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# The synthesis of new donor–acceptor polymers containing the 2,3-di (2-furyl) quinoxaline moiety: Fast-switching, low-band-gap, p- and n-dopable, neutral green-colored materials



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# ABSTRACT

Three donor–acceptor type  $\pi$ -conjugated polymers were synthesized electrochemically:poly[2,3-di(2-furyl)-5,8-bis(2-(3,4-ethylenedioxythiophene)) quinoxaline] (PFTQ), poly[2,3-di(2-furyl)-5,8-bis(2-thienyl) quinoxaline] (PFTQ) and poly[2,3-di(2-furyl)-5,8-bis(2-(3-methoxythiophene)) quinoxaline] (PFMTQ). All of the synthesized polymers, contained the 2,3-di(2-furyl) quinoxaline moiety in the backbone as the acceptor unit and different thiophene derivatives as the donor units. The electroactivity of the monomers and the electrochemical properties of their polymers were investigated by cyclic voltammetry. The presence of the strong electron-donating ethylenedioxy and methoxy groups on the aromatic structure increased the electron density. Thus, the oxidation potential of FETQ and FMTQ shifted to a lower value than that of FTQ. The optical properties of the polymers were investigated by UV-vis-NIR spectroscopy. Both PFETQ and PFMTQ reveal two distinct absorption bands in the red and blue regions of the visible spectrum, while PFTQ has only one dominant wavelength at 596 nm in the visible region. The colorimetry analysis revealed that while PFTQ has a light blue color, PFETQ and PFMTQ are green in the neutral state. The optical band gaps, defined as the onset of the  $\pi$ - $\pi$ \* transition, were found to be 1.15 eV for PFETQ, 1.2 eV for PFMTQ and 1.34 eV for PFTQ. Moreover, all three polymers showed both n-doping and fast switching times.

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# 1. Introduction

Since the discovery of the fact that polyacetylene can reach high electrical conductivity when doped, [1] conductive polymers have become a major research interest in both the academic and industry fields. Among the conductive polymers, electrochromic (EC) polymers, which can reversibly change color by altering their redox states, have attracted considerable attention over the past decades. These electrochromic conjugated polymers have been widely investigated for a variety of applications, such as electrochromic devices, [2,3] optical displays, [4] smart windows, [5] and sensors [6].

Because the band gap  $(E_g)$  is one of the most important factors controlling the opto-electronic properties of electrochromic polymers, band-structure engineering has become important in the field of materials science. Attempts to design low-band-gap

http://dx.doi.org/10.1016/j.electacta.2015.02.033 0013-4686/© 2015 Elsevier Ltd. All rights reserved. polymers are of high interest due to their electrochemical and optical properties. At present, there have been some published reports on the design and characteristics of low-band-gap conjugated polymers. The most common approach toward the construction of low band gap systems was employing alternating strong electron-donating and electron-accepting units in one polymer, as mixing monomer segments with higher HOMOs and lower LUMOs is effective in reducing the band gap due to interchain charge transfer [7,8]. The use of fused aromatics with electron-withdrawing imine nitrogens (C=N) as acceptor units and different thiophene derivatives as donor units has drawn great interest in the design of these alternating systems. Recently, the use of quinoxaline derivatives as this type of organic electron-accepting group within donor-acceptor conjugated polymers has made a great contribution to the electrochromic research field.

It should be noted that polymers of this system usually not only have low band gap but also can reveal an n-doped character. It is well-known that only a fraction of the conjugated polymers can exhibit this n-doped property due to their poor stability at the reduction potential that leads to the n-doped state. Thus, n-doped

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semiconducting polymers are expected to have a great contribution to organic electronics in the near future because it will be possible to manufacture light emitting diodes, bipolar transistors, and the polymeric analog of silicon field-effect transistors [9]. Thus, conducting polymers with stable negatively doped states have drawn great attention in the field of electrochromism.

Following this strategy, we previously reported the synthesis of poly[2,3-di(5-methylfuran-2-yl)-5,8-bis(2-(3,4-ethylenedioxy-thiophene)) quinoxaline] (PMFEQ), poly[2,3-di(5-methylfuran-2-yl)-5,8-bis(2-thienyl) quinoxaline] (PMFTQ) and poly[2,3-di(5-methylfuran-2-yl)-5,8-bis(2-(3-methoxythiophene)) quinoxaline] (PMFMQ) containing the strong electron-accepting 2,3-di(5-methylfuran-2-yl) quinoxaline as the acceptor unit. The electro-chemical band-gaps of these three polymers have been reported to be between 0.90 and 1.20 eV, and all of them present significant n-type doping [10].

