

Polyselenopheno[3,4-*b*]selenophene for Highly Efficient Bulk Heterojunction Solar Cells

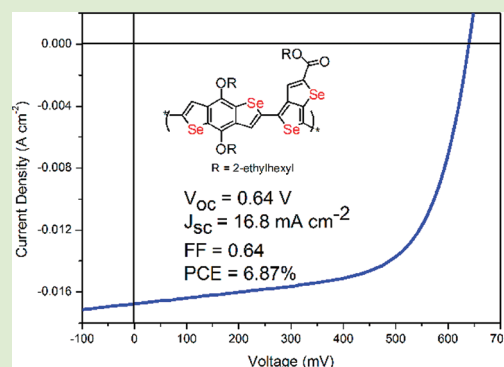
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S Supporting Information

ABSTRACT: Herein we describe the synthesis of a new series of copolymers (PSeB x) containing selenopheno[3,4-*b*]selenophene and benzodiselenophene, which exhibited a high power conversion efficiency (PCE) of 6.87% in a bulk heterojunction (BHJ) solar cell device (PSeB2/PC₇₁BM). In comparison with its thiophene analogue, PTB9, the new polyselenopheno[3,4-*b*]selenophene-*co*-benzodiselenophene (PSeB2) showed a lower band gap and improved charge carrier mobility as high as $1.35 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.



The bulk heterojunction solar cell device architecture is known to represent a promising alternative to inorganic *p-n* junction solar cells.^{1–10} However, the low dielectric constant of most organic materials relative to those of inorganic materials has a detrimental effect on charge carrier mobility and impedes charge separation, thus, limiting PCEs obtained from polymer solar cells.^{11–13} It is generally accepted that a PCE of around 10% will be required to commercialize organic photovoltaic devices; thus, much research effort has been devoted to improving PCE to this level.^{4,5} In general, a polymer's physical properties determine the open-circuit voltage (V_{oc}), the short-circuit current density (J_{sc}), and the fill factor (FF), and the PCE is defined as $P_{out}/P_{in} = V_{oc}J_{sc}FF/P_{in}$. Thus, the research on developing novel semiconducting polymers has focused on (1) lowering the band gap to enhance the J_{sc} and (2) lowering the energy level of the highest occupied molecular orbital (HOMO) to improve the V_{oc} .

Previously, our group reported PCEs of nearly 8% for the PTB series of polymers based on benzodithiophene (BDT) and thieno[3,4-*b*]thiophene (TT) units.^{14–17} Herein we describe the synthesis of a new series of polymers in which selenium atoms are introduced to replace the sulfur atoms on the thienothiophene units. We developed this series based on the following: (1) the selenium-based polymers should have lower band gaps than the sulfur based analogues and (2) selenium is more polarizable than sulfur, thus, the interchain Se...Se interactions will improve hole mobility. Three new polymers were synthesized, namely, polyselenopheno[3,4-*b*]selenophene-*co*-benzodithiophene (PSeB1), polyselenopheno[3,4-*b*]selenophene-*co*-benzodiselenophene (PSeB2), and polythieno-

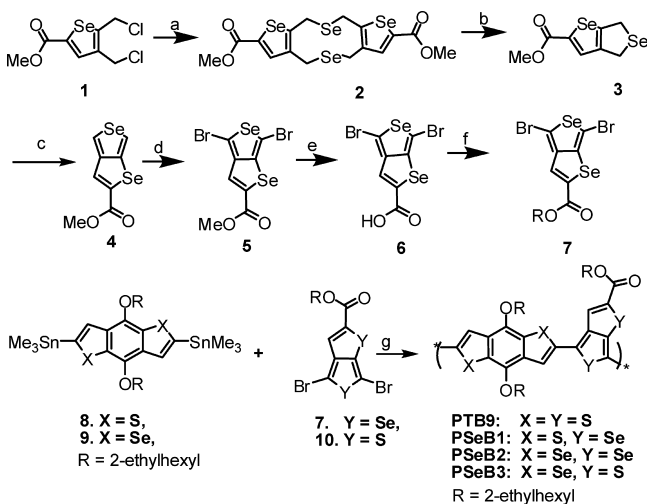
[3,4-*b*]thiophene-*co*-benzodiselenophene (PSeB3; Scheme 1). Significant PCE enhancement was observed in these polymers when compared with their sulfur analogue (PTB9; Scheme 1). BHJ devices with promising PCEs of 6.87% were achieved when PSeB2 was blended with PC₇₁BM, an almost 21% increase in PCE from the corresponding PTB9 polymer. Most importantly, very high short circuit current density ($J_{sc} \sim 16.8 \text{ mA cm}^{-2}$ from PSeB2) was observed in these polymers.

