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# Observation of Electroluminescence at Room Temperature from a Ruthenium(II) Bis-Terpyridine Complex and Its Use for Preparing Light-Emitting Electrochemical Cells

**Henk J. Bolink,* Luca Cappelli, Eugenio Coronado, and Pablo Gaviña**

*Institute of Molecular Science, University of Valencia, Dr. Moliner 50. 46100 Burjassot, Valencia, Spain*

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A terpyridine ruthenium (II) complex containing a substituted and an unsubstituted terpyridine ligand was synthesized, and its luminescence properties were studied in a solid-state single-layer light-emitting electrochemical cell. The obtained devices emitted light of a very deep red color (CIE, $x = 0.717$ $y = 0.282$) at low external applied bias. It is the first example of an electroluminescence device based on a bis-chelated ruthenium complex. Its ambient atmosphere decay is remarkably different from analogous devices using tris-chelated ruthenium complexes.

Organic light emitting diodes (OLEDs) are becoming increasingly successful as a new display technology.[1] Most OLEDs are based on neutral molecules or polymers and rely on properly chosen electrodes for electron and hole injection into the light-emissive layer. In most cases, metals unstable in air, such as calcium, barium, or aluminum, are used as cathodes to support electron injection. These metals are one of the reasons for the thorough encapsulation needed to obtain long lifetimes in these devices. Light emitting electrochemical cells (LEC) are among the youngest generation of OLEDs and contain ionic charges in addition to light-emitting complexes and charge-transporting molecules or polymers.[2] These ionic charges facilitate electronic charge injection into the light-emitting film independent of the metallic electrode employed, opening the road for unencapsulated stable devices. Additionally, these devices have a larger tolerance to the thickness of the emitting layer, which facilitates the production process. First examples of LECs were based on polymeric OLEDs to whom salts, such as $Li(SO_3CF_3)$, were added to facilitate the charge injection.[3] Later examples used a single-molecule approach in which a single molecule acts both as the charge-transporting species and as the emitter.[4] Most of these LECs make use of the positively charged metal organic complex, tris-bipyridine ruthenium, $Ru(bpy)_3{}^{2+}$, balanced by a large negative counterion such as hexafluorophosphate.[2] The possibility to use air-stable electrodes combined with the architectural simplicity of the single-molecular LEC devices are the main advantages over nonionic OLEDs. Additionally, large efficiencies can be obtained at low driving voltage, resulting in high power efficiencies required for lighting applications.[5]

The drawback of LEC devices is the limited amount of emission colors available and their limited lifetimes with respect to OLEDs. Although studies to determine the degradation mechanism have been performed on $Ru(bpy)_3{}^{2+}$ complexes, a clear picture of the degradation process is still lacking.[6]

It is therefore interesting to increase the number of available emitting complexes useful for LEC devices in order to a) increase the amount of emitting colors available and b) study and improve the device stability.

One class of ruthenium complexes that is possible to use is that of the bis-chelated ruthenium complexes. These complexes are chemically robust, which may increase the device stability. Additionally, the emission color of most bis-chelated ruthenium complexes is a deep red, which is a necessary color for full-color display applications. However, these complexes are not an immediately obvious choice for this purpose as they generally do not emit at room temperature. In fact, the complex ruthenium bis-terpyridine ($Ru(tpy)_2{}^{2+}$) has a very short-lived excited state and subsequently a very low luminance efficiency such that room-temperature emission is not observed.[7] Nevertheless, when substituting the terpyridine with electron-withdrawing or -donating entities on the 4′ positions para to the nitrogen atoms, the excited-state lifetime and the emission quantum yield are enhanced

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* E-mail: henk.bolink@uv.es.

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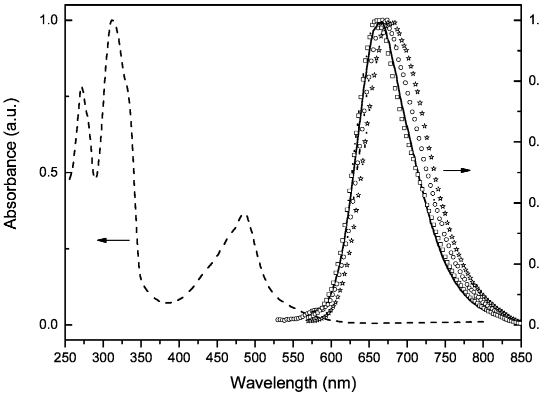
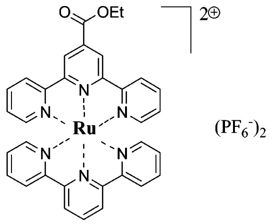


**Figure 1.** Absorption (dashed line), photoluminescence spectra for a solution in dichloromethane (squares), acetonitrile (triangles), and dimethyl sulfoxide (stars), and photoluminescence of a thin film containing 80% **1** and 20% PMMA (solid line).

