



The electrochemiluminescence of an iridium complex induced by hydroxide and ethoxide ions in organic solvents



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ABSTRACT

The electrochemical and the electrochemiluminescence (ECL) reaction between an iridium complex (phenylquinoline)₂Ir(acetylacetonate) [(pq)₂Ir(acac)] and water were studied in organic solvents. In the presence of a base, hydroxide ions, formed from the dissociation of trace water, can act as coreactants to induce strong luminescence upon application of an appropriate voltage. The mechanism study revealed that the electrochemically produced hydroxyl radicals were the key components for the ECL reaction. As the light emission intensity was proportional to the water contents, hence the method can be used for the determination of trace water in organic solvents. The linear response ranges were 0.001–0.05%, 0.003–1.00%, 0.01–1.00%, 0.01–1.00% (v/v), respectively in dichloromethane, acetonitrile, acetone and N,N'-dimethylformamide (DMF). The limit of detections as low as ppm levels were readily achievable in these solvents. When ECL experiment was carried out in ethanol, the ECL emission was observed even without the presence of water. Further experiments proved that ethoxide ion can also act as a coreactant and the ECL intensity was linearly correlated with the sodium ethoxide concentration in the range from 0.01 to 10 μM, suggesting that the ECL approach is able to quantify the sodium ethoxide content in ethanol.

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1. Introduction

The electrochemiluminescence (ECL) is a perfect combination of electrochemistry and spectroscopy. The analytical methods based on the ECL detection have drawn considerable attention during the past several decades because they can offer low background noise, high sensitivity, good controllability, fast analysis and requires simple and inexpensive instruments [1–5]. A large number of chemical compounds, including oxalates, amines, persulfates and peroxides, can act as the coreactants in an ECL system to produce strong light emission, hence they can be directly detected with an ECL method [6–8]. Among these substances, organoamines were most extensively exploited as the coreactants [9]. More recently, other organic compounds such as phenanthrene derivatives, glyoxal and methylglyoxal were also investigated as the coreactants in the ECL analysis [10–12]. However, to the best of our knowledge, the ECL reaction involving water (hydroxide ions) or ethoxide ions as the coreactants have not been fully exploited so far.

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On the other hand, it is well known that the background signal of Ru(bpy)₃²⁺ at elevated pH was ascribed to the light emissive reaction between Ru(bpy)₃³⁺ and the hydroxide ions [4,13,14]. As the reactive intermediates such as OH[•] or O₂^{•-} could be formed in the electrochemical oxidation of hydroxide ions, and which have a lifetime long enough to react with Ru(bpy)₃³⁺, leading to the increase in the background emission at alkaline conditions [15,16]. In the presence of the coreactants, however, the hydroxide ion could compete with the coreactant for the available Ru(bpy)₃³⁺, resulting in a decrease of the Ru(bpy)₃²⁺ ECL at elevated pH [9,15,17]. In any case, the hydroxide ion can be regarded as the coreactant in the ECL processes. As trace water in the organic solvent could undergo dissociation in the presence of alkali reagent and produce hydroxide ions, so it is reasonable to deduce that the light emission would be proportional to the water content and the presence of trace water in organic solvents may be quantified with the ECL method.

The determination of water content in organic solvents is very important in both the fundamental studies and the practical applications, especially in polar organic solvents in which water is easily soluble [18,19]. The direct determination of water content is normally achieved by the exploitation of the Karl Fischer reagent system [18]. The Karl Fischer method is applicable not only to organic solvents but also to many other inorganic and organic materials.

However, it is restricted by some disadvantages such as the tedious reagent preparation in harsh conditions, the complicated procedures and the use of toxic reagents. To overcome these problems, many more advanced instrumental methods were proposed, which could be exemplified by the spectrophotometry [19], infrared spectroscopy [20], gas chromatography [21], voltammetry [22], fluorescent spectroscopy [23] and optical fiber sensor methods [24]. Nevertheless, these approaches often need the specialized or expensive instruments and the sensitivity of measurements were often not good enough for trace water determination, hence they are not desirable for the sensitive, rapid and in situ analysis. Based on such considerations, the ECL reaction between a luminescent reagent and trace water was studied in organic solvents and it was hoped that a highly sensitive and relatively simple ECL method can be established for the determination of water content in organic solvents. The iridium complexes $(pq)_2Ir(acac)$ (where pq is phenylquinoline, acac is acetylacetonone and the chemical structure was shown in Fig. 1) was used as the luminescent reagent, because it was proved to have higher ECL efficiency than the most frequently utilized luminescent reagent $Ru(bpy)_3^{2+}$ in organic solvents [25–28].

On the study of the ECL reaction in ethanol, it was found that the ethoxide ion can also act as a coreactant to induce the strong ECL emission even without the presence of water. Sodium ethoxide is a strong base and a good nucleophile reagent. However, it is not very stable in ambient condition and it could gradually turn dark on storage due to the oxidation by oxygen. The study of its ECL reaction can not only propose a new coreactant for the ECL system and elucidate the reaction mechanism, but also provide a potentially useful analytical method for the quantification of the ethoxide content in organic solvents.

