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Solid-State Light-Emitting Devices Based on the Tris-Chelated Ruthenium(II) Complex. 4. High-Efficiency Light-Emitting Devices Based on Derivatives of the Tris(2,2′-bipyridyl) Ruthenium(II) Complex

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Abstract: Light-emitting devices from the tris(2,2′-bipyridyl)ruthenium(II) complex [Ru(bpy)$_3$$^{2+}$] and new derivatives thereof were prepared. Due to the electrochemical nature of the device operation, single-layer devices in an ITO/ Ru(bpy)$_3$$^{2+}$ complex + PMMA/Ag sandwich configuration achieved very high external quantum efficiencies. The derivatives of the Ru(bpy)$_3$$^{2+}$ complex were designed and synthesized to inhibit self-quenching of the excited state by adding different alkyl substituents on the bipyridyl ligands. As a result, devices that contain these new Ru(bpy)$_3$$^{2+}$ complexes show a higher photoluminescence and electroluminescence efficiency than devices made from the unmodified Ru(bpy)$_3$$^{2+}$ complex. External quantum efficiencies up to 5.5% at brightnesses in the range of 10−50 cd/m^2 are reported. In addition, the response time of such devices (which is a result of the electrochemical operation) has been shortened dramatically. An “instantaneous” light emission is achieved for devices that employ smaller counterions such as BF$_4$$^-$ to increase the ionic conductivity. Such a device shows a response time of less than 1 s to emit 10−20 cd/m^2 after the operating voltage of 2.4 V has been applied.

1. Introduction

Organic light-emitting devices (OLEDs) have become very attractive due to their potential application in flat panel displays. The field of OLEDs can broadly be divided into two groups of electroluminescent materials, namely small molecules and polymeric materials.[1,2] Devices fabricated with these materials generally require a multilayer structure and cathodes made of low work function metals in order to achieve high efficiencies and low operating voltages. Recently, the efficiency of small molecule devices has been further increased by employing phosphorescent dyes in the electroluminescent layer since phosphorescent molecules emit from their triplet state.[3]

A different type of light-emitting device is the light-emitting electrochemical cell (LEC).[4] An example of an LEC is a conjugated polymer such as poly(phenylene vinylene) (PPV) blended with a solid electrolyte that provides mobile ions. In such a device, the charge injection is more balanced and becomes fairly insensitive to the electrode work function due to the electrochemical nature of the operation. With such systems, high-efficiency, single-layer, light-emitting devices were demonstrated.[5]

It has been shown that the tris(2,2′-bipyridyl)ruthenium(II) complex [Ru(bpy)$_3$$^{2+}$] can be employed in solid-state organic light-emitting devices.[6−8] Recently, the performance of such devices was improved by blending the Ru(bpy)$_3$$^{2+}$ layer with PMMA. Blend devices that were prepared by spin coating employing cathode materials such as Ag or Al achieved external quantum efficiencies in the range of 2.0−3%.[7] Since the Ru(bpy)$_3$$^{2+}$ complex is a charged molecule, it is associated with generally mobile counterions. Consequently, devices employing the Ru(bpy)$_3$$^{2+}$ complexes operate similar to LECs. However, since mobile counterions are already present, no additional electrolyte is necessary. Furthermore, because the emission of a Ru(bpy)$_3$$^{2+}$ complex comes from a triplet state, such devices have the potential to exhibit very high efficiencies.

The stability of LECs is very sensitive to the operating voltage and devices degrade quickly when the applied bias exceeds the window of the electrochemical stability of the system. However, it has been shown that the stability of LECs can be increased by operating a device with a pulsed voltage scheme.[7,9]

LECs in general exhibit a delay between the time when the device is turned on and the time when a steady-state light emission is reached. This time delay (response time) is caused by the redistribution of ions that must occur to support the hole

