

Efficient and Stable Solid-State Light-Emitting Electrochemical Cell Using Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) Hexafluorophosphate

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One of the latest types of organic light-emitting devices (OLEDs) makes use of ionic charges to facilitate electronic charge injection from the metal electrodes into the organic or inorganic molecular semiconductor.¹ 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. The first example of such light-emitting electrochemical cells (LECs) was reported when an ionic salt was added to a poly(phenylenevinylene) light-emitting polymer.² More recently, the focus has shifted to organometallic compounds that yield single-component solid-state light-emitting devices. The compound most widely used in these single-component devices is tris(bipyridine)ruthenium ($\text{Ru}(\text{bpy})_3^{2+}$), balanced by a large negative counterion such as hexafluorophosphate.^{3,4} Nevertheless, the LECs still have a low stability, ranging from several hours to days, and a limited amount of colors available. Making use of heteroleptic iridium and ruthenium pyridyl complexes, the range of available emission colors has been widened.^{5,6} Also, significant research has been done toward the identification of the stability-limiting factors of LECs using $\text{Ru}(\text{bpy})_3^{2+}$ as the emitting entity.^{7–9} One of the reasons for the low stability of $\text{Ru}(\text{bpy})_3^{2+}$ devices seems to be the creation of the quenching molecule $\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2^{2+}$.⁸ Therefore, it is exciting to examine the use of the amphiphilic ruthenium complex tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) ($\text{Ru}(\text{dpp})_3^{2+}$) in LEC devices, as this complex exhibits photoluminescence quantum yields 6 times higher than the $\text{Ru}(\text{bpy})_3^{2+}$ and is more robust toward water-induced substitution reactions.¹⁰ However, the reported synthetic route for this complex involves long reaction times (several days), multiple synthetic steps, and low yields, often <5%.^{11,12} In an attempt to simplify the preparation of the $\text{Ru}(\text{dpp})_3^{2+}$ complex, we have adopted the microwave-assisted synthetic method as described for similar complexes.^{13,14} Here we describe the efficient microwave-assisted one-pot synthesis of the title compound and its application in solid-state light-emitting electrochemical cells.

In a typical reaction, dichloro(*p*-cymene)ruthenium(II) dimer is dissolved with an excess of 4,7-diphenyl-1,10-phenanthroline in DMF and subjected to 300-W microwave irradiation at 250 °C for 5 min. After cooling and precipitating in a mixture of dichloromethane:diethyl ether (2:5), the solid was recrystallized, yielding 89% of analytically pure tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) dichloride. This was then converted to the PF_6^- salt using a simple metathesis reaction.

Solid films of $\text{Ru}(\text{dpp})_3^{2+}$ were obtained by spin-coating from acetonitrile solutions. To improve the film-forming properties, $\text{Ru}(\text{dpp})_3^{2+}$ was blended with 20% poly(methyl methacrylate) (PMMA).

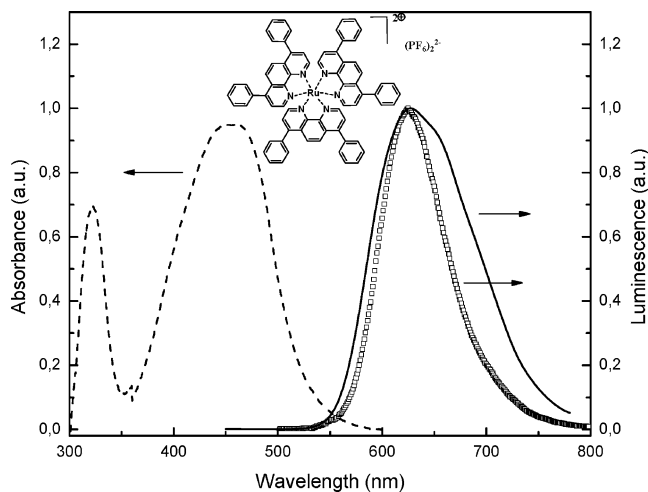


Figure 1. Absorption (dashed line), photoluminescence (open squares), and electroluminescence (solid line) spectrum of a thin film of $\text{Ru}(\text{dpp})_3^{2+}$: PMMA. Inset: chemical structure of $\text{Ru}(\text{dpp})_3^{2+}(\text{PF}_6^-)_2$.

The thickness of these films ranged between 100 and 200 nm, measured using a profilometer. Devices were prepared by depositing gold or silver electrodes on top of the spin-coated thin films, which were evaporated under vacuum ($<2 \times 10^{-6}$ mbar) to a thickness of 100 nm. Structured ITO-containing glass plates were used as the substrates. Device preparation and characterization were performed in an inert atmosphere (<0.1 ppm H_2O and <0.1 ppm O_2).

Upon applying a bias of 3 V to an ITO/ $\text{Ru}(\text{dpp})_3^{2+}$:PMMA/Au device, light emission, slowly increasing in intensity with time, is observed. The electroluminescence spectrum of $\text{Ru}(\text{dpp})_3^{2+}$ is broad and slightly red-shifted with respect to the photoluminescence spectra obtained from solution (Figure 1). Similar shifts have been reported for other complexes and are attributed to polarity effects of the medium of the luminescent complexes.^{5,6} The emission spectrum has a maximum at 630 nm. The CIE coordinates¹⁵ of the emitted light are $x = 0.631$, $y = 0.366$, corresponding to an orange-red color and very similar to those observed for the $\text{Ru}(\text{bpy})_3^{2+}$ complex.

