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Electropolymerization of Acenaphtho[1,2-*k*]fluoranthene Derivatives: Formation of a New Conductive Electroactive Electrochromic Hydrocarbon Ladder Polymer

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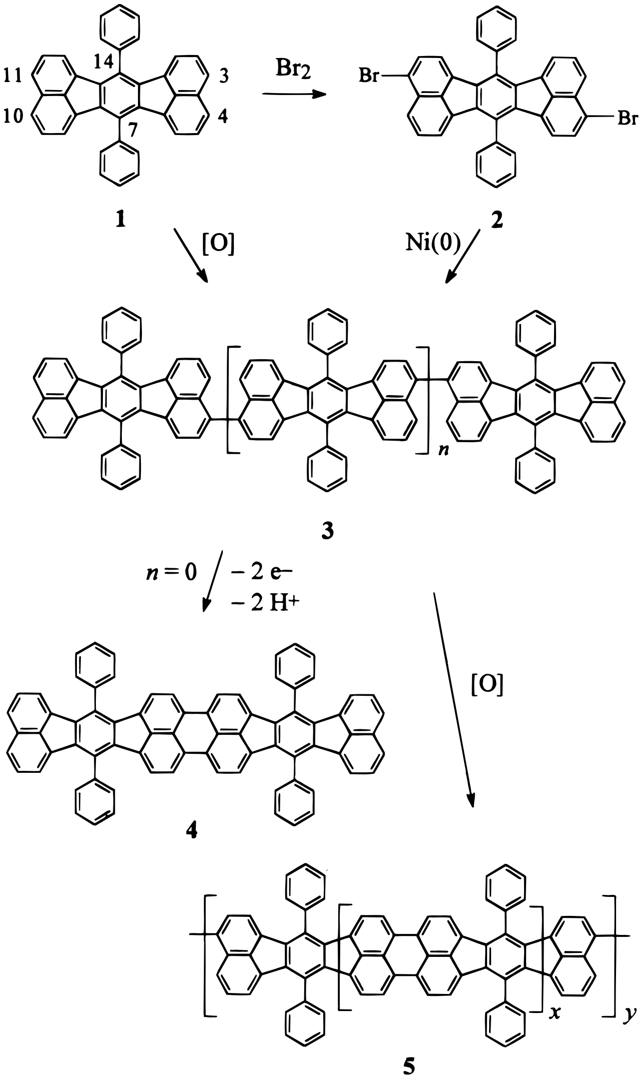
We describe here the electrochemical oxidation of a symmetric fluoranthene that produces a new type of polymer-modified electrode with interesting properties. Electropolymerization of polycyclic aromatic hydrocarbons, such as naphthalene,[1] fluorene, fluoranthene, triphenylene, pyrene,[2] and azulene[2a,3] has been reported. The structures of these polymers are ill-defined, not only because of their insolubility but also because oxidative coupling can occur at a number of different positions on the aromatic monomers, leading to unpredictably branched systems that are difficult to characterize. In a recent study, we reported that oxidation of a fluoranthene derivative leads to a dimerization reaction in which two carbon−carbon bonds form between the naphthalenic ends of two monomer units, producing a larger polyaromatic compound with a perylene core.[4] The dimerization reaction proceeds through an intermediate containing a single bond between monomer units, which undergoes intramolecular oxidative coupling to form the ultimate product. We hypothesized that if a polyaromatic molecule containing two such reactive sites was oxidized, similar oxidation chemistry would lead to ladder-type polymers with large, extended π systems. We report here our studies of an acenaphthofluoranthene derivative that displays this reactivity and upon oxidation forms an electroactive and electrochromic polymer.

