A low band gap, solution processable oligothiophene with a dialkylated diketopyrrolopyrrole chromophore for use in bulk heterojunction solar cells

Arnold Bernarte Tamayo, Xuan-Dang Dang, Bright Walker, Junghwa Seo, Tyler Kent, and Thuc-Quyen Nguyen[a]
Department of Chemistry and Biochemistry and Center for Polymers and Organic Solids, University of California-Santa Barbara, California 93106, USA

Bulk heterojunction solar cells are fabricated from blends of oligothiophene with a dialkylated diketopyrrolopyrrole chromophore:[6,6]-phenyl C_{71} butyric acid methyl ester. Absorption and photocurrent of the films extend to 800 nm. A power conversion efficiency (PCE) of 3.0% is obtained under simulated 100 mW/cm^2 AM1.5 illumination with a 9.2 mA/cm^2 short-circuit current density and an open-circuit voltage of 0.75 V. The hole and electron mobilities in the 50:50 blend are fairly balanced, 1.0×10^{-4} and 4.8×10^{-4} cm^2/V s, respectively. This is the highest PCE reported to date for solar cells using solution processable small molecules. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3086897]

Interest in using solution processable small molecule semiconductors as alternatives to conjugated polymers[1] in bulk heterojunction (BHJ) solar cells has increased in the past few years because of several key advantages.[2] In general, crystalline molecular organic materials exhibit better charge transport properties than polymeric semiconductors because they are more likely to exhibit long range order. Small molecule semiconductors are also easy to reproducibly synthesize, functionalize, and purify. There are several classes of small molecules in the literature that have been used as solution processable donor materials in BHJ solar cells.[1,3] However, the power conversion efficiencies (PCEs) remain lower than those of polymer-based devices that have yielded PCEs of >5% when blended with soluble fullerene acceptors [e.g., [6,6]-phenyl C_{61} (C_{61}-PCBM) or [6,6]-phenyl C_{71} butyric acid methyl ester (C_{71}-PCBM)].[4] The reasons for low efficiencies in small molecule based BHJ solar cells are mainly due to poor spectral overlap, poor solubility, poor solid state miscibility with acceptor materials, and low solution viscosity.[3]

Recently, we have reported that thiophene-based oligomers incorporating a diketopyrrolopyrrole (DPP) chromophore are excellent donor materials for BHJ solar cells.[5] This class of materials shows nanoscale ordering in the solid state that can be tuned by changing the nature of the alkyl substituent attached to the DPP core and the number of thiophene units in the backbone.[6] These materials exhibit intense absorption at long wavelengths and good field effect mobilities.[7] We demonstrated solar cells with PCEs of 2.3% using an oligothiophene-DPP with a *t*-Boc protecting group as the donor and C_{61}-PCBM fullerene as the acceptor.[5] This oligothiophene-DPP material, however, might not be thermally stable in the long term as the *t*-Boc protecting groups can be cleaved off at high temperatures.[8]

Here we report a low band gap oligothiophene-DPP molecule as a donor material, 2,5-di-(2-ethylhexyl)-3,6-bis-(5″-*n*-hexyl-[2,2′,5′,2″]terthiophen-5-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (SMDPPEH), which contains ethylhexyl

substituents (see Fig. 1). The ethylhexyl groups make the donor material more soluble (>20 mg/ml in chloroform, chlorobenzene or toluene) and thermally stable (mp =160 °C) relative to the *t*-Boc derivative, where the *t*-Boc group is thermally cleaved at temperatures above 140 °C.[8] With C_{71}-PCBM as the acceptor, the BHJ solar cells show a large short circuit current density (>9 mA/cm^2), good external quantum efficiency (EQE) (~40% at wavelengths above 600 nm), and good spectral match to solar spectrum with photoresponse extended to 800 nm. Figure 1 gives the structures of the donor and the acceptor materials as well as their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels.

