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Influence of heteroaryl group on electrochemical and spectroscopic properties of conjugated polymers

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ABSTRACT

During our search for novel conjugated compounds, novel monomers and their polymers with selenophene and tellurophene group were synthesized and characterized. Conjugated poly(p-phenylenevinylenes)s (PPV) derivatives attracted a large attention due to their photolouminescence properties. The stereocontrolled synthesis of 1,4-bis(2-(heteroar-2-yl) ethenyl)benzenes and 1,4-bis(heteroar-2-yl)benzenes with tellurophene, selenophene, thiophene and furan-based monomers has been successfully performed. Eight of *p*-phenylene derivatives have been synthesized, electrochemically polymerized and characterized.

1. Introduction

Organic semiconductor materials based on extended linear π-conjugated systems have been intriguing and significantly developed over the past several years [1–3], but there are always difficulties with synthesis of compounds with proper properties. By manipulation of their chemical structure it is possible to make them suitable for use in liquid form for spin-coating or printing process [4–7]. Since the 1960s, polyphenylenes and their derivatives have been developed and used many important applications [8–10]. A number of PPV polymers and their derivatives have been extensively studied. Coupling benzene molecules *via* their *para* positions is the easiest pathway to enhance the conjugation but this influence on other properties. Typical unsubstituted linear polyphenylenes have low solubility and because of that have practically no industrial application. The main requirement of optoelectronics is the ability to prepare a well defined material, featuring desirable electronic properties, stable, durable and preferably soluble in common organic solvents for inkjet printing, or low molecular weight molecules for PVD deposition [11–15]. The main modification of molecular structure is adding alkoxy groups to enhance solubility which influence on torsion within polymer and unfortunately decreasing conjugation length [16–18]. To avoid problems with decreasing of conjugation length conjugated spacer like vinyl group is applied. The conjugated spacer between mers in conjugated polymers influence on conjugation length, narrows the energy gap of polymer and providing color tuning for optoelectronic applications. Bisubstituted poly(thienylenevinylene)s exhibited significant bathochromic shifts in comparison with their heterocyclic analogs [19–21]. Conjugated poly(*p*-phenylenevinylene)s (PPV) derivatives attracted a large attention due to their photoluminescence properties. PPV is the first reported polymer used in organic light-emitting diode applications [22]. Its derivatives remain the most popular conjugated polymers for this application and continue to generate considerable interest and much research form photovoltaic applications. Pure PPV is insoluble substance and therefore difficult to process into the solid state. The previous electrochemical investigation of MEH-PPV (poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylene vinylene]) showed band gap of 2.18 eV stable *p*-doping process [23,24]. Substitution of heteroarylphenylene derivatives with long alkoxy group influence on solubility and processability of synthesized polymers [25–32]. Heteroaryl-*p*-phenylenevinylenes derivatives are shifted bathochromic than his phenylenevinylenes analog and shifted hypochromic than his heteroaryl analogs [33]. Elongation of alkoxy chain in poly[1,4-bis(2-(thien-2-yl)ethenyl)benzenes] influenced by increasing on band gap value and polaron absorption wavelength peak [34]. Formerly we have shown that monomers with conjugated system of multiple bonds bearing two terminal residues of chalcogens (furan, thiophene, and selenophene) with free positions in C5 are able to

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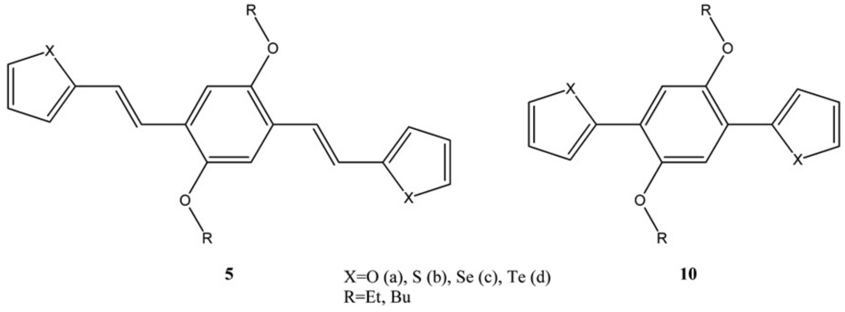


Fig. 1. Investigated compounds.

electropolymerize leading to linear PPV-type conducting systems that show strong electroluminescence [34–37]. The (*E*,*E*)-1,4-diethoxy-2,5-bis[2-(tellurophen-2- yl)ethenyl]benzene presenting higher absorption peak and fluorescence wavelength than thiophene and selenophene analogs [38]. There are many techniques to determine properties of materials for optoelectronic applications [39]. The electrochemical and spectroelectrochemical analyses give a possibility to determine oxidation and reduction potentials of compounds which are directly related to HOMO and LUMO values, kind of charge carriers responsible for the process of conductivity and other parameters for optoelectronic applications [39–41].

The synthesis of investigated compound (Fig. 1) was associated with examination of influence of heteroaryl and vinyl group to obtained polymer during electrochemical polymerization. Typically benzene ring in the middle of heteroaryl group influences on decreasing of oxidation potential but influence of vinyl linker was not fully characterized.

2. Experimental

2.1. Materials

All solvents for synthesis were dried and then distilled before the use. Other commercial substances and reagents were used without purification. Electrochemical measurements were conducted in 1.0 mM concentration of all monomers for all of cyclic voltamperometry measurements. Electrochemical studies were conducted in 0,1 M solution of Bu_4NBF_4 (Sigma–Aldrich 99%) in dichloromethane (DCM) solvent (anhydrous for HPLC) at room temperatures. UV–vis spectroelectrochemical measurements were conducted on polymeric layers synthesized on indium tin oxide (ITO) quartz glass working electrode in condition compared to cyclic voltammetric measurements. Fluorescence was measured for 10 μM concentration of all monomers in DCM solvent.

2.2. Measurements

Melting points (not corrected) were determined on Boetius HMK apparatus. NMR spectra were taken in $CDCl_3$ with TMS as an internal reference by Varian XL-300 at 300 MHz for ^1H and at 75.5 MHz for ^{13}C. EA results were obtained using Perkin-Elmer CHN automatic analyzer. Electrochemical investigation has been carried out using Eco Chemie Company's AUTOLAB potentiostat "PGSTAT20". All measured spectra have been collected using GPES (General Purpose Electrochemical System) software. The electrochemical cell comprised platinum wire with 1 mm diameter of working area and ITO glass as working electrode, Ag/AgCl electrode as reference electrode and platinum coil as auxiliary electrode. Cyclic voltammetric measurements were conducted at 50 mV/s potential rate and calibrated versus ferrocene/ferrocenium redox couple. The specific charge and capacitance were measured on 10 MHz Au coated electrode with 0.209 cm^2 active area, on UELKO M106 QCM combined with AUTOLAB PGSTAT20 potentiostat. UV–vis spectroscopy was performed on HP Agilent 8453 spectrometer. Fluorescence measurements were conducted on Hitachi F-2500 Fluorimeter.

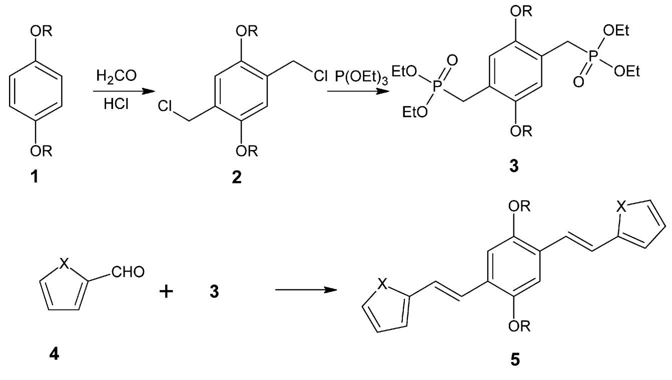
2.3. General synthesis of 1,4-bis(2-(heteroar-2-yl) ethenyl)benzenes (5)

A stereocontrolled three steps synthesis of a furan, thiophene, selenophene, tellurophene-based monomers of 1,4-bis(2-(heteroar-2-yl)ethenyl)benzenes (**5**) has been successfully performed starting from 1,4-dialkoxybenzene (**1**) as it is shown in Scheme 1. Compound **1** was treated with paraformaldehyde and gaseous hydrogen chloride in the solution of glacial acetic acid and concentrated hydrochloric acid to give 2,5-bis(chloromethyl)-1,4-dialkoxybenzene (**3**). The latter compound on heating at 150 °C with ca 20% excess of triethoxyphosphine afforded 2,5-bis(diethoxyphosphononomethyl)-1,4-dialkoxybenzene. Furan-2-carboaldehyde (**4a**) and thiophene-2-carboaldehyde (**4b**) were bought from Sigma–Aldrich Company.

Therefore, a stereocontrolled condensation of **3** with 2-heteroarylcarbaldehyde leading to the most stable EE isomer was a method of choice for the synthesis of **5**.

2.3.1. 1,4-Dibutoxybenzene (*1*) [42]

To a stirred solution of 50 cm^3 DMSO, 5.50 g (0.05 mole) hydroquinone and 5.00 g (0.12 mole) NaOH under nitrogen 20.24 g (0.11 mole) butyl iodide was added drop wise. Stirring was continued with precipitating product of reaction, after 2 h mixture was poured on 400 cm^3 of cold distilled water. Precipitated product was filtered off under vacuum, washed with water and dried under



Scheme 1. A stereocontrolled three steps synthesis of (*E*,*E*)-1,4-dialkoxy-2,5-bis [2-(heteroar-2-yl)ethenyl]benzene (**5**).

nitrogen. Dried product was recrystalized from methanol and dried in vacuo (8.38 g, 37.69 mmol, 56%). Product as white flakes with t_m = 45–46 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.97 (t, J = 7.20 Hz, 6H, 2× $-CH_3$), 1.42–1.54 (m, 4H, 2× $-CH_2-$), 1.69–1.79 (m, 4H, 2× $-CH_2-$), 3.90 (t, J = 6.30 Hz, 4H, 2× $-CH_2O-$), 6.82 (s, 2H, 2× H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 13.89 (2× $-CH_3$), 19.27 (2× $-CH_2-$), 31.47 (2× $-CH_2-$), 68.33 (2× $-OCH_2-$), 115.38 (2× $C_{Ar}-H$), 153.20 (2× $\underline{C}$OAlk).

