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Effect of the acceptor moiety on the electrochemical and electrochromic properties of Donor-Acceptor-Donor polymer films

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The aim of this work is to synthesize EC polymers having green or blue colour in the neutral state and transparent oxidized state by using the D-A-D approach. Two different monomers, diphenylthienopyrazine (M1) and diphenylquinoxaline (M2) are synthesized. The monomers are successfully electropolymerized to P1 and P2, respectively, by cyclic voltammetry on ITO substrates. The effect of the acceptor moiety on the electrochemical and electrochromic properties of the polymer films is investigated. Both polymers exhibit the characteristic redox couple due to their oxidation/reduction at 0.95 V/0.62 V for P1 and at 1.05 V/0.35 V for P2; their doping/dedoping reaction is reversible. The two polymers have different optical properties; namely, the phenyl ring in the acceptor unit (P2) caused hypsochromic shift. The acceptor moiety affects mainly the LUMO level; specifically, the LUMO level shifted to less negative values by replacing thiophene with phenyl. The electrochromic properties of the polymer films are strongly affected by the acceptor moiety. Polymer P1 changes its colour from green (neutral state), to grey (intermediate oxidised state), to transparent grey/sky blue (oxidized state) and to lemon green (reduced state). Correspondingly, P2 starts from royal blue (neutral state), going to blue purple, grey-blue and light grey (intermediate oxidised states) and then to green (oxidized state); additionally, it became also oil green and light blue (reduced states). Both polymers are multi-coloured and were good candidates for application in electrochromic devices.

Keywords: Thiophene-pyrazine, quinoxaline, copolymers, elctroctrochromic, spectroelectrochemisty, cyclic voltammetry.

1. INTRODUCTION

Electrochromism (EC) was first described in transition metal oxides during the late 1960s. Nowadays, this effect has been observed not only in inorganic materials but also, and more importantly, in organic compounds such as dyes and conducting polymers (CPs). CPs switch their colour due to the doping/dedoping process. By doping, the electronic structure of the polymer is altered leading to the formation of new electronic states; this affects the optical properties of the material and, consequently, its colour [1-5]. CPs have generally facile synthesis (most of the times through electropolymerization), environmental stability and easy processability (mainly through solutions). As EC materials, CPs have outstanding coloration efficiency, fast switching ability, multiple colours, and the ability to fine-tune their band gap (and therefore optical properties) by modifying their chemical structure [6-9]. A very promising route to achieve this is to use specially designed monomers with a structure combining both electron donor (D) and electron acceptor (A) moieties; the most promising results were derived using D-A-D structure combinations [8,10,11].

EC polymer materials have been used in many applications, including smart windows, mirrors, electrochromic inks, switchable displays, etc. [1,9,12]. As already mentioned, CPs have the advantage that their optical properties and their colours can be manipulated by modifying their chemical structure. EC polymers can be classified in three categories, depending on their optical states. The first category concerns polymers that have (at least) one coloured state and one bleached state (e.g. PEDOT); these have been applied in optical shutters and smart windows. The second category includes polymers having two distinct coloured states and no bleached state (e.g. polythiophenes); these are suitable for EC displays. The third and most important category concerns polymers that have more than two coloured states, so they are termed multi-coloured materials; these have gained much interest the last years, particularly due to their application in multi-coloured electrochromic devices [3,11]. For these devices, the polymers should switch between transparent state and at least one of the primary colours (i.e. red, blue or green). One important advantage of the D-A-D structure approach is that the CPs synthesized exhibit more than two redox states, meaning that they are multichromic from start [3].

Even though there are many works about multichromic CPs, there are only a few about polymers with green colour in the neutral or reduced state. The main reason is the dominant single-wavelength character of the two other basic colours, i.e. blue and red. From the other hand, in order to achieve a green coloured polymer in the neutral (or reduced) state, the polymer should have two absorption bands, centered at the blue and the red regions of the visible spectrum; this is not easy to happen in the non-oxidized state of a polymer. The challenge is that these absorption bands have to be manipulated in the same manner at different applied potentials [13,14]. There are some references about neutral state green polymeric materials, but they are still very rare [14-16]. Additionally, there are many blue coloured neutral polymers [17], but still the researchers are trying to improve their properties.

The aim of this work is the synthesis of EC polymers that will have a stable neutral (or reduced) green or blue state and a transparent oxidized state. The D-A-D approach will be used; specifically, the thiophene unit was chosen as the donor and diphenylthienopyrazine or diphenylquinoxaline as acceptors. The effect of the acceptor on the electrochemical and electrochromic properties of the polymer films will be also investigated.

2. EXPERIMENTAL

2.1. Materials

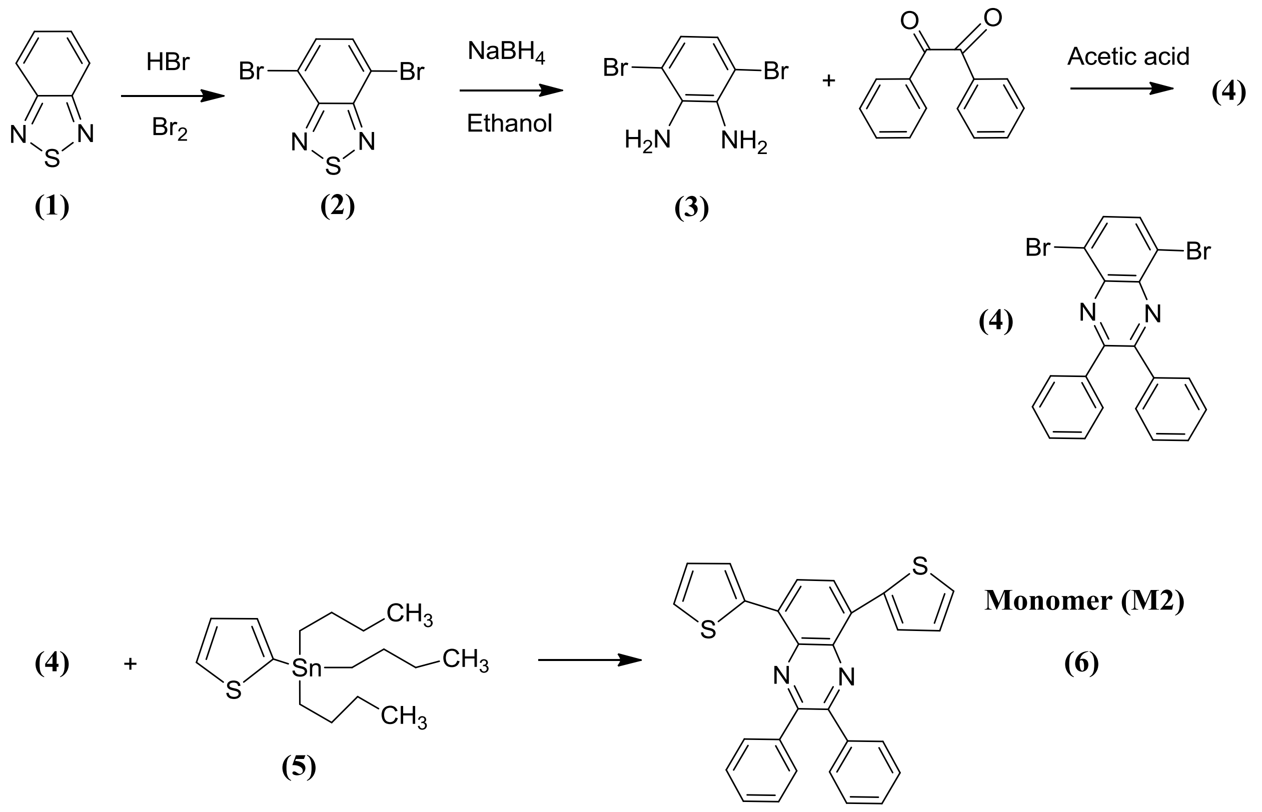
5,7-di(thiophene-2-yl)2,3-diphenyl-thieno[3,4-b]pyrazine, monomer M1, was synthesized according to the procedure describing in the literature [18]. 5,8-di(thiophene-2-yl)2,3-diphenylthieno[3,4-b] quinoxaline, monomer M2, was synthesized starting from benzo(1,2,5)thiadiazole (Sigma-Aldrich B10900). Sodium borohydride $NaBH_4$ (Sigma-Aldrich 452173), ethanol (Sigma-Aldrich 32205), benzil $(C_6H_5CO)_2$ (Sigma-Aldrich B5151), acetic acid CH_3COOH, (tributylstannyl)thiophene (Sigma- Aldrich 414492), tetrakis(triphenylphosphine) palladium (0) (Sigma-Aldrich 697265) were used as received. Dichloromethane (DCM, anhydrous, Sigma-Aldrich 270997) and acetonitrile (ACN, anhydrous, Sigma-Aldrich 494445) were used directly without further purification. Tetrabutylammonium tetrafluoroborate (for electrochemical analysis, ≥ 99.0%, Fluka 86896) was dried at 120 ^oC under vacuum prior to use.

