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Electrosynthesis and characterization of an electrochromic material containing biscarbazole–oxadiazole units and its application in an electrochromic device

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ABSTRACT

Electroactive poly(2,5-Bis(9-methyl-9 H-carbazol-3-yl)-1,3,4-oxadiazole) (PolyBCO) film was synthesized to form a highly stable conducting polymer with excellent electrochromic properties. The polymer was characterized by cyclic voltammetry, UV–Vis-NIR spectroscopy and colorimetry. Spectroelectrochemistry analysis demonstrated that the polymer can undergo both p-type and n-type doping processes. The polymer has four accessible color states. Further kinetic studies demonstrated that the polymer revealed high contrast ratio (75%), fast response time (0.9 s), excellent stability and color persistence. A dual-polymer electrochromic device was constructed in sandwich configuration where PolyBCO was used as the anodically coloring material. The device switches between a transmissive light gray state and a blue-colored state with a fast response time and high stability.

1. Introduction

There is a rapid growth in the field of organic electronics in the last two decades. Developments in science and technology have revealed new application possibilities for conducting homopolymers and their derivatives.

On the contrary the majority of the polyheterocycles exhibit p-type doping, the synthesis of n-type doping material is limited due to their susceptibility towards oxygen. This limits the use of conducting polymers in the construction of devices. One of the approaches for the synthesis of n-type materials is donor–acceptor theory [14]. This theory involves the alternation of electron-rich (donor, D) and electron-deficient (acceptor, A) units in the polymer structure. The use of this alternating donor–acceptor strategy allows the synthesis of low band gap polymers that is most significant for the control of the optical properties of synthesized polymers [5,6].

From the electronic point of view, polycarbazole based compounds attract great attention due to their unique optical properties and strong hole-transporting ability in optoelectronics [7,8], such as organic solar cells [9], organic field effect transistors [10], and organic light emitting diodes [11] and electrochromic device applications [12,13]. Carbazoles are very promising materials for tailoring functional groups since they can be easily functionalized at their (3,6-), (2,7-) or N-positions [15–17].

1,3,4-Oxadiazoles are one of the important heterocyclic compounds with a wide range of pharmaceutical and biological activities, such as anti-inflammatory [18], antibacterial [19], insecticidal [20], anticonvulsant [21] and antimitotic [22] activities. Small molecules bearing carbazole and 1,3,4-oxadiazole moieties have been used to prepare a number of donor–acceptor molecules with a π-electron-rich aromatic ring [23,24].

In the present research, 2,5-bis(9-methyl-9 H-carbazol-3-yl)-1,3,4-oxadiazole (BCO) was synthesized and structure of monomer was analyzed by spectral methods (^{1}H-, ^{13}C-Nuclear Magnetic Resonance spectroscopy (NMR)). Electropolymerization was performed to obtain the conducting polymer having multichromic properties. Furthermore, electrochemical and spectroscopic analyses of the donor–acceptor–donor type polymer and the corresponding electrochromic device were carried out.

2. Experimental

2.1. Materials and equipments

All chemicals were purchased from Aldrich, Merck and Acros. They were used without further purification. Solvents were of analytical

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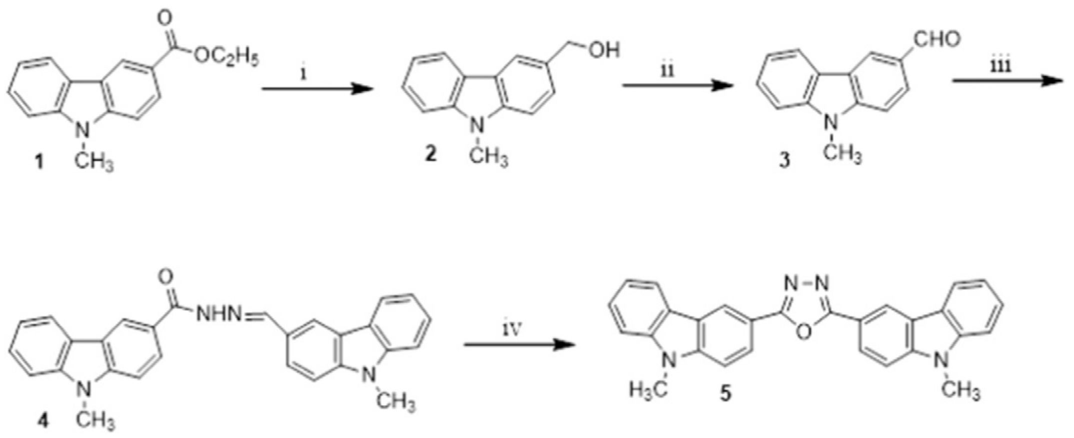

