

# Electroluminescence of Poly(vinylcarbazole) Doubly Doped with Two Phosphorescence Dyes: Investigation of Spectral Change as a Function of Driving Voltage

Fangzhong Shen, Hong Xia, Chengbo Zhang, Dong Lin, Lin He, and Yuguang Ma\*

Key Lab for Supramolecular Structure and Materials, Jilin University, Changchun 130023, P. R. China

Received: July 19, 2003; In Final Form: September 24, 2003

The utilization of molecular phosphorescent dyes in polymer-based organic light emitting diodes (OLEDs) was investigated by codoping several phosphorescent dopants into poly(*N*-vinylcarbazole) (PVK)-based single layer light emitting diodes (LEDs). In particular, green *fac*-tris(2-phenylpyridine)iridium(III), [Ir(ppy)<sub>3</sub>], red tris(4,7-diphenyl-1,10-phenanthroline)rhenium dications, [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup>, and (2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphyrin)platinum(II) (PtOEP) were used. In the phosphorescence dye doubly doped PVK system ca. *x* wt % [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup>:1 wt % Ir(ppy)<sub>3</sub>:PVK(*x* = 0.5–5), the intensity ratio (*R<sub>i</sub>*) of red emission vs green emission as a function of doping ratio (*R<sub>c</sub>*) of [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> vs Ir(ppy)<sub>3</sub> is found according to a power-law function with the exponent of  $\sim 2.0 \pm 0.2$  for photoluminescence, which obey the power law with  $R_i \propto R_c^2$  predicated by the Förster energy transfer model modified by concentration quenching factor. The red emission of these systems in EL spectra is found to be distinctly decreased compared to the PL spectra at the same doping ratio, and also to be further decreased as driving voltage increased, resulting in a driving voltage dependent power law of  $R_i \propto R_c^{1.5}$  at low voltage and  $R_i \propto R_c^{1.0}$  at high voltage, respectively. The relationship between *R<sub>i</sub>* and *R<sub>c</sub>* in the EL spectrum shifted to a power law of Förster energy transfer is likely due to the presence of additional emission mechanism in EL process ca. carrier trapping.

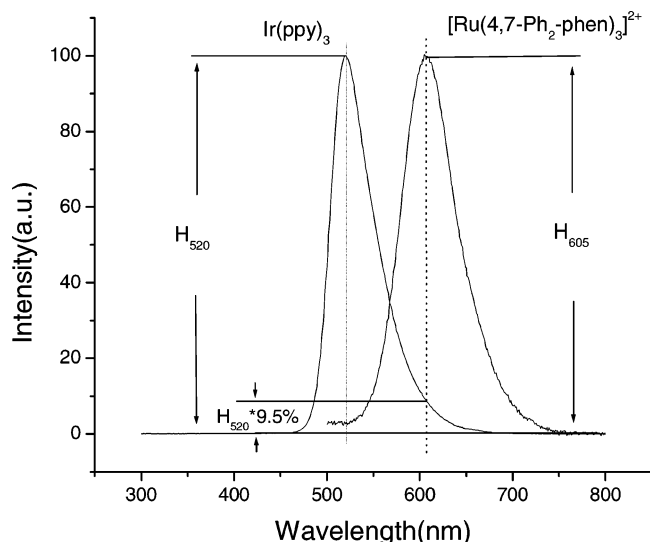
## Introduction

Operation of polymer light emitting diodes (PLEDs) brings electrons and holes from opposite electrodes and generates singlet and triplet excitons. If a PLED emits from singlet excitons only, triplet excitons are wasted because a radiative decay from triplets is spin-forbidden and often very inefficient. Heavy metal complexes ca. *fac*-tris(2-phenylpyridine)iridium, [Ir(ppy)<sub>3</sub>], that enable the otherwise spin-forbidden triplet to ground-state transition (phosphorescence), due to the heavy atom induced spin–orbit coupling effect, are especially attractive for LED applications.<sup>1–6</sup> In devices based on these complexes, it is expected that both singlet and triplet excitons generated by electrical injection and charge recombination can be utilized for EL emission through Förster-type singlet–singlet exciton transfer<sup>7</sup> or Dexter-type triplet–triplet exciton transfer.<sup>8</sup> Several groups observed the existence of triplet–triplet energy transfer from polymer hosts to phosphorescence dopants by a time-resolved electroluminescence (EL) experiment<sup>9</sup> and phosphorescence decay dynamics at low temperature.<sup>10</sup> However, Lane et al.<sup>11</sup> could not observe the triplet–triplet energy transfer from poly(9,9-dioctylfluorene) (PFO) to PtOEP by investigating the modulation frequency dependence of photoinduced absorption (PA) signal and Gong et al.<sup>12–14</sup> made the same conclusion by the investigation of the Ir complex doped poly(vinylcarbazole) (PVK) system. Speculatively, triplet excitons formed in the polymer host are, though unexpected, difficult to contribute to resultant emission in an EL device because of their very low oscillator strength based on the fact that no obvious phosphorescence is observed in the polymer system at room temperature. In other words, the transfer probability of the Dexter mechanism falls off exponentially with the distance between donor and

