Ruthenium(II) Complex as Phosphorescent Dopant for Highly Efficient Red Polymers Light-Emitting Diodes

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Red electrophosphorescence from light-emitting devices based on a ruthenium(II) complex [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$-doped wide-band-gap semiconductive polymers, e.g., poly(vinylcarbazole) (PVK), polydihexylfluorene (PF), and ladder-like polyphenylene (LPPP), as the emitting layer are reported. These polymers show the short-wavelength electroluminescence emission peaking ranged from 410 to 490 nm, which overlaps well with the absorption band of [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$; however, very efficient energy transfer was investigated in the PVK system, likely due to relative long excited-state lifetimes of PVK than that of PF and LPPP and good chemical compatibility of [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ with PVK. The EL spectra show the characteristic spectrum of [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$, with a peak at 612 nm and CIE of (0.62, 0.37) which is comparable with standard red color. The optimized device ITO/PVK 5 wt % [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$/PBD/Alq$_3$/LiF/Al shows the maximum luminance efficiency and power efficiency of 8.6 cd/A and 2.1 lm/W, respectively.

Introduction

Significant progress has been witnessed since the report on the organic thin-film heterojunction device reinvigorated the research interest and activities in organic light-emitting diodes (LEDs).[1] Extensive research on organic electroluminescence (EL) in recent years is improving both the reliability and efficiency of its devices, which realized its commercial use for mobile applications. However, new materials with better properties are still needed in order to fully realize the advantages that organic and polymer LED technology can potentially offer. Heavy-metal complexes that enable the otherwise spin-forbidden triplet to ground-state transition (phosphorescence), due to the heavy atom induced spin−orbit coupling effect, are attractive for organic light-emitting devices (OLEDs), especially for improvement in device efficiency.[2−15] It has been demonstrated that efficient electrophosphorescence was obtained from a class of heavy-metal complexes that feature a metal-to-ligand charge transfer (MLCT) excited state with short lifetime phosphorescence.[4] Frequently used electrophosphorescence materials, e.g., PtOEP, Ir(ppy)$_3$, and their derivatives, all feature the MLCT electronic states.[2−8] High-performance electrophosphorescence devices are also realized from other heavy-metal ion complexes with MLCT state.[9−15] Among the many MLCT metal complexes currently under investigation, tris(bipyridine) ruthium(II) dication, Ru(bpy)$_3{}^{2+}$, and their derivatives are the most typical ones. The Ru complex has played the pivotal role in the development of inorganic photochemistry in the past decades,[16−19] and as most active materials, it still plays a continuing role in the field up until today.[20−25] The electrochemically generated luminescence (ECL) of these materials in a liquid cell has been extensively studied, and recently, there are some reports on the use of these materials as emitters in solid-state ECL devices.[20−26] The mechanism of luminescence in these Ru-based solid devices, which are fabricated by either a Ru complex neat film or a heavily doped Ru complex/polymer film, has been demonstrated to be in a way similar to ECL in solution as originally proposed by Tokel and Bard for a liquid cell.[19] High-brightness and high-efficiency emissions with low-driving voltage of those Ru-complex-based solid-state ECL cells have been achieved.[21,23] However, stability of these cells are far away from the organic EL devices, and the turn-on times to reach maximum emission are relatively long associated with the low mobility of the counterion in solid state. In addition, the strong interaction between Ru complexes in the device may decrease the emission efficiency due to the self-quenching and triplet−triplet annihilation.[26] In principle, a molecular dispersion of a Ru complex in the semiconductive matrix and using a carrier injection diode structure may overcome these drawbacks. These ion-like Ru complexes are not suitable for vacuum deposition in OLED fabrication due to decomposition in the process of thermo-evaporation; however, some of them are well soluble in organic solvents and, thus, can be doped into semiconductive polymers for LEDs fabrication. In doped OLEDs, the Ru complexes may be excited through energy transfer from the host and/or charge trapping-induced direct recombination on the dopant site, and they differed in their mechanism with the ECL cell where an electrochemical redox pathway is required.[19] In this paper, we report the photoluminescence and electroluminescence characteristics of a Ru complex doped semiconductive polymer films. The results indicate that, by a careful design of the chemical structure of the Ru complex and device structure as well as the choice of appropriate host materials, red-emitting LEDs with efficiencies up to 8.3 cd/A can be achieved.

Experimental Section

Materials. PVK, Alq$_3$, PBD, and BCP (all from Aldrich) were used as received without further purification. PF was synthesized by the Suzuki coupling process according to ref 29. The LPPP was synthesized by modifying the method in ref 30, and the details of the synthesis and characteristics will be published elsewhere.

