

High-performance Fullerene-free Polymer Solar Cells with Solution-processed Conjugated Polymers as Anode Interfacial Layer*

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Abstract A series of conjugated polymers based on PFS derivatives with π -conjugated 5-(9H-fluoren-2-yl)-2,2'-bithiophene (fluorene-*alt*-bithiophene) backbones, namely PFS-3C, PFS-4C and PFS-6C, were synthesized for their use as the anode interfacial layers (AILs) in the efficient fullerene-free polymer solar cells (PSCs). Alkyl sulfonate pendants with different lengths of alkyl side chains were introduced in the three polymers in order to investigate the effect of the alkyl chain length on the anode modification. The obtained three polymers exhibited similar absorption bands and energy levels, indicating that changing the length of the alkyl side chains did not affect the optoelectronic properties of the conjugated polymers. Based on the PBDB-T:ITIC active layer, we fabricated the fullerene-free PSCs using the three polymers as the AILs. The superior performance of the fullerene-free PSC device was achieved when PFS-4C was used as the AIL, showing a power conversion efficiency (PCE) of 10.54%. The high performance of the PFS-4C-modified device could be ascribed to the high transmittance, suitable work-function (WF) and smooth surface of PFS-4C. To the best of our knowledge, the PCE obtained in the PFS-4C-modified device is among the highest PCE values in the fullerene-free PSCs at present. These results demonstrate that the PFS derivatives are promising candidates in serving as the AIL materials for high-performance fullerene-free PSCs.

Keywords Polymer solar cells; Interfacial layer; Power conversion efficiency; Fullerene-free

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INTRODUCTION

Since many highly efficient non-fullerene acceptors, such as ITIC and N2200, were discovered, the study on fullerene-free polymer solar cells (PSCs) has been rapidly progressed^[1–9]. To date, the state-of-the-art fullerene-free PSCs have exhibited a power conversion efficiency (PCE) of 10.8%, which is comparable to the highest record of PCE obtained in the fullerene-based PSCs^[10, 11]. At present, however, poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and MoO₃, the two typical hole-transporting materials, still remain as the predominant AIL materials in fullerene-free PSCs. The application of other AIL materials in fullerene-free PSC devices is rarely reported. Therefore, in order to further enhance the PCEs of the fullerene-free PSC devices, exploring new solution-processable AIL materials with superior properties is of great

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importance.

Owing to the good solution-processing ability and adjustable photoelectric properties, conjugated polymers have been successfully developed as the anode interfacial materials for PSCs^[12–16]. One remarkable advantage of the conjugated polymers as the AIL materials is their molecular structures that can be easily modified through versatile synthetic chemistry, which offers opportunities for tuning the chemical, optical and electrical properties of the materials. Based on the rational molecular design, conjugated polymers can effectively increase the work-function (WF) of the anode, which facilitates the hole collection in PSCs^[17]. For instance, several polythiophene derivatives were employed as AILs in P3HT-based PSCs and the device exhibited a PCE of 4.4%^[18, 19]. Although these polythiophene derivatives have been developed as the AIL materials, their molecular structures were not further optimized. This limited the application range of the AIL materials, *i.e.* the polythiophene derivatives as AILs were only used in the P3HT-based PSC devices.

In the past several years, conjugated polymers with sulfonate pendants have been widely studied as the AIL materials for the PSC devices^[20–22]. A representative example was CPE-K, a water/alcohol-soluble conjugated polymer developed by Bazan *et al.*, who used it in the single-junction PSCs with PTB7 as the active layer^[23, 24]. The device using CPE-K AIL exhibited a PCE of 8.9%. Recently, our group designed and synthesized the alkyl sulfonate functionalized conjugated polymer PFS that could be used as the AIL material in PSCs^[25]. The PSC device modified with PFS AIL exhibited a high PCE of 9.7%, which was comparable to that of the PEDOT:PSS-modified device. However, the molecular structure of PFS was not fully optimized and its application as AIL in PSCs needed to be further explored.

Herein, we report a series of PFS derivatives with π -conjugated 5-(9H-fluorene-2-yl)-2,2'-bithiophene (fluorene-*alt*-bithiophene) backbones, namely PFS-3C, PFS-4C and PFS-6C, containing alkyl sulfonate pendants but with different lengths of alkyl side chains. Based on these materials, we can probe the effect of alkyl chain length on the anode modification of these polymers in fullerene-free PSCs. The structures of PFSs (henceforth referred to as PFS-3C, PFS-4C and PFS-6C) are shown in Scheme 1. The work function (WF) of the ITO substrate modified with these polymers was tuned to *ca.* 4.95 eV, which could form the ohmic contact at the anode/active layer surface and facilitate charge collection. Based on the PBDB-T:ITIC active layer, the fullerene-free PSC devices were fabricated using PFSs as AILs, and the superior performance with a PCE of 10.54% was achieved in the fullerene-free devices when PFS-4C was used. This work demonstrates that PFS derivatives are promising candidates in serving as the AIL materials for high-performance fullerene-free PSCs.

