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SYNTHESIS OF A NEW ELECTROCHROMIC POLYMER BASED ON TETRAPHENYLETHYLENE CORED TETRAKIS CARBAZOLE COMPLEX AND ITS ELECTROCHROMIC DEVICE APPLICATION

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ABSTRACT

Poly-1,1,2,2-tetrakis(4-9H-carbazol-9-yl)phenyl)ethene P(TCP) was successfully synthesized by electrochemical oxidation of corresponding monomer, namely, 1,1,2,2-tetrakis(4-9H-carbazol-9-yl)phenyl) ethene (TCP) using dichloromethane as the solvent and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. Spectroelectrochemical properties of P(TCP) were investigated *in situ* recording the electronic absorption spectra of the polymer film coated on indium-tin oxide (ITO) at various potentials. P(TCP) displayed transparent to military green color in 1.80 s with an optical contrast of 23.0% (at 770 nm) and an optical band gap of 3.1 eV. The objective evaluation of the colors of P(TCP) at various potentials was performed through colorimetry studies on the basis of “Commission Internationale de l'Eclairage” (CIE) standards. The morphology of the polymer film was investigated by AFM analysis. A dual type electrochromic device based on P(TCP) was constructed and its spectroelectrochemical properties were investigated. The electrochromic device exhibits color change from transparent to dark blue with a good open circuit memory.

1. Introduction

Functional conjugated polymeric materials continue to be promising candidates in a variety of advanced technological applications such as sensors [1–3], light emitting diodes [4,5], photovoltaic cells [6–8], transistors [9,10], electrochromic devices [11–13], optical displays [14] and energy storage applications [15]. Among conjugated polymers, polycarbazole (PC) and its derivatives have recently held the attention of synthetic chemists due to their well known charge-transport properties, luminescence and high thermal stability [16,17]. They were mostly used in light emitting diodes, electroxerography, microcavity photoconduction, electrochromic and photovoltaic devices [18]. PC's have been extensively investigated since functionalization of carbazole monomer prior to polymerization is possible via N-substitution both in the main chain as building blocks and in the side chain as pendant groups [19]. This opens new routes for synthesizing new hybrid materials. N-substituted carbazole based polymers are generally colorless or near-colorless at their neutral state and then can be converted to multiple colors at their excited states, which is an important property for neutral state colorless electrochromic device applications [20–22]. To obtain a colorless regime, these types of materials do not need any potential or energy. Therefore conjugated polymers containing N-substituted carbazole moiety have received great attention for electrochromic technology in the last three decades [19,23,24].

In this context, tetraphenylethylene (TPE) can also be a good candidate core for the functional carbazole because TPE and its derivatives are valuable organic fluorophores exhibiting aggregation induced emission (AIE) phenomenon which can be used in various applications including explosive and pH sensors, fluorescent sensory systems, cell imaging and biomedical applications [25–30]. In our previous work, new luminogenic molecules with the tetraphenylethylene core having excellent AIE property were synthesized and their OLED (organic light emitting device)'s were constructed [31]. Although there are a lot of application areas of TPE and its derivatives, only a few polymers of TPE have been reported in literature [32–37].

Herein we wish to unveil our results concerning the synthesis and characterization of a new hybrid material based on carbazole

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and tetraphenylethylene core of which electrochemical and optical properties were investigated in detail for any potential application. Introduction of tetraphenylethylene core along a polymer matrix will not only impart these unique properties to the polymers but also enhance the properties of the resulting hybrid material in terms of sensor and electronic device applications. For this purpose, the compound named as 1,1,2,2-tetrakis(4-9H-carbazol-9-yl) phenyl)ethene (TCP) was first synthesized then, the named polymer as poly-1,1,2,2-tetrakis(4-9H-carbazol-9-yl) phenyl)ethene P(TCP) was synthesized via electrochemical polymerization in 0.1 M $TBAPF_6$ supporting electrolyte in dichloromethane. The monomer, TCP, was polymerized via potential cycling and the electrochromic properties of the resulting polymer, P(TCP), were investigated via *in situ* spectroelectrochemical techniques. A dual electrochromic device, switching from −1.0 V at neutral state to 2.0 V at oxidized state, was also prepared by utilizing P(TCP) and PEDOT as anodically and cathodically coloring electrochromic materials, respectively.