Considering the contribution of the steric interaction between the repeating units within the polymer backbone, polymers with more-planar geometries exhibit several special properties and advantages, including lower band gaps, stronger intermolecular interactions, and greater degrees of doping [11]. Thus, the 2,3-di(2furyl) quinoxaline moiety with a stronger electron-accepting ability and a greater degree of coplanarity was used as a substitute for the previous acceptor unit to combine with different thiophene donors. As a result, three new polymers were electrochemically synthesized. These were poly[2,3-di(2-furyl)-5,8-bis(2-(3,4-ethylenedioxythiophene)) quinoxaline] (PFETQ), poly[2,3-di(2-furyl)-5,8-bis(2-thienyl) quinoxaline] (PFTQ) and poly[2,3-di(2-furyl)-5,8-bis(2-(3-methoxythiophene)) quinoxaline] (PFMTQ). The amount of decrease in the band gap and the bathochromic shift of the maximum absorption wavelength of the newly synthesized polymers containing 2,3-di(2-furyl) quinoxaline demonstrated a definite improvement in the electrochemical and optical properties in contrast to the previously reported ones. In addition, it is worth noting that both PFETQ and PFMTQ showed a green color in the neutral state and a high transmissivity in the oxidized state. The effect of the different thiophene derivatives on the photoelectrical properties was further investigated in detail in this article.

# 2. Experimental

#### 2.1. General

All chemicals were purchased from commercial sources and used without further purification except for tetrahydrofuran which was dried and distilled over benzophenone and sodium under nitrogen before use. The compounds 3,6-dibromo-1,2-phenylenediamine (2), [12] 2-hydroxy-1,2-di(2-furyl) ethanone (4), [13] 1,2-di(2-furyl) ethanedione (5) [14] and tributylstannane compounds [15] were prepared according to the methods described in the literature. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the monomers were recorded on a Varian AMX 400 spectrometer in CDCl3 at 400 MHz, and chemical shifts ( $\delta$ ) were reported relative to tetramethylsilane as the internal standard. Electrochemical behaviors were investigated by cyclic voltammetry (CV). Electrochemical synthesis and experiments were performed in a onecompartment cell with a CHI 760 C Electrochemical Analyzer under the control of a computer, employing a platinum wire with a diameter of 0.5 mm as a working electrode, a platinum ring as a counter electrode, and a Ag wire (0.03 V vs. SCE.) as a pseudoreference electrode. Scanning electron microscopy (SEM) measurements were taken by using a Hitachi SU-70 thermionic field emission SEM. UV-Vis-NIR spectra were recorded on a Varian Cary 5000 spectrophotometer connected to a computer. A threeelectrode cell assembly was included in which the working electrode was an ITO/glass electrode, the counter electrode was a stainless steel wire, and a Ag wire (0.03 V vs. SCE.) was used as a pseudo-reference electrode. The polymer films for spectroelectrochemistry were prepared by potentiostatic deposition on an ITO/glass electrode with an active area of  $0.9 \text{ cm} \times 2.0 \text{ cm}$ . The thickness of the polymer films grown potentiostatically on the ITO/glass was controlled by the total charge passed through the cell. Colorimetry measurements were obtained by a SP 60 spectrophotometer (X-Rite, USA) with illuminator D65 used as the simulated light source and CIE  $10^{\circ}$  as the illuminating/viewing geometry. Digital photographs of the polymer films were taken by a Canon Power Shot A3000 IS digital camera.

# 2.2. Synthesis

#### 2.2.1. 2,3-Bis(2-furyl)-5,8-dibromoquinoxaline (6)

To a mixture of 3,6-dibromo-1,2-phenylenediamine (1.33 g, 5 mmol) and 1,2-di(2-furyl) ethanedione (0.95 g, 5 mmol) in EtOH (50 mL), a catalytic amount of p-toluene sulfonic acid (PTSA) was added, and the solution was then refluxed while being magnetically stirred overnight. At the end of the reaction, a cloudy mixture was observed. The solution was cooled to 0 °C and filtered. The separated solid was washed with EtOH several times and dried in a vacuum oven to give a yellow-green powder (1.8 g, 85.7%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  = 7.88 (s, 2H, ArH), 7.63 (d, 2H), 6.97 (d, 2H), 6.60 (q, 2H). (See Supporting Information Fig. S1).

## 2.2.2. General procedure for the synthesis of FTQ.FETQ, FMTQ

2,3-Bis(2-furyl)-5,8-dibromoquinoxaline (1.68 g, 4 mmol) was subjected to the Stille coupling reaction with excess tributyl-stannane (16 mmol) in anhydrous THF (60 mL) using Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.28 g, 0.4 mmol) as the catalyst. After the reaction mixture was deaerated, the temperature was immediately raised to reflux temperature. The solution was refluxed with stirring under nitrogen atmosphere for 24 h, cooled and concentrated on the rotary evaporator. Lastly the residue was purified by column chromatography on silica gel using hexane- dichloromethane as the eluent.

2.2.2.1. 2,3-*Di*(2-*furyl*)-5,8-*bis*(2-*thienyl*) *quinoxaline* (*FTQ*). The crude mixture was chromatographed on silica gel by eluting with hexane: dichloromethane (15:1, v/v) to give FTQ as an orange solid (1.3 g, 76.5%). <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  = 8.10 (s, 2H, ArH), 7.90 (d, 2H), 7.62 (d, 2H), 7.54 (d, 2H), 7.20 (q, 2H), 7.12 (d, 2H), 6.63 (q, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz, ppm):  $\delta$  = 148.35, 144.32, 134.85, 133.08, 131.45, 125.74, 123.58, 121.61, 121.59, 119.35, 110.31, 104.43. (See Supporting Information Fig. S2) HRMS (m/z, EI<sup>+</sup>) calcd for C<sub>24</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> 426.5066, found 426.5058.

