Copolymerisation as a way to enhance the electrochromic properties of an alkylthiophene oligomer and a pyrrole derivative: copolymer of 3,3''' Dihexyl-2,2':5',2'':5'',2'''-quaterthiophene with (*R*)-(-)-3-(1-pyrrolyl)propyl-*N*-(3,5-dinitrobenzoyl)-α-phenylglycinate

Ana Julia C. Silva[a,b], Viviane C. Nogueira[b], Thebano E. A. Santos[b], Craig J. T. Buck[c], David R. Worrall[c], Josealdo Tonholo[a,c], Roger J. Mortimer[c], Adriana S. Ribeiro[a,c*]

[a] *Instituto de Química e Biotecnologia,Universidade Federal de Alagoas, Campus A. C. Simões, Tabuleiro do Martins 57072-970, Maceió-AL, Brazil*

[b] *Centro de Tecnologia da Informação Renato Archer, Divisão de Mostradores da Informação 13069-901, Campinas-SP, Brazil.*

[c] *Department of Chemistry, Loughborough University, LE11 3TU, Leicestershire, United Kingdom*

Abstract

The copolymerisation of 3,3''' Dihexyl-2,2':5',2'':5'',2'''-quaterthiophene (DHQT) and (*R*)-(-)-3-(1-pyrrolyl)propyl-*N*-(3,5-dinitrobenzoyl)-α-phenylglycinate (DNBP) was successfully performed electrochemically in acetonitrile (CH_3CN) containing tetrabutylammonium tetrafluoroborate ((C_4H_9)$_4NBF_4$) by direct oxidation of monomer mixtures in different feed ratios. Copolymerisation improved the properties of the films of both polymers PDHQT and PDNBP, in respect to the adhesion of PDHQT onto ITO/glass surface and the chromatic contrast of these electrochromic materials. PDHQT, PDNBP and P(DHQT-co-DNBP) films

---

* Corresponding author: Tel.+55-82-3214-1393; fax: +55-82-3214-1389

E-mail address: aribeiro@qui.ufal.br (A.S. Ribeiro)

were characterised by FTIR spectroscopy, fluorescence spectroscopy, Scanning Electron Microscopy (SEM) and spectroelectrochemical techniques. Solutions of PDHQT and its copolymers with DNBP (independently of the feed ratio) in N-methylpyrrolidone are fluorescent with emission bands at 555 and 585 nm when excited at 375 nm. Reversible changes in the hue and saturation occur in all the copolymer films from yellow or orange in the reduced state to green or blue in the oxidised state, but were dependent on the proportion of the comonomers used to prepare the copolymers. These changes are more significant for P(DHQT-co-DNBP) films deposited onto ITO/glass with 1:5 feed ratio, as shown by the track of the CIE 1931 xy chromaticity coordinates and by the electrochromic parameters in which this film (thickness 0.8 ± 0.2 μm) presented chromatic contrast ($\Delta\%T$) at 660 nm of 62 %, coloration efficiency (η) of 266 cm^2 C^{-1} and stability to redox cycling ($\Delta\%T = 17$ % at the 1000th cycle). Therefore, these copolymers are potentially applicable in displays and optoelectronic devices as electrochromic and fluorescent materials.

Keywords: Copolymerisation; Electrochromism; Fluorescence; Pyrrole derivative; Alkylthiophene oligomers.

1. Introduction

Electrochromic materials based on conjugated polymers have become one of the main research topics due to their notable advantages, such as low cost and simple production methods, processability, and the possibility of tuning the band gap (and the colour states) of the polymer by suitable choice of the monomer substituent [1,2].

A major focus in the study of electrochromic polymer materials has been that of controlling their colours by main-chain and pendant group structural modification as well as copolymerisation [3,4]. However, the structural modification of these conjugated polymers with the aim to improve their properties is still a challenge. For example, the introduction of large functionalities onto a conjugated polymer can lead to a significant steric effect on the polymer backbone, adversely affecting the optical and electronic properties of the polymer [5,6]. Otherwise, copolymerisation is an easy, facile method to combine the electrochromic properties of monomers and it is a common approach to obtain materials with tailored properties [7,8]. Usually these properties are determined by the structure, ratio, and sequence of the repeat units derived from the co-monomers [9].

Copolymerisation of oligothiophenes is particularly attractive because the oligomers themselves have tunable properties that affect the behaviour of the resulting polymers and they can provide reduced steric interactions between polymer backbone and substituent allowing better control of the polymer regiochemistry [10,11]. Among the variety of oligomers used in the synthesis of semi-conducting materials, oligothiophenes have received a high interest, mainly due to the π-electron delocalisation, high polarisability of sulphur atoms and supramolecular organisation coupled with synthetic accessibility [12-14]. In particular, alkyl derivatives of oligothiophenes, such as terthiophene and quaterthiophene, constitute an interesting class of electroactive polymers with potential application in organic electronics [15] that can be used as components of active layers for application in electronic devices such

as Organic Field Effect Transistors (OFETs) [16,17], photovoltaic cells [18] and electrochromic devices [19]. 3,3'" Dihexyl-2,2':5',2":5",2"'-quaterthiophene (DHQT) is largely investigated for such applications and is usually deposited onto a conductive surface to assemble a device by means of high vacuum evaporation [16,20]. However, due to the presence of the alkyl substituents in the oligomer chain, that confer solubility to the polymer [21], its electropolymerisation directly onto the electrode surface is highly dependent on the concentration and the applied potential and can lead to a loosely-adherent film deposited onto the electrode [22]. A tool to improve the formation of a uniform and well adhered film electrodeposited onto the electrode surface is its copolymerisation with another monomer that presents some other desired property. Therefore electrochemical copolymerisation is an efficient approach for the modification of the properties of DHQT and then to obtain a variety of conjugated polymers with different electrical, optical and morphological properties [23-25]. In order to modify the properties of DHQT and thus enhance the adherence and film formation capability of this polymer, this work has focused on the electrochemical copolymerisation of DHQT with a pyrrole derivative, (*R*)-(-)-3-(1-pyrrolyl)propyl-*N*-(3,5-dinitrobenzoyl)-α-phenylglycinate, DNBP.

The polymer PDNBP has already been investigated by our group and presents good results concerning its application as an electrochromic material [26,27]. In a previous work, DNBP was copolymerised with EDOT giving a multielectrochromic film with good chromatic contrast and great stability [28]. Herein, DHQT and DNBP were successfully polymerised by electrochemical oxidation of the monomer mixtures. The copolymer films were homogenously deposited and with good adherence onto ITO/glass and they were characterised by FTIR spectroscopy, fluorescence spectroscopy, SEM and spectroelectrochemical techniques. In this case the copolymerisation of DHQT with DNBP enhanced the electrochromic properties, such as chromatic contrast, multiple change of colour

upon redox switching and long-term switching stability, of the individual constituents, as well as maintaining the fluorescence inherent to the DHQT.

2. Experimental

2.1. Chemicals

Anhydrous acetonitrile 99.8 % (CH_3CN, < 0.001 % water, Sigma-Aldrich), DHQT (Sigma-Aldrich), and tetrabutylammonium tetrafluoroborate (($C_4H_9)_4NBF_4$, Aldrich) were used as received. DNBP was synthesised as previously described [29].

2.2. Characterisation

Electrochemical experiments were carried out using an Autolab PGSTAT30 potentiostat/galvanostat. FTIR spectra were recorded on a Nicolet 510 FTIR spectrometer. A Hewlett-Packard 8453 diode array spectrophotometer was used for the visible-near infrared (vis-NIR) spectra acquisition in the spectroelectrochemical experiments. SEM analysis was conducted on a JEOL JSM 6340F microscope. Thickness measurements were obtained using a NanoMap-500LS 3D contact stylus surface profilometer (AEP Technology).

2.3. Synthesis of copolymers of DHQT with DNBP

Solutions of DHQT (10.00, 3.33, 2.00 and 1.25 mmol L^{-1}) and DNBP (10.00 mmol L^{-1}) were prepared with different feed ratios of each monomer in a supporting electrolyte consisting of 0.1 mol L^{-1} ($C_4H_9)_4NBF_4/CH_3CN$, providing DHQT:DNBP feed ratios of 1:1, 1:3, 1:5 and 1:8. Films of PDHQT, PDNBP and P(DNBP-co-DHQT) (Scheme 1) were deposited onto ITO/glass electrodes (covered area = 1.0 cm^2, R_s 8-12 $\Omega \square^{-1}$; Delta Technologies) using a platinum foil as the counter electrode and an Ag/Ag^+ reference electrode (0.10 mol L^{-1} $AgNO_3/CH_3CN$, calibrated to the Fc/Fc^+ redox couple, E_{Fc/Fc^+} - E_{Ag/Ag^+}

= 70 mV [30]). Cyclic voltammograms were acquired at a scan rate (ν) of 20 mV s^{-1} within the potential scan range of $0.0 \leq E \leq 0.50$ V for polymerisation of DHQT and copolymerisation of DHQT with DNBP in a 1:1 feed ratio, $0.0 \leq E \leq 0.55$ V for preparation of the copolymers with 1:3, 1:5 and 1:8 feed ratios, and $0.0 \leq E \leq 0.85$ V for polymerisation of DNBP. The number of voltammetric cycles was varied in order to obtain films with similar deposition charge ($Q_{dep} \sim 60$ mC cm^{-2}), *i.e.* with similar thickness (0.8 ± 0.2 μm) [31,32] to avoid ambiguities in the colorimetric measurements.

To obtain a sufficient amount of polymer for FTIR spectroscopic characterisation, a platinum foil was employed as working electrode. After polymerisation, the films were washed several times with CH$_3$CN to remove the supporting electrolyte and the unreacted monomers and oligomers.

2.4. Fluorescence spectroscopy

The monomer DHQT (~ 0.05 mg), its polymer PDHQT and the copolymer films deposited onto ITO/glass were solubilised in 5.0 mL of N-methylpyrrolidone (NMP). Before the measurements all solutions were purged with N$_2$ for 10 minutes. The photoluminescence emission spectra and lifetime data were recorded with a FLS920 Fluorescence Spectrometer equipped with a TMS300 monochromator, a S900 single photon photomultiplier detection system and an EPL-375 picosecond pulsed diode laser (Edinburgh Instruments).

2.5. Spectroelectrochemistry

The polymer and copolymer films deposited onto ITO/glass were characterised by cyclic spectrovoltammetry and double step spectrochronoamperometry in 0.1 mol L^{-1} (C$_4$H$_9$)$_4$NBF$_4$/CH$_3$CN solution as supporting electrolyte, using a platinum wire as the counter electrode and an Ag/Ag$^+$ (0.1 mol L^{-1} in CH$_3$CN) electrode as reference. Cyclic

voltammograms were acquired within the potential scan range of $0.0 \leq E \leq 0.45$ V *vs.* Ag/Ag^{+} (0.1 mol L^{-1} in CH$_3$CN), and chronoamperograms were obtained by application of pulses of $E_1 = 0.0$ and $E_2 = 0.45$ V for 20 s. Spectra in the range of 300 to 1100 nm were recorded simultaneously with the electrochemical experiments.

CIE (Commission Internationale de l'Eclairage) principles [33] were applied in order to quantify the colour changes of each deposited polymer or copolymer films. CIE 1931 *xy* chromaticity coordinates and CIELAB 1976 colour space coordinates (*L*a*b**) were acquired using a Microsoft® Excel® spreadsheet developed by Mortimer and Varley [34,35]. For simulation of midmorning to midafternoon natural light, the relative power distribution of a D55 constant temperature (5500 K blackbody radiation) standard illuminant was used in the calculations. As the chromaticity coordinates vary with film thickness [36] it is important to emphasise that all data were calculated for films prepared with similar thickness. The track of the CIE 1931 *xy* chromaticity coordinates in the CIE chromaticity diagram was obtained using a Spectra Lux® Software v.2.0 Beta [37].

