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The synthesis, physicochemical properties, and electrochemical polymerization of fluorene-based derivatives as precursors for conjugated polymers

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ABSTRACT

Two novel monomers, 2,7-bis[(thien-2-yl)cyanovinyl]-9,9-dipentylfluorene (**FPT**) and 2,7-bis-[(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)cyanovinyl]-9,9-dipentylfluorene (**FPE**) are synthesized and their electrochemical polymerization is achieved via potentiostatic methods. The corresponding polymers, poly(2,7-bis[(thien-2-yl)cyanovinyl]-9,9-dipentylfluorene) (**PFPT**) and poly(2,7-bis[(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)cyanovinyl]-9,9-dipentylfluorene) (**PFPE**), are characterized by cyclic voltammetry, FT-IR, and UV–vis spectroscopy. The band gap values (E_g) of the polymers are found to be 2.21 and 1.92 eV for **PFPT** and **PFPE**, respectively.

Conjugated polymers have attracted significant attention due to the possibility of their applications in photovoltaic cells, electroluminescent displays, field effect transistors, plastic lasers, and optical sensors.[1,2] Among these applications, polymer-based light-emitting diodes have attracted the particular interest of researchers.[3,4] The first demonstration of efficient polymer light-emitting diodes (PLEDs) in 1990[5] resulted in great interest in display applications for conjugated polymers.[6] Compared with conventional LEDs, PLEDs offer a wide variety of advantages, such as easy fabrication by spin coating and low cost.[7,8] Among the large number of conjugated polymers with different emissive colors, polyfluorenes (PFs) are of significant importance as blue light emitting emissive layers, not only due to their high thermal and chemical stability, but also for their high photoluminescence efficiency and good photostability.[9–11] These properties make polyfluorene a material of interest and a large number of PF derivatives have been reported. Moreover, PFs can be substituted at the C-9 position; this facile process provides the opportunity to improve both the solubility and functionality of the resulting polymers. Conducting polymers are prepared by chemical or electrochemical oxidation of monomeric compounds.[12–15] Electrochemical methods of preparation include potentiostatic, potentiodynamic, and galvanostatic.[13] The potentiodynamic method is reported to produce films with superior adhesion, smoothness, and optical properties.[16–18] PF films obtained by constant potential electrolysis are brittle and hydrogen-rich with electrical conductivity of 10^{-4} S/cm. Rault-Berthelot et al. have reported several articles on anodic polymerization and spectroelectrochemical studies of PFs in acetonitrile.[19–21]

In this letter, we describe the electrochemical behavior and the anodic electropolymerization of new fluorene derivatives consisting of a central alkylfluorene unit substituted at the 2,7-positions with two cyanovinylene-thiophenes or two cyanoviny-lene-(3,4-ethylene-dioxythiophenes).

Scheme 1 shows the synthetic route to the monomers. The syntheses of 2,7-bis[(thien-2-yl)cyanovinyl]-9,9-dipentylfluorene (**FPT**) and 2,7-bis[(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)cyanovinyl]-9,9-dipentylfluorene (**FPE**) started with the alkylation of fluorene followed by chloromethylation to give 2,7-bis(chloromethyl)-9,9-dipentylfluorene (**2**). Compound **3** was obtained by cyanation of compound **2**. Finally, condensation reactions of compound **3** with thiophene-2-carboxaldehyde and 3,4-ethylenedioxythiophene-2-carboxaldehyde gave the desired monomers, **FPT** and **FPE**.

