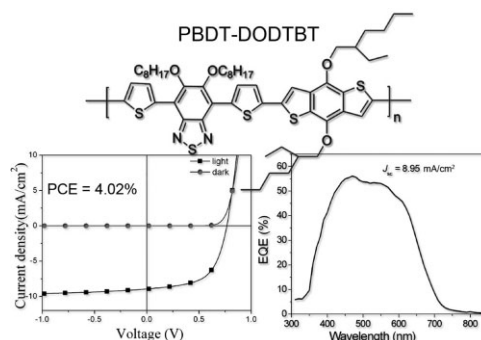


# A High-Mobility Low-Bandgap Copolymer for Efficient Solar Cells<sup>a</sup>

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A new high-mobility low-bandgap polymer, PBDT-DODTBT, based on benzodithiophene and 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzothiadiazole has been synthesized through a standard Stille coupling reaction. The polymer is soluble in common organic solvents, such as chloroform, tetrahydrofuran, and chlorobenzene and has excellent film forming properties. Preliminary studies of the copolymer showed the charge mobility as high as  $7.15 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  from SCLC measurement. Initial photovoltaic cells based on the composite structure of ITO/PEDOT:PSS/PBDT-DODTBT: $\alpha$ PC<sub>71</sub>BM (1:2)/Ca/Al showed an open-circuit voltage of 0.76 V, a power conversion efficiency of 4.02%, and a short-circuit current of  $8.96 \text{ mA} \cdot \text{cm}^{-2}$ .



## Introduction

Polymer solar cells (PSCs) have attracted significant research interest from industry and the academic community for tomorrow's photovoltaics, because of their advantages of easy fabrication, low cost, lightweightedness, and flexibility.<sup>[1]</sup> In the past few years, such solar cells have witnessed tremendous progress. A power conversion

efficiency (PCE) of 5–8% has been reached.<sup>[2]</sup> Although present research indicates that PSCs have a bright future, the efficiency and stability need to be improved towards commercialization. To achieve high performance PSCs, the greatest challenge is to develop low bandgap polymers with broad absorption and high hole mobility.<sup>[3]</sup> The use of an electron rich donor and electron deficient acceptor in the backbone was proved to be the most effective strategy for obtaining low bandgap polymers.<sup>[4]</sup> Coplanar geometries and rigid structures usually lead to high charge mobility.<sup>[5]</sup> Last year, Bo et al.<sup>[6]</sup> reported a planar alternating copolymer, HXS-1, obtained from 2,7-carbazole and 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzothiadiazole, which shows a promising PCE of 5.4% using 1,8-diiodooctane as an additive. However, the disadvantage of this polymer is the solar spectral mismatch between its absorption spectrum and solar irradiation with an absorption edge of  $\approx 650 \text{ nm}$ , which limited the ultimate efficiency of this polymer. Inspired by the purpose of harvesting more sunlight, there is a necessity to further lower the bandgap of this kind of polymer.

In the past two years, copolymers based on electron donating benzodithiophenes (BDTs) have demonstrated great potentials in polymer photovoltaics. A class of BDT-

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<sup>a</sup> Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mcp-journal.de>, or from the author.