**Scheme 1**



dramatically, leading to deep red emissive complexes at room temperature.[8] To investigate the possibility of using substituted tpy ligands in combination with a ruthenium core as the emitting species for LECs, we have prepared the heteroleptic ruthenium complex, [Ru(tpy)(tpy-$CO_2Et$)][$PF_6$]$_2$, **1** (Scheme 1) and studied its luminescence properties.

The electrochemistry (given as voltage versus the ferrocenium couple) of **1** is similar to that of Ru(tpy)$_2{}^{2+}$ with a single one-electron oxidation, predominately metal-based in nature, and a series of ligand-based reductions. The oxidation potential of **1** (0.096 V) is very similar to that of Ru(tpy)$_2{}^{2+}$ (0.092 V). The ligand-based reduction potentials for **1** (−1.269 V) and (−1.45 V) are shifted with respect to Ru(tpy)$_2{}^{2+}$ (−1.67 V) due to the electron-withdrawing substituent.

Solid films of **1** were obtained by spin-coating from acetonitrile solutions. To improve the film forming properties, **1** was blended with 20% poly(methyl methacrylate) (PMMA). The absorption spectrum of a thin film of **1** mixed with 20% PMMA is shown in Figure 1. The intense absorption bands, around 280 and 325 nm, can be assigned to ligand-centered $\pi-\pi^*$ transitions. The relative intense and broad absorption band in the visible region is due to a spin-allowed d−$\pi$ metal-to-ligand charge transfer (MLCT) transition. The absorption spectrum is practically identical to that reported in the literature for Ru(tpy)$_2{}^{2+}$ in acetonitrile solution.[7] Unlike the unsubstituted compound that showed no detectable photoluminescence at room temperature, compound **1** shows a deeply red photoluminescence. The emission spectra depend only slightly on the polarity of the solvent. A 20 nm shift in the maximum of the emission spectrum is observed when changing the solvent from dichloromethane to dimethyl sulfoxide. The photoluminescence in a solid film is almost identical to that in dichloromethane solution. This indicates that there is no noticeable effect of the charged complexes on the emission wavelength. Using charged iridium complexes, large (up to 80 nm) shifts in emission spectra have been observed when changing from a solution to a solid film.[9] This leads us to conclude that the photoluminescence of ruthenium bis-terpyridines is less sensitive to its medium than tris-chelated charged iridium complexes.

**Table 1.** Photophysical Properties of **1**

| | abs[a] 298 K | emission 298[a] K | | |
|---|---|---|---|---|
| | $\lambda$ (nm) | $\lambda$ (nm) | $\tau^b$ (ns) | $\varphi_{em}{}^c$ |
| **1** | 485 | 667 | 32 | $2.7 \times 10^{-4}$ |

[a] Acetonitrile. [b] Luminescence emission lifetime (±10%). [c] Luminescence quantum yield (±10%), using Ru(bpy)$_3$:($PF_6$)$_2$ as the reference.

The photoluminance lifetime and efficiency are depicted in Table 1. The emission lifetime of **1** in acetonitrile solution is in the same order of magnitude as other ruthenium terpyridines substituted with electron-withdrawing moieties.[8] Its emission maximum is red-shifted with respect to the emission spectrum of Ru(tpy)$_2{}^{2+}$, caused by a decrease in the LUMO level associated with the substituted tpy ligand. The photoluminescence efficiency, although much larger than that of Ru(tpy)$_2{}^{2+}$, is a factor 2 smaller than that of Ru(bpy)$_3{}^{2+}$. Compound **1** does have a much deeper red emission than Ru(bpy)$_3{}^{2+}$. Having established that the bis-chelated ruthenium complex, **1**, shows photoluminescence at room temperature, it is of interest to verify whether it can be used to prepare a solid-state LEC and obtain room-temperature electro-emission.

Devices were prepared by depositing gold or silver electrodes on top of the spin-coated thin films. Structured ITO-containing glass plates were used as the substrates. Physical characterization was performed in ambient atmosphere.

Upon applying a bias of 3 V to an ITO/**1**:PMMA/Au device, light emission, slowly increasing in intensity with time, is observed. The electroluminescence spectrum of **1** is broad and slightly shifted with respect to the photoluminescence spectra obtained from the thin film (Figure 2, inset). The emission spectrum has a maximum at 706 nm which corresponds to an energy of 1.76 eV for the lowest excited state in this system. The CIE coordinates[10] of the emitted light are; $x = 0.717$ $y = 0.282$ which is at the far end of the red corner of the CIE diagram. This is the deepest red light emission observed so far in LEC devices. Such a color point can be useful in display application, as in combination with a green and blue emitter it allows the formation of all colors lying between the red, blue, and green. From the comparison of the emission spectra with the sensitivity of the human

