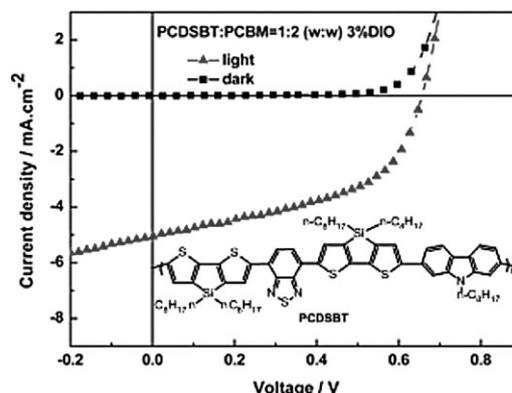


Synthesis and Photovoltaic Properties of a Poly(2,7-carbazole) Derivative Based on Dithienosilole and Benzothiadiazole

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A low bandgap poly(2,7-carbazole) derivative PCDSBT containing dithienosilole and benzothiadiazole is synthesized by Stille polymerization. The incorporation of dithienosilole and carbazole causes PCDSBT to have a broad absorption from 350 to 800 nm and a relatively low HOMO level. Solar cell devices fabricated by blending PCDSBT with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) at a 1:2 weight ratio in a mixed solvent of 3% (by volume), 1,8-diiodooctane, and 97% dichlorobenzene lead to a power conversion efficiency of 1.65% under the illumination of AM 1.5G (100 mW · cm⁻²).

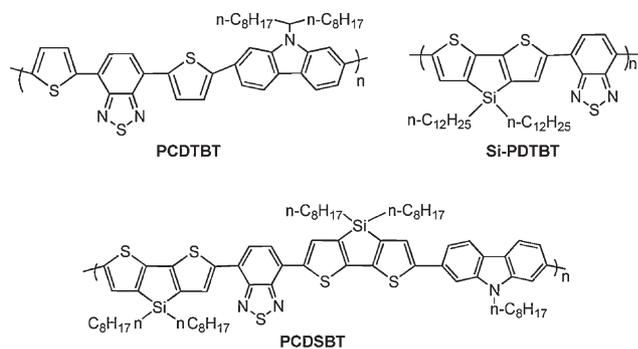


Introduction

Polymer bulk heterojunction (BHJ) solar cells based on conjugated polymer donor and fullerene acceptor blends have attracted considerable research interest over previous decades.^[1–7] Up to now, BHJ solar cell performances have been greatly improved with power conversion efficiencies (PCEs) of over 8%.^[8] To achieve the predicted 10% efficiency,^[9] the open circuit voltage (V_{oc}) and short circuit current (J_{sc}) are two important parameters of any solar cell to be improved. In polymer BHJ solar cells, the above two parameters mainly depend on the energy level, bandgap, and the hole mobility of the conjugated polymer. To obtain high V_{oc} and J_{sc} simultaneously, much effort has been made to approach an “ideal photovoltaic polymer” that possesses a low highest occupied molecular orbital (HOMO) energy level of -5.4 eV and a small bandgap of 1.5 eV.^[9,10]

To solve this problem, several classes of low bandgap polymers as the donor have been developed to better harvest the solar spectrum with deeper HOMO energies that can potentially increase V_{oc} .^[10–12] Among the various conjugated polymers, poly(2,7-carbazole) derivatives with deep HOMO levels and thus a high V_{oc} are excellent potential candidates for BHJ solar cells owing to their air stability, and tunable optical and electrochemical properties.^[13–15] Leclerc et al. reported a low bandgap copolymer based on the carbazole unit, namely poly[*N*-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT).^[16] The optical bandgap of this polymer is 1.88 eV with the HOMO and LUMO energy levels at -5.45 and -3.60 eV, respectively. The photovoltaic devices based on PCDTBT and PC₇₁BM showed a high PCE at 6.1% with a V_{oc} of 0.88 V and a J_{sc} of 10.6 mA · cm⁻².^[17] Although the V_{oc} of PCDTBT is high, it seems that the J_{sc} is limited by weak light absorption at long wavelengths between 700 and 800 nm. Therefore, if we can keep its high V_{oc} , but improve its J_{sc} simultaneously by modifying the polymer structure, it could be expected to achieve an overall

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■ Scheme 1. Structures of PCDTBT, Si-PDTBT, and PCDSBT.

