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Selenophene Bearing Low Band Gap Conjugated Polymers: Tuning Optoelectronic Properties via Fluorene and Carbazole as Donor Moieties

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Abstract: In this study, two donor-acceptor (D-A) type conjugated polymers namely PQSeCz and PQSeFl were designed and synthesized. Selenophene was incorporated as a π -bridge, quinoxaline as an acceptor unit while carbazole and fluorene were used as the donor units. Polymers were synthesized via palladium catalyzed Suzuki polymerization reaction. All molecules were characterized by ^1H and ^{13}C NMR Spectroscopy. The weight and number average molecular weights of the two polymers were determined by gel permeation chromatography (GPC). Electrochemical and spectroelectrochemical characterizations of the polymers were performed to investigate their optoelectronic properties. Oxidation potentials were 1.15 V/ 0.82 V and 1.11 V/ 0.82 V for PQSeCz and PQSeFl respectively, while reduction potentials were -1.26 V /-1.14 V and -1.48 V/ -1.23 V, respectively. In the visible region, maximum absorption wavelengths for the two polymers were 551 nm and 560 nm, respectively. Optical band gaps (E_g^{op}) were found from the lowest energy $\pi - \pi^*$ transition onsets as 1.71 eV and 1.58 eV, respectively. Both polymers showed good solubility in common solvents.

Keywords: conjugated polymer; selenophene; fluorine; carbazole band; gap; Suzuki coupling

1. Introduction

Conjugated polymers, without any doubt, have been recognized as one of the most important materials for plastic electronics. The advantage of them over other semiconductors is the possibility of solution processability, structural modification, low cost and light weight. Conjugated polymers due to their ability to combine tunable electronic and optical properties are ideal semiconductors for the future low-cost plastic electronics [1]. For many years, polymers have been used as insulators until the discovery that polymers can be provided with conductivity and conductivity can be increased substantially upon doping process. Applications of conjugated polymers have been limited until 2000s. Synthesizing new polymeric materials with better conductivity and processability gave a new impulse to the field. The interest in conjugated polymers has increased significantly after the discovery of the fact that the electrical conductivity of conjugated polymers can be increased upon oxidation [2]. Conjugated polymers have a large range of applications like light emitting diodes, biosensors, batteries, and solar cells due to flexibility, electronic properties, low cost, manipulation of structure, and ease of processing [3-14]. For conjugated polymers, HOMO and LUMO energy levels and the magnitude of the band gap are the most important parameters to identify the optoelectronic properties [15]. Engineering of the band gap can give desired conjugated polymers with desired properties, like electrical and optical properties. Preparation of low band-gap polymers mainly depends on two approaches, stabilization of quinoid resonance structure and donor-acceptor approach. Conjugated polymers have two resonance structures; aromatic and quinoid. Having a smaller band gap, the quinoid structure is less stable compared to aromatic structure. Adaptation of quinoid structure is succeeded via destruction of aromaticity resulting in the loss of stabilization energy. Donor-Acceptor (D-A) interaction is another approach in the preparation of low band gap conjugated polymers. The concept is to employ alternating electron donating and electron withdrawing units in the backbone of the conjugated polymer to reduce the band gap. Such conjugated polymers are called as "D-A" polymers [16].

For the design of new polymeric materials, among many acceptor moieties utilized in conjugated polymers, quinoxaline is one of a kind. Quinoxaline based polymers are highly used for organic electronics as acceptor comonomer. It has desirable properties like strong electron withdrawing capability, simple preparation and side-chain modification. Due to ease of controlling the morphology with introducing new substituents easily, quinoxaline unit is highly attractive. It is obvious that quinoxaline unit has high performance for preparation of low band gap conjugated polymers. Energy levels and band gap of quinoxaline bearing conjugated polymers are tuned due to the structure of quinoxaline that has an electron deficient N-heterocycle. Furthermore, aromatic groups can be introduced to this core unit resulting in both red-shift absorption spectra of the conjugated polymers and tuning the solubility of polymers with chemical modification such as introducing alkyl chains. Conjugated polymers bearing quinoxaline units as acceptor have low band gaps with a deep highest occupied molecular orbital (HOMO) and high solubility [17-21].

Carbazole is one of the most popular moieties used in organic semiconductor devices such as OLED, solar cells, and non-linear optical (NLO) materials either as a main core/or as a substituent because of its excellent hole-transporting capacity, high charge carrier mobility, the formation of stable radical cations coupled with efficient thermal, morphological and photophysical properties [22]. On the other hand, fluorene has been extensively used in optoelectronic devices due to ease of synthetic versatility at aromatic 2,7 and C-9 positions along with thermal and chemical stability [23]. So far, high efficiency, charge-transport properties, excellent solubility and film-forming ability, good chemical and thermal stability, and tunable properties through chemical modifications and copolymerization make polyfluorenes as the most attractive blue-emitting materials [24]. Generally, fluorene based compounds are appropriate for use in OLEDs in terms of their solubility and photoluminescent quantum yield however, it is difficult to inject charges to such materials limiting their use in OLEDs which could be improved by introducing different electron donor and acceptor substituents in their structure in order to adjust the HOMO and LUMO energy levels. Carbazole is more favorable than fluorene or other heterofluorene derivatives since the nitrogen atom provides a lone electron pair that gives a fully aromatic structure and, therefore, better stability [25].

