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# Synthesis, Characterization, and Field Effect Transistor Properties of Regioregular Poly(3-alkyl-2,5-selenylenevinylene)

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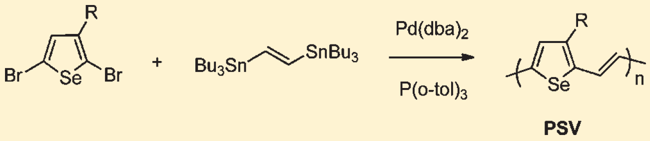
S *Supporting Information*

**ABSTRACT:** Here we report the synthesis of novel poly(3-alkyl-2,5-selenylenevinylene)s (PSV) by the polymerization of 2,5-dibromo-3-alkylselenophene and (*E*)-1,2-bis(tributylstannyl)ethylene under microwave-assisted Stille coupling conditions. Polymers containing hexyl and decyl side chains were prepared. The decyl-substituted polymer exhibited good solubility in common organic solvents, and $^1$H NMR analysis indicated a side-chain regioregularity in excess of 90%. The polymer exhibits an absorption maxima at 621 nm in solution, with a significant red shift in absorption upon film formation. Thin film transistors fabricated from PSV exhibited hole carrier mobilities up to 0.01 cm$^2$/(V s). The polymer displayed balanced ambipolar performance when hydroxyl free organic dielectrics were used as the gate insulator.



## INTRODUCTION

Thiophene-containing conjugated polymers have been the subject of intensive research over recent years as a result of their interesting optical and electronic properties. A variety of approaches have been investigated to tune their properties for application in a number of areas, for example as the active layer in organic field effect transistors, organic solar cells, organic light-emitting diodes, or photochromic devices.[1−3] One promising class of material for these applications is poly(thienylenevinylene) (PTV).[4] The unsubstituted polymer is insoluble in common organic solvents which renders it of limited practical application. However this can be overcome by preparing thin films of PTV *in situ* by the use of a soluble precursor polymer, which can be thermally converted into the active material after deposition. The resulting polymer displays high hole charge carrier mobility in field effect transistors,[5] good electrical conductivity upon doping with oxidizing agents,[6] and promising performance in organic solar cells.[7,8] Solution-processable polymers have also been developed in order to avoid the requirement for high-temperature thermal treatments. The inclusion of a single solubilizing chain onto the thiophene ring affords a noncentrosymmetric polymer which can be polymerized to afford both regioregular and regiorandom regiochemistries of the side chains.[9−12] The regioregular polymers have small optical band gaps and have shown promising performance as the donor material in bulk heterojunction organic solar cells when blended with PCBM.[13−17] Disubstituted thiophenes have also been used as comonomers to avoid the issue of side-chain regioregularity.[12]

In contrast to their thiophene analogues, selenophene-containing polymers have been far less studied,[18,19] perhaps due to the additional synthetic complexity involved in their preparation.[20] Theoretical calculations have predicted that selenophene-containing polymers are expected to have a reduced optical band gap in comparison to their thiophene analogues, while the inclusion of the larger more polarizable selenium atom may be expected to have a significant influence on the charge transport behavior.[21] We recently reported that the selenophene analogue of the well-investigated poly(3-hexylthiophene), poly(3-hexylselenophene) (P3HS), was a promising low band gap material for organic solar cells.[22−24] Selenophene substitution results in a reduction of band gap of 0.3 eV, mainly as a result of the stabilization of the polymer LUMO (lowest unoccupied molecular orbital).[21,22] Poly(3-octyl)selenophene and related selenophene copolymers also exhibit high electron charge carrier mobility and ambipolar behavior in organic field effect transistor devices.[25] Again, the low-lying LUMO energy levels are thought to both facilitate electron injection and transport. Polymers containing fused selenolo[3,2-*b*]thiophene,[26] selenolo[3,2-*b*]selenophene,[27] benzodiselenophene[28] and biselenophene comonomers[29,30] have demonstrated high hole carrier mobility in transistor devices. Oxygen- and sulfur-substituted selenophene polymers have also shown recent promise as electrochromic[31−35] and hole conducting[36,37] materials. However, despite the interest in PTV, the selenophene analogues have, to our knowledge, not yet been reported. Here we report

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the first synthesis and characterization of regioregular poly(3-alkyl-2,5-selenylenevinylene) (PSV).

