Electrochimica Acta 128 (2014) 430–438

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Unusual properties of electropolymerized 2,7- and 3,6- carbazole derivatives

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ARTICLE INFO

Article history:
Received 7 July 2013
Received in revised form
28 November 2013
Accepted 17 December 2013
Available online 3 January 2014

Keywords:
Carbazole
UV-Vis spectroelectrochemistry
Selenophene
Pyrene
Band-gap

ABSTRACT

Differently linked carbazole derivatives possessing pyrene and selenophene moieties were electrochemically investigated. Cyclic voltammetric as well as differential pulse voltammetric studies demonstrated that they display comparatively low oxidation potentials. One-step cyclic voltammetric process was used for the preparation of their highly dimensional, stable and electroactive polymers. The electrodeposited polymers displayed unusual properties upon electrochemical doping that may help tailoring the dimensional features of these polymers. The electrodeposited polymers were investigated by electrochemical and optical tools and correlation between different parameters such as oxidation characteristics or absorption behavior and the effective conjugation length was established. Spectroelectrochemical investigations showed the polaronic and bipoloronic features of the electropolymers. Multielectrochromic properties of electrodeposited polymers on successive doping suggested their application as electroactive layers in electrochromic devices.

1. Introduction

The era of flexible and highly stable electronic devices demands π-conjugated organic polymers with the certain sets of properties including mechanical strength and with the possibilities of tailoring of the properties by structural modification. Thus, it is necessary to develop novel materials with the required sets of properties for specific applications. A large number of applications of conjugated polymers depend mainly on their electrochromic properties, which rely on the reproducible switching of characteristics of conjugated polymers [1–6]. The properties of conducting polymers strongly depend on their structural characteristics, which imply the modification of their monomer structures to tune the properties of the polymers (electronic, optical, charge-transporting etc.) according to the intended applications. The physical and chemical properties of the conjugated polymers can be controlled efficiently by some basic factors such as bond length alternation, variation of aromaticity and substitution [7]. For this purpose, functionalization of the electroactive monomer structures prior to electropolymerization and combination of the conducting polymers with other materials are widely used [8,9].

Conjugated polymeric systems based on selenophene or carbazole are among the most promising materials for the development of new generation, highly efficient OLED devices [10–12]. Carbazole and selenophene-based monomer units, especially in combination with electron-poor aromatic units, lead to novel polymeric electron donor structures [13–17] that possess a number of properties useful for the improvement of the photovoltaic characteristics [11], such as energy level alignment with that of electron acceptors [18], low energy gap which favors light harvesting and increase the short-circuit current of the device [13], high charge mobility [19] and good solubility in organic solvents and good film-forming properties [20]. Polycarbazoles are known not only as efficient short wavelength emitters but also as strong electro-donating (p-type) chromophores [21–26]. The advantage of carbazole moiety is that it can be easily functionalized at its C-2, C-3, C-6, C-7 or N-positions [27–29]. Furthermore, poly (3,6-carbazole)s demonstrate interesting electrochromic properties because of the conjugation breaks that are present due to the possession of 3,6-linkages. The ability of poly (3,6-carbazole) derivatives to form multi-oxidation states results in the exhibition of many colors on the ITO/glass surface upon applied positive potentials [30,31]. Since 2,7-substituted carbazoles have been theoretically found to have

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http://dx.doi.org/10.1016/j.electacta.2013.12.108

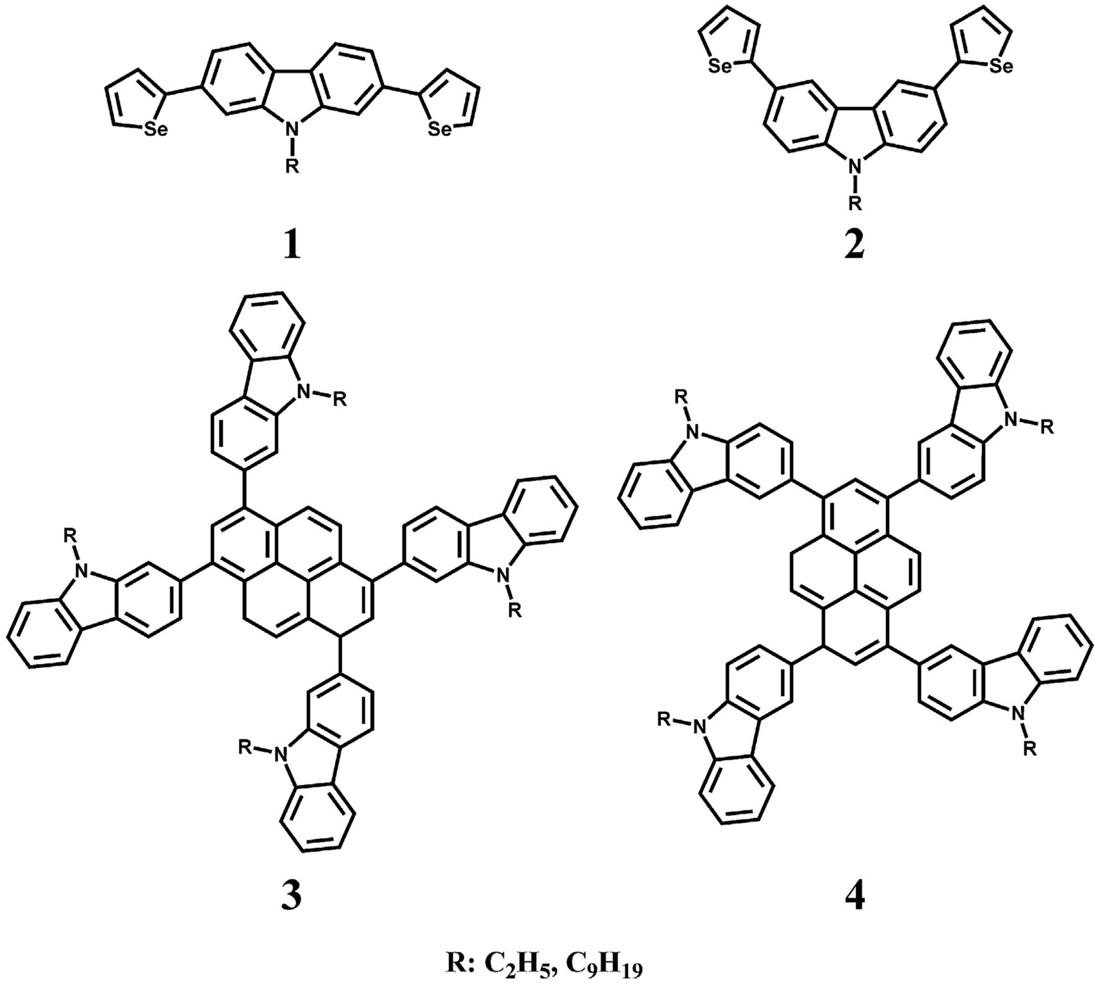


Fig. 1. Structures of investigated compounds.

