Issue 34, 2017

From the journal:
Physical Chemistry Chemical Physics

Electroluminescence of $[Ru(bpy)_3]^{2+}$ at gold and silver screen-printed electrodes followed by real-time spectroelectrochemistry

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https://doi.org/10.1039/C7CP04568A

View Article Online
DOI: 10.1039/C7CP04568A

Journal Name

COMMUNICATION

Electroluminescence of $[Ru(bpy)_3]^{2+}$ at gold and silver screen-printed electrodes followed by real-time spectroelectrochemistry

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Real-time spectroelectrochemistry of $[Ru(bpy)_3]^{2+}$ electroluminescence showed a strong correlation with electrochemical processes occurring at metal screen-printed electrodes. Luminescence was quenched when the metal oxidation takes place, but it behaved differently when gold or silver were reduced, which suggests that changes in the structural characteristics of metallic electrodes play a decisive role in luminescence spectroelectrochemistry.

The main text of the article should appear here. Headings and subheadings are not permitted in articles submitted to *Chemical Communications*, although they are permitted in communications submitted to other journals. Electroluminochromic compounds[1,2] show a different luminescent response depending on their redox state. They are useful in applications such as sensors[3] or optical devices[4]. For instance, Tris(2,2'-bipyridyl)dichlororuthenium(II) ($[Ru(bpy)_3]^{2+}$) is one of the electroluminochromic species most widely studied[5–7] since it shows different luminescent properties depending on its oxidation states (+2,+3) and exhibits a fast and reversible electrochemical response[8]. Metal-enhancing luminescence[9,10], widely reported in several works[11], is an effect that increases the emission intensity of certain luminescent species when some metallic substrates are used. This effect is normally produced by the interaction of the excited-state luminophores with free electrons from the metal (surface plasmon electrons). Metal-enhancing luminescence is typically studied by preparing ex-situ suitable metal structures, such as silver[12] or gold[13] nanostructured surfaces, or nanoparticles in solution[14]. However, few information is known about the *in situ* luminescence behaviour of electroluminescent species in real time when different redox processes occur at the metal surface.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Bizotto et al. have reported different studies on the fluorescence behaviour of adsorbed species on gold electrodes[15-16], however, the effect of electrode oxidation and reduction processes was not studied. In order to obtain this information, powerful techniques are needed to characterize the involved processes, being the luminescence spectroelectrochemistry[17-19] the most appropriate for these studies. Typically, luminescence spectroelectrochemical cells[20] are used in a 90^0 or similar configuration to discriminate between excitation and emission lights, and therefore, it increases the complexity of the system, being difficult their design and the possibility to use different electrodes (they are devices for very specific setups). The development of spectroelectrochemical instrumentation able to collect simultaneous and time-resolved optical-electrochemical data coupled with low-cost disposable electrodes[21,22] could boost the number of spectroelectrochemical studies and provide more information on the behaviour of these species in different environments. These disposable electrodes avoid the need of cleaning treatments, which could be an issue with easily adsorbable luminochromic species or oxidised products. In this work, we report the use of simple luminescence spectroelectrochemical instrumentation in reflection mode (epiluminescence measurements), which allows to study the electroluminescent response of $[Ru(bpy)_3]^{2+}$ at metal electrodes (gold and silver screen-printed electrodes) with a high time and potential resolution. **Figure 1A** shows an image of the instrumentation used in these studies (see description in the Experimental section) composed of a compact spectroelectrochemical instrument, a luminescence reflection probe and a spectroelectrochemical cell for screen-printed electrodes. $[Ru(bpy)_3]^{2+}$ displays an emission band with a maximum at 610 nm when it is irradiated with a 395 nm LED (**Figure 1B**), whose intensity varies depending on the redox processes that occur at the electrode surfaces as shown in this work.

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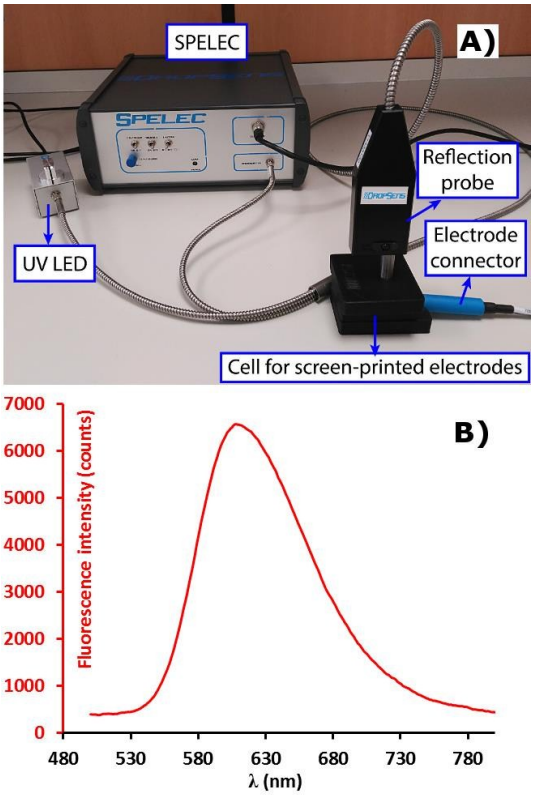

