Original Research Paper

Chemistry

Donor −Acceptor-Type of Electrochromic Polymer with Low Band-gap based on Pyridine as an Acceptor Unit

Kamila Olech	Wrocław University of Science and Technology, Faculty of Chemistry, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
Jadwiga Sołoducho	Wrocław University of Science and Technology, Faculty of Chemistry, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
Szczepan Roszak	Wrocław University of Science and Technology, Faculty of Chemistry, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
Katarzyna Łaba	Centre of Polymer and Carbon Materials of the Polish Academy of Sciences, M. Curie-Sklodowskiej 34, 41-819 Zabrze, Poland, Silesian University of Technology, Faculty of Chemistry, Strzody 9, 44-100 Gliwice, Poland.
Przemysław Data	Centre of Polymer and Carbon Materials of the Polish Academy of Sciences, M. Curie-Sklodowskiej 34, 41-819 Zabrze, Poland, Silesian University of Technology, Faculty of Chemistry, Strzody 9, 44-100 Gliwice, Poland.
Mieczysław Łapkowski	Centre of Polymer and Carbon Materials of the Polish Academy of Sciences, M. Curie-Sklodowskiej 34, 41-819 Zabrze, Poland, Silesian University of Technology, Faculty of Chemistry, Strzody 9, 44-100 Gliwice, Poland.

ABSTRACT A novel alternating conjugated polymers, based on pyridine moieties, were synthesized via the Suzuki-Miyaura couple approach. Polymers were characterized by 1H NMR, gel permeation chromatography, UV–Vis spectroscopy, fluorescence and cyclic voltammetry. The luminescence of the copolymer exhibited extraordinary bright blue. The electrochemical study shows that the new alternating polymers do not merely have the properties of the two units that constitute it but has mutual hole and electron charge carrier properties which might be promising material for applications in high efficiency, single or low number layers functional devices.

KEYWORDS : Pyridine-based polymers, organic semiconductors, Suzuki-Miyaura polymerisation, cyclic voltammetry, UV-Vis spectroelectrochemistry, computational study, electrochromic polymers, donor–acceptor polymers, luminescence

1. Introduction

Combining high contrast ratio, superior coloration efficiency, and multicolor, conjugated polymers have been developed to be the most attractive electrochromic materials [1,2]. Toward electrochromic polymers with specific colors, numerous procedures have been employed to manage the color of the polymer, including increasing the conjugation length, utilizing donor−acceptor effect, modifying the HOMO−LUMO levels, and using sterically hindered substituent [3,4]. Against, side chain substituents provide a feasible method to tune optical properties of the polymer [1]. The most common and effective strategy toward electrochromic polymers consists of tailoring the nature and structural control of donors and acceptors in the donor−acceptor-type (D−A) polymers. It has clearly been shown that compositions not only change the redox potentials and band gap of these polymers but modify the electrochromic performances either. For D−A polymers, band gap (Eg) reduction has been proved to be an effieeient way to achieve optical contrast and stable electro-chromic polymers [5]. Previous studies proved that band gaps of D−A conjugated polymers primarily depend on the acceptor moiety [6]. Therefore, inserting an electron-deficient accept-or into the π - conjugated system probably develops a decreased band gap material. Due to the π-electron nature of pyridine unit compared to benzene, pyridine would be a stronger acceptor unit relative to i.e. benzothiadiazole [7]. In the donor−acceptor-type neutral electrochromic polymer library, in sharp contrast to benzothiadiazole derivatives and thieno[3,4-b]pyrazine derivatives extensively employed as acceptor units, pyridine has scarcely been explored (Scheme 1) [8,9]. Recently, Zhou et al. [10] incorporated thiadiazolo-[3,4-c]pyridine derivative with weak donor units to yield a series of polymers showing better solubility, lower band gap, and deeper HOMO and LUMO levels.

Conjugated copolymers with pyridine rings in the main chain of macromolecule are promises candidates for application in luminescence devices. They are well known as materials for light electroluminescence diodes [11]. Poly(2,5-pyridine) are good blue light emitters as it is characterized by appropriate wide band gap [12]. Importantly, conjugated polymers of pyridine show good electrons transport ability, high electron affinity and stability under oxidative

condition [13]. Additionally, the nitrogen loan electrons pair in pyridine ring activated it for an electrophilic attack. Due to this fact polymers of pyridine can act as a ligands. They coordination complexes often show ionochromic properties what make they suitable for application in selective sensors [13,14].