The synthesis of the selenium monomers is detailed in the Supporting Information (SI). The approach used for the synthesis of ethylhexyl 4,6-dibromoselenolo[3,4-*b*] selenophene carboxylate monomer 7 is shown in Scheme 1. Sodium selenide was prepared by slow addition of sodium borohydride to a mixture of selenium powder in a basic aqueous solution. The resultant colorless aqueous Na₂Se solution was added dropwise into an ethanol solution of 2,3-bis(chloromethyl)-5-carbomethoxyselenophene 1¹⁸ over 30 min, which resulted unexpectedly in the formation of the dimer 2 in 73% yield. However, this was then converted into the desired dihydroselenoselenophene 3 in good yield (56%) under reduced pressure via flash pyrolysis.^{19,20} Aromatization of 3 by oxidation using H₂O₂ gave the *N*-selenoxide. This compound, upon careful treatment (to prevent decomposition of starting material due to instant spontaneous exothermic reaction) with cold acetic anhydride gave the corresponding methyl selenolo[3,4-*b*]thiophene carboxylate 4. Bromination using NBS gave the methyl 4,6-

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Scheme 1. Synthesis of Monomer 7 and Stille Polycondensation of Polymers PSeBx and PTB9^a


^aReagents and conditions: (a) Na₂Se, ethanol, 73%; (b) under vacuum, 600 °C, 56%; (c) H₂O₂, THF, Ac₂O, 62%; (d) NBS, DMF, 80%; (e) LiOH·H₂O, 1 M HCl, 85%; (f) 2-ethyl-1-hexanol, DCC, DMAP, 88%; (g) 7, Pd(PPh₃)₄, toluene, DMF, 120 °C, 92%.

dibromoselenolo[3,4-*b*]thiophene carboxylate 5, which upon hydrolysis under basic conditions yielded 4,6-dibromoselenolo[3,4-*b*]thiophene carboxylic acid 6. To enhance the solubility of the polymer, carboxylic acid 6 was esterified by the branched 2-ethyl-1-hexanol using DCC and DMAP to give the

corresponding ethylhexyl 4,6-dibromoseleno[3,4-*b*]thiophene carboxylate 7 monomer in a high yield (88%).

The synthesis of monomer 9 is detailed in the SI. Polymerization was carried out via Stille polycondensation.²¹ The weight-average molecular weights (M_w) for PSeB1, PSeB2, PSeB3, and PTB9, as characterized by gel permeation chromatography (GPC), were 15.4×10^3 , 41.0×10^3 , 52.1×10^3 , and 74.0×10^3 g mol⁻¹ with PDIs of 1.68, 2.68, 1.85, and 2.08, respectively. Thermal gravimetric analysis (TGA) indicates that the polymers are stable up to 200 °C. The UV-vis spectra in chloroform solution showed absorption maxima at 702, 712, and 697 nm, respectively (PTB9-672 nm; Figure 1a). The absorption spectra of the solid polymer films showed a slight red shift to 708 nm for PSeB1 and PSeB3 polymers, but for PSeB2 and PTB9 films, the maximum absorption values were still around 712 and 672 nm without any red shift when compared to the solution state (Figure 1b). After mixing with PC₇₁BM, PSeB1 and PSeB3 blend films showed minimal shifts when compared with the pristine polymer films, but the maximum absorption of PSeB2 showed a red shift of approximately 12 nm to 724 nm after blending with PC₇₁BM (Figure 1c). This extended absorption and was expected to improve the overall device PCE. An optical band gap of 1.60 eV (Figure 1b) was estimated based on the spectral onset, verifying our presumption about the effect of selenium on the polymer bandgap. The electrochemical behavior of the polymer thin films on a glassy carbon electrode was investigated using cyclic voltammetry. The energy levels of the frontier molecular orbitals can be deduced from the onset point using the equation of $E_{LUMO} = -(4.71 + E_{red})$ and $E_{HOMO} = -(4.71 +$

