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Organic Electro-Phosphorescent Devices Using 2,4,6-Triphenothiazino-1,3,5-Triazine as a Host Material

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A new 1,3,5-triazine derivative containing the phenothiazine moiety (PTZ-TRZ) has been synthesized for use as a host material of phosphorescent dye. The photoluminescence and electroluminescence properties of PTZ-TRZ were examined. We have fabricated phosphorescent organic light-emitting devices with tris(2-phenylpyridine) iridium [$Ir(ppy)_3$] as a triplet emissive dopant in PTZ-TRZ host. The emission spectrum of the device exhibited a green emission from $Ir(ppy)_3$, indicating that the energy transfer occurs from PTZ-TRZ to [$Ir(ppy)_3$]. The device with 8% doping concentration of [$Ir(ppy)_3$] in PTZ-TRZ showed external quantum efficiency of 3.72% and the peak luminance 6,870 cd/m^2.

Keywords Host materials; organic phosphorescent device; phenothiazine; 1,3,5-triazine

Introduction

Red, green and blue light-emitting materials with high efficiency and color purity are necessary for full color organic light-emitting display. Up to now organic materials used for the EL device fabrication have been mostly fluorescent dyes, which utilize the emission from a singlet exciton. Energy in triplet exciton in the materials is wasted by non-radiative decay [1–3]. Therefore utilization of fluorescence has some limit in quantum efficiency of EL devices.

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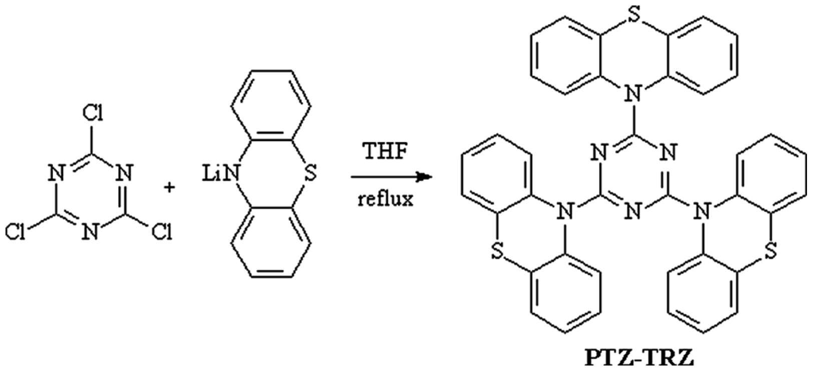

Scheme 1. Synthetic route for 2,4,6-triphenothiazino-1,3,5-triazine.

Recently phosphorescent materials have attracted much scientific and technological research interest to overcome the limit of fluorescence in quantum efficiency because they can generate emission from both triplet and singlet excitons [4–6]. Many phosphorescent materials containing various heavy metals such as platinum, terbium or iridium have been extensively developed, and RBG phosphorescent EL devices have been achieved using the materials. To fabricate an efficient phosphorescent EL devices host material is also very important. 4,4′-N, N′-Dicarbazole biphenyl (CBP), 2,9-dimethyl-4,7-diphenyl-9,10-phenanthrolinme (BCP), triazole (TAZ), oxadiazole and carbazole (CVZ) derivatives have been used as good host materials. Recently Inomata *et al.* reported that 1,3,5-triazine derivatives as efficient host materials for triplet emitters can be used as a host for tris(2-phenylpyridine)-iridium ($Ir(ppy)_3$) [7].

In this present work, we report the synthesis of a new 1,3,5-triazine derivative containing the phenothiazine moiety, 2,4,6-triphenothiazino-1,3,5-triazine (PTZ-TRZ) and the fabrication and characterization of an EL device using PTZ-TRZ as a host material for phosphorescent devices. The synthetic route we used to obtain PTZ-TRZ is shown in Scheme 1.

