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Chemiluminescent investigation of tris(2,2'-bipyridyl)ruthenium(II) immobilized on a cationic ion-exchange resin and its application to analysis

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Abstract Tris-(2, 2'-bipyridyl)ruthenium(II) complex, $\text{Ru}(\text{bpy})_3^{2+}$, was immobilized on the Dowex-50 W cationic ion-exchange resin. The chemiluminescent characteristics of $\text{Ru}(\text{bpy})_3^{2+}$ in solution and in resin form were compared by using batch and flow injection methods. A strong chemiluminescence was observed during the reaction of $\text{Ru}(\text{bpy})_3^{2+}$ both in solution and in resin with KMnO_4 or $\text{Ce}(\text{SO}_4)_2$ under acidic or basic conditions. The $\text{Ru}(\text{bpy})_3^{2+}$ immobilized resin is stable, which can be used at least for 6 months when it reacts with the dilute KMnO_4 solution. Based on this property, $\text{Ru}(\text{bpy})_3^{2+}$ immobilized in the resin phase was developed as a flow-through chemiluminescent sensor that could be used to determine oxalate, sulfite and ethanol chemically or electronically with $\text{Ru}(\text{bpy})_3^{3+}$ generation on the surface of resin. The limits of detection were 1×10^{-6} M for oxalate, 0.5% (v/v) for ethanol and 1×10^{-7} M for sulfite. The method has been successfully applied to determine sulfite in sugar.

Keywords Chemiluminescence ·

Tris(2, 2'-bipyridyl)ruthenium(II) · Cationic ion-exchange resin

Introduction

Since the first report of tris(2, 2'-bipyridyl)ruthenium(II) [$\text{Ru}(\text{bpy})_3^{2+}$] as analytical chemiluminescent (CL) reagent by Hercules and Lytly in 1966 [1], the studies and the applications of $\text{Ru}(\text{bpy})_3^{2+}$ have been widely carried out in the last 30 years [2,3]. It has been successfully used for

quantitation of NADH [4], ketones [5], oxalate [6], β -lactam antibiotics and β -lactamases [7], aliphatic amines [8], amino acids and proteins [9]. The formation of $\text{Ru}(\text{bpy})_3^{3+}$ from $\text{Ru}(\text{bpy})_3^{2+}$ is often realized with chemical, photochemical and in-situ electrogenerated methods [2, 3]. The strong reducing intermediate of $\text{Ru}(\text{bpy})_3^{3+}$ can exist at the excited stated as $[\text{Ru}(\text{bpy})_3^{2+}]^*$. The emission is observed at a maximum wavelength of 610 nm when the excited state molecule returns to the ground state [10, 11, 12].

Based on this principle, many detection devices and chemical sensors have been developed [2, 3, 13, 14] for the determination of a variety of biologically important molecules. In order to reduce the waste solution from the reaction and to save some expensive reagents, many efforts have been made for the preparations of the CL flow sensors [15, 16, 17]. Downey and Nieman [18, 19] have reported a promising technique by which $\text{Ru}(\text{bpy})_3^{2+}$ could be immobilized on glassy carbon disk coated with Nafion. $\text{Ru}(\text{bpy})_3^{3+}$ was electrochemically generated from $\text{Ru}(\text{bpy})_3^{2+}$ at the glassy carbon electrode followed by incorporation of $\text{Ru}(\text{bpy})_3^{2+}$ with Nafion. Khranov and Collinson [20, 21] reported the electrochemiluminescence (ECL) of $\text{Ru}(\text{bpy})_3^{2+}$ ion-exchanged in Nafion-silica composite films or encapsulated in sol-gel glasses. This approach was used in a flowing stream configuration, and the ECL response was examined for several analytes. This technique can save $\text{Ru}(\text{bpy})_3^{2+}$ because $\text{Ru}(\text{bpy})_3^{2+}$ is recycled on the electrode. However, the lifetime of $\text{Ru}(\text{bpy})_3^{2+}$ sensor is affected by possible dissolution of Nafion films in the solution containing the high concentration of the organic solvent. To our knowledge, this is the first report of $\text{Ru}(\text{bpy})_3^{2+}$ immobilized on Dowex-50 W cationic ion-exchange resin. The aim of the present study was to compare the CL characteristics of $\text{Ru}(\text{bpy})_3^{2+}$ in solution and

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Fig. 1 Schematic diagram of chemiluminescent flow sensor. *P*, Peristaltic pump; *PMT*, photomultiplier tube

in resin form by using batch and flow injection methods. The features of two different $\text{Ru}(\text{bpy})_3^{3+}$ generation methods, chemically and electronically, were also compared. The possible applications of the $\text{Ru}(\text{bpy})_3^{2+}$ immobilized on resin in analytical chemistry are described.

