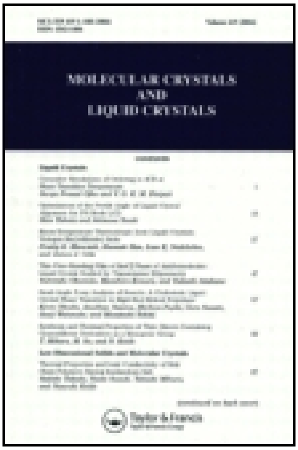

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# Characteristics of Polymer Light Emitting Diode Using a Phosphorescent Terpolymer Containing Perylene, Triazine and $Ir(ppy)_3$ Moieties in the Polymer Side Chain

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# Characteristics of Polymer Light Emitting Diode Using a Phosphorescent Terpolymer Containing Perylene, Triazine and $Ir(ppy)_3$ Moieties in the Polymer Side Chain

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*We have synthesized a novel nonconjugated phosphorescent terpolymer, PPPMA-co-DTPM-co-Ir(ppy)$_3$, containing perylene and Ir complex moieties as lightemitting units and a triazine moiety as electron transporting unit in the polymer side chain. The single-layered electroluminescence (EL) device consisting of ITO/nonconjugated phosphorescent terpolymer/Al exhibited maximum external quantum efficiency and good carrier balance when the Ir feed concentration was 8%. The emission spectrum showed no emission peak from perylene unit, indicating that the energy transfer from perylene unit to guest Ir unit is efficient. The drive voltage decreased below 6.5 V. The CIE coordinate was $x = 0.22$ and $y = 0.54$.*

**Keywords:** carrier balance; drive voltage; phosphorescent terpolymer; quantum efficiency; single-layered EL device

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## INTRODUCTION

The quantum efficiency of organic EL devices emitting from fluorescent materials is limited by the low theoretical value of singlet exciton (25%) compared to triplet exciton (75%) which is formed upon electron-hole recombination in the electroluminescent process [1,2]. Recently, highly efficient organic light emitting diodes (OLEDs) doped with phosphorescent dyes have been studied [3–6]. However, polymer LEDs (PLEDs) using phosphorescent dyes as dopant have not reached high quantum efficiency compared to multilayered OLEDs using phosphorescent dyes [7,8]. The cause of low quantum efficiency for those PLEDs is not well known, however, it may be caused to the incompatibility of the phosphorescent dye molecules in the polymer blend. Thus, PLEDs using phosphorescent copolymers have received a great deal of attention [9–11].

Previously, we synthesized a novel side chain blue light-emitting polymer (PPPMA) with a pendant perylene group and carrier transporting copolymer incorporating hole transporting and electron transporting units in order to improve the performance of single-layered PLED [12–14]. We also reported the structural effects of a blue light-emitting copolymer (PPPMA-co-DTPM) containing pendant triazine moiety as electron transporting unit on the quantum efficiency and drive voltage in a single layered PLED. In the present work, a PLED employing PPPMA-co-DTPM incorporated with Ir(ppy)$_3$ unit was demonstrated. The PPPMA-co-DTPM-co-Ir(ppy)$_3$ gave good external quantum efficiency and carrier balance, comparable to recently reported polymer blend system using the same dopant.

## EXPERIMENTAL

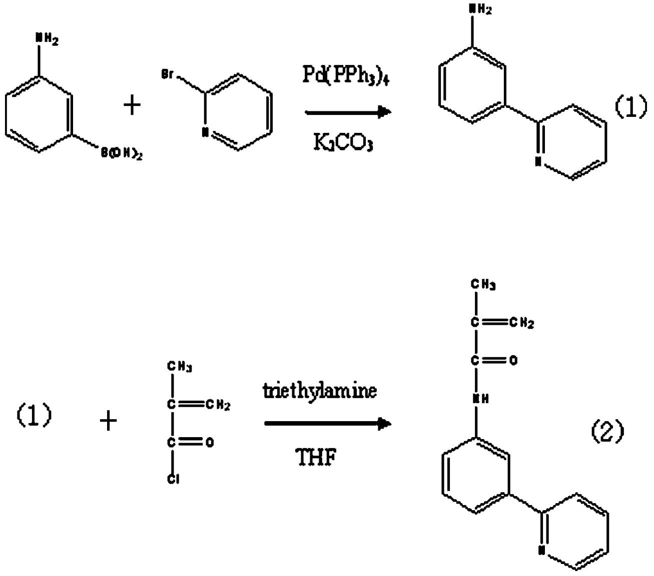
### Reagents

3-Aminophenylboronic acid (Fluka), 2-bromopyridine (Aldrich) and Ir(III)(acetylacetonate) (TCI) were used as received without further purification. THF, triethylamine, methacryloyl chloride and ethylene glycol were purchased from Aldrich.

