Mixed selenium-sulfur fused ring systems as building blocks for novel polymers used in field effect transistors[†][‡]

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Eight novel polymer materials for transistor applications were prepared based on the fused ring building block selenolo[3,2-b]thiophene. The molecular structure of selenolo[3,2-b]thiophene was determined by single-crystal X-ray diffraction and was further modified for use as a monomer during the Stille synthesis of various copolymers containing substituted and unsubstituted thiophenes, thiazoles, dithienopyrroles (DTP) and benzothiadiazole subunits. The resultant polymers were analyzed for UV-Vis absorption and show a significant red shift when compared to regioregular poly(3-hexylthiophenes) (P3HT), attributed to the increased planarity and conjugation of the polymer backbone. Cyclic voltammetry experiments on the new polymers show that almost all of the new structures have a higher oxidation potential compared to P3HT, making them more stable toward oxidative doping under ambient atmospheres. The polymers were also evaluated for their electrical properties through their performance as the active layer in field effect transistors. The polymers showed relatively high mobility values, of which the highest observed value is 0.11 cm² V⁻¹ s⁻¹, with on/off ratios of about 10⁵.

1. Introduction

Organic field effect transistors (OFETs) have recently become more important because of their use in low cost devices, such as smart cards, printable backplanes to drive circuits of large area display devices, etc.¹ The use of conjugated polymers in OFETs is increasing exponentially even though their field effect mobilities remain lower than corresponding inorganic thin film transistors.² The increased interest is due to advantages of cheap manufacturing and potential for printable electronics. Such advantages have made them preferable for large-scale, low-cost commercial applications.³ Another advantage of these materials is that they allow for easy structural modifications through molecular engineering, enabling the tuning of optical and electronic properties.⁴ One goal of this research is to produce OFETs with high charge carrier mobilities as well as high on/off ratios with better air stability.⁵ Solubility in common organic solvents and reproducible mobilities are other requirements for easy device fabrication by spin coating, stamping or inkjet printing.⁶ Many of the organic semiconductors used for p-channel OFETs have been derived from thiophene based π -conjugated systems,⁷ oligo-thiophenes,8 acenes,9 porphyrins and phthalocyanines,10 polythienylenevinylenes11 and carbon-sulfur fused rings12 as well as other fused-ring systems.13

Among these materials, polymers containing carbon-sulfur fused rings have been shown to some of the highest carrier mobilities when used as the active layer in field effect transistors.¹² It is believed that the presence of fused rings with a high degree of planarity and rigidity results in greater crystallinity, extended π overlap and result in overall improvements in device performance. We also believe that the fused rings prevent detrimental chain folding. Furthermore, the presence of fused rings in the polymer backbone lowers the molecular reorganization energy and facilitates intermolecular charge hopping, thereby increasing mobility.¹⁴ All of these factors have led many groups to focus on the use of fused ring-containing organic polymers to fabricate p-channel OFETs derived from thiophenebased systems.¹¹⁻¹³

Selenophenes are chalcogenophene homologues with chemical and physical properties similar to those of thiophene, but have not been well studied.15 Although various oligomeric fused ring containing selenium atoms have been synthesized and the OTFT properties studied, to the best of our knowledge polymers containing fused selenophenes are unknown. This could be due to low solubility^{16a} and lack of suitable synthetic methods for making such types of monomers and polymers.¹⁶ As a design principle, it has been found that the replacement of the sulfur atom by selenium can lead to electronic improvements, such as the increase in room temperature conductivity in organic metals such as tetrathiafulvalene (TTF) compared to tetraselenafulvalene (TSF) derivatives.¹⁷ Similarly, it has been shown in literature that as compared to polythiophenes, polyselenophenes have better conductivity and mobility due to the larger p-overlap in Se derivatives due to the larger p-orbitals.¹⁸ Theoretical studies,¹⁹ as well as experimental evidence,²⁰ also indicate that polyselenophenes should have a lower band gap compared to polythiophenes. Polyselenophenes are also expected to have lower

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oxidation and reduction potentials, easier polarizability and to be more suitable to inter-chain charge transfer due to the intermolecular Se-Se interactions,²¹ all of which are attractive properties for organic electronics.

Considering the superior properties of selenophenes over thiophenes, it was expected that the replacement of sulfur by selenium could be an interesting approach toward different materials for organic thin film transistors. In this paper, we report on the synthesis, characterization and performance in field effect transistors of a series of polymers containing selenopheno[3,2-b]thiophene used in conjunction with other electron rich and electron poor components to modify the polymer optoelectronic properties.

2. Experimental

2.1 General

Gel permeation chromatography (GPC) of all polymers was performed on a Water 2690 separations module and a Water 2487 dual λ absorbance detector, with chloroform as the eluent and a series of three Styragel columns (10⁴, 500 and 100 A°; Polymer Standard Service). To determine the molecular weight, toluene was taken as an internal standard and polystyrene was used for calibration. ¹H NMR was recorded on a Bruker Advance 300 MHz spectrometer. UV-vis-NIR spectra of all the polymers were recorded on a Varian Cary 5000 spectrometer in chloroform solution and polymer thin films cast onto 22 mm square cover glass slide.