2.2. Characterization

Stille coupling was carried out in microwave oven (CEM Discover DU8107). The 5,8-di(thiophene-2-yl)2,3-diphenyl-thieno[3,4-b]quinoxaline, monomer M2, was purified using Comni Flash (Teledyne ISCO) chromatography. High resolution (500 MHz) 1H-NMR spectra were recorded on a UNITY INOVA 500 spectrometer from Varian at room temperature. Elemental analysis was obtained using a Thermo Scientific Flash EA 1112 CHNS/O Automatic Elemental Analyzer. The UV-Vis spectra were recorded by a Lambda 19-UV/VIS/NIR spectrometer of PerkinElmer. Atomic force microscopy (AFM) was performed with an ‘autoprobe CP’ from Park Scientific Instruments (Digital Instruments, Santa Barbara) operating in contact mode. The instrument was equipped with a 100x100 μm^2 hardware linearized scanner and commercial silicon tips (modelCSG01, the force constant was 0.1 N/m and the tip radius was smaller than 30 nm). The scanning electron microscopy investigations (SEM) were carried out using a HITACHI S-4100 scanning electron microscope with a cold field emission cathode.

2.3. Synthesis of 5,8-di(thiophene-2-yl)2,3- diphenyl-thieno[3,4-b]quinoxaline, monomer M2

The first step was the bromination of benzo(1,2,5-thiadiazole), reagent (1) in Scheme 1. 2.5 g of (1) (183.5 mmol) were mixed with 62.5 ml HBr (2.8 mmol). Then, 15 ml of pure bromine were added dropwise under stirring and the mixture was heated under reflux (at about 95 ^oC) for 5 h; afterwards, the mixture was cooled down and the solid product was filtrated, neutralized with water and from a methanol/toluene mixture (yield = 47.3 %). In the following step, 5 g of 4,7-dibromo benzo[c][1,2,5]thiadiazole (17 mmol), reagent (2) in Scheme 2, were dissolved in 200 ml ethanol and the mixture was cooled down to 2 °C. Subsequently, 11.5 g of sodium borohydride (300 mmol) was added slowly and then the reaction mixture was stirred at room temperature overnight. Afterwards, the solvent was removed by rotary evaporation, diethyl ether was added and the organic layer was separated and washed with water. Then, NaCl was added and after washing with water, the organic layer was dried over $MgSO_4$ and filtered. The solvent was removed to afford a white product. The product (3) 3,6-dibromobenzene-1,2-diamine, was recrystallized in hexane two times (yield = 50 %). Following, 0.5 g of (3) (1.85 mmol) and 0.583 g of benzyl (2.775 mmol) were dissolved in 40 ml of fuming acetic acid and the mixture was stirred at room temperature for 8 h. The solid product was filtrated, washed with methanol and dried. It was purified by recrystallization with methanol and then dried to give 5,8-dibromo-2,3-diphenyl-quinoxaline, reagent (4) (yield=95 %).



Scheme 1. Synthetic route monomer M2: 5,8-di(thiophene-2-yl)2,3-diphenyl-thieno[3,4-b] quinoxaline

The monomer M2, 5,8-di(thiophene-2-yl)2,3-diphenyl-thieno[3,4-b] quinoxaline, was synthesized by Stille coupling of (4) with (tributylstannyl)thiophene, reagent (5). For this reaction, 0.25 g (0.568 mmol) of (4), 0.486 g (1.305 mmol) of (5) and 15.43 mg (0.015 mmol) of tetrakis (triphenylphosphine)palladium were dissolved in 6 ml of anhydrous p-xylene in a glove box. Stille coupling was carried out in a microwave oven with a heating step program (5 min at 120 °C, 5 min at 140 °C and 40 min at 170 °C). The resulting mixture was diluted by chloroform and washed with aqueous solution of ammonium chloride. The organic layer (oil green colour) was separated, washed with water and stirred with KF solution (0.5 M) for two days. The organic layer was separated, washed with water, dried over $MgSO_4$ and filtered. The product was purified by Flash Chromatography using a hexane and ethyl acetate mixture as eluent and the pure product is a yellow solid. This solid was further purified by recrystallization with methanol (yield = 60%), having a melting point of 135 °C.

NMR spectrum of the monomer 5,8-di(thiophene-2- yl)2,3-diphenyl-thieno[3,4-b]quinoxaline, Figure 1 : δ (ppm, $CDCl_3$) : 8.15 (s, 2H), 7.88 (d, 2H), 7.75 (d, 4H), 7.53 (d, 2H), 7.4 (d, 6H) and 7.18 (t,2H). Anal. Calcd for $C_{28}H_{18}N_2S_2$ (M_w 446.59 g/mol): C 75.30, H 4.06, N 6.27, S 14.36; found C: 74.77, H 4.12, N 5.89 and S 13.96.

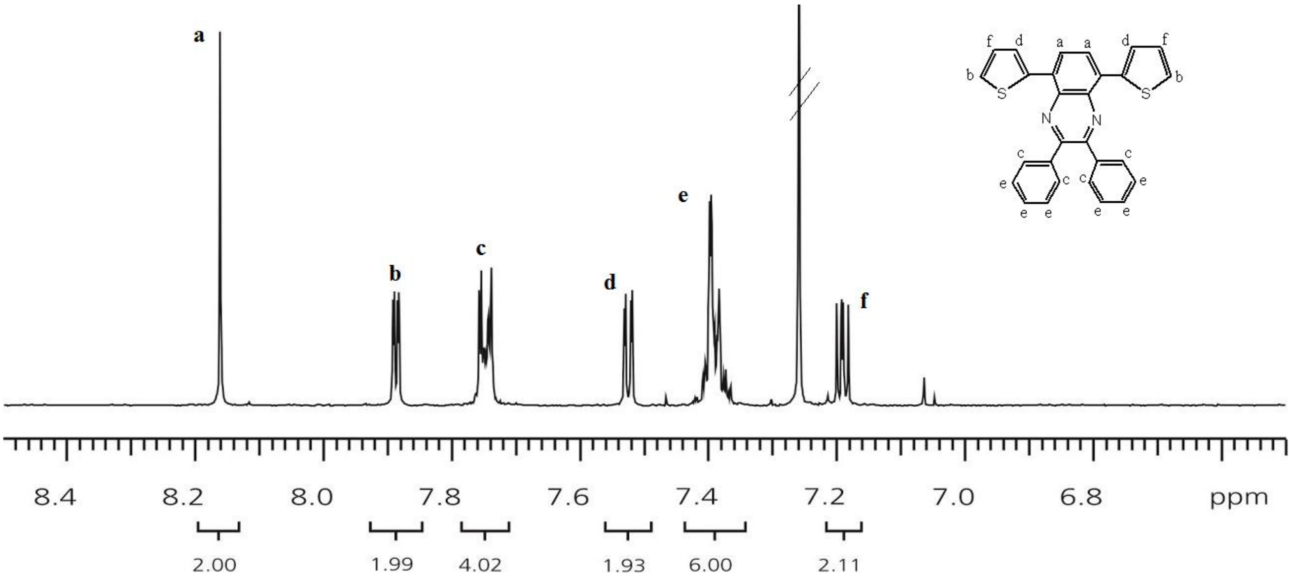


Figure 1. ^{1}H-NMR spectrum of monomer (M2) in $CDCl_3$.

