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# Electrochemical Investigation of a Tm(III)–5,10,15,20-Tetrakis(4-isopropylphenyl)porphyrin Complex Modified Glassy Carbon Electrode and its Interaction with Bovine Serum Albumin

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The electrochemical behavior of a glassy carbon (GC) electrode modified with a thin Tm(III)–5,10,15,20-tetrakis(4-isopropylphenyl)porphyrin complex ([Tm(iPPP)( $\mu$ -OH)(H<sub>2</sub>O)]<sub>2</sub>) film was investigated. Two pairs of voltammetric current peaks  $P_1$  and  $P_2$  located at about +0.75 and +1.00 V were observed in the potential range 0.00 to +1.20 V. It was found that anions greatly affect the electrochemical characteristics of the [Tm(iPPP)( $\mu$ -OH)(H<sub>2</sub>O)]<sub>2</sub> film on the GC electrode. A near Nernstian response of ClO<sub>4</sub><sup>-</sup> was observed. Furthermore, the interaction of the [Tm(iPPP)( $\mu$ -OH)(H<sub>2</sub>O)]<sub>2</sub> film with bovine serum albumin (BSA) was studied. The shape of the voltammetric current peaks changed greatly after soaking the modified electrode in BSA solution for 50 min. An irreversible reduction peak was appeared at +0.367 V,  $P_2$  disappeared and  $I_{p1}$  decreased with the concentration of BSA increased. This result was also verified by fluorescence spectrophotometry. Analysis of the modified electrode's surface morphology confirmed that BSA has indeed interacted with the complex modified on the electrode.

**Keywords:** Thulium–porphyrin complex; Bovine serum albumin; Modified electrode; Voltammetry

## INTRODUCTION

Although rare earth metals (REMs) are biologically nonessential elements, a large number of agricultural tests of REMs indicate that appropriate amounts can improve the photosynthesis in plants [1], and REMs

injected into human body may greatly affect the performance of respiration and the cardiovascular system [2]. Additionally, REM porphyrin and texaphyrin complexes have been utilized extensively as diagnostic agents and radiation sensitizer in clinical research [3,4]. It was found that REMs possess a special affinity to tumor cells [5], for example, 70% of <sup>169</sup>Yb was found to accumulate in tumors 10 minutes after intravenous injection. Among the REMs, thulium was considered as the most suitable element for the detection of tumors, because it has the highest affinity for them [6].

Furthermore, some synthetic porphyrins and metalloporphyrins have been applied to the diagnosis and treatment of diseases [7], especially in the detection of early-stage tumors [8–10] and in the field of photodynamic therapy (PDT) of cancers [11–13]. Nevertheless, selective delivery of porphyrins to tumor cells was the major challenge in the detection and PDT of tumor tissues. This has been achieved partly by using selective delivery systems such as monoclonal antibodies, liposomes, and albumins [14,15]. The amphiphilic porphyrins were carried largely by serum albumins and serum proteins after they are given by intravenous injection. These carrier molecules can interact preferentially or specifically with cancer cells [14,16]. PDT using porphyrins and their analogues as photosensitizers has been found to be mediated

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mainly by mitochondrial benzodiazepin receptors [17]. Studies on specific serum albumin binding might be highly pertinent as a model for mitochondrial interactions with porphyrins [18]. Hematoporphyrin derivatives also showed cooperative binding with human serum albumin (HSA) [19]. Therefore, we decided to study the electrochemical characteristics of thulium–porphyrin complex and its interaction with bovine serum albumin (BSA).

In this paper, the electrochemical behavior of a  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]$  modified GC electrode in 0.1 mol/l  $\text{NaClO}_4$  was studied in detail. The effect of anions on the voltammetric behavior of the modified electrode illustrated that  $\text{ClO}_4^-$  incorporated into the film during the redox processes of the film and a new complex was formed after the modified electrode had been soaked in BSA solution.

## EXPERIMENTAL

### Materials

A schematic illustration of the synthesis of  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]$  complex is shown in Fig. 1. Details of the synthesis will be published elsewhere [20]. BSA was obtained from BoAo Biological Co. (Shanghai, China). Other reagents were of analytical grade and used without further purification. A  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]$  solution was prepared by dissolving an appropriate amount of  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]$  in  $\text{CH}_2\text{Cl}_2$ . All other solutions were prepared with distilled water.

