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Novel conjugated alternating copolymer based on 2,7-carbazole and 2,1,3-benzoselenadiazole

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ABSTRACT

A novel conjugated alternating copolymer (PCzDBSe) based on N-9′-heptadecanyl-2,7-carbazole and 5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzoselenadiazole) was synthesized by Suzuki polycondensation. The polymer reveals excellent thermal stabilities with the decomposition temperature (5% weight loss) of 390 °C and the glass-transition temperature of 140 °C. The absorption peaks of the polymer are located at 412 and 626 nm, respectively, while the absorption onset is extended to 716 nm, which is 56 nm red-shifted as compared with its analogue, poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT). The HOMO and LUMO levels of the polymer were estimated to be −5.28 and −3.55 eV, respectively, with an optical bandgap of 1.73 eV. The hole mobility of PCzDBSe as deduced from a solution-processed organic field effect transistor (OFET) was found to be 3.9×10^{-4} cm^2 V^{-1} s^{-1}. Polymer solar cells (PSCs) based on the blends of PCzDBSe and [6,6]-phenyl-C$_{71}$-butyric acid methyl ester (PC$_{71}$BM) with a weight ratio of 1:4 were fabricated. Under AM 1.5 (AM, air mass), 100 mW cm^{-2} illumination, the devices were found to have an open-circuit (V_{oc}) of 0.75 V, a short-circuit current density (J_{sc}) of 7.23 mA cm^{-2}, a fill factor (FF) of 45% and a power conversion efficiency (PCE) of 2.58%. The primary results indicate that 5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzoselenadiazole) is a promising unit for low bandgap polymer for polymer solar cells.

1. Introduction

Since the discovery of the ultrafast photo-induced charge transfer between conjugated polymers and fullerene, polymer solar cells (PSCs) have attracted much attention as potential large-area, flexible, and low-cost solar cells [1]. Many conjugated polymers such as poly(p-phenylenevinylene)s (PPV) [2], poly(fluorene)s (PFO) [3], poly(3-alkylthiophene) [4], and polythiophene derivatives [5] were extensively studied. As a result of the development of new materials and the optimization of processing techniques, so far, the power conversion efficiency of the device based on these conjugated polymers and fullerene derivatives had exceeded 6.0% [4–7].

In order to further enhance the PCE of the polymer based solar cells, an effective method is to develop donor polymers with low bandgap to enable photocurrent generation from lower energy photons. It had been demonstrated that the incorporation of electron donating and accepting units along the polymer backbone can lead to intramolecular charge transfer thus resulting in lower bandgap polymer [8]. As compared with many other conjugated polymer donors, poly(2,7-carbazole) derivatives exhibit some unique merits such as high hole mobility, low energy lying highest occupied molecular orbital (HOMO), and therefore can result in high air stability and high V_{oc} [9–12]. Furthermore, the absorption spectra could be easily tuned for optimal solar spectral match. In the past several years, some of the 2,7-carbazole based polymers were synthesized as donor materials for highly efficient polymer solar cells [13], especially a low bandgap polymer, poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) with an absorption spectrum onset extended to 660 nm was reported [6,11,12,14]. Inspired by the purpose of harvesting the lower energy photons in the solar spectra, there is a need to further lower the bandgap of the 2,7-carbazole based polymer. As compared to 2,1,3-benzothiadiazole (BT), an electron deficient unit, which was widely used as the backbone in low bandgap polymers [2,3,5,15], its analogue 2,1,3-benzoselenadiazole (BSe) is more effective in extending the absorption spectrum towards the infrared

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region. For example, Hou et al. demonstrated that as a result of incorporating the BSe unit in benzo[1,2-b:4,5-b]dithiophene (BDT) based polymers, the bandgaps can be lowered from 1.70 eV (BDT-BT) to 1.52 eV (BDT-BSe) [16].

In this paper, 2,7-carbazole-alt-DBSe copolymer (PCzDBSe) with an extended absorption spectrum was synthesized. The photophysical properties of the DBSe based polymer and its photovoltaic properties to act as an electron donor to PCBM were investigated and discussed.

2. Experimental section

2.1. Materials

All the starting materials were purchased from Aldrich or Alfa Aesar and used without further purification. All the reactions were carried out under argon at 1 atmosphere unless mentioned otherwise. THF and CH_3CN were distilled from sodium and CaH_2 before use, respectively.

