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The study of ferrocenium complexes-DNA interaction based on Langmuir–Blodgett films modified electrode

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ABSTRACT

In this paper, electrochemical method was used to investigate the interactions between DNA and amphiphilic ferrocenylimine. The method was developed using the system of electrode modified with the amphiphilic ferrocenylimine LB films. Electrochemical results obtained from amphiphilic ferrocenylimine LB films modified electrode suggested that the forrocenium derivative could interact strongly with dsDNA. It was observed that the binding of amphiphilic ferrocenylimine to DNA led to a significant peak current decrease of amphiphilic ferrocenylimine LB films modified electrode. The interactions between amphiphilic ferrocenylimine and four basic groups were also investigated, the results revealed that the basic groups cytosine, thymine and adenine could interact with forrocenium complex, but guanine showed no interaction with forrocenium complex. The order of interaction intensity for four basic groups with forrocenium complex (from strong to feeble) is cytosine > thymine > adenine > guanine. Therefore, the amphiphilic ferrocenylimine interacted with DNA through the basic groups cytosine, thymine and adenine.

1. Introduction

Recently, cyclopalladated ferrocenylimine have attracted enormous attention because of their antitumor activity [1]. Many ferrocenyl derivatives have shown good effect as antitumor agents, and some of them have been applied in clinical trials [2,3]. Kiipf-Maier et al. [4] reported on the anti-tumour properties of ferrocenium salts against Ehrlich ascites tumour (EAT). Jaouen and co-workers [5–7] prepared several ferrocenyl derivatives which were biologically examined in vitro and in vivo. The results showed that these ferrocifens were discovered firstly which could show active against both hormone-dependent and hormone-independent breast cancer cells. Champdore et al. [8] prepared some adducts by incorporating the ferrocenemethyl moiety into a heterocyclic base. The ferrocenyl derivatives of 3′-deoxy-3′-azidothymidines were the sole compounds which were active against HIV-1.

Due to the importance of DNA as the primary holder of genetic information for cells, the study and detection of this substance has become an important research area in the life science [9]. So the work focused on the interactions of ferrocenium complexes with DNA has enormous significance. Liepold et al. [10] described a new and simple electrochemical approach for hybridization detection without the need for labeling the target DNA. The EDDA (electrically detected displacement assay) method was used to characterize the hybridization state of label-free capture probe DNA immobilized on gold electrodes with a solution of short redox-labeled signaling oligonucleotides. Brisset et al. [11] reported the synthesis and the characterization of the first electro-active ferrocene-labeled oligonucleotide phosphorothioate ferrocene derivative probe obtained by automated synthesis and confirmed the potential of ferrocene-labeled oligonucleotide phosphorothioate to develop electrochemical DNA chips.

Ferrocene and its derivatives are often used in DNA detection because of their favorable electrochemical properties [12,13]. Electrochemical studies on ferrocenium complexes–DNA interactions have recently attracted much attention due to the using of low cost, simple and small devices with respect to the spectroscopic methods. At the same time, numerous voltammetric methods especially using chemically modified electrodes (CME) have been developed [14–16].

LB technique is a useful way to form ultrathin organic films [17] with sequential layers in which the thickness and the order of the film at the molecular scale can be precisely controlled [18]. In this paper, the forrocenium derivatives LB films modified electrode was employed to analyse the interaction between forrocenium

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Abbreviations: (LB), Langmuir–Blodgett; (GCE), glassy carbon electrode; (SCE), saturated calomel electrode; (π-A isotherm), surface pressure–area isotherm; (CV), cyclic voltammograms; (DPV), differential pulse voltammetry; (DNA), deoxyribonucleic acid.

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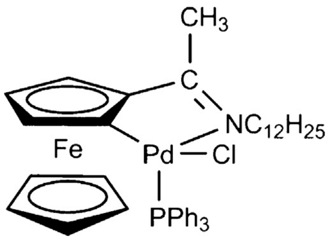

Fig. 1. Structure of the forrocenium complex.

derivatives with DNA, which is expected to be used as electrochemical DNA biosensors.

2. Experimental

2.1. Chemicals and reagents

Cyclic voltammetry and Differential Pulse Voltammetry was performed with a Model 650A electrochemical system (CH Instruments Company, USA). A glassy carbon electrode (GCE, 3 mm in diameter) coated LB films of forrocenium complex as the working electrode, with a saturated calomel electrode (SCE) and a platinum wire acting as reference and counter electrodes, respectively. All potentials were reported versus SCE. All measurements were conducted in solutions deaerated by bubbling N2 for 10 min.