2.3.2. *1,4-Bis(chloromethyl)-2,5-dialkoxybenzene (**2**) [35]*

To a stirred solution of 60 cm^3 acetic acid and 15 cm^3 concentrated hydrochloric acid filled with gaseous hydrochloric acid, 2.70 g (90.00 mmol) paraformaldehyde was added. After clarification of stirred solution 3.33 g (15.00 mmol) dibutoxybenzene was added. Stirring was continued with precipitating product of reaction for 24 h and then mixture was poured on 300 cm^3 of cold distilled water. Precipitated white product was filtered under vacuum, washed with water and dried under vacuum and P_4O_{10}. Crude product was recrystallized from methanol (4.37 g, 13.69 mmol, 91%) as white solid with t_m = 81–82 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.98 (t, J = 7.20 Hz, 6H, 2× $-CH_3$), 1.46–1.58 (m, 4H, 2× $-CH_2-$), 1.74–1.83 (m, 4H, 2× $-CH_2-$), 3.99 (t, J = 6.60 Hz, 4H, 2× $-OCH_2-$), 4.63 (s, 4H, 2× $-CH_2Cl$), 6.91 (s, 2H, 2× H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 13.85 (2× $-CH_3$), 19.28 (2× $-CH_2-$), 31.41 (2× $-CH_2-$), 41.35 (2× $-CH_2Cl$), 68.80 (2× $-OCH_2-$), 114.29 (2× $C_{Ar}-H$), 127.03 (2× C_{Ar}), 153.56 (2× $\underline{C}$OAlk).

2.3.3. *1,4-Dibutoxy-2,5-bis(diethoxyphosphonomethyl)benzene (**3**) [43]*

A solution of 0.32 g (1.00 mmol) 2,5-bis(chloromethyl)-1,4-dibutoxybenzene and 0.50 g (0.52 cm^3, 3.00 mmol) triethoxyphosphine was stirred at 150 °C for 4 h. Triethoxyphosphine excess was distilled off under low pressure and obtained product was purified chromatographically (2.5% vol. methanol in chloroform) to gave light yellow oil liquid (0.75 g, 1.44 mmol, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.97 (t, J = 7.30 Hz, 6H, 2× $-CH_3$), 1.24 (t, J = 7.30 Hz, 12H, 4× $-CH_3$), 1.49 (sekst., J = 7.50 Hz, 4H, 2× $-CH_2-$), 1.75 (q, J = 7,50 Hz, 4H, 2× $-CH_2-$), 3.23 (d, J = 20.40 Hz, 4H, 2× $-CH_2P-$), 3.93 (t, J = 6.50 Hz, 4H, 2× $-OCH_2-$), 4.00 (q, J = 7.30 Hz, 8H, 4× $-OCH_2-$), 6.92 (s, 2H, 2× $C_{Ar}-H$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 13.97 (2× $-CH_3$), 16.42 (2× $-CH_2-$), 19.38 (4× $-CH_3$), 26.57 (d, $^1J_{P-C}$ = 139.50 Hz, 2× $-CH_2P-$), 31.62 (2× $-CH_2-$), 61.91 (4× $-OCH_2-$), 68.72 (2× $-OCH_2-$), 114.96 (2× $C_{Ar}-H$), 119.51 (2× C_{Ar}), 150.41 (2× $\underline{C}$OAlk).

2.3.4. *Selenophene-2-carboaldehyde (**4c**) [44]*

The solution of 2.71 g (2.47 cm^3; 20.00 mmol) N-methylformanilide and 3.07 g (1.87 cm^3, 20.00 mmol) $POCl_3$ under nitrogen was stirred for 30 min. Mixture was cooled to 15 °C and 2.50 g (19.10 mmol) selenophene was added drop wise. Reaction was conducted in room temperature under nitrogen for 12 h. Reaction mixture was poured on 300 cm^3 of cold distilled water with ice. Obtained solution extracted three times with diethyl ether. Ether layer was flushed with $NaHCO_3$ solution and dried with $MgSO_4$. After solvent evaporation the crude product was obtained (1.95 g, 12.30 mmol, 64%) as orange liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.48 (dd, J = 3.90 Hz, J = 5.40 Hz, 1H, C_4H_3Se, H^4), 8.03 (dd, J = 1.20 Hz, J = 3.90 Hz, 1H, C_4H_3Se, H^3), 8.50 (dt, J = 1.20 Hz, J = 5.40 Hz, 1H, C_4H_3Se, H^5), 9.82 (d, J = 1.20 Hz, 1H, $-CHO$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 130.87, 139.57, 141.14, 150.39 (C^2), 184.38 ($-CHO$).

2.3.5. *(EE)-1,4-dibutoxy-2,5-bis[2-(furan-2-yl)etenyl]benzene (**5a**) [43]*

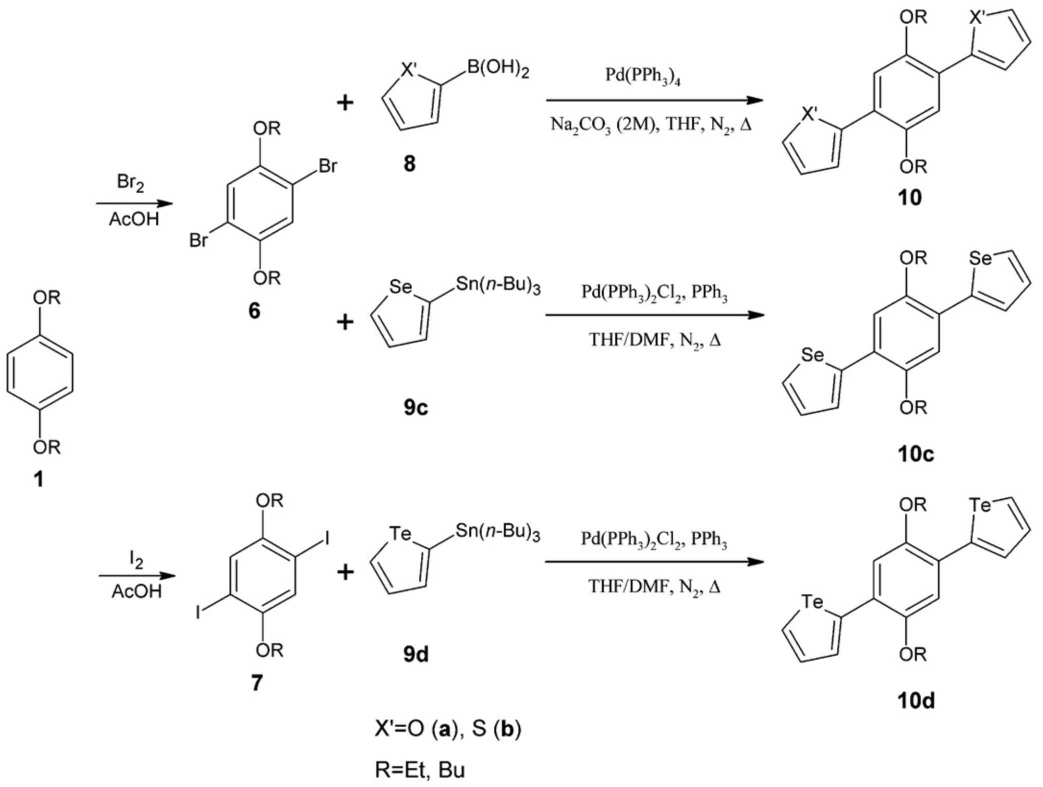
To a stirred solution of 10 cm^3 DMF and 1.02 g (9.20 mmol) t-BuOK in ice bath 0.35 g (0.67 mmol) 1,4-dibutoxy-2,5-bis(diethoxyphosphonomethyl)benzene was added and next 0.15 g (0.13 cm^3, 1.56 mmol) of furfural in 10 cm^3 DMF was added drop wise. Reaction mixture was stirred for 3 h in room temperature. Reaction mixture was poured on 100 cm^3 of cold distilled water with ice and 2 cm^3 of concentrated hydrochloric acid. Suspension was extracted with dichloromethane (3 × 50 cm^3). Organic layer was dried with $MgSO_4$ and after solvent distillation under low pressure, crude product (0.19 g, 0.47 mmol, 70%) was obtained as yellow solid with t_m = 124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.03 (t, J = 7.50 Hz, 6H, 2× $-CH_3$), 1.58 (sext., J = 7.50 Hz, 4H, 2× $-CH_2-$), 1.85 (q, J = 6.60 Hz, 4H, 2× $-CH_2-$), 4.03 (t, J = 6.60 Hz, 4H, 2× $-OCH_2-$), 6.35 (d, J = 3.30 Hz, 2H, C_4H_3O, 2× C^3-H), 6.21–6.42 (m, 2H, C_4H_3O, 2× C^4-H), 6.81–7.06 (m, 2H, 2× H_{vinyl}), 7.01 (s, 2H, 2× H_{Ar}), 7.32 (d, J = 16.50 Hz, 2H, 2× H_{vinyl}), 7.41 (d, J = 1.20 Hz, 2H, C_4H_3O, 2× C^5-H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 14.08 (2× $-CH_3$), 19.56 (2× $-CH_2-$), 31.69 (2× $-CH_2-$), 69.28 (2× $-OCH_2-$), 108.33 (C_4H_3O, C^3), 110.94 (C_4H_3O, 2× C^4), 111.76 (2× C_{vinyl}), 117.14 (2× $C_{Ar}-H$), 122.44 (2× C_{vinyl}), 126.56 (2× C_{Ar}), 142.19 (C_4H_3O, 2× C^5), 151.26 (2× $\underline{C}$OAlk), 154.14 (C_4H_3O, 2× C^2). UV–vis (CH_2Cl_2): λ = 401.0 nm, $\varepsilon = (4.47 \pm 0.28) \times 10^4$; λ = 346.5 nm, $\varepsilon = (2.40 \pm 0.15) \times 10^4$; λ = 236.5 nm, $\varepsilon = (1.47 \pm 0.10) \times 10^4$ [dm^3/mol cm]. EA calc. C(76.82%) H(7.44%), found C(76.64%) H(7.51%).