### Synthesis of 2-(3-aminophenyl)pyridine mathacrylamide (Scheme 1)

#### *2-(3-Aminophenyl)pyridine (1)*

3-Aminophenylboronic acid (3.0 g, 20 mmol) was reacted with 2-bromopyridine (6.32 g, 40 mmol) using potassium carbonate aqueous solution ($K_2CO_3$ 4.0 g, $H_2O$ 50 ml) and tetrakis(triphenylphosphine)



**SCHEME 1** Synthetic route of 2-(3-aminophenyl)pyridine mathacrylamide.

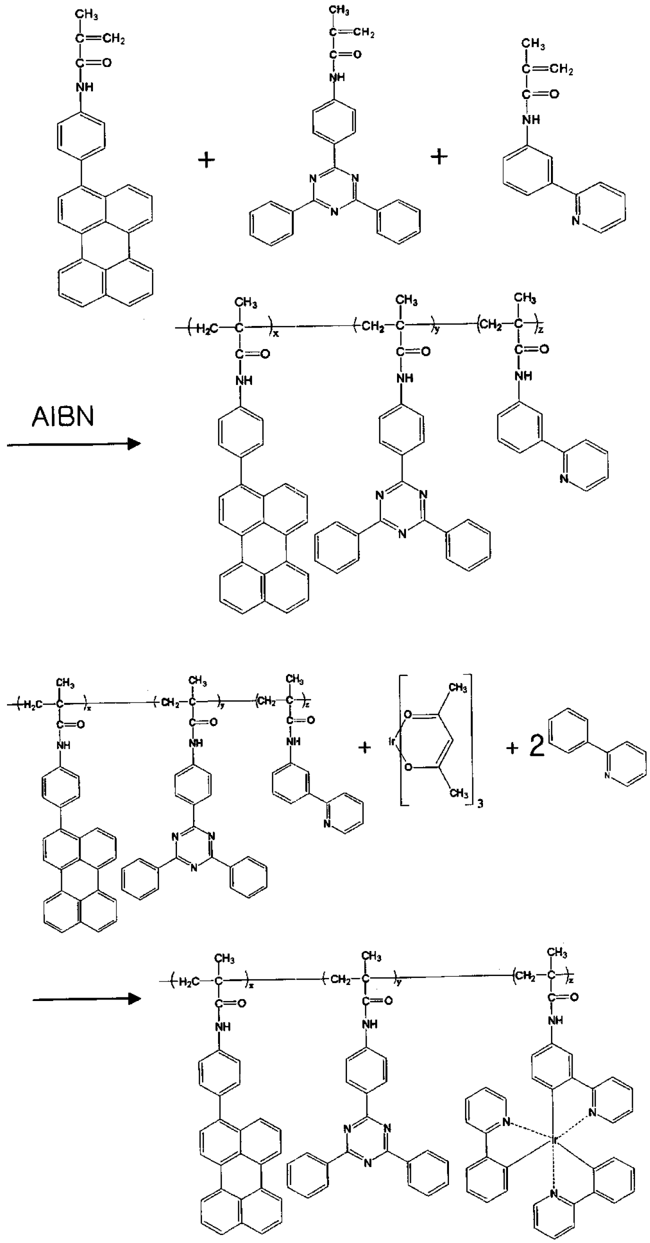
palladium (Pd(pph$_3$)$_4$ 0.06 g) as catalyst in THF at 70°C for 24 hrs under nitrogen atmosphere. After 24 hrs, the solvent was evaporated under reduced pressure, and the 2-(3-aminophenyl)pyridine was purified by using column separation (yield 85%).

### *2-(3-Aminophenyl)pyridine (1) mathacrylamide (APMA) (2)*

THF solution (10 ml) of methacryloyl chloride (1.6 g, 15 mmol) was added dropwise to the solution of 2-(3-aminophenyl)pyridine (2.5 g, 15 mmol) and triethylamine (2.3 g, 22 mmol) in THF below 10°C. The mixture was allowed to react for 24 hrs, and then cooled to room temperature. After extraction with HCl aqueous solution (1 N), water and NaOH aqueous solution (1 N), 2-(3-aminophenyl)pyridine methacrylamide was recrystallized from acetone (2.8 g, yield 80%) [11]. The detail synthetic routs of N-[p-(4,6-diphenyl-1,3,5-triazine-2-yl)phenyl]methacryl amide and N-[p-(perylen-3-yl)phenyl]methacryl amide monomers were reported in the previous publication [14].