In this study, selenophene was incorporated into polymer backbone as a π-bridge while fluorene, carbazole and quinoxaline were used as donor and acceptor units, respectively. Selenophene is highly used in conjugated polymers due to its similar physical and chemical properties compared to thiophene. Hursthouse *et al.* revealed that selenophene containing conjugated polymers have higher mobility than thiophene containing analogs [26-27]. Ionization potential of selenophene is lower than that of thiophene, thus incorporation of selenium atom decreases LUMO level of polymers. This results in a reduced band gap in conjugated polymers compared to thiophene derivatives. Replacing sulfur atom in thiophene structure with selenium results in enhanced charge transport characteristics such as charge mobility. Incorporation of selenophene leads to a red shift in absorption. Despite of those, lone pairs of selenophene atoms are more mobile than of thiophene atoms since less participating in aromaticity results in the improvement of the chain interaction among chains [28–33]. Introducing alkyl chains to fluorene improves solubility and extends conjugation. Incorporation of carbazole with selenophene in the polymer backbone results in extraordinary photochemical stabilities. Although carbazole bearing conjugated polymers demonstrate excellent properties for photovoltaics, they generally have low molecular weights.

2. Materials and Methods

2.1 Materials

All chemicals were all purchased from Aldrich except THF which was purchased from Acros. Toluene and tetrahydrofuran were freshly distilled using Na/benzophenone ketyl. Jasco V-770 UV–Vis spectrophotometer and GAMRY Reference 600 potentiostat were used to examine the electrochemical and spectroelectrochemical properties of the polymers. Chemical shifts were recorded in ppm downfield from tetramethylsilane. A platinum wire was the counter electrode, Ag wire was the reference electrode and Indium Tin Oxide (ITO) doped coated glass was the working electrode. Except for syntheses of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole, 3,6-dibromobenzene-1,2-diamine, 2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl)quinoxaline and 2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromofuran-2-yl)quinoxaline, all reactions were performed under argon atmosphere. Products were purified by column chromatography employing Silica Gel 60 (Merck, 0.063-0.200mm/70-230 mesh ASTM).

2.2 Syntheses of monomers and polymers

4,7-Dibromobenzo[*c*][1,2,5] thiadiazole was synthesized according to the literature [34]. Benzo[*c*][1,2,5] thiadiazole (5.0 g, 37 mmol) was dissolved in HBr solution (90 mL) and heated to reflux. Br_2 (12.4 g, 77.6 mmol, dissolved in 40 mL HBr) was added drop wise to the reaction medium at 100 °C. The temperature was increased to 135 °C and the mixture was refluxed overnight. The mixture was cooled to ambient temperature and kept in ice bath for two hours. The precipitate was washed with $NaHSO_3$, dissolved in DCM. Combined organic layers were washed with water and dried over Na_2SO_4. . DCM was removed under vacuum and the product was washed with diethyl ether to remove side product. Yield: 9.7 g, 90 %.

^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.73 (s, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ: 153.0, 132.3, 114.1

3,6-Dibromobenzene-1,2-diamine was synthesized according to the literature [34]. 4, 7-Dibromobenzo[*c*][1,2,5] thiadiazole (1.0 g, 3.4 mmol) was dissolved in ethanol (25 mL) then the solution was placed in an ice bath. $NaBH_4$ (5.0 g, 0.13 mol) was added portion wise to the solution and the mixture was stirred overnight at room temperature. After completion of the reaction, ethanol was evaporated under reduced pressure. The product was dissolved in diethyl ether and the organic phase was washed three times with water. Collected organic phases were dried over anhydrous $MgSO_4$ and filtered. The product was obtained as a white solid after evaporation of the solvent. Yield: 0.75 g, 83 %.

^1H NMR (400 MHz, $CDCl_3$): δ: 6.85 (d, 2H), 3.89 (s, 4H)

^{13}C NMR (100 MHz, $CDCl_3$): δ: 133.7, 123.3, 109.7

1,2-Bis(octyloxy)benzene was synthesized according to the literature [35]. Catechol (4.0 g, 36 mmol), K_2CO_3 (13 g, 94 mmol) and 1-bromooctane (14 g, 73 mmol) were put into a two-neck 100 mL flask under argon atmosphere. Anhydrous DMF (35 mL) was added to the flask and the solution was heated to 100 °C. Thin layer chromatography (TLC) controlled reaction was stirred overnight. The solvent was removed under reduced pressure and the crude product was dissolved in dichloromethane and washed with water and brine several times. Na_2SO_4 was used to dry organic layer. The solvent was removed under reduced pressure and the product was recrystallized from methanol. A milky brown solid was obtained. Yield: 9.9 g, 81 %.