## RESULTS AND DISCUSSION

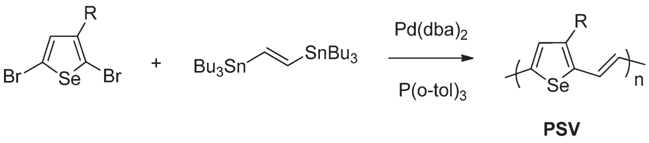
The synthesis of regioregular poly(3-alkyl-2,5-selenylenevinylene) is shown in Scheme 1. 3-Hexyl- and 3-decylselenophene were prepared as previously reported.[20] Bromination with 2 equiv of *N*-bromosuccinimide in THF afforded the 2,5-dibromo-3-alkylselenophenes in good yield. Following previous protocols for the synthesis of PTV, polymerization was performed by a Stille cross-coupling with (*E*)-1,2-bis(tributylstannyl)ethylene in the presence of a Pd(0) catalyst.[9] Our initial attempts focused upon reaction of the hexyl-substituted monomer.

Polymerization under the conditions previously reported for the thiophene analogue ($Pd_2(dba)_3/Ph_3As$ in NMP, 100 °C for 12 h[9]) afforded a sparingly soluble polymer, which was purified by precipitation into methanol and then Soxhlet extraction with acetone to remove catalyst residues. The resulting polymer had a rather low molecular weight by high-temperature GPC against polystyrene standards ($M_n$ 7.6 kDa, $M_w$ 12 kDa). We attribute the low molecular weight to the poor solubility of the polymer in the polar NMP solvent used for the polymerization resulting in precipitation of the growing chain. Attempts to increase the molecular weight by changing the solvent to the less polar chlorobenzene resulted in the isolation of mainly insoluble material, presumably due to the high polymer molecular weight. Changing the catalyst to $Pd(dba)_2/(o\text{-tol})_3P$ and reducing the reaction time by microwave heating[38] was more successful, resulting in good molecular weights, following precipitation and extraction of low weight material ($M_n$ 18 kDa, $M_w$ 45 kDa). However, the hexyl-substituted polymer had poor solubility in most organic solvents, only dissolving at high temperature (>140 °C) in chlorinated solvents like 1,2,4-trichlorobenzene. We therefore prepared the decyl-substituted polymer, P3DSV, using the optimized microwave conditions in good yield (80%) and reasonable molecular weight ($M_n$ 25 kDa, $M_w$ 62 kDa). The resulting P3DSV was soluble in lower boiling point solvents like chloroform or toluene.

The regioregularity or percentage of head-to-tail couplings of the decyl side chains of the P3DSV polymer was investigated by $^1H$ NMR in chloroform at 50 °C, chlorobenzene at 80 °C, and tetrachloroethane at 130 °C. Interpretation of the spectra was complicated by the fact that the polymers aggregated strongly in solution, even upon warming, which resulted in broadening of peaks and some loss of resolution. Nevertheless, three signals can clearly be resolved in the $CDCl_3$, as broad doublets at 6.80, 6.89, and a broad singlet at 6.96 ppm, which we attribute to the two vinyl protons on the conjugated backbone and the 4-proton on the selenophene ring (Figure 1). These occur at similar shifts to the regioregular PTV analogue.[9] The methylene protons were also clearly observable as a broad peak at 2.61 ppm, similar to PTV. We do not see appreciable contribution from methylene protons around 2.5 ppm, which have been attributed to head-to-head/tail-to-tail couplings in PTV.[9] The aromatic region is more clearly resolved in tetrachloroethane at 130 °C, in which the two vinyl protons can be resolved as doublets at 6.92 and 7.00 ppm, with the aromatic proton observable as an overlapping singlet at 7.08 ppm (Figure S4).

Regioregularity in the analogous PTV has been assigned by integration of the main methylene signal at 2.6 ppm against the upfield protons associated with miscouplings around 2.5 ppm. In the present case the poor resolution of the methylene signals in $CDCl_3$ makes estimation difficult, so higher temperature spectra were also obtained in deuterated chlorobenzene at 80 °C and deuterated tetrachloroethane at 130 °C (Figures S3 and S4). In both cases the methylene peak was sharper, although the expected triplet was still poorly resolved. In chlorobenzene at 80 °C, a small peak is distinguishable just upfield of the methylene signal at 2.79 ppm (Figure S3). Integration of the two signals gives an estimated regioregularity of at least 90%. This high regioregularity is in agreement with other measurements (*vide infra*) which suggest a degree of polymer ordering that would not be expected in a regiorandom polymer. Attempts to obtain $^{13}C$ NMR were unsuccessful, with only signals from the side chain being resolved even with long acquisition times (overnight) in chloroform at room temperature. Shorter runs at elevated temperature were also uninformative. This is not uncommon in conjugated polymers which have a high tendency to aggregate in solution.

**Scheme 1. Synthetic Route to Poly(3-alkyl-2,5-selenylenevinylene)**



Similarly high regioregularities have been observed in the polymerization of 2,5-dibromo-3-dodecylthiophene with (*E*)-1,2-bis(tributylstannyl)ethylene.[9] The high regioregularity is likely a result of a number of factors. First, in analogy to the thiophene system, the bromine in the 5-position group is likely to show higher reactivity toward oxidative addition of the palladium catalyst than the more sterically hindered 2-bromo substituent.[39,40] Second, it has been reported that the cross-coupling of the first tributylstannyl group is much faster than the second in 1,2-bis(tributylstannyl)ethylene.[41] Taken together, these factors may result in the preferential *in situ* formation of 5-(2′-tributylstannylvinyl)-2-bromo-3-alkylselenophene, which is then able to self-polymerize in a regioselective manner.

