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Improvement of Open-Circuit Voltage and Photovoltaic Properties of 2D-Conjugated Polymers by Alkylthio Substitution

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ABSTRACT: Low bandgap and two-dimensional (2D)-conjugated copolymers based on benzo[1,2-*b*:4,5-*b'*]dithiophene with conjugated thiophene side chains (BDTT) and thieno[3,4-*b*]thiophene with electron-withdrawing substituents (TT) are attractive high efficiency polymer donor materials in polymer solar cells (PSCs). In this work, we introduced alkylthio substituent on the thiophene side chain in the polymer and synthesized a new low bandgap 2D-conjugated polymer PBDTT-S-TT. The alkylthio substituent increased the hole mobility of the polymer to $4.08 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and down-shifted the HOMO energy level of the polymer by 0.11 eV with absorption of the polymer film red-shifted slightly. The PSCs based on PBDTT-S-TT as donor and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₀BM) as acceptor without solvent additive

treatment demonstrated a high open-circuit voltage (V_{oc}) of 0.84 V, leading to a high power conversion efficiency (PCE) of 8.42%, under the illumination of AM 1.5 G 100 mW cm⁻². For comparison, the V_{oc} and PCE of the devices based on the corresponding parent polymer PBDTT-TT with the device optimization of 3% DIO additive treatment are 0.77 V and 7.38%, respectively. The enhanced V_{oc} value of 0.84 V for the PSC based on PBDTT-S-TT should be benefited from the down-shifted HOMO energy level of the polymer. The results indicate that the alkylthio substitution is an effective way to further improve the photovoltaic performance of the 2D-conjugated polymer donor materials in PSCs.

Keywords: conjugated polymers, polymer solar cells, alkylthio substituent, open-circuit voltage, side chain engineering

1. INTRODUCTION

Polymer solar cells (PSCs) have attracted great attention in recent years due to their advantages of low cost, light weight, easy fabrication and capability to be fabricated into large area flexible devices.¹⁻¹¹ Typically, the PSCs are composed of a photoactive blend layer of a conjugated polymer donor and a fullerene derivative acceptor, sandwiched between an anode and a cathode (at least one of them should be transparent).⁶⁻⁷ The key issue in the studies of PSCs is the increase of power conversion efficiency (PCE) of the devices. The PCE is proportional to the values of short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF) of the PSC. The J_{sc} depends on the

wavelengths of the absorption bands and charge carrier mobilities of the donor and acceptor materials, whereas V_{oc} is proportional to the difference between the LUMO of the acceptor and the HOMO of the donor,^{12, 13} and FF is related to the charge carrier mobilities and device fabrication conditions. The electron acceptor used in PSCs at present is mainly [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) or [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₀BM). Therefore, for increasing PCE of the PSCs, it is very important to design and synthesize new conjugated polymer donor materials with narrower bandgap (broader absorption) for higher J_{sc} , higher hole mobility for higher J_{sc} and larger FF, and relatively lower-lying HOMO energy level for higher V_{oc} .

Low bandgap copolymers based on benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) and thieno[3,4-*b*]thiophene (TT) units have drawn great research interests since the first report by Yu *et al.* in 2009,¹⁴ because of their broad absorption, higher hole mobility and attractive photovoltaic properties.¹⁴⁻¹⁹ By further structural modifications to tune the energy levels, such as introducing fluorine atom into a 2-ethylhexyl carboxylate substituted TT unit (designated as PTB7)¹⁵ or an *n*-heptylacyl group substituted TT unit (designated as PBDTTT-CF)¹⁶, PCE of the PSCs based on the polymer donor reached up to 7.4~7.7%. Recently, Huo and Hou *et al.* attached conjugated thiophene side chains instead of alkoxy substituents on BDT unit (BDTT) and synthesized 2-dimensional (2D)-conjugated polymers PBDTTT-E-T and PBDTTT-C-T.¹⁷ The 2D-conjugated copolymer PBDTTTs based on BDTT and TT units show red-shifted absorption, lower-lying HOMO energy level, greatly enhanced hole mobility and further improved photovoltaic properties.^{4, 18} Nevertheless, the HOMO energy levels of this kind of

copolymers are relatively high in the range of -4.90 to -5.22 eV, which limit V_{oc} of the devices to less than 0.8 V.

Side chains in conjugated polymers play an important role in tuning solubility, absorption spectra and electronic energy levels of the conjugated polymers.²⁰⁻²² Electron-donating side chains can donate some electron density to the conjugated polymer backbones through connecting moieties such as alkoxy and alkylthio groups. It is well known that the electron-donating ability of sulfur is weaker than oxygen. Moreover, sulfur atom has some π -acceptor capability due to the formation of $p_{\pi}(C)$ - $d_{\pi}(S)$ orbital overlap where divalent sulfur accepts π -electron from the p -orbital of carbon-carbon double bond into its empty $3d$ -orbitals.²³ This causes the polymers containing alkylthio side chain to exhibit unique optoelectronic properties. In 2006, Hou and Li *et al.*²⁴ introduced alkylthio side chain in poly(*p*-phenylenevinylene) (PPV) for tuning the optoelectronic properties of PPV derivatives, and found that the PPV derivatives with the alkylthio side chain possess down-shifted HOMO energy level than that of the PPV derivatives with alkoxy side chain such as MEH-PPV. The HOMO energy levels of the PPV derivatives with an alkylthio side chain and with an alkylthio and an alkoxy side chain were -5.37 eV (onset oxidation potential is 0.66 V vs. Ag/Ag^+)²⁴ and -5.17 eV (onset oxidation potential is 0.46 V vs. Ag/Ag^+),²⁴ respectively, while the HOMO energy level of MEH-PPV with two alkoxy side chains is -5.07 eV.²⁵ Later on, Huo and Li *et al.*²⁶ studied the effect of the alkylthio side chain on the optoelectronic properties of polythiophene derivatives in comparison to the alkyl and alkoxy side chains. The alkylthio side chain made polythiophene absorption slightly red-shifted and HOMO energy level down-shifted by ca. 0.1 eV than that of the

alkyl substituted polythiophene.²⁶ Recently, Lee and Ferraris *et al.*^{27,28} attached the alkylthio side chains on benzodithiophene (BDT) unit in the conjugated polymers based on BDT unit, and the HOMO energy levels of the conjugated polymers based on BDT unit were also effectively down-shifted, so that high open-circuit voltage of the PSCs with the polymer as the donor was achieved.

