

Increased open-circuit voltage in bulk-heterojunction solar cells using a C₆₀ derivative

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The fullerene derivative C₆₀-fused N-methyl-2-(3-hexylthiophen-2-yl)pyrrolidine (C₆₀-TH-Hx) is used as the acceptor material in bulk-heterojunction (BHJ) solar cells fabricated with the low band-gap polymer poly[(4,4'-bis(2-ethylhexyl)dithiene[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl]. Direct comparison with BHJ solar cells based on [6,6]-phenyl-C₆₁-butyric methyl ester and Si-PCPDTBT indicates that the C₆₀-TH-Hx acceptor yields a larger open-circuit voltage because of higher lowest unoccupied molecular orbital energy level of C₆₀-TH-Hx. © 2010 American Institute of Physics. [doi:10.1063/1.3518066]

Bulk-heterojunction (BHJ) solar cells comprising a phase separated mixture of a semiconducting (conjugated) donor polymer with a soluble fullerene acceptor are great of interest as next generation renewable energy sources. BHJ solar cells are flexible, rugged, and lightweight. Significant effort has been devoted to develop materials and device structures to facilitate enhanced device performance.¹ Consequently, encouraging progress has been made with power conversion efficiency (PCE) demonstrated at approximately 8%.²⁻⁵ With efficiencies evolving toward 10%, BHJ solar cells will be produced in large area at low cost.¹

There are two main strategies for increasing the PCE: (1) increasing the short circuit current (J_{sc}) by synthesis of low band-gap polymers that absorb light extending into the red or infrared spectral range^{6,7} and (2) obtaining higher open-circuit voltage (V_{oc}) by lowering the energy of the highest occupied molecular orbital (HOMO) of the semiconducting polymer and/or raising the energy of the lowest unoccupied molecular orbital (LUMO) of the fullerene acceptor. In BHJ solar cells, V_{oc} is determined by the difference between the HOMO energy of the semiconducting polymer and LUMO energy of the fullerene derivative.^{8,9}

Many fullerene derivatives have been synthesized and tested in BHJ solar cells. However, [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM) continues to be the best known acceptor. In BHJ solar cells with low band-gap polymers, V_{oc} is limited by the LUMO energy of PC₆₀BM. Although some PC₆₀BM analogs have succeeded in demonstrating higher LUMO values, the performances in solar cells are poor because of their poor charge transport properties.^{10,11}

The C₆₀-fused N-methyl-2-(3-hexylthiophen-2-yl)pyrrolidine [C₆₀-TH-Hx; see Fig. 1(a)] shows high electron mobility of $1.4-1.8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in n-type FETs; i.e., one order of magnitude higher than that of PC₆₀BM.¹² Interestingly, the LUMO energy of C₆₀-TH-Hx is 3.8 eV, well

above that of PC₆₀BM.¹³ Therefore, higher V_{oc} is expected from BHJ solar cells fabricated with C₆₀-TH-Hx as the acceptor.

We have investigated the photovoltaic performance of C₆₀-TH-Hx as an acceptor material in BHJ solar cell. The low band-gap polymer, poly[(4,4'-bis(2-ethylhexyl) dithiene [3,2-b:2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] (Si-PCPDTBT) was used as the donor polymer.¹⁴ Higher V_{oc} (0.675 V) and PCE=4% were obtained. The result implies that C₆₀-TH-Hx is a promising acceptor for high performance BHJ solar cells and supports the strategy of synthesis of fullerene derivatives for BHJ solar cells.

BHJ solar cells were fabricated on an indium tin oxide (ITO) coated glass substrate. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin-casted in air at 5000 rpm for 40 s onto the precleaned ITO/glass. The substrate was subsequently dried for 10 min at 140 °C and then transferred into a N₂ filled glove box. The blend solutions of Si-PCPDTBT:PC₆₀BM (1:2 w/w) and Si-PCPDTBT:C₆₀-TH-Hx (1:2 w/w) in solu-