high PCE. Recently, a low bandgap dithienosilole-containing polymer named poly[(4,4'-didodecyl)dithieno[3,2-*b*:2',3'-*d*]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl] (Si-PDTBT) was synthesized.^[18,19] With a broad absorption spectrum from 350 to 850 nm, devices fabricated from this polymer and PC₇₁BM gave a J_{sc} as high as $17.3 \text{ mA} \cdot \text{cm}^{-2}$, however, a low V_{oc} (0.57 V) was obtained because of its relatively high HOMO level. As shown by this polymer, dithienosilole has a unique property of narrowing the bandgap.^[20–24] Meanwhile, with such an enlarged coplanar skeleton, the less steric hindrance created in the dithienosilole core will lead to good π - π stacking and a high hole mobility of the polymer.^[25–27]

Thus, our intention in this work is to combine these two types of polymers structurally, and hopefully take advantage of their combined properties for better photovoltaic performance. Specifically, based on the study above, carbazole with a deep HOMO as the electron-rich moieties could lead to higher values for V_{oc} and dithienosilole may help to lower the bandgap for a better solar spectrum match and a better J_{sc} . By replacing the two thiophene units in the first polymer PCDTBT^[17] with two dithienosilole units used in the second type of polymer,^[18,19] we synthesized and characterized a new low bandgap polymer named poly[*N*-9'-octyl-2,7-carbazole-*alt*-5,5-(4',7'-di(4,4'-dioctyl-dithieno[3,2-*b*:2',3'-*d*]silole)-2-yl-2',1',3'-benzothiadiazole)] (PCDSBT, shown in Scheme 1) as a promising electron donor polymer for BHJ solar cells. The synthesis, optical and electrochemical properties, along with the photovoltaic device performances of PCDSBT are described. BHJ solar cell devices prepared by blending PCDSBT with PC₆₁BM (denoted PCBM) at a 1:2 weight ratio in a mixed solvent of 3% (by volume) 1,8-diiodooctane (DIO), and 97% dichlorobenzene leads to a PCE of 1.65%.

Experimental Section

Instruments and Measurements

The ¹H NMR spectra were recorded on a Bruker AV400 Spectrometer. Gel permeation chromatography (GPC) analysis was

conducted on a Waters 510 system using polystyrene as the standard and tetrahydrofuran (THF) as the eluent at a flow rate of $1.0 \text{ mL} \cdot \text{min}^{-1}$ at 40°C . Thermal gravimetric analysis (TGA) was performed on a NETZSCH STA 409PC instrument under purified nitrogen gas flow with a $10^\circ\text{C} \cdot \text{min}^{-1}$ heating rate. The temperature of degradation (T_d) corresponds to a 5% weight loss. The UV-vis spectra were obtained with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer-based electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. CH₃CN was distilled over calcium hydride under dry argon immediately prior to use. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M) in CH₃CN was used as the supporting electrolyte, and the scan rate was $100 \text{ mV} \cdot \text{s}^{-1}$. HOMO and LUMO levels were estimated relative to the energy level of a ferrocene reference (4.8 eV below vacuum level).^[28] Hole mobility was measured according to a similar method described in the literature, using a diode configuration of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/PCDSBT/Al by taking dark current in the range of 0–6 V and fitting the results to a space charge limited form, where the space charge limited current (SCLC) is described by:

$$J = 9\epsilon_0\epsilon_r\mu_h V^2 / 8L^3 \quad (1)$$

where J is the current density, L is the film thickness of the active layer, μ_h is the hole mobility, ϵ_r is the relative dielectric constant of the transport medium, ϵ_0 is the permittivity of free space, V is the internal voltage in the device, and $V = V_{app} - V_r - V_{bi}$, where V_{app} is the applied voltage to the device, V_r is the voltage drop as a result of contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage attributable to the relative work function difference of the two electrodes. Atomic force microscopy (AFM) studies were performed using a Digital Instruments Dimension 3100 microscope in the tapping mode.

Device Fabrication

All the photovoltaic devices were fabricated by using a common process.^[6] An ITO-coated glass substrate was cleaned stepwise in detergent, water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried in a vacuum oven at 60°C for 12 h. A thin layer ($\approx 40 \text{ nm}$) of PEDOT:PSS (Baytron P VP AI4083) was spin-coated onto the ITO surface in air. After being baked at 150°C for 30 min, the ITO/PEDOT:PSS substrate was transferred into an argon filled glove box ($<0.1 \text{ ppm O}_2$ and H_2O). The active layer was then spin-coated from a blend of polymer ($20 \text{ mg} \cdot \text{mL}^{-1}$)/PCBM solution in *o*-dichlorobenzene (ODCB) at 1500 rpm for 1 min on the ITO/PEDOT:PSS substrate to obtain an active layer with a thickness of 70–80 nm. Subsequently, the device was completed by depositing 0.8 nm thick LiF and 80 nm thick Al under $<10^{-6}$ torr pressure. The active area of the device was $\approx 4 \text{ mm}^2$.

