

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/264695088>

5,6-Bis(tetradecyloxy)-2,1,3-benzoselenadiazole-based polymers for photovoltaic applications

ARTICLE *in* JOURNAL OF APPLIED POLYMER SCIENCE · JUNE 2013

Impact Factor: 1.77 · DOI: 10.1002/app.38586

CITATIONS

2

READS

15

6 AUTHORS, INCLUDING:



Yingping Zou

Central South University

95 PUBLICATIONS 2,818 CITATIONS

SEE PROFILE



Chunyue Pan

Central South University

20 PUBLICATIONS 363 CITATIONS

SEE PROFILE

5,6-Bis(tetradecyloxy)-2,1,3-benzoselenadiazole-Based Polymers for Photovoltaic Applications

Wanjun Tang,¹ Xuwen Chen,¹ Yingping Zou,¹ Bo Liu,² Hong Zhong,¹ Chunyue Pan¹

¹College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

²State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, China

Correspondence to: Y. Zou (E-mail: yingpingzou@csu.edu.cn)

ABSTRACT: A series of new 5,6-bis(tetradecyloxy)-2,1,3-benzoselenadiazole-based copolymers (PBDT-DTBSe, PC-DTBSe, and PF-DTBSe) have been first synthesized by Stille or Suzuki coupling polymerization reaction. The synthesized copolymers show good solubility in common organic solvents, such as chloroform, tetrahydrofuran, and chlorobenzene with excellent film-forming properties. The molecular weight was determined by gel permeation chromatography and the thermal properties were investigated by thermogravimetric analysis. All the copolymers exhibited broad absorption from 350 to 700 nm. The preliminary results showed the device based on the structure of indium tin oxide/PEDOT:PSS/PC-DTBSe:PC₆₁BM (1 : 2, w/w)/Ca/Al displayed the best photovoltaic performance with a power conversion efficiency of 1.35%, a V_{oc} of 0.87 V, a J_{sc} of 3.84 mA/cm² and a fill factor of 40.4%, under illumination of AM 1.5 G (100 mW/cm²). © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 3678–3686, 2013

KEYWORDS: copolymers; photochemistry; conducting polymers

Received 4 August 2012; accepted 13 September 2012; published online 8 October 2012

DOI: 10.1002/app.38586

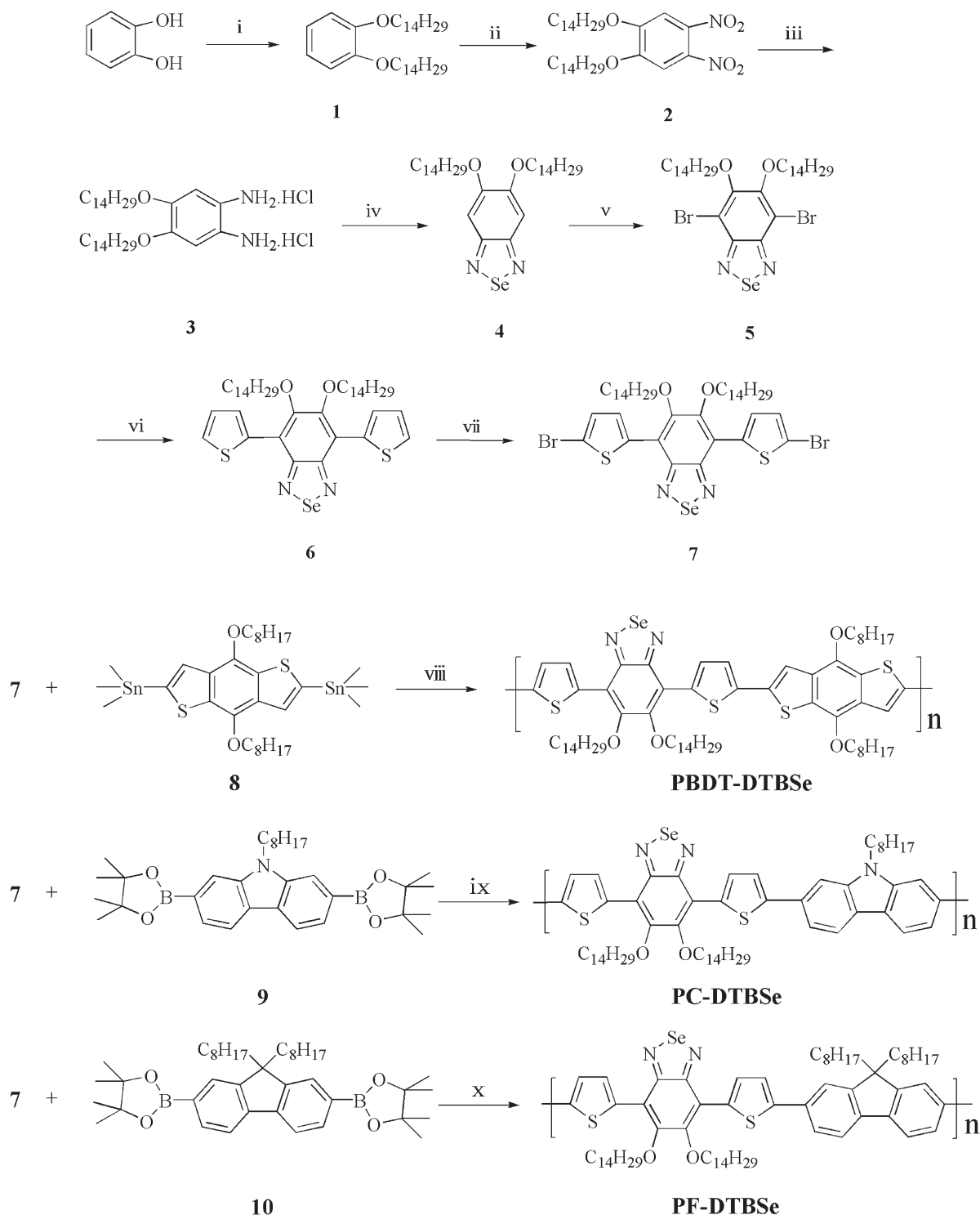
INTRODUCTION

Polymer solar cells (PSCs) have gained considerable attention recently due to their advantages of low cost, light weight, easy fabrication, and compatibility with flexible substrates.^{1–3} So far, the most representative high-performance PSCs reported in the literatures have been fabricated using the bulk heterojunction concept^{4–8} where a light-absorbing polymer (electron donor) and a soluble fullerene (electron acceptor) form a three-dimensional matrix possessing a large-area phase separation interface for efficient exciton dissociation.^{1,9} The resulting power conversion efficiencies (PCEs) of 5–8% have been reached.^{5–8} In the past few years, great progress in PSCs has been witnessed, but PCE is still a big challenge toward commercialization.^{10,11} To further improve the PCE, it is very important to design and synthesize excellent donor and acceptor materials with broad absorption, high charge carrier mobility, and suitable energy levels.^{5,12,13}