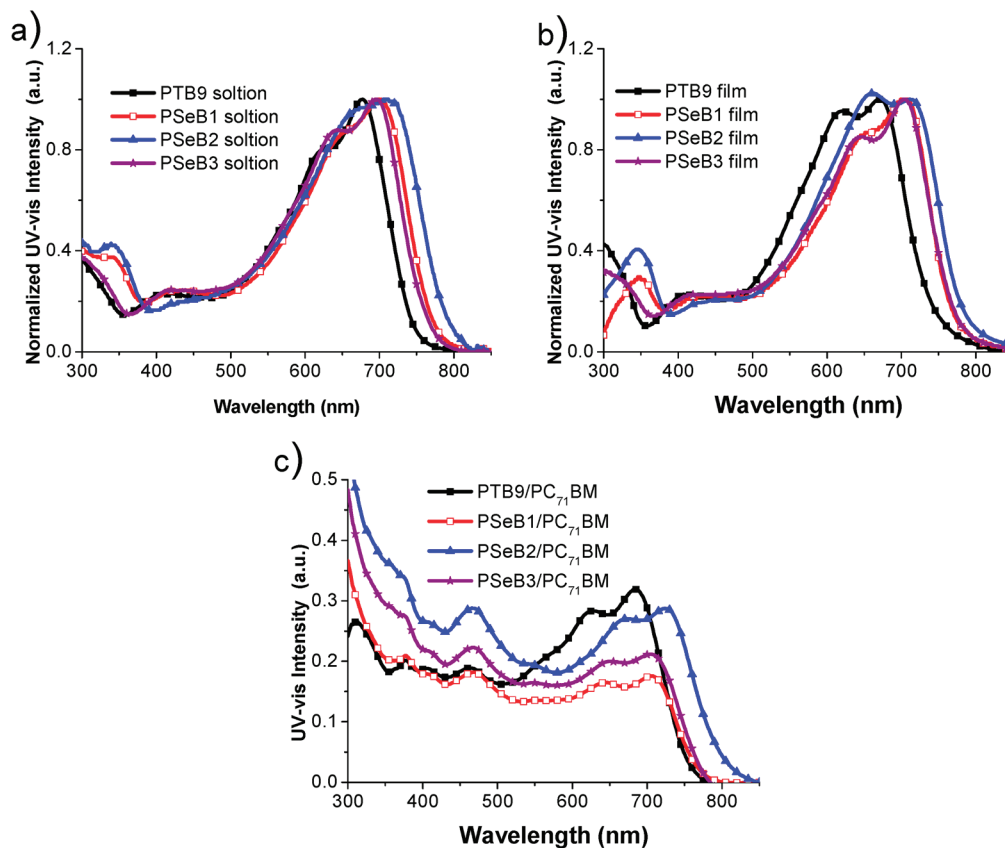


Figure 1. (a) UV-vis spectra of polymers in CHCl₃ solution; (b) UV-vis spectra of polymer films; (c) UV-vis spectra of polymer/PC₇₁BM films (PTB9, black line; PSeB1, red line; PSeB2, blue line; PSeB3, purple line).

E_{ox}). The calculated lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels for PTB9 were -3.13 eV and -5.00 eV, respectively, while those for PSeB1 were -3.27 and -5.05 eV, respectively, and those for PSeB2 are -3.26 and -5.04 eV, respectively, while those for PSeB3 were -3.27 and -5.05 eV. A band gap of 1.78 eV was obtained for all selenium containing polymers, which was about 0.08 eV smaller than that of PTB9 polymer.

Photovoltaic effects of these polymers were investigated in BHJ polymer solar cells with the device structures of (ITO/PEDOT)/(PSS/polymer)/(fullerene/Ca/Al). The active layer was spin-cast by using the weight ratio of 1:1, 1:1.2, and 1:1.5 for polymer to PC₆₁BM and PC₇₁BM, respectively. Figure 2a

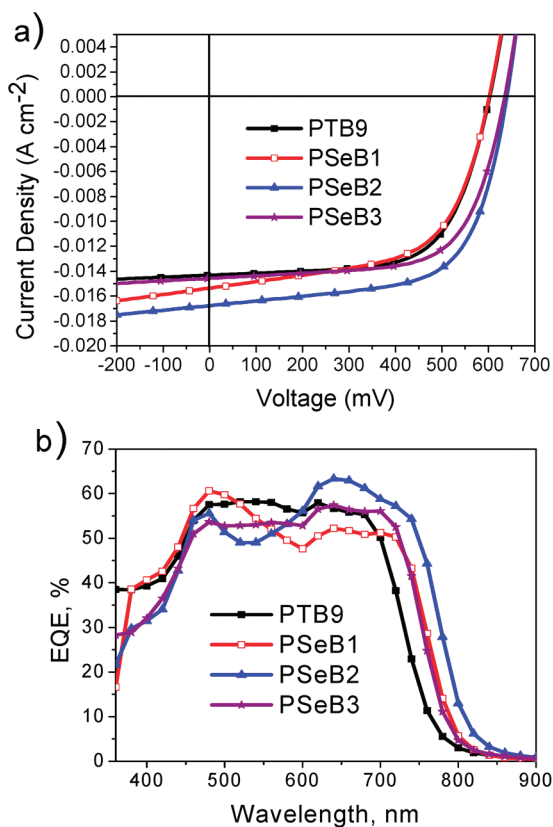


Figure 2. (a) Current–voltage characteristics of polymer solar cells under AM 1.5 G condition (100 mW cm^{-2}). (b) External quantum efficiency (EQE) of polymer solar cells (PTB9, black line; PSeB1, red line; PSeB2, blue line; PSeB3, purple line).