### Measurements

A glassy carbon (GC) electrode (2 mm in diameter) was polished to a mirror finish with polish paper and 0.3–0.05  $\mu\text{m}$  alumina slurry and cleaned thoroughly in an ultrasonic bath with 1:1 nitric acid solution, alcohol and water. Then the electrode was coated by applying 1  $\mu\text{l}$  of  $2.0 \times 10^{-4}$  mol/l  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]$  solution on the electrode surface, and dried under an infrared lamp.

The surface morphology of the modified electrode was examined using atomic force microscopy with contact model (Molecular Imaging, PicoScan) (scanner was 6  $\mu\text{m}$ ). Voltammetric and chronoamperometric data were obtained with a three-electrode system using a CHI 660A electrochemical workstation (CH Instruments, Texas, USA). The modified electrode was used as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. A small beaker containing 10 ml 0.1 mol/l  $\text{NaClO}_4$  was used as the electrochemical cell. Electrochemical experiments were carried out at room temperature ( $20 \pm 2^\circ\text{C}$ ).

Fluorescence spectra were taken on a RF-5000 spectrofluorimeter (Shimadzu, Japan) with a slit width of 5 nm for both excitation and emission spectra at room temperature. In all experiments, a fresh BSA solution was prepared daily.

## RESULTS AND DISCUSSION

### Voltammetric Behavior of the $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]$ Modified Electrode

Figure 2a shows a typical cyclic voltammetric response of the  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]$  modified electrode in a 0.1 mol/l  $\text{NaClO}_4$  solution. On the first cycle, only an anodic peak at +1.104 V followed by a cathodic peak at +0.668 V was observed. On the other hand, two pairs of current peaks were recorded from the second cycle, the first pair ( $P_{1c}/P_{1a}$ ) was located at +0.664 and +0.832 V, and the second ( $P_{2c}/P_{2a}$ ) at +0.948 and +1.089 V, respectively. In subsequent potential cycling, all current peaks shifted slightly towards negative potentials. A pronounced decrease of  $P_{2a}$  was found to be different from a slow increase of the peak currents of  $P_{1c}$ ,  $P_{1a}$  and  $P_{2c}$ . After five cycles at 100 mV/s in the potential range of 0.00 ~ +1.20 V, the peak currents of  $P_{1c}$ ,  $P_{1a}$  and  $P_{2c}$  reached their maximal. Then they started to deteriorate and all current peaks disappeared completely after numerous cycles indicating that the  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]$  thin film was electro-

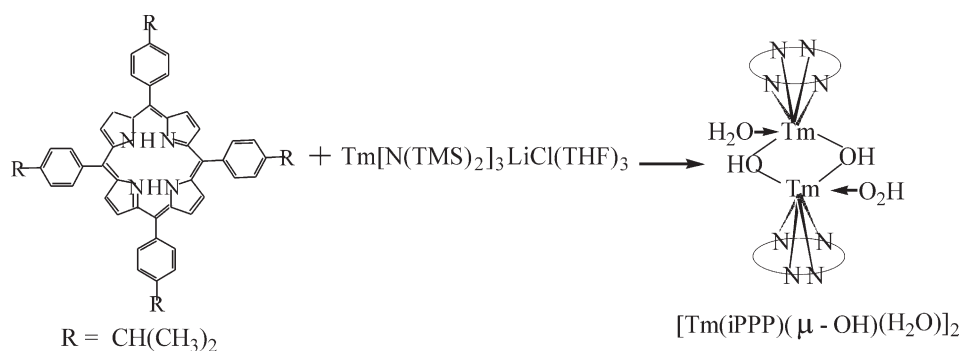


FIGURE 1 Scheme of the synthesis of  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]$ .

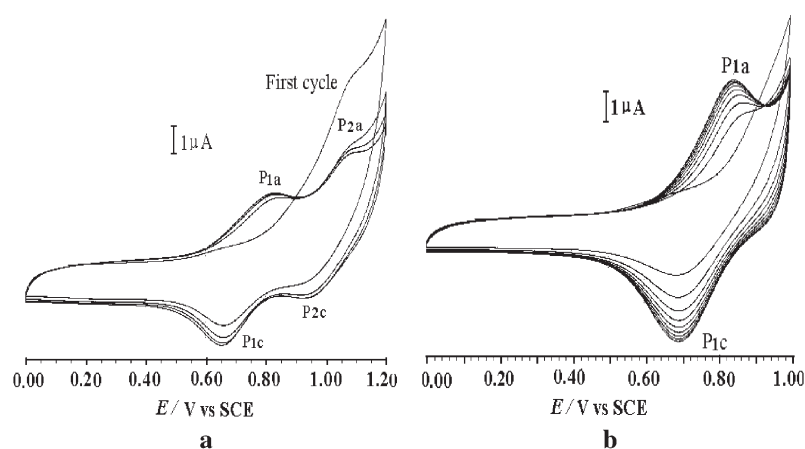


FIGURE 2 Cyclic voltammograms of the modified electrode in different potential cycling range. Supporting electrolyte: 0.1 mol/l  $\text{NaClO}_4$ ; scan rate: 100  $\text{mV/s}$ .

