# Macromolecules

# Toward Purple-to-Green-to-Transmissive-to-Black Color Switching in Polymeric Electrochrome

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**Supporting Information** 

**ABSTRACT:** A novel 3,4-ethylenedioxythiophene (EDOT)-based donor-acceptor electroactive monomer (HCQE) bearing carbazole subunit is synthesized, and then the corresponding polymer, poly(HCQE), is directly deposited onto ITO/glass surface via electrochemical process. Spectroelectrochemical studies demonstrate that poly(HCQE) is capable of showing both n- and p-doping processes. Hence, this low band polymer serves the multielectrochromic feature at three separate states (-0.4 to -2.0 V, -0.4 to 1.2 V, and 1.2 to 2.0 V) with a highly unique near colorless and colored states, fast switching times, redox switching stability, and exceptional transmittance change. To the best of our knowledge, this is the first report of a neutral state green multielectrochromic polymer exhibiting successive switching of colored-to-bleached-to-colored in three distinct regimes.

# INTRODUCTION

A major breakthrough with the discovery of polyacetylene in 1970 has imparted a great effect on the development of conductive polymers.<sup>1–3</sup> Since then, the area has grown enormously and also brought about many new and astonishing applications due to unique features of polymers such as easy processing, flexibility, light weight, tunability of band gaps, and redox behavior as well as low cost.<sup>6</sup> During the past three decades, conjugated polymers are widely used for industrial applications such as organic light-emitting diodes (OLEDs),<sup>7,8</sup> organic solar cells (OSCs),<sup>9,10</sup> organic field effect transistors (OFETs),<sup>11,12</sup> smart windows,<sup>13,14</sup> and electrochromic devices.<sup>15,16</sup> It is observed that a large number of device applications based upon electrochromism rely on the reproducibility of switching characteristics and the stability of conducting polymers under operating conditions.<sup>17</sup>

Electrochromism is a phenomenon in which a material shows a reversible color change upon applied electric field. New absorption bands at different parts of the visible and NIR regions can be generated by switching between different redox states. The resulting color changes of the material are examined by the spectroelectrochemical measurement by the utilization of both electrochemical and spectroscopic methods. This measurement offers a new route to study and clearly analyze electroactive species or products of redox reactions. However, it is a main prerequisite to produce the entire color spectrum for a possible utilization of electrochromic materials in display technologies.<sup>18</sup> So far, most of the electrochromic materials have exhibited mainly blue and red colors and lacked a green



color. It requires the absorption bands in the red and blue parts of the visible spectrum at the neutral state and also depletion in the oxidized state with the same applied potential. However, a dual control of both chromophores with the same applied potential is rather challenging. For that reason, a limited number of studies referring neutral state green polymer have come out. In 2004, Wudl et al. reported the first example of neutral state green polymer based upon a synthetic design relying on the insertion of two separate chromophores generating a dual absorbance in the visible spectrum. Nevertheless, the polymer showed inadequate transmissivity in the oxidized state.<sup>16,19</sup> Later, the Reynolds and Toppare groups overcame this by synthesizing and studying donoracceptor polymers based on benzothiadiazole and quinoxaline moieties along the polymer backbone. These neutral-state green polymers having a single chromophore demonstrated excellent transmissivity in the oxidized state.<sup>20-24</sup> Furthermore, in 2008, the first neutral-state black polymeric electrochrome was reported on the use of the donor-acceptor approach by Reynolds et al.<sup>25</sup>

Among the electrochromic polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives have taken the lead in electrochromic applications due to easy processability, easy switching between two redox states, low band gap, and high chemical stability given by an electron-donating ethylenedioxy

