

A New Narrow Band Gap Electroactive Polymer: Poly[2,5-bis{2-(3,4-ethylenedioxy)thienyl}silole]

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In recent years, there has been tremendous research interest in the design and synthesis of narrow band gap (E_g) electroactive polymers because of their unique optoelectronic properties, which includes high visible light transparency as doped conductors, their ability to be p - and n -type doped, and the possibility of metallic conduction of zero E_g polymers.¹ Our group has developed an interest in these polymers as they can exhibit multicolor electrochromism with three distinct color states in the neutral, reduced, and oxidized forms.² A number of structural parameters control the optical properties of narrow E_g polymers, which include the manipulation of bond length alteration, inter-ring torsion angle, resonance energy, interchain effects, and substituent effects.¹ Among these methods, electron-releasing or -withdrawing substituents have been used as extremely versatile means for tuning the E_g by modification of the HOMO and LUMO levels of conjugated polymers. The use of alternating donor–acceptor (D–A) units along the main chain falls into this category.³

Here, we report on a new narrow gap, redox-active D–A conjugated polymer composed of the highly electron-rich dimer unit of 3,4-ethylenedioxythiophene (EDOT) alternated with a silole repeat unit, which presents a low LUMO level. EDOT is electron-rich because of the presence of electron-donating alkoxy substituents on thiophene, which effectively elevates the HOMO energy level of the backbone. Its polymer (PEDOT) stands out for its high degree of visible light transmissivity ($E_g =$

1.6 eV) and high environmental stability in the conducting state, along with a propensity toward multiple redox switches due to its ease of oxidation.⁴ Silole derivatives have been utilized as a building blocks for conjugated polymers because of their unique electronic structure.⁵ They have a low-lying LUMO level, which is ascribed to the $\sigma^*-\pi^*$ interaction in the ring, that is, the orbital interaction between the σ^* orbital of the two exocyclic σ bonds on the silicon with the π^* orbital of the butadiene moiety.⁶ In addition, the cisoid-1,3-butadiene fragment of the silole may impart gap-narrowing characteristics to copolymers with heterocyclic repeat units. This has been illustrated for thiophene–silole copolymers of varying composition where the band gap could be controlled by the ratio of the components.^{5h}

Specifically, we have synthesized 1,1-dihexyl-3,4-diphenyl-2,5-bis{2-(3,4-ethylenedioxy)thienyl}silole, (BEDOT-silole) as shown in Scheme 1 and found it to effectively polymerize electrochemically. By using EDOT as the terminal polymerizable moiety,^{2,4,7} along with optimal electrolyte conditions, facile oxidative polymerization occurs at an especially low potential to yield a stable p -type dopable polymer exhibiting a narrow E_g at 1.3–1.4 eV.

BEDOT-silole was synthesized by a Pd-catalyzed cross-coupling reaction of the 1,1-dihexyl-3,4-diphenyl-2,5-dibromosilole and 2-stannyl-EDOT in THF as shown in Scheme 1. The dibromosilole and stannylated EDOT were synthesized according to published methods.^{5c,3g} The monomer was purified by silica gel column chromatography to afford the product in a 65% yield. The structure of the monomer was characterized using ¹H NMR, ¹³C NMR, and elemental analysis. Furthermore, the electronic structure of BEDOT-silole was characterized by UV–vis spectroscopy. The $\pi-\pi^*$ transition was observed at $\lambda_{\max} = 437$ nm, which is red-shifted relative to the value of 409 nm observed for bis(2-thienyl)siloles.^{5e}

Poly(BEDOT-silole) was synthesized by utilizing repeated potential scan electrochemical polymerization at a scan rate of 100 mV/s in 0.01 M monomer and 0.1 M LiClO₄ in a mixed solvent system of acetonitrile (ACN) and water (90/10, v/v) using a bare glassy carbon working electrode and a Fc/Fc⁺ reference electrode. The addition of a small amount of water into the ACN effectively improved the kinetics of the polymerization by decreasing the solubility of the polymer to afford good film formation on the electrode. Use of a 100% organic