Cyclic voltammetry was carried out on an Autolab PGSTAT 100 using a three-electrode cell. A platinum stick electrode coated with a polymer thin film was used as the working electrode and a platinum wire was the counter electrode. An Ag/Ag+ electrode (Ag in a 0.01 mol/L of AgNO₃) was used as the reference electrode. At the beginning of the experiment, the instrument was calibrated against the Fc/Fc⁺ couple (0.01 V *vs.* Ag/Ag⁺). An anhydrous 0.1 M solution of tetrabutylammonium-tetrafluoroborate (Bu₄N⁺BF₄⁻) in acetonitrile, saturated with nitrogen, was used as the supporting electrolyte.

2.2 Fabrication and characterization of FET devices

FET devices were fabricated in a bottom gate, bottom contact configuration on n-type silicon substrates as the gate and thermally grown 250 nm SiO₂ as the dielectric layer. Source and drain electrodes were patterned using standard photolithography and were deposited on SiO_2 by sputter deposition of 5 nm of titanium (for adhesion) and 50 nm of gold. The devices were cleaned using a UV cleaner (Novascan PSD-UVT) for 40 min by exposure to UV light in air at a temperature of 120 °C. The devices were surface treated by immersing in a 30 mM solution of octyltrichlorosilane (OTS-8, Acros) in anhydrous hexadecane at room temperature for 2.5-3 h. The devices were then washed several times with HPLC grade toluene, dried with N₂ flow followed by vacuum for at least 1h. A 5 µL solution of 1 mg/mL polymer in chloroform was deposited on the devices and allowed to evaporate slowly in a glass Petri dish saturated with chloroform. After film formation, the OFETs were kept under vacuum overnight prior to being tested. All measurements were carried out under a slow continuous flow of argon. However the devices were

exposed to air while being delivered to the probe station for measurement. While measuring the current–voltage curves and transfer curves, V_G was scanned from -80 V to +40 V. The field effect mobilities were obtained from the transfer curves in the saturation regime at $V_{DS} = -80$ V.

2.3 Monomer synthesis

The dibromo compounds of \mathbf{B}^{22} \mathbf{C}^{23} \mathbf{G}^{24} and \mathbf{H}^{25} and the distannyl compound of \mathbf{D}^{26} and \mathbf{E}^{27} were synthesized as reported in literature.

Ethyl 2-(thiophen-3-ylselanyl)acetate (1). A stirred solution of 3-bromothiophene (30.0 g, 0.18 mol) in Et₂O (300 mL) was cooled to -78 °C and *n*-BuLi (2.5 M solution in hexane, 73.6 mL) was added dropwise over 30 min. After stirring for 1h, selenium powder (16.6 g, 0.210 mol) was added in portions. The solution stirred for another 1h at -78 °C and then warmed to -30 °C for 4h. Ethyl 2-bromoacetate (35.1 g, 0.210 mol) was added dropwise to the reaction and it warmed gradually to room temperature overnight. The reaction was then quenched with H₂O (100 mL) and the organic layer separated. The aqueous layer was back extracted with Et₂O (2×50 mL) and the combined organics dried over MgSO₄ and evaporated in vacuo. The residue was distilled under reduced pressure to yield the required compound as a light yellow liquid. Yield 78%; ¹H NMR (CDCl₃, 300 MHz) δ 7.42 (dd, $J_1 = 3.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.29 (dd, $J_1 = 5.1$ Hz, $J_2 = 3.0$ Hz, 1H), 7.14 (dd, $J_1 =$ 5.1 Hz, $J_2 = 1.2$ Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 3.39 (s, 2H), 1.19 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 170.76, 132.35, 128.90, 126.46, 121.85, 61.27, 28.15, 14.06; GC MS: 250 [M]⁺, 163, 97.

Ethyl 2-(2-formylthiophen-3-ylselanyl)acetate (2). To a solution of ethyl 2-(thiophen-3-ylselanyl)acetate (1) (30 g, 0.12 mol) and DMF (17.5 g, 0.238 mol) in 1,2-dichloroethane (200 mL) at 0 °C was added POCl₃ (27.5 g, 0.179 mol) drop wise. After addition, the cooling bath was removed and the reaction heated at reflux for 4h. It was subsequently cooled to rt and added to an ice-cold aqueous solution of sodium acetate. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organics were washed several times with H₂O, dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (3 : 1 hexane and ethylacetate mixture) to yield the pure compound 2 as a yellow oil. Yield 81%; ¹H NMR (CDCl₃, 300 MHz) δ 9.98 (s, 1H), 7.73 (dd, $J_1 = 5.1$ Hz, $J_2 = 0.6$ Hz, 1H), 7.33 (d, J = 5.1 Hz, 1H), 4.12 (q, J = 7.2 Hz, 2H), 3.54 (s, 2H), 1.20 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 182.75, 170.15, 138.32, 135.18, 134.74, 132.05, 61.60, 27.10, 14.01; GC MS: 278 [M]⁺, 191.

Ethyl selenopheno[3,2-b]thiophene-5-carboxylate (3). In a 500 mL round bottom flask, ethyl 2-(2-formylthiophen-3ylselanyl)acetate (2) (25.0 g, 89.9 mmol) was taken with DMF (125 mL) and K_2CO_3 (37.2 g, 0.269 mol) was added. The mixture was stirred at room temperature for 24h under N₂. It was quenched by adding H₂O (100 mL) and the compound extracted with ethylacetate. The organic phase was washed several times with H₂O, dried over MgSO₄ and evaporated in vacuo. Purification was accomplished by column chromatography using silica gel and hexane-ethylacetate mixture (9 : 1) to obtain the yellow oil. Yield 89%; ¹H NMR (CDCl₃, 300 MHz) δ 8.25 (d, J = 0.6 Hz, 1H), 7.57 (d, J = 5.1 Hz, 1H), 7.35 (dd, $J_1 = 5.4$ Hz, $J_2 = 0.9$ Hz, 1H), 4.39 (q, J = 7.2 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 163.65, 143.70, 140.11, 138.46, 131.0, 128.25, 122.99, 61.45, 14.93; GC MS: 260 [M]⁺, 215, 188.