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(1) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913−915.
(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539−541.
(3) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature (London)* **1998**, *395*, 151−154.
(4) Pei, Q. B.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. *Science* **1995**, *269*, 1086−1088.
(5) Yang, Y.; Pei, Q. B. *J. Appl. Phys.* **1997**, *81*, 3294−3298.
(6) Handy, E. S.; Pal, A. J.; Rubner, M. F. *J. Am. Chem. Soc.* **1999**, *121*, 3525−3528.
(7) Rudmann, H.; Rubner, M. F. *J. Appl. Phys.* **2001**, *90*, 4338−4345.
(8) Gao, F. G.; Bard, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 7426.
(9) Yu, G.; Cao, Y.; Zhang, C.; Li, Y. F.; Gao, J.; Heeger, A. J. *Appl. Phys. Lett.* **1998**, *73*, 111−113.

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(oxidation) and electron (reduction) injection at the electrodes. In a two-phase system consisting of an electrolyte and a conjugated polymer, the response time is also governed by the distance the ions have to move from the electrolyte into the semiconducting polymer.[10] Consequently, faster response times were achieved by introducing ion-conducting side groups to the conjugated polymer in order to minimize phase separation.[11] In general, single-phase systems such as devices employing Ru$(bpy)_3^{2+}$ complexes have the potential to show faster response times compared to two-phase systems since the light emission and ion conduction occurs within the same phase.

In this work, we demonstrate highly efficient solid-state light-emitting electrochemical cells based on new derivatives of the $Ru(bpy)_3^{2+}$ complex. Devices employing these new complexes show an up to two times higher external quantum efficiency compared to devices with the unmodified $Ru(bpy)_3^{2+}$ complex. In addition, the response time of these devices is dramatically shortened, and "instantaneous" light emission is achieved by increasing the ion conductivity by employing smaller counterions.

2. Experimental Section

Three different $Ru(bpy)_3^{2+}$ complexes were prepared for this study. Complex **I** is the unmodified $Ru(bpy)_3^{2+}$ complex. Complex **II** is a tris(4,4′-di-*tert*-butyl-2,2′-bipyridyl)ruthenium(II) complex, and complex **III** is a bis(4,4′-di-*tert*-butyl-2,2′-bipyridyl)(4,4′-dinonyl-2,2′-bipyridyl)-ruthenium(II) complex. A more detailed description of the synthesis of these complexes will be reported in a future publication.

Light-emitting devices with the three different $Ru(bpy)_3^{2+}$complexes were prepared in a ITO/$Ru(bpy)_3^{2+}$ + PMMA/Ag sandwich configuration. The electroluminescent (EL) layer was prepared by spin coating a solution containing the $Ru(bpy)_3^{2+}$ complex and PMMA. The final films had a thickness of ~1200−1300 Å and contained about 25 vol % PMMA to improve the film quality.[7] Ag cathodes were thermally evaporated. A more detailed description of the device preparation and testing can be found in our earlier work.[7]

All devices were tested under a dc voltage and with a pulsed voltage (5 V, 50% duty cycle). The operating voltages where chosen to lie within the window of stable operation of the devices. At such voltages, the devices showed brightnesses in the range of 5−100 cd/m^2. Devices with complexes **II** and **III** showed a lower light emission relative to devices with complex **I** at a given voltage, because of the hindered charge hopping caused by the alkyl side groups. Higher brightnesses were achieved at higher operating voltages, however, at the expense of the device stability and efficiency. The emission of all devices was red-orange with a maximum emission at around 630 nm.

The ionic conductivity of the devices was measured by impedance analysis using an HP4284A LCR meter in the frequency range from 1 MHz to 20 Hz at 0 V bias with a 50 mV amplitude. From the complex plane plot of the impedance, the resistance and consequently the ionic conductivity of a device was determined. It is assumed that the Ru$(bpy)_3^{2+}$ complexes are immobile in the EL layer and only the smaller counterions can move.

