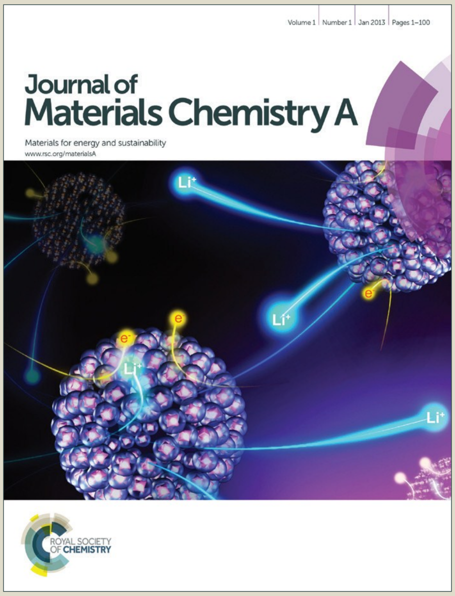

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ARTICLE TYPE

Synthesis and Photovoltaic Properties of Dithieno[3,2-b:2',3'-d]silole-Based conjugated copolymer

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A new low band gap conjugated polymer containing a dithieno[3,2-b:2',3'-d]silole (DTS) donor unit and a fluorinated 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTffBT) acceptor unit were synthesized by Stille cross-coupling polymerization. The structural and thermal properties of copolymer were characterized by using nuclear magnetic resonance, gel permeation chromatography and thermogravimetric analysis. This copolymer shows good thermal stability with decomposition temperature of 325 °C and broad absorption band from 300 to 800 nm. The HOMO and LUMO energy levels were estimated to be -5.28 and -3.66 eV, with an electrochemical band gap of 1.62 eV. Efficient bulk heterojunction solar cells were fabricated by blending this copolymer with $PC_{71}BM$, and it reached a power conversion efficiency up to 5.26% under 100 mW/cm^2 AM 1.5 illumination, indicating that PDTS-DTffBT is a potential candidate for polymer solar cells.

Introduction

Polymer solar cells (PSCs) have attracted wide attention in recent years due to their advantages of low cost, easy processing, light weight, being mechanically flexible and suitable for large-area fabrication.[1] The most efficient used architecture of polymer photovoltaic devices is so-called bulk heterojunction (BHJ) in which the active layer consists of a blend of conjugated polymer donors and fullerene derivative acceptors.[2] Over the past decade, BHJ solar cells based on regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) blend have been extensively studied and power conversion efficiencies (PCEs) have reached 4-5%.[3] Although P3HT exhibits good charge transfer and separation properties, further improvement in PCE is difficult due to its relatively large band gap.[4] To enhance light harvesting ability, many low band gap conjugated polymers have been designed and synthesized successfully.

One feasible approach for obtaining low band gap polymers is to design donor-acceptor (D-A) conjugated copolymers with alternating electron donor and electron acceptor unit among the polymer main chain.[5] Thus, through the design and selection of donor and acceptor building units, the electronic and optical properties of D-A copolymers can be tuned. The intramolecular charge transfer (ICT) from electron donor to the electron acceptor unit can enhance the π-π stacking between polymer main chains and effectively reduce the band gap.[6] Many D-A low band gap copolymers have been applied to PSCs as donors and exhibited high short circuit current and PCE. However, these devices usually exhibit low open circuit voltage (Voc), which limits their PCEs.[7] According to the BHJ photovoltaic device model and experimental result, the Voc is determined by the energy difference between the HOMO level of the copolymer and the lowest unoccupied molecular orbital (LUMO) level of the PCBM.[8]

Introduction of fluorine atoms into the polymer backbone is very popular, since its small size is expected to minimize the undesired steric hindrance, and its high electron affinity property could reduce the HOMO and LUMO energy levels of resulting polymers.[9] Therefore, solar cell devices based on fluorinated polymers showed higher Voc and PCE in comparison with the corresponding non-fluorinated polymers. For instance, Luping Yu and co-authors reported higher Voc when fluorine atom is introduced to the thieno[3,4-b] unit, and PCE of 6.1% was achieved.[10] Hou and co-authors synthesized PBDTTT-C with a fluorine atom to lower the HOMO energy level and obtained a relatively high Voc of 0.76 V, and PCE of 7.73%.[11] Recently, a novel fluorinated electron acceptor unit, 5,6-difluoro-4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTffBT) has been developed based on which the conjugated polymers have attracted much attention and showed PCE up to 8%. [12]

Recently, dithieno[3,2-b:2',3'-d]silole (DTS)-based conjugated copolymers have shown very promising properties for in PSCs, since the planar conjugated structure that are favorable for cofacial stacking, thus benefiting charge transportation and the absorption in long wavelengths.[13] DTS was copolymerized with electron acceptor 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) unit, and the resulting polymer, PDTS-DTBT, exhibited PCE up to 3.45%.[14] However, the Voc of these devices was only 0.6 V, which limits their PCEs.

