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Synthesis and simultaneously enhanced photovoltaic property of poly [4,4,9,9-tetra(4-octyloxyphenyl)-2,7-indaceno[1,2-*b*:5,6-*b*']dithiophene-*alt*-2,5-thieno[3,2-*b*]thiophene]

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ABSTRACT

An alternating conjugated polymer derived from 4,4,9,9-tetra(4-octyloxyphenyl)indaceno[1,2-*b*:5,6-*b'*] dithiophene and thieno[3,2-*b*]thiophene was synthesized by Stille coupling reaction. The copolymer shows extensive absorption from 360 nm to 590 nm with optical band gap of 2.12 eV. The highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) energy levels of the copolymer, determined by cyclic voltammetry (CV), are about -5.29 eV and -3.01 eV, respectively. A field-effect hole mobility of 8.1×10^{-4} cm²/(V s) and an on/off ratio of 2.0×10^3 are obtained in the field-effect transistors based on the copolymer. The J_{sc} , V_{oc} and *FF* of the polymer photovoltaic cells (PVCs) based on the copolymer were enhanced simultaneously via the inserting of alcohol soluble conjugated polymer interlayer between active layer and metal cathode, and the maximal power conversion efficiency of 4.19% was achieved in the modified devices under an AM 1.5 simulator (100 mWcm⁻²).

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1. Introduction

In recent years, the conjugated polymers (CPs) derived from heteroacene with fused thiophene have emerged as the forefront of polymer heterojunction photovoltaic cells [1]. Many CPs based on heteroacene with two fused thiophene have been synthesized, and the polymer photovoltaic cells (PVCs) with power conversion efficiencies (PCEs) of 3-9% have been achieved in last decade. Among them, the narrow band gap CPs based on benzo[1,2-b:4,5-b'] dithiophene (BDT) have been proven the most promising electron donor materials for high performance PVCs and BDT has been proven to be the most promising electron donor building blocks for CPs used in high performance PVCs. For example, in 2009, Yu et al. had reported a CP derived from benzo[1,2-b:4,5-b']dithiophene (BDT) and thieno[3,4-b]thiophene derivatives, and named PTB1. The PCE of 4.8% was achieved in the devices based on the PTB1 and PC₆₁BM blend [2]. After that, Yu et al. [3] Yang et al. [4] Hou et al. [5] Li et al. [6] and Huang et al. [7] have reported more promising CPs based on BDT through the optimization of the energy level and

chemical structure of the BDT-based CPs. The PCEs of 5–9% have been achieved in the PVCs with BDT-based CPs as electron donor materials.

Whereas electron-rich heteroacenes with more fused thiophene units not only hold promise as a suitable donor constituent in the building of donor-acceptor type narrow band gap copolymers for heterojunction blend PVCs, but also the presence of large coplanar structure and extended π -conjugation of heteroacenes with more fused thiophene units are beneficial to enhance the rigidity of the molecular backbone and the degree of conjugation, thus enhance π - π overlap and π - π effective approaches to increase the hole mobility of CPs [8]. Then, CPs based on heteroacenes with more fused thiophene units have been pinned much hope on developing more promising electron donor materials as comparison to the notable BDT-based copolymers. Unfortunately, the synthesis procedures of heteroacenes with more fused thiophene units suitable to use as building blocks to CPs encountered tedious synthesis, and more importantly difficult introduction of suitable alkyl chains for solubility [9].