3. Results and Discussion

The different $Ru(bpy)_3^{2+}$ complexes (**I**−**III**) that were used in this work and the device structure are shown in Figure 1. Table 1 summarizes the external efficiencies that were achieved for light-emitting devices prepared from complexes **I**−**III**. Devices with the unmodified complex **I** exhibited an external quantum efficiency of around 2.7 ± 0.2% (3.3 ± 0.2 lm/W) when operated under a dc voltage. In comparison, devices containing the chemically modified $Ru(bpy)_3^{2+}$ complexes showed higher external quantum efficiencies. For devices made with complex **II** and **III**, 4.1 ± 0.2% (4.9 ± 0.2 lm/W) and 4.8 ± 0.2% (5.6 ± 0.2 lm/W), respectively, were achieved under dc operation. To our knowledge, these are the highest reported external quantum efficiencies for light-emitting electrochemical cells. With a power efficiency of 5.6 ± 0.2 lm/W, such devices are also among OLEDs with the highest efficiencies that emit red-orange to red light.[12]

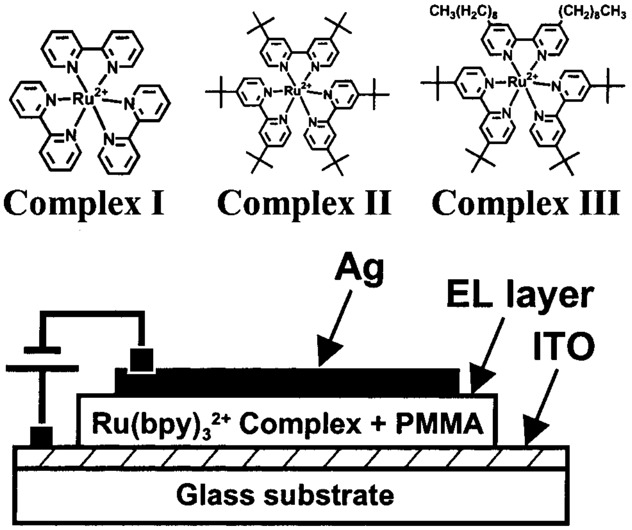

Figure 1. Chemical structures of the $Ru(bpy)_3^{2+}$ complex (complex **I**) and chemically modified $Ru(bpy)_3^{2+}$ complexes (complex **II** and **III**) and the device structure of a $Ru(bpy)_3^{2+}$ LEC.

It is believed that the increased EL efficiency is the result of a higher photoluminescence (PL) efficiency of the modified Ru$(bpy)_3^{2+}$ complexes. Table 1 shows that the PL efficiencies of complexes **II** and **III** are a factor of 1.3 ± 0.2 and 2.1 ± 0.2 higher, compared to the unmodified complex **I**. The PL efficiencies of the chemically modified complexes (**II** and **III**) were measured relative to the PL efficiency of the unmodified complex (complex **I**) on films that contained no PMMA. Adding 25 vol % PMMA to any of these complexes generally increased the PL efficiency by ~15−30% compared to the unblended complex (data not shown). In addition, this increase in PL efficiency due to blending appeared more pronounced in chemically modified complexes than in the unmodified complex, probably due to a better compatibility between the chemically modified complexes and the PMMA. All $Ru(bpy)_3^{2+}$ films were excited with a light source at ~450 nm. The PL spectra of spun films containing complexes **I**−**III** are shown in Figure 2. The corresponding EL emission spectra of devices made of complexes **I**−**III** were essentially the same.

Generally, an increased PL efficiency of an electroluminescent material yields a higher EL efficiency in a device. It has been shown that the PL efficiency of $Ru(bpy)_3^{2+}$ can be increased by molecular dispersing the $Ru(bpy)_3^{2+}$ complex in a polymer matrix.[13] However, this approach is not practical for fabricating

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(10) Cao, Y.; Yu, G.; Heeger, A. J.; Yang, C. Y. *Appl. Phys. Lett.* **1996**, *68*, 3218−3220.

(11) Holzer, L.; Wenzl, F. P.; Tasch, S.; Leising, G.; Winkler, B.; Dai, L.; Mau, A. W. H. *Appl. Phys. Lett.* **1999**, *75*, 2014−2016.

(12) Adachi, C.; Baldo, M. A.; Kwong, R. C. *Appl. Phys. Lett.* **2001**, *78*, 1622.