3. Results and Discussion

3.1. Electrochemical copolymerisation

In order to prepare copolymer chains with alternating monomer units, the oxidation potential of the starting monomers should be relatively close [23,38,39], usually below 0.2 V. As can be seen in Figure 1, the onset of the oxidation potential of DHQT is ~ 0.42 V while the onset of the oxidation potential of DNBP is ~ 0.78 V, so the difference between the oxidation potential of each one is *ca.* 0.36 V. As this difference is above 0.2 V we used the diffusion method strategy proposed by Kuwabata *et al.* [40] to guarantee that the copolymerisation has been achieved. This strategy consists of oxidising DHQT at potentials where DNBP oxidation occurs, *i.e.* using a higher concentration of the monomer with the highest oxidation potential

(DNBP). In order to confirm the suitable feed ratios of DHQT and DNBP, a series of experiments with different feed ratios were carried out.

Cyclic voltammograms recorded during the electropolymerisation of DHQT (Figure 2a) show the formation of a sharp redox couple with anodic peak potential (E_{pa}) ~ 0.39 V and cathodic peak potential (E_{pc}) ~ 0.32 V. On repetitive scanning the current of each peak increased, implying that a layer of redox-active and conductive material was deposited on the electrode, however, when the modified electrodes were withdrawn from solution the film either partially re-dissolved or became dislodged from the electrode surface forming heterogeneous films. A similar behaviour was observed by Jones and Higgins [22] with other alkyl-terthiophene and -quaterthiophenes and by Zotti *et al.* [41] with a series of dialkoxy-substituted thiophene oligomers which may be ascribed to the high solubility of the polymers/oligomers from the former and to the low rate of coupling of the latter leading to the exclusive deposition of soluble oligomers [9]. Therefore, as can be seen in Fig. 2a, the low current values observed during the reduction process of the as-formed PDHQT can be attributed to the solubility of the fresh formed oxidised polymer/oligomers.

When the proportion of DHQT and DNBP was the same (1:1), the cyclic voltammograms recorded during the copolymerisation were similar to the results observed for DHQT (Figure 2b), however an adherent and homogeneous film was deposited onto ITO/glass or Pt. Increasing the concentration of DNBP in the mixture leads to the formation of polymer films electrodeposited at slightly higher oxidation potentials (0.55 V) presenting two redox peaks that tend to overlap as the proportion of DNBP in the copolymer increases. So, the evolution of new redox pairs at potentials different from the potentials of both homopolymers indicated the formation of a copolymer. It seems that a synergic behaviour occurs displacing both the oxidation potential of the DNBP, even in higher proportion of DNBP in the mixture, as well as the E_{pa} and E_{pc} of the copolymer when compared with each

homopolymer. This effect can be explained by the diminution of the steric hindrance caused by the voluminous groups present in DNBP and by the lateral alkyl chains present in DHQT [5,42].

3.2. FTIR spectra

PDHQT, PDNBP and P(DHQT-co-DNBP) films deposited onto Pt were analysed by FTIR spectroscopy (diffuse reflectance) as shown in Figure 3. According to the spectrum recorded for PDHQT, the diagnostic bands at about 3066 and 790 cm^{-1} are attributed to the C-H$_\beta$ stretching and bending vibrations, respectively. The bands at 1500, 1461 and 1376 cm^{-1} originate from the stretching modes of C=C and C–C in the thiophene ring [15,21,43]. Furthermore, vibrations from the C–S bond in the thiophene ring of DHQT appear at 926, 875 and 832 cm^{-1}, which also can be observed for the copolymer main chain independently of the co-monomer proportion used. Moreover it is possible to notice a band at around 1095 cm^{-1} in all spectra attributed to the vibrations corresponding to the BF_4^- anion, used as electrolyte/dopant agent. Bands related to the $(C_4H_9)_4N^+$ cation occur in the same region (2960-2870 cm^{-1}) as the DHQT alkyl chain vibrations and could not be identified.

The FTIR spectrum of PDNBP shows characteristic bands at 1743 and 1670 cm^{-1} that are assigned to the ester and amide C=O stretching, respectively. Both bands can be observed in the spectra of the copolymers in all different comonomer proportions. The bands at 1627, 1453, and 730 cm^{-1} are ascribed to the stretching and bending modes of the benzene ring. Due to the low intensity of the peaks at 1627 and 1453 cm^{-1}, it was not possible to identify them in the spectra of the copolymers, but the peak at 730 cm^{-1} can be seen.

The evolution of the bands in the fingerprint region (Figure 3 inset) with increase of the concentration of DNBP is also interesting. The peaks at 832 and 790 cm^{-1} appear in the spectra of all copolymers, but their intensity decreases with an increase in DNBP

concentration, which infers there is a decrease of DHQT units incorporated into the copolymer. Another interesting feature is the evolution of the bands at around 926, 875 and 725 cm^{-1} (in the PDHQT spectrum) in the spectra of the copolymers. In this case, the peaks move from 926 to 921 cm^{-1}, 875 to 883 cm^{-1} and 725 to 735 cm^{-1} with the increase of the ratio of DNBP in the copolymer. This may be regarded as evidence of copolymerisation distinguishing itself from the simple addition of the spectra of PDHQT and PDNBP indicating that the DNBP units are incorporated into the copolymer chain. Analysis of these results, together with data from the fluorescence spectra, SEM images and cyclic voltammograms, gives evidence that the copolymerisation of DHQT and DNBP was successfully achieved independently of the copolymer's proportion.

3.3. Photoluminescence properties

DHQT and PDHQT are good light emitters while DNBP and PDNBP are not fluorescent, therefore the characterisation of these materials by fluorescence spectroscopy provides additional information about the formation of copolymers. The photoluminescence properties of DHQT and derivatives have previously been reported in the literature [44-46]. The spectra show two emission bands at 450 and 480 nm. Spectra of the solutions of PDHQT and P(DHQT-co-DNBP) in NMP show that they are also fluorescent with two emission bands at 555 and 585 nm when excited at 375 nm, but the photoluminescence intensity decreases when the proportion of DHQT in the copolymer is lowered (Figure 4). Similar behaviour was observed by Yue e*t al.* [47] when they investigated a copolymer of benzanthrone and thiophene in which the emission intensities of the copolymer films dissolved in DMSO decreased as the feed ratios of benzanthrone/thiophene decreased.

It is possible to observe two additional bands at 458 and 488 nm in the spectra of PDHQT, attributed to the presence of oligomers formed during the electropolymerisation

process. These emission bands attributable to oligomers are absent in the copolymer spectra, suggesting that the copolymerisation of DHQT with DNBP avoids the formation of soluble oligomers. Furthermore, the splitting of bands due to vibronic coupling can be clearly seen in the fluorescence spectra of DHQT, PDHQT and of copolymers. This coupling can be attributed to the planarisation of the system upon excitation, *i.e.* the solution ground state is on average twisted, while the excited state is more planar, having greater quinoid character [44,47]. Compared with the DHQT, is it possible to observe a large bathochromic shift in the emission wavelength of PDHQT and all copolymers. This red-shift of emission spectra can be attributed to the higher conjugation of the polymer/copolymer backbone in comparison with the DHQT [48,49]. There is no shift in emission wavelength as the copolymer ratio is changed, suggesting formation of block copolymers. These aspects of the fluorescence of these materials are the subject of ongoing investigation.

3.4. Morphology

The properties of conjugated polymers are strongly dependent on their morphology and structure. According to Turkarslan *et al.* and Nie *et al.* the analysis of the morphology of the polymer and its copolymer films by SEM technique can provide evidence of copolymerisation [24,25]. Therefore, SEM micrographs of PDHQT, PDNBP and copolymer films prepared in different proportions were examined. Figure 5 shows SEM images of each polymer and of the P(DHQT-co-DNBP) deposited onto ITO/glass with 1:5 feed ratio. The morphology of the PDHQT film is sponge-like (Figure 5a) with pores of less than 1 μm diameter. These pores could originate from the dissolution of the oligomers and/or polymer during the electropolymerisation process [9]. On the other hand, the morphology of PDNBP is compact and homogeneous with globular grains (Figure 5c) [32,50]. Meanwhile, the morphology of the copolymer film (Figure 5b) was between PDHQT and PDNBP, further

confirming the occurrence of copolymerisation. For other proportions the morphologies of the copolymers are quite similar, except for the copolymer deposited onto ITO/glass with 1:1 feed ratio. In this case the morphology was the same as PDHQT.

3.5. Spectroelectrochemical characterisation

PDHQT and its copolymer films deposited onto ITO/glass electrodes were characterised by cyclic spectrovoltammetry in monomer-free CH_3CN containing 0.1 mol L^{-1} $(C_4H_9)_4NBF_4$, in order to determine the potential window that would provide the maximum colour contrast and also to measure the wavelengths of maximum absorption (λ_{max}) of the film in the reduced and oxidised states. PDNBP films have already been investigated previously and the results of their spectroelectrochemical characterisation are shown and discussed in refs. [26] and [28].

The cyclic voltammograms of the copolymer films presented the same behaviour shown during the electropolymerisation, *i.e.* the features of the cyclic voltammograms were dependent on the feed ratio of the comonomers. The cyclic voltammogram of P(DHQT-co-DNBP) deposited onto ITO/glass with a 1:1 feed ratio shows similar behaviour of the PDHQT film, presenting just one redox couple with an anodic peak (E_{pa}) at 0.39 V and a cathodic peak (E_{pc}) at 0.32 V *vs.* Ag/Ag^+ (0.1 mol L^{-1} in CH_3CN), while the cyclic voltammograms of the copolymers deposited with 1:3, 1:5 and 1:8 feed ratios show two oxidation peaks and just one broad reduction peak (Figure 6 and Table 1). These two oxidation peaks tend to overlap as the proportion of DNBP increases in the copolymer film. Although PDHQT and P(DHQT-co-DNBP) deposited with 1:1 feed ratio have presented the same E_{pa} and E_{pc} values, it is possible to observe differences in the symmetry between their oxidation and reduction peaks in the cyclic voltammogram. This difference can be attributed to the higher solubility of the PDHQT (oligomers) in comparison with its copolymers.

The changes in the absorbance spectra of the copolymer films as a function of the potential applied to the electrode during cyclic voltammetry are presented in Figure 7. The spectrum of the P(DHQT-co-DNBP) film deposited onto ITO/glass with 1:1 feed ratio is quite similar to the spectrum of the PDHQT film (not shown). Spectroelectrochemical characterisation of PDNBP films was discussed earlier in ref. [26]. Spectra of the copolymer films prepared using 1:3, 1:5 and 1:8 feed ratios presented similar behaviour and exhibited a band with λ_{max} in the range of 440-453 nm in the reduced state (0.0 V). With increasing potential the peak intensity of this band decreases and is displaced to shorter wavelengths. It is possible to observe the formation of a new band at *ca.* 660 nm for the copolymer films prepared using 1:3 or 1:5 feed ratios or at 692 nm for the P(DHQT-co-DNBP) film deposited with 1:8 feed ratio (Table 1). Besides this, a rise in the absorbance in the overall near infrared region (NIR, above 800 nm) was identified for all copolymer films. This reveals the formation of bipolarons, attributed to the highly conducting state of the polymer film [51,52].

As can be seen in Table 1, comparison of the band gap energy (E_g) values (estimated from the optical absorption edge in the onset of the π-π* transition of the film in the neutral state using the Tauc relation [53,54], see Figure S1 in *Supplementary Information*) obtained for PDHQT, the copolymers, and PDNBP shows that introduction of DNBP into the PDHQT chain led to an intermediate λ_{max} value for the copolymers. Furthermore, the E_g value for PDHQT (1.97 eV) is quite lower than that calculated by Facchetti *et al.* [44] for the DHQT (2.88 eV), indicating that even with the dissolution of oligomers during the electropolymerisation process, a conjugated chain is deposited onto the electrode surface.

The description of colour, or the comparison of two colours is a subjective process and it is difficult to describe this accurately. So in order to give a better interpretation of the changes in the spectral absorption bands according to the potential applied to the system, the CIE 1931 *xy* chromaticity coordinates were calculated from the *in situ* spectra of each film

and their trajectories for PDHQT, P(DHQT-co-DNBP) deposited onto ITO/glass in different proportions and PDNBP are shown in Figure 8 (see also Tables S1-S6 and Figure S2 in *Supplementary Information*). It can be clearly seen that whilst the colour variation for the films of PDHQT, PDNBP and P(DHQT-co-DNBP) deposited onto ITO/glass with 1:1 feed ratio is very low, the other copolymer films present a remarkable change in their colour according to the applied potential. In this case, their colours change from orange in the reduced state (0.0 V) through light yellow and finally to green or blue in the reduced state (0.45 V) depending on the proportion of each comonomer used to prepare the films.