## Copolymerization and Metalization (Scheme 2)

PPPMA-co-DTPM-co-APMA was synthesized by solution polymerization of N-[p-(4,6-diphenyl-1,3,5-triazine-2-yl)phenyl]methacrylamide, N-[p-(perylene-3-yl)phenyl]methacrylamide and 2-(3-aminophenyl)



**SCHEME 2** Synthesis of PPPMA-co-DTPM-co-Ir(ppy)$_3$.

pyridine methacrylamide monomers at 75°C in THF using AIBN as an initiator [12]. The polymerization solution was poured into methanol, filtered and washed 3 times with methanol. For the synthesis of Ir complex terpolymer (PPPMA-co-DTPM-co-Ir(ppy)$_3$), the PPPMA-co-DTPM-co-APMA (0.03 g, 0.03 mmol) was added to the solution of 2-phenylpyridine (0.06 mmol) and Ir(ppy)$_3$ in ethylene glycol (50 ml), and then refluxed for 12 hrs. The reaction solution was cooled down to room temperature, and poured to 1 M HCl aqueous solution. After extraction with chloroform, the organic solvent was evaporated. The Ir complex copolymer was precipitated in methanol, and finally dried in vacuum oven. The crude product was column-separated using ethylacetate and methylene chloride to remove Ir(ppy)$_3$ (yield 90%, Mn: 15,000). ANAL. Calcd. for PPPMA-co-DTPM-co-Ir(ppy)$_3$ (7:3:0.8; feed ratio) C, 81.38%; H, 4.89%; N, 6.70%; Found: C, 81.88%; H, 4.95%; N, 6.71%.

## Device Fabrication and Characterization

The prepared terpolymer was spin-cast from THF solution onto an ITO coated glass (16 $\Omega/\text{cm}^2$), at the spin casting speed of ca. 2000 rpm. The ITO substrate was cleaned in deionized water and treated with ultraviolet/ozone prior to use. Aluminum was deposited onto the castfilms using a vacuum evaporator (ULVAC VPC-260F) at $10^{-6}$ torr. Photoluminescent (PL) and electroluminescence (EL) spectra were obtained by using an Acton 300i spectrofluorometer. Current-voltage-luminance characteristics were investigated using a Kiethley 237 programmable electrometer and a Newport 1830-c photodiode.

## RESULTS AND DISCUSSION

Figure 1 shows the UV-Visible absorption spectrum and PL spectrum of Ir(ppy)$_3$ monomer and PPPMA-co-DTPM (7:3) in THF, respectively. This system shows a good spectral overlap between the emission spectrum of PPPMA-co-DTPM and the Soret band (290 nm) and Q-band (380 nm) of Ir(ppy)$_3$ monomer, implying that the energy transfer from PPPMA-co-DTPM to Ir(ppy)$_3$ unit will be efficient. Thus, the good spectrum overlap between the PPPMA-co-DTPM host emission and the singlet metal-to-ligand chargetransfer ($^1$MLCT) state of Ir complex copolymer (PPPMA-co-DTPM-co-Ir(ppy)$_3$) is evident from the Figure 1.

The energy transfer mechanism can involve either Förster process or Dexter process, but the Förster transfer process is expected to dominate, since photoexcitation gives only singlet excitons. The PL spectra of

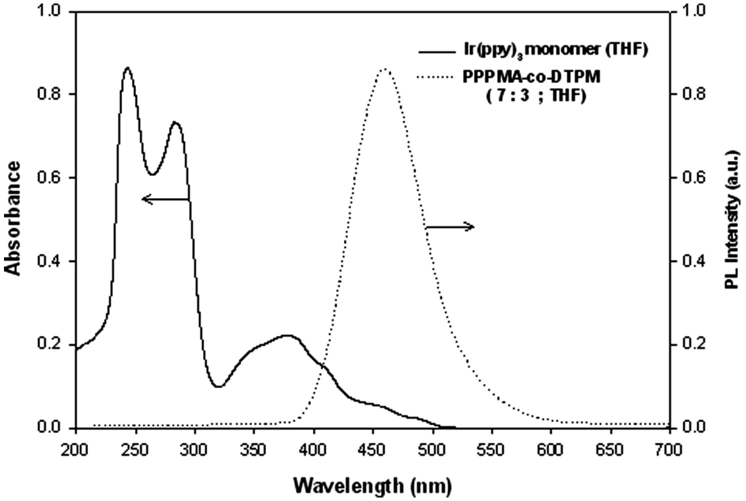


**FIGURE 1** UV-Visible absorption spectrum of $Ir(ppy)_3$ monomer and emission spectrum of PPPMA-co-DTPM in THF.

PPPMA-co-DTPM-co-$Ir(ppy)_3$ containing 6%, 8% and 10% of $Ir(ppy)_3$ feed concentration are shown in Figure 2. With the small feed concentration of 6%, the characteristic emission of Ir complex was shown, and