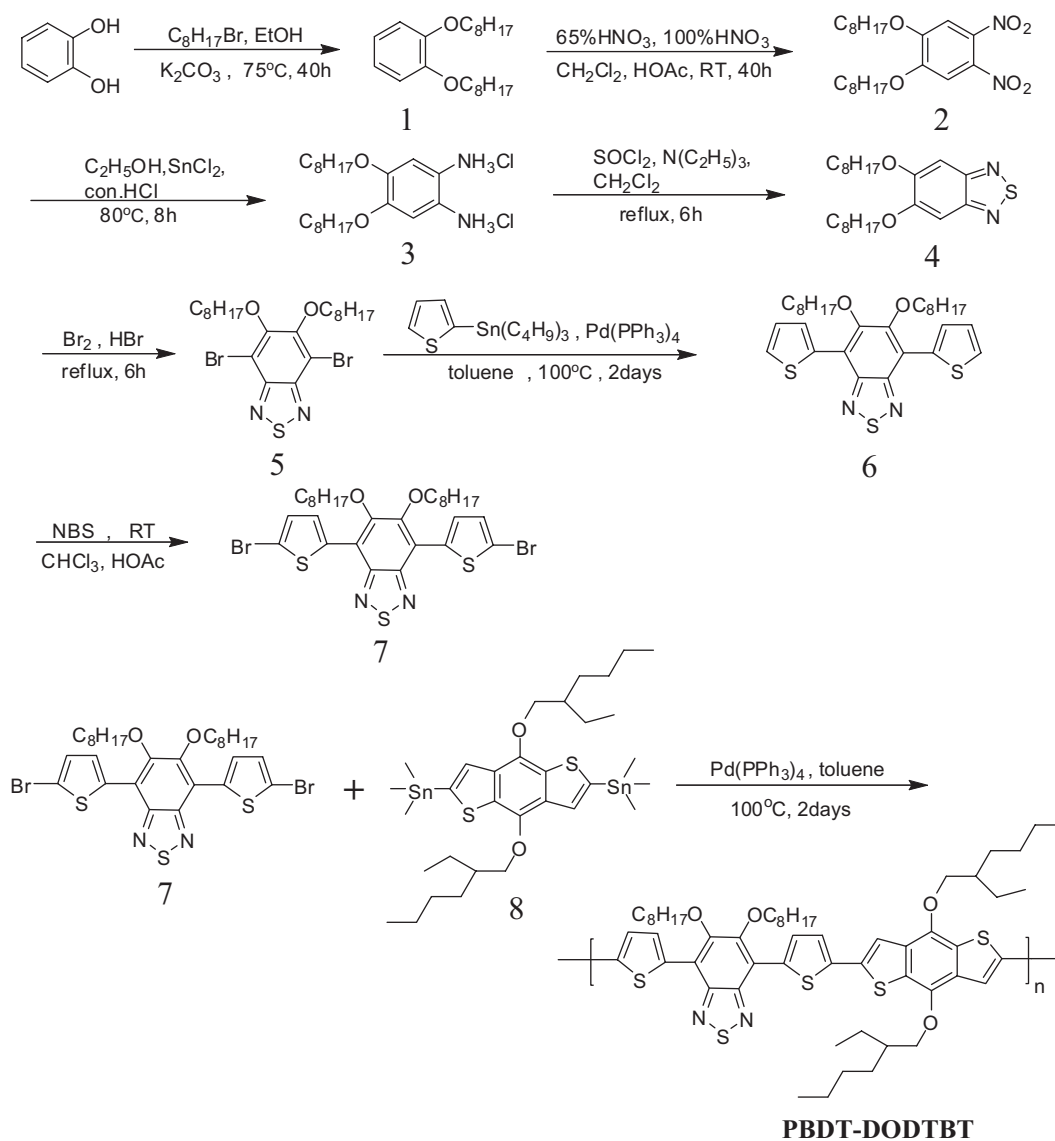
based copolymers with optimized electronic and optical properties led to promising PCEs as high as 7.4%.<sup>[7]</sup> By fusing a benzene with two flanking electron donating thiophene units, the BDT unit seems to be a more electron-rich building block than those units such as fluorene or carbazole, moreover, BDT has an entirely planar and symmetrical structure, which is beneficial to obtaining high charge mobility. Taking all this into account, copolymerizing BDT with 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzothiadiazole should lead to some interesting features such as broad absorption, high mobility, etc.

In this work, a new copolymer, PBDT-DODTBT, obtained from BDT units and 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzothiadiazole (DODTBT), as shown in Scheme 1, was designed, synthesized, and used in solar cells. This low-

bandgap polymer shows good solubility in common organic solvents, broad absorption in the wavelength range from 360 to 758 nm, and a high hole mobility up to  $7.15 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ . The polymer solar cells based on PBDT-DODTBT as the donor and PC<sub>71</sub>BM as the acceptor exhibit a high PCE of 4.02% under the AM 1.5G one sun condition.