Selenopheno[3,2-b]thiophene-5-carboxylic acid (4). Ethyl selenopheno[3,2-b]thiophene-5-carboxylate (3) (22.0 g, 84.6 mmol) was dissolved in a mixture of THF and methanol (1 : 1, 200 mL) and 10% aqueous solution of NaOH (70 mL) was added. The reaction was stirred at rt for 3h. The excess solvents were distilled off and the white solid dissolved in H₂O. To the aqueous solution, conc. HCl was slowly added to maintain a pH between 2–3. The white precipitate was filtered, washed several times with H₂O until the filtrate became neutral and vacuum dried to afford the required compound. Yield 78%, ¹H NMR (CD₃OD, 300 MHz) δ 8.21 (s, 1H), 7.68 (d, *J* = 5.1 Hz, 1H), 7.39 (d, *J* = 5.1 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.47, 144.02, 140.10, 138.68, 131.01, 128.25, 122.83.

Selenopheno[3,2-b]thiophene (5). To a solution of selenopheno[3,2-b]thiophene-5-carboxylic acid (4) (15.0 g, 64.9 mmol) in quinoline (75 mL) was added 2 CuO.Cr₂O₃ (0.760 g, 2.59 mmol) and this was heated to 200 °C. When the evolution of CO_2 stopped (3h), the reaction cooled to rt and was added slowly to a 50% solution of HCl (300 mL). It was extracted twice with chloroform and the organic layer washed several times with H₂O until the aqueous layer became neutral. The chloroform layer was dried over MgSO4 and evaporated. Purification was done by column chromatography using silica gel and hexane-chloroform mixture (95 : 5) to obtain an off white solid. Yield 83%, ¹H NMR (CDCl₃, 300 MHz) δ 7.98 (dd, $J_1 = 5.7$ Hz, $J_2 = 1.5$ Hz, 1H), 7.53 (dd, $J_1 = 5.7$ Hz, $J_2 = 0.6$ Hz, 1H), 7.40 (dd, $J_1 = 5.4$ Hz, $J_2 = 1.5$ Hz, 1H), 7.34 (dd, $J_1 = 5.1$ Hz, $J_2 = 0.6$ Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 141.0, 138.7, 130.54, 126.97, 122.52, 122.05; GC MS: 188 [M]+.

2,5-dibromoselenopheno[3,2-b]thiophene (6). To an ice-cooled stirred solution of selenopheno[3,2-b]thiophene (**5**) (8.00g, 42.7 mmol) in DMF (100 mL), NBS (15.2 g, 85.5 mmol) was added in portion and the reaction mixture was allowed to stir overnight at room temperature. The mixture was poured into H₂O and the compound filtered using a Buckner funnel. The filtrate was washed several times with H₂O and recrystallized in MeOH to obtain a light yellow solid. Yield 87%, ¹H NMR (CDCl₃, 300 MHz) δ 7.36 (s, 1H), 7.17 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 139.53, 138.28, 124.81, 124.64, 115.15, 113.37; GC MS: 346 [M]⁺, 265, 186, 106.

2,5-bis(3-dodecylthiophen-2-yl)selenopheno[3,2-b]thiophene (7). To a stirred THF (50 mL) mixture of 2-(3-dodecylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.56 g, 17.3 mmol), 2,5-dibromoselenopheno[3,2-b]thiophene (6) (2.00 g. 5.78 mmol), and tetrakis(triphenylphosphine)palladium (0.26 g, 0.23 mmol) was added 2 M aqueous potassium carbonate (50 mL). The mixture was heated at reflux with vigorous stirring for 48 h under N₂. The excess solvent was distilled and the compound extracted with chloroform. The organic phase was washed with water, dried over MgSO₄ and evaporated. The residue was purified by column chromatography using hexane and chloroform (9 : 1) to obtain a yellow solid. Yield 53%, ¹H NMR (CDCl₃, 300 MHz) δ 7.38 (d, J = 0.3 Hz, 1H), 7.26 (d, J = 0.6 Hz, 1H), 7.19 (dd, $J_1 = 5.4$ Hz, $J_2 = 3.6$ Hz, 2H), 6.94 (dd, $J_1 = 5.1$ Hz, $J_2 = 1.2$ Hz, 2H), 2.74–2.80 (m, 4H), 1.64 (quin, J = 7.2 Hz, 4H), 1.25–1.40 (m, 36H), 0.87 (t, J = 6.9 Hz, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 140.81, 140.54, 140.18, 139.85, 139.03, 137.41, 133.02, 130.67, 130.13, 130.09, 124.26, 121.18, 120.27, 31.99, 30.87, 29.73, 29.68, 29.63, 29.55, 29.43, 29.35, 29.32, 22.76, 14.18.

