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PAPER
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Synthesis and photophysical properties of 2,2'-Bis(oligothiophene)-9,9'-bifluorenylidene derivatives

Tianzhi Yu[1,*], Weijia Guan[1], Xin Wang[1], Yuling Zhao[2], Qianguang Yang[1], Yanmei Li[1], Hui Zhang[1]

[1]Key Laboratory of Opto-Electronic Technology and Intelligent Control (Ministry of Education), Lanzhou Jiaotong University, Lanzhou 730070, China

[2]School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

Abstract: Three novel 9,9'-bifluorenylidene derivatives containing thiophenyl, terthiophenyl and tetrathiophenyl groups at 2- and 2'-position of 9,9'-bifluorenylidene skeleton, respectively, were synthesized and characterized. Their photophysical and electrochemical properties were investigated systematically. The ground state geometries and electronic distributions in HOMO and LUMO energy levels of the 9,9'-bifluorenylidene derivatives were calculated by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at B3LYP/6-31G(d) level.

Keywords: 9,9'-Bifluorenylidene derivative; Oligothiophene; Electron acceptor; DFT study; HOMO and LUMO energy levels

1. Introduction

Nowadays, with concerns about environmental pollution and depletion of fossil energy, the

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[*] Corresponding Author. Tel. +86-931-4956935; Fax: +86-931-4938756; e-mail: yutzh@mail.lzjtu.cn (T.Z. Yu).

renewable energies and all kinds of green energy have attracted more and more attentions. The renewable energies mainly involve natural resources such as sunlight, wind, water, biomass, tides and geothermal energy. Among the possible renewable energy resources, solar energy is one kind of clean, renewable, abundant and the most promising energy resource, which is an ideal alternative to the traditional energy resources. Over the past few decades, silicon-based inorganic solar cells have got great development and achievement, their power conversion efficiency (PCE) has closely reached 40% [1]. However, high material and manufacturing costs and high environmental pollution limit its wide applications. Organic photovoltaics (OPVs) have drawn great attention over the last two decades as alternative photovoltaic cells. Compared with the inorganic solar cells, the organic photovoltaics have some advantages of easy fabrication, low cost, light weight and the possibility to fabricate flexible devices [2-4]. At present, the field of organic photovoltaics has progressed quite significantly, particularly through the development of solution-processed bulk heterojunction (BHJ) OPVs, and the highest efficiency is over 12% [5-7].

Contemporary organic photovoltaic cells are based on a bulk heterojunction that results from the contact between electron donor and electron acceptor materials. In a typical BHJ OPVs, the photoactive blend layer consists of a conjugated polymer donor and a soluble electron acceptor, which is sandwiched between a PEDOT:PSS coated ITO positive electrode and a low work function metal negative electrode. The conjugated polymer donor serves as the main solar light absorber and as the hole transporting phase, whereas the electron acceptor transports electrons. Broad visible absorption, higher charge carrier mobility, and suitable electronic energy levels of both the donor and acceptor materials are crucial and momentous for highly efficient polymer solar cells (PSCs) [8]. In order to improve the power conversion efficiency of polymer solar cells,

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various new donor and acceptor photovoltaic materials have been investigated in recent years [3,5-7,9-17]. Among the donor materials, the polythiophene derivatives are the most representative donor materials, such as polythiophene derivatives with conjugated side chains for broad absorption [18,19], cross-linking polythiophene derivatives with conjugated bridges for higher hole mobility [18,20], poly(thienylene vinylene) derivatives with broad visible absorption [21], and the copolymers of benzodithiophene and thieno[3,4-b]thiophene with lower HOMO energy levels and broad absorption band [22-24]. In addition to the polymer donor materials, there are various small-molecular donor materials. The small-molecular donor materials for OPVs have attracted increasing attention due to their advantages such as well-defined molecular structures, definite molecular weights and high purities [25]. Some representative small-molecular donors, such as dyes [26,27], oligothiophenes [28,29] and triphenylamine-based molecules [30,31], have been applied successfully in OPV devices. In the OPVs, although the acceptor materials play an equally important role as the donor materials for high-performance OPV devices, the research efforts devoted to the acceptor materials have been much less than those on the donor materials. The fullerene derivatives, such as phenyl-$C_{61/71}$-butyric acid esters ($PC_{60/70}BM$) and indene-$C_{60/70}$ bisadducts ($IC_{60/70}BA$), have been the most successful acceptors in OPV devices for higher power conversion efficiency so far, which have unique π-electron system, excited state electronic properties, higher electron affinity and good electron transporting ability [3,32]. Despite fullerene derivatives have many excellent optoelectronic properties and even dominated the field of acceptors of BHJ solar cells, they still have some shortcomings, such as weak absorption in the visible region, poor solubility in common solvents, lengthy synthetic routes, low yields and difficult purification processes. Therefore, it is very important and urgently required for higher

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PCE to synthesize non-fullerene acceptors with higher absorption in the visible spectrum, low-cost synthesis and controllable frontier orbital energy levels. Recently, researchers have reported some representative nonfullerene small molecule acceptors with adjustable energy level, excellent solubility and wide absorption in the visible spectrum for high-performance OPV devices [5-7,33,34], including diketopyrrolopyrrole[35,36], rylene diimide [37,38], indacenodithieno[3,2-b]thiophene (ITIC) [5-7], benzothiadiazole[39] derivatives and so on.

Oligothiophenes consist of π-conjugated units with highly delocalized π-systems, imbuing them with unique electrical and optical properties that can be easily tuned via rational structural modifications [40]. Some functionalized oligothiophenes have now been rationally designed, synthesized and validated as efficient materials for organic electronic devices [41,42]. The electron-withdrawing substituents, such as dicyanovinyl, perfluoroalkyl and perfluoroarene, introduction into π-electron frameworks has proven to be a promising approach to enhance electron injection and electron transport properties of these materials. In comparison to polymeric materials, π-conjugated small molecules and oligomers have the distinct advantages of straightforward synthesis and purification leading to defined molecular structures, which greatly improve the fabrication reproducibility and avoid batch-to-batch variations.