We herein report the synthesis of donor-acceptor pyridine-based polymers with mutual hole and electron charge carrier properties required for functional devices. Actually, we synthesized poly(pyridine-based) polymer *via* Suzuki coupling [15] method initially reported by Miyaura et al. The newly synthesized polymers containing electron-donating phenoxazine, phenothiazine and diphenylamine units and the electron-accepting pyridine, is expected to expand the scope of chemistry of macrostructures with such a charge-transferred rings.

In this paper, we wish to report on the synthesis of p–n conjugated polymer, an alternating phenoxazine/phenothiazine, diphenylamine, and pyridine backbone, obtained by Suzuki couple method [15]. The electron donating and accepting groups on consecutive repeat units are introduced to stimulate intramolecular charge transfer along polymer chains. The optical properties, density functional theory calculations, and electrochemical behavior of the polymers were reported.

2. Experimental Part

2.1. Materials and Instruments

Tetrakis(triphenylphosphine)-palladium(0) (99%), bromobenzene (99%), phenylboronic acid (95%), 2,5-dibromopyridine (98%) and tetrabutylammonium tetrafluoroborate (99%) were received from Aldrich. Anhydrous potassium carbonate (99%) was purchased from Chempur. Tetrahydrofuran (POCH) was dried over Na/benzophenone ketal before used. Other commercial available solvents were used without prior purification. The 2-isopropoxy-4,4,5,5-tetramethyl-2,1,3-dioxoborolane derivatives of phenothiazine (**1a**) phenoxazine (**1b**) and diphenylamine (**1c**) were synthesized according to our previous works [16].

1H NMR spectra were recorded in deuterated chloroform CDCl₃ on

Bruker Avance II 600 Instrument. Chemical shifts were locked to chloroform δH 7.26 (s) signal. Gel Permeation Chromatography (GPC) analysis of the polymers was performed on a Jordi Gel DVB 1000Å 250 × 10 mm gel columns with the UV/Vis detector set at 415 nm. The polymer solution (140 µL) were injected into a THF stream with a flow rate of 1 mL/min. Polystyrene calibration standards were used.

2.2. Electrochemical measurements

Electrochemical and spectroelectrochemical studies were performed in dichloromethane (Chempur) containing 0.1M tetrabutylammonium tetrafluoroborate Bu_4NBF_4 (Aldrich) as a supporting electrolyte. The solutions of 0.8 mM concentration of **1a-c FOA-P, FOT-P, DFA-P** were used for all cyclic voltammetry (CV) measurements. Solutions used for cyclic voltamperometric measurements were purged by argon bubbling for 15 minutes prior to each experiment. The electrochemical investigation was carried out using EDAQ EA161 potentiostat. The experiments were carried out in the conventional three electrode system, comprised of platinum disk with 1-mm diameter of working area as working electrode (CV) and ITO glass (spectroelectro chemistry) as a working electrode, Ag wire as a pseudo-reference electrode and platinum coil as an auxiliary electrode. All potentials were referenced to the redox potential of the ferrocene (Fc⁺/Fc) couple as an internal standard. Spectroelectrochemical measurements were carried out in 2mm quartz cuvette-type cell by using UV–Vis spectrophotometer Avantes connected with EDAQ EA161 potentiostat. The UV–Vis spectra was recorded in the increasing electrode potential mode. Fluorescence measurements were carried out in 10 mm quartz cuvette by using fluorescence spectrophotometer Hitachi F-2500. All measurements were conducted at ambient temperature.