The reaction scheme leading to the formation of oligomers and polymer films by oxidation of 7,14-diphenylacenaphtho[1,2-*k*]fluoranthene (**1**) is given in Scheme 1. Molecular orbital calculations[5] performed on acenaphtho[1,2-*k*]fluoranthene reveal that the highest electron density for the compound is located mainly on the central (positions 7 and 14) and end (positions 3, 4, 10, and 11) carbons, so reactions of the radical cation of the compound, such as intermolecular coupling, would be expected to occur primarily at these positions. However, substitution of the central 7 and 14 hydrogens with alkyl or aryl groups prevents reactions at these carbons and directs reactivity of the radical cation toward the two ends of the molecule, allowing for the possibility of producing linear polymers via an oxidative coupling route. The cyclic voltammogram of **1** is shown in Figure 1a. In contrast to the two reversible reduction processes (at −1.62 and −2.07 V), the oxidation wave ($E_{pa} = +1.6$ V) is chemically irreversible, indicating that the radical cation, **1**$^{\bullet+}$, is not stable and quickly undergoes a chemical reaction. By analogy with results in a previous study,[4] this process involves coupling of electrogenerated **1**$^{\bullet+}$, a process common to many aromatic species and the electrogeneration of their polymers.

When the potential of the electrode was cycled between 0 V and the oxidation wave for **1**, a broad reversible pair of waves grew with time and a blue electroactive film deposited on the electrode (Figure 1b), as is found for the deposition of conducting polymer films on electrodes following oxidation of monomer, e.g., polyaniline.[6] The films adhered well to platinum or ITO electrodes and looked homogeneous and transparent. Another route to thin films of this material was by the direct oxidation in MeCN of a solid film of **1** that was spin-coated on the electrode surface.

Scheme 1



Thin-layer chromatography of solutions used for electrodeposition experiments revealed that many new solution species form upon oxidation of **1**. A series of yellow compounds exhibiting yellow-green fluorescence were identified as poly(3,10-(7,14-diphenylacenaphtho[1,2-*k*]fluoranthene)) oligomers (**3**, Scheme 1) by comparison to identical compounds synthesized by nickel(0) catalyzed polymerization of the 3,10-dibromo derivative of **1** (Scheme 1). The oligomers were formed electrochemically by the oxidative coupling of the **1**$^{\bullet+}$ species by analogy to oligomerizations observed during the electropolymerization of many aromatic compounds.[7] The electrodeposition of the blue, insoluble films probably proceeds through the initial formation of these

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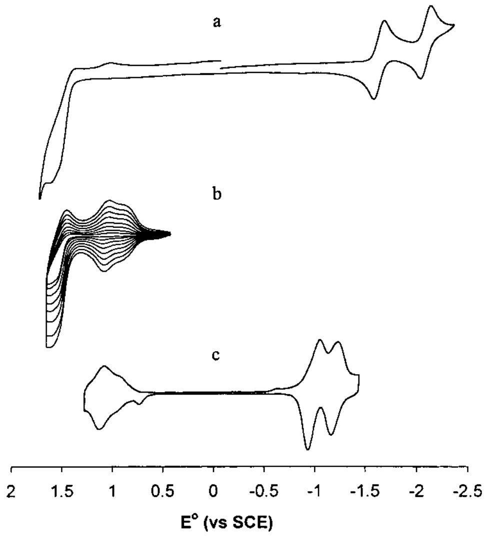

Figure 1. Cyclic voltammograms of (a) **1** in benzene:MeCN (4:1), 0.2 M $TBAPF_6$, at 200 mV/s at a Pt electrode, (b) polymer growth during repeated oxidation cycles, and (c) a thin film of the polymer deposited as in b on an ITO electrode in MeCN, 0.1 M $TBAPF_6$.

oligomers near the electrode surface, since in separate experiments the oxidation of the pure oligomers led to the deposition of films with identical properties to those formed by oxidation of **1**.

Purple and blue compounds were also produced in solution during electropolymerization of **1**. One of these species was isolated and identified as the dimer **4** (Scheme 1) by high-resolution mass spectrometry. The formation of this compound is analogous to the reaction of fluoranthene derivatives,[4] such that oxidation of the singly bound dimer (**3**, $n = 0$) triggers an intramolecular coupling process, forming a second carbon−carbon bond to generate the fully aromatic product. The other blue and purple species formed in solution during the oxidation of **1** were undoubtedly oligomers (**3**) that had undergone this intramolecular coupling in at least one position along the chain or compounds formed by the polymerization of ladder species such as the dimer, which should also be prone to intermolecular oxidative coupling. Many of these species fluoresce red under illumination, similar to the dimer **4**.