Recently, 9,9′-bifluorenylidene (99'BF) derivatives as non-fullerene type electron acceptors have attracted much attentions because 99'BF skeleton could easily accept one electron to form 14- π-electron system and thus it could have aromaticity [43-48]. Brunetti et al. fabricated the first BHJ solar cell with P3HT/D99'BF (12-(3,6-dimethoxy-fluoren-9-ylidene)-12*H*-dibenzo[*b*,*h*]fluorene), which showed a reasonable photovoltaic effect (V_{oc} = 1.10 V, PCE = 1.7%) [43]. Most noticeably, when blended with P3HT,

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D99'BF increases the optical density and allows the ultrafast charge transfer and the charge separation, and an electron transfer between the LUMO energies offset lower than the empirical value of 0.3–0.5 eV. Though several 99'BF derivatives have been synthesized as small molecule electron-acceptors for PSCs [46-48], their BHJ solar cells have lower PCE due to their lower electron mobility.

In this work, we synthesized three novel 9,9'-bifluorenylidene derivatives containing thiophenyl, terthiophenyl and tetrathiophenyl groups at 2- and 2'-position of 9,9'-bifluorenylidene skeleton, respectively, and investigated their photophysical and electrochemical properties. The synthetic routes and chemical structures of the 9,9'-bifluorenylidene derivatives are shown in Scheme1.

2. Experimental

2.1. Materials and methods

2-Bromo-3-octylthiophene, 2-bromine-9-fluorenone, 5,5'-dibromo-2,2'-bithiophene were purchased from Puyang Huicheng Electronic Material Co., Ltd (China). n-BuLi, tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$), Lawesson’s reagent, bis(pinacolato)diboron, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($PdCl_2$(dppf)) and tetrabutyl ammonium bromide (TBAB) were bought from Energy Chemical (China). 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was purchased from Yurui (Shanghai) Chemical CO., LTD (China). Potassium acetate was bought from Tianjin Kaixin Chemical Industry CO., LTD (China), and *N*-bromobutanimide (NBS) was purchased from Shanghai Crystal Pure Reagent CO., LTD (China). THF, toluene and 1,4-dioxane were purified and freshly distilled prior in the related reaction. All the other chemicals were analytical grade reagent.

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^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury Plus 400 MHz and Agilent Technologies DDZ 600 MHz. IR spectra (400–4000 cm^{-1}) were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer with KBr pellets. Mass spectrum was recorded using a Thermo Scientific Orbitrap Elite mass spectrometer. UV-vis absorption was recorded on a Shimadzu UV-2550 spectrometer. CV (CH Instruments 760 B) was performed with a 0.10 mol/L solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in dichloromethane, with the analyte present in a concentration of 10^{-3} mol/L and employing a scan rate of 100 mV/s at room temperature. A Pt electrode was used as the working electrode, while a Pt wire and an Ag/Ag+ electrode were used as the counter electrode and reference electrode, respectively.

2.2 Synthesis and characterization of the 9,9'-bifluorenylidene derivatives (**STBF**, **TTBF** and **FTBF**)

2.2.1. Synthesis and characterization of **STBF**

4,4,5,5-Tetramethyl-2-(3-octylthiophen-2-yl)-1,3,2-dioxaborolane: Under N_2 atmosphere, 2-bromo-3-octylthiophene (2 g, 7.27 mmol) and 50 mL anhydrous tetrahydrofuran were placed in a round bottom flask (250 mL), then n-BuLi (3 mL, 2.5 M in hexane) was added the reaction mixture under - 78 ^{o}C and stirred for 2 h. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.66 mL, 8.0 mmol) was added into the mixture and the mixture was stirred at -78 ^{o}C for 5 h. Afterwards, saturated salt water was added, and the mixture was extracted with dichloromethane (3 × 100 mL). The combined organic layer was dried by anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using dichloromethane/petroleum (1:6, v/v) as eluent to yield brownish yellow oily compound (1.5 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm):

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7.48 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 2.89 (t, *J* = 8.0 Hz, 2H), 1.57 (t, *J* = 8.0 Hz, 2H), 1.33 (s, 12H), 1.30–1.26 (m, 10H), 0.87 (t, *J* = 4.0 Hz, 3H).

2-(3-octylthiophen-2-yl)-9*H*-fluoren-9-one: Under N_2 atmosphere, 4,4,5,5-Tetramethyl-2-(3-octylthiophen-2-yl)-1,3,2-dioxaborolane (2.25 g, 6.98 mmol), 2-bromine-9-fluorenone (2 g, 7.72 mmol), $Pd(PPh_3)_4$ (0.8 g, 0.7 mmol) and TBAB (0.112 g, 0.35 mmol) was dissolved in 50 mL freshed toluene, then 10 mL of 2M Na_2CO_3 was added in the mixture solution. The mixture was refluxed for 30 h. After cooling, saturated salt water was added and the product was extracted with dichloromethane (3 × 100 mL), then the combined organic layer was dried by anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum (1:20, v/v) as eluent to yield brown oily compound (2.02 g, 77.3%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.73–7.70 (m, 1H), 7.70–7.65 (m, 1H), 7.56–7.47 (m, 4H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 6.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 2.66 (t, *J* = 8.0 Hz, 2H), 1.65–1.54 (m, 2H), 1.35–1.14 (m, 10H), 0.84 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 193.55, 144.21, 143.04, 139.45, 136.48, 135.98, 135.30, 134.79, 134.44, 129.66, 129.07, 125.07, 124.39, 124.09, 120.35, 31.84, 30.88, 29.40, 29.33, 29.21, 28.73, 22.64, 14.07.