Experimental

Apparatus

A schematic diagram of the CL flow sensor is shown in Fig. 1. It consists of a peristaltic pump (*P*: SJ-1211, Atto, Tokyo), a flow-through sensor (glass tube, effective length 1.5 cm $\times$ 3.0 mm i.d., which is filled with the resin particles), a CL detector (Lumiflow LF-800, Microtec NITI-ON, Funabashi, Japan) and a 50- μL loop injector placed close to the flow-through sensor. When two platinum electrodes (diameter 1.0 mm) were inserted into the resin phase and an electronic power was supplied, the flow system was used to study the CL of some reductant compounds. The power potential supplied on the platinum electrodes was from a Model 524B regulated DC power supply (Metronix Corporation, Tokyo). The batch method for the comparison of the CL profiles from the reactions of the $\text{Ru}(\text{bpy})_3^{2+}$ complex immobilized on Dowex 50 W and its solution with oxidants was carried out at a Lumicounter 600 (Microtec NITI-ON, Funabashi). An intensified multichannel photodetector IMUC-7000 (Otsuka Electronics, Osaka, Japan) was used for the analysis of the CL spectra.

Reagents

Chemicals of analytical grade were used as received. Dowex 50W-X2 (200–400 mesh) resin in hydrogen form was a product of Dow Chemical Company (MI, USA). Tris(2, 2'-bipyridyl)dichloro-ruthenium(II) hexahydrate was from Aldrich Chem. Co. (Milw., USA). Potassium permanganate (KMnO_4), sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$), sodium hydrogensulfite (NaHSO_3) and ethanol were purchased from Nacalai Tesque (Kyoto, Japan) and their solutions were prepared with water. The $\text{Ce}(\text{SO}_4)_2$ diluted solution was prepared from a 0.1 M cerium(IV) sulfate solution (Kanto Chemicals Co., Inc., Tokyo). The water used was prepared using a Millipore Elix 3 system (Japan Millipore, Tokyo).

Procedure

Dowex-50 W X2 resin was regenerated with 2 M HCl, thoroughly washed with H_2O . A 2.0 mL of resin was added into a 20 mL of

1.0 mg/mL $\text{Ru}(\text{bpy})_3^{2+}$ solution and then vibrated by a SS-8 Shaker (Tokyo Rikakikai Co. Ltd., Japan) for ca. 1 h. The resin was filtrated and washed with water. A ca. 0.3 mL of resin was filled into the glass tube, which was placed at the front of photomultiplier tube (Fig. 1). The carrier solution was water, 2×10^{-3} M H_2SO_4 or 1×10^{-5} M KMnO_4 in 2×10^{-3} M H_2SO_4 solution. A 50- μL of sample or standard solution was injected into the carrier stream through the sample valve. The CL signals were recorded with a U-125MN recorder (Shimadzu, Tokyo).

A sample solution of sugar was prepared by dissolving 5.0 g of sugar in water and diluting with water to 100 mL. This solution should contain 1×10^{-6} – 5×10^{-5} M sulfite.

Results and discussion

CL reactions of $\text{Ru}(\text{bpy})_3^{2+}$ solution and $\text{Ru}(\text{bpy})_3^{2+}$ immobilized resin with KMnO_4