Here, we introduced DTffBT unit as an acceptor unit to synthesize a DTS-based copolymer, poly{4,4′-bis(2-ethylhexyl)dithieno[3,2-b:2′,3′-d]silole-alt-5,6-Difluoro-4,7-bis(4-hexylthiophen-2-yl)-2,1,3-benzothiadiazle}(PDTS-DTffBT). The DTffBT unit has a strong electron affinity and should behave as electron withdrawing unit in the polymer backbone leading to low HOMO energy level, which is desired property to increase the air stability of the polymer and the Voc in PDTS-DTffBT based photovoltaic devices. UV-vis absorption spectrum exhibited that the PDTS-DTffBT solid film covered a strong broad absorption range from 300 to 800 nm, which is an extremely desirable absorption for PSCs application. PDTS-DTffBT displayed a deeper HOMO energy level -5.28 eV and the PCE of the PSC with PDTS-DTffBT as donor and [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) as acceptor reached 5. 26%.

Experimental

Measurements and Characterization

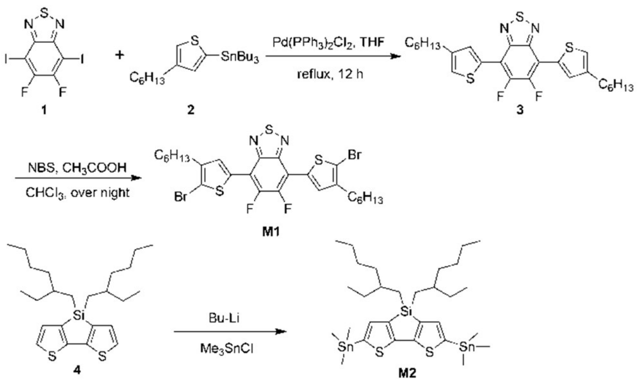
^{1}H NMR spectra were recorded on Bruker AVANCE 600-MHz spectrometer with chloroform-d as solvent and tetramethylsilane (TMS) as internal standard. The elemental analysis was carried out with a Thermoquest CHNS-Ovelemental analyzer. The gel permeation chromatographic (GPC) analysis was carried out with a Waters 410 instrument with tetrahydrofuran as the eluent (flowrate: 1mL/min, at 35 °C) and polystyrene as the standard. The thermogravimetric analysis (TGA) was performed on a Perkine Elmer Pyris 1 analyzer under nitrogen atmosphere (100 mL/min) at a heating rate of 10 °C/min. UV–visible absorption spectra were measured using a Shimadzu UV–3600 spectrophotometer. Electrochemical measurement of the copolymer was performed with a Bioanalytical Systems BAS 10 B/W electrochemical workstation.