2,5-bis(5-bromo-3-dodecylthiophen-2-yl)selenopheno[3,2-b]thiophene (8). A THF (50 mL) solution of 2,5-bis(3-dodecylthiophen-2-yl)selenopheno[3,2-b]thiophene (7) (2.0 g, 2.9 mmol) was cooled to 0 °C and NBS (1.08 g, 6.09 mmol) was slowly added. The reaction was stirred overnight at rt. The THF was evaporated and the compound dissolved with EtOAc. The organic phase was washed several times with H₂O, dried over MgSO₄ and evaporated. The crude product was purified by column chromatography (silica gel, hexane) to obtain a yellow solid. Yield 73%, ¹H NMR (CDCl₃, 300 MHz) δ 7.32 (d, J = 0.6 Hz, 1H), 7.20 (d, J = 0.6 Hz, 1H), 6.90 (d, J = 0.9 Hz, 2H), 2.66–2.72 (m, 4H), 1.60 (quin, J = 7.8 Hz, 4H), 1.24–1.40 (m, 36H), 0.86 $(t, J = 6.9 \text{ Hz}, 6\text{H}); {}^{13}\text{C} \text{ NMR} (\text{CDCl}_3, 75 \text{ MHz}) \delta 140.90, 140.66,$ 140.56, 139.60, 139.27, 136.30, 134.28, 132.77, 132.73, 131.94, 121.48, 120.62, 111.19, 111.15, 31.95, 30.65, 29.68, 29.59, 29.45, 29.39, 29.22, 22.72, 14.14.

2,5-bis(3-dodecyl-5-(trimethylstannyl)thiophen-2-yl)selenopheno-[3,2-b]thiophene (9). To a clear solution of 2,5-bis(5-bromo-3dodecylthiophen-2-yl)selenopheno[3,2-b]thiophene (8) (1.50 g, 1.77 mmol) in THF (40 mL), n-BuLi (1.80 mL, 2.5 M solution in hexane) was added dropwise at -78 °C. The solution was stirred for 1 h and a THF solution of trimethyltinchloride (5.30 mL, 1M solution) was added. The solution was then stirred at rt for an additional 4 h and quenched with H₂O. The compound was extracted with Et₂O, washed several times with H₂O, dried over MgSO₄ and evaporated. The dark, sticky liquid obtained was washed with methanol and dried to obtain the required compound in pure form. Yield 73%, ¹H NMR (CDCl₃, 300 MHz) δ 7.35 (s, 1H), 7.24 (s, 1H), 7.00(s, 2H), 2.74–2.81 (m, 4H), 1.63 (quin, J = 7.5Hz, 4H), 1.19, 1.31 (m, 36H), 0.88 (t, J = 6.6 Hz, 6H), 0.36 (s, 18H); ¹³C NMR (CDCl₃, 75 MHz) δ 141.20, 140.91, 140.54, 138.94, 138.79, 138.40, 137.54, 137.18, 137.12, 136.42, 130.86, 128.82, 120.65, 119.69, 31.96, 30.96, 29.70, 29.51, 29.51, 29.39, 29.27, 29.22, 22.73, 14.15, -8.19.

Representative example for the polymerization by stille crosscoupling reaction. Tris(dibenzylideneacetone)dipalladium(0) (4.32 mg, 2.00 mol %) and tri(o-tolyl)phosphine (5.74 mg, 8.00 mole %) were dissolved in chlorobenzene and allowed to stir for 10 min. A solution of 2,5-bis(5-bromo-3-dodecylthiophen-2yl)selenopheno[3,2-b]thiophene (8) (200 mg, 0.236 mmol) and 2,5-bis(3-dodecyl-5-(trimethylstannyl)thiophen-2-yl)selenopheno[3,2-b]thiophene (9) (239.6 mg, 0.236 mmol) was added. The resulting solution was heated to reflux under N_2 for 72h. After cooling to room temperature, the reaction mixture was added to 100 mL of MeOH containing conc. HCl (5 mL) and stirred for 2h. The polymers were filtered, then Soxhlet extracted with methanol and hexane to remove the inorganic impurities and oligomers. Finally, the soluble fraction was collected by extracting with chloroform and evaporated to obtain the polymer PMA.

3. Results and discussion

3.1. Monomer synthesis and polymerization

The selenopheno[3,2-b]thiophene (5) was synthesized from 3bromothiophene by a multi-step synthetic route (Scheme 1). First, 3-bromothiophene was lithiated at -78 °C in dry ether; then selenium powder was added and the reaction warmed to -30 °C to facilitate insertion of selenium metal into the thiophene ring. Finally subsequent addition of ethyl 2-bromoacetate gave compound 1 in a 78% yield. Compound 1 was then converted to the corresponding 2-subtituted carbonyl compound (2) by a Vilsmeier formylation reaction. Compound 2 was then treated with K₂CO₃ in DMF to yield the ring closed product selenopheno[3,2-b]thiophene-2-ethylester (3) as a yellow oil in 89% yield. Compound 3 was hydrolyzed by aqueous NaOH in a THF/ methanol mixture followed by acidification to obtain the corresponding acid 4. The hydrolysis reaction was found to proceed only in aqueous THF, using a mixture of methanol and THF increased the reaction rate. Acid 4 was then decarboxylated with copper chromite in quinoline (as a solvent) to afford selenopheno[3,2-b]thiophene (5) as off-white crystals in very good vield.

