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Green to highly transmissive switching multicolored electrochromes: Ferrocene pendant group effect on electrochromic properties

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ABSTRACT

Two new quinoxaline and ethylenedioxythiophene (EDOT) based polymers; poly(5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-(phenyll)-3-ferrocenylquinoxaline) (**P1**) and poly(5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(naphthalen-2-yl) quinoxaline) (**P2**) were synthesized and characte- rized in terms of their electrochemical and spectroelectrochemical properties. The polymers were both p and n-type dopable. The polymers can be switched between green and transparent states during p-doping/dedoping. They were compared with their previously reported analogues in order to investigate ferrocene pendant group effect on electrochromic characteristics.

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1. Introduction

The reversible and visible change in optical properties, i.e. transmittance or reflectance upon external bias is called as electrochromism [1,2]. Conjugated polymers as next generation semiconductors are mostly employed in electrochromic devices because of their fast switching times [3], high optical contrasts [4], processability [5], and fine tuning in electronic and optical properties via small structural alternations [6].

There are numerous applications for electrochromic materials such as optical displays [7] and smart windows [8]. Altering colors for different redox states determine the potential application areas. Red, green, blue (RGB) are the three main colors for display technology since all other subtractive colors can be achieved by mixing these three [9]. Among RGB colors, neutral state green polymers with highly transmissive oxidized states were missing until benzothiadiazole and quinoxaline based EDOT bearing polymers were synthesized and characterized in terms of their electrochromic properties [10]. This investigation opened the way of commercialization for electrochromic display devices. However; in the context of low cost and high performance display devices, the main demand is becoming to achieve multi-colored redox achievable states from a single polymer [11]. Towards the future display technologies, investigation and improvement of multicolored electrochromes are crucial.

Metal functionalized conducting polymers attracted attention of a great deal of scientists in recent years and different metals such as Pt [12], Rh [13], Au [14] and Ru [15] were used to functionalize conducting polymers. However, most of the interest focused on introducing ferrocene units into conducting polymers [16]. Discovery of ferrocene increased the popularity of organometallic chemistry and even after 60 years it is still receiving a great deal of interest. Incorporation of ferrocene into conjugated polymers either on main chain or as pendant group leads different redox behaviors due to its reversible and narrow electrochemical signal which is affected by its electronic and steric environment [17]. Electron rich character of ferrocene, stability in both Fe(II) and Fe(III) oxidation states and easy substitution on aromatics make ferrocene a great candidate for functionalization of conducting polymers [17]. In this context, recent studies showed that ferrocenyl (Fc) group bearing polymers posses a significant potential for optoelectronic applications such as electrochromics and memory devices [18]. Oligothienylferrocene complexes [16] were also reported. Conducting polymers functionalized by ferrocene is aroused since these type of polymers show the redox properties of both groups [19]. These are useful in a range of applications and studies such as sensors [20,21], electro active Langmuir/Blodgett films [22], free-standing redox-active films [23]. Conducting polymers containing ferrocene on main conjugation path of polymer backbone were also synthesized [16,24].





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We report here the synthesis and electrochemical properties of two newly designed donor–acceptor–donor type green electrochromic polymers 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-(phenyl)-3-ferrocenylquinoxaline (**P1**) and 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(naphthalen-2-yl)quinoxaline (**P2**). Both polymers are green in their neutral states and revealed highly transmissive oxidized states. Effect of pendant Fc unit on electrochemical and spectral behavior of the resulting polymers by a comparison between their Fc free counterparts were given in detail.

2. Experimental

2.1. General

All chemicals and reagents were obtained from commercial sources and used without further purification. THF was dried over sodium and benzophenone. 2-Hydroxy-2-phenyl-1-ferrocenylethanone (3) [25], 2-hydroxy-1,2-di(naphthalen-2-yl)ethanone (9) [25], 1-ferrocenyl-2-phenylethanedione (4) and 1,2-di(naphthalen-2-yl)ethane-1,2-dione (10) [25], 4,7-Dibromo-2,1,3benzothiadiazole [26], 3,6-Dibromo-1,2-phenylenediamine [27], 5,8-dibro-mo-2-phenyl-3-ferrocenylquinoxaline and 5,8-dibromo-2,3-di-(naphthalen-2-yl)quinoxaline [28], tributyl(2,3-dihydrothieno-[3,4-b][1,4]dioxin-5-yl)stannane [29] were synthesized according to previously published procedures. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Spectrospin Avance DPX-400 Spectrometer with TMS as the internal standard and CDCl₃ as the solvent. All shifts were given in ppm. Electrochemical studies were performed in a three-electrode cell consisting of an indium tin oxide doped glass slide (ITO) as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo reference electrode under ambient conditions using a Voltalab 50 potentiostat. HOMO-LUMO values were calculated taking the value of NHE as -4.75 eV vs vacuum. Cary 5000 UV-Vis spectrophotometer was used to perform the spectroelectrochemical studies of polymers.