The absorption spectra of regioregular P3DSV in solution and as a thin film are shown in Figure 2. In solution maximum absorbance is at 621 nm, with a prominent shoulder at 670 nm. The higher energy shoulder is typically associated with vibronic coupling and is suggestive of some degree of structural order even in solution.[42] Spun-cast films show a considerable broadening and red shift of absorbance, with a maxima at 653 nm and a pronounced shoulder at 730 nm, as well as additional shoulders below the absorption peak. This suggests enhanced structural ordering in the solid state compared to solution. For PTV, it has been shown that the regiorandom polymer exhibits only a small red shift (20 nm) in absorption maxima on going from solution to the solid state, with no observation of longer wavelength shoulders, whereas the regioregular polymer exhibits a larger shift and the observation of pronounced long wavelength vibronic shoulders.[10] Together with the NMR data, this suggest that PSV is synthesized with a high degree of regioregularity.

The onset of absorption for PSV is 775 nm, corresponding to an optical band gap of 1.6 eV. Compared to the analogous regioregular alkyl-substituted P3ATV's, which have a reported

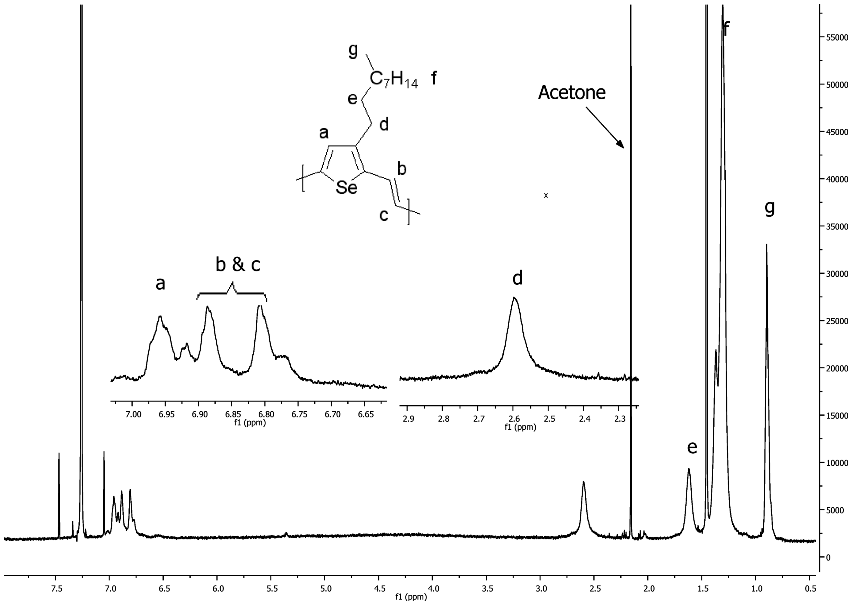


**Figure 1.** $^1$H NMR of P3DSV in $CDCl_3$ at 50 °C.

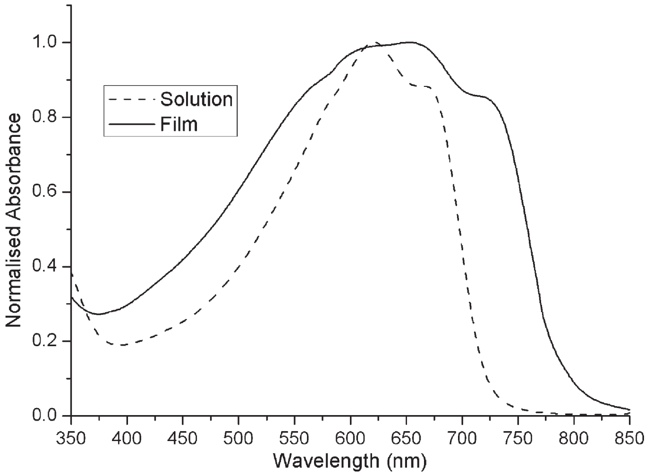


**Figure 2.** UV–vis spectra of P3DSV in 1,2,4-trichlorobenzene (dashed) and solid state (solid).

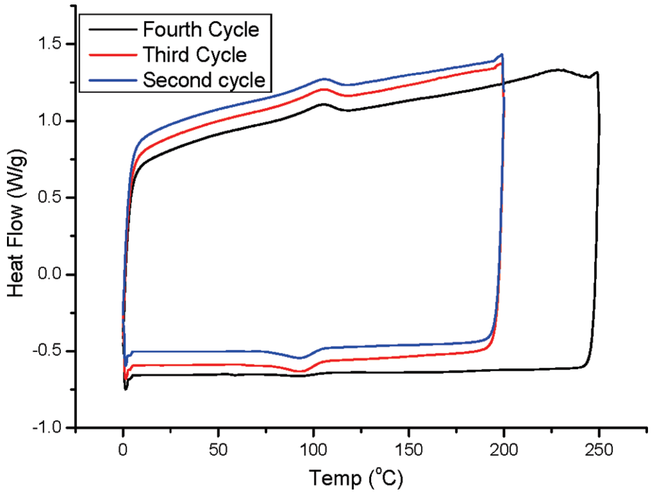


**Figure 3.** DSC plots (endo up) showing the second, third, and fourth heating/cooling cycle at 10 °C/min for P3DSV.

maximum absorbance of 577 nm in solution, and between 607 and 616 nm as a thin film,[9,10,15,42] it is apparent that selenophene substitution results in a considerable reduction in optical band gap in common with other selenophene copolymers.

The ionization potential for P3DSV as a thin film, as measured by photo electron spectroscopy in air (PESA), was 4.95 eV (Figure S2). PESA uses a low-power, tunable UV source to generate photoelectrons that ionize oxygen molecules that are in turn detected by an open counter.[43] It has previously been shown that ionization potentials determined by PESA are comparable with those obtained by other techniques.[44]

The thermal properties of P3DSV were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA (Figure S1) shows the onset of decomposition occurring around 250 °C with 5% weight loss occurring at 380 °C. The DSC of a cast film (Figure 3) shows an endothermic transition at 104 °C upon heating, with an exotherm upon cooling at 93 °C. These transitions were thermally stable and observable upon repeated cycling up to 200 °C. However, if the temperature was then increased to 250 °C, an endotherm was apparent at 240 °C upon initial heating, but the exotherm at 93 °C was not observed upon subsequent cooling, and the peaks at 104 and 240 °C were not observed upon further heating. This, in combination with the TGA, suggests an irreversible change in the polymer upon heating above 240 °C and may be indicative of some chemical cross-linking or degradation occurring. Similar changes have been observed in PTV polymers.[45]