Through many years of in-depth investigations, some basic principles have become clear to obtain an efficient p-type polymer material for photovoltaic applications¹⁴: (i) reducing the bandgap of polymers so as to better match the solar spectrum to harvest more sunlight, which leads to higher short-circuit current density (J_{sc}) and (ii) lowering the highest occupied molecular orbital (HOMO) energy level of the polymers, which increases the open-circuit voltage (V_{oc}). Up to date, donor–acceptor (D–A)

approach is proved to be the most efficient strategy for obtaining low bandgap polymers and modulating their electronic properties. Based on this, D–A copolymers have witnessed great success in achieving high performance PSCs.^{3,6} During the past few years, fluorene,¹⁵ carbazole,¹⁶ and benzodithiophene (BDT)^{3,5,13} are the typical D-type units for polymer photovoltaic donors with high open-circuit voltage (V_{oc}); 2,1,3-benzothiadiazole (BT),^{15,16} 1,2,3-benzotriazole,^{17,18} thieno[3,4-b]pyrazine,¹⁹ and diketopyrrolopyrrole^{20,21} as A-type aromatic heterocycles are also promising for their notable performances in PSCs.

Recently, our group have synthesized some A-type units such as BT, 2,1,3-benzooxadiazole and their derivatives. Therein, PBDT-DODTBT, based on BDT and 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzothiadiazole, which acts as the donor and PC₇₁BM as the acceptor, exhibited a high PCE of 4% with a high hole mobility up to 7.15×10^{-3} cm²/(V s).²² Because the selenium atom has a much larger size and is more electron rich than those of the sulfur atom, it makes selenium-containing polymers the redshift in the absorption spectra compared with those of sulfur counterparts.^{23,24} In this work, a series of new copolymers, PBDT-DTBSe, PC-DTBSe, and PF-DTBSe were first designed, synthesized, and used in solar cells. The relationship between the structure and properties was well investigated. The synthetic route of the copolymers is shown in Scheme 1. The copolymers show good solubility in common organic solvents



Scheme 1. Synthetic routes of the monomers and polymers. Reagents and conditions: (i) $\text{C}_{14}\text{H}_{29}\text{Br}$, dry dimethyl formamide (DMF), K_2CO_3 , 100°C , 40 h, 92% yield; (ii) 65% HNO_3 , 100% HNO_3 , CH_2Cl_2 , HOAc, room temperature (RT), 40 h, 75% yield; (iii) Sn(II)Cl_2 , ethanol, conc. HCl, 85°C , 12 h, 94% yield; (iv) SeO_2 , $\text{N}(\text{C}_2\text{H}_5)_3$, CH_2Cl_2 , reflux, 12 h, 65% yield; (v) Br_2 , CH_2Cl_2 , HOAc, RT, 36 h, 91%; (vi) $\text{Pd(PPh}_3)_4$, 2-(tributylstannyl)thiophene, toluene, reflux, 20 h, 95% yield; (vii) *N*-bromosuccinimide (NBS), CHCl_3 , HOAc, RT, 24 h, 81% yield; (viii) $\text{Pd(PPh}_3)_4$, toluene, reflux, 48 h, 62% yield; (ix) $\text{Pd(PPh}_3)_4$, toluene, K_2CO_3 , H_2O , reflux, 48 h, 65% yield; (x) $\text{Pd(PPh}_3)_4$, toluene, K_2CO_3 , H_2O , reflux, 48 h, 59% yield.

and broad absorption. The absorption onsets of **PBDT-DTBSe**, **PC-DTBSe**, and **PF-DTBSe** are located at 738 nm, 690 nm, and 677 nm, respectively, from their absorption spectra. In addition,

the photovoltaic characteristics of the devices were measured. PSCs based on **PC-DTBSe** as the donor and **PC₆₁BM** as the acceptor demonstrated a PCE up to 1.35% with a V_{oc} of 0.87 V,

a J_{sc} of 3.84 mA/cm², and a fill factor (FF) of 40.4%, under the illumination of AM 1.5 G, 100 mW/cm².

EXPERIMENTAL SECTION

Materials

Pd(PPh₃)₄, 2-(tributylstannyl)thiophene, catechol, and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctyl-9H-fluorene (**10**) were obtained from Aladdin and Alfa Asia Chemical, and they were used as received. Toluene was dried over Na/benzophenone ketyl and freshly distilled prior to use. Other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification. Column chromatography was performed on silica gel (size: 200–300 mesh). 2,6-Bis(trimethyltin)-4,8-dioctoxyl-benzo[1,2-b:3,4-b']dithiophene (**8**),^{25,26} 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-9-octylcarbazole (**9**),^{27,28} and 4,5-bis(tetradecyloxy)benzene-1,2-diaminium chloride (**3**) were synthesized by a previously reported procedure.²⁹ All the other compounds were synthesized following the procedures described herein.

Characterization

¹H-NMR was recorded using a Bruker AV-400 spectrometer in deuterated chloroform solution at 298 K, unless specified otherwise. Chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane standard. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene as standard. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 with a heating rate of 20 K/min under a nitrogen atmosphere. The temperature of degradation (T_d) corresponds to a 5% weight loss. Mass spectra were obtained with a Shimadzu QP2010 spectrometer. The UV-Vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. For solid state measurements, polymer solution in chloroform was spin-coated on quartz plates. Optical bandgap was calculated from the onset of the absorption spectra. The cyclic voltammogram was recorded with a Zahner IM6e electrochemical workstation (Germany) with a three-electrode system in a solution of 0.1M Bu₄NPF₆ in acetonitrile at a scan rate of 50 mV/s. The polymer films were spin-coated on a glassy carbon electrode (1.0 cm²) by dipping the electrode into the corresponding solutions and then drying with a platinum wire as the counter electrode and Ag/Ag⁺ (0.1M) as the reference electrode. Hole mobilities of the polymers were measured by the space-charge-limited current (SCLC) method with a device structure of indium tin oxide (ITO)/PEDOT:PSS/Polymer:PC₆₁BM (1 : 2)/Au. The morphologies of the polymer/PC₆₁BM blend films were investigated by a SPI 3800N atomic force microscopy (AFM) in contacting mode with a 5 μ m scanner.