chemically unstable in the potential overrun +1.20 V. A possible reason might be that the sharp increase in oxidation current at extremely positive potentials ( $>1.20$  V) is due to the oxidation of the porphyrin ring of the complex and the oxidation product is not stable in aqueous solution.

By varying the potential cycling range, evident changes in the electrode response were observed. The voltammetric response of the modified electrode obtained in the potential range from 0.00 to +1.00 V is shown in Fig. 2b. At the first cycle, only one cathodic peak located at +0.706 V was recorded. An ill-defined anodic peak appeared upon the second cycle. The peak currents increased with slightly negative shifts in peak potentials of both peaks in subsequent cycling and a steady-state was achieved after 5 min. When the steady-state had been achieved, the peak potentials were fixed +0.838 V for  $E_{P1a}$  and +0.694 V for  $E_{P1c}$ , respectively. A peak-to-peak potential separation ( $\Delta E_p$ ) of 140 mV was obtained, and the ratio of  $I_{P1a}$  to  $I_{P1c}$  is approximately unity. Figure 3a shows the dependence of the cathodic peak current on the scan rate for the modified electrode. The cathodic peak current up to 50  $\text{mV/s}$  is proportional to the scan rate (---), showing thin layer like behavior. A deviation was seen when scan rate was higher than 50  $\text{mV/s}$ . The

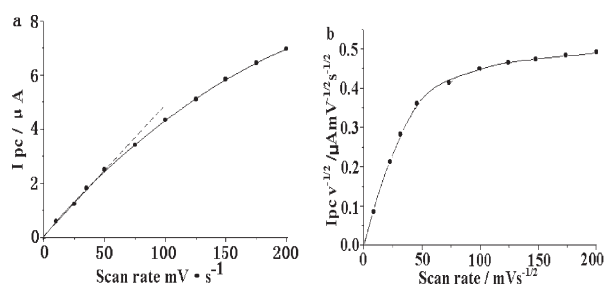


FIGURE 3 (a) The relationship of  $I_{P1c}/v$  for the modified electrode in 0.1 mol/l  $\text{NaClO}_4$ . (b) Plot of  $I_{P1c}/v^{-1/2}$  vs.  $v$  for the modified electrode in 0.1 mol/l  $\text{NaClO}_4$ .

plot of  $I_{P1c}/v^{-1/2}$  vs.  $v$  for the modified electrode indicated the independence of  $I_{P1c}/v^{1/2}$  on  $v$  at higher scan rate, especially higher than 100  $\text{mV/s}$ , suggesting that  $I_{P1c}$  was proportional to  $v^{1/2}$  and corresponding to a diffusion controlled process [21].

Potential step chronoamperometric experiments were carried out to more closely examine the charge diffusion behavior, with the results shown in Fig. 4. The  $i-t^{-1/2}$  predication of the semi-infinite diffusion-based control equation is observed at sufficiently short time in the current-time decay. The fall-off of current indicates that at longer times the process cannot be taken as infinite diffusion and a finite diffusion boundary condition must be invoked [22,23].

#### Influence of Supporting Electrolytes on the Voltammetric Behavior of the Modified Electrode

The effect of cations in the supporting electrolytes on the voltammetric behavior of the modified electrode was investigated in solutions of 0.1 mol/l  $\text{LiClO}_4$ ,

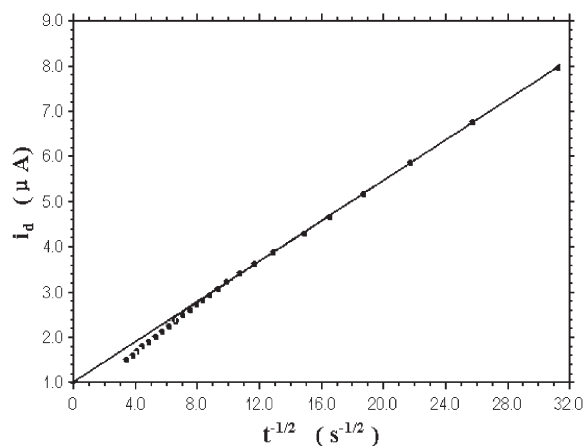


FIGURE 4 Cottrell plot for the modified electrode following potential step from +0.40 to +1.00 V vs. SCE. Supporting electrolyte 0.1 mol/l  $\text{NaClO}_4$ .

