



## Donor acceptor type neutral state green polymer bearing pyrrole as the donor unit

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### ABSTRACT

A new neutral state green polymer, poly (2,3-bis(4-tert-butylphenyl)-5,8-di(1H-pyrrol-2-yl) quinoxaline) (PTBPPQ) was synthesized and its potential use as an electrochromic material was investigated. Spectroelectrochemistry studies showed that polymer reveals two distinct absorption bands as expected for a donor–acceptor type polymer, at 408 and 745 nm. In addition, polymer has excellent switching properties with satisfactory optical contrasts and very short switching times. Outstanding optical contrast in the NIR region and stability make this polymer a great candidate for many applications. It should be noted that PTBPPQ is one of the few examples of neutral state green polymeric materials with superior switching properties. Hence, PTBPPQ can be used as a green polymeric material for display technologies.

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## 1. Introduction

Conjugated polymers have attracted a great attention after their discovery [1], since these materials can be used as active layers in polymer light emitting diodes [2], sensors [3], batteries [4], artificial noses and muscles [5], transistors [6] and electrochromic devices [7]. Electrochromism is defined as the reversible and visible change in the transmittance and/or reflectance of a material caused by an applied voltage [8,9]. First studies in the field of electrochromism were on inorganic materials such as tungsten oxide (WO<sub>3</sub>) and iridium dioxide (IrO<sub>2</sub>) [10]. Inorganic materials lack color tuning and require use of relatively high voltages to operate devices. Organic compounds such

as conducting polymers became great candidates for electrochromic devices. As regards to the advantages of conducting polymers; high optical contrasts [11], short switching time [12,13], processability [14], fine tuning of the band gap via structure modification [15], and more importantly low applied voltages [16] are worth to mention.

Due to the extended delocalization of  $\pi$  electrons along the polymer backbone, an optical absorption band in the visible region of the electromagnetic spectrum occurs. The insertion of an anion or a cation occurs when the redox processes generate charge carriers on the conjugated backbone [17]. One of the method of increasing stability of the doping process is to incorporate donor–acceptor (D–A) units into the polymer backbone. Moreover, D–A method is also used for reducing the band gap energy [18–20]. While electron donor group raises the HOMO energy and lowers the oxidation potential, electron acceptor group

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lowers the energy of conduction band (LUMO) hence; reduction occurs easily [21–23].

Several pyrrole derivatives were employed in the field of electrochromism, such as; the use of modified pyrrole [16], in situ synthesis of pyrrole [24–27], and use of pyrrole in donor acceptor type polymers. Up to date there are few studies where pyrrole has been used as the donor/acceptor unit [28]. In our previous studies, quinoxaline derivatives [29–31] were efficiently used as the acceptor unit. Ethylenedioxythiophene (EDOT) and thiophene derivatives were used as the donor units for those studies. Pyrrole was rarely used as the donor unit with a quinoxaline acceptor unit in D–A type polymers [32,33].

There are a number of electrochromic polymers reflecting red and blue color in their neutral states [34,35] whereas few studies have been reported related to polymers reflecting green color [36–38]. In order to have red or blue color in reduced state, the materials have to absorb at only one dominant wavelength. On the contrary, for a green color, there should exist at least two simultaneous absorption bands in the red and blue regions of the visible spectrum where these bands should be controlled with the same applied potential.

Here we report the synthesis of a newly designed donor–acceptor type polymer. The unique polymer bears pyrrole as the donor unit. The polymer, namely 2,3-bis(4-tert-butylphenyl)-5,8-di(1H-pyrrol-2-yl)quinoxaline, revealed higher optical contrast in near IR region and faster switching time compare to 2,3-bis(4-tert-butylphenyl)-5,8-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7yl)quinoxaline (TBPEQ) [30] and (2,3-bis(4-tert-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl)quinoxaline) (HTQ) [31].

## 2. Experimental

### 2.1. Materials

All chemicals were purchased from Aldrich except anhydrous tetrahydrofuran (THF) which was purchased from Acros. 4,7-Dibromobenzo[1,2,5]thiadiazole [39], 3,6-dibromo-1,2-phenylenediamine [40], benzoin [41], benzyl [41], 1,2-bis(4-tert-butylphenyl)-2-hydroxyethanone [42], 1,2-bis(4-tert-butylphenyl)ethane-1,2-dione [42], 5,8-dibromo-2,3-diphenylquinoxaline [43], tert-butyl pyrrole-1-carboxylate [44], *N*-(tert-butoxycarbonyl)-2-(trimethylstannyl)pyrrole [44] were synthesized according to previously described methods. Electropolymerization was performed with a Voltalab 50 potentiostat in a three-electrode cell consisting of platinum wire or Indium Tin Oxide (ITO) coated glass as the working electrodes, platinum wire as the counter electrode, and an Ag wire as the pseudo reference electrode. Electrodeposition was performed from a 0.1 M solution of tetrabutylammonium perchlorate (TBAPC) at a scan rate of 100 mV/s for 15 cycles. UV–Vis–NIR spectra were recorded on a Varian Cary 5000 spectrophotometer at a scan rate of 2000 nm/min. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on Bruker Spectrospin Avance DPX-400 Spectrometer. Colorimetry measurements were performed via Minolta CS-100 Spectrophotometer.