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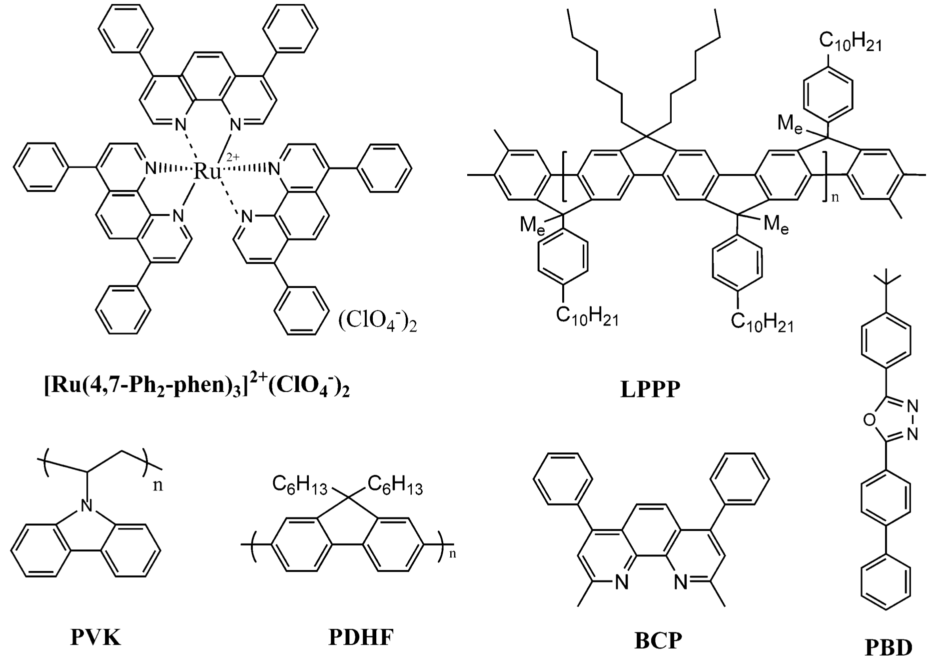


Figure 1. Molecular structures of [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$, PVK, PF, LPPP, BCP, and PBD.

Synthesis of [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$. The synthesis of [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ was done according to the literature.[28] A mixture of the RuCl$_3$ precursor (208 mg) and 4,7-Ph$_2$-phen (1.330 g) in ethanol (25 mL) was refluxed for 48 h under a nitrogen atmosphere. The resulting mixture was evaporated to dryness under reduced pressure. The crude product was purified by recrystallization from a KClO$_4$ saturated aqueous solution to give bright orange crystalline powder (yield 47%). ^{1}H NMR (500 MHz, DCCl$_3$): δ8.835 (d, 2H, $J = 5.5$ Hz, H6,6′), δ8.623 (S, 2H, H3,3′), δ8.158 (d, 2H, $J = 6$ Hz, H5,5′), δ2.55(s, 6H, CH$_3$). Elemental analysis calcd (%) for: C 66.66, H 3.72, N 6.48; found: C 65.24, H 3.75, N 6.26.

UV−vis and PL Spectra. UV−vis absorption spectra were recorded on a UV-3100 spectrophotometer. Fluorescence measurements were carried out with RF-5301PC. The films for photoluminescence (PL) experiments were formed on a precleaned quartz plate at air. Polymers were dissolved in chloroform at a concentration of 20 mg/mL.

Device Fabrication. Indium−tin−oxide (ITO)-coated glass with a sheet resistance of $<50\ \Omega\ \square^{-1}$ was used as the substrate. The substrate was pre-patterned by photolithography to give an effective device size of 4 mm^2. Pretreatment of ITO includes a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. Active layers were spin-coated from chloroform solutions containing 20 mg/mL of x% by weight [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ in polymer on ITO substrates to give a film thickness of 80−100 nm. The hole block layer BCP or PBD and electron injecting layer Alq$_3$ were deposited by thermo-evaporation. The cathode barium (Ba) or LiF/Al was deposited (50 nm) by thermo-evaporation and followed by a thick Al capping layer. The electroluminescence and luminance were recorded on a PR65 spectrometer. Current voltage and light intensity measurements were made at room temperature and ambient conditions.

