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# Electrochemiluminescence quantum yield of some Ru(II) polypyridine complexes

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## Abstract

The electrochemiluminescence quantum yield ($\varphi_{ecl}$) is a parameter difficult to measure experimentally, but significant in the comprehension of electron transfer mechanisms. We report a new experimental method which tries to control the influence of different parameters (double layer charge, 'geometric' factors, efficiencies of electrolytic processes, etc.) in determining the $\varphi_{ecl}$ values. This method does not allow absolute value measurements but requires the use of a standard. The $\varphi_{ecl}$ obtained for some Ru(II) polypyridine complexes are reported and both the results and the validity of the method are discussed.

## Introduction

Electron transfer reactions in which excited states are generated as a product (chemiluminescence, cl) are very important in the connections between chemistry and light [1–6]. Electrogenerated chemiluminescence (ecl), where the reacting species are prepared electrochemically *in situ*, has been extensively studied in recent years owing to the possibility of practical applications (lasers or display devices) [7, 8] and because they can offer a better understanding of the kind of electron transfer processes taking places in homogeneous solution [9], a field of research that the formulation of the Marcus electron-transfer theory [10] has strongly stimulated.

In this direction efforts have been made to develop systems characterized by high ecl quantum yields, defined as the number of emitted photons over the number of faradaic electrons, $\varphi_{ecl}$. Electrochemiluminescence resulting from electron transfer reactions which involve oxidized or reduced species of metal ion chelates appears to be a rather evident phenomenon [9, 11–17]. Moreover, quantitative determination of $\varphi_{ecl}$ remains a difficult goal owing to the numerous experimental parameters that can affect such measurements.

We report here a method for quantitative $\varphi_{ecl}$ determination and the results obtained in a homogeneous family of Ru(II) polypyridine complexes that are widely known to be among the more useful compounds which can be used in luminescence processes.

## Experimental

$Ru(bpy)_3(ClO_4)_2$ (bpy = 2,2′-bipyridine), $Ru(bpy)_2$(i-biq)$(PF_6)_2$ (i-biq = 2,2′-biisoquinoline), Ru(bpy)(i-biq)$_2(PF_6)_2$, $Ru(bpy)_2$(biq)$(PF_6)_2$ (biq = 2,2′-biquinoline), Ru(bpy)(biq)$_2(PF_6)_2$ were available from our laboratory. Carlo Erba polarographic grade $CH_3CN$ (ACN) was dried over activated molecular sieves for 14 days, then over $P_2O_5$ for the same time and finally distilled under dried $N_2$ in the presence of $P_2O_5$.

Fluka tetraethylammonium tetrafluoroborate ($TEABF_4$), used as the supporting electrolyte, was stored at 70 °C.

The ecl experiments were performed in a specially suited three electrode cell (Fig. 1). The working electrode (W), a Pt square 16 mm$^2$ large, was fixed at the top of a glass tube. The counter-electrode (C), a Pt foil with a 80 mm$^2$ large surface, was semicylindrically arranged around W. The reference electrode (R), a KCl saturated calomel electrode (SCE; $E° = 0.2444$ V versus SHE at 25 °C), was contained in a separate tube connected to the test solution via a fritted glass disk. When not in use the cell and electrodes were stored under vacuum. The purpose of the cell was to make it possible to keep constant the W position and the W–C distance, on which the flowing electrical current, that is the concentration near the electrode of the reduced and

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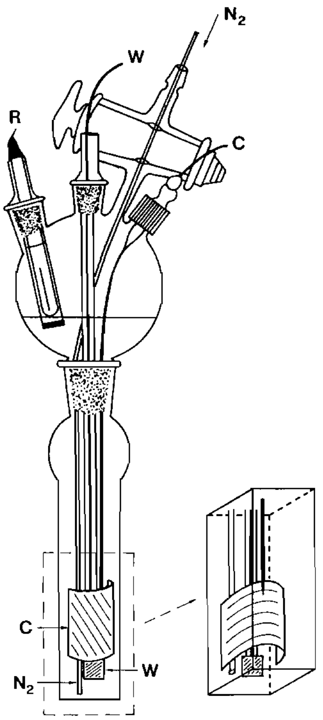

Fig. 1. Three electrodes cell for ecl measurements. R: reference electrode; W: working electrode; C: counter electrode.

oxidized species, strongly depends. The samples were stirred and deaerated by bubbling dried, acetonitrile saturated, $N_2$.