shows the plot of the photocurrent density versus voltage recorded under the AM 1.5 G irradiation at different solvent processing conditions for all polymers. The corresponding physical parameters are shown in Table 1. The parameters for each device are listed in the SI. Use of chlorobenzene (CB) with 1,8-diiodooctane (DIO) as an additive yielded superior results for all polymers.

The blend films of PSeB1/PC₆₁BM prepared from the solvent of CB and *o*-dichlorobenzene (DCB) were investigated. Both the V_{oc} and J_{sc} obtained using CB were much higher than that obtained with DCB, indicating CB is a better solvent for this system. Addition of DIO (2% v/v) into CB and DCB effectively enhanced the fill factor (FF), leading to a high PCE of 5.33% from CB/DIO solution. DIO showed no apparent

Table 1. Optimized Solar Cell Parameters of Devices with New Donor Polymers

entry	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF	PCE_{avg} (%)	PCE_{max} (%)
PTB9 ^a	603	14.3	0.66	5.54	5.66
PSeB1 ^b	602	15.4	0.59	5.39	5.47
PSeB2 ^c	640	16.8	0.64	6.46	6.87
PSeB3 ^d	635	14.6	0.66	5.84	6.13

^a1:1.5 PTB9/PC₇₁BM. ^b1:1.2 PSeB1/PC₇₁BM. ^c1:1.2 SeB2/PC₇₁BM. ^d1:1.5 PSeB3/PC₇₁BM. The cosolvent used here is CB/2%DIO (v/v).

effect on the V_{oc} . Because PC₇₁BM has better absorption in the visible region while maintaining similar electronic properties as PC₆₁BM, the active layer was prepared by using the weight ratio of PSeB1/PC₇₁BM at 1:1.2. A high J_{sc} of 15.4 mA cm^{-2} was obtained. The device had a V_{oc} of 602 mV, a FF of 0.59, and resulted in a very promising PCE of 5.47%. Devices fabricated under similar conditions with the other polymers also yielded very high values (Table 1).

Similar to PSeB1, BHJ solar cells with PSeB2 cast in CB showed superior performance compared to those from DCB. Using DCB with DIO as an additive led to a V_{oc} of 628 mV, a J_{sc} of 13.3 mA cm^{-2} , a FF of 0.58, and a PCE of 4.82%. When DCB was replaced by CB, J_{sc} increased to 16.8 mA cm^{-2} , similar to the increase we found in PSeB1. However, the FF increased to 0.64, while the V_{oc} remained relatively unchanged. This is in stark contrast with PSeB1, which exhibited an increase in V_{oc} and J_{sc} with a static FF when switching from DCB to CB. Under these optimum conditions, PSeB2 provided a PCE of 6.87%, which was considerably higher than the 5.47% exhibited by PSeB1. PSeB3 was studied to compare the importance of Se placement on the polymers. Devices fabricated using PC₆₁BM as an acceptor from CB/DIO solution exhibited relatively poor performance with a low FF of 0.43. J_{sc} was only 12.0 mA cm^{-2} . V_{oc} was moderately high at 597 mV to yield a PCE value of 3.11%. To achieve maximum PCE values, we found that using PC₇₁BM as an acceptor in a 1:1.5 ratio yielded optimum results. Devices fabricated under these conditions had an increased V_{oc} of 635 mV. The J_{sc} and FF , on the other hand, dramatically increased to 14.6 mA cm^{-2} and 0.66, respectively. This nearly doubled the PCE value of the device to 6.13%.

The EQE values for both PSeB1 and PSeB2 under optimized conditions were measured and found to be nearly identical (Figure 2b). Both span a wide range of wavelengths (350 – 800 nm) with a maximum at 645 nm. The maximum EQE value is 63% for PSeB1 and 61% for PSeB2, respectively. The trace for PSeB2 is slightly red-shifted compared to that of PSeB1, which is due to PSeB2's absorbance being red-shifted (Figure 1b). This enables PSeB2 to harvest a broader span of energy compared to PSeB1. The EQE values for PTB9 and PSeB3 are somewhat more level across the active spectral region (Figure 2b). Again we see that the selenium polymer has a red-shifted active region due to the broader absorption of the polymer.

