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Disulfide-linked symmetric *N*-alkyl carbazole derivative as a new electroactive monomer for electrochromic applications

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ABSTRACT

In this study, we reported a novel and an unusual method for the preparation of the disulfide-linked symmetrical carbazole derivative and investigated the electrical and optical properties of crosslinked conductive polymer obtained as a result of its electropolymerization. The disulfide-linked *N*-alkyl substituted carbazole monomers are comparatively polymerized in different solvents. It has been found that the conductive polymer obtained in Boron trifluoride diethyl etherate (BFEE) has the high optical contrast and stability compared to other *N*-alkyl substituted carbazoles in literature.

1. Introduction

Disulfide compounds display interesting behaviours both in biology and chemistry [1]. Disulfides have been produced from related thiol and interconversion reaction between thiol and they exploit high stability which makes their oxydated derivatives easily synthesizable due [2]. There is a great interest in synthesizing disulfide compound which can be used for the preparation a new types self-assembled monolayers and monolayer-protected clusters [3,4].

Polycarbazoles and their derivatives are still active research area due to their good electron donating and light emitting properties [5–10]. They are used as light emitting diodes in OLED technology either as dopands or host materials because of conjugation properties [11,12]. In addition to that, these kinds of compounds are also used as organic photoconductors, charge carrier transport materials, organic dyes for solar energy cells [13,14] and drug delivery material [15]. It is well known that carbazoles are active against cancer, cardiovascular disorders [16,17].

Electrochromic materials can have different colors at different applied potential. During the chemical redox processes, they change their colors accordingly. One of the most important application areas of these materials, which attracted great attention for academia and industry, are smart windows [18,19]. Smart windows technology has already advanced, but one of the typical and deadly obstacles of these technologies is low optical contrast [20]. For this reason, electrochromic material used in smart window needs to be totaly transparent in the one oxidation state and it should exhibit high optical contrast between different redox states [21–25]. Usage of the polycarbazole derivatives in electrochromic application has limited, because of theirs poor film forming properties and having low optical contrast. Recently, conductive polymers with high optical contrast and good film quality can be obtained by polymerizing two or more carbazole-containing electroactive monomers [26–29]. This high quality polycabazole films has been obtained by providing conductivity in three dimensions due to cross-links [25,30,31].

In this study, we report a novel and an anusual method for the preparation of the symmetrical carbazole linked disulfide electroactive monomer. Conducting polymer film obtained by electrochemical polymerization of this bifunctional carbazole monomer has showed the high optical contrast (62.5%) among the polycarbazole derivatives in literature. Furthermore it has showed good optical transparency in its neutral state. Due to the high optical contrast value and good tranparency property, this material is an excellent electrochromic material for smart window applications.

2. Experimental

2.1. Materials

All reactions were carried out under an argon atmosphere using Schlenk techniques connected vacuum line. 6-(9H-Carbazol-9-yl) hexane-1-thiol [31] and 3,6-bis(4'-methylphenylsulfoxyloxy) phthalonitrile [32] were synthesized following the literature procedures. All solvents were fresly purified by standard procedures before use [33] ^{1}H

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and ^{13}C NMR were recorded on an Agilent NMR-vnmrs spectrometer using TMS as internal standard. Infrared spectra were recorded on a Perkin Elmer UATR Two spectrometer. Mass spectra were determined on a Bruker Daltonicis Microflex Mass Spectrometer equipped with a nitrogen UV-Laser operating at 337 nm. Melting points were determined on an electrothermal apparatus and are uncorrected. An Ivium Compact Stat Potentiostat was used for all electrochemical measurements. Optical characterization of polymer was performed using Agilent 8453 UV–vis spectrophotometer. A Perkin Elmer 100 series FT-IR spectrophotometer was used characterization of the polymers.