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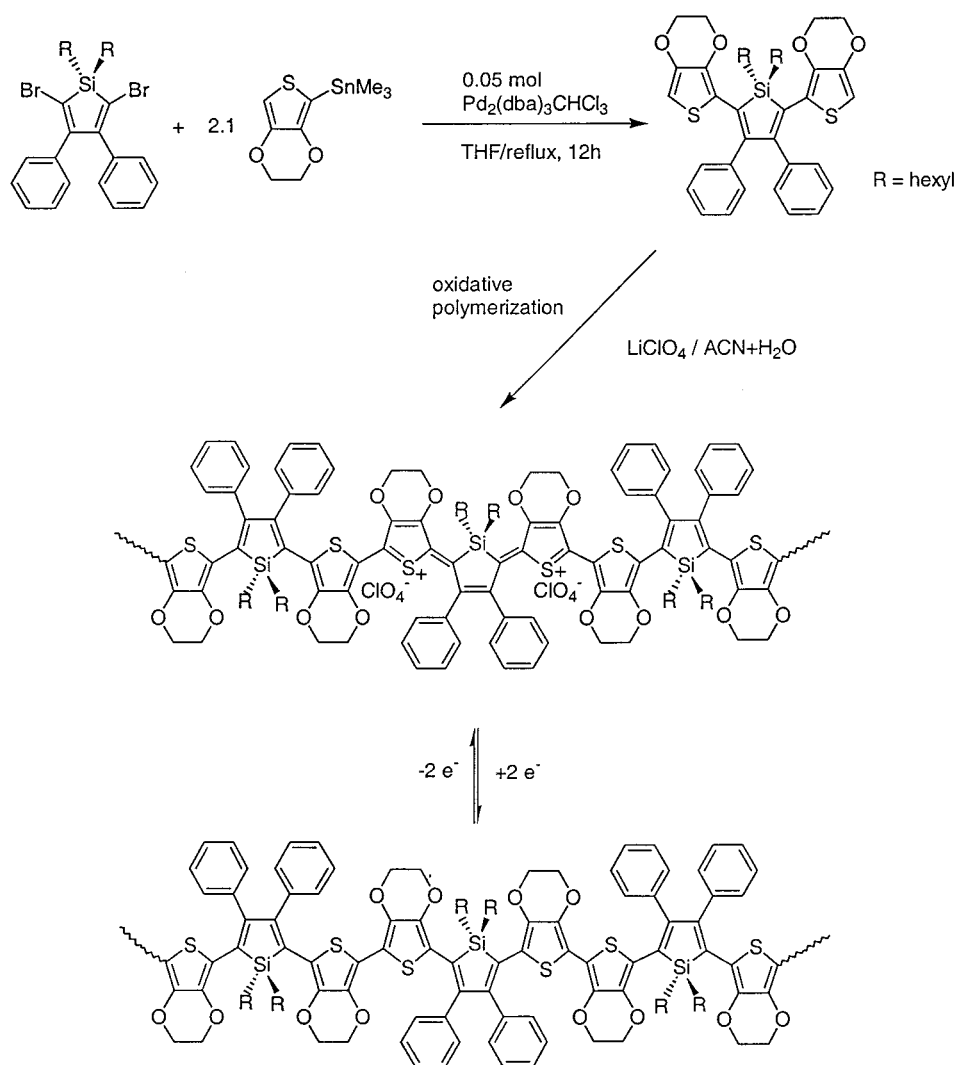
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Scheme 1



electrolyte led to soluble oligomers during electropolymerization as the hexyl groups of the silole enhance organic solubility. Figure 1a shows electrodeposition of the highly electroactive poly(BEDOT-silole) during the repeated potential scan experiment. A peak for monomer oxidation ($E_{p,m}$) is observed at 0.29 V vs Fc/Fc⁺ and a rapid and regular growth of the polymer on the electrode was observed. The monomer's $E_{p,m}$ is quite low and comparable to that of BEDOT-thiophene (0.33 V), BEDOT-furan (0.30 V), and ter-EDOT (0.20 V).^{7a} Initially, a simple polymer redox process is observed to evolve with an $E_{1/2}$ at -0.11 V. After a few successive scans, a second, lower potential, polymer oxidation peak is observed at -0.15 V and a broad reduction peak is observed ranging from -0.15 to -0.3 V.

Figure 1b shows a series of cyclic voltammograms of poly(BEDOT-silole) in 0.1 M LiClO₄/propylene carbonate as a function of scan rate between 40 and 100 mV/s. The oxidative peak of the polymer is observed at -0.01 V and two reduction peaks are observed at -0.19 and -0.35 V with a half wave potential ($E_{1/2,p}$) at -0.13 V for the main redox process. The evolution of the anodic and cathodic peak current densities is linear as a function of the scan rate, which indicates that the redox centers are surface-confined. While the monomer's $E_{p,m}$ is comparable to other BEDOT-heterocycles as men-

tioned above, the resultant poly(BEDOT-silole) exhibits a higher $E_{1/2,p}$ by 440, 30, and 210 mV when compared to poly(BEDOT-thiophene), poly(BEDOT-furan), and poly(ter-EDOT), respectively.^{7a} This confirms that the silole unit has an effect on the polymer's redox properties.