## Experimental Part

The general synthetic route of the comonomers and copolymer is sketched in Scheme 1 and the detailed synthesis is given in the Supporting Information. Device fabrication and characterization are also shown in the Supporting Information.



■ Scheme 1. Synthesis of comonomers and the polymer PBTD-DODTBT.

## Results and Discussion

### Synthesis and Characterization of PBBDT-DODTBT

The synthetic routes of the comonomers and the corresponding polymer are outlined in Scheme 1. Compounds **5**<sup>[8]</sup> and **8**<sup>[9]</sup> were prepared according to the known literature procedures. Compound **5** underwent a Stille coupling reaction with 2-(tributylstannyl) thiophene to obtain compound **6**, this step revealed a quite satisfactory yield. A dibromination step of compound **6** using *N*-bromosuccinimide (NBS) as brominating agent gave comonomer **7** in 78% yield. Compound **7** copolymerized with compound **8** through a Stille coupling reaction to afford the target polymer, PBBDT-DODTBT. The polymer was purified by sequential Soxhlet extraction with methanol, hexane, and CHCl<sub>3</sub>. The CHCl<sub>3</sub> fraction was then reduced in volume, precipitated into methanol, and collected by filtration, to yield a purple-dark solid with a 91% yield. The chemical structure of the polymer was verified by <sup>1</sup>H NMR spectroscopy as shown in Figure 1. The copolymer displayed excellent solubility in common solvents such as tetrahydrofuran (THF), CHCl<sub>3</sub>, dichlorobenzene, and so forth. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) in THF solution relative to polystyrene standards. The weight-average molecular weight ( $\bar{M}_w$ ) was 25.7 kg · mol<sup>-1</sup>, with a PDI of 2.7.

### Thermal Stability

The thermal stability of the polymer was investigated by thermogravimetric analysis (TGA) as shown in Figure 2. The

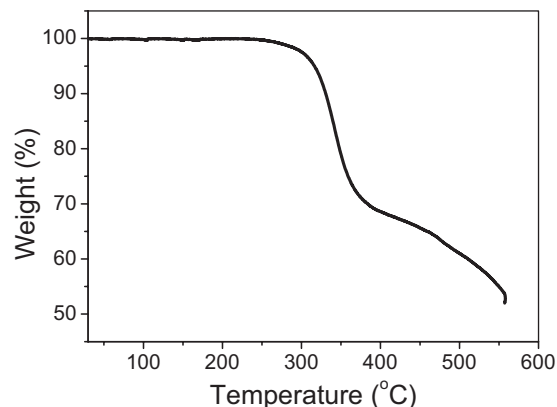


Figure 2. TGA curve of PBBDT-DODTBT with a heating rate of 20 °C · min<sup>-1</sup>.

TGA analysis reveals that the 5% weight loss temperature ( $T_d$ ) of PBBDT-DODTBT is 323 °C in air, mainly because of the removal of the alkoxy groups. The thermal stability of the polymer is favorable for its application in PSCs and other optoelectronic devices.

### Optical Properties

The photophysical characteristics of PBBDT-DODTBT were investigated by UV-vis absorption spectra in dilute chloroform solution and in a solid film spin-coated on a quartz substrate. Figure 3a shows the UV-vis absorption spectra of the polymer solution and film. The absorption peak of the polymer in solution was 548 nm, whereas in the film state

the absorption peak shifted to 600 nm with the onset wavelength at 758 nm. The absorption showed a red shift from the solution to the film probably resulting from the stronger interchain interaction of the polymer in the solid state.<sup>[10]</sup> The optical bandgap ( $E_g$ ) was calculated from the onset of the absorption to be 1.64 eV, which is lower than that of HXS-1 (ca. 1.95 eV). These results indicate that BDT is a more efficient electron rich low band-gap unit compared to that of carbazole.

