Dedicated to the Memory of Prof. M. Bendikov

Oligoselenophenes (*n* and *p* Type): Synthesis and Properties

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Abstract—An array of semiconducting oligoselenophenes (*n* and *p* types), up to hexamer units, has been synthesized by the double Stille coupling methods using tetrakis(triphenylphosphine)palladium(0) as a catalyst. A series of semiconducting oligomers (*n* and *p* types) containing mixed hetero-units (hexamers of thiophene and selenophene) have been also synthesized using the Stille coupling reaction. Their thermal properties are systematically studied and compared with those of π -conjugated thiophene based oligomers using DSC and TGA. The field-effect mobility of synthesized *n* and *p* type oligomers is analyzed.

Keywords: selenophene, oligomer, oligoselenophene, sexiselenophenes, Stille coupling, *n* and *p* type oligomers **DOI:** 10.1134/S1070363219090287

INTRODUCTION

Over past few years, conjugated oligomers (or polymers) have been attracting close attention due to their potential application in organic light-emitting diodes (OLEDs) [1, 2], photovoltaic cells [3, 4], organic fieldeffect transistors (OFETs) [5-8], and electrochromic devices [9]. Thiophene based π -conjugated systems demonstrated significant characteristics in the field of *n* and *p* type OFETs [10–12]. Selenophene is the heavy member of chalcogenophenes series and its properties are similar to some extend to those of thiophene [13, 14]. The electron-donating [15] and polarizable [16] properties of selenophenes are more pronounces than those of thiophenes. The inter-chain charge transfer facilitated by Se \cdots Se contact is also higher than by S \cdots S contacts. These facts indicate that selenophene containing oligomers and polymers should be particularly attractive as electronic materials. Nevertheless, only recently some new polyselenophenes were synthesized (chemically and electrochemically) and their electronic properties were studied systematically [9, 17]. Because of variation of chain length of polymers, comparison of the properties of polyselenophene and polythiophene does not provide complete information on contributions of chalcogen atoms in electronic structures of the conjugated systems. Comparison between oligoselenophenes and oligothiophenes having the same chain length provides some important information regarding contribution of chalcogen atoms in the electronic structures. Taking in consideration importance of oligomers (especially oligothiophenes) for OFETs application [10–12], we were determined to synthesize and study properties of *n* and *p* type oligomers based on selenophene hetero-units.

Bendikov and co-authors [18] have studied oligoselenophenes at B3LYP/6-31G(d) level for comparing those with the corresponding oligothiophenes. It was indicated that oligoselenophenes had more quinoid characters than the corresponding oligothiophenes. The inter-ring bond distances in oligoselenophenes are considerably shorter than the related distances in oligothiophenes. The HOMO-LUMO gap (band gap), bond length alternation (BLA) and charge distribution of oligoselenophenes are







strongly dependant on twisting, which costs very little energy. However, twisting of oligoselenophenes requires higher energy than their corresponding thiophene analogues. The energy required for twisting around inter-ring bonds in 6Se is small, however, it is notably greater than that in 6T. Twisting to a 36° inter-ring dihedral angle requires only 3.4 kcal/mol per inter-ring bond for 6Se (2.5 kcal/mol for 6T), and twisting to a 20° inter-ring dihedral angle requires only 0.7 kcal/mol per inter-ring bond for 6Se (0.4 kcal/mol for 6T). These calculations suggest



Scheme 3. Synthesis and reactions of unsubstituted oligomers [p-type].

X = Se (1), S (2), Se, 61% (3), S, 62% (4), Se, 75% (5), Se, 40% (6), Se, 78% (7), S, 80% (8), Se, 18% (9), S (10), Se (11); Y = Se, 18% (9), Se, 32% (10), S, 23% (11).

that selenophene containing oligomers should maintain planarity with a wider range of substituents (Scheme 1).

Keeping in mind high importance of oligothiophenes for organic electronic materials, and inspired by the structural differences between selenophenes and thiophenes, we paid particular attention to the synthesis and properties of electron-transporting as well as hole-transporting organic materials for OFETs applications. For the first time, Inoune and co-workers [19] reported the synthesis of chalcogen selenophene series up to pentamer using the Stille coupling methods. They also studied the electrochemical, spectroscopic properties and the crystal structure of tetraselenophene [20, 21]. Millefiori and Alparone [22] published theoretical investigation data on structures and conformational behavior of small selenophene oligomers. Zade and Bendikov [23] studied the hopping transport in long oligothiophenes and oligoselenophenes.

A number of *n*-channel semiconductors developed up to now is far less than that of *p*-channel ones. Incorporation of electron-withdrawing groups such as cyano [24], nitro [25], dicyanomethylene [26], ester [27], perfluoroalkyl [8, 11, 28], perfluoroaryl [29], and perfluoroalkylphenyl [30] into the π -conjugated systems is an efficient way of converting *p*-type into *n*-type organic semiconductors. Suzuki and co-workers [31] described perfluorinated oligo(*p*-phenylene) derivatives and perfluoro-*p*-sexiphenyl as an efficient *n*-type of semiconductors for electron-transport layer of OLEDs.

Here, we report synthesis of *p*-type (Scheme 2a) and *n*-type (Scheme 2b) oligomers.