The diffraction-derived molecular structures of colorless crystals (from EtOH) of compound 5 is shown in Fig. 1A. Each individual molecule consists of a selenophene ring fused to a thiophene ring. The similarity of size and shape for these fused rings produces a pseudo-centrosymmetric molecule that can pack in a neatly ordered fashion but with two possible orientations for the Se...S vector. The two packing orientations for 5 would have nearly identical positions for the carbon and hydrogen atoms but the Se and S positions would be interchanged. It is therefore not surprising that the nearly planar (to within 0.005 Å) molecules of 5 utilize a crystallographic inversion center in the crystal. This inversion center lies at the midpoint of the common C-C bond for the two fused rings. The C_i-related sites specified as Se/S and SeS' in Fig. 1a are therefore each occupied by a Se atom 50% of the time and a S atom 50% of the time. This planar conformation is highly desirable since its incorporation in the polymer structure could decrease the polymer π -stacking distance as well as increase polymer

rigidity. This effect should manifest itself as a red shift in the UV-vis peaks between the solution and solid-state and is supported by the observed data (vide infra). Fig. 1B shows hydrogen bonding between the hydrogen on C2 and a neighboring Se/S atom appears to strongly influence the crystal packing; the 3.90 Å C2…Se/S" separation produces a short H… Se/S contact distance of 3.04 Å. The two ring centers of gravity for a single molecule of 5 are separated by 2.12 Å and the shortest intermolecular ring center of gravity separation is 4.59 Å. The normals to the least-squares mean planes for the two molecules of 5 shown in Fig. 1b make an angle of 93.5° with each other. Although one could speculate that the chalcogenide atoms would also seek to interact with other H-atoms in the polymer, we do not believe this is the case since the low band gaps and UV-vis data for the derived polymers completely support a cofacial arrangement of polymer units, to be discussed later.

Selenopheno[3,2-b]thiophene (5) was then di-brominated using NBS in DMF at low temperature to yield compound 6. It was observed that the presence of trace mono-bromo product resulted in product decomposition. However the di-bromo compound 6, without the mono-bromo derivative, was sufficiently stable under ambient conditions. Di-bromoselenopheno[3,2-b]thiophene (6) was used for the coupling reaction with the 2-boronic ester of 3-dodecyl thiophene to yield compound 7 as a yellow solid. Compound 7 was di-brominated using NBS in THF to yield monomer 8 that was used as a precursor for the polymers. The di-stannyl monomer 9 was easily synthesized from precursor 8, by dilithiation at -78 °C, followed by the addition of trimethyltinchloride. The di-stannyl compound 9 was found to be unstable when attempts were made to purify by either silica or basic alumina column chromatography, and thus, was used without further purification. However, after washing the crude compound with methanol to remove the unreacted tin(IV)chloride and some dark-colored material, compound 9 was found to be reasonably pure for polymerization reactions. For synthesizing the polymers, either monomer 8 or monomer 9 was used with the other di-stannyl or di-bromo precursor respectively, keeping in mind that the di-stannyl compound should be the more electron rich aromatic precursor during Stille coupling.

Copolymerizations using either compound 8 or 9 (mentioned as M in Scheme 2) with different thiophene derivatives (A-H) were performed by reacting equimolar amounts of the di-bromo and di-distannyl derivatives and a catalytic amount of tris-(dibenzylideneacetone)dipalladium (0) and tri(o-tolyl)phosphine in chlorobenzene at 150 °C for 72 h to obtain the polymers **PMA-PMH**. After the polymerization reaction was complete, the polymers were obtained by precipitation with acidic methanol and purified by successive Soxhlet extractions, using methanol, hexane and finally chloroform to give polymer yields of 76–89%. However, only a very small fraction of polymer **PME** was found to be soluble in chloroform and thus the yield was found to be insoluble in most solvents. Hence it could not be characterized and will not be discussed further here.

Before performing any material study, all polymers were kept under vacuum overnight. Molecular weights were determined by GPC analysis using chloroform as eluent and polystyrene as

[§] CCDC 763008 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. Crystal data for Selenolo[3,2-b]thiophene: C₆H₄SSe, FW 187.11, orthorhombic, space group P_{bca}, a = 9.9543(7) Å, b = 5.9678(4) Å, c = 10.1404(7) Å, α = 90°, β = 90°, γ = 90°, V = 602.39 Å³, Z = 4, ρ_{calcd} = 2.063 g/cm³, μ = 6.450 mm⁻¹, T = 100 K, 6449 reflections collected, 916 unique (R_{int} = 0.054), R1 = 0.0201, wR2 = 0.05585 [I > 2σ(I)]. Supporting information contains additional experimental procedures, ¹H-NMR and X-ray data.



i) *n*-BuLi, ether, -78 °C, Se powder, ii) Ethyl 2-bromoacetate, rt, iii) POCl₃, DMF, 1, 2-dichloroethane, reflux iv) K_2CO_3 , DMF, rt, v) NaOH, THF, MeOH, rt, vi)2CuO.Cr₂O₃, quinoline, 200 ⁰C, vii) NBS, DMF, 0 °C-rt, viii) 2-(3-dodecylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, Pd(PPh₃)₄, K₂CO₃, THF, water, reflux, ix) NBS, THF, 0 °C-rt, x) *n*-BuLi, THF, -78 °C, xi) Me₃SnCl, rt

Scheme 1 Synthesis of selenopheno[3,2-*b*]thiophene containing monomer.