^1H NMR (400, $CDCl_3$): δ: 6.89 (s, 4H), 3.99 (t, *J*= 6.7 Hz, 4H), 1.81 (m, *J*=6.9 Hz, 4H), 1.47 (m, 4H), 1.28-1.37 (m, 16H), 0.88 (t, *J*=6.4 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ: 149.1, 121.0, 114.1, 69.27, 31.85, 29.41, 26.06, 22.69, 14.11

1,2-Bis(3,4-bis(octyloxy)phenyl) ethane-1,2-dione was synthesized according to the literature [35]. 1,2-Bis(octyloxy)benzene (1.9 g, 5.5 mmol), urea (0.31 g, 5.2 mmol) and $AlCl_3$ (1.1 g, 8.4 mmol) were dissolved in dichloromethane (15 mL). The solution was cooled to 0°C in an ice bath and stirred under argon atmosphere. Oxalylchloride (0.30 mL, 3.4 mmol) was added drop wise to the reaction medium. The mixture was stirred overnight at ambient temperature. Then the solution was poured into cold water and the organic phase was extracted with dichloromethane. Organic phase was washed with $NaHCO_3$, dried over Na_2SO_4 and concentrated under vacuum to afford a yellow solid. Yield: 0.99 g, 50 %.

^1H NMR (400, $CDCl_3$): δ: 7.56 (d, *J*=2.0 Hz, 2H), 7.43 (dd, J_1= 1.86 Hz, J_2= 8.4 Hz, 2H), 6.86 (d, *J*=8.5 Hz, 2H), 4.05 (t, *J*= 5.3 Hz, 8H), 1.84 (m, 8H), 1.45 (m, 8H), 1.28 (m, 32H), 0.88 (m, 12H)

^{13}C NMR (100 MHz, $CDCl_3$): δ: 202.1, 155.0, 149.3, 126.1, 93.21, 69.12, 31.82, 29.35, 28.92, 25.92, 22.68, 14.11

2,3-Bis(3,4-bis(octyloxy)phenyl)-5,8-dibromoquinoxaline was synthesized according to the literature [36]. 3,6-Dibromobenzene-1,2-diamine (0.22 g, 0.85 mmol), 1,2-bis(3,4-bis(octyloxy)phenyl) ethane-1,2-dione (0.62 g, 0.85 mmol) and *p*-toluene sulfonic acid were dissolved in ethanol (10 mL) in a two-neck flask under argon atmosphere. The mixture was heated to reflux overnight. After completion of the reaction, the solution was cooled to 0°C in an ice bath. The precipitate was filtered and washed with ethanol to obtain the product as a yellow solid. Yield: 0.57 g, 66 %.

^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.85 (s, 2H), 7.56 (d, *J*= 2.0 Hz, 2H), 7.43 (dd, J_1= 2.0 Hz, J_2= 8.4 Hz, 2H), 6.85 (d, *J*= 2.1 Hz, 2H), 4.0 (t, *J*= 6.7 Hz, 8H), 1.74 (m, 8H), 1.47 (m, 8H), 1.29 (m, 32H), 0.89 (m, 12H)

^{13}C NMR (100 MHz, $CDCl_3$): δ: 151.5, 148.6, 146.6, 136.9, 130.4, 128.5, 121.3, 113.5, 110.9, 67.11, 29.73, 27.31, 26.99, 23.90, 20.54, 11.96

Tributyl(selenophen-2-yl) stannane was synthesized according to the literature [37]. Selenophene (5.0 g, 38 mmol) was dissolved in anhydrous tetrahydrofuran (70 mL) in a two-neck flask under argon atmosphere. After the solution was cooled to -78 °C, n-butyl lithium (15.3 mL, 38.2 mmol in 2.5 mL hexane) was added drop wise. Then, tributyltin chloride (11 mL, 41 mmol) was added drop wise to the solution. The temperature was maintained at -78 °C for 4h and then the reaction mixture was stirred overnight at room temperature. After evaporation of solvent, the crude product was dissolved in dichloromethane and organic phase was washed with $NaHCO_3$, water and brine. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed using rotary evaporator to afford the product as a pale yellow oil. Yield: 14 g, 95 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, *J*= 8.4 Hz, 1H), 7.53 (m, 1H), 7.5 (dd, J_1= 2.4 Hz, J_2= 9.4 Hz, 1H), 1.59 (m, 6H), 1.37 (m, 6H), 1.12 (m, 6H), 0.91 (t, *J*= 7.3 Hz, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ: 143.6, 137.9, 135.3, 130.6, 29.00, 27.30, 13.67, 11.13

2,3-Bis(3,4-bis(octyloxy)phenyl)-5,8-di(selenophen-2-yl) quinoxaline was synthesized according to the literature [38]. 2,3-Bis(3,4-bis(octyloxy)phenyl)-5,8-dibromoquinoxaline (0.40 g, 0.42 mmol), tributyl(selenophen-2-yl) stannane (0.88 g, 2.10 mmol) and $PdCl_2(PPh_3)_2$ (45 mg, 0.06 mmol) were dissolved in dry tetrahydrofuran (35 mL) in a two-neck flask under argon atmosphere. The reaction mixture was stirred for 18 hours at 100°C. The mixture was cooled to ambient temperature and removal of the solvent under vacuum gave a red solid subjected to column chromatography (hexane: chloroform, 1:1). Yield: 0.36 g, 95 %.

