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Organosilicate thin film containing Ru(bpy)$_3^{2+}$ for an electrogenerated chemiluminescence (ECL) sensor†

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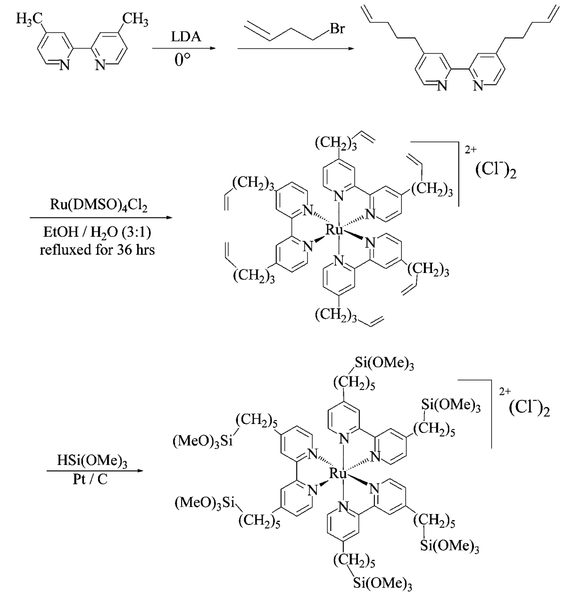
Received (in Cambridge, UK) 4th April 2003, Accepted 13th May 2003
First published as an Advance Article on the web 4th June 2003

An insoluble organosilicate gel containing a Ru(bpy)$_3^{2+}$ complex was formed on an ITO electrode surface and its ECL responses toward several analytes were investigated for the sensitive ECL sensor application having long-term stability.

Since electrogenerated chemiluminescence (ECL), the emission from an excited molecule generated by an electrochemical redox reaction, was observed from Ru(bpy)$_3^{2+}$ complex,[1] ECL has attracted much attention as a powerful analytical tool that combines a clear mechanism and simple equipment with inherent sensitivity, selectivity, and wide linear dynamic range for amine containing analytes, such as alkylamines, NADH, hydrazine, amino acids, biomolecules and a variety of pharmaceutical compounds.[2–6] In order to develop regenerable ECL-based chemical sensors and detection devices in flowing streams, much effort has been focused on the immobilization of Ru(bpy)$_3^{2+}$ complexes on an electrode surface, thus in theory recycling the Ru(bpy)$_3^{2+}$ complex permanently. For example, Ru(bpy)$_3^{2+}$ complexes immobilized on the electrode surface by SAM (self-assembled monolayer) formation[7–9] or physically embedded in a polymer matrix such as Nafion[10–12] and silica-ionomer composite[13–15] films have been reported. However, the SAM layer is so easily detached from the surface during the positive potential scan that this limits the actual application of ECL sensors. The physically embedded Ru(bpy)$_3^{2+}$ complex in Nafion matrix has proven to be promising but the migration of the Ru(bpy)$_3^{2+}$ complex into electrochemically inactive hydrophobic regions of Nafion causes a serious problem with the long-term stability of the ECL sensor. Some polymeric systems where Ru complexes were chemically attached to polymer chains have been reported to enhance the stability of ECL sensors, however, their ECL signals are low due to the inhibited mass transport and poor permeation of analyte molecules through the matrix.[16–18]

As an alternative new immobilization method, we present the novel synthesis of a functionalized Ru(bpy′)$_3^{2+}$ complex having polymerizable trimethoxysilyl end groups, –Si(OMe)$_3$, on each bipyridine ligand and the formation of insoluble porous gel films on an ITO electrode. ITO was chosen as the electrode because it is transparent and it has many –OH groups on the surface where the modified Ru(bpy′)$_3^{2+}$ complexes will also be chemically bound through –Si–O– bond formation. Preliminary data for sensing various analytes in the buffered aqueous solution and the long-term stability of the coated gel film containing Ru(bpy′)$_3^{2+}$ will also be discussed.