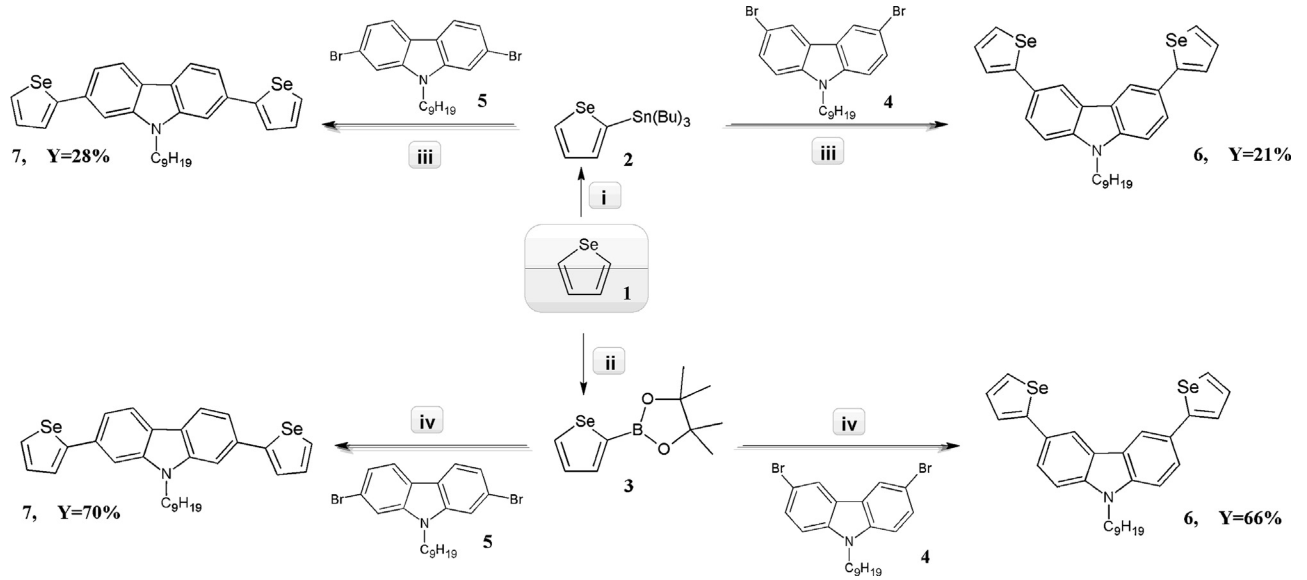
smaller band gaps than the 3,6-substituted carbazoles, the small energy gaps of these monomers are expected to contribute to a lowering of the band gaps in the resulting polymers [22–25]. Due to the simplicity of the synthesis, there are many reports regarding poly (3,6-carbazole)s [32]. Oligo- and poly(2,7-carbazole) derivatives have been successfully used in polymer light emitting diodes (PLEDs) and organic field-effect transistors (OFETs) [31]. Carbazole moiety is fully aromatic and possess good chemical and environmental stability. Taking all these considerations into account we expect, that development of new carbazole-based low-band gap copolymers will lead to interesting properties useful for photovoltaic applications. However, one possible problem that still concerns 2,7-carbazole-based copolymers is their electrochemical instability due to the build-up of charge at the free para-(3- and 6-) positions [33]. Big progress has been made recently in the field of electrochemically deposited polyselenophene derivatives for electrochromic devices [34,35], and chemically synthesized regioregular poly(3-hexylselenophene) for solar cells [36–38]. In addition, there are also some applications of the copolymers in organic light emitting diodes [39], OFETs [40] and near IR emitter [39,41] applications. The new aspect of the investigation into selenophene derivatives is use of selenophene moieties as a donor groups in donor-acceptor copolymers. Lee and co-workers [42] presented the synthesis, optical and photovoltaic characteristics of alkylselenophene-substituted quinoxaline based donor-acceptor low band-gap polymers. It was observed that the length of the C-C bond between selenophene rings is shorter than that between thiophene rings (ref). Therefore oligoselenophenes with enhanced conjugation in the polymer backbone show red shift in the absorption spectra as compared to oligothiophenes [42–46]. In the present study, a comparison of differently linked carbazole derivatives is presented. In selenophene derivatives 2,7- and 3,6-substituted carbazole moieties are inside the molecules while in pyrene-based derivatives they serve as the side arms.

Fig. 1.

2. Experimental

2.1. Materials

All solvents for the synthesis were dried and then distilled before use. Other commercially available substances and reagents were used as received. The solutions of 1.0 mM concentration of all monomers were used for all cyclic voltammetry measurements. Electrochemical studies were conducted in 0.1 M solutions of Bu_4NBF_4, 99% (Sigma Aldrich) in dichloromethane (DCM) solvent, (CHROMASOLV®, 99.9% from Sigma Aldrich) at room temperature. UV-Vis spectroelectrochemical measurements were performed on Indium Tin Oxide (ITO) quartz glass working electrode coated with polymers. Polymeric layers were synthesized on an ITO electrode under conditions similar to those of cyclic voltammetry measurements.



Scheme 1. Synthesis of selenophene derivatives. Conditions of reactions: (**i**) *n*-BuLi, $Sn(Bu)_3Cl$, THF_{anh}, -10 °C–rt, N_2, 5 h; (**ii**) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxoboralane, THF_{anh}, -78 °C–rt, N_2, 18 h; (**iii**) $Pd(PPh_3)_4$, toluene, N_2, 110 °C, 24 h; (**iv**) $Pd(PPh_3)_4$, 2 M K_2CO_{3aq}, toluene, N_2, 90 °C, 72 h.

