



# Synthesis and characterization of fluorescent nitrobenzoyl polythiophenes



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## ABSTRACT

Two thiophene derivatives named 4"-nitrobenzoyl (thiophene-3'-yl)-1-ethylate (**NTh**) and 3",5"-dinitrobenzoyl (thiophene-3'-yl)-1-ethylate (**DNTh**) were synthesized and characterized. Both monomers were electrochemically polymerized onto platinum or glassy carbon electrodes by potentiodynamic method in 0.1 mol L<sup>-1</sup> TBABF<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> + boron trifluoride diethyl etherate (**BFEE**) (1:1, v/v). These monomers were also successfully polymerized by chemical oxidation using FeCl<sub>3</sub>/CHCl<sub>3</sub>. Spectroscopic and electrochemical properties of the monomers and polymers were investigated. Films of both polymers showed well-defined reversible redox system at the anodic branch (1.0 V vs. Ag/AgCl, KCl (sat.)), attributed to thiophene doping/dedoping process; and another redox process at the cathodic branch (**PNTTh**) (or two redox processes for **PDNTTh**) was attributed to the reduction of the 4-nitrobenzoyl or 3,5-dinitrobenzoyl substituent groups. The THF solutions of monomers and polymers are fluorescent, with emission bands at  $\lambda_{\text{max}} = 488$  nm (**NTh**), 511 nm (**DNTh**), 440 nm (**PNTTh**) and 546 nm (**PDNTTh**). The monomers are also fluorescent in the solid state.

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## 1. Introduction

The synthesis and characterization of novel  $\pi$ -conjugated polymers have attracted a great deal of interest, mainly because of their properties: electrical conductivity, electrochromism, electroluminescence, nonlinear optical characteristics and chemical sensing [1], which are useful for a wide range of applications, including electrochromic devices [2,3], organic light emitting diodes (OLEDs) [4], organic solar cells (OSCs) [5], organic field effect transistors (OFETs) [6], energy storage [7] and biosensors [8]. All these applications usually require the rational design and modification of the monomer structure. Therefore, the creative design and strategies to synthesize new derivatives of conjugated polymers can lead to materials with enhanced performance.

Some of the conjugated polymer properties are assigned to their ability on changing the electronic and spectral features, upon the modification of their chemical structure, *i.e.*, the tailoring of the band gap ( $E_g$ ) of these polymers allows the shift of the absorption and emission wavelengths [9], or even in the electrochemical response [10]. Therefore, the properties can be adjusted by

modification of the monomer structure by attaching different functional groups, such as, electron-donating and/or electron-withdrawing, n-dopable, or fluorescent substituents [10–13]. For instance, the appendage of a nitro group on the monomer structure would make the resulting polymers amenable for use in sensors or electrochemical capacitors [14,15].

The presence of nitro groups in conjugated polymers may provide interesting applications: i) during the redox process of corresponding conjugated polymers, the nitro group can be reduced, ii) the NO<sub>2</sub> group can be reduced to NH<sub>2</sub> at less negative potential, and iii) the introduction of the nitro groups in the conjugated polymer structure can provide a post-functionalization approach, *e.g.*, reduction of NO<sub>2</sub> into NH<sub>2</sub> [16]. In addition, polymers bearing nitro groups have not been extensively investigated.

The presence of the electron-withdrawing nitro group in the monomer structure usually leads to a higher oxidation potential, culminating in poor polymer film quality or no electropolymerization [16–18]. The nitro group can stabilize the radical cation intermediates, allowing its diffusion away from the electrode that prevents the polymerization on the anode surface [19,20]. Therefore, its preparation still remains as a challenge.

Thiophene and pyrrole electropolymerizations has been largely studied, and follow the same reaction mechanism. The pyrrole

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oxidation potential ( $\sim 1.2$  V vs. Ag/AgCl) is lower than the thiophene oxidation potential ( $\sim 1.6$  V) that can reach 2.4 V, depending on the substituent group; thus, thiophene electropolymerization is very difficult to be carried out in aqueous medium. Polypyrrole is more susceptible to oxidation than polythiophene, leading to the carbonyl group formation at the position 3 and breakup of the conjugation. Polythiophene presents a better thermal stability than polypyrrole, and the conductivity of both polymers can vary ( $10^{-3}$  to  $10^3$  S cm $^{-1}$ ) according to the substituent, dopant and experimental conditions of electropolymerization [21,22]. Therefore, numerous applications can be associated to intrinsic characteristics and properties of these polymers.

A series of polypyrrole and polythiophene derivatives bearing nitro- and dinitro- substituents have been synthesized and characterized by our research group aiming their application in electrochromic devices (ECDs) [3,23–25], fluorescent layers [26] or as material for energy storage [14]. In an earlier study, Welzel et al. [19] synthesized two thiophene derivatives substituted with nitro- and dinitro- groups and tried to electropolymerize these derivatives under standard conditions (such as TBAP/CH<sub>3</sub>CN), but they were not successful. According to their results, the high potential (up to 2.3 V vs. Ag/AgCl) necessary for the monomers oxidation caused an overoxidation process destroying the aromatic structure of the thiophene units.