[Ru(bpy′)$_3$]Cl$_2$ (**1**) was quantitatively prepared by the hydrosilylation of a precursor complex with terminal olefin groups, which was synthesized in high yield from Ru(DMSO)$_4$Cl$_2$ and modified bpy ligands† (Fig. 1). Although the precursor complex was stable in air, complex **1** with trimethoxysilyl groups, –Si(OMe)$_3$, was not stable in air especially with regard to moisture. Therefore, complex **1** was stored in a glove box as an anhydrous methanol solution. A solution of complex **1** (30 wt%) in the mixed solvent isopropanol–methanol (1 : 1, w/w) was spin-coated on the pre-cleaned ITO surface at 3000 rpm for 30 s. A thin film of [Ru(bpy′)$_3$]Cl$_2$ was stored in ambient air for 18 h at room temperature to remove solvent and to initiate the gelation, and then was cured at 170 °C for 24 h to complete the gelation.



[Ru(bpy')$_3$]Cl$_2$ (1)

Fig. 1 Modification of bpy ligand and preparation of [Ru(bpy′)$_3$]Cl$_2$ complex.

Completion of the gelation could be confirmed by the comparison of UV-Vis absorption spectra of coated films before and after the thermal curing process followed by methanol washing which removed the unreacted [Ru(bpy′)$_3$]Cl$_2$ as well as the unbound portion of gel film from the ITO substrate. The curing conditions mentioned above were the optimized ones where no differences in UV measurement were observed. This chemically immobilized gel film containing [Ru(bpy′)$_3$]Cl$_2$ units showed stable CV and ECL characteristics as well as long-term stability in acetonitrile solution (results not shown). The coated gel film was characterized by field emission SEM (FE-SEM) to show the porous structure having nanopores in the range of 50–150 nm with a film thickness of about 400 nm (Fig. 2).

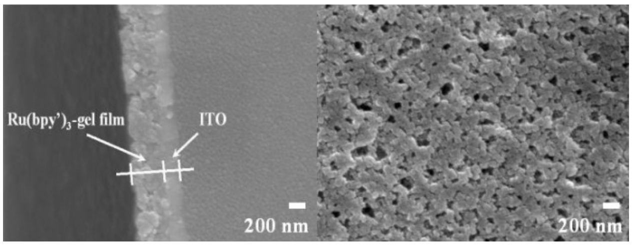


Fig. 2 FE-SEM images of coated gel film containing [Ru(bpy′)$_3$]Cl$_2$ complexes (left: cross-sectional view, right: surface view).

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b303766e/

DOI: 10.1039/b303766e

All chemicals used for ECL measurement were of analytical reagent grade and distilled deionized water (Milli-Q grade, Millipore Corp.) was used to prepare the solutions. Tripropylamine (TPrA), sodium oxalate, proline, tryptophan, ascorbic acid, tartaric acid and quinacrine were obtained from Aldrich Chemicals and were used without further purification. ECL intensity *versus* potential profiles was monitored using a photomultiplier tube (Hamamatsu HC 135) in conjunction with a an EG&G 273A potentiostat/galvanostat. The experiments employed a conventional three-electrode configuration in a 15 mL electrochemical cell (sample volume: 10 mL). The $Ru(bpy)_3^{2+}$ modified ITO electrode ($A = 1 \times 1$ cm^2) was employed as the working electrode, Pt wire auxiliary and Ag/AgCl in 3 M NaCl reference electrode.

Similar to the previously reported CV and ECL phenomena from immobilized $[Ru(bpy)_3]Cl_2$, the ITO electrode coated with $[Ru(bpy')_3]Cl_2$ gel film showed a $Ru(bpy')_3^{2+}$ anodic peak current at 1.0 V *vs*. Ag/AgCl (3 M NaCl) in 0.05 M phosphate buffer (pH 7.0) during CV scanning between 0.8 and 1.35 V at a scan rate of 50 mV s^{-1}. Under slow scan rate conditions, almost all the $Ru(bpy')_3^{2+}$ units in the coated gel film are electrochemically active. In the presence of TPrA, the anodic current increases significantly and the cathodic current decreases due to the catalytic oxidation of TPrA. In the presence of TPrA, the onset of ECL emission was coincident with the oxidation of $Ru(bpy')_3^{2+}$ units. The maximum of the ECL emission was 630 nm, red-shifted from that of the $Ru(bpy')_3^{2+}$ in solution because of the strong interactions among the immobilized $Ru(bpy')_3^{2+}$ molecules. The ECL response for TPrA increased with increasing pH from 4 to 8, then decreased at pH higher than 9 as similar to the previous report.[15]

TPrA has proved an most efficient amine for this ECL reaction, and it has been commonly used as a model analyte by which to compare the ECL activity.[12] In our experiments, the coated gel film containing $Ru(bpy')_3^{2+}$ units gave a linear response for TPrA concentration having correlation coefficient of 0.9981 with a reasonable detection limit ($S/N = 2$) of 1.0 μM (Fig. 3).