2.2. Synthesis of 5,8-dibromo-2-phenyl-3-ferrocenylquinoxaline (11)

A solution of 3,6-dibromo-1,2-phenylenediamine (166 mg, 0.63 mmol) and 1-ferrocenyl-2-phenylethanedione (200 mg, 0.63 mmol) in EtOH (50 mL) was refluxed overnight with a catalytic amount of *p*-toluene sulfonic acid (PTSA). The mixture was cooled to 0 °C and concentrated on the rotary evaporator. The residue was subjected to column chromatography (silica gel, hexane:EtOH, 10:1). Compound **11** was obtained as a purple solid in 73.0% yield (249 mg, 0.45 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, 1H), 7.76 (d, 1H), 7.59–7.55 (m, 2H), 7.41–7.35 (m, 3H), 4.57–4.53 (m, 2H), 4.28–4.25 (m, 2H), 3.91 (s, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 156.3, 153.73, 139.7, 138.7, 138.3, 132.7, 131.8, 129.8, 129.3, 128.1, 123.8, 123.1, 96.1, 82.1, 71.6, 70.2, 70.2.

2.3. Synthesis of 5,8-dibromo-2,3-di(naphthalen-2-yl)quinoxaline (12)

A solution of 3,6-dibromo-1,2-phenylenediamine (86 mg, 0.33 mmol) and 1,2-di(naphthalen-2-yl)ethane-1,2-dione (100 mg, 0.322 mmol) in EtOH (25 mL) was refluxed overnight with a catalytic amount of *p*-toluene sulfonic acid (PTSA). The mixture was cooled to 0 °C. The precipitate was isolated by filtration and washed with EtOH several times then the residue was subjected to column chromatography (silica gel, CHCl₃:hexane, 1:1) to get the product as a yellow solid in 67% yield (116 mg, 0.214 mmol). ¹H NMR (400 MHz, CDCl₃) δ 8.96–8.81 (m, 1H), 8.55–7.99 (m, 7H), 7.95 (d, 2H), 7.92–7.65 (m, 4H), 7.56–7.46 (m, 2H). ¹³C NMR

(101 MHz, CDCl3) δ 152.8, 147.0, 135.4, 134.5, 133.9, 130.8, 130.3, 129.1, 128.9, 128.4, 126.2, 125.4, 125.0, 124.8.

2.4. Synthesis of 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-(phenyll)-3-ferrocenylquinoxaline (**M1**)

5,8-Dibromo-2-phenyl-3-ferrocenylquinoxaline (240 mg, 0.438 mmol) and tributyl (2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (1.393 g, 2.19 mmol) were dissolved in dry THF (100 mL). The solution was purged with argon for 30 min. and $PdCl_2(PPh_3)_2$ was added under argon atmosphere. The mixture was stirred at 100 °C under argon atmosphere for 18 h, cooled and concentrated on the rotary evaporator. The residue was subjected to column chromatography (silica gel, CHCl₃:hexane, 2:1) to afford a red solid in 68.0% yield (198 mg, 0.295 mmol). $^1\mathrm{H}$ NMR (400 MHz, CDCl_3) δ 8.63 (d, 1H), 8.55 (d, 1H), 7.78–7.70 (m, 2H), 7.46 (dd, J = 8.0, 3.0 Hz, 3H), 6.65 (s, 1H), 6.49 (s, 1H), 4.79-4.76 (m, 2H), 4.41 (dd, *J* = 5.2, 2.4 Hz, 2H), 4.37 (dd, *J* = 5.2, 2.4 Hz, 2H), 4.34–4.32 (m, 2H), 4.31 (dd, J = 3.7 Hz, 2H), 4.27 (dd, J = 4.1 Hz, 2H), 3.95 (s, 5H). ¹³C NMR (101 MHz, CDCl₃) & 151,9, 150,1, 141.4, 141.3, 140.3, 140.2, 137.5, 136.9, 135.9, 133.3, 133.1, 129.6, 128.9, 128.6, 128.0, 127.8, 127.7, 127.6, 127.5, 127.0, 126.6, 126.2, 113.4, 103.1, 102.7, 82.3, 71.8, 70.0, 64.9, 64.3.

