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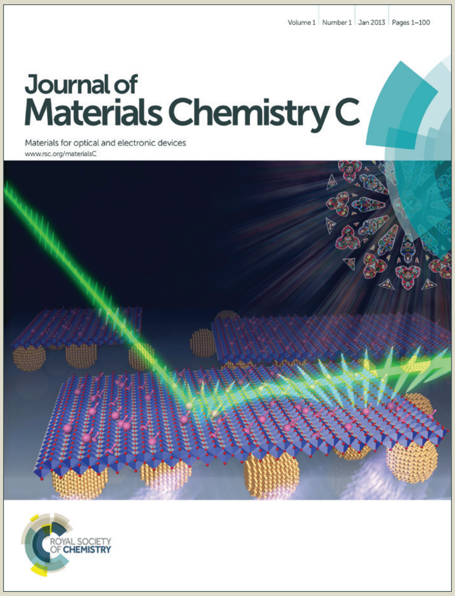

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ARTICLE

5,6-Difluorobenzothiadiazole and silafluorene based conjugated polymers for organic photovoltaic cells

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To achieve 5,6-difluorobenzothiadiazole and 2,7-linked silafluorene based soluble conjugated polymers, flexible side chains were attached at different positions of the conjugated polymers. Three soluble polymers **PSiF-D(OT)DFBT**, **PSiF-TTDFBT**, and **PDOSiF-DTDFBT** were prepared and used as donor materials for polymer solar cells. **PSiF-D(OT)DFBT** exhibits a band gap of 2.06 eV with a deep HOMO of -5.64 eV. **PSiF-TTDFBT** shows a band gap of 1.75 eV with the HOMO of -5.23 eV. **PDOSiF-DTDFBT** is of a band gap of 1.86 eV with the HOMO level of -5.37 eV. Among these three polymers, **PDOSiF-DTDFBT** shows the highest field effect transistor (FET) hole mobility up to 3.31×10^{-2} $cm^2V^{-1}s^{-1}$, **PDOSiF-DTDFBT**:$PC_{71}BM$ blend films show the highest SCLC mobility up to 5.10×10^{-4} $cm^2V^{-1}s^{-1}$, and polymer solar cells (PSCs) with the blend of **PDOSiF-DTDFBT**:$PC_{71}BM$ (1:1, by weight) as the active layer gave a power conversion efficiency (PCE) of 4.03% with an open circuit voltage (V_{oc}) of 0.73 V, a short circuit current (J_{sc}) of 8.55 mA/cm^2, and a fill factor (*FF*) of 0.65. Our studies also reveal the structure-property relationship of 2,7-linked silafluorene and 5,6-difluorobenzothiadiazole based conjugated polymers.

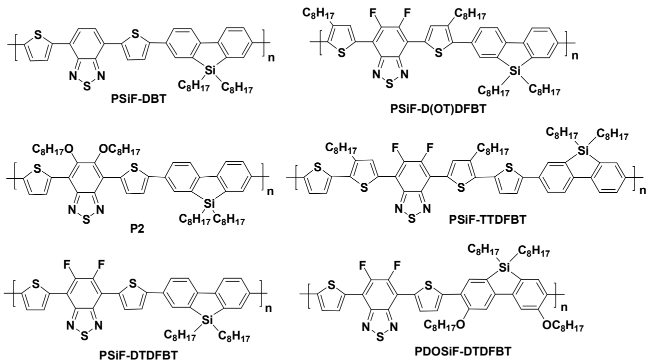
Introduction

The synthesis of new donor-acceptor (D-A) alternating conjugated polymers with high power conversion efficiency (PCE) is still an important topic in the research field of polymer solar cells (PSCs).[1-7] Benzothiadiazole (BT) is a widely used acceptor unit, and many BT containing D-A alternating conjugated polymers have afforded high device performance when blended with $PC_{71}BM$ as the active layer for PSCs.[8-12] The introduction of two fluoro atoms in the 5,6-positions of benzothiadiazole unit not only lowers the HOMO and LUMO energy levels of the resulted conjugated polymers to achieve higher open circuit voltage (V_{oc}), but also increases the intramolecular polymer chain interactions to afford higher hole mobility.[13] Compared with the corresponding BT based conjugated polymers, 5,6-difluorobenzothiazole (DFBT) based conjugated polymers usually gave better device performance.[14-16] Except the above mentioned advantages, the introduction of DFBT into polymer main chain usually brings about the DFBT containing polymers with poor solubility.[3]

Silafluorene has been used as donor unit for the construction of D-A alternating conjugated polymers for high efficiency PSCs.[12,17-19] Conjugated polymer **PSiF-DBT**, as shown in Chart 1, with BT as the acceptor unit, silafluorene as the donor unit, and thiophene as the spacer has been reported as donor material with good device performance.[12,20,21] In our previous paper, we have reported the synthesis of 5,6-bis(octyloxy)benzothiadiazole and silafluorene based conjugated polymer **P2**, as shown in Chart 1, for high efficiency PSCs.[21] Due to the good solubility, high molecular weight **P2** has been synthesized and PSCs with **P2**:$PC_{71}BM$ as the active layer gave a PCE of 6.05%.

