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Multifunctional Surface Design by Carbazole and Fluorescein Functionalized Conducting Polymer: High-Contrast Electrochromic Devices Application

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In this work, a star shaped monomer including carbazole and fluorescein namely 2-(6-((4,6-bis((9H-carbazol-2-yl)oxy)-1,3,5-triazin-2-yl)oxy)-3-oxo-3H-xanthen-9-yl)benzoic acid (TFC) was synthesized. As an electroactive functional group, carbazole has been used to electrochemically polymerize the monomer and allows the resulting conductive film to be used in different electrochemical and optical applications. On the other hand, fluorescein functional group will bring fluorescence property to the molecule and it will be used in different applications such as biosensor and metal sensor via acid functional group in its structure. This monomer has been electrochemically polymerized on the ITO surface to obtain a multifunctional modified surface. This thin film (PTFC) has been used in electrochromic application. Spectroelectrochemical studies have showed that the conducting polymer film exhibit between transparent and green color. Furthermore, electrochromic device (ECD) which containing PTFC and poly(3,4-ethylenedioxythiophene) (PEDOT) was designed. Electrochromic properties of the device were studied.
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Recently, super-structural polymers[1–6] are attracted more attention than linear counterparts. Great efforts have been made the design and synthesis of super-structural conducting polymers to achieve multi-functional properties in various fields. These polymers have gained considerable attention owing to their potentials for excellent optical and electrochemical properties[7–9] multiple color exhibitions,[10–12] high optical contrast[13] and multifunctional material design ability. Therefore, they can be used in many fields such as OLEDs,[14,15] photovoltaics devices,[16] field-effect transistors,[17] sensor applications[18–25] and electrochromic devices.[26,27]

Due to its high photostability and a big fluorescence quantum yield, fluorescein[28,29] with large rigid π-conjugated structure is widely used as fluorescent probes in chemistry, biology and material science.

2,4,6-trichloro-1,3,5-triazine[30,31] is a unique starting molecule for the synthesis of multifunctional materials. By controlling the temperature, three chloride atom of 2,4,6-trichloro-1,3,5-triazine can be substituted any nucleophilic reactant like amines, alcohols, or phenol. The substitution of first chloride atom of 2,4,6-trichloro-1,3,5-triazine is exothermic. For this reason, the temperature of reaction mixture has to be controlled about 0°C. The second chloride can be substituted at 30–35°C. Finally, the third chloride of 2,4,6-trichloro-1,3,5-triazine is performed under reflux of the solvents.[32–34] Therefore, three different functional molecules can be added to the triazine molecule with temperature controlled reactions which allows the synthesis of new materials with multifunctional properties.

Therefore we have synthesized a triazine cored carbazole and fluorescein functionalized star shaped monomer namely 2-(6-((4,6-bis((9H-carbazol-2-yl)oxy)-1,3,5-triazin-2-yl)oxy)-3-oxo-3H-xanthen-9-yl)benzoicacid (TFC). As an electroactive functional group, carbazole has been used to electrochemically polymerize the monomer and allows obtaining conductive film to be used in different electrochemical and optical applications. On the other hand, fluorescein functional group will bring fluorescence property to the molecule and it will be used in different applications such as biosensor and metal sensor via acid functional group in its structure. This monomer has been electrochemically polymerized (PTFC) on the ITO surface to obtain a multifunctional modified surface.

This multifunctional material with has been used in electrochromic device applications. Optical and electrical properties of device with ITO/PTFC/gel electrolyte/PEDOT/ITO design have been investigated.

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Experimental

Chemical reagents and equipments.—Fluorescein, 2-hydroxycarbazole, 3,4-ethylenedioxythiophene, poly(methyl methacrylate) (PMMA), lithium perchlorate ($LiClO_4$), acetone, sodium hydrogen carbonate ($NaHCO_3$), propylene carbonate (PC), sodium hydroxide (NaOH), acetic acid were purchased from Sigma-Aldrich. 2,4,6-trichloro-*s*-triazine was purchased from Merck. The phosphorus pentoxide (P_2O_5) was used to dry acetonitrile (ACN) (Aldrich).

The ^1H NMR spectra in DMSO-d_6 was attained using a Varian (400-MHz) spectrometer. Perkin Elmer 100 series FT-IR spectrophotometer with Universal ATR Polarization Accessory (4000–400 cm^{-1}) was used for FT-IR measurements. Elemental analyses were performed with LECO-CHNS-932 analytical instrument. Surface morphology of the polymer was analyzed in Zeiss Evo LS 10 scanning electron microscope. Perkin Elmer LS55 Luminescence Spectrometer was used to measure fluorescence properties. Fluorescence image of polymer was investigated using an Olympus CKX41 model inverted microscope containing a DC30 camera. Electrochemical polymerization and analysis were fulfilled by Ivium potentiostat/galvanostat equipment. The spectroelectrochemical properties of polymer were identified by using an Agilent 8453 UV–Vis spectrophotometer. Background correction for electrochemical measurements was not done. Minolta CS-100 spectrophotometer was used to investigate of colorimetry measurements.

Synthesis of 2-(6-(4,6-dichloro-s-triazin-2-yloxy)-3-oxo-3H-xanthen-9-yl)benzoic acid (TF).—2,4,6-trichloro-*s*-triazine (0.184 g, 1 mmol) in 10 mL acetone, a mixture of sodium hydroxide(0.8 g, 2 mmol), and fluorescein(0.333 g, 0.01 mol) in 10 mL acetone-water (4:1 v/v) was added slowly at 0–5°C. The reaction was stirred further for 4 h. At the end of the reaction, the mixture was poured into cold acidified water and filtered. Precipitate as brick color was rinsed several times with water and dried at 80°C, giving the product in 70% yield. Its melting point was 190°C. Elemental analysis; % Calculated: C 57.52, H 2.31, N 8.75, $C_{23}H_{11}Cl_2N_3O_5$, % Found: C 57.81, H 2.42, N 8.48.

Synthesis of 2-(6-(4,6-bis(9H-carbazol-2-yloxy)-s-triazin-2-yloxy)-3-oxo-3H-xanthen-9-yl)benzoic acid (TFC).—2-hydroxycarbazole (0.183 g, 1 mmol) and NaOH (0.04 g, 1 mmol) were dissolved in 10 mL acetone/water (9:1, v/v) and added dropwise at 0°C to a cooled solution of (0.240 g, 0.5 mmol) TF in 10 mL acetone. The mixture was reacted for 1 h at 0–5°C, 4 h at 30–35°C then resultant mixture was refluxed for overnight. After the reaction mixture was cooled and poured into acidified water. Then crude