RESULTS AND DISCUSSION

The Stille coupling reaction was used efficiently in constructing a series of oligoselenophenes. Bromination of dicyclic compounds 1 and 2 by *N*-bromosuccinimide (NBS) yielded the corresponding monobrominated derivates 3 (61%) and 4 (62%). Tributyltin derivatives 7 and 8 were accumulated in good yields upon lithiation of 1 and 2 followed by quenching with tributyltin chloride. Synthesis of sexiselenophene (α -6Se) and mixed oligo-





X = Se, 35% (12), S, 85% (13), Se, 78% (14), S, 64% (15), Se, 70% (16), S, 88% (17), Se, 22% (18), S, 27% (19); Y = Se, 22% (18), Se, 27% (19); $R = C_6H_{13}$.

mers (α -4S-2Se, α -4Se-2S) was based on the double Stille coupling reaction involving stannic derivatives of bis-selenophene or bis-thiophene using monobrominated derivatives of bis-selenophene or bis-thiophene tetrakis(triphenylphosphine)palladium(0) as catalysts (Scheme 3). Similarly, synthesis of tetraselenophene **6** was accomplished in 40% yield by the Stille coupling reaction of dibromo derivative **5** with 2-(*n*-tributyltin)selenophene using Pd catalyst.

It could be expected that introduction of alkyl groups would support solubility of oligoselenophenes. For this reason we have planned to synthesize DH-6Se and DH-4S-2Se bearing hexyl groups at the terminal positions. 2-Hexyl bisselenophene and 2-hexyl bisthiophene were used as the starting materials for obtaining DH-6Se and DH-4S-2Se. As presented in Scheme 4, these were achieved in moderate yield by the Friedel–Crafts acyla-



Fig. 1. UV-Vis spectra of sexi-selenophene and mixed oligomers in 1,2-dichlorobenzene: (1) 6Se, (2) 4S-2Se, and (3) 4Se-2S.

tion of derivatives 1 and 2 followed by reduction of the corresponding acylated derivates 12 and 13 by AlH_3 (LAH+AlCl₃). Bromo derivatives 16 and 17 were synthesized in good yields by bromination of the corresponding compounds 14 and 15 by NBS. The Stille coupling reaction of compound 7 with bromoderivatives 16 and 17 using the Pd catalyst gave the corresponding oligomers 18 (DH-6Se) and 19 (DH-4S-2Se) in moderate yields. All oligoselenophenes were purified by sublimation.

As presented in Scheme 5, the required starting materials were produced by lithiation of bithiophene 2 and bi-selenophene 1 with an equivalent of *n*-BuLi followed by treatment with (PhSO₂)₂NF that yielded the respective 2-fluorobithiophene and 2-fluorobiselenophene in moderate yields. Bromination of 2a and 2c with by NBS afforded the respective monobromoderivatives 2b and 2d. Tributyltin derivatives 8 and 7 were prepared in 80% and 78% yield by lithiation of compounds 2 and 1 followed by quenching with *n*-Bu₃SnCl. The *n*-type oligomers 20–22 were synthesized by the double Stille coupling reaction based on tin analog of bithiophene 8 or biselenophene 7 and monobrominated derivatives 2b or 2d using tetrakis(triphenylphosphine)palladium(0) as a catalyst. All *n*-type oligomers were purified by sublimation.

UV-Vis spectra. UV absorbance maxima recorded for the dimer (2Se 331 nm), trimer (3Se 389 nm), tetramer (4Se 432 nm), and hexamer (6Se 452 nm) were higher than their corresponding thiophene analog. UV absorbance maxima of 4S-2Se (441 nm) and 4Se-2S (438 nm) were lower than that of sexi-selenophene (6Se 452 nm) (Fig. 1). The profiles of absorption and emission spectra Scheme 5. Synthesis and reactions of *n*-type oligomers.



of alkylated oligomers (*p*-type) in 1,2-dichlorobenzene and chloroform respectively were almost identical. The absorption maximum of DH-6Se was recorded at 460 nm and its emission maximum at 548 nm. UV-Vis spectral data of synthesized oligoselenophenes are presented in Table 1.

Thermal properties. Thermal behavior of the oligomers was determined by a repeated heating-cooling cycle using DSC. Figures 2, 3 demonstrate the comparison of DSC scans of sulfur and selenium analogs. Melting points of oligoselenophenes were substantially higher than those of the corresponding oligothiophenes, α -2Se, α -3Se and α -4Se melt at 48, 170, and 296°C respectively, whereas α -2S, α -3S and α -4S melt at 34, 92, and 208°C. The higher melting points of α -oligoselenophenes indicated stronger π - π intermolecular interaction among the neighboring components in their molecules. The calculated enthalpy of fusion (ΔH) for α -3Se (5.14 kcal/mol) and α -4Se (12.89 kcal/mol) were also higher than their corresponding thiophene analogs [4.87 kcal/mol (α -3T) and 12.55 kcal/mol (α -4T)]. Generally, melting points became higher as the number of hetero rings in a given



Fig. 2. DSC scans of **3S** and **3Se** under the atmosphere of N₂: (*1*) 3S and (*2*) 3Se.

oligomer chain increases. The melting point of α -4Se (296°C) was higher than its corresponding shorter chain analogue α -3Se (170°C) (Fig. 4). Longer chain oligomers were expected to have stronger π - π intermolecular interactions between the neighboring molecules than the corresponding shorter chain oligomers. This could also be the reason for the higher melting points of the former compounds. DSC analysis of α -6T exhibited the liquid crystalline phase at higher temperature [21–23]. Our DSC studies of α -6T matched these results. DSC analysis of α -4S-2Se demonstrated two phase transitions at 339°C

 Table 1. UV-Vis spectral data of oligoselenophenes

Compound	Absorbance,	Emission,	
Compound	λ_{max} , nm	λ_{max} , nm	
2Se	331	_	
3Se	389	_	
4Se	432	_	
6Se	452	_	
4S-2Se	441	_	
4Se-2S	438	_	
$\alpha - 6T$	435	508	
DH-6Se	460	548	
DH-4S-2Se	446	538	
DH-6T	440 521, 551		
DF-6T	444	508, 542	
DF-6Se	431	_	
DF-4S-2Se	439	_	



Fig. 3. DSC scans of **4S** and **4Se** under the atmosphere of N_2 : (1) 4S and (2) 4Se.

and 353°C, that were higher than those of α -6T. DSC analysis of DH- α -6T demonstrated three phase transitions at 296, 305, 316°C. The data were in accord with the earlier studies [24]. DSC study of DH-4S-2Se exhibited two phase transitions at 338 and 366°C. All phase transitions were determined to be reversible in oligoselenophenes. TGA data accumulated for DH-6Se and DH-4S-2Se revealed inflections at 233 and 358°C that indicated their decomposition processes.