2.2. Characterization

^{1}H and ^{13}C NMR spectra were recorded by Bruker DRX 300 and Varian INOVA 500NB spectrometers operating at 300 MHz and 125 MHz respectively, in $CDCl_3$ at 298 K. Chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane (TMS) standard. The FTIR spectrum was recorded with a Bruker Vector 33 FTIR spectrometer. Elemental analysis was performed on a ELEMENTAR Vario ELIII Elemental Analyzer. Number-average (M_n) and weight-average (M_w) molecular weights were determined by GPC, using polystyrene as standards. Thermogravimetric analysis (TGA) was performed on Netzsch TG 209 in nitrogen, with a heating rate of 20 °C min^{-1}. Differential scanning calorimetry (DSC) analysis was performed on Netzsch DSC 204 in nitrogen, with a heating rate of 20 °C min^{-1}.

Cyclic voltammograms (CV) were recorded on a CHI 660A electrochemical workstation. A conventional three-electrode system consisting of a platinum electrode as working electrode, an Ag/AgCl reference electrode and a platinum wire as counter electrode was used. The polymer film was deposited on the working electrode of platinum electrode by solvent casting. The electrode was polished by using 0.3 μm Al_2O_3 slurry followed by rinsing with de-ionized water and acetonitrile, dried over 105 °C before use. A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile was used as the supporting electrolyte. Argon was bubbled through the solution for 10 min to remove the dissolved oxygen and also over the solution throughout the experiment.

Photoluminescence spectra (PL) of the polymer were recorded with a CCD spectrophotometer (Instaspec IV, Oriel Co.) under excitation of a 325 nm HeCd laser.

2.3. Fabrication and characterization of organic field effect transistor

Heavily p-doped Si wafers with 600 nm thermal SiO_2 grown, were used both as the substrate and the gate electrode. The substrates were cleaned by subsequent soaking in acetone, isopropanol and de-ionized water in ultrasonic bath for 10 min, and dried with nitrogen. Then, the substrates were treated with oxygen plasma for 5 min to remove any residual organic materials and to create a high density of silanol groups at the surface. To improve the chemical and electrical properties of the gate dielectric, the SiO_2/Si substrates were modified with a self-assembled monolayer (SAM) octyltrichlorosilane (OTS) solution in dry toluene at room temperature for 24 h. After the OTS SAM formation, the substrates were rinsed with toluene, and dried in a vacuum oven. Films of PCzDBSe were deposited on pre-treated SiO_2/Si substrates by spin-coating a 10 mg mL^{-1} solution of the polymer in chlorobenzene, followed by annealing under nitrogen to remove the residual solvent. The source and drain electrodes were defined by thermally evaporating gold (70 nm) through a shadow mask on top of the organic thin film forming top contact geometry transistors. Channel length and width of the obtained OFET were 0.1 and 10 mm, respectively. The OFET was characterized under ambient conditions by a semiconductor parameter analyzer (model: 4155B).

2.4. Fabrication and characterization of polymer solar cells

Patterned indium tin oxide (ITO) coated glass with a sheet resistance of 15–20 ohm/square was cleaned by a surfactant scrub, then underwent a wet-cleaning process inside an ultrasonic bath, beginning with de-ionized water, followed by acetone and isopropanol. After oxygen plasma cleaning for 5 min, a 40 nm-thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast on the ITO substrate and then dried by baking in a vacuum oven at 80 °C overnight. The active layer, with thickness in the 60–80 nm range, was then deposited on top of the PEDOT:PSS layer, by casting from a chlorobenzene solution (20 mg mL^{-1}) containing PCzDBSe:PCBM (1:*x*, w/w). The thickness of the PEDOT:PSS and active layer was verified by a surface profilometer (Tencor, Alpha-500). Finally, 100 nm aluminum layer was thermally evaporated with a shadow mask at a base pressure of 3×10^{-4} Pa. The overlapping area between the cathode and anode defined a pixel size of 0.15 cm^2. The thickness of the evaporated cathodes was monitored by a quartz crystal thickness/ratio monitor (model: STM-100/MF, Sycon). Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of nitrogen dry-box (Vacuum Atmosphere Co.) containing less than 10 ppm oxygen and moisture. The power conversion efficiency of the resulting polymer solar cells was measured under 1 sun AM 1.5G (air mass 1.5 global) spectrum from a solar simulator (Oriel model 91192) (1000 W m^{-2}). The current density–voltage (*J*–*V*) characteristics were recorded with a Keithley 2410 source unit. The spectral response of the devices was measured with a commercial EQE/incident photon to charge carrier efficiency (IPCE) measurement setup (Oriel). A calibrated silicon detector was used to determine the absolute photosensitivity at different wavelengths.

2.5. Synthetic procedures

2,7-Bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-N-9″-heptadecanylcarbazole [14,17] and 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzoselenadiazole [18] were prepared according to the literature procedure.

