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Clickable, versatile poly(2,5-dithienylpyrrole) derivatives

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ABSTRACT

In this study a novel, clickable, azide containing conducting polymers based on 1-(2-azido-ethyl)-2,5-dithiophene-2-yl-1H-pyrrole (SNS-N_3) were synthesized and characterized. Optical and electronic properties of homopolymer (PSNS-N_3) were investigated and colorimetric studies were performed. The homopolymer has a band gap of 2.49 eV and it displays yellow to blue coloration upon doping. Electrochemically prepared copolymers of SNS-N_3 and 3,4-ethylenedioxythiophene (EDOT) formed multichromic, color tunable electrochromic materials with continuous color gradient from cinnamon, mustard, lime green, blue and dark blue. Spectroelectrochemical analyses revealed that the neutral copolymers possess two absorption maxima (~320 and 450 nm) where the relative intensity and position of the two depends on polymerization potential. Copolymer films could be fully switched between their neutral and oxidized forms in ~1.2 s with a percent transmittance of ~65% at 950 nm. Moreover, a PSNS-N_3 coated ITO electrode was subjected to click reaction using ethynylferrocene. CV and FTIR studies revealed that ferrocene could easily be attached onto the electrode surface without loss of electroactivity of both ferrocene and PSNS backbone. Our results suggest that electrochemically prepared PSNS-N_3 films offer a novel and multipurpose platform for simple, effective post-functionalization of poly(2,5-dithienylpyrrole)s under mild conditions.

1. Introduction

Conducting polymers take an interest in academic and industrial research centers because of their electrical, optical, electrophysical and electrochemical properties. These unique properties make them suitable in various applications of technology such as LED [1], solar cells [2], chemical sensors [3], organic transistors [4] and electrochromic devices [5]. Poly(2,5-dithienylpyrrole) derivatives (PSNS) have been known and investigated for almost 20 years. PSNS derivatives are one of the most promising conducting polymers due to their low oxidation potential, effortless chemical and electrochemical polymerization. In literature there are a few SNS derivatives, having substituted alkyl derivatives [6,7], phenyl derivatives [8–15], ferrocene [16], BODIPY [17], anthraquinone [18]. Nevertheless, SNS derivatives which contain azide groups have not been reported hitherto.

Azide groups are known to undergo several high yield cycloaddition reactions which could serve as a reactive site for the covalent binding of functional units. Among those, azide alkyne Huisgen cycloaddition reactions using Cu catalyst, which is also acknowledged as the most popular "Click" reaction, is the widely used in synthesis of sophisticated polymers from simple building blocks. Utilization of click chemistry in the field of conducting polymers have recently started, and they are mainly devoted on PEDOT derivatives which are functionalized by click reaction both prior to and after the polymerization [19–24].

Until now all PSNS derivatives in literature are achieved though electrochemical/chemical polymerization of SNS monomers which are synthesized through Paal–Knorr reaction having significantly low yields, especially in case of bulky- acceptor groups. Thus, it was clear that introduction of new groups to classical PSNS structure depends mainly on success in monomer synthesis, which seriously limits the available structures. This study proposes the use of a modular, conveniently synthesized PSNS derivative which could readily undergo click reaction after its electrochemical deposition on electrode. This approach it is expected to embody the superior attributes of poly(2,5-dithienylpyrrole) derivatives with an active group in a single electrode, where the active group could be chosen according to requirements of the field of interest without concerning the limitations of Paal–Knorr reaction.

Herein we disclose construction of clickable PSNS-based electrochromic films and provide a pioneer study which demonstrates capability and versatility of click chemistry in efficient functionalization of PSNS-based electrochromic films on electrode surface. For this purpose, a novel SNS derivative 1-(2-azido-ethyl)-2,5-dithiophen-2-yl-1H-pyrrole (SNS-N_3) was designed, synthesized and characterized for the first time. SNS-N_3 was subjected to electrochemical polymerization and optoelectronic properties of the homopolymer were investigated by cyclic voltammetry,

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spectroelectrochemistry, switching and colorimetry studies. Additionally, based on SNS-N_3 and 3,4-ethylenedioxythiophene (EDOT) novel multicolored electrochromic copolymers, having tunable composition, were achieved by controlling electrochemical copolymerization conditions. Finally, in order to prove the design strategy of this material, we realized post polymerization functionalization of PSNS-N_3 films on electrode surface through clicking of ethynylferrocene.

2. Experimental

2.1. General

All chemicals were purchased from Aldrich, Merck Chemical as analytical grade. Lithium perchlorate and tetrabutylammonium perchlorate (TBAP) were electroanalytical grade and thiophene, succinyl chloride, ethanolamine, p-toluene sulfonic acid (PTSA), triethylamine (TEA), dimethylaminopyridine (DMAP), p-toluene sulfonyl chloride (TsCl), sodium azide, 3,4-ethylenedioxythiophene (EDOT) were used as received. Acetonitrile (ACN) was distilled over calcium hydride and kept on 4 Å molecular sieves. 1,4-di(2-thienyl)-1,4-butanedione and *2-(2,5-di-thiophene-2-yl-pyrrol-1-yl)-ethanol (SNS-etOH)* were synthesized according to literature [25].

2.2. Equipments

Electrochemical synthesis and characterization studies were performed on Ivium stat potentiostat/galvanostat. Thermo Evolution Array UV–Visible spectrophotometer was utilized for spectroelectrochemistry and kinetic studies. Colorimetry measurements were recorded on a Minolta CS-100A Chroma Meter in a proper box having D-50 illumination. NMR spectra were recorded with a Bruker Spectrospin Avance DPX-500 spectrometer at 500 MHz for ^{1}H NMR and 250 MHz for ^{13}C NMR. Chemical shifts (δ) were given relative to tetramethylsilane (TMS) as the internal standard. The FTIR spectra were recorded on a Brucker Tensor 27 spectrometer.