EXPERIMENTAL

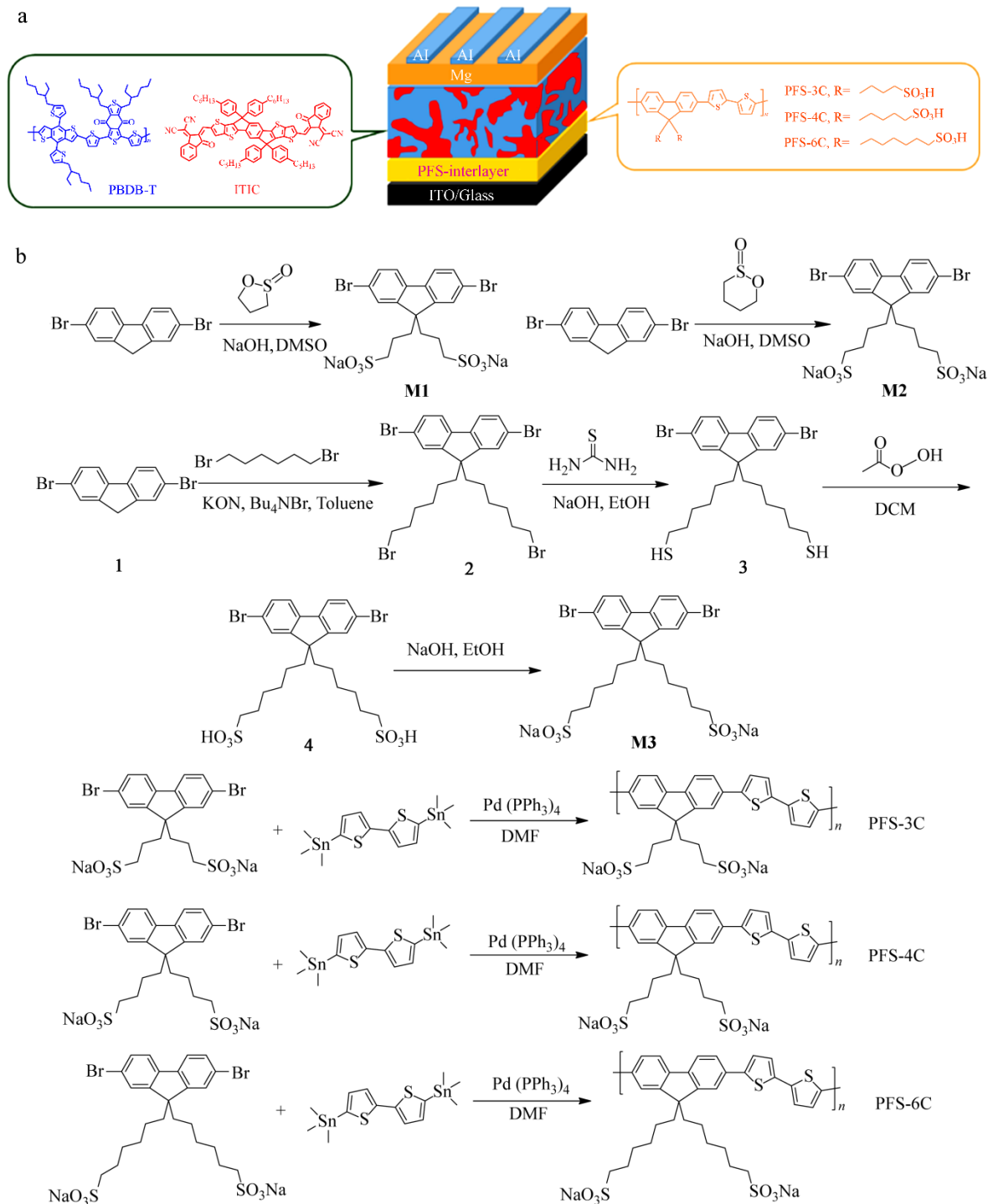
Materials and Synthesis

The monomers M1, M2 and compound (2) were synthesized according to the literature report^[23]. Pd(PPh₃)₄ was purchased from Frontier Scientific Inc. Other reagents were common commercial level and used without further purification.

Compound (3) (2,7-dibromo-9,9-di(6-thiohexyl)fluorene)^[27]: compound (2) (1.30 g, 2.0 mmol) and thiourea (0.340 g, 4.5 mmol) were dissolved in 50 mL of refluxing ethanol and stirred for 16 h. NaOH (15 mL, 1.0 mol/L) was added to the reaction, causing the mixture to become cloudy. After that, the reaction mixture was refluxed for 3 h for clearing the solution. 6 mol/L H₂SO₄ was added dropwise until the precipitation of white solid completed. The reaction mixture was extracted with ether (200 mL $\times$ 3) and the organic extractions were combined and dried with MgSO₄. The solvent was removed to give white solid. Yield: 0.923 g (83%). ¹H-NMR (CDCl₃, 400 MHz, δ): 7.53 (s, 2H), 7.45 (d, 4H), 2.44 (t, 4H), 1.94 (t, 4H), 1.47 (m, 4H), 1.39 (2H), 1.13 (m, 8H), 0.88 (t, 4H).

Compound (4) (2,7-dibromo-9,9-di(6-sulfonic acid-hexyl)fluorene): peracetic acid (30 mL) was added to the solution of compound (3) (1.10 g, 2.0 mmol) and the mixture was stirred at room temperature for 8 h. After the reaction was finished, the mixture was extracted with dichloromethane (200 mL $\times$ 3). The organic extractions were combined and then washed with distilled water, dried with MgSO₄. Solvent was removed under vacuum to

give the pale-yellow solid. Yield: 1.174 g (91%). $^1\text{H-NMR}$ (DMSO, 400 MHz, δ): 7.79 (s, 2H), 7.50 (d, 4H), 2.29 (t, 4H), 2.02 (t, 4H), 1.37 (m, 4H), 1.07 (8H), 0.43 (m, 4H).