The charge transport properties of P3DSV were investigated in both bottom and top gate transistor configurations. Bottom gate (doped Si), bottom contact (Au) devices were fabricated by spin-coating hot solutions in 1,2,4-trichlorobenzene, followed

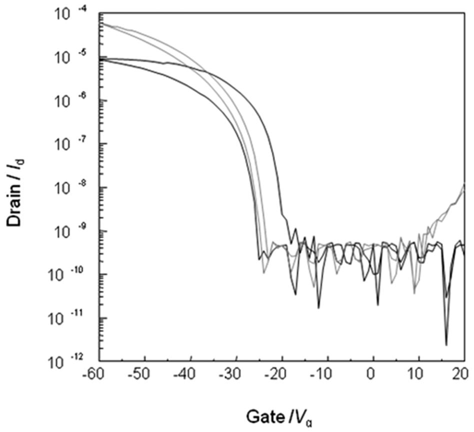


**Figure 4.** Transfer (left) and output (right) characteristics on bottom gate, bottom contact devices treated with OTS ($L$ = 10 $\mu$m, $W$ = 10 mm).

by drying at 100 °C for 20 min in nitrogen. The $SiO_2$ dielectric was treated with either octadecyltrichlorosilane (OTS) or HMDS prior to semiconductor deposition, to both passivate the $SiO_2$ surface and enhance the ordering of the semiconductor at the dielectric interface. The resulting devices showed p-type transistor behavior, with saturated hole mobilities up to 0.01 $cm^2/(V\ s)$ and on/off ratios of $10^5$ observed with the OTS-treated devices (Figure 4). HMDS-treated devices exhibited a slightly worse performance with saturated mobilities around 0.005 $cm^2/(V\ s)$, possibly as a result of reduced order at the dielectric/semiconductor interface. There was no evidence of electron transport in either device, possibly due to difficulties injecting electrons into the LUMO of the polymer from the Fermi level of the Au (~4.8 eV) source/drain electrodes and/or due to electron trapping at the interface due to free silanol surface groups as a result of incomplete OTS coverage.[46,47]

In order to investigate the possible electron transporting characteristics of P3DSV, bottom gate, top contact devices were investigated. A thin layer of the cross-linkable dielectric divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) was used as the passivation layer of the $SiO_2$, since it is known to contain very few electron trapping groups.[47] Low workfunction (~2.9 eV) bilayer Ca/Al electrodes were deposited by shadow masking under high vacuum ($10^{-6}$ mbar) in order to promote electron injection. Gratifyingly, both hole and electron transport were observed in this configuration, with hole and electron mobilities, measured from as-prepared devices, of $\mu_{e,sat}$ ($2 \times 10^{-5}$ $cm^2/(V\ s)$) and $\mu_{h,sat}$ ($9 \times 10^{-5}$ $cm^2/(V\ s)$), respectively. Thermal annealing at 140 °C resulted in improved device performance, with balanced hole and electron mobilities around $1 \times 10^{-4}$ $cm^2/(V\ s)$ observed (Figure 5).

