



# Synthesis and electrochemiluminescence properties of a new ternary terbium complex and its application for the determination of norfloxacin



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## ARTICLE INFO

### Article history:

Received 19 January 2014

Received in revised form 1 May 2014

Accepted 3 May 2014

Available online 29 May 2014

### Keywords:

Electrochemiluminescence (ECL)

Terbium complex

Norfloxacin

## ABSTRACT

A new ternary terbium complex with 2,6-pyridinedicarboxylic acid (DPA) and 2,2'-bipyridyl (bipy) as ligand was synthesized and characterized by EDTA titration, elemental analysis and FTIR. The complex showed strong and stable electrochemiluminescence (ECL) property in  $\text{NaBO}_4\text{-NaOH}$  buffer solution ( $\text{pH} = 10.0$ ) with the coreactant of potassium peroxydisulfate. The possible mechanism for the ECL behavior of terbium complex was discussed. Based on the ECL of the complex, a simple and ultrasensitive detection method for norfloxacin (NFX) was thus established. Under the optimized conditions, the enhanced ECL intensity versus the concentration of norfloxacin was in a good linear relationship over a concentration range from  $1.0 \times 10^{-9}$  to  $4.0 \times 10^{-7}$  mol/L. The detection limit was found to be  $6.9 \times 10^{-10}$  mol/L. The mechanism of ECL enhancement of NFX was also studied. The results obtained by the proposed ECL system, in terms of sensitivity, were much better than those obtained previously reported methods. In addition, the method was applied successfully to determine the total residuals of the norfloxacin in urine samples, the recoveries obtained were from 98.0% to 101.0%.

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## 1. Introduction

Electrogenerated chemiluminescence (ECL), the process of light emission by the excited state of a luminophore that results from an initial electrochemical reaction at the electrode surface, has aroused widespread concern interest [1–6]. It provides an important and powerful tool for various applications owing to its high versatility, simplified optical setup, good temporal and spatial control, fast sample analysis, and a very low background signal. So a large number of ECL detection methods was established in food, biosensors, immunoassays and environmental pollutant testing.

Among many ECL systems in metal–organic complex, ECL based on  $\text{Ru}(\text{bpy})_3^{2+}$  and its derivatives has been most studied owing to their relatively high emission quantum yield and long excited-state lifetimes in aqueous media [7–10]. Other metal complexes like Os [11], Ir [12], Pt [13], Re [14] were also investigated.

Based on the advantageous properties of rare earth complexes, especially the lowest excited state properties and the high quantum emission efficiencies from the metal-to-ligand charge-transfer (MLCT) excited state, rare earth complexes have been extensively studied in the last few decades [15], most studies of rare earth complex was focused on their chemical reactivity, structural topologies and photoluminescence (PL) properties [16–17].

However, ECL properties of rare earth complexes are rare. To our best knowledge, Cui et al. reported cathodic ECL behaviours of the acetonitrile, acetonitrile-phen and acetonitrile-ternary  $\text{Eu}(\text{III})$  complex systems at a gold electrode [18]. Shi-lv Chen, Fen Ding, Yu Liu, Hui-chun Zhao also researched the electrochemiluminescence (ECL) of  $\text{Tb}^{3+}$ -enoxacin- $\text{Na}_2\text{SO}_3$  system (ENX system) and  $\text{Tb}^{3+}$ -ofloxacin- $\text{Na}_2\text{SO}_3$  system (OFLX system) in aqueous solution [19]. Other researches like Krzysztof Staninski studied the electro-generated chemiluminescence of chosen terbium complexes deposited into  $\text{Al}_2\text{O}_3$  layer at the aluminum cathode [20]. With the increasing application of ECL, it is of considerable interest to develop new and efficient ECL systems in the area of metal complex, so it is important to find the new electrochemiluminescence reagent to broaden the scope of ECL in organic–metal complexes.

Norfloxacin (NFX), the chemical structure shown in Fig. 1a) is one of the third generation members of quinolone antibiotics, which is widely used in the clinic [21]. It is used effectively in both human and veterinary therapeutic medicines for the treatment of a wide variety of diseases caused by urinary, respiratory and gastrointestinal tract infections.

In recent years, the coordination complexes of metal ions especially rare earth ions as a probe to study norfloxacin have attracted much attention [22]. A series of analytical methods have been reported for the determination of NFX by spectrophotometry [23], fluorometry [24], electrochemical analysis [25] and high performance liquid chromatography (HPLC) [26]. Electrochemical

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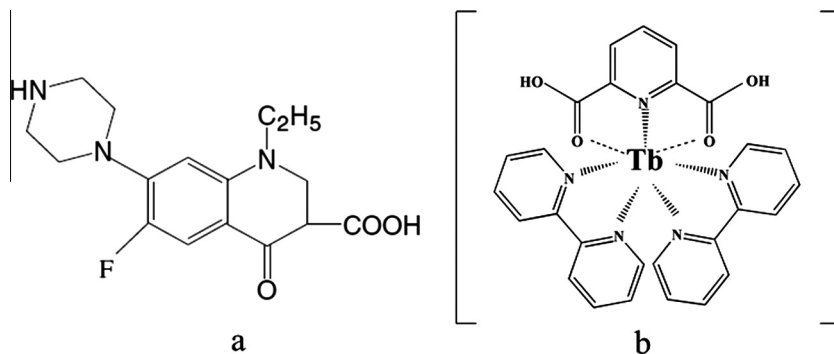


Fig. 1. Chemical structure of norfloxacin (a) and Tb(III) complex (b).

detection of analyte is a very elegant method in analytical chemistry. However, few electrochemical determination of norfloxacin has been reported [27,28]. Therefore, novel techniques for the determination of norfloxacin are still needed to be developed.