As an attractive heteroacene with more fused thiophene units, indaceno[1,2-*b*:5,6-*b'*]dithiophene (IT) not only holds larger coplanar fused structure, which enables enhanced π -conjugation, π - π intermolecular interaction and improved charge carrier



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mobility, but also has two sites for attaching side alkyl chains to optimize the solubility of the CPs. Therefore, IT can be used as a promising building block to develop novel CPs for high performance PVCs. For example, Ko et al. and Zhang et al. have reported series of CPs derived from 4,4,9,9-tetra(4-hexylphenyl)indaceno [1,2-b:5,6-b']dithiophene, respectively. And the PCEs of 3-6.2% have been achieved in the PVCs based on the copolymers [10]. On the other hand, we have demonstrated that the open circuit voltage, short current density and fill factor of PVCs with narrow band gap CPs derived from indeno[1,2-b]fluorene – a similar fused coplanar structure unit to IT, can be simultaneously enhanced via the incorporation of polyelectrolyte interlayer between active layer and metal cathode [11]. Wu et al. [12,13a] and Bazan et al. [13b] also have demonstrated that the open circuit voltage (V_{oc}), short current density (J_{sc}) and fill factor (FF) of PVCs based on CPs derived from benzo[1,2-b:4,5-b']dithiophene and/or carbazole-based CPs, can be simultaneously enhanced via the method through the incorporation of alcohol soluble conjugated polymer interlayer or polyelectrolytes interlayer between active layer and metal cathode, respectively. Unfortunately, it has been found that the validity of the method on the increase of J_{sc} , V_{oc} and FF of the PVCs, have only taken effects on some specific donor materials system such as fluorene, carbazole and benzo[1,2-*b*:4,5-*b*']dithiophene etc [11–14]. In order to broaden the materials systems, the method through which the photovoltaic parameters of PVCs such as J_{sc} , V_{oc} and FF are increased via the incorporation of polyelectrolyte or alcohol soluble conjugated polymer interlayer between active layer and metal cathode, and optimize the PVCs from IT-based CPs, further development of novel IT-based CPs and implement of devices configuration with modified cathode, is interesting and promising for the achievement of high performance PVCs from IT-based copolymers.

In this paper, we present our results on the synthesis and characterization of an alternating copolymer derived from 4,4,9,9-tetra(4octyloxyphenyl)indaceno[1,2-*b*:5,6-*b*']dithiophene and thieno[3,2-*b*] thiophene. The resulted polymer, named PITT, is soluble in common organic solvents and exhibits extensive absorption from 330 nm to 600 nm. The chemical structure, molecular weight, thermal stability, field-effect charge carrier property and electrochemical properties of the copolymer have been characterized. Moreover, the application of the copolymer as electron donor material for PVCs was investigated, and the optimization of the devices through the cathode modification through alcohol soluble conjugated polymer interlayer was implemented.

2. Experimental section

2.1. Materials

All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co., and used as received. All the solvents were further purified under a nitrogen flow. 1-bromo-4-octyloxybenzene [15], diethyl 2,5-dibromoterephthalate [16] and 2,5-bis(trimethystannyl)thieno[3,2-b]thiophene [17] were prepared following the published procedures and characterized by ¹H NMR and GC–MS before use. Poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) were prepared and characterized by the procedure as reported reference [18].

2.2. General methods

¹H NMR spectra were recorded on a Bruker DRX 400 spectrometer operating at 400 MHz and were referred to tetramethylsilane (TMS). Analytical GPC was obtained using a Waters GPC 2410 in tetrahydrofuran (THF) via a calibration curve of polystyrene standard. UV–visible absorption spectra were measured on a UV-2550 spectrophotometer (Shimadzu). Photoluminescence (PL) spectra were taken by 970 CRT spectrofluorometer (Sanco, Shanghai) through 500 nm excitation. Thermogravimetric analysis (TGA) was measured on a TGA 2050 (TA instruments) thermal analysis system under a heating rate of 10 °C min⁻¹ and a nitrogen flow rate of 20 mL min⁻¹.

Cyclic voltammetry (CV) was measured on a CHI 660 electrochemical workstation (Shanghai Chenhua Co.) at a scan rate of 50 mV/s with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile (CH₃CN) with platinum and Ag/AgCl electrodes as the working and reference electrodes, respectively.

