ELECTROPOLYMERIZATION OF A NEW CARBAZOLE-TETRA SUBSTITUTED PHENYLETHENE DERIVATIVE AND ITS ELECTROCHROMIC DEVICE APPLICATION

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Abstract—A new carbazole derivative monomer 1,1,2,2-tetrakis(4-(9H-carbazol-9-yl)phenyl)ethene (TCP) was synthesized and characterized by Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared (FT-IR), and UV–vis spectroscopies and then electropolymerized. The electrochemical polymerization of this newlysynthesized TCP monomer was performed in dichloromethane(DCM)/ 0.1 M tetrabutylammonium hexafluoraphosphate ($TBAPF_6$) solvent/ electrolyte couple.An insoluble film was deposited on the electrode surface, both during repetitive cycling and constant potential electrolysis at 1.6 V. Resulting polymer film, P(TCP), was characterized utilizing UV–vis andFT-IR spectroscopic techniques and its electrochemical behavior was investigated via cyclic voltammetry (CV). Spectroelectrochemical behavior of the polymer film on indium tin oxide (ITO) working electrode was investigated by recording the electronic absorption spectra, in situ, in monomer-free electrolytic solution at different potentials and it is found that the P(TCP) film can be reversibly cycled between 0.0 and 1.65 V anddemonstrates a stable electrochromic behavior; transparent in the neutral state, olive green in the intermediate state and green in the oxidized state. It is also noteworthy that the device shows good environmental and redox stabilityFurthermore, a dual type electrochromic device based on P(TCP) was constructed and its spectroelectrochemical properties were investigated. Optical density and response time of the dual-type electrochromic device based on P(TCP) were found to be 0.20 and 0.6 s at 600 nm, respectively.

Index Terms—Polycarbazole, Electrochemical Polymerization, Electrochromic Device.

I. INTRODUCTION

Most of the research groups still are of interested in conjugated polymers because they are promising candidates for a large number of advanced technological applications including solar cells [1,2], light emitting diodes [3,5], optical displays and sensors [6-8]. The first generation electrochromic materials were mainly inorganic oxides [9-12] due to their advantages. However, functional conjugated polymers have been also widely employed as electrochromic materials in electrochromic devices [13-15]. The advantages of this kind of polymeric materials used in electrochromic devices include not only multicolors and high contrast ratio but also include fast switching capability and long cycle times. Furthermore, these properties can be tuned via structural tailoring of the starting materials. Because of that, significant effort has been dedicated to design and synthesize new polymeric electrochromics based on conjugated polymers [16].

Among various conjugated polymers, polycarbazole (P(C)), have been widely investigated, since they are one of the most promising candidates for hole-transporting and photoluminescence efficiencies units. Furthermore, P(C)'s have the possibility of substitution at N position, which provides the opportunity to improve both the solubility and functionality of the resulting polymer [17-20].Herein, we report the electrochemical polymerization of a new monomer,1,1,2,2-tetrakis(4-(9H-carbazol-9-yl)phenyl)ethene (TCP)bearing carbazoleside groups. The monomer, TCP, was polymerized via potential cycling and the electrochromic properties of the resulting polymer, P(TCP), was investigated via *in-situ*spectroelectrochemical techniques. An electrochromic device, switching from -1.0 V at neutral state to 1.8 V at oxidized state was also prepared utilizing P(TCP) and EDOT as anodically and cathodically coloring electrochromic materials.

II. DETAILS EXPERIMENTAL

2.1. Materials

All chemicals were purchased from Aldrich Chemical and used as received. For electrochemical experiments, tetrabutylammoniumhexafluoraphosphate ($TBAPF_6$), dissolved in freshly distilled dichloromethane (DCM) (over CaH_2 under N_2 or Aratm) solvents were used as electrolyte solutions. Polished platinum electrodes were used as WE and counter electrodes.