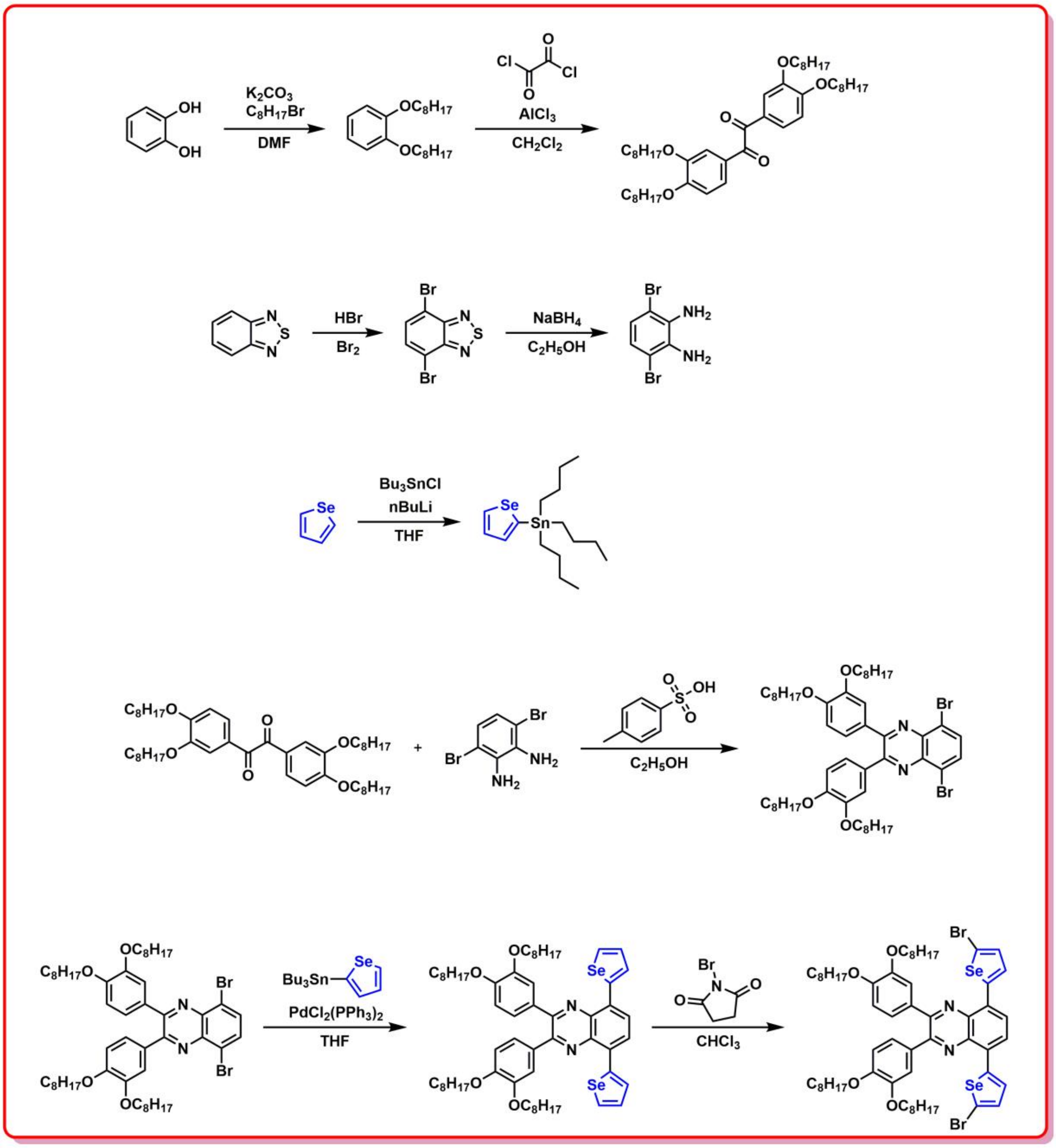
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (2H, s), 8.19 (d, *J*= 6.5 Hz, 2H), 8.05 (d, *J*= 3.2 Hz, 2H), 7.45 (dd, J_1= 4.0 Hz, J_2= 5.8 Hz, 2H), 7.36 (d, *J*= 2.0 Hz 2H), 7.23 (dd, J_1= 2.0 Hz, J_2= 2.1 Hz, 2H), 6.86 (d, *J*= 8.5 Hz, 2H), 4.04 (t, *J*= 6.7 Hz, 4H), 3.93 (t, *J*= 6.7 Hz, 4H), 1.86 (m, 4H), 1.78 (m, 4H), 1.40-1.25 (m, 40H), 0.9 (t, *J*= 6.6 Hz, 12H)

^{13}C NMR (100 MHz, $CDCl_3$): δ: 163.0, 159.2, 151.7, 110.3, 102.4, 85.34, 31.86, 29.37, 26.08, 22.69, 22.23, 14.12