A further interesting observation is the large value of the switch-on voltage ($V_{ON}$) for holes, i.e., the gate voltage at which injected charges start accumulating in the device channel, for both hole-only and ambipolar transistors. For both types of devices $V_{ON}$ appears to be relatively high and in the range −20 to −30 V. The latter is an indication of the presence of a nonideal interface (i.e., an interface where a significant concentration of hole traps exists) between OTS−PSV as well as BCB−PSV interfaces for hole transport. One way of circumventing this problem and hence further enhancing the device performance could be through the use of improved trap-free gate dielectrics such as fluoropolymers.[24] Use of source-drain electrodes with better hole injecting characteristics (e.g., platinum) could also be explored as a mean for improving the hole mobility in PSV-based transistors. However, device optimization would require a significant amount of additional investigation that is beyond the scope of this work.

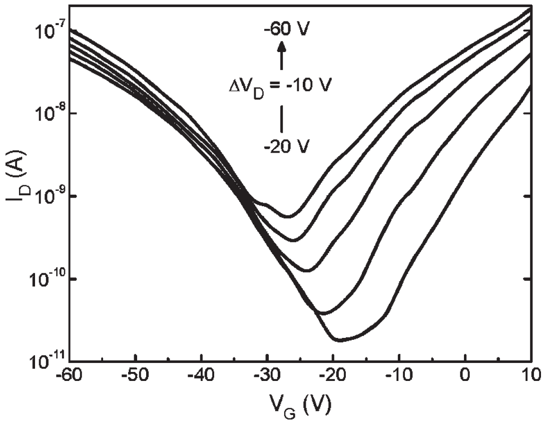


**Figure 5.** Ambipolar transfer characteristics measured from a P3DTV transistor after it has been annealed at 140 °C. The transistor channel length and width were 20 $\mu$m and 2 mm, respectively.

Although polymers with higher ambipolar mobilities have been reported,[48] we believe that these results demonstrate that the substitution of thiophene for selenophene is a potentially attractive strategy to tune polymer band gap and induce ambipolar charge transport.

## ■ CONCLUSION

In conclusion, we have reported the first synthesis of regioregular poly(3-alkyl-2,5-selenylenevinylene). The polymer exhibits a reduced optical band gap in comparison to the well-investigated thiophene analogue as a result of the stabilizing effect of selenophene on the polymer LUMO. Field effect transistors fabricated with PSV exhibit hole mobilities up to 0.01 $cm^2/(V\ s)$, with balanced ambipolar transport observed when hydroxyl free gate dielectrics were used. Such properties further demonstrate the potential of selenophene-based polymers for optoelectronic devices.

## ■ EXPERIMENTAL SECTION

**Materials and Methods.** (*E*)-1,2-Bis(tributylstannyl)ethylene was purchased from TCI Europe. All other chemicals were purchased from Aldrich or Fisher. All reactions were carried out under $N_2$ using solvents and reagents as commercially supplied, unless otherwise stated. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of $CDCl_3$ or TMS as an internal reference and are given in ppm. Microwave reactions were run in a Biotage Initiator in constant temperature mode. Number-average ($M_n$) and weight-average ($M_w$) were determined by either an Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C or a high-temperature Polymer Laboratories PL-GPC 220 running in 1,2,4-trichlorobenzene at 160 °C. Both systems used two PL mixed B columns in series and were calibrated against narrow polydispersity polystyrene standards. Electrospray mass spectrometry was performed with a Thermo Electron Corp. DSQII mass spectrometer. UV–vis spectra were recorded on a Perkin-Elmer Lambda 900 UV–vis spectrometer. Thin film samples were prepared by spin-coating a 0.5 wt % solution in hot 1,2,4-trichlorobenzene at 500 rpm for 30 s, followed by 2000 rpm for 30 s. Flash chromatography was performed on silica gel (Merck Kieselgel 60 F254 230–400 mesh) unless otherwise indicated. Thin layer chromatography (TLC) was performed on Merck aluminum-backed plates precoated with silica (0.2 mm, 60 F254). Thermogravimetric analysis (TGA) and differential scaning calorimetry (DSC) were conducted under a $N_2$ atmosphere at a scan rate of 10 °C/min with a Perkin-Elmer TGA7 and a Mettler Toledo DSC822 instrument, respectively. For DSC, the sample weight was ~4 mg. Photoelectron spectroscopy in air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. Samples for PESA were prepared on glass substrates as drop-cast films.

