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Synthesis of 3,4-Ethylenedioxyselenophene (EDOS): A Novel Building Block for Electron-Rich π-Conjugated Polymers

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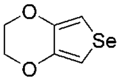
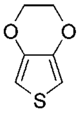
ABSTRACT



A multistep synthesis of the electron-rich 3,4-ethylenedioxyselenophene (EDOS) monomer is described. The electrochemical properties as well as the electropolymerization of EDOS are presented.

Conjugated macromolecules have attracted considerable interest in the past 2 decades for their unique electrical and optical properties.[1] In this context, the design, synthesis, and physical properties of π-conjugated polymers derived from 3,4-ethylenedioxythiophene (EDOT, **1**) and its derivatives is a field of enormous growth.[2] The research efforts of the past decade have brought poly-EDOT to the forefront of the field of conducting polymers.[2,3] Polymers derived from EDOT and its derivatives provide highly conducting and especially stable doped states, a range of optical properties with electronic band gaps varying across the entire visible spectrum, and enhanced redox properties, making them useful for numerous electrochemical devices.[2,4] The high stability of the p-doped poly-EDOT has been attributed to favorable ring geometry and the electron-donating effect of the oxygen atoms in the 3,4-positions, which stabilize the positive charge in the polymer backbone. The electrochemical polymerization of EDOT takes place at a relatively low oxidation potential, and the corresponding polymer (**2**) exhibits an optical band gap of 1.6 eV.[3a] The final aim of further reducing the oxidation potential of the monomers and consequently the band gap of the corresponding polymers is a challenging research field. A general trend that proved to be promising involves the synthesis of EDOT derivatives substituted with variety of π-conjugated moieties in the 2- and/or 5-position; recently, electronically disconnected tetrathiafulvalene (TTF) derivatives have been grafted to long chains on the ethylenedioxy bridge.[5]



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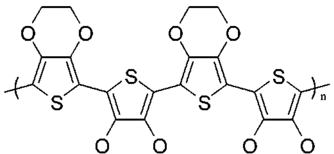

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The properties of polymers derived from EDOT and its derivatives depends largely on the degree of backbone conjugation and conformational stability, which in turn may be influenced by the heteroatom properties (electronegativity, polarizability, ring aromaticity). It is notable that selenophenes received only scant attention in the fabrication of

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(1) (a) Roncali, J. *Chem Rev*. **1997**, *97*, 173. (b) Kraft, A.; Grimsdal, C. A.; Holmes, B. A. *Angew. Chem., Int. Ed*. **1998**, *37*, 402. (c) Roncali, J. *J. Mater. Chem*. **1999**, 9, 1875. (d) McCullough, R. D. *Adv. Mater*. **1998**, *10*, 93.

(2) For recent review on poly(3,4-ethylenedioxythiophene) see: Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater*. **2000**, *12*, 481 and references therein.

(3) (a) Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, F. *J. Electroanal. Chem*. **1994**, *369*, 87. (b) Jonas, F.; Heywang, G. *Electrochim. Acta* **1994**, *39*, 1345. (c) Heywang, G.; Jonas, F. *Adv. Mater*. **1992**, *4*, 116. (d) Yamato, H.; Ohawa, M.; Wernet, W. *J. Electroanal. Chem*. **1995**, *397*, 163.

(4) Reynold, J. R.; Kumar, A.; Reddinger, J. L.; Sankaran, B.; Sapp, S. A.; Sotzing, G. A. *Synth. Met*. **1997**, *85*, 1295.

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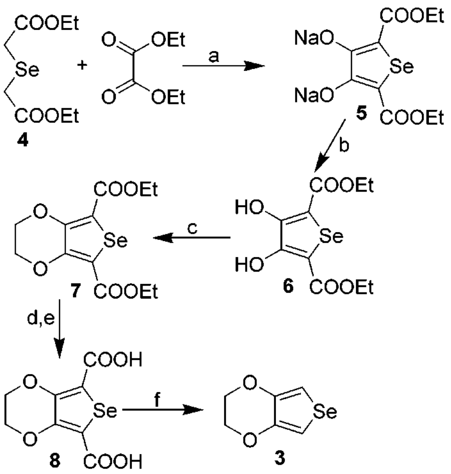
conjugated polymers,[6] and the potential of selenophene as a constituent unit of conducting polyconjugated systems as well as the role of the selenium atom in the structure−properties relationship still remains unclear. Moreover, despite the remarkable growth in orgonoselenium chemistry, the number of chemical approaches and types of selenophenes are still rather limited. The replacement of the sulfur atom in EDOT by the more polarizable selenium atom presents a novel approach for lowering of the oxidation potential of the monomer and consequently for fine-tuning of the electrochemical and optical properties of the corresponding polymer. Here we report the synthesis of the selenium analogue of EDOT, namely, 3,4-ethylenedioxyselenophene (EDOS, **3**, Scheme 1).