The polymer obtained from the oxidation of **1** is believed to possess a structure like that of **5** shown in Scheme 1. Further oxidative coupling within the oligomers (**3**) that were initially formed at the electrode led to planar sections of ladder structure that eventually became insoluble and precipitated onto the electrode surface. The insolubility of the film precluded complete characterization; however, spectroscopic data support this assignment. A thin film of the polymer deposited on ITO absorbed light at much lower energy (up to 800 nm, Figure 2) than the dimer **4**, which absorbs to only 620 nm, suggesting that the polymer contains sections of ladder structure made up of more than two monomer sections in length. This trend was mirrored by the fluorescence of the dimer ($\lambda_{em} = 640$ nm) and of the solid polymer ($\lambda_{em} = 750$ nm).

Fully conjugated ladder polymers with similar structure to that proposed for the electopolymerized material prepared here have been chemically synthesized using Diels−Alder reactions.[8] Polymers of this type are highly insoluble given their rigidity, and efforts to produce soluble precursors that can be chemically or thermally treated to form the ladder polymer have received much attention. The electropolymerization method described here presents an alternative route to such polymers and also a facile route to polymer films that are easily studied.

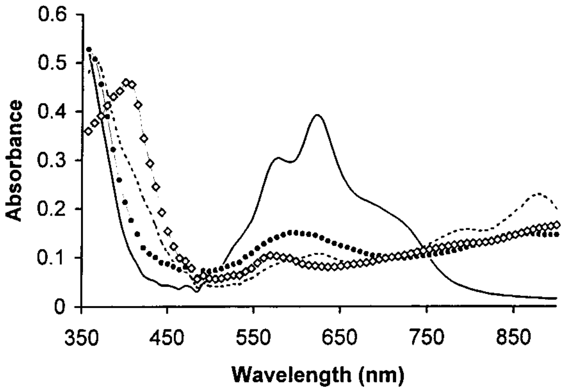

Figure 2. Absorption spectra of different oxidation states of a thin polymer film on ITO: neutral (—), oxidized (•), reduced at −1.1 V (- - -), and reduced at −1.4 V (◇).

The electrochemical and electrochromic properties of the film were studied by transferring the film-coated electrode to an MeCN/0.1 M $TBAPF_6$ solution. A representative voltammogram of a thin film on ITO is shown in Figure 1c. Identical electrochemistry was observed for films produced from solutions of the oligomers (**3**) or by electropolymerization in MeCN of solid films of **1** or **3** spin-coated onto ITO electrodes. The oxidation ($E° = +1.25$ V) and two reduction waves (−0.88 and −1.12 V) are characterized by a small ΔE_p, which is typical of a solid-state redox process. The waves shown in Figure 1c are due to the longest ladder sections within the polymer, while shorter ladder sections are presumably responsible for the additional redox processes that can be observed at more extreme potentials than those shown.

When care was taken to remove oxygen and water from the system, the films could undergo at least 20 000 cycles through both reduction peaks (0 to −1.4 V at 0.5 V/s) with no change in the shape of the voltammetric features. An initial small decrease in the amount of charge incorporated into the film occurred during the first 10 000 scans, presumably due to the dissolution of lower molecular weight species that become soluble when charged. However, repeated oxidation of the films (0 to +1.4 V) resulted in a change in the size and shape of the oxidation wave, although several hundred cycles were required for any noticeable change. Loss of charged material from the electrode or further oxidative processes occurring within the film such as cross-linking could account for these observations.

The thin films formed by electropolymerization of compound **1** are transparent blue and exhibit dramatic color changes when oxidized or reduced. Electrochemical oxidation in MeCN initiates a rapid color change to pale gray, while reduction to the first or second reduction waves causes the film to become pale green or pale orange, respectively. Absorption spectra recorded for the neutral, oxidized, and both reduced forms of the polymer are shown in Figure 2. To our knowledge this is the only example of this type of polymer to show such behavior. The neutral polymer was stable in air for at least several months. The electrochromic effects were stable and reversible under anerobic and anhydrous conditions, and the films continued to exhibit strong color changes after 30 000 reduction cycles in MeCN. In addition to its interesting electrochromic properties, this material may be useful in electroluminescent devices and in electrogenerated chemiluminescence. Such studies are under investigation.

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Supporting Information Available: Experimental details (3 pages). See any current masthead page for ordering information and Web access instructions.

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