The light emission was detected by means of a Hamamatsu R928 photomultiplier tube; the electrochemical control was assured by using an AMEL 568 programmable function generator and an AMEL 552 potentiostat; light and current signals were sent to a programmable digitizer Tektronix 7612D. All the sets of points collected by the digitizer were stored and processed by an Apple IIe computer.

The whole experimental equipment was protected from daylight in order to avoid as much as possible scattered light detection.

The luminescence quantum yields were measured by a Perkin-Elmer 650-40 spectrofluorimeter and corrected for the photomultiplier sensitivity, taking aerated $Ru(bpy)_3^{2+}$ in water as a standard ($\varphi_{em}=0.028$) [18]. A correction coefficient was also found for the integrated light emitted intensity which we found the $\varphi_{ecl}$ from, to take into account the different emission spectra.

## Results and discussion

All the experiments were carried out in ACN solution at 25 °C.

Ecl emission spectra are similar, in all the cases studied, to the photoemission spectra.

Before each ecl experiment a cyclic voltammogram of the solution was recorded (with the experimental set-up), in order to establish the exact positions of the reduction and oxidation peaks. Then the experiments were performed by stepping the potential between values suited to reduce and/or to oxidize the complex. These values were chosen in order to reduce differences in relevant experimental parameters between the samples (*vide infra*).

The potential square wave was conferred in a continuous mode, in order to achieve an electrochemical cyclic steady state and only current flowing and light emitted during the 32nd potential stepping cycle were collected. The light intensity–time transient (1024 points) and the current intensity–time transient (1024 points) were integrated, by using the trapezia formula, to obtain the total quantity of light emitted and the quantity of charge flowed through.

An important problem was to estimate the entity of the double layer charge and of the electrolytic processes different from the one we want. In particular, everytime we invert the applied potential from, for example, the reduction value to the oxidation one, the just reduced complex lying near the W surface is oxidized to the parent complex. Other possible undesired electrolytic processes involve impurities present in the solvent or samples [9, 13].

To estimate the double layer charge we made use [19] of eqn. (1)

$$i=\frac{E}{R}\,e^{-t/RC} \qquad (1)$$

where $i$ is the current intensity owing to the double layer charging process, $E$ the applied potential, $R$ the solution resistance, $C$ the double layer capacity and $t$ the time. By exploiting the first points of each measured current–time transient we were able to estimate the unknown parameters of eqn. (1), that is $E/R$ and $1/RC$, so as to make it possible for us to rebuild a complete double layer current–time transient and, by integrating this, the double layer charge.

Moreover, in order to get the entity of the waste electrolytic events, we collected a set of points stepping the 32nd cycle potential between one of the working potentials (e.g. anodic) and a potential at the foot of the other voltammetric wave (in this example cathodic). The desired quantity was computed as the difference between the total flowing charge and the double layer one in this case.

In order to obviate the very difficult absolute photomultiplier setting, we carried out relative $\varphi'_{ecl}$ measurements by using as an absolute standard the

$\varphi_{ecl}$ reported by Wallace and Bard [11d] for deaerated $Ru(bpy)_3(ClO_4)_2$ in ACN ($\varphi_{ecl}=0.05$). The absolute values were obtained by comparing, under identical experimental conditions, the $\varphi'_{ecl}$ value obtained for the sample and that obtained for the standard

$$\varphi_{ecl}=\frac{\varphi_{ecl,s}}{\varphi'_{ecl,s}}\varphi'_{ecl} \tag{2}$$

The process leading to the $\varphi_{ecl}$ values is schematized in Fig. 2 where

$\eta_{e,ox}$ (or $\eta_{e,red}$)

$$=\frac{\text{no. of } A^+ \text{ (or } A^-\text{) produced}}{\text{no. of electrons flowed through}} \tag{3}$$

are the efficiences of the electrolytic processes which furnish the chemiluminescence reagents;

$$\eta_i=\frac{\text{no. of precursor complexes formed in useful space and time}}{\text{no. of reagent pairs produced}} \tag{4}$$

is the efficiency of encounter of $A^+$ and $A^-$ in such a time and space that the eventual light emission could be detected;

$$\eta_{et}=\frac{\text{no. of } {}^*A \text{ obtained}}{\text{no. of electron transfer events in useful space and time}} \tag{5}$$

is the efficiency of the electron transfer reaction leading to the emissive excited state. Another possible electron transfer process leads directly to the ground state.

$$\eta_{em}=\frac{\text{no. of emitted photons}}{\text{no. of } {}^*A} \tag{6}$$

finally is the luminescence quantum yield of the complex relative to the emissive excited state.

