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Synthesis and photovoltaic performance of novel thiophenylmethylene-9*H*-fluorene-based low bandgap polymers



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Jiefeng Hai^a, Baofeng Zhao^b, Fujun Zhang^c, Chuan-Xiang Sheng^d,*, Liangming Yin^a, Yang Li^a, Enwei Zhu^a, Linyi Bian^a, Hongbin Wu^b,*, Weihua Tang^{a,*}

^a Key Laboratory of Soft Chemistry and Functional Materials (Ministry of Education of China), Nanjing University of Science and Technology, Nanjing 210094, PR China

^b Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices,

South China University of Technology, Guangzhou 510640, PR China

^c Key Laboratory of Luminescence and Optical Information (Ministry of Education of China), Beijing Jiaotong University, Beijing 100044, PR China

^d School of Electronic and Optical Engineering, Nanjing University of Science and Technology, Nanjing 210094, PR China

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ABSTRACT

Three novel donor-acceptor polymers have been synthesized with Suzuki cross-coupling between thiophenyl-methylene-9*H*-fluorene donating unit with thiazolo[5,4-*d*]thiazole (**PFTTTz**), benzothiadiazole (**PFTODTBT**) or [1,2,3]triazolo[4,5-g]quinoxaline (**PFTDTBTzQ**) accepting unit. The polymer **PFTTTz**-THF prepared from tetrahydrofuran (THF) presented higher molecular weight and narrower polydiversity than that from toluene (**PFTTTz**-toluene), leading to higher photovoltaic performance in BHJ devices of these polymers blended with PC₇₁BM ([6,6]-phenyl-C₇₁-butyric acid methyl ester). These good solution processable polymers exhibit a bandgap of 1.66–1.93 eV and a low highest occupied molecular orbital (HOMO) energy level ~ -5.32 eV. Polymers **PFTTTz** and **PFTOTBTT** displayed strong absorption in the range of 300–650 nm, while **PFTDTBTzQ** showed a further 100 nm extended absorption band. Overall efficiencies over 1.5% are achieved for BHJ devices fabricated from blends of **PFTTTz** with PC₇₁BM as active layer. A maximum power conversion efficiency of 2.21% is obtained by the use of interlayer poly [(9,9-dioctyl-2,7-fluorene)-alt-(9,9-bis(3'-(N, N-dimethylamino)propyl)-2,7-fluorene)] (PFN) and Ca between active layer and Al anode.

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1. Introduction

In the past decade, polymer solar cells (PSCs) adopting bulk heterojunction (BHJ) device structure have attracted considerable attention owing to their easy tunability of polymers' chemical properties and potential in fabricating lightweight, low-cost, and flexible large area devices [1–5]. Tremendous progress in the research of PSCs has been made in recent years, whose power conversion efficiencies (PCEs) have been improved from 1% to over 9% and even a highest record of 10.6% under the collective efforts of both device physicists and material chemists [6–8]. However, there are still some key issues needed to be solved before its commercial application, such as dependable encapsulation technology to secure long-life working devices, and robust large-area processing for device making [2–4,9].

* Corresponding authors. Fax: +86 25 84317311.

Some design criteria for an ideal donor polymer materials can be summarized as follows: (1) the donor polymer should have high extinction coefficient and optimal optical bandgap (E_g); (2) the donor polymer should have good solubility and appropriate compatibility with fullerene derivatives; (3) the molecular energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the donor polymer should well match with those of acceptors; (4) the donor polymer should have high hole mobility [10]. To meet the these criteria, a large library of donor polymers designed by alternating electronrich (D) and electron-deficient (A) units along the conjugated backbone have been developed as D-A alternating copolymers for highly efficient PSCs [6–8,11–22].

Recently, 9-alkylidene-9*H*-fluorene has been explored as a donating unit in the synthesis of D-A alternating narrow bandgap polymers for PSCs, with a highest PCE reaching 6.2% [15,23,24]. Featuring a sp²-hybridized carbon at the 9-position, 9-alkylidene-9*H*-fluorene presents a more planar conformation than 9,9-dialkyl-substituted fluorene, which facilitates the formation of close



E-mail addresses: cxsheng@mail.njust.edu.cn (C.-X. Sheng), hbwu@scut.edu.cn (H. Wu), whtang@mail.njust.edu.cn (W. Tang).

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packing of polymer backbones in solid state to enhance charge carrier transport [25]. In order to improve the isotropic hole transport along polymer backbone and extend absorption spectrum of the as-designed polymers, a novel conjugated donating unit, thiophenyl-methylene-9H-fluorene, was designed by introducing a thiophene unit into 9-alkylidene-9H-fluorene. New D-A polymers were further prepared by alternating the thiophenylmethylene-9H-fluorene donating unit with accepting unit including thiazolo[5,4-d]thiazole (TTz) [26-31], 4',7'-di-2-thienyl-5',6'-dialkoxy-2',1',3'- benzothiadiazole (ODTBT) [15,32-36] and [1-3]triazolo[4,5-g]quinoxaline (DTBTzQ) [37-39]. These novel copolymers possesses two distinctive characteristics in molecular design: i) the first time to use thiophenyl-methylene-9H-fluorene as electron donating unit for D-A copolymer construction for PSCs; ii) thiophenyl-methylene-9H-fluorene increases conjugate length comparing with 9-alkylidene-9H-fluorene, which has higher electron density. The thiophenyl-methylene-9H-fluorene unit enhances the coplanarity of the polymer backbone and extent the π conjugation.

In this paper, the synthesis, characterization and photovoltaic properties of thiophenyl-methylene-9*H*-fluorene based narrow bandgap polymers are reported. The thermal, optical and electrochemical properties of the resulting polymers were systematically studied. Importantly, the promising potential of blends of **PFTTZ** with $PC_{71}BM$ as the active layer for photovoltaic cells was demonstrated, with a best PCE of 2.21% obtained in the initial device measurement.

2. Experimental section

2.1. Characterization

¹H NMR and ¹³C NMR spectra were characterized on Bruker AVANCE 500-MHz (Bio-Spin Corporation, Europe) spectrometer with chloroform-d as solvent and tetramethylsilane (TMS) as internal standard. Gel permeation chromatography (GPC) analysis were measured with on a Waters 717-2410 instrument with polystyrenes as the standard and THF as an eluant (flow rate 1.0 mL/min). The thermogravimetric analysis (TGA) analysis was conducted with a TA instrument TGA/SDTA851e under nitrogen atmosphere at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analysis was performed on a DSC instrument DSC823 under N₂ with a heating rate from 0 °C to 280 °C. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a UVvis instrument Evolution 220. The electrochemical cyclic voltammetry was conducted in 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution at a scan rate of 50 mV/s on electrochemistry workstation (CHI660D, Chenhua Shanghai) with the polymer film on Pt plate, Pt slice, and saturated calomel electrode (SCE) as working electrode, counter electrode and reference electrode, respectively.