The relative luminance (%Y) can offer a different perspective on light transmittance of the film relative to spectroelectrochemistry where a low value of luminance corresponds to an opaque material while a high value is characteristic of a highly transparent material giving a perception of the changes in brightness. So both luminance and chromaticity coordinates provide valuable information that allows the observer to understand changes in the colour of the material [4]. The potential dependence of the relative luminance (Figure 9) shows that PDHQT and P(DHQT-co-DNBP) films deposited onto ITO/glass with 1:1 feed ratio presented similar behaviour with a small variation of the luminance between the reduced and oxidised states. Besides PDNBP film has shown small variation in the luminance values according to the potential applied; their luminance values are lower (*c.a.* 50-60 %) than PDHQT and the 1:1 copolymer indicating that this film is more opaque. However, the changes in brightness are more pronounced in the copolymers deposited onto ITO/glass with 1:3 or 1:5 feed ratios.

The values of the CIELAB 1976 *L*a*b** coordinates for each polymer and their copolymers deposited onto ITO/glass in different proportions are shown in Table 2. *L** can be interpreted as being the lightness variable of the material, while *a** and *b** are concerned with the red-green and yellow-blue saturation of the colour, respectively. The PDHQT and all

copolymer films show positive values for $a*$ (colour perceived as red) and for $b*$ (colour perceived as yellow) in the reduced state, reaching a maximum ($a* = 27$) for the copolymer deposited onto ITO/glass with 1:5 feed ratio. PDHQT and P(DHQT-co-DNBP) deposited onto ITO/glass with 1:1 feed ratio are yellow and the other copolymers are orange in the reduced state. For PDNBP film in the reduced state $a*$ is negative indicating that the perceived colour is green and $b*$ is positive (yellow) giving a yellowish green colour. When the applied potential increases (from 0.00 to 0.45 V), a negative change (towards green) in $a*$ occurs, coupled with a decrease in $b*$ for PDHQT and all copolymer films quantifying the perceived colour state as a combination of green and yellow at 0.45 V. This change is more significant for the copolymer deposited onto ITO/glass with 1:5 feed ratio, where $b*$ changes to negative values (towards blue) and the colour of this copolymer is a combination of green and blue. For PDNBP film in the oxidised state $a*$ and $b*$ values are positive but small and the colour of the film is light blue.

3.6. Electrochromic properties

The electrochromic performance of the copolymer films with respect to chromatic contrast ($\Delta\%T$), coloration efficiency (η) and stability to redox cycles was investigated by double step potential spectrochronoamperometry. As can be seen in Table 1 the λ_{max} of the polymers and its copolymers are different, therefore $\Delta\%T$ and η were measured at different wavelengths (close to their λ_{max}) in order to achieve the highest contrast for each film. For the copolymers deposited onto ITO/glass with 1:3, 1:5 and 1:8 feed ratio, the chromatic contrast ($\Delta\%T$) was 55, 62 and 50 %, respectively (Table 2), which is 30 - 40 % higher than that of the PDNBP deposited onto ITO/glass with $Q_{dep} = 60$ mC cm^{-2} at 485 nm in its first cycle ($\Delta\%T = 11.0$) [26]. The stability of the copolymer film deposited onto ITO/glass with 1:5 feed ratio following long-term switching between the oxidised and reduced states was tested and

showed $\Delta\%T = 17$ % at the 1000th cycle with the changes in the colour still perceived by the eye. Otherwise, when PDHQT or PDNBP films were switched in the same experimental conditions, these films reached just 100 and 350 double step potential cycles, respectively, and presented a severe decrease in the chromatic contrast ($\Delta\%T < 10$ %).

Coloration efficiency, η, was calculated according to Eq. (1) using the data obtained from spectrochronoamperometry experiments at λ_{max} of each sample:

$$\eta(\lambda) = (\log T_b - \log T_c) / Q \tag{1}$$

where T_b is the transmittance of the bleached form at a certain wavelength, T_c the transmittance of the coloured form at the same wavelength and Q the charge density (in C cm^{-2}) necessary to produce the chromatic change.

Coloration efficiency (η) for the copolymer film deposited onto ITO/glass with 1:5 feed ratio was 266 cm^2 C^{-1}, which is *ca.* 10 times higher than the values reached for PDNBP deposited with the same Q_{dep} (60 mC cm^{-2}) [26] and are in accordance with the values cited in the literature for polymers obtained from thiophene and pyrrole derivatives [55,56]. These results suggest that the copolymer films can be used to assemble electrochromic devices, since a relatively small amount of charge injected per unit area is necessary for attainment of a perceptible colour change.

4. Conclusions

Copolymerisation of DHQT and DNBP leads to an interesting combination of the properties observed in the corresponding homopolymers and is an excellent tool for the fine-tuning of colour with a view to electrochromic applications. P(DHQT-co-DNBP) films presented higher chromatic contrast (35 – 62 %) as compared to the homopolymers, but these properties were dependent on the proportion of each comonomer used to prepare the copolymers. Accordingly, this synergic effect observed when the two monomers are

polymerised can be explained by the diminishing of the steric effect of the voluminous groups present in both thiophene and pyrrole derivatives facilitating the electropolymerisation process and permitting that the copolymer can adopt a highly conjugated planar conformation.

Similarly to the analysis of the morphology of the films, the characterisation by fluorescence spectroscopy has helped to obtain additional information about the structure of the copolymer, suggesting the formation of a block copolymer. Furthermore, fluorescence measurements show that the PDHQT and its copolymers with DNBP are good yellow light emitters. The enhanced electrochromic properties of the P(DHQT-co-DNBP) copolymer films are interesting for the application of these materials as active layers in optoelectronic devices, such as displays and smart windows. Therefore, the combination of DHQT and DNBP make these structures useful for promising applications as electrochromic and fluorescent materials.

References

[1] R.J. Mortimer, Organic electrochromic materials, Electrochimica Acta 44 (1999) 2971-2981.

[2] P.M.S. Monk, R.J. Mortimer, D.R. Rosseinsky, Electrochromism: Fundamentals and Applications, VCH, Weinheim, 1995.

[3] I. Schwendeman, R. Hickman, G. Sönmez, P. Schottland, K. Zong, D.M. Welsh, J.R. Reynolds, Enhanced contrast dual polymer elctrochromic devices, Chemistry of Materials 14 (2002) 3118-3122.

[4] B.C. Thompson, P. Schottland, K. Zhong, J.R. Reynolds, In situ colorimetric analysis of electrochromic polymers and devices, Chemistry of Materials 12 (2000) 1563-1571.

[5] K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, D.L. Officer, A multiswitchable poly(terthiophene) bearing a spiropyran functionality: understanding photo- and electrochemical control, Journal of the American Chemical Society 133 (2011) 5453-5462.

[6] J. Roncali, Synthetic principles for band gap control in linear π-conjugated systems, Chemical Reviews 97 (1997) 173-206.

[7] P.M. Beaujuge, J.R. Reynolds, Color control in π-conjugated organic polymers for use in electrochromic devices, Chemical Reviews 110 (2010) 268-320.

[8] R. Holze, Copolymers - A refined way to tailor intrinsically conducting polymers, Electrochimica Acta, 56 (2011) 10479-10492.

[9] P.T. Henderson, D.M. Collard, Thiophene: Alkylthiophene copolymers from substituted dialkyl oligothiophenes, Chemistry of Materials 7 (1995) 1879-1889.

[10] M.C. Gallazzi, L. Castellani, R.A. Marin, G.J. Zerbi, Regiodefined substituted poly(2,5-thienylene)s, Journal of Polymer Science, Part A: Polymer Chemistry 31 (1993) 3339-3349.

[11] D.K. Grant, K.W. Jolley, D.L. Officer, K.C. Gordon, T.M. Clarke, Towards functionalized poly(terthiophenes): regioselective synthesis of oligoether-substituted bis(styryl)sexithiophenes**,** Organic and Biomolecular Chemistry 3 (2005) 2008-2015.

[12] A. Mishra, C.-Q. Ma, P. Baüerle, Functional oligothiophenes: molecular design for multidimensional nanoarchitectures and their applications, Chemical Reviews 109 (2009) 1141-1276

[13] H. Dong, C. Wang, W. Hu, High performance organic semiconductors for field-effect transistors, Chemical Communications (2010) 5211-5222.

[14] M. Jenart, C. Niebel, J.Y. Balandier, J. Leroy, A. Mignolet, S. Stas, A.V. Vooren, J. Cornil, Y.H. Geerts, Quatertiophene-based dimers containing an ethylene bridge: molecular design, synthesis, and optoelectronic properties, Tetrahedron 68 (2012) 349-355.

[15] K. Kotwica, E. Kurach, G. Louarn, A.S. Kostyuchenko, A.S. Fisyuk, M Zagorska, A. Pron, Alternating copolymers of thiadiazole and quaterthiophenes – synthesis, electrochemical and spectroelectrochemical characterization, Electrochimica Acta 111 (2013) 491-498.

[16] J. Ackermann, C. Videlot, P. Rayanal, A. El Kassmi, P. Dumas, Effect of end-substitution of hexyl chains on the growth and electrical properties of quaterthiophene thin films, Applied Surface Science 212-213 (2003) 26-32.

[17] G. Generali, R. Capeli, S. Toffanin, A. Facchetti, M. Muccini, Ambipolar field-effect transistor based on α,ω-dihexylquaterthiophene and α,ω-diperfluoroquaterthiophene vertical heterojunction, Microelectronics Reliability 50 (2010) 1861-1865.

[18] E. Lim, S. Lee, K.K. Lee, I.-N. Kang, S.J. Moon, H.-Y. Kong, H. E. Katz, Solution-processable oligothiophenes with solubilizing β-alkyl groups for organic photovoltaic cells, Solar Energy Materials and Solar Cells 107 (2012) 165-174.

[19] B. Yin, C, Jiang, Y. Wang, M. La, P. Liu, W. Deng, Synthesis and electrochromic properties of oligothiophene derivatives, Synthetic Metals 160 (2010) 432-435.

[20] J. Ackermann, C. Videlot, P. Dumas, A. El Kassmi, R. Guglielmetti, V. Safarov, Control of growth and charge transport properties of quaterthiophene thin films via hexyl chain substitutions, Organic Electronics 5 (2004) 213-222.

[21] M. Lanzi, L. Paganin, D. Caretti, New photoactive oligo- and poly-alkylthiophenes, Polymer 49 (2008) 4942-4948.

[22] C.L. Jones, S.J. Higgins, Symmetrical alkyl-substituted oligothiophenes as ligands: complexation of the $[(\eta\text{-}C_5H_5)Ru]^+$ moiety by hexyl-substituted ter- quater- and quinque-thiophenes, Journal of Materials Chemistry 9 (1999) 865-874.

[23] S. Varis, M. Ak, I.M. Akhmedov, C. Tanyeli, L. Toppare, A novel multielectrochromic copolymer based on 1-(4-nitrophenyl)-2,5-di(2-thienyl)-1H-pyrrole and EDOT, Journal of Electroanalytical Chemistry 603 (2007) 8-14.

[24] O. Turkarslan, M. Ak, C. Tanyeli, I.M. Akhmedov, L. Toppare, Enhancing electrochromic properties of conducting polymers via copolymerization: copolymer of 1-(4-fluorophenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole with 3,4-ethylene dioxythiophene, Journal of Polymer Science: Part A: Polymer Chemistry 45 (2007) 4496-4503.

[25] G. Nie, L. Qu, J. Xu, S. Zhang, Electrosynthesis and characterizations of a new soluble conducting copolymer of 5-cyanoindole and 3,4-ethylenedioxythiophene, Electrochimica Acta 53 (2008) 8351-8358.

[26] A.S. Ribeiro, A.U. da Silva, M. Navarro, J. Tonholo, Electrochromism of dinitrobenzoyl-derivatised polypyrrole films deposited on ITO/glass electrodes, Electrochimica Acta 51 (2006) 4892-4896.