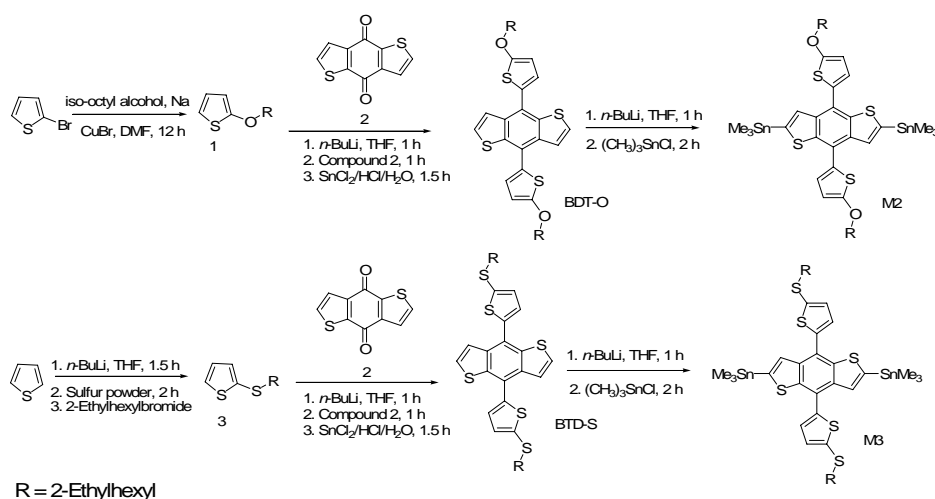
For further improving the photovoltaic performance of the 2D-conjugated copolymer PBDTTs, in this work, we introduced alkylthio substituent on the conjugated thiophene side chains of the 2D-conjugated copolymer and synthesized a new 2D-conjugated polymer PBDTT-S-TT with alkylthio substituent. For comparison, the corresponding polymers PBDTT-O-TT with alkoxy substituent and PBDTT-TT with alkyl substituent on the thiophene side chains were also synthesized. Molecular structures of the polymers are shown in Scheme 1. The absorption edge of PBDTT-S-TT film was red-shifted by ca. 5 nm and the HOMO energy level of PBDTT-S-TT was down-shifted by 0.11 eV than that of PBDTT-TT. As a result, PSCs based on PBDTT-S-TT as donor and PC₇₀BM as acceptor demonstrated a high V_{oc} of 0.84 V, leading to a higher PCE of 8.42% under the illumination of AM 1.5 G at 100 mW cm⁻². While the V_{oc} and PCE of the devices under the optimized device fabrication conditions are 0.77 V and 7.42% for PBDTT-TT.

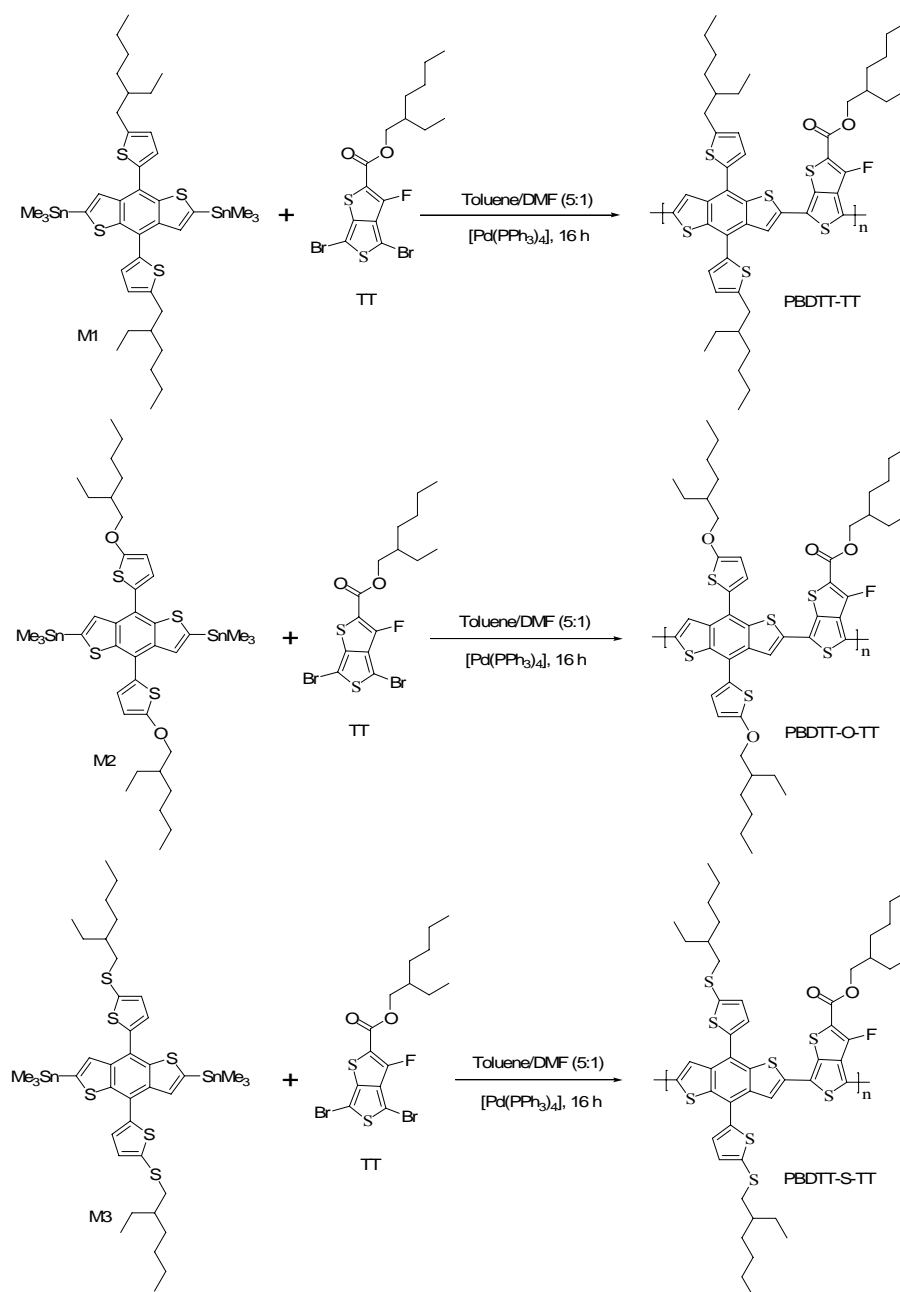
2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of the Polymers