2.2. Instrumentation

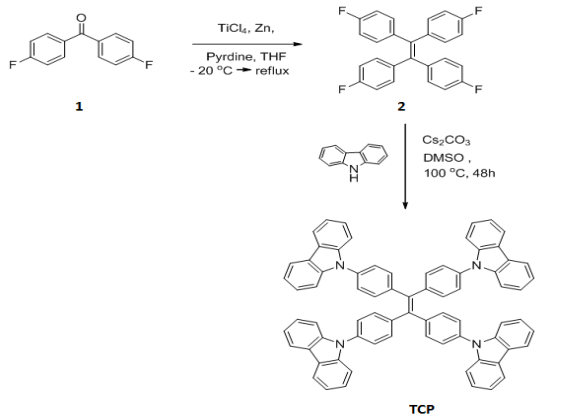
^{1}H-NMR and ^{13}C-NMR spectra of the monomer was recorded on a Bruker-Instrument-NMR Spectrometer (DPX-400) with $CDCl_3$ as the solvent and chemical shifts (δ) were given relative to tetramethylsilane as the internal standard. FTIR spectra were recorded on Nicolet 510 FT-IR with an attenuated total reflectance (ATR). UV measurements were carried out with a Hewlett-Packard 8453A diode array UV-vis and SPECORD S 600 spectrometers using a well-considered designed three electrode cell to allow

potential application as monitoring the absorbtion spectra.

2.3. Electrochemistry

Prior to electrochemical polymerization, redox behavior of TCP was investigated using cyclic voltammetry (CV) in 0.1 M $TBAPF_6$ /dichloromethane (DCM) electrolyte-solvent couple. The monomer was successfully electropolymerized via potentiodynamic or potentiostatic methods using three-electrode system containing a platinum disc (d=1.6 mm), a platinum wire as working and counter electrodes, respectively, as well as Ag wire as a pseudo-reference electrode (calibrated externally using a solution of ferrocene/ferrocenium couple). Electrochemical behavior of correspondingpolymer films, coated on working electrode,was investigated in monomer-free electrolyticmedium. For electro-optical studies, indium-tin oxide(ITO, Delta Tech. 8–12 X, 0.7 cm x 5 cm) electrodeswere coated by the polymer film and the coatedelectrode was dipped into a UV cuvette with 1.0-cmpath length together with Pt wire and Ag wire ascounter and reference electrodes, respectively. Prior tospectroelectrochemical investigations, the polymerfilm was switched between neutral and doped
states several times to equilibrate its redox behaviorin monomer-free electrolytic solution.

2.4.SynthesisofTCP



Scheme 1.Syntheticroute of TCP

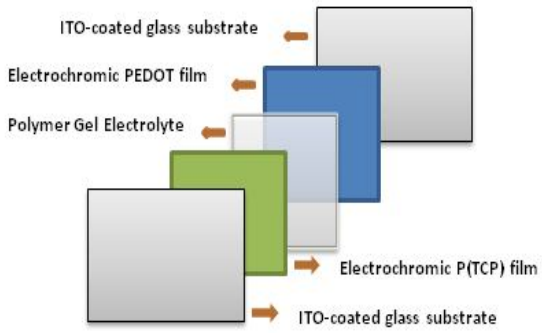
2.4.1. Synthesis of 1,1,2,2 – Tetrakis (4-fluorophenyl) ethane (2)

