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Donor-Acceptor Type Super-Structural Triazine Cored Conducting Polymer Containing Carbazole and Quinoline for High-Contrast Electrochromic Device

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Star shaped functionalized molecules allow the production of sophisticated nano devices by using them as the building blocks for the formation of superstructured macromolecules. Here, we address star-shaped molecule which is formed by quinoline and electroactive carbazole functionalized triazine (TQEC). Using quinoline as electron accepting (A) and carbazole as electron donating (D) moiety, the resulting conductive polymer is designed to have high optical contrast. The cross-linked polymer (PTQEC) characterized after the electropolymerization of the A/D type molecule has been found to have superior optical and electrical properties. It has high optical contrast (71% at 675 nm), fast switching time about 3 s and high long time redox stability (91.75%). As a result of the spectroelectrochemical and electrochromic characterization, it is determined that PTQEC is transparent and green colored in its neutral and oxidized states, which is a desirable property for smart windows. Therefore electrochromic devices (ECDs) depending on PTQEC and PEDOT were established, where PEDOT functioned as the cathodically coloring layer. Optical and electrochemical characterizations of the device in the way of the optical contrast (51% at 540 nm), switching time (about 3 s), open circuit memory, redox stability (95.36%) and colors were investigated.
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1,3,5 triazine ring used to form star-shaped[1–4] molecules have become the focus of research in recent times. Star-shaped polymer derivatives formed by this core structure have given some special advantage to the polymer structure. These materials are used in wide range of technological areas including sensors[5,6] light emitting diodes (LEDs)[7,8] and electrochromic device (ECDs)[9,10] Compared with linear polymers, star shaped polymers[11,12] have superior properties. These properties are good electrochromic reversibility and excellent stability. Therefore, the synthesis of star-shaped triazine derivatives is among the studies that are in consideration.

One of the most necessary and active components used in electrochromic device is[13–18] electrochromic materials such as metal oxides,[19,20] metal coordination complexes,[21] viologens,[22] conducting polymers[23–25] and metal hexacyanometallates.[26] Conjugated polymer-based electrochromic materials[27–29] are able to reversible change the optical properties of a material during electrochemical process. These classes of polymers have much more attention due to theirs fast response time, good stability and high optical density[30–32] as electrochromic material.

Due to their good optical and efficient hole transporting properties, carbazole-based polymers[33,34] are used in many potential application areas such as OLEDs[35–37] electrophosphorescence[38] and electrochromic devices.[39]

8-Hydroxyquinoline (8-HQ)[40–42] is a ligand that has various advantages, which has been extensively used in the conjugated polymers as an electron accepting moiety. Especially using quinoline group, it can be produce conjugated polymers with controlled band gaps and electronic structures contains constructing A/D type polymers, in which the A and D groups are both powerful electron withdrawing and electron donating moieties. Therefore, 8-hydroxyquinoline-containing conducting polymers can be widely used especially in optical devices.

In this study, TQEC was synthesized by introducing 8-hydroxyquinoline unit and 2-(9H-carbazol-9-yl)ethanole unit at 2,4,6-trichloro-1,3,5-triazine and electrochemically polymerized. Electrochemical, spectroelectrochemical and electrochromic properties of PTQEC were examined dual type ECDs composed of PTQEC and poly(3,4-ethylenedioxythiophene) (PEDOT) were established and characterized.

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Experimental

Chemicals and equipment.—TQ was synthesized according to the former literature.[43] Acetonitrile (ACN) (Aldrich) was dried by using phosphorus pentoxide (P_2O_5). The chemical used in the all of the experiments are 2,4,6-trichloro-1,3,5-triazine (TCT) (Merck), 9H-Carbazole-9-ethanol (Sigma-Aldrich), 8-hydroxyquinoline (Sigma-Aldrich), 3,4-Ethylenedioxythiophene (Sigma-Aldrich), lithium perchlorate (Sigma-Aldrich), dichloromethane(Sigma-Aldrich), acetone (Sigma-Aldrich), $MgSO_4$ (Sigma-Aldrich) and sodium hydroxide (Sigma-Aldrich), which were used directly without further purification.

FTIR, elemental analysis and ^{1}H-NMR were used to characterize the synthesized monomer structure. The ^{1}H-NMR data of the TQEC were collected on a Varian 400 MHz spectrometer. The infrared spectra were recorded from Fourier Transform Infrared FTIR on a PerkinElmer 100 spectrometer (ATR). Elemental analyses were applied at Leco CHNS-932 analyzer. Melting points of the compounds was specified on a Stuart melting point SMP30 apparatus in a sealed capillary and are uncorrected. For surface morphology of the polymer film coated ITO electrode, scanning electron microscope (SEM) (Zeiss Evo LS 10 model) was used. All electrochemical polymerization were performed by an Ivium potentiostat/galvanostand interfaced. The spectroelectrochemical studies of the polymer were performed using UV–Vis spectrophotometer (Agilent 8453), and Minolta CS100 spectrophotometer was measured in order to analysis the colorimetric measurements.

Synthesis of 8-(4,6-dichloro-1,3,5-triazinoxy) quinoline (TQ).—8-hydroxyquinoline (0.145 g, 1 mmol) and sodium hydroxide (0.04 g, 1 mmol) were dissolved in 5 mL acetone/water (4:1 v/v), then added drop by drop to a solution of TCT (0.184 g, 1 mmol) in 5 ml acetone at 0–5°C (Scheme 1). The reaction mixture was stirred at 0–5°C for 1 hour and 10 mL crushed ice was added to the medium. The precipitate was filtered. Product as white powdered solid was washed large amount of cold water and 30 mL cold acetone/water (1:2 v/v). After storing in desiccator to dry the obtained chemical compound, compound was purified by recrystallization from acetone/n-hexane (1:1 v/v). The melting point of the light yellow product (TQ) was 199–200°C.

Synthesis of 9,9′-(2,2′-(6-(quinolin-8-yloxy)-1,3,5-triazine-2,4-diyl)bis(oxy)bis(ethane-2,1-diyl))bis(9H-carbazole) (TQEC).—To stirred TQ (0.293 g, 1 mmol), dissolved in 20 mL acetone, was added