2.2.2. 2,3-Di(2-furyl)-5,8-bis(2-(3,4-ethylenedioxythiophene)) quinoxaline (FETQ). The crude mixture was chromatographed on silica gel by eluting with hexane: dichloromethane (3:1, v/v) to give FETQ as a deep red solid (1.6 g, 73.8%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  = 8.58 (s, 2H, ArH), 7.58 (d, 2H), 7.12 (d, 2H), 6.60 (q, 2H), 6.57 (s, 2H), 4.33 (dd, 8H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz, ppm):  $\delta$  = 151.62, 143.95, 141.33, 140.42, 139.35, 136.54, 128.48, 128.16, 113.67, 113.17, 111.90, 103.28, 64.91,64.28. (See Supporting Information Fig. S3) HRMS (m/z, El<sup>+</sup>) calcd for C<sub>28</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub> 542.5782, found 542.5810.

2.2.2.3. 2,3-Di(2-furyl)-5,8-bis(2-(3-methoxythiophene)) quinoxaline (FMTQ). The crude mixture was chromatographed on silica gel by eluting with hexane: dichloromethane (8:1, v/v) to give FMTQ as a bright red solid (1.5 g, 77.2%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  = 8.02 (s, 2H, ArH), 7.62 (d, 2H), 7.59 (d, 2H), 7.10 (d, 2H), 6.63 (d, 2H), 6.48 (q, 2H). 3.88 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz, ppm):

δ = 153.85, 150.62, 143.80, 139.86, 131.53, 129.82, 125.08, 120.24, 114.51, 107.49, 105.19, 102.34, 58.17. (See Supporting Information Fig. S4) HRMS (m/z, El<sup>+</sup>) calcd for C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> 486.5582, found 486.5563.

## 3. Results and discussion

#### 3.1. Synthesis of monomers

The synthetic route to the monomers is presented in Scheme 1. In the first step, the reduction of 4,7-dibromo-2,1,3-benzothiadiazole (1) by  $NaBH_4$  as described in the literature [12] yielded the desired 3,6-dibromo-1,2-phenylenediamine (2). 2-Hydroxy-1,2-di (2-furyl) ethanone (4) [13] was synthesized by the benzoin condensation of furfural (3). To a solution of  $CuSO_4 \cdot 5H_2O$  and pyridine, 2-hydroxy-1,2-di(2-furyl) ethanone (4) was added, and then oxidation of **4** gave yellow acicular crystals of 1,2-di(2-furyl) ethanedione (5) [14]. Then, a simple condensation reaction was performed with the compounds 2 and 5 to afford the corresponding 2,3-bis(2-furyl)-5,8-dibromoquinoxaline (6). To increase the reaction yields, p-toluene sulfonic acid was used as the catalyst. Finally, Stille coupling in the presence of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> as a catalyst was used to attach different thiophene donor moieties to the acceptor quinoxaline unit to give the target monomers FTQ, FETQ and FMTQ in satisfactory yields (70-80%).

#### 3.2. Electrochemistry

Cyclic voltammetry (CV) is a very useful method that reveals the electroactivity of monomers and the electrochemical properties of their polymers. Electrochemical polymerizations of FTQ, FETQ and FMTQ were carried out by cyclic voltammetry (CV) in an acetonitrile (ACN)/dichloromethane (DCM) (1:1, by volume) solvent mixture containing 0.1 M tetrabutylammonium hexafluor-ophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte and 0.005 M in the respective monomers. Voltammetry curves for the repeated scanning electropolymerization of FETQ are shown in Fig. 1 and the others are given in the Supporting Information. (See Supporting Information Fig. S5 and Fig. S6)

The first cycle of the CV test corresponds to the irreversible monomer oxidation at the platinum wire electrode. For the FTQ monomer, the onset of oxidation is observed at 1.03 V vs. the Ag wire pseudo-reference electrode. The oxidation potential of FETQ and FMTQ shifted to 0.79 V and 0.85 V owing to the presence of the strong electron-donating group on the donor moiety. Comparing the onsets of monomer oxidation, FETQ and FMTQ were much more easily oxidized than FTQ. As the cyclic scan continued, the current densities of the oxidation/reduction peaks increased, indicating the formation of the conducting polymers on the surface of the working electrodes [16].



Scheme 1. Synthetic route of the monomers. (a) NaBH<sub>4</sub>, EtOH, 0 °C, 24 h (b) KCN (c) CuSO<sub>4</sub> · 5H<sub>2</sub>O, pyridine, reflux, 2.5 h (d) PTSA, EtOH, reflux, overnight (e–g) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, tributyl(thiophen-2-yl) stannane (e), tributyl(2-(3,4-ethylenedioxythiophene))stannane (f), tributyl(2-(3-methoxythiophene))stannane (g), dry THF, reflux, 24 h.