Received: September 24, 2014 Revised: November 25, 2014 group.<sup>26,27</sup> PEDOT polymers containing carbazole moieties inserted in the main chain as building blocks and also in the side chain as pendant groups have been used as electroactive and photoactive materials in various electrochromic applications.<sup>15,28,29</sup> The multielectrochromism in the systems of carbazole moiety incorporated into the polymer backbone at the 3,6-position is due to the effective conjugation break. The radical cations formed upon initial oxidation and dications upon further oxidation at higher potentials are well separated from one another and do not combine. Thus, two distinct oxidation states provide a three-color electrochromism resulting in the separate colors found at three states.<sup>30,31</sup> In addition, Hsiao and Liu have shown the multielectrochromism studies with distinct colors present for different states in a design of carbazole moiety introduced into main chain as a pendant group.<sup>32–36</sup>

Herein, we report the synthesis of a new monomer named as 3-(5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-3-(9hexyl-9H-carbazole-3-yl)quinoxalin-2-yl)-9-hexyl-9H-carbazole (HCQE). Poly(HCQE) has an ambipolar character (n- and pdopable) which implies that the same polymer can behave as both the cathodically and anodically coloring material in an electrochromic device. It exhibits a green color in the neutral state, near colorless in the first oxidized state, and then cyan, blue, and black colors in the second oxidized state of the pdoping. On the other hand, the green color of the film turns into red, violet, and purple on n-doping. Since the electroactive carbazole pendant groups have a separate oxidation potential and their oxidation has no color interference due to near colorless first oxidation state, the resulting polymer film exhibits a highly unique near colorless and colored oxidized states, fast switching times, redox switching stability, and exceptional transmittance change with a multielectrochromism behavior at three distinct states of -0.4 to -2.0 V, -0.4 to 1.2 V, and 1.2 to 2.0 V (Figure 1). For the first time, we have demonstrated by



Figure 1. Color changes of poly(HCQE) at different potentials.

this work a neutral state green multielectrochromic polymer possessing the consecutive transitions of colored-to-bleachedto-colored oxidation states, thereby allowing this material as a possible electrochrome for display applications.

#### EXPERIMENTAL SECTION

All synthetic steps are given in the Supporting Information. FT-IR spectra were recorded by a PerkinElmer FT-IR Spectrum One using an ATR system (4000–650 cm<sup>-1</sup>). <sup>1</sup>H NMR (Bruker Avance DPX-400) data were recorded at 25 °C using CHCl<sub>3</sub>-d solvent and TMS as internal standard.

Electrochemical measurements were carried out using a Biologic SP-50 electrochemical workstation. The electrochemical cell consists of a Ag wire as reference electrode (RE), a Pt wire as counter electrode (CE), and platinum as a working electrode (WE) immersed in 0.1 M TBAHF<sub>6</sub> as the supporting electrolyte. All measurements were carried out under an argon atmosphere. To calculate the HOMO–LUMO

energy levels, oxidation and reduction potential onsets of HCQE and poly(HCQE) were used, and the onset potentials of oxidation and reduction were determined from intersection of the tangents between the baseline and the signal current. The potentials were calibrated to the ferrocene redox couple  $E^{\circ}(Fc/Fc^+) = 0.38$  V (vs Ag wire) in CH<sub>2</sub>Cl<sub>2</sub> using the equation  $E_{HOMO} = -e(E_{ox} - E_{Fc}) + (-4.8 \text{ eV}).^{37}$  UV–vis absorption spectra were measured using an Analytic Jena Speedcord S-600 diode-array spectrophotometer. The optical band gaps ( $E_{g}$ ) of products were calculated from their absorption edges ( $\lambda_{onset}$ ) using the equation  $E_{g} = 1241/\lambda_{onset}$ .<sup>38</sup> Photoluminescence spectra were recorded on a PTI QM1 fluorescence spectrophotometer.

Spectroelectrochemical measurements were performed using absorption spectra of this polymer film upon applied potentials.<sup>39</sup> The spectroelectrochemical cell includes a quartz cuvette, an Ag wire (RE), a Pt wire counter electrode (CE), and ITO/glass as transparent working electrode (WE). These measurements were carried out in 0.1 M TBAPF<sub>6</sub> as supporting electrolyte in CH<sub>3</sub>CN.