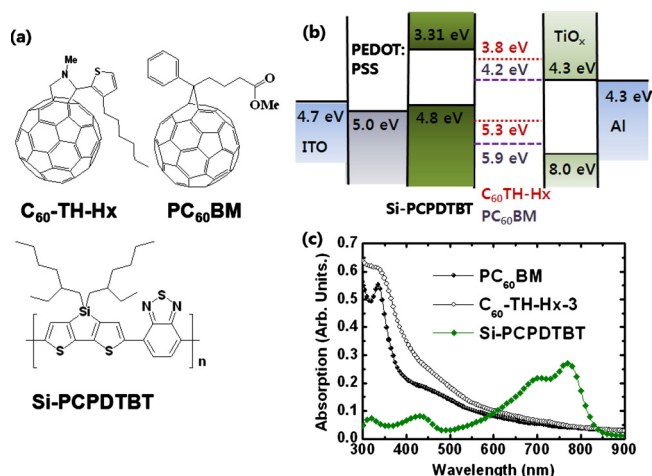


FIG. 1. (Color online) (a) Molecular structures of C₆₀-TH-Hx, PC₆₀BM, and Si-PCPDTBT. (b) Energy level diagrams of the BHJ components. (c) Absorption spectra of PC₆₀BM, C₆₀-TH-Hx, and Si-PCPDTBT.

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tion in 1,2-dichlorobenzene (concentration of 7 mg/ml) were spin-casted onto the PEDOT:PSS/ITO/glass. As described in detail in earlier publications, TiO_x solution (diluted by 1:200 in methanol) was spin-casted in air on top of Si-PCPDTBT:PC₆₀BM or Si-PCPDTBT:C₆₀-TH-Hx BHJ film (5000 rpm for 40 s) as the symmetry-breaking and electron extraction layer.¹⁵ The devices were heated at 80 °C for 10 min in air. Finally, Al metal was deposited by thermal evaporation in high vacuum (4×10^{-6} mbar).

Current-voltage characteristic curves were measured using a Keithley 2400 source meter. Solar cell performance was measured using an Air Mass (AM) 1.5 global solar simulator (100 mW/cm²). An aperture (9.84 mm²) was used on top of the cell to eliminate extrinsic effects such as cross talk, wave guiding, and shadow effect. External quantum efficiency (EQE) spectra were measured using a solar cell spectral response/QE/IPCE measurement system (PV Measurements Inc., Model QE7). All devices were encapsulated with UV epoxy and a cover glass (inside a glove box filled with N₂). Tapping mode atomic force microscope (AFM) images were obtained using a multimode microscope with a Nanoscope IIIa controller (Veeco).

The molecular structures of C₆₀-TH-Hx, PC₆₀BM, and Si-PCPDTBT are presented in Fig. 1(a). C₆₀-TH-Hx was prepared by Prato reaction between fullerene and 3-hexylthiophene-2-carbaldehyde with N-methylglycine refluxing in 1,2-dichlorobenzene for 48 h (45% isolated yield). The reaction provides better product yields and purity compared with the reaction for the synthesis of PC₆₀BM which commonly gives 32%–41% yield.¹⁶ The size of thiophene functional group in C₆₀-TH-Hx is slightly smaller than the benzene ring in PC₆₀BM. In addition, the hexyl side chain on thiophene functional group increases the solubility of fullerene derivative. Thus, good solubility in common solvents was obtained. Energy level diagrams of the two components are depicted in Fig. 1(b).

Figure 1(c) shows the UV-visible (UV-vis) absorption spectra of PC₆₀BM, C₆₀-TH-Hx, and Si-PCPDTBT thin films, respectively. Si-PCPDTBT can harvest photons in the long wavelength range because of the strong absorption from 550 to 850 nm. The absorption spectra of PC₆₀BM and C₆₀-TH-Hx show strong absorptivity below 550 nm. Between 400 and 550 nm, the absorption coefficient of C₆₀-TH-Hx is larger than that of PC₆₀BM. In the short wavelength region below 400 nm, PC₆₀BM exhibits the well-known resolved peaks. However, for the C₆₀-TH-Hx, it is difficult to resolve these peaks in the same wavelength region. This indicates that the change of functional group on fullerene induces the increase of absorption in the visible range and affects on the electronic structure of the fullerene.¹⁷

Initially, to find the optimum blend ratio, devices were prepared and tested with various mixture ratios (1:1, 1:2, and 1:4, w/w). As shown in Fig. 2(a), the performance depends on the amount of C₆₀-TH-Hx. The 1:1 ratio Si-PCPDTBT:C₆₀-TH-Hx yields PCE=1.514% with J_{sc} = 5.084 mA/cm², V_{oc} = 0.608 V, FF = 0.49, while device with 1:2 ratio resulted PCE=4.023% with J_{sc} = 10.62 mA/cm², V_{oc} = 0.675 V, and FF = 0.561. In the case of 1:4 ratio solar cell, the performance was decreased in PCE=3.278% with J_{sc} = 8.922 mA/cm², V_{oc} = 0.644 V, FF = 0.571. We conclude that the optimum Si-PCPDTBT:C₆₀-TH-Hx mixture ratio is