Due to the fascinating properties of both DFBT and silafluorene, herein we would like to report the rational design and synthesis of DFBT and silafluorene based conjugated polymers. To achieve polymers with good photovoltaic performance, four D-A conjugated polymers **PSiF-DTDFBT**, **PSiF-D(OT)DFBT**, **PSi-TTDFBT**, and **PDOSiF-DTDFBT**, as shown in Chart 1, have been designed and synthesized. We first designed and synthesized **PSiF-DTDFBT**, which is insoluble even at elevated temperature in commonly used organic solvents such as chloroform, chlorobenzene (CB), 1,2-dichlorobenzene (DCB), and 1,2,4-trichlorobenzene (TCB), and can’t be used for the fabrication of PSCs. To obtain soluble polymers, we have attached an octyl chain on the 4-position of thiophene unit, and synthesized polymer **PSiF-D(OT)DFBT**. The disadvantage of such design is that the octyl chain on the thiophene unit will give rise to a large dihedral angle between the thiophene unit and silafluorene and result in poorer conjugation. To enhance the polymer chain conjugation, we incorporated two additional thiophene units into the polymer main chain and synthesized polymer **PSiF-TTDFBT**. It is worth noting that similar fluorene based D-A polymers **PFO-M1-3** with four thiophene units in each repeating unit have been reported by Wang and Cao et al. and **PFO-M3** exhibited improved photovoltaic performance in compared with **PFO-DTBT**.[22] Alternatively, we have designed and synthesized **PDOSiF-DTDFBT** via attaching four flexible chains onto the silafluorene unit to enhance the solubility of polymers. The structures of three soluble polymers were fully characterized, and their optical, electrochemical, and photovoltaic properties were investigated in detail to explore their structure and property relationships.

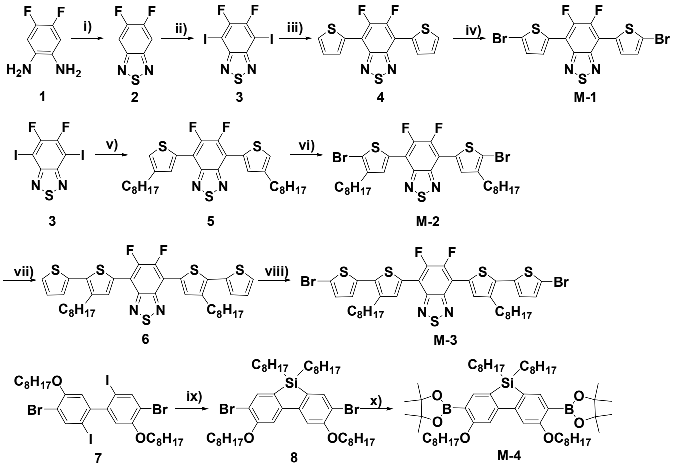
Chart 1



Results and discussion

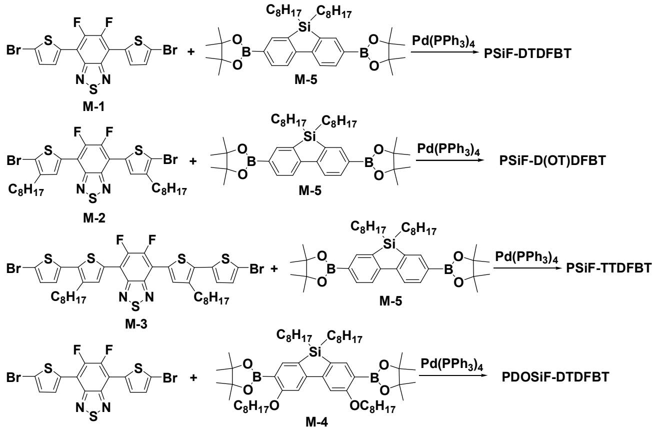
Material Synthesis and Characterization

The syntheses of monomers **M-1**, **M-2**, **M-3**, and **M-4** are outlined in Scheme 1. **M-1** was synthesized using commercially available 4,5-difluorobenzene-1,2-diamine as the starting material according to the literature procedures.[23] Suzuki cross-coupling of **3** with 4-octylthiophene-2-boronic acid pinacol ester was followed by bromination of the cross-coupling product with Br_2 in methylene chloride at room temperature to afford **M-2**, which bears two octyl chains on the two thiophene units. Coupling of **M-2** and thiophene-2-boronic acid pinacol ester using Suzuki-Miyaura cross-coupling reaction furnished compound **6** in a yield of 75%, which was converted to **M-2** by bromination with NBS in a solvent mixture of chloroform and DMF at room temperature. Compound **8** was synthesized according to literature procedures.[19] Reaction of **8** and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane under Miyaura conditions afforded **M-4** in a yield of 59%. The synthesis of polymers **PSiF-DTDFBT**, **PSiF-D(OT)DFBT**, **PSiF-TTDFBT**, and **PDOSiF-DTDFBT** are outlined in Scheme 2. Suzuki polycondensation of **M-1** with **M-5**,[21] **M-2** with **M-5**, **M-3** with **M-5**, and **M-1** with **M-4** afforded **PSiF-DTDFBT**, **PSiF-D(OT)DFBT**, **PSi-TTDFBT**, and **PDOSiF-DTDFBT**, respectively. Except **PSiF-DTDFBT**, all the other polymers are fully soluble in CB, DCB, and TCB at elevated temperature. Molecular weights and molecular weight distributions of these three soluble polymers were measured by gel permeation chromatography (GPC) using TCB as an eluent at 150 °C with narrowly distributed polystyrenes as the calibration standards, and the results are summarized in Table 1. **PSiF-D(OT)DFBT** showed a number average molecular weight (M_n) of 69.6 kg/mol, a weight average molecular weight (M_w) of 218.3 kg/mol, and a polydispersity index (PDI) of 3.14. **PSiF-TTDFBT** showed a M_n of 31.0 kg/mol, a M_w of 100.6 kg/mol, and a PDI of 3.25. **PDOSiF-DTDFBT** showed a M_n of 40.0 kg/mol, a M_w 119.8 kg/mol, and a PDI of 3.00. For many polymers, the photovoltaic performance of devices is highly dependent on their molecular weight. Only high molecular materials can furnish good device performance. It is worthy noting we have obtained soluble and high molecular weight **PSiF-D(OT)DFBT**, **PSiF-TTDFBT**, and **PDOSiF-DTDFBT**. These three polymers are of good thermal stability as indicated by thermo gravimetric analysis (TGA) measurements. The 5% decomposition temperatures of **PSiF-D(OT)DFBT**, **PSiF-TTDFBT**, and **PDOSiF-DTDFBT** are 447 °C, 440 °C, and 397 °C, respectively. Differential scanning calorimetry (DSC) measurements from 20 to 300 °C under nitrogen atmosphere showed that there is no obvious glass transition for these polymers. Powdery X-ray diffraction (XRD) measurements were carried out to investigate the packing of polymer chains in solid state. As shown in Figure 1, XRD diffraction patterns of **PSiF-D(OT)DFBT**, **PSiF-TTDFBT,** and **PDOSiF-DTDFBT** exhibited two diffraction peaks. The first peak at small angle region, which reflexes the distance of polymer backbones separated by the flexible side chains, is located at 2θ of 4.36 ° for **PSiF-D(OT)DFBT,** 5.69 ° for **PSiF-TTDFBT**, and 4.57 ° for **PDOSiF-DTDFBT**, corresponding to a distance of 20.27, 15.53, and 19.69 Å, respectively. The three diffraction peaks at the wide angle region reflex the π-π stacking distances between polymer backbones, which are located at 2θ of 20.94 ° for **PSiF-D(OT)DFBT**, 25.43 ° for **PSiF-TTDFBT**, and 24.16 ° for **PDOSiF-DTDFBT**, corresponding to π-π stacking distances of 4.24, 3.50, 3.68Å, respectively.