SMDPPEH was synthesized following a previously reported procedure.[6] C_{71}-PCBM was purchased from Nano-C and used as received. Blended films of SMDPPEH and C_{71}-PCBM for optical and photovoltaic measurements were spun cast at 2500 rpm for 30 s from chloroform solutions (20 mg/ml) onto a 40 nm layer of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate 4083 (PE-DOT:PSS) (H.C. Starck) on indium tin oxide (ITO)-coated glass. For the photovoltaic devices, an aluminum cathode
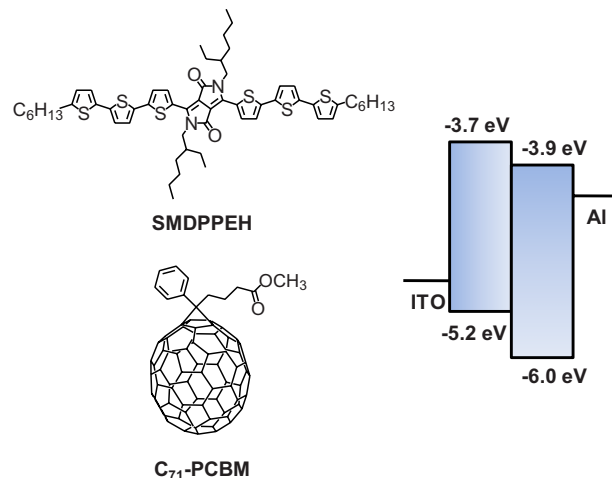

FIG. 1. (Color online) Chemical structures of SMDPPEH and C_{71}-PCBM and approximate HOMO and LUMO levels.

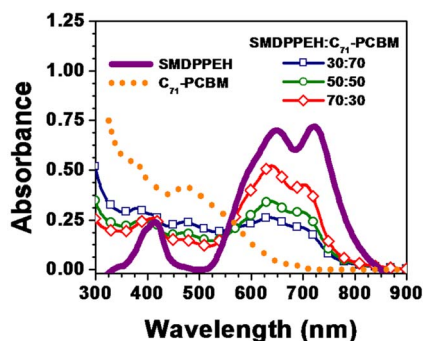[a]Author to whom correspondence should be addressed. Electronic mail: quyen@chem.ucsb.edu.

FIG. 2. (Color online) Optical absorption spectra for SMDPPEH film (solid purple line), C_{71}-PCBM film (orange dotted line), and SMDPPEH:C_{71}-PCBM films as a function of blend ratios: 30:70 (blue open squares), 50:50 (green open circles), and 70:30 (red open diamonds).
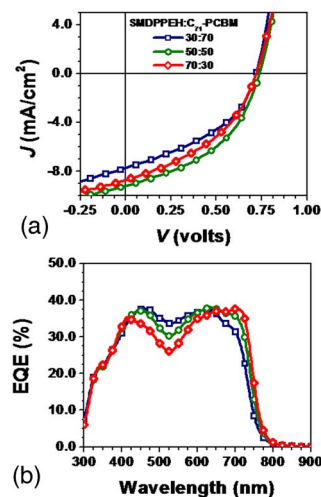

FIG. 3. (Color online) (a) Current density-voltage characteristics and (b) EQE of BHJ solar cells as a function of SMDPPEH: C_{71}-PCBM donor-acceptor ratio: 30:70 (blue open squares), 50:50 (green open circles), and 70:30 (red open diamonds).

was thermally evaporated through a shadow mask giving a device area of 17 mm². Solar cells were characterized under simulated 100 mW/cm² AM1.5G irradiation from a Xe arc lamp with an AM1.5 global filter. Simulator irradiance was characterized using a calibrated spectrometer, and illumination intensity was set using an NREL certified silicon diode with an integrated KG1 optical filter. Quantum efficiencies were measured with a Xe lamp, monochromator, optical chopper, and lock-in amplifier. Photoflux was determined by a calibrated silicon photodiode. Mobility measurements were done using the following diode structures: ITO/PEDOT:PSS/active material/Au for hole mobility and Al/active material/Ba/Al for electron mobility. The charge carrier mobilities were calculated using the space-charge limited current (SCLC) model.[9] Au (1000 Å) and Al (500 Å) electrodes were thermally evaporated at a pressure of 1×10^{-7} Torr at room temperature using a shadow mask (Angstrom Engineering, Inc.). The active layers of all devices obtained were approximately 80 nm as determined by using Ambios XP-100 profilometer. All device fabrication and characterization were conducted under a nitrogen atmosphere.