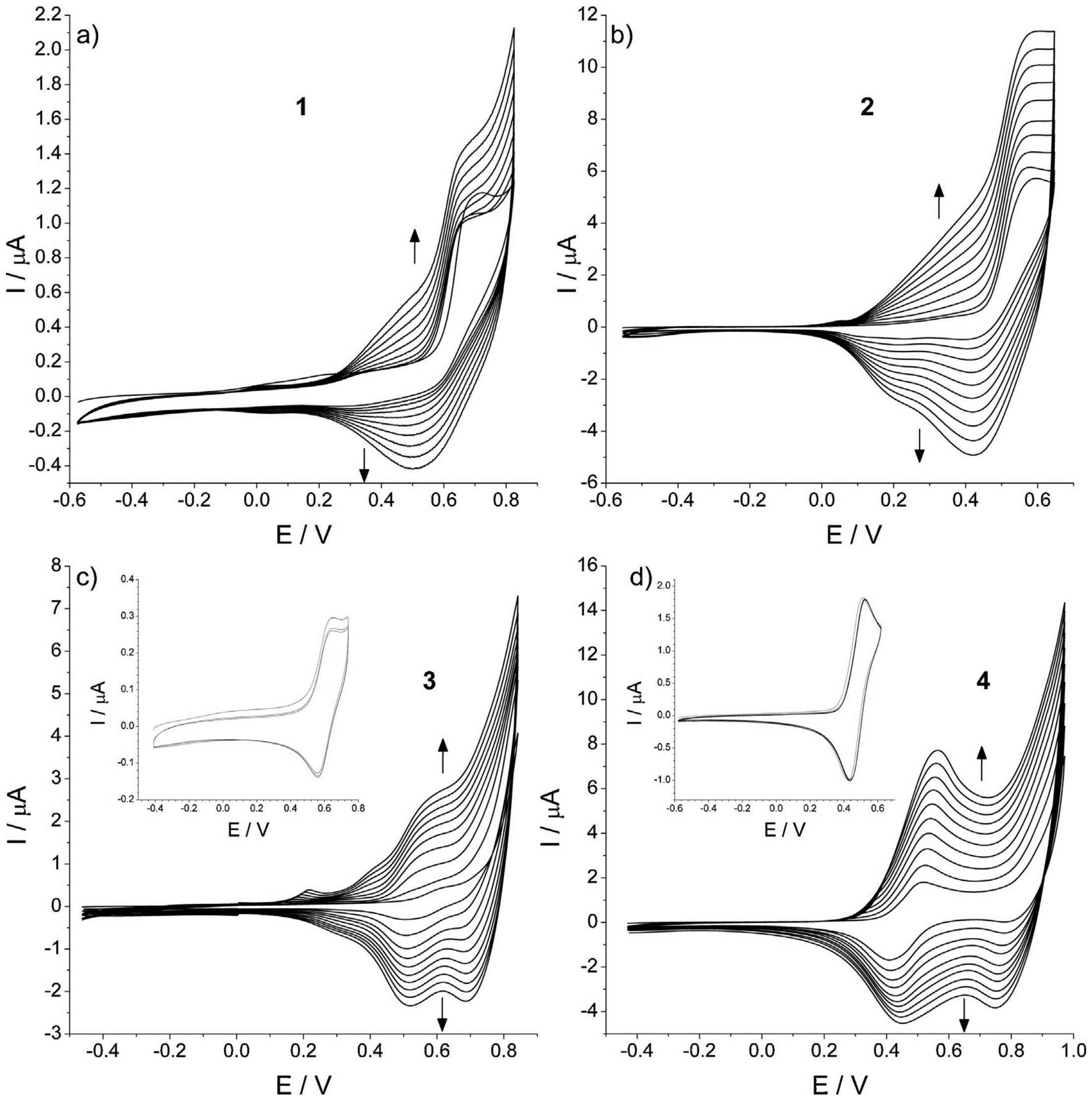


Fig. 2. Cyclic voltammograms of investigated monomers. Measurement conditions: scan rate 50 mV/s, calibrated against ferrocene/ferrocenium redox couple.

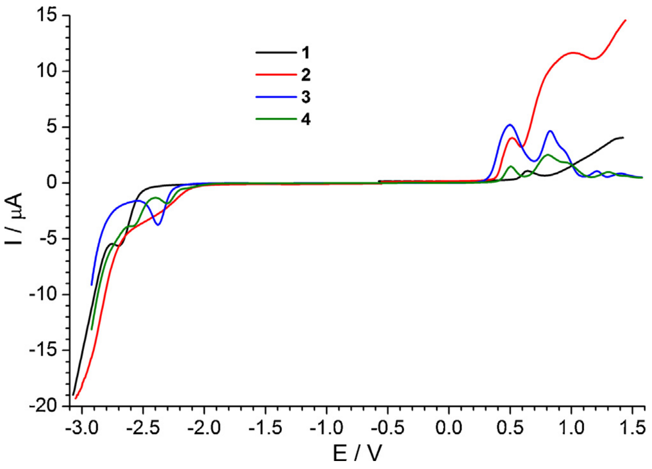


Fig. 3. DPV of investigated monomers. Measurement conditions: scan rate 50 mV/s, Ag/AgCl - quasireference electrode, calibrated against a ferrocene/ferrocenium redox couple.

2.1.1. *General synthesis of bis(selen-2-yl)-N-nonylcarbazole*

The synthesis of compounds **1** and **2** was based on our previous work [47]. It was established that the Stille and Suzuki procedures allowed the preparation of these carbazole derivatives. However, it was found that using Suzuki reaction, resulted in significantly higher yields (by *ca.* three times) (Scheme 1). The synthesis of selenophene-based monomers of 2,7- and 3,6-bis(selenophen-2-yl)-*N*-nonylcarbazole was performed starting from carbazole. *N*-nonylcarbazole [48] was successfully brominated in position 3 and 6 (**8**) using a modified procedure [49], requiring the usage of N-bromosuccinimide (NBS) and equal volume mixture of glacial acetic acid and dichloromethane. Whereas, 2,7-dibromo-*N*-nonylcarbazole (**9**) was synthesized by alkylation of commercially available 2,7-dibromocarbazole with 1-bromononane in toluene and sodium hydroxide solution in the presence of benzyltriethylammonium chloride as a catalyst. Boron- (**7**) and tin-derivatives (**6**) of selenophene were prepared as described in the literature [50–52].