2.2. Photovoltaic device fabrication and characterization

The BHJ solar cells were prepared with a device structure of ITO/ PEDOT:PSS(40 nm)/polymer:PC₆₁BM (1:1, 1:2, 1:3, w/w) or PC₇₁BM (1:2, w/w)/PFN or Ca/Al (80 nm). The ITO glass substrates were sonicated sequentially in deionized water, acetone, deionized water and isopropanol. Immediately prior to device fabrication, the substrates were treated by oxygen plasma for 4 min. Firstly, poly(3,4ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS, H.C. Starck) thin film (40 nm) was spin-coated and then baked at 150 °C for 15 min. Secondly, the **PFITTz**:PC₇₁BM (1:2 weight ratio) or PFTDTBTzQ:PC₆₁BM (1:1, 1:2, 1:3 weight ratio) active blend layer, with a nominal thickness of ~80 nm, was spin-coated on top of the PEDOT/PSS from a solvent of *o*-dichlorobenzene (*o*-DCB) solution (concentration, 10 mg/mL) at 1000 rpm for 2 min. Thirdly, a 5 nm interlayer material PFN was spin-coated on the top of active layer through its methanol solution in the presence of small amount of acetic acid or Ca layer was deposited under high vacuum. Finally, Al layer was subsequently evaporated through a shadow mask to define the active area of the devices ($\sim 2 \times 8 \text{ mm}^2$) and form a top anode to complete the photovoltaic device fabrication. The current–voltage (*J*–*V*) characteristics and PCE were measured with a Keithley 2400 sourcemeter under 1 sun, AM 1.5G spectrum from a solar simulator (Oriel model 91192) at room temperature in a nitrogen filled glove-box. Solar simulator illumination intensity was determined using a monocrystal silicon reference cell (Hamamatsu S1133, with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL).

2.3. Materials

All starting materials and reagents were purchased from Sigma– Aldrich Chemical Co. or Acros and used without further purification. THF was dried over sodium/benzophenone and freshly distilled before use. Chloroform and dichloromethane were distilled from CaH₂ under nitrogen. 2-Dodecylthiophene [40], (4',7'-di-2-thienyl-5',6'-didodecyloxy)-2',1',3'-benzothiadazole (ODTBT)[36]2-dodecyl-4,7-bis(4-(2-ethylhexyl)thiophen-2-yl)-5,6-dinitro-2H-benzo[d] [1– 3]triaz-ole [37], and 1,2-bis(3,4-bis(dodecyloxy)phenyl)ethane-1,2dione [41,42] were prepared according to the known literature procedures.

2.4. Synthesis

2.4.1. 5-Dodecylthiophene-2-carbaldehyde (1) [43]

To a stirred solution of 5-dodecylthiophene [40] (4.00 g, 15.84 mmol) in anhydrous DMF (3.47 g, 47.53 mmol), POCl₃ (7.29 g, 47.53 mmol) was added slowly at 0 °C and stirred for 20 min at this temperature. The mixture was warmed to 75 °C and refluxed for 2 h, and then it was poured into ice water and neutralized by NaOH to neutrality. After extraction with CHCl₃, the combined organic layers were washed with water and brine, dried with MgSO₄, filtered, and concentrated via rotary evaporation. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (4:1, v/v) to give the pure product as a pale yellow solid (3.26 g, 73%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 9.81 (s, 1H), 7.60 (d, J = 3.7 Hz, 1H), 6.90 (d, J = 3.7 Hz, 1H), 2.86 (t, J = 7.6 Hz, 2H), 1.74–1.67 (m, 2H), 1.31–1.23 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H).

2.4.2. 2,7-Dibromo-fluorene (2) [44]

To a solution of fluorene (14.7 g, 88.44 mmol) in dry chloroform (150 mL) at 0 °C was added with a solution of Br₂ in chloroform (80 mL). The reaction was stirred overnight at room temperature in darkness. After quenched with saturated aqueous Na₂S₂O₃, the reaction mixture was separated and the organic phase was washed with water, dried with MgSO₄ and concentrated *in vacuo*. The crude product was recrystallized in ethanol to give the *title* product as a white solid (26.3 g, 92%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.68 (s, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 3.87 (s, 2H).

2.4.3. 2,7-Dibromo-9-((5-dodecylthiophen-2-yl)methylene)-9H-fluorene (**3**) [45]

2,7-Dibromo-fluorene (**2**) (0.648 g, 2.00 mmol), potassium *tert*-butoxide (0.247 g, 2.20 mmol) were dissolved in ethanol (100 mL). The mixture was refluxed for 1 h before added with 5-dodecylthiophene-2-carbaldehyde (**1**) (0.617 g, 2.00 mmol). The mixture was refluxed for another 2 h. The reaction was cooled to

room temperature and water (100 mL) was added. The crude product was extracted with dichloromethane and the combined organic layers were washed with water and brine, dried with MgSO₄, filtered, and concentrated via rotary evaporation. The residue was purified by column chromatography on silica gel using petroleum ether to give the *title* compound as a yellow solid (1.05 g, 90%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.50 (d, J = 1.6 Hz, 1H), 7.84 (d, J = 1.6 Hz, 1H), 7.60–7.53 (m, 3H), 7.50–7.45 (m, 2H), 7.32 (d, J = 3.6 Hz, 1H), 6.86 (d, J = 3.6 Hz, 1H), 2.91 (t, J = 7.6 Hz, 2H), 1.78–1.71 (m, 2H), 1.46–1.39 (m, 2H), 1.37–1.20 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 150.77, 141.83, 138.85, 137.74, 136.44, 135.96, 131.82, 131.29, 130.74, 127.29, 125.35, 123.32, 122.45, 121.25, 121.07, 32.22, 31.79, 30.68, 29.96, 29.67, 29.45, 23.00, 14.44.

