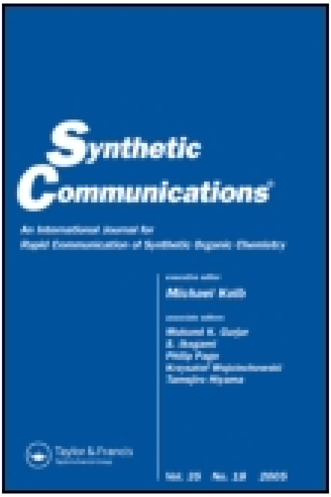

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ORGANIC MONOLAYERS AS NUCLEATION SITES FOR EPITAXIAL GROWTH:
II. SYNTHESIS OF ω-*N*- PYRROLO-FUNCTIONALIZED n-DIALKYL DISULFIDE

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Abstract: Pyrrole terminated dialkyl disulfides were synthesized. The molecules self assemble on gold and can be used for the electrochemical epitaxial growth of poly(n-alkyl)pyrrole.

Alkylthiols or dialkyldisulfides spontaneously form monolayers via dissociative adsorption on metal surfaces by forming a metal-thiolate bond, which are called self-assembled monolayers (SAMs)[1]. SAMs have been a subject of fundamental and applied researches for the last decade. The fundamental interests stem from the formation of well defined monolayers that lead to the construction of model systems in order to understand physical and chemical properties of nm thick dielectric layers in terms of orientation and packing structures on numerous substrates[2]. Furthermore, SAMs show a great promise for a number of applications such as sensors[3], lithography[4], corrosion[5], adhesion[6], and modified electrodes[7]. Thus, it is very clear that the advance of SAMs will provide a significant improvement in the basic and applied science.

There has been a large amount of study on SAMs but most of them are limited to simple alkylthiols and a few ω-substituted alkylthiols such as hydroxyl, carboxyl, amine, and pyrrole[1]. Sayre and Collard, Willicut and McCarley recently reported the synthesis and electrochemical characterization of the pyrrole terminated alkylthiols self-assembled on a gold electrode, and they showed the oxidation of surface confined pyrroles and the improvement of adhesion for the subsequent growth of polypyrrole on the surface confined pyrrole[1d, 6]. We believe this is very important evidence to achieve epitaxial growth of conducting polymers and extend the synthesis of ω-functionalized dialkyl disulfides which is relatively straight forward and provides a high yield.

We are interested in the electrochemical *epitaxial* growth of conducting polymers containing a long alkyl chain. This would be achieved by electrochemical coupling of surface confined monomers with monomers in the solution as depicted in Figure 1. Thus, it is very important to synthesize molecules terminated with monomers such as pyrrole, thiophene, and aniline. Fundamental as well as practical aspects on the electronic, optical, and topographic studies of highly oriented conducting polymers motivated us to epitaxially grow conducting polymers.

Here we report a simple synthetic method of monomer terminated dialkyl disulfides such as di-11,11'-*N*-pyrroylundecano-1,1'-disulfide. Furthermore, this method can be used toward a general synthetic procedure of ω-functionalized dialkyl disulfides that easily form SAMs on metal surfaces.

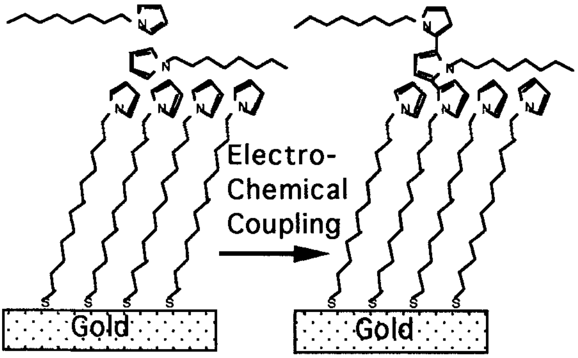
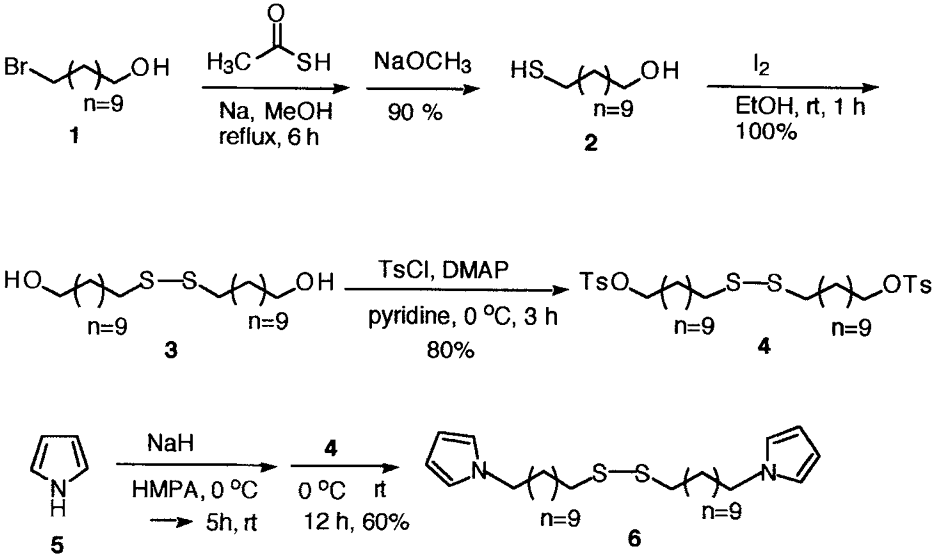


Figure 1.