2.3. Synthesis

The general procedure of polymerization. In the three neck round bottom flask 0.38 g (0.70 mmol) of 2,5-dibromopyridine (**3**) and 0.70 mmol of **2a-c** was dissolved in THF (25 ml). The 2M aqueous solution of potassium carbonate (10 ml) was added and reaction mixture was purged with nitrogen for 15 minutes before adding 0.6 mol% tetrakis(triphenylphosphine)palladium(0) (4.8 mg, 4.2 µmol). Reaction was refluxed under an inert atmosphere of nitrogen for 20 (**1a, 1b**) to 43 hours (**1c**). Polymerisation was finished by adding 0.1 mol% of each - bromobenzene, palladium catalyst and phenylboronic acid. Solvent was evaporated under reduced pressure. The residue was washed with a distilled water followed by methanol. The polymer was dissolved in chloroform and selectively precipitated in methanol. This process was repeated three times. Filtration yielded compounds **1a-c** as pure yellow polymers powders.

Poly[(*N*-nonylphenothiazin-3,7-diyl-*alt*-(2,5-pyridine)] (**1a**): Y=92%, light yellow powder, 1H NMR (300 MHz, CDCl3), δ (ppm): δ 8.83 (s, 1H, Ar-H), 7.88–7.72 (m, 3H, Ar-H), 7.69 (d, ^3J = 8.1 Hz, 1H, Ar-H), 7.45–7.34 (m, 2H, Ar-H), 6.99–6.87 (m, 2H, Ar-H), 3.91 (d, ^3J = 5.7 Hz, 2H, CH₂), 1.86 (d, ^3J = 6.9 Hz, 2H, CH₂), 1.47 (d, ^3J = 6.0 Hz, 2H, CH₂), 1.40–1.13 (m, 10H, CH₂), 0.87 (t, ^3J = 7.0 Hz, 3H, CH₃); GPC: M_w = 3433 Da, M_n = 1648 Da, PDI = 2.084

Poly[(*N*-nonylphenoxazine-3,7-diyl-*alt*-(2,5-pyridine)] (**1b**): Y=62%, yellow powder, 1H NMR (600 MHz, CDCl3), δ (ppm): δ 8.69 (m, 1H, Ar-H), 7.91–6.70 (m, 6H, Ar-H), 6.51 (s, 2H, Ar-H), 3.49 (s, 2H, CH₂), 2.04–0.65 (m, 14H, CH₂), 0.89 (s, 3H, CH₃); GPC: M_w = 1206 Da, M_n = 852 Da, PDI = 1.416

Poly[(*N*-nonyldiphenylamine-4,4'-diyl-*alt*-(2,5-pyridine)] (**1c**): Y=89%, light yellow powder, ¹H NMR (600 MHz, CDCl₃), δ (ppm): δ 8.91 (s, 1H, Ar-H), 7.99 (d, ^3J = 8.4 Hz, 2H, Ar-H), 7.91 (d, ^3J = 8.2 Hz, 1H, Ar-H), 7.75 (d, ^3J = 8.2 Hz, 1H, Ar-H), 7.58 (d, ^3J = 8.3 Hz, 2H, Ar-H), 7.22 – 7.13 (m, 4H, Ar-H), 3.86 – 3.75 (m, 2H, CH₂), 1.75 (br, 2H, CH₂), 1.43–1.16 (m, 12H, CH₂), 0.89 (m, 3H, CH₃); GPC: M_w = 12112 Da, M_n = 7151 Da, PDI = 1.69

2.4. Computational study

Energy gap between frontier orbitals, molecular structures, nature of molecular orbitals and electronic density distribution were studied for monomers and short oligomers of synthesized oligomers. The computational studies are based of density functional theory (DFT) procedure. The B3LYP three-parameter functional [17] and cc-pVDZ basis set [18] was applied. The energies of excited states were calculated within the time-dependent density functional theory

(TDDFT) [19]. Twenty excited electronic states were considered for each molecule. The electron distribution was examined by using NBO and Mulliken electron population analysis schemes [20]. The computations were performed using Gaussian-09 suite of codes [21]. The graphic was produced applying the GaussView and GaussSum programs [22].

