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Asymmetric Star-Shaped Functionalized Triazine Architecture and Its Electrochromic Device Application

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A new asymmetric functionalized star shaped triazine derivative, namely 2,2'-((6-(quinolin-8-yloxy)-1,3,5-triazine-2,4-diyl)bis(oxy))bis(9H carbazole) (TQC) was synthesized from 2-hydroxy carbazole and 8-hydroxyquinoline. The electrically conductive PTQC film was synthesized via electropolymerization on ITO in a 0.1 M lithium perchlorate/acetonitrile ($LiClO_4$/ACN) electrolyte–solvent couple. ^{1}H-NMR, FTIR and elemental analysis were used to analyze the structure of the TQC. Both electrochemical and spectroelectrochemical studies of the polymer were examined. PTQC revealed color changes between transparent and dark green in the reduced and oxidized states, respectively. Dual type polymer electrochromic devices (ECDs) based on PTQC and poly(3,4-ethylenedioxythiophene) (PEDOT) have been constructed. A potential range of 0 to 2.5 V was found to be proper for working the PTQC/PEDOT device between transparent and blue colors. The spectroelectrochemistry, electrochromic switching, open circuit memory and stability of the device were studied. The properties of the electrochromic device have been investigated such as spectroelectrochemistry, electrochromic switching, stability and open circuit memory.
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Star-shaped polymers[1–3] have drawn considerable interest in research throughout the years owing to their unique architectures and its various properties. Based on the core and functionalization of the peripheral units it is likely to acheieve star-shaped molecules with different geometry and symmetry. The most important class of star shaped polymers consist of 1,3,5 triazines. 1,3,5-Triazines[4–8] (s-triazines) has both high electron affinity and structural symmetry, which makes it advantage for the design and synthesis of star-shaped polymers and hyperbranched polymers.

Electron donors like 1,3,5-triazine[9] and carbazole[10] possess not only photochemical but also and thermal stability.[11] Carbazole-containing polymers have received enormous attention because of the versatile application of the materials in many fields, including electrochromic devices (ECDs),[12,13] hole-transporting layers,[14] sensors[15–17] and as photovoltaic[18–21] components. Moreover, these compounds are attractive as photoconductors or charge transporting materials.

8-Hydroxyquinoline[22–24] as a very useful ligand, has often been incorporated into conjugated coordination polymers. This molecule indicates a wide importance in organic light emitting diodes (OLED)[25] owing to their exceptional optical and thermal stability properties as well as electrochemical characteristic.

Asymmetric structures[26] in star-shaped polymers have attracted considerable attention in recent times. The ongoing peak of interest in asymmetric functionalized containing polymers is connected mostly with of polymeric light emitting diodes and organic photorefractive materials. These advantages have remarkably used the applications of the asymmetric functionalized star shaped polymers in optical and electrochromic devices.

Electrochromic (EC)[27] materials and polymer electrolytes are the most essential and active components in an ECDs. Electrochromism contains electroactive materials that present a reversible change in optical properties when the material is electrochemically oxidized or reduced. This process modifies the polymer electronic structure, producing new electronic states in the bandgap, causing color changes. To create multicolor electrochromics[28–30] conjugated polymer-based electrochromic materials[31] have gained popularity owing to their ease of processability and rapid response times.

This study comes in two parts. In the first part, novel asymmetric functionalized star shaped derivative (TQC) of 2,4,6-trichloro-1,3,5-triazine containing 2-hydroxy carbazole and 8-hydroxyquinoline was designed, synthesized and characterized. Electrochemical polymerization of PTQC was achieved by electrochemical polymerization in 0.1 M $LiClO_4$/ACN. Electronic and optoelectronic properties of polymer was investigated by cyclic voltammetry and spectroelectrochemical studies, and their oxidation potentials, HOMO/LUMO energy level, bandgap (Eg), optical contrast ($\Delta T\%$) and switching time were reported in detail. When the polymeric film prepared by electrochemical process has been subjected to a repetitive cyclic scan between 0 V and 1.5 V, it has switched among five different colors.

In the second part of the study, to explore the use of this material in electrochromic device we constructed a dual-type electrochromic device with ITO/ PTQC /gel electrolyte/PEDOT/ITO configuration, where the polymer and PEDOT functioned as the anodically and the cathodically coloring layers respectively. The device displayed impressive color changes and electrochemical stability make it become promising candidate for electrochromic layer in ECD application.

Materials and Methods

Materials.—2-hydroxy carbazole, 8-hydroxyquinoline, 3,4-Ethylenedioxythiophene, lithium perchlorate, acetone, sodium hydrogen carbonate and sodium hydroxide were purchased from Sigma-Aldrich and used any further purification. The electrolysis solvent, acetonitrile (Aldrich) was dried with using phosphorus pentoxide (P_2O_5) and 2,4,6-trichloro-1,3,5-triazine (Merck) was purified by recrystallizations from pure petroleum ether (60–90°C). 8-(4,6-dichloro-1,3,5-triazinoxy)quinoline (TQ) was synthesized according to the published procedure.[22]

Instrumentations.—The chemical structure of the monomer (TQC) was characterized using ^{1}H-NMR, FTIR and elemental analysis. ^{1}H-NMR spectra of the monomer were recorded by the Varian, 400-MHz Spectrometer at room temperature using DMSO-d_6 as solvent. FTIR spectra were performed on a Perkin Elmer Spectrum 100 using Universal ATR Polarization Accessory in the range 4000–400 cm^{-1}. The melting point of the synthesized monomer was measured by Stuart Melting Point Apparatus SMP30 instrument. The surface morphologies of the polymer film were evaluated using Zeiss Evo LS 10 scanning electron microscope. Elemental analyses were carried out using LECO-CHNS-932 elemental analyzers. Electropolymerization and electrochemical properties were performed with an Ivium potentiostat/galvanostand. An Agilent 8453 UV–Vis spectrophotometer was used in order to perform the spectroelectrochemical studies of the polymer. No background correction was done for all electrochemical measurements. A Minalto CS 100 spectrophotometer was used for colorimetric measurements.

Synthesis of 8-(4,6-dichloro-1,3,5-triazinoxy)quinoline (TQ).—A solution of 8-hydroxyquinoline (0.145 g, 1×10^{-3} mol) and NaOH

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