Electrochemical methods have been found as a highly-sensitive, convenient and effective tool for the analysis of important biomolecules including drugs in pharmaceutical formulations and human body fluids owing to their simplicity, low cost and relatively short analysis time as compared to the other routine analytical techniques. Thus, the aim of this study is to develop a simple and rapid method for the analysis of norfloxacin in urine samples and also to quantitate the compound in marketed formulations.

In this paper, we investigated the ECL behavior of Tb complex- $K_2S_2O_8$  system in aqueous solution at a glass carbon electrode, and the possible mechanism for the ECL behavior of Tb(bipy) $_2$ (DPA)- $K_2S_2O_8$  system and ECL enhancement of NFX was proposed. In addition, it was found that the ECL intensity versus the concentration of Norfloxacin was linear over the range of  $1.0 \times 10^{-9}$  to  $4.0 \times 10^{-7}$  mol/L with a correlation coefficient of 0.998 with a low detection limit of  $6.9 \times 10^{-10}$  mol/L. Terbium complex as a new electrochemiluminescence reagent show a good luminous efficiency and great potential in medicine determination.

## 2. Experimental

### 2.1. Reagents and chemicals

All materials employed in the present investigation were of analytical reagent (A.R.) grade products. 2,2-bipyridyl and 2,6-pyridine dicarboxylic acid were purchased from Shanghai Chemical Regents (Shanghai, China) and used without purification. Solid lanthanide metal salts were prepared by dissolving precisely of weighed amounts in bi-distilled water.

### 2.2. Apparatus and measurements

ECL measurements were carried out with a tailor-made setup controlled by a computer, which consisted of a MPI-E ECL analytical system (Xi'an Remax Analyse Instrument Co. Ltd., Xi'an, China) and a CHI 660C Electrochemical Analyzer (Shanghai Chenhua Instrument Co., China). A conventional three electrode configuration was employed, with a glass carbon-working electrode (GCE) (3 mm) used as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl (sat. KCl) electrode as the reference electrode. The voltage of the photomultiplier tube (PMT) was biased at 600 V in the experiment and the potential range for ECL measurements was from 0 to  $-1.6$  V at 0.10 V/s.

Fluorescence spectra were run using a Hitachi (Tokyo, Japan) F-4500 spectrofluorimeter. The absorption and fluorescence

spectra in solution were performed at room temperature, and whole excitation and emission slit widths were 5 nm. And the IR spectra were recorded from 4000 to  $400$   $cm^{-1}$  in KBr (FT-IR 8900, Hitachi, Japan).

### 2.3. Preparation of Tb(III) complex

#### 2.3.1. Synthesis of terbium(III) complexes

The synthesis procedure was similar to our previous work [29]. 2,6-Pyridinedicarboxylic acid (DPA) (0.1671 g, 1.0 mmol) and 2,2'-bipyridyl (Bipy) (0.3124 g, 2.0 mmol) were dissolved in 40 ml ethanol. After adjusting the pH value of the solution to about 6 with dilute ammonia, an ethanol solution of 1.0 mmol of  $Tb(NO_3)_3$  was added dropwise with stirring. The pH value of the mixed solution was readjusted to 6.0–7.0 with dilute ammonia. Reaction of the mixture was maintained for 4 h with heating in water bath under a constant temperature of 60 °C. Then the precipitate was filtered and washed twice with absolute ethanol and acetone. After dried to constant mass at 50 °C, the terbium complex  $Tb(bipy)_2(DPA)(NO_3)_2(H_2O)_3$  was obtained.

### 2.4. Composition analysis of the complexes

#### 2.4.1. Element analysis data (C, H and N) of the complexes

The element analysis data were determined by elemental analysis and total rare earth element content by EDTA titration were shown in Table 1.

The results indicated that the formulas of the complexes may be that  $Tb(bipy)_2(DPA)(NO_3)_2(H_2O)_3$ . The chemical structure of the complex was shown in Fig. 1b.

#### 2.4.2. Infrared spectroscopy

IR spectra of the complexes and ligands were all determined. IR spectra of lanthanide complexes and ligands show the different features. It revealed that after the reaction the formation of the ligand had changed. As shown in Fig. 2.

2,2-Pyridine shows the absorption peak at  $1577$   $cm^{-1}$ , which could be ascribed to the stretching vibration of C=N bond. 2,2-Pyridine shows the absorption peaks at  $3055$   $cm^{-1}$ , which could be ascribed to the stretching vibration of C—H bond. After the coordination, the absorption peaks of 2,2-pyridine ( $1577$   $cm^{-1}$  C=N) move to  $1496$   $cm^{-1}$ . This indicates that carboxylate groups of both the two ligands coordinate with rare earth ions in the complexes.

Table 1  
Element analysis data (C, H, N and Tb) of the complexes.

| Tb (%) | C (%) | N (%) | H (%) |
|--------|-------|-------|-------|
| 16.52  | 33.68 | 20.37 | 2.81  |

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