The film absorption properties of SMDPPEH (solid purple line) and C_{71}-PCBM (dotted orange line) are shown in Fig. 2. The film absorption of SMDPPEH extends up to 800 nm and exhibits two bands centered at 650 nm and 720 nm. The 720 nm band in the film has been observed previously in highly ordered oligothiophene-DPP systems and assigned to strong intermolecular interactions.[5,6] When mixed with the fullerene acceptor, which has an absorption band centered at 480 nm, the resulting blended film gives a very good spectral coverage. The hole mobility of a pure SMDPPEH film is $\sim 1.0 \times 10^{-4}$ cm²/V s based on the SCLC model, which is two orders of magnitude higher than that of the *t*-Boc derivative.[5] The SMDPPEH hole mobility is comparable to that of the widely used donor polymer poly(3-hexyl thiophene) (P3HT).[10,11]

Figure 2 also shows the film absorption spectra of the various blend ratios. It can be seen that as the amount of C_{71}-PCBM decreases, the absorption peak at 480 nm assigned to C_{71}-PCBM decreases with the concomitant increase in the absorption bands at 620 and 710 nm, which are assigned to SMDPPEH. These DPP absorption bands are blueshifted by 20 and 30 nm, respectively, compared to the absorption peaks in the pure film probably due to disruption of the solid state packing of SMDPPEH by the addition of C_{71}-PCBM. A similar blueshift has been observed for the

t-Boc-functionalized oligothiophene-DPP system as well as in conjugated polymers upon the addition of PCBM.[5,12]

Figure 3(a) shows the current density versus voltage (*J-V*) characteristics for devices using 30:70, 50:50, and 70:30 blend ratios of SMDPPEH:C_{71}-PCBM. A summary of photovoltaic properties is given in Table I. The open-circuit voltages (V_{OC})=0.72–0.75 V for the three sets of devices are independent of the blend ratios. This value is slightly higher than that of the *t*-Boc derivative (0.67 V). The slight increase in V_{OC} is consistent with the lower HOMO energy level of SMDPPEH [5.2 eV as determined by ultraviolet photoelectron spectroscopy (UPS)] compared to HOMO energy level of the *t*-Boc derivative (4.9 eV as determined by UPS). In contrast, the short-circuit current densities (J_{SC}) are dependent on the donor-acceptor ratio. The devices based on 30:70 blend ratios delivered a short circuit current density of 7.7 mA/cm² and a fill factor of 0.41 giving a PCE of 2.4%. The short-circuit current density increases to 9.2 mA/cm² when the donor-acceptor blend ratio was changed to 50:50. Combined with a slightly increased fill factor of 0.45, a PCE of 3.0% is achieved, which is the highest reported J_{SC} and PCE for solution-processed, small molecule based BHJ solar cells. Changing the blend ratio to 70:30, however, slightly decreases both J_{SC} and fill factor to 8.7 mA/cm² and 0.35, respectively, giving a PCE of 2.2%.

From the EQE spectra shown in Fig. 3(b), it is clear that the absorption bands at 480, 620, and 710 nm significantly contribute to the device photocurrent in all blend ratios. The EQE spectra show that the contribution of C_{71}-PCBM decreases as its concentration changes from 70% to 50% to 30%. This is consistent with the decrease in the amount of

TABLE I. Summary of hole and electron mobilities and solar cell characteristics of various SMDPPEH:C_{71}-PCBM ratios.

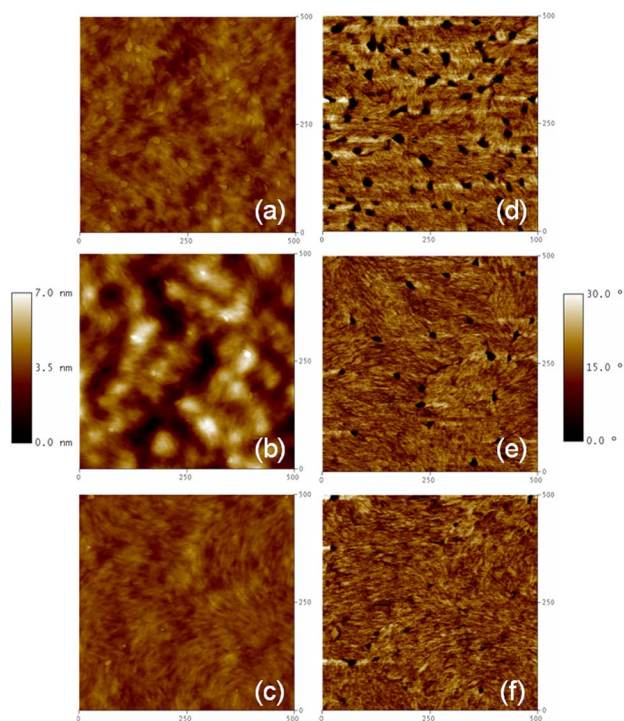| SMDPPEH:C_{71}-PCBM ratio (20 mg/ml)	V_{OC} (V)	J_{SC} (mA/cm²)	FF	η (%)	μ_{hole} (cm²/V s)	$\mu_{electron}$ (cm²/V s)
30:70	0.72	7.7	0.41	2.4	0.4×10^{-4}	6.3×10^{-4}
50:50	0.75	9.2	0.44	3.0	1.0×10^{-4}	4.8×10^{-4}
70:30	0.72	8.7	0.35	2.2	1.6×10^{-4}	1.9×10^{-4}

