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Rapid-scan time-resolved FT-IR spectroelectrochemistry – Study on the electron transfer of ferrocene-substituted thiophenes

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ABSTRACT

A series of ferrocene-substituted thiophenes, 2-ferrocenylthiophene, 2,5-diferrocenylthiophene and 2,3,5-triferrocenylthiophene have been synthesized. The electron transfer mechanism during redox process of the ferrocenyl complexes was studied by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and rapid-scan time-resolved FT-IR spectroelectrochemistry (RS-TRS FT-IR). Electrochemistry and RS-TRS FT-IR spectroelectrochemistry results indicated the redox process of 2,5-diferrocenylthiophene and 2,3,5-triferrocenylthiophene involved two and three consecutive one-electron steps, respectively. IR absorption peaks arisen from intermediate appearing and disappearing on the experimental time scale in the oxidation and reduction process of 2,5-diferrocenylthiophene and 2,3,5-triferrocenylthiophene were clearly observed by the RS-TRS FT-IR spectroelectrochemistry. A kinetics simulation experiment, based on the results of RS-TRS FT-IR spectroelectrochemistry, was conducted to give the kinetics parameters of 2,5-diferrocenylthiophene.

1. Introduction

The study of electron or energy transfer between two redox active centers across an unsaturated organic bridge has attracted extensive attention. The electron transfer (ET) or Electron donor–acceptor (EDA) of ferrocene complexes has been extensively investigated because of the good thermal stability and exceptional electrochemical properties of ferrocene. These properties also make ferrocene-based complexes good candidates for the preparation of new materials which can be applied in organic synthesis, catalysis and materials science [1,2]. For decades, research into the synthesis and electronic properties of ferrocene complexes has been focused on [3–7] .

Thiophene derivatives show great optical and electronic properties, and several studies of ferrocenyl complexes containing thiophene ring have been carried out [8–11]. In the literature [8,12], CV and Osteryoung square waver voltammetry (OSWV) were used to evaluate the redox properties, the degree of interaction and the possibility of "electronic communication" among the ferrocene centers. Recently, there is a growing interest in the spectroelectrochemistry studies on these complexes [10,13–15], UV–Visible and in situ FT-IR spectroscopy were most widely used to investigate the mechanism of electron transfer. Although a good amount of experimental and theoretical work has been done on such complexes, a lot more remains to be performed.

Fourier transform IR absorption spectroscopy is one of the useful tools for molecular characterization and identification. In situ infrared spectroelectrochemistry can provide the property of electrode/electrolyte interfaces at the molecular level. What is more, the time-resolved Fourier transform infrared spectroscopy (TRS FT-IR) helps us to understand the dynamic characteristics in fast reactions. In the previous work [16], it was demonstrated that the RS-TRS FT-IR spectroelectrochemistry was a powerful method for the study on electron transfer mechanism during redox process. The technique provides the detailed information about the intermediates producing and vanishing during the electrochemical process. 1,4-Benzoquinone and 1,4-bis(2-ferrocenylvinyl)benzene were studied by this method.

In the present study, a series of ferrocenyl complexes containing thiophene ring have been prepared by Suzuki and cross-coupling reaction of bis(ferrocenyl)mercury (Fc_2Hg) with aryl iodides. Then CV, DPV and RS-TRS FT-IR spectroelectrochemistry were used to study the redox properties. RS-TRS FT-IR spectroelectrochemistry provides a clear demonstration of the electrochemical process. The intermediate, produced by electrode reaction, is facilely observed by the technique and help us to have a complete unstanding of the electron transfer mechanism.

2. Experimental

2.1. Preparation of 2-ferrocenylthiophene

2-Ferrocenylthiophene was synthesized according to the method in the literature [17].

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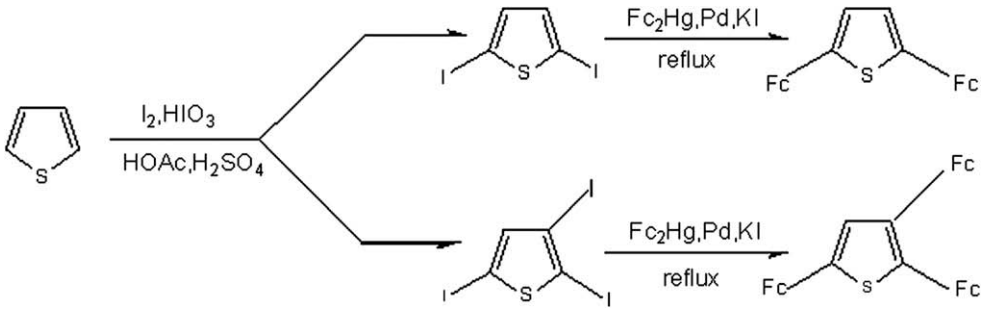

Scheme 1. Reaction Scheme for Preparation of 2,5-diferrocenylthiophene and 2,3,5-triferrocenylthiophene.