2-Ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate (TT)¹⁴ and 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophen

e (M1)¹⁷ were synthesized by the literature methods. The detailed synthetic procedures of (4,8-bis(5-((2-ethylhexyl)oxy)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl) bis(trimethylstannane) (M2) and (4,8-bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl) bis(trimethylstannane) (M3) were described in Experimental Section. The polymers PBDTT-TT, PBDTT-O-TT and PBDTT-S-TT were synthesized by the Stille coupling reaction, as shown in Scheme 1. The polymerization was carried out with Pd(PPh₃)₄ as catalyst and refluxed for 16 h under argon protection. The polymers were purified by extraction with methanol, hexane and chloroform. The polymers possess good solubility in chloroform, chlorobenzene, and *o*-dichlorobenzene. Molecular weight of the polymers was estimated by gel-permeation chromatography (GPC) using tetrahydrofuran as the eluent. The number-average molecular weight (M_n) of PBDTT-TT, PBDTT-O-TT and PBDTT-S-TT was 95 kDa, 78 kDa and 118 kDa, with polydispersity (PDI) of 1.39, 1.52 and 1.46, respectively.





Scheme 1. Synthetic routes and chemical structures of the polymers.

Thermogravimetric analysis (TGA) measurements were carried out to evaluate the thermal stability of the polymers, and the TGA plots of the three polymers are shown in Figure 1. The TGA profile reveals that the decomposition temperatures (T_d) at 5% weight loss of PBDTT-O-TT and PBDTT-S-TT are approximately 308 °C and 291 °C, respectively, which are lower than that of PBDTT-TT (383 °C), indicating that the alkoxy

and alkylthio hybrid electron-donating side chains decreases thermal stability of the polymers slightly in comparison to the normal alkyl chain in PBDTT-TT. Nevertheless, the thermal stability of PBDTT-O-TT and PBDTT-S-TT is still good enough for their application in PSCs.

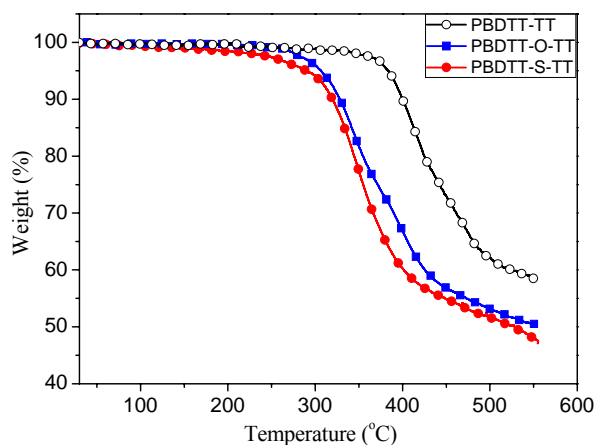


Figure 1. TGA plots of PBDTT-TT, PBDTT-O-TT and PBDTT-S-TT with a heating rate of 10 min s^{-1} under an inert atmosphere.

2.2. Absorption Spectra

Figure 2 shows the absorption spectra of PBDTT-TT, PBDTT-O-TT and PBDTT-S-TT in dilute *o*-dichlorobenzene and thin solid film. The three polymers showed broad and strong absorption in the wavelength region from 450 nm to ca. 800 nm. The well-defined absorption peaks with vibronic shoulder at the long wavelength range (700~800 nm) implies the existence of ordered aggregation and strong π - π stacking. The main absorption bands of PBDTT-O-TT and PBDTT-S-TT are red-shifted by 25 nm and 5 nm, respectively, and broadened to some extent, in comparison with that of PBDTT-TT, which should result from introduction of the alkoxy or alkylthio electron-donating side chains onto the

polymers. The absorption edge of PBDTT-O-TT film is ~ 20 nm more red-shifted than that of the PBDTT-S-TT film, which is attributed to the stronger electron-donating ability of the alkoxy group than that of alkylthio group.^{24, 29, 30}

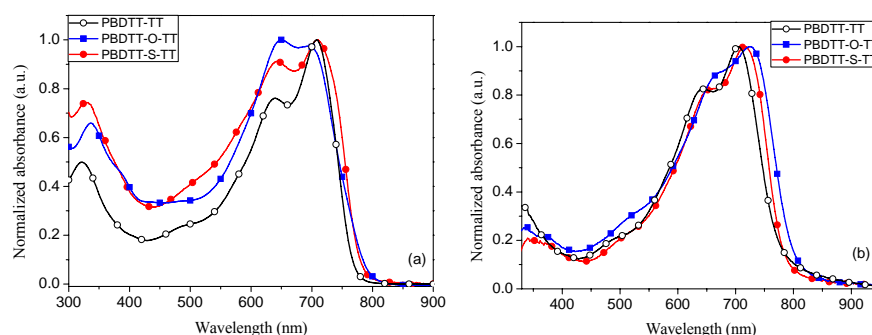


Figure 2. Normalized absorption spectra of PBDTT-TT, PBDTT-O-TT, and PBDTT-S-TT in (a) *o*-dichlorobenzene solution and (b) thin film on quartz.