The CL reactions of $\text{Ru}(\text{bpy})_3^{2+}$ solution with the strongly oxidants, e.g., KMnO_4 and $\text{Ce}(\text{SO}_4)_2$ have been applied in the analysis [22, 23, 24, 25]. The applications of the chemically generated $\text{Ru}(\text{bpy})_3^{3+}$ in the analysis were relatively few due to the oxidant reagent reacted not only with $\text{Ru}(\text{bpy})_3^{2+}$ complex but also with the analytes in the mixture solution. In the present work, in order to compare the CL reactions of $\text{Ru}(\text{bpy})_3^{2+}$ solution and $\text{Ru}(\text{bpy})_3^{2+}$ in resin form with the strong oxidants, the batch CL method was used. The CL profiles from the reactions of the $\text{Ru}(\text{bpy})_3^{2+}$ immobilized on Dowex 50 W resin and its solution with 1×10^{-3} M KMnO_4 solution are shown in Fig. 2. The two CL profiles with the similar feature indicated that the CL reactions of $\text{Ru}(\text{bpy})_3^{2+}$ in solution and in solid states with the strong oxidant were of the same CL character. From these CL profiles, we noticed that only $\text{Ru}(\text{bpy})_3^{2+}$ was mixed with KMnO_4 solution, the CL emissions could also be recorded. It seems that the present observation was contradictory to the reactions in Eqs. 1–3. Indeed, the CL emission of the electronically generated $\text{Ru}(\text{bpy})_3^{3+}$ in water has been reported by Fiaccabrino et al. [26] recently and they declared that it was the first discovery, but the

Fig. 2 Chemiluminescence profiles in batch system. **a** 1×10^{-4} M $\text{Ru}(\text{bpy})_3^{2+}$ 200 μL + 1×10^{-3} M KMnO_4 100 μL . **b** $\text{Ru}(\text{bpy})_3^{2+}$ immobilized resin ca. 15 mg+ 1×10^{-3} M KMnO_4 100 μL

CL reaction mechanism was not described clearly in their report. To our knowledge, there were two explanations for this phenomenon. The first one is that the emission may also be generated from the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^{3+}$ [27, 28, 29].

Potential for the ground- and excited-state couples involving $\text{Ru}(\text{bpy})_3^{2+}$ have been noted in previous papers [30, 31, 32, 33]. The redox potential data summarized by Bock [34] are listed below.

The oxidizing and reducing powers of $\text{Ru}(\text{bpy})_3^{2+}$ are enhanced in the excited state by difference of the free-energy (ΔG_{ES}) between the excited state and the ground state. The enhanced oxidizing and reducing properties of the excited state mean that it is unstable with respect to disproportionate into $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^{3+}$ and Meyer et al. have confirmed that the disproportionation reaction can be catalyzed chemically [30, 34].

Another possible mechanism is the so-called “solvent reduction” of $\text{Ru}(\text{bpy})_3^{3+}$ proposed by Vogler [35]. The reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with water in dilution sulfuric acid has been reported [26, 33, 36].

The oxidation potential for water to form oxygen ($\text{O}_2/\text{H}_2\text{O}$) is 1.23 V, but the standard reduction potential for the $\text{Ru}(\text{bpy})_3^{3+}/[\text{Ru}(\text{bpy})_3^{2+}]^*$ couple is 0.87 V. It seems that the reaction in Eq. 8 could hardly take place. It was known that $\text{Ru}(\text{bpy})_3^{3+}$ is relatively stable in weakly acidic solution, and to be reduced in alkaline solution to form $\text{Ru}(\text{bpy})_3^{2+}$ through a reaction with hydroxide ion. Because of this reaction, the lifetime of $\text{Ru}(\text{bpy})_3^{3+}$ complex at pH 10 is greatly reduced in comparison to that at pH 5–7 [36]. However $[\text{Ru}(\text{bpy})_3^{2+}]^*$ lies about 2.2 V above the ground state, which also has been reported in the previous work [34], indicating that the intermediate involved in the CL step must be a fairly high energetic one. The $\text{Ru}(\text{bpy})_3^{3+}$ complex could be reduced by hydroxide, the same as their reaction in homogeneous system [28, 33].

In order to confirm Eq. 9, an experiment was carried out. After a 1×10^{-3} M KMnO_4 solution flowed through the $\text{Ru}(\text{bpy})_3^{2+}$ immobilized resin, a 0.1 M NaOH solution was passed through the resin, a very strong CL was recorded. It was bright enough to be watched by the naked eye in a dark room. The CL spectra of this emission are showed in Fig. 3. The CL intensity was increased with increasing reaction time and reached its strongest CL at 20 s when the NaOH flowed through the resin phase. The maximum wavelength is at 610 nm, indicating that the emitter