2.4. Electrochemistry

Electrochemical synthesis (electropolymerization) and electrochemistry experiments were performed with a Cyclic EG&G Parc model 273 potentiostat controlled by an IBM P70 computer. An one-compartment electrochemical cell with a three- electrode set up was used. An indium-tin oxide coated glass (ITO, Balzers, 30 nm fully oxidized ITO on SIO_2 with a resistance 78 Ohm / sq, 2.5 x1.0 cm) or Pt plate (0.15 cm^2) were used as working electrodes for the deposition of the films, a Pt wire or Pt mesh as counter electrode and Ag/AgCl (3M NaCl and sat. AgCl) as reference electrode. The ITO electrodes were cleaned prior to their use by sequential ultrasonication in acetone, water and isopropyl alcohol (10 min each solvent). Then, they were further cleaned by exposure for 2 min on air plasma and were dried on a hot plate at 120 ^{o}C for 10 min. The electropolymerization solution was a mixture of acetonitrile with dichloromethane (ACN:DCM = 1:1 v/v), with tetrabutylammonium tetrafluoroborate ($TBABF_4$, 0.1 M) as supporting electrolyte and the monomers (M1) or (M2) in a concentration of 1 mM. In order to remove the residues of polymerization and the soluble oligomers, the polymer films were rinsed with ACN:DCM=1:1 v/v solution after the electropolymerization and then they were dried with argon flow. The electrochemical behaviour of the already formed films on

ITO or Pt electrodes was studied using the same electrode set-up in a monomer-free solution of $TBABF_4$ (0.1 M) in acetonitrile. All the electrochemistry experiments were performed at room temperature; in all cases, the solutions were deoxygenated with argon prior to their use. The electrochemical cell was calibrated by the use of a ferrocene standard and the half-wave potential has been estimated to be 435 mV for this assembly.

2.5. Spectroelectrochemistry

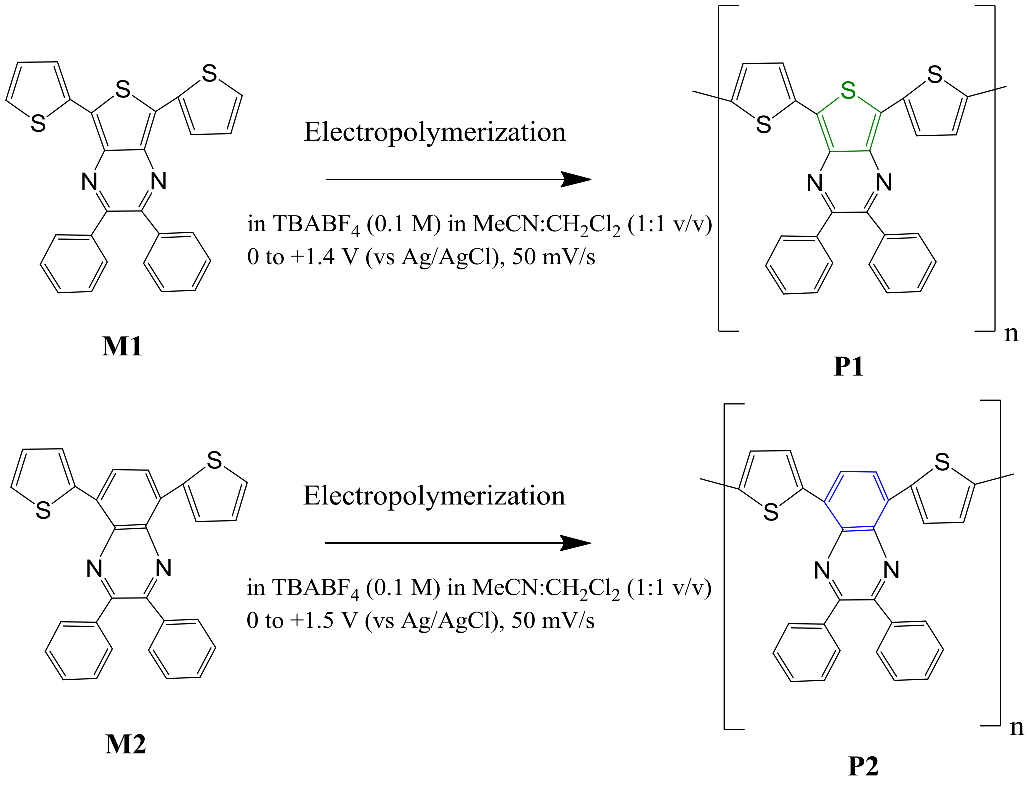
Spectroelectrochemical data were recorded on an 8453 UV− 358 visible Spectophotometer (Agilent, Germany). The potential was obtained with the potentiostat PGSTAT 302N (AUTOLAB), controlled by a PC running under GPES for Windows (ECO Chemie B. V.). The polymer films on ITO electrodes were measured in a cell of 1 cm path length. A three electrode cell assembly was used, where the working electrode was the ITO/polymer system, a Pt wire as counter and Ag/AgCl (2 M KCl / EtOH) as a reference electrode. The measurements were carried out at room temperature under Ar and the equilibration time for each measurement was 20 sec.

3. RESULTS AND DISCUSSION

3.1. Electropolymerization of M1 and M2

The electropolymerization of monomer M1, Scheme 2, was carried out using cyclic voltammetry (CV) between 0 and 1.4 V with a scan rate of 50 mV/s. In Figure 2 the first 10 scans are presented. During the first scan, the oxidation of the monomer appears at 1.1 V and its reduction at 0.90 V. Moreover, the reduction of the already formed polymer can be observed at 0.50 V.

From the second scan and onwards, the oxidation peak due to the doping of the already formed polymer is clearly shown at 0.82 V. With increasing the number of scans, the oxidation peak of the polymer shifted in the anodic direction and the reduction peak shifted to the cathodic one. This electrochemical behaviour indicated that conducting polymer film was formed on the working electrode. The current of oxidation (anodic) and reduction (cathodic) peak increase by increasing the number of scans, indicating that the deposition of polymer on the electrode did not stop. The polymer growth continued until the 40th scan and then practically stopped (i.e. the current was almost constant). After five scans, a polymer deposition could be clearly seen on ITO, which has a light green colour. The charge due to oxidation Q_{ox} and the corresponding due to the reduction Q_{red} were calculated for every scan, as well as their absolute ratio (Q_{ox}/Q_{red}). The dependence between this ratio and the number of scans is presented in the inset of Figure 2. During the first scan, mainly oxidation took place and this lead to the high Q_{ox}/Q_{red} value of 6.5. After the 1st scan, the reduction started to increase, thus the ratio decreased reaching the value of 2.3 after 5 scans. This means that the polymer P1 synthesized under these scans was partially reduced.



Scheme 2. Electropolymerization of monomer M1 and monomer M2.

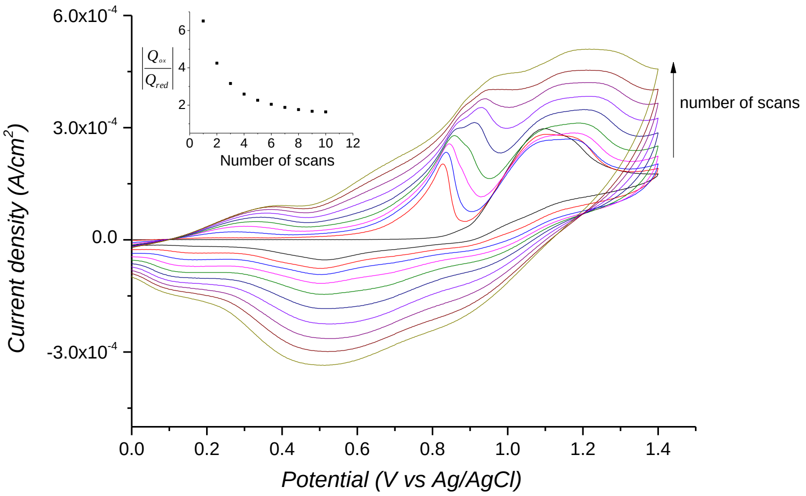


Figure 2. Cyclic voltammograms during the electropolymerization of M1 with 1 mM in 0.1 M TBABF$_4$, in MeCN:CH$_2$Cl$_2$ (1:1 v/v) on ITO electrode (area: 1.5 cm^2), scan rate 50 mV/s, vs. Ag/AgCl.

The electropolymerization of monomer M2, Scheme 2, was carried out also using cyclic voltammetry between 0 to 1.5 V with a scan rate of 50 mV/s. In Figure 3 the first 10 scans are presented. During the first scan, the oxidation of the monomer appeared at 1.35 V, its reduction at around 1.00 V and the reduction of the already formed polymer at 0.65 V. From the second scan the oxidation peak due to the doping of the already formed polymer was present at 0.90 V. As the number of scans increase, the reduction peaks (of monomer and that of polymer) became one broad peak in the potential region from 0.55 to 0.85 V. The polymer growth continued until the 30th scan and then practically stopped. After five scans, a polymer deposition was present on ITO, which has a blue colour. The ratio Q_{ox}/Q_{red} (inset of Figure 3) started from a value of 4.5 (for the 1st scan) and gradually decreased to the value of 1.8 (for 5th scan). The polymer P2 synthesized after 5 scans was partially reduced.