2.1.2. *2,7-dibromo-N-nonylcarbazole (**9**)*

To a stirred solution of 2,7-dibromocarbazole (2 g, 6.15 mmol), 50 ml toluene, 20 ml 50% $NaOH_{aq}$ 1-bromononane (1.27 g,

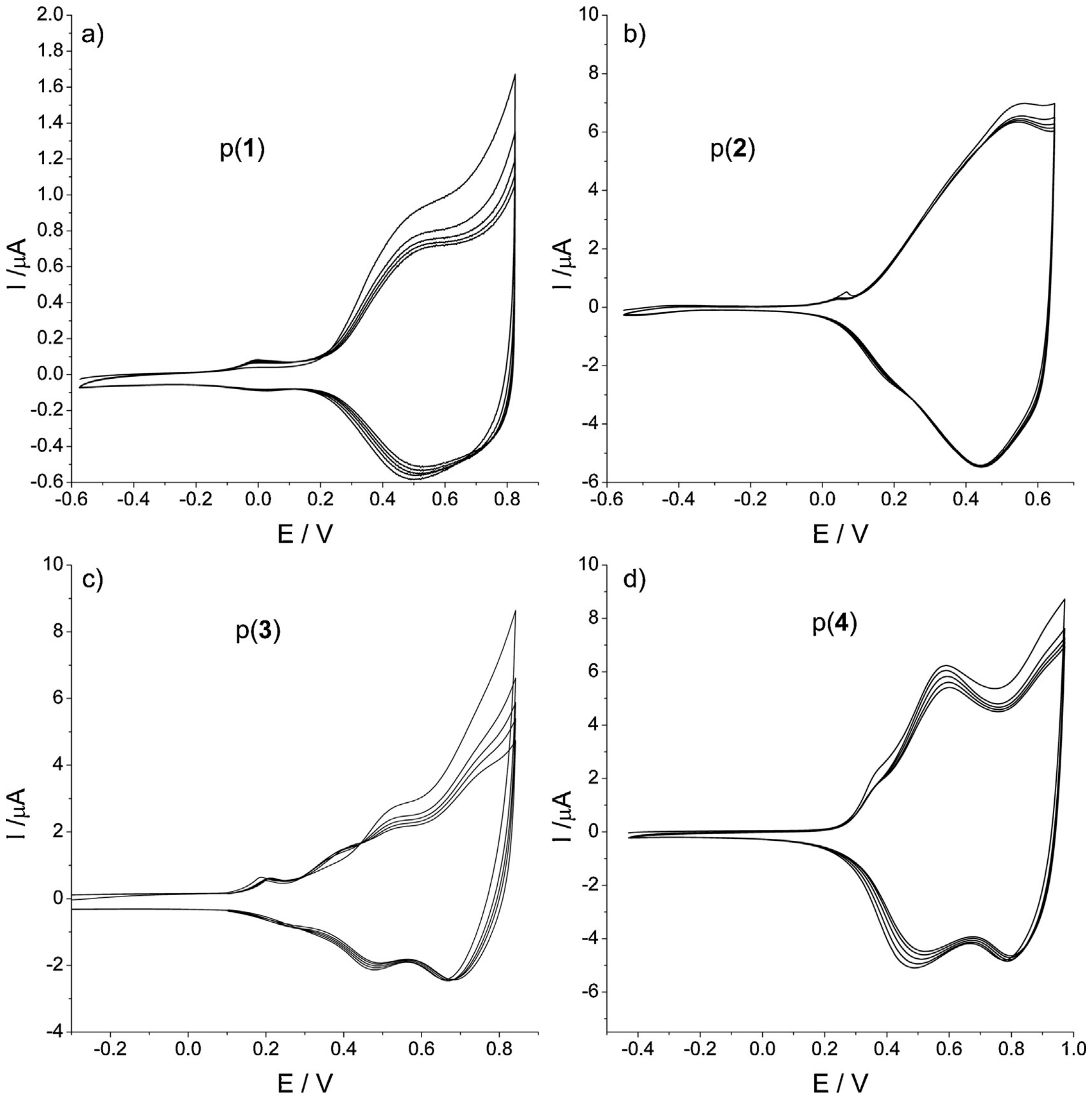


Fig. 4. Cyclic voltammograms of the electrochemical doping-dedoping process of polymers. Measurement conditions: scan rate 50 mV/s, calibrated against ferrocene/ferrocenium redox couple.

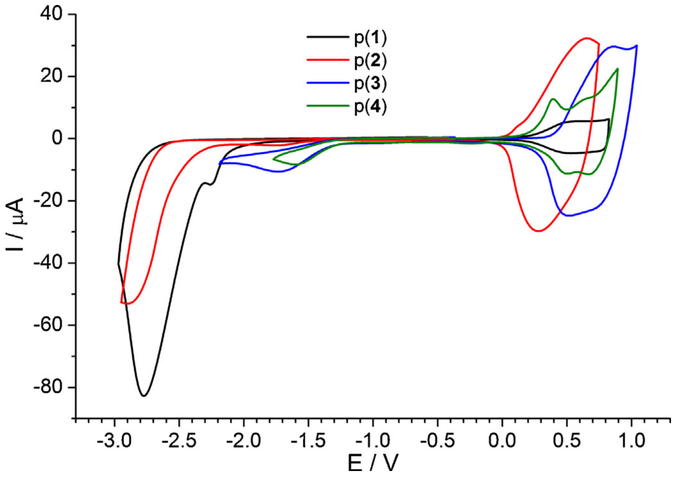


Fig. 5. Cyclic voltammograms of the doping-dedoping process of electropolymerization products in a monomer free medium. Measurement conditions: scan rate -300 mV/s, calibrated against ferrocene/ferrocenium redox couple.

6.13 mmol) and benzyltriethylammonium chloride (0.55 g, 2.41 mmol) were added. Reaction mixture was stirred for 20 h at 40 °C, then toluene phase was washed with water and ammonium chloride, while water phase was extracted with dichloromethane. The residue was purified by silica gel column chromatography (eluent–hexane) followed by evaporation to afford a cream-colored crystals with 98% yield (2.78 g, 6.15 mmol), t_m = 72 °C. ^{1}H NMR (300 MHz, CDCl$_3$): 7.89 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 1.6 Hz, 2H), 7.36-7.32 (dd, *J* = 1.6 Hz, *J* = 8.3 Hz, 2H), 4.19 (t, *J* = 7.3 Hz, 2H), 1.88-1.79 (m, 2H), 1.36-1.26 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H).