acceptor and an acceptor concentration of 10% is required for appreciable transfer.<sup>8</sup> However, the investigations in various phosphorescence dye doped polymer systems noted that the efficient electrophosphorescence can be achieved at a concentration as low as 0.01 wt %.<sup>4,9,12–14</sup> Actually, long-range Förster energy transfer plays a more important role in phosphorescence dye doped polymer devices as it does in fluorescence dye doped devices, but Förster energy transfer only cannot explain the fact that the efficiency of phosphorescence dye doped polymer devices is higher than the ones with undoped polymer or fluorescence dye doped polymer as well as the enhanced triplet contribution in EL spectra compared with corresponding PL spectra.<sup>4,12–15</sup> Thus an alternative explanation for enhanced emission from phosphorescence dopants and increased device efficiency was proposed as charge trapping-induced direct recombination on the phosphorescence dopant site.<sup>16,17</sup> It is supported in advance by significantly higher driving voltage of doped devices than that of undoped devices.<sup>14</sup>

In this paper, we investigate the spectral characteristics of PVK film doubly doped with two phosphorescent dyes ca. green Ir(ppy)<sub>3</sub> and red [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> (or PtOEP) in photoexcitation and EL devices. The intensity ratio (*R<sub>i</sub>*) of red and green bands of the blend emission spectrum is obtained by Gaussian deconvolution of experimental spectra, as  $R_i = I_{\text{red}}/I_{\text{green}}$ . The *R<sub>i</sub>* as a function of doping ratio (*R<sub>c</sub>*) of [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> and Ir(ppy)<sub>3</sub> (or PtOEP) in PVK host is carefully measured. One of our aims is to establish a relationship between the emission spectra (color) and doping ratios (*R<sub>c</sub>*) for the design of the EL spectrum simply by intermixing dye molecules in solution. The other aim is to reveal the mechanism of electrophosphorescence in doped polymer devices because emission in different mechanism may exhibit different relationship between *R<sub>i</sub>* and *R<sub>c</sub>*.

\* Corresponding author. Telephone: +86 431 8498981. Fax: +86 431 8980729. E-mail: ygma@jlu.edu.cn.



**Figure 1.** EL emission spectra of PVK doped Ir(ppy)<sub>3</sub> or [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup>. The device structure is ITO/PEDOT:PSS/polymer layer/LiF/Al.

### Experimental Section

**Materials.** Ir(ppy)<sub>3</sub> and [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> were synthesized according to the literature.<sup>3,18</sup> Other chemicals were purchased from Aldrich (PVK), Porphyrin Products Inc. (PtOEP), and Bayer [PEDOT (poly(3,4-ethylene dioxythiophene))].

**UV–Vis and PL Spectra.** UV–vis absorption spectra were recorded on a UV-3100 spectrophotometer. Fluorescence measurements were carried out by RF-5301PC. The films for photoluminescence (PL) experiments were formed on precleaned quartz plate at air atmosphere. Doped PVK was dissolved in chloroform at a concentration of 10 mg/mL.

**Device Fabrication.** The LEDs have the structure ITO/PEDOT (100 nm)/PVK:1 wt % Ir(ppy)<sub>3</sub>:0.5–5 wt % [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> (80 nm)/LiF(0.5 nm)/Al (200 nm). Indium–tin oxide (ITO)-coated glass with a sheet resistance of <50 Ω/□ was used as substrate. The substrate was prepatterned by photolithography to give an effective device size of 4 mm<sup>2</sup>. Pretreatment of ITO includes a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. The PEDOT+PSS (Bayer) [PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)] was coated from a water dispersion, yielding a 100 nm thick layer after drying (ca. 105 °C; 5 min). Active layers were spin-coated from chloroform solution containing 10 mg/mL of *x* wt % dyes in PVK on PEDOT:PSS to give a film with the thickness of 80–100 nm. The cathode LiF (0.5 nm) and Al (200 nm) was deposited by thermo-evaporation. The electroluminescence and luminance were recorded by a PR65 spectrometer. Current voltage and light intensity measurements were made at room temperature and ambient condition. We measured the spectral change of three to five devices at the same composition, and the dependence of the relative emission intensity (*R<sub>i</sub>*) on the doping ratio (*R<sub>c</sub>*) can be obtained independently from these measurements. The obtained exponent in power law of *R<sub>i</sub>* ~ *R<sub>c</sub>* relationship for the same composition was found to be reproducible with the highest error of less than 6%. For each composition, we selected an exponent value that approaches average level of repetitious experiments to calculate.