The replacement of the usual organic media (CH<sub>3</sub>CN) by a Lewis acid, such as boron trifluoride diethyl etherate (BFEE) is a good strategy to prepare good-quality conjugated polymer films bearing electron-withdrawing substituents [17,23]. BFEE solution has been widely used as catalyst to electropolymerize aromatic monomers, such as thiophene and its derivatives, selenophene and pyrene [27–29]. In the presence of BFEE, the monomer oxidation occurs at a lower potential, rather than in CH<sub>3</sub>CN, by virtue of the interaction between the Lewis acid and the aromatic monomer [30]. It occurs because the strong electrophilic nature of BFEE catalyzes the deprotonation of aromatic compounds, decreasing the oxidation potential of such compounds [31,32]. In the specific case of thiophene derivatives, the formation of  $\pi$ -complexes with BFEE suppresses the resonance stability of the thiophene ring, thus facilitating the loss of electrons from the ring [33]. So the catalytic effect of BFEE enables the formation of high quality polymer films.

In the present work, we report a new synthetic route for the preparation of two thiophene derivatives bearing nitro- and dinitro- groups: 4"-nitrobenzoyl (thiophene-3'-yl)-1-ethylate (**NTh**) and 3",5"-dinitrobenzoyl (thiophene-3'-yl)-1-ethylate (**DNTh**), improving the previous route proposed by Welzel et al. [19]. Polymer films of **PNTh** and **PDNTh** were successfully electropolymerized by direct anodic oxidation of the monomers onto platinum or glassy carbon electrodes by using a mixed electrolyte containing TBABF<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> and BFEE (1:1, v/v). The electrochemical and spectroscopic properties of the monomers and polymers were investigated in details.

## 2. Experimental

### 2.1. Chemicals and equipments

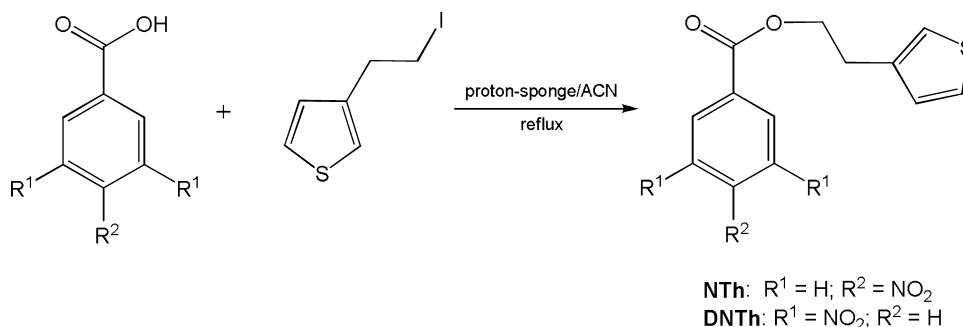
Most chemicals and solvents were purchased and used without further purification. The solvents CH<sub>3</sub>CN, CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> were dried and then distilled before the use, the first two under P<sub>2</sub>O<sub>5</sub> and the last one under CaH<sub>2</sub> [34]. The starting materials 3-(2'-Bromoethyl) thiophene and 3-(2'-Iodoethyl) thiophene were synthesized according to the previous literature [35]. The monomers **NTh** and **DNTh** were obtained as described below. BFEE was distilled and freshly used. Tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) was dried under high vacuum at 100 °C for 3 h before use.

NMR spectra (<sup>1</sup>H, <sup>13</sup>C and Cosy NMR) were obtained in a Varian spectrometer (Unity Plus, 300 and 400 MHz) using CDCl<sub>3</sub> as solvent. Infrared spectra were registered using a Bruker FTIR (IFS66, 1% sample KBr pellets) and ATR Varian FTIR (640-IR, film electropolymerized on Pt foil) spectrometers. Melting points were determined on Electrothermal equipment (Mel-Temp, analogic mode). Elemental analyses were performed in a Carlo Erba (EA 1110) and a Perkin-Elmer (CHN 2400) equipment. Gas chromatograms were carried out in a Varian (CP-3380) (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m DB-5 capillary column) using a 60–200 °C temperature range (10 °C min $^{-1}$ ). Gas chromatograms/mass spectra were carried out in a Shimadzu (GC/MS-QP5050A), using the same column and temperature ramp. UV-Vis spectra of the monomers and polymers, both solubilized in THF solvent, were carried out in a Perkin Elmer spectrophotometer (Lambda 650, double beam). Excitation and emission fluorescence spectra were recorded in a Shimadzu spectrofluorophotometer (RF-5301PC). All electrochemical experiments were carried out using an Autolab potentiostat/galvanostat PGSTAT30 (NOVA software v.1.10).

### 2.2. Synthesis of the monomers

#### 2.2.1. 4"-Nitrobenzoyl (thiophene-3'-yl)-1-ethylate - **NTh**

3-(2'-Iodoethyl) thiophene (0.712 g, 3.0 mmol), 4-nitrobenzoic acid (0.500 g, 3.0 mmol) and proton-sponge<sup>®</sup> (1.280 g, 6.0 mmol) were stirred for 5 hours in dry CH<sub>3</sub>CN (10 mL) at 75 °C. In the first hour of reaction, a white solid precipitated (proton-sponge iodine). This solid was removed by filtration and rigorously washed with diethyl ether. The reaction solution was rotaevaporated for diethyl ether extraction, and the reaction was continued until its completeness to be confirmed by GC. The remaining proton-sponge iodine precipitate was filtrated and washed with ethyl ether. The resulting solution (orange color) was rotaevaporated and the crude product was extracted with 0.01 mol L $^{-1}$  HNO<sub>3</sub>/CHCl<sub>3</sub> (1:1) biphasic solution (2  $\times$  50 mL, each extraction). The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and rotaevaporated. The crude product was solubilized in 10 mL of ethyl acetate/



Scheme 1. **NTh** and **DNTh** monomer preparations.

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