



Diphenylanthrylene and diphenylfluorene-based segmented conjugated polymer films as fluorescent chemosensors for nitroaromatics in aqueous solution



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ABSTRACT

A new regularly segmented conjugated polymer with diphenylanthryl chromophores bearing oxyethylene side chains was synthesized. The amorphous polymer was solution-processable. The formation of aggregated species in solid phase was hindered by the bent microstructure while fluorescence depolarization measurements showed high exciton mobilities among the short chromophores. The fluorescence quenching of films of **PA** toward nitroaromatics in aqueous solution was evaluated and compared with the behavior of **PF**; a diphenylfluorenylene-based segmented CP bearing non-polar aliphatic side chains. Films of both polymers exhibit remarkable sensing abilities in the micromolar range thus showing that hydrated films have porosity at the molecular level. The fluorene-based **PF** had higher overall quenching responses to NACs than the anthryl-based **PA** while nitrophenols were more effective than nitrotoluenes in quenching the fluorescence of both **PA** and **PF**. Such differences are rationalized in terms of polymer–analyte interactions. The binding strengths between analytes and sensing materials were evaluated by their Hansen solubility parameters. We concluded that strong analyte cohesive interactions with the polymer could drag analyte diffusion and impair polymer sensing ability and should be avoided in the design of responsive polymers to be used in the present sensing configuration.

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1. Introduction

Nitro aromatic compound (NAC) sensing is necessary for environmental pollution control, security matters and industrial applications [1–3]. For instance, phytotoxic nitrophenols are primary and secondary pollutants found in air, dew and rain in city downtown and industrial areas [4]. In addition, the characterization of soil and groundwater at munitions production, distribution and storage facilities usually reveals contamination with toxic nitrotoluene derivatives. Chemosensing methods based in responsive polymers have raised interest because of high sensitivity, stability, reproducibility, affordability and feasibility for miniaturization [5,6]. Thus, fluorescent quenching of conjugated macromolecular films is a promising approach for detection of NACs because they display sensory signal amplification by energy migration along the

conjugated polymer (CP) chain. The best sensory responses in solid state have been observed when bulky groups attached to the CP main chain bring porosity to the films that foster analyte diffusion into the sensing layer [7,8]. However, luminescent molecular structures such as dendrimers [9,10] or hyperbranched polymers [11] or monolayers [12,13] that also facilitate fluorophore–quencher interactions have proven to be very sensitive toward nitroaromatics.

Our approach to generating film porosity involves the use of CPs with broken conjugation whose microstructure consists of conjugated aromatic segments tethered along the main chain by saturated 2,2-isopropylene spacers; the latter structural motif induced twisted arrangements of the attached geminal fluorophores [14]. The contorted conformations adopted by the regularly segmented CP main chain produce amorphous morphologies, introduce porosity of molecular dimensions and reduce any potential π -stacking that usually leads to polymer self-quenching. Thus, previous reports from our group detailed the high quenching sensitivity of these new segmented CPs toward methanolic solutions of NACs thus demonstrating the amplified quenching effect

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that an array of structurally well-defined chromophoric units can display in solid state [15,16]. We also encountered in these studies the difficulties already mentioned by other authors [13,17] in establishing trends for quenching responses of NACs in condensed phase, e.g. films of a quaterphenylene-based segmented CP were very sensitive toward picric acid but showed no response to trinitrotoluene [16]. Although these empirical types of findings could be of interest for the design of selective sensors, their serendipity makes them less valuable in building a rationale for polymer tailoring.

In this paper we selected two sets of NACs with increasing molecular volume and decreasing reduction potential for our experiments in order to implement a more systematic approach to studying the quenching efficiency of phytotoxic nitrophenols and nitrotoluene derivatives. The first set was composed of nitrophenol (NP), dinitrophenol (DNP) and trinitrophenol (TNP) while the second one was constituted by nitrotoluene (NT), dinitrotoluene (DNT) and trinitrotoluene (TNT). We also report herein the synthesis and electro-optical characterization of a new amorphous diphenylanthrylene-based segmented CP bearing polar oxyethylene side chains, **PA**, see Scheme 1. Its electrochemical and photophysical properties were investigated using cyclic voltammetry (CV) and both UV–visible absorption and steady state photoluminescence emission (PL) spectroscopies. Then, the fluorescence quenching response of hydrated films of **PA** to the two series of NACs in aqueous solution was evaluated and the results were compared with those obtained in similar quenching experiments with a diphenylfluorenylene-based segmented CP bearing non-polar aliphatic side chains, **PF**, in order to observe whether either the polymer bearing polar side chains or the one with the non polar chains show selectivity to either one of the two NAC sets.

2. Experimental

2.1. General methods and instrumentation

Melting points reported are not corrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX300 spectrometer on samples dissolved in CDCl_3 . Mass spectra were measured with Varian MAT CH-7A instrument. Gel permeation chromatography analyses were carried out on THF solutions at room temperature using a Waters model 600 furnished with a Waters 2487 UV detector set at 254 nm. Calibration of the instrument was done using polystyrene standards. Thermal analysis was carried out on a TA Q20 instrument under nitrogen flow at a scan rate of $10^\circ\text{C}/\text{min}$. The thermal behavior was observed on an optical polarizing microscope (Leitz, Model Ortolux) equipped with a hot stage (Mettler).