Results and Discussions

Figure 1 shows the chemical structure of the Ru complex and three emitting polymer hosts used in this study, and their electronic spectra are shown in Figure 2. The ruthenium complex, referred to here as [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$, containing three 4,7-diphenyl-1,10-phenanthroline (4,7-Ph$_2$-phen) and two ClO$_4^-$ counteranions was selected in this study due to its high emission efficiency in solution ($\varphi = 27\%$ in toluene[18] and this value might be increased as doped in polymer matrixes[2]) as well as good solubility in organic solvents, e.g., toluene, THF, and dichloromethane. [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ shows the MLCT singlet absorption band centered around 460 nm and the MLCT triplet emission band centered at 600 nm with fresh red color. Three blue-emitting polymers, polyvinylcarbzole (PVK), polydihexylfluorene (PF), and a modified ladder-type polyphenylene (LPPP), were selected as the host to facilitate Förster energy transfer,[27] because their emission spectra overlap the MLCT absorption band of [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ as shown in Figure 2. [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ is synthesized and purified according Meyer et al.[28] PVK was obtained from TCI Co.; PF with molecular weight of □20000 g/mol and polydispersion index of 2.5 was synthesized and purified according reference's method.[29] LPPP is a novel ladder-type polyphenylene derivative synthesized by our groups. LPPP has a slight difference in structure with Me-LPPP reported by Mullen et al.,[30] in which a alkyl substituted fluorene ring replaces the phenylene ring in

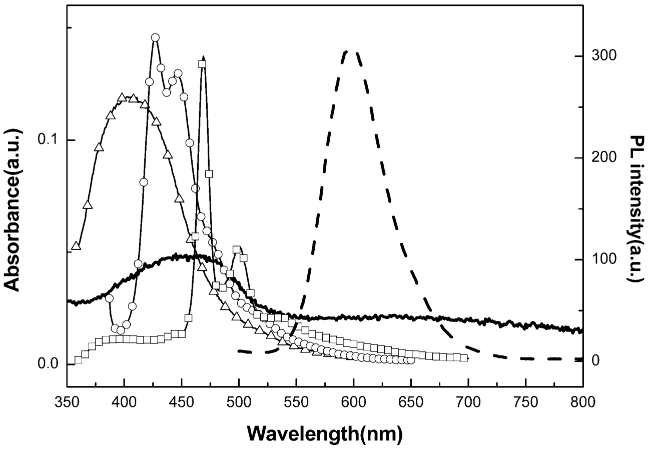
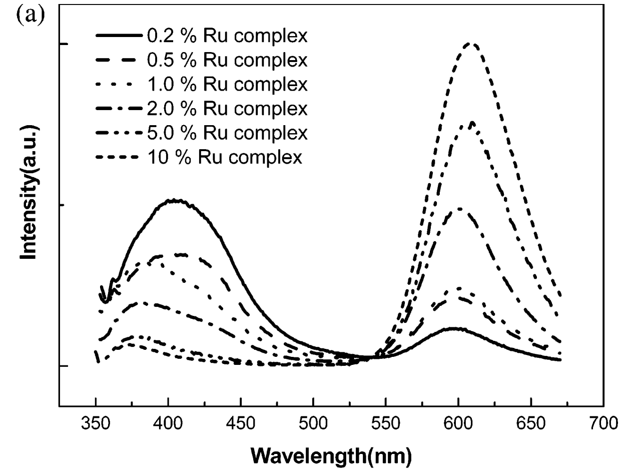


Figure 2. Normalized spectra of absorption (solid line) and emission (dash line) of [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ in polycarbonate film, and photoluminescence spectra of PVK (triangle), PF (circle), and LPPP (square) in neat film.



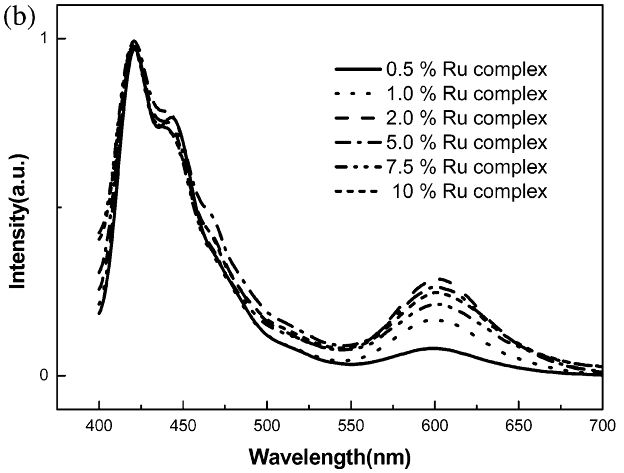


Figure 3. PL spectra of $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ doped PVK (a) and PF (b) film with different $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ concentrations.