Colorimetry measurements were performed using an Analytic Jena Specord S600 UV–vis spectrophotometer which consists of a chromometer module (standard illuminator D65, CIE system; the color is made up of three attributes: luminance (L), hue (a), and saturation (b)).<sup>40</sup> Platinum cobalt DIN ISO 621, iodine DIN EN 1557, and Gardner DIN ISO 6430 are the references of colorimetric measurement. These parameters were applied for the neutral and oxidized states of the polymer deposited onto ITO/glass surface.

#### RESULTS AND DISCUSSION

Synthesis and Characterization. The HCQE monomer has been synthesized in four steps (Scheme 1). The initial compound, 9-hexyl-9H-carbazole, was prepared according to the previously reported work.<sup>41</sup> 1,2-Bis(9-hexyl-9H-carbazole-3yl)ethane-1,2-dione was obtained via standard Friedel-Crafts reaction between 9-hexyl-9H-carbazole and oxalyl chloride in the presence of  $AlCl_3$  in DCM. The yield of the compound 1 is very low (35%) because of the formed polymeric side products. Then, the dibromo compound bearing carbazole subunits, compound 2, was synthesized from the condensation reaction between carbazole-dione compound 1 and 3,6-dibromobenzene-1,2-diamine in the presence of PTSA as a catalyst in toluene. Finally, the standard Stille reaction was applied to obtain target donor-acceptor compound of HCQE. After completion of the synthetic works, the chemical structures of the initial compounds and the target product were elucidated by using FT-IR and <sup>1</sup>H NMR spectroscopy (Figures S1–S5).

Poly-HCQE was synthesized in a reaction medium containing 2.0  $\times$  10<sup>-3</sup> M HCQE and 0.1 M TBAPF<sub>6</sub>/ CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>CN (3:1 v/v) via repetitive cycling at a scan rate of 100 mV s<sup>-1</sup>. The electroactive polymer was directly deposited onto the working electrode (platinum disk or ITO/glass surface). Potentiodynamic electrochemical polymerization of HCQE was studied by repetitive cycling between 0 and 1.10 V exhibiting a new redox couple at lower potentials (Figure 2). The increase in current density after each successive cycle clearly indicated the deposition of poly(HCQE) onto the surface of working electrode (WE). The polymer film deposited onto ITO/glass surface was electrochemically dedoped in monomer-free electrolyte solution and then partly dissolved in chloroform by sonicating for UV–vis absorption and fluorescence measurements.

**Optical and Electrochemical Properties.** The UV-vis absorption and fluorescence spectra of HCQE and poly-(HCQE) were recorded in CHCl<sub>3</sub> solution (Figure 3). In the UV-vis absorption spectrum of HCQE, the absorption peak at 316 nm is attributed to the  $\pi$ - $\pi$ \* transition; the peak at the 429 nm charge transfer band is associated with electronic transition

#### Scheme 1. Synthetic Route for HCQE Monomer<sup>a</sup>



"Reagents and conditions: (a) 1-hexyl bromide, KOH, toluene, 110 °C, 24 h; (b) oxalyl chloride,  $AlCl_3$ , DCM, rt, 18 h; (c) 3,6-dibromobenzene-1,2-diamine, PTSA, toluene, 24 h, 110 °C; (d)  $Pd(PPh_3)_4$ , 3 M KOH, toluene, 120 °C, 24 h.



Figure 2. Repeated potential scans of HCQE in 0.1 M TBAHF<sub>6</sub> in  $CH_3CN/CH_2Cl_2$  (1/3; v/v) with a scan rate of 100 mV s<sup>-1</sup>.

from the donor moieties to the electron-withdrawing quinoxaline unit (Figure 3). Because of increased effective conjugation on the polymer backbone, the charge transfer band was broadened and bathochromically shifted (about 230 nm) relative to corresponding monomer, suggesting  $\pi - \pi$  interaction between polymer chains. Moreover, two specific absorption bands which are crucial for neutral state green conducting polymers were determined. The emission spectrum of poly-(HCQE) showed that emission maxima shifted to NIR region ( $\lambda_{max}$ : 778 nm) relative to the corresponding monomer HCQE ( $\lambda_{max}$ : 538 nm) due to a red-shift in absorbance of the charge transfer band upon polymerization, and the intensity was quite quenched relative to the corresponding monomer HCQE.