Fig. 1 Diffraction derived molecular structure of 5 (thermal ellipsoids at 50%) and the H-bond.

standard. The number average molecular weight of all the polymers were obtained ranging from 10,000 to 33,000 as shown in Table 1 with the exception of **PME** in which M_n was found to be 5,600.

3.2 Optical properties

The solution UV-vis spectra of all polymers were studied using chloroform solutions, and thin films cast from chloroform solutions before and after annealing. The spectra of the cast films are shown in Fig. 2 and the absorption maxima for all measurements are summarized in Table 2. When compared to regioregular poly(3-alkylthiophene)s, a distinct red shift was observed for all the polymers in both solution and thin film. This red shift is attributed to the presence of the rigid selenothiophene unit, which leads to the slightly more planar structure of the polymer chain even in solution, thus increasing its effective conjugation. In dilute chloroform solutions, the polymers exhibited blue shifted spectra as compared to the thin films. This blue shift for the solutions' spectra is because of the more disturbed interchain association in the liquid state as compared to the solid state.

For thin films, polymers **PMB**, **PMC**, **PME** and **PMH** showed absorption maxima between 520 nm to 533 nm whereas **PMA**



Where M is either (8) or (9) and Ar =



 $X = -Sn(Me)_3$ when Y = -Br (for polymer PMA-PMC, PMG and PMH) and X = -Br when $Y = -Sn(Me)_3$ (for polymer PMD-PMF)

Scheme 2 Polymerization of selenopheno[3,2-b]thiophene containing monomer with various other monomers.

Table 1 Molecular weight and the yield of the synthesized polymers

Polymer	$M_n^{\ a}$	M_w/M_n^a	Yield ^b	
PMA	10,000	1.8	81%	
PMB	15,000	1.6	76%	
PMC	21,000	1.6	89%	
PMD	21,000	1.3	89%	
PME	5,600	1.2	27%	
PMF	insoluble	-na-	-na-	
PMG	20,000	1.8	87%	
PMH	33,000	1.9	83%	

 a Calculated from GPC (using chloroform as eluent w.r.t polystyrene standards). b Yields are calculated based on the chloroform soluble fraction.

showed slightly red-shifted spectra compared to these. This could be due to the presence of a larger number of selenolo[3,2-b]thiophene in the polymer, which makes the backbone more planar and thus more conjugated. Similarly, polymer **PMD** showed an increased red shift than polymer **PMA**, probably because of the increased planarity of the polymer backbone due to the presence of the larger DTP fused ring structure.²⁸ Surprisingly, polymer **PMG** showed very broad absorption spectra having two absorption maxima at 472 nm and 623 nm. The probable explanation for this broadness is the presence of a donor–acceptor group in the highly electron rich selenothiophene and the electron poor benzothiazole in the same backbone, resulting in a lower band gap polymer.

To study the effect of annealing, all polymer films were annealed at a temperature of $150 \,^{\circ}$ C for 30 min inside a glove box. An obvious red shift in the absorption spectra was observed for most of the polymers, which may be due to increased ordering

of the polymer chains leading to an increase in effective conjugation length. However for polymers **PMB** and **PMC**, a significant red shift was not identified for the λ_{max} but a shoulder toward longer wavelength was observed, which indicates better ordered structures.²⁸

Optical band gaps were calculated from the onset of UV-vis absorption spectra and are shown in Table 2.²⁹ The band gaps of polymers **PMA-PMF** and **PMH** were found to be 1.72–1.93 eV, which are slightly smaller or closer to the band gap of rr-P3HT (1.9 eV). However polymer **PMG** showed a band gap of 1.57 eV, which is much smaller than that of rr-P3HT, mainly due to the strong donor–acceptor interaction between the electron rich selenopheno[3,2-b]thiophene and the electron poor benzothiazole. Another factor to consider is that the large number of fused rings in **PMG** may have led to the increased planarity in the structure, which can lead to extended conjugation in the polymer chain and a lower bandgap. Because of its decreased bandgap and absorption in a broad area of the visible region, polymer **PMG** may be a viable material for organic photovoltaic applications.

3.3 Electrochemical properties

The redox properties of all the polymers, as well as rr-P3HT, were determined by cyclic voltammetry. All polymers displayed a partial reversible oxidation process as seen in Fig. 3. The onset of oxidation (E_{ox}) was calculated for each polymer, and was found to be between 0.08V to 0.35V vs. Ag/Ag⁺, most of which is higher than the E_{ox} of rr-P3HT. Because of their higher oxidation potential, these polymers are expected to be more stable in their neutral state than rr-P3HT. Table 2 summarizes the HOMO levels of all the polymers, which were calculated from the onset of the oxidation peak (E_{ox}), assuming that the



Fig. 2 UV-vis absorption spectra of the polymer thin films.

