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Synthesis of 2,5-Bis[(3,4-ethylenedioxy)thien-2-yl]-3-Substituted Thiophenes

Michael F. Pepitone, Kalya Eaiprasertsak, Stephen S. Hardaker,† and Richard V. Gregory*

School of Materials Science and Engineering, Clemson University,
Clemson, South Carolina 29634-0971

richar6@clemson.edu

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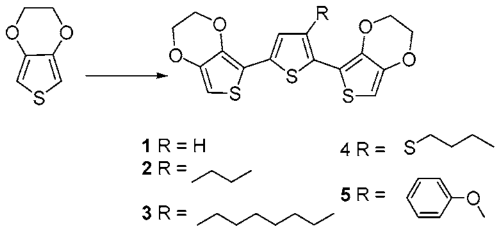
ABSTRACT



Synthesis of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-substituted thiophene monomers afforded compounds with blue emission characteristics and having a quantum yield of 3–5%. Cyclic voltammetry was employed to investigate the electrochemical behavior of the four monomers reported here. Polymer films were deposited by repeated potential cycling. These materials are considered for use in tailoring properties in optoelectronic device applications.

The past decade has seen a growth in the application of conductive polymers for potential use in electrochromic devices, sensors, and light-emitting diodes (LEDs), etc.[1] Poly(*p*-phenylenevinylene) (PPV) and its derivatives, poly(*p*-phenylene)s (PPP), polythiophenes, and polyfluorenes, and their copolymers have been used as the emissive layer in polymeric LEDs (PLEDs).[2] Thiophene-based linear π-conjugated oligomers have been investigated for their potential applications as active materials in organic electronic and photonic devices.[3] Extensive research has been done on poly(3,4-ethylenedioxythiophene) (PEDOT);[4] however, in contrast to oligothiophenes, 3,4-ethylenedioxythiophene (EDOT) oligomers have received less attention. Recently, EDOT has been used as a building block in several conjugated systems that incorporate unique properties such as electrochromic behavior[5] and low-band-gap polymers.[6] Functionalization of 3,4-ethylenedioxythiophene has led to the formation of a variety of monomers, oligomers, and polymers with unique electronic and optical properties,[4] as well as the formation of its sulfur[7] and selenophene[8] derivatives.

With respect to other oligothiophenes, EDOT derivatives have seen limited use as the emissive component in PLEDs.[9] Herein we report the synthesis and photoluminescent proper-

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† Current address: Battelle Memorial Institute, 505 King Avenue, 10-210J, Columbus, OH 43201.

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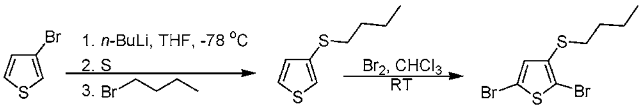
ties of EDOT-thiophene based materials, containing alkyl, alkylsulfanyl, and 4′-methoxyphenyl groups substituted on the 3-position of the thiophene ring, as potential materials for optoelectronic devices, including the emissive layer of LEDs and microring organic lasers.

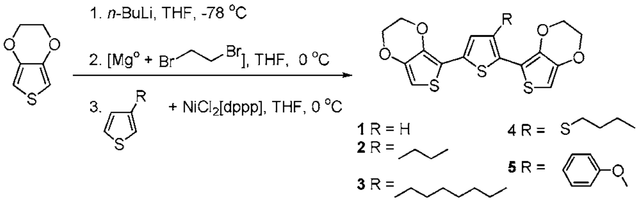
The synthesis of 3-bromothiophene from literature procedures[10] allowed functionalization into the corresponding 3-alkyl,[11] alkylsulfanyl, and 4′-alkoxyphenyl[12] derivatives. Scheme 1 depicts the synthesis of 3-(butylsulfanyl)thiophene by generation of the 3-lithio adduct and then reacting with sulfur powder to form the 3-sulfate anion, which was then reacted with bromobutane to afford the product in 51% yield. Although this yield is slightly lower than that of the method employed by Rieke et al.[13] using a mixed solvent system of hexane and THF to provide room-temperature stable 3-lithiothiophenes, which can then react with alkyl disulfides for the formation of the 3-(alkylsulfanyl)thiophenes, it provided a convenient method for synthesizing different alkylsulfanyl thiophenes by employing various alkyl bromides.