To study on the electrochemical properties, three polymer films were prepared on Pt wire by sweeping the potentials for three cycles. The electrochemical behaviors of the deposited polymers were investigated at different scan rates between 100 and  $300 \text{ mV s}^{-1}$  in monomer-free electrolyte solution. As shown in Fig. 2, the maximum current density of the three polymers increased with the scan rate.

The fine electrochemical properties of the D-A type conjugated polymers were that the polymers can be p-doped/dedoped at proper positive potentials and n-doped/dedoped at certain negative potentials. During the p-doping process, the conjugated chain loses electrons and doping anions could move into the polymer film.

$$CP - e^- + A^- \leftrightarrow CP^+ (A^-)$$

where CP is the conjugated polymer and  $A^-$  denotes the doping anions.

During the n-doping process, the conjugated chain gains electrons and doping cations could move into the polymer film.

 $CP + e^- + M^+ \leftrightarrow CP^-(M^+)$ 

where CP is the conjugated polymer and  $M^{\ast}$  denotes the doping cations.

As is well known, only a fraction of the conjugated polymers can exhibit n-doped properties due to their poor stability at the reduction potential. However, a single conjugated polymer system that contains donor-acceptor units can undergo a transport mechanism that reduces the degradation effects associated with water and air, [17] thus enhancing the stabilization of the n-doped state. For this reason, three donor-acceptor conjugated polymers



**Fig. 1.** Repeated potential scan electropolymerization of FETQ at  $100 \text{ mV s}^{-1}$  in 0.1 M TBAPF<sub>6</sub>/ACN/DCM on a platinum wire electrode (with a diameter of 0.5 mm).

(PFETQ, PFMTQ and PFTQ) were synthesized, and all of them exhibited distinct but different redox peaks in the n-doping process. The 2,3-di(2-furyl) quinoxaline moiety used as the electron-accepting unit is critical to driving this process. In addition, it is worth noting that the redox peak of the n-doping/dedoping is much stronger than that of the p-doping/dedoping process. The results indicate that these three conjugated polymers are strong electron-acceptors and good n-type conjugated polymers [18]. Through analysis, the reversible sharp peaks corresponding to reversible n-doping of the polymers appear in the range of -1.5 V to -1.2 V and the corresponding n-dedoping peaks appear at approximately -1.2 V vs. Ag wire.



**Fig. 2.** (a) CV curves of the PFETQ film on a platinum electrode at different scan rates between 100 and 300 mV s<sup>-1</sup> in the monomer-free 0.1 M TBAPF<sub>6</sub>/ACN/DCM solution. (b) CV curves of the PFMTQ film on a platinum electrode at different scan rates between 100 and 300 mV s<sup>-1</sup> in the monomer-free 0.1 M TBAPF<sub>6</sub>/ACN/DCM solution. (c) CV curves of the PFTQ film on a platinum electrode at different scan rates between 100 and 300 mV s<sup>-1</sup> in the monomer-free 0.1 M TBAPF<sub>6</sub>/ACN/DCM solution. (c) CV curves of the PFTQ film on a platinum electrode at different scan rates between 100 and 300 mV s<sup>-1</sup> in the monomer-free 0.1 M TBAPF<sub>6</sub>/ACN/DCM solution.

It is well known that the stability and robustness of the polymer films for long-term multiple redox switching have important practical applications. Hence, cyclic voltammograms of the polymers deposited on the Pt electrode were investigated by potential scanning between neutral and oxidized states in monomer-free 0.1 M TBAPF6/ACN/DCM at a potential scan rate of 200 mV s<sup>-1</sup>. The PFETO film was tested by cyclic voltammetry at the applied potential between -0.8 and 1.0 V with 200 mV s<sup>-1</sup> to evaluate the stability of the device (Fig. 3a). During the above observation of the ability to switch between oxidized and reduced states of PFMTQ, 82.1% of its electroactivity is retained after 1000 cycles for the PFMTQ film. PFETQ and PFTQ displayed even better stability, with 93.8% and 92.6% of the exchange charge still remaining after sweeping 1000 cycles, respectively. These results indicate that all three polymers have fine redox stability, and their long lifetimes mean they have good effective charge compensation ability.

Likewise, the stability and robustness of the polymer films for long-term multiple switching between the reduced and neutral states were also investigated. As seen from Fig. S7, the stability during the n-doping process was poor. The films were almost completely dissolved in electrolyte solution after 1000 cycles. Note that the stability test was carried out in air in order to test the environmental stability of the polymers because the observed loss is most probably due to the degradation effects associated with water and air. Further research is needed under nitrogen conditions, and the samples should be placed in a completely dry environment, such as a glove box containing a desiccant.