Scheme 1 (a) The device structure of the fullerene-free PSCs; (b) The synthesis route to PFS-3C, PFS-4C and PFS-6C

M3 (2,7-dibromo-9,9-di(6-sodium sulfonate-hexyl)fluorene): sodium hydroxide (1.20 g, 30 mmol) was

added in the methanol solution of compound (**4**) (1.30 g, 2 mmol) in one portion. Then, the mixture was stirred at room temperature for 8 h. After the reaction finished, the methanol was removed under vacuum, providing the crude product as a white solid. The crude product was recrystallized several times in ethanol until all the sodium hydroxide was removed. Yield: 0.944 g (68%). $^1\text{H-NMR}$ (DMSO, 400 MHz, δ): 7.79 (s, 2H), 7.50 (d, 4H), 2.26 (t, 4H), 2.02 (t, 4H), 1.35 (m, 4H), 1.07 (8H), 0.42 (m, 4H).

The preparation of polymers PFS-3C, PFS-4C and PFS-6C was presented as follows.

PFS-3C: to a 50 mL flask, monomer **M1** (0.6099 g, 1.0 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.4939 g, 1.0 mmol) were dissolved in 6 mL anhydrous DMF. After being flushed with argon for 5 min, $\text{Pd}(\text{PPh}_3)_4$ (0.015 g, 0.013 mmol) was added. Then the mixture was purged with argon for another 15 min. The reaction mixture was vigorously stirred at 95 °C for 48 h. After the reaction was finished, the polymer was poured into 500 mL 1 mol/L hydrochloric acid and the mixture was stirred for 0.5 h at room temperature. Afterwards, the polymer was precipitated and filtered in a Buchner funnel. The polymer was purified by precipitation in ethyl ether several times with a yield of 48%. $^1\text{H-NMR}$ (DMSO, 400 MHz, δ): 8.42–7.41 (m, br, 10H), 2.51–1.90 (m, br, 8H), 0.86 (m, br, 4H); GPC: $M_n = 8300$, $M_w = 9100$, PDI = 1.09.

PFS-4C: the synthetic procedure was same as that of PFS-3C. Monomer **M2** (0.6379 g, 1.0 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.4939 g, 1.0 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.015 g, 0.013 mmol) were added in 6 mL of anhydrous DMF. Yield: 43%. $^1\text{H-NMR}$ (DMSO, 400 MHz, δ): 8.23 (br, 2H), 7.84 (br, 3H), 7.66 (br, 3H), 7.44 (br, 2H), 2.22 (m, 6H), 1.40 (br, 4H), 1.22 (m, 2H), 0.59 (m, 4H); GPC: $M_n = 3800$, $M_w = 3900$, PDI = 1.03.

PFS-6C: the synthetic procedure was same as that of PFS-3C. Monomer **M3** (0.6939 g, 1.0 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.4939 g, 1.0 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.015 g, 0.013 mmol) were added in 6 mL of anhydrous DMF. Yield: 65%. $^1\text{H-NMR}$ (DMSO, 400 MHz, δ): 8.20–7.79 (m, br, 10H), 2.20 (m, 4H), 2.17–1.87 (m, br, 16), 0.87 (m, 4H); GPC: $M_n = 3800$, $M_w = 3900$, PDI = 1.03.

Instruments and Characterization

$^1\text{H-NMR}$ spectra were recorded at 298 K on a Bruker AVANCE 400 MHz spectrometer to confirm the structures of the compounds. Absorption spectra of the polymers in solution and solid thin films were measured by Shanghai Lab-spectrum 1900PC UV-Vis spectrophotometer. Molecular weight and polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) using *N,N*-dimethylformamide (DMF) as the eluent at room temperature. The film thicknesses of the PFSs films for the measurement of the transmittance spectra were *ca.* 8 nm, which were the same thicknesses as they were used in the photovoltaic devices. The absorption and transmission spectra of the polymer films were measured on quartz substrate. Cyclic voltammetry (CV) was conducted on a CHI650D Electrochemical Workstation at a scan rate of 20 mV/s with a three-electrode cell in 0.1 mol/L tetrabutylammoniumtetrafluoroborate (Bu_4NBF_4) dichloromethane solution.

Atomic force microscope (AFM) measurement was performed on VecooNanoscopeIIIa on tapping mode. Ultraviolet photoelectron spectroscopy (UPS) analyses were carried out on Thermo Scientific ESCALab 250Xi. The thickness of different buffer layer was independently measured *via* the surface profilometer Bruker Dektak XT.

Current density-voltage (*J-V*) characteristics were measured under 100 mW/cm² standard AM1.5G spectrum using a solar simulator (AAA grade). The simulator was calibrated by A NIM certificated silicon solar cell (KG3 color filter). The external quantum efficiency (EQE) data were collected by an integrated IPCE measurement system named QE-R3011 (Enli Technology Co. Ltd., Taiwan).

Fabrication of the PSC Devices

The fullerene-free PSCs were fabricated with a configuration of ITO/PEDOT:PSS (30 nm)/PBDB-T:ITIC/PFN-Br/Al. ITO glass substrate was precleaned in an ultrasonic bath of acetone and isopropyl alcohol, and treated in an ultraviolet-ozone chamber (Jelight Company, Irvine, CA) for 20 min. A thin layer of PEDOT:PSS was deposited through spin-coating on the ITO glass at about 3000 r/min and dried subsequently at 150 °C for 15 min in air. Then the device was transferred to a nitrogen glove box, where the active blend layer containing a

blend of PBDB-T and ITIC was spin-coated from chlorobenzene solution onto the PEDOT:PSS layer. Afterwards, the methanol solution of 0.5 mg/mL PFN-Br was deposited atop the active layer at 3000 r/min for 30 s to afford a thickness of *ca.* 10 nm. Finally, 80 nm of Al were deposited onto the active layer under high vacuum successively. The active area of the device was 4 mm².