3. Result and discussion

3.1. Synthesis

Palladium–catalyzed coupling *via* Suzuki approach was established in formation of novel pyridine-based polymers **1a-c**. The reactions generally result in a very good yield when performed at temperatures near 70°C. Because of the fact, it is of high interest to adapt this procedure as resin mounted procedure. The polymerization was end-capped by adding small amounts of phenylboronic acid, bromobenzene and tetrakis(triphenylphosphine)palladium(0) [23] Scheme 1. Final compounds were separated from low-molecular weight monomers and by-products by selective precipitation in methanol. Structures of copolymers were confirmed and characterized by ¹H NMR spectroscopy.
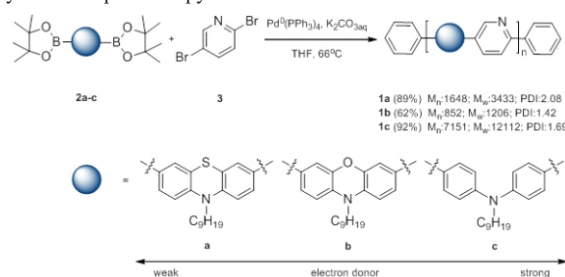
Scheme 1. General synthetic route of oligomers **3a-c** *via* Suzuki-Miyaura condensation. Number average molar mass (M_n) and mass average molar mass (M_w) are given in gmol⁻¹.

The dioxaborolane derivatives **1a-c** were synthesized with good yield according to previous reported methods [16]. Solubility of the final compounds (**3a-c**) were improved significantly by introduction of aliphatic chains at very beginning synthetic step [24].

Gel permeation chromatography (GPC) against polystyrene standards was used to estimate the molecular weight of each polymers, Table 1. It was determined that the oligomers were all of rather low molecular weight. They number-average molecular weights were about 1500-3000 g/mol. These values corresponds to a degree of polymerization of seven to eight, meaning that the polymers synthesized here consist commonly about 25 aromatic rings per chain. The obtained molecular weights were adequate for processing and film formation, and thus, further optimization of the polymerization was not attempted. As for synthesized polymers the low polydispersity index was obtained (average near 1.7).

Table 1. Summary of GPC data (polystyrene standard) for pyridine-based polymers.

polymer	M_n [g/mol]	M_w [g/mol]	PDI
1a	7151	12112	1.69
1b	852	1206	1.42
1c	1648	3433	2.08

3.2. Electrochemical properties

Electrochemical properties of the copolymers were investigated by cyclic voltammetry. Electrochemical investigation of the solutions of the compounds in dichloromethane demonstrated that all molecules are very stable as is evidenced by recording repetitive voltammetric waves during multiple doping and de-doping process (Fig.1). The electronic properties of these donor–acceptor polymers should be varied significantly with the acceptor moiety [23]. The highest oxidation potential (0.64V) was observed for copolymer **1c** (DFA-P) where pyridine units are linked to *N*-nonyldiphenylamine. For structures **1b** and **1a** (Fig.1), redox couples were observed at almost the same oxidation potentials: at 0.42 V for **1b** (FOA-P) and 0.41 V for **1a** (FOT-P). The difference between the two potentials was 0.01 V which indicated that the electron-withdrawing pyridine in compound's main chain exerts no influence on electron-accepting effect in the π-system. Thus, both kinds of polymers have the same conjugation among

created polymer main chain. It is assumed that obtained polymers have the same electron moieties, which have the same effect among polymer main chain, the only one factor which can lower the energy-gap and LUMO level is acceptor unit. Measurements of electrochemical bad-gap and the estimation of HOMO and LUMO levels for obtained polymers were investigated by commonly used method. The difference in onset potentials obtained from p- and n-doping sides can be taken as a measure of the Ionization Potential (E_{IP}) and Electron Affinity (E_{EA}) of electroactive compounds. The electrochemical band gap corresponds to a value of difference between E_{EA} an E_{IP} which can be related to HOMO and LUMO bands [25-27]. LUMO levels are estimated at -2.64eV for **1b** (FOA-P), -2.74eV for **1a** (FOT-P) and -2.69eV for **1c** (DFA-P). The energy difference indicates that the N-nonylphenothiazine moiety adds stronger electron-accepting (weaker electron-donating) character among polymer main chain. The lower LUMO level ensures easier reduction of the polymer. The electron character is also proven by the magnitude of the estimated band-gap of copolymers, which are changed in order **1a** - FOT-P (-2.57eV) < **1b** - FOA-P (-2.62eV) < **31c** - DFA-P (-2.83eV) – Table 2. As expected, it was found that the oxidation potentials of the EDOT-based polymers are lower than their pyridine-based analogues [16], while the reduction is easiest for the pyridine-type copolymers [23,28]. Semiconducting materials should reveal a band-gap value between 0.1 eV and 3.0 eV. This requirement is crucial for various optoelectronic applications.
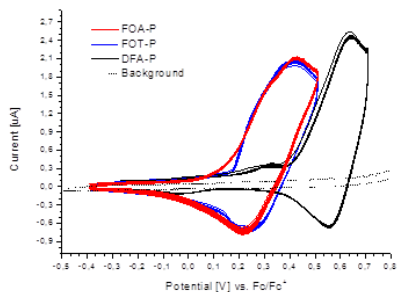
Fig. 1. Cyclic voltammograms of the electrochemical doping-dedoping process of polymers **1a-c**. Measurement conditions: scan rate 50 mV/s, calibrated against ferrocene/ferrocenium redox couple.