Fig. 3 Chemiluminescent spectra of the resin in $\text{Ru}(\text{bpy})_3^{2+}$ form reacting with NaOH solution. Conditions: After a 1×10^{-3} M KMnO_4 solution flowing through the $\text{Ru}(\text{bpy})_3^{2+}$ immobilized resin phase for 5 min at 2.0 mL/min, a 0.1 M NaOH solution was passed through the resin with the same flow rate. The spectra from the bottom to up are corresponding to the time of NaOH solution to flow through the resin phase in 0, 4, 8, 12, 16, 20 s, respectively

is $[\text{Ru}(\text{bpy})_3^{2+}]^*$. These CL spectra could be explained by the fact that the $\text{Ru}(\text{bpy})_3^{2+}$ immobilized on the surface of resin was oxidized to $\text{Ru}(\text{bpy})_3^{3+}$ by KMnO_4 solution. When NaOH solution passed through the resin surface, $\text{Ru}(\text{bpy})_3^{3+}$ reacted with OH^- ions and emitted the light. If instead of KMnO_4 the solution was replaced by $\text{Ce}(\text{SO}_4)_2$ solution, the same phenomenon was also observed. When the resin particles were filled into the glass tube and used as a CL sensor as shown in Fig. 1, the CL analysis for the injection of KMnO_4 solution from the valve into the carrier was examined. The CL intensity was affected by the acidity of the water carrier and increased quickly with increasing the concentration of H_2SO_4 in the carrier until 0.1 M. Using a 0.01 M NaOH solution as carrier, there was no CL emission recorded for a 1×10^{-4} M KMnO_4 solution. In acidic solution, the standard potential of $\text{MnO}_4^-/\text{Mn}^{2+}$ is 1.51 V, which is high enough to oxidize the $\text{Ru}(\text{bpy})_3^{2+}$ complex to the $\text{Ru}(\text{bpy})_3^{3+}$ form.

But in alkaline solution, the oxidation ability of MnO_4^- is decreased to 0.34 V.

This potential is not strong enough to oxidize $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Ru}(\text{bpy})_3^{3+}$. Agater et al. [37] reported that under acidic conditions, when the permanganate was reduced, a CL emission was appeared at wavelength of 650 ± 10 nm. They ascribed that the CL emission due to an intermediate oxidation state of manganese, which is independent of reductant. The different maximum wavelengths of $[\text{Ru}(\text{bpy})_3^{2+}]^*$ and the manganese intermediate species verified that the

CL emitted from the heterogeneous reaction system is also the result of $[\text{Ru}(\text{bpy})_3^{2+}]^*$ emitter.

Flow-through sensor using KMnO_4 solution as carrier

The $\text{Ru}(\text{bpy})_3^{2+}$ immobilized resin was developed as a material to prepare a flow-through sensor (see Fig. 1) for the determinations of reducing compounds. The dilution KMnO_4 solution was used as carrier. As discussed at the above section, $\text{Ru}(\text{bpy})_3^{2+}$ in resin form can react with KMnO_4 to form $\text{Ru}(\text{bpy})_3^{3+}$. Using oxalate sodium solution as model sample, the optimum conditions for the present flow-through sensor were examined. The CL intensity was measured as a function of the concentrations of KMnO_4 and H_2SO_4 in the carrier and the flow rate. The concentrations of KMnO_4 in the range from 1×10^{-4} M to 1×10^{-6} M were compared. The high concentration ($>5 \times 10^{-5}$ M) of KMnO_4 in the carrier caused a very strongly background CL emission and an unstable baseline. The baseline CL noise was also increased with increasing the KMnO_4 concentration. But too low concentration ($<5 \times 10^{-6}$ M) of KMnO_4 caused a very weak CL emission or no CL observed. The low concentration of KMnO_4 also caused a poor reproducibility of analysis. A concentration of KMnO_4 at 1×10^{-5} M was chosen as the most convenient one for the following experiments. It was known that the oxidation ability of KMnO_4 was strongly affected by the acidic or alkaline concentration in the solution. The relationships between the ratio of CL signal-to-noise (S/N) and the concentrations of H_2SO_4 in the KMnO_4 carrier solution are plotted in Fig. 4. The effect of H_2SO_4 concentrations on the CL intensity is significant. The higher concentration of H_2SO_4 in the carrier the stronger CL emission (peak height) was recorded, but the background CL and the noise were also increased by an