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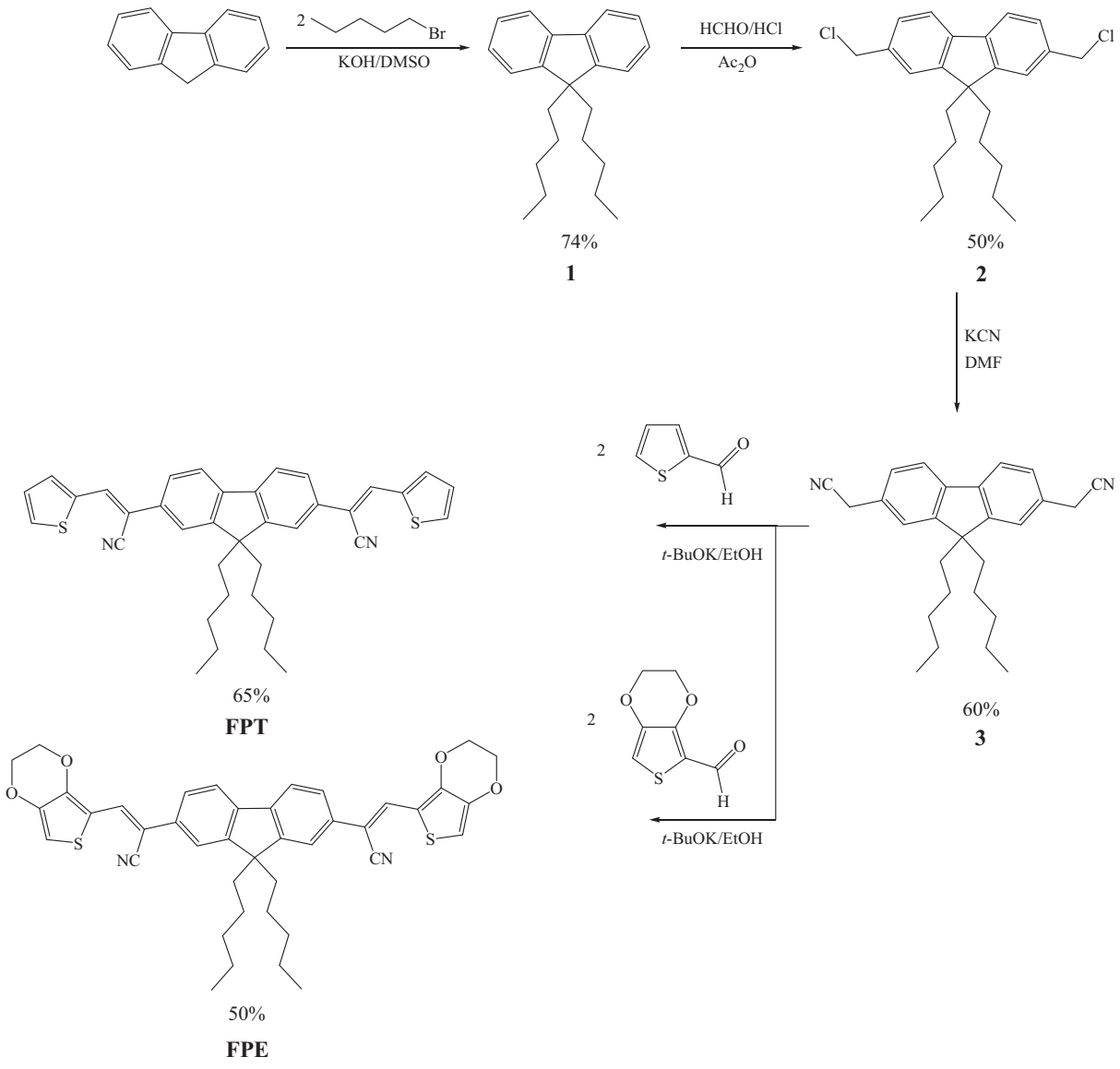

Scheme 1. Synthesis of the monomers **FPT** and **FPE**.

Next, the electrochemical behavior of these fluorene-based monomers was investigated by cyclic voltammetry. During the first positive scan, **FPT** and **FPE** exhibited irreversible peaks (E_m^{Ox}) at 1.40 V and 1.20 V versus SCE, respectively. (Fig. 1), which correspond to the transfer of an electron from the HOMO level of the monomer to the working electrode of the electrochemical system.

After the determination of the redox behavior of **FPT** and **FPE**, repetitive anodic scans were performed to obtain their corresponding polymers, **PFPT** and **PFPE**. For **FPE**, The electrochemical polymerization was performed with a platinum disk electrode between 0.36 V and 1.26 V. Due to the limited solubility of **FPE** in MeCN, a mixture of CH_2Cl_2 and MeCN (1:10 by volume) was used as the solvent. On the other hand, repetitive cycling between 0.36 V and 1.46 V was used for the polymerization of **FPT** in Bu_4NBF_4 (0.1 M)/MeCN electrolyte solution. As shown in Figure 2, new redox couples intensified during each successive scan indicating the formation of electroactive polymer films on the surface of the working electrode, with increasing polymer film thickness.[22] The electrochemical behavior of the polymeric films previously

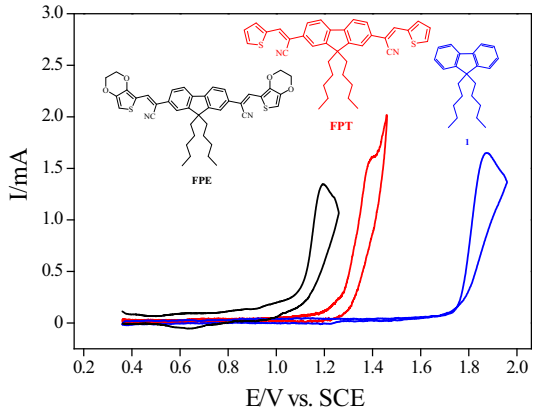

Figure 1. Cyclic voltammograms of **FPE** (2.0×10^{-3} M), **FPT** (2.0×10^{-3} M) and 9,9-dipentylfluorene (**1**) (2.0×10^{-3} M) in Bu_4NBF_4 (0.1 M)/MeCN solution at a scan rate of 100 mV/s.