2.3. Fabrication and characterization of field-effect transistor

Heavily *p*-doped Si wafers with 100 nm thermal SiO₂ grown, were used both as the substrate and the gate electrode. The substrates were cleaned followed by a wet-cleaning process inside an ultrasonic bath, beginning with deionized water, followed by acetone and isopropanol for 10 min, and dried with nitrogen. Then, the substrates were treated with oxygen plasma for 5 min to remove any residual organic materials and to create a high density of silanol groups at the surface. On the other hand, to improve the chemical and electrical properties of the gate dielectric, a selfassembled monolayer (SAM) octyltrichlorosilane (OTS) film on the wafers were prepared as the following procedure [19], beginning with immersed the wafers in a 0.1 M solution of the OTS in toluene at 60 °C for 30 min, then rinsed with toluene and 2propanol, and dried in a vacuum oven. After that, the films of PITT were deposited on pre-treated SiO₂/Si substrates by spincoating a 10 mg mL⁻¹ solution of the polymer in chlorobenzene, followed by annealing under nitrogen to remove the residual solvent. The source and drain electrodes were defined by thermally evaporating gold (70 nm) through a shadow mask on top of the organic thin film forming top contact geometry transistors. Channel length and width of the obtained OFET were 0.1 and 10 mm, respectively. The OFET was characterized under ambient conditions by a semiconductor parameter analyzer (model: 4155B).

2.4. Fabrication and characterization of PVCs

A patterned indium tin oxide (ITO) coated glass with a sheet resistance of 10–15 Ω /square was cleaned by a surfactant scrub, followed by a wet-cleaning process inside an ultrasonic bath, beginning with deionized water, followed by acetone and isopropanol. After oxygen plasma cleaning for 5 min, a 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spincasted onto the ITO substrate and then dried by baking in a vacuum oven at 80 °C overnight. The active layer, with a thickness in the 70–80 nm range, was then deposited on top of the PEDOT:PSS layer, by spin-casting from a chlorobenzene solution containing PITT/PC₆₁BM (1:2 w/w), PITT/PC₆₁BM (1:4 w/w), PITT/PC₇₁BM(1:4 w/w). The PFN solution in methanol was spin-coated on the top of the obtained active layer to form a thin interlayer of 5 nm. The thickness of the PEDOT:PSS and active layer were verified by a surface profilometer (DektakXT, Boyue In. Co.). Determination of the thickness of the PFN interlayer followed as previously described [18], and thickness control was achieved by adjusting the concentration of the solution and the spin speed (between 600 and 2500 rpm). The thickness of the PFN interlayer was determined using a surface profilometer, in combination with extrapolation from an absorbance-thickness curve that assumes a linear dependence of absorbance at 380 nm on the film thickness. Finally, a 100 nm aluminium layer was thermally evaporated with a shadow mask under vacuum of 3 \times 10⁻⁵ Pa. The overlapping area between the cathode and anode defined a pixel size of device of 0.15 cm². The thickness of the evaporated cathode was monitored by a quartz crystal thickness/ratio monitor (SI-TM206, Shenyang Sciens Technology Co.). Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere in a nitrogen drybox (Etelux Co.) containing less than 1 ppm oxygen and moisture. The PCEs of the resulting polymer solar cells were measured under 1 sun, AM 1.5G (Air mass 1.5 global) condition using a solar simulator (XES-70S1, San-EI Electric Co.) (100 mW cm⁻²). The current density–voltage (*I*–*V*) characteristics were recorded with a Keithley 2410 source-measurement unit. The spectral responses of the devices were measured with a commercial EQE/incident photon to charge carrier efficiency (IPCE) setup (7-SCSpecIII, Bejing 7-star Opt. In. Co.). A calibrated silicon detector was used to determine the absolute photosensitivity.