2.4.4. 2,2'-(9-((5-dodecylthiophen-2-yl)methylene)-9H-fluorene-2,7-diyl)bis(4,4,5,5- tetramethyl-1,3,2-dioxaborolane) (**M1**) [15]

A mixture of (9-((5-dodecylthiophen-2-yl)methylene)-9H-fluorene (3)) (1.00 g, 1.71 mmol), bis-pinacoldiboron (1.04 g, 4.09 mmol), PdCl₂(dppf)₂ (62 mg, 0.08 mmol), and potassium acetate (1.67 g, 17.05 mmol) in MDF (50 mL) was stirred for 20 h at 100 °C. The reaction mixture was cooled to room temperature and water (50 mL) was added. The crude product was extracted with diethyl ether and the combined organic layers were washed with water and brine, dried with MgSO₄, filtered and concentrated via rotary evaporation. The residue was purified with column chromatography on silica gel using petroleum ether/ethyl acetate (30:1) to give a vellow oil: after recrystallization from ethanol to give the desired product as a pale vellow solid (1.16 g, 70%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.97 (s, 1H), 8.20 (s, 1H), 7.83–7.78 (m, 3H), 7.77–7.73 (m, 2H),7.36 (d, *J* = 3.4 Hz, 1H), 6.83 (d, *J* = 3.4 Hz, 1H), 2.89 (t, *J* = 7.7 Hz, 2H), 1.79 (m, 2H), 1.39 (s, 12H), 1.35 (s, 12H), 1.33–1.23 (m, 18H), 0.88 (t, J = 7.0 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 149.46, 143.54, 141.26, 140.33, 137.22, 136.25, 134.99, 134.55, 133.48, 131.37, 128.11, 127.83, 126.59, 125.09, 120.68, 119.81, 119.63, 84.08, 83.92, 32.25, 31.93, 30.78, 30.00, 29.72, 29.56, 25.22, 23.03, 14.48.

2.4.5. 3-Methoxythiophene (4) [46]

To a stirred solution of sodium methanolate (3.18 g, 58.88 mmol) in methanol (50 mL) were added with N-methyl pyrrolidone (50 mL) and 3-bromothiophene (8 g, 49.07 mmol). The mixture was heated to 110 °C and then Cul (934 mg, 4.91 mmol) was added in one portion and kept reflux overnight. The reaction was cooled to room temperature and water (100 mL) was added. The crude product was extracted with dichloromethane and the combined organic layers were washed with water and saturated aqueous NH₄Cl, dried with MgSO₄, filtered, and concentrated via rotary evaporation. The residue was further distilled under reduced pressure to afford the *title* compound as a colorless liquid (4.95 g, 88%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.19–7.16 (m, 1H), 6.76-6.74 (m, 1H), 6.26-6.24 (m, 1H), 3.81 (s, 3H).

2.4.6. 3-((2-Octyldodecyl)oxy)thiophene (5) [46]

A mixture of 3-methoxythiophene (**4**) (5.26 g, 46.07 mmol), 2-octyldodecan-1-ol (27.51 g, 92.15 mmol), potassium bisulfate (1.25 g, 9.21 mmol) were dissolved in toluene (50 mL) and heated at 115 °C for 20 h under N₂. The reaction mixture was cooled to room temperature and water (50 mL) was added. The crude product was extracted with dichloromethane and the combined organic layers were washed with water and brine, dried with MgSO₄, filtered, and concentrated via rotary evaporation. The residue was purified by column chromatography on silica gel using petroleum ether to give the pure product as a colorless liquid (8.70 g, 50%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.20–7.16 (m, 1H), 6.80–6.77 (m, 1H), 6.25–6.23 (m, 1H), 3.85 (d, *J* = 5.7 Hz, 2H), 1.82–1.77 (m, 1H), 1.27–1.50 (m, 32H), 0.93 (t, *J* = 7.0 Hz, 6H).

2.4.7. 3-((2-Octyldodecyl)oxy)thiophene-2-carbaldehyde (6) [26]

To the stirred solution of anhydrous DMF (40 mL) at 0 °C under nitrogen atmosphere was added with POCl₃ (2.42 g, 15.76 mmol) over 10 min. After addition, the reaction mixture was stirred at that temperature for 3 h. Then 3-((2-octyldodecyl)oxy)thiophene (5) (5.00 g, 13.13 mmol) was added dropwise at 0 °C. The reaction mixture was heated to 70 °C for 12 h. The reaction was cooled to room temperature and poured it into ice water and then slowly neutralize with 10% NaOH solution. The crude product was extracted with dichloromethane and the combined organic layers were washed with water and brine, dried with MgSO₄, filtered, and concentrated via rotary evaporation. After column chromatography on silica gel using petroleum ether/ethyl acetate (8:1), the title product was obtained as a colorless liquid (4.03 g, 75%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 10.00 (s, 1H), 7.61 (d, J = 5.4 Hz, 1H), 6.83 (d, J = 5.4 Hz, 1H), 4.03 (d, J = 5.6 Hz, 2H), 1.83–1.77 (m, 2H), 1.48–1.19 (m, 32H), 0.88 (t, J = 7.0 Hz, 6H).

2.4.8. 2,5-Bis(3-((2-octyldodecyl)oxy)thiophen-2-yl)thiazolo[5,4-d] thiazole (7) [26]

Dithiooxamide (220 mg, 1.84 mmol), phenol (1.5 g), and 3-((2-octyldodecyl)oxy)thiophene-2-carbaldehyde (**6**) (1.50 g, 3.67 mmol) were combined in a round-bottom flask and refluxed at temperature 160 °C for 3 h. The crude product was purified by column chromatography on silica gel using petroleum ether/chloroform (3:2) to give pure product as brown yellow solid (800 mg, 24%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.32 (d, *J* = 5.5 Hz, 2H), 6.89 (d, *J* = 5.5 Hz, 2H), 4.14 (d, *J* = 4.8 Hz, 4H), 1.88–1.82 (m, 2H), 1.64–1.57 (m, 4H), 1.55–1.47 (m, 4H), 1.40–1.20 (m, 56H), 0.86 (t, *J* = 7.0 Hz, 12H).

2.4.9. 2,5-Bis(5-bromo-3-((2-octyldodecyl)oxy)thiophen-2-yl) thiazolo[5,4-d]thiazole (TTz-Br) [26]

To a solution of 2,5-bis(3-((2-octyldodecyl)oxy)thiophen-2-yl) thiazolo[5,4-d] thiazole (**7**) (0.80 g, 0.89 mmol) in CHCl₃ (16 mL) and acetic acid (8 mL) solution, NBS (348 mg, 1.96 mmol) solution in CHCl₃/AcOH (10/5 mL) was added dropwise and stirred at 0 °C for 2 h. Then the reaction solution was stirred at room temperature overnight. The mixture was washed with water and brine, dried with MgSO₄, filtered, and concentrated via rotary evaporation. After column chromatography on silica gel using petroleum ether/chloroform (5:1), the pure product was obtained as a yellow solid (800 mg, 85%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 6.90 (s, 2H), 4.09 (d, *J* = 4.9 Hz, 4H), 1.88–1.78 (m, 2H), 1.62–1.44 (m, 8H), 1.38–1.18 (m, 56H), 0.86 (t, *J* = 7.0 Hz, 12H).