(*E*)-2,2'-Bis(3-octylthiophen-2-yl)-9,9'-bifluorenylidene (STBF): To a toluene solution (20 mL) of 2-(3-octylthiophen-2-yl)-9*H*-fluoren-9-one (1g, 2.67 mmol) was added Lawesson's reagent (0.62 g, 1.53 mmol) under N_2 atmosphere. The mixture was stirred and refluxed overnight. The cooled solution was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using dichloromethane/petroleum (1:10, v/v) as eluent to yield dark brown sticky compound, then it was freeze-dried under reduced pressure to give dark brown solid

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STBF (0.5 g, 52.2%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.50–8.33 (m, 4H), 7.73–7.60 (m, 4H), 7.43–7.06 (m, 8H), 6.89 (dd, J = 8.0, 8.0 Hz, 2H), 2.69–2.46 (m, 4H), 1.58–1.37 (m, 4H), 1.28–0.97 (m, 20H), 0.93–0.70 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 141.13, 140.24, 138.75, 138.69, 138.60, 138.49, 138.43, 138.38, 137.98, 133.63, 130.38, 129.55, 129.43, 129.40, 127.91, 127.45, 127.07, 126.98, 126.74, 123.57, 120.02, 119.90, 119.83, 31.91, 31.09, 31.00, 29.53, 29.47, 29.43, 29.36, 29.32, 28.79, 28.59, 22.74, 14.18, 14.15. HRMS: Calcd. for $C_{50}H_{52}S_2$, 716.35; Found: 717.3572.

2.2.2. Synthesis and characterization of **TTBF**

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluoren-9-one: A stirred mixture of 2-bromine-9-fluorenone (2 g, 7.72 mmol), bis(pinacolato)diboron (3.8 g, 14.96 mmol), Pd(dppf)Cl_2 (0.28 g, 0.386 mmol), potassium acetate (2.9 g, 29.55 mmol) and 1,4-dioxane (60 mL) was refluxed for 24 h. After cooling, saturated salt water was added and the product was extracted with dichloromethane (3 × 100 mL), then the combined organic layer was dried by anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum (1:6, v/v) as eluent to yield yellow solid compound (2.0g, 84.6%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.12 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.56–7.46 (m, 3H), 7.31 (t, J = 8.0 Hz, 1H), 1.36 (s, 12H).

5''-bromo-3-octyl-2,2':5',2''-terthiophene (1): The preparation of the compound **1** was similar to that described for the compound 2-(3-octylthiophen-2-yl)-9*H*-fluoren-9-one, which was obtained from the reaction between 4,4,5,5-Tetramethyl-2-(3-octylthiophen-2-yl)-1,3,2-dioxaborolane (1.5 g, 4.654 mmol) and 5,5'-dibromo-2,2'-bithiophene (1.961 g, 6.05 mmol) in the presence of Na_2CO_3 (1.48 g, 13.96

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mmol), TBAB (0.075 g, 0.233 mmol) and $Pd(PPh_3)_4$ (0.269 g, 0.233 mmol). The crude product was purified by column chromatography on silica gel using petroleum as eluent to yield yellow oily compound (1.0 g, 49 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.17 (d, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 6.98 (dd, *J* = 8.0, 7.4 Hz, 2H), 6.92 (dd, *J* = 8.0, 7.6 Hz, 2H), 2.75 (t, *J* = 8.0 Hz, 2H), 1.69–1.58 (m, 2H), 1.39–1.22 (m, 10H), 0.87 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 139.98, 138.63, 136.88, 136.72, 130.61, 130.06, 130.00, 126.42, 124.16, 123.97, 123.60, 110.91, 31.87, 30.63, 29.50, 29.39, 29.24, 29.23, 22.66, 14.11.

2-(3''-octyl-[2,2':5',2''-terthiophen]-5-yl)-9H-fluoren-9-one (4): The preparation of the compound **4** was similar to that described for the compound 2-(3-octylthiophen-2-yl)-9*H*-fluoren-9-one, which was obtained from the reaction between 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluoren-9-one (0.669 g, 2.184 mmol) and 5''-bromo-3-octyl-2,2':5',2''-terthiophene (0.80 g, 1.82 mmol) in the presence of Na_2CO_3 (0.695 g, 6.552 mmol), TBAB (0.029 g, 0.090 mmol) and $Pd(PPh_3)_4$ (0.105 g, 0.091 mmol). The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum (1:6, v/v) as eluent to yield orange powdery compound **4** (0.64 g, 65.3%). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.88 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 3H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.21–7.11 (m, 3H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 2.79 (d, *J* = 6.0 Hz, 2H), 1.66 (d, *J* = 12.0 Hz, 2H), 1.43–1.23 (m, 10H), 0.88 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 193.45, 144.20, 142.94, 141.64, 139.92, 137.11, 136.62, 135.64, 135.00, 134.92, 134.85, 134.32, 131.06, 130.23, 130.11, 128.99, 126.50, 124.49, 124.41, 124.09, 123.90, 121.02, 120.78, 120.33, 31.89, 30.65, 29.55, 29.43, 29.30, 29.27, 22.68, 14.12.

(*E*)-2,2'-bis(3''-octyl-[2,2':5',2''-terthiophen]-5-yl)-9,9'-bifluorenylidene (TTBF): The

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preparation of the compound **TTBF** was similar to that described for the compound **STBF**, which was obtained from the compound **4** in the presence of Lawesson's reagent. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum (1:8, v/v) as eluent to yield dark brown oily compound, then it was cured from cold methanol to give brown powdery solid **TTBF** (45% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 8.60 (s, 1H), 8.56 (s, 1H), 8.34 (d, *J* = 7.8 Hz, 2H), 7.61–7.49 (m, 4H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.31–7.24 (m, 2H), 7.15 (m, 4H), 7.07–6.80 (m, 9H), 2.80–2.68 (m, 4H), 1.70–1.57 (m, 4H), 1.43–1.23 (m, 20H), 0.95–0.85 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 143.28, 143.00, 141.13, 141.02, 141.00, 140.44, 140.34, 139.73, 139.55, 138.63, 138.56, 138.27, 137.00, 136.85, 136.38, 136.19, 135.20, 135.12, 132.76, 132.49, 130.55, 130.46, 130.09, 129.99, 129.52, 129.45, 126.87, 126.71, 126.69, 126.42, 126.33, 124.50, 124.40, 123.86, 123.81, 123.76, 123.75, 123.70, 123.59, 120.30, 120.23, 120.08, 119.96, 31.96, 30.69, 30.61, 29.63, 29.59, 29.51, 29.35, 29.34, 29.32, 22.75, 14.20. HRMS: Calcd. for $C_{66}H_{60}S_6$, 1044.30; Found: 1045.3076.