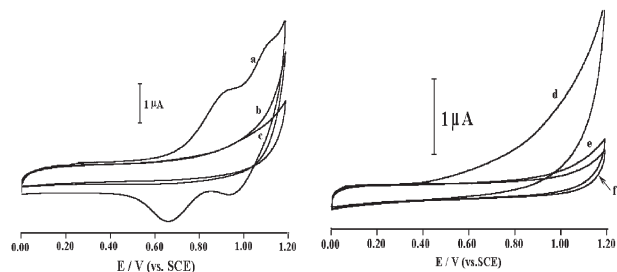


FIGURE 5 Cyclic voltammograms of the modified electrode in 0.1 mol/l NaClO<sub>4</sub> (a); 0.1 mol/l NaCl (b); 0.1 mol/l NaNO<sub>3</sub> (c); 0.1 mol/l Na<sub>2</sub>CO<sub>3</sub> (d); 0.1 mol/l Na<sub>2</sub>HPO<sub>4</sub> (e); and 0.1 mol/l Na<sub>2</sub>SO<sub>4</sub> (f). Scan rate: 100 mV/s.

NaClO<sub>4</sub>, KClO<sub>4</sub> and NH<sub>4</sub>ClO<sub>4</sub>. It was found that the cations had little effect on the voltammetric behavior of the modified electrode.

The effect of anions on the electrochemical behavior was studied, respectively, in 0.1 mol/l solutions of NaCl, NaClO<sub>4</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>. In each case the modified electrode was cycled in the supporting electrolyte solution to achieve a steady-state. As shown in Fig. 5, the anions had marked effect on the voltammetric behavior of the modified electrode. Only in 0.1 mol/l NaClO<sub>4</sub> solution, two pairs of voltammetric current peaks were observed in the potential range of 0.00– +1.20 V.

In addition, the concentration of ClO<sub>4</sub><sup>-</sup> (C) has significant influence on the voltammetric behavior of the film. Figure 6 illustrates cyclic voltammograms of the modified electrode in solutions containing different amounts of NaClO<sub>4</sub> (keeping the total ionic strength constant at 0.1 mol/l by adding KCl to the solution), peak potentials shifted positively and ΔE<sub>P</sub> turned broader with the decrease of the concentration of NaClO<sub>4</sub>. No oxidation peak was observed when the concentration of ClO<sub>4</sub><sup>-</sup> was lower than 5.0 × 10<sup>-5</sup> mol/l. The insert summarizes the formal potentials, E<sub>0</sub> (estimated from the average of anodic peak and cathodic peak potentials), for one complete set of measurements performed in solution containing various amounts of NaClO<sub>4</sub> from 1 × 10<sup>-4</sup> to 10<sup>-1</sup> mol/l. It was found that the modified electrode displayed a near Nernstian response for ClO<sub>4</sub><sup>-</sup>. E<sub>0</sub> was linear dependence on the logarithm of ClO<sub>4</sub><sup>-</sup> concentration and the linear regression equation was E<sub>0</sub> = -0.0578 logC + 0.7131 with a correlation coefficient r<sup>2</sup> = 0.993. It is probably due to the fact that ClO<sub>4</sub><sup>-</sup> fulfils the requirement of electroneutrality of the film while the complex was oxidized and the coordinating molecule H<sub>2</sub>O was substituted by the ClO<sub>4</sub><sup>-</sup> incorporated into the film. Hence, the reduction and oxidation processes of the [Tm(iPPP)(μ-OH)(H<sub>2</sub>O)]<sub>2</sub> film in the NaClO<sub>4</sub> solution can be proposed as follow:

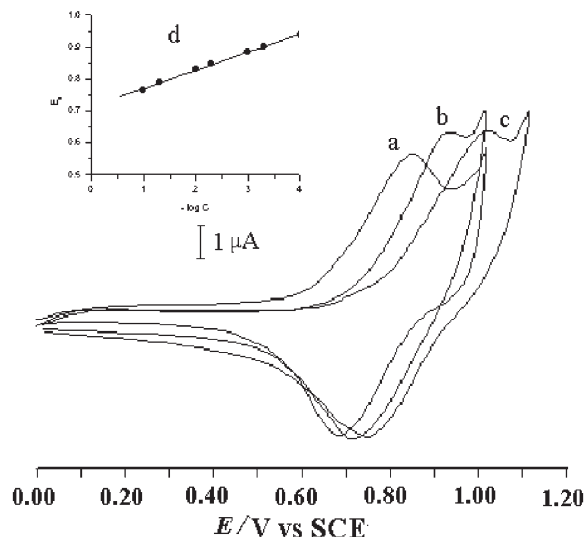
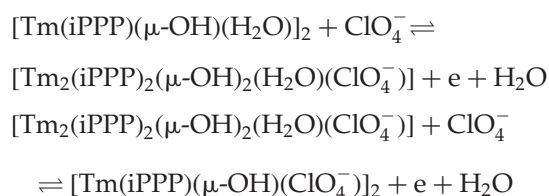


FIGURE 6 Cyclic voltammograms of the modified electrode in (a) 0.1 mol/l NaClO<sub>4</sub>, (b) 0.01 mol/l NaClO<sub>4</sub> + 0.09 mol/l KCl, (c) 0.001 mol/l NaClO<sub>4</sub> + 0.1 mol/l KCl, respectively. (d) A plot of formal peak potentials vs. -logC. Scan rate: 100 mV/s.



#### Effect of pH on the Voltammetric Behavior of the Modified Electrode

The dependence of the oxidation and reduction peak potentials (E<sub>P1a</sub> and E<sub>P1c</sub>) on the pH of the supporting electrolyte was studied by adjusted the solution to appropriate value with NaOH and HCl solution. No observable changes in the peak potentials were obtained in the pH range 0.170–7.20. The anodic peak shifted positively and cathodic peak shifted negatively with further increase of pH from 8.00 to 13.20. This may be ascribed to the coordination of OH<sup>-</sup> to the metal centers within the film [24].

#### The Effect of the Surface Coverage of [Tm(iPPP)(μ-OH)(H<sub>2</sub>O)]<sub>2</sub> Deposited on the GC Electrode

The CV response of the modified electrode was also affected by the surface coverage of [Tm(iPPP)(μ-OH)(H<sub>2</sub>O)]<sub>2</sub> deposited on the GC electrode. When the surface coverage was varied from 6.37 × 10<sup>-9</sup> mol/cm<sup>2</sup> to 3.19 × 10<sup>-8</sup> mol/cm<sup>2</sup>, the steady-state peak current obtained in the potential range of 0 ~ +1.00 V increased with the increase of the amount deposited. However, the peak current



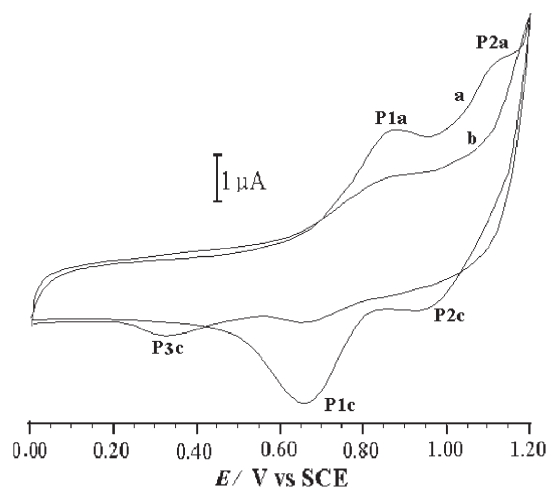


FIGURE 7 Cyclic voltammograms of the modified electrode soaked in (a) water and (b)  $1.0 \times 10^{-3}$  mol/l BSA for 50 min. Supporting electrode: 0.1 mol/l  $\text{NaClO}_4$ ; Scan rate: 100 mV/s.

decreased and  $\Delta E_p$  became broad when the surface coverage was over  $3.19 \times 10^{-8}$  mol/cm<sup>2</sup>. This was presumably because the excessive surface coverage results in large IR drop values.

The modified electrode with different amounts of surface coverage was also investigated before and after soaking in water or aqueous solution. No significant change in peak currents was seen after soaking the modified electrode in water or different electrolyte solutions for 5 h. The stability of modified electrode in aqueous solution is fairly good although it is simply constructed.