Fabrication and Characterization of PSCs

The PSCs were fabricated in the configuration of the common sandwich structure with an ITO glass anode and a Ca/Al cathode. Patterned ITO glass with a sheet resistance of 10 Ω/\square was purchased from CSG HOLDING (China). The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone and isopropanol, then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company) for 20 min. PEDOT:PSS (poly(3,4-ethylene diox-

thiophene):poly(styrene sulfonate)) (Clevios P 4083, Germany) was used as anode buffer layer to smooth the ITO surface and was filtered through a 0.45 μ m polyvinylidene difluoride (PVDF) filter and spin-coated at 2000 rpm for 40 s on the cleaned ITO electrode. Subsequently, the PEDOT:PSS film was baked at 150°C for 15 min in air to dry and resulted in a thin film with a thickness of 35 nm. A blend of polymer/PC₆₁BM was dissolved in *o*-dichlorobenzene (ODCB) overnight, filtered through a 0.45 μ m poly(tetrafluoroethylene) filter, and spin-cast at 1000 rpm for 40 s onto the PEDOT:PSS layer. The thickness of the photoactive layer was about 80 nm measured by a surface profilometer (XP-2, Ambios Technology). Finally, the substrates were transferred into a thermal evaporator and pumped down to 5×10^{-5} Pa. Subsequently, the cathode of devices, consisting of 20 nm Ca and 80 nm aluminum, was thermally deposited onto the active layer. The overlap area between the cathode and anode defined a pixel size of 4 mm². Current density versus potential curves (J - V characteristics) was conducted on a computer-controlled Keithley 236 source measure unit. A xenon lamp with AM 1.5 filter was used as a white-light source and the optical power was 100 mW/cm². The external quantum efficiency (EQE) measurements of PSCs were performed by Stanford Research Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500 W xenon lamp. A calibrated silicon detector was used to determine the absolute photosensitivity at different wavelengths. All the fabrication processes after cleaning of ITO substrates were performed in a glove box.

Synthesis of Monomers and Copolymers

The synthetic routes of the monomers and copolymers are shown in Scheme 1. The detailed synthetic processes of other compounds and polymers are as following:

5,6-Bis(tetradecyloxy)[2,1,3]-benzoselenadiazole (4). Monomer **3** (5.85 g, 9.67 mmol), triethylamine (143.76 mmol, 20 mL), selenium dioxide (7.16 g, 64.5 mmol), and 150 mL dichloromethane were added to a 250 mL flask. After addition, the mixture was heated to reflux for 12 h. The reaction mixture was concentrated in vacuum followed by trituration in water. After stirring for 1 h, the product was filtered. The residue was chromatographically purified on a silica gel column eluting with ethyl acetate/petroleum ether (1 : 10, v/v) to afford **4** as an fluffy needle-like off-white solid (5.81 g, 65%). ¹H-NMR (CDCl₃): δ = 6.98 (s, 2H), 4.09 (t, 4H), 1.94–1.89 (m, 4H), 1.58–1.32 (m, 44H), 0.9 (m, 6H). MS: 607 (M⁺).

4,7-Dibromo-5,6-bis(tetradecyloxy)[2,1,3]-benzoselenadiazole (5). To a solution of **4** (2.84 g, 4.67 mmol) in a mixture of dichloromethane (250 mL) and acetic acid (100 mL) was added bromine (2 mL, 38.26 mmol), and the reaction mixture was stirred at room temperature for 36 h. The mixture was then poured into water (300 mL), extracted with dichloromethane, sequentially washed with water, saturated NaHCO₃ (aq), and 1M Na₂SO₃ (aq), and the solvent was removed under reduced pressure. The residue was chromatographically purified on a silica gel column eluting with ethyl acetate/petroleum ether (1 : 10, v/v) to afford **5** as a yellow solid (3.24 g, 91%).

Table I. Molecular Weights and Thermal Properties of the Copolymers

Polymers	M_n	M_w	PDI	T_d (°C)
PBDT-DTBS _{Se}	6417	11,457	1.7	262
PC-DTBS _{Se}	9970	24,076	2.4	303
PF-DTBS _{Se}	14,263	41,075	2.8	323

M_w , M_n , and PDI of the polymers were determined by GPC using polystyrene standards in THF. T_d is the 5% weight-loss temperatures of the polymers under inert atmosphere.

$^1\text{H-NMR}$ (CDCl_3): δ = 4.05 (t, 4H), 1.91–1.88 (m, 4H), 1.59–1.31 (m, 44H), 0.89 (m, 6H). MS: 763 (M^+).

4,7-Di(thiophen-2-yl)-5,6-bis(tetradecyloxy)[2,1,3]-benzoselenadiazole (6). To a solution of **5** (2.00 g, 2.62 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.37 g, 0.32 mmol) in dry toluene (125 mL) was added 2-(tributylstannyl)-thiophene (2.42 g, 6.49 mmol) and the reaction mixture was heated to reflux for 20 h under nitrogen atmosphere. The reaction mixture was concentrated under reduced pressure. The residue was chromatographically purified on a silica gel column eluting with ethyl acetate/petroleum ether (1 : 20, v/v) to afford **6** as an orange solid (1.91 g, 95%). $^1\text{H-NMR}$ (CDCl_3): δ = 8.21–8.18 (d, 2H), 7.31–7.29 (d, 2H), 7.10–7.08 (t, 2H), 4.03 (t, 4H), 1.93–1.90 (m, 4H), 1.61–1.29 (m, 44H), 0.90–0.86 (m, 6H). MS: 770 (M^+).

4,7-Bis(5-bromothiophen-2-yl)-5,6-bis(tetradecyloxy)[2,1,3]-benzoselenadiazole(7). To a solution of **6** (1.00 g, 1.30 mmol) in glacial acetic acid (50 mL) and chloroform (50 mL) was added NBS (0.51 g, 2.86 mmol) in one portion. The mixture was stirred at room temperature in dark for 24 h. The solution was concentrated in vacuum, the residue was chromatographically purified on silica gel column eluting with dichloromethane/petroleum ether (1 : 10, v/v) to afford **7** as an orange-red crystal (0.976 g, 81%). $^1\text{H-NMR}$ (CDCl_3): δ = 8.15–8.10 (d, 2H), 7.19–7.05 (d, 2H), 4.04–4.01 (t, 4H), 1.89–1.80 (m, 4H), 1.57–1.21 (m, 44H), 0.88–0.81 (t, 6H). MS: 928 (M^+).