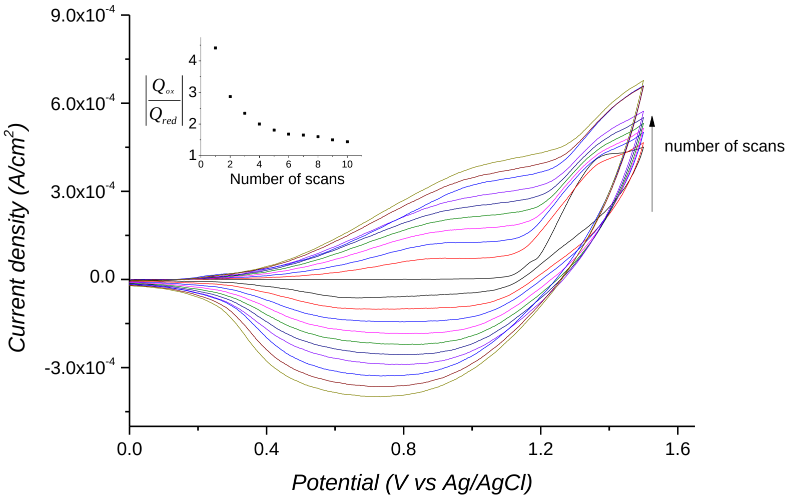
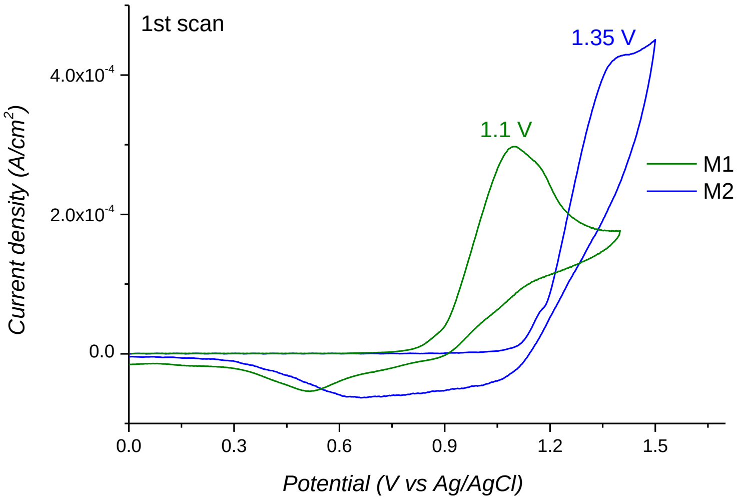


Figure 3. Cyclic voltammograms during the electropolymerization of M2 with 1 mM in 0.1 M $TBABF_4$, in $MeCN:CH_2Cl_2$ (1:1 v/v) on ITO electrode (area: 1.5 cm^2), scan rate 50 mV/s, vs. Ag/AgCl.

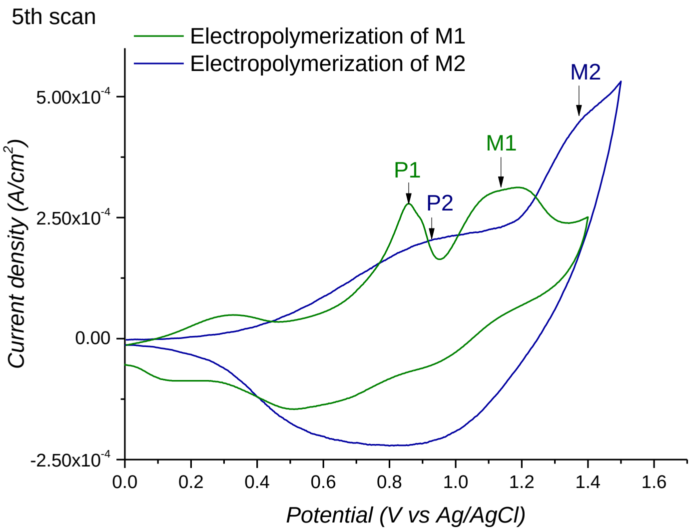
The influence of the different acceptor unit on the oxidation and reduction potentials can be seen in the comparative Figure 4, where the 1st and the 5th scan for the electropolymerization of M1 and M2 are presented. By replacing the thiophene ring with phenyl in the acceptor unit (i.e. going from M1 to M2), the oxidation and reduction potentials shift to higher values, for both monomer and polymer. This is due to the electron rich character of the thiophene, which facilitated the oxidation.

3.2 Morphology of the films

The morphology of P1 and P2 films were investigated by SEM and AFM and the corresponding photos are presented in Figure 5. The thickness of the polymer P1 and P2 was estimated by SEM as 40 and 100 nm, respectively. P1 had a dense network with rod-like structures (50 nm diameter), whereas P2 seems to had aggregates of round shape (with diameter of about 80 nm). According to Figure 5(d), the nucleation clusters can be seen; in some regions they had started to join together. On the other hand, P1 seems to be more uniform having some localized region with high concentration of granules. From the AFM the average surface roughness was estimated for P1 as 4.0 nm and for P2 as 18 nm, confirming that P1 is more uniform.



(a)

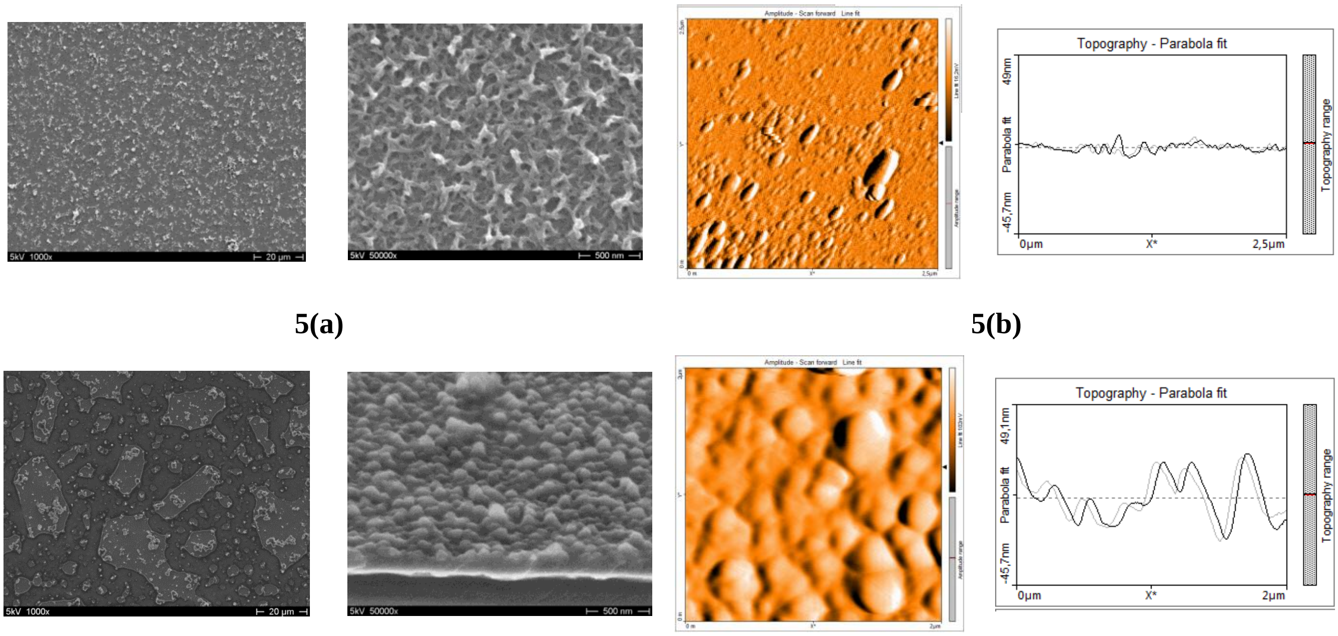


(b)

Figure 4. (a)1st and (b) 5th cyclic voltammogram during the electropolymerization of M1 and M2.

