



Synthesis of a new π -conjugated redox oligomer: Electrochemical and optical investigation



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ABSTRACT

A new π -conjugated redox oligomer was prepared according a two-Step Synthesis. Firstly, an oligo-phenylene (OMPA) was obtained from the anodic oxidation of the (4-methoxyphenyl)acetonitrile. Then, the resulting material was chemically modified by the Knoevenagel condensation with the ferrocene-carboxaldehyde. This reaction led to a redox-conjugated oligomer the Fc-OMPA. The synthesized material was characterized using different spectroscopic techniques: NMR, FTIR, UV–vis and photoluminescence (PL) spectroscopy. The Fc-OMPA was used to modify a platinum electrode surface and the electrochemical response of the ferrocene redox-center was investigated by cyclic voltammetry. Moreover, the room temperature PL spectra of Fc-OMPA revealed that the ferrocene moiety, which acts as an electron donor, can effectively quench the oligomer luminescence. However, when ferrocene was oxidized to ferrocenium ion, the intramolecular charge transfer process was prevented which consequently enhanced the light emission. Thus, the oligomer light-emission can be, chemically or electrochemically tuned. The obtained results showed that the prepared material is a good candidate for the elaboration of electrochemical sensors and for the development of luminescent Redox-switchable devices.

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1. Introduction

Attaching metal groups to conjugated polymers and oligomers is currently an active area in the field of functional material design [1]. In fact, the resulting hybrid materials, where the properties of both metal complex and conjugated backbone may be coupled, exhibit great potential of applications in various fields, including energy, optoelectronic and sensors [2–14]. Metal-containing conjugated polymers can be divided into three categories according to the metal's position in the polymer chain structure. For the first type, the redox sites are covalently attached to the conjugated backbone by a non-conjugated spacer. In Type II, polymers have the metal directly coupled to the polymer backbone or coupled to the backbone by a conjugated linker. In the latter case, polymers

showed a greater degree of interaction with metal ions. The third type of polymer has the metal directly incorporated into the conjugated backbone.

Recently, we were interested on the synthesis of conjugated oligomers from the polyphenylene family [15–18]. In this work we report the synthesis of a Type II conjugated oligophenylene having a conjugated pendant group with ferrocene. In fact, ferrocene is widely used as a redox center for conjugated metallopolymers elaboration [12–14]. This organometallic sandwich compound presents distinct physical and chemical characteristics such as high redox activity, good electrochemical reversibility and generation of stable redox forms at a relatively low potential. The localization of these redox centers result in a charge transport mechanism through the redox-polymer film (electron hopping).

The designed material was prepared according a two-Step Synthesis. Firstly, a conjugated oligomer (OMPA) was electro-synthesized from the anodic oxidation of the (4-methoxyphenyl) acetonitrile. Secondly, this oligomer was chemically modified by the Knoevenagel condensation with the ferrocene-carboxaldehyde.

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The resulting material (Fc-OMPA) was characterized by different physico-chemical techniques and its electrochemical and optical properties were investigated.

2. Experimental section

2.1. Reagents

(4-methoxyphenyl)acetonitrile, ferrocenecarboxaldehyde and potassium tert-butoxide were provided by ACROS. Tetrahydrofuran, chloroform, diethyl ether and sodium tetrafluoroborate were purchased from SIGMA ALDRICH.

2.2. Electrochemical techniques

The voltammetric study was performed with a Voltalab10 apparatus from Radiometer driven by the Volta Master software. The working electrode and the counter electrode were a 2 mm diameter platinum disk and a platinum wire, respectively. An Ag/AgCl/KCl electrode was used as a reference electrode.

2.3. Spectroscopic analysis

FTIR analysis was performed with a Perkin Elmer Spectrum Two ATR-FTIR spectrometer, over the wave number range between 4000 and 450 cm^{-1} . ^{13}C and ^1H NMR studies were performed with a Bruker 300 MHz in CDCl_3 . The absorption spectra were recorded with a spectrophotometer Cary 5000. The PL spectra were measured at the room temperature using laser diode emitting at 375 nm as an excitation source.

2.4. Synthesis

2.4.1. OMPA synthesis

OMPA was synthesized by preparative electrolyses carried out at a constant current of 150 mA [15]. The supporting electrolyte used was tetraethyl ammonium tetrafluoroborate (NEt_4BF_4). The (4-methoxyphenyl)acetonitrile (MPA) concentration was about 0.1 M. Homogenization of the solution was performed by mechanical stirring. The electrolyses were stopped after consumption of 2 F/mole of the starting material. The electrolysis solutions were evaporated under vacuum for eliminating the major part of the acetonitrile, then 50 mL of water was added and an extraction with dichloromethane was performed to eliminate the supporting salt. The organic phase, containing the electrolysis products, was concentrated and then precipitated in diethyl ether. OMPA was obtained by filtration as a brown powder. The results of gel permeation chromatography analyses indicated that the average chain length for OMPA was about 5–6 units.