Amphiphilic ferrocenylimine was synthesized by ourselves with pure of >95%. The structure of the forrocenium derivative is shown in Fig. 1. The synthesis steps consulted the reference [19]. All chemicals were purchased in analytical regent grade and used without further purification. The water was redistilled in quartz vessel. Measurement of surface pressure (π)-area (A) isotherms was carried out with a Langmuir–Blodgett system (KSV-5000-3, KSV Instruments, Helsinki, Finland). The monolayer was transferred onto a glassy carbon electrode at 20 ± 0.5 °C. De-ionized water was obtained by Milli-Q ultrapure water apparatus (the specific resistance is 18.2 MΩ cm)

2.2. Preparation of LB films

The experiments were carried out at room temperature, approximately 22 °C. Prior to deposition, the GCE was polished with 0.1 mm aluminum slurry, rinsed thoroughly with redistilled water and sonicated successively in ethanol and redistilled water, each for 3 min. The electrodes were electrochemically pretreated by cycling the electrode in 0.5 mol/L H2SO4 (scan rate, 100 mV/s − 1; potential-scan range, −1.0–1.0 V). A sample of amphiphilic ferrocenylimine in a chloroform solution was spread onto pure water using a syringe, allowing the solvent to evaporate for 30 min before compression with two parallel barriers which compress or expand symmetrically at the same rate from two sides of the trough. A Wilhelmy balance was used as a surface pressure sensor and situated in the middle of the trough. The Langmuir film was compressed at a rate of 10 mm/min and then transferred to GCE with a rate of 3 mm/min (vertical dipping) under surface pressure of 15 mN/m.

3. Results and discussion

3.1. π–A isotherms

The π–A isotherm of the forrocenium derivative on the pure water surface was presented in Fig. 2. The face pressure was low with a relatively high area per molecule, and further compression showed a continuous rise of isotherms. During the compression process of the apparently condensed phase, a sharp rise of the surface pressure at the air/water interface was observed. The monolayer film began to collapse at surface pressure of 48 mN/m, suggested that the forrocenium derivative could form stable monolayer film on the water surface. And the limiting area of per molecule was 0.7 nm^2, which obtained by extrapolating the linear part of the isotherm to $\pi = 0$.

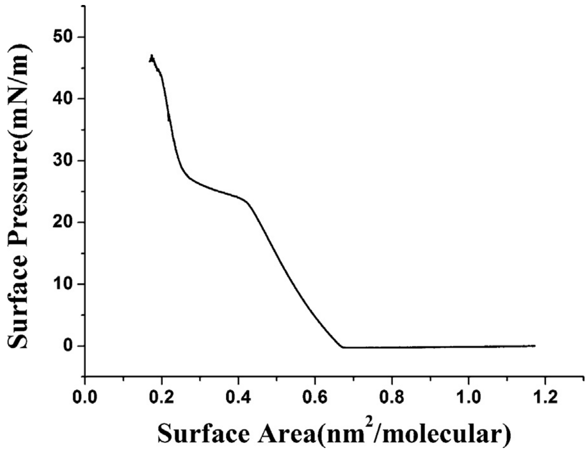

Fig. 2. Surface pressure (π)–area (A) isotherm of forrocenium complex.

3.2. Electrochemical behavior of the forrocenium complex LB film modified electrode

3.2.1. Cyclic voltammetry behavior

Fig. 3 shows the Cyclic voltammogram of the forrocenium complex LB films modified electrode in 0.1 M KClO4 buffer solution (pH 1.5) at scan rate of 100 mV/s. Forrocenium complex LB films were obtained at surface pressure of 15 mN/m. One pair of well-defined and stable redox peaks were observed for the compound, which were attributed to the redox of ferrocene (Fc). Generally, this pair of redox peaks were attributed as Fc/Fc$^+$. The anodic peak potential Epa, cathodic peak potential Epc and formal potential E0 (taken as the average of Epa and Epc) of the compound were 0.552 V, 0.456 V and 0.504 V respectively. The peak potential difference ΔEp (Epa − Epc) was about 96 mV and peak current ratio (ipa/ipc) is about 1 for the compound.

The current character of the electrode process was identified by the relationship between peak currents (i_p) and scan rate (ν). Fig. 4 shows the Cyclic voltammograms of forrocenium complex LB films modified electrode at different scan rates. Scan rates from inner to outer were 20, 40, 60, 80, 100, 120, 140, 160, and 180 mV/s, respectively. Fig. 5 shows the relationship between peak currents

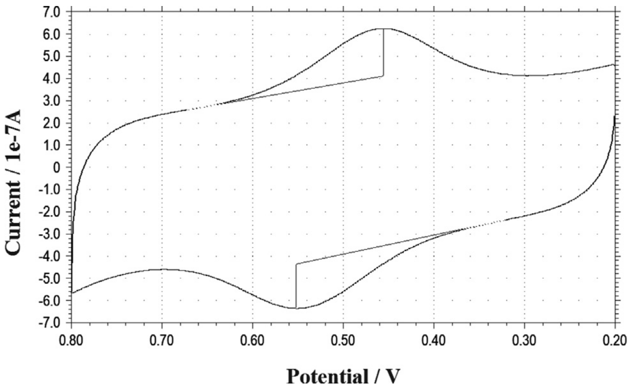

Fig. 3. The Cyclic voltammograms of the forrocenium complex LB film modified electrode. Solution: 0.1 M KClO4 (pH 1.5); Scan rate: 100 mV/s.