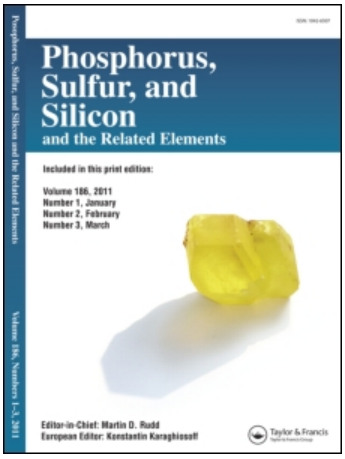

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Functionalization of Conductive Poly(thiophenes) and Poly(pyrroles)

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New methods for functionalization of conductive poly(thiophenes) and poly(pyrroles) using fused aromatics or crown ethers are discussed.

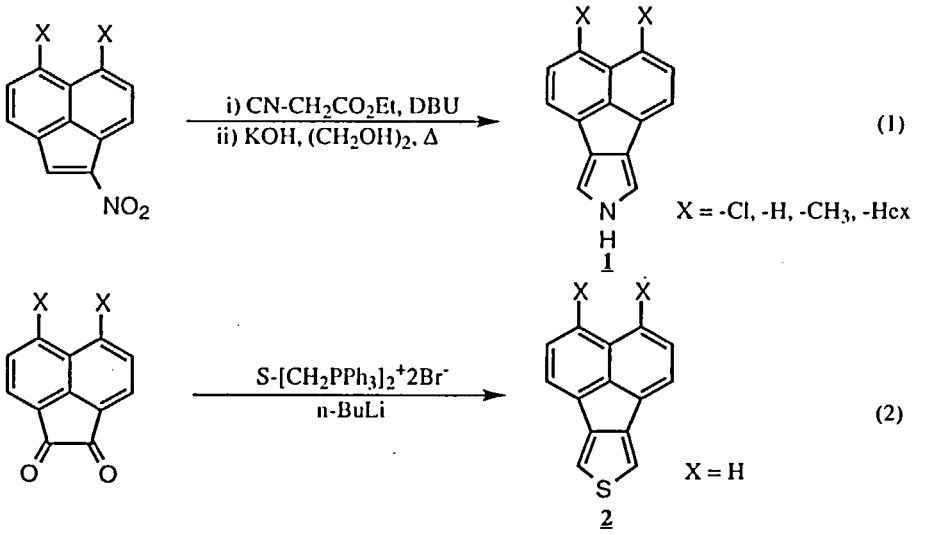
POLY(THIOPHENES), POLY(PYRROLES), CONDUCTIVE POLYMERS

INTRODUCTION

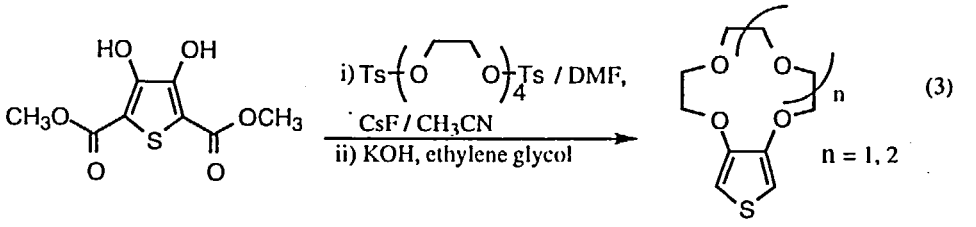
Functional electrodes which are obtained by electrooxidative polymerization of thiophenes or pyrroles have received much attention as sensors or display-devices. The function of these conductive polymers can be controlled by the fine tuning of the band structure of the polymers or by the covalent bonding of various groups which possess recognition properties toward the chemical and physical environment. In this paper we present two methods for the functionalization of conductive polymers, 1) the control of band gap of polymers using fused aromatics and 2) synthesis of thiophenes and pyrroles fused with crown ethers.

SYNTHESIS OF MONOMERS

Pyrroles fused with aromatic rings were prepared by the reaction of nitro aromatic compounds with ethyl isocyanoacetate followed by deethoxycarbonylation. For example, the reaction starting from 1-nitro-5,6-disubstituted-acenaphthylene gave 3,4-disubstituted acenaphtho[1,2-c]pyrrole **1**[1]. The corresponding thiophene derivatives **2** were prepared by Wittig reaction of the bisylide with acenaphthene quinones.



Thiophene fused with crown ethers were prepared as shown in equation 3. And the corresponding pyrroles were also prepared by the same procedure.



ELECTROOXIDATIVE POLYMERIZATION

The oxidation potentials of polymer **1** and **2** were measured by the CV method. They were affected by substituents X. This is due to the coplanarity of the thiophene or pyrrole ring and fused aromatics. The absorption wavelengh of polypyrrole **1** (X=Hex) was 482 nm and the absorption edge was 620 nm. Thus, the band gap of polypyrrole **1** (X=Hex) was estimated to be 2.0 eV. The band gap of polythiophene **2** was determined to be 1.3 eV (determined from gap of oxidation and reduction potentials). The properties of these polymers depend of X. And the fluorescence wavelength of neutral polypyrrole **1** (Hex) was 563 nm. Thus, fine tuning of the band structure of the polypyrroles **1** can be achieved by changing X. The conductivity of **1** was 0.1-4.0 Scm^{-1} and that of **2** was 10^{-3} Scm^{-1}.

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