Scheme 1 Synthesis of monomers, Reagents and conditions: i) aniline, $SOCl_2$, toluene, 100 °C; ii) NIS, AcOH, H_2SO_4, rt; iii) $Pd_2(dba)_3$, P(o-tol)$_3$, thiophene-2-

boronic acid pinacol ester, $NaHCO_3$, THF/H_2O, reflux; iv) Br_2, CH_2Cl_2, rt; v) $Pd_2(dba)_3$, P(*o*-tol)$_3$, 4-octylthiophene-2-boronic acid pinacol ester, $NaHCO_3$, THF/H_2O, reflux; vi) Br_2, CH_2Cl_2, rt; vii) $Pd_2(dba)_3$, P(o-tol)$_3$, thiophene-2-boronic acid pinacol ester, $NaHCO_3$, THF/H_2O, reflux; viii) NBS, $CHCl_3$/DMF, rt; ix) *n*-BuLi, dichlorodioctylsilane, -100 °C; x) 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, $PdCl_2(PPh_3)_2$, Et_3N, 1,2-dichloroethane, 80 °C



Scheme 2 Synthesis of polymers

Table 1 Physical Properties of the polymers

polymer	M_n (kg/mol)^a	M_w (kg/mol)^a	PDI	T_d (°C)^b
PSiF-D(OT)DFBT	69.6	218.3	3.14	447
PSiF-TTDFBT	31.0	100.6	3.25	440
PDOSiF-DTDFBT	40.0	119.8	3.00	397

^{a} M_n, M_w, and PDI of polymers were determined by GPC at 150 °C using polystyrene standards with TCB as an eluent. ^{b} Decomposition temperatures were determined by TGA under N_2 based on 5% weight loss.

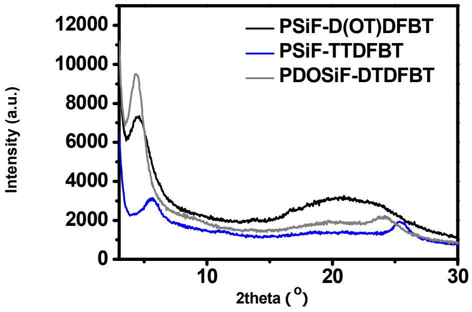


Fig. 1 Powdery XRD patterns of polymers.

Optical Properties. UV-vis absorption spectra of polymers **PSiF-D(OT)DFBT**, **PSiF-TTDFBT**, and **PDOSiF-DTDFBT** in DCB solutions at 100 °C and as thin films are shown in Figure 2. To eliminate the influence of aggregation of polymer chains in DCB solutions, UV-vis absorption spectra of polymer solutions were measured at 100 °C. All polymers exhibit two absorption peaks both in solutions and as thin films, and the peak locations are summarized in Table 2. In comparison with their solution spectra, the film ones are all red-shifted and broadening due to the aggregation of polymer chains in the solid state. For **PSiF-D(OT)DFBT**, due to the steric hindrance of octyl chain on the thiophene unit, the absorption spectrum of **PSiF-D(OT)DFBT** is much narrower, and its film absorption onset is 603 nm, corresponding to an optical band gap of 2.06 eV. For **PSiF-TTDFBT**, in comparison with **PSiF-D(OT)DFBT**, the introduction of two additional thiophene units in the polymer main chain can release the steric hindrance of the octyl chain and result in small dihedral angel between the two adjacent thiophene units. Therefore, the film absorption spectrum of **PSiF-TTDFBT** is much broad, and the film absorption onset is 708 nm, which gave an optical band gap of 1.75 eV. For **PDOSiF-DTDFBT**, due to the supramolecular S-O interaction, the two octyloxy substituents on the silafluorene can planarize the polymer main chain in some extent.[24,25] As a result, **PDOSiF-DTDFBT** as film exhibited broader absorption with an absorption onset at 668 nm, giving an optical band gap of 1.86 eV. The absorption onsets and optical band gaps ($E_{g,opt}$) are also summarized in Table 2.

