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## Experimental Details

Tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) (SACHEM, Austin, TX) was recrystallized from EtOH/H<sub>2</sub>O (4:1) twice and dried at 100 °C before use. Dimethylformamide (DMF), benzene (Aldrich, anhydrous), and MeCN (Burdick and Jackson, UV grade) were used as received after being transported unopened into an inert atmosphere drybox (Vacuum Atmospheres). Bis(1,5-cyclooctadiene)nickel(0) (Johnson Matthey), bromine, acenaphthylene, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 1,3-diphenylacetone (Aldrich), and acenaphthenequinone (Lancaster) were used as received.

NMR spectra were recorded on a Varian Unity Plus 300 spectrometer as solutions in deuteriochloroform (CDCl<sub>3</sub>). Chemical shifts are expressed in parts per million (ppm,  $\delta$ ) downfield from tetramethylsilane (TMS) and are referenced to CDCl<sub>3</sub> (7.24 ppm) as internal standard. Exact mass determinations were obtained on a VG analytical ZAB2-E instrument. Fluorescence spectra were recorded on a SLM Aminco SPF-500 spectrofluorometer, and UV spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer.

A Model 175 universal programmer and a Model 173 potentiostat (Princeton Applied Research) were used for electropolymerization. Cyclic voltammograms were recorded on a Model 660 electrochemical workstation (CH Instruments). The working electrode consisted of either an inlaid platinum disk or indium tin oxide-coated (ITO) glass ( $R_s \leq 40 \Omega/\text{cm}^2$ , Delta Technologies, MN). Platinum gauze served as a counter electrode, and a silver wire was utilized as a quasi-reference electrode which was calibrated vs SCE by the addition of ferrocene as an internal standard using  $E^\circ(\text{Fc}/\text{Fc}^+) = 0.424 \text{ V vs SCE}$ .

**7,14-Diphenylacenaphtho[1,2-*k*]fluoranthene (1).** This compound was prepared by a route similar to those previously reported.<sup>1</sup> The cyclopentadienone intermediate was prepared by refluxing 1,3-diphenylacetone (3.72 g, 17.7 mmol) and acenaphthenequinone (3.23 g, 17.7 mmol) in ethanolic KOH for 6 h. The solvent was removed under vacuum, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered (the cyclopentadienone can be isolated at this step by addition of pentane to the filtered solution to precipitate the compound; however, isolation is not required for the following preparation). The solvent was removed and acenaphthylene (2.70 g, 17.8 mmol) and xylenes (40 mL) were added and the resulting solution was refluxed for 2 days. The solvent was removed by distillation and the residue was placed under vacuum to remove unreacted acenaphthylene. DDQ (4.0 g, 18 mmol) and enough CH<sub>2</sub>Cl<sub>2</sub> to dissolve the residue were added and the solution was stirred at 45 °C for 1 h. The solution was filtered through silica (3 cm) and the solution volume was reduced under vacuum. The product precipitated as yellow crystals, which were isolated by filtration. The supernatant was reduced further and cooled to induce more product to crystallize (5.15 g total, 61%). The compound was recrystallized from toluene before use in electropolymerization experiments.

**3,10-Dibromo-7,14-diphenylacenaphtho[1,2-*k*]fluoranthene (2).** 1 and 2.5 equivalents of bromine were stirred under reflux in CH<sub>2</sub>Cl<sub>2</sub> until the starting material was consumed, as

judged by TLC (~ 4 h). The solvent was removed under vacuum to leave a bright yellow solid which was used without further purification.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.47 (2H, d,  $J = 7.5$  Hz,  $\text{H}_{2,9}$ ), 6.70 (2H, d,  $J = 6.9$  Hz,  $\text{H}_{4,11}$ ), 7.37 (2H, vt,  $J = 8$  Hz,  $\text{H}_{5,12}$ ), 7.53 (2H, d,  $J = 7.8$  Hz,  $\text{H}_{1,8}$ ), 7.6 (4H, m, phenyl), 7.7 (6H, o,p, phenyl), 7.88 (2H, d,  $J = 7.8$  Hz,  $\text{H}_{6,13}$ ). MS (CI+) 637 ( $\text{M}^+ + 1$ ), 556 ( $\text{M}^+ - \text{Br}$ ). EA calcd for  $\text{C}_{38}\text{H}_{20}\text{Br}_2$  C: 71.72, H: 3.17, Br: 25.11. Found C: 71.73, H: 3.18, Br: 25.05.