Figure 1. A) Image of the instrumentation employed for luminescence spectroelectrochemistry at metal screen-printed electrodes. **B)** Luminescence spectrum of $[Ru(bpy)_3]^{2+}$ in 0.1 M KNO_3 after excitation with a 395 nm UV LED.

The luminescent spectroelectrochemical response of $[Ru(bpy)_3]^{2+}$ was studied using a solution of 1.5 mM of $[Ru(bpy)_3]^{2+}$ in 0.1 M KNO_3 at gold screen-printed electrodes. Cyclic voltammetry was carried out from 0 V to +1.2 V to -1.1 V at 50 mV/s, covering a wide potential window to observe the different electrochemical processes at different potentials. Simultaneously, the luminescence spectra were recorded every 250 ms (integration time). **Figure 2A** shows the variation of luminescence at 610 nm as a function of cyclic voltammetry (voltaluminogram). Voltammogram of the background electrolyte is also shown for comparison. Initially, the luminescence remained quite constant up to +0.8 V where a sharp downwards change is observed. This change seems to be due to the oxidation processes that appear in the voltammogram. Two oxidation processes can be observed: the first one would correspond to the gold oxidation (peak potential at +0.91 V) since it also appeared in the blank, whereas the next one with a peak potential around +1.0 V is attributed to the oxidation of $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_3]^{3+}$. The correlation of these processes with the optical response is significant when the negative of the derivative luminescence at 610 nm is represented (**Figure 2B**). In this representation, the changes of the luminescence variation are highlighted and as the **Figure 2B** shows, they are strongly correlated with the electrochemical processes of the voltammogram. This process led to a clear decrease of the luminescence that could be in agreement with the metal-enhanced luminescence effect widely reported, as the oxidation of the gold surface could minimize this enhancing-effect. The luminescence continues to decrease until a potential near +0.93 V, which also corresponds to the onset of a new cathodic redox process. This process does not appear in the blank voltammogram, so it can be assigned to the $[Ru(bpy)_3]^{3+}$ reduction. This reduction caused an increment of the luminescence, which can be explained by the fact that the $[Ru(bpy)_3]^{3+}$ species is non-luminescent while the $[Ru(bpy)_3]^{2+}$ species is luminescent. This fact also suggests that the previous oxidation of $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_3]^{3+}$ observed in the voltammetric peak unresolved from the gold oxidation (as a shoulder at +1.0 V) should also contribute to the decrease of the luminescence observed at those potentials. A new slope change with a slight increase in the luminescence was observed at potentials near +0.5 V, which correlates with the reduction of the previously oxidized gold. This slight increase would also be in agreement with the metal-enhancing effect of the luminescence as fresh gold surface is being generated, but the enhancement is small in this case and the luminescence is not totally recovered.

This process is more clearly observed when the experiment is carried out using 0.1 M KCl as supporting electrolye, where soluble Au(III) species could be formed and more gold could also be oxidized. In this case (**Figures 2C** and **2D**), the gold reduction shows a more intense peak with lower peak-width than in KNO_3 solution, where the gold reduction appears with a wider and less intense process. In KCl, a higher increment of the luminescence can be observed when the gold reduction takes place, which also led to a more intense peak in the derivative voltaluminogram. Therefore, it is clear that the luminescence of $[Ru(bpy)_3]^{2+}$ increases when the reduction of Au(III) to Au(0) occurs. This fact could be due to some metal-enhanced luminescence as previously mentioned (by the effect of surface plasmons), although it does not seem very significant, or due to the recovery of an electrode surface with a higher power of light reflection that leads to a higher absorption yield and, therefore, to a higher-intensity emission. However, at these range of potentials the initial luminescence is not recovered from the initial one, so it seems that there has been some irreversible quenching. If the electrodes surface plays a significant role in the luminescence as it appears to do, then, it is obvious that the surface after the oxidation/reduction processes is not in the same conditions than initially and a different luminescence intensity is expected. Starting from -0.40 V towards negative potentials, a new luminescence increment was observed, related to a new cathodic process, assigned to the oxygen reduction reaction (ORR). In this case, the increment of the luminescence is significant, obtaining values higher than those obtained initially. Oxygen acts as a luminescence quencher, usually produced by dynamic collisions between molecules (charge-transfer processes)[23], and therefore, when the ORR takes place at the electrode surface, less O_2 molecules are available for quenching leading to a significant increase in the luminescence of $[Ru(bpy)_3]^{2+}$. This process is observed in the derivative voltaluminogram with the presence of a new peak at the same potential as the peak potential of the ORR in the voltammogram.