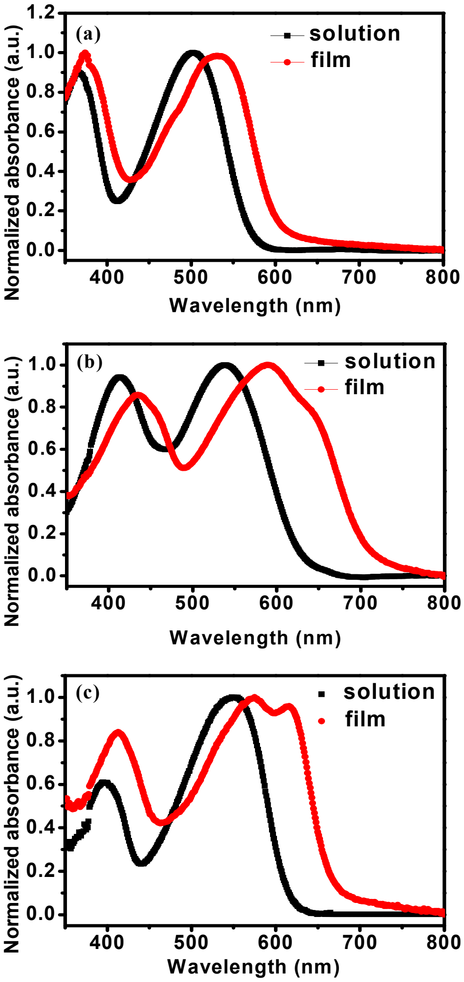


Fig. 2 UV-vis absorption spectra of **PSiF-D(OT)DFBT** (a), **PSiF-TTDFBT** (b) and **PDOSiF-DTDFBT** (c) in DCB solutions at 100 °C and as thin films.

Table 2 Electrochemical and optical properties of polymers.

polymer	λ_{max} [nm] solution^a	$E_{g,\ opt}$ (eV)^b	HOMO (eV)	LUMO (eV)^c
PSiF-D(OT)DFBT	366,501	2.06	-5.64	-3.58
PSiF-TTDFBT	411,538	1.75	-5.23	-3.48
PDOSiF-DTDFBT	397,548	1.86	-5.37	-3.51

^{a} measured at 100 °C. ^{b} calculated from the absorption band edge of the copolymer film, $E_{g,opt}$ = 1240/$\lambda_{edge.}$ ^{c} calculated by the equation $E_{LUMO} = E_{HOMO} + E_{g,opt}$. ^{d} shoulder peak.

Electrochemical Properties. Cyclic voltammetry (CV) was used to study the electrochemical properties of polymers and the CV curves are shown in Figure 3. The onset oxidation potentials of **PSiF-D(OT)DFBT**, **PSiF-TTDFBT**, and **PDOSiF-DTDFBT** determined by CV are 0.93 V, 0.52 V, and 0.66 V, respectively. According to the equation $E_{HOMO} = -e(E_{ox} + 4.71)$, HOMO levels were calculated to be -5.64 eV for **PSiF-D(OT)DFBT**, -5.23 eV for **PSiF-TTDFBT**, and -5.37 eV for **PDOSiF-DTDFBT**. Among these three polymers, **PSiF-D(OT)DFBT** is of the lowest HOMO level; compared with **PSiF-D(OT)DFBT**, the introduction of two additional thiophene in the main chain has lifted the HOMO level of **PSiF-TTDFBT** for 0.41 eV to -5.23 eV. Compare with **PSiF-D(OT)DFBT**, the introduction two electron donating octyloxy substituents on the silafluorene has raised the HOMO level of **PDOSiF-DTDFBT** for 0.27 eV to -5.37 eV. LUMO levels calculated according to the equation $E_{LUMO} = E_{HOMO} + E_{g,opt}$ to be -3.58 eV for **PSiF-D(OT)DFBT**, -3.48 eV for **PSiF-TTDFBT**, -3.51 eV for **PDOSiF-DTDFBT**. The data are also summarized in Table 2. The low-lying HOMO level of **PSiF-D(OT)DFBT** is favorable for achieving higher open circuit voltage (V_{oc}), as confirmed by device results (vide infra).