Experimental

Measurements and LED Fabrication

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AM 300 MHz spectrometer. The steady-state photoluminescence (PL) spectra were recorded on a Spex FL3-11. We fabricated electrophosphorescent diodes with the following structure: indium tin oxide CuPc (50 Å)/α-NPD (350 Å)/PTZ-TRZ (200 Å):$Ir(ppy)_3$/Balq (100 Å)/Alq_3 (400 Å)/LiF (5 Å)/Al (1000 Å). Organic layers of copper phthalocyanine (50 Å), α-NPD (350 Å), PTZ-TRZ (200 Å) doped with $Ir(ppy)_3$, $BAlq_3$ (100 Å), Alq_3 (400 Å), LiF (0.5 nm) and Al (1000 Å) electrodes were deposited on top of the ITO glass through successive vacuum depositions, without breaking vacuum. The doping concentrations of $Ir(ppy)_3$ in the PTZ-TRZ host layer were 5.0, 8.0 and 11.0%. The area of the overlap of the Al and ITO electrodes was about 9.0 mm^2. The device performance was studied by measuring its current-voltage-EL (I-V-L) characteristics, spectra, and CIE coordinates. The I-V-L characteristics were measured with a Keithley 238 source-measure unit and a Keithley 2000 multimeter equipped with a PMT through an ARC 275 monochromator. The external quantum efficiency (QE) of the device's EL, defined as the ratio of emitted photons to injected charges, was calculated from the EL intensity measured with a calibrated Si photodiode.

Synthesis of PTZ-TRZ

2,4,6-Triphenothiazino-1,3,5-triazine (PTZ-TRZ). Phenothiazine (4.85 g, 24.0 mmol) was dissolved in 50 mL of dry tetrahydrofurane (THF) and cooled to −78°C using dry ice and acetone under nitrogen atmosphere. A 1.6 M n-butyllithium/hexane solution (15.0 mL) was slowly added to the reaction mixture by syringe for 30 min. A cyanuric tricloride (1.0 g, 5.4 mmol) solution in 15 mL of dry THF was slowly added to the reaction mixture by syringe for 30 min. The cold bah was then removed and the reaction mixture was stirred for 24 h at room temperature. The reaction was quenched by adding 10 mL of methanol to the reaction solution. The reaction mixture was extracted using ethylacetate and distilled water. The organic layer was separated, dried with magnesium sulfate and concentrated by evaporation. The residue was purified by silica gel column using a hexane/ethylacetate (8/2) co-solvent. The obtained solid was re-crystallized in methanol. A white power (1.69 g, 2.5 mmol) was obtained. The product yield was 46.3%. mp: 128°C. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.92~7.10 (m, 12H), 7.24~7.34 (m, 12H). m/e = 672 (M+).

Results and Discussion

The synthesized PTZ-TRZ was soluble in common organic solvents. UV-visible absorption spectrum of PTZ-TRZ was obtained in chloroform solution. The peak absorptions of the PTZ-TRZ solution were 239 and 277 nm as shown in Figure 1. The maximum PL of the same PTZ-TRZ solution was observed at 452 and

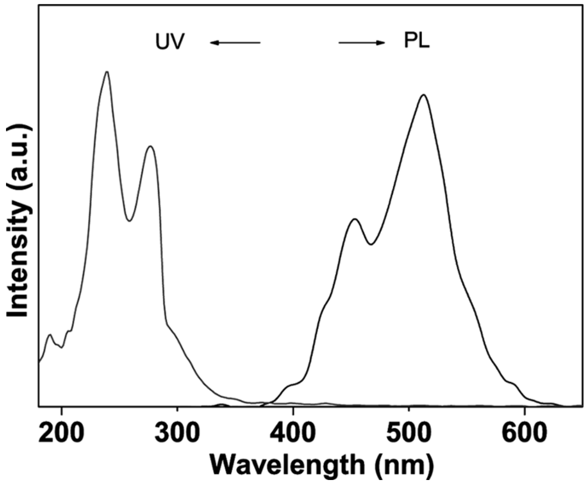

Figure 1. UV-visible absorption spectrum of PTZ-TRZ in chloroform (10^{-5} mol).