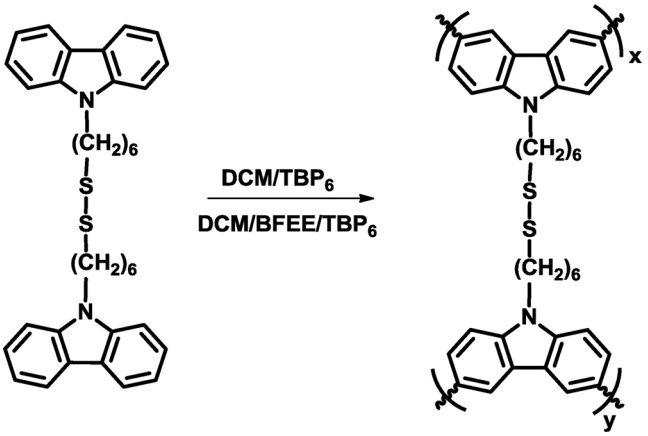
2.2. Synthesis of monomer (CS)

1,2-Bis[6-(9-carbozol-9-yl)hexyl]disulfane (CS) was prepared as follow. A mixture of 3,6-bis(4'-methylphenylsulfoxyloxy)phthalonitrile (2.06 g, 4.38 mmol) and 6-(9H-carbazol-9-yl)hexane-1-thiol (3.1 g, 10.96 mmol) was dissolved in dry dimethyl sulfoxide (DMSO) (40 mL) under argon atmosphere at room temperature and stirred for 1 h. Anhydrous K_2CO_3 (2.42 g, 17.52 mmol) was drop-wise added to the reaction mixture and the mixture was stirred for 20 h under the same conditions and monitored by a TLC [silica gel (chloroform:hexane) (9:1)]. After the reaction was complete, the mixture was poured into 400 mL of distilled water and extracted with dichloromethane (3 × 150 mL). The organic layer was subsequently washed with 100 mL of water, dried over anhydrous $MgSO_4$ and then filtered. Solvent was evaporated to dryness under reduced pressure and solidified with adding of diethylether (50 mL). The pale yellow product was purified by column chromatography to obtain 3,6-bis((6-(9H-carbazol-9-yl) hexyl)thio)phthalonitrile compound. The etheric phase was dried with $MgSO_4$ and evaporated to dryness under reduced pressure. The oily crude product was chromatographed on silica gel eluting with chloroform:hexane (8:2), chloroform:hexane (7:3) and hexane, succesively. The residue in chromatography column was re-chromatographed eluting with stepwise gradient mixtures of chloroform:hexane (95:5, 90:10, 80:20). The oily product was evaporated to dryness under reduced pressure and then crystalized by using a mixture of diethyl ether:petroleum ether (1:3). Yield: 0.42 g (17%), mp: 82 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.03-8.00 (d, J = 7.62 Hz, 4H, Ar-H), 7.40-7.32 (m, 8H, Ar-H), 7.16-7.12 (t, J = 6.7 Hz, 4H, Ar-H), 4.22-4.17 (t, J = 7.03 Hz, 4H, NCH_2), 2.52-2.47 (t, J = 7.15 Hz, 4H, SCH_2),182-1.75 (m, 4H, CH_2), 1.57-1.53 (m, 4H, CH_2), 1.31-1.28 (m, 8H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.29, 124.53, 121.71, 119.30, 117.67, 107.55, 41.84, 37.64, 27.86, 27.41, 25.83. FT-IR (ATR, cm^{-1}): 3050, 3021, 2923-2853, 1596, 1484, 1461, 1325, 1238, 1152. MS (ESI) m/z: 564.054 $[M]^+$. Anal. Calcd. for $C_{36}H_{40}N_2S_2$: C, 76.59; H, 7.09; N, 4.96. Found: C, 76.40; H, 7.26; N, 5.13.

2.3. Electrochemistry

The redox behaviour and electropolymerization of the monomer (CS) were investigated by cyclic voltammetry technique. All electrochemical measurements including cyclic voltammetry were carried out by using an Ivium Compact Stat potentiostat at room temperature. Electrochemical cell was consist of an ITO-coated glass slide (Delta Technologies, 8–12 Ω, 0.7 × 5.0 cm^2) as working electrode, Pt counter electrode and silver wire as reference electrode which calibrated by using 0.5 mM of ferrocene solution.