The temporal behavior of an ITO/ $\text{Ru}(\text{dpp})_3^{2+}$:PMMA/Au device is depicted in Figure 2. The buildup of the light output is synchronous with that of the current density. This time-delayed response is one of the striking features of the operation of an electrochemical cell and reflects the mechanism of device operation. Under the influence of the applied electric field, the PF_6^- anions start to migrate toward the positively charged electrode, leaving at the side of the negatively charged electrode a surplus of positive charges. With increasing amount of ions near the electrode–organic layer interface, the amount of electronic charges that are injected

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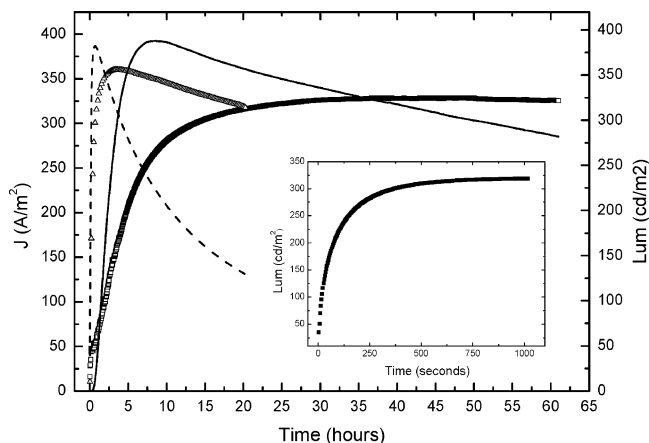


Figure 2. Current density and luminance evolution as a function of time for an ITO/Ru(dpp)₃²⁺:PMMA/Au device (open squares and solid line, respectively) and for an ITO/Ru(bpy)₃²⁺/Au device (open triangles and dashed line, respectively) under an applied bias of 3 V. Inset: recovery of the light emission of an ITO/Ru(dpp)₃²⁺:PMMA/Au device after turning off the bias for 2 min after 40 h of operation.

increases, which results in the observed increase in current density and luminance. A maximum light output of 390 cd/m² is reached after approximately 8 h. This slow temporal response is due to the low migration rate of the PF₆⁻ ions through the solid films and can be greatly enhanced by replacing this counterion with smaller ones, such as BF₄⁻.¹⁶ At the maximum light output, a power efficiency of 1.9 Lum/W and a current efficiency of 1.85 cd/A are reached. The external quantum efficiency is 1.25%, which is significantly higher than the ones observed for ruthenium(II) tris-(4,7-diphenyl-1,10-phenanthroline disulfonate)-containing devices.¹⁷

The power efficiency is similar to that observed for Ru(bpy)₃²⁺ and among the highest obtained for red-orange emitters. It demonstrates the potential of this type of device for commercial display applications.^{16,18} Even more striking than the power efficiency is the long temporal stability of the device. When taking the lifetime as the point in time where the luminous intensity reaches 50% of the maximum intensity, we reach a room-temperature lifetime of 115 h under dc driving at 3 V. As different values for the lifetime have been reported in the literature^{8,18,19} for devices using Ru(bpy)₃²⁺ complexes, we have prepared devices using Ru(bpy)₃²⁺:(PF₆)₂ under conditions identical to the ones used for the Ru(dpp)₃²⁺ devices. As is clearly noted from Figure 2, the lifetime of Ru(bpy)₃²⁺-based devices is approximately 12 h. These results show that the lifetime of Ru(dpp)₃²⁺-based devices is significantly increased with respect to that of devices using Ru(bpy)₃²⁺. A remarkable difference in the luminance decay is observed with respect to the decay of the current density of devices using the Ru(dpp)₃²⁺ complex. The current density is maintained over the full range of the measurement time, indicating that there is practically no decay of the charge injection or transport on this time scale. However, on the same time scale, the luminance is decreasing, indicative of the degradation of the emitting complex or, as reported previously by Kalyuzhny et al., the generation of a luminescent quencher.⁸ It is not unlikely that a quenching molecule, as a result of a reaction of the title complex with H₂O, is formed

analogous to the complex formed in Ru(bpy)₃²⁺-containing LEC devices. However, due to the more hydrophobic nature of the title complex, the formation of such a quenching molecule would be strongly retarded, hence explaining partly the increased stability of the LEC devices using the Ru(dpp)₃²⁺ complex. Further studies will be performed with the Ru(dpp)₃²⁺ complex in different device architectures and utilizing different driving schemes to examine the maximum achievable lifetime at high brightness. For example, it has been shown in this kind of devices that the lifetime is greatly enhanced when an ac driving mode is applied.¹⁹

In conclusion, the complex Ru(dpp)₃²⁺ shows very promising electroluminescence behavior when operated in a solid-state light-emitting electrochemical cell, reaching a high power efficiency of 1.9 Lum/W at a luminous brightness of 390 cd/m². These devices have the longest dc lifetimes reported so far, showing their potential for use in solid-state lighting and display applications. Additionally, a simple microwave-assisted synthetic method is described to prepare the Ru(dpp)₃²⁺ complex, which makes the complex easily accessible for further investigation.

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Supporting Information Available: Experimental procedures and analytical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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