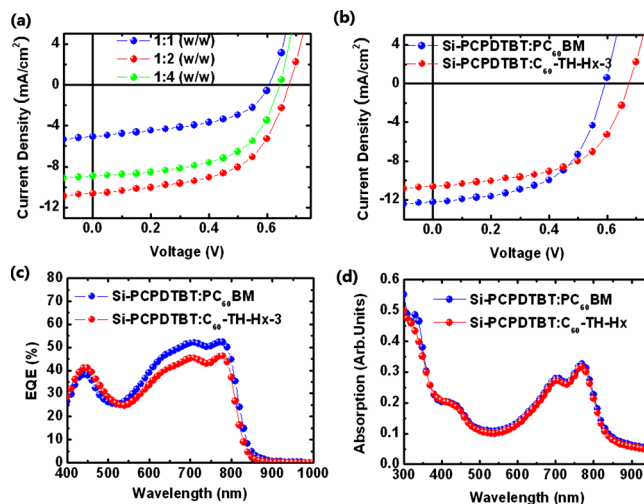


FIG. 2. (Color online) (a) Current density-voltage (J - V) characteristics of Si-PCPDTBT:C₆₀-TH-Hx solar cell with various ratios, 1:1, 1:2, and 1:4 under AM 1.5 G irradiation with 100 mW/cm² intensity from calibrated solar simulator. (b) J - V characteristics of Si-PCPDTBT:PC₆₀BM and Si-PCPDTBT:C₆₀-TH-Hx devices. (c) External quantum efficiencies spectra of BHJ solar cells fabricated by Si-PCPDTBT:PC₆₀BM and Si-PCPDTBT:C₆₀-TH-Hx. (d) UV-vis absorption spectra of Si-PCPDTBT:PC₆₀BM (1:2, w/w) and Si-PCPDTBT:C₆₀-TH-Hx (1:2, w/w) films.

1:2. This result is similar with the optimum condition of Si-PCPDTBT:PC₆₀BM.¹⁴

Figure 2(b) shows the direct comparison of J - V characteristics between the Si-PCPDTBT:C₆₀-TH-Hx solar cell and Si-PCPDTBT:PC₆₀BM solar cell. The solar cell with PC₆₀BM yields the PCE=4.038% with J_{sc} = 12.21 mA/cm², V_{oc} = 0.594 V, and FF = 0.557. This result is consistent with that in the literature.¹⁸ Although Si-PCPDTBT:C₆₀-TH-Hx solar cell shows a slight decrease of (value) in J_{sc} , and PCE \approx 4%; because of the larger V_{oc} (0.675 V) and FF (0.561). Particularly, the V_{oc} increases approximately 0.1 V.

For the Si-PCPDTBT based BHJ solar cells in the literature, V_{oc} was shown around 0.58 V.¹⁴ From the energy level diagram shown in Fig. 1(b), the difference between Si-PCPDTBT HOMO and PC₆₀BM LUMO is around 0.6 eV. For C₆₀-TH-Hx, the LUMO value is higher around 0.4 eV than that of PC₆₀BM. Since the most important factor that determines V_{oc} in BHJ solar cell is the difference between HOMO of donor and LUMO of acceptor, we attribute the increase in V_{oc} obtained with C₆₀-TH-Hx to the higher LUMO value of C₆₀-TH-Hx.

Figure 2(c) shows the EQE measurement for both Si-PCPDTBT:C₆₀-TH-Hx and Si-PCPDTBT:PC₆₀BM solar cells. Overall EQE spectrum of Si-PCPDTBT:PC₆₀BM was higher than that of Si-PCPDTBT:C₆₀-TH-Hx, consistent with J_{sc} as obtained from the J - V characteristics. To analyze EQE spectra, we also measured absorption spectra of Si-PCPDTBT:PC₆₀BM (1:2, w/w) and Si-PCPDTBT:C₆₀-TH-Hx (1:2, w/w) thin films as shown in Fig. 2(d). Comparing the EQE spectra of devices with the absorption spectra of blend films, the photoresponse of devices between 400 and 900 nm is similar to the corresponding absorption spectra of each material. However, since the absorption intensities of each film are almost identical, the decreased EQE in the Si-PCPDTBT:C₆₀-TH-Hx solar cell implies a reduction in the probability of carrier collection.