[27] A.J.C. da Silva, F.A.R. Nogueira, J. Tonholo, A.S. Ribeiro, Dual-type electrochromic device based on polypyrrole and polythiophene derivatives, Solar Energy Materiais and Solar Cells 95 (2011) 2255-2259.

[28] A.J.C. Silva, S.M.F. Ferreira, D.P. Santos, M. Navarro, J. Tonholo, A.S. Ribeiro, A multielectrochromic copolymer based on pyrrole and thiophene derivatives, Solar Energy Materials and Solar Cells 103 (2012) 108-113.

[29] A.S. Ribeiro, A. Kanazawa, D.M.A.F. Navarro, J.-C. Moutet, M. Navarro, Synthesis of (R)-(−) and (S)-(+)-3-(1-pyrrolyl)propyl-N-(3,5-dinitrobenzoyl)-α-phenylglycinate and derivatives. A suitable chiral polymeric phase precursor, Tetrahedron Asymmetry 10 (1999) 3735–3745.

[30] G. Gritzner, J. Kuta, Recommendations on reporting electrode potentials in nonaqueous solvents, Pure and Applied Chemistry 56 (1984) 461-466.

[31] J.N. Barisci, R. Stella, G.M. Spinks, G.G. Wallace, Characterisation of the topography and surface potential of electrodeposited conducting polymer films using atomic force and electric force miscroscopies, Electrochimica Acta 46 (2000) 519-531.

[32] A.S. Ribeiro, A.U. Silva, L.M.O. Ribeiro, J.G. Silva Jr., M. Navarro, J. Tonholo, Electrochemical and morphological characterization of poly[(R)-(-)-3-(l-pyrrolyl)propyl-N-(3,5-dinitrobenzoyl)-α-phenylglycinate] films deposited on ITO electrodes, Journal of Electroanalytical Chemistry 580 (2005) 313–319.

[33] G. Wyszecki, W.S. Stiles, Color Science: Concepts and Methods, Quantitative Data and Formulae, 2nd ed., John Wiley and Sons, New York, 1982.

[34] R.J. Mortimer, T.S. Varley, Quantification of colour stimuli through the calculation of CIE chromaticity coordinates and luminance data for application to in situ colorimetry studies of electrochromic materials, Displays 32 (2011) 35-44.

[35] R.J. Mortimer, T.S. Varley, *In situ* spectroelectrochemistry and colour measurement of a complementary electrochromic device based on surface-confined Prussian blue and aqueous solution-phase methyl viologen, Solar Energy Materials and Solar Cells 99 (2012) 213-220.

[36] R.J. Mortimer, K.R. Graham, C.R.G. Grenier, J.R. Reynolds, Influence of the film thickness and morphology on the colorimetric properties of spray-coated electrochromic disubstituted 3,4-Propylenedioxythiophene polymers, ACS Applied Materials and Interfaces 1 (2009) 2269-2276.

[37] P.A. Santa-Cruz, F.S. Teles, Spectra Lux Software v.2.0 Beta, Ponto Quântico Nanodispositivos 2003, RENAMI.

[38] R.M. Latonen, C. Kvarnström, A. Ivaska, Electrochemical synthesis of a copolymer of poly(3-octylthiophene) and poly(paraphenylene), Electrochimica Acta 44 (1999) 1933-1943.

[39] X.B. Wan, W. Zhang, S. Jin, G. Xue, Q.D. You, B. Che, The electrochemical copolymerization of pyrrole and furan in a novel binary solvent system, Journal of Electroanalytical Chemistry 470 (1999) 23-30.

[40] S. Kuwabata, S. Ito, H. Yoneyama, Copolymerization of pyrrole and thiophene by electrochemical oxidation and electrochemical behavior of the resulting copolymers, Journal of the Electrochemical Society 135 (1988) 1691-1695.

[41] G. Zotti, M.C. Gallazzi, G. Zerbi, S.V. Meille, Conducting polymers from anodic coupling of some regiochemically defined dialkoxy-substituted thiophene oligomers, Synthetic Metals 73 (1995) 217-225.

[42] N. Xiang, Y. Liu, W. Zou, H. Huang, X. Guo, Z. Tan, B. Zhao, P. Shen, S. Tan, Synthesis and characterization of porphyrin-terthiophene and oligothiophene π-conjugated copolymers for polymer solar cells, European Polymer Journal 46 (2010) 1084-1092.

[43] K.I. Seo, I.J. Chung, Reaction analysis of 3,4-ethylenedioxythiophene with potassium persulfate in aqueous solution by using a calorimeter, Polymer 41 (2000) 4491-4499.

[44] A. Facchetti, M.-H. Yoon, C.L. Stern, G.R. Hutchison, M.A. Ratner, T.J. Marks, Building blocks for n-type molecular and polymeric electronics. Perfluoroalkyl- versus alkyl-functionalized oligothiophenes (nTs; n = 2-6). Systematic synthesis, spectroscopy, electrochemistry, and solid-state organization, Journal of the American Chemical Society 126 (2004) 13859-13874.

[45] J. Wan, A. Ferreira, W. Xia, C.H. Chow, K. Takechi, P.V. Kamat, G. Jones II, V.I. Vullev, Solvent dependence of the charge-transfer properties of a quaterthiophene-anthraquinone dyad, Journal of Photochemistry and Photobiology A: Chemistry 197 (2008) 364-374.

[46] M. Jenard, C. Niebel, J.-Y. Balandier, J. Leroy, A. Mignolet, S. Stas, A.V. Vooren, J. Cornil, Y.H. Geerts, Quaterthiophene-based dimers containing an ethylene bridge: molecular design, synthesis and optoelectronic properties, Tetrahedron 68 (2012) 349-355.

[47] R.-r. Yue, J.-k. Xu, B.-y. Lu, C.-c. Liu, Z.-j. Zhu, Z. Zhang, Electrosyntheses and characterization of a fluorescent conducting polymer of benzanthrone and thiophene, Chinese Journal of Polymer Science 28 (2010) 771-780.

[48] X. Xie, W. Lei, X. Liu, Q. Hao, M. Xia, F. Wang, W. Si, Facile electrosynthesis of poly (pyrene-1-sulfonic acid sodium salt) film: A good candidate for blue light-emitting diodes applications, Materials Letters 65 (2011) 1234–1237.

[49] B.Y. Lu, J.K. Xu, C.I. Fan, F.X. Jiang, H.M. Miao, Facile electrosynthesis of nitro-group-substituted oligopyrene with bicolored emission, Electrochimica Acta 54 (2008) 334–340.

[50] A.S. Ribeiro, L.M.O. Ribeiro, J.G. Silva Jr., M. Navarro, J. Tonholo, Characterization by Atomic Force Microscopy of electrodeposited films of polypyrrole dinitrobenzoyl-derivative, Microscopy and Microanalysis 11 (supp 3) (2005) 146-149.

[51] M. Sato, S. Tanaka, K. Kaeriyama, Electrochemical preparation of conducting poly(3-methylthiophene): comparison with polythiophene and poly (3-ethylthiophene), Synthetic Metals 14 (1986) 279–288.

[52] T.C. Chung, J.H. Kaufman, A.J. Heeger, F. Wudl, Charge Storage in Doped Poly(thiophene): Optical and Electrochemical Studies, Physical Reviews B 30 (1984) 702–710.

[53] J. Tauc, R. Grigorovici, A. Vancu, Optical properties and electronic structure of amorphous germanium, Physica Status Solidi B 15 (1966) 627-637.

[54] A. Misra, P. Kumar, R. Srivastava, S.K. Dhawan, M.N. Kamalasanan, S. Chandra, Electrochemical and optical studies of conjugated polymers for three primary colours, Indian Journal of Pure and Applied Physics 43 (2005) 921-925.

[55] G.E. Gumbas, P. Camurlu, I.M. Akhmedov, C. Taniely, A.M. Önal, L. Toppare, A fast switching, low band gap, p- and n- dopable, donor-acceptor type polymer, Journal of Electroanalytical Chemistry 615 (2008) 75-83.

[56] P. Data, P. Zassowski, M. Lapkowski, W. Domagala, S. Krompiec, T. Flak, M. Penkala, A. Swist, J. Soloducho, W. Danikiewicz, Electrochemical and spectroelectrochemical comparison of alternated monomers and their copolymers based on carbazole and thiophene derivatives, Electrochimica Acta 122 (2014) 118-129.

Table 1. Anodic peak potential (E_{pa}), cathodic peak potential (E_{pc}), λ_{max} at reduced (0.0 V) and oxidised (0.45 V) states and band gap energy (E_g) of the copolymer films prepared using different feed ratios.
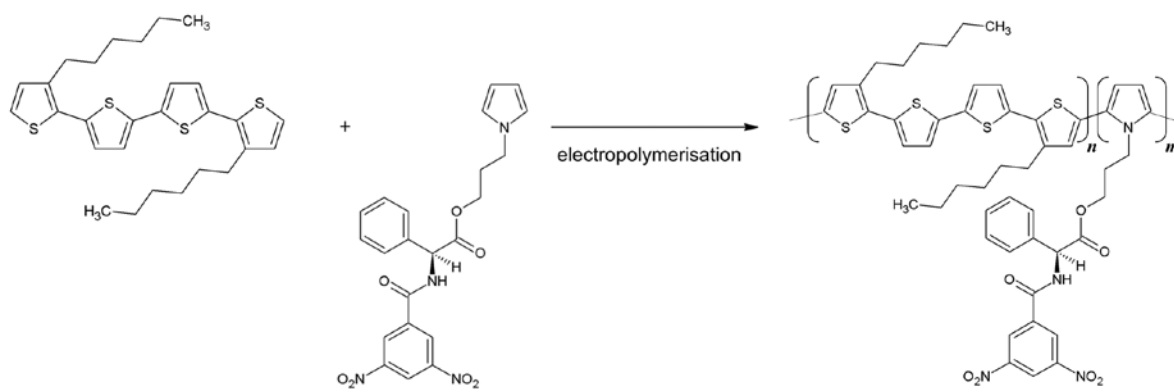
	Epa_I (V)	Epa_{II} (V)	Epc_I (V)	λ_{max} (nm)		E_g (eV)[a]
				0.0 V	0.45 V	
PDHQT	0.39	-	0.32	381, 474[b]	381, 638	1.97
P(DHQT-co-DNBP) 1:1	0.39	-	0.32	380, 475[b]	380, 641	2.08
P(DHQT-co-DNBP) 1:3	0.27	0.33	0.25	446	390, 659	2.11
P(DHQT-co-DNBP) 1:5	0.24	0.30	0.24	453	459, 657	2.11
P(DHQT-co-DNBP) 1:8	0.23	0.30	0.24	440	431,692	2.10
PDNBP	0.35	-	0.27	350, 390[a]	460	2.38

[a] calculated from the onset of the π–π* transition; [b] shoulder.

Table 2. Colorimetry and electrochromic properties of the polymers and its copolymer films deposited onto ITO/glass with different feed ratios.