Scheme 1. Reagent and Conditions: i) THF, $LiAlH_4$, reflux, 5 h; ii) MnO_2, CH_2Cl_2, refluxed, 5 h; iii) 9-Methyl-9 H-carbazole-3-carbohydrazide, ethanol, AcOH, refluxed, 6 h; iv) acetone, $KMnO_4$, refluxed, 4 h.

grade and used as received. NMR spectra were recorded on Varian AS-400 NMR at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR. Combustion analyses of compounds were performed on a CHNS-932-LECO. Voltalab 50 potentiostat/galvanostat was used to supply a constant potential during electrochemical synthesis and for cyclic voltammetry. Spectroelectrochemical and kinetic studies of the polymers were performed on Varian Cary 5000 spectrophotometer at a scan rate of 2000 nm/min. Colorimetric measurements were achieved by a Minolta CS-100A Chroma Meter with a 0/0 (normal/normal) viewing geometry as recommended by The Commission Internationale de l'Eclairage (CIE). During measurement, samples were placed in a light booth system where it was illuminated from behind by a D65 light source.

2.2. Synthesis

2.2.1. (9-methyl-9 H-carbazol-3-yl)methanol (2)

A solution of **1** (5.0 g, 19 mmol) of in anhydrous tetrahydrofuran was added to a stirred solution of lithium aluminum hydride (1.0 g, 30 mmol) in 50 mL of tetrahydrofuran. The mixture was refluxed under nitrogen for 5 h and then cooled to 0 °C and the excess lithium aluminum hydride was quenched with water and the product was extracted with ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was recrystallized from diethyl ether to yield 4 g (96%) of **2**, mp: 137 °C; IR (KBr, ν_{max}, cm^{-1}): 3436 (OH), 3048 (CH), 2919 (CH); ^1H NMR (d_6-DMSO, 400 MHz): δ 3.86 (s, 3 H, CH_3), 4.66 (d, 2 H, J = 5.7 Hz, CH_2), 5.16 (t, 1 H, J = 5,7 Hz, OH), 7.19 (t, 1 H, J = 7.5 Hz, ArH), 7.42–7.48 (m, 2 H, ArH), 7.54 (d, 1 H, J = 8.0 Hz, ArH), 7.57 (d, 1 H, J = 8.0 Hz, ArH), 8.09 (s, 1 H, ArH), 8.13 (d, 1 H, J = 7.6 Hz, ArH).

Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.42; H, 6.31; N, 6.59.

2.2.2. 9-methyl-9 H-carbazole-3-carbaldehyde (3)

To a solution of **2** (1.0 g, 4.7 mmol) in dichloromethane (25 mL) actived MnO_2 (1.5 g) was added and the mixture was refluxed for 5 h. The solvent was removed under reduced pressure and the residue was recrystallized from diethyl ether to yield 0.80 g (80%) of **3**, mp: 76 °C; IR (KBr, ν_{max}, cm^{-1}): 3046 (CH), 2931 (CH), 1700 (C = O); ^1H NMR ($CDCl_3$, 400 MHz): δ 3.87 (s, 3 H, CH_3), 7.32 (t, 1 H, J = 8.4 Hz, ArH), 7.43 (d, 1 H, J = 8.0 Hz, ArH), 7.46 (d, 1 H, J = 8.0 Hz, ArH), 7.54 (t, 1 H, J = 7.6 Hz, ArH), 8.00 (dd, 1 H, J = 8.8 and 1,4 Hz, ArH), 8.13 (dd, 1 H, J = 8.0 and 1.6 Hz, ArH), 8.58 (d, 1 H, J = 1.6 Hz, ArH), 10.08 (s, 1 H, CHO).

Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.09; H, 5.21; N, 6.57.

2.2.3. 9-methyl-N'-((9-methyl-9 H-carbazol-3-yl)methylene)-9 H-carbazole-3 carbohydrazide (4)

To an equimolar ethanolic solution of carbazole carbaldehyde **3** (1.0 g, 4.2 mmol) and 9-methyl-9 H-carbazole-3-carbohydrazide [25] (0.87 g, 4.2 mmol), a few drops of glacial acetic acid were added. The mixture was then refluxed for 6 h. It was then allowed to cool and filtered. The crude product was recrystallized from methanol to yield 1.75 g (85%) of **4**, mp: 259 °C; IR (KBr, ν_{max}, cm^{-1}): 3180 (NH), 3050 (CH), 2950 (CH), 1642 (C = O), 1615 (C = N); ^1H NMR (d_6-DMSO, 400 MHz): δ 3.89 (s, 3 H, CH_3), 3.92 (s, 3 H, CH_3), 7.23 (t, 1 H, J = 7.6 Hz, ArH), 7.29 (d, 1 H, J = 7.2 Hz, ArH),7.49 (t, 1 H, J = 7.6 Hz, ArH), 7.52 (t, 1 H, J = 7.6 Hz, ArH), 7.59–7.72 (m, 4 H, ArH), 7.93 (d, 1 H, J = 8.4 Hz, ArH), 8.11 (d, 1 H, J = 8.4 Hz, ArH), 8.23 (t, 2 H, J = 7.6 Hz, ArH), 8.47 (s, 1 H, ArH), 8.68 (s, 1 H, ArH), 8.82 (s, 1 H, N = CH), 11.81 (s, 1 H, NH).

Anal. Calcd for $C_{28}H_{22}N_4O$: C, 78.12; H, 5.15; N, 13.01. Found: C, 77.98; H, 5.11; N, 13.12.

2.2.4. 2,5-bis(9-methyl-9 H-carbazol-3-yl)-1,3,4-oxadiazole (5)

A solution of carbazole hydrazide **4** (1.0 g, 2.3 mmol) and potassium permanganate (1 g) in acetone (25 mL) was refluxed for 4 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to remove acetone. The residue was added with a saturated sodium sulfite aqueous solution (30 mL) and extracted with ethyl acetate. The organic phase was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude product was chromatographed with ethyl acetate-hexane (1:1) using silica gel. Organic solvents were evaporated and the residue was recrystallized from diethyl ether to yield 0.62 g (62%) of biscarbazole–oxadiazole **5**, mp: 238 °C; IR (KBr, ν_{max}, cm^{-1}): 3047 (CH), 2942 (CH), 1607 (C = N); ^1H NMR (d_6-DMSO, 400 MHz): δ 3.94 (s, 6 H, 2 × CH_3), 7.27 (t, 2 H, J = 8.0 Hz, ArH), 7.53 (t, 2 H, J = 8.0 Hz, ArH),7.65 (d, 2 H, J = 8.4 Hz, ArH), 7.81 (d, 2 H, J = 8.8 Hz, ArH), 8.25 (d, 2 H, J = 7.6 Hz, ArH), 8.37 (d, 2 H, J = 7.6 Hz, ArH), 9.00 (s, 2 H, ArH).

Anal. Calcd for $C_{28}H_{20}N_4O$: C, 78.49; H, 4.70; N, 13.08. Found: C, 78.35; H, 4.76; N, 12.98.

2.3. Electrochemistry

The potentiodynamic electropolymerization of monomer (10^{-2} M) was carried out in 0.1 M tetrabutylammonium tetrafluoroborate/acetonitrile ($TBABF_4$/ACN) supporting electrolyte–solvent couple. Electrochemical synthesis of polymer was performed in a three-electrode cell consisting of an indium tin oxide (ITO) glass slide as the working electrode, platinum (Pt) wire as the counter electrode and Ag wire as the pseudo-reference electrode (calibrated against