Table 2 Optical and electronic properties of the synthesized polymers

Polymer	λ_{max} (film)	λ_{\max} (film after annealing) ^{<i>a</i>}	λ_{max} (solution)	$Eg(eV)^b$	E_{ox} (V vs. Ag/Ag ⁺)/Homo (eV) ^c	LUMO $(eV)^d$
РМА	538	543	465	1.8	0.30/-5.03	-3.2
PMB	520	520	453	1.8	0.50/-5.23	-3.4
PMC	520	520	459	1.9	0.48/-5.21	-3.3
PMD	554	556	514	1.7	0.58/-5.31	-3.6
PME	521	524	478	1.9	0.30/-5.03	-3.1
PMG	472, 623	467. 627	420, 539	1.6	0.50/-5.23	-3.7
PMH	533	533	470	1.9	0.40/-5.13	-3.2
rr-P3HT	504		442	1.9	0.35/-5.08	-3.2

^{*a*} Films were annealed at a temperature of 150 °C for 30 min in nitrogen atmosphere. ^{*b*} Optical band gap evaluated from the onset of absorption spectra of the polymer film. ^{*c*} The potentials are reported *vs.* Fc/Fc⁺ based on the assumption that the redox couple of Fc/Fc⁺ is 4.8 eV relative to vacuum. ^{*d*} Calculated from the optical band gap and homo from CV.

energy level of ferrocene/ferrocenium (Fc/Fc⁺) is at 4.8 eV from vacuum.³⁰ The calculated HOMO energy levels of all the polymers were found to be between -5.0 to -5.3 eV, which are all deeper when compared to that of rr-P3HT (-4.8 eV). LUMO levels were then calculated from the HOMO level and the optical band gap.

3.4 Field effect transistor

Table 3 reports the average field-effect mobilities, on/off ratios and threshold voltages for all the polymers. All measurements were performed on at least five different days, using different devices. The calculated field effect mobilities were found to be consistent and reproducible from batch to batch.

Polymers **PMA** and **PMH** showed comparatively high mobility compared to the other polymers. All the components in these polymers comprise of highly electron-rich groups, which could enhance charge injection, which in turn, could be a factor in having a relatively high hole mobility.³¹ It should also be noted that the solubilizing alkyl groups present in these polymers are well separated and symmetrical, which may enable the polymers to better self-assemble into lamellar π -stacking microstructures that could provide efficient pathways for charge transport.³² We also feel that the homogeneity of the π -system appears to be



Fig. 3 Cyclic voltammetry of the polymers at a scan rate of 100 mV s^{-1} .

Table 3 Field effect mobility, on/off ratio and threshold voltage (V_T) of the polymer devices before and after annealing

Polymer	Mobility (cm ² V ⁻¹ s ⁻¹) ^{a,b}		On/off ratio ^{<i>a,c</i>}		
	\mathbf{A}^{e}	\mathbf{B}^{f}	$\overline{\mathbf{A}^g}$	B^h	$V_{T}(V)^{d}$
РМА	0.07–0.08	0.1 - 0.11	5×10^4 to 4×10^5	2×10^5 to 4×10^5	-10
PMB	0.006-0.008	0.007 - 0.008	4×10^3 to 6×10^3	7×10^3 to 8×10^3	-29
PMC	0.003-0.03	0.03	4×10^3 to 1×10^4	4×10^4 to 7×10^4	-11
PMD	0.052-0.054	0.03	5×10^1 to 1×10^2	113–146	-14
PME	10^{-4} - 10^{-5}	10^{-4} - 10^{-5}	5×10^1 to 2×10^2	2×10^2 to 4×10^2	-23
PMG	0.032-0.034	0.029-0.039	6×10^2 to 3×10^3	3×10^4 to 7×10^4	-9
PMH	0.08-0.11	0.10	3×10^4 to 9×10^4	$3 \times 10^{5} - 4 \times 10^{6}$	+4

^{*a*} Devices have $L = 10 \mu m$. ^{*b*} Evaluated from the saturated regime at $V_{SD} = -80 \text{ V}$. ^{*c*} Calculated from $I_{SD} = -80 \text{ V}$ (on) and 40 V (off). ^{*d*} Evaluated from the onset of the transfer curve showing highest mobility. ^{*e*} mobility before annealing. ^{*f*} mobility after annealing at 150 °C for 30 min. ^{*g*} on/off ratio before annealing. ^{*h*} on/off ratio after annealing at 150 °C for 30 min.

important in these polymers. This could also explain why PMB and PMD, although composed of electron rich units, showed relatively lower mobility. The higher side-chain density of PMB could be interfering with its packing, while the unsymmetrical DTP in PMD, which promotes poorly-formed nanofibrillar morphologies, could also be a factor in the decreased transport properties. PMB and PMC have similar structures, so though they both have similar mobility values. However, the electron-poor thiazole group in PMC increases its ionization potential, making it more stable to oxidative doping and having a higher on/off ratio. Both PMC and PMG include electron-rich and electron-poor units, and both of them have good on/off ratios, which can be attributed to their higher oxidation potential. The on/off ratio of polymer PMD was found to be much smaller because of the presence of the highly electron rich DTP ring (D) in the polymer backbone, which is prone to oxidation (doping) that can increase the off current. On the other hand, PME showed a very low mobility, which could be due to its relatively low molecular weight. Thermal annealing led to an increase in on/off ratios and could be attributed to the removal of charge traps within the polymer films.¹² On the other hand, mobilities showed only a very slight increase after thermal annealing.

3.5 Microstructure characterization

The surface morphologies of thin films were analyzed by tapping mode atomic force microscopy (TMAFM). Polymer sample thin films were prepared by drop-casting from dilute solutions (chloroform) onto OTS treated devices. TMAFM characterizations of thin film surface morphologies were then performed directly inside the channel of OFET devices. In order to facilitate the equilibration of nanostructures, polymer deposition was carried out under saturated solvent vapor by placing the substrate in a covered Petri dish partially filled with the solvent. Sample thin films were subjected to additional thermal annealing at 150 °C for 30 min followed by slowly cooling to room temperature in a glove box under an inert atmosphere. Polymer thin films were examined before and after annealing to study the evolution of surface morphologies and microstructures.