DSC scans of DF-6T and DF-4S-2Se demonstrated sharp melting endotherms at 317 and 358°C, accordingly, which was followed by crystallization at 313 and 352°C. The melting endotherms of DF-6T and DF-4S-2Se were higher than 6T. Similarly, the melting endotherm of DF-4S-2Se was also higher than DF-6T. The higher melting endotherms of *n*-type oligomers indicated the stronger π - π interaction between the molecules.

The detailed shelf-live tests of hole mobility (μ), threshold voltage (V_t), on current (I_{on}), and off current (I_{off}) under atmospheric conditions of OTFTs based on α -6T, α -6-Se, α -4S-2Se, and α -4Se-2S indicated their environmental stability over time (Table 2).

Table 2. Properties of sublimed oligomers

Compound	Mobility	$I_{\rm on}/I_{\rm off}$	V_T
α- 6Τ	2.1×10-3	106	-20
α-6Se	1.1×10-2	106	-20
α -4S-2Se	2.0×10-2	106	-20
α -4Se-2S	4.0×10 ⁻²	106	-20

EXPERIMENTAL

The chemicals used were purchased from Aldrich, Lancaster, Fluka, Merck, SRL, and Spectrochem, and distilled or recrystallized whenever required, or prepared according to literature procedures. All manipulations were performed under an inert atmosphere using standard vacuum lines and Schlenk techniques. All solvents used for the synthesis were deoxygenated, dried and distilled by standard methods. Pre-coated silica gel 60F254 (Merck) was used for TLC and silica gel 60-120 and 100-200 mesh (SRL) was used for column chromatography. IR spectra were recorded on a Nicolet 6700 single beam FTIR spectrophotometer. ¹H NMR spectra were measured on a Brucker-AC 250 MHz and a Brucker-AC 400 MHz spectrometers at 300 K. Chemical shifts are reported in δ unit (ppm) from TMS with the solvent resonance used as the internal standard (CDCl₃ in ¹H NMR spectra 7.26 ppm and in ¹³C NMR spectra 77.0 ppm). EIMS (70 eV) spectra were measured on a VG MicroMass 7070H and a VG Autospec M mass spectrometers. Elemental analysis was carried out on a Perkin Elmer Instruments 2400 Series II CHNS/O Analyzer and a Vario EL, Elementar. Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected. DSC was run on a TA instrument DSCQ200 analyzer at a heating/cooling rate of 10/-10°C/min under nitrogen flow.

2,2'-Biselenophene (1) and 2,2'-bithiophene (2) were synthesized according to the earlier developed procedure [19, 32].

2-Bromo-5-(selenophene-2-yl)selenophene (3). Into a stirred solution of biselenophene (1) (1 g, 3.84 mmol) in chloroform-acetic acid (1 : 1 v/v 50 mL) was portionwise added NBS (0.68 g, 3.84 mmol), and the mixture was stirred at room temperature for 1 h, then poured into water (100 mL) and extracted with dichloromethane. The extract was washed with water, 5% aqueous solution of sodium hydrogen carbonate and brine solution. The mixture was dried over MgSO₄, the solvent was evaporated, and the residue was purified by column chromatography on silica gel with hexane to give compound **3** as a white solid. Yield 61%, mp 75°C. ¹H NMR spectrum, δ , ppm: 6.94 d (J = 4.0 Hz, 1H), 7.14–7.25 m (3H), 7.87 d (J = 5.2 Hz, 1H). Found, %: C 28.37, H 1.46. C₈H₅BrSe₂. Calculated, %: C 28.35, H 1.49.

2-Bromo-5-(thiophene-2-yl)thiophene (4) was synthesized according to the earlier developed procedure [32].



Fig. 4. DSC scans of **2Se**, **3Se** and **4Se** under the atmosphere of N_2 : (1) 2Se, (2) 3Se, and (3) 4Se.

5,5'-Dibromo-2,2'-biselenophene (5) was synthesized according to the earlier developed procedure [19].

2,2':5',2'':5'',2''' Quaterselenyl (6). A mixture of 2,5-dibromobiselenophene 5 (0.50 g, 1.20 mmol) with 2-tributylstannylselenophene (1 g, 2.38 mmol) and tetrakis(triphenylphosphine)palladium (0.14 g, 0.12 mmol) in dry toluene (20 mL) was refluxed for 24 h under the atmosphere of nitrogen. The precipitate was filtered off under suction and sublimed at 220°C to give compound 6 as an orange solid. Yield 40%, mp 296°C. IR spectrum, v, cm⁻¹: 1503, 1456, 1437, 1204, 1062, 1039, 823, 795, 754, 687, 675. MS (EI): *m/z*: 518 $[M]^+$. Found, %: C 37.11, H 1.94. C₁₆H₁₀Se₄. Calculated, %: C 37.09, H 1.95.