2.3.6. *(EE)-1,4-dibutoxy-2,5-bis[2-(tiophen-2-yl)ethenyl]benzene (**5b**)*

To a stirred solution of 10 cm^3 DMF and 1.02 g (9.20 mmol) t-BuOK in ice bath 0.40 g (0.77 mmol) 1,4-dibutoxy-2,5-bis(diethoxylphosphonomethyl)benzene was added and next 0.20 g (0.20 cm^3, 1.77 mmol) of 2-thienyl aldehyde in 10 cm^3 DMF was added drop wise. Reaction mixture was stirred for 3 h in room temperature. Reaction mixture was poured on 100 cm^3 of cold distilled water with ice and 2 cm^3 of concentrated hydrochloric acid. Suspension was extracted with dichloromethane (3 × 50 cm^3). Organic layer was dried with $MgSO_4$ and after solvent distillation under low pressure, crude product (0.23 g, 0.52 mmol, 67%) was obtained as yellow solid with t_m = 159–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.03 (t, J = 7.50 Hz, 6H, 2× $-CH_3$), 1.57 (sext., J = 7.50 Hz, 4H, 2× $-CH_2-$), 1.85 (q, J = 6.60 Hz, 4H, 2× $-CH_2-$), 4.04 (t, J = 6.00 Hz, 4H, 2× $-OCH_2-$), 7.00 (dd, J = 3.60 Hz, J = 5.10 Hz, 2H, C_4H_3S, 2× C^4-H), 7.03 (s, 2H, 2× H_{Ar}), 7.06 (d, J = 3.60 Hz, 2H, C_4H_3S, 2× C^3-H), 7.18 (d, J = 5.10 Hz, 2H, C_4H_3S, 2× C^5-H), 7.24 (d, J = 16.20 Hz, 2H, 2× H_{vinyl}). 7.31 (d, J = 16.20 Hz, 2H, 2× H_{vinyl}). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 14.11 (2× $-CH_3$), 19.61 (2× $-CH_2-$), 31.69 (2× $-CH_2-$), 69.35 (2× $-OCH_2-$), 110.82 (2× $C_{Ar}-H$), 122.26 (2× C_{vinyl}), 123.54 (2× C_{vinyl}), 124.32 (C_4H_3S, 2× C^3), 125.83 (C_4H_3S, 2× C^4), 126.52 (2× C_{Ar}), 127.72 (C_4H_3S, 2× C^5), 143.97 (C_4H_3S, 2× C^2), 151.17 (2× $\underline{C}$OAlk). UV–vis (CH_2Cl_2) λ = 398.5 nm, $\varepsilon = (4.42 \pm 0.27) \times 10^4$, λ = 341.0 nm, $\varepsilon = (2.11 \pm 0.14) \times 10^4$, λ = 246.5 nm, $\varepsilon = (1.15 \pm 0.08) \times 10^4$ [dm^3/mol cm].

2.3.7. *(EE)-1,4-dibutoxy-2,5-bis[2-(selenophen-2-yl)ethenyl]benzene (**5c**)*

To a stirred solution of 10 cm^3 DMF and 0.99 g (8.83 mmol) t-BuOK in ice bath 0.27 g (0.54 mmol) 1,4-dibutoxy-2,5-bis(diethoxylphosphonomethyl)benzene was added and next 0.14 g (0.88 mmol) of 2-selenophenyl aldehyde in 10 cm^3 DMF was added drop wise. Reaction mixture was stirred for 3 h in room temperature. Reaction mixture was poured on 100 cm^3 of cold distilled water with ice and 2 cm^3 of concentrated hydrochloric acid. Suspension was extracted with dichloromethane (3 × 50 cm^3). Organic layer was dried with $MgSO_4$ and after solvent distillation under low pressure, crude product (0.08 g, 0.15 mmol, 29%) was obtained as yellow solid with t_m = 173–175 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.03 (t, J = 7.50 Hz, 6H, 2× CH_3), 1.58



Scheme 2. A stereocontrolled three steps synthesis of 1,4-dialkoxy-2,5-bis (heteroar-2-yl)benzene (**10**).

(sext., $J = 7.50$ Hz, 4H, 2× —CH_2—), 1.85 (pent., $J = 6.60$ Hz, 4H, 2× —CH_2—), 4.04 (t, $J = 6.30$ Hz, 4H, 2× —OCH_2—), 7.03 (s, 2H, 2× H_{Ar}), 7.14 (d, $J = 16.50$ Hz, 2H, 2× H_{vinyl}), 7.33 (d, $J = 16.50$ Hz, 2H, 2× H_{vinyl}), 7.22–7.34 (m, 4H, C_4H_3Se, 2× C^3—H, 2× C^4—H), 7.82 (d, $J = 4.50$ Hz, 2H, C_4H_3Se, 2× C^5—H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 14.12 (2× —CH_3), 19.64 (2× —CH_2—), 31.68 (2× —CH_2—), 69.38 (2× —OCH_2—), 110.89 (2× C_{Ar}—H), 124.78 (2× C_{vinyl}), 124.87 (2× C_{vinyl}), 126.62 (2× C_{Ar}), 128.63 (C_4H_3Se, 2× C^5), 128.83 (C_4H_3Se, 2× C^4), 130.30 (C_4H_3Se, 2× C^3), 150.23 (C_4H_3Se, 2× C^2), 151.19 (2× $\underline{C}$OAlk). UV–vis (CH_2Cl_2) $\lambda = 413.5$ nm, $\varepsilon = (4.82 \pm 0.31) \times 10^4$, $\lambda = 356.0$ nm, $\varepsilon = (2.03 \pm 0.13) \times 10^4$, $\lambda = 291.0$ nm, $\varepsilon = (0.93 \pm 0.06) \times 10^4$ [dm^3/mol cm]. EA calc. C(58.65%) H(5.68%), found C(58.09%) H(5.93%).

2.3.8. *(EE)-1,4-diethoxy-2,5-bis[2-(tellurophen-2-yl)ethenyl]benzene (**5d**)*

Synthesis and characterization were previously reported in publication [38].

2.4. *General synthesis of 1,4-bis(heteroar-2-yl) benzenes (**10**)*

A two steps synthesis of a furan, thiophene, selenophene, tellurophene-based monomers of 1,4-bis(heteroar-2-yl) benzenes (**10**) has been successfully performed starting from 1,4-dialkoxybenzene (**1**) as it is shown in Scheme 2. Compound **1** was treated with bromine in acetic acid to give 2,5-dibromo-1,4-dibutoxybenzene (**6**). The synthesis of tellurophene derivatives only works with 2,5-iodo-1,4-alkoxybenzenes (**7**) as starting materials. Furan and thiophene derivatives were synthesized by Suzuki coupling reaction and selenophene derivative by Still coupling. 2-Furylboronic acid **(8a)** was bought from Maybridge company and 2-thienylboronic acid **(8b)** was bought from Acros Organics Company.

2.4.1. *1,4-Dibutoxy-2,5-dibromobenzene (**6**) [45]*

To a stirred solution of 2.07 g (9.31 mmol) 1,4-dibutoxybenzene, 1.90 g (23.16 mmol) sodium acetate and 15 cm^3 acetic acid, a 3.02 g (0.96 cm^3, 18.90 mmol) Br_2 in 2 cm^3 acetic acid was added drop wise. After 3 h of stirring in room temperature, mixture was poured on 50 cm^3 of cold distilled water with ice and filtered under vacuum. Precipitate as crude product was recrystallized from dichloromethane to obtained (2.67 g, 7.02 mmol, 78%) white solid with $t_m = 70–72$ °C. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.98 (t, $J = 7.20$ Hz, 6H, 2× —CH_3), 1.52 (sekst., $J = 7.50$ Hz, 4H, 2× —CH_2—), 1.79 (q, $J = 6.90$ Hz, 4H, 2× —CH_2—), 3.95 (t, $J = 6.30$ Hz, 4H, 2× —OCH_2—), 7.09 (s, 2H, 2× H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 13.96 (2× —CH_3), 19.34 (2× —CH_2—), 31.35 (2× —CH_2—), 70.15 (2× —OCH_2—), 111.29 (2× C_{Ar}—Br), 118.63 (2× C_{Ar}—H), 150.25 (2× $\underline{C}$OAlk).

2.4.2. *1,4-Diethoxy-2,5-diiodobenzene (**7**) [46]*

To a stirred solution of 2.00 g (12.01 mmol) 1,4-diethoxybenzene in 20 cm^3 acetic acid and 5 cm^3 CCl_4, a 3.05 g (12.03 mmol) I_2, 1 cm^3 of conc. H_2SO_4, 1 cm^3 of water and 2.57 g (12.03 mmol) KIO_3 were added in order. After 24 h of stirring under reflux, mixture was poured on 200 cm^3 of cold distilled water with ice and extracted with chloroform (3× 50 cm^3). Organic layer was dried with $MgSO_4$ and after solvent distillation under low pressure, crude product (3.32 g, 7.78 mmol, 65%) was obtained as white solid with $t_m = 144–146$ °C. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.44 (t, $J = 6.90$ Hz, 6H, 2× —CH_3), 4.01 (q, $J = 6.90$ Hz, 4H, 2× —OCH_2—), 7.18 (s, 2H, 2× H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 14.94 (2× —CH_3), 66.19 (2× —OCH_2—), 86.63(2× C_{Ar}—I), 123.17 (2× C_{Ar}—H), 152.95 (2× $\underline{C}$OAlk).