2,3-Bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl) quinoxaline was synthesized according to the literature [37]. 2,3-Bis(3,4-bis(octyloxy)phenyl)-5,8 di(selenophen-2-yl) quinoxaline (0.46 g, 0.43 mmol) was dissolved in $CHCl_3$ in a two-neck flask. N-bromosuccinimide (0.15 g, 0.86 mmol) was added in several portions. After stirring the mixture overnight at ambient temperature, 65 mL distilled water was added. The organic layer was extracted with $CHCl_3$, dried over Na_2SO_4 and concentrated under vacuum. The product was obtained as a red solid by recrystallization from ethanol. Yield: 0.46 g, 89 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (s, 2H), 7.73 (d, *J*= 4.4 Hz, 2H), 7.41 (s, 2H), 7.36 (d, *J*= 4.4 Hz, 2H), 7.07 (dd, J_1= 2.0 Hz, J_2= 8.3 Hz, 2H), 6.83 (d, *J*= 8.4 Hz, 2H), 4.03 (t, *J*= 6.7 Hz, 8H), 1.85 (m, 8H), 1.50 (m, 8H), 1.25-1.36 (m, 32H), 0.90 (t, *J*= 6.7 Hz, 12H)

^{13}C NMR (100 MHz, $CDCl_3$): δ: 150.1, 148.1, 146.7, 140.4, 133.6, 129.7, 129.26, 128.3, 123.6, 121.4, 120.8, 113.8, 110.4, 67.31, 29.70, 27.20, 24.00, 20.55, 11.94



Scheme 1. Synthetic pathway and structure of the monomers

Poly[2-(5-(2,3-bis(3,4-bis(octyloxy)phenyl)-8-(selenophen-2-yl)quinoxalin-5-yl)selenophen-2-yl)-9-(heptadecan-9-yl)-9H-carbazole]-PQSeCz and Poly [(2,3-bis(3,4-bis(octyloxy)phenyl)-5-(5-(9,9-dioctyl-9H-fluoren-2-yl)selenophen-2-yl)-8-(selenophen-2-yl)quinoxaline]- PQSeFl were synthesized according to the literature [39].

PQSeCz

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2,3-Bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl) quinoxaline (0.23 g, 0.19 mmol), 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (0.13 g, 0.19 mmol), 2M K_2CO_3 (0.4 mL), Aliquat 336 (1-2 drops) and $Pd(PPh_3)_4$ (5 mol %) were dissolved and refluxed in dry toluene (10 mL) in a two neck flask under argon atmosphere for 48h. The reaction was controlled by TLC. Then, chlorobenzene and tributyl(furan-2-yl) were added as end-capping reagents. After evaporation of solvent under reduced pressure, the crude product was extracted with $CHCl_3$: H_2O several times to remove alkali solution. The organic layers were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. Cold methanol was added to the crude product. Sodium diethyldithiocarbamate trihydrate was added to the solution as Pd scavenger and the solution was stirred for 1.5 h. Then, the polymer was filtered through a Soxhlet thimble and washed with acetone and hexane to remove oligomers. The polymer was recovered with chloroform. Corresponding polymer was obtained as a dark green solid. Yield: 145 mg, 52 %.

^1H NMR (400 MHz, $CDCl_3$) δ: 8.26, 8.10, 7.86, 7.68 (Carbazole), 8.22-8.20, 7.62-7.57, 6.92-6.80 (Quinoxaline), 7.73, 7.48, 7.32 (Selenophene), 4.06-3.95 ($-OCH_2$), 1.87, 1.71, 1.31-1.14 ($-CH_2$), 0.90-0.78 ($-CH_3$)