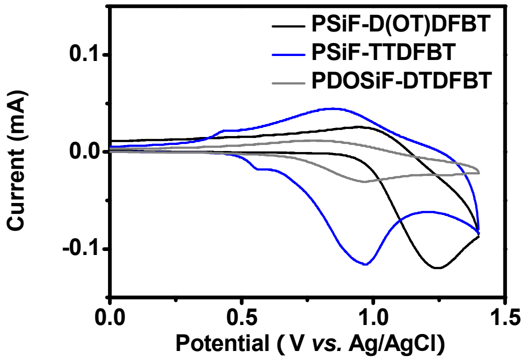


Fig. 3 Cyclic voltammograms of the polymers

Field-effect transistor fabrication and characterization

Hole mobility up to 10^{-3} $cm^2V^{-1}s^{-1}$ is usually required for polymer donors in order to obtain balanced electron and hole mobility for the polymer and PCBM blends, and balanced mobility is very crucial for achieving high performance polymer solar cells. Transport properties of polymers were therefore investigated by fabrication of field effect transistors (FETs). Bottom-contact devices were fabricated on Si/SiO_2 substrates with the low resistance Si as gate and SiO_2 (500 nm) as gate insulator. Polymer thin films were spin-coated on the OTS-modified Si/SiO_2 substrates from DCB solutions, and Au electrodes with a thickness of 25 nm were vacuum deposited onto polymer thin films. The transfer and output characteristic curves of FET devices are shown in Figure 4. Hole mobility (μ) was deduced from the derivative plots in the saturated regime through equation $I_{DS} = \mu(W/2L)C_i(V_G - V_T)^2$ where I_{DS} is the drain current, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer (SiO_2, 300 nm, C_i = 11 nF/cm^2), V_G and V_T is the gain voltage and threshold voltage, respectively. Hole mobilities of **PSiF-D(OT)DFBT, PSiF-TTDFBT**, and **PDOSiF-DTDFBT** are 6.94×10^{-3}, 3.09×10^{-2} and 3.31×10^{-2} $cm^2V^{-1}s^{-1}$, respectively, which are close to the electron mobility of $PC_{71}BM$. Hole mobilities, V_T, and on/off ratios are summarized in Table 3.

Table 3 FET properties of the pure polymer films

polymers	on/off	μ (cm^2/Vs)	V_T (V)
PSiF-D(OT)DFBT	8.4×10^5	6.94×10^{-3}	-40
PSiF-TTDFBT	2.0×10^6	3.09×10^{-2}	-37
PDOSiF-DTDFBT	4.7×10^6	3.31×10^{-2}	-35

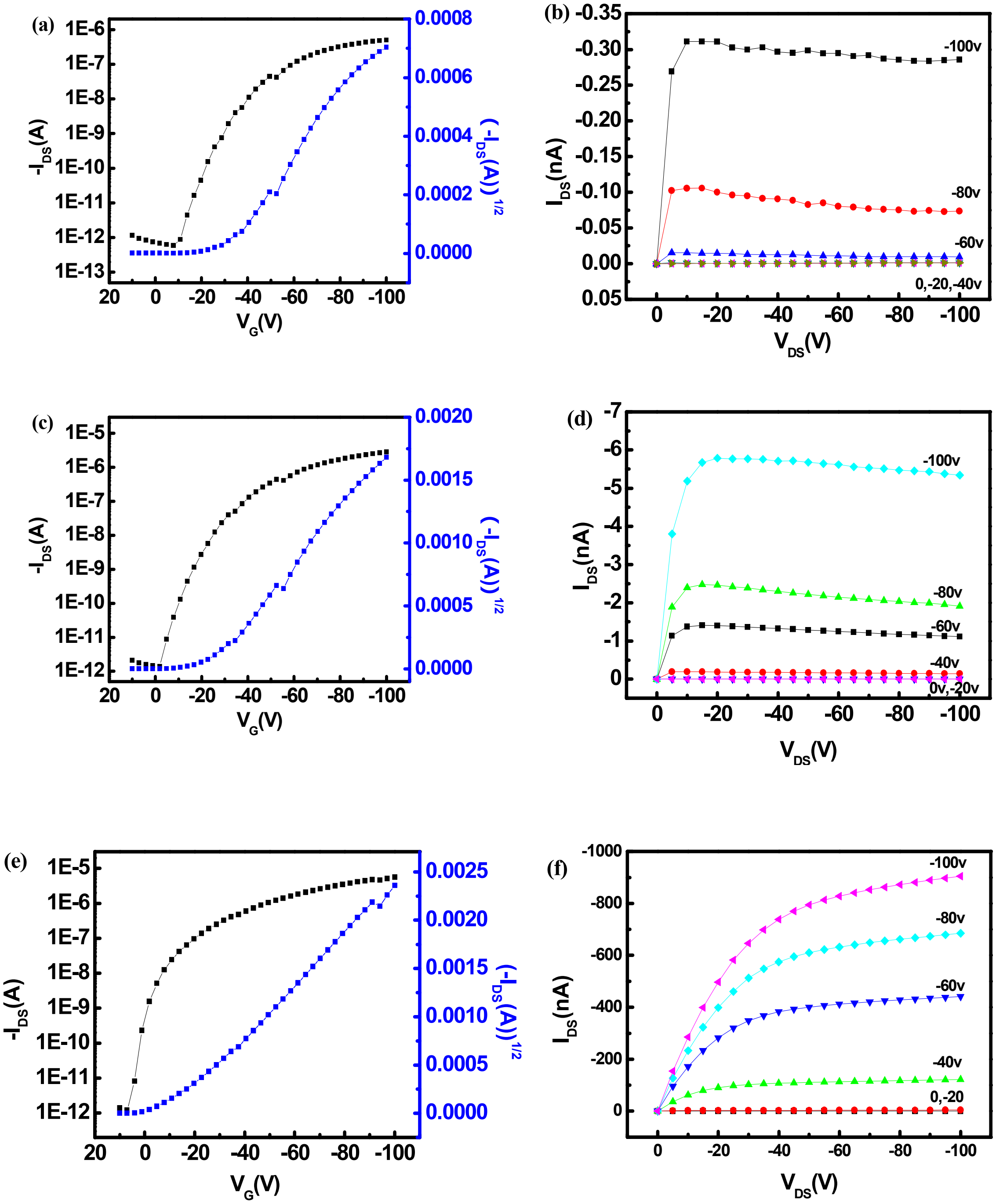


Fig. 4 Transfer and output characteristics of **PSiF-D(OT)DFBT** (a, b), **PSiF-TTDFBT** (c, d), and **PDOSiF-DTDFBT** (e, f) devices, respectively.