2.4.3. *Tri-n-butyl(selenophen-2-yl)tin (**9c**) [47]*

To a stirred solution of 1.54 g (1.02 cm^3, 11.75 mmol) selenophene in10 cm^3 dried diethyl ether under nitrogen at

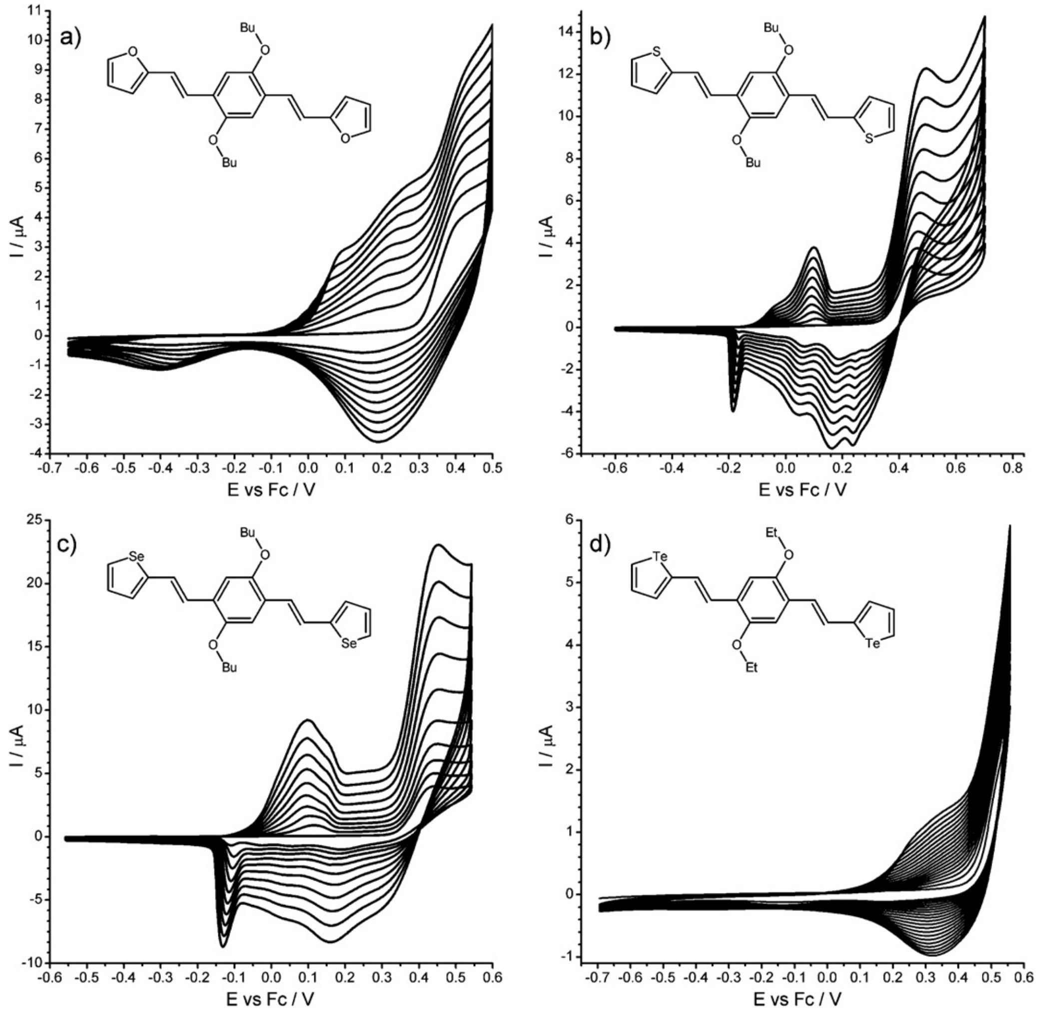


Fig. 2. Cyclic voltammetry of investigated monomers of polymerization. Measurement conditions: scan rate 50 mV/s, Ag/AgCl – quasireference electrode, calibrated against ferrocene/ferrocenium redox couple.

temperature −10 °C 0.75 g (1.06 cm^3, 11.71 mmol) *n*-butyllithium (2.5 M hexane) was added drop wise. Mixture was stirred for 1.5 h at room temperature and next reaction were cooled down to 0 °C for adding 3.83 g (3.19 cm^3, 11.77 mmol) of tri-*n*-butyltin chloride in 10 cm^3 dried diethyl ether. Reaction was conducted for 1 h at room temperature and filtered under vacuum. Solvent was evaporated and crude product (3.50 g, 8.34 mmol, 71%) was obtained as light yellow oil liquid.

2.4.4. *Tri-n-butyl(tellurophen-2-yl)tin (**9d**)*

To a stirred solution of 1.00 g (5.57 mmol) tellurophene[33] in 10 cm^3 dried diethyl ether under nitrogen at temperature −10 °C 0.36 g (2.23 cm^3, 5.57 mmol) of *n*-butyllithium (2.5 M hexane) was added drop wise. Mixture was stirred for 1.5 h at room temperature and as next step reaction was cooled down to 0 °C for adding 1.81 g (1.59 cm^3, 5.57 mmol) of tri-*n*-butyltin chloride in 10 cm^3 dried diethyl ether. Reaction was conducted for 1 h at room temperature and filtered under vacuum. Solvent was evaporated and crude product (2.56 g, 5.47 mmol, 98%) was obtained as light yellow oil liquid. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 0.90 (t, J = 7.30 Hz, 9H, 3× —CH$_3$), 0.95–1.20 (m, 6H, 3× —CH$_2$—), 1.34 (sext., J = 7.20 Hz, 6H, 3× —CH$_2$—), 1.45–1.65 (m, 6H, 3× —CH$_2$—), 8.00 (dd, J = 3.60 Hz, J = 6.40 Hz, 1H, $\mathrm{H^4}_{\mathrm{Ar}}$), 8.12 (dd, 1H, J = 0.80 Hz, J = 3.60 Hz, $\mathrm{H^3}_{\mathrm{Ar}}$), 9.25 (dd, 1H, J = 0.80 Hz, J = 6.40 Hz, $\mathrm{H^5}_{\mathrm{Ar}}$). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm) 11.72, 13.80, 27.47, 29.14, 130.12, 140.08, 145.66.

2.4.5. *1,4-Dibutoxy-2,5-bis(furan-2-yl)benzene (**10a**)*

The reaction mixture of 0.31 g (0.82 mmol) 2,5-dibromo-1,4-dibutoxybenzene, 0.20 g (1.79 mmol) 2-furanboronic acid, 0.02 g (0.014 mmol) Pd(PPh$_3$)$_4$, 3 cm^3 2 M Na$_2$CO$_3$ (3.39 mmol) in 10 cm^3 THF was stirred for 24 h at temperature 70 °C. Solution after synthesis was extracted (50 cm^3 water, 50 cm^3 dichloromethane) and organic layer was washed with water (2×), salty water (1×) and dried by MgSO$_4$. Solvent was evaporated and crude product was purified by column chromatography method (hexane – eluent) to obtained light green solid (0.29 g, 0.82 mmol, 83%) with t_m = 140–141 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 1.02 (t, J = 7.50 Hz, 6H, 2× —CH$_3$), 1.57 (sext., J = 7.50 Hz, 4H, 2× —CH$_2$—), 1.90 (q, J = 7.20 Hz, 4H, 2× —CH$_2$—), 4.14 (t, J = 6.30 Hz, 4H, 2× —OCH$_2$—), 6.51 (dd, J = 1.80 Hz, J = 3.30 Hz, 2H, C$_4$H$_3$O, 2× C^4—H), 7.03 (d, J = 3.30 Hz, 2H, C$_4$H$_3$O, 2× C^3—H), 7.45 (s, 2H, 2× H$_{\mathrm{Ar}}$), 7.47 (d, J = 1.80 Hz, 2H, C$_4$H$_3$O, 2× C^5—H). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm) 14.09 (2× —CH$_3$), 19.67 (2× —CH$_2$—), 31.74 (2× —CH$_2$—), 68.71 (2× —OCH$_2$—), 109.50 (C$_4$H$_3$O, 2× C^3), 110.35 (C$_4$H$_3$O, 2× C^4), 112.13 (2× C$_{\mathrm{Ar}}$—H), 118.91 (2× C$_{\mathrm{Ar}}$), 141.08 (C$_4$H$_3$O, 2× C^5), 149.08 (C$_4$H$_3$O, 2× C^2), 150.47 (2× $\underline{\mathrm{C}}$OAlk). UV–vis (CH$_2$Cl$_2$) λ = 368.0 nm, $\varepsilon = (2.12 \pm 0.14) \times 10^4$, λ = 351.5 nm, $\varepsilon = (2.18 \pm 0.14) \times 10^4$, λ = 309.5 nm, $\varepsilon = (2.25 \pm 0.14) \times 10^4$, λ = 295.0 nm, $\varepsilon = (1.68 \pm 0.11) \times 10^4$, λ = 247.0 nm, $\varepsilon = (0.91 \pm 0.06) \times 10^4$ [dm^3/mol cm]. EA calc. C(68.35%) H(6.78%), found C(68.15%) H(6.79%).