2.2.3. Synthesis and characterization of **FTBF**

3,3'''-dioctyl-2,2':5',2'':5'',2'''-quaterthiophene (2): The preparation of the compound **2** was similar to that described for the compound 2-(3-octylthiophen-2-yl)-9*H*-fluoren-9-one, which was obtained from the reaction between 4,4,5,5-Tetramethyl-2-(3-octylthiophen-2-yl)-1,3,2-dioxaborolane (1.8 g, 5.585 mmol) and 5,5'-dibromo-2,2'-bithiophene (0.778 g, 2.40 mmol) in the presence of Na_2CO_3 (1.776 g, 16.755 mmol), TBAB (0.0387 g, 0.12 mmol) and $Pd(PPh_3)_4$ (0.139 g, 0.12 mmol). The crude product was purified by column chromatography on silica gel using petroleum as eluent to yield yellow oily compound **2** (57% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J*

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= 7.6 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 4H), 1.70–1.60 (m, 4H), 1.41–1.23 (m, 20H), 0.87 (t, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 139.87, 136.78, 135.29, 130.28, 130.07, 126.51, 123.84, 123.80, 31.88, 30.67, 29.52, 29.41, 29.26, 22.68, 14.12.

5-bromo-3,3'''-dioctyl-2,2':5',2'':5'',2'''-quaterthiophene (3): The compound **2** (1.8 g, 3.24 mmol) was dissolved in 30 mL chloroform. NBS (0.534 g, 3.0 mmol) was dissolved in a mixed solvent of acetic acid (20 mL) and chloroform (20 mL), and then the resulting solution was added dropwise to the compound **2** solution. The mixture was stirred overnight at room temperature. Afterwards, the mixture was neutralized with KOH solution, and the product was extracted with chloroform (3 × 100 mL), then the combined organic layer was dried by anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum as eluent to yield yellow oily compound **3** (1.06 g, 51.6%). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 7.19 (t, *J* = 8.0 Hz, 1H), 7.16–7.10 (m, 2H), 7.05 (t, *J* = 8.0 Hz, 1H), 7.00–6.94 (m, 2H), 6.92 (s, 1H), 2.82 (t, *J* = 6.0 Hz, 2H), 2.74 (t, *J* = 6.0 Hz, 2H), 1.75–1.61 (m, 4H), 1.46–1.26 (m, 20H), 1.00–0.87 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 140.39, 139.88, 137.37, 136.47, 135.63, 133.82, 132.71, 131.90, 130.31, 130.11, 126.90, 126.48, 124.01, 123.89, 123.76, 110.61, 31.98, 31.96, 30.72, 30.58, 29.62, 29.51, 29.46, 29.36, 29.33, 29.29, 22.77, 14.21.

2-(3''',4-dioctyl-[2,2':5',2'':5'',2'''-quaterthiophen]-5-yl)-9H-fluoren-9-one (5): The preparation of the compound **5** was similar to that described for the compound 2-(3-octylthiophen-2-yl)-9*H*-fluoren-9-one, which was obtained from the reaction between 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluoren-9-one (0.348 g, 1.137 mmol) and the

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compound **3** (0.60 g, 0.947 mmol) in the presence of Na_2CO_3 (0.361 g, 3.406 mmol), TBAB (0.015 g, 0.047 mmol) and $Pd(PPh_3)_4$ (0.055 g, 0.047 mmol). The residue was purified by column chromatography on silica gel using dichloromethane/petroleum (1:2, v/v) as eluent to yield reddish-brown oily compound **5** (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.87 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 3H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 2.78 (t, *J* = 8.0 Hz, 4H), 1.73–1.62 (m, 4H), 1.42–1.25 (m, 20H), 0.88 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 193.54, 144.26, 142.91, 140.85, 140.48, 139.90, 136.99, 136.61, 135.48, 135.03, 134.90, 134.86, 134.35, 131.09, 130.66, 130.26, 130.08, 128.97, 126.78, 126.51, 126.49, 124.42, 123.92, 123.89, 123.86, 120.98, 120.77, 120.32, 31.89, 31.88, 30.65, 30.50, 29.59, 29.58, 29.53, 29.43, 29.41, 29.27, 29.26, 22.67, 14.11.

(*E*)-2,2'-bis(3''',4-dioctyl-[2,2':5',2'':5'',2'''-quaterthiophen]-5-yl)-9,9'-bifluorenylidene (FTBF): The preparation of the compound **FTBF** was similar to that described for the compound **STBF**, which was obtained from the compound **5** in the presence of Lawesson's reagent. The residue was purified by column chromatography on silica gel using dichloromethane/petroleum (1:4, v/v) as eluent to yield black oily compound, then it was freeze-dried under reduced pressure to give black powdery solid **FTBF** (45% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.76 (s, 1H), 8.64 (s, 1H), 8.42 (t, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 8.0 Hz, 4H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.35 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.28–7.05 (m, 8H), 7.04–6.83 (m, 8H), 2.83–2.59 (m, 8H), 1.71–1.58 (m, 6H), 1.49 ((t, *J* = 6.0 Hz, 2H), 1.44–1.07 (m, 40H), 1.00–0.64 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 142.09, 141.55, 141.17, 141.08, 140.59, 140.40, 139.85, 139.69, 138.65, 138.27, 136.75, 136.44, 135.22, 132.76, 130.41, 130.01, 129.80, 129.50, 126.92, 126.75, 126.49, 126.38, 126.29,