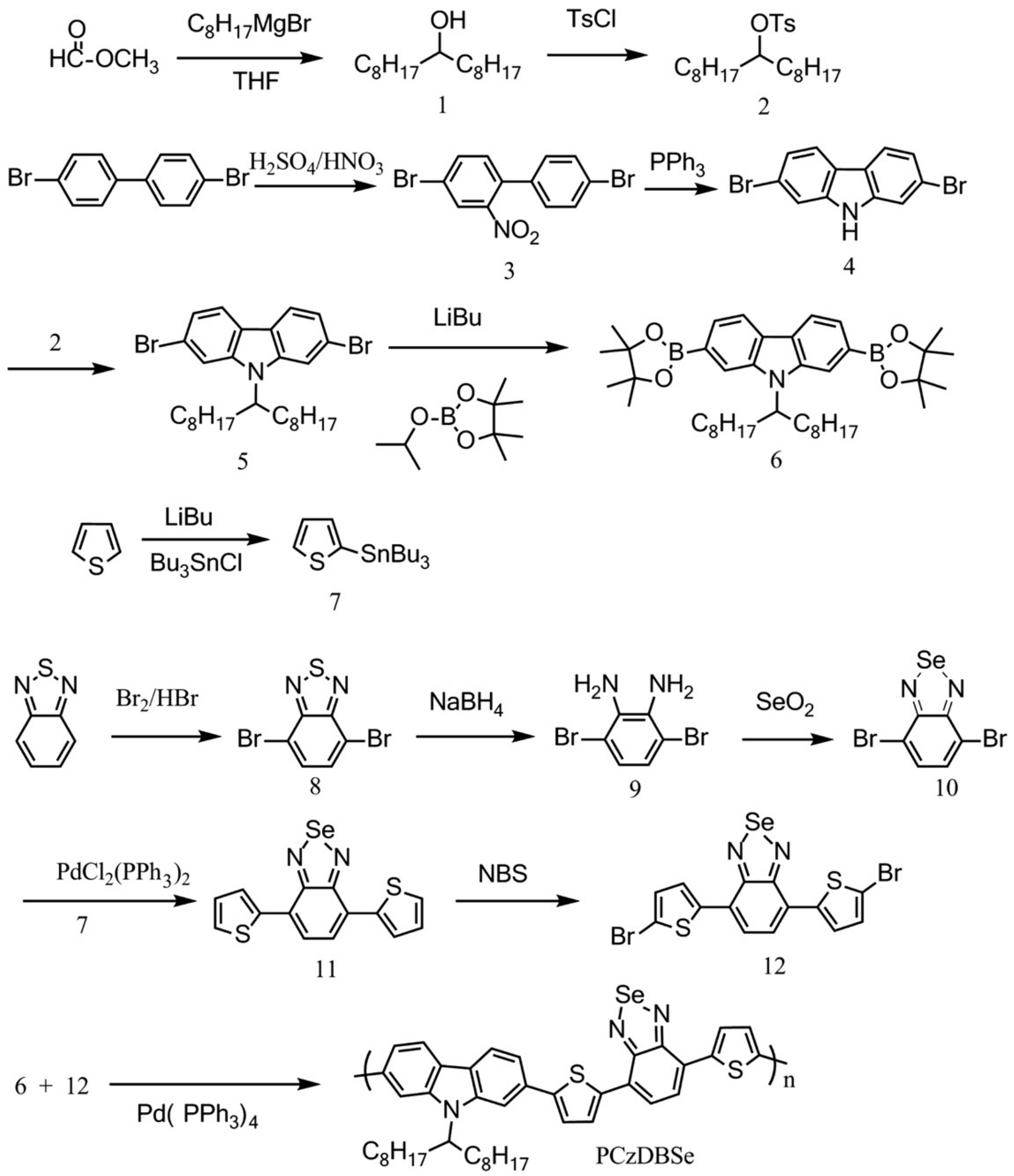
Synthesis of poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzoselenadiazole)](PCzDBSe).