3.3. Electrochemistry of films

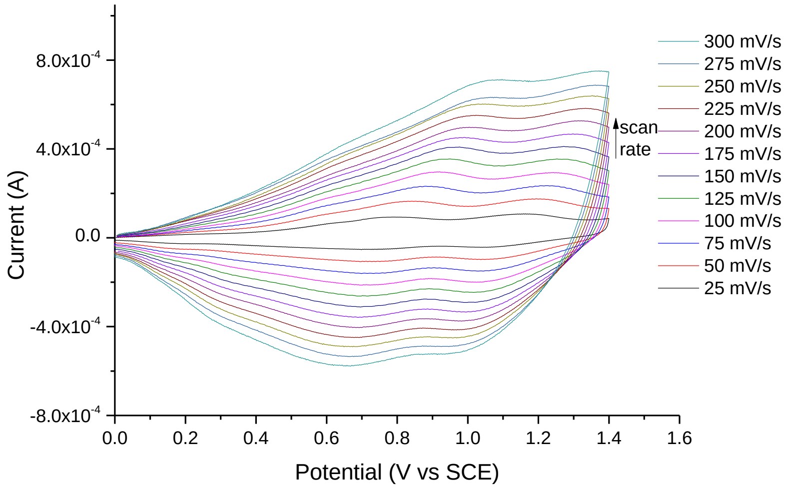
For application in ECDs, it is important to have a film that switches reversible between oxidation/reduction process. In order to investigate this, an already formed polymer film P1 on ITO (synthesized by scanning the potential form 0 to 1.4 V, scan rate 50 mV/s, 5 scans) underwent scans in a monomer free solution for different scan rates, Figure 6(a). The redox couple due to doping/dedoping of the P1 polymer can be observed at around 0.95 V and 0.62 V, respectively. As the scan rate increased, the peak current also increased, indicating an electroactive polymer film on the electrode surface. The anodic and the cathodic peak currents depended linearly on the scan rate, Figure 6(b); additionally, the position of the peaks was not affected by the scan rate. These observations indicated that the electrochemical oxidation/reduction is reversible and not diffusion limited [19], even at high scan rates.



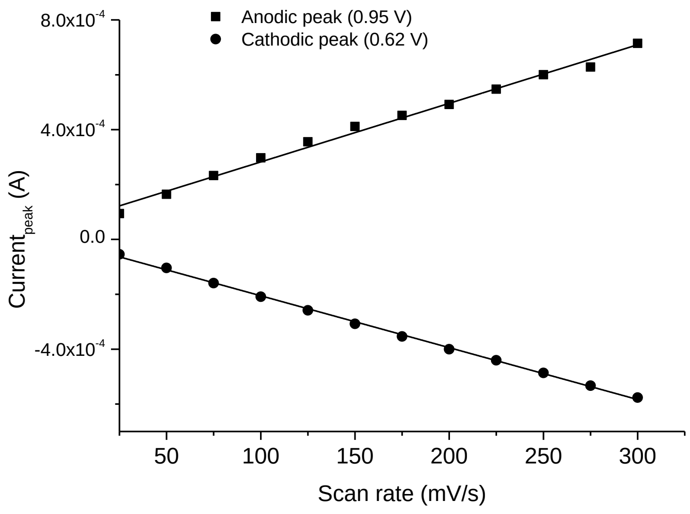
5(a) 5(b)

5(c) 5(d)

Figure 5. (a) SEM photos of P1, (b) AFM photos of P1, (c) SEM photos of P2, (d) AFM of P2. P1 and P2 are formed films on ITO; they deposited after 5 scan, with a scan rate of 50 mV/s in the potential range 0 to 1.4 V (P1) or 0 to 1.5 V (P2).



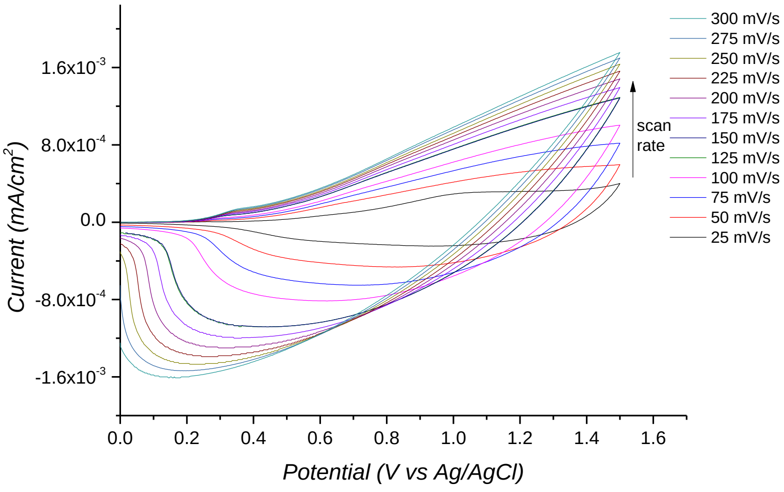
6(a)



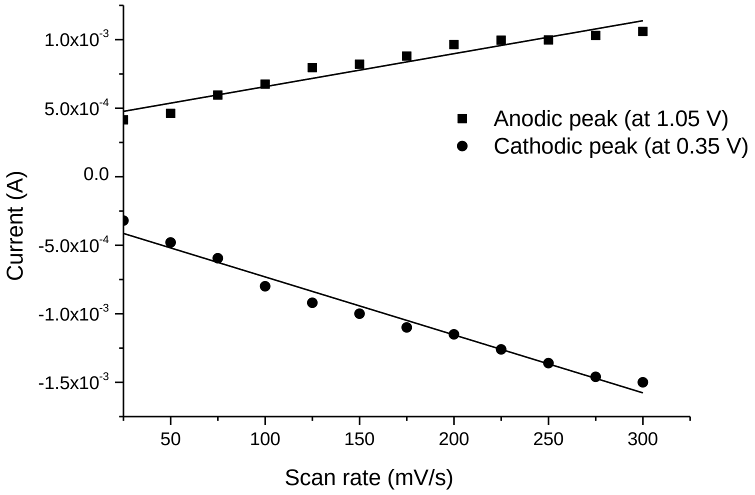
6(b)

Figure 6. (a) Cyclic voltammetry curves of the P1 polymer ready film on ITO electrode at different scan rates between 25 mV/s and 300 mV/s. A monomer-free solution of 0.1 M TBABF$_4$ in acetonitrile was used. The ready film had synthesized by scanning the potential form 0 to 1.4 V, scan rate 50 mV/s, for 5 scans, on ITO electrode (b) Scan rate dependence of current of the anodic (0.95 V) and the cathodic (0.62 V) peak.

Similarly, the reversibility of the polymer P2 was also investigated following the same procedure. In Figure 7(a) the electrochemical behavior P2 (synthesized by scanning the potential form 0 to 1.5 V, scan rate 50 mV/s, 5 scans) at different scan rates is presented. The dependence of the anodic (1.05 V) and cathodic current peak (0.35 V) with the scan rate is presented in Figure 7(b). Like P1, in P2 polymer a reversible oxidation/reduction process was also observed.



7(a)



7(b)

Figure 7. (a) Cyclic voltammetry curves of the P2 polymer ready film on ITO electrode at different scan rates between 25 mV/s and 300 mV/s. A monomer-free solution of 0.1 M TBABF$_4$ in acetonitrile was used. The ready film had synthesized by scanning the potential form 0 to 1.5 V, scan rate 50 mV/s, for 5 scans, on ITO electrode (b) Scan rate dependence of current of the anodic (1.05 V) and the cathodic peak (0.35 V).

3.4. Optical and electrochemical properties

Figure 8 presents the UV-Vis spectra of neutral films P1 and P2 on ITO substrates. The films were synthesized after 5 scans (scan rate 50 mV/s) in the potential range from 0 to 1.4 V, and 0 to 1.5 V, respectively. After synthesis, they were dedoped in a monomer-free solution. P1 exhibits two absorption bands, one at 475 nm and another broad, from 600 to 855 nm. This is a typical behaviour for a green colour material [13,14]. The first peak is attributed to the absorption of the violet and blue colours and the second one to the absorption of yellow, orange and red colours. Polymer P2 has a different spectrum; it exhibits one small band at 385 nm and another at 580 nm. It seems that the phenyl ring of the acceptor unit caused a hypsochromic shift. From the onset of absorption maximum (λ_{onset}), the optical band gap was estimated as 2.3 eV for P1 and 2.7 eV for P2.