Scheme 1



Dibromination[14−16] of the 3-substituted thiophenes afforded the corresponding 2,5-dibromo-3-substituted thiophenes, which were then used in a nickel(II) chloride-catalyzed Grignard coupling starting with lithiation of 3,4-ethylenedioxythiophene and conversion into the 2-magnesium bromide derivative via an entrainment procedure, as depicted in Scheme 2.

Scheme 2



2,5-Bis[(3,4-ethylenedioxy)thien-2-yl]-thiophene **1** (BEDOT-THIO) was synthesized via a modification of literature procedures and used as a reference material.[2a] Synthesis of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-butylthiophene **2** (BEDOT-3BT) and 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-octyllthiophene **3** (BEDOT-3OT) was reported previously from our group and is included in this discussion.[17] Synthesis of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-(butylsulfanyl)-thiophene **4** (BEDOT-3TBS) was obtained in 40% yield.[18] 2,5-Bis[(3,4-ethylenedioxy)thien-2-yl]-3-(4′-methoxyphenyl)-thiophene **5** (BEDOT-3MPT) was obtained in 58% yield.[19] Formation of a 3-alkoxythiophene derivative was attempted by the synthesis of 3-methoxy thiophene[20] and 2,5-dibromo-3-methoxythiopehene[21] from literature procedures using the same organonickel chemistry as depicted in Scheme 2; however, product isolation during purification was not possible due to decomposition during column chromatography. Formation of the 3-alkoxy derivatives is still being investigated in our labs.

Figure 1 shows the absorbance and emission spectra of the 3-substituted thiophene derivatives. The different substituents show a slight effect on the absorption wavelength, ranging from 361 to 382 nm. Corrected emission spectra were

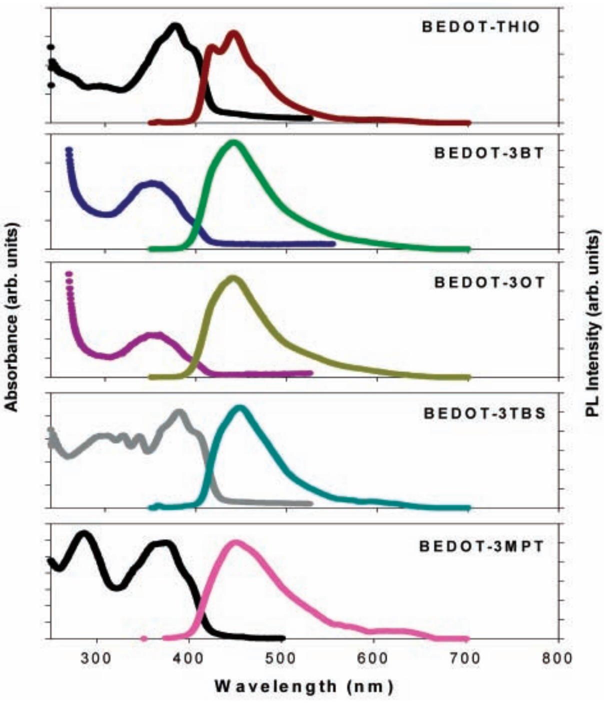


Figure 1. Absorbance and corrected emission of spectra of **1**−**5** in $CHCl_3$.

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obtained in dilute chloroform solution and quantum yields were calculated using quinine sulfate as a standard. All materials have blue emission with λ_{max} ranging from 441 to 450 nm, with quantum yields ranging from 0.020 to 0.053. Under the same conditions, the unsubstituted thiophene derivative had the highest quantum yield. These results are summarized in Table 1.

Table 1. Optical and Electrochemical Data for Monomers (Poly)

monomer	Abs $\lambda_{max}{}^{a}$	PL^{a} λ_{max}	$\Phi_f{}^{b}$	$E_{pa,m}{}^{c}$	$E_{pa,p}$	$E_{pc,p}$
1	378	442	0.053	466	−265	
2	361 (560)	441 (595)	0.034	446	−259	−320
3	361 (548)	441 (616)	0.032	426	−200	−394
4	382 (558)	441 (596)	0.032	403	−235	−415
5	371 (554)	450 (592)	0.020	451	−269	−299

[a] In $CHCl_3$. [b] Quinine sulfate as a standard. [c] Versus Ag/Ag$^+$ in 0.1 M $TABPF_6$/MeCN, GCE working electrode, 100 mV/s.