5,5'-Bis-tributylstannyl-2,2'-biselenophene (7). Into a stirred solution of bis-lithiobiselenophene, prepared from biselenophene 1 (1 g, 3.84 mmol) and *n*-butyllithium (3.4 mL, 8.43 mmol) in dry ether (50 mL) and cooled down to -78°C, was added tributyltin chloride (2.75 g, 8.44 mmol) in the atmosphere of nitrogen, and the mixture was stirred overnight at room temperature, then treated with hexane (50 mL), washed with brine, and dried over MgSO₄. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (hexane and few drops of TEA) to give product 7 as a pale yellow oil. Yield 78%. ¹H NMR (400 MHz) spectrum, δ, ppm: 0.89 t (*J* = 7.2 Hz, 18H), 1.06–1.10 m (12H), 1.30–1.37 m (12H), 1.52-1.60 m (12H), 7.31 d (J = 3.6 Hz, 2H), 7.34 d (J = 3.6 Hz, 2H). Found, %: C 45.91, H 6.94. C₃₂H₅₈Se₂Sn₂. Calculated, %: C 45.86, H 6.98.

5,5'-Bis-tributylstannyl-2,2'-bithiophene (8). Into a stirred solution of bis-lithiobithiophene, prepared from

bithiophene **2** (2 g, 12.02 mmol) and *n*-butyllithium (11 mL, 27.65 mmol) in dry ether (50 mL) and cooled down to -78° C, was added tributyltin chloride (8.23 g, 25.28 mmol) in the atmosphere of nitrogen, and the mixture was stirred overnight at room temperature, then treated with hexane (50 mL), washed with brine and dried over MgSO₄. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (hexane with few drops of TEA) to give compound **8** as a pale yellow oil. Yield 80%. ¹H NMR (400 MHz) spectrum, δ , ppm: 0.92 t (J = 7.2 Hz, 18H), 1.09–1.15 m (12H), 1.28–1.40 m (12H), 1.55–1.62 m (12H), 7.05 d (J = 3.5 Hz, 2H), 7.29 d (J = 3.3 Hz, 2H). Found, %: C 51.66, H 7.84. C₃₂H₅₈S₂Sn₂. Calculated, %: C 51.63, H 7.85.

2, 2': 5', 2'': 5'', 2''': 5''', 2'''' Sexiselenophene (α -6Se) (9). A mixture of 2-bromo-5-(selenophene-2-yl)selenophene (3) (0.48 g, 1.43 mmol) with 5,5'-bis-tributylstannyl-2,2'-biselenophene (7) (0.60 g, 0.71 mmol), and tetrakis(triphenylphosphine) palladium (0.16 g, 0.14 mmol) in dry toluene (30 mL) was refluxed for 24 h under the atmosphere of nitrogen. The red precipitate was filtered off under suction. Its following sublimation at 320°C gave compound 9 as a dark red solid. Yield 18% (first sublimation), 5% (second sublimation), mp 307°C. IR spectrum, v, cm⁻¹: 1500, 1456, 1436, 1261, 1202, 1096, 1065, 1037, 818, 789, 752, 675. MS (EI): *m/z*: 777 [*M* + 1]⁺. Found, %: C 37.17, H 1.79. C₂₄H₁₄Se₆. Calculated, %: C 37.14, H 1.82.

Oligomer (a-4S-2Se) (10). A mixture of 2-bromo-5-(thiophen-2-yl)thiophene (**4**) (0.20 g, 0.81 mmol) with 5,5'-bis-tributylstannyl-2,2'-biselenophene (**8**) (0.34 g, 0.40 mmol) and tetrakis(triphenylphosphine)palladium (0.1 g, 0.09 mmol) in dry toluene (20 mL) was refluxed for 24 h under the atmosphere of nitrogen. The precipitate was filtered off under suction and sublimed at 260°C to give compound **10** as a red solid. Yield 32% (sublimation), mp > 300°C. IR spectrum, v, cm⁻¹: 1495, 1451, 1427, 1224, 1202, 1069, 838, 827, 798, 793, 702, 688. MS (EI): *m/z*: 589 [*M* + 1]⁺. Found, %: C 48.99, H 2.39. C₂₄H₁₄S₄Se₂. Calculated, %: C 48.98, H 2.40.

Oligomer (a-4Se-2S) (11). A mixture of 2-bromo-5-(selenophene-2-yl)selenophene (**3**) (0.50 g, 1.28 mmol) with 5,5'-bis-tributylstannyl-2,2'-bisthiophene (**8**) (0.47 g, 0.64 mmol) and tetrakis(triphenylphosphine)palladium (0.15 g, 0.13 mmol) in dry toluene (30 mL) was refluxed for 24 h under the atmosphere of nitrogen. The precipitate was filtered off under suction and sublimed at 320°C to give compound **11** as a red solid. Yield 23%, mp > 300°C. IR spectrum, v, cm⁻¹: 1496, 1457, 1436, 1201, 1120, 1068, 1037, 818, 790, 763, 754, 723, 686, 675 cm⁻¹. MS: m/z: 683 $[M + 1]^+$. Found, %: C 42.27, H 2.06. C₂₄H₁₄S₂Se₄. Calculated, %: C 42.25, H 2.07.

1-[5-(Selenophen-2-yl)selenophen-2-yl]hexan-1-one (12). SnCl₄ (1.05 g, 4.03 mmol) Was added to a mixture of 2,2'-biselenophene 1 (1 g, 3.84 mmol) with hexanoyl chloride (0.54 g, 4.03 mmol) in anhydrous benzene (50 mL) cooled down to 0°C. The reaction mixture was stirred for 15 min at 0°C. After addition of ice and dilution with CH_2Cl_2 , the mixture was washed successively with water and saturated aqueous solution of NaHCO₃, dried over MgSO₄, and concentrated to dryness affording crude yellow solid which was purified by column chromatography on silica gel with hexane to give compound 12 as a yellow solid. Yield 35%, mp 95°C.