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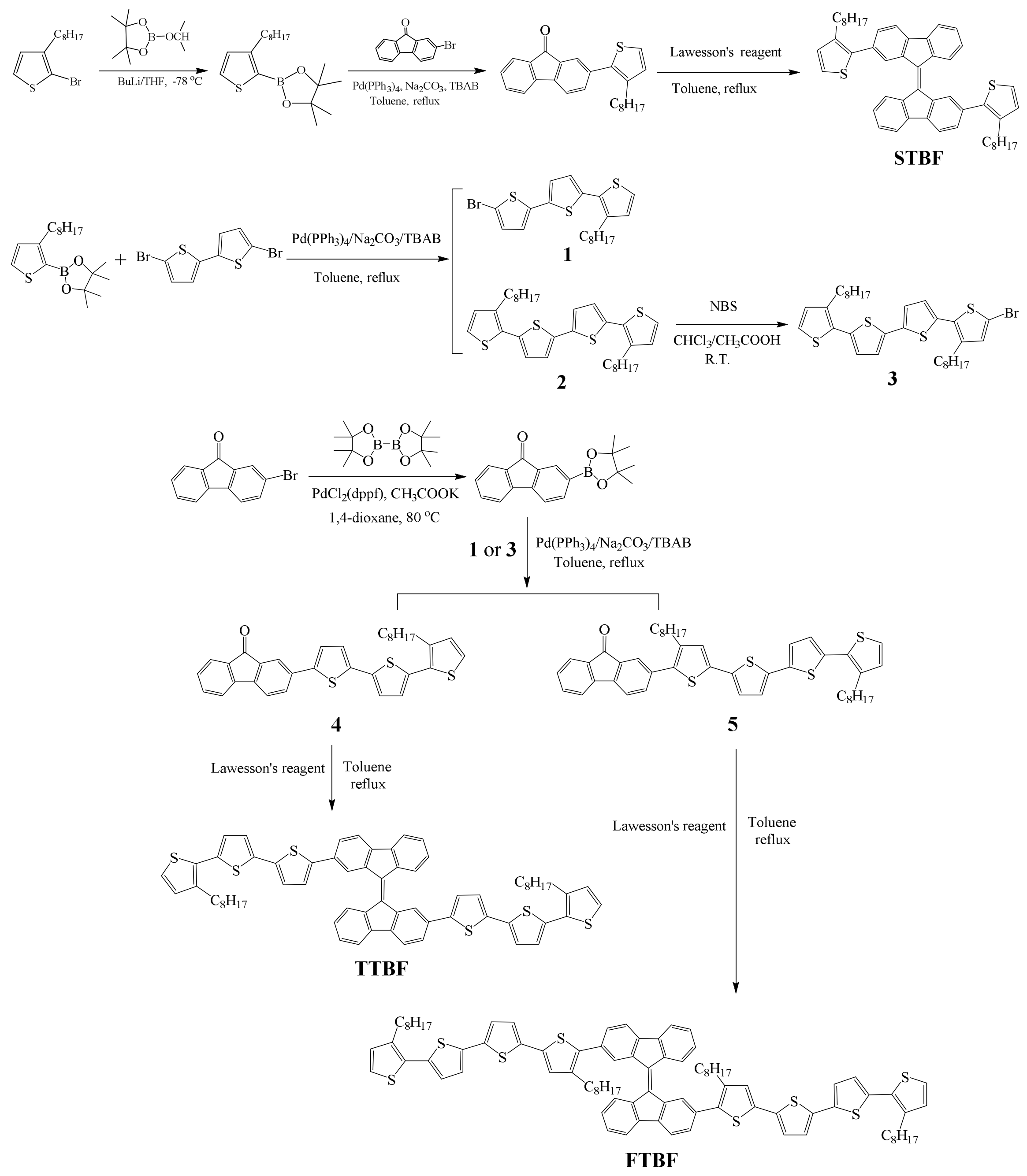
126.14, 126.01, 123.80, 123.69, 120.26, 119.93, 31.92, 31.89, 30.66, 30.63, 30.48, 30.33, 29.65, 29.54, 29.44, 29.38, 29.31, 29.27, 22.71, 22.69, 14.14, 14.12. HRMS: Calcd. for $C_{90}H_{96}S_8$, 1432.52; Found, 1433.5321.



Scheme 1. The synthetic routes and chemical structures of the 9,9'-bifluorenylidene derivatives (STBF, TTBF and FTBF).

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3. Results and discussion

STBF, **TTBF** and **FTBF** had been synthesized by two key synthetic approaches, namely, Suzuki-Miyaura cross coupling reaction [49] and one-pot conversion of fluorenone derivatives to 9,9'-bifluorenylidene derivatives in the presence of Lawesson's reagent in boiling toluene [50]. The synthetic routes were outlined in Scheme 1. Firstly, using Suzuki-Miyaura cross coupling reaction, the appropriate fluorenone intermediates were synthesized by stirring bromofluorenone and thiopheneboronic ester or bromooligothiophenes and fluorenoneboronic ester under nitrogen atmosphere in a mixture of H_2O and toluene overnight at 110 °C together with K_2CO_3 and catalytic amounts of $Pd(PPh_3)_4$. Next, the target 9,9'-bifluorenylidene derivatives (**STBF**, **TTBF** and **FTBF**) were obtained from a one-pot reaction by treating the appropriate fluorenone intermediates in the presence of Lawesson's reagent in boiling toluene. For the step of conversion of fluorenone derivatives to 9,9'-bifluorenylidene derivatives, Agranat et al. [50] proposed that the process undergoes the formation of fluorene-thione, and then desulfuration and dimerization *via* the carbene fluorenylidene and 2,4-bis(fluorenylidene)-1,3-dithiane leading to 9,9'-bifluorenylidene derivative, while Steliou et al. [51] suggested a possible pathway for the conversion of fluorene-thione to 9,9'-bifluorenylidene, which involves the 1,2-dithietane intermediate generated from the fluorene-thione and the formation of a carbon-carbon double bond upon extrusion of the diatomic sulfur.

