



# Novel multicolored electrochromic polymers containing phenanthrene-9,10-quinone and thiophene derivatives moieties



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## ABSTRACT

Two novel monomers 2,7-bis(3-ethylthiophen-2-yl)-9,10-phenanthrenequinone (ETPQ) and 2,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9,10-phenanthrenequinone (DDPQ) were successfully synthesized via Stille cross coupling reaction. Meanwhile, the corresponding polymers PETPQ and PDDPQ were synthesized electrochemically and characterized carefully. Both polymer films displayed multi-colored electrochromism. The PETPQ film showed a yellow color at neutral state, and with the increase of the applied potential, its color switched from yellowish green to green, and then light blue, finally a blue color in the oxidized state was observed. The color of the PDDPQ film was red in its neutral state, and turned to blue in the oxidized state, in intermediate states, violet red and purple colors were observed. Moreover, the parameters (coloration efficiency, optical contrast and response time) of the two interesting polymers were all reasonable and satisfactory. The dual-type electrochromic device based on PETPQ film (or PDDPQ film) and PEDOT film was constructed and characterized as well. Both of them revealed excellent properties.

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## 1. Introduction

Owing to the great interest, researchers have made significant efforts to design and synthesis of the novel conjugated polymers with unique optical and electrical properties. The electrochromic conjugated polymers have been widely investigated for a variety of applications, such as electrochromic devices [1,2], optical displays [3], smart windows [4], sensors [5]. Compared with the inorganic compounds, organic electrochromic materials have distinct advantages toward high coloration efficiency, fast switching ability, and multiple colors within the same material [6]. In addition, the structural modification of the organic electrochromic materials can be easily performed, and the pendant substituents on the backbone play a important role on the changing of electrochemical and optical properties of conjugated polymers. This strategy allows a fine-tuning of the band gaps of the polymers toward generating different colors [7].

The electrochromic conjugated polymers with thiophene unit [8], 3,4-alkylenedioxythiophene (EDOT) unit [9], or pyrrole unit [10] have been pursued quite actively. In recent years, the kind of poly(heterocycle-arylene-heterocycle) compound has been drawn much attention due to the fine-tuning of the bandgap of the

polymers by the choice of the arylene units. In this way, some of the polymers with excellent electrochromic properties have been synthesized and characterized. Osman Atwani and coworkers [11] have reported a kind of electrochromic polymer, poly(4,7-dithien-2-yl-2,1,3-benzothiadiazole), which was highly stable and had low band gap. And our group also reported the electrosynthesis and characterization of an electrochromic material from poly(1,4-bis(2-thienyl)-benzene) [12], which has a structure of poly(thiophene-arylene-thiophene). As a candidate for arylene unites, it is interesting to find that phenanthra-9,10-quinone turns out to be a ideal  $\pi$ -electron system as which is fully conjugated. The two carbonyl groups present in phenanthra-9,10-quinone provide a unique opportunity for molecular modification. Some of the previous works have been done to modify the phenanthra-9,10-quinone unit, and the incorporation of the modified unites in poly(thiophene derivatives) often resulted in the formation of donor-acceptor type polymers, such as the series of conjugated monomers containing 10,11,12,13-tetrahydridibenzo[a,c]phenazine moiety and thiophene derivatives, made by Elif Kose Unver and coworkers [6]. And the group of Simge Tarkuc also synthesized and characterized the electrochromic material of 10,13-bis(4-hexylthiophen-2-yl)dibenzo[a,c]phenazine, based on phenanthra-9,10-quinone [13]. Meanwhile, phenanthra-9,10-quinone displays a large dipole by reason of the fact that two carbonyl groups are on the same 'side' of the molecule. And, easy electron transfer along the polymer backbone is expected by the stacking of the quinone units [14]. So it

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was expected that the unmodified phenanthra-9,10-quinone only be also suitable as the arylene unit for the modification of the backbone of the electrochromic conjugated polymers. And, to the best of our knowledge, the synthesis and characterization of thiophene derivatives–bis-substituted phenanthra-9,10-quinone monomers and the corresponding polymers have not been reported previously.

In the present paper, two structurally related polymers containing phenanthra-9,10-quinone unit and different thiophene derivatives were synthesized and characterized in detail to show the effect made by substitution on electrochemical and optical properties. Although, the typical behaviors of donor–acceptor type polymers such as n-doping were not found, the polymers we obtained exhibited satisfactory electrochemical and optical properties.

Based on the consideration above, two novel monomers 2,7-bis(3-ethylthiophen-2-yl)-9,10-phenanthrenequinone (ETPQ) and 2,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9,10-phenanthrenequinone (DDPQ) were synthesized via Stille cross coupling reaction, and the corresponding polymers were electrochemically synthesized. In addition, the spectroelectrochemical and electrochromic properties of the two polymers were investigated in particular. Both of the two polymers exhibited multiple colors (yellow, yellowish green, green, light blue and blue for PETPQ film, and red, violet red, purple, blue for PDDPQ film). Moreover, the PETPQ film had prominent high optical contrast ( $\Delta T\%$ ) of 61.6%, and PDDPQ film revealed excellent response time of 0.34 s. Both of the properties have a significant influence on the electrochromic applications. Simple dual-type electrochromic devices based on target polymer film and PEDOT film were fabricated and characterized as well, and a satisfactory result was achieved.