In a 50 mL flask, 328.5 mg (0.5 mmol) of 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-N-9″-heptadecanylcarbazole, 253.6 mg (0.5 mmol) of 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzoselenadiazole, 3 mg (0.003 mmol) of $Pd(PPh_3)_4$, were dissolved in 15 mL of toluene and 0.6 mL of 20% aqueous tetraethylammonium hydroxide. The reaction mixture was refluxed with vigorous stirring for 48 h under argon atmosphere. Bromobenzene (5 μL, 0.05 mmol) was added to the reaction mixture, 4 h later, phenylboronic acid (6.1 mg, 0.05 mmol) was added to the reaction mixture, and then the reaction was continued for 4 h. After cooling to room temperature, the mixture was poured into 500 mL methanol, and filtered. The precipitate was washed in a Soxhlet apparatus with hexane, acetone, toluene, dichloromethane and chloroform for 24 h, respectively. The chloroform fraction was condensed to 10 mL, and precipitated in methanol and finally dried overnight (150 mg, yield: 40%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.10 (br, 4H); 7.88 (br, 4H); 7.60 (br, 2H); 7.51 (br, 2H); 4.70 (br, 1H); 2.38 (br, 2H); 2.00 (br, 2H); 1.20 (m, 24H); 0.80 (t, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 158.26, 157.93, 147.26, 143.11, 141.04, 139.88, 138.93, 131.93, 130.27, 128.77, 137.33, 126.62, 126.28, 125.52, 125.35, 123.93, 123.25, 122.16, 120.80, 119.50, 117.63, 117.22, 115.36, 115.03, 108.75, 106.06, 56.61, 33.89, 31.77, 29.70, 29.48, 29.35, 29.22, 26.87, 24.96, 22.59, 14.04; FTIR (KBr disk cm^{-1}): 3028, 1430, 761, 722, 686, 2919, 2850. Anal. calcd. (%) for $C_{43}H_{47}N_3S_2Se$: C, 68.96; H, 6.33; N, 5.61; S, 8.56; Se,10.54. Found: C, 68.69; H, 6.38; N, 5.64; S, 8.64.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes of monomers and copolymer are outlined in Scheme 1. 2,7-Dibromocarbazole (4) was synthesized according to the literature [14,17] under PPh_3-mediated reductive cyclization. Alkylation of (4) with 9-heptadecane-p-toluenesulfonate afforded N-9′-heptadecanyl-2,7-dibromocarbazole (5) [14]. The Y-shaped long alkyl chain in the carbazole unit makes the polymer with high solubility and relative high molecular weight. 2,7-Bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-N-9″-heptadecanylcarbazole (6) was synthesized through a double lithiation of (5) with LiBu at −78 °C, and subsequent quenching with isopropoxy boronic ester. 4,7-Dibromo-2,1,3-benzothiadiazole (8) was reduced by $NaBH_4$, and subsequently oxidated by SeO_2 to give 4,7-dibromo-



Scheme 1. Synthetic route of monomers and the polymer.

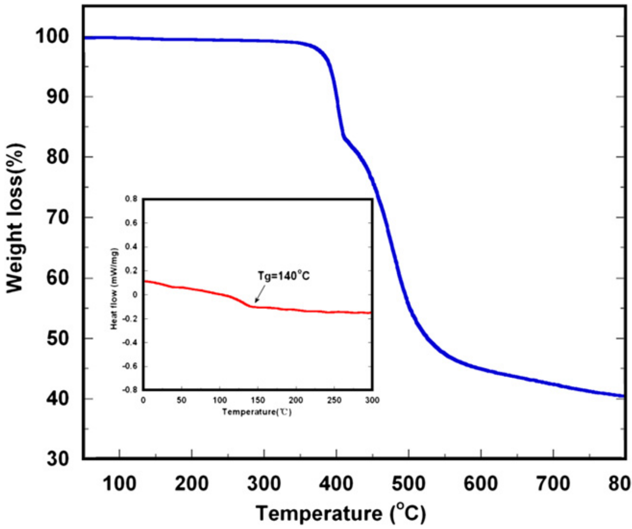


Fig. 1. TGA and DSC plots of PCzDBSe in nitrogen.

2,1,3-benzoselenadiazole (10), which was converted to 4,7-bis(2-thienyl)-2,1,3-benzoselenadiazole (11) by Stille coupling reaction with tri-N-butylstannyl-2-thiophene (7) in the presence of $PdCl_2(PPh_3)_2$, and subsequently brominated by N-bromosuccinimide (NBS) to give 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzoselenadiazole (12). The alternating copolymer was synthesized via a Suzuki polycondensation of (6) and (12).

The weight-average molecular weight (M_w) and number-average molecular weight (M_n) are 17,000 and 14,000 respectively, with a polydispersity (PDI) of 1.21. The copolymer is soluble in common organic solvents, such as chloroform, THF and chlorobenzene.

The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) plots are shown in Fig. 1 and the thermal analytical data are summarized in Table 1. The polymer reveals excellent thermal stability with a high decomposed temperature (corresponding to 5% weight loss) at 390 °C, while the glass-transition temperature is determined at 140 °C.

