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Facile synthesis of 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole-based narrow band gap small molecules for solar cell applications

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ABSTRACT

In this study, 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole-based two new low band gap organic small molecules, **TPT-SM1** and **TPT-SM2**, were prepared and their optical, electrical and photovoltaic properties were investigated. **TPT-SM1** was synthesized by simply linking the electron rich 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole and electron deficient tricyanovinyl (−C(CN)=C(CN)$_2$) units. On the other hand, **TPT-SM2** was prepared by attaching the electron donating non planar triphenyl amine and electron accepting tricyanovinyl groups respectively on both side of 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole unit. Interestingly, the absorption band of **TPT-SM1** and **TPT-SM2** was found to be located exactly at the maximum solar flux region of the solar spectrum and their strong absorption band appears at the region of 470–800 nm and 490–900 nm, respectively, in film state. The optical band gap of **TPT-SM1** and **TPT-SM2** was calculated to be 1.58 eV and 1.42 eV, respectively, and the electrochemical studies revealed that the HOMO energy level was located at around −5.15 eV. The solution processed small molecule organic solar cells (SMOSCs) prepared by using **TPT-SM1** and **TPT-SM2** as an electron donor and $PC_{71}BM$ as an electron acceptor at 1:2 wt% donor:acceptor blend ratio showed maximum power conversion efficiency (*PCE*) of 1.19% and 1.68%, respectively.

1. Introduction

Bulk heterojunction solar cells (BHJ) are considered as one of the promising candidates for renewable energy sources due to their advantages such as low cost, light weight, solution processable, and the capability to fabricate flexible large-area devices [1,2]. In BHJ solar cells, the blends of electron donor and electron acceptor materials have been utilized for the sun light harvesting and charge separation. After many efforts, polymer based BHJ solar cells (PSCs) which made up with the photoactive layer containing the interpenetrating network of the electron donating polymer and electron accepting PCBM showed impressive performances in converting solar energy to electrical energy. Finally, the power conversion efficiency (*PCE*) was improved in the range of 7–9.2% [3–10] for single layer PSCs and 10.6% [3] for tandem structured PSCs. Unfortunately, the *PCE* of the PSCs device is found to be highly affected by the synthetic characteristics of the donor polymers. Presently, the poor reproducibility of the synthetic characteristics such as purity, molecular weight, regioregularity and polydispersity of each batch of the polymerization bit delays their commercial application [11,12]. On the other hand, organic small molecules compete with the polymeric donor materials in BHJ solar cell applications due to their advantages such as facile synthesis, reproducibility of the purity, more number of possibilities for the structural modification of molecules to tune their molecular energy levels for optimizing the photovoltaic device performances [13]. Presently, the *PCE* was improved in the range of 4–7% [14–24] for solution-processed small molecule organic solar cells (SMOSCs) and 10.7% [15] for vacuum-processed tandem SMOSCs. The overall *PCE* of SMOSCs is quite similar to the maximum *PCE* obtained from the PSCs. This inspires us to develop new low band gap small molecules for SMOSCs application. In order to achieve high current density in SMOSCs, utilizing new donor molecules that can efficiently absorb the sun light at the maximum solar flux region (500–900 nm) of the solar spectrum is crucial, because the energy conversion efficiency of SMOSCs is directly proportional to the light harvesting ability of the electron donor molecules. In addition, the HOMO energy levels of the donor molecules should be deeper than −5.0 eV to get high open circuit voltage, which is defined as the energy difference between

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the HOMO and LUMO levels of the donor and acceptor materials, respectively.

In our laboratory, we have been interested in utilizing 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole (*N*-aryl TPT)-based π-conjugated materials in solar cell applications. Recently, synthesis of a series of *N*-aryl TPT-based polymers showing dissimilar absorption band at visible part of the solar spectrum was reported from our group [25–32] and the PSCs fabricated form *N*-aryl TPT-based polymeric donor and $PC_{71}BM$ acceptor units were found to show relatively high current density (J_{sc}) (up to ~9.3 mA cm^{-2}) [25–32]. The good light harvesting ability of *N*-aryl TPT-based units induced us to develop *N*-aryl TPT-based dyes for dye sensitized solar cells (DSSCs) application. Interestingly, the DSSCs sensitized by *N*-aryl TPT-based dyes were found to show relatively high *PCE* (6.71%) and J_{sc} (13.5 mA cm^{-2}) [33,34]. In this continuity, to evaluate the potential of *N*-aryl TPT-based small molecules in SMOSCs application, we tried to develop new low band gap small molecules by coupling the *N*-aryl TPT unit with tricyanovinyl unit, an electron acceptor group showing very strong electron attracting ability [35]. Here, we wish to report the synthesis of two new *N*-aryl TPT-based low band gap small molecules containing tricyanovinyl electron acceptor group and their SMOSC applications.

2. Experimental

2.1. Materials and general procedure

All reagents were commercially available from Aldrich or TCI chemicals and used without further purification. Solvents were purified by normal procedure and handled in a moisture-free atmosphere. Flash column chromatography was performed on silica gel (Merck Kieselgel 60, 70–230 mesh).