Transmission electron microscopy (TEM) was performed to study the morphology of blend films (Figure 3). The PSeB1/PC₇₁BM film cast from CB without the DIO additive exhibited a coarse morphology, indicating the formation of large separate domains of aggregated polymer and fullerene. PSeB1/PC₇₁BM films cast from CB/DIO exhibited uniform and fine features, indicating nanoscale phase separation and resulted in an effective donor–acceptor interaction. This characteristic feature facilitates the charge separation. Detailed structural character-

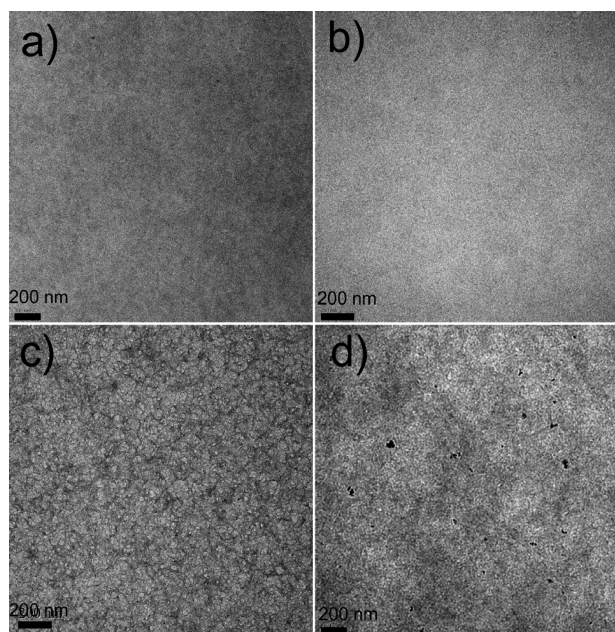


Figure 3. TEM images of the active layer deposited with optimized conditions with (a) PTB9, (b) PSeB1, (c) PSeB2, and (d) PSeB3. The scale bar is 200 nm.

ization using grazing incidence wide-angle X-ray scattering (GIWAXS) is under way. The hole mobilities of PSeB1 and PSeB3 were determined by using the space charge limited current (SCLC) method, which were found to be $\sim 3.2 \times 10^{-4}$ and $3.45 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. These values fall in the same level as that of the PTB9 polymer ($4.08 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The PSeB2/PC₇₁BM film cast from CB/DIO showed a surprisingly coarse morphology, despite being structurally similar to PSeB1. Indeed, its morphology was closer to that of the PSeB1/PC₇₁BM film cast from CB without the DIO additive (SI). However, the PSeB2/PC₇₁BM films cast from CB/DIO exhibited a high PCE, which was in stark contrast to our observations of the PTB series of polymers. The hole mobility of PSeB2 was about $1.35 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, much higher than that of other three polymers, which would definitely favor the charge transportation in the blend film and result in high solar cell performance.

Numerous theoretical studies have hypothesized that selenophene derivatives would exhibit superior oxidative and charge-transferring properties compared to their thiophene counterparts.^{22–25} A few selenophene polymers have been synthesized, which demonstrated a decreased E_g and higher hole mobility, which would suggest that polyselenophenes could be ideal in bulk-heterojunction solar cells.^{23,26} Direct comparisons between polythiophenes and polyselenophenes in such devices are rare. Despite their promising characteristics, many polythiophenes have been shown to outperform their polyselenophene counterparts in organic solar cell (OSC) devices. McCulloch et al. found that regioregular (rr) poly(3-hexylselenophene) had a much lower PCE compared to rr poly(3-hexylthiophene), despite having a lower E_g .^{27,28} This was attributed to poor film morphology of the polyselenophene. Our own results would indicate that polyselenophenes tend to aggregate into large domains in the solid state, however, the high polarizability of the Se atoms as well as the high mobility provided by the Se...Se contacts create a large J_{sc} which results in high PCE values for the PSeB2 polymer.

In summary, the results described above unambiguously disclosed the potentials of these novel semiconducting polymers as the active components in BHJ solar cells. Preliminary photovoltaic study indicates that the PSeB2 is a very promising material for BHJ solar cells. An excellent PCE of 6.87% was achieved after blending with PC₇₁BM, a 21% enhancement in PCE from the corresponding sulfur version. The high PCE is clearly the result of a synergistic effect combining various physical properties including band gap, charge carrier mobility, and optimal overlap of optical absorption with the region of maximum solar photon flux. All of these parameters underscore the promise of selenium-based polymers for highly efficient organic solar cells.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures, synthesis of monomers and polymers, detailed device results, cyclic voltammograms, and TEM experiments are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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