### Electrochemical Properties

In order to investigate the electrochemical properties of PBBDT-DODTBT, and estimate its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, cyclic voltammetry (CV) was carried out in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in

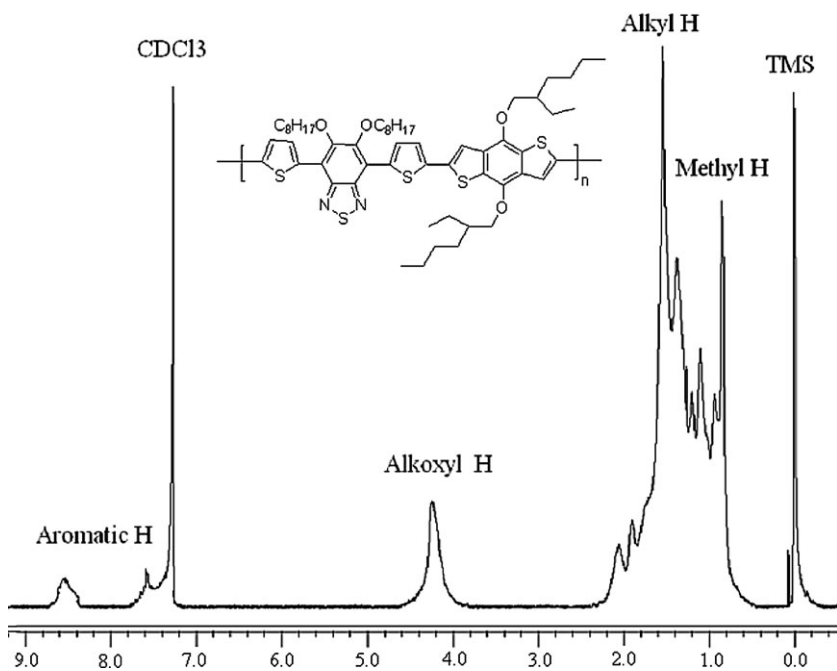


Figure 1. <sup>1</sup>H NMR spectrum of PBBDT-DODTBT in CDCl<sub>3</sub>.

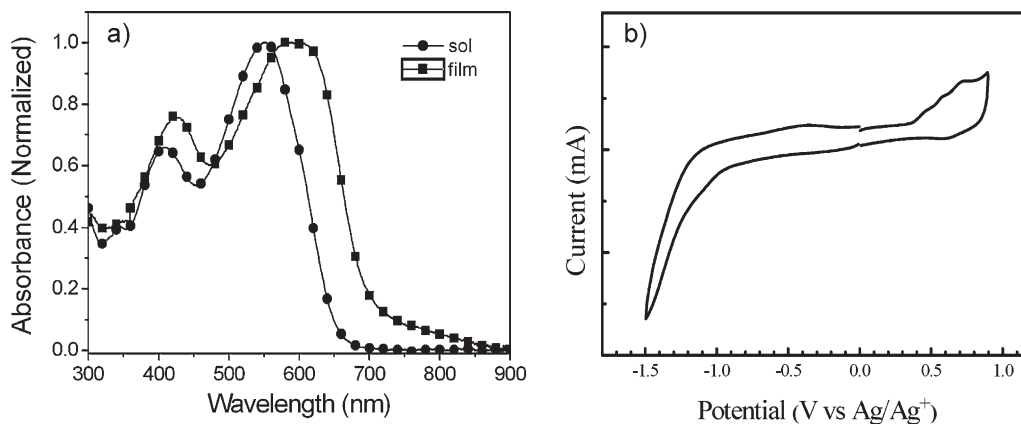


Figure 3. a) UV-Vis absorption spectra of PBDT-DODTBT in chloroform solution and in film state. b) Cyclic voltammogram of a PBDT-DODTBT film on a platinum electrode in  $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ Bu}_4\text{NPF}_6$ ,  $\text{CH}_3\text{CN}$  solution at a scanning rate of  $50 \text{ mV} \cdot \text{s}^{-1}$ .