Scheme 1[a]



[a] (a) C_2H_5ONa/C_2H_5OH, room temperature, 15 h. (b) HCl 3 N. (c) $BrCH_2CH_2Br$, K_2CO_3, DMF, 110 °C. (d) KOH/C_2H_5OH, reflux, 5 h. (e) HCl 3 N. (f) melt.

The five-step synthetic methodology of EDOT is well documented.[7] The synthesis of diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate using the classical Hinsberg synthesis[8] is a key step. Surprisingly, only a few examples of the application of the Hinsberg method for the synthesis of selenophenes have been reported.[9] The multistep synthesis of EDOS is outlined in Scheme 1. Diethyl selenodiglycolate (**4**) was synthesized from sodium selenide and ethyl chloroacetate according to a general procedure.[10] By applying the Hinsberg original synthesis, we found that condensation of **4** with diethyl oxalate in the presence of excess of sodium ethoxide at reflux leads to the formation of the disodium salt of diethyl-3,4-dihydroxyselenophene-2,5-dicarboxylate (**5**) in low yield. Noteworthy is the formation of selenium observed as a side reaction, which may be attributed to the cleavage of the carbon−selenium bond. Better results were obtained when the reaction was carried out at room temperature for 15 h. Acidification of **5** gave diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**6**) in 48% overall yield.

The etherification of **6** with 1,2-dibromoethane in DMF in the presence of dry potassium carbonate gave 2,5-dicarboethoxy-3,4-ethylenedioxyselenophene **7** in good yield. Hydrolysis of the ester groups in **7** was achieved by treatment with potassium hydroxide in ethanol and subsequent acidification. The yield of the diacid **8** was high as expected. The decarboxylation of the diacid **8** was found to occur in the melt, giving rise to the EDOS (**3**)[11] in 56−58% yield as a colorless liquid that slowly turns brown upon exposure to air and light.

The electrochemical behavior of EDOS was studied by cyclic voltammetry (CV).[12] The first voltammetric anodic scanning of EDOS in acetonitrile exhibited one irreversible oxidation peak at 1.18 V (Figure 1), a value which is lower than that observed for EDOT (1.44 V) under the same experimental conditions. This indicates the moderate enhancement of the EDOS electron-donating ability. The cation radical intermediate formed upon electrochemical oxidation

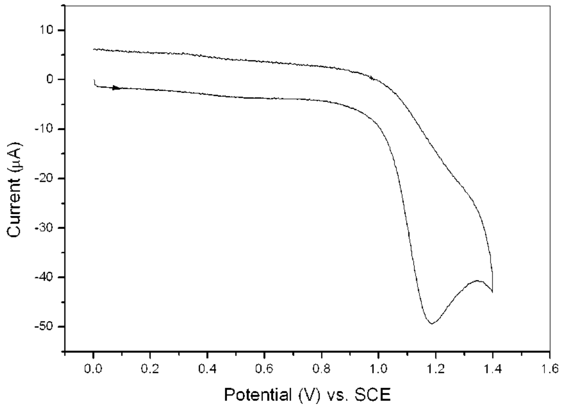


Figure 1. Cyclic voltammogram (first cycle) of EDOS (**3**).[12]

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(5) (a) Irvin, J. A.; Schwendman, I.; Lee, Y.; Abboud, A. A.; Reynolds, J. R. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 2164. (b) Wang, F.; Wilson, M. S.; Rauh, R. D.; Scottland, P.; Thompson, B. C.; Reynolds, J. R. *Macromolecules* **2000**, *33*, 2083. (c) Sotzing, G. A.; Thomas, C. A.; Reynolds, J. R.; Steel, P. J. *Macromolecules* **1998**, *31*, 3750. (d) Sotzing, G. A.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun*. **1995**, 703. (e) Fu, Y.; Cheng, H.; Elsenbaumer, R. L. *Chem. Mater*. **1997**, *9*, 1720. (f) Besbes, M.; Trippe, G.; Levillain, E.; Mazari, M.; Le Derf, F.; Perepichka, F. I.; Derdour, I.; Gorgues, A.; Roncali, J. *Adv. Mater*. **2001**, *13*, 1249.

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(7) (a) Gogte, V. N.; Shah, L. G.; Tilak, B. D.; Gadekar, K. N.; Sahasrabuldhe, M. B. *Tetrahedron* **1967**, *23*, 2437. (b) Coffey, M.; McKellar, B. R.; Reinhardt, B. A.; Nijakowski, T.; Feld, W. A. *Synth. Commun*. **1996**, *26*, 2205.

(8) Hinsberg, O. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 901.

(9) Nakayama, J.; Shibuyra, M.; Hoshino, M. *Heterocycles* **1987**, *26*, 909.