*2.1.3. 3,6-bis(selenophen-2-yl)-N-nonylcarbazole (**2**)*

Suzuki's procedure was used for the preparation of the compounds **1** and **2**. To a three-necked flask the following chemicals were added: 3,6-dibromo-*N*-nonylcarbazole (**8**) (1.0 g, 2.22 mmol), 4,4,5,5-tetramethyl-2-(selenophen-2-yl)-1,3,2-dioxoboralane (**7**) (1.38 g, 5.35 mmol), and a mixture of anhydrous toluene (35 ml) and 2 M aqueous potassium carbonate solution (15 ml). The flask equipped with a condenser was then evacuated and filled with nitrogen several times to remove traces of the air. The catalyst Pd(PPh$_3$)$_4$ (0.08 g, 0.07 mmol) was then added under a nitrogen atmosphere and the mixture was heated at 90 °C for 72 h under nitrogen. The separated aqueous layer was extracted with dichloromethane (3 × 15 ml). The organic phase was washed thrice with water (15 ml). Combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography with hexane:ethyl acetate (10:1, V/V) as eluent. Product **2** was obtained as a yellow-green solid with yield 66% (0.81 g, 1.46 mmol), t_m = 53-54 °C. ^{1}H NMR (300 MHz, CDCl$_3$): 8.30 (d, *J* = 1.8 Hz, 2H), 7.94-7.92 (dd, *J* = 1.1 Hz, *J* = 5.6 Hz, 2H), 7.72-7.69 (dd, *J* = 1.8 Hz, *J* = 8.5 Hz, 2H), 7.52-7.51 (dd, *J* = 1.1 Hz, *J* = 3.8 Hz, 2H), 7.38-7.35 (m, 4H), 4.28 (t, *J* = 7.2 Hz, 2H), 1.91-1.83 (m, 2H), 1.41-1.25 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (300 MHz, CDCl$_3$): 152.2, 140.6, 130.8, 128.8, 128.0, 125.0, 124.2, 123.3, 118.4, 109.3, 43.3, 32.0, 29.6, 29.5, 29.4, 29.1, 27.4, 22.8, 14.3.

*2.1.4. 2,7-bis(selenophen-2-yl)-N-nonylcarbazole (**1**)*

The synthesis of compound **1**, performed similar to that of compound **2**, which allowed to obtain 0.85 g (1.54 mmol, 70%) of product in form of yellow-green solid with 70% yield, t_m = 56-57 °C. ^{1}H NMR(300 mHz, CDCl$_3$): 8.03 (d, *J* = 8.2 Hz, 2H), 7.99-7.97 (dd, *J* = 1.1 Hz, *J* = 5.6 Hz, 2H), 7.58-7.56 (dd, *J* = 1.1 Hz, *J* = 3.8 Hz, 2H), 7.54 (d, *J* = 1.1 Hz, 2H), 7.48-7.45 (dd, *J* = 1.5 Hz, *J* = 8.1 Hz, 2H), 7.39-7.36 (dd, *J* = 3.8 Hz, *J* = 5.6 Hz, 2H), 4.35 (t, *J* = 7.2 Hz, 2H), 1.95-1.90 (m, 2H), 1.48-1.25 (m, 12H), 0.86 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (300 mHz, CDCl$_3$): 152.1, 141.5, 134.3, 130.7, 129.9, 125.2, 122.3, 120.7, 118.5, 106.4, 43.1, 32.0, 29.7, 29.5, 29.4, 29.2, 27.3, 22.8, 14.2.

1,3,6,8-Tetra(9-ethyl-9H-carbazol-2-yl) Pyrene (3) and 1,3,6,8-Tetra(9-ethyl-9H-carbazol-3-yl) Pyrene (4) monomers were synthesized according to our previously published procedures[53].

2.2. Measurements

Melting points were determined on automatic melting point SMP40 (Stuart) apparatus. NMR spectra were obtained in CDCl$_3$ by Avance 400 (Bruker) at 300 MHz for ^{1}H and at 75.5 MHz for ^{13}C. The electrochemical investigation was carried out using potentiostats Autolab PGSTAT20 and PGSTAT100 (Metrohm Autolab). The electrochemical cell comprised of platinum disk with 1-mm diameter of working area as working electrode (CV, DPV) and ITO glass

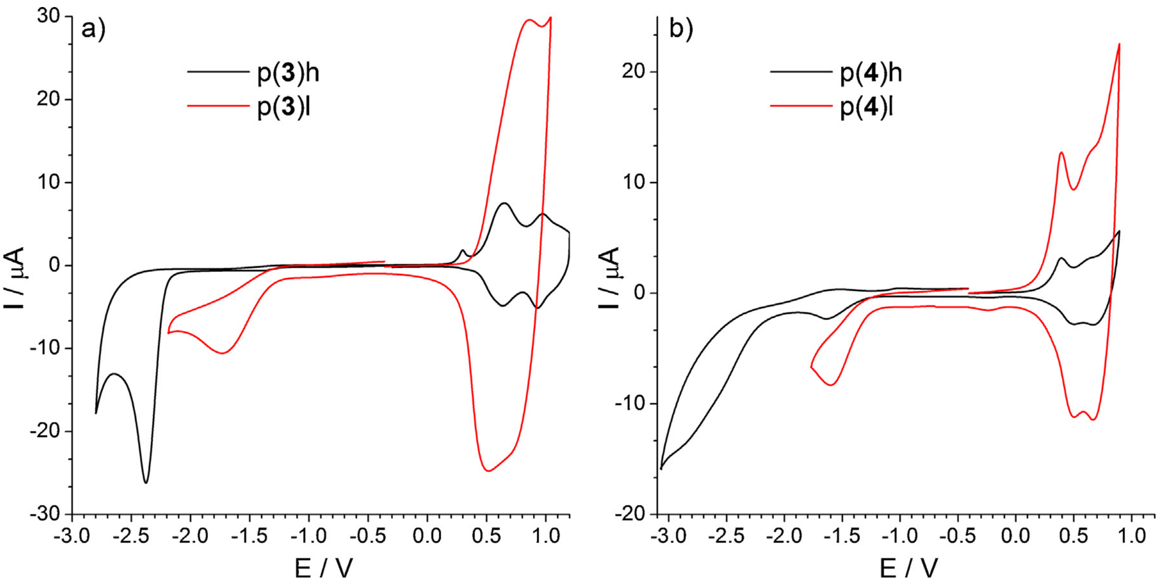


Fig. 6. Cyclic voltammograms of the doping-dedoping process of the electrodeposited polymers at low oxidation limit p(3)l, p(4)l and high oxidation limit p(3)h, p(4)h in a monomer free media. Measurement conditions: scan rate – 300 mV/s, calibrated against ferrocene/ferrocenium redox couple.