**Deconvolution of Overlapped Emission Peaks.** From EL spectra of Ir(ppy)<sub>3</sub> and [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> single doped PVK devices (Figure 1), it can be found that the emission peak of Ir(ppy)<sub>3</sub> and [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> at 520 and 605 nm,

respectively. The separation of emission peaks of both dopants is large enough (85 nm). We can use a height (*H*) in emission spectra at peak wavelength of 520 and 605 nm to represent their peak area (*S*) (emission intensity), because peak area is in direct proportion to peak height and the spectral shape of both single doping devices remains unchanged with changes in driving voltage. From Figure 1, *H*<sub>520</sub> can represent the emission intensity of Ir(ppy)<sub>3</sub> guest because it is independent of emission from the [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> guest. Although *H*<sub>605</sub> contains both contribution from [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> and Ir(ppy)<sub>3</sub> due to the low-energy band of Ir(ppy)<sub>3</sub> emission, which has the intensity of about 9.5% in height of Ir(ppy)<sub>3</sub> at 520 nm. Accordingly, the real contribution from [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> dopant can be obtained by subtracting the contribution of Ir(ppy)<sub>3</sub> at 605 nm from the total height, that is, *H*<sub>605</sub> – *H*<sub>520</sub> × 9.5%. Thus *R<sub>i</sub>* can be calculated accurately as follows:

$$R_i = I_{Ru}/I_{Ir} = (H_{605} - H_{520} \times 9.5\%)/H_{520}$$

### Results and Discussion

**Theoretical Speculation for the Relationship of *R<sub>i</sub>* and *R<sub>c</sub>* in Förster Energy Transfer and Charge Trapping Models.** The emission intensity (*I*) of a dopant in Förster energy transfer system

$$I \propto k_{et}\eta_e C \quad (1)$$

is in proportion to the rate of energy transfer from host to dopant (*k<sub>et</sub>*), emission quantum efficiency of dopant (*η<sub>e</sub>*), and concentration of dopant in the host (*C*). According to the Förster equation, *k<sub>et</sub>* = (*R<sub>0</sub>*/*r*)<sup>6</sup>/τ, where *R<sub>0</sub>* is the Förster radius that depends on the overlap of the absorption and emission spectra of host and dopant, τ is the radiative lifetime of the emitting species, and *r* is the distance between dopant molecules, which is in proportion to *C*<sup>−1/3</sup>.<sup>19</sup> If we assume in the first approximation that in our systems *R<sub>0</sub>* as well as τ does not greatly vary, we can obtain emission intensity (*I*)

$$I \propto \eta_e C^3 \quad (2)$$

and

$$R_i = I_1/I_2 \propto \eta_{e1}/\eta_{e2} \times (C_1/C_2)^3 \quad (3)$$

Furthermore, if we consider the concentration quenching and assume that the emission quantum yield, *η<sub>e</sub>*, follows a simple relationship inverse proportional to dopant concentration, *η<sub>e</sub>* ∝ *C*<sup>−1</sup>, the obtained expression of the *R<sub>i</sub>* ~ *R<sub>c</sub>* results is

$$R_i \propto (C_1/C_2)^2 = R_c^2 \quad (4)$$

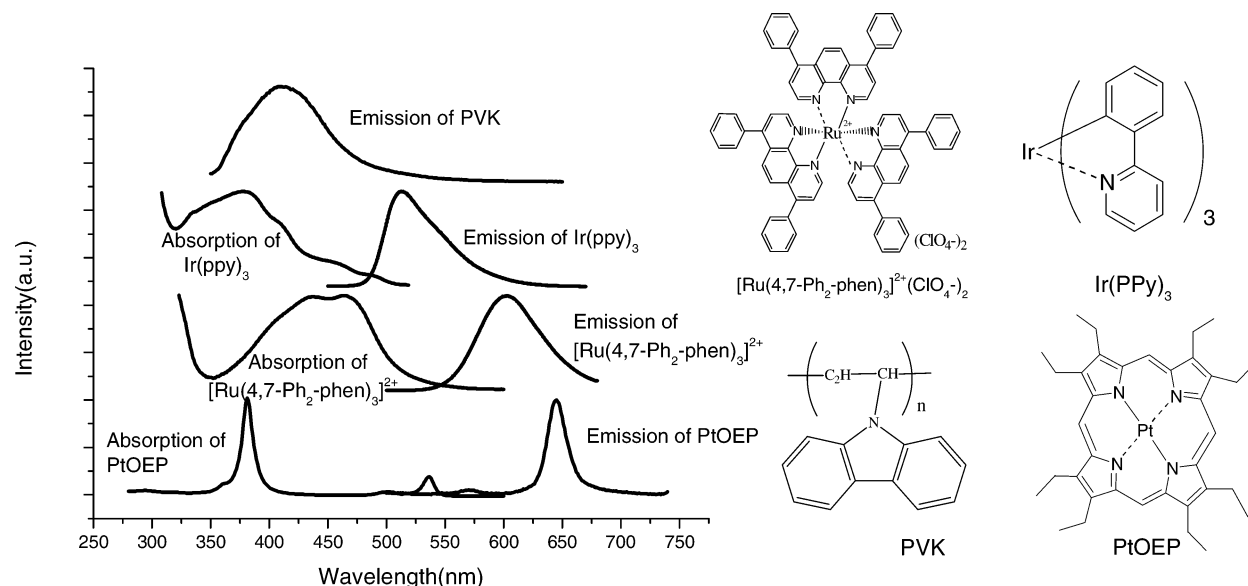
whereas the emission intensity (*I*) of the dopant by a trapping mechanism

$$I \propto \eta_t \eta_e C \quad (5)$$

where *η<sub>t</sub>* is the probability of carriers trapped by dopant, which should be directly proportional to its concentration. Similarly, considering concentration quenching, the following relationship is obtained.