Materials and Reagents

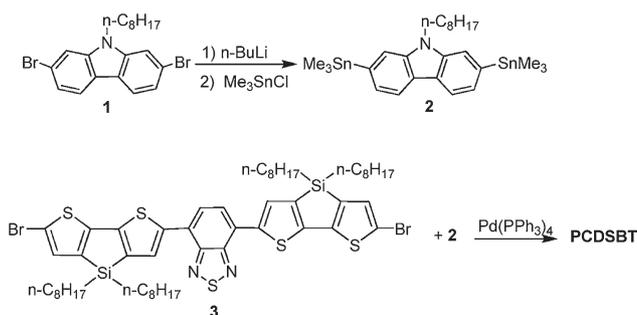
All reagents were purchased from commercial sources. Solvents were purified by standard procedures. Reactions were carried out under argon unless otherwise noted. 2,7-Dibromo-*N*-octyl-carbazole (**1**)^[29] and 4,7-di(4,4'-dioctyl-5-bromodithieno[3,2-*b*:2',3'-*d*]silole)-2-yl-2,1,3-benzothiadiazole (**3**)^[30–32] were prepared according to the reported methods. All other compounds were synthesized following procedures described below as shown in Scheme 2.

Synthesis of 2,7-Di(trimethyltin)-*N*-octyl-carbazole (**2**)^[33]

Compound **1** (1.5 g, 3.43 mmol) was dissolved in 50 mL of dry THF and cooled to -78°C . A solution of *n*-BuLi in hexane (3.3 mL, 8.23 mmol, 2.5 M) was added over a 15 min period and the mixture was stirred for 1 h at -78°C . A solution of trimethyltin chloride in THF (8.9 mL, 8.9 mmol) was subsequently added, and the mixture was allowed to warm to room temperature and stirred overnight. The reaction was next quenched by adding 100 mL of water, and the aqueous layer was extracted with ethyl acetate. The organic phase was washed with water and dried over Na_2SO_4 . After filtration, the solvent was evaporated to afford a brown oil which was used for the next step without further purification ($\approx 90\%$ purity). $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 8.08 (d, 2H), 7.51 (s, 2H), 7.33 (d, 2H), 4.33 (t, 2H), 1.89 (m, 2H), 1.42–1.20 (m, 10H), 0.85–0.93 (m, 3H), 0.37 (s, 18H).

Synthesis of PCDSBT

Compound **2** (229 mg, 0.38 mmol) and compound **3** (406 mg, 0.36 mmol) were dissolved in a mixture of 20 mL of dry toluene and 5 mL of dry *N,N*-dimethylformamide (DMF). The mixture was purged with argon for 10 min, and then $\text{Pd}(\text{PPh}_3)_4$ (132 mg, 0.114 mmol) was added. After being purged with argon for another 10 min, the mixture was refluxed at 110°C for 24 h, the solvent was evaporated, and 100 mL of methanol was added, resulting in a precipitate (note: adding the product polymer in the reaction solvent to a large amount of methanol did not produce a precipitate). The mixture was filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform, respectively. The chloroform fraction was concentrated to afford a dark solid, which was further purified by chromatography using chloroform as the eluent. The final polymer PCDSBT was obtained as a black solid after removal of chloroform (224 mg, 50%, $\bar{M}_n = 11.7$ KDa, PDI = 1.8). $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 8.13–7.42 (br, 12H), 4.28 (br, 2H), 1.90 (br, 2H), 1.42–1.20 (br, 66H), 0.85–0.93 (br, 15H). Anal. calcd for $(\text{C}_{74}\text{H}_{57}\text{N}_3\text{S}_5\text{Si}_2)_n$ (1245.09) $_n$: C 71.39, H 7.63, N 3.37; found: C 69.94, H 6.66, N 3.33.