2.5. Synthesis of 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(naphthalen-2-yl)quinoxaline (**M2**)

5,8-Dibromo-2,3-di(naphthalen-2-yl)quinoxaline (400 mg, 0.74 mmol) and tributyl (2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (2.35 g, 3,7 mmol) were dissolved in dry THF (130 mL). The solution was purged with argon for 30 min. and PdCl₂(PPh₃)₂ was added under argon atmosphere. The mixture was stirred at 100 °C under argon atmosphere for 18 h, cooled and concentrated on the rotary evaporator. The residue was subjected to column chromatography (silica gel, CHCl₃:hexane, 2:1) to afford a red solid in 65.0% yield (318.48 mg, 0.48 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.23–8.44 (m, 6H), 8.38–7.60 (m, 8H), 7.59–7.39 (m, 2H), 6.51 (s, 2H), 4.35 (dd, *J* = 3.55, 4H), 4.25 (dd, *J* = 3.78, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 148.9, 146.4, 141.4, 140.6, 139.1, 137.4, 135.4, 134.3, 131.1, 129.01, 128.9, 125.9, 125.1, 124.9, 124.3, 123.2, 112.1, 103.4, 65.0, 64.3.

3. Results and discussions

3.1. Synthesis

The synthetic route to the monomers was outlined in Scheme 1. 2-Hydroxy-2-phenyl-1-ferrocenylethanone (3) and 2-hydroxy-1,2di(naphthalen-2-yl)ethanone (9) were synthesized by benzoin condensation of ferrocene carboxaldehyde (1) and β -naphtaldehyde (2, 8) [5]. Oxidation of 2-hydroxy-2-phenyl-1-ferrocenylethanone (3) by MnO₂ gave 1-ferrocenyl-2-phenylethanedione (4) as a red solid with sufficient yields [25]. Oxidation of 2-hydroxy-1,2-di(naphthalen-2-yl)ethanone (9) took place and 1,2-di(naphthalen-2-yl)ethane-1,2-dione (10) was afforded via refluxing in HNO₃. Bromination of 1,3-benzothiadiazole yielded dibrominated compound **6** in high vield [26]. Then the reduction of this compound by NaBH₄ as described in the literature [27] gave desired dibromodiamine **7**. Condensation of **7** with diketones in ethanol afforded 5,8-dibromo-2-phenyl-3-ferrocenylquinoxaline (11) and 5,8-dibromo-2,3-di(naphthalen-2-yl)quinoxaline (12) [28]. The Stille coupling of these compounds with tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane [29] gave the desired monomers M1 and M2 (Scheme 1).



Scheme 1. Synthetic routes for M1 and M2.

3.2. Cyclic voltammetry

The potentiodynamic electropolymerizations for **M1** and **M2** were performed in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile (ACN)/dichloromethane (DCM) (95:5, v:v) mixture. Indium tin oxide coated glass slides (ITO)

were used as the working electrode whereto polymer films produced electrochemically. Fig. 1 represents cyclic voltammetry (CV) results for both **M1** and **M2** monomers and formation of corresponding polymers **P1** and **P2**. In the first cycle of oxidative electrochemical polymerization of **M1**, characteristic ferrocene oxidation (Fc/Fc⁺) peak was recorded at 0.58 V. The monomer



Fig. 1. Repeated potential scan electropolymerization of: (a) M1 and (b) M2 in 0.1 M TBAPF₆/ACN/DCM on ITO electrode.

oxidation was achieved at 0.8 V which accompanied with a reversible redox couple resulting from the presence of oligomers and polymer chains. During the first scan, reduction of Fc⁺ was blanketed due to the reduction of preliminary chains (Fig. 1a). Monomer oxidation potential for **M2** was observed at 0.85 V which was the lowest potential for monomer oxidation among its analogues (Table 1).