Table 2. Electrochemical and optical band-gap.

| Polymer	$E_{IP} = E_{HOMO}$ [eV]	$E_{EA} = E_{LUMO}$ [eV]	E_{GCV} [eV]	λ_{ab} [nm]	E_{GOpt} [eV]
1a FOT-P	-5.31	-2.74	2.57	299, 397	2.66
1b FOA-P	-5.26	-2.64	2.62	282, 434	2.61
1c DFA-P	-5.52	-2.69	2.83	389	2.86

3.3. Spectroclectrochemical UV-Vis properties

Spectroelectrochemical properties of the polymers **1a-c** were investigated in due to examine the impact of the introduction of electron-donating groups in copolymer main chain on the optoelectronic features and to meet the relationship between redox processes and UV–Vis absorption. UV–Vis spectroelectrochemistry can bring information about charge carriers formed during doping processes and clarify doping processes.

UV–Vis spectra of p-doping copolymers recorded with increasing applied electrode potential are given in Fig. 2. The provided spectra show the absorption of copolymer solutions at different applied potentials between the neutral and fully oxidized states.

The insertion a heteroatom (Oxygen or Sulphur) bridge between benzene rings results in a red-shifted spectrum by about 8 nm of **1c** (DFA-P) compared to **1a** (FOT-P) and 45 nm compared to N-nonylphenoxazine derivative (**1b**). The absorption bands corresponding to the polymers with maximum at 389 nm for **1c**, 397 nm for **1a**, 434 nm for **1b** are associated with π-π* electron transitions and were found to gradually decrease the intensity as the applied potential increases. A considerable longer wavelength reflects a higher order of contribution of charge transfer in electronic state of **1b** due to its strong electron-accepting property. Moreover, in the neutral state, the copolymers **1b** and **1a**, are also characterized with low-energy broad transition bands with maximum at 282 nm (**1b**) and 299 nm (**1a**),

respectively, which are assigned to n-π* electron transitions. For all copolymers are found the stable isosbestic point at approximately 461 nm for **1b**, 436 nm for **1a** and 413 nm for **1c**, which indicates that only two stable species are found in the systems, namely: structure and an oxidized product. After reduction at 0V (**1b**) or 0.15V (**1a**, **1c**) the broad absorption bands decrease and a new peak appears with maximum at approximately 548 nm for **1b**, 547 nm for **1a** and 467nm for **1c**. The neutral product presents a batochromic shift in comparison to its monomer. This points out a conjugation increase. New well-defined absorption band of charge carriers appears in the range of 470–640 nm for **1b**, 460-670 nm for **1a** and 430-540 nm for **1c** due to the formation of radical cations (polarons).