2.4.10. 2-Dodecyl-4,7-bis(4-(2-ethylhexyl)thiophen-2-yl)-2Hbenzo[d] [1-3]triazole- 5,6-diamine (**9**) [37]

2-Dodecyl-4,7-bis(4-(2-ethylhexyl)thiophen-2-yl)-5,6-dinitro-2H-benzo[d] [1–3]tri-azole (**8**) (3.48 g, 4.54 mmol), iron powder (5.07 g, 90.85 mmol) and acetic acid (100 mL) were added into a round bottom flask purged with nitrogen. The reaction was stirred at 70 °C for 4 h, after which was allowed to cool to room temperature, poured into water (200 mL) and extracted using dichloromethane. The combined organic layers were washed with water and brine, dried with MgSO₄, filtered, concentrated via rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate to give the pure product as a brown oil (2.64 g, 82%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.25 (s, 2H), 7.05 (s, 2H), 4.58 (t, *J* = 7.4 Hz, 2H), 3.54–2.86 (br, 4H), 2.63 (d, *J* = 6.8 Hz, 4H), 2.07–2.00 (m, 2H), 1.66–1.58 (m, 2H), 1.41–1.20 (m, 34H), 0.94–0.86 (m, 15H). 2.4.11. 6,7-Bis(3,4-bis(dodecyloxy)phenyl)-2-dodecyl-4,9-bis(4-(2-ethylhexyl) thiophen-2-yl)-2H- [1-3]triazolo[4,5-g]quinoxaline (11) [37]

2-Dodecyl-4,7-bis(4-(2-ethylhexyl)thiophen-2-yl)-2H-benzo[d] [1-3]triazole-5,6-diamine (9) (844 mg, 1.20 mmol) and 1,2-bis(3,4bis(dodecyloxy)phenyl)ethane-1,2-dione (10) [42] (1.36 g, 1.43 mmol) was dissolved in acetic acid (50 mL). The reaction flask was purged with nitrogen and heated at 100 °C for 24 h. The reaction mixture was cooled to room temperature and water (100 mL) was added. The crude product was extracted with dichloromethane and the organic layer was washed thoroughly with water and then diluted sodium bicarbonate solution. The combined organic layers were washed with water and brine, dried with MgSO₄, filtered and concentrated via rotary evaporation. The residue was purified with column chromatography on silica gel using petroleum ether/ethyl acetate to give the *title* compound as a purple black liquid (1.85 g, 95%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.77 (d, J = 1.2 Hz, 2H), 7.58 (d, J = 2.0, 2H), 7.30 (dd, J = 2.0, 8.3 Hz, 2H), 7.14 (s, 2H), 6.84 (d, J = 8.5 Hz, 2H), 4.96 (d, J = 7.2 Hz, 2H), 4.06–3.97 (m, 8H), 2.71 (d, J = 5.1 Hz, 2H), 2.35-2.29 (m, 2H), 1.88– 1.78 (m, 8H), 1.73-1.68 (m, 2H), 1.53-1.19 (m, 106H), 0.98-0.81 (m, 27H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 151.09, 150.11, 148.61, 142.20, 141.24, 135.38, 133.54, 133.27, 131.33, 126.40, 123.86, 118.84, 116.01, 112.57, 77.25, 69.08, 57.54, 40.40, 34.48, 32.59, 31.92, 29.67, 29.46, 29.38, 29.11, 29.012, 26.73, 26.11, 26.06, 25.70, 23.10, 22.68, 14.20, 14.09, 10.97.

2.4.12. 6,7-Bis(3,4-bis(dodecyloxy)phenyl)-4,9-bis(5-bromo-4-(2ethylhexyl)thiophen-2-yl)-2-dodecyl-2H- [1–3]triazolo[4,5-g] quinoxaline (**DTBTzQ-Br**)

A solution of 6,7-bis(3,4-bis(dodecyloxy)phenyl)-2-dodecyl-4,9-bis(4- (2-ethylhexyl)thiophen-2-yl)-2H- [1-3]triazolo[4,5-g] quinoxaline (11) (1850 mg, 1.14 mmol) in CHCl₃ was cooled to 0 °C. Then NBS (458 mg, 2.57 mmol) was added in small portions over 30 min and then the mixture was stirred overnight. The combined organic layers were washed with water and brine, dried with MgSO₄, filtered, and concentrated via rotary evaporation. After column chromatography on silica gel using petroleum ether/ethyl acetate, the title compound was obtained as a black purple solid (960 mg, 47%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.66 (d, J = 3.7 Hz, 2H), 7.76 (s, 2H), 7.07 (dd, J = 2.0, 8.4 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 4.95–4.90 (m, 2H), 4.18 (t, J = 6.6 Hz, 4H), 4.03 (t, J = 6.5 Hz, 4H), 2.64 (d, J = 7.0 Hz, 4H), 2.33–2.26 (m, 2H), 1.92– 1.82 (m, 8H), 1.80-1.76 (m, 2H), 1.46-1.19 (m, 106H), 0.98-0.84 (m, 27H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 151.67, 150.43, 149.23, 141.77, 140.48, 135.27, 133.00, 131.20, 124.41, 118.23, 117.30, 115.67, 112.32, 69.57, 69.28, 57.70, 40.22, 33.84, 32.79, 32.22, 29.98, 29.69, 29.41, 29.09, 26.98, 26.55, 26.38, 25.95, 23.38, 22.94, 14.39, 11.19.

2.4.13. PFTTTz-THF

TTz-Br (259 mg, 0.381 mmol), **M1** (400 mg, 0.381 mmol), and Pd(PPh₃)₄ (16 mg, 0.02 mmol) were dissolved in a mixture of THF (15 mL) and aqueous Na₂CO₃ (7 mL, 2 mol/L). The mixture was refluxed with vigorous stirring for 65 h under at 85 °C under N₂. After cooling to room temperature, the mixture was poured into methanol. The precipitated material was collected and was Soxhlet-extracted sequentially with methanol, acetone and then with chloroform. The chloroform solution was concentrated to a small volume to precipitate out the polymer out of methanol. Finally, the purple black polymer **PFTTTz**-THF was collected by filtration and dried under vacuum at 40 °C overnight (327 mg, 65%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 9.08–8.06 (br, 2H), 8.05–7.33 (br, 5H), 7.19–6.58 (br, 4H), 4.45–3.81 (m, 4H), 3.14–2.82 (br, 2H), 2.04–0.77 (m, 101H).