Fig. 4 Effects of H_2SO_4 concentration of KMnO_4 carrier solution on the chemiluminescence intensity. Conditions: The concentration of oxalate sample solution was 1×10^{-5} M. The concentration of KMnO_4 carrier solution was 1×10^{-5} M. Flow rate: 2.0 mL/min

evident level. Therefore the signal-to-noise ratio of the CL decreased when the concentration of H_2SO_4 was above 2×10^{-3} M. The addition of small amount of NaOH into the carrier could make not only the CL decrease but also the noise increase. These results demonstrated that the suitable medium for the KMnO_4 carrier is in 2×10^{-3} M H_2SO_4 solution. Another experiment condition is the flow rate of the carrier. Similarly to the usual flow injection analysis, the low flow rate caused a broad CL signal. The higher flow rate the bigger and shaper CL peak height was obtained until 4.0 mL/min. This is because the higher flow rate provided a faster mixing of the sample molecules with the $\text{Ru}(\text{bpy})_3^{3+}$ molecules. But the higher flow rate also made the background CL and the noise increase due to more $\text{Ru}(\text{bpy})_3^{3+}$ molecules being generated on the surface of the resin. Therefore, too high a flow rate should be avoided in this work. A flow rate at 2.0 mL/min is recommended. On the other hand, in order to achieve good reproducibility for each sample injection, control of the injection interval time was needed. With the low concentration of KMnO_4 as the oxidant reagent in the carrier, the injection interval time decided the amount of $\text{Ru}(\text{bpy})_3^{3+}$ molecules generated on the surface of resin, which influenced the reproducibility of the CL intensity. One minute for each injection is suitable, thus the flow-through sensor can handle 60 samples per hour.

Under the selected conditions given above, the CL signals were sharp and stable. Three standard curves for oxalate, ethanol and sulfite were obtained. The linear calibration response curves can be described by the following equations:

$$Y = 5.0 \times 10^6 C_{\text{Oxalate}} - 1.0 \quad (12)$$

$$(r^2=0.9123, \text{ in the range } 1 \times 10^{-6} \text{ to } \sim 1 \times 10^{-3} \text{ M})$$

$$Y = 120 C_{\text{Ethanol}} - 1.9 \quad (13)$$

$$(r^2=0.9515, \text{ in the range } 0.5 \text{ to } \sim 55\%, \text{ v/v})$$

$$Y = 1.2 \times 10^7 C_{\text{Sulfite}} + 2.3 \quad (14)$$

($r^2=0.9201$, in the range 1×10^{-7} to $\sim 5 \times 10^{-4}$ M), where Y is the ratio of the CL signal-to-noise (S/N) and r is the correlation coefficient. C_{Oxalate} , C_{Ethanol} and C_{Sulfite} are the concentrations of oxalate, ethanol and sulfite, respectively. The limits of detection were 1×10^{-6} M for oxalate, 0.5% for ethanol and 1×10^{-7} M for sulfite. The relative standard deviations ($n=14$) were 4.2% for 1×10^{-5} M oxalate, 3.8% for 10% ethanol and 5.4% for 1×10^{-5} M sulfite, respectively.

The immobilization of $\text{Ru}(\text{bpy})_3^{2+}$ on the resin is very stable. A successful prepared sensor can be used at least 6 months. During this work, we used the same sensor for all the experiments, including the chemically and electronically $\text{Ru}(\text{bpy})_3^{3+}$ generations.

Effect of some interference on the determination of sulfite and the analysis of sulfite in sugar

As compared in Table 1, the present method for the determination of sulfite is of higher sensitivity than some re-

Table 1 Comparison the present method for the determination of sulfite with other reported methods

Method	Detection limit	Dynamic linear range	Ref.
Proposed CL	1×10^{-7} M	1×10^{-7} – 5×10^{-4} M	
Na_2CO_3 – NaHCO_3 – Cu^{2+} CL system	5×10^{-7} M	1×10^{-6} – 5×10^{-4} M	[38]
Spectrophotometry	1×10^{-5} M	1.5×10^{-5} – 3.1×10^{-4} M	[39]
	25 ng	1.3–6.3 $\mu\text{g/mL}$	[40]
Fluorimetry	0.01 $\mu\text{g}/25$ mL	0.01–0.4 $\mu\text{g}/25$ mL	[41]
Potentiometry	5×10^{-6} M	5×10^{-6} –0.1 M	[42]
	2×10^{-6} M	2×10^{-6} – 5×10^{-4} M	[43]