Bottom gate, bottom contact OFETs were fabricated on a highly doped silicon substrate, which acted as a common gate electrode. A thermally grown 300 nm layer of silicon dioxide as the dielectric and the source drain was photolithography patterned. The substrates were thoroughly cleaned in an ultrasonic bath with acetone, deionized water, and isopropyl alcohol and exposed to UV-light for ~20 min. This was followed by surface treatment of the substrate using octadecyltrichlorosilane (OTS). A 80 °C solution of the P3DSV (0.5 wt %) in 1,2,4-trichlorobenzene (TCB) was spin-coated onto the substrate, followed by drying at 100 °C for 20 min under nitrogen.

Bottom gate, top contact OFETs were fabricated on bare silicon substrates with a 400 nm thermally layer grown silicon oxide $SiO_2$. For the p-type devices, the substrates were exposed to a plasma ashing at 80 W for 1 min. Then HMDS solution contained in a small crucible was evaporated on a hot plate at 70 °C covered by a big beaker. For the n-type devices, the substrates were subjected to a plasma ashing at 80 W for 3 min. BCB, diluted in trimethylbenzene (TMB) with the ratio 1:20, was spin-coated at 3000 rpm for 60 s. The BCB layer was cross-linked by annealing the samples at 250 °C for 2 h in a nitrogen ($N_2$) atmosphere. The P3DSV polymer was dissolved in 1,2,4-trichlorobenzene (TCB) with a concentration of 10 mg/mL. The solution was heated at 150 °C for 15 min and then at 100 °C for 10 min. The solution was spin-coated at 500 rpm for 30 s and then 2000 rpm for 60 s. On the p-type devices, 36 nm gold source drain electrodes were deposited through shadow masks, whereas on the n-type devices, a combination of 20 nm calcium and 40 nm aluminum electrodes was deposited. The FET characterization was acquired in $N_2$ glovebox using a Keithley 4200 semiconductor parameter analyzer.

Field effect was calculated from the saturation regime employing the relationship

$$\mu_{\mathrm{e,\,sat}} = \frac{L}{C_i W}\frac{\partial^2 I_D}{\partial {V_G}^2}$$

where $I_D$ is the source-drain current (saturation regime), $V_G$ and $V_D$ are gate and source-drain voltage, respectively, $C_i$ is the insulator capacitance, and $W$ and $L$ are the channel width and length.

*2,5-Dibromo-3-decylselenophene.* To a solution of 3-decylselenophene[20] (2 g, 7.37 mmol) in THF (110 mL) at 0 °C was added *N*-bromosuccinimide (2.62 g, 14.74 mmol) in six portions over 40 min. The resulting solution was stirred at room temperature in the dark for 16 h. The solvent was removed under reduced pressure, and the resulting residue was dissolved in ethyl acetate (45 mL) and washed with water (2 × 25 mL). The aqueous layers were combined and further extracted with ethyl acetate. The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude oil was filtered through a plug of silica (petroleum ether 40–60 °C) to afford a colorless oil (2.25 g, 71%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.05 (s, 1H), 2.51 (t, $J$ = 7.8 Hz, 2H), 1.48–1.55 (m, 2H), 1.24–1.30 (m, 14H), 0.89 (t, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 144.9, 134.2, 113.6, 111.1, 31.9, 30.7, 29.8, 29.7, 29.6, 29.4, 29.4, 29.2, 22.8, 14.2. MS (EI) 430 (t, $M^+$).

*P3DSV.* To 2,5-dibromo-3-decylselenophene (0.5 g, 1.17 mmol) in a 20 mL microwave vial was added $Pd(dba)_2$ (17 mg, 2.5 mol %), P-(*o*-tol)$_3$ (36 mg, 10 mol %), and chlorobenzene (10 mL). The reaction mixture was degassed under argon for 30 min, and an equal molar amount of (*E*)-1,2-bis(tributylstannyl)ethylene (0.72 g, 1.17 mmol) was added via syringe. The resultant mixture was degassed for 30 min with argon and securely sealed. The glass vial was placed into a microwave reactor and heated at 140 °C for 2 min, 160 °C for 2 min, and followed by 180 °C for 30 min. After being cooled to room temperature, the reaction mixture was precipitated into a mixture of methanol (200 mL) and concentrated hydrochloric acid (2 mL) and stirred for 1 h at RT. The precipitate was filtered and extracted (Soxhlet) with methanol, acetone, and hexane. The remaining polymer was dissolved in hot chloroform, filtered, and precipitated into methanol to afford the desired polymer after drying under vacuum (250 mg, 72%). GPC (chlorobenzene at 80 °C): $M_w$ = 62 000; $M_n$ = 25 000 g/mol. $^1$H NMR (400 MHz, $CDCl_3$ at 50 °C) $\delta$: 6.95–6.80 (m, 3H), 2.62 (br, 2H), 1.60 (br, 2H) 1.31–1.49 (br, 12H), 0.90 (br, 3H). Found: C, 63.4; H, 8.06. Calcd for $C_{16}H_{24}Se$: C, 65.1; H, 8.14.