acetonitrile ( $\text{CH}_3\text{CN}$ ) at room temperature under argon with a scanning rate of  $50 \text{ mV} \cdot \text{s}^{-1}$ . All the potentials are reported vs.  $\text{Ag}/\text{Ag}^+$  with the ferrocene/ferrocenium couple as an internal standard. The CV curve of the polymer is shown in Figure 3b. The copolymer exhibited a quasi-reversible oxidation and irreversible reduction. From the value of the onset oxidation potential and the onset reduction potential of the polymer, the HOMO and the LUMO levels were estimated to be  $-5.17$  and  $-3.61$  eV, respectively.<sup>[11]</sup> The HOMO level is lower than that of P3HT ( $-4.76$  eV),<sup>[12]</sup> which is expected to be more stable than that of P3HT. We calculated the HOMO and LUMO energy levels of the polymer according to the equations:<sup>[13]</sup>  $\text{HOMO} = -e(E_{\text{on}}^{\text{ox}} + 4.71 \text{ V})$ ,  $\text{LUMO} = -e(E_{\text{on}}^{\text{red}} + 4.71 \text{ V})$ . The corresponding electrochemical bandgap is  $1.56$  eV, which is similar to the optical bandgap within the experimental error.

### X-Ray Analysis

To evaluate the crystallinity of the polymer, X-ray diffraction measurements were taken for the spin-coated films on  $\text{SiO}_2$  substrate. Figure 4 shows the XRD spectrum of the thin film of PBDT-DODTBT at room temperature. It is clear that there is no apparent peak at the small angle region, but the peak at  $24.7^\circ$  corresponds to a short  $\pi$ - $\pi$  distance of  $3.6 \text{ \AA}$  between the polymer main chains, which is even shorter than that of HXS-1, indicating that PBDT-DODTBT possesses strong long range  $\pi$ - $\pi$  stacking crystallinity.<sup>[14]</sup>

### Hole Mobility

Hole mobility is an important parameter of the conjugated polymers for photovoltaic applications. We investigated the hole mobility of PBDT-DODTBT with the space-charge-limited current (SCLC) model with a device structure of indium/tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):

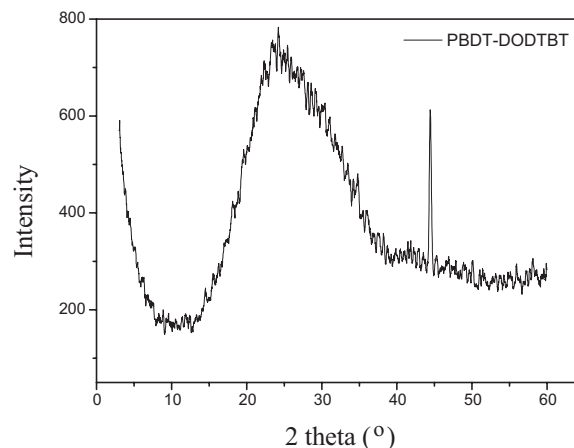


Figure 4. X-Ray diffraction pattern of a powdery PBDT-DODTBT sample.

poly(styrenesulfonate) (PEDOT:PSS)/PBDT-DODTBT (210 nm)/Au (100 nm). Details concerning the SCLC method are shown in the Supporting Information. The results are plotted as  $\ln(Jd^3/V^2)$  vs.  $(V/d)^{0.5}$ , as shown in Figure 2c. Herein,  $J$  stands for current density,  $d$  is the thickness of the device, and  $V = V_{\text{appl}} - V_{\text{bi}}$ , where  $V_{\text{appl}}$  is the applied potential and  $V_{\text{bi}}$  is the built-in potential.

$$J_{\text{SCLC}} = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0 \frac{(V - V_{\text{bi}})^2}{d^3} \exp \left[ 0.89 \gamma \sqrt{\frac{V - V_{\text{bi}}}{d}} \right] \quad (1)$$

According to Equation (1)<sup>[15]</sup> and Figure 5, the hole mobility of the polymer is evaluated to be  $7.15 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ . The high hole mobility is mostly because of the rigidity, short  $\pi$ - $\pi$  stacking distance, and planarity of the polymer backbone. Obviously, the hole mobility of PBDT-DODTBT is relatively high as the photovoltaic donor material in PSCs. The high hole mobility