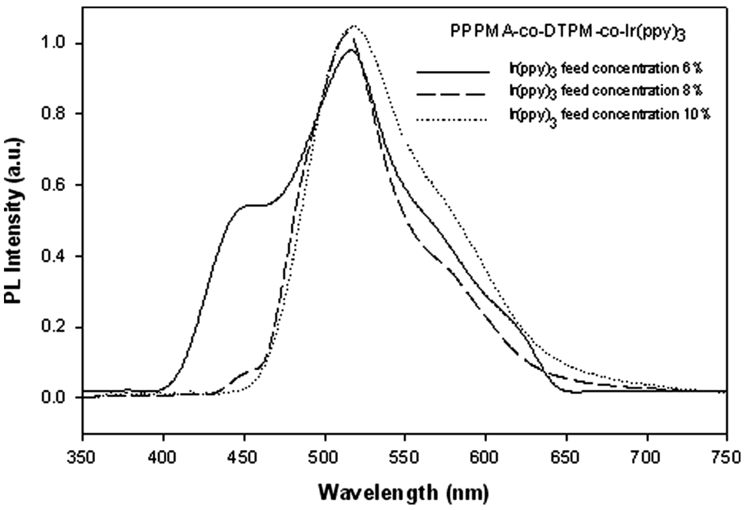


**FIGURE 2** PL spectra of PPPMA-co-DTPM-co-$Ir(ppy)_3$ at various $Ir(ppy)_3$ concentrations in THF.

the emission of perylene unit was not even observed. The complete quenching of PPPMA-co-DTPM emission is achieved at Ir(ppy)$_3$ concentration of 8%. This result shows that intramolecular energy transfer from PPPMA-co-DTPM to Ir(ppy)$_3$ unit is also very efficient.

The EL spectra of three PLEDs using phosphorescent terpolymer are shown in Figure 3. No change in the EL spectra according to the concentration of Ir(ppy)$_3$ was observed. The peak of green emission corresponding to Ir(ppy)$_3$ was appeared at 515 nm. No emission could be detected at the 480 nm peak corresponding to the PPPMA-co-DTPM singlet. The EL spectra showed the shoulder peaks at 550 nm, which is characteristic to Ir(ppy)$_3$ quenching emission. This result is in agreement with PL spectra of Figure 2. The EL spectra clearly exhibited that the light emission is mainly due to the phosphorescence from each iridium complex unit of the terpolymer. It should be noted that this phosphorescent emission is caused to the energy transfer from perylene unit to the iridium complex unit and the direct excitation of iridium complex unit owing to the recombination of injected holes and electrons.

The quantum efficiencies of PLEDs using PPPMA-co-DTPM-co-Ir(ppy)$_3$ are shown in Figure 4. The maximum quantum efficiency of 0.17% was obtained at a Ir(ppy)$_3$ concentration of approximately 8%. The quantum efficiency of Ir complex terpolymer showed high value while high current is applied. Figure 5 shows the radiance vs.