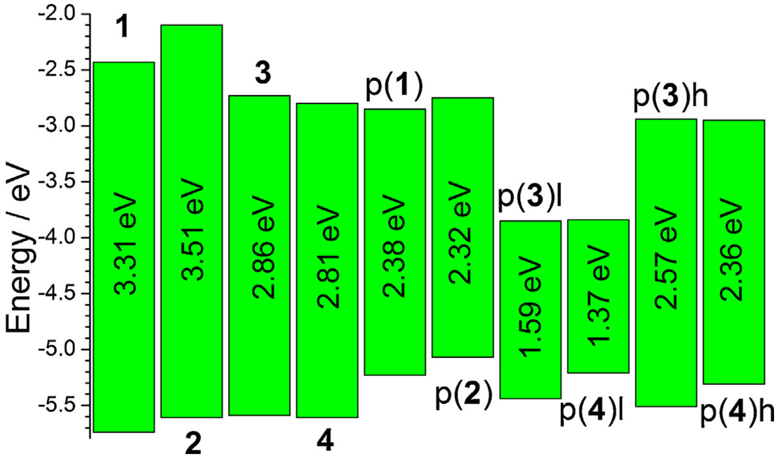


Fig. 7. Energy diagrams of HOMO-LUMO levels and band-gaps of monomers and polymers.

(spectroelectrochemistry) as a working electrode, Ag/AgCl electrode as reference electrode and platinum coil as auxiliary electrode. Cyclic voltamperometric measurements were conducted at room temperature under argon atmosphere and at scan rate of 50 mV/s and were calibrated against ferrocene/ferrocenium redox couple. UV-Vis-NIR spectroscopy and spectroelectrochemistry analyses were recorded by QE6500 and NIRQuest detectors (Ocean Optics).

3. Results and Discussion

It is known that introduction of substituents at C-2, C-3, C-6, C-7 positions carbazole moiety affects the optical and electronic properties of carbazole derivatives [22–33]. In this study, cyclic voltammetry (CV) measurements were performed to understand the effect of 2,7- and 3,6- substitution on the electronic structures of two different types of carbazole derivatives. Electrochemical investigation of the solutions of the compounds in dichloromethane demonstrated that all molecules underwent multi-electron oxidation processes (Fig. 2). The lowest oxidation potential was observed for monomer **4** where carbazole units are linked to pyrene core *via* C-3 position. During successive CV scan of 1 mM solution of monomers **1** and **2**, potentiodynamic growth of the conductive layer was observed (Fig. 2**a,b**) above the first oxidation peak. During the first scan, because of absence of the redox couple, irreversible peaks were observed at 0.71 V (for **1**) and 0.59 V (for **2**), respectively. For monomers **3** and **4** (Fig. 2**c,d**), redox couples were observed at first oxidation stage at 0.64 V (for **3**) and 0.52 V (for **4**). At higher oxidation potentials but below the second irreversible oxidation peak the current growth in successive scan was observed.

During successive voltammetric scans, the formation and growth of new wide bands at lower potential compared to those of monomers were observed. New peaks were not observed and only the growing peaks of monomers were observed. These observations suggested the formation of electroactive moieties on the electrode. The potential shift between the monomer peak and two peaks of electrodeposited layer suggests that the layer is formed by a species more conjugated than the monomer; i.e, in this case it was the conjugated polymer. The peakless behavior of electrodeposited layers suggested the formation of polymers with wide molecular weight distribution. The comparison the CV peaks with absolute peaks of oxidation and reduction processes in Differential Pulse Voltammetry (DPV) measurements (Fig. 3) revealed the lowest oxidation potential peaks for monomer **3**. The first oxidation of monomers **3** and **4** is related to the oxidation of pyrene core [53]. For monomers **1** and **2**, selenophene group was accountable for the first oxidation process (ref).

When it is assumed that the oxidation peak is related with the HOMO band and the reduction peak with the LUMO band, the electrochemical band-gap value for monomers will be the in the range between these two peaks. In the investigated series of carbazolyl derivatives, monomer **4** with a 3-linkage to pyrene core possessed the lowest band gap. For selenophenyl derivatives, where the carbazole group is inside the two selenophene units, the lowest band-gap was observed for monomer **1**.

Cyclic voltammetric experiments were carried out in electropolymerization conditions to investigate the synthesized polymers. Polymers were immersed into a monomer-free Bu_4NBF_4 DCM electrolyte and it was noted that the electrochemical stability of polymers during doping-dedoping process under polymerization conditions was moderate (Fig. 4). Comparatively good stability was observed for polymer p(**2**) obtained from monomer 2. Similar behavior was observed for the previously reported thiophene analogue of this polymer [54]. Polymer p(**1**) with 2,7-bis(selenophen-2-yl) group possessed the lowest potential value of oxidation peak, while polymer p(**4**) with carbazolyl substituted pyrene core via C-3 position of carbazole moiety displayed the highest oxidation peak potential.

HOMO and LUMO energy levels as well as electrochemical band-gap values were estimated by electrochemical analysis of doping-dedoping processes. Fig. 5 represents the cyclic voltammograms of polymers upon p- and n-doping at a scan rate of 300 mVs^{-1}. For all the investigated compounds, both p- and n- redox processes were observed. However, it was noted that the n- redox cycles were irreversible. Unusual results were observed during the analysis of CV curves of polymers p(**3**) and p(**4**) CV curves. In contrastr to the previous investigation [53], the peak at ca. 1.5 V was not observed and the band-gap values were by almost 1 eV lower.

To explain the aforementioned unusual behavior, both experiments are compared in Fig. 6. The main differences between both the experiments were in the thickness of the electrodeposited polymer layers and in the voltage range of electropolymerizations. In the present study, polymers p(**3**)l and p(**4**)l were formed at lower oxidation potentials of 0.85 V and 0.95 V as compared to 1.15 V and 1.10 V observed in the previous study [53]. Moreover, the polymers were electrodeposited during 10 scans rather than 3 scans as it was in the previous case [53]. It is interesting to note that the current density observed in both the cases was different. This observation can be due to the different thickness of polymer layers since the active area in CV curves was found to be the same in both the measurements. It is also assumed that the more linear forms