A schematic representation of epitaxial growth by electrochemical coupling between surface confined pyrroles and pyrroles derivatized with a long alkyl chain.



11-Bromo-1-undecanol (**1**) was converted by treatment of thioacetic acid in sodium and followed by addition of sodium methoxide, into 11-

hydroxyundecan-1-mercaptan (**2**) in 90 % yield. However, the resulting thiol is unstable and easily undergoes air oxidation to afford disulfide as a minor component along with the product during workup. Although the two products are inseparable by usual methods, it does not matter since the disulfide was a desired product in the next step. Oxidation of **2** with iodine in alcoholic solution afforded disulfide in quantitative yield which was easily purified by recrystallization in aqueous methanol. Tosylation of the resulting disulfide **3** was carried out in pyridine and a catalytic amount of DMAP to afford **4** in good yield (80 %)[8]. During the past twenty years, several new procedures have been developed in which *N*-alkylation of pyrrole or indole can be accomplished with little or no interference from *C*-alkylation[9]. The method developed by Rubottom was employed for *N*-alkylation of pyrrole with **4**[10]. Treatment of pyrrole with sodium hydride in HMPA, followed by addition of **4**, afforded the desired product **6** in 60% yield[11].

In conclusion, we have synthesized a very interesting compound, di-11,11'-*N*-pyrroylundecano-1,1'-disulfide (**6**) for the epitaxial growth of poly(n-alkyl)pyrrole. Product 6 formed SAMs on gold in a hexane solution within an hour[12]. The promising results were obtained from the initial study and further study is undergoing.

ACKNOWLEDGMENT

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8. A white solid; mp 38-40 °C; ^{1}H NMR (360 MHz, $CDCl_3$) d 7.80 (d, *J* = 8.3 Hz, 4 H), 7.35 (d, *J* = 8.3 Hz, 4 H), 4.05 (t, *J* = 6.6 Hz, 4 H), 2.68 (t, *J* = 7.3 Hz, 4 H), 2.45 (s, 6 H), 1.75-1.55 (m, 8 H), 1.45-1.15 (m, 28 H); ^{13}C NMR (90 MHz, $CDCl_3$) d 144.57, 133.27, 129.76, 127.84, 70.65, 39.14, 29.38 (C X 2), 29.31(C X 2), 29.17, 28.88, 28.79, 28.47, 25.29, 21.60.
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11. General procedure for alkylation: A solution of pyrrole (1.69 g, 25.2 mmol) in HMPA (56 mL) was flushed with nitrogen and cooled to 0 °C. To the solution was added with stirring sodium hydride (538 mg, 22.4 mmol; previously washed with hexane to remove mineral oil) over a period of 10 min. The reaction mixture was stirred at room temperature for 5h and then cooled to 0 °C again. **4** (4.0 g, 5.60 mmol) was added and the resulting mixture was allowed to room temperature and stirred at room temperature for 12 h. The mixture was diluted with water (50 mL) and extracted with diethyl ether (3 x 60 mL). The combined organic layers were washed with water (2 x 50 mL) anddried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure and purified by chromatography on silica gel (80 g, 10:1 hexane/diethyl ether as a eluent) to afford the product as a pale yellow oil (1.73 g, 60 %). ^{1}H NMR (360 MHz, $CDCl_3$) d 6.63 (dd, *J* = 2.1, 2.1 Hz, 4 H), 6.13 (dd, *J* = 2.1, 2.1 Hz, 4 H), 3.86 (t, *J* = 7.2 Hz, 4 H), 2.70 (t, *J* = 7.3 Hz, 4 H), 1.80-1.50 (m, 8 H), 1.50-1.20 (m, 28 H); ^{13}C NMR (90 MHz, $CDCl_3$) d 120.43, 107.74, 49.61, 39.19, 31.56, 29.73, 29.45 (C X 2), 29.44, 29.20 (C X 2), 29.19, 28.50, 26.76; Anal. Calcd for $C_{15}H_{26}NS$: C, 71.37; H, 10.38. found: C, 71.26; H, 10.84.

12. Wurm, B. D.; Brittain, S. T.; Kim, Y. -T. submitted to Langmuir.

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