$$R_i \propto (C_1/C_2) = R_c \quad (6)$$

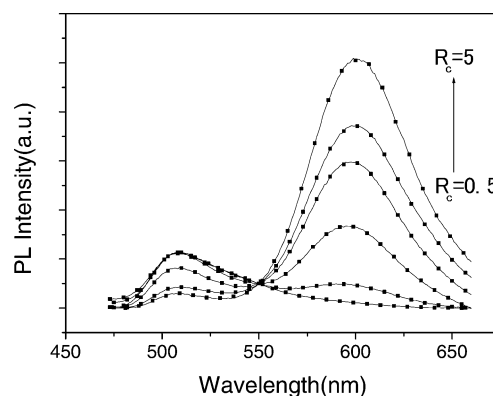
**Photoluminescence Spectra of PVK:Ir(ppy)<sub>3</sub>:[Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> (or PtOEP) Systems.** In this research, the guest materials are Ir(ppy)<sub>3</sub> and [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> (or PtOEP) and



**Figure 2.** Normalized absorption and emission spectra of Ir(ppy)<sub>3</sub>, [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup>, and PtOEP in solution, photoluminescence spectra of PVK in neat film, and molecular structures of all the materials used.

the host is PVK. Ir(ppy)<sub>3</sub> and PtOEP are well-studied phosphorescence dyes emitting a green light and red light, respectively. [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup>, a derivative of well-known tris(bipyridine) ruthium(II) dication Ru(bpy)<sub>3</sub><sup>2+</sup> emitting a red light, is selected in this study due to its high emission efficiency in solution ( $\phi = 27\%$  in toluene,<sup>20</sup> and this value may increase with doping in polymer matrixes<sup>1</sup>) as well as good solubility in organic solvents such as toluene, THF, and dichloromethane. The Ru complex has played a pivotal role in the development of inorganic photochemistry in the past decades,<sup>21</sup> and as most active materials it still plays the continuing role in the field up to today.<sup>22,23</sup> Recently, we study the [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup>-based polymer LEDs, in which a 5 wt % [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> doped PVK device showed red emission with luminance efficiency up to 8.4 cd/A, which demonstrated great potentials of Ru complexes as electrophosphorescence materials. Blue-emitting PVK was selected as the host because its emission spectrum overlaps the absorption spectrum of Ir(ppy)<sub>3</sub>, [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup>, and PtOEP. PVK is known to be a suitable host material for a phosphorescence guest.

The absorption and emission spectra of Ir(ppy)<sub>3</sub>, [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup>, and PtOEP in solution, and the emission spectra of PVK alone as a film, are shown in Figure 2. The emission spectra of PVK peaking at  $\lambda_{\text{max}} = 430$  nm showed the large spectral overlap with the absorption of metal-to-ligand-charge-transfer (MLCT) bands of Ir(ppy)<sub>3</sub> ( $\lambda_{\text{max}} = 390$  nm), [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> ( $\lambda_{\text{max}} = 450$  nm), and PtOEP ( $\lambda_{\text{max}} = 390$  nm). Thus, efficient singlet energy transfers from PVK to these complexes are expected. Ir(ppy)<sub>3</sub> shows a green emission peaking at 510 nm, [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> a red emission peaking at 610 nm, and PtOEP a red emission peaking at 650 nm. It is worth noting that the spectral overlap between the emission of Ir(ppy)<sub>3</sub> and absorption of [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> and PtOEP is very weak, indicating that there are weak or low-energy exchanges between the three metal complexes. Therefore in PVK:Ir(ppy)<sub>3</sub>: [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> (or PtOEP) systems, an independent energy transfer from the PVK host to both metal complexes is expected. This is greatly different from an intermixing fluorescence dye molecule system, for which we must take energy transfer among dye molecules into account due to the energy overlap among dye molecules, which induces