Me-LPPP. The new LPPP exhibited blue-green photoluminescence and electroluminescence, and the single-layer EL device with barium (Ba) as cathode showed luminance efficiency of 0.6 cd/A and maximum brightness up to 6000 cd/m^2. Three polymers have been extensively applied as the host materials for phosphorescence dopants in LEDs.

The electronic structure and photophysic properties of Ru complexes including $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ have been extensively studied.[16−18] The MLCT excited states are considered to be generated by the promotion of an electron from the bivalent Ru(II) ion-centered dπ-orbital to a π^* orbital localized on the ligand, and it has been shown that efficient light emission was obtained as pumped by light localized at MLCT absorption band. From this view, it seems that three polymers should transfer their energy efficiently to $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ due to spectral overlap as shown in Figure 2; however, from the PL emission spectrum of $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ in these polymers as shown in Figure 3, parts a and b, just the $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$−PVK film showed efficient energy transfer and distinct red emission from $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ peaking at 600 nm. The excitation wavelength for the PL measurements was 345 nm, where the absorption by $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ is minimal so that most of the excitation light is absorbed by the hosts. The energy transfer in the $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$−PF and −LPPP films is relatively inefficient. For $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$−PF in 1 wt % doping level, only very weak red emission was observed, and for $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$−LPPP even, there isn't any red emission (no shown). Furthermore, as the $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ dopant concentration increases up to 10 wt %, the emission from PVK in the $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$−PVK film is completely quenched, whereas the emission spectra of the $Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$−PF and −LPPP films do not have a distinctly observed difference with spectra of 1 wt % doped concentration. For Förster energy transfer, the efficiency is proportional to the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor.[27] A calculation based on spectral overlap for three Ru-doped polymer systems gives the Förster radius R_0 with the similar value of about 3.0 nm. Therefore, it is indicated that there are other factors for achieving efficient energy transfer. One possibility is in the difference of the exciton lifetime of polymer hosts. In three polymer hosts, PVK showed the longest exciton lifetime of several tens of nanoseconds,[31] whereas PF and LPPP showed much shorter lifetimes of typically less than 1 ns.[32] Thus, it is reasonable that a long-lived exciton of PVK increases the probability of reaching a low energy trap ($[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$). The other possibility is in the difference of the chemical compatibility of $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ with three polymer hosts as suggested by Noh et al.[33] recently. They found that the formation of aggregates prevents dopant molecules from being in close proximity with host molecules thereby inhibiting energy transfer processes, as in the case of $Ir(ppy)_3$ in PF, whereas $Ir(ppy)_3$:PVK films were homogeneous, efficient energy transfer from PVK to $Ir(ppy)_3$. The efficient energy transfer in PVK/$[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ films was further unequivocally confirmed by photoluminescence excitation (PLE) spectra shown in Figure 4. The PLE spectrum of $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ emission (600 nm) in a doped polycarbonate film showed a distinct peak at 460 nm originating from a singlet MLCT band of $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ itself, whereas the PLE spectrum of a $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ emission in a doped PVK film showed a peak at 350 nm originating from PVK. Thus, we consider that the resonant energy transfer from PVK supplied the energy of red light emission from $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ molecules.

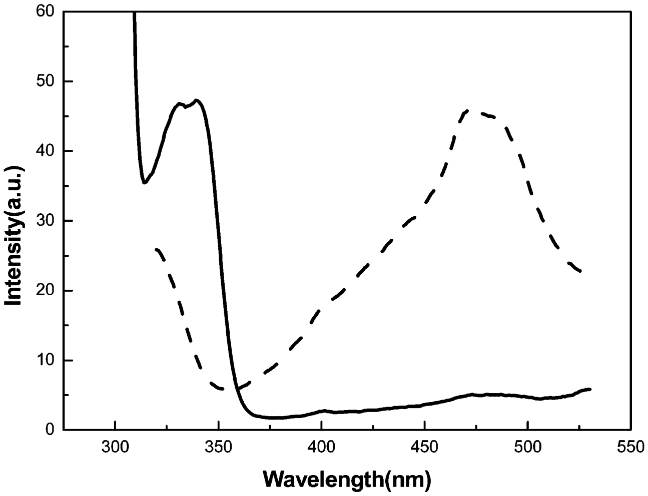


Figure 4. PLE spectra of PVK film with $Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ concentrations of 1 wt % (solid) and $Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ in polycarbonate film (dash).