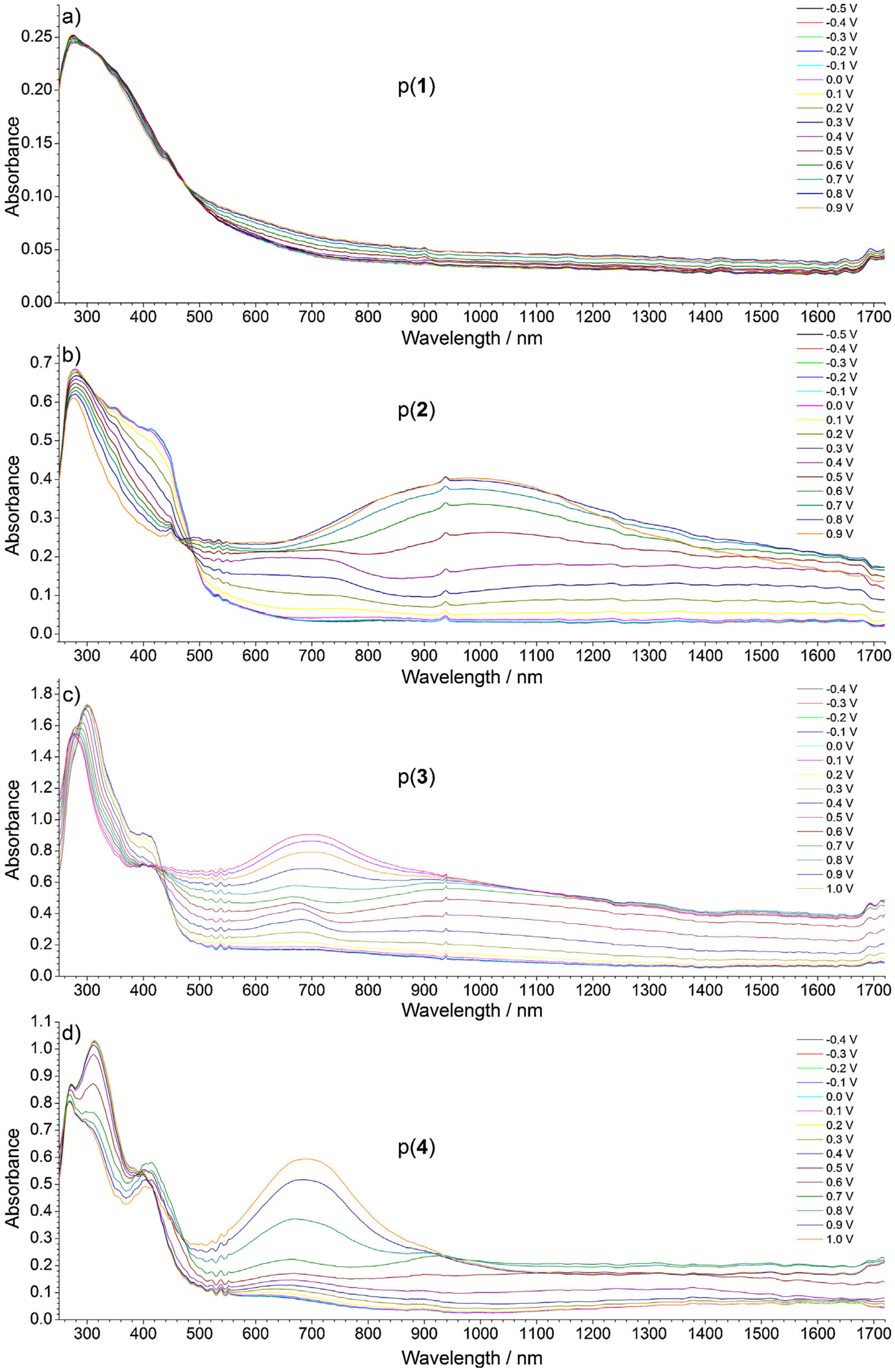


Fig. 8. UV-Vis spectra recorded during electrochemical oxidation of polymers p(1), p(2), p(3), p(4).

(2-arm connection) of p(**3**)l and p(**4**)l were deposited on the electrode at lower oxidation potentials. This assumption is supported by the absence of new peaks in higher oxidation range. It should be noted that it is almost impossible to oxidize all four carbazolyl arms of the monomers at mild electrochemical conditions to form fully branched polymers. Hence, to conclude, the oxidative peak at ca. 1.5 V might be originated from the pyrene core that apparently stronger for the linear polymers compared to the branched ones

The HOMO–LUMO energy levels and the electrochemical bandgap values of the electrochemically generated polymers are

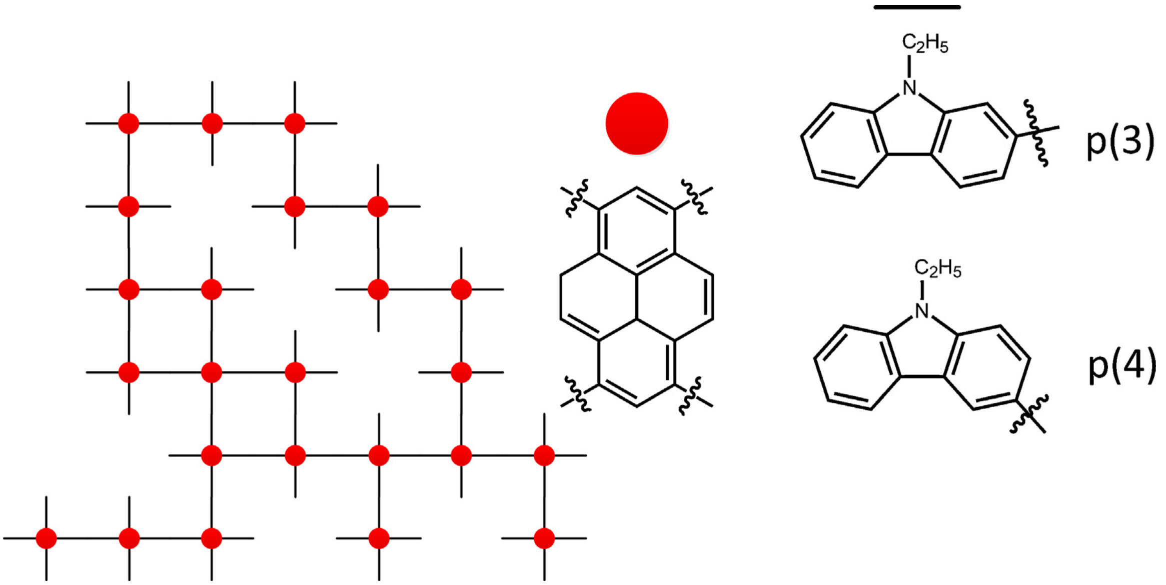


Fig. 9. Proposed structure of the electrodeposited polymers.

provided in Fig. 7 and tabulated in Table 1. These values were calculated from the first oxidation and reduction potential onsets. The difference in onset potentials obtained from the p- and n-doping sides can be taken as a measure of the band gap (E_G) values of the polymers (Fig. 5, **6**).