*P3HSV.* Following the procedure above, using 2,5-dibromo-3-hexylselenophene (0.5 g, 1.34 mmol) in a microwave vial was added $Pd(dba)_2$ (19.26 mg, 2.5 mol %), P-(*o*-tol)$_3$ (40.79 mg, 10 mol %), and chlorobenzene (10 mL) to afford P3HSV (260 mg). GPC (1,2,4-trichlorobenzene at 160 °C): $M_w$ = 45 500, $M_n$ = 18 000 g/mol). The polymer was too insoluble for NMR analysis.

## ASSOCIATED CONTENT

**Supporting Information.** TGA, PESA, and full $^1$H NMR spectra of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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## REFERENCES

(1) Mishra, A.; Ma, C.-Q.; Bäuerle, P. *Chem. Rev.* **2009**, *109*, 1141.

(2) Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem. Rev.* **2010**, *110*, 3.

(3) Pron, A.; Gawrys, P.; Zagorska, M.; Djurado, D.; Demadrille, R. *Chem. Soc. Rev.* **2010**, *39*, 2577.

(4) Jen, K. Y.; Maxfield, M.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 309.

(5) Fuchigami, H.; Tsumura, A.; Koezuka, H. *Appl. Phys. Lett.* **1993**, *63*, 1372.

(6) Yamada, S.; Tokito, S.; Tsutsui, T.; Saito, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1448.

(7) Nguyen, L. H.; Gunes, S.; Neugebauer, H.; Sariciftci, N. S.; Banishoeib, F.; Henckens, A.; Cleij, T.; Lutsen, L.; Vanderzande, D. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2815.

(8) Banishoeib, F.; Henckens, A.; Fourier, S.; Vanhooyland, G.; Breselge, M.; Manca, J.; Cleij, T. J.; Lutsen, L.; Vanderzande, D.; Nguyen, L. H.; Neugebauer, H.; Sariciftci, N. S. *Thin Solid Films* **2008**, *516*, 3978.

(9) Loewe, R. S.; McCullough, R. D. *Chem. Mater.* **2000**, *12*, 3214.

(10) Zhang, C.; Matos, T.; Li, R.; Sun, S. S.; Lewis, J. E.; Zhang, J. A.; Jiang, X. M. *Polym. Chem.* **2010**, *1*, 663.

(11) Qin, Y.; Hillmyer, M. A. *Macromolecules* **2009**, *42*, 6429.

(12) Banishoeib, F.; Adriaensens, P.; Berson, S.; Guillerez, S.; Douheret, O.; Manca, J.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Vanderzande, D. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1026.

(13) Huo, L. J.; Chen, T. L.; Zhou, Y.; Hou, J. H.; Chen, H. Y.; Yang, Y.; Li, Y. F. *Macromolecules* **2009**, *42*, 4377.

(14) Smith, A. P.; Smith, R. R.; Taylor, B. E.; Durstock, M. F. *Chem. Mater.* **2004**, *16*, 4687.

(15) Girotto, C.; Cheyns, D.; Aernouts, T.; Banishoeib, F.; Lutsen, L.; Cleij, T. J.; Vanderzande, D.; Genoe, J.; Poortman, J.; Heremans, P. *Org. Electron.* **2008**, *9*, 740.

(16) Kim, J. Y.; Qin, Y.; Stevens, D. A.; Ugurlu, O.; Kalihari, V.; Hillmyer, M. A.; Frisbie, C. D. *J. Phys. Chem. C* **2009**, *113*, 10790.

(17) Horie, M.; Shen, I. W.; Tuladhar, S. M.; Leventis, H.; Haque, S. A.; Nelson, J.; Saunders, B. R.; Turner, M. L. *Polymer* **2010**, *51*, 1541.

(18) Patra, A.; Bendikov, M. *J. Mater. Chem.* **2010**, *20*, 422.

(19) Dian, G.; Barbey, G.; Decroix, B. *Synth. Met.* **1986**, *13*, 281.

(20) Mahatsekake, C.; Catel, J. M.; Andrieu, C. G.; Ebel, M.; Mollier, Y. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *47*, 35.

(21) Zade, S. S.; Zamoshchik, N.; Bendikov, M. *Chem.—Eur. J.* **2009**, *15*, 8613.

(22) Heeney, M.; Zhang, W.; Crouch, D. J.; Chabinyc, M. L.; Gordeyev, S.; Hamilton, R.; Higgins, S. J.; McCulloch, I.; Skabara, P. J.; Sparrowe, D.; Tierney, S. *Chem. Commun.* **2007**, 5061.