2.4.14. PFTTTz-toluene

Toluene was used for the synthesis of **PFTTTz** with Suzuki crosscoupling reaction. Typically, a mixture of **TTz-Br** (259 mg, 0.381 mmol), **M1** (400 mg, 0.381 mmol), toluene (15 mL) and aqueous Na₂CO₃ (7 mL, 2 mol/L) was carefully degassed before and after Pd(PPh₃)₄ (16 mg, 0.02 mmol) was added. The mixture was refluxed with vigorous stirring for 65 h under at 85 °C under nitrogen. By following the same work-up procedure as for **PFTTTz**-THF, the *title* polymer **PFTTTz**-toluene was obtained as a purple black polymer (246 mg, 49%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.85–7.89 (br, 2H), 7.88–7.31 (br, 5H), 7.16–6.70 (br, 4H), 4.50–3.88 (br, 4H), 3.09–2.84 (br, 2H), 2.12–0.75 (m, 101H).

2.4.15. PFTODTBT

Standard Suzuki cross-coupling reaction was employed for the synthesis of PFTODTBT. Typically, **ODTBT-Br** (335 mg, 0.492 mmol), **M1** (407 mg, 0.492 mmol), and Pd(PPh₃)₄ (16 mg, 0.02 mmol) were dissolved in a mixture of toluene (12 mL) and aqueous Na₂CO₃ (5 mL, 2 mol/L). The mixture was refluxed with vigorous stirring for 48 h under an argon atmosphere. After cooling to room temperature, the mixture was poured into methanol. The precipitated material was collected and was Soxhlet-extracted in order with methanol, acetone and then with chloroform. The chloroform solution was concentrated to a small volume to precipitate the polymer out of methanol. Finally, the purple black polymer **PFODTBT** was collected by filtration and dried under vacuum at 40 °C overnight (324 mg, 60%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.85-8.21 (m, 4H), 7.88-7.32 (m, 8H), 6.93-6.84 (br, 1H), 4.33-3.99 (br. 4H). 3.03–2.82 (m. 2H). 2.10–1.89 (br. 4H). 1.87–1.71 (br. 2H). 1.52-1.00 (m, 54H), 0.93-0.77 (br, 9H).

2.4.16. PFTDTBTzQ

By following similar procedure as for PFODTBT, PFDTBTzQ was prepared by the cross-coupling between DTBTzQ-Br (510 mg, 0.287 mmol) and M1 (196 mg, 0.287 mmol) under the catalysis of $Pd(PPh_3)_4$ (16 mg, 0.02 mmol) in a mixture solution of toluene (20 mL) and 20% agueous tetraethylammonium hydroxide (5 mL). The mixture was refluxed with vigorous stirring for 48 h under an N₂ atmosphere. After cooling to room temperature, the mixture was poured into methanol. The precipitated material was collected and was Soxhlet-extracted in order with methanol, acetone and then with chloroform. The chloroform solution was concentrated to a small volume to precipitate the polymer out of methanol. Finally, the purple black polymer **PFDTBTzQ** was collected by filtration and dried under vacuum at 40 °C overnight (483 mg, 82%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.98–8.87 (m, 2H), 8.63 (s, 1H), 7.98 (s, 1H), 7.88-7.81 (m, 2H), 7.76 (s, 1H), 7.74-7.69 (m, 2H), 7.66-7.59 (m, 2H), 7.34-7.28 (m, 2H), 6.82-6.71 (m, 2H), 6.63 (s, 1H), 5.01 (br, 2H), 3.95 (br, 4H), 3.84 (br, 4H), 2.91-2.78 (m, 4H), 2.72 (br, 2H), 2.40 (br, 2H), 1.77 (br, 8H), 1.53–1.02 (m, 128H), 0.93–0.79 (m, 30H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 151.14, 150.18, 149.34, 144.50, 144.22, 142.28, 140.63, 139.78, 137.81, 136.78, 136.374, 135.03, 134.03, 133.80, 133.37, 131.38, 130.86, 129.88, 129.38, 125.57, 124.82, 123.96, 121.10, 119.50, 118.58, 115.61, 112.47, 69.11, 57.60, 40.73, 32.71, 31.92, 31.50, 30.35, 29.67, 29.36, 26.82, 26.04, 25.807, 23.14, 22.68, 14.10.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes for donating monomer **M1** and accepting monomers **TTz-Br** and **DTBTZQ-Br** are outlined in Scheme 1. The thiophenyl-methylene-9*H*-fluorene based donating unit was constructed by a condensation between 5-dodecylthiophene-2-carbaldehyde (**1**) and 2,7-dibromo-fluorene (**2**) with a yield of 90%.



Scheme 1. Synthetic route for monomers.



Scheme 2. Synthetic route for the target copolymers PFTTTz-THF, PFTTTz-toluene, PFTODTBT and PFTDTBTzQ.

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A further boration of 2,7-dibromo-(9-((5-dodecylthiophen-2-yl) methylene)-9H-fluorene (**3**)) afforded the desired thiophenylmethylene-9H-fluorene based donating monomer **M1** in 70% yield. The thiazolo[5,4-*d*]thiazole based accepting monomer **TTz-Br** was prepared with a five-step protocol starting from 3-bromothiophene. The diamine **9** which was the reduction of **8** underwent a condensation with 1,2-bis(3,4-bis(dodecyloxy)phenyl)ethane-1,2-dione (**10**) in acetic acid to afford the key intermediate compound **11** in 95% yield. Bromination of **11** with N-bromosuccinimide in a solution of chloroform afforded **DTBTz-Br** with a good yield.

As depicted in Scheme 2, three polymers PFTTTz, PFTODTBT and PFTDTBTzQ were prepared using Suzuki cross-coupling reaction with a yield of 49-82%. For the synthesis of PFTTTz, THF and toluene were explored for the reaction, and the resulted polymers are named as PFTTTz-THF and PFTTTz-toluene, respectively. The as-synthesized four polymers exhibit excellent solubility in common organic solvents, including tetrahydrofuran, chloroform, o-dichlorobenzene, toluene, etc. Molecular weight of the polymers and polydispersity (PDI) was measured by gel permeation chromatography (GPC) method using polystyrene as standard and chloroform as eluant (Table 1). The as-prepared polymers PFTTTz-THF, PFTTTz-toluene, PFTODTBT and PFTDTBTzQ possess a number-average molecular weight (M_n) of 11,190, 9456, 6393 and 14,230, respectively, and a corresponding polydispersity index (PDI) of 1.22, 1.40, 1.66 and 1.69. A close look at the M_n and PDI data of PFTTTz-THF and PFTTTz-toluene would find that THF is a better solvent than toluene for the synthesis of **PFTTTz**, indicated by the higher $M_{\rm p}$ and narrower PDI.

The thermal property of the polymer was investigated with TGA (Fig. 1). The onset temperature (T_d) with 5% weight loss of **PFTTTz**-THF, **PFTTTz**-toluene, **PFTODTBT** are 352, 315 and 317 °C, respectively. These high T_d values indicate the good thermal stability of the polymers, which are beneficial for their application in optoelectronic devices. PFTDTBTzQ, however, exhibits a relatively low T_d (270 °C). Interestingly, no obvious phase transition process could be observed in the range from 0 to 300 °C for all the resulting polymers even in several cycles of DSC testing.