Three final compounds (**STBF**, **TTBF** and **FTBF**) were characterized by ^{1}H NMR, ^{13}C NMR, MS and FT-IR spectra. In the ^{1}H NMR spectra of the **STBF**, **TTBF** and **FTBF**, the aromatic moieties (H^1 and H^8) could be differentiated by the low field ^{1}H NMR signals (> 8 ppm), while in their corresponding precursors the chemical shifts of the aromatic moieties appeared in higher

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field (< 8 ppm). In the ^{13}C NMR spectra, the characteristic chemical shifts of C=O for the corresponding precursors of **STBF**, **TTBF** and **FTBF** separately appeared at 193.55 ppm, 193.54 ppm and 193.54 ppm. However, these characteristic chemical shifts disappeared in the ^{13}C NMR spectra of the three target compounds. In the FT-IR spectra of the corresponding precursors of **STBF**, **TTBF** and **FTBF**, the characteristic absorption bands of C=O appeared at 1722, 1719 and 1714 cm^{-1}, respectively. In the FT-IR spectra of **STBF**, **TTBF** and **FTBF**, the characteristic stretching vibration of C=O disappeared completely. **STBF**, **TTBF** and **FTBF** were further identified by their high resolution mass spectra, their molar masses were detected clearly.

Figure 1 shows the UV-vis absorption spectra measured for PCBM and the bifluorenylidene derivatives **STBF**, **TTBF** and **FTBF** in CH_2Cl_2 solutions and solid thin films. The corresponding photophysical data are listed in Table 1. As shown in Fig. 1a, the absorption spectrum of **STBF** in solution exhibits two intense absorption bands at 247 and 298 nm, and one weak absorption band at 466 nm. The band below 350 nm is attributed to the correspond π–π* transition of thiophene units, whereas the band of longer wavelength at 466 nm is assigned to π–π* transition of the bifluorenylidene structure [48]. From the structure of **STBF**, the presence of two octyl chains at 3-position of the thiophene rings reduces the coplanarity between thiophene units and bifluorenylidene due to the steric hindrance of the two octyl groups. Thus, the π–π* transition of thiophene units and the π–π* transition of the bifluorenylidene structure emerged clearly. Moreover, the presence of two octyl chains increases the conjugation of the thiophene units and the molar absorptivity of the thiophene units due to the hyperconjugation effects between thiophene rings and aliphatic chains. In the absorption spectrum of **TTBF** in solution, there are two intense absorption bands at 249 and 380 nm, and one weak absorption band at 475 nm. The

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former two absorption bands correspond to the π–π* transition of terthienyl units, and the last absorption band is assigned to the π–π* transition of the bifluorenylidene skeleton. Because the thiophene rings adjacent to the bifluorenylidene skeleton were not grafted by octyl chains, the coplanarity between terthienyl units and bifluorenylidene skeleton is larger, which leads to partial overlapping of the absorption bands of terthienyl units and bifluorenylidene skeleton, and causes red-shifts of the absorption bands in contrast with **STBF**. The absorption spectrum of **FTBF** in solution only shows two intense absorption bands at 249 and 407 nm, corresponding to the π–π* transition of the quaterthiophene units. The absorption band of the bifluorenylidene skeleton was not observed in its absorption spectrum. The presence of two octyl chains at 3-position of the thiophene rings adjacent to the bifluorenylidene skeleton reduces the coplanarity between the quaterthiophene units and the bifluorenylidene skeleton due to the steric hindrance of the two alkyl groups. Besides, there are stronger hyperconjugation effects between two quaterthiophene rings and four octyl chains, which increases the molar absorptivity of the quaterthiophene rings. Thus, the absorption band of the bifluorenylidene skeleton is probably packaged in the absorption bands of the quaterthiophene units. Compared with **TTBF**, the absorption band at longer wavelength of **FTBF** is red-shifted by about 27 nm because the conjugation of the quaterthiophene unit is larger than that of terthienyl unit. The absorption spectrum of PCBM in solution exhibits four characteristic absorption peaks at 261, 329, 430 and 493 nm [52]. The former two absorption bands are relatively strong, but the latter two bands are very weak. Compared with PCBM, the absorption of STBF, TTBF and FTBF is stronger than that of PCBM in 250–600 nm regions.

As shown in Fig. 1b, the absorption spectra of **STBF**, **TTBF**, **FTBF** and PCBM in solid thin

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films were similar to that of them in CH_2Cl_2 solutions. Due to more intermolecular interaction in the solid state, their absorption spectra were much broader than that in CH_2Cl_2 solutions, and the maximum absorptions and edge wavelengths of solid thin films moved slightly to longer wavelength regions than those of solutions. The maximum absorption bands of **STBF**, **TTBF** and **FTBF** in solid thin films were located at 472, 388 and 413 nm, respectively.