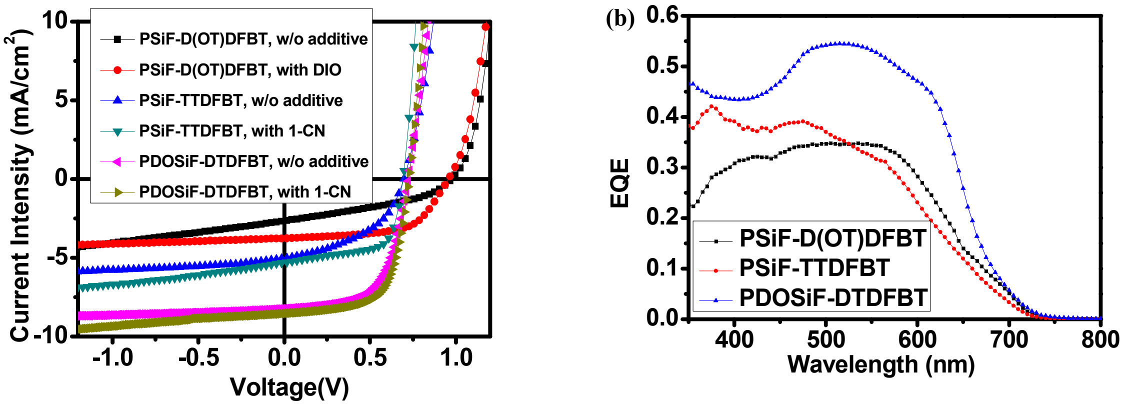


Fig. 5 (a) *J-V* curves of PSiF-D(OT)DFBT, PSiF-TTDFBT, and PDOSiF-DTDFBT solar cells; (b) External Quantum Efficiency curves for the solar cells devices with the best conditions

Table 4 Photovoltaic cells performance of three polymers

active layer	Solvent	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE	Thickness	SCLC mobilities
PSiF-D(OT)DFBT:PC$_{71}$BM (1:3)	DCB	0.97	2.63	0.38	0.96%	95	4.56×10^{-5}
PSiF-D(OT)DFBT:PC$_{71}$BM (1:3)	DCB^a	0.96	3.75	0.61	2.19%	97	6.52×10^{-5}
PSiF-TTDFBT:PC$_{71}$BM (1:3)	DCB	0.70	5.09	0.45	1.61%	102	1.21×10^{-5}
PSiF-TTDFBT:PC$_{71}$BM (1:3)	DCB^b	0.70	5.34	0.65	2.39%	105	9.65×10^{-5}
PDOSiF-DTDFBT:PC$_{71}$BM (1:1)	DCB	0.72	8.23	0.61	3.61%	101	1.25×10^{-4}
PDOSiF-DTDFBT:PC$_{71}$BM (1:1)	DCB^b	0.73	8.55	0.65	4.03%	106	3.21×10^{-4}

^{a} with 2% DIO (by volume); ^{b} with 2% 1-CN (by volume)