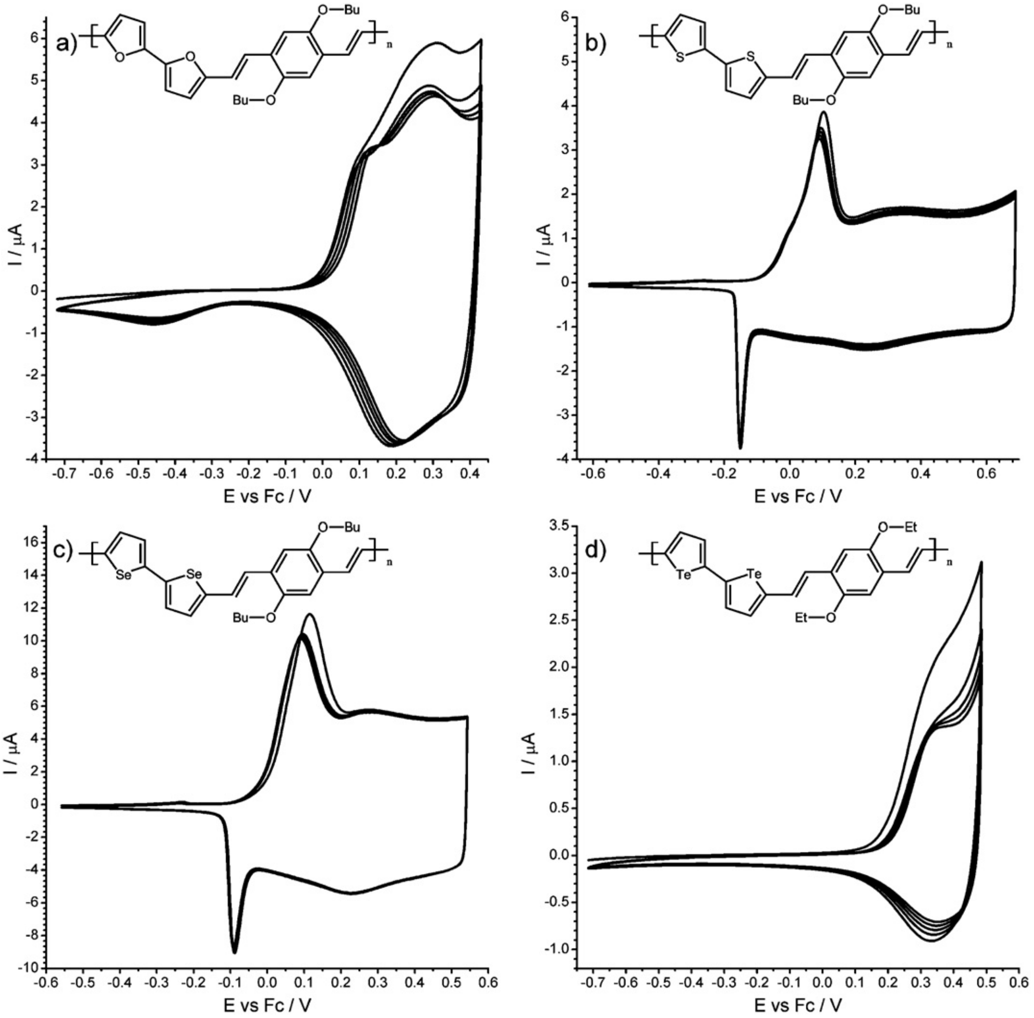


Fig. 3. Cyclic voltammetry of electrochemical doping–dedoping process of the electrodeposited polymers in monomer free medium. Measurement conditions: scan rate 50 mV/s, Ag/AgCl – quasireference electrode, calibrated against ferrocene/ferrocenium redox couple.

*2.4.6. 1,4-Dibutoxy-2,5-bis(thiophen-2-yl)benzene (**10b**)*

0.50 g (1.32 mmol) 2,5-dibromo-1,4-dibutoxybenzene, 0.37 g (2.89 mmol) 2-thienylboronic acid, 0.03 g (0.026 mmol) $Pd(PPh_3)_4$, 3 cm^3 (3.39 mmol) 2 M Na_2CO_3, 10 cm^3 THF-u. Reaction time 24 h. Received product 0.28 g (0.72 mmol, 54%) as white solid with t_m = 93–95 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.00 (t, J = 7.50 Hz, 6H, 2× —CH_3), 1.56 (sext., J = 7.50 Hz, 4H, 2× —CH_2—), 1.82 (q, J = 6.60 Hz, 4H, 2× —CH_2—), 4.09 (t, J = 6.30 Hz, 4H, 2× —OCH_2—), 7.09 (dd, J = 3.60 Hz, J = 5.10 Hz, 2H, C_4H_3S, 2× C^4—H), 7.26 (s, 2H, 2× H_{Ar}), 7.34 (dd, J = 0.90 Hz, J = 5.10 Hz, 2H, C_4H_3S, 2× C^5—H), 7,53 (dd, J = 0.90 Hz, J = 3.60 Hz, 2H, C_4H_3S, 2× C^3—H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 14.07 (2× —CH_3), 19.63 (2× —CH_2—), 31.65 (2× —CH_2—), 69.51 (2× —OCH_2—), 112.91 (2× C_{Ar}—H), 123.09 (2× C_{Ar}), 125.27 (C_4H_3S, 2× C^3), 125.82 (C_4H_3S, 2× C^4), 126.85 (C_4H_3S, 2× C^5), 139.44 (C_4H_3S, 2× C^2), 149.36 (2× $\underline{C}$OAlk). UV–vis (CH_2Cl_2) λ = 361.5 nm, $\varepsilon = (2.26 \pm 0.14) \times 10^4$, λ = 305.0 nm, $\varepsilon = (1.61 \pm 0.10) \times 10^4$, λ = 256.5 nm, $\varepsilon = (0.94 \pm 0.06) \times 10^4$ [dm^3/mol cm].

*2.4.7. 1,4-Dibutoxy-2,5-bis(selenophen-2-yl)benzene (**10c**)*

To a stirred solution of 0.30 g (0.79 mmol) 2,5-dibromo-1,4-dibutoxybenzene, 0.02 g (0.024 mmol) $Pd(PPh_3)_2Cl_2$, 0.03 g (0.13 mmol) triphenylphosphine in 3 cm^3 DMF and 3 cm^3 THF, 0.66 g (1.57 mmol) tributyl(selenophen-2-yl)tin in 2 cm^3 was added drop wise. Reaction was conducted under nitrogen for 18 h at temperature 75 °C. Rection mixture was poured into 50 cm^3 of concentrated KF solution with 20 cm^3 of dichloromethane and stirred for 1 h. Aqueous layer was extracted with dichloromethane (3 × 10 cm^3) and collected organic phases were washed by KF solution and water. Organic phase was dried by $MgSO_4$ and solvent was evaporated. Crude product was purified by column chromatography (hexane) to give yellow solid (0.18 g, 0.37 mmol, 48%) with t_m = 120–121.5 °C (hexane), 120–122 °C (methanol), 121–122 °C (diethyl ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.02 (t, J = 7.20 Hz, 6H, 2× —CH_3), 1.51 (sext., J = 7.20 Hz, 4H, 2× —CH_2—), 1.94 (pent., J = 7.20 Hz, 4H, 2× —CH_2—), 4.14 (t, J = 6.60 Hz, 4H, 2× —OCH_2—), 7.26 (s, 2H, 2× H_{Ar}), 7.36 (dd, J = 3.90 Hz, J = 5.70 Hz, 2H, C_4H_3Se, 2× C^4—H), 7.72 (d, J = 3.90 Hz, 2H, C_4H_3Se, 2× C^3—H), 8.06 (d, J = 5.70 Hz, 2H, C_4H_3Se, 2× C^5—H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 13.92 (2× —CH_3), 19.57 (2× —CH_2—), 31.56 (2× —CH_2—), 69.48 (2× —OCH_2—), 111.06 (2× C_{Ar}—H), 124.59 (2× C_{Ar}), 125.83 (C_4H_3Se, 2× C^3), 128.86 (C_4H_3Se, 2× C^4), 131.76 (C_4H_3Se, 2× C^5), 143.06 (C_4H_3Se, 2× C^2), 148.59 (2× $\underline{C}$OAlk). UV–vis (CH_2Cl_2) λ = 374.0 nm, $\varepsilon = (2.57 \pm 0.16) \times 10^4$, λ = 323.5 nm, $\varepsilon = (1.37 \pm 0.09) \times 10^4$, λ = 313.0 nm, $\varepsilon = (1.38 \pm 0.09) \times 10^4$, λ = 290.0 nm, $\varepsilon = (0.93 \pm 0.06) \times 10^4$ [dm^3/mol cm]. EA calc. C(55.01%) H(5.46%), found C(54.64%) H(5.38%).

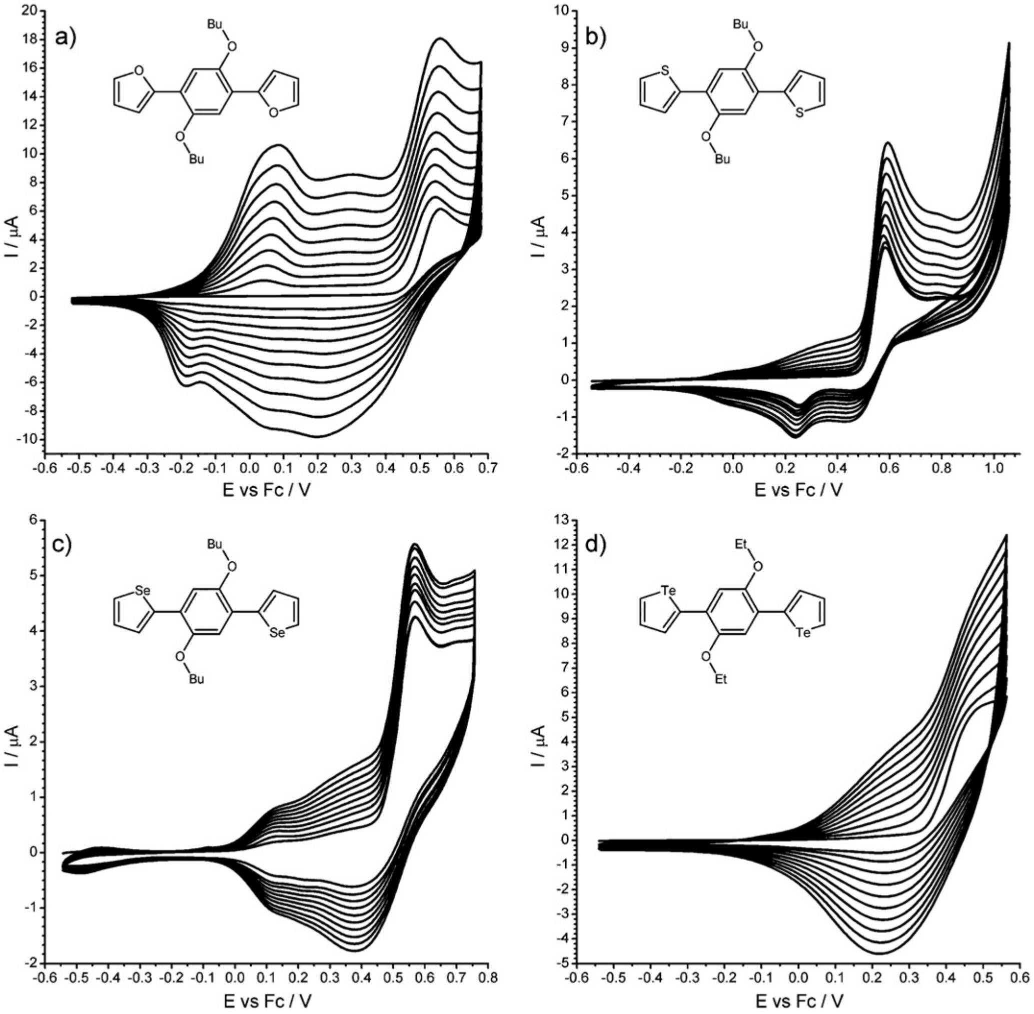


Fig. 4. Cyclic voltammetry of investigated monomers of polymerization. Measurement conditions: scan rate 50 mV/s, Ag/AgCl – quasireference electrode, calibrated against ferrocene/ferrocenium redox couple.