2.3. Electronic Energy Levels

Cyclic voltammetry was employed to measure the electronic energy levels of the conjugated polymers,^{25,31} and the HOMO and LUMO energy levels were calculated from the onset oxidation and reduction potentials by assuming the energy level of ferrocene/ferrocenium (Fc/Fc^+) to be -4.8 eV below the vacuum level.³² Figure 3 displays the cyclic voltammograms of ferrocene and the three polymer films on a glassy carbon electrode in 0.1 mol L^{-1} Bu_4NPF_6 acetonitrile solution at a scan rate of 100 mV s^{-1} . The onset reduction potentials (ϕ_{red}) of PBDTT-TT, PBDTT-O-TT and PBDTT-S-TT are -1.16 , -1.18 and -1.06 V vs. Ag/AgCl, respectively, while the onset oxidation potentials (ϕ_{ox}) are 0.97 , 0.85 and 1.08 V vs. Ag/AgCl, respectively. The formal potential of Fc/Fc^+ was 0.47 V vs. Ag/AgCl measured in this work, so the HOMO and LUMO levels of the polymers were calculated according to the equations, $\text{HOMO} = -e(\phi_{\text{ox}} + 4.33)$ (eV); $\text{LUMO} =$

$-e(\varphi_{\text{red}} + 4.33)$ (eV). The HOMO and LUMO energy level values of the polymers are -5.30 and -3.17 eV for PBDTT-TT, -5.18 and -3.15 eV for PBDTT-O-TT, -5.41 and -3.27 eV for PBDTT-S-TT, respectively, as listed in Table 1. PBDTT-O-TT showed a higher HOMO energy level due to the strong electron-donating ability of alkoxy substituent. Interestingly, the HOMO level of PBDTT-S-TT with alkylthio side chain was decreased by 0.11 eV as compared to PBDTT-TT, indicating that the thiophene side chains in the 2D-conjugated copolymers are in conjugation with the polymer main chain and the substituents on the thiophene conjugated side chains influence the electronic properties of the 2D-conjugated polymers significantly. Obviously, the red-shifted absorption and down-shifted HOMO energy level of PBDTT-S-TT are desirable for its application as the donor material in PSCs.

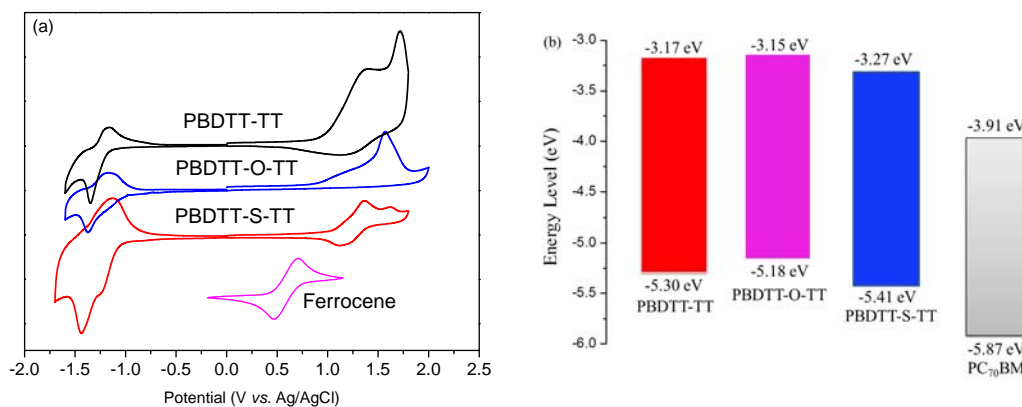


Figure 3. (a) Cyclic voltammograms and (b) HOMO and LUMO energy levels of PBDTT-TT, PBDTT-O-TT and PBDTT-S-TT.

2.4. Theoretical Calculations

Molecular simulation with density functional theory (DFT) was carried out to understand the structure-property relationship of the three polymers. The geometries of

the compounds were optimized using density functional theory (DFT) with B3LYP functional and 6-31G (d, p) basis set. In particular, the HOMO and LUMO levels and related electron distributions were calculated. The alkyl chains were replaced by methyl groups to save the computational time within a reasonable simplification. The frontier molecular orbitals and the corresponding LUMO and HOMO energy levels are shown in Figure S1 in Supporting Information (SI) and Table 1, respectively. The trend of variation for molecular orbital energy levels is consistent with the results obtained from the CV measurements. As depicted in Figure S1 in SI, the electron density distributions at LUMO of the three polymers are mainly localized on the TT unit while their HOMO surfaces are delocalized along the whole π -conjugated backbones.

Table 1. Absorption spectral properties and energy level data of the polymers.

Polymer	λ_{\max} (nm)				E_g^{opt} (eV)	HOMO ^[a] (eV)	LUMO ^[a] (eV)	E_g^{cv} (eV)	HOMO ^[b] (eV)	LUMO ^[b] (eV)
	Solution		Film							
PBDTT-TT	640	708	643	705	1.58	-5.30	-3.17	2.13	-5.04	-2.66
PBDTT-O-TT	650	698	670	726	1.53	-5.18	-3.15	2.03	-4.97	-2.62
PBDTT-S-TT	644	709	657	716	1.57	-5.41	-3.27	2.14	-5.22	-2.77

^[a] Calculated from the cyclic voltammograms. ^[b] Obtained by DFT calculations.

2.5. Hole Mobility

Hole mobility is an important parameter for the photovoltaic donor materials. Hole mobility of the three polymers were measured by using the space-charge-limited current

(SCLC) method with the device structure of ITO/PEDOT:PSS/polymer/Au. For the hole-only devices, SCLC is described by³³

$$J \cong (9/8)\varepsilon\varepsilon_0\mu_0V^2 \exp(0.89\sqrt{V/E_0L})/L^3 \quad (1)$$

where ε is the dielectric constant of the polymers, ε_0 is the permittivity of the vacuum, μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, and L is the thickness of the film. Figure 4 shows the $\ln(JL^3/V^2)$ vs. $(V/L)^{0.5}$ plots of the polymers measured by the SCLC method. The hole mobility values of the PBDTT-TT, PBDTT-O-TT and PBDTT-S-TT films are 2.83×10^{-3} , 1.50×10^{-3} and $4.08 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The results indicate that substitution with alkylthio side chains in PBDTT-S-TT increased hole mobility of the polymer.