(13) Nagai, K.; Takamiya, N.; Kaneko, M. *J. Photochem. Photobiol. A: Chem.* **1994**, *84*, 271−277.

Table 1. External EL Efficiencies, Relative PL Efficiencies, and Ionic Conductivities of Ru(bpy)$_3^{2+}$ Devices[a]

		external EL efficiency				
		dc V		pulsed V[b]	rel PL	conductivity
complex	counterion	ph/el [%]	[lm/W]	ph/el [%]	efficiency[c]	σ [S/cm]
I	PF_6^-	2.7 ± 0.2	3.3 ± 0.2 (2.6 V)	2.9 ± 0.2	1.00	4.0×10^{-12}
II	PF_6^-	4.1 ± 0.2	4.9 ± 0.2 (2.6 V)	4.6 ± 0.2	1.3 ± 0.2	1.0×10^{-11}
II	ClO_4^-	3.0 ± 0.2	3.9 ± 0.2 (2.4 V)	3.6 ± 0.2	1.2 ± 0.2	1.3×10^{-10}
II	BF_4^-	3.0 ± 0.2	3.9 ± 0.2 (2.4 V)	3.6 ± 0.2	1.4 ± 0.2	0.8×10^{-9}
III	PF_6^-	4.8 ± 0.2	5.6 ± 0.2 (2.7 V)	5.5 ± 0.2	2.1 ± 0.2	5.0×10^{-12}

[a] All devices contained 25% PMMA by volume. [b] 50% duty cycle, 5 V. [c] Without PMMA.

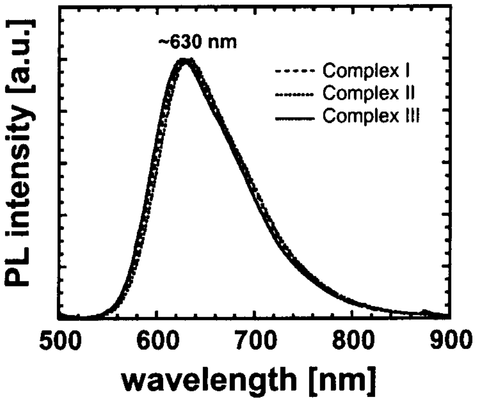

Figure 2. Photoluminescence (PL) emission spectra of spin-coated films containing complexes **I**−**III**.

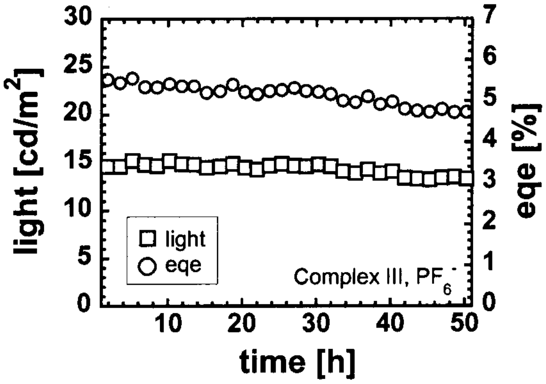

Figure 3. Light emission and efficiency vs time of a device containing complex **III** with PF_6^- counterions. The device was operated at 5 V with a 50% duty cycle at 1 kHz.

light-emitting devices. By dispersing the Ru(bpy)$_3^{2+}$ complex in a polymer matrix the charge transport becomes impeded and therefore a higher voltage is required to operate the device. The addition of PMMA as used in this study is too small to significantly affect the operating voltage of a device. The small amount of PMMA in the films, however, lowers the chances of pinholes in the EL layer and consequently increases the yield of working devices.[7]

To increase the PL efficiency without significantly compromising the charge hopping we followed a different approach in which the Ru(bpy)$_3^{2+}$ complex was chemically modified. By adding relatively small but bulky alkyl side groups to the bpy ligands as shown in Figure 1, the Ru(bpy)$_3^{2+}$ complex is “wrapped” in alkyl groups and therefore a “dispersion” is achieved without significantly increasing the distance between the Ru(bpy)$_3^{2+}$ centers. In addition, the compatibility between the PMMA and the chemically modified complexes in devices might be increased. Devices fabricated with these complexes can still be operated at the same low operating voltage as a device employing the regular Ru(bpy)$_3^{2+}$ complex. A low operating voltage is essential for LECs to exhibit long lifetimes.