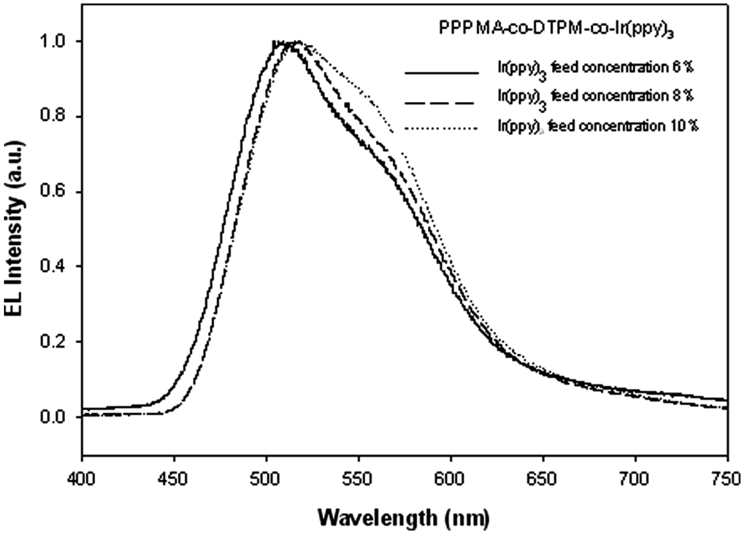


**FIGURE 3** EL spectra of ITO/PPPMA-co-DTPM-co-Ir(ppy)$_3$/Al devices at various Ir(ppy)$_3$ concentrations.

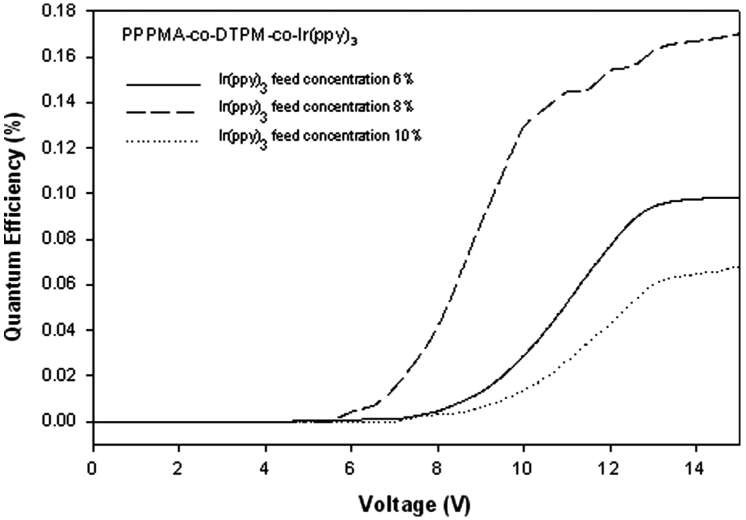


**FIGURE 4** External quantum efficiency of ITO/PPPMA-co-DTPM-co-Ir (ppy)$_3$/Al devices at various Ir(ppy)$_3$ concentrations.

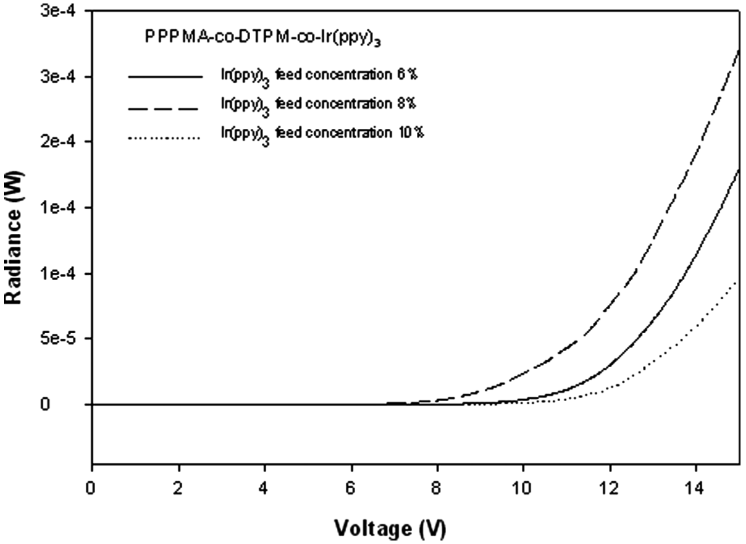


**FIGURE 5** Radiance-voltage characteristics of ITO/PPPMA-co-DTPM-co-Ir(ppy)$_3$/Al devices of various Ir(ppy)$_3$ concentrations.

applied voltage characteristics of ITO/PPPMA-co-DTPM-co-Ir(p-py$)_3$/Al devices at various Ir(ppy$)_3$ concentrations. Light emission was observed at a 6.5 V DC for Ir(ppy$)_3$ feed concentration of 8%. The PLED using terpolymer containing Ir(ppy$)_3$ concentration of 8% had a low turn-on voltage, which is consistent with the result of quantum efficiency. The maximum luminance of the device was 1600 cd/m$^2$ at a 15 V DC.

## CONCLUSIONS

We have synthesized a novel terpolymer containing perylene, triazine and Ir complex as side groups, and then fabricated electrophosphorescent PLEDs. PL and EL results of the terpolymer film exhibited that the energy transfer from perylene unit to Ir unit takes place primarily by the intramolecular energy transfer mechanism. Green emission light is obtained, and a high quantum efficiency of 0.17% is achieved at a Ir(ppy$)_3$ feed concentration of 8%. The luminance of 1,600 cd/m$^2$ was observed at a 15 V DC. It can be concluded that the present phosphorescent terpolymer suggests a simple solution process for achieving high performance of flexible polymer display panel.

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