3.2. Photophysical properties

Fig. 2 shows the UV–vis absorption spectra of PCzDBSe. The polymer presents two absorption bands both in chloroform solution and in thin film, which is in accordance with other D-A copolymers [13,14]. The absorption peak at long wavelength could be attributed to the $\pi-\pi^*$ transition of the low bandgap units, while the absorption peak at short wavelength is possibly the result of the $\pi-\pi^*$ transition of carbazole units [15,19]. We note that the absorption peak of the film is red-shifted 16 nm as compared with that in solution, as a result of the intermolecular interaction in solid state [20]. The optical bandgap of the polymer is 1.73 eV, deduced from the absorption onset of the film at 716 nm. The optical properties of PCzDBSe were summarized in Table 2. The absorption of PCzDBSe has a red-shift of 56 nm compared with that of its BT analogue (PCDTBT) [6,14].

Table 1
Molecular weight and thermal properties of PCzDBSe

Polymer	M_n	M_w	PDI	T_g (°C)	T_d (°C)[a]
PCzDBSe	14,000	17,000	1.21	140	390

[a] Temperature of 5% weight loss.

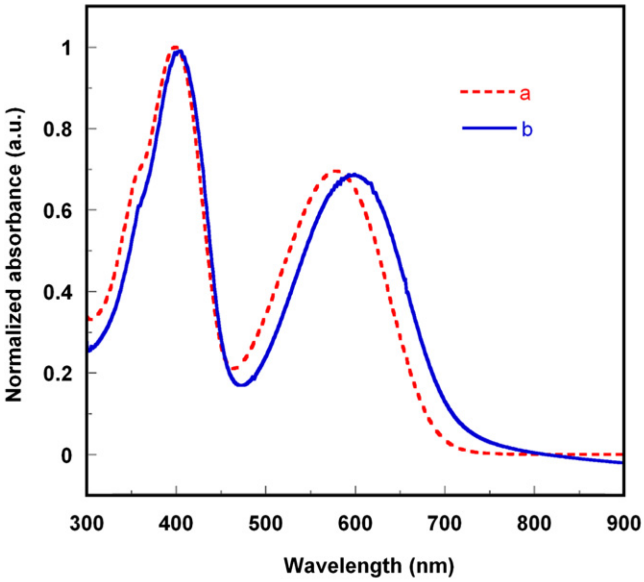


Fig. 2. UV–vis absorption spectra of PCzDBSe in chloroform solution (a) and in thin film (b).

To get an insight into the charge transfer process in the donor–acceptor blend films, the photoluminescence (PL) of blends along with that of the pure polymer has been investigated. As shown in Fig. 3, the PL of the polymer in film locates in the near-infrared region with a maximum emission at 724 nm, and is thoroughly quenched by the addition of 6,6-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) or 6,6-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$), indicating a highly efficient exciton dissociation at the interface between the polymer and PCBM [1]. Therefore efficient PSCs can be constructed based on the PCzDBSe:PCBM blend.

3.3. Electrochemistry

As shown in Fig. 4, the cyclic voltammogram of PCzDBSe presents one oxidation process ($E_{ox}^{1/2} = 1.03$ V) and one reduction process ($E_{re}^{1/2} = -1.17$ V). Based on the recorded oxidation potential, PCzDBSe should show good air stability [21]. From the onset oxidation potential ($E_{ox} = 0.88$ V) and the onset reduction potential ($E_{re} = -0.85$ V) of the polymer, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels were calculated to be −5.28 and −3.55 eV, respectively (Table 2). The HOMO of PCzDBSe is 0.22 eV higher than that of PCDTBT. The corresponding electrochemical bandgap is 1.73 eV, which is similar to the optical bandgap within the experimental error. Given these electrochemical data and the observed PL quenching as shown above in the PCzDBSe:PCBM blend, and taking into account that the LUMO energy of PCBM is −4.3 eV, one can assume that the PCzDBSe can potentially lead to PSCs with PCE over 6% under ideal conditions [22].

Table 2
Absorption and electrochemical properties of the copolymer

Polymer	In $CHCl_3$	In film			p-Doping		n-Doping		E_g^{EC} (eV)
	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	$E_{ox,onset}$ (V)	HOMO (eV)	$E_{re,onset}$ (V)	LUMO (eV)	
PCzDBSe	610	626	716	1.73	0.88	−5.28	−1.17	−3.55	1.73