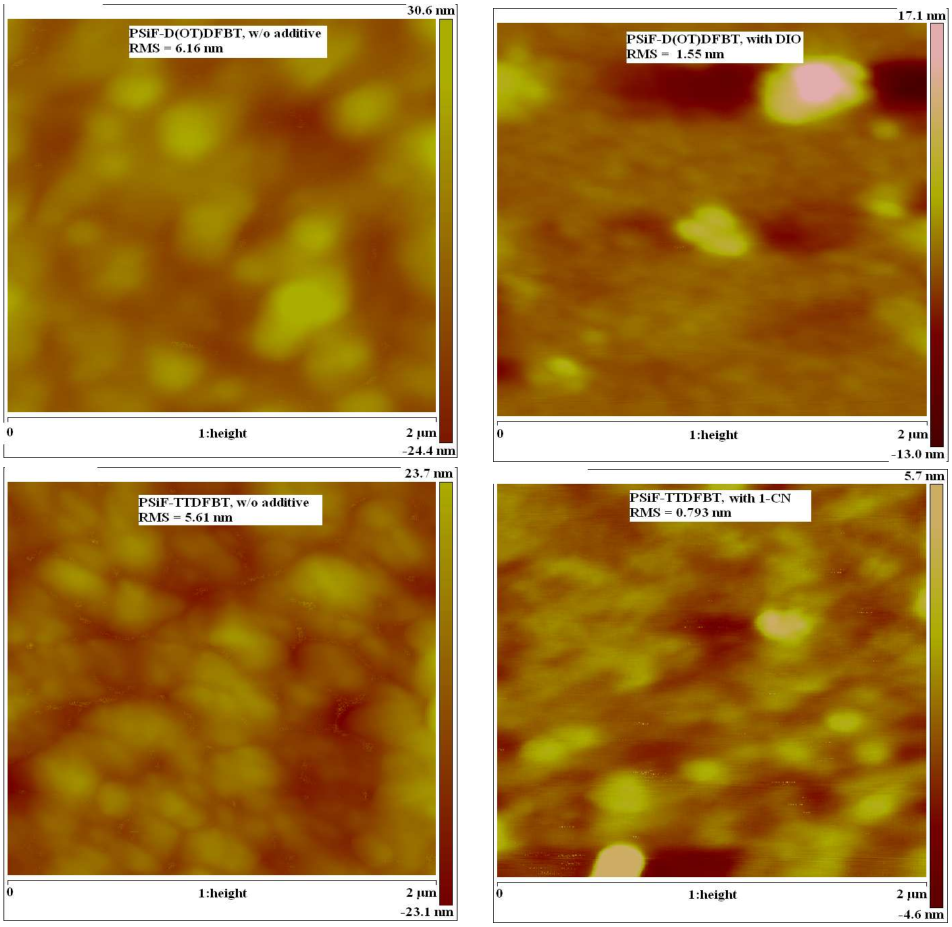
Photovoltaic Properties

Photovoltaic properties of polymers were evaluated by using the device configuration of ITO/PEDOT:PSS/active layer/LiF/Al. The performance of devices was optimized by variation of the weight ratio of polymer to PC$_{71}$BM, the concentration of blend solution, the spin-coating speed, and the volume of 1,8-diiodooctane (DIO) or 1-chloronaphthalene (1-CN) as additives. The J-V curves of these polymer solar cells are illustrated in Figure 5a. The use of DIO as the additive only showed a positive effect for **PSiF-D(OT)DFBT** based PSCs, but a negative effect for **PSiF-TTDFBT** and **PDOSiF-DTDFBT** based PSCs. The use of 1-CN as the additive have positive effect for polymer **PSiF-TTDFBT** and **PDOSiF-DTDFBT** and a negative effect for **PSiF-D(OT)DFBT**. For **PSiF-D(OT)DFBT**, the active layer spin-coated from polymer:PC$_{71}$BM in a weight ratio of 1:3 in DCB solutions gave the best device performance with a PCE of 0.96%, a V_{oc} of 0.97 V, a J_{sc} of 2.63 mA/cm^2, and an *FF* of 0.38. The high V_{oc} of devices agrees well with the wide band gap and the deep HOMO level of **PSiF-D(OT)DFBT** (vide supra). The use of DIO (2%, by volume) as the additive, the PCE was increased to 2.19% with a V_{oc} of 0.96 V, a J_{sc} of 3.75 mA/cm^2, and an *FF* of 0.61. For **PSiF-TTDFBT** based PSCs, the active layer spin-coated from polymer:PC$_{71}$BM in a weight ratio of 1:3 using DCB as the solvent gave a PCE of 1.61% with a V_{oc} of 0.70 V, a J_{sc} of 5.09 mA/cm^2, and an *FF* of 0.45. The use of 1-CN (2%, by volume) as the additive, the PCE was increased to 2.39% with a V_{oc} of 0.70 V, a J_{sc} of 5.34 mA/cm^2, and an *FF* of 0.65. For **PDOSiF-DTDFBT**, devices fabricated from DCB solutions with a polymer to PC$_{71}$BM weight ratio of 1:1 gave the highest PCE of 3.61% with a V_{oc} of 0.72 V, a J_{sc} of 8.23 mA/cm^2, and an *FF* of 0.61. The use of 1-CN (2%, by volume) as the additive, the PCE was increased to 4.03% with a V_{oc} of 0.73, a J_{sc} of 8.55 mA/cm^2, and an *FF* of 0.65. The data are summarized in Table 4. Comparing **PSiF-TTDFBT** with **PDOSiF-DTDFBT**, we should mention here that the solubility of **PSiF-TTDFBT** was poorer than **PDOSiF-DTDFBT**, which makes it difficult to make high concentration solution for spin-coating. The high V_{oc} for **PDOSiF-DTDFBT** based PSCs is consistent with the fact that **PDOSiF-DTDFBT** is of a deep HOMO level. Among these polymers, the pure **PDOSiF-DTDFBT** film showed the highest hole mobility and **PDOSiF-DTDFBT**:PC$_{71}$BM blend film gave the highest space charge limited current (SCLC) mobility (vide infra). The hole mobility of **PDOSiF-DTDFBT**:PC$_{71}$BM blend film is almost three times higher than that of the **PSiF-TTDFBT**:PC$_{71}$BM blend film. As we described (vide supra), the best photovoltaic performance was achieved for **PSiF-TTDFBT**:PC$_{71}$BM in a polymer to PC$_{71}$BM weight ratio of 1:3; whereas for **PDOSiF-DTDFBT** based PSCs, the best photovoltaic performance was achieved in polymer to PC$_{71}$BM weight ratio of 1:1. Therefore we think the high J_{sc} for **PDOSiF-DTDFBT** based PSCs for the following two reasons: (1) the high hole mobility of the blend film, which is confirmed by the SCLC measurement; (2) the high polymer content blend films can absorb more photons, which is proved by the high absorption coefficient of **PDOSiF-DTDFBT**:PC$_{71}$BM (1:1) blend films. UV-visible absorption coefficient curves of **PSiF-D(OT)DFBT**:PC$_{71}$BM (1:3), **PSiF-TTDFBT**:PC$_{71}$BM (1:3), and **PDOSiF-DTDFBT**:PC$_{71}$BM (1:1) blend films fabricated under optimized conditions are shown in Figure S1. The absorption coefficient was calculated by film absorbance/film thickness (nm). We can clearly see that the absorption coefficient of **PDOSiF-DTDFBT**:PC$_{71}$BM (1:1) blend film is markedly higher than that of **PSiF-D(OT)DFBT**:PC$_{71}$BM (1:3) blend film in the range of 350 to 700 nm. The poorer solubility of **PSiF-TTDFBT**:PC$_{71}$BM in 1,2-dichlorobenzene prohibited to fabricate device with a high polymer concentration. Compared with fluorene based D-A polymers **PFO-M1-3**,[22] the introduction of two fluorine atoms on the benzothiadiazole ring resulted in poorer solubility of the final polymers, and led to poorer performance of **PSiF-TTDFBT**:PC$_{71}$BM based PSCs. Hole mobilities of blend films were measured by SCLC method, and the results are also summarized in table 4. **PDOSiF-DTDFBT** and PC$_{71}$BM film exhibit the highest hole mobilities among these blend films, which is consistent with the highest short circuit current obtained from **PDOSiF-DTDFBT** based PSCs.