The optical band-gap values obtained for **1b** and **1a** were quite similar from those of the electrochemical ones, which proposes that the absorption onsets in general might be related to π-π* band transitions. For polymer **1c** the E_{GCV} and E_{GOpt} were slightly different which implies that the absorption onset might be not always related to only π-π* band transitions. The electronic band gap is calculated from the onset of the π–π* transition of neutral film. Optical band gap was calculated from onset of polymer absorption (λ_{onset}) by conversion of wavelength to the energy [25-27]. The results are shown in Table 2.
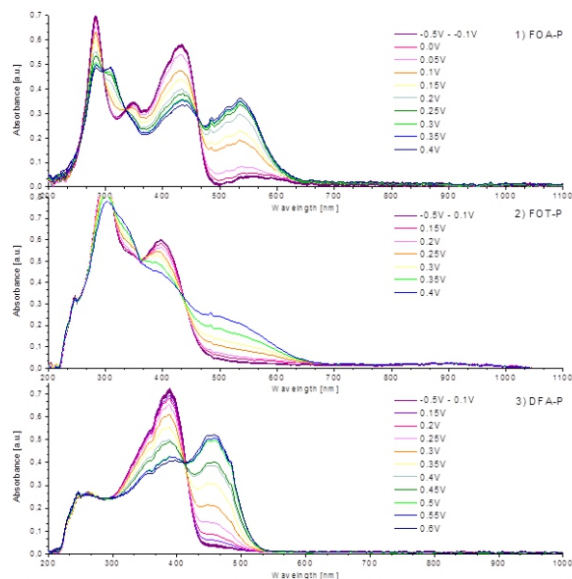
Fig. 2. UV–Vis spectra recorded during potentiostatic oxidation of 1b-FOA-P, 1a-FOT-P, 1c-DFA-P dissolved in 0.1M Bu_4NBF_4 in dichloromethane.

3.4. Fluorescence properties
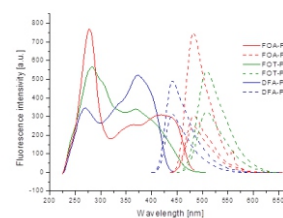
Fig. 3. Fluorescence excitation (solid line) and emission (dashed line) spectra of 0.1 μM of **1b**-FOA-P, **1a**-FOT-P, **1c**-DFA-P in dichloromethane.

In all cases the fluorescence effect was observed. Fluorescence properties of the investigated polymers were observed at room temperature under ambient conditions. The excitation and emission spectra of polymers **1a-c** were recorded in a dilute dichloromethane solution (0.8 μmol/dm³). The fluorescence emission were recorded at the excitation maximum (Fig. 3). The excitation of diluted solution of **1c**-DFA-P at 269 or 373 nm led to the emission with maximum at 442 nm. Insertion a heteroatom (Oxygen or Sulphur) bridge between benzene rings results in a clear bathochromic shift. The emission maxima changed in order: **1c**-DFA-P < **1b**-FOA-P < **1a**-FOT-P with

maximums at 442, 482, 508 nm, respectively. Fluorescence emission spectra were not found to be a mirror image of their respective absorption spectra implying large changes in the solution during the transition from the excited to the ground state. The strongest quenching is found for **1c**. The analysis of the fluorescence spectra reveal their complex character. The largest Stokes shift was found for **1a** (139 nm). These large Stokes shifts are desirable as re-absorption of the emitted photons and can be minimized. The values of Stokes shifts are rather different what means that different factors affect on value of the emission. The fluorescence properties are collected in Table 3.

Table 3. The fluorescence properties of 0.1 μM of **1b**-FOA-P, **1a**-FOT-P, **1c**-DFA-P in dichloromethane.

Polymer	λ_{exc}	λ_{em}	Stokes shift
1a FOT-P	283, 369	508	139
1b FOA-P	277, 364, 417	482	118, 48
1c DFA-P	269, 373	442	69

3.5. Computational study
The goal of a computational study was discovery of new conducting materials and early phase identification of designed compound properties ranging from geometry of polymers chain, over electron distribution to energy band gap value. DFT calculation was performed for monomers of synthetized polymers and their short oligomers up to tetramers. Analysis of natural bond orbitals (NBO) atomic charges distribution show that in each investigated D-A system pyridine acts as an acceptor of electrons. The charge distribution within the mers is almost the same, with an atomic charge on the pyridine N atom about - 0.5 electrons. A highest negative charge is localized on pyridine coupled with *N*−nonyldiphenylamine. It revealed a stronger donor properties of *N*−nonyldiphenylamine then *N*-nonylphenoxazine and *N*−nonylphenothiazine. However, the **1c** chain growing leads to decreasing of NBO atomic charge concentration on pyridine moiety and smaller difference between donor and acceptor charges. Opposite trend is observed for **1a** and **1b** polymer where charge separation between a donor and an acceptor become more significant with increasing of polymer chain.