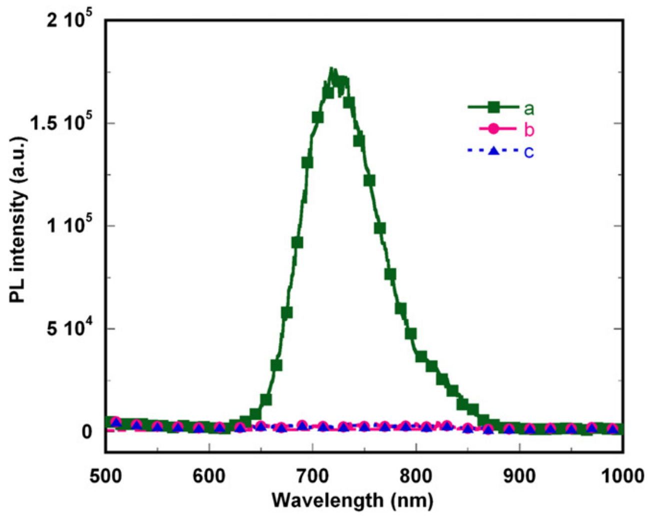


Fig. 3. PL spectra of PCzDBSe (a), PCzDBSe:$PC_{61}BM$ (1:4, w/w) (b), and PCzDBSe:$PC_{71}BM$ (1:4, w/w) (c) blends excited at 325 nm by a HeCd laser.

3.4. *Field effect transistor performances*

Top contact OFET of PCzDBSe was fabricated on pre-treated SiO_2/Si substrates as described in Section 2.3. Fig. 5 shows the output at different gate voltages and the transfer characteristics for OFET using spin-coating PCzDBSe on OTS-treated SiO_2/Si substrates. The copolymer was found to exhibit typical p-type organic semiconductor characteristics, and the hole mobility of PCzDBSe was calculated in the saturated regime at $V_{DS} = -30$ V to be 3.9×10^{-4} cm^2 V^{-1} s^{-1} with a current on/off ratio of 1.4×10^2. The results are consistent with the reported data [11,12], in which the field effect hole mobility of a series of polycarbazole derivatives on OTS-treated SiO_2/Si substrates was found to between 2×10^{-5} cm^2 V^{-1} s^{-1} and 1×10^{-3} cm^2 V^{-1} s^{-1}. The high hole mobility of the PCzDBSe is expected to facilitate charge transport and reduce recombination loss in the PSCs; therefore it can lead to an improved device performance.

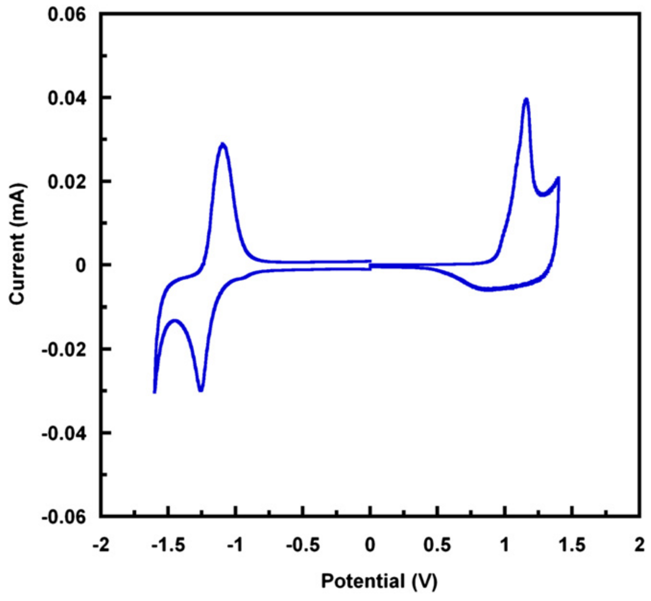


Fig. 4. Cyclic voltammogram of PCzDBSe in acetonitrile solution of 0.1 mol L^{-1} $[Bu_4N]PF_6$.