For device characteristics, at first we employed a simple single-active-layer configuration ITO/Polymer host: x wt % $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$(80 nm)/LiF/Al. The emitting layer, $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ doped polymers (PVK, PF and LPPP), was spin-cast onto the ITO surface from the chloroform solution. The typical thickness of the $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ doped polymer film was approximately 80 nm. The $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ doping level for device fabrication was limited below 10 wt % in order to rule out the ECL process where the Ru

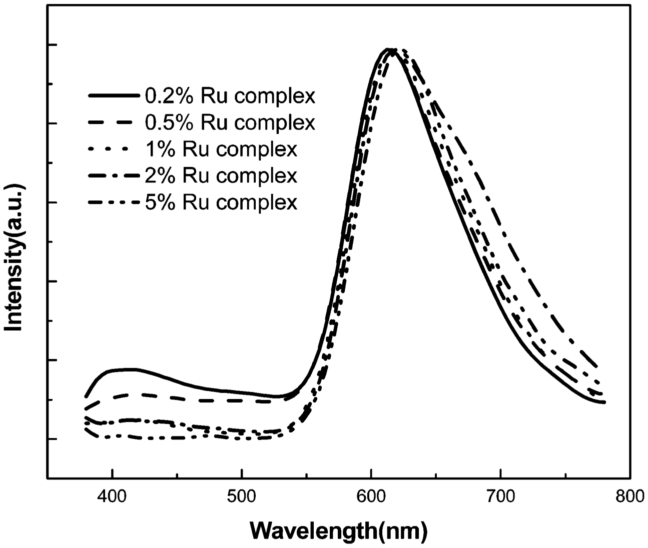


Figure 5. EL spectra of single layer device ITO/PVK: x % [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$/LiF/Al.

complexes need to come close to each other. The electroluminescence of undoped polymer single layer devices showed blue emission peaking at 416 (PVK), 427 (PF) and 470 nm (LPPP) (no shown), respectively, which is in agreement with their PL spectra in the film state. The undoped polymers in single devices show the luminance efficiency (LE) of LPPP (~0.5 cd/A) > PF (~0.1 cd/A) > PVK (~0.01 cd/A). However, [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$-doped polymer devices showed a reversal order in efficiency: the [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$-doped PVK device is the best, and performance of the [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$-doped PF and LPPP devices is very poor, even very instable. It has been observed that in a platinum(II) porphyrin (PtOX) doped semiconductive polymer system electron accumulation in the emitting layer and trapping in PtOX induced a rapid decomposition of PtOX due to instability of PtOX in the reduction state.[34] However, it may be not a case of [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$-based devices because [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$ exhibited reversibility both in oxidation and reduction state in cyclic voltammetry measurements.[16] This indicated that the efficient energy transfer plays a very important role for device performance. Due to poor performance of devices of [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$ in PF and LPPP, we focus the studies on the [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$:PVK system.

The EL spectrum of single layer device changes with doping concentration as shown in Figure 5. Most of the light was emitted from [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$ in the EL devices even as the doping concentration was lower than 0.2%. As the doping concentration was increased up to 1 wt. %, devices show the pure red emission from [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$, indicating that the energy transfer is almost complete at this doping concentration. The EL spectrum changes with the applied voltage at the same doping concentration ca. 2 wt % as shown in Figure 6. No PVK emission was detected from devices as the [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$ doping level of >1 wt % and the driving voltage ranged from turn-on (about 11 V) to 21 V. Compared to PL in the same doping level, the triplet emission of [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$ centered at 612 nm is distinctly enhanced in the EL device. That triplet contribution in total emission was enhanced in the EL device compared to photoexcitation seems the common phenomena in electrophosphorescence devices, especially with polymers as hosts. The investigations by Cleave et al.,[35] Cao et al.,[36] and Gong et al.[7] for various phosphorescence dye doped polymer systems also noted that the efficient electrophosphorescence can be achieved at a concentration as low as 0.01 wt %. The absence of a PVK emission peak at both low and high applied voltages suggests the present of a process of charge trapping and then recombination with opposite charged carriers in [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$ in the Ru-based EL device. The charge trapping, and likely combined with Förster transfer, is the dominant EL mechanism in the Ru-based LEDs.

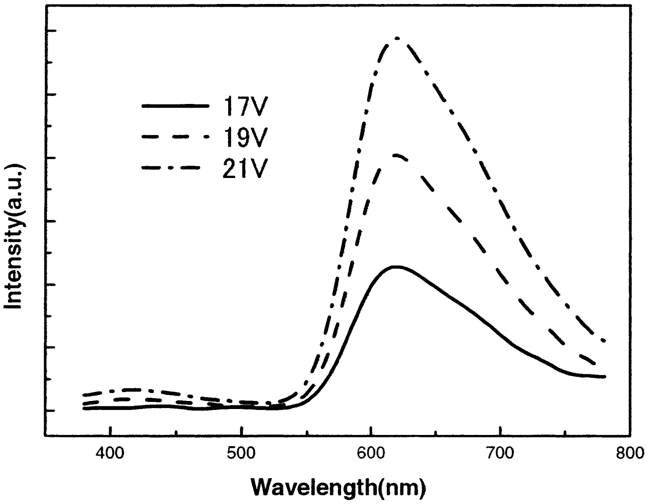


Figure 6. EL spectra of single layer device ITO/PVK: 2 wt % [Ru-(4,7-Ph_2-phen)$_3$]$^{2+}$/LiF/Al at different bias voltages.