Because LECs exhibit better stability when operated with a pulsed voltage, the devices were tested at 5 V with a 50% duty cycle at 1 kHz (Table 1). During the pulsed operation, all devices showed a higher external quantum efficiency compared to the dc operation. The power efficiency in this operation mode was not measured since it is a function of the frequency of the pulsed voltage. At a low frequency, the power efficiency approaches the dc power efficiency. Under a pulsed voltage, devices employing complex **III** showed the highest external quantum efficiency of 5.5%. With such an operation scheme, these devices show very good stability. Figure 3 shows the light emission and efficiency of a device with complex **III** and PF_6^- counterions that has been operated at 5 V with a 50% duty cycle at 1 kHz for around 50 h. The initial light output was around 15 cd/m^2 and did not change significantly over the test period. In the same time, the efficiency decreased from initially 5.5% to around 4.8%. Very good stabilities have also been observed for devices made of complexes **I** and **II**. In addition, by employing Ag as the cathode material, these devices exhibit excellent storage life, and no change in performance has been observed after devices were stored in inert atmosphere for several months. A good operational stability was also observed for devices with an Al cathode, although these devices degrade rapidly due to chemical reactions with the Al cathode when stored in the off-state.[7] For example, an Al device made with complex **III** showed only a ∼20% decrease in light output and efficiency after 500 h of continuous operation. The estimated half-life of this device exceeds 1000 h. The light output and external quantum efficiency of this device was about 50 cd/m^2 and 3%, respectively.

The response time of light-emitting electrochemical cells has always been a hindrance for their practical application. In general, the response time can be decreased by increasing the ionic conductivity of the ion-containing phase. This is especially effective in Ru(bpy)$_3^{2+}$ devices since the light emission and ion conduction occurs within the same phase. The ionic conductivity of Ru(bpy)$_3^{2+}$ devices can be increased by changing the chemical structure of the Ru(bpy)$_3^{2+}$ complex itself or by decreasing the size of the mobile counterion.

Table 1 shows that a device with complex **II** and PF_6^- exhibits around 1 order of magnitude higher ion conductivity compared to devices with complex **I** and **III** with PF_6^- counterions. The most dramatic increase in ion conductivity, however, is achieved by changing the size of the counterion. In devices that were prepared with complex **II** and ClO_4^- or