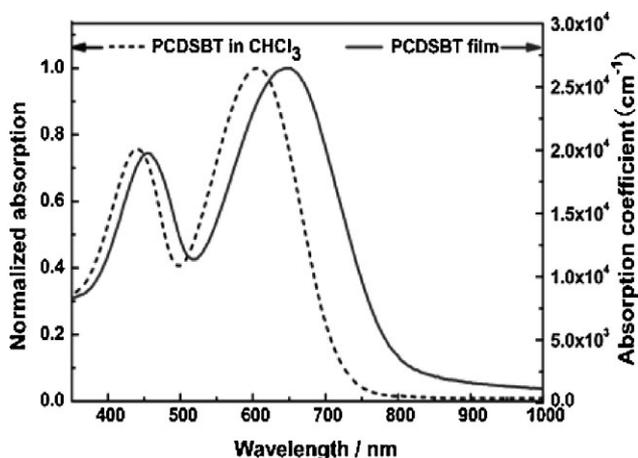
■ Scheme 2. Synthesis and structure of polymer PCDSBT.

Results and Discussion

The low bandgap polymer PCDSBT was synthesized by Stille polymerization of the monomers **2** and **3** using palladium(0) tetrakis(triphenylphosphine) ($\text{Pd}(\text{PPh}_3)_4$) as the catalyst in a mixed solvent of toluene and DMF (4:1). The polymer has readily good solubility in common organic solvents such as chloroform and dichlorobenzene owing to the existence of five octyl chains in each repeat unit. The number average molecular weight (\bar{M}_n) of PCDSBT is 11.7 kDa with a polydispersity index (PDI) of 1.84 determined by GPC. The molecular weight is not as high as desired, probably because of the low reactivity of **2** in the Stille polymerization.^[34] An attempt was made to use the Suzuki coupling method^[35] to obtain a higher molecular weight polymer, however, because of instability of the dithienosilole unit in the alkaline reaction,^[36] no desired polymer was obtained. Other methods to improve the molecular weight such as changing the Stille coupling catalyst system^[34] and using a microwave-assisted Stille polycondensation method^[10,19] are to be tested further. TGA suggests that PCDSBT exhibits good stability with a T_d greater than 367°C under a N_2 atmosphere.

Optical and Electrochemical Properties

Figure 1 presents absorption spectra of PCDSBT in dilute chloroform solution and in the solid state. The absorption bands of PCDSBT in dilute chloroform solution are at 440 and 603 nm, while PCDTBT has two peaks at 390 and 545 nm.^[16] Indeed, as was expected, replacing the thienylene electron-rich block in PCDTBT with dithienosilole causes a significant red-shift of the UV-vis absorption. Compared with the solution absorption spectrum, the PCDSBT thin film exhibits two absorption peaks at 455 and 650 nm with a maximum absorption coefficient of 2.7×10^4



■ Figure 1. Absorption spectra of PCDSBT in dilute chloroform solution (dashed line) and as a film (solid line).



Figure 2. Cyclic voltammograms of PCDSBT films on a platinum electrode in 0.1 mol · L⁻¹ Bu₄NPF₆, CH₃CN solution.

cm⁻¹ (calculated from the thin film absorption and the film thickness). A red-shifted absorption was observed as expected in the solid state. The optical bandgap of PCDSBT is estimated to be 1.53 eV by extrapolation of the low energy edge of the absorption spectrum, compared with 1.88 eV for PCDTBT.^[16]

The HOMO and LUMO levels of PCDSBT were measured by electrochemical CV. Figure 2 displays the CV curves for PCDSBT. Both the anodic oxidation and cathodic reduction processes are reversible, with the HOMO and LUMO levels of PCDSBT at -5.28 and -3.29 eV, respectively. The HOMO level is 0.23 eV lower than that of Si-PDTBT (-5.05 eV) because of the presence of the low HOMO lying carbazole unit, which indicates a high V_{oc} should be obtained in the PCDSBT-based devices.