2.2. Instruments and measurements

^{1}H and ^{13}C NMR spectra were recorded using a 300-MHz Varian Mercury Plus spectrometer in deuterated chloroform. Infrared spectra were obtained on a Nicolet 380 FTIR spectrophotometer with samples prepared as KBr pellets. Melting points were determined using Gallenkamp Variable Heater. The absorption spectra were recorded at 25 °C in chloroform and as thin films on glass using a JASCO V-570 spectrophotometer. The electrochemical studies were performed using a CH Instruments Electrochemical Analyzer in acetonitrile (ACN) containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as the supporting electrolyte, Ag/AgCl as reference electrode and platinum as counter and working electrodes. Atomic force microscopy (AFM) images of blend films were obtained on a Veeco-Multimode AFM operating in the tapping mode.

2.3. Fabrication and characterization of solar cell devices

2.3.1. Fabrication

The small molecule organic solar cells (SMOSCs) were constructed as follows. The transparent ITO electrode (300 nm thick, 4 Ω/sq sheet resistance) was coated on glass substrates and cleaned by ultrasonication sequentially in detergent, deionized water, acetone, and isopropyl alcohol. After drying the substrates, a 40 nm thick layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (CLEVIOUS P) was spin-coated onto the pre-cleaned and UV-ozone treated ITO substrates and baked in air at 150 °C for 5 min. Subsequently, the 80 nm thickness of active layer (**TPT-SM1** or **TPT-SM2**:$PC_{71}BM$ blend solution) was spin coated onto the ITO/PEDOT:PSS substrates. The **TPT-SM1** or **TPT-SM2**:$PC_{71}BM$ blend solution was prepared by mixing **TPT-SM1** or **TPT-SM2** with $PC_{71}BM$ at a weight ratio of 1:1 and 1:2 wt% in 1,2-dichlorobenzene. After drying the solvent, the 0.7 nm thickness of LiF was spin-coated onto the active layer and subjected to heating at 80 °C for 30 min in glove box. After being subjected to a vacuum (3×10^{-6} Torr), an Al electrode with thickness of around 100 nm was deposited onto the LiF layer. The top metal electrode area, comprising the active area of the solar cells, was found to be 0.36 cm^2. All fabrication steps and characterization measurements were performed in an ambient environment without a protective atmosphere.

2.3.2. Characterization of solar cell devices

The performances of the SMOSCs were measured under simulated AM 1.5 illumination with an irradiance of 100 mW cm^{-2} (PEC-L11, Pecell Technologies Inc.). The irradiance of the sunlight-simulating illumination was calibrated using a standard Si photodiode detector fitted with a KG5 filter. The *J–V* curves were recorded automatically using a Keithley 2400 SourceMeter source measurement unit. The quantum efficiency measurements (IPCE) were carried out by using Oriel IQE-200. Oriel IQE-200 is made up by using 250 W quartz tungsten halogen (QTH) lamp, monochromator, an optical chopper, a lock-in amplifier, and a calibrated silicon photodetector. The thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ±1 nm.

2.4. Synthesis

2.4.1. Synthesis of 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole (**1**)

Compound **1** was prepared via the procedure, which was slightly modified from the procedure reported previously from our group [25]. 1,4-Bis(2-thienyl)-1,4-butanedione (1) (5.0 g, 20 mmol), which was prepared via the previously reported procedure [25], 2,6-diisopropylaniline (15.2 mL, 80 mmol) and *p*-toluenesulfonic acid monohydrate (0.76 g, 4.00 mmol) were heated at 110 °C for 36 h with stirring and then cooled to room temperature. To this mixture, 80 mL of ethyl acetate was added and stirred for 15 min. The insoluble material was filtered off and the organic solution was washed with saturated Na_2CO_3 solution. The organic layer was separated and washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane) to afford the pure product 1. Yield: 5.9 g (76%). mp 106–107 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.55 (t, 1H), 7.28 (d, 2H), 6.98 (dd, 2H), 6.77 (dd, 2H), 6.67 (s, 2H), 6.40 (dd, 2H) 2.42–2.58 (m, 2H), 0.90 (d, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 148.3, 135.4, 134.5, 130.5, 130.3, 127.1, 124.8, 123.3, 123.0, 109.3, 28.5, 23.9; HRMS (EI$^+$, *m*/*z*) [m$^+$] Calcd for $C_{24}H_{25}NS_2$ 391.1428, found 391.1426.

2.4.2. Synthesis of 1-(5-(1-(2,6-diisopropylphenyl)-5-(thiophen-2-yl)-1H-pyrrol-2-yl)thiophen-2-yl)ethene-1,2,2-tricarbonitrile (***TPT-SM1***)

To a stirred solution of compound **1** (1.17 g, 3.00 mmol) in DMF was added tetracyanoethylene (TCNE) (0.4 g, 3.10 mmol) at room temperature and the resulting solution was stirred for 24 h. Then, the reaction mixture was concentrated by using rotary evaporator and the residue was dissolved in ethyl acetate (100 mL). The organic solution was washed with brine and dried over anhydrous Na_2SO_4. The solution was filtered and concentrated by using a rotary evaporator. The blue residue was purified by column chromatography (silica gel, $CHCl_3$) to afford pure product, **TPT-SM1**. Yield 1.35 g (91%). mp 224–225 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.73 (d, 1H), 7.67 (t, 1H), 7.39 (d, 2H), 7.17 (d, 1H), 7.13 (dd, 1H), 6.80–6.90 (m, 3H), 6.70 (dd, 1H), 2.32–2.48 (m, 2H), 0.97 (d, 6H), 0.92 (d, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 150.0, 147.8, 140.6, 136.9, 133.2,