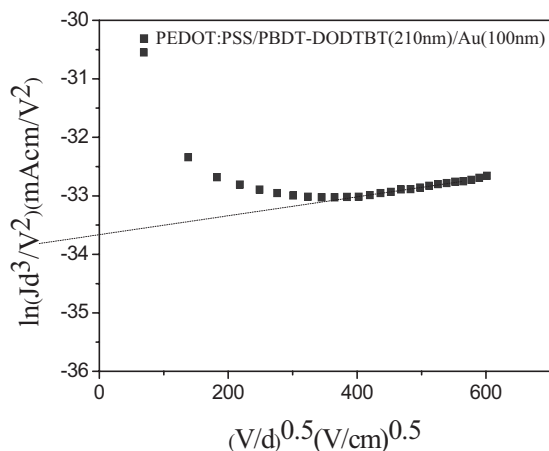


Figure 5. Current/voltage data from the device ITO/PEDOT:PSS/polymer/Au, plotted in the format of  $\ln(Jd^3/V^2)$  vs.  $(V/d)^{0.5}$ , where  $J$  is the current density and  $d$  is the thickness of the polymer layer.

of the polymer is expected to facilitate charge transport and reduce recombination loss in the PSCs, therefore, it can lead to an improved device performance.

### Photovoltaic Properties

All these characteristics (low bandgap, high hole mobility, preferred energy levels, etc) indicate that the copolymer PBDT-DODTBT should be an excellent candidate for photovoltaic applications. Therefore, bulk heterojunction PSCs with the use of PBDT-DODTBT as the donor and fullerene derivative PC<sub>71</sub>BM as the acceptor were fabricated with the structure of ITO/PEDOT:PSS/PBDT-DODTBT:PC<sub>71</sub>BM (1:2)/Ca/Al. Details concerning device fabrication and characterization are provided in the Supporting Information. Figure 6 shows a typical current

density/voltage ( $J/V$ ) curve and the external quantum efficiency (EQE) of the polymer solar cells. The device demonstrated a high short-circuit current density ( $J_{sc}$ ) of  $8.96 \text{ mA} \cdot \text{cm}^{-2}$ , an open-circuit voltage ( $V_{oc}$ ) of  $0.76 \text{ V}$ , and a good fill factor (FF) of  $0.59$ . A high FF indicates a balanced transport in the PSCs. The resulting PCE reached up to  $4.02\%$  without annealing and additives. The complementary absorbance of PC<sub>71</sub>BM and PBDT-DODTBT gives a relatively high photoconversion efficiency over the wavelength range of  $390\text{--}630 \text{ nm}$ , with monochromatic EQE values above  $40\%$ . It is worth noting that the  $J_{sc}$  calculated by integrating the EQE curve with an AM 1.5G reference spectrum agrees well with the  $J_{sc}$  value obtained from the  $J/V$  measurements.<sup>[16]</sup> Initial results are promising and we are currently aiming at trying this polymer with other electron acceptors and different device conditions.

### Morphology

The morphology of the photoactive layer is very important for the performance of PSCs, and in some cases the performance of the device strongly depends on its morphological features.<sup>[17]</sup>

Therefore, we used atomic force microscopy (AFM) to investigate the surface morphology of the active layer. AFM topographic and phase images prepared of PBDT-DODTBT:PC<sub>71</sub>BM (1: 2) in dichlorobenzene are shown in Figure 7. The film is smooth [RMS (root mean square) roughness =  $1.3 \text{ nm}$ ] and connective between the neighboring domains from the topographic image, which can in part explain the high hole mobility of this copolymer. In addition, from AFM, the polymer and fullerene domains are homogeneously distributed throughout the surface of the film, in other words, the nanometer-scale interpenetrating network can be formed in this blend, which can benefit not only the charge separation but also the charge transport, therefore, leading to a high FF. The very fine