3.2. Photophysical properties

Fig. 2 shows the UV–vis absorption spectra of the polymers in dilute (10^{-5} M) chloroform solutions and solid films, with the absorption maximum (λ_{max}) data summarized in Table 1. **PFTTTz**-THF film showed absorption band in the range of 350–650 nm with a λ_{max} at 581 nm, which was 12 nm red-shifted than its solution. **PFTTTz**-toluene film showed absorption band in the range of 350–650 nm with a λ_{max} at 577 nm, which was 7 nm red-shifted than its solution. The red-shifted λ_{max} of **PFTTTz**-THF than **PFTTTz**-toluene film can be explained with longer conjugation length of **PFTTTz**-THF due to its larger M_n . **PFTODTBT** film showed absorption band in the range of 450–650 nm with a λ_{max} at 548 nm, which was





^a $M_{\rm w}$ and PDI of the polymers determined by GPC using polystyrene standards in THF.

 $^{\rm b}$ 5% weight-loss temperatures under N₂ and heat from 50 to 800 $^\circ$ C at a rate of 20 $^\circ$ C/min.

^c UV-vis absorption in dilute CHCl₃ solution.

^d UV–vis absorption in thin films.

^e Optical bandgap calculated as $E_{\rm g} = 1240/\lambda_{\rm onset}$ (eV).

^f LUMO = HOMO + E_g^{opt} (eV).



Fig. 1. TGA curve of copolymers at the heating rate of 20 $^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

35 nm red-shifted than that of its solution. **PFTDTBTzQ** film showed absorption band in the range of 550–750 nm with a λ_{max} at 669 nm, which was 19 nm red-shifted than that of its solution. The red-shifted absorption of polymers film indicated that strong intermolecular interaction and aggregation exist in the solid-state of these polymers, which is probably related to the increased extent of π - π stacking of the backbones and increased polarizability of the solid-state. **PFTODTBT** and **PFTDTBTzQ** exhibited two evident absorption bands, the first absorption band at the shorter wavelength was attributed to the π - π * transition of the conjugated main chain and the second band at the longer wavelength was owed to the intramolecular charge transfer (ICT) interaction between the 9-((5-dodecylthiophen-2-yl)methylene)-9H-fluorene donating unit and **TTz** or **DTBTzQ** accepting unit.

The optical bandgaps (E_g) of these copolymers were determined from the UV–vis absorption onsets in the solid state according to the empirical equation: $E_g = 1240/\lambda_{onset}$ eV. The E_g of **PFTTZ**-THF, **PFTTTZ**-toluene, **PFTODTBT** and **PFTDTBTZQ** was determined to be 1.93, 1.96, 1.92, and 1.66 eV, respectively. From the E_g data of **PFTTTZ**-THF, **PFTTTZ**-toluene, **PFTODTBT** and **PFTDTBTZQ**, one could conclude that the electron-withdrawing ability of accepting **DTBTZQ** is stronger than those of **ODTBT** and **TTZ** units. **PFTTTZ** exhibited a lower E_g than structure analog PCDTTz (2.07 eV) [47]. The E_g of **PFTODTBT** is smaller than benzothiadiazole based polyfluorene (2.04 eV), but larger than 9-alkylidene-9*H*-fluorene based **PADFTBT** (1.84 eV) [15]. It showed that 9-((5-dodecylthiophen-2yl)methylene)-9H-fluorene unit could effectively adjust the optical property of the resulting polymers.



Fig. 2. Absorption spectra of four polymers in chloroform solution and solid films.

3.3. Electrochemical properties

The highest occupied molecular orbital (HOMO) energy levels of the conjugated polymers were determined by electrochemical cyclic voltammetry (CV). Fig. 3 shows the CV traces of polymers film on Pt electrode in 0.1 M Bu₄NPF₆ acetonitrile solution at a scan rate of 50 mV/s. The potential of ferrocene 0.40 V versus SCE is used as internal standard. On the basis of 4.8 eV below vacuum for the energy level of Fc/Fc⁺, the HOMO level of the polymers is calculated from the onset oxidation potentials (E_{ox}^{onset}), while the LUMO levels are calculated using HOMO and optical E_{g}^{opt} according to the following equations:

$$HOMO = -e(E_{ox}^{onset} + 4.4)(eV);$$

 $LUMO = HOMO + E_g^{opt}(eV)$

The onset potential for oxidation (E_{0x}^{onset}) was observed to be 0.84, 0.83, 1.03, and 0.92 eV for **PFTTTz**-THF, **PFTTTz**-toluene, **PFTODTBT** and **PFTDTBTzQ**, respectively. Accordingly, the corresponding HOMO energy level of **PFTTTz**-THF, **PFTTTz**-toluene, **PFTODTBT** and



Fig. 3. Cyclic voltammograms of polymers films on platinum electrode in 0.1 M Bu_4NPF_6 acetonitrile solutions at a scan rate of 50 mV/s.

PFTDTBTzQ are calculated to be -5.24, -5.23, -5.43 and -5.32 eV, respectively (Table 1). The deep HOMO levels of these polymers should be beneficial to their chemical stability in ambient conditions. In addition, the deep HOMO levels of copolymers are desirable for higher V_{oc} of the PSCs with copolymers as donor materials [1]. The LUMO level of **PFTTTz**-THF, **PFTTTz**-toluene, **PFTODTBT** and **PFTDTBTzQ** were thus calculated to be -3.31, 3.27, -3.51, -3.66 eV, which were calculated from the E_{go}^{opt} and HOMO energy levels of the polymers, respectively. The difference E_{ox}^{onset} of **PFTTTz**-THF and **PFTTTz**-toluene is attributed to the difference M_n of them.







Fig. 5. Current density versus voltage (J-V) characteristics of devices using different **PFTDTBTzQ**:PC₆₁BM weight ratios as active layer under AM 1.5 G irradiation with an intensity of 100 mW cm⁻².