In monomers **1a-c** dihedral angles between donor and acceptor rings are similar and measure 171-178°. However, only **1a** and **1b** are planar despite a slightly deviation of heteroatoms (N, O, S) from the molecule plane. In monomer **1c** due to low rotation barrier of C-N-C bond, aromatic rings of diphenylamine are twisted to each other so only two rings of monomer stay in a one plane. Dihedral angles between monomer subunits in dimers of **1a-c** are close to 145° what allow for electrons delocalization between polymers building blocks. The dihedral angles remain almost unchanged with increasing of polymers chain. Angles containing heteroatoms C-N-C, C-O-C and C-S-C as well as C-C bond length between D-A moiety are also preserved. This fact suggest almost perfect additivity of polymers building blocks.
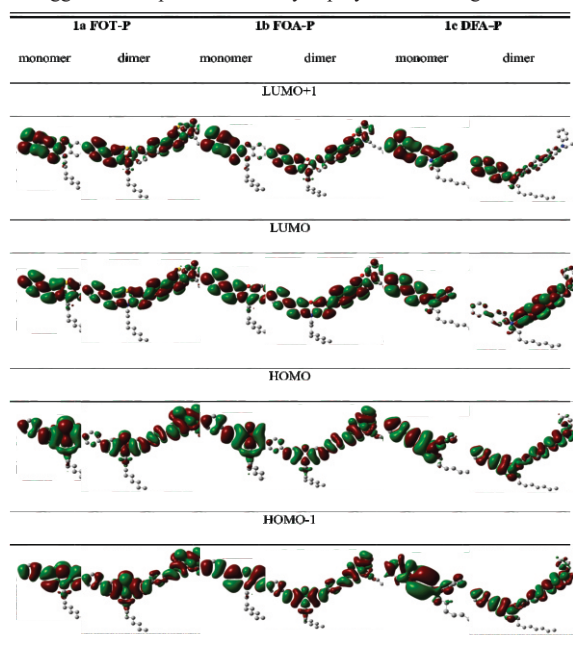
Fig 4. Molecular orbitals obtained from B3LYP/cc-pVDZ studies for the neutral form of monomers and dimers of **1a-c**. Hydrogen atoms are removed for better clarity.

Table 4. Calculated (ΔE_g, $\Delta E_{excited}$ singlet and triplet electronic excited states) and corresponding experimental (optical and cyclic voltammetry) energy gap between valence and conduction bands for **1a-c**. All energies are in eV.

Nr	E_{HOMO}	E_{LUMO}	E_g	$E_{singlet}^{T}$ D	$E_{tryplet}^{T}$ D	E_{IP} (E_{HOMO})	E_{EA} (E_{LUMO})	λab nm	E_g^{CV}	E_g^{Opt}
	calculated							experimental		
1a	-4,85	-1,55	3,30	2,84	2,31	-5,31	-2,74	299 397	2,57	2,64
1b	-4,67	-1,48	3,19	2,76	2,19	-5,26	-2,64	282 434	2,62	2,61
1c	-5,12	-1,37	3,74	3,28	2,57	-5,52	-2,69	389	2,83	2,86

4. Conclusion
The results presented in the paper report the investigation of alternating copolymer of pyridine. All copolymers are electronically and optically active. All of copolymers appear to be stable during multiple doping and de-doping processes. Heterocyclic ring influences on ionisation potential of molecule. As expected, it is found that the oxidative potentials of the EDOT-based polymers are lower than their pyridine-based analogues, while the reduction is easiest for the pyridine-type polymers. The LUMO energy difference indicates that the N-nonylphenothiazine moiety adds stronger electron-accepting character among polymer main chain. The lower LUMO level ensures easier reduction of the polymer. Spectroelectrochemical investigation of electro-oxidation products suggested the formation of charged species like polarons. Electrochemical properties of investigated compounds make this material of great interest for electrochromic applications.

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