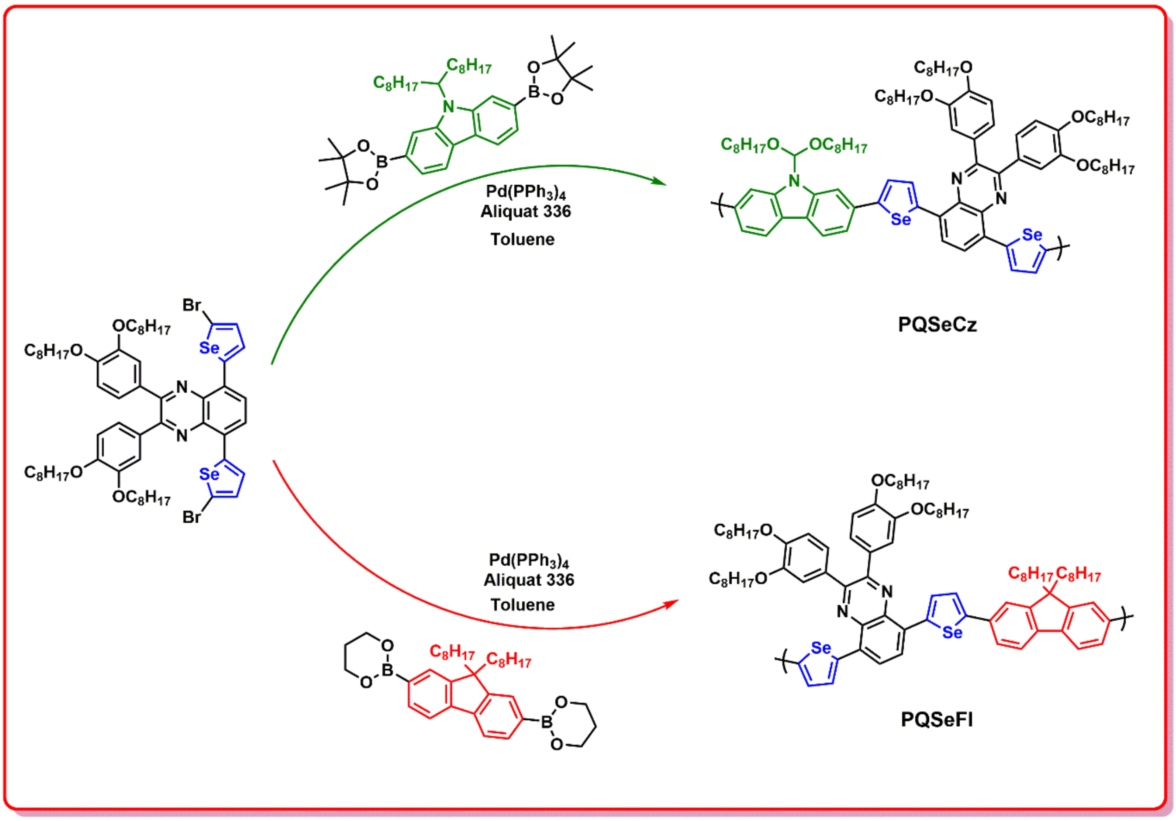
Mw: 31000 Da, Mn: 10700 Da, PDI: 2.89

PQSeFl

The polymer was synthesized with the same procedure described for PQSeCz. The copolymerization of the monomers; 2,3-bis(3,4-bis(octyloxy)phenyl)-5,8-bis(5-bromoselenophen-2-yl) quinoxaline (210 mg, 0.173 mmol), 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl) bis(1,3,2-dioxaborinane) gave the polymer as a dark red solid. Yield: 195 mg, 80 %.

^1H NMR (400 MHz, $CDCl_3$) δ: 8.28-8.24, (Fluorene), 8.22-8.20, 7.62-7.57, 6.92-6.80 (Quinoxaline), 7.73, 7.48, 7.32 (Selenophene), 4.07-3.96 ($-OCH_2$), 2.04-1.09 ($-CH_2$), 0.91-0.78 ($-CH_3$)

Mw: 9600 Da, Mn: 7200 Da, PDI: 1.33



Scheme 2. Synthetic pathways and structures of the polymers

2.3 Characterizations

In order to determine the structures and purity of synthesized molecules and polymers, a Bruker Avance DPX 400 NMR Spectrometer was implemented to obtain ^1H and ^{13}C NMR spectra in $CDCl_3$. Chemical shifts were recorded in ppm with respect to tetramethylsilane internal reference. To investigate the redox properties of synthesized polymers cyclic voltammetry (CV) was implemented. A three-electrode system was used to perform cyclic voltammetry. Silver and platinum wires were used as reference and counter electrodes, respectively. Indium tin oxide (ITO) cast glass substrate was used as the working electrode in an electrolyte containing 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Highest Occupied Molecular Orbital (HOMO) and Lowest Occupied Molecular Orbital (LUMO) levels were determined with respect to Normal Hydrogen Electrode (NHE), -4.75 eV in vacuum.