The electrochemical properties of HCQE and poly(HCQE) were investigated by cyclic voltammetry (CV). An explicit

difference in redox behavior of poly(HCQE) and the initial compound HCQE can be deduced from the CV depicted in Figure 4. During CV scan in the anodic regime, HCQE exhibited an oxidation peak at  $E_{m,a}^{ox} = 0.80$  V vs Ag wire at anodic scan, and this oxidation potential is higher than that of poly(HCQE) ( $E_{m,a}^{ox} = 0.55$  V and  $E_{m,c}^{ox} = 0.45$  V;  $E_{m,1/2}^{ox} = 0.50$  V vs Ag wire) (Figure 4a,b). Because of the extended conjugation along the polymer backbone, an oxidation potential was observed at lower potentials compared to the corresponding initial compound (HCQE). It is clearly seen that the electroactive pendant carbazole moiety in both monomer and polymer structures can be easily oxidized at 1.5 V upon applied higher potentials (Figure S6).

On the other hand, during the cathodic regime, the cyclic voltammogram of HCQE exhibits a characteristic reduction peak at -1.35 to -1.41 V ( $E_{m,1/2}^{red} = -1.38$  V) attributed to the reversible reduction process of the quinoxaline moiety (Figure 4a). Besides, a more negative shift was observed upon the polymerization since the donor character of the main chain rises with increasing  $\pi - \pi$  conjugation on the polymer backbone. Finally, a reduction peak was observed with a half-wave potential ( $E_{m,1/2}^{red} = -1.49$  V) of -1.40 to -1.58 V for poly(HCQE).

The scan rate dependence of the polymer film was studied by cyclic voltammetry. The linear relationship between peak current and scan rate demonstrates that the polymer film firmly attaches onto ITO electrode, and the electrochemical process is consistent with non-diffusion-controlled behavior (Figure 5).<sup>42,43</sup> The linear behavior indicates that the redox-active species pursue the characteristic of the surface confined nature of the electrochemical process. Thus, it is seen that the polymer on the ITO/glass surface does not diffuse into the electrolyte solution even in the high scan rates. On the other hand, the positive or negative charges can diffuse through the polymer



Figure 3. UV-vis absorbance and fluorescence spectra of HCQE (a) and poly(HCQE) (b). Insets: the corresponding photos of compounds with (right) and without (left) UV light (366 nm).



Figure 4. Cyclic voltammograms of HCQE (a) and poly(HCQE) (b) in 0.1 M TBAPF<sub>6</sub>/DCM with a scan rate of 100 mV s<sup>-1</sup> vs Ag wire.



Figure 5. Scan rate dependence of the poly(HCQE) film deposited onto the ITO electrode in 0.1 M TBAPF<sub>6</sub>/CH<sub>3</sub>CN at different scan rates from 25 to 1000 mV  $s^{-1}$  vs Ag wire.

Table 1. Electrochemically Determined HOMO and LUMO Energy Levels, Electrochemical Band Gaps $(E_g)$ ,	and
Spectroscopically Estimated Optical Band Gap $(E_g)$ Values of HCQE and Poly(HCQE)	

molecules	reduction potential (V)	oxidation potential (V)	HOMO (eV)	LUMO (eV)	$E'_{g'}$ electrochem band gap (eV)	$E_{\rm g'}$ optical band gap (eV)
HCQE	$E_{\rm m,c}^{\rm red} = -1.41$	$E_{\mathrm{m,a}}^{\mathrm{ox}} = 0.80$	-5.10	-3.15	1.95	2.27
	$E_{m,a}^{red} = -1.35$	$E_{\rm m,on}^{\rm ox} = 0.68$				
	$E_{\rm m,on}^{\rm red} = -1.27$					
poly(HCQE)	$E_{\rm p,c}^{\rm red} = -1.40$	$E_{\rm p,a}^{\rm ox} = 0.55$	-4.40	-3.06	1.34	1.63
	$E_{\rm p,a}^{\rm red} = -1.58$	$E_{\rm p,c}^{\rm ox} = 0.45$				
	$E_{\rm p,on}^{\rm red} = -1.36$	$E_{\rm p,on}^{\rm ox} = -0.02$				

film under applied potentials referring to as having diffusive characteristics at the redox states.