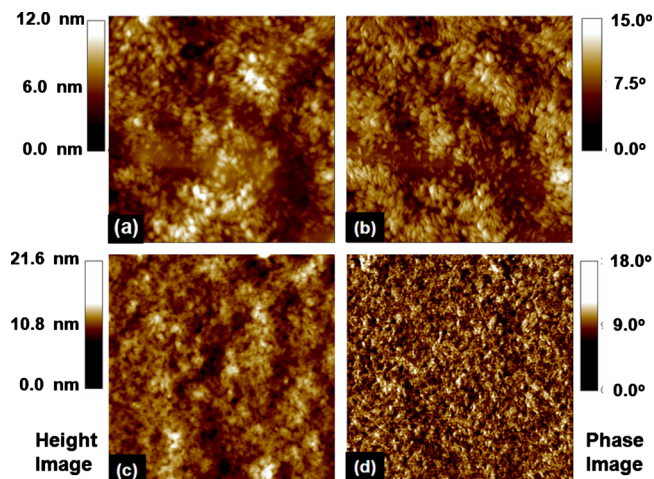


FIG. 3. (Color online) AFM images ($1 \times 1 \mu\text{m}^2$) of films casted from 1,2-dichlorobenzene solution with Si-PCPDTBT:PC₆₀BM or C₆₀-TH-Hx (1:2, w/w): height image (a) and phase image (b) of Si-PCPDTBT:PC₆₀BM blend and height image (c) and phase image (d) of Si-PCPDTBT:C₆₀-TH-Hx.

In general, the performance of BJJ solar cells strongly depends on the nanomorphology of film.^{2,7,14,19} Fig. 3 shows the height and phase images of Si-PCPDTBT:PC₆₀BM and Si-PCPDTBT:C₆₀-TH-Hx films recorded by tapping mode AFM. For the Si-PCPDTBT:PC₆₀BM film, the AFM height image exhibits a rough film morphology consisting of oval shape grains. Apparently, these valleys characterize an uneven surface with route-mean-square (rms) roughness of 1.56 nm for a $1 \times 1 \mu\text{m}^2$ scan area. This feature is also clearly observed in phase image [see Fig. 3(b)]. In the Si-PCPDTBT:C₆₀-TH-Hx film, similar oval shape grains with valleys were observed. However, the roughness of these features is slightly reduced with rms value of 1.39 nm. This distinctive change can be easily recognized in phase image. Therefore, we can conclude that the smaller functional group of C₆₀-TH-Hx provides a more homogeneous surface morphology. The smoother surface morphology suggests fine intermixing of polymer and fullerene in Si-PCPDTBT:C₆₀-TH-Hx blend. The details of the morphology within the film must be explored by an TEM.

According to morphological studies on the mixture of polymer and fullerene derivatives, a too fine intermixing of polymer and fullerene can lead to recombination loss in a BJJ device.^{20,21} For example, Morana and co-workers demonstrated that relatively homogeneous morphology brought relatively low J_{sc} from the comparative study of morphology for polymer-fullerene BJJ solar cells using carbon-bridged (C-PCPDTBT) and silicon-bridged (Si-PCPDTBT) dithiophene donor-acceptor copolymer.¹⁴ In our system, the Si-PPDTBT has well phase separated morphology when it mixed with PC₆₀BM as shown in Figs. 3(a) and 3(b). However, replacement of PC₆₀BM with C₆₀-TH-Hx suggests a decrease in the length scale of the phase separation as shown in Figs. 3(c) and 3(d). Note that the J_{sc} value also decreased slightly in Si-PCPDTBT:C₆₀-TH-Hx device. This suggests that if the phase separation in the device with Si-PCPDTBT:C₆₀-TH-Hx can be changed by controlling the BJJ morphology by using a processing additive,¹⁸ change of solvent,^{2,19} or by fine tuning of blend ratio²² of Si-PCPDTBT and C₆₀-TH-Hx, a higher photocurrent and higher PCE could be achieved in BJJ solar cells using C₆₀-TH-Hx.

In conclusion, we have demonstrated BJJ solar cells using Si-PCPDTBT and newly synthesized fullerene derivative, C₆₀-TH-Hx with PCE > 4% (AM 1.5 G with 100 mW/cm²). The BJJ solar cell using the C₆₀-TH-Hx exhibited higher V_{oc} (0.675 V) and slightly lower J_{sc} in comparison with PC₆₀BM based devices because of more homogeneous phase separation morphology. We anticipate additional improvements in the PCE by further optimizing the morphology of the Si-PCPDTBT:C₆₀-TH-Hx system.

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