The electrochemical behaviors of these systems were studied by cyclic voltammetry (CV).[22] Figure 2 shows the first voltammetric anodic scanning applied to a 1 mM solution of **2**, **4**, and **5** in 0.10 M Bu_4NPF_6/MeCN. These compounds show quasi-reversible oxidation peaks ranging from 446 to 403 mV vs Ag/Ag$^+$. As expected, increasing the electron-donating ability of the substituent resulted in a lower oxidation potential than that of **1** under the same conditions.

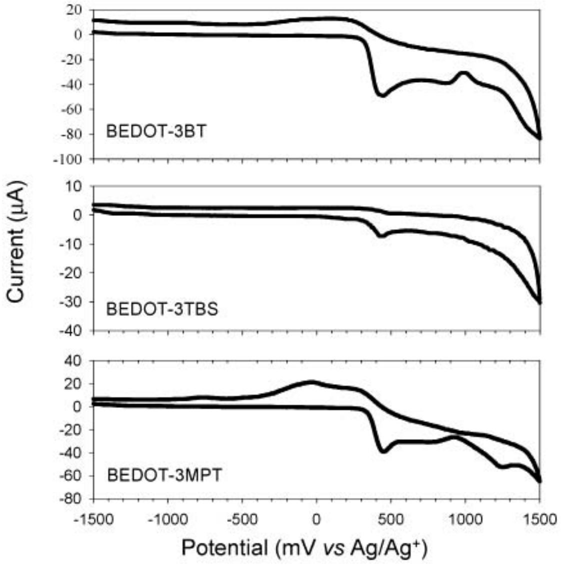

Figure 2. Cyclic voltammogram of monomers **2**, **4**, and **5**.[22]

Application of recurrent potential scans of each monomer solution with a positive limit set at the first of the oxidation wave of the monomer leads to the development of a new redox process at a lower potential. The current of this new redox process continues to increase in intensity upon additional cycling consistent with the deposition of an electroactive polymer onto the surface of the working electrode (Figure 3). Further evidence for the formation of the polymer is the observation of a dark blue film on the surface of the working electrode.

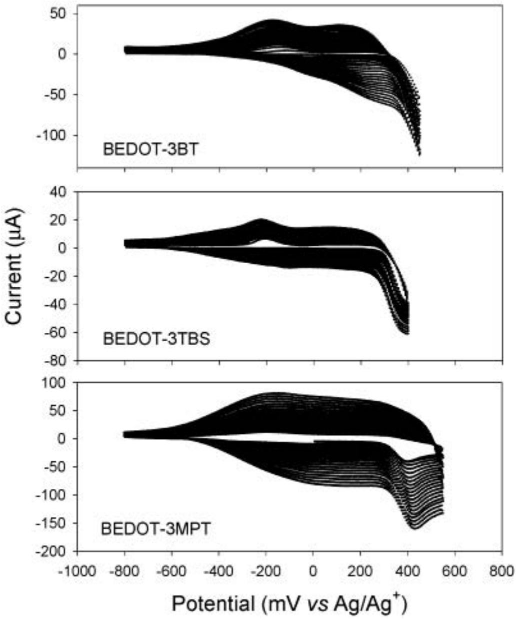

Figure 3. Cyclic voltammetric scanning electropolymerization of **2**, **4**, and **5** in 0.1 M Bu_4NPF_6/MeCN cycled at 100 mV/s.

The electrochemically polymerized films of each of the monomers, poly(**2**), poly(**4**), and poly(**5**), were thoroughly washed with MeCN to remove excess monomer, and subsequent cyclic voltammetry was performed in monomer-free electrolyte. Figure 4 shows the scan rate dependence of poly(**5**), exhibiting an anodic wave peak ranging from −235 to −265 mV vs Ag/Ag$^+$, which is lower than the oxidation potential of PEDOT.[23] For each of the polymers investigated

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(18) **Compound 4.** ^{1}H NMR 300 MHz ($CDCl_3$) δ: 7.16 (s, 1H), 6.35 (s, 1H), 6.25 (s, 1H), 4.32 (m, 4H), 4.25 (m, 4H), 2.86 (t, 2H), 1.58, (m, 2H), 1.39 (m, 2H), 0.89 (t, 3H). ^{13}C NMR 75 MHZ ($CDCl_3$) δ: 141.75, 141.02, 138.57, 137.68, 136.88, 132.38, 131.91, 127.25, 111.46, 111.07, 99.42, 97.04, 64.99, 64.88, 64.43, 64.32, 36.25, 31.47, 21.78, 13.37.