In addition, the HOMO-LUMO energy levels and the electrochemical band gap  $(E'_g)$  of the compounds were

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estimated from the onset oxidation and reduction potentials (Table 1). The electrochemical band gaps of HCQE and poly(HCQE) were found as 1.95 and 1.34 eV, respectively.

The frontier molecular orbitals of the monomer HCQE were investigated by using density functional theory (DFT) with the Spartan10 program at the parameters of B3LYP and  $6-31+G^*$  basis sets. The charge distribution in the frontier molecular orbitals is shown in Figure 6. All hexyl chains were replaced



Figure 6. Molecular orbital diagrams of the HOMO and LUMO levels of HCQE.

with an ethyl chain for simplicity. As shown in Figure 6, the LUMO orbital is more localized on the electron-accepting quinoxaline moiety, while HOMO orbitals (HOMO and HOMO-1) are delocalized on the electron-donating thiophene and pendant carbazole moiety, respectively. Hence, the results of DFT calculation also confimed that the structure shows an increase in stability against over oxidation and also explain the formation of two distinct state electrochromism in the anodic regime.

**Spectroelectrochemical Properties.** Oxidation and reduction of the polymer film are accompanied by impressive color changes based upon the chemical structure of the polymer. To study these color changes in detail, the electro-optical properties of the poly(HCQE) film were investigated by monitoring absorption spectra upon applied different potentials to the film. Poly(HCQE) has absorption bands at two distinct wavelengths (400 and 700 nm) which are necessary to produce a green color at the neutral state (Figure 7). Upon applied positive potential of -0.4 to +1.2 V to the poly(HCQE) film, the intensity of the valence band–conduction band  $(\pi - \pi^*$  transitions) at about 400 nm and charge transfer band at about 700 nm decreased, and a new intense absorption band centered at about 950 nm emerged due to low-energy charge carriers. This depletion in absorption bands of the visible region makes



Figure 7. Electronic absorption spectra and the color changes of poly(HCQE) deposited onto ITO/glass surface with the applied potential of -0.4 to 1.2 V in 0.1 M TBAPF<sub>6</sub>/CH<sub>3</sub>CN on p-doping.

the polymer film nearly colorless in a stepwise fashion with a residual absorption tail starting at 500 nm. Apparently, a high level of transparency can be seen by the naked eye upon oxidation. Finally, the green color (L\*:57; a:-46; b:15) of the polymer film was converted to nearly colorless (L\*:72; a:-3; b:-2) after application of positive potential.

As the applied potential was gradually increased (1.2-2.0 V), a new broad absorption peak at about 650 nm appeared and the peak intensity increased drastically (Figure 8). The pendant



Figure 8. Spectroelectronic absorption spectra and the color changes of poly(HCQE) deposited onto ITO/glass surface with the applied potential of 1.2-2.0 V in 0.1 M TBAPF<sub>6</sub>/CH<sub>3</sub>CN on p-doping.

carbazole units may oxidize and dimerize at higher applied voltages leading to a biscarbazole structure, which may be a result of NIR absorption due to the intervalence charge transfer (IVCT) effect. The IVCT effect is known as one electron transfer from a neutral to a positively charged nitrogen atom on carbazoles.<sup>44,45</sup> As a consequence of oxidation of carbazole moiety on the polymer subunit, the poly(HCQE) film switched from a nearly colorless oxidized state to a fully oxidized state by revealing colors of (L\*:82; a:-3; b:-2) cyan (L\*:55; a:-31; b:-10), dark blue (L\*:31; a:2; b:-19), and black (L\*:22 ; a:0; b:-6).