### The Study of the Interaction of the Modified Electrode with BSA Solution

#### *Voltammetric Investigation of the Interaction of the Modified Electrode with BSA*

The modified electrode was immersed in a  $1 \times 10^{-3}$  mol/l BSA solution for 50 min at 37°C, then, it was rinsed thoroughly with water. The voltammetric behavior of the modified electrode was investigated in the 0.1 mol/l  $\text{NaClO}_4$  solution. The second cycle of cyclic voltammograms are shown in Fig. 7b. In comparison with that of a modified electrode after

soaking in water for 50 min at 37°C (Fig. 7a), the disappearance of  $P_2$  and the appearance of an irreversible reduction current peak at +0.367 V (Fig. 7,  $P_{3c}$ ) were the main differences between two conditions. Otherwise, no current peaks were observed at a bare GC electrode in the 0.1 mol/l  $\text{NaClO}_4$  solution containing  $1 \times 10^{-3}$  mol/l BSA. Evidently, the  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})]_2$  complex film must have been bound with BSA, and formed a new complex. To further probe the binding of the complex with BSA, experiments were performed at various concentrations of BSA at 37°C. It was found that the peak current decreased with the increase of BSA concentration, and the minimum current was obtained as the BSA concentration reached  $1.5 \times 10^{-3}$  mol/l. The detection limit of BSA was  $5 \times 10^{-6}$  mol/l.

### The Analysis of the Surface Morphology of the Modified Electrode

The surface morphology of the modified electrode before and after soaking in BSA solution was characterized by atomic force microscopy. As shown in Fig. 8, the  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})]_2$  modified electrode presents a rough surface, with irregular protuberances and no visible pores. The size of the particles after soaking the film in BSA was larger than before, and the shape of the particles on the modified electrode surface has been changed into regular ovals. Thus, the molecule of BSA has indeed interacted with the complex modified on the electrode surface.

### The Fluorescence Spectrophotometric Study of the Modified Electrode with BSA

Spectrograms of fluorescence experiments are shown in Fig. 9, from which it was seen that the fluorescence intensity of BSA decreased with the increase of  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})]_2$  concentration. This experimental result was consistent with that of voltammetry.

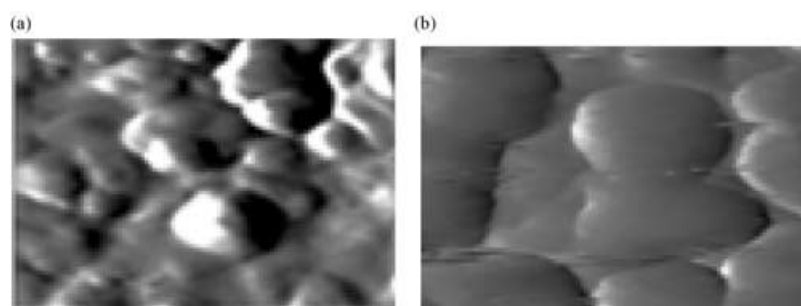


FIGURE 8 The surface morphology of the modified electrode before (a) and after (b) soaking in BSA solution.

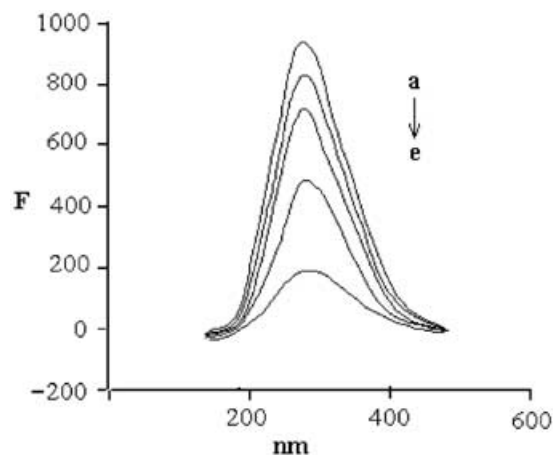


FIGURE 9 Fluorescence spectrogram of BSA with  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]_2$ . The concentration of  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]_2$  increased in the order 0, 5, 10, 20,  $50 \times 10^{-6}$  mol/l for curves  $a \rightarrow e$ .

## CONCLUSIONS

The electrochemical behavior of the  $[\text{Tm}(\text{iPPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]_2$  film modified GC electrode was affected greatly by anions. A near Nernstian response of  $\text{ClO}_4^-$  indicates that the complex would be a promising electroactive component of ion-selective electrode for  $\text{ClO}_4^-$ . The interaction of the metalloporphyrin complex in film with BSA suggested that a new complex was formed and could be applied to determining BSA in solution. Further work is under way in our laboratory to pursue this goal.

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