Hole Mobility

The introduction of dithienosilole was anticipated to enhance the polymer hole mobility, whereas the vertical

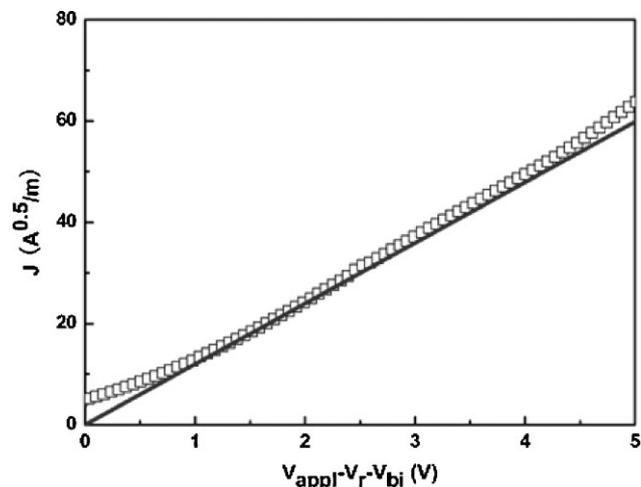


Figure 3. J^{0.5} vs V plots for the PCDSBT film at room temperature. The solid lines are fits of the data points.

hole mobility through the hole-only device measured by using the SCLC^[37,38] method is 1 × 10⁻⁴ cm² · V⁻¹ · s⁻¹. The result is plotted in Figure 3. The moderate value of the hole mobility may be ascribed to the relatively low molecular weight^[39] and the large number of octyl side chains in the repeat units which influences the packing of the polymer.^[40,41]

Photovoltaic Properties

The photovoltaic performance of PCDSBT was studied by fabricating BHJ solar cells with a device structure of ITO/PEDOT:PSS/polymer (20 mg · mL⁻¹ PCDSBT in dichlorobenzene):PCBM/LiF/Al. Device optimizations were conducted by varying the ratios of polymer versus PCBM and using different solvents as shown in Table 1. The series (R_s) and shunt (R_{sh}) resistances were calculated from the inverse slope of the current density–voltage (J–V) curve in the first quadrant and the forth quadrant, respectively.^[42]

Table 1. Photovoltaic properties of polymer solar cells incorporating PCDSBT:PCBM blends prepared at various weight ratios and with different solvents.

Ratio (w/w)	V _{oc} [V]	J _{sc} [mA · cm ⁻²]	FF	η [%]	R _s [Ω · cm ²]	R _{sh} [kΩv · cm ²]
1:1	0.68	4.23	0.36	1.03	37.0	0.23
1:2	0.68	6.15	0.35	1.48	37.5	0.24
1:2 DIO ^{a)}	0.66	5.05	0.49	1.63	2.50	0.31
1:3	0.64	4.12	0.32	0.87	47.4	0.22
1:4	0.65	4.47	0.31	0.90	57.1	0.23

^{a)}Devices prepared from a mixed solvent of dichlorobenzene/1,8-diiodooctane (97:3, v:v).

For the devices without any additive, the optimal efficiency was obtained from the device with an active layer that comprised a blend of PCDSBT and PCBM at a weight ratio of 1 : 2, which gave a value for the V_{oc} of 0.68 V, a J_{sc} of $6.15 \text{ mA} \cdot \text{cm}^{-2}$, a fill factor (FF) of 0.36, and a PCE of 1.48%. The V_{oc} is higher than most of the dithienosilole-containing polymers.^[19–21] However, the J_{sc} is not as high as expected, this may be attributable to the molecular weight being not as high as required and the relatively low absorption coefficient. Usually low-molecular-weight polymers cannot obtain the maximum current as promised by their optical bandgap.^[39] Moreover, in each device at different weight ratios without additive, the large R_s and low R_{sh} lead to a FF as low as 0.31–0.36. Note that the poly(3-hexylthiophene) (P3HT)-based BHJ devices possess R_s and R_{sh} values, respectively, of around 3 and $1\,000 \Omega \cdot \text{cm}^2$.^[42] Both R_s and R_{sh} have clear correlation with the molecular weight and the charge transport of the polymer, thus a higher molecular weight PCDSBT (\bar{M}_n larger than 17 kDa) may exhibit a better photovoltaic performance.^[43]

Figure 4 shows the effect of mixed solvents on the polymer solar cell performance. It is obvious that, with the addition of DIO, the R_s decreased significantly from 37.5 to $2.5 \Omega \cdot \text{cm}^2$; meanwhile, the R_{sh} increased from 0.24 to $0.31 \text{ k}\Omega \cdot \text{cm}^2$. Therefore, after the addition of DIO to the blend solution, the FF dramatically increased from 0.36 to 0.50, whilst the efficiency of the devices did not improve considerably, with only a small enhancement from 1.48% to 1.65%. The use of high-boiling-point additives has been shown to improve the morphology of the blend film by avoiding excessive crystallization of PCBM.^[12,44–46] The effect of additive on the morphology was studied by AFM. AFM topography images and phase images were measured on a film cast from a PCDSBT:PCBM blend with and without additive. As shown in the AFM images (Figure 5), the