Under an Ar atmosphere, a three-necked flask equipped with a magnetic stirrer was charged with zinc powder (3.00 gr, 45.83 mmol) and 50 mL freshly distilled THF. The mixture was cooled to -20 °C, and $TiCl_4$ (4.35 gr, 22.92 mmol) was slowly added by a syringe with the temperature kept under 0 °C. The suspending mixture was warmed to room temperature and stirred for 0.5 h, then heated at reflux for 2 h. The mixture was cooled to 0 °C, charged with pyridine (0.91 gr, 11.46 mmol) and stirred for 15 min. Bis(4-fluorophenyl)methanone (**1**) (2.0 gr, 9.17 mmol) in 40 mL THF was added slowly. After addition, the reaction mixture was heated at reflux until the carbonyl compound was consumed. The reaction was quenched with 10% K_2CO_3 aqueous solution and taken up with CH_2Cl_2. The organic layer was collected and dried over Na_2SO_4 and evaporation of the solvent afforded the desired product. The crude material was purified by chromatography eluting with dichloromethane–n-hexane (1 : 3, v/v).85% chemical yield, as a white powder.^{1}H NMR (500 MHz, DMSO): δ ppm 8.24 (d, J=7.1Hz, 16H), ^{13}C NMR (125 MHz, DMSO):δ ppm 162.3, 160.3, 139.5, 133.1, 115.3.

2.4.2. Synthesis of 1,1,2,2-tetrakis(4--9H-carbazol-9-yl)phenyl)ethene (TCP)

1,1,2,2-Tetrakis(4-fluorophenyl)ethene (1.00 gr, 2.47 mmol) and carbazole (3.31 gr, 19.78 mmol) were dissolved in DMSO (40 mL). Cesium carbonate (6.45 gr, 19.78 mmol) was added to the solution with stirring. The suspension mixture was stirred at 100 °C for 2 days. The mixture was cooled to room temperature, and poured into ice–water (100 mL) and filtered. The crude product was purified by column chromatography on silica, eluting with dichloromethane–n-hexane (1:3, v/v). 70% chemical yield, as a white powder.^{1}H NMR (500 MHz, DMSO): δ ppm 8.24 (dd, J_1=4.5Hz, J_2=7.6Hz, 8H), 8.05 (d, J=8.5Hz, 4H), 8.0 (d, J=8.5Hz, 4H), 7.61 (d, J=8.6Hz, 4H), 7.54 (d, J=11.5Hz, 4H), 7.35 – 7.25 (m, 24H).

2.5.Fabrication of electrochromic device



For a dual type electrochromic device (ECD) fabrication, PEDOT as a cathodically coloring polymer was electropolymerized onto a 1.25 cm^2 ITO glass surface from an ACN solution containing 2×10^{-3} M EDOT and 0.1 M $TBAPF_6$ via constant potential electrolysis at 1.2 V. After coating PEDOT onto the ITO-glass surface, the film was rinsed with ACN to remove all the unreacted monomers on the electrode surface. **P(TCP)** was also electropolymerized using CV method in DCM solution containing 0.1 M $TBAPF_6$ on ITO electrode. The device was constructed using the electrochromic electrodes stacked face-to-face separated by gel electrolyte ($TBABF_4$; ACN; poly(methyl methacrylate); polycarbonate in the ratio of

3:70:7:20). The electrochromic device was allowed to dry for 48 h at room temperature under atmospheric pressure. The electro-optical properties of the device were recorded *in situ* under various applied potentials. Finally, square wave potential method was used to perform switching between the colored states.

3. RESULTS AND DISCUSSION

3.1. Electrochemicalpolymerization of TCP

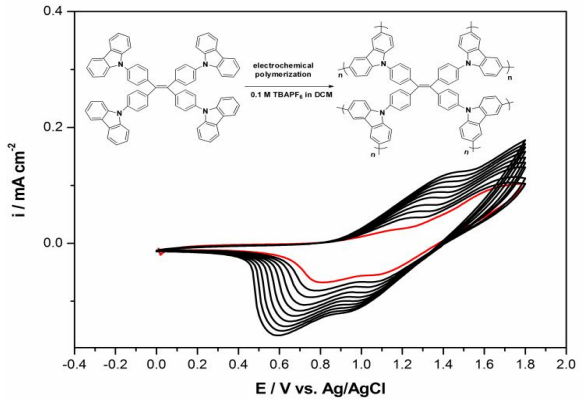


Fig.1. Repeatedpotentialscanelectropolymerization of 1 mM TCP on a Ptdiscelectrode at 100 mV s^{-1} in 0.1MTBAPF$_6$/DCM.