(23) Ballantyne, A. M.; Chen, L.; Dane, J.; Hammant, T.; Braun, F. M.; Heeney, M.; Duffy, W.; McCulloch, I.; Bradley, D. D. C.; Nelson, J. *Adv. Funct. Mater.* **2008**, *18*, 2373.

(24) Clarke, T. M.; Ballantyne, A. M.; Tierney, S.; Heeney, M.; Duffy, W.; McCulloch, I.; Nelson, J.; Durrant, J. R. *J. Phys. Chem. C* **2010**, *114*, 8068.

(25) Chen, Z. Y.; Lemke, H.; Albert-Seifried, S.; Caironi, M.; Nielsen, M. M.; Heeney, M.; Zhang, W. M.; McCulloch, I.; Sirringhaus, H. *Adv. Mater.* **2010**, *22*, 2371.

(26) Mishra, S. P.; Javier, A. E.; Zhang, R.; Liu, J. Y.; Belot, J. A.; Osaka, I.; McCullough, R. D. *J. Mater. Chem.* **2011**, *21*, 1551.

(27) Kong, H.; Jung, Y. K.; Cho, N. S.; Kang, I. N.; Park, J. H.; Cho, S.; Shim, H. K. *Chem. Mater.* **2009**, *21*, 2650.

(28) Leenen, M. A. M.; Vian, F.; Cucinotta, F.; Pisula, W.; Thiem, H.; Anselmann, R.; De Cola, L. *Macromol. Chem. Phys.* **2010**, *211*, 2286.

(29) Chung, D. S.; Kong, H.; Yun, W. M.; Cha, H.; Shim, H. K.; Kim, Y. H.; Park, C. E. *Org. Electron.* **2010**, *11*, 899.

(30) Kong, H.; Chung, D. S.; Kang, I. N.; Park, J. H.; Park, M. J.; Jung, I. H.; Park, C. E.; Shim, H. K. *J. Mater. Chem.* **2009**, *19*, 3490.

(31) Li, M.; Patra, A.; Sheynin, Y.; Bendikov, M. *Adv. Mater.* **2009**, *21*, 1707.

(32) Li, M.; Sheynin, Y.; Patra, A.; Bendikov, M. *Chem. Mater.* **2009**, *21*, 2482.

(33) Zade, S. S.; Das, S. *Chem. Commun.* **2010**, *46*, 1168.

(34) Patra, A.; Wijsboom, Y. H.; Leitus, G.; Bendikov, M. *Chem. Mater.* **2011**, *23*, 896.

(35) Ozkut, M. I.; Atak, S.; Onal, A. M.; Cihaner, A. *J. Mater. Chem.* **2011**, *21*, 5268.

(36) Patra, A.; Wijsboom, Y. H.; Zade, S. S.; Li, M.; Sheynin, Y.; Leitus, G.; Bendikov, M. *J. Am. Chem. Soc.* **2008**, *130*, 6734.

(37) Wijsboom, Y. H.; Patra, A.; Zade, S. S.; Sheynin, Y.; Li, M.; Shimon, L. L. W.; Bendikov, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5443.

(38) Tierney, S.; Heeney, M.; McCulloch, I. *Synth. Met.* **2005**, *148*, 195.

(39) Amb, C. M.; Rasmussen, S. C. *Eur. J. Org. Chem.* **2008**, 801.

(40) Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. *Macromolecules* **1992**, *25*, 1214.

(41) Haack, R. A.; Penning, T. D.; Djuric, S. W.; Dziuba, J. A. *Tetrahedron Lett.* **1988**, *29*, 2783.

(42) Gavrilenko, A. V.; Matos, T. A.; Bonner, C. E.; Sun, S. S.; Zhang, C.; Gavrilenko, V. I. *J. Phys. Chem. C* **2008**, *112*, 7908.

(43) Kirihata, H.; Uda, M. *Rev. Sci. Instrum.* **1980**, *52*, 68.

(44) Davis, R. J.; Lloyd, M. T.; Ferreira, S. R.; Bruzek, M. J.; Watkins, S. E.; Fahlman, M.; Anthony, J. E.; Hsu, J. W. P. *J. Mater. Chem* **2011**, *21*, 1721.

(45) Henckens, A.; Colladet, K.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Gelan, J.; Vanderzande, D. *Macromolecules* **2005**, *38*, 19.

(46) Ito, Y.; Virkar, A. A.; Mannsfeld, S.; Oh, J. H.; Toney, M.; Locklin, J.; Bao, Z. A. *J. Am. Chem. Soc.* **2009**, *131*, 9396.

(47) Chua, L.-L.; Zaumseil, J.; Chang, J. F.; Ou, E. C.-W.; Ho, P. K.-H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194.

(48) Sonar, P.; Singh, S. P.; Li, Y.; Soh, M. S.; Dodabalapur, A. *Adv. Mater.* **2010**, *22*, 5409.