RESULTS AND DISCUSSION

Synthesis

The synthetic routes for the polymers PFS-3C, PFS-4C and PFS-6C are shown in Scheme 1. The commercially available 2,7-dibromo-9*H*-fluorene was alkylated with 1,3-propanesultone and 1,4-butanedisultone under basic conditions, providing the water-soluble monomers **M1** and **M2** in good yield^[23]. The synthesis of **M3** is more complex than that of **M1** and **M2**. The pendent sulfonate acid group was introduced into **M3** through the oxidation of its thiol-functionalized precursor. Towards this end, the thiol group was first introduced into 2,7-dibromo-9,9-bis(6-bromohexyl)-fluorene (**2**) through nucleophilic attack by thiourea in refluxing ethanol, which was then hydrolyzed with sodium hydroxide and neutralized with sulfuric acid^[26]. The resulting thiol-functionalized 2,7-dibromo-9,9-di(6-thiolhexyl)-fluorene (**3**) was then oxidized by using peracetic acid to give the desired sulfonate acid functional compound (**4**)^[27]. However, compound (**4**) could not be purified by the conventional approaches such as chromatographic column separation and recrystallization. Therefore, the compound (**4**) was stirred with sodium hydrate in methanol to give the sulfonate sodium functionalized monomer 2,7-dibromo-9,9-di(6-sodium sulfonate-hexyl)-fluorene (**M3**) which could be purified by recrystallization. The overall yield of **M3** was approximately 40%.

The polymers PFSs were synthesized *via* Stille coupling reaction and were then acidified by hydrochloric acid to give the final products PFS-3C, PFS-4C and PFS-6C. The detailed synthetic methods of the polymers are provided in the experimental section. The chemical structures of these polymers were confirmed by ¹H-NMR. Molecular weights of the polymers were determined by GPC with DMF as the eluent. The number-average molecular weight (*M_n*) of PFS-3C, PFS-4C and PFS-6C were 8.3, 3.8 and 3.8 kDa, respectively. The three polymers can be easily dissolved in high polar solvents such as methanol, DMF and *N*-methyl-2-pyrrolidone. Notably, PFSs exhibit poor solubility in some organic solvents such as chloroform, toluene and chlorobenzene which are widely used in the active layer processing. Therefore, the processing solvents of these polymers are completely orthogonal with that of the active layer, which facilitates the solution-processing of these polymers as interfacial layers in the PSCs.

Thermo gravimetric analysis (TGA) measurements were carried out to evaluate the thermal stability of PFSs. The TGA curves of the three polymers are shown in Fig. S1 (in SI). The TGA profile reveals that the decomposition temperatures (*T_d*) at 5% weight loss for the three polymers are all above 300 °C. The thermal stability of the PFSs is adequate for their applications in PSCs.

Optoelectronic Properties

The UV-Vis absorption spectra of PFS-3C, PFS-4C and PFS-6C in solution and as solid films are shown in Figs. 1(a) and 1(b). The three polymers showed similar absorption bands in solution and as solid films. In diluted methanol solution, the absorption band of the PFSs is located at *ca.* 440 nm, which is originated from the intramolecular π - π^* transition of the polymer backbones. Compared with the polymer solution, the UV-Vis absorption bands of the PFSs films were obviously red-shifted to *ca.* 458 nm. Meanwhile, weak absorption shoulder appeared at around 487 nm for all the three polymer films. The absorption shoulders at the long wavelength range were mainly derived from the intermolecular π - π^* transition, indicating the existence of inter-chain interactions in the polymer films. The absorption edge (λ_{edge}) of the three polymer films are 527 nm, corresponding to the optical bandgap of 2.35 eV. The transmittance spectra of PFSs in solid films are shown in Fig. 1(c). In the long wavelength region (> 540 nm), the transmittance of the three polymer films is over 98%. It is worth noting that, among the three polymer films, PFS-4C exhibits the highest light transmittance in the wavelength range from 360 nm to 520 nm, which should be ascribed to the low molar absorption coefficient of

the PFS-4C film. Practically, the influence factors on the optical absorption of polymers are highly complicated, such as the crystallinity, anisotropy, aggregation, backbone kinks, surface morphology and roughness. Although the PFS-4C has a little difference from PFS-3C and PFS-6C in alkyl length, the multiple factors from the intrinsic property of PFS-4C may lead to an exceptive equilibrium value of the absorption coefficient. As shown in Fig. S2 (in SI), the molar absorption coefficients at 458 nm of the PFSs films were determined to be 0.013/nm for PFS-3C, 0.006/nm for PFS-4C and 0.010/nm for PFS-6C, respectively. The high transparency of PFS-4C film is favorable to a sufficient light-harvesting of the photoactive layer; which is crucial for realizing high short-circuit current (J_{sc}) in PSC devices.

Cyclic voltammetry (CV) measurements were performed to determine the highest occupied molecular orbital (HOMO) levels of the PFSs (Fig. 1d). On the basis of the onset oxidation potential of the polymers, the HOMO levels of PFS-3C, PFS-4C and PFS-6C were calculated to be -5.15 , -5.13 and -5.15 eV, respectively^[28]. Apparently, length variation of the alkyl side chains did not change the energy levels of the polymers. Considering that the HOMO level of PBDB-T^[29, 30], a polymer donor typically used in fullerene-free PSCs, is -5.25 eV, the HOMO levels of ~ -5.15 eV of the PFSs can assure an ohmic contact and satisfy the hole extraction from the donor materials, showing the potential use of PFSs as the AILs in fullerene-free PSCs.

