

# Synthesis of a new phenothiazine-carbazole polymer derivative and utilization in an electrochromic cell

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## ABSTRACT

In this study, a phenothiazine-carbazole electrochromic copolymer (CNU-CKP) was designed and prepared and fully confirmed by their  $^1\text{H}$  NMR, FT-IR, UV-vis, GPC and CV analyses. For this copolymer, we investigated its electrochromic properties by making an electrochromic cell. This cell consisted of polymer-spray-coated ITO glass and a gel electrolyte. We achieved good cyclic stability and electrochromic switching results with interesting color changes. Finally, the experimental results were compared with theoretical studies.

## 1. Introduction

According to J.R. Platt's [1] theoretical explanations, by the application of a strong electric field the absorption and emission spectra of some compounds shifts by hundreds of angstroms and this phenomenon is called the electrochromism, broadly, optical change in a material influenced by an external voltage in a reversible manner. Many inorganic and organic compounds display electrochromism throughout their electromagnetic spectra [2]. In this phenomenon, a reversible and visible change in reflectance or transmittance is accompanied with an electrochemically produced oxidation and reduction reaction. The color change is usually between a bleached state and a colored state or between two colored states. The first report on electrochromic applied materials and devices were manifested by Deb et al. [3]. Electrochromic compounds are mainly helpful for the construction of mirrors, windows, displays, and chameleon materials [4–7].

Phenothiazine consists of  $sp^3$ -hybridized electron-rich nitrogen and sulfur atoms, and it can form ordered structures between polymer chains via interactions of the side chains [8]. The heterocyclic ring of phenothiazine is more interesting due to its specific electron-donating ability and the butterfly conformation, which is useful for the effective prevention of intermolecular and inter-chain aggregation [9,10]. Because of the great optical and electrochemical properties, phenothiazine derivatives are useful in different applications, such as light emitting diodes [11–13], solar energy materials [14–16], organic semiconductors and organic thin film transistors [17–19]. On the other side, carbazole is well known as a good electron-donating chromophore [20,21]. attributable to their effective carrier-transport properties, carbazole-containing polymers can certainly form stable polarons and

bipolarons when applied with a external potential or doping agent [22] and are useful for different applications, such as electrochromic materials, electro-xerography, LEDs, and photovoltaic devices [23–27].

In the series of our chromic studies [28,29], particularly electrochromic studies [30], we designed and synthesized a conjugated polymer with phenothiazine and carbazole moieties with the purpose of developing an adaptive camouflage electrochromic material. The synthesized copolymer (CNU-CKP) was perfectly confirmed and characterized by  $^1\text{H}$  NMR, GPC, thermogravimetric analysis, UV-vis spectral analysis, cyclic voltammetry (CV), and spectroelectrochemical studies. The resulting copolymer was nicely soluble in most of the organic solvents, like tetrahydrofuran, chloroform, dichloromethane and DMF. Here, we created a solid-state electrochemical cell for CNU-CKP using a method of spray-coating with DMF solution of the copolymer on the glass (ITO-coated) and used the gel as an electrolyte (Fig. 1).

## 2. Experimental section

### 2.1. Chemicals, materials and instruments

Analytical reagents and solvents were used and purchased from Sigma-Aldrich, TCI and Alfa Aesar. The FT-IR experiment conducted on an ALPHA-P spectrometer. The ESI mass spectra were recorded by a 4000 Q TRAP mass spectrometer. The  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded by using an AVANCE III spectrometer operating on 600 MHz and 150 MHz respectively with  $\text{CDCl}_3$  and  $\text{DMSO-}d_6$  as the solvents. The chemical shifts ( $\delta$ ) values were given in ppm downfield from tetramethyl silane (internal standard). The cyclic voltammetry (CV) studies were performed by using a Versa STAT 3 instrument with polymer films

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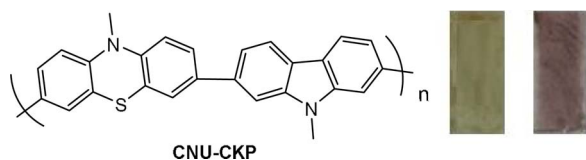


Fig. 1. Copolymer and its color transitions.

sprayed on platinum buttons; 0.1 M TBABF<sub>4</sub> electrolyte was used in propylene carbonate; an Ag/Ag<sup>+</sup> electrode used as the reference electrode, and a platinum wire was as the counter electrode. XPS analysis was done by using multilab 2000 spectrometer.

UV-Visible absorption spectral experiments were performed with an Agilent 8453 spectrophotometer. Number-average (M<sub>n</sub>), weight-average (M<sub>w</sub>) and molecular weights were confirmed by GPC (gel permeation chromatography) with waters company 2690 instrument using THF as an eluting solvent. Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo instrument using rate of heating 20 °C/min with a nitrogen flow rate of 50 mL/min. Polymer film, spectroelectrochemical experiment was conducted by using an Instek model GPS-3303 instrument as direct current (DC) power source. The electrochromic cell of polymer film was made by spray coating of a solution of the polymer (5 mg/mL in DMF solvent) on indium tin oxide coated glass slides (surface resistivity: 8–12 Ω/sq, 25 mm × 25 mm × 1.1 mm with rectangular shape, Sigma-Aldrich) at the active surface side of the ITO plate by using a mask. The gel electrolyte was prepared by adopting previously reported procedures.