2.2. Preparation of 2,5-diferrocenylthiophene

Scheme 1 shows the route for preparation of 2,5-diferrocenylthiophene and 2,3,5-triferrocenylthiophene. Bis(ferrocenyl)mercury was prepared according to the method in the report [18,19]. Firstly, a 250 mL, round-bottom flask was charged with thiophene (1.68 g) and 70 mL mixture solution of HOAC/H_2O/H_2SO_4 (90:7:3, v/v/v), the reaction mixture was stirred for 20 min. Then, I_2 (5.07 g) and HIO_3 (2.12 g) were added. The reaction was heated to 70 °C for 10 h. Then, the mixture was cooled and a spin-like solid, 2,5-diiodothiophene was collected and dried [20]. At last, we get the product via this reaction: to THF-acetone (3:2, v/v), which was added 2,5-diiodothiophene, bis(ferrocenyl)mercury, 4 eq. KI and purged with nitrogen for 30 min, was added $Pa(PPh_3)_4$, then, the reaction was heated to refluxed for 5 h under a nitrogen atmosphere. The solvent was then removed, the residue taken up in CH_2Cl_2 and filtered. The CH_2Cl_2 solution was washed with water and then dried over anhydrous sodium sulfate overnight. The solvent was then removed and the residue chromatographed on a chromatotron. Yield 75% for the product. ν_{max}(KBr)/cm^{-1} 3084, 2923, 2853, 1406, 1248, 1103, 1024, 1020, 1001; δ_H($CDCl_3$) 6.72(2H, ArH), 4.60(4H, C_5H_4), 4.31(4H, C_5H_4), 4.11(10H, C_5H_5); *m*/*z* 450(30%), 452(M^+, 100), 453(32%).

2.3. Preparation of 2,3,5-triferrocenylthiophene

First, a 250 ml, round-bottom flask was added thiophene (2.1 g), acetic acid (16 ml), water (7.4 ml), carbon tetrachloride (6 ml), sulfuric acid (0.42 ml), iodine (7.6 g), and iodic acid (2.7 g) were refluxed for 100 h. Then water and CH_2Cl_2 were added. The organic layer was washed with water, 0.1 M $Na_2S_2O_3$, and water again. The organic phase was dried over Na_2SO_4. The solvent was evaporated and the residue was crystallized from ethanol to give 2,3,5-triiodothiophene [21]. The second, the product 2,3,5- triferrocenylthiophene was synthesized via the same reaction as 2,5-diferrocenylthiophene. The yield is 75%. ν_{max}(KBr)/cm^{-1} 3091, 2924, 2853, 1447, 1408, 1108,

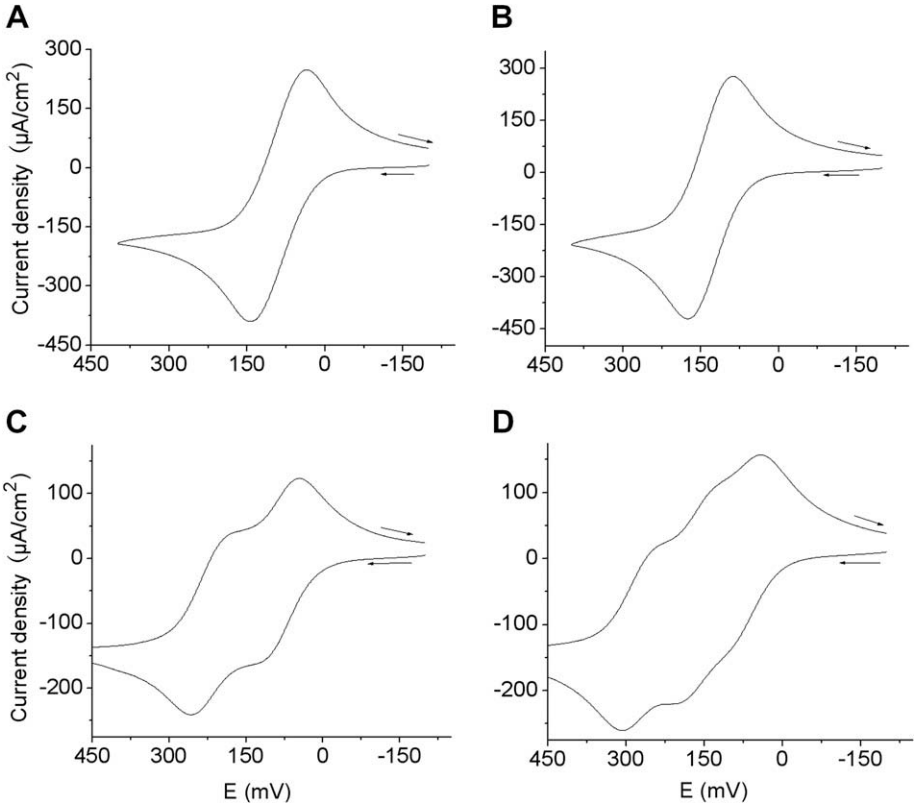

Fig. 1. Cyclic voltammograms of 1 mM solution of (A) ferrocene, (B) 2-ferrocenylthiophene, (C) 2,5-diferrocenylthiophene and (D) 2,3,5-triferrocenylthiophene in 0.3 M TBAP/CH_2Cl_2 (vs. Ag/Ag^+). Scan rate, 50 mV s^{-1}.