To correct the J_{sc} results obtained from J-V measurements, external quantum efficiencies (EQEs) of devices used for the J-V investigation were measured and shown in Figure 5b. In the range of 360 to 600 nm, EQEs of **PSiF-D(OT)DFBT** and **PSiF-TTDFBT** are around 35%; whereas EQE of **PDOSiF-DTDFBT** is around 50%. For all devices, J_{sc} obtained from the integration of the EQE with an AM 1.5G reference spectrum matched well with the J_{sc} obtained from the J-V measurements.

Film Morphologies

The morphology of polymer:PC$_{71}$BM blend films, which has a significantly influence on exciton separation, charge carrier mobility, and photovoltaic performance, was investigated by atomic force microscopy (AFM) in tapping-mode. AFM images of **PSiF-D(OT)DFBT**:PC$_{71}$BM (1:3), **PSiF-TTDFBT**:PC$_{71}$BM (1:3), and **PDOSiF-DTDFBT**:PC$_{71}$BM (1:1) blend films fabricated from DCB solutions without and with additives are shown in Figure 6. For **PSiF-D(OT)DFBT**, the use of DIO as an additive led to smaller domain size with the root-mean-square (rms) value decreased from 6.16 nm to 1.55 nm; whereas for **PSiF-TTDFBT** and **PDOSiF-DTDFBT**, the use of 1-CN as an additive also led to smaller domain size with the rms values decreased from 5.61 nm to 0.793 nm for **PSiF-TTDFBT** and from 0.401 nm to 0.364 nm for **PDOSiF-DTDFBT**. As an experiential rule, DIO prefers to dissolve PCBM; whereas CN prefers to dissolve the conjugated polymers. Usually, the use of DIO can reduce the domain size of PC$_{71}$BM;[26] whereas the use of CN can usually reduce the domain size of polymers.[27,28] The morphology changing after the addition of additive is consistent with the enhancing of the performance of PSCs.



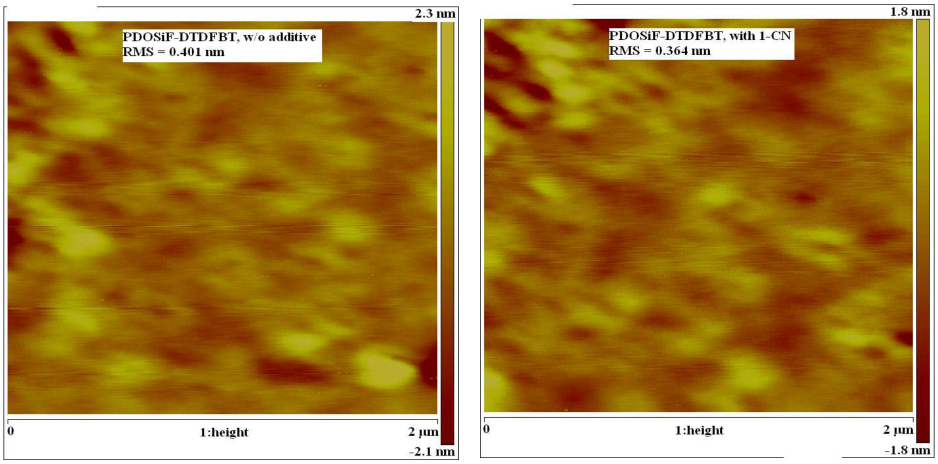


Fig. 6 AFM height images of polymer:$PC_{71}BM$ blend films without and with additive

Conclusions

We have designed and synthesized four D-A alternating conjugated polymers based on 5,6-difluorobenzothiadiazole and 2,7-linked silafluorene. **PSiF-DTDFBT** is insoluble in common organic solvent and not suitable for fabrication of PSCs by solution processing. **PSiF-D(OT)DFBT**, **PSiF-TTDFBT**, and **PDOSiF-DTDFBT** are soluble in DCB and TCB and could be used for the fabrication of PSCs. **PSiF-D(OT)DFBT** with an octyl chain on the thiophene unit is of a band gap of 2.06 eV with a deep HOMO of -5.64 eV. **PSiF-TTDFBT** with two additional thiophenes at each repeating unit in polymer main chain exhibits a band gap of 1.75 eV with the HOMO of -5.23 eV. **PDOSiF-DTDFBT** with two additional octyloxy chains on the silafluorene unit has a band gap of 1.86 eV with the HOMO level of -5.37 eV. The hole mobilities of these polymers are in the range of 6.94×10^{-3} to 3.31×10^{-2} $cm^2V^{-1}s^{-1}$, which match the electron mobility of $PC_{71}BM$. Hole mobilities of polymer:$PC_{71}BM$ blend films measured by SCLC method are in the range of 1.92×10^{-5} to 5.10×10^{-4} $cm^2V^{-1}s^{-1}$. PSCs with the blends of **PSiF-D(OT)DFBT**:$PC_{71}BM$, **PSiF-TTDFBT**:$PC_{71}BM$, and **PDOSiF-DTDFBT**:$PC_{71}BM$ as the active layer gave PCEs of 2.19%, 2.39%, and 4.03%, respectively. Additionally, our research also provides a better understanding on the structure-property relationship of silafluorene and 5,6-difluorobenzothiadiazole based conjugated polymers.

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Notes and references

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Table of contents entry

Three novel 5,6-difluorobenzothiadiazole and silafluorene based conjugated polymers have been synthesized and used as donor materials for polymer solar cells.