Photovoltaic Device Fabrication and Characterization

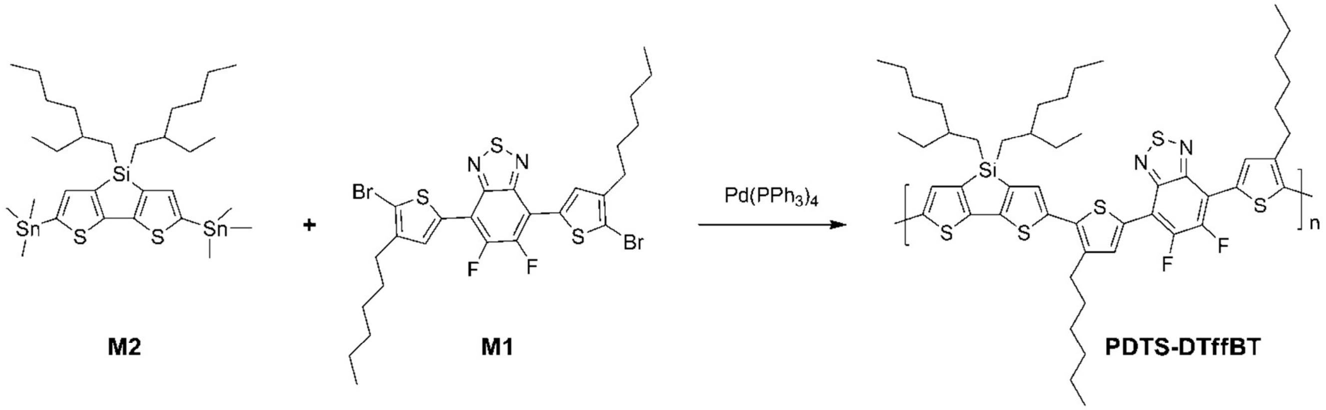
The solar cells were fabricated with a device structure of ITO/PEDOT:PSS/Polymer:$PC_{71}BM$ Blend/LiF/Al. The ITO glass substrates were pre-cleaned by detergent, deionized water, acetone and isopropyl alcohol sequently. After UV/ozone treatment for 10 min, highly conducting poly(3,4-ethylenedioxythiophene):poly(sty-enesulfonate) (PEDOT:PSS, Baytron P, Al 4083) was spin-casted (5000 rpm) at a thickness of ~ 40 nm from aqueous solution (after passing through a 0.22 μm filter). The substrate was annealed at 140 °C for 30 min on hot plate. The active layer contained a blend of copolymers as electron donor and $PC_{71}BM$ as electron acceptor, which was prepared by different weight ratio (1:1~1:4, w/w) in dichlorobenzene (10 mg/mL) for copolymer. The active layers were obtained by spin coating the blend solutions on top of the PEDOT:PSS film and the thickness of films were ~ 95 nm, as measured with the Ambios Technology XP-2. Subsequently, LiF (0.6 nm) and Al (100 nm) electrodes were deposited via thermal evaporation in vacuum (5×10^{-4} Pa) in thickness of approximately. The active area was about 6.4 mm^2. Current-voltage (*J-V*) characteristics were recorded using Keithley 2400 Source Meter in the dark and under 100 mW/cm^2 simulated AM 1.5 G irradiation (Sciencetech SS-0.5K Solar Simulator). The light intensity was measured by a photometer (International light, IL1400) and corrected by a standard silicon solar cell. All the measurements were performed under ambient atmosphere at room temperature.

Materials

All reagents were purchased from either Acros or Aldrich Chemical Co. and used without further purification, unless otherwise noted. In synthetic preparations, diethyl ether, THF and toluene were dried by distillation from sodium/benzophenone under nitrogen. Similarly, DMF and dichloromethane were distilled from CaH_2 under nitrogen. 5,6-difluoro-4,7-diiodo-2,1,3-benzothiadiazle (**1**), [9a] 4-(hexyl-2-thienyl)-stannane (**2**),[16] 5,6-Difluoro-4,7-bis(4-hexylthiophen-2-yl)-2, 1, 3-benzothiadiazle (**3**), [9a] and 4,4'-Bis(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole (**4**)[18] were prepared according reported procedures. All the reactions were carried out under nitrogen atmosphere.



Scheme 1. Synthesis of monomers (M1 and M2).



Scheme 2 Synthesis of copolymer PDTS-DTffBT.

5,6-Difluoro-4,7-bis(5-bromo-4-hexylthiophen-2-yl)-2, 1, 3-benzothiadiazle (**M1**)

To a solution of compound 3 (1.80 g, 3.566 mmol) in chloroform (80 mL) and acetic acid (15 mL) was added N-bromosuccinimide (NBS) (1.33 g, 7.489 mmol) at room temperature (RT). The reaction mixture was stirred in the dark at RT overnight. Then, the reaction mixture was poured into distilled water, and the organic layers were extracted with chloroform (3×50). The organic layer was washed with distilled water, dried over anhydrous magnesium sulphate ($MgSO_4$). After drying over $MgSO_4$ and removal of organic solvent under reduced pressure, the crude product was purified by column chromatography to provide a product of 1.86 g (yield: 79%).

^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ(ppm) 7.95 (s, 2H), 2.66 (t, *J*=7.8, 4H), 1.68 (m, 4H), 1.45-1.39 (m, 4H), 1.38-1.33 (m, 8H), 0.92 (t, *J*=7.2, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ(ppm) 150.69, 150.52, 148.61, 148.45, 148.29, 142.58, 131.67, 131.22, 114.48, 110.94, 110.87, 31.65, 29.72, 29.56, 28.97, 22.65, 14.12. Anal. Calch for $C_{26}H_{28}Br_2F_2N_2S_3$: C, 47.14; H, 4.26; N, 4.23; S, 14.52. Found: C, 47.13; H, 4.11; N, 4.08; S, 14.54. MALDI-TOF MS: Calch for $C_{26}H_{28}Br_2F_2N_2S_3$ m/z=662.51; Found 662.54.