2.5. Synthesis procedure

2.5.1. Diethyl 2,5-di(thiophen-2-yl)terephthalate (I) [20]

A solution of anhydrous zinc chloride (5.4 g, 40 mmol) suspended in 30 mL anhydrous THF was added dropwise into 30 mL of 2-thienylmagnesium bromide (1 M in THF) solution at 0 °C, and the reaction was kept at 0 °C for another 0.5 h under argon atmosphere. A solution of diethyl 2,5-dibromoterephthalate (4.38 g, 11.5 mmol) and Pd(PPh₃)₄ (226 mg) in 100 mL THF was added in one portion. After the mixture was refluxed overnight, the reaction mixture were cooled to room temperature and quenched by distilled water, then extracted with diethyl ether for three times. The organic phase was combined and the solvent was removed under reduced pressure. The product was purified by chromatography (petroleum ether/ethyl acetate = 8:1, V/V) to give 4.29 g white solid with yield of 96%. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.81 (s, 2H), 7.38 (dd, *J* = 5.2, 1.6 Hz, 2H), 7.10–7.06 (m, 4H), 4.22 (q, *J* = 7.2 Hz, 4H), 1.15 (t, *J* = 7.2 Hz, 6H). GC–MS: Cacld for C₂₀H₁₈O₄S₂, 386.48, Found: 386.15.

2.5.2. Diethyl 2,5-bis(5-bromothiophen-2-yl)terephthalate (II) [10b]

A solution of *N*-bromosuccinimide (NBS, 2.0 g, 11.2 mmol) dissolved in 20 mL chloroform was added dropwise into the solution of I (2.0 g, 5.2 mmol) in the 90 mL chloroform and 35 mL acetic acid at room temperature under dark. After the reaction was carried on for another 3 h, 80 mL distilled water was added and the mixture was extracted with chloroform for three times. The combined organic was dried with anhydrous Na₂SO₄, the solvent was removed under reduced pressure. Then the yellow solid was recrystallized from acetone to led 2.59 g yellow flake (yield, 92%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.77 (s, 2H), 7.04 (d, *J* = 4.0 Hz, 2H), 6.84 (d, *J* = 3.6 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 4H), 1.21 (t, *J* = 6.8 Hz, 6H). C₂₀H₁₆Br₂O₄S₂, Calcd:44.13; H, 2.96; Br, 29.36; S, 11.78. Found: C, 44.09; H, 2.94; Br, 29.4; S, 11.81.

2.5.3. 2,5-bis(5-bromothien-2-yl)-1,4-bis(1,1-di(4-octyloxyphenyl-hydroxylmethyl) benzene (III) [20]

A solution of 4-octyloxyphenylmagnesium bromide prepared by 1-bromo-4-octyloxybenzene (18.0 g, 63.15 mmol) and magnesium (1.82 g, 75.8 mmol) in 80 mL THF, was added slowly to a solution of II (4.3 g, 7.9 mmol) at 0 °C under argon atmosphere. After the reaction was carried on for another 1.5 h at 0 °C, then refluxed overnight, the reaction was quenched by water and extracted with ethyl acetate. The combined organic phase was dried with anhydrous Na₂SO₄, the solvent was removed under reduced pressure. The resulted product was used for the next step directly without further purification.

2.5.4. 2,7-dibromo-4,4,9,9-tetra(4-octyloxyphenyl)indaceno[1,2-

b:5,6-b']dithiophene (IV) [20]

Compound **III** 2.0 g was dissolved into a 100 mL acetate acid and stirred for 20 min. Then two drops of concentrated sulfuric acid was added, and the mixture was refluxed for 4 h. After the reaction was cooled to room temperature, 100 mL distilled water was added. The resulted solution was extracted with ethyl acetate for three times. The combined organic phase washed with saline solution and dried with anhydrous Na₂SO₄. Then the solvent was removed under reduced pressure, and the product was purified with chromatography (petroleum ether/ethyl acetate = 30:1, V/V) to afford 0.87 g white solid (yield 45%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.28 (s, 2H), 7.10 (d, *J* = 8.8 Hz, 8H), 6.96 (s, 2H), 6.77 (d, *J* = 8.8 Hz, 8H), 3.90 (t, *J* = 6.8 Hz, 8H), 1.74 (m, 8H), 1.42 (m, 8H), 1.31–1.26 (m, 32H), 0.87 (t, *J* = 7.2 Hz, 12H). FAB–MS: Cacld for C₇₂H₈₈Br₂O₄S₂, 1241.4, Found: 1241.