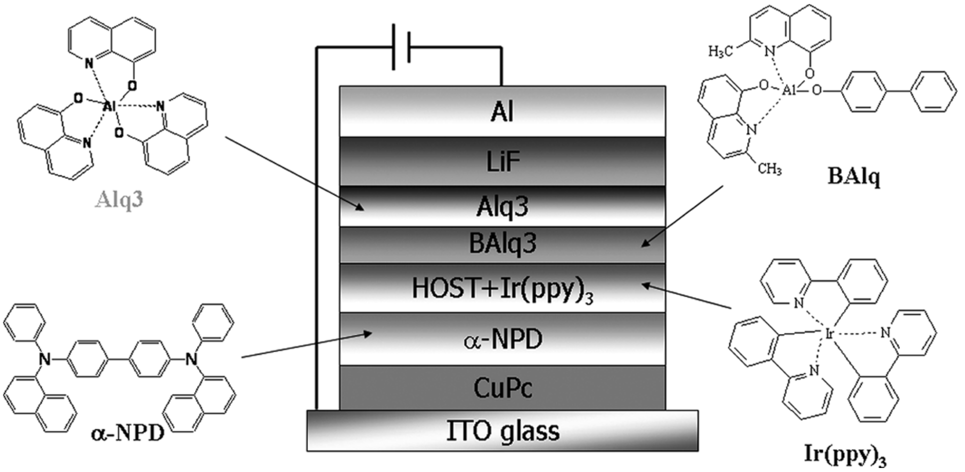

Figure 2. Schematic diagram of the multi-layer EL device constructed for this work.

512 nm. We fabricated an EL device using the PTZ-TRZ as the host material of phosphorescent diode. The EL device was constructed with the following structure: CuPc (50 Å)/α-NPD (350 Å)/PTZ-TRZ (200 Å):Ir(ppy)$_3$/Balq (100 Å)/Alq$_3$ (400 Å)/LiF (5 Å)/Al (1000 Å). A schematic diagram of the device is shown in Figure 2. Copper phthalocyanine (Cu-PC) was used as the buffer layers and α-NPD as the hole-transporting layer. Green phosphorescent Ir(ppy)$_3$ was doped in the PTZ-TRZ host layer with different doping ratios. BAlq$_3$ was used as the exciton-blocking layer, and undoped Alq$_3$ was used as the electron-transporting layer. The Ir(ppy)$_3$-doped PTZ-TRZ emission layer was prepared by co-evaporating PTZ-TRZ and Ir(ppy)$_3$ simultaneously from two sources at calibrated rates to achieve the desired mass ratio. ITO-coated glass with a sheet resistance of 10 Ω/square was used as both the substrate and the anode. Thick aluminum (100 nm)

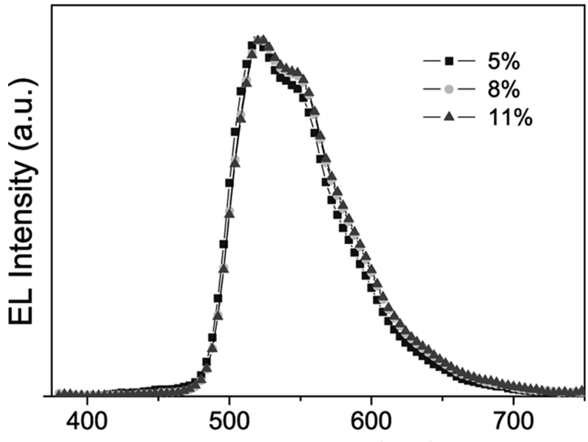

Figure 3. EL spectra of the devices with various doping concentrations.