2. Experimental Details

2.1. Materials and Instrumentation

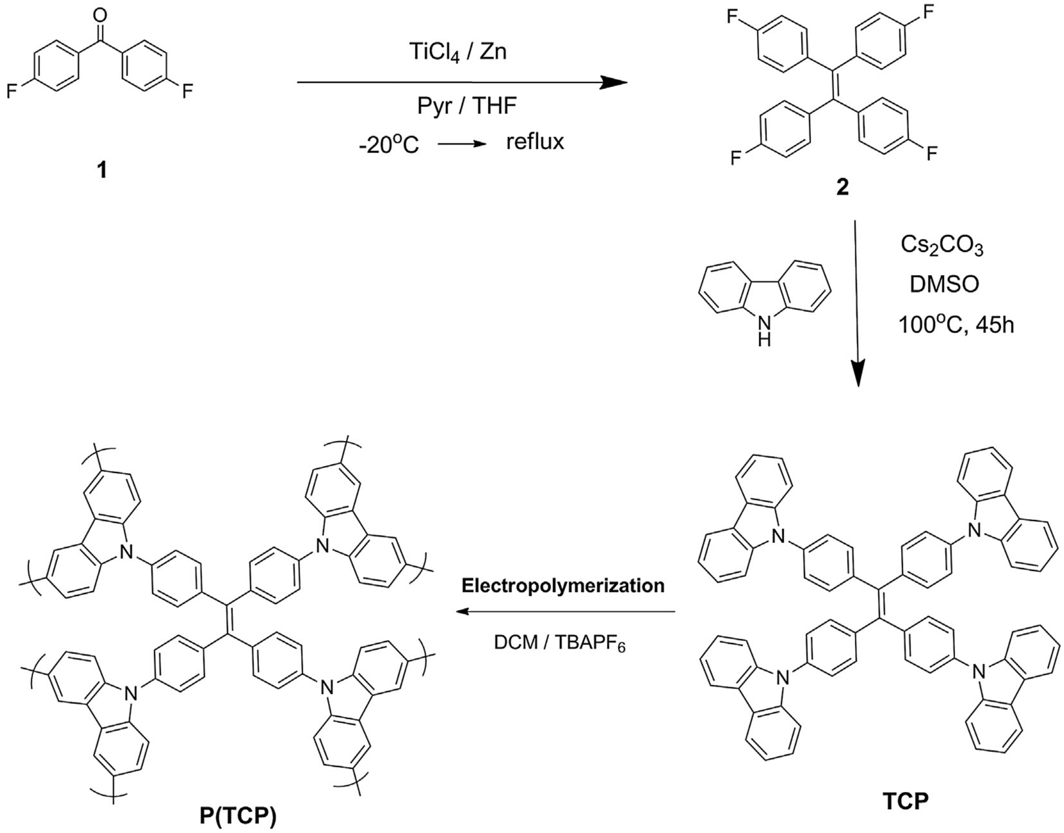
All chemicals were purchased from Aldrich Chemical and used as received NMR spectra were recorded with Bruker Spectrospin Avance 500 MHz spectrometer. Infrared spectra were measured on a Perkin Elmer Instruments, Spectrum One Spectrophotometer. Mass spectra (MS) were obtained on Bruker Daltonics MicroToF II mass spectrometer. An AFM from Nanomagnetics Instruments was used for investigating the morphologies of the films under ambient laboratory conditions. AFM imaging was performed in the tapping mode using PPP-NCLR cantilevers. Horiba Jobinyvon, FluoroLog was used for fluorescence spectroscopy studies. Electrochemical synthesis and cyclic voltammetry studies were performed on Ivium stat potentiostat/galvanostat under argon atmosphere. A platinum wire was used as the counter electrode and Ag/AgCl electrode was used as the reference electrode. A Specord S600 spectrometer UV-Visible spectrophotometer was utilized for spectroelectrochemistry and kinetic studies. Colorimetry measurements were recorded on a Minolta CS-100A Chroma Meter in a proper box having D-50 illumination. Measurements were performed with a 0/0 (normal/normal) viewing geometry as recommended by CIE.

2.2. Synthesis of TCP and P(TCP)

Synthetic route for monomer and its polymer was given in Scheme 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 g, 45.83 mmol) and 50 mL freshly distilled THF. The mixture was cooled to –20 °C, and $TiCl_4$ (4.35 g, 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 g, 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



Scheme 1. The synthetic route for monomer TCP and its polymer P (TCP).