The electropolymerization process of CS monomer was carried out comparatively in the BFEE (Boron trifluoride diethyl etherate) containing and BFEE-free electrolytic solutions. Electrolytic solution was composed of 0.01 M monomer and 0.1 M tetrabutylammonium hexafluorophosphate (TBP_6) in dichloro methane (DCM) solvent. After electrodynamic electropolymerization using CV technique, prepared conducting polymer film of CS was washed with the solvent to remove the unreacted monomer and the excess supporting electrolyte. Optical and electrical characterizations of the PCS such as switching studies, redox stability and spectroelectrochemical properties were performed in the same electrolyte media in the absence of monomer. Electrochemical polymerization of CS is shown in Scheme 1.



Scheme 1. Electrochemical polymerization of CS.

3. Results and discussion

3.1. Synthesis and characterization of CS

The classical methods for the preparation of disulfides are based on the oxidation of appropriate thiols by using oxygen, iodine, hydrogen peroxide, chromates, DMSO and bromine [34]. There is only one report for the synthesis of carbazole substituted disulfide [35]. In the mentioned literature, tosylated undecyl linked carbazole was reacted with NaSH at 45 °C. The conversion reaction of thiols to disulfide requires an oxydation agent. In this study, the preparation of alkyl linked carbazole disulfide was achieved in inert atmosphere presence of 3,6-bis(4'-methylphenylsulfoxyloxy) phthalonitrile, dry K_2CO_3 and 1,2-bis[6-(9-carbozol-9-yl)hexyl]disulfane in dry DMSO at room temperature. To prepare 3,6-bis(6-carbazol-9-yl-hexyl-sulfanyl)phthalonitrile as a starting material for synthesis of zinc(II) phthalo-cyanine was an aim of this study. 1,2-bis[6-(9-carbozol-9-yl)hexyl]disulfane can be prepared precursor compound [2,3-dicyano-1,4-phenylene bis(4-methylbenzenesulfonate)] and chalcogenyl anions via S_NAr reaction in the presence of dry K_2CO_3 by using DMSO as solvent at room temperature under standard conditions [32]. We have accomplished the synthesis of carbazole terminated dihexyl disulfide that has spontaneously formation ability. Competitive reaction of thiol and tosylated precursor indicated that formation of 3,6-bis(6-carbazol-9-yl-hexylsulfanyl)-phthalonitrile is preferred over disulfide. Although, the yield of substituted phthalonitrile looked convenient in 47.7%, but thiol gave disulfide in 17.0%. Synthetic route of CS was given in Scheme S1 (Supporting information). Disulfide displayed the expected molecular ion peak at m/z = 564 $[M]^+$. MS spectrum of 6-(9-carbozolyl)-1-hexyldisulfide (CS) was given in Fig. S1 (Supporting information). ^1H NMR spectrum of this compound (Fig. 1a), expectation signals concerning NCH_2, CH_2 and SCH_2 protons belonging to carbazole and substituted disulfide moieties gave significant signals at δ = 4.22–4.17, 1.82–1.28, 252–247 ppm, respectively. Characteristic chemical shifts concerning carbazole moiety observed at δ = 8.03–8.00, 7.40–7.32 and 7.16–7.12 ppm as expected [36]. In the proton-decoupled ^{13}C NMR spectrum of CS (Fig. 1b), the signals observing at δ = 41.84, 37.64, 27.86-25.83 and range of 107.55, 119.30, 121.71, 124.53 and 139.29 ppm should be related to CH_2N, CH_2S, CH_2, and aromatic carbons. FT-IR spectrum of CS (Fig. S2, Supporting information) clearly indicates that disapperance of the S—H groups at 2553 cm^{-1} after the S_NAr reaction, which shows the formation of disulfide compound [31].