2.5.5. Synthesis of the polymer

A mixture of toluene (6 mL) and N,N-dimethylformamide (0.5 mL) was added to a 25 mL two-neck flask containing monomers IV (372.30 mg, 0.3 mmol), 2,5-bis(trimethylstannyl)thieno [3,2-b]thiophene (139.65 mg, 0.3 mmol) and Pd(PPh₃)₄ (4.0 mg). The solution was refluxed with vigorous stirring for 36 h under an argon atmosphere. At the end of polymerization, the polymer was end-capped with 2-tributylstannylthiophene and 2bromothiophene to remove bromo and trimethystannyl end groups. The mixture was then poured into methanol, and the precipitated material was collected and extracted with ethanol. acetone, hexane and toluene in a Soxhlet extractor. The solution of the copolymer in toluene was condensed to about 5 mL and then poured into methanol (500 mL). The precipitation was collected and dried under vacuum overnight (yield: 75%).¹H NMR (400 MHz, CDCl₃), δ (ppm): 6.98–7.45 (m, 22H); 3.93 (t, 8H); 1.74 (m, 8H); 1.41-1.26 (m, 40 H); 0.87 (t, 12H); Anal. Found: C 75.78, H 7.37,N 2.49,1 S 14.28; $M_n = 16,500$ g/mol with a polydispersity index (PDI) of 1.47.

3. Results and discussion

3.1. Synthesis and characterization

The general synthetic route toward the monomers and copolymer is outlined in Scheme 1. Diethyl 2,5-di(thiophen-2-yl)terephthalate (I) was synthesized by 2-thienylzinc chloride and diethyl 2,5-dibromoterephthalate through the $Pd(PPh_3)_4$ catalyzed coupling reaction, then I was brominated by NBS under dark to led II. Then II was reacted with 4-octvloxyphenylmagnesium bromide to led a corresponding alcohol **III**. Without further purification. compound III was then treated to acid-mediated to afford the IV in 45% yield [20]. 2,5-Bis(trimethylstannyl)thieno[3,2-b]thiophene was prepared following the modified procedures [17]. All the compounds were characterized with ¹H NMR spectra and GC-MS or FAB-MS. The alternating conjugated copolymer (PITT) was synthesized by the palladium-catalyzed Stille coupling reaction and end-capping reactions were performed using 2tributylstannylthiophene and 2-bromothiophene [21]. The obtained copolymer is soluble in common organic solvents, such as toluene, THF and chloroform etc. The number-average molecular weight of PITT determined by GPC using a polystyrene standard, is 16,500 g mol⁻¹ with a polydispersity index (M_w/M_n) of 1.47. Freestanding films can be easily obtained from the solution of PITT in toluene. Furthermore, the copolymer shows excellent thermal stability (5%, degradation at 380 °C, Fig. 1).



Scheme 1. The synthetic route of the monomer and polymer.

3.2. Optoelectronic properties of the copolymer

Fig. 2 shows the normalized UV—vis absorption and photoluminescence spectra of the polymer in the solution of THF and solid thin film. There are one absorption peak at around 510 nm and a shoulder absorption peak at around 535 nm for the copolymer in



Fig. 1. TGA plots of PITT in nitrogen.