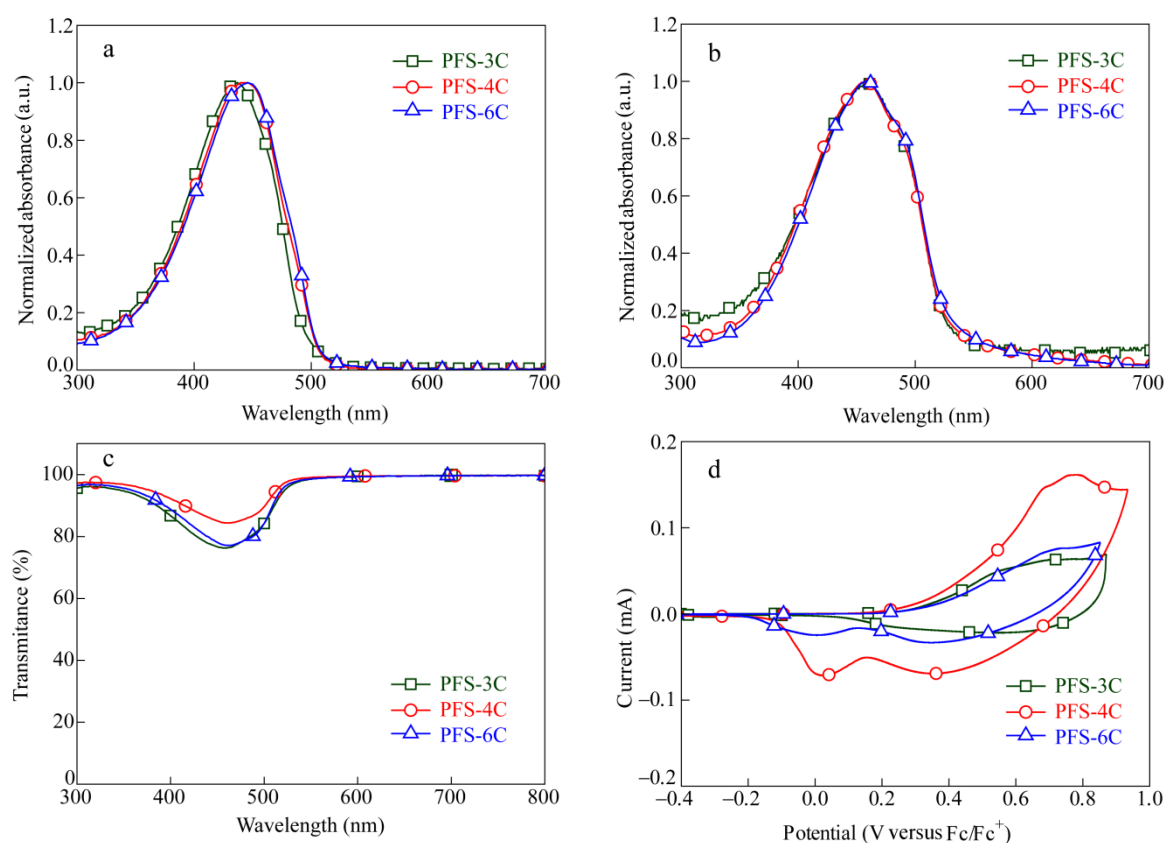


Fig. 1 Normalized absorption spectra of PFS-3C, PFS-4C and PFS-6C in (a) methanol solution and (b) thin film on quartz; (c) transmittance spectra of PFS-3C (8 nm), PFS-4C (8 nm) and PFS-6C (9 nm) in solid films; (d) cyclic voltammograms of PFS-3C, PFS-4C and PFS-6C films

Work Function Tuning with PFS Derivatives

To investigate the effect of electronic properties of the polymer interlayers on the photovoltaic performance, UPS measurement was carried out to study the energy levels of the bare ITO and ITO covered with PFSs. As shown in Fig. 2, the bare ITO showed a WF of 4.54 eV. After the ITO substrate was modified by PFS-3C,

PFS-4C and PFS-6C, the WF of the ITO substrates was tuned to 4.90, 4.98 and 4.93 eV, respectively. The increased WF of ITO can reduce the energy barrier at the active layer/anode interface, which is of considerable importance for the interfacial modification of ITO anode. Among the three polymers, PFS-4C is the most effective material in adjusting the WF of ITO anode. Moreover, the WF of PFS-4C-modified ITO is similar to the value obtained in PEDOT:PSS-modified ITO (5.01 eV), suggesting that PFS-4C has the similar effect to PEDOT:PSS on increasing the WF of ITO anode.

Fullerene-free Polymer Solar Cell Performance

In recent years, great progress has been made in fullerene-free PSCs due to the newly developed non-fullerene acceptors. PCEs over 9% in fullerene-free PSCs have been reported by several groups, which are comparable to those of the fullerene-based PSCs. Herein, fullerene-free PSC devices were fabricated to evaluate the applicability of PFSs films in high-performance fullerene-free PSCs. PBDB-T:ITIC blend film was selected as the model active layer material due to its broad optical absorption, favorable molecular stacking and high charge mobility^[31]. The chemical structures of PBDB-T and ITIC are shown in Scheme 1. The configuration of the fullerene-free PSC devices was ITO/PFSs/PBDB-T:ITIC/PFN-Br/Al and the device using PEDOT:PSS AIL was also fabricated as a control.