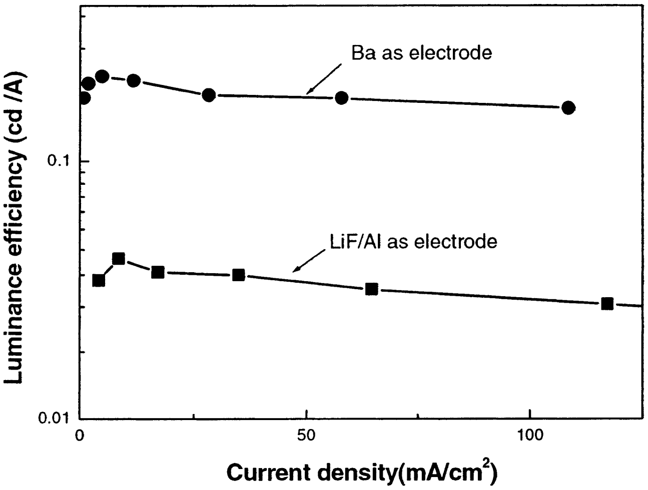


Figure 7. Luminance efficiency as a function of current density of 1 wt % Ru(4,7-Ph_2-phen)$_3$)$^{2+}$ in PVK in the single layer device.

Figure 7 is the luminescence efficiency as a function of current density of 1 wt % Ru(4,7-Ph_2-phen)$_3$)$^{2+}$ in PVK in the single layer device. The efficiency of a [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$−PVK single layer device with LiF/Al electrode is relative low (e.g., LE = 0.04 cd/A), likely due to lower electron injection efficiency which induces a poor balance of the electron and hole within the device. A significant enhancement in device efficiency was achieved by using a more active metal, e.g., Ba,[36] instead of LiF/Al as electrode to increase electron injection. The 1 wt % [Ru(4,7-Ph_2-phen)$_3$]$^{2+}$−PVK device of Ba as electrode shows an efficiency of 0.21 cd/A, which is five times that of the LiF/Al device. The performance of the present device changed with the change of electrodes indicating again that the emission mechanism of the present device is different with the ECL cell of which the performance is independent of the work function of electrodes.[22,23] A measurement of device response as upon a driving voltage (Figure 8) shows that a response time to reach a maximum of light emission is less than 0.02 s (an

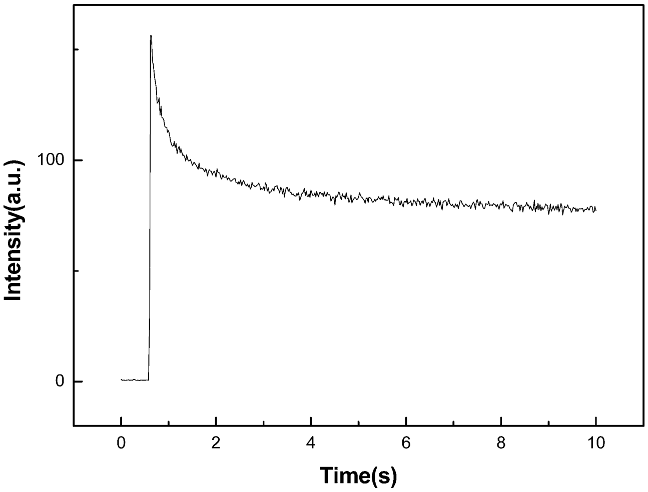


Figure 8. Light emission as a function of time of driving field applied for device ITO/PVK: 5 wt % [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$/LiF/Al.