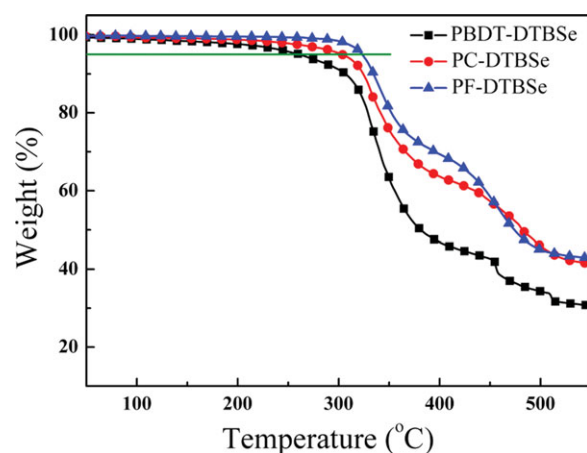


Figure 1. TGA curves of the copolymers with a heating rate of 20 K/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Synthesis of PBDT-DTBS_{Se}. 4,7-Bis(5-bromothiophen-2-yl)-5,6-bis(tetradecyloxy) [2,1,3]-benzoselenadiazole (**7**) (185.6 mg, 0.2 mmol) and 2,6-bis(trimethyltin)-4,8-di(octoxyl)benzo[1,2-b:3,4-b']dithiophene (**8**) (154.4 mg, 0.2 mmol) were dissolved in toluene (6 mL). The solution was flushed with nitrogen for 20 min, and then $\text{Pd}(\text{PPh}_3)_4$ (20 mg, 0.016 mmol) was added into a two-necked flask. The flask was purged three times with successive vacuum and nitrogen filling cycles. The polymerization reaction was heated to 110°C and the mixture was stirred for 48 h under nitrogen atmosphere. The mixture was cooled to room temperature and poured slowly into methanol (100 mL), and the resulting precipitate was collected by filtration. The crude polymer was washed with methanol and hexane by a soxhlet apparatus to remove the oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The polymer chloroform part was concentrated to about 20 mL and slowly poured in methanol (200 mL). The precipitate was collected by filtration and dried under vacuum to afford PBDT-DTBS_{Se} as a blue black solid (153.0 mg, 69%). GPC (tetrahydrofuran [THF]): M_n = 6417 g/mol; M_w = 11457 g/mol; polydispersity index (PDI) = 1.7.

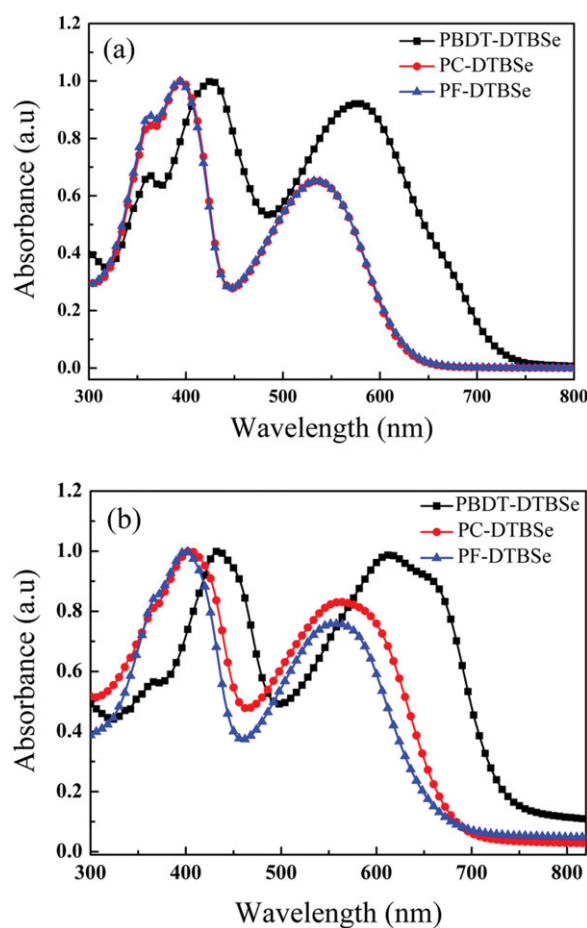


Figure 2. UV-Vis absorption spectra of the polymers: (a) solutions in diluted CHCl_3 at room temperature; (b) films drop-casting from polymer in CHCl_3 solutions on quartz. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table II. Optical and Electrochemical Properties of the Copolymers

Copolymers	Absorption spectra				CV Energy levels	
	Solution ^a		Film ^b		$E_{\text{on}}^{\text{ox}}/\text{HOMO}^{\text{d}}$ (V)/(eV)	LUMO (eV)
	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	$E_{\text{g}}^{\text{opt}}$ (eV) ^c		
PBDT-DTBSe	426	434	738	1.68	0.50/−5.21	−3.53
PC-DTBSe	396	404	690	1.80	0.70/−5.41	−3.61
PF-DTBSe	394	400	677	1.83	0.87/−5.58	−3.75

^aMeasured in chloroform solution.^bSpin-coated from chloroform solution.^cBand gap estimated from the onset wavelength of the optical absorption.^dHOMO = −e(+4.71) (eV) using Ag/Ag⁺ as the reference electrode.

Synthesis of PC-DTBSe. Monomer (**7**) (185.6 mg, 0.2 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-9-octylcarbazole (**9**) (106.2 mg, 0.2 mmol), and K₂CO₃ (0.66 g) were dissolved in toluene (10 mL) and H₂O (2.4 mL). The solution was flushed with nitrogen for 20 min, and then Pd(PPh₃)₄ (5 mg, 0.0043 mmol) was added into a two-necked flask. The flask was purged three times with successive vacuum and nitrogen filling cycles. The reaction was heated to 95°C, and the mixture was stirred for 48 h under nitrogen atmosphere. Its postprocessing step was the same to **PBDT-DTBSe**. The final product as a purple solid was obtained (134.1 mg, 64%). GPC (THF): M_n = 9970 g/mol; M_w = 24076 g/mol; PDI = 2.4.