(10) Rheinboldt, H. *Methoden Org. Chem. (Houben-Weyl), 4th Ed. 9*, 976.

(11) All new compounds were characterized by spectroscopic means and elemental analysis. Detailed experimental procedures will be described elsewhere. Compound **3**: ^1H NMR (acetone-d_6) δ 4.19 (s, 4H), 6.82 (s, 2H); ^{13}C NMR (acetone-d_6) δ 65.20, 102.32, 143.93. Anal. Calcd For $C_6H_6O_2Se$: C, 38.11; H, 3.20. Found: C, 37.91; H, 3.14.

can further couple to form poly-EDOS. Thus, repetitive cyclic voltammetry leads to EDOS electropolymerization as evident by the formation of a deep blue oxidized polymer deposit at the surface of the platinum working electrode.

Cyclic voltammetry of the polymer electrode was performed in contact with electrolyte in the absence of EDOS. The voltammogram exhibits redox behavior of poly-EDOS in the potential range −1.0 to +1 V (Figure 2). The peak currents are linearly proportional to the scanning rate, indicating surface-bound redox species. A thin film of transparent sky-blue doped poly-EDOS was obtained electrochemically on optically transparent indium−tin oxide (ITO) coated glass electrode. Similar to poly-EDOT,[5e] the oxidized doped form of the polymer exhibits an absorption band in the near-IR region with absorption maximum at about 6480 cm^{-1}.

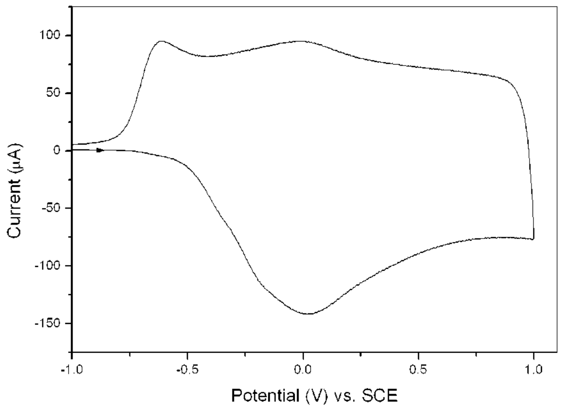

Figure 2. Cyclic voltammogram of poly-EDOS film on Pt electrode.[12]

The oxidation of EDOS was also studied chemically. The oxidative polymerization of EDOS was achieved by using 1 equiv of $FeCl_3$ in acetonitrile. Unlike the chemically prepared insoluble poly-EDOT,[5e] the resulting dark blue poly-EDOS exhibits moderate solubility in common organic solvents. Comparison of the ^1H NMR spectrum of the monomer and the polymer showed complete disappearance of the singlet at 6.82 ppm, attributed to the lone selenophene proton, indicating a reasonably high molecular weight polymer with no visible end group. The acetonitrile solution of the chemically prepared poly-EDOS exhibits an absorption band in the visible region with $\lambda_{max} = 594$ nm, indicating the neutral (nondoped) form of the polymer (Figure 3).

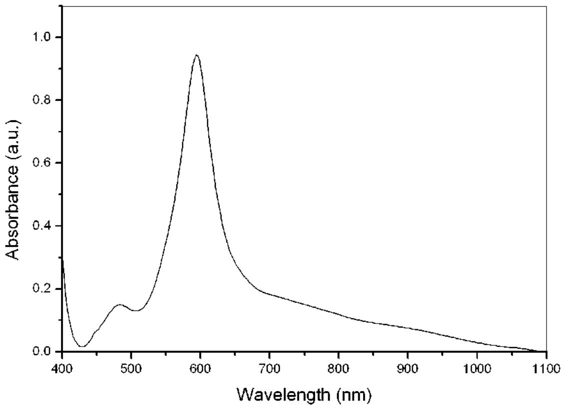

Figure 3. Absorption spectrum of neutral poly-EDOS in CH_3CN.

In conclusion, an efficient synthesis of the selenium analogue of the well studied EDOT was developed. Our preliminary results show that polymerization of EDOS can be achieved electrochemically or chemically. Further characterization, conductivity measurements, and detailed spectroelectrochemical investigations of the new polymers are currently under way in our laboratory.

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(12) Cyclic voltammetry was carried out with a three-electrode two-component cell equipped with a platinum working electrode, platinum wire counter electrode, and saturated calomel reference electrode (SCE). The electrolytic medium consisted of dry acetonitrile, 0.1 M tetrabutylamonium hexafluorophosphate. Scan rate 100 mV s^{-1}; Fc/Fc^+ shows 0.33 V under conditions. Electropolymerizations on Pt working electrode or indium−tin oxide (ITO) coated glass electrode were carried under the same experimental conditions by application of repeated potential scans between 0.50 and 1.40 V, the monomer concentration was 0.05 M.