2.4.8. *1,4-Diethoxy-2,5-bis(tellurophen-2-yl)benzene (**10d**)*

To a stirred solution of 0.42 g (1.00 mmol) 2,5-diiodo-1,4-diethoxybenzene, 0.04 g (0.035 mmol) Pd(PPh_3)$_4$, 0.01 g (0.05 mmol) CuI in 5 cm^3 DMF, 0.94 g (2.00 mmol) tributyl(tellurophen-2-yl)tin in 3 cm^3 DMF was added drop wise. Reaction was conducted under nitrogen for 18 h at temperature 75 °C. As next step reaction mixture was poured into 50 cm^3 of concentrated KF solution and 20 cm^3 of dichloromethane and stirred for 1 h. Aqueous layer was extracted with dichloromethane (3× 15 cm^3) and collected organic phases were washed by KF solution and water. Organic phase was dried by $MgSO_4$ and solvent was evaporated. Crude product was purified by column chromatography (hexane) to give yellow solid (0.24 g, 0.46 mmol, 46%) with t_m = 214–216 °C (hexane). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.62 (t, J = 6.90 Hz, 6H, 2× —CH_3), 4.29 (q, J = 6.90 Hz, 4H, 2× —OCH_2—), 7.44 (s, 2H, 2× H_{Ar}), 7.94 (dd, J = 4.50 Hz, J = 7.20 Hz, 2H, C_4H_3Te, 2× C^4—H), 8.15 (dd, J = 0.90 Hz, J = 4.50 Hz, 2H, C_4H_3Te, 2× C^3—H), 8.98 (dd, J = 0.90 Hz, J = 7.20 Hz, 2H, C_4H_3Se, 2× C^5—H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 15.52 (2× —CH_3), 65.63 (2× —OCH_2—), 108.63 (2× C_{Ar}—H), 127.39 (2× C_{Ar}), 129.32 (C_4H_3Te, 2× C^3), 131.82 (C_4H_3Te, 2× C^4), 136.29 (C_4H_3Te, 2× C^5), 136.62 (C_4H_3Te, 2× C^2), 147.63(2× $\underline{C}$OAlk). UV–vis (CH_2Cl_2) λ = 406.0 nm, $\varepsilon = (3.00 \pm 0.19) \times 10^4$; λ = 388.0 nm, $\varepsilon = (3.23 \pm 0.20) \times 10^4$, λ = 322.0 nm, $\varepsilon = (1.63 \pm 0.11) \times 10^4$ [dm^3/mol cm].

3. Results and discussion

3.1. *Electrochemical properties*

To understand influence of heteroatom in the electronic structures of the molecules, cyclic voltammetry (CV) measurements were performed. Fig. 2 shows the results of electrochemical measurements of the monomers in the potential ranges from −0.7 V up to 0.8 V for thiophene derivative. Cyclic voltammetric curves in positive potentials range show multistep irreversible oxidation process, and both the shape of the curves and the individual oxidation potentials of peaks depend on the type of heteroatom. Series of reduction peaks are observed at lower potentials than the first oxidation peak, which indicates that the reactions give us products with a higher conjugation degree compared to the initial monomer. The reduction process is irreversible, although less complicated, but in the case of monomers containing tellurophene several independent peaks are shown. In order to better visualize of individual processes and to obtain the absolute values of the peaks of oxidation and reduction differential pulse voltammetry (DPV) measurements in Fig. 6 are shown.

The synthesized monomers were electropolymerized by cyclic voltammetric process in the dichloromethane solutions (Fig. 2). In all of investigated monomers electropolymerization

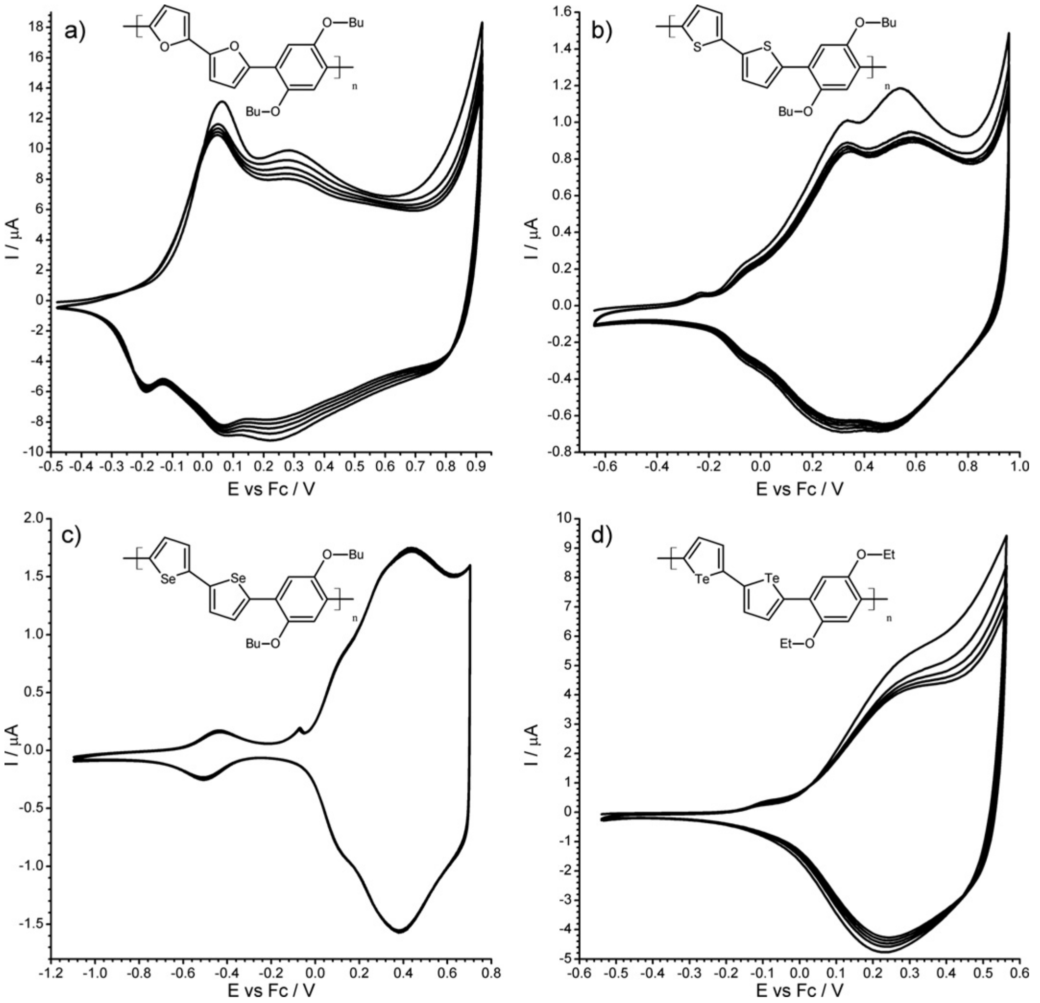


Fig. 5. Cyclic voltammetry of electrochemical doping–dedoping process of the electrodeposited polymers in monomer free medium. Measurement conditions: scan rate 50 mV/s, Ag/AgCl – quasireference electrode, calibrated against ferrocene/ferrocenium redox couple.

process occurred only above first oxidation peak potentials. During electropolymerization, the current is growing in successive scans what corresponding to formation of conducting species on working electrode as polymer layer (Figs. 2 and 4). The monomers electropolymerization under potentiostatic control provides information about the formation and polymer growth stages on electrode. Electrochemical investigation of compounds in dichloromethane showed that all molecules undergo multi-electron oxidation processes but the initial potentials depend on the molecular structure and were found 0.15 V for (**5a**), 0.26 V for (**5b**), 0.23 V for (**5c**) and 0.21 V for (**5d**), respectively, as shown in Fig. 3. The first oxidation peak potentials of compounds occur at 0.43 V (**5a**), 0.46 V (**5b**), 0.44 V (**5c**) and 0.53 V (**5d**). The peak of tellurophene monomer is not clearly shown because of large peak of second oxidation step of decomposition of tellurophene ring, which was described in previous investigations [38].

As is shown in Fig. 3 the poly(**5a**) with bifuran unit has two oxidation peaks and two reduction peaks at potentials 0.12 V, 0.31 V and 0.18 V, −0.46 V. The poly(**5b**) with bithiophene have similar two oxidation and two reduction peaks at 0.10 V, 0.36 V and 0.23 V, 0.16 V, the sharp peak shape suggesting high speed of doping–dedoping process. Oxidation and reduction peaks of poly(**5c**) are 0.12 V, 0.28 V and 0.23 V, −0,09 V. Peaks from redox process of poly(**5d**) are 0.37 V and 0.32 V. The poly(**5b**) had the lowest oxidation potential what was observed in previous investigations. Normally the poly(**5d**) should have lowest oxidation potential, but probably tellurium twist molecule structure, similar process was observed in selenophene compounds [48,49].

In all poly(**5**) and poly(**10**) we observed shifting of oxidation peak which was related with activation barrier of neutral polymers. In first cycle the polymer must oxidize from neutral state at different equilibrium state than in second and successive scans (Figs. 3 and 5).