4,4'-Bis(2-ethylhexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]silole (**M2**)

To a solution of 4,4'-Bis(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole (**4**) (2.0 g, 4.77 mmol) in anhydrous THF (45 mL) at -78 °C, n-BuLi (4.0 mL, 10.03 mmol) was added dropwise, and the mixture was stirred at -78 °C under a nitrogen atmosphere for 1 h. Then Trimethyltin chloride (11 mL, 1 M in *n*-hexane) was added, and the mixture was stirred at -78 °C for 1 h. After being stirred at ambient temperature for 12 h, the reactant was poured into cool water and extracted by diethyl ether for three times. After removal organic solvent, 4,4'-Bis(2-ethylhexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]silole (3.36 g, 4.52 mmol), monomer (M2), was obtained as sticky yellow oil with a yield of 94.7% and used without any further purification.

^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ(ppm) 7.09 (s, 2H), 1.47-1.41 (m, 2H), 1.35-1.12 (m, 16H), 0.95-0.89 (m, 4H), 0.84 (t, *J*=6.6, 6H), 0.79 (t, *J*=7.2, 6H), 0.39 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ(ppm) 154.73, 143.91, 137.95, 137.44, 35.97, 35.67, 29.01, 28.91, 23.08, 17.88, 14.27, 10.93, -8.13. MALDI-TOF MS: Calch for $C_{30}H_{54}S_2SiSn_2$ m/z=744.39; Found 744.02.

Poly{4,4′-bis(2-ethylhexyl)dithieno[3,2-b:2′,3′-d]silole-alt-5,6-Difluoro-4,7-bis(4-hexylthiophen-2-yl)-2, 1, 3-benzothiadiazle}(PDTS-DTffBT)

Monormer **1** (0.172 g, 0.259 mmol), monomer **2** (0.193 g, 0.259 mmol), dry toluene (6 mL) and N, N-dimethyl formamide (DMF) (1 mL) were added to a 25 mL double-neck round-bottom flask. The reaction container was purged with nitrogen for 30 minutes to remove oxygen, and then $Pd(PPh_3)_4$ (15 mg) was poured. The reaction was heated at 110 °C for 28 h under nitrogen. The reactant was cooled down to room temperature and poured into MeOH (200 mL) and filtered through a Soxhlet thimble, subsequently filter residue was subjected to Soxhlet extraction with MeOH, hexane, and chloroform. The fraction from chloroform was concentrated under reduced pressure and precipitated into MeOH, collected by filtration. The final polymer was dried under vaccum overnight to afford PDTS-DTffBT as a black solid (187 mg, yield: 78%).

^{1}H NMR (600 MHz, $CDCl_3$, TMS): 8.10 (br, 2H), 7.10 (br, 2H), 2.88 (br, 4H), 1.77 (br, 4H), 1.64-1.18 (m, 30H), 1.07 (br, 4H), 1.02-0.75 (m, 18H). GPC: Mn=16000, Mw=24300, PDI=1.52.

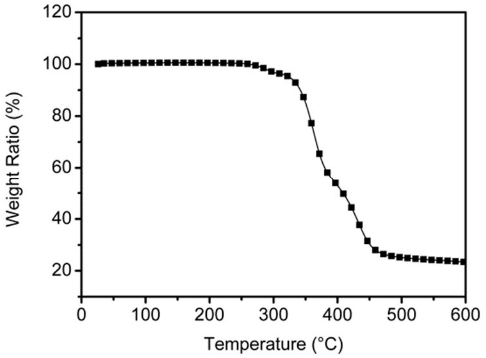


Fig. 1. TGA curve of copolymer PDTS-DTffBT at the heating rete of 10 °C/min under nitrogen atmosphere.