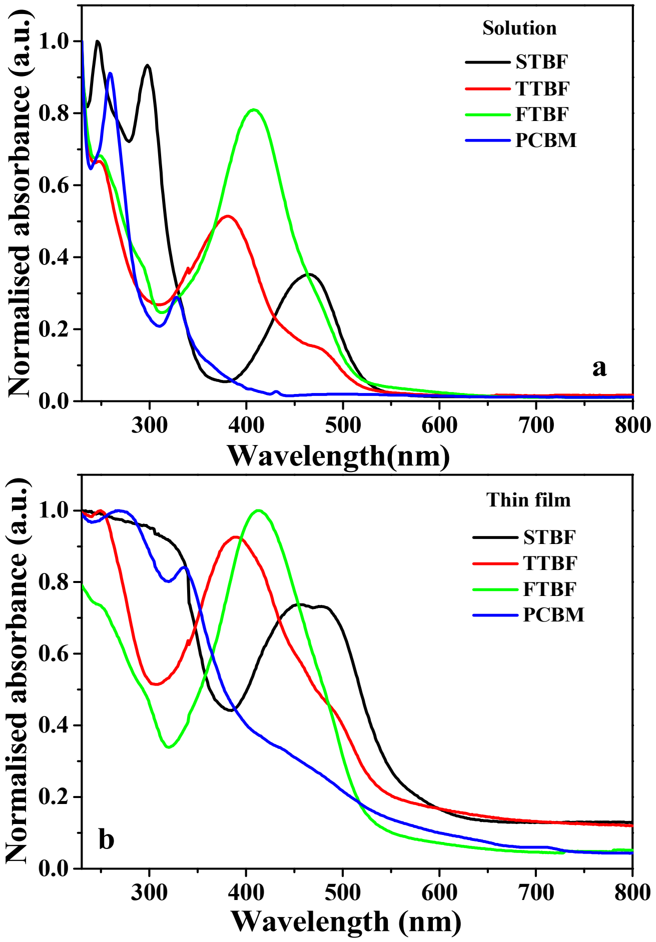

Fig. 1. UV-vis absorption spectra of **STBF**, **TTBF**, **FTBF** and PCBM in CH_2Cl_2 solutions (a) and in thin films (b).

In order to investigate the frontier orbitals of **STBF**, **TTBF** and **FTBF**, cyclic voltammetry (CV) was carried out to investigate their electrochemical behavior. Their highest occupied molecular orbital (HOMO) energy levels were calculated from the onset of the oxidation potentials of their cyclic voltammetry measurements, while their lowest unoccupied molecular

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orbital (LUMO) energy levels were deduced from their HOMO energy levels and optical band gaps determined from their extrapolated UV-Vis absorption edges [53]. The cyclic voltammograms of **STBF**, **TTBF** and **FTBF** were measured in degassed dichloromethane solution with Bu_4NPF_6 (0.1 mol/L) as the electrolyte (Fig. 2). A platinum working electrode and a saturated Ag/AgCl reference electrode were used. Ferrocene was used for potential calibration. As shown in Fig. 2, the onset oxidation potentials (E_{ox}) for **STBF**, **TTBF** and **FTBF** are 1.36, 0.94 and 0.73 V versus Ag/Ag^+, respectively. At the same condition, the Fc/Fc^+ potential was measured to be 0.52 V. Thus, the HOMO energy levels of **STBF**, **TTBF** and **FTBF** were calculated to be -5.64, -5.22 and -5.01 eV regarding the energy level of ferrocene/ferrocenium as -4.8 eV [54]. The optical band edges of **STBF**, **TTBF** and **FTBF** were estimated to be at ca. 521, 523 and 512 nm, which correspond to 2.38, 2.37 and 2.42 eV. Therefore, the LUMO energy levels of **STBF**, **TTBF** and **FTBF** were calculated to be -3.26, -2.85 and -2.59 eV, respectively.

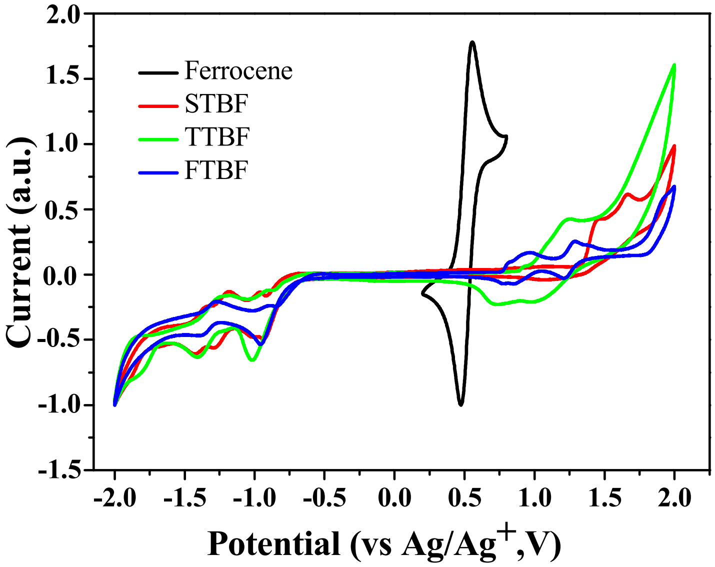

Fig. 2. Cyclic voltammograms of ferrocene and the compounds **STBF**, **TTBF** and **FTBF** in dichloromethane solutions with 0.1 mol/L Bu_4NPF_6 at a scan rate of 100 mV/s.

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Table 1. Optical and electrochemical properties of **STBF**, **TTBF** and **FTBF**

Compound	UV-vis (nm)[a]	λ_{max} (nm)[b]	λ_{onset} (nm)	E_{OX} (V)[c]	E_{opt} (eV)[d]	HOMO (eV)[e]	LUMO (eV)[f]
STBF	247, 298, 466	472	521	1.36	2.38	-5.64	-3.26
TTBF	249, 380, 475	388	523	0.94	2.37	-5.22	-2.85
FTBF	249, 407	413	512	0.73	2.42	-5.01	-2.59

[a] Absorption bands in CH_2Cl_2 solution at room temperature;
[b] Maximum absorption band in thin film at room temperature;
[c] All the values are referred to Ag/AgCl and calibrated by Fc/Fc^+;
[d] $E_{opt} \approx 1241/\lambda_{onset}$; [e] $E_{HOMO} = -e(E_{OX} - 0.52 + 4.8)$ (eV); [f] $E_{LUMO} = E_{opt} + E_{HOMO}$

For comparing the energy levels of the synthesized compounds and the traditional donor and receptor materials P3HT and PCBM, Figure 3 depicts the corresponding HOMO/LUMO energy diagram of **STBF**, **TTBF**, **FTBF**, P3HT and PCBM. The HOMO and LUMO energy levels of P3HT and PCBM are from the data reported by Koster et al. [55].