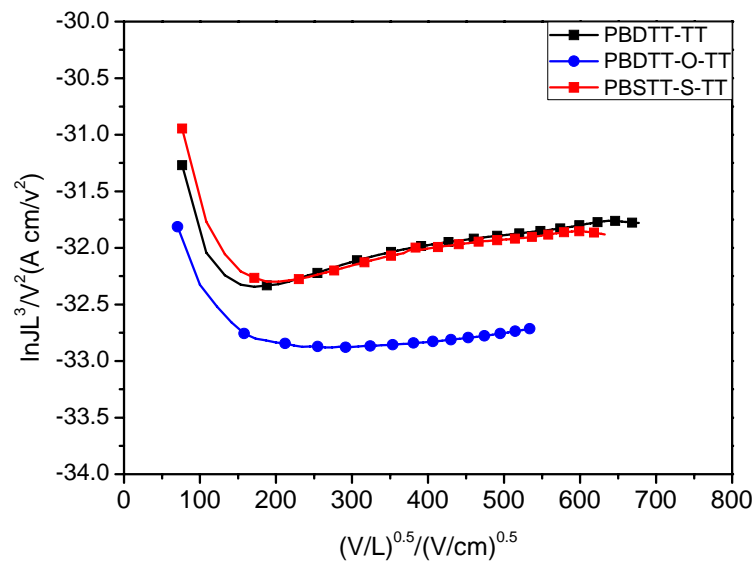


Figure 4. Plot of $\ln(JL^3/V^2)$ vs. $(V/L)^{0.5}$ of the polymers for the measurement of hole mobility by the SCLC method with the device structure of ITO/PEDOT:PSS/polymer/Au.

2.6. Photovoltaic Performance

The device structure of the PSCs for characterizing photovoltaic properties of the

polymers is ITO/PEDOT:PSS/polymer:PC₇₀BM/Ca/Al. The devices were fabricated by employing PBDTT-S-TT, PBDTT-O-TT or PBDTT-TT as a donor material and PC₇₀BM as an acceptor material in the photoactive layer. The active layer was prepared by spin-coating the blend solution of polymer:PC₇₀BM with the ratio of 1:1.5 (w/w) in *o*-dichlorobenzene. The current density-voltage (J - V) curves are shown in Figure 5 and the key device parameters are summarized in Table 2.

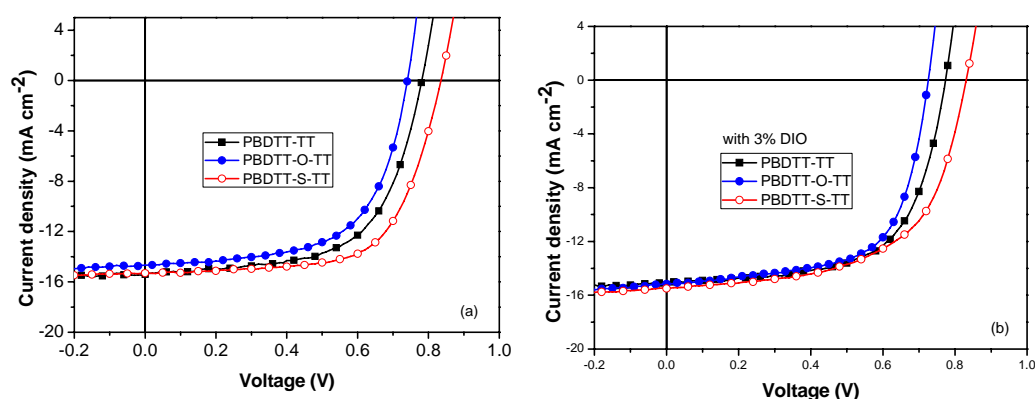


Figure 5. J - V curves of the PSCs with the device structure of ITO/PEDOT:PSS/the polymers:PC₇₀BM (1:1.5, w/w)/Ca/Al (a) without DIO and (b) with 3% DIO additive under illumination of AM 1.5 G at 100 mW cm⁻².

The device based on PBDTT-TT exhibited a PCE of 7.38% with $V_{oc} = 0.78$ V, $J_{sc} = 15.41$ mA cm⁻², and FF = 61.25%. The treatment of 3% 1,8-diiodooctane (DIO) additive improved the PCE of the PSC only a little to 7.42%. For the PSC based on PBDTT-O-TT, the V_{oc} was decreased to 0.74 V due to the higher HOMO energy level of PBDTT-O-TT, resulting in a lower PCE of 6.68%. By the treatment of 3% DIO additive, PCE of the PSC based on PBDTT-O-TT was improved to 7.10%, but it is still lower than that of the PSC based on PBDTT-TT. Very importantly, PCE of the PSC based on PBDTT-S-TT without

DIO additive treatment demonstrated a high V_{oc} of 0.84 V and a high PCE of 8.42%. The V_{oc} of the PSC based on PBDTT-S-TT is 0.07 V higher than that of the PSC based on PBDTT-TT, which is benefitted from the lower HOMO energy level of PBDTT-S-TT. To our best knowledge, the V_{oc} of 0.84 V is the highest V_{oc} value among all the copolymers based on BDT and TT units in the literature. In addition, FF value of the PSC based on PBDTT-S-TT was also improved to 65.49%, which could be attributed to the higher hole mobility of PBDTT-S-TT. It is noteworthy that the excellent photovoltaic performance of the PSC based on PBDTT-S-TT was obtained without any processing additive or post treatments, which should be a great advantage for future large-scale production and commercial application of PSCs.

For a better understanding of the effect of DIO additive on the active layers, X-ray diffraction (XRD) analysis and atomic force microscopy (AFM) morphology of PBDTT-S-TT:PC₇₀BM (1:1.5, w/w) blend films processed without or with DIO additive were studied. As shown in Figure S2 in SI, DIO additive influences the crystalline property of PBDTT-S-TT:PC₇₀BM (1:1.5, w/w) blend film a little. When processed with 3% DIO additive, the XRD pattern of the blend film exhibits stronger (100) and (010) diffraction peaks than that of the blend film processed without DIO additive. Figure S3 shows surface topography (left) and phase images (right) of the PBDTT-S-TT:PC₇₀BM (1:1.5, w/w) blend films processed without or with DIO additive. The topography and phase images of the two blend films exhibited clear well-defined interpenetrating donor/acceptor networks, but the blend film with DIO additive showed larger domain size, which could result in the decreased photovoltaic performance of the devices with DIO

additive.

Table 2. Photovoltaic performance of the PSCs with the device structure of ITO/PEDOT:PSS/the polymers/PC₇₀BM (1:1.5, w/w)/Ca/Al under the illumination of AM 1.5 G at 100 mW cm⁻².