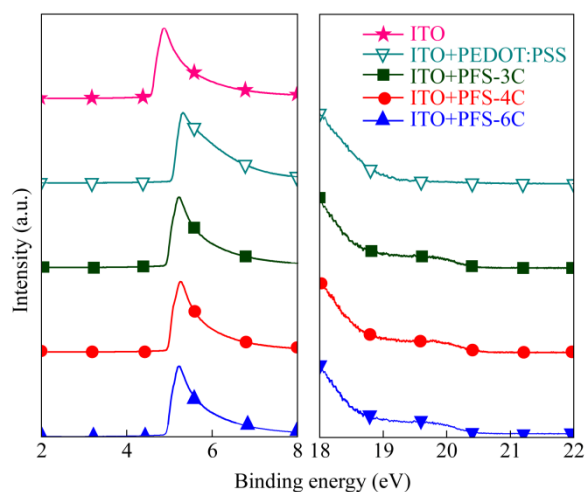


Fig. 2 UPS spectra of pristine ITO, PEDOT:PSS, PFS-3C, PFS-4C and PFS-6C deposited on the top of ITO

We first examined the effect of PFSs thickness on the performance of the fullerene-free PSCs in order to optimize the thickness of PFSs AILs in PSCs. The PFSs thickness was regulated by spin-coating of the PFSs solution at different concentrations at 3000 r/min for 30 s. The J - V curves of the fullerene-free PSCs with PFSs in various film thicknesses (from 2 nm to 14 nm) are shown in Fig. S3 and the photovoltaic parameters are summarized in Table S1. The photovoltaic parameters are plotted as a function of PFSs thickness as shown in Fig. 3. The PFSs-modified devices exhibited almost independent open circuit voltage (V_{oc}) values on the PFSs thickness. The J_{sc} values of the PFS-3C-modified PSCs declined with increasing the thickness of PFS-3C, while the J_{sc} of the devices incorporated with PFS-4C and PFS-6C AILs reached the maximum values as the thickness increased to 8 nm for PFS-4C and 9 nm for PFS-6C, respectively. Moreover, in the thickness range from 8 nm to 14 nm, the PFS-4C-modified PSC devices exhibited higher fill factor (FF) compared with that of the devices modified with PFS-3C and PFS-6C (see Fig. 3c), suggesting the superior capacity of PFS-4C AIL in the hole collection. Upon the thickness optimization, the superior PSC performance could be achieved with the PFSs thickness of *ca.* 8 nm, demonstrating the optimal thickness of the PFSs as AILs in PSCs (see Fig. 3d). The enhanced PCE values of the devices with optimal PFSs thickness could be ascribed to the reduced series resistance (R_s) of the devices (see Fig. 3e). For example, with the optimal thickness of PFS-4C, the R_s of the

PFS-4C-modified device was reduced to $4.8 \Omega\cdot\text{cm}^2$, leading to the simultaneous enhancement in J_{sc} and FF.