Surprisingly, initial results from tapping mode atomic force microscopy analysis revealed that surface morphologies exhibited no discernable variations resulting from thermal annealing for all of the polymer thin films. Consequently, only the surface morphologies after thermal treatment are subjected to consideration and discussion. Fig. 4 provides sample TMAMF images of the surface morphologies of representative polymer thin films inside the transistor channel. The left figure for each polymer shows topographic images where the right figures shows phase contrast images. Close examination of phase contrast TMAFM images revealed that the morphologies of the selenolo[3,2-b]thiophene containing polymers seemed to highly depend on the molecular nature of the copolymer units. Most of the polymer thin films exhibited a relatively featureless and smooth surface with the exception of polymers PMD and PMH. The morphology of the PMD thin film exhibited fibrillar features, most likely corresponding to PMD microcrystalline structures (Fig. 4 A and B). The needle-shaped



Fig. 4 Tapping mode AFM images of the polymer films PMD (A, B), PMH (C, D) and PMA (E, F) drop cast on OTS treated surfaces. (Left column represents the topographic images and the right column shows phase images).

features self-assembled into bundles with a width of approximately 20 nm. The formation of needle-shaped features in **PMD** thin films is most likely due to the presence of the large, highly planar DTP rings in the polymer chain, which forces the polymer chain to maintain extended conjugation and improve inter-planar interactions resembling the mechanism of nanofibril formation in rr-P3HTs. In comparison, TMAFM images of the **PMH** thin film, presented in Fig. 4 C and D, shows undulating nanofibrillar morphology. The relatively larger PDI values of the **PMH** may have led to larger phase separation of the polymer, thus leading to the non-uniformity of the fibrils. The polymer could actually be capable of forming more compact structures, but didn't due to polymer's relatively high polydispersity. Azimuthally averaged radial profiles of the 2D Fourier transforms of the phase contrast image exhibited a sharp peak centered at $q = 0.1097 \text{ nm}^{-1}$ revealing a domain size of around 57 nm.

The rest of the other polymer films exhibited smooth surfaces and a general lack of features, a representative example of which is polymer **PMA** (Fig. 4 E and F). Such morphology may be beneficial in achieving charge carrier transport in semiconducting polymer thin films, as in the case of **PMA**. It has been said that the formation of nanofibrillar morphologies or large crystalline domains is believed to give rise to high mobility,³⁰ however, we believe that well-defined fibril boundaries or crystalline domain boundaries create rate-limiting boundaries for charge transport. The quality of having smooth surfaces with indiscernible grain boundaries is highly desirable to assisting the development of inter-domain/interchain connectivity (presumably facilitated by sparse placement of alkyl side chains), thus becoming more effective in allowing inter-domain or interchain hopping. Phase contrast AFM images of **PMA** thin films revealed a fairly amorphous morphology with the presence of very small particles/ aggregates. We have found that systems with this type of morphologies give good charge transport properties.

X-ray data on thin films of PMC reveal highly crystalline microstructures with preferred orientations with the π -system normal to the surface (Fig. SI2-SI4[†]). PMC thin films appeared to be more isotropic, with one preferred orientation parallel to the substrate and another ~ 45 degree to the substrate. On the other hand, PMD thin films before and after thermal annealing revealed relatively poorly crystalline microstructures, but still with preferred orientation. Both these polymers showed no improvement in the intensity of the scatter peaks after thermal annealing. The film of polymer PMG revealed highly crystalline microstructures with preferred orientation. The peak intensities increase substantially after thermal annealing, the FWHM of the peaks become narrower and peaks up to the fourth order also appear in the thermally annealed film (Fig. SI2[†]). Though polymers PMC and PMG showed similar molecular ordering to P3HT, these polymers showed decreased charge mobilities. This could be due to charge trapping within the polymer. On the other hand, PMA and PMH showed similar scatter profiles (Fig. SI5[†]), indicating a fairly amorphous morphology (although PMH has a nanofibrillar structure). It is interesting to note that the polymers that gave the highest mobilities (PMA and PMH) were the least crystalline, while polymers that were highly crystalline had poor mobilities. PMD, which has intermediate crystallinity, also showed intermediate charge transport properties.

4. Conclusions

We surveyed a series of novel and solution processable semiconducting polymers based on selenolo[3.2-b]thiophene. Polymers were characterized by UV-Vis spectroscopy and cyclic voltammetry, and show excellent optoelectronic properties. Polymer analysis of device performance in field-effect transistors showed high field-effect mobility values and on/off ratios even without annealing. The deeper HOMO levels may also indicate increased stability towards doping at ambient conditions. All in all, these characteristics may promote the use of these polymers for large area device fabrication. The performance of the polymers as the active layer in field effect transistors showed promise for use in printable electronics. We also observed that there seemed to be a relationship between polymer crystallinity and charge transport properties - the most amorphous (least crystalline) polymers gave the highest mobilities. Although our main focus was on the OFET properties, the very broad absorption in the UV-Vis region, as well as the low band gap properties, also point toward some of the polymers as attractive materials for organic solar cells.

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