 Table 2

 Photovoltaic properties of polymer solar cells based PFTDTBTzQ:PC₆₁BM blends at different ratios.

| Cells | Polymer/PC ₆₁ BM | D/A | $V_{\rm oc} [V]$ | J _{sc} [mA/cm ²] | FF [%] | PCE [%] |
|-------|-----------------------------|-----|-------------------|---------------------------------------|--------|---------|
| A | PFTDTBTzQ | 1:1 | 0.79 | 1.59 | 39.8 | 0.50 |
| B | PFTDTBTzQ | 1:2 | 0.76 | 1.73 | 43.3 | 0.57 |
| C | PFTDTBTzQ | 1.3 | 0.74 | 1.54 | 46.2 | 0.53 |

The HOMO-LUMO energy diagrams of the polymers and PC₇₁BM are shown in Fig. 4. It is obvious that the HOMO energy levels of the four polymers are almost identical due to the presence of the same polyfluorene backbone. However, their LUMO energy levels are strongly dependent upon the accepting unit. Among the three accepting units used, the [1–3]triazolo[4,5-g]quinoxaline based **PFTDTBTzO** has the lowest lying LUMO level, due to the strongest electron-deficiency of this aromatic moiety. Therefore, **PFTDTBTzO** has the narrowest E_{σ} of 1.66 eV and thus much wider absorption band. The relatively low HOMO levels of polymer donors not only endows polymer with good chemical stability in ambient conditions but also higher open circuit voltage (V_{oc}) for OPV devices, as the $V_{\rm oc}$ is proportional to the difference between the LUMO level of fullerene acceptor and the HOMO level of the donor [1]. Importantly, the frontier energy levels of the as-prepared polymers are appropriately aligned with those of PC₇₁BM.

3.4. Photovoltaic properties

The photovoltaic property of **PFTDTBTzQ** was evaluated in BHJ device by blending **PFTDTBTzQ** with $PC_{61}BM$ acceptor as active layer. The photoactive layers were prepared by spin-coating of the blend solution of **PFTDTBTzQ**:PC₆₁BM dissolved in o-DCB, in which **PFTDTBTzQ** shows good solubility, on ITO/PEDOT:PSS patterned substrates (40 nm). The thickness of all the blends is around 80 nm. The active area of the cells is 0.16 cm². The typical device structure is ITO/PEDOT:PSS/polymer:PC₆₁BM/PFN/Al. All devices were prepared under an inert nitrogen atmosphere and characterized in air without encapsulation, where *J*–*V* measurements were performed under simulated AM 1.5 G illumination (100 mW/cm²). Different **PFTDTBTzQ**/PC₆₁BM weight ratios, such as 1:1, 1:2, and 1:3 have been investigated to optimize the photovoltaic properties. The corresponding photovoltaic performances of devices with different ratios are summarized in Table 3. The polymer/PC₆₁BM weight ratio



Fig. 6. Current density versus voltage (J-V) characteristics of devices based on **PFTDTBTzQ**:PC₇₁BM as active layer under AM 1.5 G irradiation with an intensity of 100 mW cm⁻².

Table 3

Table /

Photovoltaic properties of polymer solar cells based $\ensuremath{\text{PFTDTBTzQ}}\xspace;\ensuremath{\text{PC}}\xspace_{71}\ensuremath{\text{BM}}\xspace$ (1:2) blends.

| Cells | Polymer/PC71BM | D/A | $V_{\rm oc}$ [V] | $J_{\rm sc} [{\rm mA/cm}^2]$ | FF [%] | PCE [%] |
|-------|------------------------|-----|------------------|------------------------------|--------|---------|
| A | PFTDTBTzQ ^a | 1:2 | 0.79 | 1.59 | 39.8 | 0.50 |
| B | PFTDTBTzQ ^b | 1:2 | 0.81 | 1.81 | 40.7 | 0.60 |

^a No annealing.

^b Annealing at 90 °C.

| Tuble 1 | | | | | | | | |
|--------------|------------|----|---------|-------|-------|-------|-----------------|-------|
| Photovoltaic | properties | of | polymer | solar | cells | based | PFTODTBT:PC71BM | (1:2) |
| blends. | | | | | | | | |

| Cells | Polymer/PC71BM | D/A | $V_{\rm oc}$ [V] | J _{sc} [mA/cm ²] | FF [%] | PCE [%] |
|-------|----------------|-----|------------------|---------------------------------------|--------|---------|
| A | PFTODTBT | 1:1 | 0.76 | 5.17 | 33.1 | 1.30 |
| B | PFTODTBT | 1:2 | 0.67 | 4.54 | 31.8 | 0.97 |

of 1:2 showed the best device performance. The **PFTDTBTzQ**/ PC₆₁BM (1:2, w/w) device gave an open-circuit voltage (V_{oc}) of 0.76 V, a short circuit current (J_{sc}) of 1.73 mA cm⁻², a fill factor (FF) of 43.3%, and resulted in a power conversion efficiency (PCE) of 0.57% (Fig. 5 and Table 2).

PC₇₁BM was further used to optimize the device performance because PC₇₁BM had electronic properties similar to those of PC₆₁BM but possessed a much stronger absorption in the visible region [33], which could improve the absorption of the donor material. The current density-voltage (*J*–*V*) curves of devices based on the **PFTDTBT2Q**/PC₇₁BM blend before and after thermal annealing are compared in Fig. 6. The polymer/PC₇₁BM (1:2, w/w) after thermal annealing at 90 °C showed improved device performance. The **PFTDTBT2Q**/PC₇₁BM device gave a *V*_{oc} of 0.81 V, a *J*_{sc} of 1.81 mA cm⁻², a FF of 40.7%, and resulted in a PCE of 0.60% (Fig. 6 and Table 3).

Different **PFTODTBT**/PC₇₁BM weight ratios, such as 1:1, 1:2 have been investigated to optimize the photovoltaic properties. The typical device structure is ITO/PEDOT:PSS/polymer:PC₇₁BM/PFN/AI. The corresponding photovoltaic performances of devices with different ratios are summarized in Table 4. The polymer/PC₇₁BM weight ratio of 1:2 showed the best device performance. The **PFTODTBT**/PC₇₁BM (1:2, w/w) device gave a V_{oc} of 0.76 V, a J_{sc} of 5.17 mA cm⁻², a FF of 33.1%, and resulted in a PCE of 1.30% (Fig. 7 and Table 4).



Fig. 7. Current density versus voltage (J-V) characteristics of devices based on **PFTODTBT**:PC₇₁BM as active layer under AM 1.5 G irradiation with an intensity of 100 mW cm⁻².



Fig. 8. (a) Current density versus voltage (*J*–*V*) characteristics of devices using **PFTTZ**-toluene (device A, B and C) or **PFTTZ**-THF (device D, E and F):PC₇₁BM (1:2) as active layer under AM 1.5 G irradiation with an intensity of 49.1 mW cm⁻². (b) *J*–*V* characteristics of the same devices in the dark.