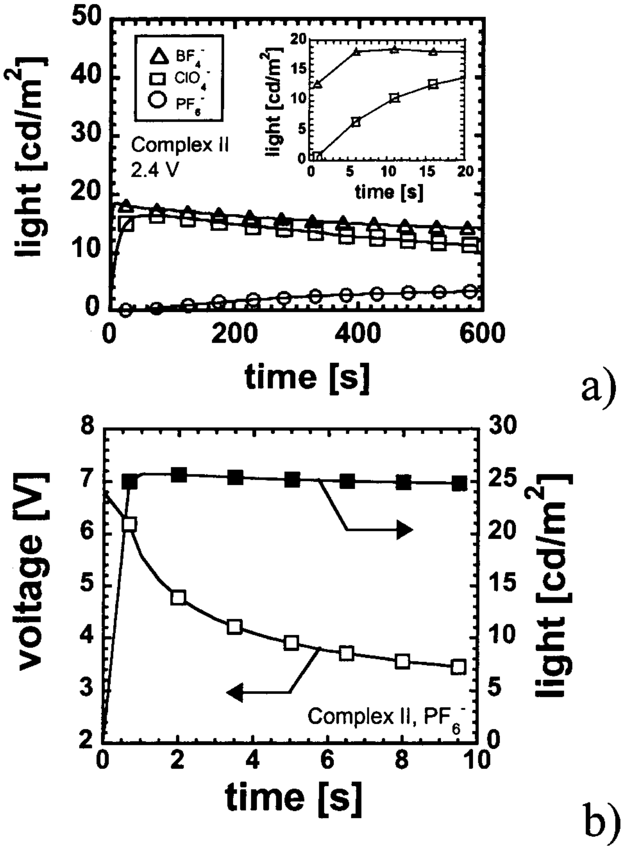

Figure 4. Transient time to reach steady-state light emission of devices containing complex **II** with PF_6^-, ClO_4^-, or BF_4^- operated at 2.4 V dc (a) and a device containing complex **II** with PF_6^- operated with a constant current (b).

BF_4^- as the counterions, the ion conductivity increased to 1.3×10^{-10} and 0.8×10^{-9} S/cm, respectively. This is a 3 orders of magnitude increase in ionic conductivity for devices with complex **II** and BF_4^- compared to the unmodified complex **I** with PF_6^-. Consequently, such devices show "instantaneous light" when started from the fresh or discharged state, where the counterions are completely relaxed.

Figure 4a shows the light emission vs time of devices with complex **II** and PF_6^-, ClO_4^-, or BF_4^- as counterions after a 2.4 V bias was applied. The inset of this figure shows the first 20 s of operation. From Figure 4a it can be seen that the response time of a device decreases as the ion conductivity is increased. At 2.4 V, the BF_4^- device reaches 50% of its maximum emission in less than 1 s compared to several minutes for the PF_6^- device. Such a device no longer requires a pre-operation at a higher voltage to achieve fast response times. However, at a higher voltage, light emission occurs even faster. Very fast response times were also reported for $[Ru(bpy)_3](ClO_4)_2$ devices using a Ga:In cathode.[8] In addition to a faster response time, devices with ClO_4^- or BF_4^- counterions exhibited a 2−3 times higher brightness than devices employing PF_6^- counterions. The external quantum efficiency of devices with ClO_4^- or BF_4^- counterions was ~3% and such devices showed a half-life of a few hours when operated with a pulsed voltage. Possible explanations why these devices exhibit a poorer stability compared to devices employing PF_6^- counterions are currently being investigated.

A fast response time can also be achieved by applying a higher initial operating voltage. This can be done by operating a device under a constant current. With a constant current, the voltage is adjusted automatically to achieve the set current flow. Figure 4b shows the response time of a device with complex **II** and PF_6^- counterions. The device emits around 25 cd/m^2 after ~0.5 s (which is the time resolution of the experimental setup) after a constant current has been applied. Initially 7 V is required in order to move the counterions and inject charge carriers. As the injection barriers become smaller at the electrode interfaces, the required operating voltage decreases. This shows that with an initial voltage pulse of ~7 V, "instantaneous" light can be achieved for a device with complex **II** and PF_6^- counterions. With such an operation scheme, this device exhibited an external quantum efficiency of around 3%, which is a lower efficiency compared to when the device was turned on at 2.6 V. This indicates that the conditions under which a device is turned on influence the device efficiency.

It is important to note that these response times have been measured on devices that were fresh or fully discharged. In comparison, very fast response times were also reported for LECs that were operated with a continuously pulsed voltage.[10,11] However, with such an operation scheme, the ions are not completely relaxed.

4. Conclusions

In summary, light-emitting electrochemical cells based on phosphorescent $Ru(bpy)_3^{2+}$ complexes have been demonstrated. By chemically modifying the $Ru(bpy)_3^{2+}$ complex, the external quantum efficiency of such devices was increased to as high as 5.5%. Such devices show excellent storage stability and a very good operational stability when operated with a pulsed voltage. The response time of $Ru(bpy)_3^{2+}$ devices was dramatically decreased by employing smaller counterions such as BF_4^-, which resulted in "instantaneous" light (<1 s) at very low turn-on voltages. We believe that the combination of very high efficiencies and fast response times makes light-emitting electrochemical cells based on $Ru(bpy)_3^{2+}$ complexes very attractive candidates for practical applications.

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