Polymer	DIO (%)	Thickness (nm)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^[a] (%)
PBDTT-TT	0	95	0.78	15.41	61.25	7.38 [7.29]
PBDTT-TT	3	90	0.77	14.99	63.92	7.42 [7.35]
PBDTT-O-TT	0	92	0.74	14.67	61.50	6.68 [6.56]
PBDTT-O-TT	3	93	0.73	15.17	64.44	7.10 [7.01]
PBDTT-S-TT	0	95	0.84	15.32	65.49	8.42 [8.35]
PBDTT-S-TT	3	90	0.83	15.49	59.01	7.58 [7.46]

^[a] The values in square bracket are the average PCE obtained from 20 devices.

The external quantum efficiency (EQE) of the devices was measured to further confirm the accuracy of the measurements. The EQE curves are shown in Figure 6. All the devices exhibited rather efficient photo-conversion efficiency in the wavelength range of 400-700 nm, with EQE values of 60~70%. The J_{sc} values of all the devices integrated from the EQE curves are rather consistent (less than 5% error) with the values obtained by J - V measurements.

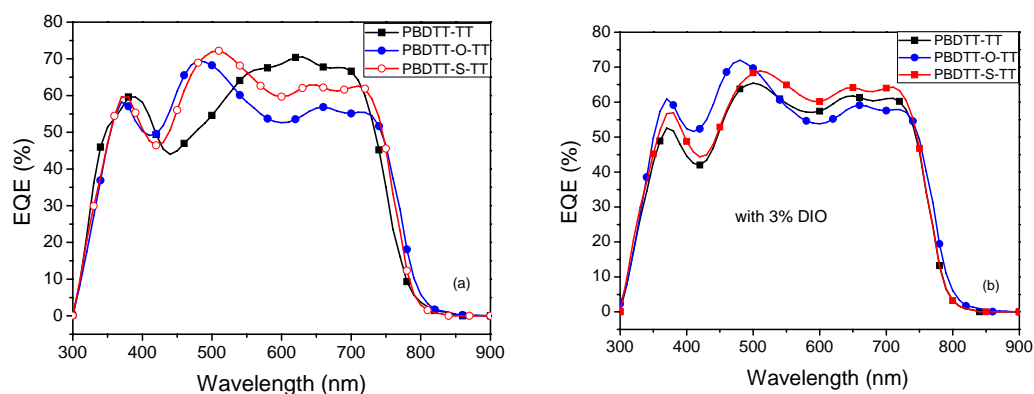


Figure 6. EQE curves of the corresponding PSCs (a) without DIO and (b) with 3% DIO additive treatment under the illumination of AM 1.5 G at 100 mW cm^{-2} .

3. CONCLUSIONS

In conclusion, a new 2D-conjugated polymer based on the BDTT and TT units with alkylthio substitution on thiophene side chains of BDT unit, PBDTT-S-TT, was designed and synthesized for further improving the photovoltaic performance of the 2D-conjugated polymers. It was found that the alkylthio side chains down-shifted the HOMO energy level by ca. 0.11 eV and slightly red-shifted the absorption of the 2D-conjugated polymers in comparison to the corresponding polymer with alkyl substitution on the conjugated thiophene side chains. The HOMO energy level of PBDTT-O-TT with alkoxy side chain is up-shifted from that of PBDTT-TT, which is expected from the effect of substitution of electron-donating side chains. The PSC device based on PBDTT-S-TT showed an enhanced V_{oc} of 0.84 V, which is among the highest one in the reported copolymers based on BDT and TT units, leading to an enhanced PCE of 8.42%. The results indicate that molecular modification by introducing alkylthio side chain will be a promising strategy to broaden the absorption, down-shift the HOMO energy level and increase the hole

mobility of the low bandgap 2D-conjugated polymers for further enhancing the photovoltaic performance of PSCs.

4. EXPERIMENTAL SECTION

4.1 Materials and Measurements

Solvents were dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification. NMR spectra were measured in CDCl_3 on Bruker AV 400 MHz FT-NMR spectrometer and chemical shifts are quoted relative to tetramethylsilane for ^1H and ^{13}C nuclei. Molecular weight for the polymers was measured by gel permeation chromatography (GPC) with polystyrene as a standard. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7. Mass spectra were obtained with a Shimadzu QP2010 spectrometer. UV-vis absorption spectra were obtained on a Hitachi U-3010 spectrometer. Cyclic voltammetry was performed on a Zahner IM6e electrochemical workstation with a three-electrode system in a solution of 0.1 M $[\text{Bu}_4\text{N}]\text{PF}_6$ acetonitrile solution at a scan rate of 100 mV s^{-1} . Glassy carbon disc coated with polymer film was used as the working electrode. A Pt wire was used as the counter electrode and Ag/AgCl was used as the reference electrode.

4.2 Device Fabrication and Characterization

PSCs were fabricated with ITO glass as a positive electrode, Ca/Al as a negative electrode and the blend film of the polymer/ PC_{70}BM between them as a photosensitive layer. The ITO glass was pre-cleaned and modified by a thin layer of PEDOT:PSS which

was spin-cast from a PEDOT:PSS aqueous solution (Clevious P VP AI 4083 H. C. Stark, Germany) on the ITO substrate, and the thickness of the PEDOT:PSS layer is about 30 nm. The photosensitive layers, consisting of polymers and PC₇₀BM with a weight ratio of 1:1.5 w/w, were dissolved at the concentration of 1% (10 mg/mL) in *o*-dichlorobenzene and spin-coated on the ITO/PEDOT:PSS electrode. Finally, the Ca/Al cathode was deposited on the active layer by vacuum evaporation under 1×10^{-4} Pa. The typical effective area of the investigated devices was 4 mm². The current density-voltage (*J-V*) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit in a dry box under an inert atmosphere. A xenon lamp with AM 1.5 filter was used as the white light source, and the optical power at the sample was 100 mW cm⁻². The external quantum efficiency (EQE) was measured using a Stanford Research Systems model SR830 DSP lock-in amplifier coupled with a WDG3 monochromator and 500 W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. All the measurements were performed under ambient atmosphere at room temperature.