Electrochemical investigation of monomers **10** showed that all molecules undergo similar electrochemical processes. The initial potentials were found 0.35 V for (**10a**), 0.41 V for (**10b**), 0.39 V for (**10c**) and 0.24 V for (**10d**) and the first oxidation peak potentials of compounds occurred at voltage 0.56 V (**10a**), 0.58 V (**10b**), 0.57 V (**10c**), and 0.49 V (**10d**) which are shown in Fig. 4.

The poly(**10a**) with bifuran unit has two peaks of the oxidation and reduction process at 0.10 V, 0.28 V and 0.23 V, −0.18 V which is shown in Fig. 5. The poly(**10b**) with bithiophene spacer have two oxidation and two reduction peaks at higher potential (0.34 V, 0.54 V and 0.47 V, 0.29 V) than polymer with bifuran unit. Oxidation and reduction peaks of poly(**10c**) are −0.44 V, 0.44 V and 0.38 V, −0,51 V and the peaks of electrochemical processes of poly(**10d**) are 0.30 V and 0.22 V. The poly(**10a**) has the lowest oxidation potential what was similar in previous investigations.

Specific charges of polymer doping calculated by area under CV's curve are shown in Table 1. Measured values in comparison with chemically synthesized polythiophene 352.8 C/g are lower but in the range of investigated electrochemically synthesized

Table 1
Electrical properties of investigated polymers.

	Specific charge (C/g)	Specific capacitance (F/g)
Poly(**5a**)	33	27
Poly(**5b**)	56	20
Poly(**5c**)	67	61
Poly(**5d**)	73	86
Poly(**9a**)	75	125
Poly(**9b**)	26	10
Poly(**9c**)	49	15
Poly(**9d**)	101	129
Polythiophene	352.8 [50]	260 [51]
Polypyrrole	44.5 [52]	–

materials like polypyrrole 44.5 C/g. The specific capacitance of polymers measured by ratio of mean value of current to CV's scan rate of doping process are much lower than for chemically synthesized polythiophene (260 F/g).

The specific charge of poly(**5d**) doping increased by half and specific capacitance by three times from previous investigation [38] only by controlling of polymerization process. The specific charge should increase with heteroatom mass in both cases but there is large influence on charge transfer when furan is directly connected to the chain without vinyl linker. Probably chain is more rigid what influence on electrical properties. The specific charge is 2.5 times larger and specific capacitance is 5 times larger than monomer with vinyl linker.

Differential pulse voltammetry (DPV) spectra (Fig. 6) are showing absolute peaks of oxidation and reduction processes. In correlation to the molecular band, oxidation peak is connected to the HOMO band and reduction peak is connected to the LUMO band. Electrochemical band gap value for monomers is the range between those peaks. DPV spectra showed that peaks of oxidation process are similar for all *p*-phenylene derivatives, only potentials for tellurophene monomers are lower. Redox processes at the potential near of 0.50 V concerns the first oxidation step of benzene unit. In respect of that, peaks of monomers with vinyl linker have lower potential than analogs without vinyl linker, which is connected to higher conjugation length in monomer.

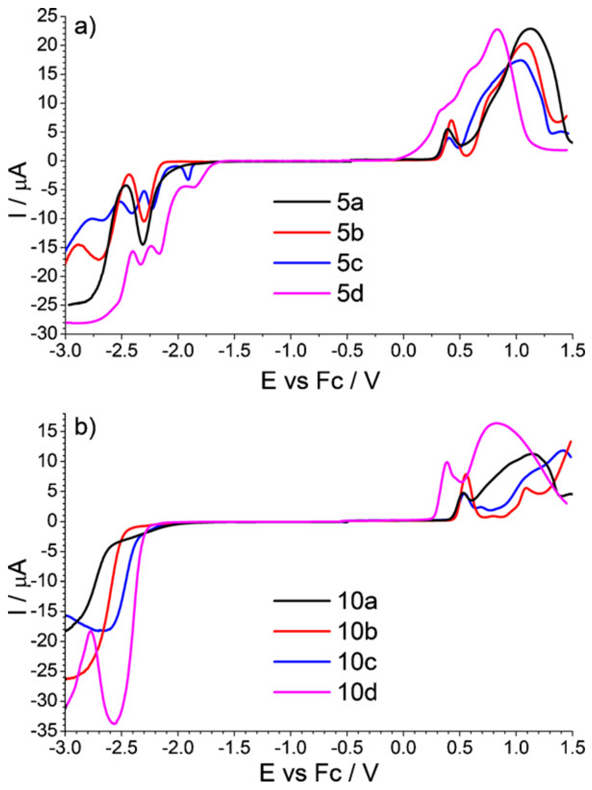


Fig. 6. DPV spectra of investigated monomers. Measurement conditions: scan rate 50 mV/s, Ag/AgCl – quasireference electrode, calibrated against ferrocene/ferrocenium redox couple.

Similar dependence is for shifting of first reduction peak, value is increasing due to higher conjugation of molecule. First oxidation potential is increasing in tellurophene < selenophene < thiophene < furan series, first reduction peak is decreasing tellurophene < selenophene < thiophene < furan series in both of cases. That means tellurophene monomers had lowest band gap in investigated series.

*3.2. Spectroelectrochemical properties of poly(**5**) and poly(**10**)*

In order to find relation between redox processes and UV–vis absorption, the spectroelectrochemical properties of polymers prepared on ITO coated glass electrode were investigated. The absorption spectra of poly(**5a–d**) films on ITO glass were represented in Fig. 7. As a result of the spectroelectrochemical measurements, both electronic structure of the poly(**5**) and their optical behavior upon doping were clarified. The neutral poly(**5a**) is characterized by two overlapping broad absorption peaks located at $\lambda_{max1} = 369$ nm and $\lambda_{max2} = 413$ nm and poorly marked shoulder. During the oxidation process of poly(**5a**) film, by increasing potential and electrochemical doping the band at 300–550 nm diminished and a new broad band developed between 500 and 1000 nm. This is indicating the formation of polarons and bipolarons in conducting polymers, while the $\pi \rightarrow \pi^*$ transitions of the neutral polymer appear in higher energies (Fig. 7a). The neutral polymer **5b** shows a maximum of absorbance at 517 nm related to the interband $\pi \rightarrow \pi^*$ transitions of the aromatic form of neutral polythiophene derivative. When the oxidation starts, new polaronic and bipolaronic levels are generated inside this band gap. The UV–vis set of spectrum recorded during the poly(**5b**) oxidation revealed the absorption band (400–650 nm) correlated with the polymer (Fig. 7b), gradually losing its intensity as the applied potential increased. In the same time the new defined absorption band occurred (600–1100 nm), owing the formation of radical cation of bithiophene and *p*-phenylenevinylene.

The neutral polytellurophene derivative poly(**5d**) shows two broad absorption peaks located at $\lambda_{max1} = 347$ nm and $\lambda_{max2} = 513$ nm. During anodic process UV–vis set of spectrum showed that the absorption band from 450 to 700 nm correlated with the polymer (Fig. 7d), gradually losing its intensity as the applied potential increased. In the same time the new defined polaron absorption band is formed at 750–1100 nm with maximum at 805 nm. Under doping polymers **5** from red for poly(**5a,b**) and violet for poly(**5c,d**) turns to dark violet and dark blue.

The absorption spectra of poly(**10a–d**) films on ITO glass were represented in Fig. 8. The neutral poly(**10a**) is characterized by two overlapping absorption peaks located at $\lambda_{max1} = 478$ nm and $\lambda_{max2} = 517$ nm. During the oxidation process of poly(**10a**) film, the band at 400–550 nm diminished and a new broad band of polarons developed between 500 and 800 nm (Fig. 8a). Formation of bipolaron band occurs with absorption band formation from 1000 to beyond 1100 nm. Bipolarons are formed by oxidation of polarons. Electrons require an average lower energy to be transferred to those bipolaronic levels from the fundamental state $\lambda_{max} > 850$ nm. The neutral polymer **10b** shows a maximum of absorbance at 442 nm related to the interband $\pi \rightarrow \pi^*$ transitions. The next UV–vis set of spectrum recorded during the poly(**10b**) oxidation showed the absorption band (350–550 nm) from neutral polymer (Fig. 8b), gradually losing its intensity as the applied potential increased. In the same time the formation of polarons and bipolarons in conducting polymer occurred by forming new absorption band

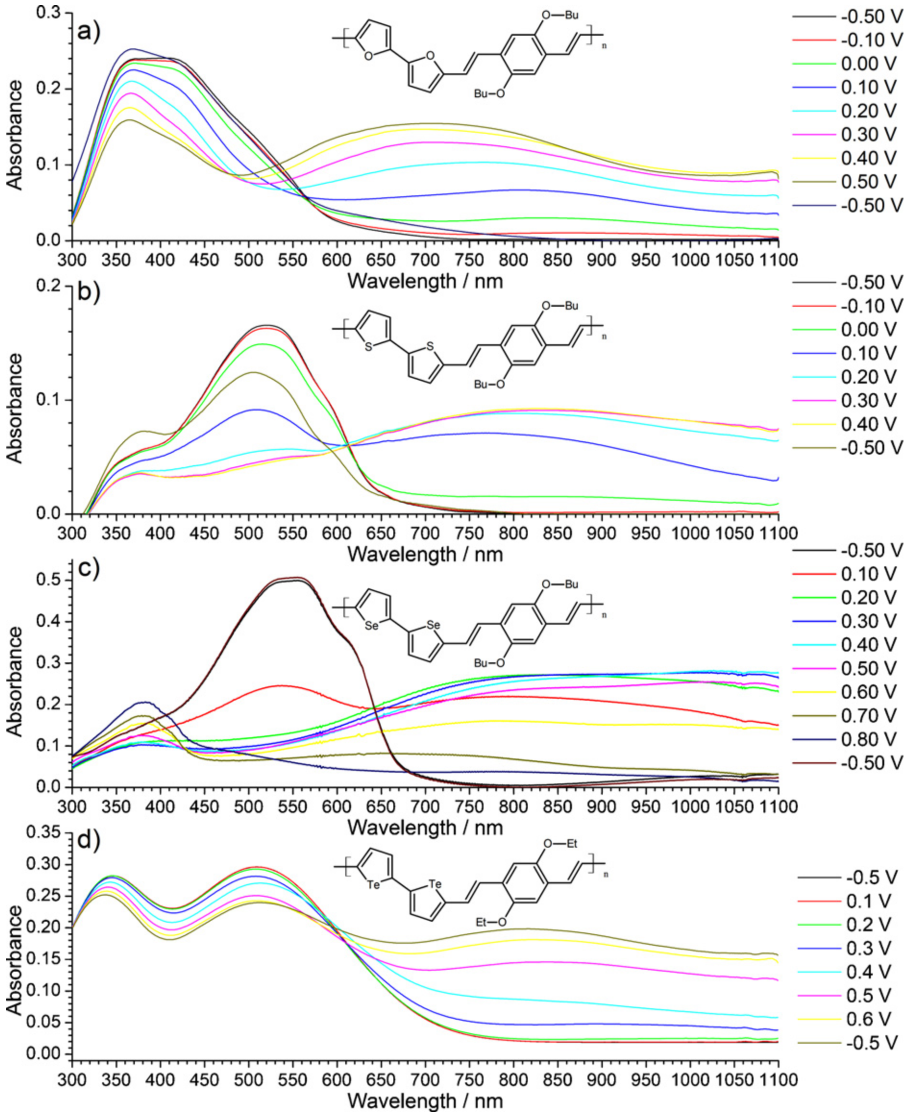


Fig. 7. UV–vis spectra recorded during electrochemical oxidation of poly(**5a**), poly(**5b**), poly(**5c**) and poly(**5d**) films.