Electrochemical behavior of TCP was investigated in DCM using 0.1 M TBAPF$_6$as supporting electrolytes. One oxidation peak at 1.60 V vs Ag/AgCl was observed during the anodic scan. During the reverse scan, a reduction peak was also noted which intensified after scan reversal at 1.25 V **(Fig.1)**. Upon successive anodic scans, this reversible peak gained intensity, which indicates the deposition of conducting polymer on the working electrode.

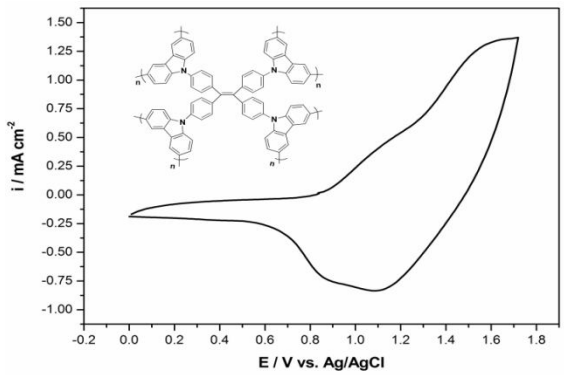


Fig.2. P(TCP), anodic scan between 0.0 and 1.6 V on a Ptdiscelectrode at 200 mV s^{-1} in 0.1MTBAPF$_6$/DCM.

After repeated scans, the polymer coated working electrode was removed from the monomer solution and rinsed with DCM to remove the oligomeric species and the electrolyte. The electrochemical behavior of the polymer film was investigated in 0.1M TBAPF$_6$ / DCM solution. The polymer film was found to exhibit two reversible redox couple representing the doping and de-doping of the polymer film (**Fig.2a**).

Polymer film was deposited on ITO and its transition between the neutral (de-doped) and oxidized (doped) states was studied in 0.1M TBAPF$_6$ / DCM solution. Fig.3 shows the *in-situ* absorption spectra of the polymer recorded at various applied potentials in terms of the reversible redox couple of **P(TCP)** between 0.0 V and 1.7 V in 0.1M TBAPF$_6$ / DCM. In the neutral state, polymer film exhibits an absorption band at 310 nm due to the π–π* transition. From the beginning of the low energy end of the π–π^* transition band in the neutral state, the band gap value of 3.1 eV was found. This value is slightly lower than that of its thiophene analogue, P(C). Upon electrochemical doping, the evolution of the spectra shows a simultaneous increase of the absorbance at 425 nm and 1075 nm indicating polaron formations, together with an isosbestic point at 360 nm indicating one step reaction due to polaron formation. . As further doped, (beyond 1.2 V) a broad band centered at 770 nm starts to intensify indicating bipolaron formation. These changes in the electronic absorption spectrum was accompanied with a multielectrochromic response and the colors of the P(TCP) film changes from transparent yellow to green.

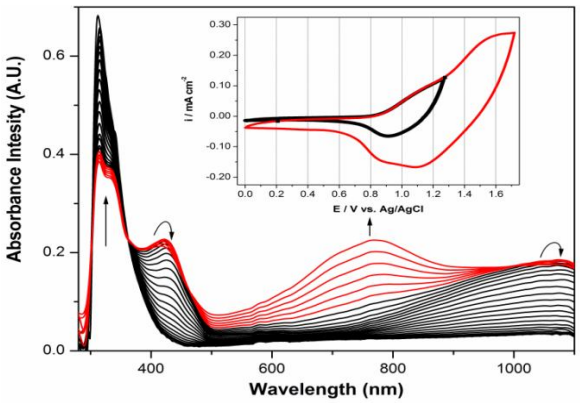


Fig.3. Electronic absorptionspectra of P(TCP) on ITO (25 mC cm^{-2}) in 0.1M TBAPF$_6$/DCM.solutionduringanodicoxidation of thepolymer film. (Inset: Anodicwaveclippingbehaviour of P(TCP).)