	E (V)	L^*	a^*	b^*	$\Delta\%T$	η (cm^2 C^{-1})
PDHQT	0.00	92	2	30	22[a]	82[a]
	0.45	87	-6	13		
P(DHQT-co-DNBP) 1:1	0.00	87	8	30	35[a]	110[a]
	0.45	83	-6	11		
P(DHQT-co-DNBP) 1:3	0.00	78	31	104	55[b]	150[b]
	0.45	51	-13	14		
P(DHQT-co-DNBP) 1:5	0.00	73	27	82	62[b]	266[b]
	0.45	50	-12	-1		
P(DHQT-co-DNBP) 1:8	0.00	76	19	73	50[c]	148[c]
	0.45	60	-4	23		
PDNBP	0.00	83	-1	5	11[d]	30[d]
	0.45	78	1	5		

[a] Calculated at $\lambda = 640$ nm, [b] calculated at $\lambda = 660$ nm, [c] calculated at $\lambda = 700$ nm, [d] calculated at $\lambda = 485$ nm.
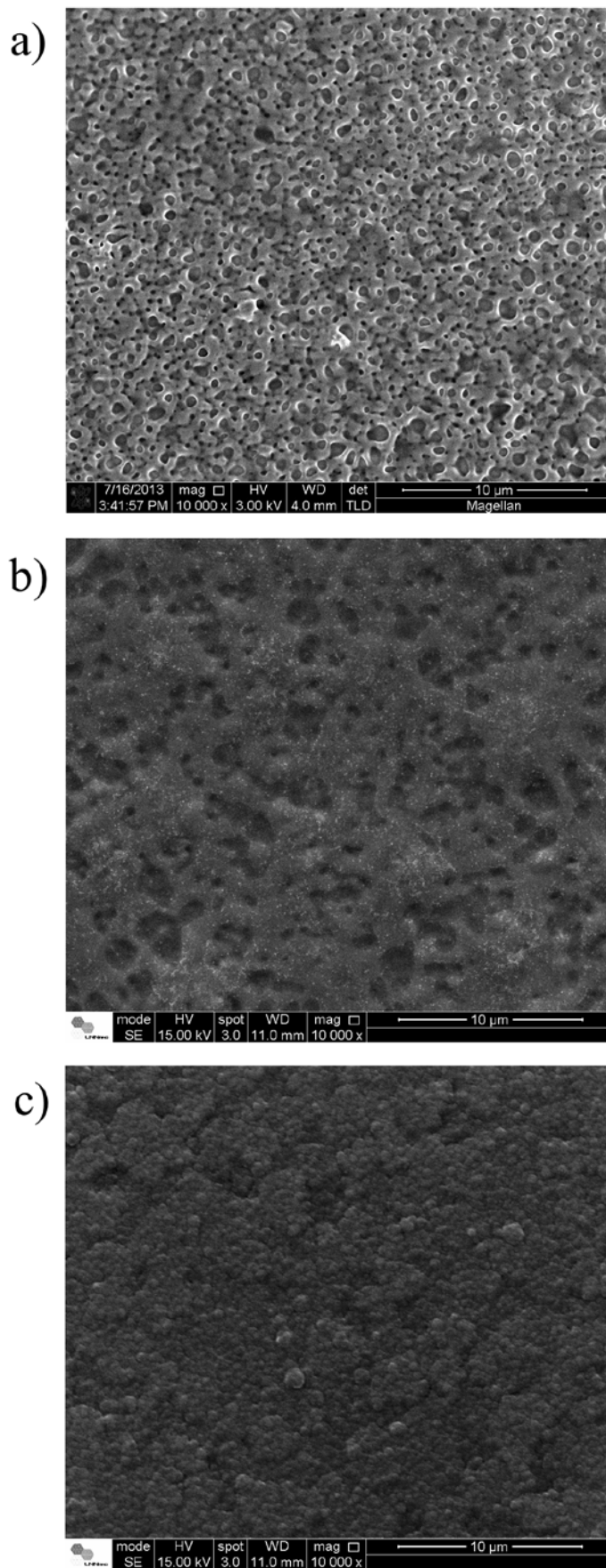
Scheme 1
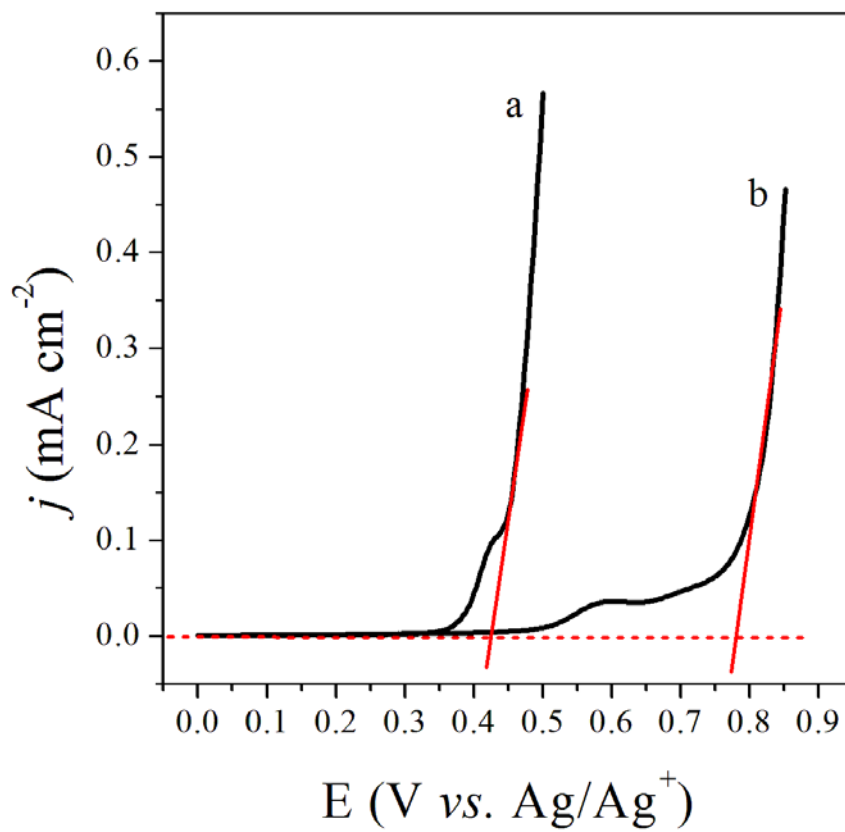
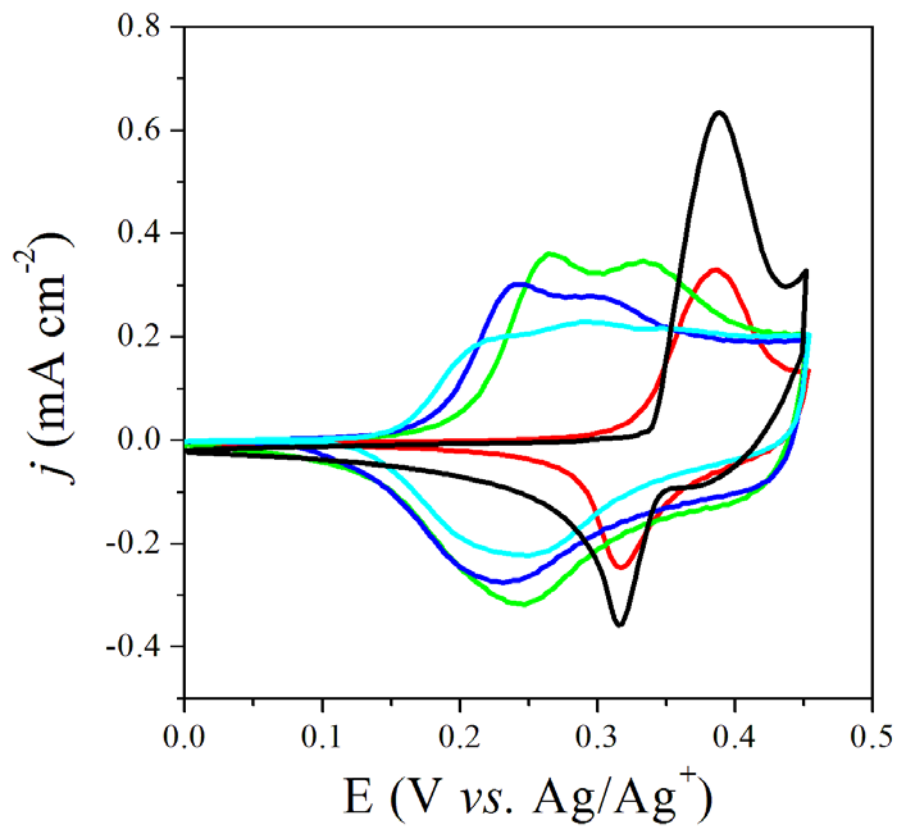**Figure 1**
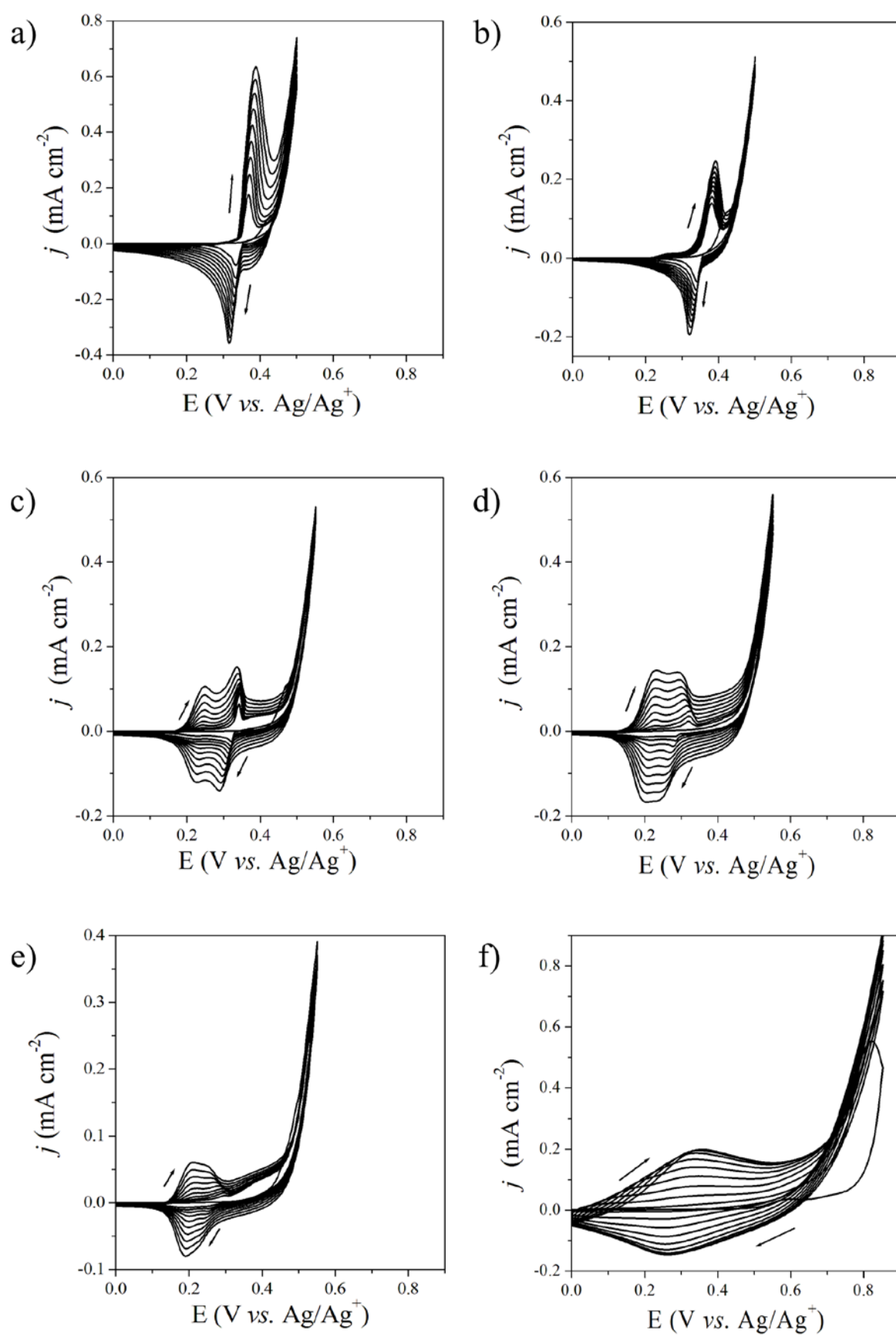
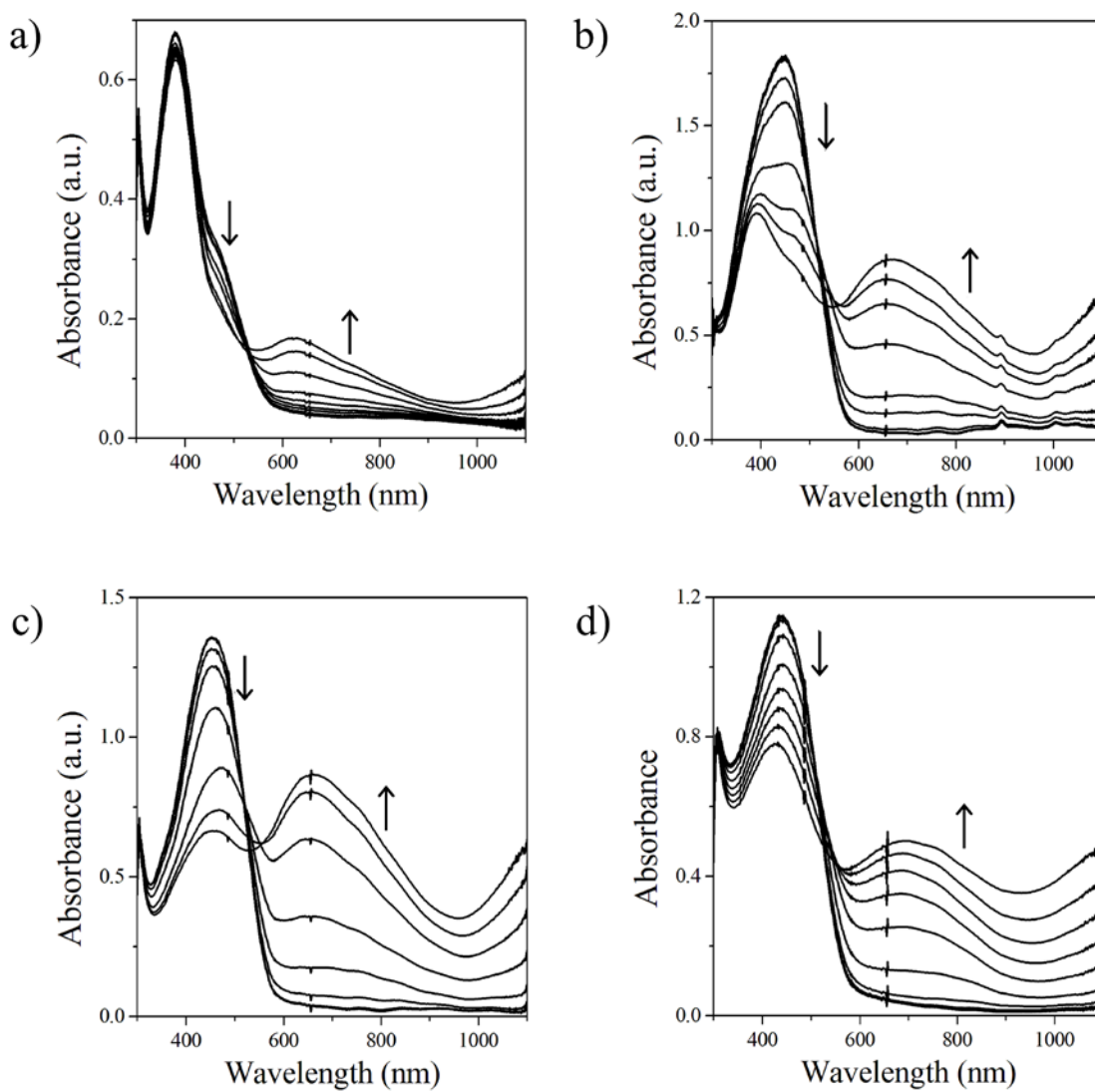**Figure 2**
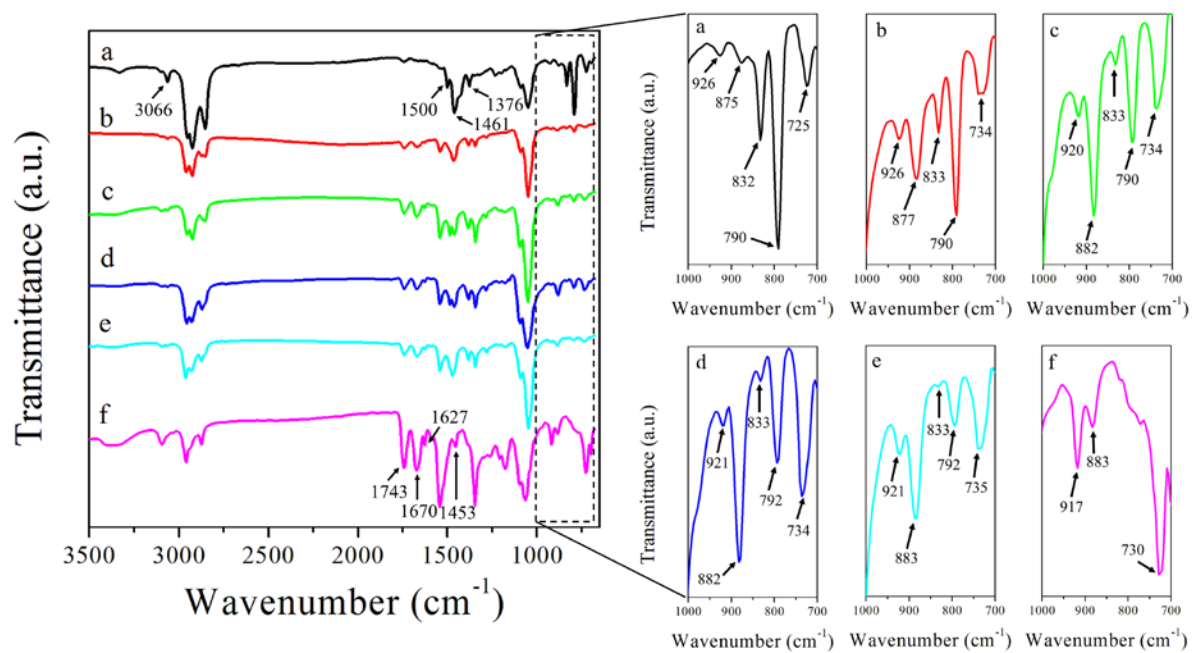
Figure 3
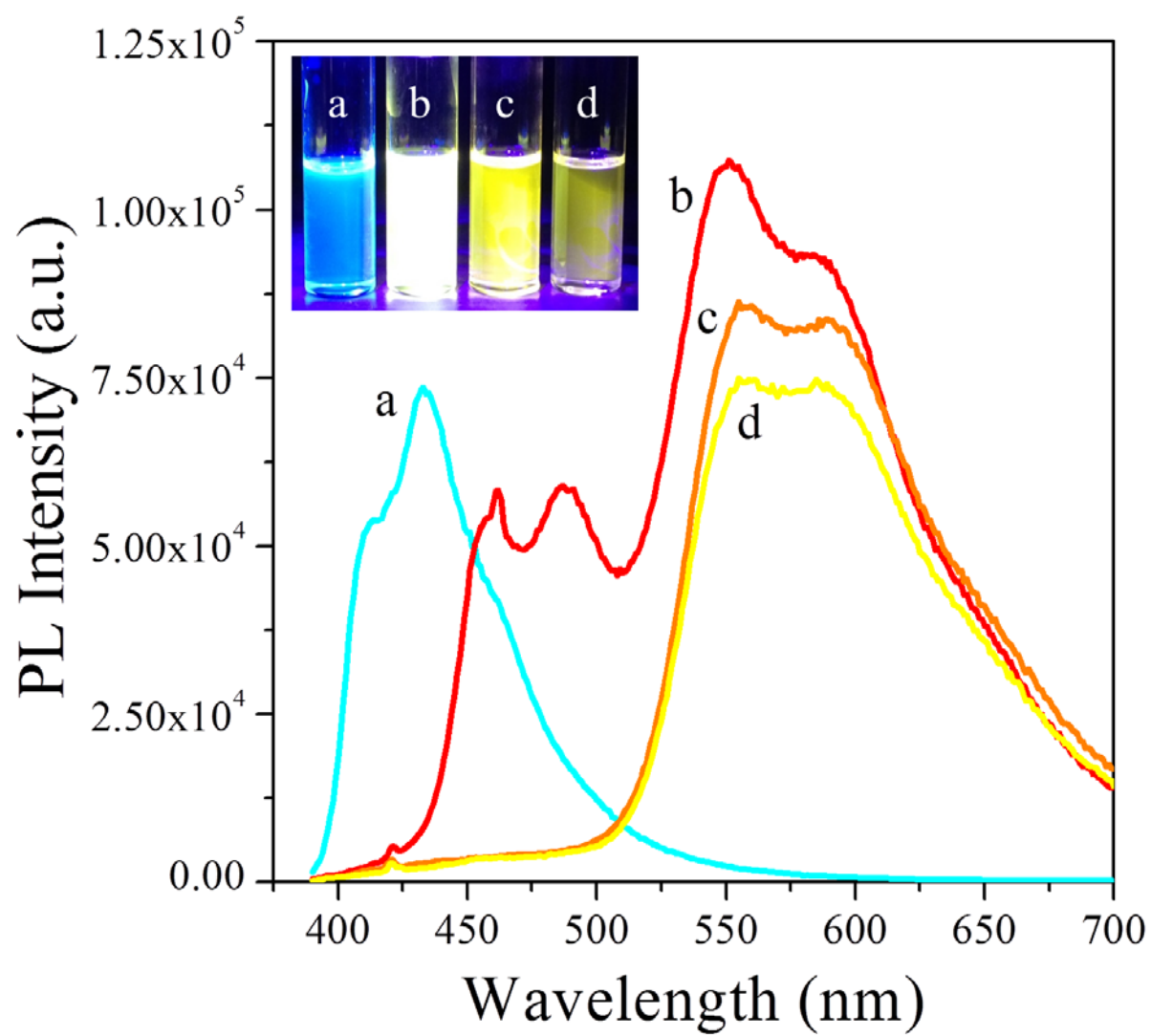
Figure 4