Table 2 Determination of sulfite in sugar

Sugar solution contents ^a ($\times 10^{-6}$ M)	Added ($\times 10^{-6}$ M)	Found ($\times 10^{-6}$ M)	Recovery (%)
2.36 $\pm$ 0.05	1.0	0.90	90
	2.0	1.89	95
	4.0	3.69	92
3.12 $\pm$ 0.07	1.0	1.02	102
	2.0	1.91	96
	4.0	3.84	96

^a $n=4$.

ported methods. The interference in the determination of 5×10^{-6} M sulfite using the proposed method was also examined. The tolerance limit was taken as the amount which caused an error of $\pm 5\%$ in peak height. 1000-fold Na^+ , Cl^- , K^+ , Ca^{2+} , SO_4^{2-} , Mg^{2+} , glucose and citrate; 500-fold HPO_4^{2-} , PO_4^{3-} , NO_3^- and Mn^{2+} ; 100-fold Cu^{2+} , NH_4^+ , Fe(III) and Br^- and 10-fold Fe(II) , Co^{2+} and S^{2-} have almost no effect on the determination of high concentration levels of sulfite. As an example, the application of the present method for the determination of sulfite in sugar was carried out. The sample solution was prepared with water and was directly injected into the flow system. The relative standard derivation was 3%–7% ($n=5$) for each sample. Based on the calibration graph, the determination results of sulfite analysis agreed well with those obtained by the iodine titration method. The recoveries were good enough for practical use and the determination results are listed in Table 2. Two sugar samples that contained sulfite in SO_2 form were 30.2 and 39.9 mg/kg respectively.

Electrogeneration of Ru(bpy)_3^{3+} on the resin solid phase

The above results indicated that the Ru(bpy)_3^{2+} immobilized on the resin could be oxidized to Ru(bpy)_3^{3+} by strong oxidants, which also told us that the Ru(bpy)_3^{2+} immobilized on resin could be oxidized by supplying a voltage on the resin phase. As shown in Fig. 1, using a 2×10^{-3} M H_2SO_4 solution as carrier (flow rate, 2.0 mL/min) and supplying a 4.0 V (constant current at 10 μA) potential on the electrodes (platinum wires, diameter 1.0 mm), injections of oxalate, ethanol or sulfite solution into the flow system, their CL emissions were observed. The CL

signals were similar to those using KMnO_4 as oxidant in the carrier solution. However, the reproducibility of the analysis was much lower than the chemical generated one. The low reproducibility for the analysis using electronically generated Ru(bpy)_3^{3+} on the surface of resin may be due to the electrode material, resin material, shape of the flow cell and the carrier electronic conductance, etc. Because of the importance and the interest of the Ru(bpy)_3^{2+} immobilized on a functional material, the detail researches for the resin treatment, a new resin synthesis and the design of a new flow-cell are the subjects of our future research.

Conclusions

The CL characters of Ru(bpy)_3^{2+} in aqueous solution and resin solid have been compared. With the dilute KMnO_4 solution as oxidant, the CL emitters, $[\text{Ru(bpy)}_3^{2+}]^*$ excited molecule of 610 nm maximum wavelength, generated from both aqueous and solid phases were evidenced. The CL emission from the reaction of KMnO_4 with Ru(bpy)_3^{2+} was discussed. The reaction of hydroxide ion with Ru(bpy)_3^{3+} produces a strong CL emission. The Ru(bpy)_3^{2+} immobilized resin has been developed as a flow-through CL sensor for the determination of oxalate, ethanol and sulfite, which can not only save the Ru(bpy)_3^{2+} reagent, but also concentrate the reagent on the surface of resin. The recommended sensor was simple and stable. Instead of the chemical generation of Ru(bpy)_3^{3+} , electronically generated Ru(bpy)_3^{3+} could also be used to determine oxalate, sulfite and ethanol by supplying a suitable electric potential on the resin phase, in this case not required in the carrier solution. The synthesis and the study of the Ru(bpy)_3^{2+} or other ruthenium complexes of luminescence immobilized functional materials may be developed as a new branch of CL research in the near future based on the saving of reagent, the low environmental pollutant and the highly analytical sensitivity of this type CL sensor.

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