UV/vis spectra were obtained from a UV–visible GBC Cindra 20 spectrometer. The absorption measurements were done either on dilute samples (less than 0.01 g/ml) or on thin films cast on quartz plates, which were placed at a 30° angle with respect to the incident beam. The molar extinction coefficients (ϵ) were obtained from the slope of the plot of the absorption with six solutions of different concentrations vs. the concentration (correlation values >0.99). Steady-state fluorescence studies were conducted using an SML AMINCO 4800 spectrofluorimeter at 25°C . The emission measurements were carried out on dilute samples (less than 0.02 mg/ml) using a quartz cuvette with a path length of 1 cm and keeping the optical densities below 0.1 to minimize aggregation and reduce artifacts introduced by self-absorption in fluorescence. Thin film spectra were recorded by front-face (30°) detection. Film specimens were drop-cast from a CHCl_3 solution on quartz substrates and dried at room temperature. Fluorescence anisotropy was measured using a couple of film polarizers on the excitation and emission beams in the spectrofluorimeter operating in

an L-format. The fluorescence anisotropy is calculated according to $\langle r \rangle = I_{vv} - G I_{vh} / (I_{vv} + G 2 I_{vh})$ where $I_{exc,em}$ is the intensity of the emission, v and h are the vertical or horizontal alignment of the excitation and emission polarizers, and $G = I_{hv} / I_{hh}$ is the instrumental correction factor which accounts for the difference in sensitivities for the detection and emission in the perpendicular and parallel polarized configurations [27].

Electrochemistry experiments were performed in a Bas Epsilon instrument with a three-electrode setup using platinum wire as working electrode, a Pt wire as counter electrode and Ag wire on which AgCl had been deposited electrolytically as the reference electrode. Cyclic voltammograms were recorded potentiostatically in CH_2Cl_2 with 0.1 M tetraethylammonium perchlorate as supporting electrolyte at a scan rate of 100 mV/s.

2.2. Materials and synthesis

Melting points reported are not corrected. 2,6-Dihydroxy-9,10-anthraquinone, bisphenol A, 1,4,7-trioxanonanol and other reagents were purchased from Aldrich and used without further purification unless otherwise specified. THF was purified by distillation from Na/benzophenone. Tetrakis(triphenylphosphine)palladium(0) was prepared from literature [18,19]. 2,4,6-Trinitrotoluene was prepared as reported elsewhere [20] and recrystallized three times from ethanol.

2.2.1. Monomer synthesis

The synthesis of the monomer 2,2-bis[3-(1,3,2-dioxaborinan-2-yl)-4-methoxyphenyl] propane has been already reported [15]. 1,4,7-Trioxanonyl-*p*-toluenesulfonate was prepared according to a reported procedure [21].

2.2.1.1. 2,6-Dihydroxyanthracene (1). A suspension of 2,6-dihydroxy-9,10-anthraquinone (20 g; 83 mmol) in 25% aqueous solution of ammonia (190 ml) was treated with Al(Hg) (6.0 g) and heated under reflux for 5 h. After cooling at r.t., 35% HCl (200 ml) was added and the precipitate was collected by filtration. The product was extracted in a sohxlet with 2-butanone and then the solvent was evaporated. The product (11.5; 65%) was used as such in the next step. M.p. 287°C (decomp.). ^1H NMR (acetone- d_6) δ 8.51 (s, 1H), 8.17 (s, 1H), 7.88 (d, 1H, $J=9.0$ Hz), 7.26 (d, 1H, $J=2.5$ Hz), 7.19 (dd, 1H, $J=9.0$ Hz and 2.5 Hz); ^{13}C NMR (acetone- d_6) δ 154.8, 132.5, 130.2, 129.6, 124.4, 121.1, 108.1.

2.2.1.2. 2,6-Bis(1,4,7-trioxanonyl)anthracene (2). A mixture of **1** (7.37 g; 35 mmol) and sodium hydride (2.11 g) was dissolved with DMF (50 ml) and after the hydrogen evolution totally receded, ca. 15 min, a solution of 1,4,7-trioxanonyl-*p*-toluenesulfonate (7.3 g; 25.3 mmol) in DMF (50 ml) was added at r.t. The green mixture was heated under reflux for 3 h. After standing overnight at r.t. the product was collected by filtration, washed with benzene (3×30 ml) and dissolved in CHCl_3 (750 ml). The solution was washed with 10% NaOH (40 ml), 5% NaHCO_3 (50 ml), brine (50 ml), dried with Na_2SO_4 , and evaporated. Crystallization at 4°C of the residue from acetone (150 ml) afforded **5** (10.78 g, 69%). M.p. $131\text{--}132^\circ\text{C}$. ^1H NMR (CDCl_3) δ 8.15 (s, 1H), 7.81 (d, 1H, $J=10.1$), 7.16 (m, 2H), 4.27 (t, 2H, $J=4.9$ Hz), 3.93 (t, 2H, $J=4.9$ Hz), 3.75 (m, 2H), 3.62 (m, 2H), 3.52 (q, 2H, $J=7.0$ Hz), 1.21 (t, 3H, $J=7.0$ Hz); ^{13}C NMR (CDCl_3) δ 155.9, 131.4, 129.4, 129, 124.5, 120.9, 105.1, 71.2, 70.1, 70.0, 67.6, 66.9, 15.3; MS (70 eV), m/z (%), 443 ($\text{M}^+ + 1$, 26), 442 (M^+ , 100), 441 (24), 210 (96), 181 (27), 117 (58), 89 (20), 73 (79). Anal. Calcd. for $\text{C}_{26}\text{H}_{34}\text{O}_6$, C, 70.56; H, 7.74. Found C, 70.45; H, 7.64.

2.2.1.3. 9,10-Dibromo-2,6-bis(1,4,7-trioxanonyl)anthracene (3). A solution of Br_2 (7.2 g; 45 mmol) in CH_2Cl_2 (65 ml) was added drop wise within 4 h to a stirred ice-cooled solution of **5** (10.0 g;

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