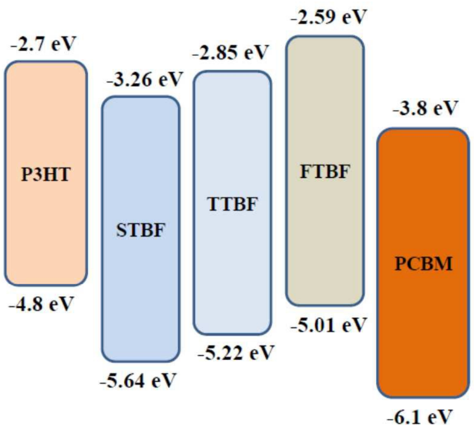

Fig. 3. Electronic energy levels of **STBF**, **TTBF**, **FTBF**, P3HT and PCBM

The bulk heterojunction polymer solar cells based on P3HT/PCBM are the most representative and attractive OPVs due to their reproducible high efficiency (> 4%) and low cost of the photovoltaic materials. However, too low LUMO energy level of PCBM results in low open circuit voltage (V_{oc}, ca. 0.6 V) of the devices, which limits further improvement of the device efficiency. For increasing efficiency of the bulk heterojunction polymer solar cells, various new donor and acceptor photovoltaic materials have been developed in recent years. With respect to the P3HT-based organic photovoltaic cells, the development of new acceptors with up-shifted LUMO energy levels is very important for higher open circuit voltage and improved photovoltaic efficiency. As shown in Fig. 3, it is found that the LUMO energy levels of the synthesized 9,9'-bifluorenylidene derivatives were gradually up-shifted to be -3.26–-2.59 eV with the number of thiophene ring in oligothiophene units increased. The LUMO energy level of **STBF** is higher than that of PCBM by 0.54 eV. The LUMO energy off-set of P3HT and **STBF** is 0.56 eV, which is roughly meeting the empirical off-set energy of 0.3–0.5 eV [44] as the driving force for the exciton dissociation at the donor/acceptor interface, suggesting that **STBF** could be used as an electron acceptor in the P3HT-based organic photovoltaic cells. The LUMO energy level of **TTBF** (-2.85 eV) is close to that of P3HT (-2.7 eV), whereas the LUMO energy level of **FTBF** (-2.59 eV) is higher than that of P3HT. Considering from the LUMO energy levels, **TTBF** and **FTBF** could be more suitable for use as electron donor materials.

Frontier molecular orbitals play an important role in electric and optical properties for materials. The ground-state geometries of **STBF**, **TTBF** and **FTBF** were fully optimized by density functional theory (DFT) at B3LYP/6-31G(d) basis set and an ethyl group was used instead of the octyl group here to make the calculation easier. The electronic distributions in HOMO and LUMO energy levels of the synthesized 9,9'-bifluorenylidene derivatives obtained from time-dependent DFT (TD-DFT) calculation are shown in Figure 4. For **STBF**, the electron densities in the HOMO and LUMO orbitals reside on the 9,9'-bifluorenylidene cores. For **TTBF** and **FTBF**, the electrons in HOMO energy levels are mainly distributed on one side of

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oligothiophene units and their adjacent fluorene rings, while the electrons are mainly distributed on the core 9,9'-bifluorenylidene units in the LUMO energy levels.

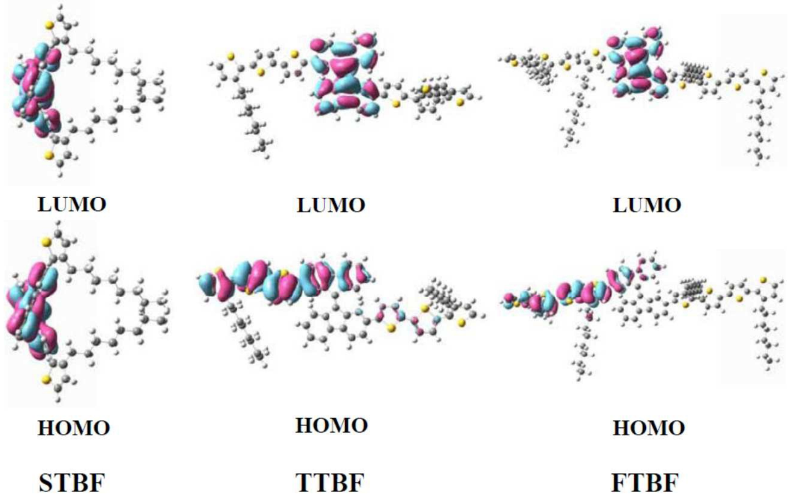

Fig. 4. The spatial electron distributions of HOMO and LUMO energy densities of **STBF**, **TTBF** and **FTBF** by DFT B3LYP/6-31G (d) calculation.

4. Conclusions

We have designed and synthesized three new 9,9'-bifluorenylidene derivatives **STBF**, **TTBF** and **FTBF**. Their UV-vis absorption bands were much broader and stronger than that of fullerene derivative PCBM. The LUMO energy levels of the synthesized 9,9'-bifluorenylidene derivatives were gradually up-shifted with the number of thiophene ring in oligothiophene units increased. Considering from the LUMO energy level, **STBF** could be used as an electron acceptor in the P3HT-based organic photovoltaic cells, whereas **TTBF** and **FTBF** could be more suitable for use as electron donor materials.

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Graphical abstract

Three 9,9'-bifluorenylidene derivatives were synthesized, in which **STBF** could be as an electron acceptor in the P3HT-based organic photovoltaic cells.