(550–800 nm). The bipolaron band occurs with absorption band formation from 900 to beyond 1100 nm.

Spectroelectrochemical processes were similar in all of polymers, differences were only in shifting of polymer and polaron band. The electrochromic properties are usually described by behavior of those bands. The color change characterization should be analyzed for materials for electrochemical windows applications, e.g. colorless layer fully turns to red or other color. Under oxidation polymers **10a–c** layer from red turns to dark violet. Poly(**10d**) turns from golden red to dark blue.

3.3. Photoluminescent properties of monomers

The photophysical characteristic of *p*-phenylene derivatives (**5**, **10**) was investigated by photoluminescence (PL) in diluted dichloromethane solution (1×10^{-5} mol/L) at ultraviolet-visible (UV–vis) maximum absorption peak of excitation. It is strictly showed that fluorescence emission is shifted to lower energies with increasing of heteroatom radius in heterocyclic ring. Heteroatom influence on separation of molecular band and it is possible to distinguished two fluorescence peaks for selenophene and

Table 2
Electrochemical and optical band-gap.

	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{g_{\mathrm{El}}}$ (eV)	$E_{g_{\mathrm{Op.}}}$ (eV)
Poly(**5a**)	−4.91	−2.70	2.21	2.10
Poly(**5b**)	−4.87	−2.78	2.09	1.91
Poly(**5c**)	−4.77	−2.90	1.87	1.82
Poly(**5d**)	−4.76	−3.00	1.76	1.75
Poly(**10a**)	−4.75	−2.34	2.41	2.25
Poly(**10b**)	−4.69	−2.45	2.24	2.21
Poly(**10c**)	−4.67	−2.65	2.02	2.14
Poly(**10d**)	−4.63	−2.80	1.83	1.94

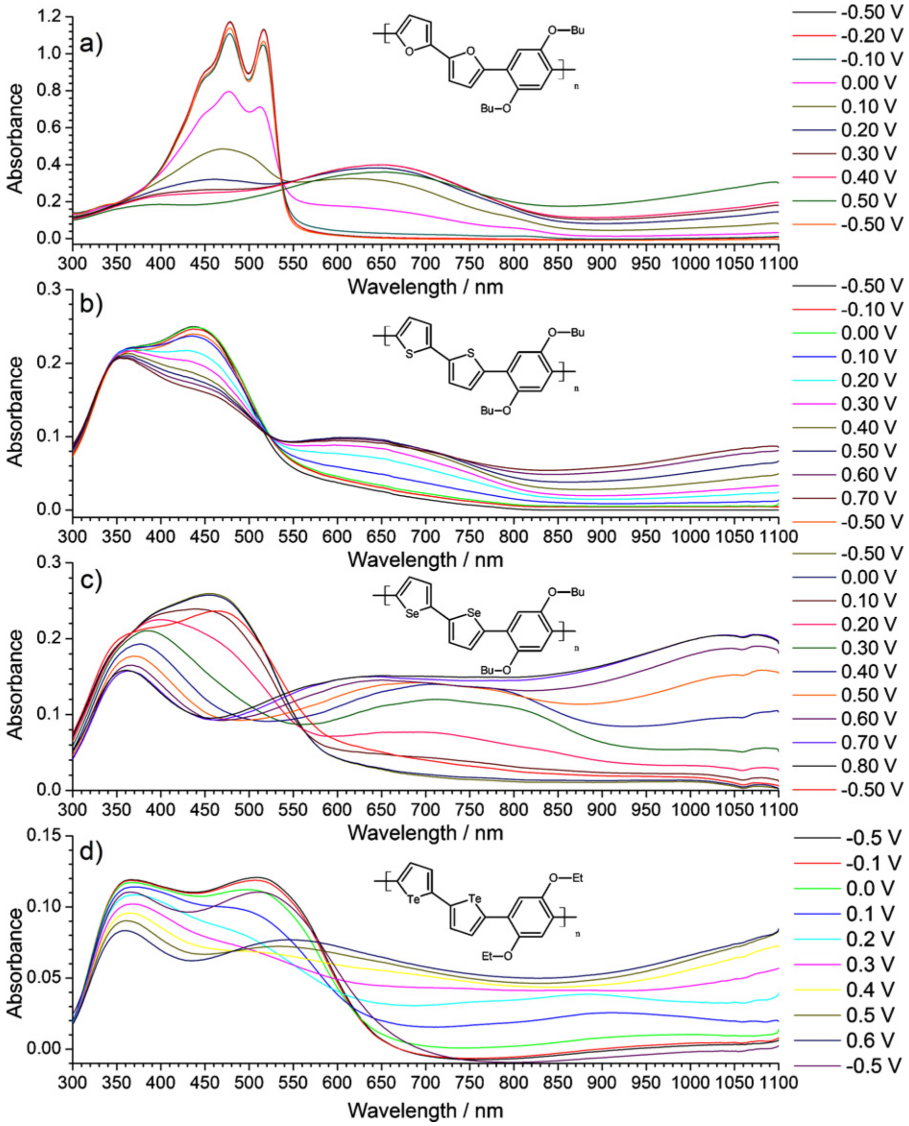


Fig. 8. UV–vis spectra recorded during electrochemical oxidation of poly(**10a**), poly(**10b**), poly(**10c**) and poly(**10d**) films.

tellurophene molecules. The vinyl *p*-phenylene derivatives are more conjugated and have higher absorption and emission peak than non-vinyl analogs (Fig. 9).

Thank to electrochemical characterization of polymers by analyzing oxidation and reduction processes it is possible to estimation of electrochemical band-gap value. In correlation to the molecular band, oxidation peak is related to the HOMO band and reduction peak is related to the LUMO band. Electrochemical band-gap value is the range between those peaks (Table 2) [53,54]. Optical band-gap was calculated from onset of polymer absorption by conversion

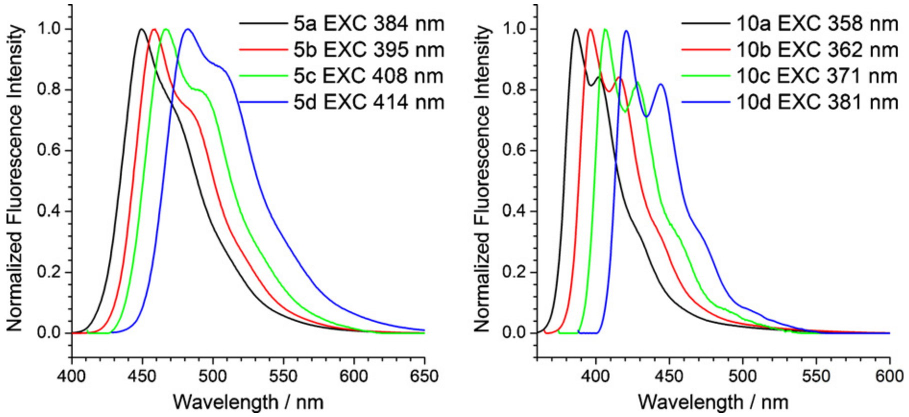


Fig. 9. Fluorescence spectra recorded at maximum absorption peak of monomers.

of wavelength to the energy [53,54]. The lowest electrochemical and optical band-gap have polymer contain bitellurophene and *p*-phenylenevinylene unit. The largest electrochemical and optical band-gap have polymer with bifuran and without vinyl unit.

4. Conclusions

New derivatives of *p*-phenylene containing different heteroaryl group were synthesized according to *Suzuki and Stille* condensation. Presented results show that (E,E)-1,4-dialkoxy-2,5-bis[2-(tellurophen)-2-yl)ethenyl]benzene can be obtained by condensation of 2-tellurophenecarbaldehyde with tetraethyl [2,5-dialkoxy-1,4-bis(methylene)]diphosphonate. The 1,4-dialkoxy-2,5-bis(selenophen-2-yl)benzenes and 1,4-dialkoxy-2,5-bis(tellurophen-2-yl)benzenes could be only synthesized from proper tri-*n*-butyltin derivative with 1,4-dialkoxy-2,5-bromobenzene for selenophene compound and 1,4-dialkoxy-2,5-diiodobenzene for tellurophene compound.

Presented results show influence of heteroatom and vinyl group in conjugated monomers and polymers on photo and electrochemical properties. All monomers electropolymerize during oxidative polymerization and formed polymers were electro and optically active. The band-gap were decreasing in furan > thiophene > selenophene > tellurophene series.

Fluorescence emission is shifted to lower energies with increasing of heteroatom radius in heterocyclic ring. Heteroatom influence on separation of molecular band and it is possible to distinguished two fluorescence peaks for selenophene and tellurophene molecules. The vinyl *p*-phenylene derivatives are more conjugated and have higher wavelength of absorption and emission peak than non-vinyl analogs.

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