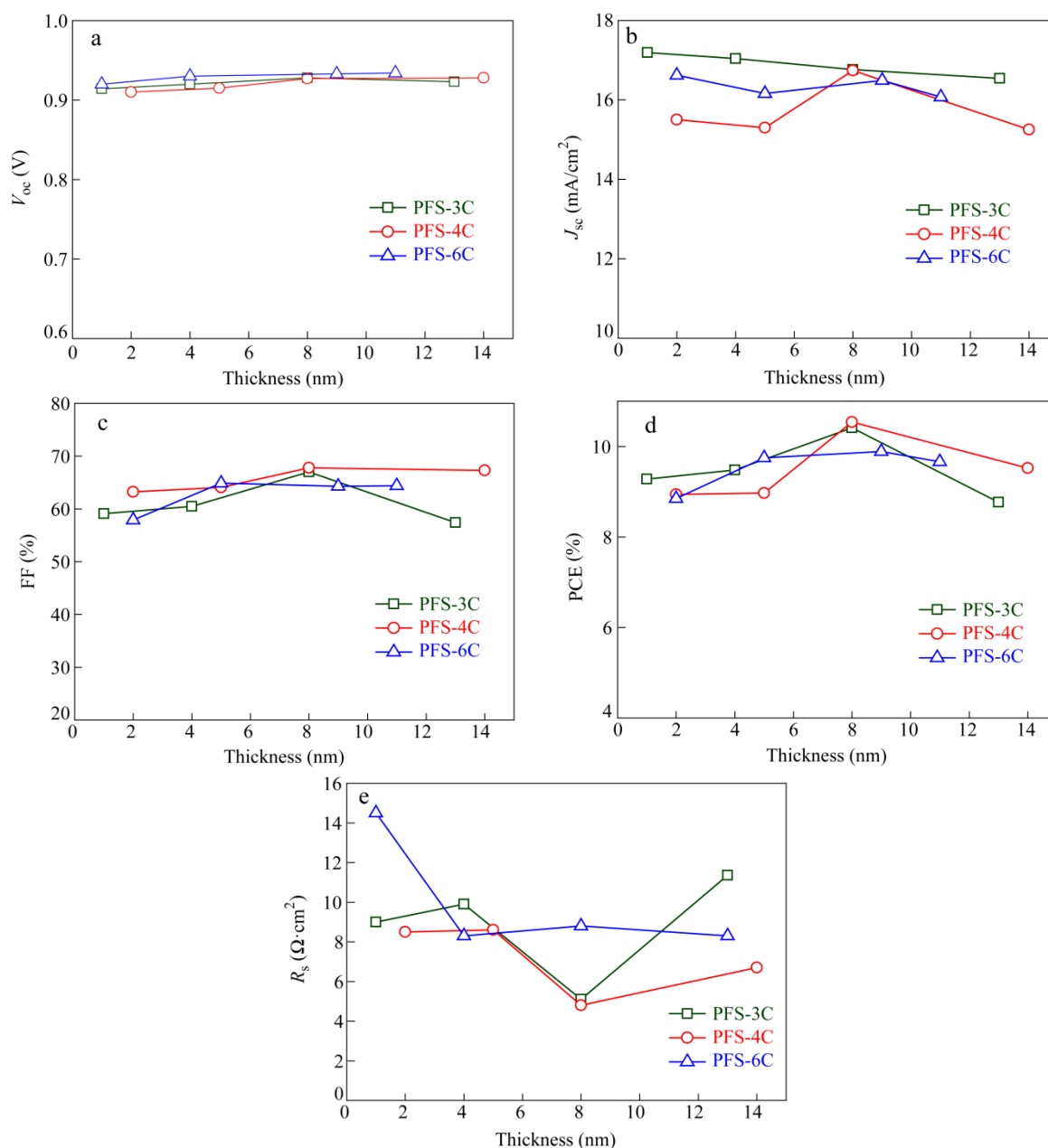


Fig. 3 Photovoltaic parameters of the fullerene-free PSCs with PFSs AILs as a function of PFSs thickness: (a) V_{oc} , (b) J_{sc} , (c) FF, (d) PCE and (e) R_s

Figure 4(a) shows the J - V curves of the fullerene-free PSC devices with optimal PFSs thickness and Table 1 lists the corresponding photovoltaic parameters. The fullerene-free PSC device using PFS-3C AIL displays PCE = 10.41%, with V_{oc} = 0.928 V, J_{sc} = 16.76 mA/cm^2 and FF = 66.97%, which is comparable to that of the device using PEDOT:PSS (PCE = 10.45%). The superior device parameters were obtained for the PFS-4C-modified PSC device, achieving a PCE of 10.54%, with V_{oc} = 0.927 V, J_{sc} = 16.74 mA/cm^2 and FF = 67.85%. In contrast, the PFS-6C-modified device only afforded a moderate PCE of 9.75%. As well known, the PCE of

10.54% is almost the highest PCE values in the fullerene-free PSCs at present. These results indicate that both PFS-3C and PFS-4C are promising AIL materials for the high-performance fullerene-free PSC devices.

Also, we investigated the EQE of the PFSs-modified PSC device and the control device, as presented in Fig. 4(b). The PFS-4C-modified device showed the highest EQE on the wavelength region from 550 nm to 700 nm. The J_{sc} integrated from the EQE spectra were 16.52, 16.38, 16.41 and 16.46 mA/cm² for the devices modified with PFS-3C, PFS-4C, PFS-6C and PEDOT:PSS, respectively. The calculated J_{sc} agreed well to the J_{sc} tested from J - V characteristics, suggesting that the J_{sc} values obtained in the J - V measurement were reliable.

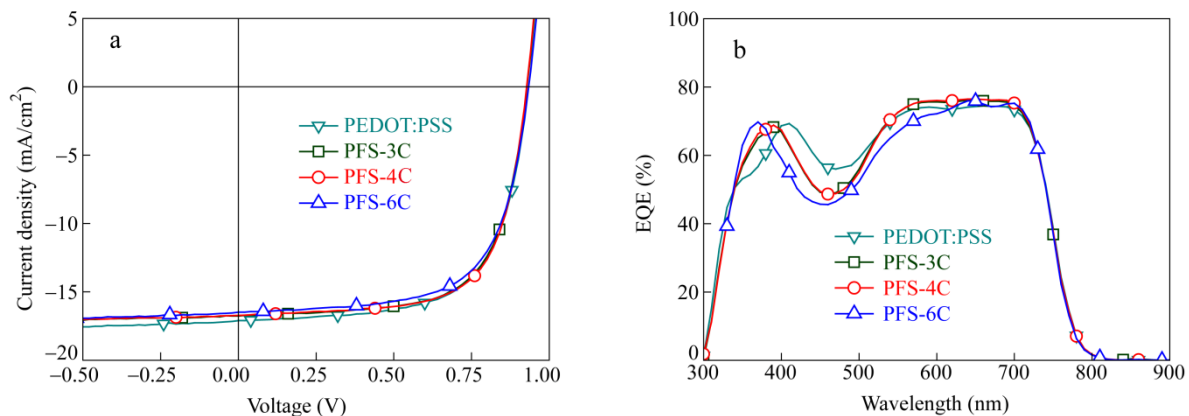


Fig. 4 J - V characteristics (a) and EQE spectra (b) of the fullerene-free PSCs with PFSs and PEDOT:PSS interlayers

Table 1 Photovoltaic characteristics of PBDB-T:ITIC polymer solar cells with optimized PFSs thickness under the illumination of AM 1.5, 100 mW/cm²

Interlayer	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	R_s (Ω ·cm ²)
PFS-3C	0.928	16.76	67.0	10.41 (10.09 $\pm$ 0.18)	5.1
PFS-4C	0.927	16.74	67.8	10.52 (10.34 $\pm$ 0.13)	4.9
PFS-6C	0.933	16.49	64.3	9.89 (9.51 $\pm$ 0.27)	8.0
PEDOT:PSS	0.934	17.10	65.5	10.46 (10.13 $\pm$ 0.27)	6.2

The statistics are from seven devices.