Poly(BEDOT-silole) films were electrochemically deposited on ITO-coated glass plates from a water/ACN mixture with 0.01 M monomer and 0.1 M LiClO₄ at a constant potential of 0.3 V vs Fc/Fc⁺ for spectroelectrochemical studies (Figure 2). The spectra were initially obtained in the fully reduced state to determine the band gap of the polymer, which is defined as the onset of the $\pi - \pi^*$ transition. The band gap of neutral polymer is estimated to be between 1.3 and 1.4 eV. The potential applied to the polymer-coated electrode was then sequentially increased to higher potentials to oxidize the polymer while monitoring the creation of the charge carriers. A broad absorption beginning at 830 nm and extending into the mid-IR region was observed in the doped form. The electrochromic properties of this polymer was also studied by in situ colorimetry.⁸ Poly-(BEDOT-silole) changes from blue in its reduced form

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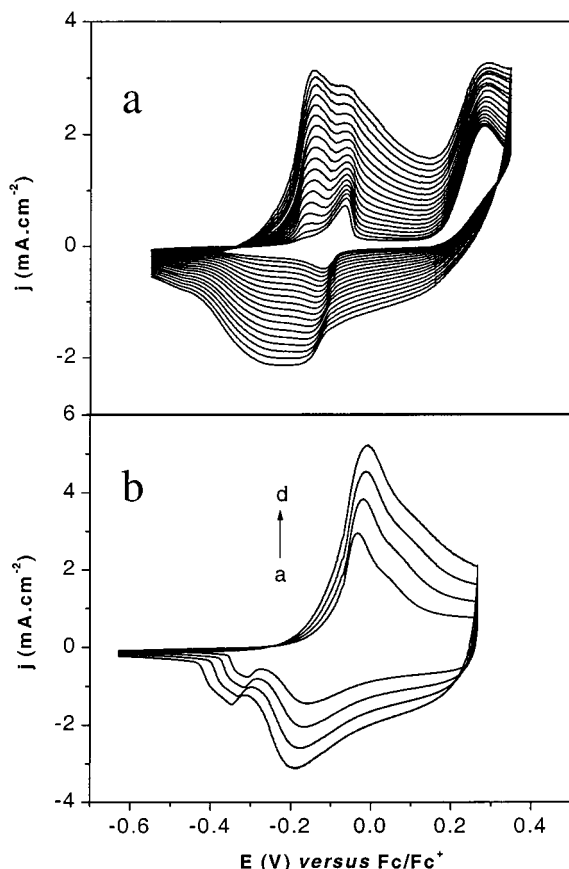


Figure 1. (a) Repeated scan electrochemical polymerization ($\nu = 100 \text{ mV s}^{-1}$) of BEDOT-silole from a 0.01 M monomer and 0.1 M $\text{LiClO}_4/\text{ACN} + \text{water}$ (90/10, v/v) solution on a glassy carbon electrode; (b) cyclic voltammetry of poly(BEDOT-silole) on a glassy carbon electrode in 0.1 M $\text{LiClO}_4/\text{propylene carbonate}$; scan rate: a, 40; b, 60; c, 80; d, 100 mV s^{-1} .

to transmissive yellow-green upon oxidation. The luminance, which represents the relative transmissivity of a color, is very informative because it provides information about the human eye perceived transparency of a sample over the entire visible range of light with only one value. The relative luminance of poly(BEDOT-silole) increased upon oxidation from 54% to 80%. This is

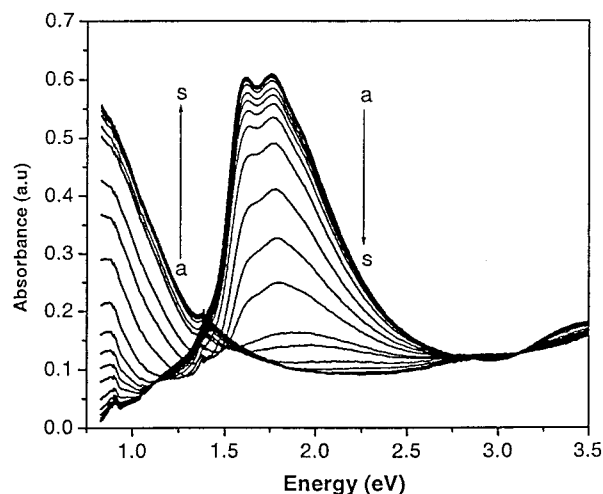


Figure 2. Spectroelectrochemical analysis of poly(BEDOT-silole) in 0.1 M LiClO_4/PC at applied potentials of (a) \rightarrow (s): $-0.43 \text{ V} \rightarrow 0.17 \text{ V}$ vs Fc/Fc^+ in 20 mV potentials steps.

expected as the absorbance of the $\pi-\pi^*$ transition located in the visible spectrum is depleted while oscillator strength is shifted to the NIR.

In conclusion, a new silole-containing monomer (BEDOT-silole) was synthesized by a Pd-catalyzed cross-coupling reaction. This monomer can be easily electropolymerized to yield an electroactive polymer with a low half-wave oxidation potential. Spectroelectrochemistry has shown that the polymer switches between blue and transmissive yellow-green upon doping. The low-lying LUMO level of the silole combined with the electron-rich character of the 3,4-ethylenedioxythiophene units confers upon this new polymer a narrow band gap of 1.3–1.4 eV.

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