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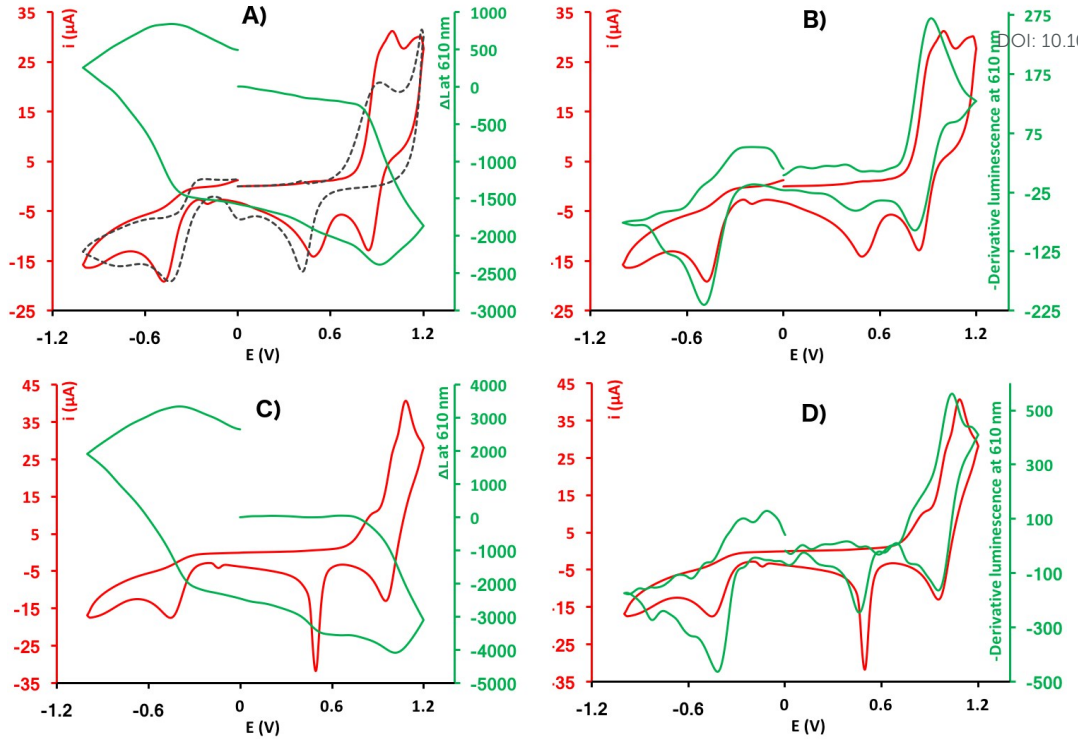

Figure 2. A) Voltaluminogram of the luminescence variation (ΔL) at 610 nm (green line) during the cyclic voltammogram (red line) of 1.5 mM $[Ru(bpy)_3]^{2+}$ in 0.1 M KNO_3 at gold screen-printed electrodes. Voltammogram in absence of $[Ru(bpy)_3]^{2+}$ is also shown (dashed line). **B)** Negative of the derivative voltaluminogram at 610 nm (green line) during the cyclic voltammogram (red line) of 1.5 mM $[Ru(bpy)_3]^{2+}$ in 0.1 M KNO_3 at gold screen-printed electrodes. **C)** Voltaluminogram of the luminescence variation (ΔL) at 610 nm (green line) during the cyclic voltammogram (red line) of 1.5 mM $[Ru(bpy)_3]^{2+}$ in 0.1 M KCl at gold screen-printed electrodes. D) Negative of the derivative voltaluminogram at 610 nm (green line) during the cyclic voltammogram (red line) of 1.5 mM $[Ru(bpy)_3]^{2+}$ in 0.1 M KCl at gold screen-printed electrodes.