#### 3.3. Optical properties of the monomers and films

The UV–vis absorption spectra of FETQ, FMTQ and FTQ monomers and the corresponding polymer films are shown in Fig. 4. For these measurements, the polymer films were potentiostatically electrodeposited onto ITO/glass with the same polymerization charge of  $1.11 \times 10^2$ C/m<sup>2</sup> at 1.0 V, 0.95 V and 1.2 V, respectively. After polymerization, the films were electrochemically dedoped at -0.7 V, -0.6 V and -0.2 V for 30 s in ACN/DCM (1:1, by volume) containing 0.1 M TBAPF<sub>6</sub>, and then washed three times with ACN/DCM(1:1, by volume) to remove the supporting electrolyte and oligomers/monomers.

As shown in Fig. 4, the absorption maximum  $(\lambda_{max})$  of the monomers FETQ, FMTQ and FTQ due to the  $\pi$ - $\pi$ <sup>\*</sup> transition is centered at 323, 315 and 314 nm, respectively. It can easily be seen that when thiophene and methoxythiophene units were replaced by EDOT, the monomer absorbance was shifted to a lower energy level. The bathochromic shift of the maximum absorption wavelength of FETQ compared with those of FTQ and FMTQ is attributed to the strong electron-donating abilities of the ethylenedioxy group that enhances the conjugation effect and decreases the intensity of the  $\pi$ - $\pi$ <sup>\*</sup> electronic transition absorption. This trend was also observed in the absorbance values of the polymer films. In their neutral state, both PFETO and PFMTO showed maximum absorption at approximately 790 nm in the visible region due to the  $\pi$ - $\pi$ <sup>\*</sup> transition, while the maximum absorption wavelength of PFTQ was located at 595 nm. Additionally, because the conjugation length was increased, all of the dominant



**Fig. 3.** (a) Electrochemical stability of PFETQ during p-doping process in the monomer-free ACN/DCM containing 0.1 M TBAPF<sub>6</sub> solutions after 1000 switching by the CV method. (Pt working electrode *versus* Ag wire pseudo reference electrode.) (b) Electrochemical stability of PFMTQ during p-doping process in the monomer-free ACN/DCM containing 0.1 M TBAPF<sub>6</sub> solutions after 1000 switching by the CV method. (Pt working electrode versus Ag wire pseudo reference electrode.) (c) Electrochemical stability of PFTQ during p-doping process in the monomer-free ACN/DCM containing 0.1 M TBAPF<sub>6</sub> solutions after 1000 switching by the CV method. (Pt working electrode versus Ag wire pseudo reference electrode.) (c) Electrochemical stability of PFTQ during p-doping process in the monomer-free ACN/DCM containing 0.1 M TBAPF<sub>6</sub> solutions after 1000 switching by the CV method. (Pt working electrode versus Ag wire pseudo reference electrode.)



**Fig. 4.** (a) UV-vis absorption spectra of FETQ, FMTQ and FTQ dissolved in dichloromethane. (b) absorption spectra of the corresponding polymers on an ITO-coated glass slide.

wavelengths were shifted to the longer wavelength region for polymers PFETQ, PFMTQ and PFTQ compared to their respective monomers, which verifies that the longer the wavelength of maximum absorption is, the higher the conjugation length in the polymer will be [19].

A regular alternation of conjugated donor and acceptor moieties along the polymer backbone increases the double-bond character and establishes an intramolecular charge transfer, allowing absorption of low-energy photons [20–22]. Low-bandgap polymers have been defined as conjugated polymers with a band gap below 1.5 eV [23]. The low optical band gap values (calculated from the onset of  $\pi$ – $\pi$ \* transition) of PFETQ (1.15 eV), PFMTQ (1.20 eV) and PFTQ (1.34 eV) indicate that the three newly synthesized polymers all have low band gaps. By contrast with the reported polymer films containing 2,3-di(5-methylfuran-2-yl) quinoxaline as the acceptor,<sup>10</sup> the band gaps of PFETQ, PFMTQ and PFTQ shift to a much lower level due to the stronger electronaccepting ability and well-defined coplanarity of the 2,3-di(2furyl) quinoxaline moiety when this was used as a substitution. The introduction of the 2,3-di(2-furyl) quinoxaline acceptor increases the double bond character which leads to a broadening of the valence and conduction bands and induces small band gaps [24–27]. Table 1 clearly summarizes the maximum absorption wavelength ( $\lambda_{max}$ ), the absorption onset wavelength ( $\lambda_{onset}$ ), the optical band gap ( $E_g$ ), and the HOMO/LUMO energy levels of the monomers and corresponding polymers.

# 3.4. Morphology

The morphologies of the polymer films were closely related to the electrochemical properties of the polymers. Thus in the present paper, scanning electron microscopy (SEM) was employed as a useful method to investigate the surface morphologies of the polymer films. Available films were prepared potentiostatically on ITO/glass with the same polymerization charge of  $5.55 \times 10^{2}$  C/m<sup>2</sup> in the ACN/DCM (1:1, by volume) solution containing 0.1 M TBAPF<sub>6</sub> and 0.005 M in the relevant monomer. In addition, the thickness of the PFETQ, PFMTQ and PFTQ films were investigated by step profilers, which were 776 nm, 710 nm and 824 nm, respectively. All of the polymers were dedoped before characterization. Fig. 5 clearly displays the SEM images of these polymer films. An accumulation state of small globules with interlinked holes among the clusters is observed on the surface of the PFETQ polymer film (Fig. 5a). The PFTQ film (Fig. 5b) exhibits similar surface morphology to PFETQ. As for PFMTQ film, there are pervasive gibbosities on the surface and some gullies are also found (Fig. 5c). The morphologies of the three polymers were quite different from each other, which might be an indication of the different aggregation structure of the conjugated polymers.