Results and discussion

On the basis of the D-A concept, the strong electron donating DTS unit and strong withdrawing DTffBT unit were utilized to synthesize the low band gap PDTS-DTffBT copolymer. The synthesis routes of the monomers and corresponding copolymer are shown (PDTS-DTffBT) Schemes 1 and 2. The PDTS-DTffBT was obtained by reacting the corresponding bis(stannyl) monomer (DTS) with monomer (DTffBT) via Stille coupling polymerization. The resulting polymer was collected by precipitating the polymer solution in methanol and filtered. It was in a Soxhlet extractor sequentially with methanol, hexane, and chloroform to remove residual catalyst and oligomers. The polymer PDTS-DTffBT exhibits an excellent film casting property, as well as good solubility in common organic solvents such as chloroform, tetrahydrofuran, and chlorobenzene. The weight average molecular (Mw) of the resulting copolymer was measured to be 24300 g/mol with a polydispersity (PDI) of 1.52 by gel permeation chromatography (GPC) with THF as the solvent. Fig. 1 shows the thermalgravimentric analysis (TGA) curve of the resulting copolymer at the heating rate of 10 °C/min under nitrogen atmosphere. It shows high thermal stability of 325 °C, which indicates that the thermal stability of PDTS-DTFBT is good enough for the application in optoelectronic devices.

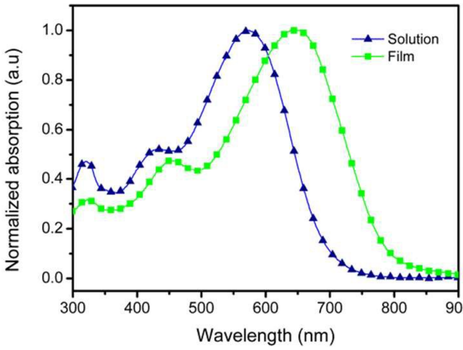


Fig. 2. Uv-vis absorption spectra of PDTS-DTffBT in chloroform solution and in thin film.

Optical properties

The normalized UV-vis absorption spectra measured for the copolymer PDTS-DTffBT in dilute solution and solid film are show in Fig. 2, and the main optical properties are summarized in Table 1. PBDT-DTffBT in dilute chloroform solution exhibits two absorption peaks at 434 and 572 nm, respectively, covering a broad wavelength range from 300 to 700 nm, which is benefited from its D-A polymer backbone. The absorption peak at 434 nm corresponds to the π-π* absorption of the conjugated copolymer backbone, and the strong absorption band in the longer wavelength region having an absorption peak at 572 nm is attributed to intramolecular charge transfer transition from DTS donor unit to DTffBT acceptor unit.[19] In solid film, the absorption of the copolymer becomes broader and is significantly red shifted with the maximum absorption peak located at 652 nm. Compared to its counterpart in dilute solution, the absorption spectrum of PBDT-DTffBT in the thin film exhibited a red shifted by about 80 nm, indicating a more planar polymer chain structure/or the degree of interchain π-stacking in the solid state.[20] The optical band gap of PDTS-DTffBT is 1.58 eV, calculated from the absorption edge of the thin solid film.

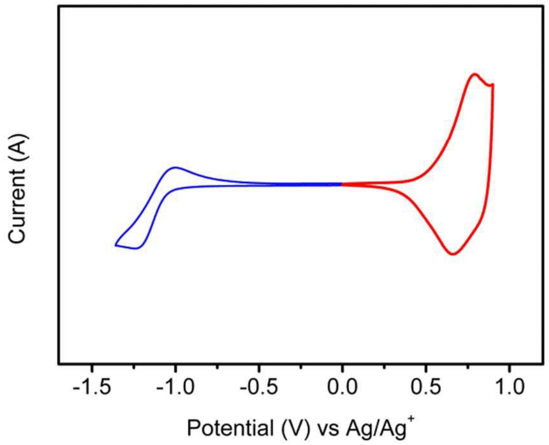


Fig. 3 Cyclic voltammogram of PDTS-DTFBT film on a platinum electrode measured in 0.1mol L^{-1} Bu_4NPF_6 acetonitrile solution at a rate of 50 mV s^{-1}.

Electrochemical properties

Electrochemical cyclic volta1mmetry has been usually used to investigate the redox behavior of a polymer and to estimate its HOMO and LUMO levels. Cyclic votammetry of the polymer in film was performed in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte at a scan retes of 50 mV s^{-1} with platinum button working electrodes, a Platinum wire counter electrode, and an Ag/$AgNO_3$ reference electrode under N_2 atmosphere. Ferrocene/ferrocenium (Fc/Fc$^+$) was used as the internal standard. The redox curve of the polymer is presented in Fig. 3. On the anodic sweep, PDTS-DTffBT showed a reversible oxidation with onset potential of 0.57 V (versus Ag/Ag$^+$). In contrast, the cathodic sweep showed an onset reversible reduction potential of 1.05 V.