THF solution. The maximal absorption and shoulder absorption peaks of the copolymer in solid thin film are red-shifted in web version to around 515 and 541 nm, respectively. The copolymer shows extensive light absorption from 350 to 583 nm in THF solution and 350–590 nm in solid thin film. The optical band gap (E_g) of PITT estimated from the onset of absorption edge in solid thin film is about 2.12 eV. The PL emission peaks of the copolymer in THF solution and solid thin film are around 580 and 592 nm, respectively (Fig. 2). The solid state photoluminescence of the copolymer with a maximal emission at 590 nm is totally quenched by the addition of [6,6]-phenyl-C₆₁ butyric acid methyl ester (PC₆₁BM) (Fig. 2b). This efficient photoluminescence quenching is the consequence of ultra-fast photo-induced charge transfer from the polymer to PC₆₁BM. It indicates that the PITT is a viable electron donor material for PVCs [21].

The electrochemical behavior of the copolymer was investigated by cyclic voltammetry (Fig. 3). We can record two oxidation process and one reduction process in the copolymer solid thin film. The reduction potential is at around -1.35 V. Two oxidation potentials are observed at around 0.83 eV and 1.32 eV. HOMO and LUMO levels of the copolymer calculated by empirical formulas ($E_{HOMO} = -e(E_{ox} + 4.46)$ (eV)) and $E_{LUMO} = -e(E_{red} + 4.46)$ (eV)) [22] are -5.29 eV and -3.11 eV, respectively. The electrochemical band gap of the copolymer of 2.18 eV is similar to the optical band gap of the copolymer ($E_{opt} = 2.12$ eV).

3.3. Field-effect transistor performances

The field-effect carrier mobility of the polymer was investigated by fabricating and evaluating thin film field-effect transistors (FETs) based on the top contact geometry. Fig. 4a displays the plots of



Fig. 2. Normalized absorption and PL spectra of the copolymer in solid thin film and the THF solution (5×10^{-5} mol L⁻¹) (a), normalized absorption and PL spectra of the blend of PITT and PC₆₁BM (b).

source-drain current (I_{DS}) as a function of source-drain voltage (V_{DS}) at different gate voltages (V_G) from 0 to -40 V. On the application of negative V_G , characteristic transistor behavior is observed, indicating that the fabricated FET holds *p*-channel characteristics. As the V_{DS} increases, the current I_{DS} approach into the saturation regime could be described by Equation (1):

$$I_{\rm DS} = (W/2L)C_0\mu(V_G - V_T)^2$$
(1)

where μ is the field-effect hole mobility, *W* is the channel width (10 mm), *L* is the channel length (0.1 mm), *C*₀ is the capacitance per unit area of the gate dielectric layer (SiO₂, 100 nm, *C*₀ = 34.5 nF/cm²), and *V*_T is the threshold voltage. The saturation region field-effect mobility was thus calculated from the transfer characteristics of the OFETs involving plotting $I_{DS}^{1/2}$ vs. *V*_G (Fig. 4b). The PITT devices show typical *p*-channel FET characteristics with good drain–current modulation and well defined linear and saturation regions. The hole mobility of PITT was calculated in the saturated



Fig. 3. Electrochemical curve of the copolymer.



Fig. 4. The output at different gate voltages (V_G) (a) and transfer characteristics in the saturation regime (b) for OFETs using spin-coated PITT on SiO₂/Si substrates.

Table 1 Device characteristics of photovoltaic cells based on PITT/PCBM blend.

Device	$V_{\rm oc}\left({\sf V}\right)$	J _{sc} (mA/cm ²)	FF (%)	η _e (AM1.5 100 mW/cm ²) (%)
PITT:PC ₆₁ BM (1:2)	0.80	3.23	43	1.11
PITT:PC61BM (1:4)	0.80	4.82	48	1.85
PITT:PC71BM (1:4)	0.80	6.97	54	3.01
PITT:PC71BM (1:4)	0.88	7.68	62	4.19
(with PFN interlayer)				

regime at $V_{\rm DS} = -30$ V to be 8.1×10^{-4} cm² V⁻¹ s⁻¹ with a current on/off ratio of 2.0×10^3 . The result is consistent with the mobility of IT-based copolymers reported by Ko et al. [10b]. The high hole mobility of the PITT is expected to facilitate charge transport and reduce recombination loss in the PVCs, therefore it can lead to an improved device performance.



