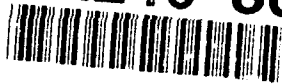


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Synthesis, Characterization, and Electropolymerization
of Ferrocene Substituted Anilines

by

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<p>The synthesis and electrochemical properties of aniline and aniline like molecules substituted with ferrocene are described [(C₅H₅)Fe (C₅H₄CH₂NHR) where R= C₆H₅, 1, C₆H₅-3-NH₂, 2, C₆H₅-3-OH, 3, and (CH₂)₂NHC₆H₅, 4). All compounds polymerize upon electrochemical oxidation of the aromatic amine portion of the complex in a CH₃CN solution containing Bu₄NClO₄ as supporting electrolyte. The phenol substituted complex shows its best polymerization characteristics when approximately one equivalent of NEt₃ is added to the electrolysis solution. The polymers, characterized by cyclic voltammetry, show well defined couples for the ferrocene but there is no electrochemical indication that the polymer backbones are electroactive. Spectroelectrochemical measurements show changes in the visible absorption spectrum characteristic for formation of the ferricinium cation, λ_{max} = 620 nm, in all of the polymers upon oxidation. In the case of the polymer from 2, an intense absorption at 480 nm also is recorded which suggests that the polymer backbone is in fact electrochemically active.</p>				
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SYNTHESIS, CHARACTERIZATION, AND ELECTROPOLYMERIZATION OF FERROCENE SUBSTITUTED ANILINES

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ABSTRACT

The synthesis and electrochemical properties of aniline and aniline like molecules substituted with ferrocene are described $[(C_5H_5)Fe(C_5H_4CH_2NHR)]$ where $R = C_6H_5$, **1**, $C_6H_5-3-NH_2$, **2**, C_6H_5-3-OH , **3**, and $(CH_2)_2NHC_6H_5$, **4**. All compounds polymerize upon electrochemical oxidation of the aromatic amine portion of the complex in a CH_3CN solution containing Bu_4NClO_4 as supporting electrolyte. The phenol substituted complex shows its best polymerization characteristics when approximately one equivalent of NEt_3 is added to the electrolysis solution. The polymers, characterized by cyclic voltammetry, show well defined couples for the ferrocene but there is no electrochemical indication that the polymer backbones are electroactive. Spectroelectrochemical measurements show changes in the visible absorption spectrum characteristic for formation of the ferricinium cation, $\lambda_{max} = 620$ nm, in all of the polymers upon oxidation. In the case of the polymer from **2**, an intense absorption at 480 nm also is recorded which suggests that the polymer backbone is in fact electrochemically active.

The ferrocene polymers that have been described exhibit a number of desirable properties which may lead to their use in practical devices. These polymers are quite stable to standard electrochemical conditions, show good stability to storage at ambient conditions, and the monomers can be synthesized using simple techniques. Furthermore, the mild positive potentials used in forming the films simplifies device fabrication. All of these aspects offer considerable improvements over existing methodologies for preparing electropolymerized polyferrocene films.

The methodology of incorporating a redox active transition metal complex onto a possible electronically conducting organic backbone holds promise for preparing novel materials. As demonstrated for the polyphenylene oxide like polymers, a synergistic effect can occur between the different components. In this example, the ferrocene aids in propagating charge through what normally would be an insulating film while the phenol backbone provides a useful means for immobilizing the ferrocene. Studies are ongoing to determine the generality of the present approach to polymer film formation.

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RESULTS

- All compounds can be electropolymerized

- Compound 2 is the best method to form polyphenylene oxide films - a new electronic conductor

- Compound 3 may have an electronically conducting polyaniline backbone

- Compound 4 has poor film forming properties
 - a) Decrease free volume for ion motion

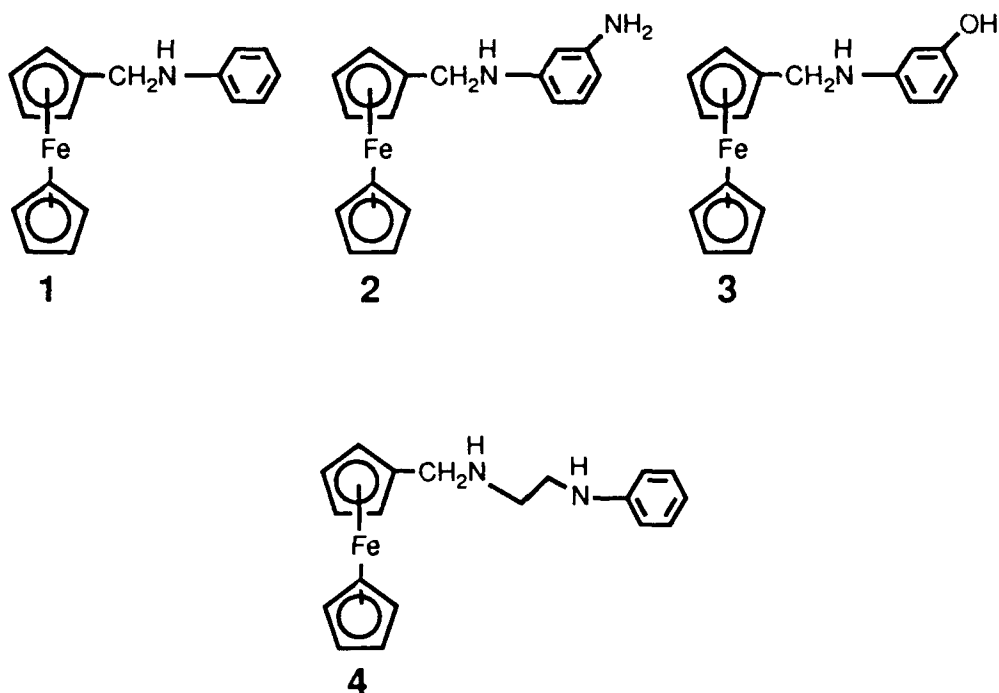
 - b) Alkyl chain is hydrophobic and rejects ions

- Promise of new materials with unique properties is being realized

COMPOSITE ELECTRONIC - REDOX HOPPING CONDUCTORS

- Organic polymers which are electronically conducting may be used for battery electrodes
- Redox hopping conductors prepared from metal complexes allow control of ion concentration
- Composite materials should have unique and novel properties

Materials synthesized, characterized, and electropolymerized



- 1) Polyaniline or polyphenyleneoxide like backbones
- 2) Metal ion can be oxidized to control anion levels
- 3) Compound 4 may be viewed as a polyethyleneimine analog