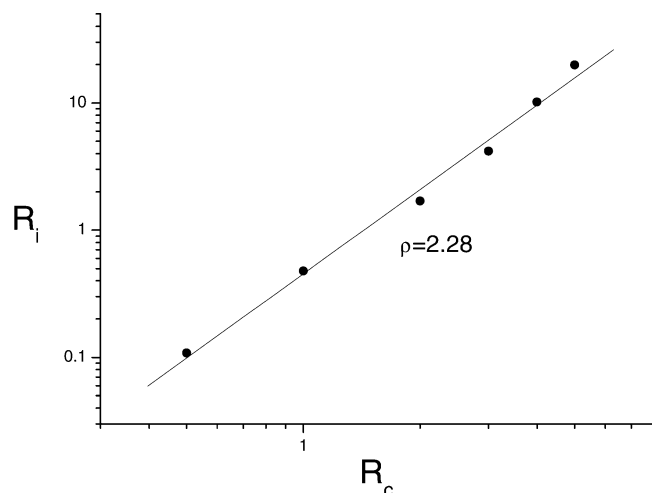


**Figure 3.** PL spectra of 1 wt % Ir(ppy)<sub>3</sub> and  $x$  wt % [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> in PVK thin films ( $x = 0.5-5$ ) at an excitation wavelength of 345 nm.

the complexity of optimization of dye composition for designed colors.<sup>24,25</sup>

To explore the feasibility of fully tunable emission color in doubly doped phosphorescence system, we prepared ternary blends by spin coating PVK chloroform solution. The blends were prepared by adding identical quantities (generally less than 5 wt %) of Ir(ppy)<sub>3</sub> and [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> (or PtOEP) in PVK. The optical excitation is selected using wavelength of 345 nm, where the absorption of Ir(ppy)<sub>3</sub> and [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> is minimal so that most of the excitation light is absorbed by the PVK host.

Figure 3 shows the normalized PL spectra of films made of 1 wt % of Ir(ppy)<sub>3</sub> and  $x$  wt % [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> ( $x = 0.5-5$ ) in PVK. The emissions from both dopants are observed as well as peaks at  $\lambda_{\text{max}} = 510$  and 610 nm, which are consistent with the emission from Ir(ppy)<sub>3</sub> and [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup>, respectively. Tunable colors from green, yellow, orange, to red are observed by increasing the [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> content from 0.5 to 5 wt % and fixing Ir(ppy)<sub>3</sub> at 1 wt %. To obtain a rule of spectra and doping ratio of both emitting species, we separately integrated the spectral contribution of both dopants, and the ratios of emission intensity of both dopants as a function of doping ratio are shown in Figure 4 on a double logarithmic scale. The relationship in power law fashions is obtained with a slope of  $2.28 \pm 0.2$ , which is consistent with the predicted



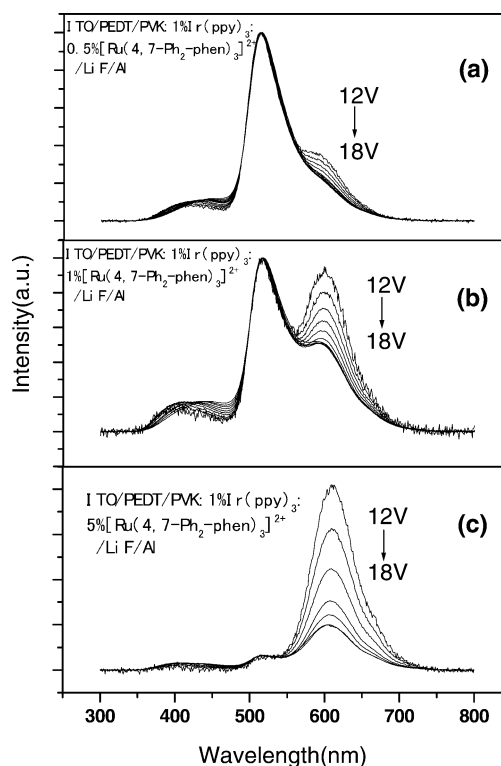
**Figure 4.**  $R_i$  vs  $R_c$  (symbols) from PL spectra on a double logarithmic scale. The solid line is the fitted curve.

value of 2 by the Förster mechanism. The results indicate again that independent Förster energy transfer from PVK host to both guest molecules occurred in the doubly doped phosphorescence dyes system. Similar experiments for  $\text{Ir(ppy)}_3$  and PtOEP doped PVK were performed. Again, the measured  $R_i \propto R_c^{2.1 \pm 0.2}$  obeyed the power law of Förster energy transfer.