Fig. 5. a. J-V characteristics of photovoltaic devices based on the blend of copolymer and PC₇₁BM. b. IPCE curves of the devices based on copolymer and PC₇₁BM.

3.4. Solar cell performances

The potential of the PITT to be employed as electron donor material for PVCs were explored in a device configuration of ITO/PEDOT:PSS/active layer/Al, with $PC_{61}BM$ and $PC_{71}BM$ as electron acceptor materials, respectively. The obtained PVCs were tested under AM 1.5G illumination at an irradiation intensity of 100 mW cm⁻², and the resulting device performances are summarized in Table 1. The PCEs of 1.11%–1.85% and the V_{oc} of 0.80 and 0.80 V, J_{sc} of 3.23 and 4.82 mA cm⁻² and fill factor (FF) of 43% and 48% are achieved in PVCs based on PITT/PC₆₁BM blend (w:w, 1:2 and 1:4), respectively. When PC₇₁BM was used as the electron acceptor material, the PCEs of the devices from PITT/PC₇₁BM (w:w; 1:4) are improved to 3.01% with V_{oc} of 0.80 V, J_{sc} of 6.97 mAcm⁻² and *FF* of 54%.

When a thin layer of PFN (5 nm) was inserted as interlayer between the active layer and metal electrode, the device performances are improved in all aspects (Table 1). The PCE of the PVCs, with PC71BM as electron acceptor material and PFN as interlayer between active layer and metal cathode, were improved from 3.01% to 4.19%. The $V_{\rm oc}$ of 0.88 V, $J_{\rm sc}$ of 7.68 mA cm⁻², FF of 62%, and the incident photons to charge efficiency (IPCE) of the PVCs based on the PITT/PC71BM blend with PFN interlayer, were simultaneously enhanced as comparison of the parameters for PVCs without PFN interlayer (Fig. 5a and 5b). The improvement of device performance may be attributed to an enhanced built-in potential across the device due to the existence of interface dipole between the active layer and cathode by the PFN layer, improvement to chargetransport properties, elimination of the buildup of space charge. and reduced recombination loss due to increase in built-in field and charge carrier mobility [12]. The results indicated that the performance of PVCs with IT-based conjugated polymers as electron donor materials could be enhanced via the incorporation of alcohol soluble conjugated polymer interlayer between active layer and metal cathode. It should open up new opportunities to improve the performance of PVCs from IT-based CPs.

4. Conclusion

An alternating copolymer derived from 4,4,9,9-tetra(4octyloxyphenyl) indaceno[1,2-*b*:5,6-*b*']dithiophene and thieno [3,2-b]thiophene was synthesized, and the chemical structure, molecular weight, thermal stability, field-effect charge carrier property and electrochemical properties of the copolymer have been characterized. The application of the copolymer as electron donor materials for polymer photovoltaic cells (PVCs) was investigated. On the other hand, the optimization of the devices through the cathode modification by alcohol soluble conjugated polymer interlayer, was also implemented. The Voc, Jsc and FF of the PVCs based on PITT were enhanced simultaneously in the PVCs with PFN interlayer, and the maximal power conversion efficiency reaches 4.19% with an open circuit voltage (V_{oc}) of 0.88 V, short circuit current densities (J_{sc}) of 7.68 mAcm⁻² and fill factor (*FF*) of 62% in the devices with PFN as cathode modification interlayer under an AM 1.5 simulator (100 mWcm⁻²). The results indicated that the performance of PVCs with IT-based conjugated polymers as electron donor materials could be enhanced via the incorporation of alcohol soluble conjugated polymer interlayer between active layer and metal cathode. It should open up new opportunities to improve the performance of PVCs from IT-based CPs.

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