Table 1. The electrochemical and spectroelectrochemical data for P(TCP).

Polymer	P(C)	P(TCP)
E^{ox}_{mon} (V)	1.40	1.70
E^{ox}_{pol} (V)	1.00 1.42	1.11 1.58
HOMO (eV)	-5.71	5.97
LUMO (eV)	2.37	2.79
E^{opt}_{gap} (eV)	3.3	3.1
λ_{max} (nm)	395/710	310/425/770
Color		
Optical contrast (%)	10/13	13/23/
Switching time (s)	1.8/2.2	2.9/2/

HOMO/LUMO energy levels of the polymers were elucidated utilizing their ionization potentials and electron affinities obtained from the experimental data. First, the ionization potentials (*Ip*) were evaluated using the following empirical relation. The onset of oxidation potentials was used as *Eox* . Electron affinities were estimated by subtracting the band gap energy from *Ip* and the results were depicted and compared with P(C) in Table 1.

A dual type electrochromic device consisting of P(TCP) and PEDOT was constructed and its spectroelectrochemical behavior was investigated by recording the optical absorbance spectra at different applied potentials. Electrochromic device showed a reversible response in a potential range of −1.0 V (neutral) and 1.8 V (oxidized) as depicted in Fig. 4. At −1.0 V, the polymer was green and PEDOT was transparent (light blue) in its oxidized state; therefore, the color of the device at −1.0 V waslight green. The color of the device at 2.0 V became blue. As the applied potential was increased, an absorption band at 600 nm was observed due to the neutral state of PEDOT layer.

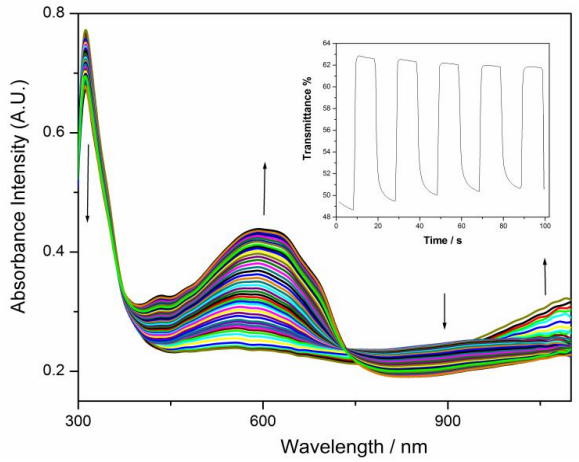


Fig.4. Optical characterization of P(TCP)/PEDOT electrochromic device by applying potentials between − 1.0 V and + 2.0 V (Inset: Optical response of P(TCP) /PEDOTelectrochromic device at 600 nm as a function of time under an applied square voltage signal between − 1.0 V (light green) and + 2.0 V (dark blue color).

CONCLUSION

In summary, a new type of tetraphenylethene complexes bearing carbazole substituent were synthesized and characterized. This new complex was polymerized by anodic oxidation in 0.1 M $TBAPF_6$/DCM. Electrochemical and spectro-electrochemical properties of the polymer film were investigated via *in situ* spectroelectrochemical and cyclic voltammetry techniques in monomer free electrolytic medium. The polymer film was found to exhibit a well-defined and reversible redox processes accompanied byelectrochromic changes which make both polymers a candidate for electrochromic material applications. The polymer film exhibits multielectrochromic behaviour under applied external potentials. The dual type complementary colored ECDs were constructed. Via spectroelectrochemical studies, a maximum absorption at 600 nm due to π to π* transition was observed. The percent transmittance change at 600 nm was found to be 20 % for P(TCP)/PEDOT. These devices exhibit good stability and optical memory. These prominent features make P(TCP) an excellent candidate for any practical issue. We try to detect thermal behaviour of polymerfim. Work in this line is currently underway in our laboratories.

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