Further, an n-type feature can be also confirmed by an absorption change in the NIR region beside a redox couple at negative potentials revealed in cyclic voltammetry. Anion radicals formed on the quinoxaline moiety of the poly(HCQE) structure upon applied negative potentials. As the negative potentials are applied to the film from -0.4 to -2.0 V (Figure 9), a decrease in the absorption bands at about 400 and 700 nm and the formation of new absorption bands at 510 and 950 nm were observed by accompanying the color change from green (L\*:57; a:-46; b:15) to violet (L\*:50; a:56; b:-33) and purple (L\*:50; a:76; b:-66).

The double step chronoamperometry technique was used to monitor the transmittance changes between the neutral and the oxidized states upon electrochromic switching of poly(HCQE). Electrochromic parameters of the polymer film were analyzed with the changes in transmittance (increments or decrements of the absorption band with respect to time) while switching the potential step wisely between the neutral and oxidized states with a residence time of 5 s. In the oxidation, the change in maximum percentage transmittance ( $\%\Delta T$ ) of poly(HCQE) between the neutral (-0.4 V) and oxidized state (1.2 V) was found 37% (Figure 10). Besides, the polymer switches very rapidly between the neutral and oxidized state, and response



Figure 9. Electronic absorption spectra and the color change of poly(HCQE) deposited onto ITO/glass surface with the applied potential of -0.4 to -2.0 V in 0.1 M TBAPF<sub>6</sub>/CH<sub>3</sub>CN on n-doping.

times in this regime were measured as 0.45 and 0.3 s. Poly(HCQE) film achieved an excellent optical activity of 98% after 1000 cycles (Figure 10).

Another important criterion for identifying the electrochemical performance of the materials is the coloration efficiency (CE). The CE is defined as the change in optical density per unit of inserted charge. The ideal material would demonstrate a large transmittance change with a small amount of charge, which eventually results in large CEs. CE is calculated using the formulas CE = OD/Q<sub>d</sub> and OD =  $\log(T_{colored}/T_{bleached})$ , where Q<sub>d</sub> is the injected/ejected charge between the neutral and oxidized states and  $T_{colored}$  and  $T_{bleached}$ are the transmittance in the oxidized and neutral states, respectively. Using these equations, CE of poly(HCQE) was calculated as 96 cm<sup>2</sup> C<sup>-1</sup> (at 700 nm), 112 cm<sup>2</sup> C<sup>-1</sup> (at 690 nm), and 403 cm<sup>2</sup> C<sup>-1</sup> (at 650 nm), with applied potential switched from -2.0 to -0.4 V, 0.4 to 1.2 V, and 1.2 to 2.0 V, respectively, by monitoring the charge and change in transmittance.

# CONCLUSION

Herein, a novel donor-acceptor monomer, HCQE, containing a pendant carbazole unit was designed, synthesized, and electrochemically polymerized yielding a neutral state green polymer exhibiting an ambipolar behavior and a multielectrochromism existing in three distinct redox states. Poly(HCQE) film prepared via electrochemical process onto transparent ITO/glass surface led to an impressive multielectrochromic material at different redox states. Because of a dual n- and p-type dopable behavior and having another electroactive carbazole moiety as a subunit, poly(HCQE) as an electrochromic material has multiple separate colors at various oxidation and reduction states. Optical and spectroelectrochemical analysis of the green conjugated polymer brought out a nearly colorless and colored oxidized states, excellent transmittance change, fast switching times, and long-term stability. To our knowledge, this is the first report of a neutral state green polymer demonstrating the consecutive switching of colored-to-bleached-to-colored oxidation states, which might open up a new horizon in electrochromic display applications.

Article

# ASSOCIATED CONTENT

#### Supporting Information

All experimental details; FT-IR and <sup>1</sup>H NMR spectra of initial compounds and HCQE monomer. This material is available free of charge via the Internet at http://pubs.acs.org.

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# Notes

The authors declare no competing financial interest. E.Ö.: deceased March 25, 2014.

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Figure 10. Chronoabsorptometry experiments for poly(HCQE) deposited onto ITO/glass surface with a switched potential of -0.4 to 1.2 V.

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