**Poly(3,10-(7,14-diphenylacenaphtho[1,2-*k*]fluoranthene)) (3).** **2** (150 mg, 0.24 mmol) and bis(1,5-cyclooctadiene)nickel(0) (70 mg, 0.25 mmol) were dissolved in DMF (350 mL) in a glove box. Benzene (100 mL) was added to improve the solubility of the products and the solution was heated in a sealed vessel at 55 °C for 6 days with constant stirring. HCl (5 mL, 0.2 M) was then added and the solution was stirred for 1 h, at which time 300 mL of water was added. The benzene layer was separated, dried ( $\text{MgSO}_4$ ), and filtered, and the solvent was evaporated. An equivalent volume of hexanes was added, and the solution was passed through 10 cm of silica. The column was washed with benzene:hexanes (1:1) until the eluate was nearly colorless, and the solvent was removed from the combined filtrates to leave a yellow-orange powder. This was dissolved in 5 mL of benzene, and 10 mL of MeCN were added dropwise with vigorous stirring to precipitate the longer oligomers. After isolating the precipitate, the procedure was repeated once more, and the product was dried under vacuum (15 mg, 13%). The oligomers could be separated using TLC ( $\text{CH}_2\text{Cl}_2$ /hexanes, 1:2) so that the degree of polymerization could be identified by mass spectrometry, and the relative amounts of each oligomer could be determined by fluorescence spectroscopy. The oligomers ranged from  $n = 0$  to  $n = 8$  (Scheme 1), with an average degree of polymerization of 6 (i.e.,  $n = 4$ ). UV ( $\text{CHCl}_3$ ) 322, 451 nm.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.7 (7H, m), 7.42 (1H, br d), 7.35 (2H, m), 7.50 (2H, br t), 6.8 (1H, m), 6.7 (2H, m). MS (CI+) examples:  $n = 4$ : 2861 ( $\text{M}^+$ );  $n = 3$ : 2385 ( $\text{M}^+$ ).

#### **Electropolymerization of 7,14-Diphenylacenaphtho[1,2-*k*]fluoranthene (1).**

**From Solution.** Solutions used for electropolymerization consisted of the monomer (**1**) in benzene/MeCN (5:1) containing 0.2 M TBAPF<sub>6</sub>. Monomer **1** shows low solubility in MeCN alone. The concentration of monomer depended upon the type of film required; homogeneous thin films were best prepared using low concentrations (0.5 mM), while 5 mM solutions were used to produce bulk polymer. The thin films appeared clear and transparent, although under magnification they looked coarse and porous. The electropolymerization cell contained two compartments separated by a fine glass frit. The working electrode was placed in one compartment along with a silver wire quasi-reference electrode that was contained inside a small fritted glass tube. The counter electrode was a large platinum mesh. Polymer was deposited on the working electrode by repeatedly sweeping the potential from 0 V to the oxidation peak of the monomer (~1.6 V) and back using scan rates of 100–200 mV/s. The solution became green during the experiments, and a TLC of the resulting solution showed the presence of oligomers (**3**) that were fluorescent yellow and other blue and purple products, some of which appeared

fluorescent red under a hand-held UV lamp. The polymer-coated electrode was washed in MeCN after removal from the electropolymerization cell. Bulk material was produced by using large ITO electrodes, from which the polymer was mechanically removed. This material was washed in electrolyte solution, MeCN, benzene, and then dried under vacuum before analysis. EA: found, C: 84.4, H: 4.7, N: 0.87. Calcd  $[(C_{38}H_{20})_n + 0.4(TBAPF_6)]$ , C: 84.4, H: 5.1, N: 0.92.

**From a Solid Film.** Films of **1** were spin-coated onto a clean ITO surface and immersed in an MeCN/TBAPF<sub>6</sub> solution. **1** is slightly soluble in MeCN, and therefore the electropolymerization solution was saturated with **1** before immersion of the film-coated electrode to decrease dissolution of the film before application of the potential (electropolymerization of the monomer directly from the saturated solution onto a clean electrode is not observed due to the low concentrations involved). The yellow film of **1** was polymerized by scanning the potential as described for the solution experiments until no further growth of the polymer was observed.

**Electropolymerization of Poly(3,10-(7,14-diphenylacenaphtho[1,2-*k*]fluoranthene)).** The same procedures used to polymerize **1** from solution or the solid state were used to electropolymerize these oligomers. The electrochemistry of the polymer thus formed was identical to that of the polymer obtained from the monomer.

**1,4,9,12-Tetraphenyldiacenaphtho[*b,p*]periflanthene (4).** Small amounts of this product were isolated from solutions used for the electropolymerization of **1**. Best results were obtained when these solutions were further electrolyzed at 1.6 V until the solution became blue and no monomer remained, whereupon the solvent was removed and the residue chromatographed on silica (20 cm column) using CHCl<sub>3</sub>/hexanes (1:2) to elute. Compound **4** appeared as a purple band. The low solubility and the small amounts isolated prevented complete characterization. UV (CHCl<sub>3</sub>): 340, 520, 555, 601 nm. Fluorescence (CHCl<sub>3</sub>, λ<sub>ex</sub> = 555 nm): 640 nm. HRMS (CI+) calcd for C<sub>76</sub>H<sub>40</sub>: 952.3130 (M<sup>+</sup>). Found: 952.3110.

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