Furthermore, the HOMO and LUMO energy levels were estimated using cyclic voltammetry. An already formed P1 polymer film on Pt plate electrode (synthesized by scanning the potential form 0 to 1.4 V, scan rate 50 mV/s, 5 scans) underwent scans in monomer free solution with a slow scan rate of 20 mV/s (Figure 9). In the oxidation direction, a reversible peak at 1.08 V was observed, due to the p-doping of the molecule, whereas in the reduction direction, a peak at -1.12 V appeared due to n-doping. The energy levels were estimated according the literature [20] as E_{HOMO}= - 5.9 eV, E_{LUMO} = - 3.7 eV and E_g = 2.2 eV.

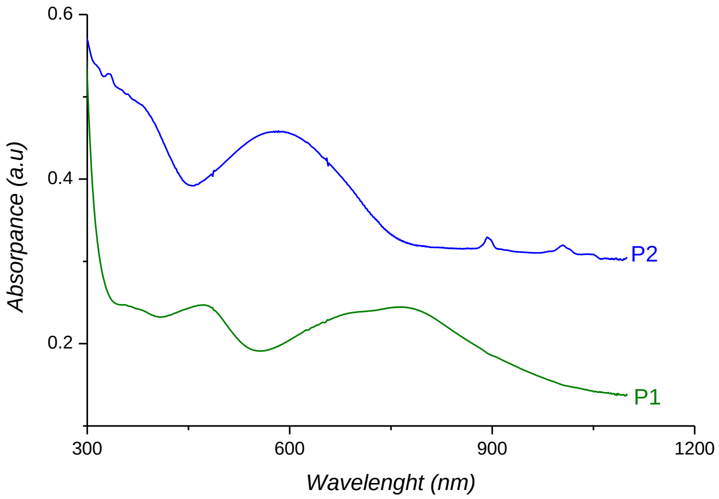


Figure 8. UV-Vis spectrum of polymer film P1 and P2 deposited on ITO electrode in the neutral state (P1 was synthesized by scanning the potential form 0 to 1.4 V, P2 by scanning the potential form 0 to 1.5 V; in both cases the scan rate was 50 mV/s, for 5 scans).

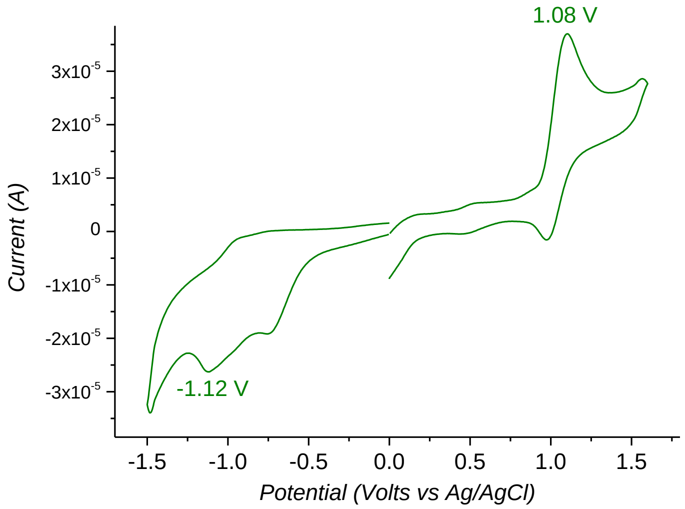


Figure 9. Cyclic voltammetry curve of polymer ready film P1 on Pt electrode in monomer-free solution of 0.1 M $TBABF_4$ in acetonitrile, scan rate 20 mV/s. The ready film had synthesized by scanning the potential form 0 to 1.4 V, scan rate 50 mV/s, for 5 scans on Pt electrode.

Similarly, the corresponding values for P2 (Figure 10) are E_{HOMO}= - 5.9 eV , E_{LUMO} = - 3.5 eV and E_g = 2.4 eV. The acceptor unit seems that affects only the LUMO level of the polymers. Namely, by replacing the thiophene by phenyl ring (i.e. going from P1 to P2) the LUMO band shifted in less negative values. Therefore, the band gap was also affected, being lower for P1 with the thiophene in the acceptor moiety. This effect has also been reported in the literature [11], i.e. that the presence of electron-rich (such as the thiophene ring) or electron-deficient groups on the polymer backbone ease the π-electron delocalization and hence lower the band gap.

Comparing the values of optical band gap with the electrochemical one, the values are not the same. From a more fundamental point of view, the optical transitions do not reveal the formation of free charge carriers: the excited state in conjugated polymers may be viewed as a bound exciton (with a binding energy that is still controversial). The formation of charge carriers will then require a higher energy of optical absorption, with no easy detection by linear optical spectroscopy; it may thus be concluded that the optical transitions cannot be directly compared to the electrochemical doping processes [21,22]. The deviation between these two values is quite larger in the case of P2; however, such high differences have been reported in the literature for other conducting polymers [5,22,23].

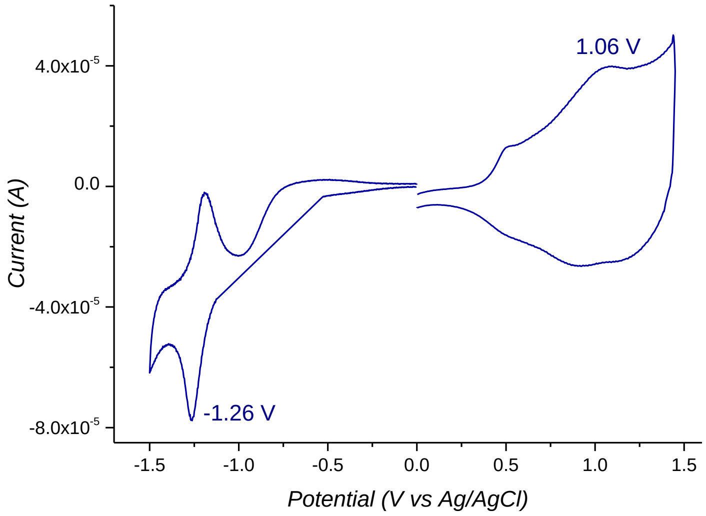


Figure 10. Cyclic voltammetry curve of polymer ready film P2 on Pt electrode in monomer-free solution of 0.1 M TBABF$_4$ in acetonitrile, scan rate 20 mV/s. The ready film had synthesized by scanning the potential form 0 to 1.5 V, scan rate 50 mV/s, for 5 scans on Pt electrode.

3.5. Electrochromic properties

In order to investigate the electrochromic properties of the films, spectroelectrochemistry was used. In this technique, an already formed polymer P1 on ITO (synthesized by scanning the potential form 0 to 1.4 V, scan rate 50 mV/s, for 5 scans) was used as working electrode and underwent a stepwise potential scan in a monomer free solution. Starting form 0 V, the potential gradually increases and it was kept constant for some seconds at every desired value; at the same time, the UV-Vis spectrum was recorded. It is a useful tool, given that the optical properties of the film due to the voltage changes can be directly studied. The in situ UV-Vis spectrum of P1 is presented in Figure 11. At 0 V, the polymer is in its neutral state having two bands; namely, one at 470 nm, due to π- π* transitions and another broad one, centered at 730 nm. By increasing the applied potential, the intensity of the bands decreased due to the doping of the polymer. For potential higher than 0.8 V, the broad band disappeared and a new one at 900 nm appeared, due to the polarons. The change of the colour of the film was also observed macroscopically during the change of the applied potential.