Synthesis of PF-DTBSe. By following the similar methods, **PF-DTBSe** was synthesized with monomer (**7**) (185.6 mg, 0.2 mmol) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctyl-9H-fluorene (**10**) (128.6 mg, 0.2 mmol). Its postprocessing step was the same to **PBDT-DTBSe**. The final product as a red solid was obtained (120.3 mg, 52%). GPC (THF): M_n = 14,263 g/mol; M_w = 41075 g/mol; PDI = 2.8.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers and Polymers

The synthetic routes of the comonomers and the D–A copolymers are outlined in Scheme 1. Monomer **3**,²⁹ monomer **8**,^{25,26} and monomer **9**^{27,28} were prepared according to the reported procedures. Monomer **7** copolymerized with monomer **8** through Stille coupling reactions to afford the target polymer-**PBDT-DTBSe**. **PC-DTBSe** and **PF-DTBSe** were synthesized by Suzuki polycondensation of an equimolecular mixture of the monomer **7** and monomer **9** or monomer **10**. The polymers were purified by sequential Soxhlet extraction with methanol, hexane, and CHCl₃. The CHCl₃ fraction was then reduced in volume, precipitated into methanol, and collected by filtration, yielding a blue black or purple or red solid. The chemical structures of the comonomers were verified by ¹H-NMR as described above. The molecular weight of the polymers was determined by gel-permeation chromatography (GPC) in THF solution relative to polystyrene standards. The number average molecular weight (M_n) of **PBDT-DTBSe**, **PC-DTBSe**, and **PF-DTBSe** is 6417, 9970, and 14,263 g/mol, with a PDI of 1.7, 2.4, and 2.8, respectively, the related data are listed in Table I.

Thermal Stability

The thermal properties of the copolymers were investigated with TGA as shown in Figure 1, and the data are summarized in Table I. TGA measurement displays that the 5% weight-loss temperatures (T_d) of **PBDT-DTBSe**, **PC-DTBSe**, and **PF-DTBSe** were 262°C, 303°C, and 323°C under inert atmosphere, respectively. The temperature of **PBDT-DTBSe** is the lowest among the three polymers mainly due to the removal of the more alkoxy groups and lowest molecular weight. The thermal stability of the three copolymers is favorable for its application in PSCs and other optoelectronic devices.

Optical Properties

The normalized UV–Vis absorption spectra of the copolymers in dilute chloroform solution and in a solid film spin-coated on a quartz substrate are shown in Figure 2, the results are listed in Table II. The absorption spectra of all the copolymers have two absorption bands. The peak at the shorter wavelength could be attributed to the absorption of 2,1,3-benzoselenadiazole and the other is possibly the result of higher energy transitions.³⁰ The absorption spectra of **PBDT-DTBSe**, **PC-DTBSe**, and **PF-DTBSe** in solution all showed two absorption peaks, 426 and

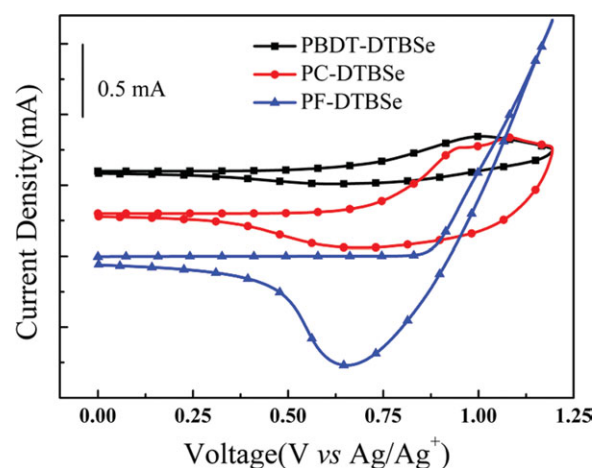


Figure 3. Cyclic voltammograms of **PBDT-DTBSe**, **PC-DTBSe**, and **PF-DTBSe** films on a glassy carbon electrode in 0.1M Bu₄NPF₆, CH₃CN solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

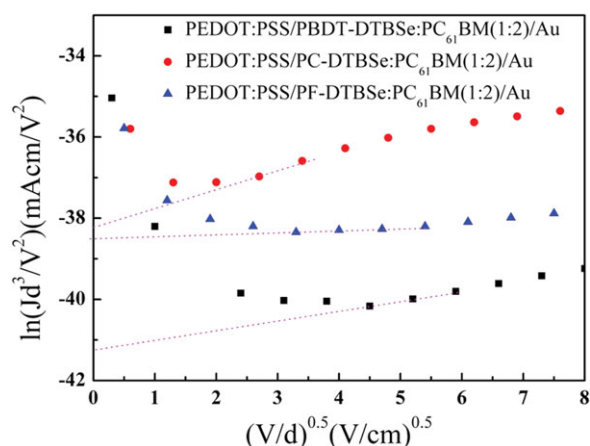


Figure 4. $\ln(Jd^3/V^2)$ versus $(V/d)^{0.5}$ plots of the polymers for the measurement of the hole mobility by the SCLC method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

598 nm, 396 and 536 nm, 394 and 535 nm, respectively. Whereas in the film states also showed two absorption peaks, and the absorption peak shows a large redshift, respectively. Compared to the solution absorption, the absorption spectra of PC-DTBSe and PF-DTBSe in the film states are similar, but PF-DTBSe film showed a less redshift than that of PC-DTBSe film, indicating carbazole group is more electron rich than that of fluorene. The absorption peaks at the longer wavelength in the polymer films have a red-shift of 20–30 nm compared with those in solution, indicating the presence of intermolecular interactions in the solid state. The optical band gaps (E_g) of the copolymers estimated from the onset absorption in the film states are 1.68 eV, 1.80 eV, and 1.83 eV for PBDT-DTBSe, PC-DTBSe, and PF-DTBSe, respectively. The results show that the photophysical properties of the copolymers can be easily tuned by simply incorporating different electron rich comonomers and all the copolymers exhibit broad absorption from 350 to 700 nm, which is beneficial for obtaining good photovoltaic properties.