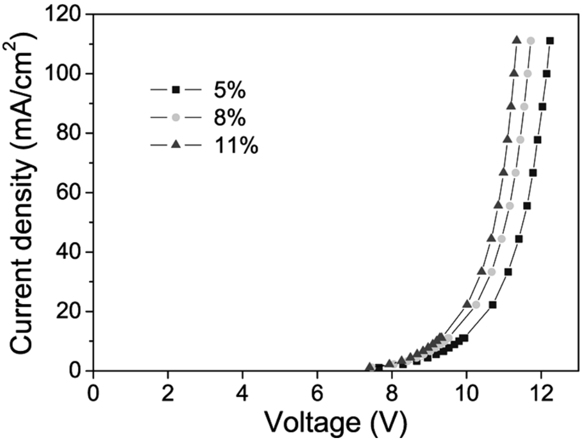

Figure 4. Current density-voltage curves of the devices.

was used as the cathode. Figure 3 shows the EL spectra of the phosphorescent diodes with different doping concentration of Ir(ppy)$_3$. The EL spectrum was not changed by varying the doping concentration of Ir(ppy)$_3$. The maximum electroluminescence was found to be at 520 nm. Figure 4 shows the current-voltage characteristics of the EL devices. Light emission from all the devices was observed at voltages less than 4 V (~1 cd/m^2). The operating voltage at a luminance of 100 cd/m^2 was 7.4 V with a current density of 1.11 mA/cm^2. The EL device exhibited a maximum brightness of 6,870 cd/m^2 at 11.6 V and at current density of 100 mA/cm^2. The CIE 1931 coordinates of the device measured at a brightness of 100 cd/m^2 are $x = 0.34$ and $y = 0.60$. The external quantum efficiency and luminescence efficiency of the 8.0% Ir(ppy)$_3$ doped device were 3.72% and 6,870 cd/m^2 respectively. The luminance-voltage characteristics were shown in Figure 5 and the device characteristics were summarized in Table 1.

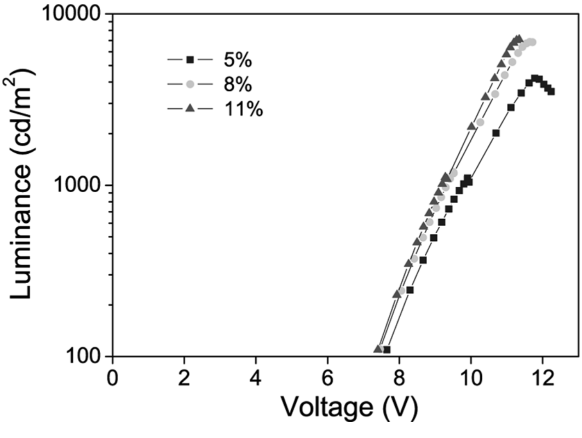

Figure 5. Luminance-voltage curves of the devices.

Table 1. Summary of characteristics of the phosphorescent devices

Doping ratio of $Ir(ppy)_3$ (%)	EL_{max}[a]	Luminance (cd/m^2)	Power efficiency (lm/W)	Q.E. (%)	CIE coordinate[a] (x, y)
5	520	4,210	4.16	3.68	(0.33, 0.60)
8	520	6,870	4.25	3.72	(0.34, 0.60)
11	521	7,080	4.17	3.47	(0.34, 0.60)

[a] Measured at $100\,cd/m^2$ brightness.

Conclusion

We have synthesized 1,3,5-triazine derivative containing phenothiazine as a new host material for phosphorescent EL devices. A phosphorescent EL devices using the PTZ-TRZ as a host layer for green phosphorescent $Ir(ppy)_3$ were fabricated with a structure of CuPc(50 Å)/NPD(350 Å)/HOST(200 Å):$Ir(ppy)_3$/Balq(100 Å)/ Alq_3(400 Å)/LiF(5 Å)/ Al(1000 Å). The emission spectrum of the device exhibited a green emission from $Ir(ppy)_3$, indicating that the energy transfer from PTZ-TRZ to [$Ir(ppy)_3$] is efficient.

Acknowledgments

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