The optical band-gap values were slightly different from those of the electrochemical ones, which suggests that the absorption onsets might be not always related to π-π band transitions. The lowest optical and electrochemical band-gap values were observed for polymer p(**4**)l whereas the highest HOMO energy level was observed for p(**3**)h.

Thin polymeric films were electrodeposited on ITO-coated quartz glass substrates using cyclic voltammetry under the conditions similar to those shown in Fig. 2. Electrochemically formed polymers were investigated by UV-Vis-NIR spectrometry. Fig. 8 demonstrates the results of spectroelectrochemical investigation of polycarbazoles at potentiostatic conditions. No significant changes during doping process was observed for p(**1**) during several experiments (Fig. 8**a**). However, neutral p(**2**) was characterized by the two overlapping absorption peaks located at λ_{max1} = 280 nm and λ_{max2} = 418 nm. During the oxidation processes of the film of p(**2**), the absorption band of neutral polymer at 200-550 nm diminished and the new broad band of polarons developed between 550 and 900 nm (Fig. 8**b**) with an isosbestic point at 482 nm. For p(**2**), absorption bands developed beyond 900 nm with maxima at λ_{max} = 986 nm which is attributed to the formation of bipolarons. The neutral p(**3**)l showed a maximum absorbance at λ_{max} = 300 nm and λ_{max} = 404 nm; which can be attributed to the interband $\pi \rightarrow \pi^*$ transitions. The UV-Vis spectra recorded during the oxidation of p(**3**)h, showed the absorption band (200–480 nm) from neutral polymer (Fig. 8**c**) which was found to be gradually losing its intensity as the applied potential was increased. Meanwhile, new wide absorption bands (480– > 1700 nm) with maxima at λ_{max} = 672 nm and λ_{max} = 960 nm and an isosbestic point at 430 nm could be accounted for polarons and bipolarons in the conducting polymer layer.

For the investigated polymers, increase in the intensity of polaronic band was observed beyond the applied potential of 0.7 V. Increase of poloronic intensity unlike the expected increase of bipolaronic band at higher doping levels suggested the oxidation of on the working electrode of polymer with low extent of conjugation [57]. It should be noted that the effective conjugation length would be different for differently linked polymers, e.g., for polymers coupled *via* 2-arms, 3-arms or 4-arms (Fig. 9). It is assumed that electrodeposited polymers possessing low conjugation levels, e.g., polymers coupled *via* 2-arms or 3-arms, might undergo further oxidation at higher applied potentials which lead to the effective increase of polaronic bands. This observation can provide a new approach for tailoring the dimensional features of electrodeposited polymers.

During doping processes, the color of the electrodeposited polymer layers was found to change to almost black (Fig. 8**c,d**), which suggested that they possess multielectrochromic properties. Thus it is possible to prepare electroactive layers with black electrochromic properties by electropolymerizatio.

Table 1
Electrochemical and optical band-gap.

	E_{Ox} [V][a]	E_{Red} [V][b]	E_{HOMO} [eV][c]	E_{LUMO} [eV][d]	E_G^{el} [eV][e]	E_G^{op} [eV][f]
1	0.64	−2.67	−5.74	−2.43	3.31	3.06
2	0.51	−3	−5.61	−2.1	3.51	3.16
3	0.49	−2.37	−5.59	−2.73	2.86	2.85
4	0.51	−2.3	−5.61	−2.8	2.81	2.82
p(**1**)	0.13	−2.25	−5.23	−2.85	2.38	2.39
p(**2**)	−0.03	−2.35	−5.07	−2.75	2.32	2.34
p(**3**)l	0.34	−1.25	−5.44	−3.85	1.59	1.54
p(**4**)l	0.11	−1.26	−5.21	−3.84	1.37	1.33
p(**3**)h	0.41	−2.16	−5.51	−2.94	2.57	2.53
p(**4**)h	0.21	−2.15	−5.31	−2.95	2.36	2.44

[a] first oxidation potentials of monomers from DPV and polymers from CV measurements;

[b] first reduction potentials of monomers from DPV and polymers from CV measurements;

[c] Energy of Highest Occupied Molecular Orbital calculated from E_{HOMO} = -(E_p + 5.1), where E_p is DPV oxidation peak potential for monomers and onset of CV oxidation potential versus *Fc*/*Fc*$^+$ [54–56];

[d] Energy of Lowest Unoccupied Molecular Orbital calculated from E_{LUMO} = -(E_n + 5.1), where E_n is DPV reduction peak potential for monomers and onset of CV reduction potential versus *Fc*/*Fc*$^+$ [54–56];

[e] Energy of band-gap calculated from the difference between Energy of HOMO and LUMO band;

[f] Energy of band-gap calculated from UV-Vis spectroscopy $E_G^{op} = hc/\lambda_{onset}$, where *h* is Planck's constant, *c* is speed of light in a vacuum, λ_{onset} is polymer onset of absorption [54–56].

4. Conclusions

In conclusion, we have demonstrated the effect of the different linkages of carbazole moieties in electroactive monomers and the corresponding electropolymers on their photo- and electro- chemical properties. All the monomers were found to be capabale of polymerization upon electro oxidation and the electrodeposited layers were electronically and optically active. Both linear and high dimensional conjugated polymers can be prepared by electrooxidation. In comparison to 2, 7- linked carbazoles, prevailing formation 3,6-carbazolyl derivatives was observed during electropolymerization. 3, 6- Substituted carbazolyl derivatives were found to be more stable under electrochemical conditions than their 2, 7-substituted analogues.

At mild electrochemical conditions, not all monomer “arms” were found to participate in polymerization. Hence, the reduction peak observed at lower oxidation potential is assumed to be accounted for pyrene core of the monomers.

Spectroelectrochemical investigation of electro-oxidation products suggested the formation of charged species like polarons and bipolarons, which indicate the multielectrochromic properties. The electrodeposited polymers p(**3**) and p(**4**) on the electrode are supposed to possess free “arms”, which might predetrmine large polaronic signals in the visible region. The branched carbazolyl derivatives showed different oxidation behavior as well as unusual absorption characteristics, which can be assigned to the presence of different effective conjugation levels in electrodeposited polymers.

Acknowledgment

This work was supported by National Science Centre, Project No. 2011/03/N/ST5/04362. This research was also funded by the European Social Fund under the Global Grant measure.

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