3. Results and discussions

3.1. Electrochemical Properties

Cyclic voltammetry is a practical and useful technique that can be used to investigate redox behaviors of polymers. For this purpose the chemically synthesized polymers (PQSeCz and PQSeFl) were dissolved in chloroform (5 mg.mL^{-1}) and coated onto ITO coated glass slides via spray coating. Prepared ITO films were used both for electrochemical and spectroelectrochemical characterizations. The cyclic voltammograms of polymer films were recorded in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$)/acetonitrile (ACN) solutions versus Ag wire pseudo reference electrode. Figure 1. illustrates the single scan cyclic voltammograms of polymers performed in the potential range between -1.8 V and 1.5 V for PQSeCz and -1.7 V and 1.4 V for PQSeFl at a scan rate of 100 mV.s^{-1}. In addition to redox behaviors, CV can be used to explore the doping characters and the HOMO and LUMO energy levels of corresponding copolymers. As seen in Fig. 1, both polymers have ambipolar character. Polymers that illustrate ambipolar character have both p-type doping and n-type doping behaviors which make them good candidates for different applications such as; batteries, supercapacitors, and light-emitting diodes. The potential at which the polymer is oxidized at the anodic region is p-doping potential and the reverse peak stands for the dedoping process whereas n-doping is the reduction peak at the cathodic region and the reverse peak is for the dedoping. The oxidation (doping/dedoping) potentials were 1.15 V/ 0.82 V for PQSeCz, 1.11V/ 0.82 V for PQSeFl, in the positive potential region. Another important parameters for the characterization of conducting polymers are HOMO/ LUMO energy levels of these materials which affect their application fields importantly. HOMO energy levels were calculated as -5.54 eV for PQSeCz, and -5.58 eV for PQSeFl. Organic anions are mostly unstable and reduction potentials are rarely obtained. For our polymers n-doping was clearly observed by CV studies. The reduction (doping/dedoping) potentials were -1.26 V /-1.14 V for PQSeCz, -1.48 V/ -1.23 V for PQSeFl, in the negative potential region. Moon and coworkers synthesized carbazole and quinoxaline based polymers with alkyl side chains and the π-bridge was thiophene in the polymer backbone. The polymers with different solubilizing side chains were not n-dopable in that study. Replacing selenium atom with thiophene provided us to obtain a polymer (PQSeCz) with a lower band gap and n-dopable character [34]. In this study, two different donor units (carbazole and fluorene) were inserted into the polymer backbones in order to explore the effect of these units on electrochemical and optical properties. Polymers have very similar oxidation potentials and electronic band gaps which may be attributed to their molecular weights. Optoelectronic properties and device performance of the polymers are improved with increasing molecular weights. In literature, Fréchet and co-workers revealed that high molecular weight polymers gave enhanced interconnectivity with high charge carrier mobility. Studies have shown that molecular weight of conjugated polymers can affect the effective conjugated chain length, and thus may vary their optical and electric properties [35]. Polymers with different electron densities did not give the expected results in terms of their redox behaviors and HOMO-LUMO energy levels. Carbazole based polymer has a higher molecular weight than its fluorene derivative. The reason of obtaining higher molecular weight for carbazole based polymer could be attributed to its fully aromatic structure with stronger chemical and air stability compared to those of fluorene [36]. Due to its air instability, we could not obtain a high molecular weight polymer with fluorene as the donor and this may lead to slight changes in the electronic properties of polymers.

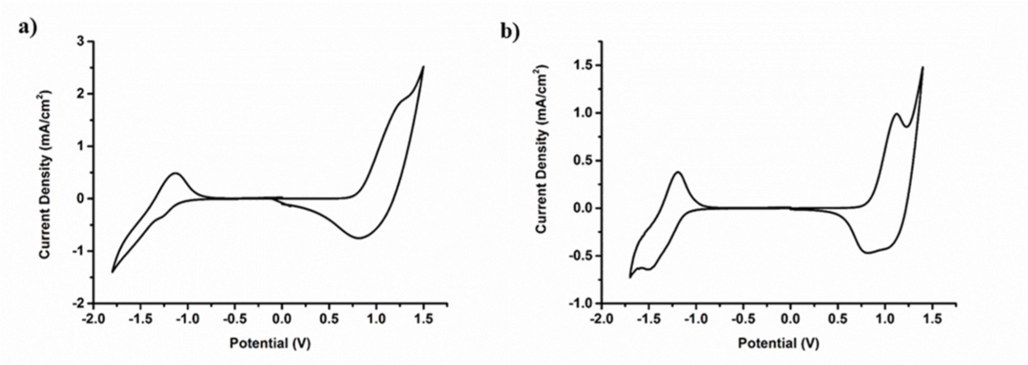


Figure 1. Single scan cyclic voltammograms of polymers **(a)** PQSeCz, **(b)** PQSeFl on ITO in 0.1 M $TBAPF_6$/ACN electrolyte/solvent couple at a scan rate of 100 mV.s^{-1}

Table 1. Comparison of electronic properties of two polymers

Polymers	**$E_{p\text{-doping}}$ (V)**	**$E_{p\text{-dedoping}}$ (V)**	**$E_{n\text{-doping}}$ (V)**	**$E_{n\text{-dedoping}}$ (V)**	**HOMO (eV)**	**LUMO (eV)**	**E_g^{el} (eV)**
PQSeFl	1.11	0.82	-1.48	-1.20	-5.58	-3.68	1.90
PQSeCz	1.15	0.82	-1.26	-1.14	-5.54	-3.68	1.86

3.2. Optical Properties

To explore optical properties of conducting polymers; λ_{max} and optical band gap, spectroelectrochemical studies were performed. In this study, in situ UV-Vis-NIR spectra were monitored in 0.1 M $TBAPF_6$/ACN solution to investigate the spectral response of the polymers to the doping processes.

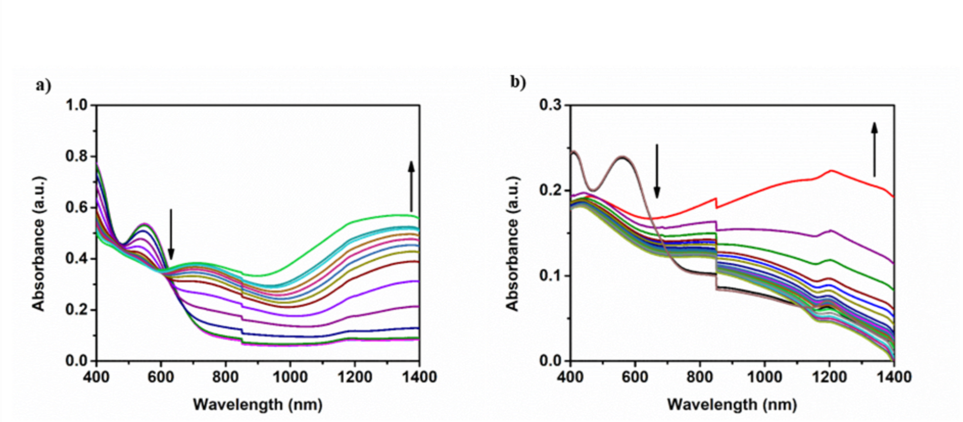


Figure 2. Electronic absorption spectra for **(a)** PQSeCz **(b)** PQSeFl in 0.1 M $TBAPF_6$/ACN solution