In terms of the mechanism of Fig. 2 the ecl quantum yield can be written as

$$\varphi_{ecl}=\eta_e\eta_i\eta_{et}\varphi_{em} \tag{7}$$

$\eta_{e,ox}$ or $\eta_{e,red}$ should be considered if, respectively, $A^+$ or $A^-$ is the less produced ecl reagent (limiting reagent).

Operatively $\varphi'_{ecl}$ can be defined as well as

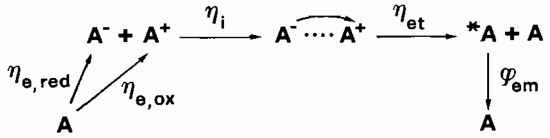

Fig. 2. Mechanicistics scheme of the electrochemiluminescence process. For the symbols, see text.

$$\varphi'_{ecl}=\frac{\int^{t_s} I\,dt}{\int^{t_s} i\,dt} \tag{8}$$

where $I$ is the light emitted, $i$ the current flowed and $t_s$ is the step duration; eqn. (8) corresponds to eqn. (7), so $i_{an}$ or $i_{cat}$ should be used according to the nature of the limiting reagent.

But we are interested in a $\varphi_{ecl}$ theoretically defined as

$$\varphi_{ecl}=\frac{\text{no. of photons emitted}}{\text{no. of reagent pairs}} \tag{9}$$

that is, to the product of eqns. (5) and (6) only. So the problem was how to get eqn. (9) from our experimental results which led to eqn. (8).

Let us analyze the constraints which the first step of ecl process depends on. As already stated (see 'Experimental'), the double layer charge and different electrolytic processes decrease the $\eta_e$ value; we tried to evaluate these factors so as to be able to subtract them from the total electric change, yielding $\eta_e=1$. As a matter of fact, the double layer charging is very fast and is completed in 10–20 ms. However its charge is so big that it constitutes more than one third of the total charge flowed in 100 ms. By increasing the step duration, the percentage of double layer charge decreases, but we saw that $\varphi_{ecl}$ decreased with increasing step time, as illustrated in Fig. 3. There it diminishes in spite of the increasing value of $\eta_e$ (due to the diminishing influence of the double layer charge, which remains constant while the total charge raises with time). So a step time 100 ms long seemed the best choice.

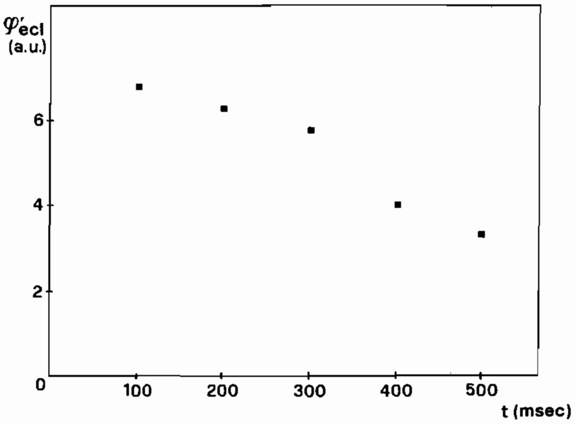

Fig. 3. Variation of $\varphi'_{ecl}$ as a function of potential step duration: $5\times10^{-4}$ M $Ru(bpy)_3^{2+}$ in ACN with $5\times10^{-2}$ M $TEABF_4$; potential stepped between −1.30 and +1.36 V.

TABLE 1. Electrochemical, photophysical and ecl data for Ru(II) polypyridine compounds

| Sample | $E_{0-0}$[a] | $E_p$(ox)[b] | $E_p$(red)[b] | $\varphi_{em}$[c] | $\varphi_{ecl}$[d] | $\eta_{et}$ |
|---|---|---|---|---|---|---|
| $Ru(bpy)_3(ClO_4)_2$ | 2.13 | 1.34 | −1.40 | 0.072[e] | 0.005 | 0.07 |
| $Ru(bpy)_2$(i-biq)$(PF_6)_2$ | 2.12 | 1.28 | −1.44 | 0.072 | 0.019 | 0.26 |
| Ru(bpy)(i-biq)$_2(PF_6)_2$ | 2.12 | 1.24 | −1.48 | 0.071 | 0.015 | 0.21 |
| $Ru(bpy)_2$(biq)$(PF_6)_2$ | 1.70 | 1.39 | −0.97 | 0.0081 | 0.00042 | 0.052 |
| Ru(bpy)(biq)$_2(PF_6)_2$ | 1.69 | 1.47 | −0.89 | 0.0067 | 0.00042 | 0.062 |

[a] Energy of the lowest excited state, from ref. 20. [b] Redox potentials vs. SCE, obtained by using the ecl cell. [c] Photoluminescence quantum yields. [d] Obtained stepping the potential between 50 mV over the oxidation peak and 30 mV under the reduction peak, getting an only cathodic light emission. All samples $5\times10^{-4}$ M in $5\times10^{-2}$ M $TEABF_4$. [e] In perfect agreement with ref. 11d.