Interestingly, the luminescence decreased at the last potentials of the cyclic sweep (from -0.5 V to 0 V). This fact is due to the diffusion of new quenching O_2 molecules to the electrode surface where it is in defect after the reduction. Therefore, the time-resolved spectroelectrochemical response is also able to provide information about non-redox processes occurring at the electrode/solution interface. These studies show how the $[Ru(bpy)_3]^{2+}$ luminescence correlates perfectly with the redox processes that take place at gold screen-printed electrodes. Moreover, the derivative of the luminescence resembles the voltammogram but inversely: the anodic processes cause a decrease in the luminescence at 610 nm, while that the cathodic processes cause an increase in the luminescence. **Video S1** is available as Supporting Information showing the voltaluminogram and the negative derivative voltaluminogram of $[Ru(bpy)_3]^{2+}$ in real time at gold screen-printed electrodes.

At silver screen-printed electrodes, the potential able to oxidize the $[Ru(bpy)_3]^{2+}$ is high enough to oxidize completely the silver working electrodes, so in this case, the potential range was chosen to produce only a slight oxidation of the electrode (up to +0.30 V). This way, the luminescence variation caused by the redox processes occurring at the electrode surface but without transforming the electroluminescent species was studied. Starting from the initial potential -0.2 V to 0.05 V, the luminescence remained practically constant as can be observed in the voltaluminogram at 610 nm (**Figure 3A**). A significant decrease in luminescence was observed from 0.05 V towards positive potentials, which correlates perfectly with an oxidation process assigned to the silver electrode. Interestingly, two oxidation processes could be observed, the first one with a peak potential around +0.1 V and a second process at higher potentials, which continues to increase after the most positive value of the cyclic sweep. Both processes could be assigned to silver oxidation, being the first one more favourable due to generation of insoluble AgCl (as the $[Ru(bpy)_3]^{2+}$ salt has chloride ions), and when all Cl^- is forming AgCl, Ag probably oxidises to a soluble form (main electrolyte is KNO_3). The decrease in the luminescence seems to be specially correlated with the first process (see derivative voltaluminogram in the **Figure 3B**), so it is probably due to the formation of AgCl in the electrode surface affecting the luminescent emission of $[Ru(bpy)_3]^{2+}$ or minimizing the metal-enhanced effect. The luminescence after this oxidation process is kept constant until reaching -0.05 V, suggesting that the decrease is related only to the first oxidation process. Unlike the behaviour at gold electrodes, when silver is reduced again (and electrodeposited) as indicated by the intense cathodic process at -0.135 V, the luminescence drops sharply between -0.05 V and –0.17 V.

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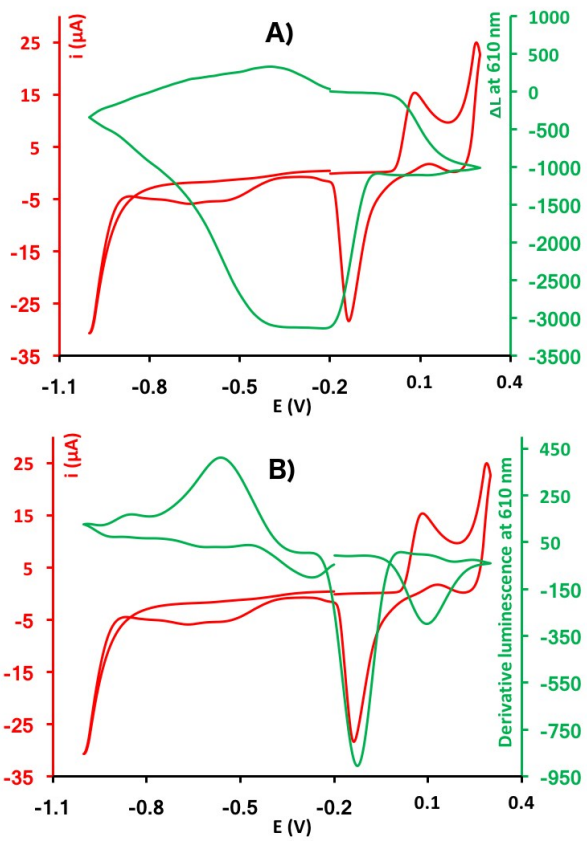

Figure 3. A) Voltaluminogram of the luminescence variation (ΔL) at 610 nm (green line) during the cyclic voltammogram (red line) of 1.5 mM $[Ru(bpy)_3]^{2+}$ in 0.1 M KNO_3 at silver screen-printed electrodes. B) Derivative voltaluminogram at 610 nm (green line) during the cyclic voltammogram (red line) of 1.5 mM $[Ru(bpy)_3]^{2+}$ in 0.1 M KNO_3 at silver screen-printed electrodes.