1-[5-(Thiophen-2-yl)thiophen-2-yl]hexan-1-one (13). $SnCl_4$ (4.94 mL, 18.9 mmol) Was added to a mixture of 2,2'-bithiophene 2 (3.0 g, 18.0 mmol) with hexanoyl chloride (2.55 g, 18.90 mmol) in anhydrous benzene (50 mL) cooled down to 0°C, and the mixture was stirred for 15 min. After addition of ice and dilution with CH_2Cl_2 , the mixture was washed successively with water and saturated aqueous solution of NaHCO₃, dried over MgSO₄ and concentrated to dryness. The crude yellow solid was purified by column chromatography on silica gel with hexane to give compound 13 as a pale yellow solid. Yield 85%, mp 80°C.

5-Hexyl-2,2'-biselenophene (14). A solution of ketone intermediate 12 (0.60 g, 1.67 mmol) in toluene (40 mL) was added to a suspension of $LiAlH_4$ (0.5 g, 13.15 mmol) with AlCl₃ (0.44 g, 3.30 mmol) in anhydrous Et₂O (100 mL) under the atmosphere of N₂. After 1 h of stirring at 20°C, EtOAc (20 mL) and a 1 M aqueous solution of HCl (30 mL) were successively added to the reaction mixture. The organic phase was separated by decantation and the aqueous phase was extracted with Et₂O. The combined organic phases were dried over MgSO₄ and concentrated in vacuo. Purification by column chromatography on silica gel with hexane gave compound 14 as a colorless oil. Yield 78%. ¹H NMR (250 MHz) spectrum, δ , ppm: 0.88 t (J = 6.6 Hz, 3H), 1.26–1.40 m (6H), 1.59–1.71 m (2H), 2.82 t (*J* = 7.5 Hz, 2H), 6.79 d (*J* = 3. 75 Hz, 1H), 7.03 d (*J* = 3.75 Hz, 1H), 7.14–7.24 m (2H), 7.78–7.81 m (1H). Found, %: C 48.85, H 5.27. C₁₄H₁₈Se₂. Calculated, %: C:48.85, H 5.27.

5-Hexyl-2,2'-bithiophene (15). A solution of ketone intermediate **13** (2 g, 7.57 mmol) in toluene (40 mL) was

1919

added to a suspension of $LiAlH_4$ (2.3 g, 60 mmol) with AlCl₃ (2.01 g, 15 mmol) in anhydrous Et₂O (100 mL) under the atmosphere of nitrogen, and the mixture was stirred for 1 h at 20°C. EtOAc (20 mL) And a 1 M aqueous solution of HCl (30 mL) were successively added to the reaction mixture. The organic phase was separated by decantation, and the aqueous phase was extracted with Et₂O. The organic phases were combined, dried over MgSO₄ and concentrated in vacuo. Purification by column chromatography on silica gel with hexane gave compound 15 as a colorless oil. Yield 64%. ¹H NMR (250 MHz) spectrum, δ , ppm: 0.88 t (J = 6.5 Hz, 3H), 1.26–1.42 m (6H), 1.60–1.69 m (2H), 2.77 t (*J* = 7.6 Hz, 2H), 6.65 d (J = 3.5 Hz, 1H), 6.95-6.98 m (2H), 7.07-7.09 m (1H),7.13–7.15 m (1H). Found, %: C 67.17, H 7.23. C₁₄H₁₈S₂. Calculated, %: C 67.15, H 7.24.

5-Bromo-5'-hexyl-2,2'-biselenophene (16). A solution of NBS (0.38 g, 2.13 mmol) in DMF (15 mL) was added dropwise in darkness to a solution of *n*-hexylbiselenophene (14) (0.7 g, 2.03 mmol) in DMF (10 mL) cooled to -20°C, and stirred for 4 h. Addition of ice to the reaction mixture was followed by extraction with CH₂Cl₂. The combined organic phases were washed with water, dried over Na_2SO_4 and concentrated in vacuo. The oily residue was purified by column chromatography on silica gel with hexane to give compound 16 as a colorless solid. Yield 70%, mp 42°C. ¹H NMR (400 MHz) spectrum, δ, ppm: 0.87 t (J = 6.8 Hz, 3H), 1.26 - 1.40 m (6H), 1.62 - 1.66m (2H), 2.80 t (J = 7.6 Hz, 2H), 6.78 d (J = 3.6 Hz, 1H), 6.83 d (*J* = 4.4 Hz, 1H), 6.94 d (*J* = 3.6 Hz, 1H), 7.09 d (J = 4.4 Hz, 1H). Found, %: C 39.77, H 4.03. C₁₄H-₁₇BrSe₂. Calculated, %: C 39.74, H 4.05.

5-Bromo-5'-hexyl-2,2'-bithiophene (17). In darkness, a solution of NBS (0.74 g, 4.15 mmol) in DMF (15 mL) was added dropwise to a solution of *n*-hexylbithiophene (15) (1 g, 4.00 mmol) in DMF (10 mL) cooled down to -20°C, and stirred for 4 h. After addition of ice to the reaction mixture and extraction with CH₂Cl₂, the organic phases were washed with water, dried over Na₂SO₄ and concentrated in vacuo. The oily residue was purified by column chromatography on silica gel with hexane to give compound 17 as a white solid. Yield 88%. ¹H NMR (400 MHz) spectrum, δ , ppm: 0.89 t (J= 6.8 Hz, 3H), 1.28–1.38 m (6H), 1.62–1.67 m (2H), 2.76 t (J = 7.6 Hz, 2H), 6.64 d (J = 3.6 Hz, 1H), 6.81 d (J = 3.6 Hz, 1H), 6.89 d (J = 3.6 Hz, 1H), 6.91 d (J = 4.0 Hz, 1H)1H). Found, %: C 51.07, H 5.16. C₁₄H₁₇BrS₂. Calculated, %: C 51.06, H 5.20.