Interfacial Modification

To understand the possible reason for the superior performance of the PFS-4C PSC devices, surface properties of the PFSs-modified ITO were characterized by contact angle (CA) measurement and tapping mode AFM. It is recognized that wetting property may influence the morphology of the active layers during the sequential deposition of the multilayered devices. For instance, Liu *et al.* demonstrated that the insertion of the hydrophobic PTB7-TV interlayer could improve the vertical composition profile in the active layer, in which the donor polymer was gradually enriched toward the anode side^[31]. Therefore, we studied the wettability of the ITO surface modified with PFSs by measuring CA. The measurements were performed by depositing the droplet of deionized water on the ITO surface (bare or covered with PFSs), where CAs were determined based on the automated image analysis. As shown in Fig. 5(a), the bare ITO surface shows obvious hydrophilicity after being treated by the ultraviolet-ozone, with a CA of $11.0^\circ \pm 0.8^\circ$. After being modified with PFSs AILs, the surface of the ITO anode became hydrophobic and the CA increased to $18.2^\circ \pm 0.3^\circ$ for PFS-3C, $27.5^\circ \pm 0.3^\circ$ for PFS-4C, and $48.5^\circ \pm 1.6^\circ$ for PFS-6C, respectively. The CA values of the modified ITO gradually increased with the extended length of alkyl side chain from the propyl group of PFS-3C to the hexyl group of PFS-6C. It is expectable that the longer side chain polymer gives more hydrophobic surface, because the increased carbon number of the alkyl chain can raise the hydrophobicity of the polymer.

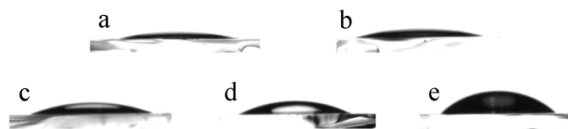


Fig. 5 Contact angle measurements (DI water) of (a) pristine ITO and ITO covered with (b) PEDOT:PSS, (c) PFS-3C, (d) PFS-4C and (e) PFS-6C

Thereafter, AFM measurements were carried out to identify the uniformity and surface roughness of ITO substrates before and after the modification. As shown in Fig. 6(a), the pristine ITO exhibits a relatively rough surface with a root mean square roughness (R_q) of 2.93 nm. After being modified by PFS-4C, the ITO substrate shows a decreased R_q value of 2.45 nm. The smooth surface of the PFS-4C-modified ITO anode can facilitate the contact quality with the active layer so as to improve the charge collection^[32]. In contrast to the PFS-4C-modified ITO anode, the R_q values of the ITO modified with PFS-3C and PFS-6C increased to 3.69 nm for PFS-3C and 4.44 nm for PFS-6C, respectively. Overall, by comparison with PFS-3C and PFS-6C, the PFS-4C film displays superior characteristics in serving as AIL, such as high transmittance, suitable WF and relatively smooth surface.

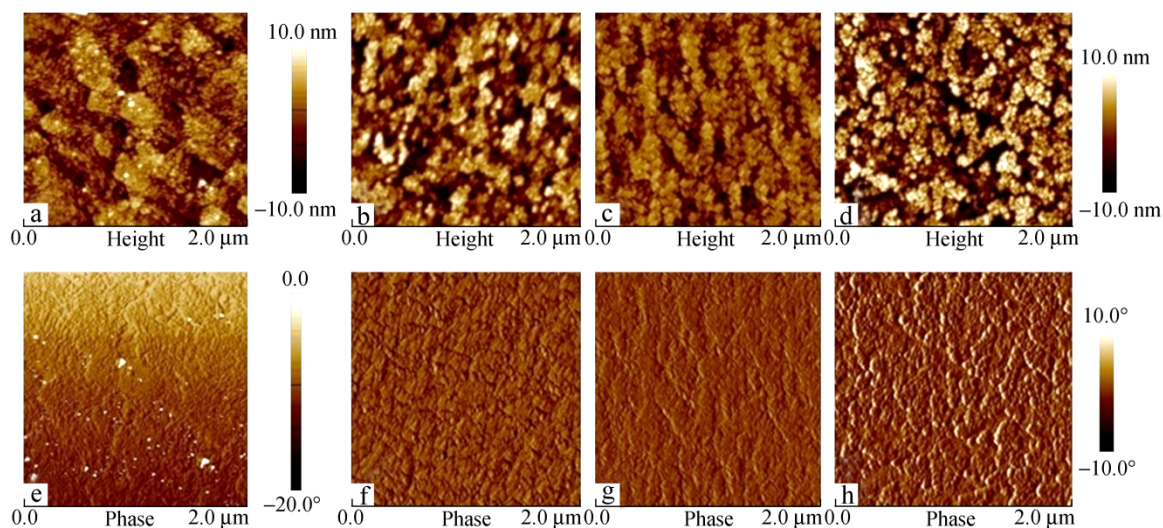


Fig. 6 AFM topography images and phase images of pristine ITO (a and e), ITO covered with PFS-3C (b and f), PFS-4C (c and g) and PFS-6C (d and h)

CONCLUSIONS

In conclusion, we synthesized a series of conjugated polymers based on PFSs derivatives and demonstrated their application in fullerene-free PSCs. These as-synthesized polymers possess deep HOMO levels at *ca.* -5.15 eV, which is beneficial to reduce the hole collection energy barrier of the anode. Among the three polymers, PFS-4C exhibits the most superior properties in serving as AIL in fullerene-free PSC devices due to its high transmittance, suitable WF and smooth surface. The fullerene-free PSC device with PFS-4C interlayer shows a high PCE of 10.54%, which is of superior PEC value in current fullerene-free PSCs. This work demonstrates that the conjugated polymers of rational design are promising candidates in developing superior AIL material for high-performance PSCs.

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