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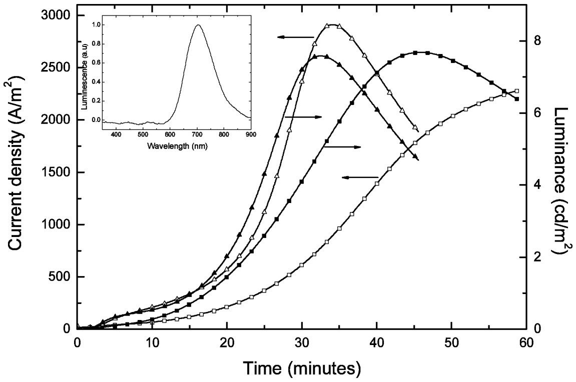

**Figure 2.** Buildup of current density (open symbols) and luminance (closed symbols) for an ITO/**1**:PMMA/Au device under a forward (up triangles) and reverse (squares) of 3 V. Inset, electroluminescence of the same device at an applied bias of 3 V.

eye toward different wavelengths, it is clear that these films are predominantly infrared light emitters. Due to the broad emission spectra, only a small fraction of the emitted photons are detectable by the human eye.

The electrical characteristics of the ITO/**1**:PMMA/Au devices are similar to those seen in devices based on tris-chelated ruthenium complexes. The most striking feature in these devices is the time-delayed response when a bias is applied. Such a behavior is shown in Figure 2. At an applied bias of 3 V, the maximum light output is observed around 30 min. This delayed response reflects the mechanism of device operation. Under the influence of the applied electric field, the negative $PF_6$ ions start to migrate toward the positively charged electrode, leaving at the side of the negatively charged electrode a surplus of positive charges. With an increasing amount of ions near the electrode-organic layer interface, the amount of electronic charges that are injected increases. The enhanced ability of electrons and holes to enter the device results in the observed increase in current density and luminance.

Additionally, in LEC devices, the electroluminescence response should be independent of the polarity of the applied bias. That is, its characteristics should be independent of positive or negative applied bias as the injection is governed primarily by the buildup of an internal electric field by the movement of the ions and not by the work function of the electrodes. When applying a negative bias to the ITO/**1**:PMMA/Au device, similar brightness levels are observed as those for forward bias operation (Figure 2). This result demonstrates that the device is operating as a LEC. The current response, however, is significantly slower and, at the maximum brightness, lower for a device in reverse bias. Therefore, even though the luminance levels are similar, the efficacy is almost a factor two higher in reverse bias due to the lower current density.

It may be interesting to compare the device properties of a bis-chelated ruthenium complex with those reported for a tris-chelated ruthenium complex. The **1**:PMMA film emits light with an efficacy reaching 0.01 cd/A, which is approximately 100 times less than that observed in LEC devices using the tris-chelated $Ru(bpy)_3^{2+}$ complexes. This efficacy is higher than expected on the basis of the low photoluminescence quantum yield and the poor overlap with the eye sensitivity curve, relative to that of $Ru(bpy)_3^{2+}$. This indicates that either the charge recombination or the light outcoupling is better in LEC devices using compound **1**. For applications in displays, the efficacy is obviously too low; however, it does demonstrate that the chemically stable ruthenium tpy complexes can be used to generate light through electroemission. The reason for the lower efficacy lies mainly in the lower photoluminescence quantum efficiency and, to a lesser extent, in the small overlap of the wavelength of the emitted light with the eye sensitivity curve.

The time to half of the maximum brightness is 25 and 35 min in forward and reverse bias, respectively. When comparing the ITO/**1**:PMMA/Au device to analogous ruthenium tris-chelated LECs operating in ambient conditions, it is noted that the bis-chelated ruthenium containing devices have a longer lifetime. The very rapid EL decay (30 s) with a much slower current density decay as reported by Kalyuzhny et al. for a device using $Ru(bpy)_3^{2+}$ in ambient conditions is not observed.[6a] In their study, the rapid emission decay is attributed to a reaction product of $Ru(bpy)_3^{2+}$ and water that acts as an emission quencher. In the devices containing compound **1** as the emitting complex, the decay in light emission and current density have a similar time response. From this behavior, it seems less likely that an emission quencher is generated. Instead, the similar decay curves for the luminance and current density are indicative of a decay mechanism that affects both these parameters simultaneously. Hinting at a disturbance of the charge injection and/or transport during device operation. A more thorough study would be necessary to address the device stability. Although the lifetime of LEC devices using **1** as the emitting complex is too low for practical applications, it offers an independent path towards studying lifetime behavior in LEC devices.

In conclusion, we have shown that a bis-chelated ruthenium complex shows electroluminescence at room temperature. Using the title complex, we have been able to prepare very deep red emissive devices that operate at low voltages. The observed efficacy is low compared to devices employing tris-chelated ruthenium complexes; however, it is higher than expected in view of its low photoluminescence efficiency. The stability of the devices is significantly longer than tris-chelated ruthenium-based LEC devices prepared in ambient atmosphere. These findings open the way to develop a new class of deep red emitters useful for preparing and improving the performance of light-emitting electrochemical cells.

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**Supporting Information Available:** Experimental details and device preparation. This material is available free of charge via the Internet at http://pubs.acs.org.

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