Resulting polymers were subjected to CV in order to examine the n-type doping property of the polymers (Fig. 2). **P1** and **P2** revealed both p- and n-doping property which were proved by well defined reversible redox couples at -1.95 V/-1.30 V (Fig. 2a) and at -2.05 V/-1.42 V (Fig. 2b) for **P1** and **P2**, respectively. Although almost all conjugated polymers have a tendency to be p doped, only handful of them reveal ambipolar characteristics which have numerous applications such as; light emitting diodes and ambipolar transistors [30]. It is striking to notice that full cycles (p and n doping) for **P1** and **P2** were recorded with consecutive cycles under ambient conditions which indicates the stability of doped states [31].

The cyclic voltammograms for both polymer films were recorded at different scan rates (between 100 and 300 mV/s) in monomer free medium and the scan rate dependence of the anodic and cathodic peak currents were observed (Fig. 3). This linear dependence illustrates that the charge transfer process for well adhered polymer films were non diffusion controlled [32].

Table 1 summarizes electrochemical behaviors of synthesized polymers and their analogues without Fc. As seen, when Fc was replaced by one phenyl unit in PDPEQ (Scheme 2), both p-and n-type doping/dedoping potentials were increased for **P1**. The trend was also observed for p-type doping/dedoping potentials of **P2** compared to PDEFNQ. This can be attributed to the electroactive behavior of the Fc unit where oxidation of Fc to Fc⁺ results in positively charged pendant group on polymer backbone which makes electron extraction from the polymer more difficult compare to Fc free analogues. Comparison between optical band gaps of all four polymers showed that incorporation of Fc unit as a pendant group increased the band gap of the polymer.

3.3. Spectroelectrochemistry

Spectroelectrochemical properties of the polymers were investigated between -0.5 and 1.0 V in 0.1 M TBAPF₆/ACN electrolytesolvent couple and UV-Vis-NIR spectra were recorded upon external bias. Electrochemically produced polymer films on ITO were reduced to their neutral states at -0.5 V in order to remove any trapped charge and dopant ion during electrochemical polymerization prior to spectroelectrochemical analysis. The spectral responses of polymer films to stepwise oxidation were noted as the potential was gradually increased. As seen in Fig. 4, P1 has maximum absorption wavelengths in the visible region were centered at 447 and 703 nm whereas P2 revealed relatively red shifted absorption maxima at 450 and 760 nm which were attributed to low and high energy $\pi - \pi^*$ transitions. Optical band gaps (E_g) for P1 and P2 were calculated from the onsets of lower energy transitions as 1.43 eV and 1.24 eV, respectively. Calculated Eg values suggest that both polymers can be regarded as low band gap polymers

Table 1

Electrochemical and optical results for P1, P2 and their counterparts.

	-		-						
Polymer (V)	$E_{\rm ox}^{\rm mon}$	$E_{\rm p-doping}$	$E_{\rm p-dedoping}$	E _{n-doping}	E _{n-dedoping}	λ_{max}	Τ%	Switching time (s)	$E_{\rm g}^{\rm op}~({\rm eV})$
P1	0.58 ^c 0.98	1.0	0.35	-1.95	-1.30	447 703 1700	40 22	1.3 1.68	1.43
PDPEQ ^a	1.05	0.3	-0.02	-1.55	-1.10	448 732 1800	35 29 77	1.2 0.7 2	1.01
PDEFNQ ^b	0.72 ^c 1.1	0.85	0.42	-1.70	-1.35	450 760 1750	33 40	0.8 1.6	1.3
P2	0.85	0.60	0.35	-2.05	-1.42	450 760 1800	21 17 57	0.6 0.5 0.9	1.24

^a Data were taken from Ref. [10b].

^b Data were taken from Ref. [33].

^c Fc/Fc⁺ oxidation potential was observed in the first cycle during CV.



Fig. 2. Single scan voltammograms for P1 and P2 in monomer free, 0.1 M TBAPF₆/ACN solutions.



Fig. 3. Scan rate dependence of: (a) P1 and (b) P2 films at 100, 150, 200, 250, and 300 mV/s.