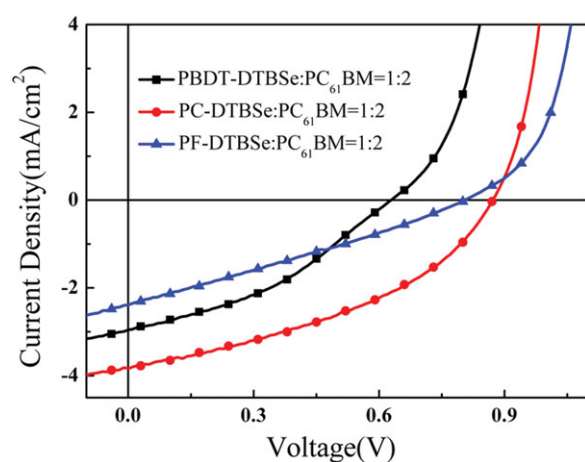


Figure 5. J - V curves of the PSCs based on PBDT-DTBSe, PC-DTBSe, and PF-DTBSe:PC₆₁BM (1 : 2, w/w) under illumination of AM 1.5 G, 100 mW/cm². [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Photovoltaic Performances of the PSCs Based on PBDT-DTBSe, PC-DTBSe, and PF-DTBSe

Polymers: PC ₆₁ BM = 1 : 2 (w/w)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Hole mobility (cm ² /V s)
PBDT-DTBSe	0.63	2.95	37.0	0.69	5.03×10^{-6}
PC-DTBSe	0.87	3.84	40.4	1.35	9.14×10^{-5}
PF-DTBSe	0.81	2.39	27.9	0.54	7.49×10^{-5}

Electrochemical Properties

The electrochemical properties of the three copolymers were investigated by cyclic voltammetry (CV). The measurements were performed in a 0.1M solution of Bu₄NPF₆ in acetonitrile at room temperature under argon with a scanning rate of 50 mV/s. All the potentials are reported versus Ag/Ag⁺ with the ferrocene/ferrocenium (Fc/Fc⁺) couple as an internal standard. The related electrochemical data are summarized in Table II. As shown in Figure 3, no reduction peaks in the n-doping region are observed for the three polymers. In a positive potential region, the oxidation is quasireversible, the onset oxidation potential (E_{on}^{ox}) is 0.50 V for PBDT-DTBSe, 0.70 V for PC-DTBSe and 0.87 V for PF-DTBSe. From the E_{on}^{ox} of the polymers, we calculated the HOMO levels of the polymers according to the equation¹³:

$$\text{HOMO} = -e(E_{on}^{ox} + 4.71) \text{ (eV)}$$

The HOMO levels of PBDT-DTBSe, PC-DTBSe, and PF-DTBSe are −5.21 eV, −5.41 eV, and −5.58 eV, respectively. Among the three copolymers, HOMO level of PBDT-DTBSe is very similar to that of PC-DTBSe. The lowest unoccupied molecular orbital (LUMO) levels were obtained from the E_g^{opt} and HOMO levels by the equation: $\text{LUMO} = E_g^{opt} + \text{HOMO}$. Accordingly, the LUMO levels of the three polymers are −3.53

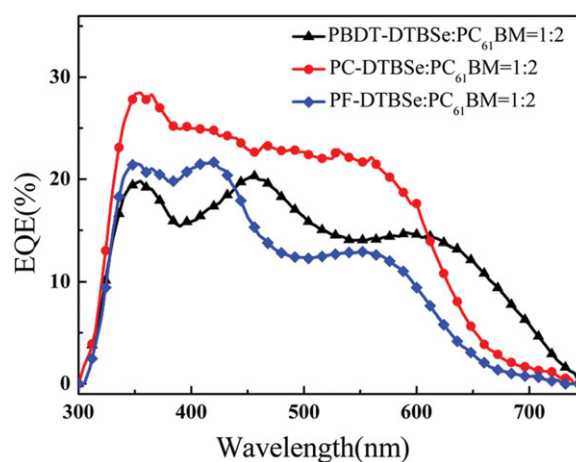


Figure 6. EQE curves of the photovoltaic cells with polymers:PC₆₁BM (1 : 2, w/w) as the active layer using Ca/Al bilayer cathode. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