# 3.5. Spectroelectrochemical properties of the polymer films

Spectroelectrochemistry is a useful method for studying the changes in the absorption spectra and information about the electronic structures of conjugated polymers as a function of the applied potential difference [28]. In situ electronic absorption spectra studies of the polymer films were performed using stepwise oxidation in a monomer-free 0.1 M TBAPF<sub>6</sub>/ACN/DCM solution. Spectroelectrochemistry and the corresponding colors of the polymeric films in the n-dopable, neutral and p-dopable states are shown in Fig. 6. The PFETQ, PFMTQ and PFTQ films were electrodeposited onto ITO/glass electrode with the same polymerization charge of  $1.11 \times 10^{2}$  C/m<sup>2</sup> under constant potentials of 0.8 V, 1.1 V and 1.2 V, respectively. After polymerization, electrochemical dedoping was carried out at -0.8 V, -0.7 V and -0.2 V, respectively, for 30 s in 0.1 M TBAPF<sub>6</sub>/ACN/DCM solution, and the samples were then washed three times using ACN/DCM (1:1, by volume) to remove the supporting electrolyte and oligomers/monomers.

Table 1

The onset oxidation potential ( $E_{onset}$ ), maximum absorption wavelength ( $\lambda_{max}$ ), absorption onsets wavelength ( $\lambda_{onset}$ ), optical band gap ( $E_{g}$ ), HOMO/LUMO energy levels of the monomers and corresponding polymers.

Polymer	E <sub>onset</sub> , vs.Ag (V) <sup>a</sup>	$\lambda_{max} (nm)$	$\lambda_{onset} (nm)$	$E_{g,op} (eV)^{a}$	HOMO <sup>b</sup> (eV)	LUMO <sup>c</sup> (eV)
PFETQ	-0.39	790	1078	1.15	-4.04	-2.89
PFMTQ	-0.22	790	1033	1.20	-4.21	-3.01
PFTQ	0.31	596	925	1.34	-4.74	-3.40
PMFEQ <sup>d</sup>	-0.40	780	986	1.26	-4.03	-2.77
PMFMQ <sup>d</sup>	-0.28	790	1014	1.22	-4.15	-2.93
PMFTQ <sup>d</sup>	0.21	558	753	1.65	-4.64	-2.99

<sup>a</sup> Calculated from the low energy absorption edges ( $\lambda_{onse}t$ ), Eg = 1240/ $\lambda_{onset}$ .

<sup>b</sup> HOMO =  $(E_{onset} + 4.4)$  ( $E_{onset}$  vs. SCE).

<sup>c</sup> Calculated by the subtraction of the optical band gap from the HOMO level.

<sup>d</sup> Data were taken from Ref. [10].







**Fig. 5.** (a) SEM images of PFETQ deposited potentiostatically onto ITO/glass electrode. (b) SEM images of PFTQ deposited potentiostatically onto ITO/glass electrode. (c) SEM images of PFMTQ deposited potentiostatically onto ITO/glass electrode.

Most of the conjugated polymers are colored in the neutral state because the energy difference between the bonding and the antibonding orbitals (the  $\pi$ - $\pi$ \*transition) occurs in the visible region. When oxidized, the lower energy transitions become more intense, and a second color appears. To obtain different UV-vis absorbance curves of the PFTQ, various potentials ranging from -0.2 V to 1.2 V were applied. As seen from Fig. 6, PFTQ exhibits a blue color with only one absorption band at 596 nm in the visible

region due to the  $\pi$ - $\pi$ \* transition at neutral state. The intensity of the absorption band decreases and a new inconspicuous absorption band in the NIR region arises due to the formation of charge carriers upon oxidation of the PFTQ. Meanwhile, the PFTQ film turned to a tile blue color at its p-doped state after being fully oxidized.