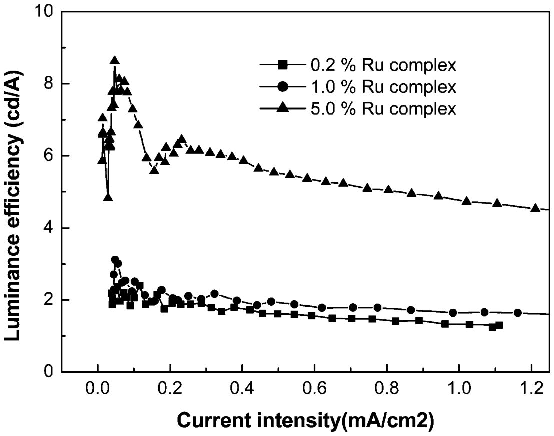


Figure 9. Luminance efficiency versus current density of multilayer device ITO/PVK:[Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$/PBD/Alq$_3$/LiF/Al with Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ concentrations of 0.2%, 1%, 5 wt %.

up-limitation of minimum time detected by RF-5301PC spectrophotometer in time-based determination), demonstrating that the device operation is most likely according to a diode-like mechanism, but a mobility of the counterion in ECL devices.[37]

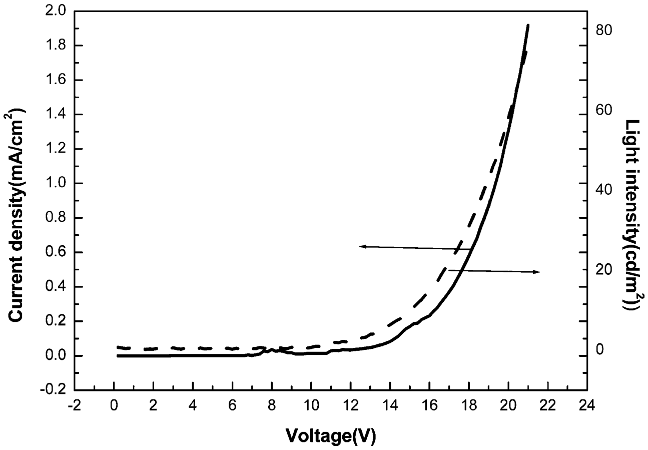


Figure 10. *J*−*L*−*V* characteristics of device ITO/PVK: 5 wt % [Ru-(4,7-Ph$_2$-phen)$_3$]$^{2+}$ (80 nm)/PBD (50 nm)/Alq$_3$ (45 nm)/LiF (1.8 nm)/Al (340 nm).

TABLE 1: Performance of Devices of 5 wt % PBD as Hole Block Layer with the Different Thickness of Alq$_3$ and PBD

PBD (nm)	Alq$_3$ (nm)	turn-on (V)	brightness at 20V (cd/m2)	max LE (cd/A)	max PE (lm/W)
13	9	17	3	0.18	0.033
36	18	11.6	41	1.53	0.36
40	17	10.6	67	0.93	0.28
40	27	11	93	1.78	0.37
40	35	10.5	53	1.93	0.39
40	45	9.8	143	7.10	1.72
50	45	11	76	8.63	2.08
50	60	10.4	60	8.32	2.46

Furthermore, a great increase in efficiency is achieved in the multilayer device by inserting an electron injection layer (Alq$_3$) and hole block layer (PBD) between the cathode and emitting layer.[38] Figure 9 shows LE−current density curves of different [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ doping concentration in the multilayer device ITO/PVK: x wt % [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ (80 nm)/PBD-(50 nm)/Alq$_3$ (45 nm)/LiF (1.8 nm)/Al (340 nm). The device with 5 wt % [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ in PVK as emitting layer gives the highest EL efficiency than that of other doping concentrations. The current density (*J*) and luminance (*L*) versus applied voltage (*V*) characteristics of the 5% [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ doped PVK multilayer device is shown in Figure 10. The turn-on voltage of this multilayer device is approximately 10 V. The device has a luminance of 140 cd/m^2 at 21 V and of □500 cd/m^2 at 26 V. The efficiency first increases and then decreases with increasing current density, similar to the behavior reported for other polymer based electrophosphorescence devices.[7,11,34] The maximum LE = 8.6 cd/A, which was among the highest reported for red OLEDs in the literature, was achieved at a current density of 0.05 mA/cm^2 and at a brightness of 4.1 cd/m^2. The LE value is approximately 6 cd/A at the higher current density and brightness. The power efficiency of this device was 2.1 lm/W at 13 V. At the higher brightness of 100 cd/m^2, LE was 2.6 cd/A and the power efficiency was about 0.39 lm/W. Note that the thickness of Alq$_3$ and PBD are found to greatly impact on device efficiency, which are ranged from 0.18 to 8.6 cd/A (Table 1); however, device performance is relatively stable as the combination of PBD 40−50 nm and Alq$_3$ 40−60 nm. The device gave red emission with the peak wavelength of 612 nm and the full width at half-maximum was 90 nm. The color coordinates in the Commission Internationale del'Eclairage (CIE 1931) chromaticity chart are coordinates of (0.62, 0.37) at 13 V, and the CIE coordinates remained nearly constant from 13 to 19 V. At a voltage up to 26 V, the weak emission band ranged from 400 to 550 nm likely from PBD and Alq$_3$ layers appeared (Figure 11a), which induced a color shift to the red-orange spectral region (CIE;0.55, 0.38).