## 2.2. Synthesis

**Poly [3-(7,9-dimethyl-9H-carbazol-2-yl)-7,10-dimethyl-10H-phenothiazine] (CNU-CKP) synthesis:** For this synthesis, 3,6-Dibromocarbazole (0.627 g, 1.85 mmol), 10-methyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenothiazine (0.8605 g, 1.85 mmol) and aqueous 2 M K<sub>2</sub>CO<sub>3</sub> (25 mL) were taken in dry THF (75 mL) and degassed this solution for 15 min. in argon atmosphere. Then Pd (PPh<sub>3</sub>)<sub>4</sub> (0.1 g,

0.085 mmol) was added to this reaction mixture and vigorously stirred at 85–90 °C for 72 h. After completion of reaction, the reaction mixture was cooled to room temperature and poured into an ice-cold mixture of methanol/distilled water (10:1 v/v). The precipitate was collected through filtration and further washed with methanol. To remove the oligomer and catalyst residues, the crude copolymer was then washed in acetone for 36 h with Soxhlet apparatus. Lastly, the polymer product was dissolved in 10 mL chloroform and precipitated from 100 mL methanol followed by dried under vacuum (515 mg, 66%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ 8.50–8.70 (m, 2H), 6.90–8.01 (m, 10H), 3.83–3.96 (m, 3H), 3.35–3.45 (m, 3H).

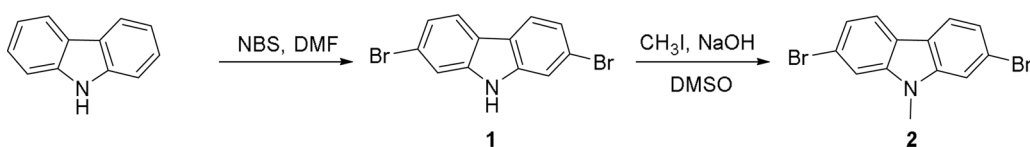
## 2.3. Theoretical calculations

The free-state geometry of phenothiazine-carbazole monomer was optimized with DFT calculations using B3LYP method at the basis set level of 6-31G(d,p). In this study for the neutral molecule, charge and multiplicity were taken as 0 and 1, and for the charged molecule, charge and multiplicity were 1 and 2. The same level of method was approached to estimate the electronic absorption properties (excitation energy and oscillator strength) of first 50 singlets with the help of time dependent-DFT (TD-DFT) technique. All the calculations were performed in the gas phase (without solvation) using the Gaussian 09 program [31].

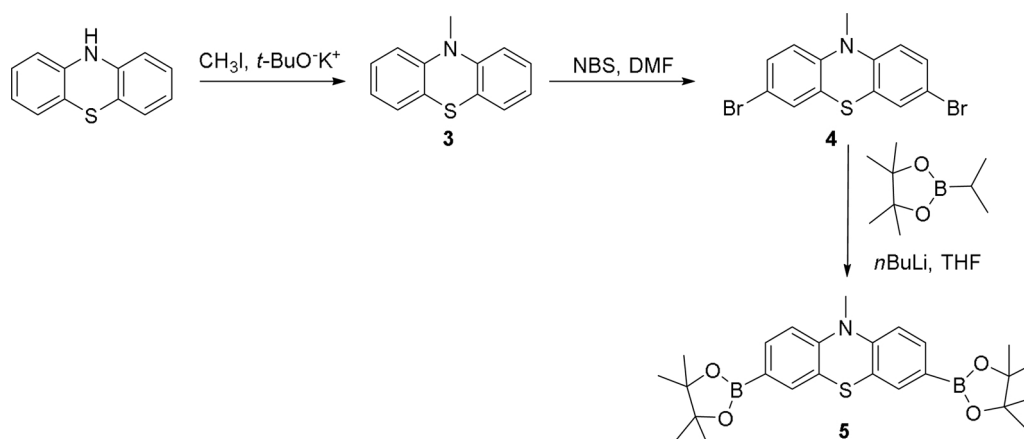
## 3. Results and discussion

### 3.1. Synthesis, GPC and TG studies

For the synthesis of CNU-CKP, first, we started with bromination followed by methylation of carbazole to yield compound **2** [32] (Scheme 1). In another reaction, phenothiazine was methylated with iodomethane [33]. Then, this compound was brominated by using N-bromosuccinimide [34] (Scheme 2). Finally, compound **2** and **5** underwent Suzuki cross-coupling for copolymerization using palladium (0), which resulted in a good yield (Scheme 3). All the precursor compounds were characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR spectroscopy and ESI mass spectrometry, and the polymer was characterized and confirmed by <sup>1</sup>H-NMR, GPC, thermogravimetric analysis, UV–vis



Scheme 1. Synthetic route for the synthesis of dibromo methyl carbazole.



Scheme 2. Synthetic route for the synthesis of boronic acid derivative.

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