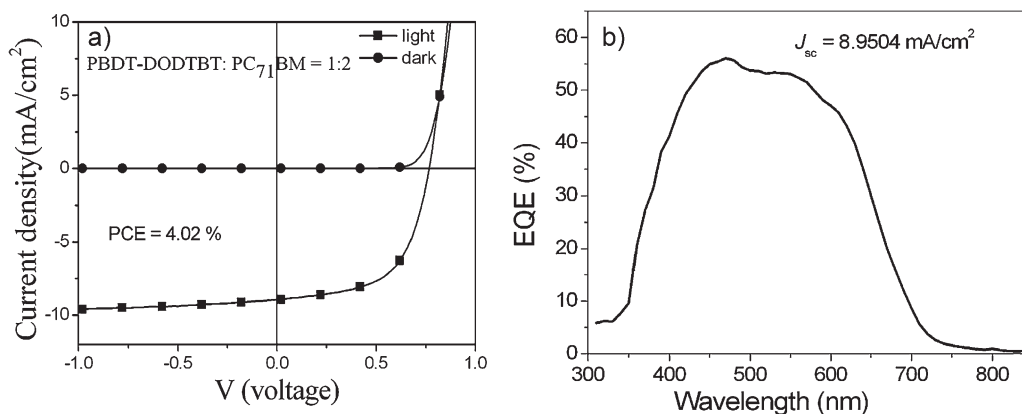


Figure 6. a) Current density/voltage ( $J/V$ ) curves of a PBDT-DODTBT:PC<sub>71</sub>BM (1:2, w/w) device under  $100 \text{ mW} \cdot \text{cm}^{-2}$ , AM 1.5 solar irradiation and in the dark. b) EQE of the PBDT-DODTBT:PC<sub>71</sub>BM BHJ solar cell.



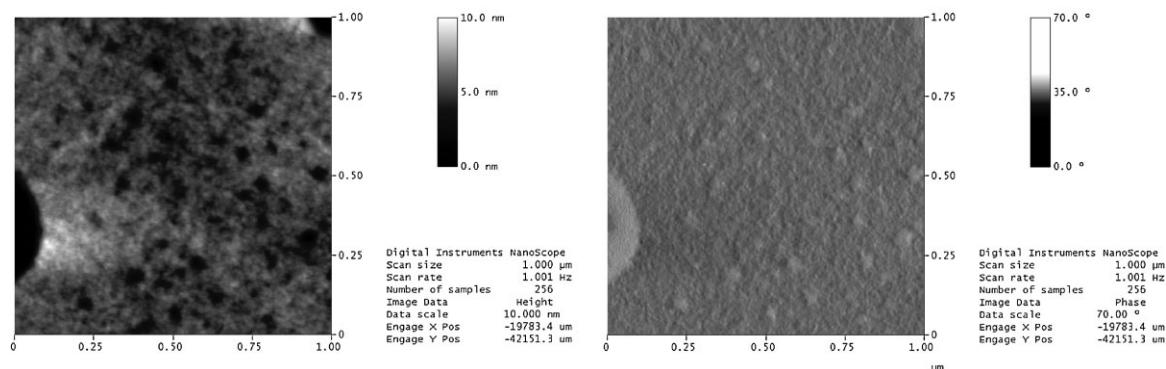


Figure 7. AFM images of PBDT-DODTBT/PC<sub>71</sub>BM (1:2) prepared from 1,2-dichlorobenzene solution: topographic image (left) and phase image (right).

domains and no large phases contributed partially to the high photovoltaic performance of the polymer.

## Conclusion

We have designed and synthesized a new high mobility low bandgap polymer, PBDT-DODTBT, based on benzodithiophene and 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzothiadiazole through a Stille coupling reaction in a good yield. Preliminary studies of the copolymer showed the hole mobility as high as  $7.15 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  from the SCLC model. Broad and good absorption, and high hole mobility combined with a nanometer-scale morphology leads to a polymer with promising photovoltaic properties. Initial bulk heterojunction solar cells based on the blends of PBDT-DODTBT with PC<sub>71</sub>BM had a high PCE up to 4% under  $100 \text{ mW} \cdot \text{cm}^{-2}$ , AM 1.5 solar illumination. A high PCE from the PSCs based on PBDT-DODTBT is ascribed to high EQE plateau values between 390–630 nm over 40%, high mobility, and good morphology. Optimization of PSCs based on PBDT-DODTBT is underway, a PCE of higher than 5% can be anticipated through careful device engineering. We firmly believe this polymer has the promising potential for future photovoltaics.

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