## 2. Experimental

### 2.1. Materials

9,10-Phenanthrenequinone, 3,4-ethylenedioxythiophene (EDOT, 98%), *N*-bromosuccinimide (NBS), dichlorobis(triphenyl phosphine)palladium(II) ( $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ ), dichloromethane (DCM) were all purchased from Aldrich Chemical and used as received without further treatment. Tributylstannane compounds were prepared according to literature methods [15–17]. Tetrahydrofuran (THF), dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF) were all purchased from Tianjin windship chemistry Technological Company Limited. THF was dried and distilled over sodium in the presence of benzophenone before use. DMSO, DMF were used directly as received. Commercial high-performance liquid chromatography grade acetonitrile (ACN, Tedia Company, INC. USA), poly(methyl methacrylate) (PMMA, Shanghai Chemical Reagent Company), propylene carbonate (PC, Shanghai Chemical Reagent Company), lithium perchlorate ( $\text{LiClO}_4$ , Shanghai Chemical Reagent Company, 99.9%) and tetra-*n*-butylammonium hexafluorophosphate ( $\text{TBAPF}_6$ , Alfa Aesar, 98%) were all used directly without further purification. Sodium perchlorate ( $\text{NaClO}_4$ , Shanghai Chemical Reagent Company, 98%) was dried in vacuum at 60 °C for 24 h prior to be used. Indium-tin-oxide-coated (ITO) glass (sheet resistance  $< 10 \Omega \square^{-1}$ , purchased from Shenzhen CSG Display Technologies, China) was respectively washed with ethanol, acetone and deionized water in turn under ultrasonic, and dried by  $\text{N}_2$  flow at last.

### 2.2. Instrumentation

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy studies were recorded with a Varian AMX 400 spectrometer and chemical shifts were recorded in

ppm units with tetramethylsilane (TMS) as the internal standard. Hitachi SU-70 thermionic field emission SEM was used to analyze the surface morphologies of the polymer films. UV–vis spectra were performed via Shimadzu UV-2550 spectrophotometer. A Canon Power Shot A3000 IS digital camera was used to obtain digital photographs of the polymer films and devices.

### 2.3. Synthesis of monomers

#### 2.3.1. Synthesis of 2,7-dibromo-9,10-phenanthrenequinone (2)

According to the reported procedures [6,14,18], 9,10-phenanthrenequinone (PQ) and *N*-bromosuccinimide (NBS) were used as the starting materials to synthesize 2,7-dibromo-9,10-phenanthrenequinone (DBPQ) as depicted in Scheme 1. The solution of PQ in concentrated  $\text{H}_2\text{SO}_4$  (98%) was stirred mechanically at the temperature of 50 °C. And then NBS dissolved in *N,N*-dimethylformamide (DMF) was added dropwise to the mixture. Excessive addition of NBS was performed to make sure the reaction was well accomplished. The mixture was stirred for 8 h under nitrogen atmosphere to remove air and be free from light. After the reaction was complete, slow addition of the mixture to water with stirring for 1 h at room temperature was performed to quench the reaction mixture, and the precipitate was obtained. Then the precipitate was filtered, washed with water, dried under vacuum. The crude product was recrystallised two times from dimethylsulfoxide (DMSO) to get the purified product which is incarnadine solid.  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ , 400 MHz, ppm):  $\delta = 8.26$  (s, 1H), 8.24 (s, 1H), 8.08 (d, 2H), 7.97–7.95 (dd, 2H) (see Supporting information Fig. S1).

#### 2.3.2. Synthesis of 2,7-bis(3-ethylthiophen-2-yl)-9,10-phenanthrenequinone (3) and 2,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9,10-phenanthrenequinone (4)

Both of 2,7-bis(3-ethylthiophen-2-yl)-9,10-phenanthrenequinone (ETPQ) and 2,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9,10-phenanthrenequinone (DDPQ) were synthesized via Stille cross coupling reaction as is described in Scheme 1. To a solution of 2,7-dibromo-9,10-phenanthrenequinone (DBPQ) in dry THF was added the corresponding tributylstannane compound, and dichlorobis(triphenyl phosphine)palladium(II) ( $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ ) used as the catalytic was also added. The mixture was stirred magnetically at room temperature under nitrogen atmosphere. After half an hour, the mixture was heated to reflux with vigorous stirring for a further 36 h, and then concentrated under reduced pressure. The reaction was followed by thin-layer chromatography (TLC). Finally, column chromatography was used to purify the reaction mixture. The purified product ETPQ is glistening yellow solid.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta = 8.14$  (s, 1H), 7.96 (s, 1H), 7.90 (s, 2H), 7.81 (d, 1H), 7.61 (d, 1H), 7.33 (s, 2H), 6.95 (d, 2H), 2.68 (q, 4H), 1.29 (t, 6H) (see Supporting information Fig. S2).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta = 204.0$ , 146.2, 136.1, 134.9, 131.9, 128.9, 125.4, 124.8, 124.0, 123.1, 120.1, 24.0, 14.9 (see Supporting information Fig. S3). The purified product DDPQ is grey yellow solid.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta = 8.26$  (s, 1H), 8.05 (s, 1H), 8.01 (d, 1H), 7.90 (d, 1H), 7.79 (d, 1H), 7.74 (d, 1H), 6.36 (d, 2H), 4.37 (t, 8H) (see Supporting information Fig. S4).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz, ppm):  $\delta = 204.2$ , 142.6, 141.6, 133.5, 132.0, 128.7, 125.5, 124.4, 123.6, 117.2, 98.9, 65.1, 64.7 (see Supporting information Fig. S5).

### 2.4. Electrochemistry

The electrochemical tests and polymerization of the monomers were carried out in a one-compartment cell using a CHI 760C Electrochemical Analyzer (Shanghai Chenhua Instrument Co., China) under computer control at room temperature. For the experiments,

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