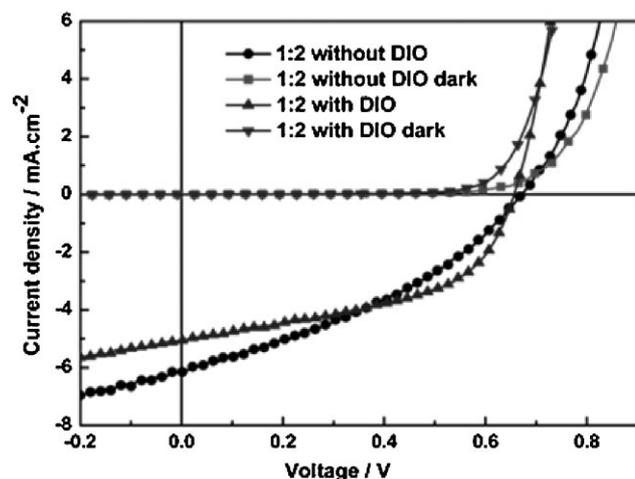


Figure 4. J - V curves of the PCDSBT:PCBM (1:2) BHJ films processed from dichlorobenzene a) without and b) with 3% DIO, under AM 1.5G illumination.

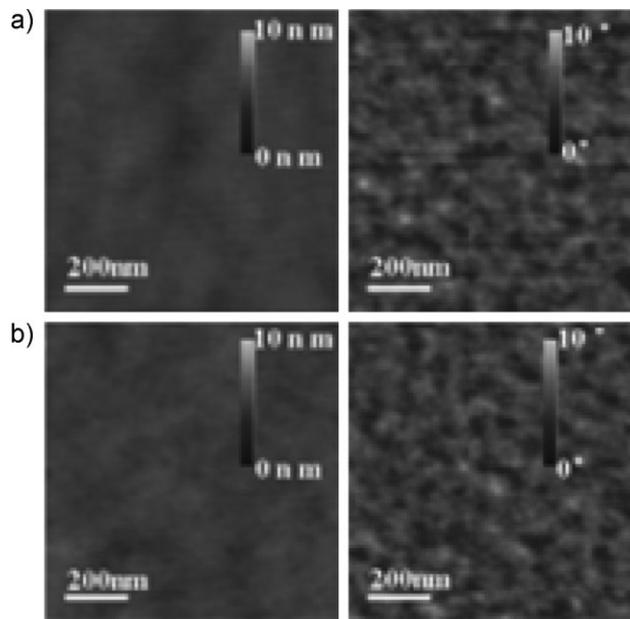


Figure 5. AFM images of the PCDSBT:PCBM (1:2) BHJ films processed from dichlorobenzene a) without and b) with 3% DIO. The topography of each film is shown in the left panels, and the corresponding phase image in the right panels.

morphology of the film with DIO was more uniform than that of the film without DIO, which led to a higher FF. However, both the domain sizes of the films with DIO and without DIO (40 and 100 nm, respectively) are larger than that of the exciton diffusion length (10 nm),^[12] which results in a loss of photocurrent and a low PCE of the photovoltaic devices. Further work is being undertaken to optimize the photovoltaic performance of PCDSBT. The photovoltaic performance of the BHJ solar cells based on PCDSBT could be improved by increasing the molecular weight of the polymer,^[43] changing the side chains in the monomers to weaken the steric hindrance,^[45,47] and using other stronger electron-accepting units to narrow the bandgap.^[14,39]

Conclusion

In summary, we envisioned and synthesized a new low bandgap poly(2,7-carbazole) derivative, i.e., poly[*N*-9'-octyl-2,7-carbazole-*alt*-5,5-(4',7'-di-(4,4'-dioctyldithieno [3,2-*b*:2',3'-*d*]silole)-2-yl-2',1',3'-benzothiadiazole)] (PCDSBT). The combination of dithienosilole and carbazole imparts PCDSBT with a narrow bandgap and a relatively low HOMO level. An overall efficiency of 1.65% has been achieved for PCDSBT-based BHJ solar cell devices. Although the PCE is not as high in this work as expected, further improvements, such as synthesizing higher molecular weight PCDSBT from

other catalyst systems and the utilization of a stronger electron-accepting unit, should lead to better performance.

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