a,*a*'-Dihexylsexiselenophene (*a*-DH-6Se) (18). A mixture of 5-bromo-5'-hexyl-2,2'-biselenophene (16) (0.5 g, 1.18 mmol) with 5,5'-bis-tributylstannyl-2,2'-biselenophene (7) (0.5 g, 0.59 mmol) and tetrakis(triphenylphosphine)palladium (0.14 g, 0.12 mmol) in dry toluene (30 mL) was refluxed for 24 h under the atmosphere of nitrogen. The precipitate was filtered off by suction and subjected to soxhlet purification (CHCl₃). Sublimation of the insoluble precipitate at 290°C gave compound **18** as a dark red solid. Yield 22%, mp > 300°C. IR spectrum, v, cm⁻¹: 2922, 1539, 1507, 1456, 1200, 1065, 788, 766. Found, %: C 45.81, H 4.01. C₃₆H₃₈Se₆. Calculated, %: C 45.78, H 4.06.

Oligomer (a-DH-4S-2Se) (19). A mixture of 5-bromo-5'-hexyl-2,2'-bithiophene (**17**) (0.50 g, 1.52 mmol) with 5,5'-bis-tributylstannyl-2,2'-biselenophene (**7**) (0.64 g, 0.76 mmol) and tetrakis(triphenylphosphine)palladium (0.18 g , 0.15 mmol) in dry toluene (30 mL) was refluxed for 24 h under the atmosphere of nitrogen. The precipitate was filtered off under suction and subjected to soxhlet purification (CHCl₃). Sublimation of the insoluble precipitate at 270°C gave compound **19** as a red solid. Yield 27%, mp > 300°C. IR spectrum, v, cm⁻¹: 2922, 1507, 1456, 1445, 1377, 1220, 1202, 1067, 857, 793. Found, %: C 57.17, H 5.01. C₃₆H₃₈S₄Se₂. Calculated, %: C 57.13, H 5.06.

2-Fluoro-5-(thiophen-2-yl)thiophene (2a). To a stirred solution of mono-lithiobithiophene, prepared from bithiophene 2 (1 g, 6.02 mmol) and *n*-butyllithium (3.1 mL, 7.81 mmol) in dry THF (50 mL) and cooled to -78°C, was added a solution of N-fluorobenzenesulfonamide (2.08 g, 6.59 mmol) in anhydrous THF under the atmosphere of nitrogen. The mixture was stirred overnight at room temperature and then treated with hexane (50 mL), washed with brine and dried over MgSO₄. The solvent was concentrated, and the residue was purified by column chromatography on silica gel with hexane to give compound 2a as a colorless oil. Yield 20%. ¹H NMR (400 MHz) spectrum, δ , ppm: 6.38 d.d (J = 2 Hz, $J_{HF} =$ 2 Hz, 1H), 6.74 t (J = 3.6 Hz, $J_{\rm HF}$ = 3.6 Hz, 1H), 6.96–7.04 m (2H), 7.17–7.18 m (1H). Found, %: C 52.17, H 2.71. C₈H₅FS₂. Calculated, %: C 52.15, H 2.74.

2-(5-Bromothiophen-2-yl)-5-fluorothiophene (2b). Into a stirred solution of 2-fluoro-5-(thiophen-2-yl)thiophene (**2a**) (0.15 g, 0.815 mmol) in chloroform-acetic acid (1 : 1 v/v 20 mL) was added portionwise NBS (0.159 g, 0.89 mmol). The mixture was stirred at room temperature for 24 h, poured into water (100 mL) and extracted with dichloromethane. The extract was successively washed with water, 5% sodium hydrogen carbonate aqueous solution, and brine, and dried over MgSO₄. The solvent was evaporated and the residue was purified by column chromatography on silica gel with hexane to give compound **2b** as a white solid. Yield 56%, mp 78°C. ¹H NMR (400 MHz) spectrum, δ , ppm: 6.37 d.d (J = 2.0 Hz, J_{HF} = 2.0 Hz, 1H), 6.67 t (J = 4.0 Hz, J_{HF} = 3.6 Hz, 1H), 6.76 d (J = 3.6 Hz, 1H), 6.92 d (J = 4.0Hz, 1H). Found, %: C 36.53, H 1.51. C₈H₄BrFS₂. Calculated, %: C 36.51, H 1.53.

DF-(4S-2Se) (20). A mixture of 2-(5-bromothiophen-2-yl)-5-fluorothiophene (**2b**) (0.10 g, 0.38 mmol) with 5,5'-bis-tributylstannyl-2,2'-biselenophene (**7**) (0.16 g, 0.19 mmol) and tetrakis(triphenylphosphine)palladium (0.044 g , 0.038 mmol) in dry toluene (30 mL) was refluxed for 24 h under the atmosphere of nitrogen. The precipitate was filtered off under suction and sublimed at 270°C to give compound **20** as a dark red solid. Yield 20%, mp > 358°C. IR spectrum, v, cm⁻¹: 1569, 1546, 1513, 1480, 1447, 1271, 1244, 1225, 1198, 1066, 1030, 858, 788, 756, 724, 712, 668, 584, 443. MS: *m/z*: 625 [*M* + 1]⁺. Found, %: C 46.17, H 1.91. C₂₄H₁₂F₂S₄Se₂. Calculated, %: C 46.16, H 1.94.