Table 5 Photovoltaic properties of polymer solar cells based PFTTTz-toluene or PFTTTz-THF:PC₇₁BM (1:2) blends.

| Cells | Polymer/PC71BM | Cathode | $V_{\rm oc} [V]$ | $J_{\rm sc} [{\rm mA/cm^2}]$ | FF [%] | PCE [%] |
|-------|----------------|-----------|-------------------|------------------------------|--------|---------|
| Α | PFTTTz-toluene | Al | 0.70 | 1.93 | 54.4 | 1.50 |
| В | PFTTTz-toluene | PFN/Al | 0.62 | 2.17 | 57.7 | 1.58 |
| С | PFTTTz-toluene | PFN/Ca/Al | 0.62 | 2.29 | 61.4 | 1.77 |
| D | PFTTTz-THF | Al | 0.60 | 2.35 | 57.7 | 1.66 |
| E | PFTTTz-THF | PFN/Al | 0.64 | 2.44 | 55.6 | 1.77 |
| F | PFTTTz-THF | PFN/Ca/Al | 0.70 | 2.48 | 62.4 | 2.21 |

The photovoltaic properties of **PFTTTz**-THF and **PFTTTz**-toluene were evaluated in BHJ device by blending PFTTTz-THF or PFTTTztoluene with PC71BM acceptor as active layer. PC71BM was chosen due to its similar electronic properties to PCBM but a much stronger absorption in the visible region. The photoactive layers were prepared by spin-coating of the blend solution of polymer:PC71BM (1:2, w/w) dissolved in o-DCB, in which PFTTTz-THF (device D, E and F) or **PFTTTz**-toluene (device A, B and C) shows good solubility, on ITO/PEDOT:PSS patterned substrates (40 nm). The thickness of all the blends is around 80 nm. The active area of the cells is 0.16 cm². All devices were prepared under an inert nitrogen atmosphere and characterized in air without encapsulation, where *I*-V measurements were performed in the dark and under simulated AM 1.5 G illumination (49.1 mW/cm²). The effect of insertion of PFN or Ca interfacial layer on device performance was studied. And thus three device structures (Fig. 8 and Table 5) were explored, i.e. ITO/PEDOT:PSS/**PFTTTz**:PC₇₁BM/Al for device A and D; ITO/PEDOT:PSS/**PFTTTz**:PC₇₁BM/PFN(5 nm)/Al for device B and E; and ITO/PEDOT:PSS/**PFTTTz**:PC₇₁BM/PFN(5 nm)/Ca(5 nm)/Al for device C and F. Typical current density-voltage (J-V) curves for devices with this blend composition are presented in Fig. 8a for two polymers.

Table 5 summarizes the photovoltaic performance of BHJ device of PFTTTz under the same device fabrication condition. Obvious impact of cathode interfacial layer was observed on the device performance. The devices of PFTTTz-toluene achieved an increased PCE from 1.50% (device A), 1.58% (device B) to 1.77% (device C) after inserting the cathode interfacial layer Ca or PFN. On the other hand, the devices with high M_n PFTTTz-THF achieved an increased PCE from 1.66% (device D), 1.77% (device E) to 2.21% (device F) after inserting the cathode interfacial layer Ca or PFN. Comparing device A, B, C, D, E, and F, we could conclude that a PFN/Ca/Al trilayer cathode is better than a PFN/Al bilayer cathode and an Al single layer cathode. Cathode interfacial layer PFN could establish better interfacial contacts by decreasing the series resistance, resulting in enhanced electron collection at the cathode and decreasing the possibility of hole-electron recombinations in the active layer [48]. A bilayer cathode or a trilayer cathode could increase the device configurations. The best performing device F in the preliminary test exhibited a maximum PCE value of 2.21%, with a V_{oc} of 0.70 V, a J_{sc} of 2.48 mA/ cm^2 , and a FF of 0.62. Efficient charge collection in the case of **PFTTTz**-THF:PC₇₁BM (device F) would be consistent with the slightly larger dark current for this blend than for any of the others (Fig. 8b). The performance of **PFTTTz**-THF:PC₇₁BM (device D, E, F) is relatively better than that of **PFTTTz**-toluene:PC₇₁BM (device A, B, C). It obviously deduced that higher $M_{\rm p}$ of polymer has positive effect on device performance through increasing V_{oc} , J_{sc} and FF.



Fig. 9. AFM image of the surface morphology of (a) PFTTTz-toulene:PC71BM (1:2) thin film and (b) PFTTTz-THF:PC71BM (1:2) thin film.

The morphology of **PFTTTz**-toluene:PC₇₁BM and **PFTTTz**-THF:PC₇₁BM (1:2) blend films was further compared to reveal the correlation of morphology with device performance. The atomic force microscopy (AFM) images of two blend films (Fig. 9) exhibits almost the same pattern, where very fine domains without large phases can be found. The film presented the largest peak-to-valley height of around 3 nm and a root-mean-square (rms) roughness [49] of around 1 nm. This nanoscale phase separation and interpenetrating network morphology between the electron donor polymer (**PFTTTz**) and acceptor material (PC₇₁BM) allow a large area of the interface for better photogenerated charges and desirable J_{sc} . However, the possibility of a recombination of hole and electron carriers at these high interfacial areas could also be enhanced. This might be the reason why the J_{sc} values of **PFTTTz** devices have not reached their utmost values.

From above, the devices based on **PFTDTBTzQ**, **PFTODTBT** had larger V_{oc} (0.81 V for the former, and 0.76 V for the latter) than the devices based on **PFTTTz**-THF and **PFTTTz**-toluene (0.70 V) which was accorded with the HOMO energy levels of polymers. The low J_{sc} and FF of **PFTDTBTzQ** were due to its too much bulk alkyl chains which hindered the intramolecular charge transfer (ICT) and $\pi - \pi$ stacking. The low FF of **PFTODTBT** was due to its low molecular weight and wider polydiversity which hinder the effective conjugated length. A best PCE of device based on **PFTTTz**-THF was due to its suitable molecular weight and HOMO energy level and most uniform and bi-continuous network blending film with PC₇₁BM.

4. Conclusion

A new electron-donating unit, thiophenyl-methylene-9*H*-fluorene, was developed and used for the design of D-A polymer for PSC application for the first time. By conjugated thiophene with flourene unit, thiophenyl-methylene-9*H*-fluorene shows more planar conformation and electron donating ability. By alternating thiophenyl-methylene-9*H*-fluorene with thiazolo[5,4-*d*]thiazole (TTz), benzothiadiazole (ODTBT), and [1–3]triazolo[4,5-g]quinoxaline (DTBTzQ) the narrow bandgap copolymers, **PFTTZ**-THF, **PFTTTZ**toluene, **PFTODTBT** and **PFTDTBTZQ** exhibited and ideal bandgap of 1.66–1.96 eV. Primary device tests on these copolymers delivered a best PCE of 2.21%. Our research results suggest that thiophenylmethylene-9*H*-fluorene unit can be a choice of new donor to construct D-A polymer for fine-tuning photophysical, electrochemical and photovoltaic properties of the resulted polymers.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.07.001.

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