To obtain a green color there should be at least two simultaneous absorption bands in the red and blue regions of the visible spectrum, and these bands should also be controlled by the same applied potential. All this complexity is expected to result in only a limited number of neutral-state green polymeric materials in the literature [29,30]. Fortunately, in its neutral state, PFETQ showed maximum absorption peaks at 458 nm and 790 nm in the visible region which are essential values to maintain a green color. Likewise, PFMTQ film with two absorption maxima at approximately 427 nm and 790 nm also reveals a green neutral state. Through the contrast analysis of the absorption values of the polymers, the strong electron-donating ethylenedioxy and methoxy groups affect not only the monomer oxidation and the polymer redox couple potentials but also the maximum absorption wavelengths of the corresponding transitions. Favorable donoracceptor matches with the quinoxaline moieties of PFETQ and PFMTQ increased the double-bond character, creating an intramolecular charge transfer, allowing absorption of low-energy photons [20-22] and producing a bathochromic shift of the maximum absorption wavelengths. For both polymers, the  $\pi$ - $\pi$ \* electronic transition absorption decreased while charge-carrier absorption bands evolved at approximately 1000 nm for PFETO and 1065 nm for PFMTO at moderate oxidation potentials. The appearance of charge carrier bands could be attributed to the evolution of polaron and bipolaron bands [31]. Finally, no significant absorption peaks can be found in the visible region for PFETQ and PFMTQ, which resulted in a highly transmissive colorless oxidized state. However, the absorption of all three polymers increased substantially in the near infrared region owing to the charge carriers.

The color changes were further investigated by colorimetric parameters and color spaces using the CIE 1976 L\*a\*b\* with the value of L\* representing lightness and the opponent color dimensions (a\* and b\*) are the red-green balance for a\* and yellow-blue balance for b\* [32]. Colorimetry measurements are obtained using an SP 60 spectrophotometer (X-Rite, USA). The PFTQ is light blue (L\*, 43.2; a\*, 14.0; b\*, -45.6) in the neutral state, while the oxidized state becomes light gray (L\*, 58.6; a\*, -6.9; b\*, 13.4). The PFETQ film changed from a green neutral state (L\*, 63.3; a\*, -42.4; b\*, 21.1) to a transmissive colorless oxidized state (L\*, 59.0; a\*, -2.4; b\*, 11.7). Although the PFMTQ film also revealed a green neutral state (L\*, 55.3; a\*, -46.2; b\*, 17.9) and a highly transmissive colorless oxidized state (L\*, 57.3; a\*, -3.6; b\*, 10.4), the colorimetric parameters were different.

Although the conjugated polymers have considerable potential to be n-doped, only a small portion of them can exhibit this property because of the easy degradation reaction associated with water and air [17]. The use of the donor-acceptor approach is one of the significant methods to enhance the stabilization of the ndoped state and display the n-doped characters of the conjugated polymers. Additionally, the n-doping of a conjugated polymer system in an n-type manner is not only an electrochemical formation of a reduced state. The introduction of charge carries to conjugated systems should yield considerable structural, conductivity and optical differences [33]. Hence, to prove that an n-type doping process is present, both the electrochemistry of the reduced state and moreover, the spectral changes that occur upon reduction should be examined [34]. To test this hypothesis, UV-vis absorption spectra of three polymers at the reduction potential of -1.6 V were investigated.



**Fig. 6.** (a) Spectroelectrochemistry of PFETQ films on ITO/glass electrode at different applied potentials in the monomer-free 0.1 M TBAPF<sub>6</sub>/ACN/DCM solution. (b) Spectroelectrochemistry of PFMTQ films on ITO/glass electrode at different applied potentials in the monomer-free 0.1 M TBAPF<sub>6</sub>/ACN/DCM solution. (c) Spectroelectrochemistry of PFTQ films on ITO/glass electrode at different applied potentials in the monomer-free 0.1 M TBAPF<sub>6</sub>/ACN/DCM solution. (c)

As seen from Fig. 6, the absorption spectra of the reduced forms were markedly different from that of the other two states. The changes in UV–vis absorption spectra were also reflected in a corresponding change in the color of the three films. For PFETQ, two coterminous absorption maxima were found at 423 and 538 nm, which resulted in a deep purple-red reduced state (L\*, 47.5; a\*, 45.2; b\*, -21.6). When a potential of -1.6 V was applied to polymer PFMTQ, the film became light purple-red in color (L\*, 51.3; a\*, 32.8; b\*, -13.3) with two separated absorption peaks at 443 and 626 nm. As for the PFTQ, the single absorption band at 537 nm in the visible region resulted in a bronze color (L\*, 52.7; a\*, 12.1; b\*, 25.4), which indicates a significant difference from that of the neutral and p-doped states. The electrochemical property of the reduced state and the spectral changes that occur upon reduction proved that the n-doping process truly occurred.

#### 3.6. Switching properties

Polymers with the ability to switch rapidly and exhibit striking color changes according to the alternate reduced and oxidized states are crucial for electrochromic applications. A repeated potential stepping method coupled with optical spectroscopy was used to observe switching times and optical contrasts for these polymers. Electrochromic switching of the polymers was performed at regular intervals of 5 s in a monomer-free ACN/DCM (1:1, by volume) solution containing 0.1 M TBAPF<sub>6</sub> as a supporting electrolyte. As seen from Fig. 7, the behaviors included only slight losses in the percent transmittance contrast value after regular switching during 300 s, indicating a certain stability of all three films.