DF-6T (21). A mixture of 2-(5-bromothiophen-2-yl)-5-fluorothiophene (**2b**) (2.0 g, 7.63 mmol) with 5,5'-bistributylstannyl-2,2'-bithiophene (**8**) (2.83 g, 3.80 mmol) and tetrakis(triphenylphosphine)palladium (0.881 g, 0.76 mmol) in dry toluene (30 mL) was refluxed for 24 h under the atmosphere of nitrogen. The precipitate was filtered off under suction and sublimed at 260°C to give compound **21** as an orange red solid. Yield 22 %, mp > 300°C. IR spectrum, v, cm⁻¹: 1569, 1546, 1509, 1480, 1442, 1353, 1273, 1246, 1228, 1199, 1072, 1067, 1031, 839, 788, 724, 712, 679, 626, 566, 465. MS: *m/z*: 530 [*M*]⁺. Found, %: C 54.35, H 2.25. C₂₄H₁₂F₂S₆. Calculated, %: C 54.31, H 2.28.

2-Fluoro-5-(selenophen-2-yl)selenophene (2c). Into a stirred solution of mono-lithiobiselenophene, prepared from biselenophene **1** (1 g, 3.84 mmol) and *n*-butyllithium (2.0 mL, 4.98 mmol) in dry ether (50 mL) and cooled down to -78° C, was added a solution of *N*-fluorobenzene sulfonamide (2.66 g, 8.43 mmol) in anhydrous THF under the atmosphere of nitrogen. The mixture was stirred overnight at room temperature and then treated with hexane (50 mL), washed with brine, and dried over MgSO₄. The solvent was evaporated and the residue was purified by column chromatography on silica gel with hexane to give compound **2c** as a white solid. Yield 25%, mp 71°C. ¹H NMR (400 MHz) spectrum, δ , ppm: 6.44 t (J = 4 Hz, $J_{HF} = 4.4$ Hz, 1H), 6.77 t (J = 4.0 Hz, $J_{HF} = 3.6$ Hz, 1H), 7.10 d (J = 3.6 Hz, 1H), 7.83 d (J = 5.6 Hz, 1H). Found, %: C 34.57, H 1.80. C₈H₅FSe₂. Calculated, %: C 34.56, H 1.81.

2-(5-Bromoselenophen-2-yl)-5-fluoroselenophene (2d). Into a stirred solution of 2-fluoro-5-(selenophen-2-yl)selenophene (2c) (0.25 g, 0.89 mmol) in chloroformacetic acid (1 : 1 v/v 20 mL) was added portionwise NBS (0.16 g, 0.89 mmol). The mixture was stirred at room temperature for 24 h, poured into water (100 mL) and extracted with dichloromethane. The extract was successively washed with water, 5% sodium hydrogen carbonate aqueous solution and brine solution, and dried over MgSO₄ The solvent was evaporated, and the residue was purified by column chromatography on silica gel with hexane to give compound 2d as a white solid. Yield 48%, mp 89°C. ¹H NMR (400 MHz) spectrum, δ, ppm: 6.45 t $(J = 4.8 \text{ Hz}, J_{\text{HF}} = 4.4 \text{ Hz}, 1\text{H}), 6.69 \text{ t} (J = 4.0 \text{ Hz}, J_{\text{HF}} =$ 4.0 Hz, 1H), 6.79 d (J = 4.0 Hz, 1H), 7.10 d (J = 4.0Hz, 1H). Found, %: C 26.95, H 1.11. C₈H₄BrFSe₂. Calculated, %: C 26.92, H 1.13.

DF-6Se (22). A mixture of 2-(5-bromoselenophen-2-yl)-5-fluoroselenophene (**2d**) (1.0 g, 2.80 mmol) with 5,5'-bis-tributylstannyl-2,2'-biselenophene (7) (1.17 g, 1.40 mmol) and tetrakis(triphenylphosphine)palladium (0.320 g, 0.28 mmol) in dry toluene (30 mL) was refluxed for 24 h under the atmosphere of nitrogen. The precipitate was filtered under suction. Found, %: C 35.51, H 1.47. $C_{24}H_{12}F_{2}Se_{6}$. Calculated, %: C 35.49, H 1.49.

CONCLUSIONS

We have synthesized new p and n types oligoselenophenes by the double Stille coupling method using tetrakis(triphenylphosphine)palladium(0) as a catalyst. A series of semiconducting oligomers (n and p) consisting of mixed hetero-units (hexamers of thiophene and selenophene) are also synthesized by the Stille coupling reaction. Thermal properties of n and p type oligoselenophenes are studied and compared with those of π -conjugated thiophene based oligomers using DSC and TGA measurements. Physical properties of the oligomers are also studied.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