doi:10.20944/preprints201805.0331.v1

The polymers were dissolved in chloroform and spray coated onto ITO substrate until homogeneous films are obtained. In situ spectroelectrochemical analyses were performed via incrementally increasing applied potentials between 0.0 and 1.15 V for PQSeCz, 0.0 and 1.20 V for PQSeFl. These potentials were obtained from cyclic voltammetry studies and electronic absorption spectra were reported in Fig. 2. Recording neutral film absorptions are very crucial to calculate λ_{max} and E_g^{op} which are important parameters as regards to several applications. While the neutral film absorptions in the visible region were depleted, new transitions in the NIR region aroused during stepwise oxidation proving the formation of charge carriers on the polymer backbone namely polarons (radical cations) and bipolarons (dications).

As seen in Fig. 2, maximum absorption wavelengths in the visible region were centered at 551 nm for PQSeCz, 560 nm for PQSeFl. Optical bandgaps (E_g^{op}) of polymers were calculated from the lowest energy $\pi - \pi^*$ transition onsets and found as 1.71 eV, and 1.58 eV, respectively. Optical properties of polymers were summarized in Table 2. The synthesized polymers are electrochromic and both reveal different colors at their neutral and doped states.

Table 2. Comparison of optical properties of the polymers

Polymers	**λ_{max} (nm)**	**$\lambda_{max,onset}$ (nm)**	**E_g^{op} (eV)**
PQSeCz	551	725	1.71
PQSeFl	560	783	1.58

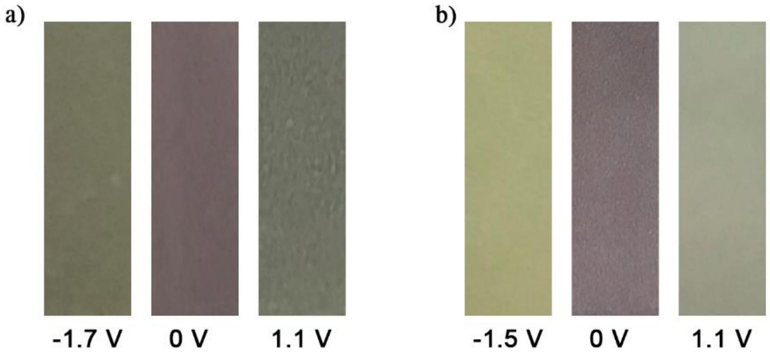


Figure 3. Colors of **(a)** PQSeCz **(b)** PQSeFl in neutral and oxidized states

For the scientific expression of the color, colorimetry measurements of the polymer films were performed and CIE (Commission Internationale de l'Eclairage) coordinates were determined. In CIE coordinates, "L" represents the brightness of the color (L= 0 yields black and L= 100 indicates diffuse white), "a" represents a color between red/magenta and green, "b" represents a color between yellow and blue. Table 3 illustrates the colorimetric values of the polymer film.

Table 3. Colorimetry measurements of the polymers

	Applied Potential (V)	L	a	b
PQSeFl	-1.5	68.08	-6.02	23.07
	0	49.26	5.98	0.92
	1.1	67.60	-4.14	11.73
PQSeCz	-1.7	48.34	-2.52	12.98
	0	42.51	5.91	2.21
	1.1	47.71	-3.20	7.46

4. Conclusions

Palladium catalyzed Suzuki polymerization was performed to obtain two donor–acceptor type alternating copolymers. Fluorene and carbazole were selected as the electron donor moieties whereas quinoxaline was used as the acceptor in the polymer backbone. Selenophene was introduced to the polymer to decrease steric hindrance between donor and acceptor groups which may arise from solubilizing alkyl chains. Moreover, selenophene can provide improved planarity, enhanced effective conjugation length, and lower band-gap energy due to its relatively lower aromaticity. Since selenophene bearing monomers have lower solubility than thiophene based counterparts, the polymers were synthesized with lower Mn. Due to its air instability, a high molecular weight polymer could not be obtained for the one with fluorene as the donor which may lead to slightly change in electronic properties of polymers compared to carbazole derivative. PQSeFl possess grayish transparent color in its doped state hence it can be used as active layer in an electrochromic device.

Author Contributions: Methodology, Mustafa Yasa and Seza Goker; Supervision, Levent Toppare

Acknowledgments: M.Y. is grateful to TÜBİTAK for 2210-C scholarship.

Conflicts of Interest: The authors declare no conflict of interest.

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