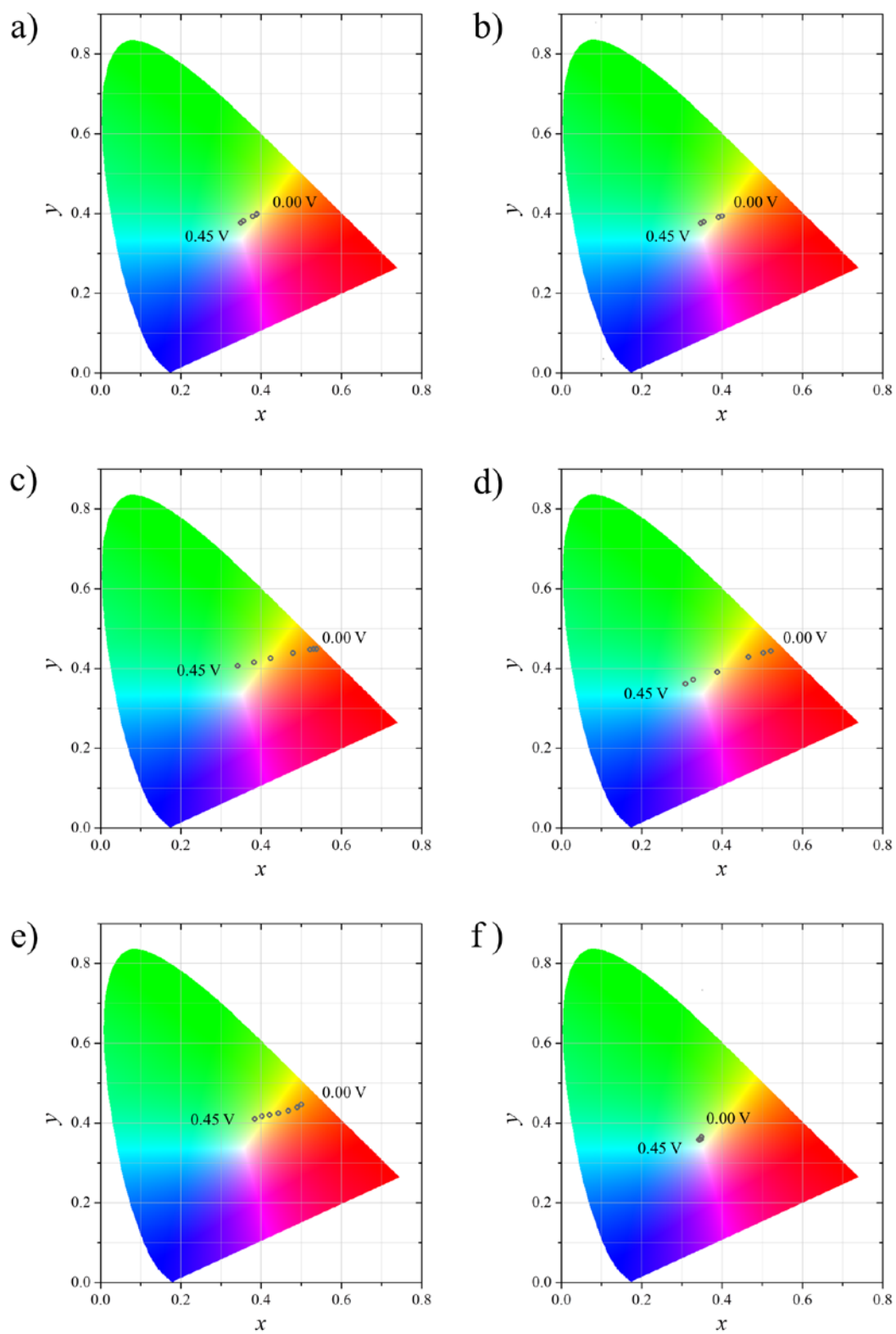**Figure 5**

Figure 6

Figure 7
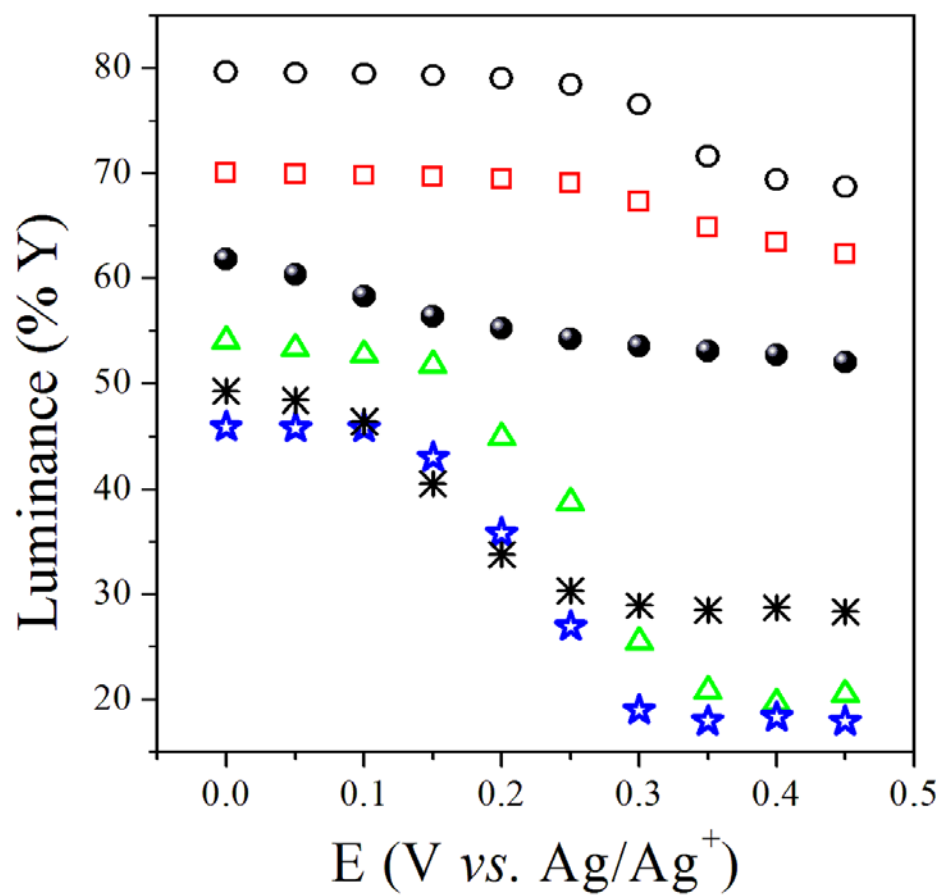
Figure 8

Figure 9

Figure Captions

Scheme 1. Electrochemical copolymerisation of DHQT and DNBP.

Figure 1. Anodic polarisation curves of (a) DHQT and (b) DNBP in 0.1 mol L^{-1} (C$_4$H$_9$)NBF$_4$/CH$_3$CN, ν = 20 mV s^{-1}.

Figure 2. Cyclic voltammograms of (a) DHQT, (b) 1:1, (c) 1:3, (d) 1:5 and (e) 1:8 DHQT:DNBP molar concentration proportions (feed ratios), and (**f**) DNBP in 0.1 mol L^{-1} (C$_4$H$_9$)NBF$_4$/CH$_3$CN, ν = 20 mV s^{-1}.

Figure 3. FTIR spectra for (a) PDHQT, P(DHQT-co-DNBP) with (b) 1:1, (c) 1:3, (d)1:5 and (e) 1:8 feed ratios, and (f) PDNBP films deposited onto Pt. Inset: Expanded view of the finger print region.

Figure 4. Emission spectra of (a) DHQT, (b) PDHQT, P(DHQT-co-DNBP) prepared with (c) 1:1 and (d) 1:5 feed ratios, in NMP solution (excitation at 375 nm). Inset: photoluminescence of (a) DHQT, (b) PDHQT, P(DHQT-co-DNBP) prepared with (c) 1:1 and (d) 1:5 feed ratios, in NMP solution, when exposed to UV light.

Figure 5. SEM images of (a) PDHQT, (b) P(DHQT-co-DNBP) deposited onto ITO/glass with 1:5 feed ratio and (c) PDNBP.

Figure 6. Cyclic voltammograms of PDHQT (—) and P(DHQT-co-DNBP) films deposited onto ITO/glass in (—) 1:1, (—) 1:3, (—) 1:5 and (—) 1:8 feed ratios in 0.1 mol L^{-1} $(C_4H_9)NBF_4/CH_3CN$, $\nu = 20$ mV s^{-1}.

Figure 7. Spectroelectrochemical characterisation of the P(DHQT-co-DNBP) films deposited onto ITO/glass with (a) 1:1, (b) 1:3, (c) 1:5 and (d) 1:8 feed ratio in $(C_4H_9)_4NBF_4$ / CH_3CN 0.1 mol L^{-1} showing absorbance as a function of the applied potential from 0.00 to 0.45 V in 0.05 V intervals.

Figure 8. Calculated colour trajectory in the CIE 1931 colour space for (a) PDHQT, P(DHQT-co-DNBP) films deposited onto ITO/glass with (b) 1:1, (c) 1:3, (d) 1:5 and (e) 1:8 feed ratios and (f) PDNBP.

Figure 9. Relative luminance (%Y) *vs.* applied potential of (○) PDHQT, P(DHQT-co-DNBP) films deposited onto ITO/glass with (□) 1:1, (△) 1:3, (★) 1:5 and (✳) 1:8 feed ratios and (◕) PDNBP.

Table 1. Anodic peak potential (E_{pa}), cathodic peak potential (E_{pc}), λ_{max} at reduced (0.0 V) and oxidised (0.45 V) states and band gap energy (E_g) of the copolymer films prepared using different feed ratios.

	Epa_I (V)	Epa_{II} (V)	Epc_I (V)	λ_{max} (nm)		E_g (eV)[a]
				0.0 V	0.45 V	
PDHQT	0.39	-	0.32	381, 474[b]	381, 638	1.97
P(DHQT-co-DNBP) 1:1	0.39	-	0.32	380, 475[b]	380, 641	2.08
P(DHQT-co-DNBP) 1:3	0.27	0.33	0.25	446	390, 659	2.11
P(DHQT-co-DNBP) 1:5	0.24	0.30	0.24	453	459, 657	2.11
P(DHQT-co-DNBP) 1:8	0.23	0.30	0.24	440	431,692	2.10
PDNBP	0.35	-	0.27	350, 390[a]	460	2.38

[a] calculated from the onset of the π–π* transition; [b] shoulder.

Table 2. Colorimetry and electrochromic properties of the polymers and its copolymer films deposited onto ITO/glass with different feed ratios.

	E (V)	L^*	a^*	b^*	$\Delta\%T$	η (cm^2 C^{-1})
PDHQT	0.00	92	2	30	22[a]	82[a]
	0.45	87	-6	13		
P(DHQT-co-DNBP) 1:1	0.00	87	8	30	35[a]	110[a]
	0.45	83	-6	11		
P(DHQT-co-DNBP) 1:3	0.00	78	31	104	55[b]	150[b]
	0.45	51	-13	14		
P(DHQT-co-DNBP) 1:5	0.00	73	27	82	62[b]	266[b]
	0.45	50	-12	-1		
P(DHQT-co-DNBP) 1:8	0.00	76	19	73	50[c]	148[c]
	0.45	60	-4	23		
PDNBP	0.00	83	-1	5	11[d]	30[d]
	0.45	78	1	5		

[a] Calculated at $\lambda = 640$ nm, [b] calculated at $\lambda = 660$ nm, [c] calculated at $\lambda = 700$ nm, [d] calculated at $\lambda = 485$ nm.
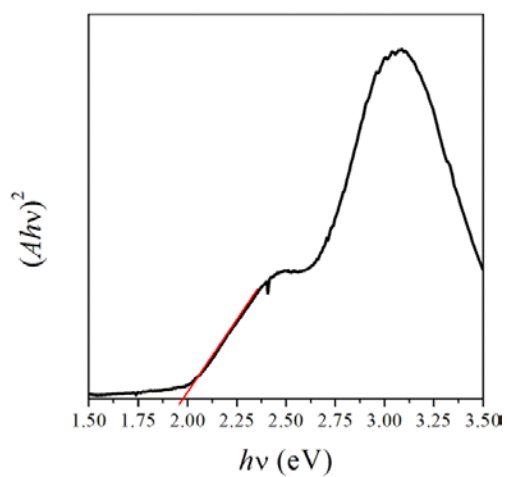
Supplementary Information

Calculation of E_g

The band gap energy (E_g) values of each polymer and its copolymers were estimated from the optical absorption edge on the onset of π-π* transition of the film in the neutral state using the Tauc relation.
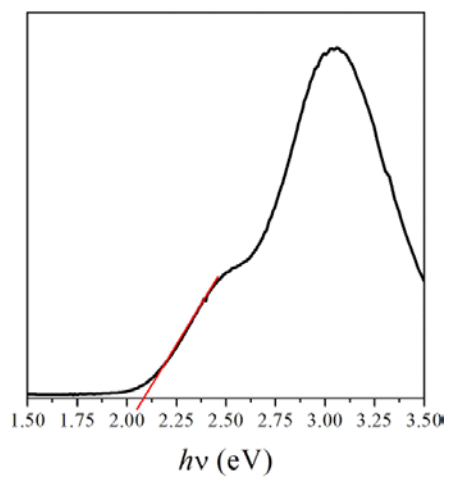
$A h\nu = (h\nu - E_g)^n$