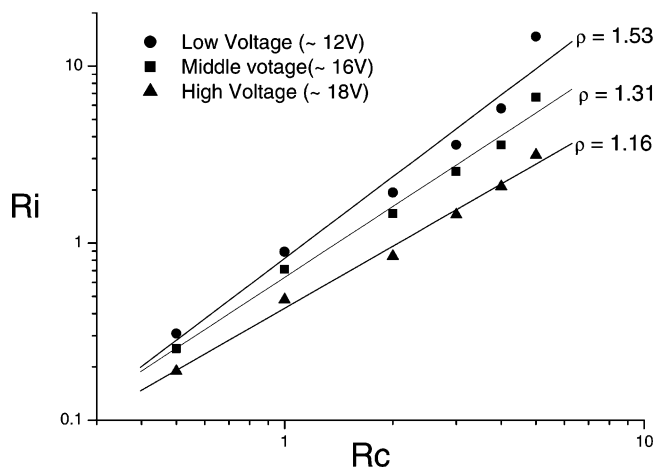
**Electroluminescence.** For device fabrication, we employed only the single-active-layer configuration with poly(3,4-ethylenedioxythiophene) (PEDOT) on indium tin oxide (ITO) as the hole-injecting bilayer electrode. The device configuration was (ITO)/PEDOT/PVK: $\text{Ir(ppy)}_3$ : $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$ /LiF/Al. The emitting layer,  $\text{Ir(ppy)}_3$ : $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$  doped into PVK, was spin-cast onto the surface of PEDOT. The typical thickness of the PVK films with different doping concentrations of both dopants was approximately 80 nm.

The EL spectra of  $\text{Ir(ppy)}_3$ : $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$ :PVK at different doping concentrations and varied applied voltages at the same doping concentration are shown in Figure 5. The light was mostly emitted from  $\text{Ir(ppy)}_3$  and  $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$  at a  $\text{Ir(ppy)}_3$  doping concentration of 1 wt % and  $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$  of 0.5–5 wt %. We found that the emission spectra changed distinctly as changing driving voltages for all devices. Figure 6 shows an  $R_i$  vs  $R_c$  plot in EL spectra at driving voltage of 12, 16, and 18 V, respectively. At lower applied voltage, the emission intensity vs doping concentration obeys power laws with  $R_i \propto R_c^{1.53 \pm 0.14}$ . The red emission clearly decreased as the applied voltage increased, and the power law exponent decreased from an initial  $1.53 \pm 0.14$  at a driving voltage near the turn on voltage  $\sim 12$  V to  $1.16 \pm 0.14$  at  $\sim 18$  V. The observed power law at high applied voltage was close to the predicted value from a trapping model, indicating that in this case, charge trapping and recombination on the dopant site become dominant in the EL process. It is reasonable that high current density passing through the polymer film increases the probability of carriers trapped by dopants. At low voltage the exponent of 1.53 is between the prediction from the Förster energy transfer and carrier trapping model, indicating a combining contribution of two mechanisms. The EL spectral change of all devices is reversible upon increasing and decreasing the voltage and cannot be attributed to the decomposition of metal complexes in EL process.

We noted the possibility that the observed change of relative EL intensities of two emissions with applied electric field could be the result of the difference in quenching efficiency for these two complexes. For example, if the quenching efficiency of the



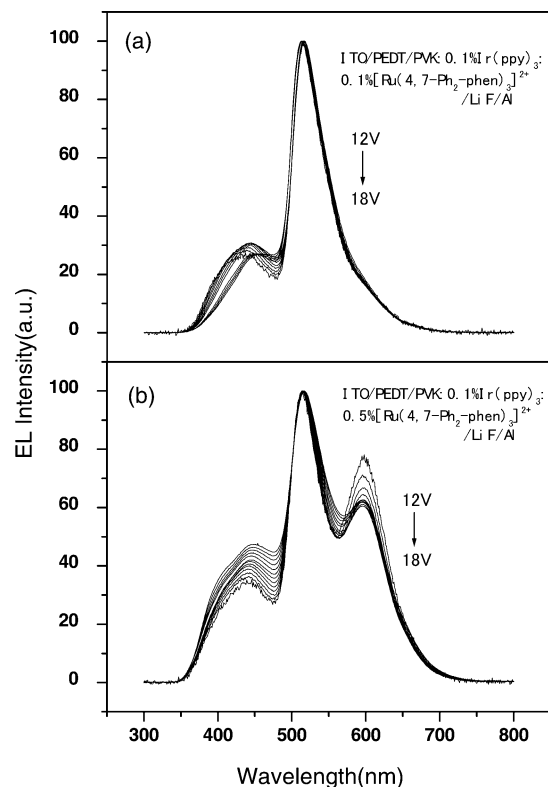
**Figure 5.** Normalized EL spectra of 1 wt %  $\text{Ir(ppy)}_3$  and  $x$  wt %  $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$  in PVK thin films at varied driving voltages: (a)  $x = 0.5$ ; (b)  $x = 1$ ; (c)  $x = 5$ . The emission bands at 510 nm for all spectra have been normalized to the same intensity.