From the onset oxidation potential and the onset reduction potential of the PDTS-DTffBT, its HOMO and LUMO levels as well as the band gap were calculated according to the following equations:[21]

$$\mathrm{HOMO(eV)} = -e(E_{\mathrm{ox}}^{\mathrm{onset}} + 4.71)$$
$$\mathrm{LUMO(eV)} = -e(E_{\mathrm{red}}^{\mathrm{onset}} + 4.71)$$
$$E_{\mathrm{g}}^{\mathrm{ec}}(\mathrm{eV}) = e(E_{\mathrm{ox}}^{\mathrm{onset}} - E_{\mathrm{red}}^{\mathrm{onset}})$$

Where, E_{ox}^{onset} and E_{red}^{onset} are the measured onset potentials relative to Ag/Ag$^+$.

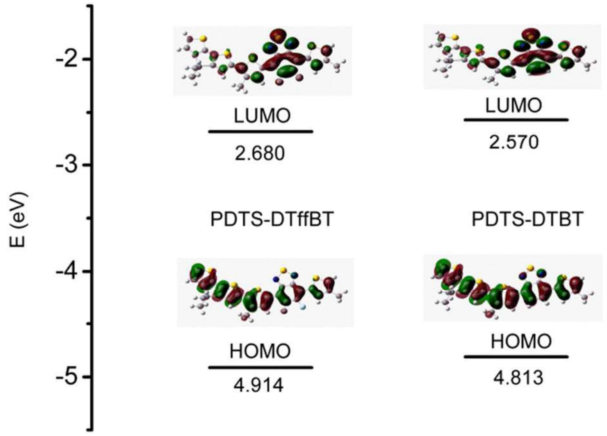


Fig. 4 DFT-calculated LUMO and HOMO of the geometry optimized structures of analogous monomers of PDTS-DTffBT and PDTS-DTBT.

The results of the electrochemical measurements and calculated energy levels of PDTS-DTffBT are listed in Table 1. The HOMO and LUMO energy levels of PDTS-DTffBT were estimated 5.28 and 3.66 eV, respectively. PDTS-DTffBT possesses deeply low-lying HOMO and LUMO energy levels than those non-fluorined polymers, which indicates the effect of incorporated electron deficient fluorine atom in decreasing the energy levers of HOMO and LUMO. In addition, the relatively low-ying HOMO level may be favored for the improvement of the Voc when fabricating the photovoltaic devices with and PCBM as acceptor. The electrochemical band gap of the copolymer PDTS-DTffBT was calculated 1.62 eV, which is slightly higher than the optical band gap within the experimental error.

Theoretical calculation

Fig. 4 depicts the electron state density distribution for the HOMO and LUMO of analogous monomer PDTS-DTffBT based on B3LYP/6-31G* level. To simplify the calculation, only one repeating unit of copolymer was subject to the calculation. The

Table 1. Summary of Optical and Electrochemical Properties of PDTS-DTffBT

$\lambda_{\mathrm{max}}^{\mathrm{abs,sol}}$ nm	$\lambda_{\mathrm{max}}^{\mathrm{abs,film}}$ nm	ε cm^{-1}	$E_{\mathrm{ox}}^{\mathrm{onset}}$ V	HOMO eV	$E_{\mathrm{red}}^{\mathrm{onset}}$ V	LUMO eV	$E_{\mathrm{g}}^{\mathrm{ec}}$ eV	$^{a}E_{\mathrm{g}}^{\mathrm{opt}}$ eV
434/572	455/652	9.1×10^{4}	0.57	-5.28	-1.05	-3.66	1.62	1.58

^{a} $E_{\mathrm{g}}^{\mathrm{opt}} = 1240/\lambda_{\mathrm{Ab}}^{\mathrm{onset}}$

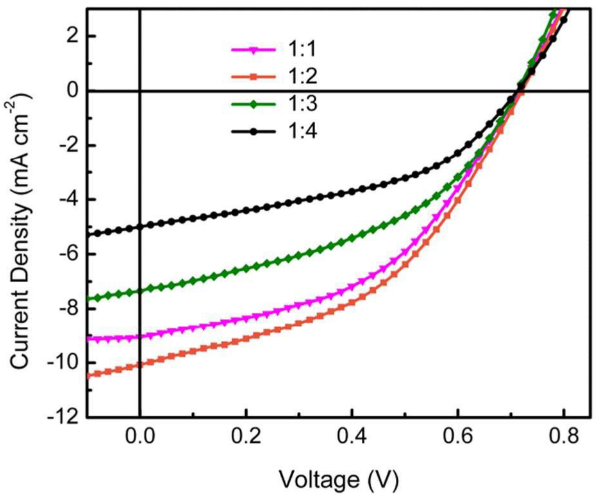


Fig. 5. *J-V* curves of the polymer solar cells based on PDTS-DTffBT: P_{71}CBM with different blend ratios (1:1, 1:2, 1:3, 1:4, w/w) under the illumination of AM 1.5G, 100 mW/cm^2.