Where A is the absorbance, $h\nu$ is the photon energy and n is ½ for allowed direct transitions in the material. The E_g of the polymers and copolymers were obtained from extrapolation of the straight line portion of their $(A h\nu)^2$ *vs.* $h\nu$ plots to $A = 0$ as shown in Figure 1S.
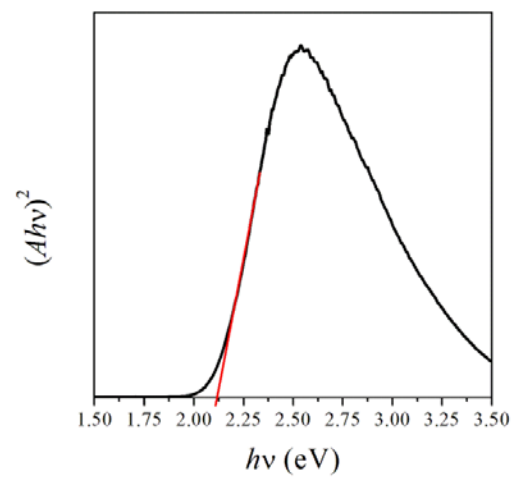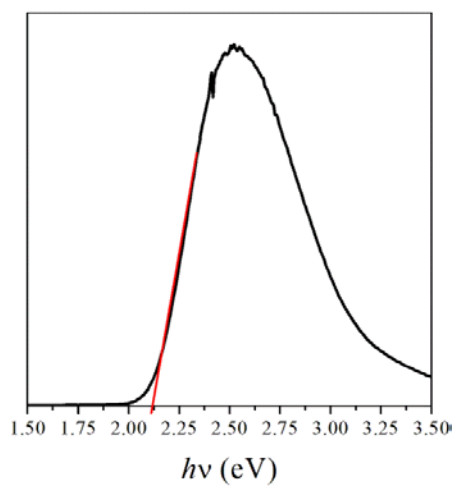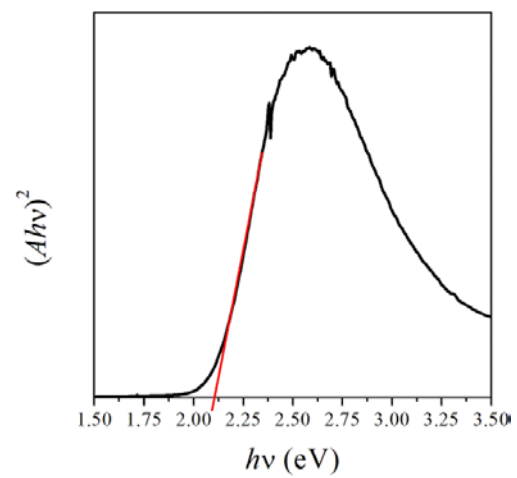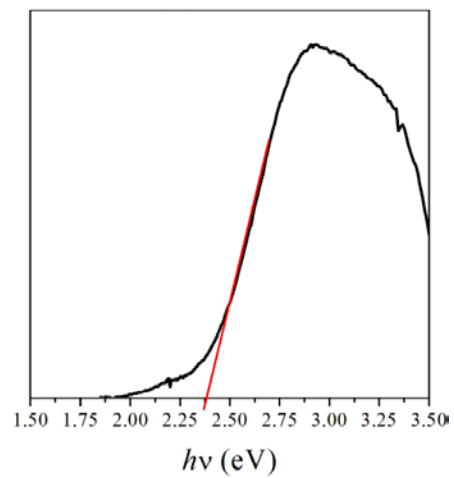
Figure S1 (*Supplementary Information*): Absorbance squared versus the photon energy (hν) extrapolated to zero absorption of the (a) PDHQT, P(DHQT-co-DNBP) deposited with (b) 1:1, (c) 1:3, (d) 1:5 and (e) 1:8 feed ratio, and PDNBP films.

Colorimetric data

All colorimetric data for the polymer and copolymer films are shown in Tables S1 – S6. Figure 2 shows an expanded region in the CIE 1931 colour space for each polymer and copolymer.

Table S1. Numerical chromaticity coordinates for PDHQT films deposited onto ITO/glass according to the applied potential.

E (V)	x	y	%Y	L*	a*	b*
0.00	0.386	0.398	79.66	92	2	30
0.05	0.387	0.398	79.54	91	2	30
0.10	0.387	0.398	79.44	91	2	30
0.15	0.387	0.398	79.28	91	2	30
0.20	0.387	0.398	79.04	91	2	30
0.25	0.385	0.397	78.43	91	2	29
0.30	0.376	0.392	76.55	90	0	25
0.35	0.353	0.381	71.63	88	-5	16
0.40	0.353	0.380	69.39	87	-5	16
0.45	0.347	0.376	68.66	87	-6	13

Table S2. Numerical chromaticity coordinates for P(DHQT-co-DNBP) films deposited onto ITO/glass with 1:1 feed ratio according to the applied potential.

E (V)	x	y	%Y	L*	a*	b*
0.00	0.397	0.393	70.03	87	8	30
0.05	0.397	0.393	69.87	87	8	30
0.10	0.397	0.393	68.78	87	8	30
0.15	0.397	0.393	69.62	87	8	30
0.20	0.397	0.393	69.39	87	8	30
0.25	0.397	0.393	69.04	87	8	29
0.30	0.388	0.389	67.29	86	6	26
0.35	0.361	0.381	64.81	84	-1	17
0.40	0.352	0.378	63.41	84	-4	14

| 0.45 | 0.344 | 0.375 | 62.29 | 83 | -6 | 11 |

Table S3. Numerical chromaticity coordinates for P(DHQT-co-DNBP) films deposited onto ITO/glass with 1:3 feed ratio according to the applied potential.

| E (V)	x	y	%Y	L*	a*	b*
0.00	0.533	0.448	54.02	78	31	104
0.05	0.533	0.447	53.29	78	31	103
0.10	0.533	0.447	52.68	78	31	103
0.15	0.533	0.447	51.72	77	30	102
0.20	0.526	0.446	44.89	73	27	92
0.25	0.518	0.446	38.68	69	24	81
0.30	0.476	0.438	25.44	57	14	51
0.35	0.420	0.424	20.76	53	4	31
0.40	0.379	0.414	20.43	52	-4	21
0.45	0.339	0.406	19.58	51	-13	14

Table S4. Numerical chromaticity coordinates for P(DHQT-co-DNBP) films deposited onto ITO/glass with 1:5 feed ratio according to the applied potential.

E (V)	x	y	%Y	L*	a*	b*
0.00	0.517	0.442	45.87	73	27	82
0.05	0.517	0.442	45.81	73	27	82
0.10	0.517	0.442	44.98	73	27	82
0.15	0.515	0.440	43.00	71	26	82
0.20	0.499	0.437	35.77	66	22	82
0.25	0.462	0.428	26.90	59	13	45
0.30	0.385	0.390	18.94	51	3	17
0.35	0.326	0.370	18.28	50	-8	4
0.40	0.303	0.360	17.91	49	-9	2
0.45	0.317	0.365	17.87	49	-12	-1

Table S5. Numerical chromaticity coordinates for P(DHQT-co-DNBP) films deposited onto ITO/glass with 1:8 feed ratio according to the applied potential.

| E (V)	x	y	%Y	L*	a*	b*
0.00	0.491	0.445	49.23	76	19	73
0.05	0.491	0.444	48.41	75	19	72
0.10	0.490	0.442	46.38	74	19	70
0.15	0.481	0.437	40.54	70	18	61
0.20	0.459	0.429	33.72	65	13	48
0.25	0.435	0.423	30.29	62	8	38
0.30	0.413	0.419	28.89	61	3	32
0.35	0.394	0.415	28.67	60	-1	27
0.40	0.377	0.409	28.50	60	-3	24
0.45	0.382	0.411	28.33	60	-4	23

Table S6. Numerical chromaticity coordinates for PDNBP films deposited onto ITO/glass according to the applied potential.

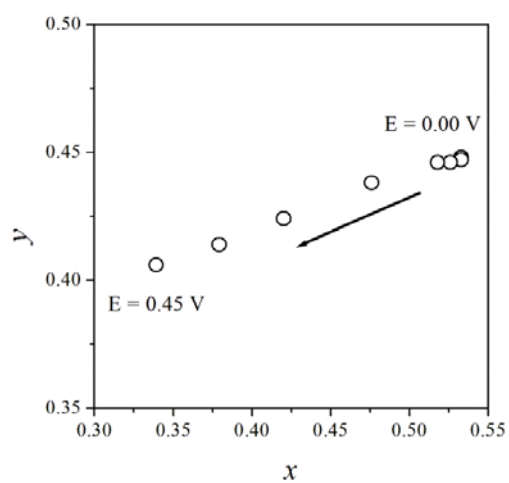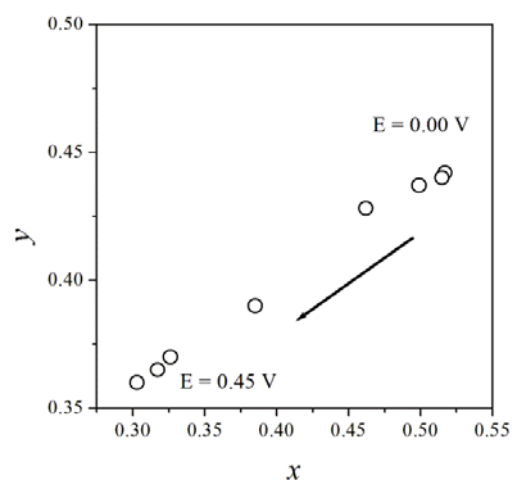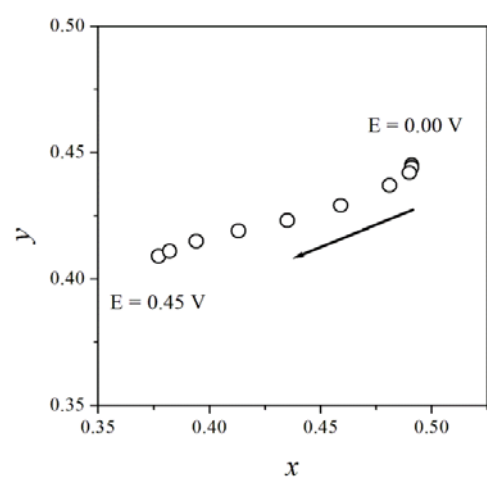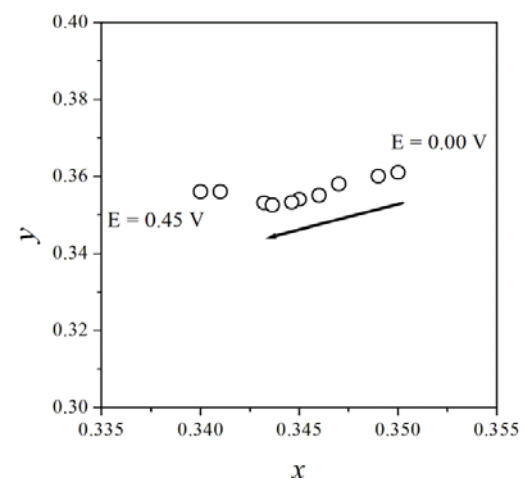| E (V)	x	y	%Y	L*	a*	b*
0.00	0.350	0.361	61.80	83	-1	5
0.05	0.349	0.360	60.35	82	0	5
0.10	0.347	0.358	58.28	81	1	4
0.15	0.346	0.355	56.36	80	2	4
0.20	0.345	0.354	55.18	79	3	4
0.25	0.345	0.353	54.24	79	3	4
0.30	0.344	0.352	53.53	78	2	4
0.35	0.343	0.353	53.05	78	1	4
0.40	0.341	0.356	52.69	78	1	5
0.45	0.340	0.356	52.00	78	1	5

a)
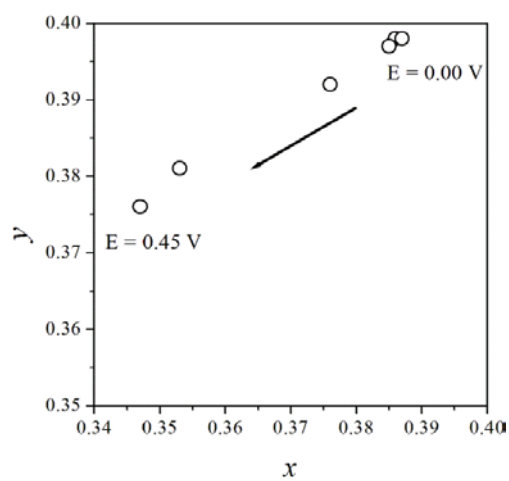
b)
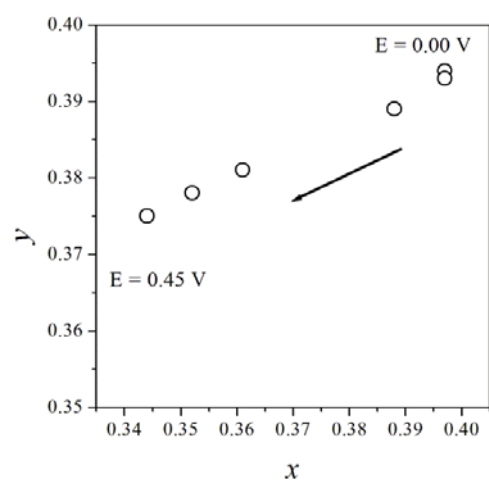
c)

d)

e)

f)

Figure S2 (*Supplementary Information*): Expanded graphs of the calculated colour trajectory in the CIE 1931 colour space for (a) PDHQT, P(DHQT-co-DNBP) films deposited onto ITO/glass with (b) 1:1, (c) 1:3, (d) 1:5 and (e) 1:8 feed ratios and (f) PDNBP film.