### 2.2. Monomer synthesis

#### 2.2.1. 5,8-Bis[*N*-(tert-butoxycarbonyl)-2-pyrrolyl]2,3-bis(4-tert-butylphenyl) quinoxaline

5,8-Dibromo-2,3-bis(4-tert-butylphenyl) quinoxaline (550 mg, 1.0 mmol), and *N*-(tert-butoxycarbonyl)-2-(tributylstannyl)pyrrole (2.29 g, 5.0 mmol) were dissolved in anhydrous THF (150 ml) and purged with argon for 30 min. Then, dichlorobis(triphenyl phosphine)-palladium(II) (75 mg, 0.068 mmol) was added at room temperature under argon atmosphere. The mixture was refluxed for 3 days. Solvent was evaporated under vacuum and the crude product was purified by column chromatography on neutral alumina (eluent DCM:hexane, 2:1 v/v) to obtain 456 mg (63%) of 5,8-bis[*N*-(tert-butoxycarbonyl)-2-pyrrolyl]2,3-bis(4-tert-butylphenyl) quinoxaline. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 0.9 (s, 18 H), 1.22 (s, 18 H), 6.26 (t, 2H, *J* = 6.4 Hz), 6.32 (d, 2H, *J* = 7.0 Hz), 7.22 (d, 4 H, *J* = 8.8 Hz), 7.43 (d, 4 H, *J* = 8.4 Hz), 7.48 (q, 2 H, *J* = 3 Hz), 7.66 (s, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 152.0, 151.2, 149.8, 139.0, 136.1, 133.3, 131.5, 129.7, 128.0, 125.1, 123.0, 115.0, 110.4, 83.0, 34.7, 31.2, 27.2.

#### 2.2.2. 5,8-Bis [2-pyrrolyl] 2,3-bis(4-tert-butylphenyl) quinoxaline (TBPPQ)

5,8-Bis [*N*-(tert-butoxycarbonyl)-2-pyrrolyl] 2,3-bis(4-tert-butylphenyl) quinoxaline (350 mg, 0.48 mmol) was dissolved in 60 ml methanol. About 120 mg Na, (5.2 mmol) was added and the reaction mixture was heated under reflux for 24 h. The solvent was evaporated and the residue was treated with water and extracted with dichloromethane. The organic extracts were dried over MgSO<sub>4</sub>, the solvent was evaporated and the residue chromatographed on a column with silica gel using hexane:DCM (2:1 v/v) as eluent. In the second fraction 180 mg (72%) of product TBPPQ isolated. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 1.31 (s, 18 H), 6.27 (m, 2H), 6.82(m, 2H), 6.90 (m, 2H), 7.35 (d, 4 H, *J* = 8.4 Hz), 7.41 (d, 4 H, *J* = 8.8 Hz), 8.00 (s, 2 H), 11.93 (s, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 152.7, 151.4, 138.0, 136.4, 131.4, 129.7, 126.3, 125.8, 125.7, 119.7, 109.5, 107.7, 35.1, 31.6. MS: *m/e* 525 (M<sup>+</sup>). IR (drift) *v*: 1084, 1112, 1392, 1473, 1608, 2962, 3350 cm<sup>-1</sup>

## 3. Results and discussion

### 3.1. Monomer synthesis

The reagent 2,1,3-benzothiadiazole was brominated in the presence of a HBr/Br<sub>2</sub> mixture (95%) and reduced with an excess amount of NaBH<sub>4</sub> to give 3,6-dibromo-1,2-phenylenediamine as pale yellow solid. The purified compound was condensed with 1,2-bis(4-tert-butylphenyl)ethane-1,2-dione in ethanol to afford 5,8-dibromoquinoxaline. In order to achieve *N*-(tert-butoxycarbonyl)-2-(tributylstannyl)pyrrole (2), pyrrole was *N*-protected by using di-tert-butyl dicarbonate (Boc)<sub>2</sub>O and reacted with tri-*n*-butylstannyl chloride after lithiation at the 2 position. Deprotection of pyrrole substituents in (3) after coupling reaction between (1) and (2) resulted in donor acceptor type monomer TBPPQ (Scheme 1).

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