Scheme 2. Chemical structures of related polymers.

with strong absorption in the visible region tailing into near IR (NIR).

Upon stepwise oxidation of polymer films, the absorption in the visible region diminished as the new bands were intensified at around 1000 nm and 1700 nm. These lower energy transitions indicate the formation of charge carriers such as polarons and bipolarons. Although both polymers switched between green and transmissive states as their two extreme states, partial oxidation of **P1** film resulted in different intermediate state colors (Fig. 4). Difference between two homologue polymers is a consequence of bridge-like absorption at 500 nm for **P1** which was not the case for **P2**. This absorption also induced a black colored intermediate state for **P1** where almost all visible light was harvested by the polymer film. Since polaronic and bipolaronic states absorptions were not in the visible region, both polymers ended up with highly transmissive oxidized forms.

Spectroelectrochemical and colorimetry studies showed that incorporation of Fc unit in polymer backbone resulted in multicolored oxidation states whereas quinoxaline based polymers without ferrocene switched only between green and highly transmissive states (Fig. 5). Intermediate colored states appeared due to



Fig. 4. Spectroelectrochemistry of: (a) P1 and (b) P2 films on an ITO coated glass slide in monomer free, 0.1 M TBAPF₆/ACN electrolyte–solvent couple between –0.5 V and 1.0 V.



Fig. 5. Colors of P1 and P2 at their neutral (0.0 V) and different oxidized states.



Fig. 6. Percent transmittance changes as a function of time for: (a) P1 and (b) P2 at their maximum absorption wavelengths in visible and NIR regions.

contribution of orange and blue colors which are the characteristic colors of Fc and Fc^+ respectively. This was also proven by the different spectral response of Fc containing polymers upon stepwise oxidation compared to that of non-containing ones.

3.4. Kinetic studies

Kinetic studies were conducted in order to determine switching times and percent transmittance changes (ΔT %) of the polymers

between their neutral and oxidized states. The polymer films were stepped between two states with 5 s time intervals. Due to multicolor formation between its two extreme states, ΔT % for **P1** in the visible region was only observable at 703 nm as 40%. However, in the visible region at the maximum absorption wavelengths (450 nm and 760 nm), **P2** film revealed 21% and 17% transmittance changes between the neutral and oxidized states. In this manner incorporation of Fc unit as pendant group increased the transparency of the oxidized states as in **P1** and PDEFNQ compared to their Fc free counterparts while resulting in a slower switching time (Table 1). In NIR region, **P2** was repetitively switched between its p-type doped/dedoped states and revealed 57% optical contrast (Fig. 6).

How fast the electrochromic materials change their colors is also an important parameter as well as percent transmittance changes at maximum absorption wavelengths for optical applications. Switching time is defined as the period required for the color change of a material between its neutral and oxidized/reduced states. Utilizing the kinetic studies of **P1** and **P2**, switching times were calculated for visible and NIR regions. **P1**, at its dominant wavelength (703 nm), switched its color from green to transmissive within 1.3 s which was outstanding since three colors were detectable in that period. For **P2**, switching times were calculated as 0.6 s, 0.5 s and 0.9 s at 450 nm, 760 nm and 1800 nm, respectively. When pristine phenyl and naphthalene containing polymers **PDPEQ** and **P2** are compared in terms of their switching abilities, it was seen that **P2** has shorter switching times than that of **PDPEQ**.

4. Conclusion

Two new guinoxaline and EDOT based polymers were synthesized electrochemically from their corresponding monomers. Structural designs for P1 and P2 were accomplished in order to have a better comparison and understanding about pendant group effect on electrochromic properties of these green to transmissive conjugated polymers. Summary of results showed that incorporation of Fc substituent enhanced the optical contrast in the visible region which in turn resulted in better transparency for the oxidized state if comparison is made between P1 and PDPEQ or between PDEFNQ and P2. Phenyl pendant group (as in PDPEQ) resulted in higher optical contrast with a longer switching time than that of naphthyl substituted **P2**. However, Fc pendant group bearing polymers (P1 and PDEFNQ) revealed multicolored electrochromism which is an effect of independent electrochromic switching of Fc. Thus, multicolored states with green to transmissive switching polymers could be achieved by Fc substitution.

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