2.4.2. Synthesis of (Z)-2-(4-methoxyphenyl)-3-(ferrocen-1-yl)acrylonitrile (Fc-MPA)

t-BuOK (226 mg, 2.02 mmol, 2.02 equiv.) was added to a stirred solution of ferrocenecarboxaldehyde (214 mg, 1.0 mmol, 1.0 equiv.) and (4-methoxyphenyl) acetonitrile (147 mg, 1.0 mmol, 1.0 equiv.) in anhydrous THF (10 mL) at 0 °C. The mixture was stirred for 2 h at room temperature, and then quenched by addition of aq. NH_4Cl . The reaction mixture was concentrated and then diluted with dichloromethane (50 mL). The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4 . The yield of the reaction is 92%. mp = 97 °C; ^1H NMR (300 Hz, CDCl_3) 3.87 (3H, s), 4.25 (5H, s), 4.52 (2H, t, $J = 1.8$ Hz), 4.96 (2H, dd, $J_1 = 2.1$ Hz, $J_2 = 1.8$ Hz), 6.95 (2H, m), 7.28 (1H, s), 7.54 (2H, m). ^{13}C NMR (300 MHz, CDCl_3) 54.94, 69.24, 69.38, 70.71, 106.03, 113.94, 118.74, 125.97, 126.90, 140.57 and 159.25.

2.4.3. Fc-oligo-methoxyphenyl acetonitrile (Fc-OMPA) synthesis

A 25 mL reaction vessel, equipped with a magnetic stirrer, was charged with OMPA (147 mg) and ferrocenecarboxaldehyde (214 mg) dissolved in 10 mL of anhydrous THF. To this mixture was added the t-BuOK (336 mg) at 0 °C. The mixture was stirred for 24 h at room temperature, and then quenched by addition of aq. NH_4Cl . The reaction mixture was concentrated and then diluted with dichloromethane (50 mL). The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4 . Finally Fc-OMPA was precipitated in diethyl ether and recovered by filtration as a purplish red powder.

2.5. Preparation of modified electrode

The modified electrode was prepared by dip-coating method: this procedure consists of immersing the platinum electrode in a solution of Fc-OMPA in methylene chloride (10 mg/mL) for a period sufficient for spontaneous film adsorption. Then the film was allowed to dry on the electrode surface.

2.6. Preparation of a chemically and electrochemically oxidized/reduced FcOMPA

The oxidation state of ferrocene was monitored by chemical oxidation of FcOMPA and subsequent reduction. Iron III ion and ascorbic acid was previously described as effective reagents for oxidizing ferrocene and reducing ferrocenium ion, respectively [19]. Therefore, the oxidation of ferrocene moiety was achieved by adding a negligible volume (5 μl) of a concentrated solution of FeCl_3 (0.5 M) to an Fc-OMPA solution (4 mg/10 mL). The chemical reduction of the chemically oxidized Fc-OMPA was performed using an excess of ascorbic acid. Both chemical oxidation and reduction were monitored by UV-visible analysis. Amounts of Fe^{3+} ions and ascorbic acid were added until no changes were observed for the recorded spectra.

The oligomer was electrochemically oxidized using a three-electrode setup in an electrolytic solution of sodium tetrafluoroborate (NaBF_4 , 0.1 M) in water. Oligomer film was spin-coated onto an indium tin oxide (ITO) coated glass slides used as working electrode. Oxidation was performed by maintaining a constant potential of 0.800 V between the working electrode and an Ag/AgCl reference electrode. For the electrochemical reduction, a potential of 0 V was applied to the working electrode. The progress of the electrochemical oxidation/reduction was followed by chronoamperometry for 30 min and by UV/visible spectrophotometry.

3. Results and discussion

3.1. Synthesis and structural characterization

The oligomer OMPA was prepared as described earlier from the electrochemical oxidation of (4-methoxyphenyl)acetonitrile [15]. Then, it was subjected to a chemical modification via the Knoevenagel condensation as depicted in Scheme 1. The resulting material was analyzed by NMR and FTIR spectroscopy. Parallely, we have prepared the (Z)-2-(4-methoxyphenyl)-3-ferrocenylacrylonitrile (Fc-MPA) resulting from the condensation of the monomer (4-methoxyphenyl) acetonitrile with the ferrocenecarboxaldehyde. Fc-MPA will serve as a model for different signal assignment.

The Fc-OMPA ^1H NMR spectrum (Fig. 1) showed broad peaks between 3.0 and 5.1 ppm assigned to protons of the unreacted $-\text{CH}_2-\text{CN}$, the methoxy and the ferrocene groups. The aromatic and ethylenic protons appear in the ranges of 6.5–7.8 ppm.

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