**Figure 6.**  $R_i$  vs  $R_c$  on a double logarithmic scale for EL spectra obtained at driving voltages of 12, 16, and 18 V, respectively. The solid lines are the fitted curves.

triplet–triplet (T–T) and triplet–charge carrier (T–q) annihilation and quenching efficiency of high-electric-field-induced quenching of phosphorescence (dissociation of exciton pairs at high field) are different for two complexes, they may be responsible for the observed change of relative intensities of the emissions of two guests at different operating voltages. However, experimental proofs are weak for the quenching effect. No evidence indicates that there is significant difference in T–T and T–q annihilation between  $\text{Ir(ppy)}_3$  and  $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$ , for both complexes have the same coordination number of six and octahedral geometry in structure and also similar lifetimes of triplet excitons (1–5  $\mu\text{s}$ ). It is necessary to note that recent studies on quenching effects in organic electrophosphorescence by Kalinowski et al.<sup>26</sup> indicate that triplet–triplet and triplet–carriers annihilation as the process

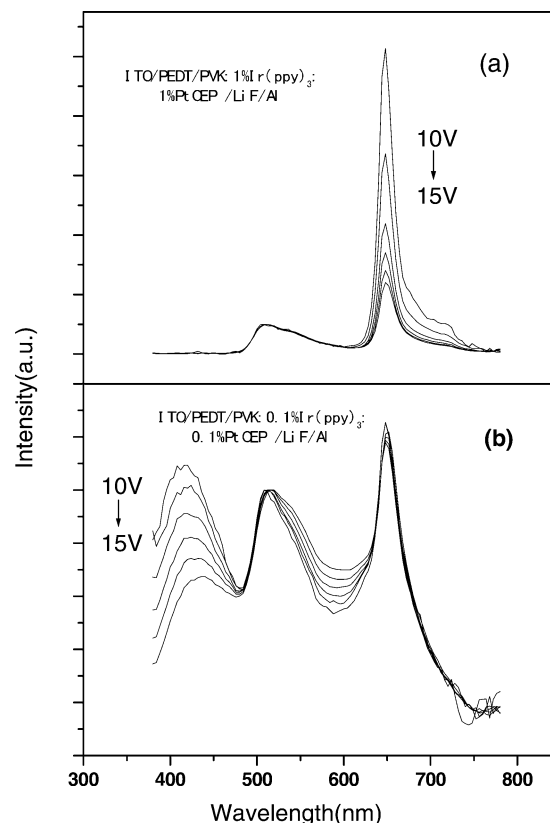




**Figure 7.** Normalized EL spectra of 0.1 wt %  $\text{Ir(ppy)}_3$  and  $x$  wt %  $[\text{Ru(4,7-Ph}_2\text{-phen)}_3]^{2+}$  in PVK thin films at varied driving voltages: (a)  $x = 0.1$ ; (b)  $x = 0.5$ . The emission bands at 510 nm for all spectra have been normalized to the same intensity.

determining the phosphorescence quenching is highly unlikely; on the other hand, electric-field-induced quenching of phosphorescence appears to be a straightforward reason for reducing the electrophosphorescence efficiency as the applied voltage increases. If Kalinowski's conclusion is right, the reducing electrophosphorescence efficiency as applied voltage increases may be independent of guest doping concentration. However, we observed that at low concentration (ca. 0.1 wt %  $\text{Ir(ppy)}_3$ /0.1 wt %  $[\text{Ru(4,7-Ph}_2\text{-phen)}_3]^{2+}$ ), relative intensities of the emissions of two guests at different operating voltages remain unchanged (see Figure 7b), which is largely different from the case at high doping concentration (1 wt %  $\text{Ir(ppy)}_3$ /1 wt %  $[\text{Ru(4,7-Ph}_2\text{-phen)}_3]^{2+}$ ). Therefore, the high-electric-field-induced quenching can be safely ruled out as the process determining the spectral changes.

The spectral investigation has enabled the design of the EL spectrum, namely color engineering, simply by intermixing phosphorescent dye molecules and host polymer in solution, and this is a promising way for improving the productivity of EL devices. In an intermixing fluorescence dye molecule system, we must take energy transfer among dye molecules into account due to the energy overlap among dye molecules, which introduces complexity in the optimization of dye compositions for designed colors.<sup>15</sup> In comparison, the energy overlap among phosphorescence dye molecules is weak in the case of present  $\text{Ir(ppy)}_3$  and  $[\text{Ru(4,7-Ph}_2\text{-phen)}_3]^{2+}$  combinations, which has the same absorption energy but largely different emission energy due to large Stokes shift between the absorption and emission in phosphorescence dyes, thus the spectral disturbance between the dyes is depressed in the phosphorescence system. However, as demonstrated in the above spectral investigation, in a phosphorescence dye molecule system, the dependence between the emission spectrum and driving voltage due to the changed emission mechanisms (energy transfer and charge trapping) in



**Figure 8.** Normalized EL spectra of  $\text{Ir(ppy)}_3$  and PtOEP in PVK thin film at varied driving voltages: (a) 1 wt %  $\text{Ir(ppy)}_3$  and 1 wt % PtOEP in PVK; (b) 0.1 wt %  $\text{Ir(ppy)}_3$  and 0.1 wt % PtOEP in PVK. The emission bands at 510 nm for all spectra have been normalized to the same intensity.