In these studies, the optical contrast ( $\Delta T$ %) of the polymer films which can be defined as the transmittance difference between the redox states was recorded at constant wavelengths. The response time, another very important characteristic of electrochromic materials, is the time necessary for 95% of the full optical switch (after which the naked eye could not sense the color change) [35]. Fig. 7a shows the switching properties of PFETQ between -0.7 and 0.8 V at two different wavelengths both in the visible and NIR regions. At 458 nm, the optical contrast for PFETQ was calculated as 30% and the switching time was 0.9 s. The polymer switches rapidly and achieves 87% of its total optical change in 0.8 s at 1600 nm.

PFMTQ was also switched from -0.6 V to 1.1 V at 5 s step intervals, while the change in transmittance at three different wavelengths was monitored. The optical contrasts for PFMTQ were calculated as 20% at 442 nm, 26% at 780 nm, and 81% at 1600 nm. PFMTQ revealed switching times of 0.45 s at 442 nm and 1600 nm, 0.9 s at 780 nm (Fig. 7b). The PFTQ revealed a 21% transmittance change upon doping/de-doping process at 590 nm and 76% at 1336 nm (Fig. 7c). The switching time was calculated as 0.8 s and 0.4 s at corresponding wavelengths from the reduced to the oxidized state. In addition, all of the polymers show high optical contrasts in the NIR region, which is a very significant property for various NIR applications.

The coloration efficiency (another important characteristic of electrochromic materials) has been used to investigate the optical behavior comparison of polymer films. It is defined as the change in the optical density ( $\Delta$ OD) for the charge consumed per unit electrode area ( $\Delta$ Q) [36]. The corresponding equations are given below [37]:

$$\Delta \text{OD} = 1 \text{g} \left( \frac{T_b}{T_c} \right) \text{and} \eta = \frac{\Delta \text{OD}}{\Delta \text{Q}}$$

where  $T_b$  and  $T_c$  are the transmittances before and after coloration, respectively,  $\Delta Q$  is the amount of injected charge per unit sample



**Fig. 7.** (a) Electrochromic switching, percent transmittance change monitored at 458 and 1600 nm for PFETQ on ITO/glass electrode between -0.7 V and 0.8 V. (b) Electrochromic switching, percent transmittance change monitored at 442, 780 and 1600 nm for PFMTQ on ITO/glass electrode between -0.6 V and 1.1 V. (c) Electrochromic switching, percent transmittance change monitored at 590 and 1336 nm for PFTQ on ITO/glass electrode between -0.2 V and 1.2 V.

area and  $\eta$  denotes the CE (coloration efficiency). The CE of the PFETQ film was calculated to be  $157.1 \text{ cm}^2 \cdot \text{C}^{-1}$  at 458 nm. The PFMTQ film was calculated to have a CE of  $130.4 \text{ cm}^2 \cdot \text{C}^{-1}$  at 442 nm, and the PFTQ had a CE of  $90.8 \text{ cm}^2 \cdot \text{C}^{-1}$  at 590 nm. The +/– error of all three polymers in the coloration efficiencies was calculated to be lower than  $1.0 \text{ cm}^2 \cdot \text{C}^{-1}$ . The results clearly demonstrate that the coloration efficiencies of PFETQ and PFMTQ are much greater than that of PFTQ.

By contrast with the reported polymer films containing 2,3-di (5-methylfuran-2-yl) quinoxaline as the acceptor [10], PFETQ and PMFEQ with the same ethylenedioxythiophene donor unit but different acceptors, showed a similar response time, while the PFETQ film displayed a prominently higher optical contrast ( $\Delta T$ %) than PMFEQ. Analogously, the PFMTQ film exhibits fast response time, despite the fact that the optical contrast is a little inferior to that of PMFMQ. A comparison between the PFTQ and PMFTQ films reveals a higher optical contrast and faster response time for PFTQ. Generally speaking, the switching properties of the newly synthesized polymers were superior to the previously reported ones [10] due to their stronger electron-accepting ability and the well-defined coplanarity of the 2,3-di(2-furyl) guinoxaline moiety that was used as a substitution. In light of the superior characteristics mentioned above, PFETQ, PFMTQ and PFTQ could be the better candidates for electrochromic display applications.

# 4. Conclusion

In this study, three monomers based on 2,3-di(2-furyl) quinoxaline as the acceptor unit were synthesized to understand the effects of donor strength on the electrochemical and

spectroelectrochemical properties of the resulting electropolymerized materials. Polymers with the stronger EDOT or methoxythiophene donor unit have lower oxidation potentials and band gaps relative to the thienyl derivative. In addition, PFTQ displayed two different colors (tile blue in the neutral state, light grav in the oxidized state), while favorable donor-acceptor matches with the quinoxaline moieties of PFETO and PFMTO resulted in a green neutral state and a highly transmissive colorless oxidized state. As a donor-acceptor-donor type of  $\pi$ -conjugated polymers, they all showed high optical contrast ( $\Delta$ T%), fast response time and good cyclic voltammetry stability. In addition, the generation of redox waves in CV at negative potentials and variation of the spectral absorption curves upon reduction proved that all three polymers have stable n-doping properties. The polymer films with their favorable electrochemical and optical properties are expected to be useful for practical use in electrochromic display applications.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2015.02.033.

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