2. Experimental

2.1. Materials and reagents

The iridium complexes $[(pq)_2Ir(acac)]$ was obtained from the Aglaia Technology Development Co., Ltd. The ionic liquid trihexyl(tetradecyl)phosphonium hexafluorophosphate (98%) was obtained from Strem Chemicals. All the solvents employed were of analytical grade and were obtained from Sinopharm Chemical Reagent Co., Ltd. Dichloromethane was refluxed with calcium hydride for 4 h and distilled prior to use [29]. Other solvents were dried over activated 4A molecular sieves [30,31]. The head space in sealed reagent bottles were flushed with dry nitrogen. Ultrapure water ($18 M\Omega$), which was obtained from SUPER Series NW

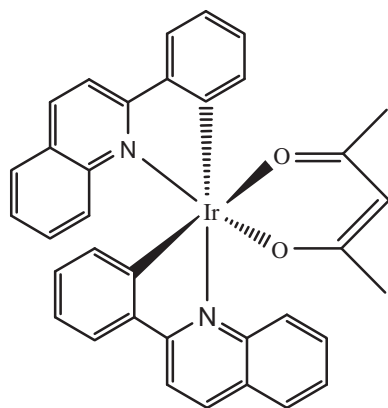


Fig. 1. The chemical structure of the iridium complex $(pq)_2Ir(acac)$.

Ultra-pure Water System (Heal Force Co. Ltd.), was used throughout the experiment.

2.2. Instruments and methods

The electrochemical and ECL measurements were carried out on the MPI-E ECL analyzer (Xi'an Remax Electro-Science & Technology Co. Ltd., China). The cyclic voltammetry (CV) was performed in the potential range 0–1.2 V to induce the ECL reaction with a scan rate of 100 mV/s. A typical three electrode configuration was used, which consists of a glassy carbon (GC) electrode (4 mm diameter) as the working electrode, a silver wire as the reference and a platinum wire as the counter electrode. Before the experiment, the GC electrode was polished with 0.05 μm alumina slurry to mirror finish and subsequently cleaned by sonication in ethanol and water for 1 min respectively. The three-electrode cell was placed directly on top the window of the photomultiplier tube (PMT). The PMT was biased at -600 V.

The testing solution typically composed of 5 mL solvent containing 5×10^{-4} M of $(pq)_2Ir(acac)$, 0.05 M supporting electrolyte and an appropriate amount of sodium hydroxide (Section 3.1). Water contents were varied by pipetting different amount of pure water in the solvents. In the case of dichloromethane, the standardized moisture content stock solution, prepared in acetonitrile, was added to the solvent to facilitate the miscibility.

To obtain the ECL emission spectra, a series narrow band interference filters (450 nm–740 nm, Beijing Trusttech Co., Ltd., Beijing, China) were inserted between the detection cell and the window of PMT in the ECL experiments.

3. Results and discussion

3.1. Rational selection of luminescent reagents and supporting electrolytes

In this work, an efficient ECL reagent, i.e., the iridium complexes $(pq)_2Ir(acac)$ was selected as the luminescent reagent. This is because that the $(pq)_2Ir(acac)$ has an appropriate solubility in many organic solvents and a very high ECL efficiency [32]. It was reported that the ECL efficiency of $(pq)_2Ir(acac)$ was about 77 times greater than that of the $Ru(bpy)_3^{2+}$ complex when the TPA was used as the coreactant [27]. Also, in contrast to the commercially available $Ru(bpy)_3^{2+}$ complex, the iridium complex $(pq)_2Ir(acac)$ does not have the crystal water in its commercial product, hence it is more suitable for trace water detection.

Supporting electrolytes are also important for the ECL experiment to be carried out in organic solvents. Lithium perchlorate and ionic liquid trihexyl(tetradecyl)phosphonium hexafluorophosphate were considered in present work. Lithium perchlorate could be used as supporting electrolyte in the DMF, acetone and ethanol. But it is practically insoluble in dichloromethane and other non-polar solvents. It was also noted that the lithium perchlorate could induce the decomposition of $(pq)_2Ir(acac)$ in acetonitrile. The phenomenon was similar to that reported by Mei et al., where a new iridium(III) complex was formed by the addition of lithium perchlorate in acetonitrile [33]. In these cases, an ionic liquid trihexyl(tetradecyl)phosphonium hexafluorophosphate was utilized as the supporting electrolyte. This reagent exhibited good solubility and conductivity in acetonitrile and dichloromethane.

In the absence of the base, a very weak ECL was observed even in the presence of high concentration water, suggesting that water dissociation was necessary. Sodium hydroxide was used to provide an alkaline condition. As sodium hydroxide does not dissolve in the most of the testing solvents (except ethanol), a small piece of solid sodium hydroxide (ca. 20 mg) was directly added to the testing

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