The other hole-block materials bathocuprine (BCP), which was frequently used in small molecule electrophosphorescence devices as hole bock and triplet exciton limiting layers, was also tried in the present [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$−PVK device. The performance of devices of 5 wt % [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ in PVK using BCP as hole block layer are tabulated in Table 2. The devices show the maximum LE = 4.1 cd/A and PE = 1.0 lm/W, which was about half of the efficiency of the PBD device. However, the BCP devices show significant improvement in spectral stability. Figure 11b showed the EL spectra of 5 wt % [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ in the PVK device using BCP as a hole block layer. The pure [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ emission is observed even at high driving voltage indicating a complete blocking of carriers (hole) and excited energy in [Ru(4,7-Ph$_2$-phen)$_3$]$^{2+}$ doped PVK layers. The CIE coordinates of the BCP device are (CIE; 0.6153, 0.3694) at a low driving voltage (13 V) and (CIE; 0.6036,0.3698) at a high driving voltage (25 V).

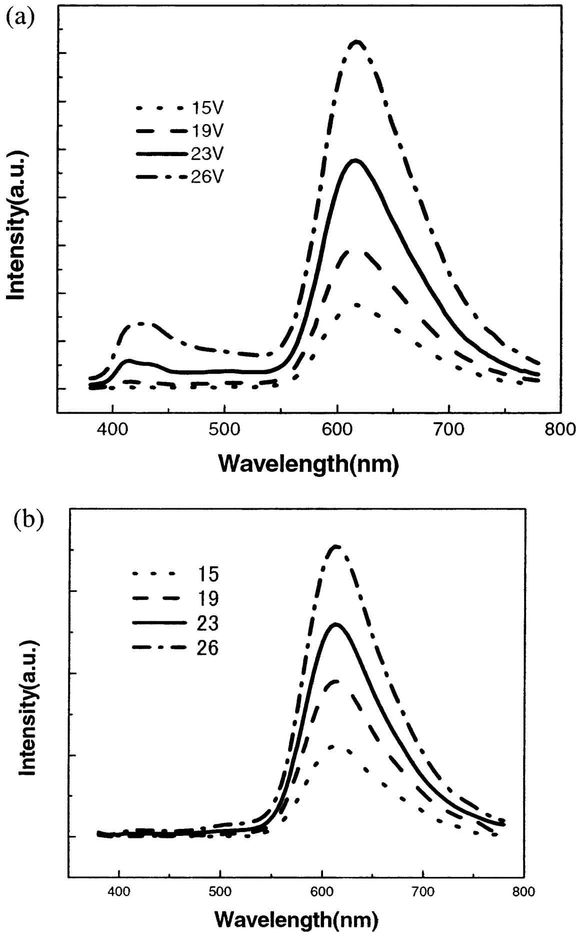


Figure 11. EL spectra of 5 wt % $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$ in PVK device using PBD (a) and BCP (b) as hole block layer at different bias voltages.

TABLE 2: Performance of Devices of 5 wt % BCP as Hole Block Layer with the Different Thickness of Alq_3 and BCP

BCP (nm)	Alq_3 (nm)	turn-on (V)	brightness at 20 V (cd/m2)	max LE (cd/A)	max PE (lm/W)
40	45	11	19	4.04	1.13
40	55	12	62	4.13	1.08
53	37	15	6	2.96	0.62
53	45	12	27	2.28	0.45
53	55	11	65	2.71	0.77

Conclusions

We demonstrated that the Ru–complex $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$, which is generally used for fabrication of an electrochemical cell with mechanism associated with electrochemical redox pathway, can be applied as a dopant in the semiconductor polymer layer for the fabrication of carrier-injection-type LEDs. The efficient energy transfer from polymer host to the Ru-complex dopant is very important for device performance. The PVK-based devices are more efficient than PF and LPPP-based devices likely due to their long exciton lifetime and good chemical compatibility with $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$. The EL spectra show the characteristic spectrum of $[Ru(4,7\text{-}Ph_2\text{-}phen)_3]^{2+}$, with a peak at 612 nm and CIE of (0.62, 0.37). Luminous efficiency of 8.6 cd/A was achieved in an optimized multilayer device, which was in comparison with the best red emitters, making this Ru-based material a promising candidate for further optimization.

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