UV–vis absorption spectrum displayed that the 8TPDC8 thin film covered a rather broad absorption range from 300 to 900 nm, which is an extremely desirable absorption spectrum for photovoltaic applications. The objective of this project is aiming at the development of new series of PD derivatives as donors for organic solar cells, we report here preliminary results on BHJ solar cell based on 8TPDC8 as donor and (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM) as acceptor. A relatively high power conversion efficiency (PCE) of 1.28% was achieved for the photovoltaic devices based on 8TPDC8:PCBM (1:2) under simulated air mass 1.5 global irradiation (100 mW/cm^2).

2. Experimental

2.1. Materials

All reagents and chemicals were purchased from commercial sources (Aldrich, Across, Fluka) and used without further purification unless stated otherwise. All solvents were distilled over appropriate drying agent(s) prior to use and were purged with nitrogen. Compound 6 was synthesized according to a previous reference [14]. The synthesis route was shown in Scheme 1.

2.2. Synthesis of compounds

3,4-Dioctyllthiophene (1): Mg (4.80 g, 0.20 mol) was placed in 60 mL of dry ether, a grain of I_2 was added as catalyst. The solution was heated to 40 °C for stimulating the reaction. 1-Bromooctane (40 mL, 0.25 mol) was added dropwise over 2 h, and the reaction mixture was stirred for another hour. This solution was then transferred slowly via a cannula to a mixture of 3,4-dibromothiophene (9.09 mL, 0.08 mol) and 200 mg of Ni(dppp)Cl_2 in 50 mL of dry ether while cooling on ice. The reaction mixture was stirred for 16 h at room temperature and subsequently poured out in 300 mL of ice/water containing 10 mL of concentrated HCl. The product was extracted with ether and the combined organic layers were washed with plenty of water and brine, successively. The organic extracts were dried over anhydrous $MgSO_4$, evaporated and purified with column chromatography on silica gel with petroleumether as the eluant to give a slight yellowish oil. 18.26 g (0.059 mol, yeild 74.3%). ^{1}H NMR (300 MHz): δ(ppm) 6.884 (s, 2H, –Ph), 2.498 (t, 4H, –CH_2), 1.614 (m, 4H, –CH_2), 1.297 (m, 20H, –CH_2), 0.886 (t, 6H, –CH_3). Elem. Anal. Calcd. for $C_{20}H_{36}S$: C, 77.85; H, 11.76. Found: C, 77.82; H, 11.77.

2,5-Dibromo-3,4-dioctylthiophene (2): Compound 1 (13.44 g) was dissolved in 80 mL of THF at room temperature, then 14.4 g *N*-bromosuccinimide was added over a period of 5 min. The solution was stirred at room temperature for 8 h. The solvent was then removed in vacuum and hexane (500 mL) was then added (to precipitate all the succinimide). The mixture was filtered through a silica plug and the solvent was removed in vacuum. Distillation under vacuum gave 15.23 g gas a colorless oil. ^{1}H NMR (300 MHz): δ(ppm) 2.511 (t, 4H, –CH_2), 1.471(m, 4H, –CH_2), 1.283 (m, 20H, –CH_2), 0.890 (t, 6H, –CH_3). Elem. Anal. Calcd. for $C_{20}H_{34}Br_2S$: C, 51.51; H, 7.35. Found: C, 51.52; H, 7.32.

5-*Bromo*-3,4-*dioctylthiophene*-2-*carbaldehyde* (3): *n*-Buli (7.5 mL of 2.5 M solution in hexane) was added dropwise to a solution of compound 2 (8.0 g) in THF (80 mL) at −78 °C under argon. The solution was stirred at −78 °C for 2 h, then dried DMF (2.2 mL) was added quickly and it was kept at room temperature and stirred for 24 h before being poured into water. The product was extracted with ether. The organic layer was subsequently washed with water and brine and dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography with CH_2Cl_2:petroleumether (1:2) to give a red brown oil 4.06 g (9.80 mmol, yeild 57.1%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ(ppm) 9.909 (s, 1H, –CHO), 2.871 (t, 2H, –CH_2), 2.541 (t, 2H, –CH_2), 1.536 (m, 4H, –CH_2), 1.283 (m, 20H, –CH_2), 0.961 (m, 6H, –CH_3). Elem. Anal. Calcd. for $C_{21}H_{35}BrOS$: C, 60.71; H, 8.49. Found: C, 60.73; H, 8.50.

5-(2,6-Dimethyl-pyran-4-ylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione (4): 2,6-Dimethyl-pyran-4-one (2.48 g, 20 mmol) and 1,3-diethyl-2-thioxo-dihydro–pyrimidine-4,6-dione (4 g, 20 mmol) were dissolved in a mixture of acetic anhydride (50 mL), The solution refluxed with vigorous stirring for 24 h. The reaction mixture was cooled to room temperature and then poured into water. After filtration, the residue was recrystallized from ethanol and the yellow solid 3.86 g (12.6 mmol, 63%) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ(ppm) 8.829 (s, 2H, –PD), 4.580 (m, 4H, –CH_2), 2.471(s, 6H, –CH_3), 1.313 (t, 6H, –CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ(ppm) 177.688, 165.579, 161.703, 158.182, 111.592, 96.546, 43.210, 20.628, 12.419. Elem. Anal. Calcd. For $C_{15}H_{18}N_2O_3S$: C, 58.80; H, 5.92. Found: C, 58.79; H, 5.95.

5-(2,6-bis((E)-2-(5-bromo-3,4-dioctylthiophen-2-yl)vinyl)-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxo-dihydropyrimidine-4,6(1H, 5H)-dione (5): A mixture of 5-bromo-3,4-dioctylthiophene-2-carbaldehyde(3.55 g), 5-(2,6-dimethyl-pyran-4-ylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione (1.19 g), piperidine (10 drops), and *n*-propyl alcohol were refluxed under N_2 for 24 h. The reaction mixture was cooled to room temperature and poured into water and extracted with dichloromethane. The combined organic extractions were washed three times with water, dried over anhydrous $MgSO_4$, evaporated under vacuum, and purified with column chromatography on silica gel with dichloromethane:petroleumether (2:1) as the eluate to a red solid 2.57 g was obtained (2.33 mmol, 60.0%). ^{1}H NMR (300 MHz,