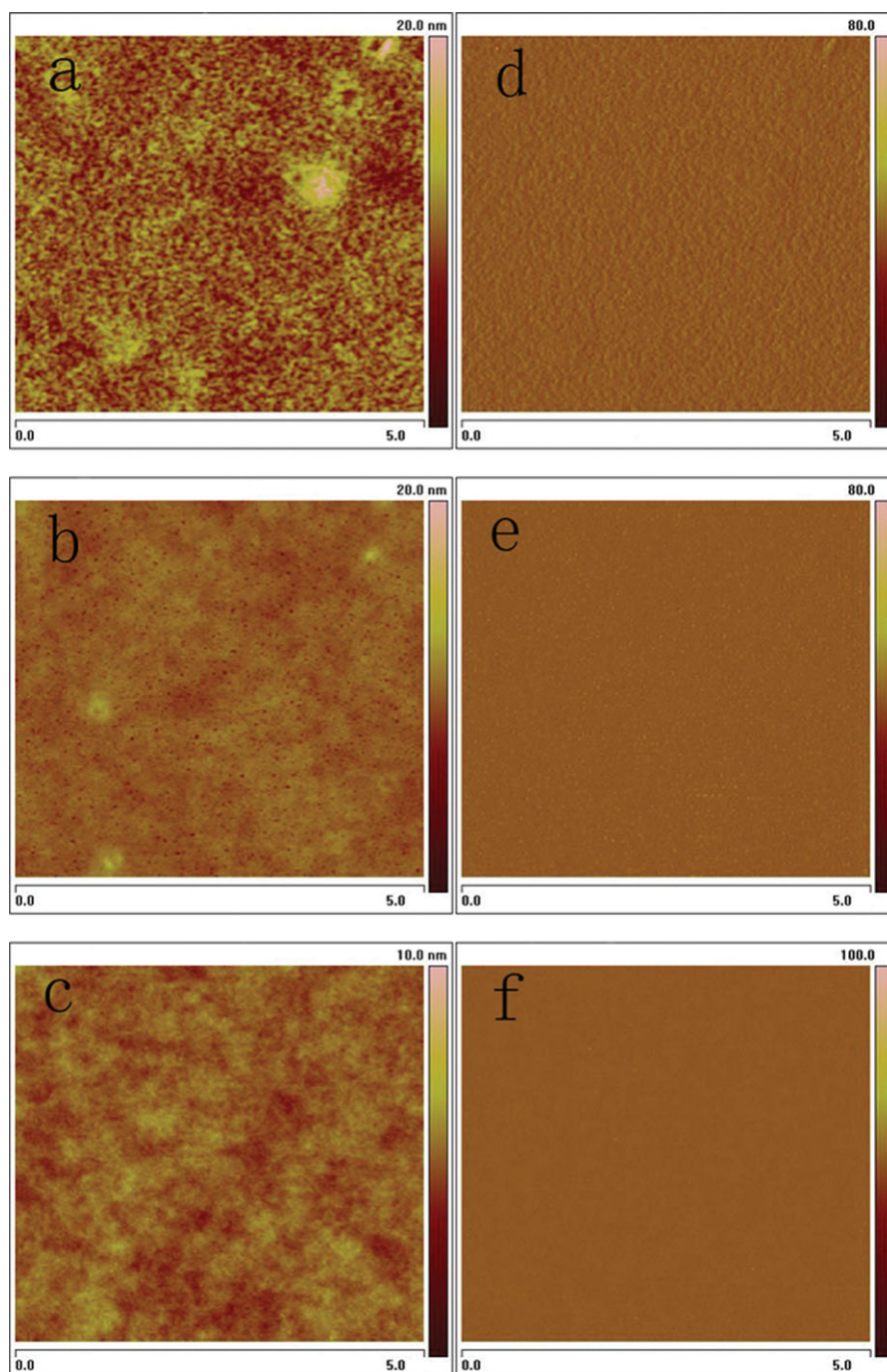


Figure 7. AFM height images (a, b, and c) and phase images (d, e, and f) for polymer:PC₆₁BM blend films (1 : 2, w/w): (a, d) PBDT-DTBSe; (b, e) PC-DTBSe; (c, f) PF-DTBSe, spin-coated from ODCB solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

eV, −3.61 eV, and −3.75 eV. The related CV data are summarized in Table II for comparison.

Hole Mobility

Hole mobility of the materials is a key factor for PSCs. We investigated the hole mobilities of the three copolymers with a typical device structure of ITO/PEDOT:PSS/polymer:PC₆₁BM/Au via the SCLC model. The SCLC current can be determined approximated by³¹

$$J_{\text{SCLC}} = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0 \frac{(V - V_{\text{bi}})^2}{d^3} \exp \left[0.89 \gamma \sqrt{\frac{V - V_{\text{bi}}}{d}} \right]$$

The results are plotted as $\ln(Jd^3/V^2)$ versus $(V/d)^{0.5}$, as shown in Figure 4. Herein, J stands for current density, d is the thickness of the device, and $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied potential and V_{bi} is the built-in potential. According to

the above equation and Figure 4, the hole mobilities of the three polymers are evaluated to be $5.03 \times 10^{-6} \text{ cm}^2/(\text{V s})$, $9.14 \times 10^{-5} \text{ cm}^2/(\text{V s})$, and $7.49 \times 10^{-5} \text{ cm}^2/(\text{V s})$ for **PBDT-DTBSe**, **PC-DTBSe**, and **PF-DTBSe**, respectively. Obviously, the hole mobility of **PC-DTBSe** is the highest ($9.14 \times 10^{-5} \text{ cm}^2/(\text{V s})$) among the three copolymers. The relatively high hole mobility of the polymer is expected to facilitate charge transport and reduce recombination loss in the PSCs. Therefore, **PC-DTBSe** is probably to obtain a relatively high PCE among the three polymers considering the moderate broad absorption.

Photovoltaic Properties

To investigate and compare the photovoltaic properties of the three polymers, PSC devices with a structure of ITO/PEDOT:PSS/Polymer:**PC₆₁BM** (1 : 2, w/w)/Ca/Al were fabricated. The polymer/**PC₆₁BM** blend layers were spin-coated from ODCB solution. Figure 5 shows the typical current density–voltage (*J*–*V*) curves of the PSCs based on **PBDT-DTBSe**, **PC-DTBSe**, and **PF-DTBSe:PC₆₁BM** (1 : 2, w/w) blend under the illumination of AM 1.5 G, 100 mW/cm². The corresponding open-circuit voltage (*V*_{oc}), short-circuit current density (*J*_{sc}), FF, and PCE of the devices are summarized in Table III. From the photovoltaic results, the device based on **PC-DTBSe:PC₆₁BM** (1 : 2, w/w) demonstrated the best device performance with a PCE of 1.35%, a *V*_{oc} of 0.87 V, a *J*_{sc} of 3.84 mA/cm², and a FF of 40.4%, which are probably affected by higher hole mobility, balanced charge transport, relatively high molecular weight, and better blend morphologies. However, the PSCs based on **PF-DTBSe** exhibit the lowest *J*_{sc} and FF among the three copolymers, which indicate that the PSCs based on **PF-DTBSe** suffer seriously from relatively poor absorption and moderate hole mobility, and so forth. Although of the broadest absorption, **PBDT-DTBSe** shows a low PCE of 0.69% due to its lowest hole mobility and high HOMO energy level. We measured the EQEs of the PSC devices based on **PBDT-DTBSe**, **PC-DTBSe**, and **PF-DTBSe:PC₆₁BM** (1 : 2, w/w) to verify the accuracy of the *J*_{sc} measurements. Figure 6 displays EQE spectra of the devices. All the devices exhibited a broad photoresponse between 300 and 750 nm, indicating that **PC₆₁BM** and copolymer absorptions reflect the photocurrents in the short-wavelength and long-wavelength regions, respectively. From EQE curves, **PC-DTBSe** shows the relatively higher EQE and broader photoresponse compared to **PF-DTBSe**, which probably results from the higher hole mobility and more redshift absorption. Although of the lowest hole mobility, however, **PBDT-DTBSe** exhibits moderate EQE values due to the compromise between its broad absorption and low hole mobility. **PF-DTBSe** has the lowest *J*_{sc} which may be from the relatively narrow absorption. The *J*_{sc} value calculated from the integration of the EQE spectra closely matches the *J*_{sc} value obtained from the *J*–*V* measurement under white-light illumination. From the photovoltaic results, the photovoltaic performances of the copolymers from 2,1,3-benzoselenadiazole derivatives are lower than the sulfur-containing counterparts, which may be from the much lower hole mobilities and unoptimized morphologies of the 2,1,3-benzoselenadiazole-based copolymers.

Morphology

The morphology of the active layer is generally important for PSCs. We used AFM to investigate the surface morphology of the copolymer:**PC₆₁BM** (1 : 2, w/w) blend films spin-coated from the ODCB solution. The AFM height and phase images are presented in Figure 7. AFM height images showed that the different surface morphology and the root-mean-square values of the polymer:**PC₆₁BM** blends are 1.37 nm, 5.68 nm, and 0.35 nm for **PBDT-DTBSe**, **PC-DTBSe**, and **PF-DTBSe**, respectively. Phase separation between polymers and PCBM in proper size (10–20 nm) can provide enough D/A interfaces for exciton dissociation. From the phase images, no appreciable nanophase separation is formed, therefore which probably lead to relative low photovoltaic properties of the three copolymers. We firmly believe that the photovoltaic performance of this kind of copolymers can be further improved by the optimization of film morphology and device fabrication conditions.