LUMO of the copolymer is mainly localized on the DTffBT acceptor unit, while the HOMO is distributed over the entire conjugated molecular backbone, which indicates that introduction of the fluorine atoms significantly affects the LUMO and HOMO level of the corresponding copolymer. For comparison, the DFT-calculated results of analogous monomer of non-fluorinated copolymer are also shown in Fig.4. Both the HOMO and LUMO levels of PDTS-DTffBT are slightly lower than that of non-fluorined copolymer, which is in agreement with the experimental results estimated from the electrochemical measurement.

Photovoltaic properties

The photovoltaic properties of PDTS-DTffBT were investigated with a conventional structure of ITO/PEDOT:PSS (P VP AI 4083)/PDTS-DTffBT:PC_{71}BM/LiF/Al, where poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was used to facilitate hole extraction and lithium fluoride (LiF) was used for hole blocking and electron extraction. The photoactive layers were spin-coated from dichlorobenzene (DCB) solutions at various PDTS-DTffBT:PC_{71}BM blend compositions.

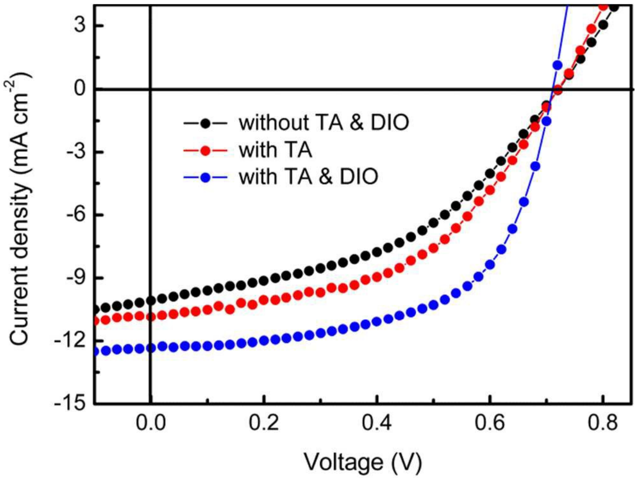


Fig. 6. *J-V* curves of the polymer solar cells based on PDTS-DTffBT: P_{71}CBM with blend ratios (1:2, w/w) under the illumination of AM 1.5G, 100 mW/cm^2.

Fig. 5 shows the typical current density-voltage (*J*-V) characteristics of various weight ratios under one sun of simulated AM 1.5G irradiation (100 mW·cm^{-2}). Corresponding performance parameters of these devices are summarized in Table 2. The Voc values of all devices range from 0.71 to 0.72 V. Based on the explanation proposed by Scharber. M. C. et.al,[8a] the Voc value of a BHJ photovoltaic device is related to the energy difference between the HOMO energy level of the donor component and the LUMO energy level of the acceptor component, and can be theoretically calculated with the following formula, $V_{\mathrm{oc}} = {}^{1}\!/_{\mathrm{e}}(|E^{Donor}HOMO| - |E^{PCBM}LUMO|) - 0.3\mathrm{V}$. Finally the theoretically estimated result of the Voc value is equal to 0.68 V, which is very close to the practically measured results ranging from 0.71 to 0.72 V for all devices. The Voc of these devices are about 0.12 V higher than those of non-fluorinated copolymers, attributed to the much lower HOMO level. Among these devices prepared using DCB as the processing solvent, the best device performance was obtained at a weight ratio of 1:2, with Voc= 0.72 V, *J*sc = 10.07 mA·cm^{-2}, a fill factor (FF) of 0.45, and an overall PCE of 3.26%. So we chose the 1:2 weight ratio for further device optimization by thermal annealing (TA). When the active layer is annealed at 120 °C for 5 min, the *J*sc improves slightly from 10.07 to 10.85 mA·cm^{-2}, the FF increases from 45 to 48, the Voc remains unchanged. As a result, the PCE improves from 3.26% to 3.78%.