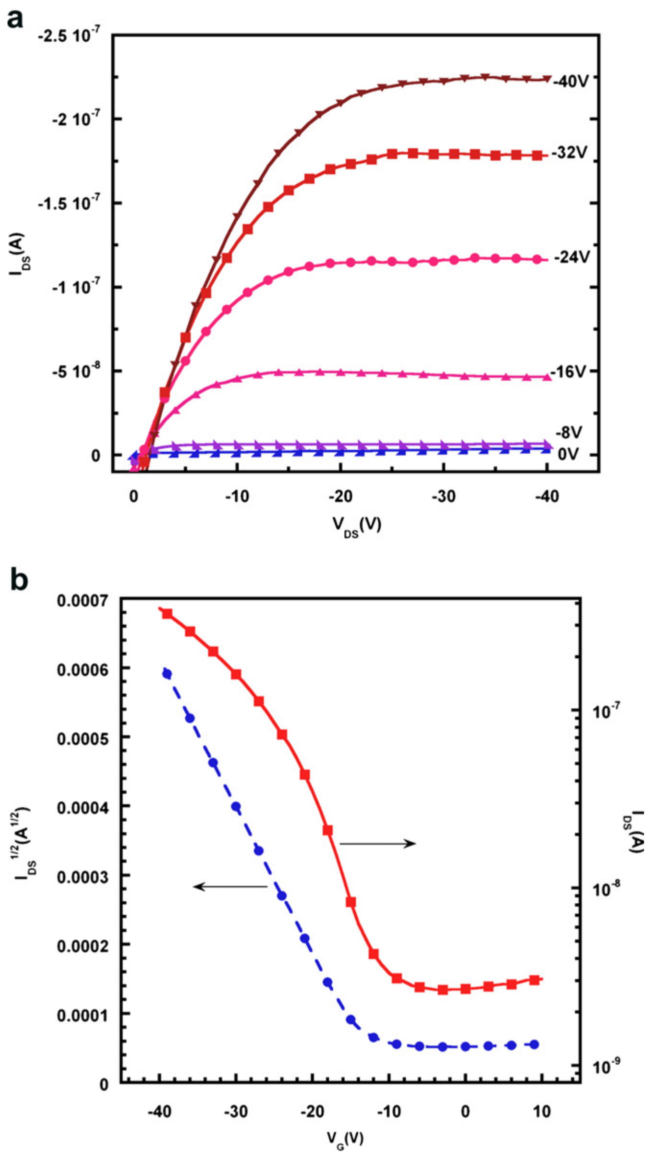


Fig. 5. The output at different gate voltages (V_G) (a) and transfer characteristics in the saturation regime at constant source–drain voltage ($V_{DS} = -30$ V) (b) for OFETs using spin-coated PCzDBSe on OTS-treated SiO_2/Si substrates.

3.5. *Solar cell performances*

PSCs with a device structure of ITO/PEDOT:PSS/PCzDBSe:PCBM/Al were fabricated following the processes described in Section 2.3 and the performances of a series of devices with different donor/acceptor blending ratios by weight are summarized in Table 3 for comparison. On increasing the weight ratio of polymer:$PC_{61}BM$ from 1:1 to 1:4, the PCE increases from 0.39% to 1.46%. This phenomenon is quite common in bulk heterojunction PSCs [23]. A

Table 3
Photovoltaic performances of the PSC devices

Polymer:PCBM (wt/wt)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
1:1[a]	1.63	0.75	32	0.39
1:2	2.17	0.8	38	0.66
1:3	3.35	0.8	42	1.13
1:4	4.15	0.8	44	1.46
1:4[b]	7.23	0.75	45	2.58

[a] $PC_{61}BM$.
[b] $PC_{71}BM$.

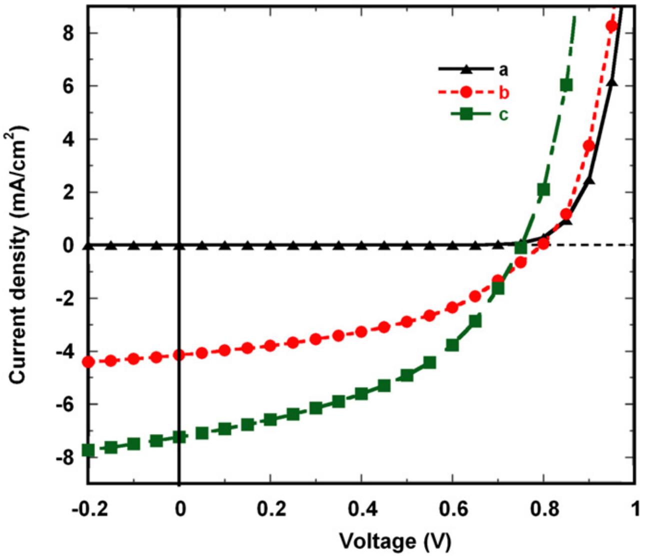


Fig. 6. *I–V* curves of PSCs in the dark (a) and under illumination of AM 1.5G, 100 mW cm^{-2} based on PCzDBSe:PC$_{61}$BM (b), and PCzDBSe:PC$_{71}$BM (c) blends.

typical *J–V* characteristic of the devices under AM 1.5G illumination (100 mW cm^{-2}) and in the dark is shown in Fig. 6. A J_{sc} of 4.15 mA cm^{-2} and a fill factor of 44% are obtained under simulated solar spectra while the V_{oc} of the device is found to be 0.80 V, slightly smaller than that of its BT analogue (PCDTBT, 0.89 V) [14]. The slightly lower V_{oc} in our PCzDBSe devices is probably due to its higher HOMO energy level since it had been suggested that V_{oc} directly correlates with the difference between the LUMO of the acceptor and the HOMO of the donor. When PC$_{61}$BM was replaced by PC$_{71}$BM and used as an electron acceptor in the devices, a significantly improved J_{sc} of 7.23 mA cm^{-2} (Fig. 6) was recorded, due to its unsymmetrical structure with significantly stronger absorption in the visible region (see Fig. 7) [24]. As a result, the overall performance of the device is improved, leading to a PCE of 2.58%.