4.3 Synthesis of the monomers and polymers

2-((2-Ethylhexyl)oxy) thiophene (1) Sodium (2.3 g, 0.1 mol) was added to iso-octyl alcohol (39 g, 0.3 mol) and stirred at room temperature until the sodium disappeared completely. The paste solution was distilled under vacuum to afford a pale powder. 60 mL dry *N,N*-dimethylformamide was added into the powder under argon protection, and then 2-bromothiophene (9.8 g, 0.06 mol) was injected into the reaction mixture. After 5 min,

cuprous bromide (1.44 g, 10 mmol) was added to the reaction mixture and stirred for 12 h at 100 °C. When the reaction temperature was cooled to room temperature, hexane (100 mL) was added and the mixture was filtered under suction. After the removal of solvent, purification was carried out by silica gel column chromatography using hexane as eluent. Compound **1** (6.6 g, yield 52%) was obtained as a colorless oil.

¹H NMR (400 MHz, CDCl₃), δ (ppm): 6.70–6.67 (m, 1H), 6.50–6.48 (m, 1H), 6.18–6.16 (m, 1H), 3.91–3.89 (d, 2H), 1.72–1.50 (m, 1H), 1.48–1.30 (m, 8H), 0.94–0.88 (m, 6H).

¹³C NMR (100 MHz, CDCl₃), δ (ppm): 166.24, 124.68, 111.55, 104.39, 76.54, 39.51, 30.43, 29.08, 23.79, 23.07, 14.10, 11.09. MS: *m/z* = 212.

4,8-Bis(5-((2-ethylhexyl)oxy)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDT-O)

Compound **1** (6.6 g, 31 mmol) and 60 mL dry THF were added into a flask under argon protection. The solution was cooled to 0 °C and 14.2 mL of *n*-butyllithium (0.034 mol, 2.4 M in hexane) was added dropwise. The mixture was then warmed to room temperature and stirred for 1 hour. Subsequently, compound **2** (1.7 g, 7.8 mmol) was added to the reaction mixture, and then stirred for 1 h at 50 °C. After cooling to ambient temperature, a mixture of SnCl₂·2H₂O (13.6 g, 60.7 mmol) in 10% HCl (30 mL) was added and the mixture was stirred for additional 1.5 h. After that, the reaction mixture was poured into water and extracted with ether. The organic layer was washed with water three times and then dried over MgSO₄. After the removal of solvent, the crude product was purified by column chromatography on silica gel using hexane as eluent to afford BDT-O (2.4 g, yield 51%) as a yellow powder.

¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.66 (s, 2H), 7.44–7.43 (d, 2H), 7.10–7.09 (d, 2H),

6.32–6.31 (d, 2H), 4.03–4.01 (d, 4H), 1.78–1.76 (m, 2H), 1.56–1.27 (m, 16H), 0.95–0.94 (d, 12H). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 166.74, 139.24, 136.70, 127.41, 125.88, 125.35, 123.83, 123.40, 104.57, 76.47, 39.56, 30.42, 29.07, 23.79, 23.03, 14.08, 11.12. MALDI-TOF MS: calcd for $\text{C}_{34}\text{H}_{42}\text{O}_2\text{S}_4$ $m/z = 610.9$; found 610.2.

(4,8-Bis(5-((2-ethylhexyl)oxy)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) M2 **BDT-O** (2.4 g, 3.9 mmol) and 50 mL dry THF were mixed under $-78\text{ }^\circ\text{C}$ with argon protection, 4.1 mL of *n*-butyllithium (9.8 mmol, 2.4 M in hexane) was added dropwise. The reaction mixture was then stirred at $-78\text{ }^\circ\text{C}$ for 1 h. Subsequently, chlorotrimethylstannane (1.0 M in hexane, 11.7 mL) was added in several portions and the mixture was stirred for 2 h at ambient temperature. Then, the mixture was extracted by diethyl ether, and the combined organic phase was washed with water three times, dried over MgSO_4 . After the removal of solvent, the crude product was purified by recrystallization using ethanol to obtain the target compound as a light-yellow solid (2.7 g, yield 75%).

^1H NMR (400 MHz, CDCl_3), δ (ppm): 7.69 (s, 2H), 7.11–7.10 (d, 2H), 6.34–6.33 (d, 2H), 4.05–4.03 (d, 4H), 1.80–1.77 (m, 2H), 1.56–1.26 (m, 16H), 0.99–0.97 (d, 12H), 0.49–0.35 (t, 18H). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 166.53, 143.55, 142.28, 137.53, 131.14, 126.16, 125.68, 122.18, 104.44, 76.36, 39.60, 30.44, 29.10, 23.81, 23.04, 14.10, 11.15, -8.31. MALDI-TOF MS: calcd for $\text{C}_{40}\text{H}_{58}\text{O}_2\text{S}_4\text{Sn}_2$ $m/z = 936.6$; found 936.2.

2-((2-Ethylhexyl)thio)thiophene (**3**) 20.8 mL of *n*-butyllithium (50 mmol, 2.4 M in hexane) was added dropwise into thiophene (4.2 g, 50 mmol) and 100 mL of dry THF at $0\text{ }^\circ\text{C}$ under argon protection. After the mixture was stirred at $0\text{ }^\circ\text{C}$ for 1.5 h, sulfur powder

(1.6 g, 50 mmol) was added in one portion, and then the resulting suspension was stirred at 0 °C for 2 h. Subsequently, 2-ethylhexylbromide (9.7 g, 50 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature. Then, ice-water containing NH₄Cl was added to the reaction, and the mixture was extracted with diethyl ether, washed with water, and dried over MgSO₄. After the removal of solvent, purification was carried out by silica gel column chromatography using hexane as eluent and compound **3** (10.5 g, yield 92%) was obtained as a colorless oil.

¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.55–7.51 (m, 1H), 7.13–7.10 (m, 1H), 7.02–6.99 (m, 1H), 3.05–2.77 (d, 2H), 1.72–1.70 (m, 1H), 1.55–1.30 (m, 8H), 0.94–0.88 (m, 6H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 137.24, 131.62, 128.35, 127.39, 42.74, 39.61, 34.34, 28.18, 27.79, 23.12, 14.10, 11.29. MS: *m/z* = 228.

