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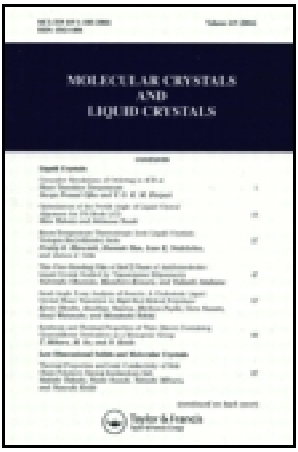

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A New Narrow Band Gap Electroactive Silole Containing Polymer

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A New Narrow Band Gap Electroactive Silole Containing Polymer

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A new silole containing monomer, 1,1-dihexyl-3,4-diphenyl-2,5-bis{2-(3,4-ethylenedioxy)thienyl}silole, was synthesized by Pd-catalyzed Stille coupling reaction of the necessary 2,5-dibromosilole and 2-stannylethylenedioxythiophene derivatives. This monomer can be easily electropolymerized ($E_{ox,m}$ = +0.29 V vs. Fc/Fc^+) and yields an electroactive polymer with a low half-wave oxidation potential ($E_{1/2}$ = -0.38 V vs. Fc/Fc^+). Spectroelectrochemistry has shown that the polymer switches between sky blue and yellow green upon doping. The low-lying LUMO levels of the siloles combined with the electron-rich character of the 3,4-ethylenedioxythiophene units confer upon this new polymer a narrow band gap of 1.4 eV (onset of the π-π^* transition).

Keywords: silole; narrow band gap; electroactive polymer

INTRODUCTION

In recent years, there has been tremendous research interest in the design and synthesis of narrow band gap electroactive polymers due to their unique properties, such as high visible transparency as doped conductors, their ability

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to be *p*- and *n*-type doped, the possibility of intrinsically conducting polymer of zero band gap.[1] The band gap of conjugated polymer originated from the interaction of the π-orbitals of the repeating units. A number of methods have been developed to synthesize low band gap polymers, which include the manipulation of bond length alteration, inter-ring torsion angle, resonance energy, interchain effect, and substituent effects.[1] One of these employs alternating electron donor and acceptor substituents which will respectively increase the HOMO level or lower the LUMO.[2] 3,4-Ethylenedioxythiophene (EDOT) is an electron rich monomer due to the presence of electron donating alkoxy substituents to result in high HOMO energy level,[3] and silole unit has an ability to provides a system with a lower LUMO level due to the σ^*-π^* interaction.[4] Here, we describe the synthesis and electropolymerization of a new silole containing monomer, 1,1-dihexyl-3,4-diphenyl-2,5-bis{2-(3,4-ethylene dioxy)thienyl}silole, (BEDOT-silole), and the electrochemical properties of it's polymer.

EXPERIMENTAL

BEDOT-silole was synthesized by Pd-catalyzed cross coupling reaction of the necessary dibromosilole with 2-stannylEDOT reagents.[5] The dibromosilole, (1,1-dihexyl-3,4- diphenyl-2,5-dibromosilole) and 2-stanyl-EDOT were synthesized according to published methods.[6,7] Electropolymerization was carried out with an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat employing platinum and glassy carbon button working electrodes, a platinum wire counter electrode, and a silver wire pseudo-reference. The electrolyte used was 0.1 M $LiClO_4$ in acetonitrile (ACN) or ACN/water mixture for electropolymerization and 0.1M $LiClO_4$ in propylene carbonate for electrochemical characterization. Spectroelectrochemical results were recorded on a Varian Cary 5E UV-Vis-NIR spectrophotometer at a scan rate of 600 nm/min.

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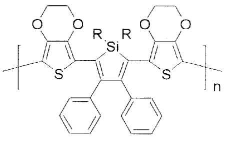
RESULTS AND DISCUSSIONS

BEDOT-silole was synthesized by a Pd-catalyzed cross coupling reaction in THF and purified by silica gel column chromatography to afford the product in a 65% yield. The structure of the monomer was characterized using ^{1}H NMR, elemental analysis, and UV-Vis spectroscopy. The π-π^* 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.[8] The monomer was polymerized by utilizing repeated potential scan electrochemical polymerization at a scan rate of 100 mV/s in0.01 M monomer and 0.1 M LiClO4 in a ACN or ACN/water (90/10, v/v) mixed solvent system to yield poly(BEDOT-silole) as shown below.



R: hexyl

It was observed that electrochemical polymerization in ACN solvent led to soluble oligomers, however the addition of small amount of water effectively afford good film formation by decreasing the solubility of the polymer. Figure 1 shows electrochemical deposition of the poly(BEDOT-silole) in ACN/water mixed solvent during the repeated potential scan experiment. A peak for oxidation ($E_{p,m}$) of silole containing monomer is observed at 0.29 V vs. Fc/Fc$^+$, which is quite low and comparable to that of BEDOT analogues of thiophene (0.33 V), furan (0.30 V), and *ter*-EDOT (0.20 V).[9] Initially, a simple polymer redox process is observed to evolve with an $E_{1/2}$ at -0.11 V and a second, lower potential, polymer oxidation peak is observed at -0.15 V after a few successive scans. A broad reduction peak is observed ranging from -0.15 to -0.3 V. Poly(BEDOT-silole) films were electrochemically deposited on ITO-coated glass plates for spectroelectrochemical studies. The band gap of neutral polymer is estimated to be between 1.3 to 1.4 eV. Two

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absorption peaks were observed at 706 and 767 nm in the neutral form and broad absorption from 830 nm extending into IR region was observed in the doped form. The electrochromic property of this polymer was also studied by *in-situ* colorimetry. Poly(BEDOT-silole) changes from blue in its reduced form to transmissive yellow-green upon oxidation.

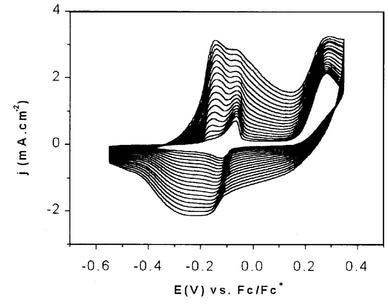

FIGURE 2. Repeated scan electrochemical polymerization (ν=100 mVs^{-1})

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