The phenomenon shown in Fig. 3 is caused by the decrease of $\eta_i$ with increasing step time, since $A^+$ and $A^-$ produced at the electrode surface have to meet and to form a precursor complex before attaining the electron transfer. The number of pairs whose reaction cannot be seen by the photomultiplier increases with increasing step time.

This last factor entity is not easy to estimate nor to diminish. But the best value of $\eta_i$ (not unity because of what we said above) would be achieved by raising the concentration of, for example, $A^+$ near W so much that all $A^-$, just formed, reacted with it. Moreover, in the above case, we would have light emission during the only cathodic step, because of the lack of left over $A^-$ when the anodic potential is applied. As a matter of fact we observed light emission during only the cathodic step, only the anodic step or both, depending on the applied potentials and also on the nature of the limiting reagent. If we hold one potential fixed at a high value and vary the other one, the $\varphi'_{ecl}$ increases increasing this potential until the light is emitted only during its application; when light begins to be visible in both steps, then the $\varphi'_{ecl}$ starts falling (Fig. 4). This is only due to the increasing concentration of both species which leads to an increase in the $\eta_i$ value, up to a maximum.

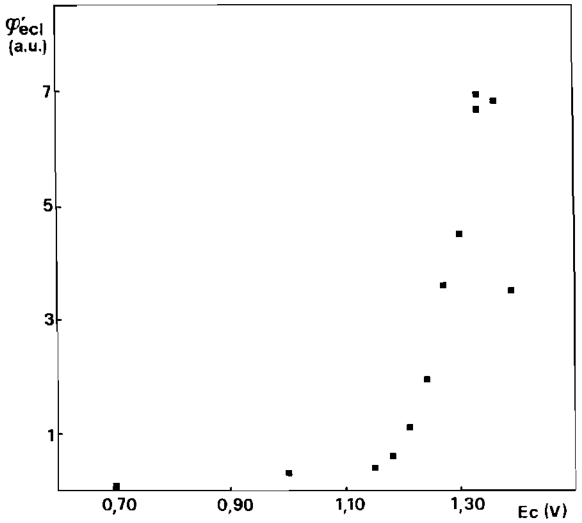

Fig. 4. Variation of $\varphi'_{ecl}$ as a function of applied reduction potential while the oxidation potential is maintained constant at +1.36 V; $5\times10^{-4}$ M $Ru(bpy)_3^{2+}$ in ACN with $5\times10^{-2}$ M $TEABF_4$.

To deal with this unavoidable factor we utilized potentials such that the $\eta_i$ values were the same for samples and standard, so it would disappear in the final ratio (eqn. (2)).

The $\varphi_{ecl}$ and $\eta_{et}$ values obtained for some Ru(II) polypyridine complexes are shown in Table 1, along with other relevant parameters. As can be seen, $\varphi_{ecl}$ and $\eta_{et}$ are smaller for the compounds containing the i-biq ligand than for $Ru(bpy)_3^{2+}$, while their $\varphi_{em}$ is identical. This could be due to the larger dimension of the i-biq ligand with respect to bpy, which hinders the orbital overlap of the redox partners and lowers the efficiency of the electron transfer.

More surprising is the sharp decrease of $\varphi_{ecl}$ in going from the i-biq to the biq ligand, where the overlap factors should not be too different. A possible explanation may be found in the larger reactivity of the excited states of the complexes containing biq ligands, that are known to undergo photosubstitution reactions [21]. In this case the efficiency of the population of the dissociative excited state may depend on the nature of the excitation process, i.e. photoexcitation versus 'chemical' redox reaction. In this hypothesis, the values of $\eta_{et}$ in Table 1 for biq containing complexes are not correct, since we could not use the $\varphi_{em}$ found in the photoluminescence.*

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*Different chemical behaviour between photochemically and 'chemically' produced excited states has been reported for Ru–polypyridine complexes [22].

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