Table 2. Photovoltaic Properties of Polymer Solar Cells Based on PDTS-DTffBT:PC_{71}BM.

polymer: PC_{71}BM	Thickness nm	*V*oc (V)	*J*sc (mA/cm^2)	FF	PCE
1: 1	98	0.72	9.06	0.46	3.00 (2.89)
1: 2	95	0.72	10.07	0.45	3.26 (3.18)
1: 3	92	0.71	7.35	0.44	2.30 (2.24)
1: 4	85	0.71	5.00	0.45	1.60 (1.52)
1: 2[a]	92	0.72	10.85	0.48	3.78 (3.65)
1: 2[b]	95	0.71	12.35	0.60	5.26 (5.12)

[a] with thermal annealing, [b]with thermal annealing and DIO

The average PCE in parentheses was obtained from over 10 devices.

It is worthwhile to note that the processing additive, 1,8-diiodooctance (DIO), played an important role in improving the performance of solar cells devices.[21] When DIO (3%) was added into the blend solution of PDTS-DTffBT/PC_{71}BM, the fabricated active layer remained annealed at 120 °C for 5 min, the device performance shows apparent improvement. The *J*sc increased from 10.85 to 12.35 mA·cm^{-2}, FF increased from 48 to 60. AS a result, PCE of the device enhanced from 3.78 to 5.26%. Incorporation of DIO leads to around 39.1% enhancement of PCE due to the notable enhanced *J*sc and improved FF. The *J-V* curves of the optimized devices (with annealing and additive) and reference device (without annealing and additive) are shown in Fig. 6, with the corresponding performance parameters summarized in Table 2.

Fig. 7 displays external quantum efficiency (EQE) spectra of the PDTS-DTffBT:PC_{71}BM devices prepared at 1:2 blend weight ratio. The EQE curves of the devices exhibit a broad response range covering from 330 to 800 nm. The device with additive exhibits the highest improvement from 420 to 800 nm with the maximum EQE value of 49%. The maximum EQE values for the reference device and the thermal annealing device are 42% and 45%, respectively. The measured EQE enhancements are consistent with the increased *J*sc values of the devices with thermal annealing and incorporation of DIO.

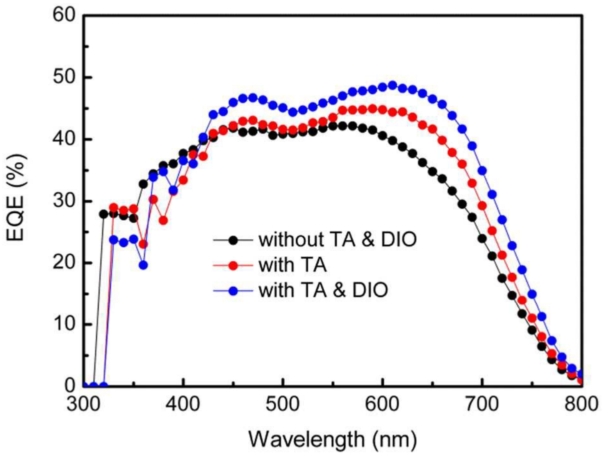


Fig. 7. The EQE of polymer solar cells based on PDTS-DTffBT:P$_{71}$CBM with blend ratios (1:2, w/w).

Conclusions

In conclusion, we have synthesized a new D-A conjugated copolymer PDTS-DTffBT containing DTS donor and DTffBT acceptor unit by the Stille-coupling reaction. This polymer possessed good thermal stability, low band gap and strong absorbance from 300 to 800 nm. PDTS-DTffBT exhibited a low-lying HOMO energy level, due to the presence of strongly electron withdrawing DTffBT unit. A preliminary device test based on the blend of PDTS-DTffBT with PC$_{71}$BM gives very promising results with PCE up to 5.26%.

Acknowledgements

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Notes and references

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Synthesis and Photovoltaic Properties of Dithieno[3,2-b:2',3'-d]silole-Based conjugated copolymer

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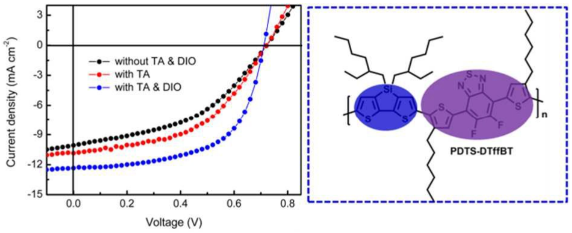

Efficient polymer solar cells were fabricated by blending PDTS-DTffBT with $PC_{71}BM$, and the power conversion efficiency reached to 5.26%.