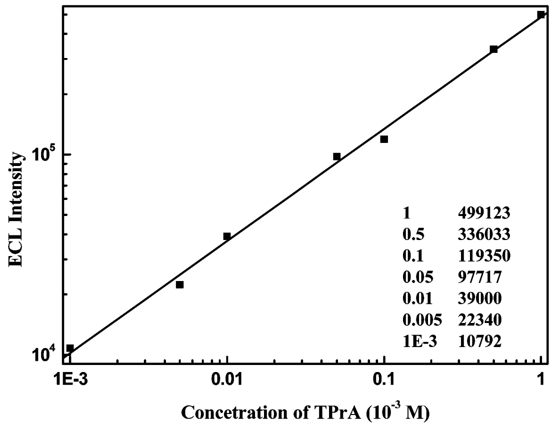

Fig. 3 ECL intensity as a function of concentration of TPrA, recorded in 0.05 M phosphate buffer (pH 7.0) with voltage scanned between 0.8 and 1.35 V at 50 mV s^{-1} (peak height was used).

Table 1 shows the ECL responses for 1 mM concentration of various analytes by employing the prepared $[Ru(bpy')_3]Cl_2$ gel film coated ITO electrode. For comparison, the relative intensities of ECL from the $Ru(bpy)_3^{2+}$ solution with bare ITO electrode and various analytes were measured and results are also summarized in Table 1. Most of the analytes showed good ECL responses with $[Ru(bpy')_3]Cl_2$ gel film coated ITO electrode similar to those with the bare ITO electrode in $Ru(bpy)_3^{2+}$ solution. This fact indicates that positively charged, neutral, and even negatively charged analytes can readily diffuse into thin films of the gel containing $[Ru(bpy')_3]Cl_2$ because of their large pore size, and thus relatively open structure.

Table 1 ECL sensitivity[a] comparison of coated gel film with $Ru(bpy)_3^{2+}$ solution for a series of analytes

Analytes	Coated gel film containing $Ru(bpy')_3^{2+}$	$Ru(bpy)_3^{2+}$ solution[b]
TPrA	100	100
Tartaric acid	8.21	0.54
Ascorbic acid	4.22	0.48
NADH	3.90	1.94
L-Tryptophan	2.39	1.44
Promazine	5.01	3.52
Oxalate	10.7	9.96
Quinacrine	1.57	2.63
L-Proline	12.0	16.8

[a] Values relative to the ECL intensity of TPrA as 100%. [b] 0.5 mM $Ru(bpy)_3^{2+}$ solution with ITO electrode.

The most interesting feature of the $[Ru(bpy')_3]Cl_2$ gel film coated ITO electrode is good long-term stability which is one of the most important factors for the actual applications of ECL sensors. The $[Ru(bpy')_3]Cl_2$ gel film coated ITO electrode showed no significant reduction of ECL intensity after storing at room temperature for more than six months (~ 10% loss in ECL intensity).

When it was operated continuously in the buffered solution under potential bias, however, ECL intensity decreased by less than 10% in 8 h, probably due to the decomposition of $[Ru(bpy')_3]Cl_2$ units on the electrode surface. Another distinctive feature of the present ECL sensor is that the coated gel film containing $Ru(bpy')_3^{2+}$ units does not dissolve in organic solvents such as acetonitrile, thus it can be used as a detection device in HPLC. In contrast, the ECL sensor based on Nafion film is slowly destroyed upon prolonged exposure to a mobile phase with high organic content.[19]

We are quite certain that our underlying concept to develop $[Ru(bpy')_3]Cl_2$ gel film coated ITO electrode from the derivatized $[Ru(bpy)_3]Cl_2$ complex having polymerizable trimethoxysilyl groups, $-Si(OMe)_3$, can be used to develop a stable and sensitive ECL sensor. It can also be readily extended to preparing various functional coating materials. We are at present investigating the detailed ECL sensitivity and selectivity of $[Ru(bpy')_3]Cl_2$ gel film coated ITO electrodes in aqueous as well as organic solution.

This work was supported by Korea Research Foundation Grant (KRF-2000-015-DP0302) through the Research Institute of Basic Sciences, SNU. S.-H. Lee and M. Kim are grateful for the award of a BK21 fellowship.

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