2.3. Synthesis of the toluene-4-sulfonic acid 2-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-ethyl ester (SNS-OTs)

A solution of TsCl (0.19 g, 1 mmol) in 5 ml DCM was added drop wise to a 3 ml of DCM solution containing SNS-etanol (0.275 g, 1 mmol), TEA (5 mmol), DMAP (0.1 mmol) at 0 °C. Reaction mixture was stirred for a total of 5 h and it was extracted with water, concentrated $NaHCO_3$, NaCl and later dried over $MgSO_4$. The crude product was purified by chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 8.0 Hz, 2 H), 7.31 (dd, J = 1.0, 5.0 Hz, 2 H), 7.26 (d, J = 8.0 Hz, 2 H), 7.05 (dd, J = 3.0, 5.0 Hz, 2 H), 6.97 (dd, J = 1.0, 3.0 Hz, 2 H), 6.27 (s, 2 H), 4.40 (t, J = 6.0 Hz, 2 H), 3.93 (t, J = 6.0 Hz, 2 H), 2.45 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 133.8, 132.25, 129.89, 128.31, 127.93, 127.48, 126.79, 125.96, 111.71, 67.66, 43.08, 21.7; FTIR (KBr, cm^{-1}): 3092, 2928, 1730, 1594, 1492, 1466, 1406, 1366, 1292, 1186, 1171, 988, 773, 706, 663.

2.4. Synthesis of 1-(2-azido-ethyl)-2,5-dithiophen-2-yl-1H-pyrrole (SNS-N_3)

To 10 ml of DMF, 0.429 g (1 mmol) SNS-OTs and 0.65 g (10 mmol) of NaN_3 were added and mixed at 50 °C for 6 h. After cooling to the room temperature, the reaction mixture was partitioned between water and DCM, and the aqueous phase was washed with DCM. The combined organic extracts were washed with concentrated $NaHCO_3$, brine and dried with $MgSO_4$. The crude product was purified by chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.36 (m, 2 H), 7.01–7.11 (m, 4 H), 6.38 (s, 2 H), 4.37 (t, J = 6.6 Hz, 2 H), 3.27 (t, J = 6.6 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.14 (C_{quat}), 128.42 (C_{quat}), 127.43 (CH), 126.55 (CH), 125.81 (CH), 111.69 (CH), 111.67 (CH), 50.77 (CH_2), 43.86 (CH_2); FTIR (KBr, cm^{-1}): 3104, 2943, 2098, 1447, 1402, 1344, 1300, 843, 770, 699.

2.5. Synthesis of homopolymer (PSNS-N_3)

PSNS-N_3 films were prepared potentiodynamically on ITO electrodes, using 0.01 M monomer in acetonitrile (ACN). Both $LiClO_4$ and TBAP were used as the supporting electrolyte. A platinum wire was used as the counter electrode and Ag/Ag^+ electrode calibrated against ferrocene was used as the reference electrode. During the electrochemical process, the color of the solution in the vicinity of working the electrode darkened progressively. However, as the polymerization proceeded, a homogeneous well adhered film deposited on the working electrode.

2.6. Synthesis of copolymers (P(SNS-N_3-EDOT))

EDOT was used as the comonomer for the syntheses of copolymer (Scheme 2). For this purpose SNS-N_3 (20 mg) was dissolved in 5 ml of ACN and 5 μL of EDOT was introduced into the same electrolysis cell which was used during homopolymerization. The films were either prepared potentiodynamically scanning the potential between 0.0 V and 1.2 V by using $LiClO_4$ or potentiostatically at 1.0–1.3 V by using TBAP as the supporting electrolyte on ITO glass electrodes.

2.7. Post-polymerization functionalization of P(SNS-N_3) with ferrocene

Post-polymerization functionalization of P(SNS-N_3) was achieved via typical click reaction where a P(SNS-N_3) coated ITO electrode was immersed in a 5 ml DMF solution containing 0.1 M ethynylferrocene, $CuSO_4$ and sodium ascorbate. After 24 h of click reaction at room temperature; the electrode was thoroughly rinsed with methanol and distilled water to in order to eliminate the art effect of any physically adsorbed ethynylferrocene and copper residue. After drying under vacuum, the specimens were subjected to CV and FTIR analyses.

3. Results and discussion

3.1. Monomer synthesis

1-(2-Azido-ethyl)-2,5-di-thiophen-2-yl-1H-pyrrole (SNS-N_3) was synthesized by four-step synthetic route, as shown in Scheme 1. The first step involves synthesis of 1,4-di(2-thienly)-1,4-butanedione through thiophene and succinyl chloride and the second step includes a Paal–Knorr reaction between 1,4-di(2-thienly)-1,4-butanedione and ethanolamine in the presence of catalytical amount of PTSA. Treatment of 2-(2,5-di-thiophene-2-yl-pyrrol-1-yl)-ethanol (SNS-ethanol) with an equimolar amount of TsCl produced toluene-4-sulfonic acid 2-(2,5-di-thiophen-2-yl-pyrrol-1-yl)-ethyl ester (SNS-OTs) and this compound is substituted using NaN_3 to give 1-(2-azido-ethyl)-2,5-di-thiophen-2-yl-1H-pyrrole (SNS-N_3). Structural investigation of monomer was performed via ^{1}H, ^{13}C NMR and FTIR. The monomer is colorless oil at room temperature.

3.2. Electrochemical synthesis and optoelectronic properties of P(SNS-N_3)

Cyclic Voltammetry (CV) was employed to demonstrate redox behavior of the monomer in $LiClO_4$/ACN system with ITO