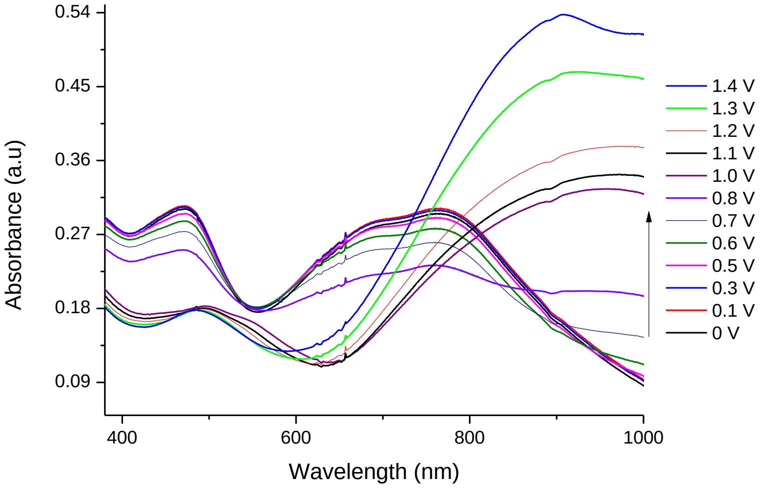
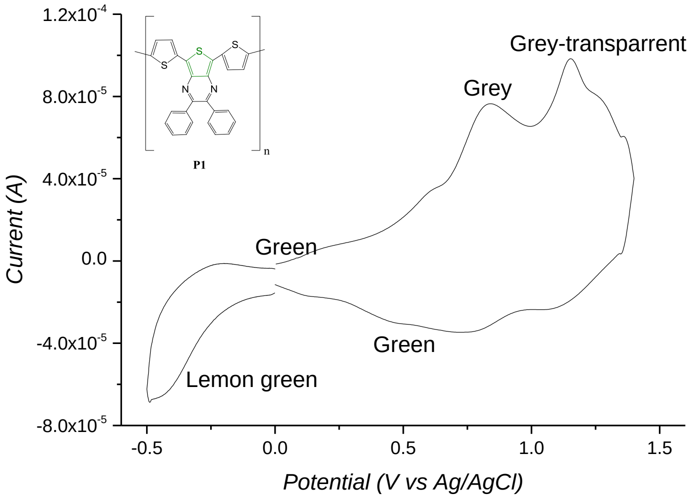
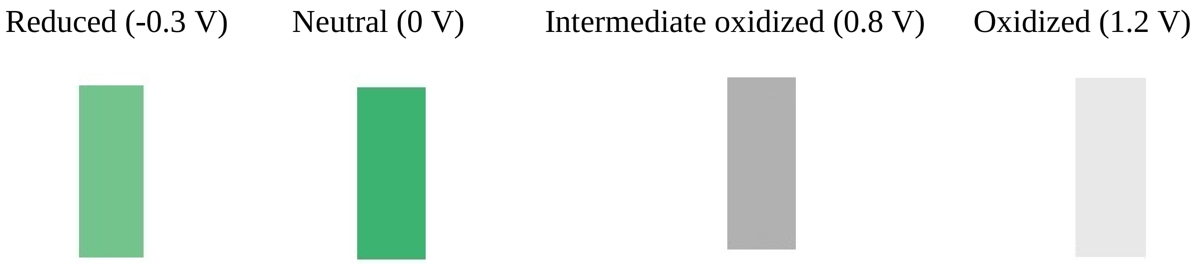


Figure 11. Spectroelectrochemical spectra of polymer film P1 on ITO in the neutral and oxidized states, in 0.1 M TBABF$_4$ in acetonitrile at several potential from 0 to 1.4 Volts. The ready film had synthesized by scanning the potential form 0 to 1.4 V, scan rate 50 mV/s, for 5 scans, on ITO electrode.

In Figure 12, the different colours of the film P1 are presented (with the corresponding potentials). When P1 is in the neutral state was green, became grey at 0.8 V (i.e. in the intermediate oxidized state) and finally exhibited transparent grey/sky blue colour (when it is fully doped). Moreover, it has lemon green colour in its reduced state. This is a significant trait in order to apply CPs in electrochromic devices and displays.



12(a)



12(b)

Figure 12. (a) Cyclic voltammogram (CV) of polymer film P1 on ITO, in 0.1 M TBABF4 in acetonitrile, scan rate 50 mV/s. The ready film had synthesized by scanning the potential form 0 to 1.4 V, scan rate 50 mV/s, for 5 scans, on ITO electrode. (b) Change of the colour of P1 during the CV potential scan in relation to the different oxidation states.

The corresponding in situ UV-Vis spectra for P2 (synthesized by scanning the potential form 0 to 1.5 V, scan rate 50 mV/s, for 5 scans) are presented in Figure 13. Starting for 0 V and increasing the potential up to 0.7 V, the intensity of the band at 580 nm decreased due to the doping of the polymer; at the same time, the peak shifted to higher wavelengths. By further increase of the applied potential (reaching 1.0 V), the spectrum shifted again, but this time to lower wavelengths. For even higher potential (1.3 V), a completely different spectrum is derived. Specifically, the one band has been replaced by two, one at 540 nm and another broad at 660 to 880 nm.

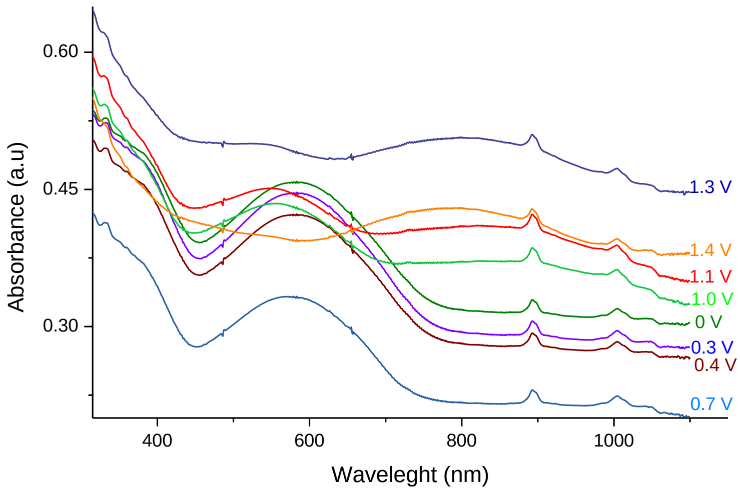
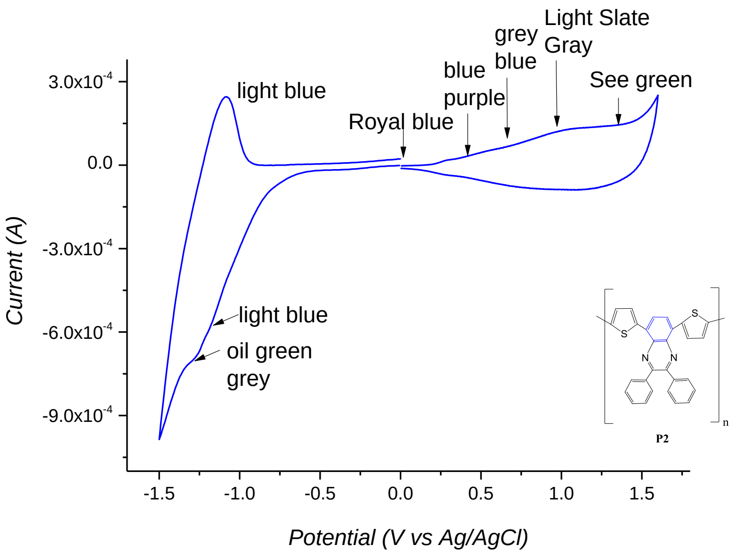
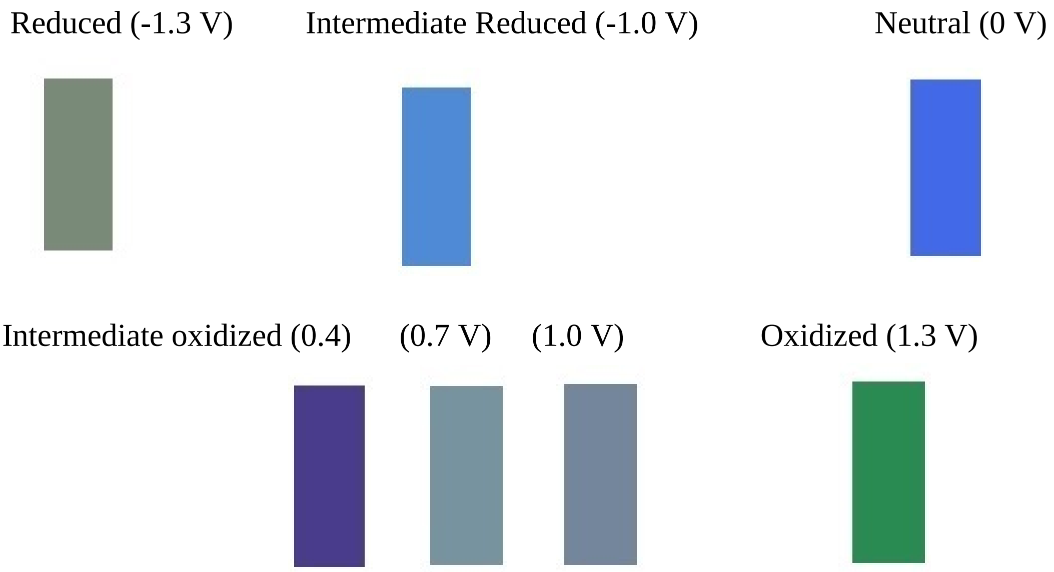


Figure 13. Spectroelectrochemical spectra of polymer film P2 on ITO in the neutral and oxidized states, in 0.1 M TBABF4 in acetonitrile at several potential from 0 to 1.3 Volts. The ready film had synthesized by scanning the potential form 0 to 1.5 V, scan rate 50 mV/s, for 5 scans, on ITO electrode.