the varied voltage region was considered. At low doping level of phosphorescence dye ca. less than 0.1 wt %, the energy transfer is inefficient due to the average larger distance of phosphorescence dye ( $r$ ) than Förster distance ( $R_0$ );<sup>7</sup> consequently, the trapping mechanism may become dominate for EL emission through the entire voltage region, and we can expect an independence of emission spectrum and driving voltage. Figure 7 shows the EL spectra of low doping concentration of  $\text{Ir(ppy)}_3$  and  $[\text{Ru(4,7-Ph}_2\text{-phen)}_3]^{2+}$  in PVK. The spectral change was relatively inconspicuous in these low-doping devices compared with high-doping devices. For example, in a device with  $[\text{Ru(4,7-Ph}_2\text{-phen)}_3]^{2+}:\text{Ir(ppy)}_3 = 0.1:0.1$ , the spectra remained unchanged, and in a device with  $[\text{Ru(4,7-Ph}_2\text{-phen)}_3]^{2+}:\text{Ir(ppy)}_3 = 0.5:0.1$ , the change of  $R_i$  was less than 20% as the driving voltage ranged from 12 to 18 V. Note that in a device with  $[\text{Ru(4,7-Ph}_2\text{-phen)}_3]^{2+}:\text{Ir(ppy)}_3 = 5:1$  (Figure 5c), the change of  $R_i$  was over 400% as driving voltages changed from 12 to 18 V. The other important difference between the EL spectra of low- and high-doping devices is that the absolute value of  $R_i$  in low-doping devices is evidently lower than that of high-doping devices though they have the same doping ratio. Because the emission of the low-doping device is mainly from charge trapping, the low intensity of the red part in the EL spectra of low-doping devices reflects the lower charge trapping ability of  $[\text{Ru(4,7-Ph}_2\text{-phen)}_3]^{2+}$  compared to  $\text{Ir(ppy)}_3$ .

To demonstrate the universality of observed spectral changes with driving voltage obtained in  $\text{Ir(ppy)}_3$  and  $[\text{Ru(4,7-Ph}_2\text{-phen)}_3]^{2+}$  system, we test another phosphorescence dye combination of  $\text{Ir(ppy)}_3$  and PtOEP in PVK. Similar experiments were performed for  $\text{Ir(ppy)}_3$  and PtOEP in PVK system, and the similar spectral change (Figure 8) was observed in  $\text{Ir(ppy)}_3$

and PtOEP system as that of Ir(ppy)<sub>3</sub> and [Ru(4,7-Ph<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup>. To our interest, in a low-doped single layer device of 0.1 wt % Ir(ppy)<sub>3</sub>:0.1 wt % PtOEP in PVK (Figure 8b), a stable white-emitting device was obtained. The green part and red part of the white spectrum can be associated with the emission of Ir(ppy)<sub>3</sub> and PtOEP, respectively, whereas the blue part in the white spectrum should come from excited PVK, which cannot transfer energy to the two phosphorescent dopants because energy transfer from the PVK host to phosphorescence dopants is very inefficient at such a low doping level (0.1 wt %). The CIE of this white device (0.317, 0.336) at 10 V and (0.338, 0.368) at 15 V is close to the standard white light (0.33, 0.33). Though the efficiency of the present device (~0.1 wt %) was not as high as that of the multi-emissive layer electrophosphorescent white device (5 wt %) using three different color Ir complexes as emitting layers reported by Forrest and Thompson et al.,<sup>27,28</sup> the present device structure was relatively simple. By the way, our present work is focused on a single layer device structure; thus, on the basis of the previous studies on the polymer-based electrophosphorescence device, the EL efficiency can be further improved by using an optimized device structure such as a blend of PVK and an electron transporting molecule like PBD as host<sup>5,12–14,19</sup> as well as using a multilayer device structure containing hole-block and electron-injection layers.<sup>29</sup> Actually, a white device with luminance efficiency up to 4 cd/A has been achieved in a multilayer device ITO/PEDOT/PVK:0.1 wt % Ir(ppy)<sub>3</sub>:0.1 wt % PtOEP/PBD/Alq<sub>3</sub>/LiF/Al. Details for this high-performance white LEDs will be reported elsewhere.

## Conclusions

In conclusion, the relative emission intensity ( $R_i$ ) and doping ratio ( $R_c$ ) dependence of phosphorescence dye in doubly doped PVK devices are measured. The relationship between  $R_i$  and  $R_c$  is found to depend on the driving voltage, which reflects that the various mechanisms (singlet energy transfer and charge trapping) may contribute to the emission process of phosphorescence polymer LEDs. At low driving voltage, the Förster transfer, likely combined with charge trapping, is the dominant EL mechanism in these doubly phosphorescence-based LEDs, and at high driving voltage, the charge trapping plays a more important role in the EL process. The voltage independent EL spectra can be realized in low-doping devices. Our results are interesting for future applications of these blends as tunable active materials for LEDs and lasers.

**Acknowledgment.** We are thankful for support by the National Science Foundation of China (grant number 20125421-

90101026) and by the Ministry of Science and Technology of China (grant number 2002CB6134003).

## References and Notes

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