- Burroughes, J.H., Bradley, D.D.C, Brown, A.R., Marks, R.N., Mackay, K, Friend, R.H., Burns, P.L. and Holmes, A.B., *Nature.*, 1990, vol. 347, p. 539. https://doi.org/10.1038/347539a0
- Perepichka, I.F., Perepichka, D.F., Meng, H., and Wudl, F., *Adv. Mater.*, 2005, vol. 17 p. 2281. https://doi.org/10.1002/adma.200500461
- Sariciftci, N.S, Smilowitz, L., Heeger, A.J., and Wudl, F., *Science.*, 1992, vol. 258, p. 1474. https://doi.org/10.1126/science.258.5087.1474
- Hoppe, H. and Sariciftci, N.S., J. Mater. Res., 2004, vol. 19, p. 1924. https://doi.org/10.1557/JMR.2004.0252
- Koyanagi, T., Muratsubaki, M., Hosoi, Y., Shibata, T., Tsutsui, K., Wada, Y., and Furukawa, Y., *Chem. Lett.*, 2006, vol. 35, p. 20. https://doi.org/10.1246/cl.2006.20
- Drury, C.J., Mutsaers, C.M.J., Hart, C.M., Matters, M., and de Leeuw, D.M., *Appl. Phys. Lett.*, 1998, vol. 73, p. 108. https://doi.org/10.1063/1.121783
- Sirringhaus, H., Tessler, N., and Friend, R.H., *Science.*, 1998, vol. 280, p. 1741. https://doi.org/10.1126/science.280.5370.1741
- Bao, Z., Lovinger, A.J., and Brown, J., J. Am. Chem. Soc., 1998, vol. 120, p. 207https://doi.org/10.1021/ja9727629
- Beaujuge, P.M., Ellinger, S., and Reynolds, J.R., *Nat. Mater*. 2008, vol. 7, p. 795. https://doi.org/10.1038/nmat2272
- Murphy, A.R. and Frechet, J.M.J., *Chem. Rev.*, 2007, vol. 107, p. 1066. https://doi.org/10.1021/cr0501386
- Sakamoto, Y., Komatsu, S., and Suzuki, T., J. Am. Chem. Soc., 2001, vol. 123, p. 4643. https://doi.org/10.1021/ja015712j
- Ando, S., Nishida, J., Tada, H., Inoue, Y., Tokito, S., and Yamashita, Y., *J. Am. Chem. Soc.*, 2005, vol. 127, p. 5336-5337. https://doi.org/10.1021/ja042219+
- Magdesieva, N.M. and Zefirov, N.S., in *Organic Selenium Compounds Their Chemistry and Biology*, Klayman, D.L. and Gunther, W.H.H., Eds., New York: John Wiley, 1973, p. 427.

- 14. Bird, C.W., *Comprehensive Heterocyclic Chemistry II* Oxford: Elsevier, 1996, vol. 2.
- 15. Djumanazarova, A.Z., Litvinov, V.P., and Konar, A., *Chem. Scr.*, 1998, vol. 20, p. 214.
- Kamada, K., Ueda, M., Sakaguchi, T., Ohta, K., Fukumi, T., *Chem. Phys. Lett.*, 1996, vol. 263, p. 215. https://doi.org/10.1016/S0009-2614(96)01185-2
- Yoshino, K., Kohno, Y., Shiraishi, T., Kaneto, K., Inoue, S., and Tsukagoshi, K., *Synth. Met.*, 1985, vol. 10, p. 319. https://doi.org/10.1016/0379-6779(85)90040-2
- Zade, S.S., Zamoshchik, N., and Bendikov, M., *Chem. Eur. J.* 2009, vol. 15, p. 8613-8624. https://doi.org/10.1002/chem.200900971
- Nakanishi, H., Inoue, S., and Otsubo, T., *Mol. Cryst. Liq. Cryst.*, 1997, vol. 296, p. 335. https://doi.org/10.1080/10587259708032331
- Inoue, S., Nakanishi, H., Takimiya, K., Aso, Y., and Otsubo, T., *Synth. Met.*, 1997, vol. 84, p. 341. https://doi.org/10.1016/S0379-6779(97)80772-2
- Nakanishi, H., Inoue, S., Aso, Y., and Otsubo, T., Synth. Met., 1999, vol. 101, p. 639. https://doi.org/10.1016/S0379-6779(98)00849-2
- Millefiori, S. and Alparone, A., Synth. Met., 1998, vol. 95, p. 217. https://doi.org/10.1016/S0379-6779(98)00058-7
- Zade, S.S. and Bendikov, M., *Chem. Eur. J.*, 2008, vol. 14, p. 6734. https://doi.org/10.1002/chem.200701182
- Hapiot, P., Demanze, F., Yassar, A., and Garnier, F., J. Phys. Chem., 1996, vol. 100, p. 8397. https://doi.org/10.1021/jp953226a
- Garcia, P., Pernaut, J.M., Hapiot, P., Wintgens, V., Valat, P., Garnier, F., and Delabouglise, D., *J. Phys. Chem.*, 1993, vol. 97, p. 513. https://doi.org/10.1021/j100104a040
- Yui, K., Aso, Y., Otsubo, T., and Ogura, F., *Bull. Chem. Soc. Jpn.*, 1989, vol. 62, p. 1539. https://doi.org/10.1246/bcsj.62.1539
- Murphy, A. R., Liu, J., Luscombe, C., Kavulak, D., Frechet, J.M.J., Kline, R. J., and Mcgehee, M.D., *Chem. Mater.*, 2005, vol. 17, p. 4892.

https://doi.org/10.1021/cm050911d

- Facchetti, A., Wang, A., Marks, T.J., Sirringhaus, H., Deng, Y., and Friend, R.J., *Polym. Mater. Sci. Eng.*, 2000, vol 83, p. 290
- Facchetti, A., Yoon, M.-H., Stern, C. L., Katz, H.E., and Marks, T.J., *Angew. Chem. Int. Ed.*, 2003, vol. 42, p. 3900. https://doi.org/10.1002/anie.200351253
- 30. Facchetti, A., Letizia, J., Yoon, M.-H., Mushrush, M.,

Katz, H.E., and Marks, T.J., *Chem. Mater.*, 2004, vol. 16, p. 4715. https://doi.org/10.1021/cm0495008

- Sakamoto, Y., Komatsu, S., and Suzuki, T., *J. Am. Chem.* Soc., 2001, vol. 123, p. 4643. https://doi.org/10.1021/ja015712j
- Kilbinger, A.F.M. and Feast, W.J., *J. Mater. Chem.*, 2000, vol. 10, p. 1777. https://doi.org/10.1039/B002899L