The colour of the P2 film changed upon the change of the potential and the corresponding colours are presented in Figure 14. Namely, P2 was royal blue in the neutral state and green in the oxidized, additionally in the intermediate oxidized states it had blue purple, grey-blue and light grey colours. Moreover, in the reduced state it is oil green, having also a light blue colour in the intermediate reduced state. This behaviour is really impressive and genuinely multi-coloured; thus, the polymers are very good candidates for electrochromic devices and displays.



14(a)



14(b)

Figure 14. Cyclic voltammogram (CV) of polymer film (P2) on ITO, in 0.1 M TBABF4 in acetonitrile, scan rate 50 mV/s. The ready film had synthesized by scanning the potential form 0 to 1.5 V, scan rate 50 mV/s, for 5 scans, on ITO electrode. (b) Change of the colour of P2 during the CV potential scan in relation to the different oxidation states.

3.6. Stability

The stability of the electrochromic polymer film was monitored by repetitive switching between oxidized and neutral states. In order to investigate the stability, P1 film (deposited on ITO, by 5 scans in the range of 0 to 1.4 V, scan rate 50 mV/s) underwent repetitive scans in a monomer free solution, in the range of interest (i.e. from 0 to 1.4 V) with a very fast scan rate, i.e. 500 mV/s. The charge involved during the doping-dedoping process was calculated for every scan. The total loss was at around 12 % after the first 150 scans and then the loss rate was low. On the other hand, P2 (deposited on ITO, by 5 scans in the range of 0 to 1.5 V, scan rate 50 mV/s) seems to be exceptionally stable. By scanning it in the range from 0 to 1.5 V (with 500 mV/s), it does not exhibit any loss until the 300th scan and then it started to have a really small loss. Finally, after 500 scans, the total loss was estimated as only 2%.

4. CONCLUSION

Two different monomers having electron donor-electron acceptor-electron donor (D-A-D) structure were synthesized. They had the same D moiety (i.e. thiophene) and different A moiety (i.e. diphenylthienopyrazine for monomer M1 and diphenylquinoxaline for monomer M2). The two monomers were successfully electropolymerized by cyclic voltammetry to polymers P1 and P2, respectively. The effect of the acceptor on the electrochemical and electrochromic properties of the polymer films was investigated. The thiophene ring causes an easier oxidation. From the microscopy analysis it was found that the different acceptor affects strongly the polymer film morphology. P1 seems to be more uniform, having a dense network with rod like structures, whereas P2 has aggregates of round shape. The already formed film P1 and P2 on ITO electrodes exhibit the characteristic redox couple due to corresponding oxidation/reduction, at 0.95 V/0.62 V and at 1.05 V/0.35 V, respectively. The reversibility of the doping/dedoping was investigating by cyclic voltammety and a reversible process was observed for both polymers. Concerning the optical properties of the films, neutral P1 exhibited two absorption bands (one at 475 nm and another broad, from 600 to 855 nm), whereas P2 had a different spectrum (one small band at 385 nm and another at 580 nm). Comparing the spectra, it seems that the phenyl ring in the acceptor unit (P2) caused a hypsochromic shift. The HOMO, LUMO energy levels, as well as the band gap for the polymer films were estimated by cyclic voltammetry. Investigating the influence of the acceptor unit, it seems that affects only the LUMO level. Specifically substituting the thiophene with phenyl ring, the LUMO level shifted to less negative values. Moreover, the band gap was also affected; it is lower for P1 (E_g =2.2 eV for P1 and E_g =2.4 eV for P2). The electrochromic properties of the polymer films were investigated by spectroelectrochemistry. Polymer P1 is green in its neutral state, becoming grey and transparent grey/sky blue colour by increasing the oxidation level. In the reduced state, it had a lemon green colour. Polymer P2 is royal blue in the neutral and green in the oxidized state; it has also three more colours (blue purple, grey blue and light grey) in intermediate oxidized states. At -1.3 V (i.e. in the reduced state) the film is oil green, having also a light blue colour in the intermediate reduced state. This behaviour is really impressive and genuinely multi-coloured. The stability of the electrochromic polymer film during repetitive switching between oxidized and neutral states was also investigated. Even though both the polymers were stable, P2 exhibits better behaviour.

Summarizing, P1 poly(5,7-di(thiophene-2-yl)2,3-diphenyl-thieno[3,4-b]pyrazine) and P2, poly(5,8-di(thiophene-2-yl)2,3-diphenyl-thieno[3,4-b] quinoxaline) exhibit interesting multi-chromism properties and they are good candidates to be applied in multi-coloured electrochromic devices.

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References

1. P. Monk, R. Mortimer and D. Rosseinsky, *Electrochromism and Electrochromic Devices,* Cambridge University Press 2007.
2. I. Yagmur, M. Ak, and A. Bayrakceken, *Smart Mater. Struct*. 22 (2013) 115022.
3. AA. Argun, PR. Aubert, BC. Thompson, I. Schwendeman, CL. Gaupp, J. Hwang, NJ. Pinto, DB. Tanner, AG. MacDiarmid and JR. Reynolds, *Chem. Mater*. 16 (2004) 4401.
4. L. Beverina, GA. Pagani and M. Sassi, *Chem. Commun*. 50 (2014) 5413.
5. P. Ledwon, A. Brzeczek, S. Pluczyk, T. Jarosz, W. Kuznika, K. Walczak and M. Lapkowskia, *Electroch. Acta*, 128 (2014) 420.
6. EK. Unver, S. Tarkuc, D. Baran, C. Tanyeli and L. Toppare, *Tetrahedron Let*. 52 (2011) 2725.
7. R. Berridge, SP. Wright, PJ. Skabara, A. Dyer, T. Steckler, A. Argun, JR Reynolds, RW. Harrington and W. Clegg, *J. Mater. Chem*. 17 (2006) 225.
8. B. Hu, X. Lv, J. Sun, G. Bian, M. Ouyang, Z. Fu, P. Wang and C. Zhang, *Org. Electr*. 14 (2013) 1521.
9. PM. Beaujuge, S. Ellinger and JR. Reynolds, *Nat. Mat.* 7 (2008) 795.
10. SO. Hacioglu, S. Toksabay, M. Sendur and L. Toppare, *J. Pol. Sci. Part A:Pol. Chem. Phys.* 52 (2014) 537.
11. AG. Nurioglu, H. Akpinar, M. Sendur and L. Toppare, *J. Pol. Sci. Part A:Pol. Chem.* 150 (2012) 3499.
12. DR. Rosseinsky and RJ. Mortimer, *Adv. Mater.*13 (2001) 783.
13. F. Algi and A. Cihaner, *Org. Electr.* 10 (2009) 704.
14. GE. Gunbas, A. Durmus and L. Toppare, *Adv. Funct. Mater.* 18 (2008) 2026.
15. A. Durmus, GE. Gunbas, P. Camurlu and L. Toppare, *Chem. Comm.* 32 (2007) 3246.
16. A. Durmus, GE. Gunbas and L. Toppare, *Chem. Mater.* 19 (2007) 6247.
17. WT. Neo, LM. Loo, J. Song, X. Wang, XM. Cho, HS On Chan, Y. Zong and J. Xu, *Polym. Chem.* 4 (2013) 4663.
18. E. Person, X. Wang, F. Zhang, W. Mammo, JL. Delgado, P. de la Cruz, O. Inganas, F. Langa and MR. Andersson, *Synth. Met.* 154 (2005) 53.
19. M. Mahmut, T. Awut, I. Nurulla ans M. Mijit, *J. Appl. Polym. Sci.* 2014, DOI: 10.1002/APP.40861.
20. S. Admassie, O. Inganas, W. Mammo, E. Perzon and MR. Andersson, *Synth. Met.* 156 (2006), 614.
21. T. Johansson, W. Mammo, M. Svensson, MR: Andersson and O. Inganas, *J. Mater. Chem.* 13 (2003) 1316.

22. E. Kaya, A. Balan, D. Baran, A. Cirpan and L. Toppare, *Org. Electr.* 12 (2010) 202.
23. S. Ozdemir, M. Sendur, G. Oktem, O. Dogan and L. Toppare, *J. Mater. Chem.* 22 (2012) 4687.

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