



## Carbazole Functionalized Star Shaped Triazine Monomer and Its Electrochromic Applications

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A new star shape monomer, 2,4,6-tris((9H-carbazol-2-yl)oxy)-1,3,5-triazine (CTR) was synthesized. It was electrochemically polymerized in boron trifluoride diethyl etherate (BFEE)/acetonitrile (ACN) solvent couple. The interaction between BFEE and the CTR lowers the oxidation potential of the monomer and the catalytic effect of BFEE facilitated the formation of high quality polymer film. Electrochemically prepared P(CTR) film was characterized via CV, SEM, FTIR, TGA and UV-vis spectroscopy. Spectroelectrochemical analysis revealed that P(CTR) has high band gap energy which provide it colorless in the neutral state. Electronic transitions of the P(CTR) were observed at 327 and 650 nm, revealing  $\pi$  to  $\pi^*$  transitions, and polaron band formation. The polymer switches between dark turquoise and transparent with a switching time of 1.5 s and an optical contrast ( $\% \Delta T$ ) of 50%. Electrochromic studies revealed that P(CTR) has opposite properties to EDOT in terms of redox color. In addition to a dual-type complementary colored polymer electrochromic device based on P(CTR) and P(EDOT) was constructed in sandwich configuration. Spectroelectrochemical studies disclosed that the oxidized state of the device shows a blue color and it is transparent in the reduced state. Switching time and maximum contrast ( $\% \Delta T$ ) of the device was measured as 3 s and 32% for 615 nm.  
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Recently, organic  $\pi$ -conjugated materials have been an issue of interest in countless studies. The photophysical properties of  $\pi$ -conjugated polymers depend on their molecular structure. Numerous experiments, aimed at developing properties of such systems by modifications of their structure, have been conducted. One of the design concepts involves well-described, branched or star-shaped macromolecular architectures, featuring properties distinct from their linear analogues.<sup>1,2</sup> This makes them encouraging materials for applications in a broad range of organic optoelectronic applications such as light-emitting devices (LED), photovoltaics<sup>3,4</sup> field-effect transistors,<sup>5</sup> nonlinear optics<sup>6</sup> and sensors.<sup>7,8</sup> Since conducting polymers have fast switching times, high optical contrasts, processibility and easy tuning of color with structural modifications, they became more popular over time as active layers in electrochromic devices.<sup>9-12</sup> During the search for the conjugated polymers with suitable electronic and optical properties for electrochromic devices, numerous organic molecules and their combinations are constructed and investigated.

Building super-structured conjugated polymers (CPs) is of substantial attention owing to the novel characteristics that could result from such structures.<sup>13-15</sup> Branched CPs with electronically attached nodes are perfect candidates among this family of super-structured CPs; with these polymers, there should be no necessity for inter-chain electronic transfer or inter-chain coupling to ensure high electronic conductivity.<sup>16,17</sup> Furthermore, these materials have three dimensional structure which could also increase the conductivity.<sup>18</sup>

The solvent and electrolyte can widely affect the optical properties, electrochemical performance, morphology and other features of CP films. As a superior solvent and electrolyte, BFEE has been proved to be the convenient electrolyte to polymerize the fused aromatic molecules, such as pyrene, benzanthrene, phenanthrene, fluoranthene and their derivatives. As previously reported, Lewis acidity of BFEE reduces the polymerization potential of many aromatic molecules, usually resulting in stable and high quality polymer films.<sup>19-22</sup>

For the forthcoming utilization of CPs, the experience of the stability and thermal behavior is crucial. Electrical conductivity and thermal stability will provide CPs with exceptionally wide applications for the practical processing of solid-state electronic devices.<sup>23-25</sup> One of the most considerable and credible factor of conducting polymers is the measurement or evaluation of their thermal stability. Thermal properties of monomer and polymer can be estimated from the oxidative degradation curves through TGA.

Star-shaped polymers, which are formed multiple polymer chains stemming from junction points, have received considerable interest over the last decade because of their distinctive three dimensional

shapes. They have potential processing benefits due to their compact architecture in comparison with linear analogues. For this reason we report the synthesis of a new star-shaped monomer, 2,4,6-tris((9H-carbazol-1-yl)oxy)-1,3,5-triazine(CTR). Electrochemical polymerization of CTR was performed using tetrabutylammonium hexafluorophosphate (TBP<sub>6</sub>) as the supporting electrolyte. The resultant product was characterized via cyclic voltammetry (CV), scanning electron microscopy (SEM), and conductivity measurements. We also successfully set and characterized a dual-type complementary-colored polymer electrochromic device using P(CTR)/poly(3,4-ethylenedioxythiophene) (PEDOT) in a sandwich configuration.

### Materials and Methods

**Materials.**— All of the reagents and solvents used in this study; acetonitrile (Aldrich), acetone (ACS reagent,  $\geq 99.5$ , Aldrich), boron trifluoride diethyl etherate (BFEE) (Aldrich), dimethyl sulfoxide (DMSO) (ACS reagent,  $\geq 99$ , Merck) 2-hydroxy carbazole (Alfa Aesar), lithium perchlorate (LiClO<sub>4</sub>) (Aldrich), NaOH (Tekkim), tetrabutylammonium hexafluorophosphate (TBP<sub>6</sub>) (Aldrich), propylene carbonate (PC) (Sigma-Aldrich), poly(methylmethacrylate) (PMMA) (Sigma-Aldrich) and 2,4,6-trichloro-1,3,5-triazine (Cyanuric chloride) ( $\geq 99$ , Merck), were used as received from their indicated commercial suppliers without any further purification.

**Instrumentations.**— Three-electrode cell geometry was used in all electrochemical experiments. ITO (indium tin oxide) coated glass rectangular slide was used as the working electrode. Pt and Ag wires were used as the counter and reference electrodes respectively. All potential values are referred to Ag/Ag<sup>+</sup> reference electrode. An Ivium potentiostat/galvanostat interfaced with a personal computer was used in all electrochemical measurements. The UV spectra were recorded with a UV-vis spectrophotometer (Agilent 8453), interfaced with a PC and spectroelectrochemical measurements were carried out in three-electrode quartz cell. The structure of the monomer was confirmed by NMR analysis. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the monomer were taken by using a 400 MHz/54 mm Ultra Shield Plus with DMSO as the solvent.

All of the TGA and differential thermal analysis (DTA) curves were obtained simultaneously by using a Shimadzu DTG-60H Thermal Analyzer. The measurements were carried out in flowing nitrogen (100 ml/min.) atmosphere and temperature ranged from 25 to 1000°C in platinum crucible.

**Synthesis of the monomer.**— 2,4,6-trichloro-1,3,5-triazine (0.46 g,  $2.5 \times 10^{-3}$  mol) was dissolved in acetone (5 ml) and a solution of 2-hydroxycarbazole (1.375 g,  $7.5 \times 10^{-2}$  mol) and NaOH (0.3 g,

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