CONCLUSIONS

In summary, a series of 5,6-bis(tetradecyloxy)benzo[c][1,2,5]selenadiazole-based copolymers have been first synthesized by Stille or Suzuki coupling polymerization and well characterized. The synthesized copolymers exhibited good solubilities, broad absorption, low bandgap, and deep lying HOMO level. The preliminary results showed that the device based on **PC-DTBSe:PC₆₁BM** (1 : 2, w/w) displayed the best device performance with a PCE of 1.35%, a *V*_{oc} of 0.87 V, a *J*_{sc} of 3.84 mA/cm², and a FF of 40.4%, under illumination of AM 1.5 G (100 mW/cm²). We believe that the photovoltaic performance based on the present polymers is likely to get improved by device fabrications and materials modifications.

ACKNOWLEDGMENTS

The authors thank the helpful discussions of Prof. Yongfang Li. This work was supported by NSFC (Nos. 51173206 and 21161160443) and the Natural Science Foundation of Hunan Province, China (No. 11JJ4010).

REFERENCES

1. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. *J. Science* **1995**, *270*, 1789.
2. Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T. Q.; Dante, M.; Heeger, A. *J. Science* **2007**, *317*, 222.
3. Zou, Y.; Najari, A.; Berrouard, P.; Beaupré, S.; Aich, R. B.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2010**, *132*, 5330.
4. Liu, X.; Zhang, J.; Tang, P.; Yu, G.; Zhang, Z.; Chen, H.; Chen, Y.; Zhao, B.; Tan S.; Shen, P. *Org. Electron.* **2012**, *13*, 1671.
5. Chen, H. Y.; Hou, J. H.; Zhang, S. Q.; Liang, Y. Y.; Yang, G. W.; Yang, Y.; Yu, L. P.; Wu, Y.; Li, G. *Nat. Photonics* **2009**, *3*, 649.
6. Hou, J. H.; Chen, H. Y.; Zhang, S. Q.; Chen, R. I.; Yang, Y.; Wu, Y.; Li, G. *J. Am. Chem. Soc.* **2009**, *131*, 15586.
7. He, Z.; Zhong, C.; Huang, X.; Wong, W.; Wu, H.; Chen, L.; Su, S.; Cao, Y. *Adv. Mater.* **2011**, *23*, 4636.

8. Li, X.; Choy, W.; Huo, L.; Xie, F.; Sha, W.; Ding, B.; Guo, X.; Li, Y.; Hou, J.; You, J.; Yang, Y. *Adv. Mater.* **2012**, *24*, 3046.
9. Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474.
10. Chen, J. W.; Cao, Y. *Acc. Chem. Res.* **2009**, *11*, 1709.
11. Li, Y. *Acc. Chem. Res.* **2012**, *45*, 723.
12. Li, Y.; Zou, Y. *Adv. Mater.* **2008**, *20*, 2952.
13. Yang, M.; Peng, B.; Liu, B.; Zou, Y. P.; Zhou, K. C.; He, Y. H.; Pan, C. Y.; Li, Y. F. *J. Phys. Chem. C* **2010**, *114*, 17989.
14. Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. *Adv. Mater.* **2006**, *18*, 789.
15. Svensson, M.; Zhang, F.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inganas, O.; Andersson, M. R. *Adv. Mater.* **2003**, *15*, 988.
16. Zou, Y.; Gendron, D.; Badrou-Aich, R.; Najari, A.; Tao, Y.; Leclerc, M. *Macromolecules* **2009**, *42*, 2891.
17. Zhang, Z.; Peng, B.; Liu, B.; Pan, C.; Li, Y.; He, Y.; Zhou, K.; Zou, Y. *Polym. Chem.* **2010**, *1*, 1441.
18. Zhang, L.; He, C.; Chen, J.; Yuan, P.; Huang, L.; Zhang, C.; Cai, W.; Liu, Z. T.; Cao, Y. *Macromolecules* **2010**, *43*, 9771.
19. Zhang, F.; Mammo, W.; Andersson, L.; Admassie, S.; Andersson, M.; Inganas, O. *Adv. Mater.* **2006**, *18*, 2169.
20. Wienk, M. M.; Turbiez, M.; Gilot, J.; Janssen, R. A. *Adv. Mater.* **2008**, *20*, 2556.
21. Zou, Y.; Gendron, D.; Rodica, N.; Leclerc, M. *Macromolecules* **2009**, *42*, 6361.
22. Ding, P.; Che, C. C.; Liu, B.; Peng, B.; Zou, Y. P.; He, Y. H.; Zhou, K. C.; Hsu, C. S. *Macromol. Chem. Phys.* **2010**, *211*, 2555.
23. Huang, F.; Hou, L.; Shen, H.; Yang, R.; Hou, Q.; Cao, Y. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 2521.
24. Yang, R.; Tian, R.; Yang, W.; Hou, Q.; Cao, Y. *Macromolecules* **2003**, *36*, 7453.
25. Liang, Y.; Wu, Y.; Feng, D.; Tsai, S. T.; Son, H. J.; Li, G.; Ray, C.; Yu, L. *J. Am. Chem. Soc.* **2009**, *131*, 56.
26. Hou, J.; Park, M. H.; Zhang, S.; Yao, Y.; Chen, L. M.; Li, J. H.; Yang, Y. *Macromolecules* **2008**, *41*, 6012.
27. Dierschke, F.; Grimsdale, A. C.; Müllen, K. *Synthesis* **2003**, *16*, 2470.
28. Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater.* **2007**, *19*, 2295.
29. Helgesen, M.; Gevorgyan, S. A.; Krebs, F. C.; Janssen, R. A. *J. Chem. Mater.* **2009**, *21*, 4669.
30. Zhou, E.; Yamakawa, S.; Zhang, Y.; Tajima, K.; Yang, C.; Hashimoto, K. *J. Mater. Chem.* **2009**, *19*, 7730.
31. Malliaras, G. G.; Salem, J. R.; Brock, P. J.; Scott, C. *Phys. Rev. B* **1998**, *58*, 13411.