The external quantum efficiency (EQE) plot of the devices under short-circuit conditions is shown in Fig. 8, in which photoresponse up to 700 nm is clearly displayed. Note that the EQE curve of the devices has two features – a peak around 400 nm and another at 600 nm, closely following the trend observed in the absorption spectra of the PCzDBSe (Fig. 2), indicating that the harvested photons over the entire absorption spectra contribute to the photocurrent. The device exhibits a maximal EQE of 58% at 390 nm and an EQE of 40% at 600 nm. Optimization of PSCs based on PCzDBSe is on the way and it is expected that PCE can be further improved under optimized fabrication conditions (film morphology, thickness of active layer, electrode buffer layer etc.).

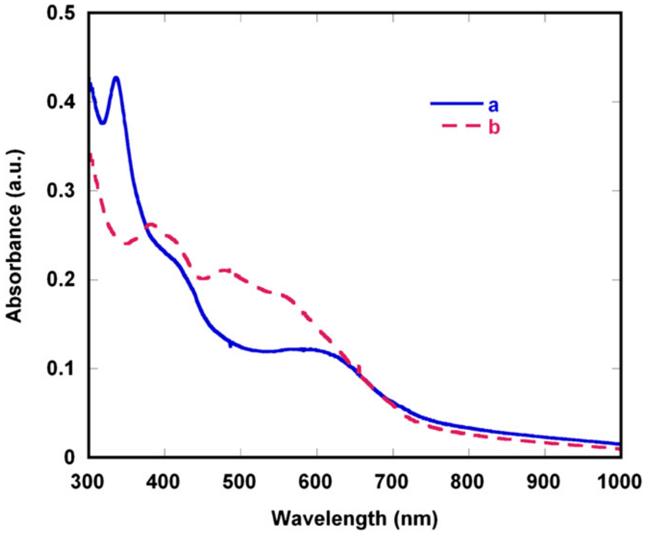


Fig. 7. Absorption spectra of PCzDBSe:PC$_{61}$BM (a) and PCzDBSe:PC$_{71}$BM (b) blends.

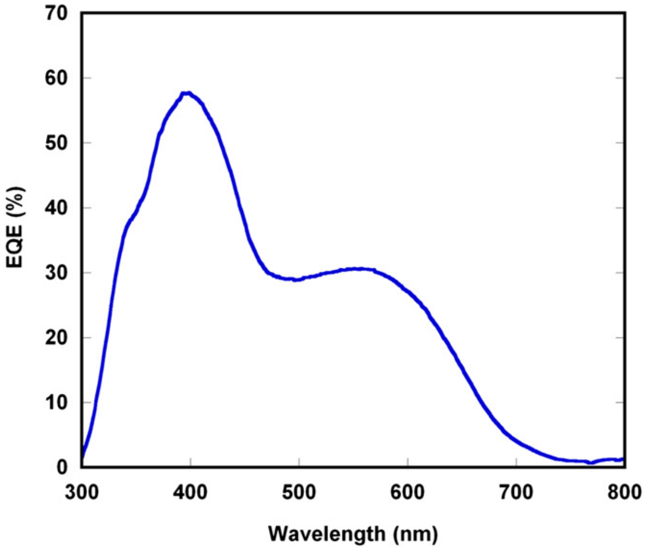


Fig. 8. Photoresponse of PSCs based on PCzDBSe:PC$_{61}$BM (1:4, wt/wt).

4. Conclusion

In conclusion, a novel conjugated alternating copolymer (PCzDBSe) based on N-9′-heptadecanyl-2,7-carbazole and 5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzoselenadiazole) was synthesized by Suzuki polycondensation. Compared with its analogue based on 2,1,3-benzothiadiazole (BT) unit, the absorption onset of the PCzDBSe is red-shifted by 56 nm, extended to 716 nm. The deduced optical bandgap of PCzDBSe is 1.73 eV, which is 0.14 eV narrower than that of PCDTBT. The hole mobility of PCzDBSe as deduced from a solution-processed OFET was found to be 3.9×10^{-4} cm^2 V^{-1} s^{-1}. V_{oc}, J_{sc} and FF of the devices fabricated from the PCzDBSe are 0.75 V, 7.23 mA cm^{-2}, and 45%, respectively, leading to a power conversion efficiency (PCE) of 2.58%.

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