4,8-Bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDT-S)

BDT-S was synthesized similarly as described above for **BDT-O** except that compound **3** (7 g, 31 mmol) was used instead of compound **1**. (2.8 g, yield 56%, light yellow powder).

¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.63–7.62 (d, 2H), 7.48–7.47 (d, 2H), 7.33–7.32 (d, 2H), 7.23–7.22 (d, 2H), 2.97–2.95 (d, 4H), 1.68–1.65 (m, 2H), 1.55–1.33 (m, 16H), 0.95–0.92 (t, 12H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 142.17, 139.03, 137.65, 136.54, 132.53, 128.40, 127.92, 123.66, 123.15, 43.56, 39.30, 32.19, 28.85, 25.42, 23.00, 14.19, 10.86. MALDI-TOF MS: calcd for C₃₄H₄₂S₆ *m/z* = 643.1; found 642.1.

(4,8-Bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) **M3** **M3** was synthesized similarly as described above for **M2** except that **BDT-S** (2.8 g, 4.4 mmol) was used instead of **BDT-O**. (3.5 g, yield 82%).

^1H NMR (400 MHz, CDCl_3), δ (ppm): 7.64 (s, 2H), 7.34–7.33 (d, 2H), 7.23–7.22 (d, 2H), 2.95–2.93 (d, 4H), 1.67–1.64 (m, 2H), 1.54–1.27 (m, 16H), 0.93–0.90 (m, 12H), 0.48–0.41 (t, 18H). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 143.09, 142.85, 142.81, 137.12, 136.83, 132.38, 130.53, 128.02, 121.73, 43.35, 39.07, 31.93, 28.57, 25.17, 22.74, 13.91, 10.63, -8.53. MALDI-TOF MS: calcd for $\text{C}_{40}\text{H}_{58}\text{S}_6\text{Sn}_2$ m/z = 968.7; found 968.2.

Synthesis of the Copolymers General procedure for the synthesis of **PBDTT-TT**, **PBDTT-O-TT** and **PBDTT-S-TT** by the Stille coupling is shown in Scheme 1. In a 25 mL flask, M1 (or M2, M3) (0.3 mmol) and M4 (0.3 mmol) were dissolved in 10 mL of toluene and 2 mL of DMF. After flushed with argon for 10 min, $[\text{Pd}(\text{PPh}_3)_4]$ (23 mg) was added as the catalyst, and the mixture was then purged with argon for 20 min. The solution was heated to reflux and stirred for 16 h under argon protection. Then, the reactant was cooled to room temperature, and the polymer was precipitated by addition of 100 mL of methanol, filtered through a Soxhlet thimble. The precipitate was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was precipitated from methanol as a solid, and the solid was dried under vacuum. The yield and elemental analytical results of the polymers are as follows.

PBDTT-TT. Yield: 43%. Elemental analysis calcd (%) for $\text{C}_{49}\text{H}_{57}\text{FO}_2\text{S}_6$: C 66.14, H 6.41; found: C 65.95, H 6.49. M_n = 95,000, PDI = 1.39. T_d = 383 °C.

PBDTT-O-TT. Yield: 39%. Elemental analysis calcd (%) for $\text{C}_{49}\text{H}_{57}\text{FO}_4\text{S}_6$: C 63.84, H 6.19; found: C 63.98, H 6.14. M_n = 78,000, PDI = 1.52. T_d = 308 °C.

PBDTT-S-TT. Yield: 51%. Elemental analysis calcd (%) for $\text{C}_{49}\text{H}_{57}\text{FO}_2\text{S}_8$: C 61.70, H 5.98; found: C 61.89, H 5.95. M_n = 118,000, PDI = 1.46. T_d = 291 °C.

Acknowledgement. This work was supported by the Ministry of Science and Technology of China (No. 2014CB643501) and NSFC (No. 91333204). W.-Y.W. also thanks Hong Kong Baptist University (FRG/12-13/083), Hong Kong Research Grants Council (HKBU202410) and Areas of Excellence Scheme, University Grants Committee of HKSAR (project no. AoE/P-03/08) for financial support.

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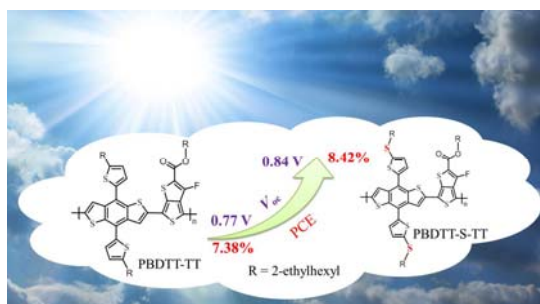
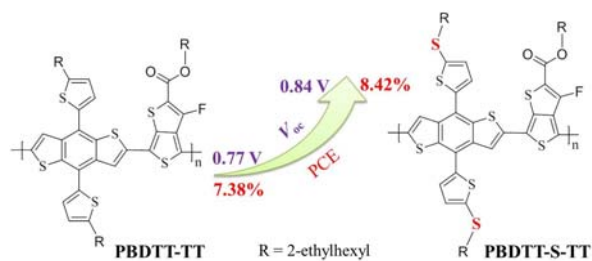
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Improvement of Open-Circuit Voltage and Photovoltaic Properties of 2D-Conjugated Polymers by Alkylthio Substitution

Chaohua Cui, Wai-Yeung Wong* and Yongfang Li*



The photovoltaic properties of the 2D-conjugated copolymer PBDTTTs were further improved by side chain engineering in 2D-conjugated polymer.

Broader context

For further improving the photovoltaic performance of the 2D-conjugated copolymer PBDTTTs, we introduced alkylthio substituent on the conjugated thiophene side chains of the 2D-conjugated copolymer to synthesize a new 2D-conjugated polymer PBDTT-S-TT. The alkylthio substituent increased the hole mobility of the polymer to $4.08 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and down-shifted the HOMO energy level of the polymer by 0.11 eV with absorption of the polymer film red-shifted slightly. The PSCs based on PBDTT-S-TT as donor without the need of solvent additive treatment demonstrated a high V_{oc} of 0.84 V, leading to a PCE of 8.42%, under the illumination of AM 1.5 G 100 mW cm^{-2} .