FIG. 4. (Color online) AFM topographic [(a), (b), and (c)] and phase [(d), (e), and (f)] images of SMDPPEH:C_{71}-PCBM films spun from 2% (w/v) solution at different ratios: 30:70 [(a) and (d)], 50:50 [(b) and (e)], and 70:30 [(c) and (f)]. Images are 500×500 nm^2 in size.

absorption at 480 nm assigned to C_{71}-PCBM in the blended film (see Fig. 2). In contrast, the peaks at 620 and 710 nm in the EQE spectra assigned to SMDPPEH do not significantly change as a function of blend ratio. The EQE does not track with the film absorption at 620 and 710 nm, which double in intensity when the amount of donor is increased from 30% to 70%. One possible explanation is that the donor domains increase in size due to increase in the donor concentration such that some generated excitons may not reach a donor-acceptor interface.[2,13]

Charge carrier mobilities in donor-acceptor films have a crucial effect on the performance of organic solar cells.[14,15] To gain insight into the solar cell performance, hole- and electron-only diodes were fabricated to extract charge carrier mobilities using the SCLC model. The hole and electron mobilites for all the blends are given in Table I. The hole mobilities are of the order of $10^{-4}-10^{-5}$ cm^2/V s and are not significantly different from the measured hole mobility of the pure donor film irrespective of the blend ratio. Similarly, the electron mobilities are also of the order of 10^{-4} cm^2/V s. These carrier mobilities are comparable to those measured for high performance BHJ solar cells based on P3HT:PCBM blends.[16] Importantly, the electron and hole mobilities of the blends are quite balanced, which may help explain the high PCEs observed for this donor-acceptor system.

Atomic force microscopy (AFM) was employed to probe the film morphological properties of the blended films. The AFM images of the as-cast films with different blend ratios are given in Fig. 4. All the films are very smooth, independent of the donor-acceptor blend ratio. The average root mean square surface roughnesses are $\sim$0.3, 0.5, and 0.3 nm for the 30:70, 50:50, and 70:30 blend ratios, respectively. No microscale phase segregation was observed in any of the films. The 30:70 SMDPPEH:C_{71}-PCBM blend shows two

distinct domains in both topographical and phase images, both fiberlike structures and oval-shaped features [Figs. 4(a) and 4(d)]. The domain sizes for the fibers increase as the amount of donor material is increased from 30% to 50% and 70%. The oval-shaped features (i.e., light spots in the height images and dark spots in the phase images) become smaller in size when the amount of C_{71}-PCBM is decreased. From these images, it can be inferred that the fiberlike structures are donor-rich domains and the oval-shaped features are acceptor-rich domains. In all the ratios, a high degree of ordering is observed. Combined with the absence of large phase separation, this favorable ordered network of donor and acceptor domains in the blended film can also help explained the high PCEs observed for the devices.

The PCEs observed with this system are the highest to date for solution processed small molecule BHJ solar cells. Attachment of ethylhexyl groups on the oligothiophene-DPP donor system increases the thermal stability and solubility, lowers the HOMO level, and further enhances film forming properties compared to the *t*-Boc derivative. The high degree of ordering in the pure donor film is maintained in blended films, resulting in good hole mobilities. The HOMO-LUMO energy levels are also different from that *t*-Boc derivative giving a significantly broader optical absorption as well as an increase in the open circuit voltage. With finer tuning of this molecular system and optimization of device processing methods, BHJ devices with efficiencies of larger than 3% are achievable.

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