(19) **Compound 5.** ^{1}H NMR 300 MHz ($CDCl_3$) δ: 7.31 (d, 2H), 7.17 (s, 1H), 6.87 (d, 2H), 6.21 (s, 1H), 6.19 (s, 1H), 4.29 (m, 2H), 4.21 (m, 2H), 4.13 (m, 4H), 3.75 (s, 3H). ^{13}C NMR 75 MHZ ($CDCl_3$) δ: 158.99, 141.78, 141.16, 139.05, 138.30, 137.66, 133.42, 130.23, 128.93, 126.16, 125.39, 113.58, 111.63, 110.92, 98.96, 96.97, 64.91, 64.70, 64.50, 64.37, 55.17.

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(22) Cyclic voltammetry was carried out with a three-electrode cell consisting of a glassy carbon working electrode, platinum wire auxiliary electrode, and a 0.01 M silver nitrate reference electrode (Ag/Ag$^+$). The electrolytic medium consisted of 0.10 M tetrabutylammonium hexafluorophosphate in acetonitrile (distilled from CaH_2). Scan rate = 100 mV/s; monomer concentration was 1 mM.

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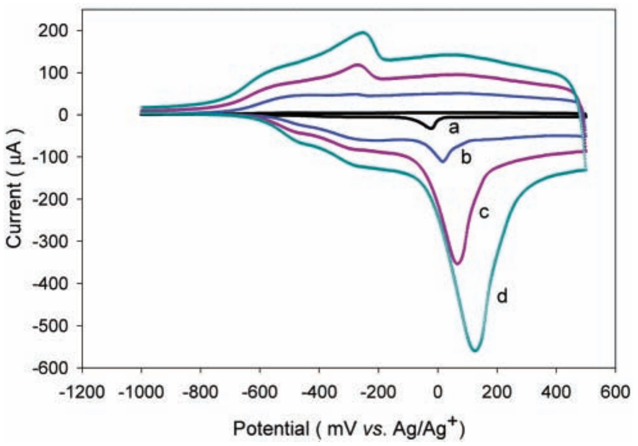

Figure 4. Scan-rate dependence of the cyclic voltammogram of poly(**5**) thin film in 0.1 M Bu_4NPF_6/MeCN. Poly(**5**) scanned at (a) 10, (b) 100, (c) 200, and (d) 300 mV/s.

here, the peak current varies linearly with the scan rate as expected for electroactive species that are surface bound. These electrochemical results are summarized in Table 1.

The oxidative polymerization of **5** was achieved by using 3 equiv of $FeCl_3$ in chloroform, followed by the reduction of the oxidized polymer using NH_4OH.[24] The resulting dark purple poly(**5**) was sparingly soluble in common organic solvents. Poly(**5**) exhibited an onset of absorption at 668 nm with λ_{max} of 530 nm in chloroform solution.

Optical measurements of poly(**2**−**5**) were obtained from electrochemically polymerized films of **2**−**5**. Those films were deposited on ITO-coated glass slides using similar conditions as on GCE at a scan rate of 50 mV/s. Reduction of the films by immersion in hydrazine hydrate for at least 24 h followed by washing with deionized H_2O, MeOH, and drying under a stream of N_2. UV−vis−NIR spectra of the oxidized films thus prepared show the characteristic charge carrier tail. The reduced poly(**2**−**5**) show the disappearance of the charge carrier tail and have Abs λ_{max} ranging from 548 to 560 nm. PL spectra were obtained at a 30° angle of incidence and a 450 nm excitation, and all polymers show similar PL spectra with λ_{max} values from 592 to 616 nm. Results are summarized in Table 1.

In conclusion, a series of bis-EDOT-3-substituted thiophenes were prepared by a Kumada-type coupling in moderate yields. The synthetic utility of 3-bromothiophene allowed the formation of the 3-substituted thiophene derivatives via organonickel and organolithium chemistry. The resulting materials were then brominated with 2 equiv of bromine and used in subsequent coupling reactions. Preliminary results show that polymerization of bis-EDOT-3-substituted thiophene monomers can be achieved by electrochemical and chemical methods. Current work involves the formation of analogous 3-substituted thiophene derivatives as well as their optical, electrical, and electrochemical characterization.

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Supporting Information Available: Experimental procedure for coupling of compounds **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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