After the peak current returned to the baseline, indicating total reduction of silver, the luminescence of $[Ru(bpy)_3]^{2+}$ remained constant until -0.45 V, suggesting that the abrupt change of luminescence is strongly correlated with the electrodeposition of silver as shown in the derivative voltaluminogram, and therefore, that the electrode surface plays an important role in the recorded luminescence. Although a fresh silver surface is generated by electrodeposition, no metal-enhancing effect was observed in this case demonstrating a totally different behaviour in comparison to gold electrodes. After -0.45 V, a new electrochemical reduction process appeared, which is attributed to the ORR in the same way that for gold electrodes, although in this case a less defined peak is obtained. Similarly, the luminescence of $[Ru(bpy)_3]^{2+}$ also increased when the ORR was produced at silver electrodes, reaching a maximum value at a potential of -0.4 V (already again in the anodic sweep) and higher that the value obtained initially. From -0.4 V to the final potential (-0.2 V), the luminescence decreases slightly again probably due to the diffusion of new O_2 molecules that diffuse towards the electrode surface to produce the quenching of the luminescence. **Video S2** is available as Supporting Information showing the voltaluminogram and the derivative voltaluminogram of $[Ru(bpy)_3]^{2+}$ in real time at silver screen-printed electrodes.

Conclusions

Real-time luminescence spectroelectrochemistry is a very interesting technique to observe changes occurring at the electrode/solution interface in real time. The simple coupling with screen-printed electrodes presented in this work allows its application using low-cost and easy to use disposable electrodes with the three electrodes of the electrochemical cell miniaturised in the same planar substrate. With these tools, we could detect changes in the luminescence of electroluminochromic species such as $[Ru(bpy)_3]^{2+}$ in two different metal screen-printed electrodes, which were strongly correlated with the electrochemical processes occurring during potentiostatic measurements. The oxidation of both metal surfaces (gold and silver) decreased the luminescence of the $[Ru(bpy)_3]^{2+}$ but the reduction of the oxidized metal affected the luminescence differently whether gold or silver electrodes are used. These results demonstrate that the electrode surface properties are an important parameter in spectroelectrochemical measurements of luminescence in reflection mode.

Experimental Section

Instrumentation and materials

All electrochemical, spectroscopic and spectroelectrochemical measurements were carried out with a SPELEC instrument (DropSens) controlled by DropView SPELEC software (2.3 version). Luminescence spectroelectrochemistry measurements were performed with a bifurcated reflection probe (DropSens, ref.DRP-FLUOPROBE) and a specific cell for screen-printed electrodes (Dropsens, ref.DRP-RAMANCELL) working in a near-normal reflection configuration. The excitation connector of the bifurcated probe was connected to a 395 nm UV LED (ref.DRP-UVLED, DropSens) and the detection connector of the probe was connected to the SPELEC. The LED was powered by an USB port of the computer and its intensity was changed with the selector on the LED box (3.5 V was the applied voltage in this work). Figure 1A of the main manuscript shows the SPELEC setup for time-resolved luminescence spectroelectrochemistry with screen-printed electrodes. Luminescence measurements were carried out with an integration time of 250 ms.

DropSens screen printed electrodes (SPEs) incorporate a three-electrode configuration printed on a planar ceramic substrate (with dimensions of 3.4 x 1.0 cm). Gold SPEs with working (disk-shaped 4 mm diameter) and counter electrodes made of low-temperature curing gold inks were employed (ref. DRP-220BT). Silver SPEs with a disk-shaped working electrode (1.6 mm diameter) made of silver ink and a counter electrode made of carbon ink were employed (ref. DRP-C013). Both gold and silver SPEs had a pseudoreference electrode and electric contacts made of silver. Therefore, the potential values are reported versus the silver pseudoreference electrode. All measurements with SPEs were carried out at room temperature and using a drop volume of 45 μL of the appropriate solution. SPEs were

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connected to the SPELEC instrument through a specific connector (DropSens, DRP-CAST).

Reagents and solutions

Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ($[Ru(bpy)_3]^{2+}$), potassium chloride and potassium nitrate were purchased from Sigma-Aldrich. Ultrapure water was obtained from a Milli-RO 3 plus/Milli-Q plus 185 purification system from Millipore.

Conflict of interest

There are no conflicts to declare.

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