Recent Progress in Phosphorescent Materials for Organic Light-Emitting Devices

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Blue phosphorescence and white phosphorescence from organic light-emitting devices (OLEDs) based on phosphorescent iridium complexes are discussed. To improve emission efficiency, 4,4'-Bis(9-carbazolyl)-2,2'-Dimethyl-biphenyl (CDBP), which has a high triplet energy, was used as the carrier-transporting host for the emissive layer. The blue phosphorescent OLED exhibited a maximum external quantum efficiency of 10.4%, which corresponds to a current efficiency of 20.4 cd/A. This result can be explained as due to the efficient confinement of triplet energy on blue phosphorescent molecules, which is consistent with the results of transient photoluminescence experiments. The white phosphorescent OLED with greenish-blue and red emissive layers exhibited a maximum external quantum efficiency of 12% and a luminous efficiency of 18 cd/A. This is primarily attributed to improved greenish-blue emission efficiency as well as the emission efficiency of the blue phosphorescent OLED.

Keywords: organic light-emitting device, phosphorescence, triplet energy, confinement, quantum efficiency

1. Introduction

Improvement in the emission efficiency of organic light-emitting devices (OLEDs) is an important goal. Blue emission in particular is essential for full-color flat-panel displays because blue is one of the three primary colors.\(^1\,^2\) White light emission is also of interest because it can be used for full-color flat-panel displays with color filters and as an alternative lighting source.\(^3\) The combination of white light emission and color filters should simplify the fabrication process for fine-pixel large-screen displays.\(^4\) To accelerate the commercialization of OLEDs, though, improved efficiency in blue and white emission is needed. A Princeton University group has demonstrated a way to break through the efficiency limitation by using certain organic materials which emit intense phosphorescence from triplet states at room temperature.\(^4,^5\) The phosphorescent materials used were iridium (Ir) and platinum (Pt) complexes with organic ligands, and they were doped as an emissive guest into a charge-transport host material of the emissive layer.\(^6\) The phosphorescence from the device can be understood in terms of the energy transfer from both the singlet and triplet states of the host
molecules to the triplet states of the phosphorescent guest molecules and/or by direct excitation of the phosphorescent guest molecules followed by charge trapping. Devices using phosphorescent materials have already shown a high external quantum efficiency of over 5% in green, red, blue, and white light emission.\(^3\)\(^,\)\(^4\)\(^,\)\(^5\) In particular, the efficiency of the green-emission device was almost 20%, implying 100% internal quantum efficiency.\(^8\)\(^,\)\(^10\) For blue emission, iridium(III)bis[(4,6-di-fluorophenyl)-pyridinato-N, C\(^5\)]picolinate (Flrpic) was used as the blue phosphorescent guest and 4,4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP) was used as the host in these devices.\(^1\) The energy difference of the triplet energies of the host and guest materials was discussed by Baldo et al. who pointed out that higher triplet energy is preferable to achieve efficient blue phosphorescence of the guest molecules.\(^1\) The triplet energy of CBP is lower than that of Flrpic, which indicates that higher efficiency cannot be attained from this host and guest combination.

In this paper, we show that the emission efficiency of a Flrpic-based blue OLED can be improved by using a new host material with a high triplet energy of 3.0 eV. This material is 4,4'-bis(9-carbazolyl)-2,2'-dimethyl-biphenyl (CDBP) which is a derivative of CBP. The blue phosphorescent OLED exhibited an external quantum efficiency of 10.4%, which is much higher than previously reported values.\(^1\) We have also demonstrated highly efficient white phosphorescent OLEDs with greenish-blue and red emissive layers. A greenish-blue phosphorescent material, bis[2-(3,5-bis-trifluoromethyl phenyl)-pyridinato-N,C\(^{5\prime}\)]-iridium(III)picolinate ((CF\(_3\))ppy)\(_2\)Ir(pic)), was used for the greenish-blue emissive layer. The well-known red phosphorescent material, bis(2-(2'-benzo[4,5-a]thienyl)pyridinato-N,C\(^3\))\(_2\)Ir(acac)), was used for the red emissive layer.\(^4\) To enhance the greenish-blue emission, CDBP was used as the host of each emissive layer. The phosphorescent devices exhibited Commission Internationale de l'Eclairage (CIE) coordinates of (0.35, 0.36), and an external quantum efficiency of 12%.

2. Experiments

Figure 1 shows the molecular structures of the phosphorescent guest and host materials used in this study. We expected high triplet energy for the new host material, CDBP, because two phenyl carbazoles were decoupled by the steric hindrance caused by the two methyl groups. The CDBP was synthesized as follows:\(^1\)\(^3\) Pd(OAc)\(_2\) and (tert-Bu)\(_2\)P were stirred at 70°C under nitrogen, then 4,4'-dibromo-2,2'-dimethyl-biphenyl, carbazole, tert-BuONa, and xylene were added and the mixture was refluxed for 5 hours. A fluorinated Ir complex, (CF\(_3\))ppy)\(_2\)Ir(pic), was also synthesized in two steps using the standard procedures.\(^1\)\(^5\) First, a cyclometalated Ir(III) m-chloro bridged dimer was synthesized by the reacting IrCl\(_3\) · n\(_2\)O and 2-(3,5-bis(trifluoromethyl)phenyl)pyridine. The dimer was then

![Molecular structures of host and guest materials for the emissive layer and the hole blocking/electron transporting material.](image-url)
reacted with picolinic acid sodium salt in 2-ethoxyethanol.\textsuperscript{14}

The triplet energies of the materials were measured from the highest energy peak of the phosphorescence spectra in methanol/ethanol solutions at 77 K. To investigate the energy transfer in the emissive layer, we also measured the transient photoluminescence decay in a CDBP thin film (50 nm) doped with 3% FIrpic and a CBP thin film (50 nm) doped with 3% FIrpic, in both cases after laser pulse excitation with a 337-nm wavelength.

Figure 2 shows the device structures of the blue and white phosphorescent OLEDs. A glass substrate coated with a 200-nm-thick indium-tin-oxide (ITO) layer with a sheet resistance of 10 $\Omega/\square$ was used at the substrate. Prior to fabrication of the organic layers, the substrate was cleaned with ultra-purified water and organic solvents, and then treated with a UV-ozone ambient. To reduce the possibility of electrical shorts within the device, poly(3,4-ethylenedioxy-thiophene)/poly(styrene sulfonic acid) (PEDOT:PSS) was spun onto the substrate from a water solution and then the 40-nm-thick PEDOT:PSS layer was baked for 30 min at 190°C.\textsuperscript{16} The other organic layers were continuously grown on the substrate by vacuum deposition under a pressure of about 4 x 10$^{-7}$ Torr without breaking the vacuum. A 40-nm-thick blue emissive layer consisting of a host material and 3% FIrpic was formed by co-deposition with precisely controlled deposition rates. A 30-nm-thick aluminum (III)bis(2-methyl-8-quinolinato)4-phenylphenolate (BAIq) layer was formed as the electron-transporting and hole-blocking layer.\textsuperscript{17} After the cathode formation, the devices were encapsulated using a UV-epoxy resin and glass plate under a nitrogen atmosphere. In the case of white phosphorescent OLED, two emissive layers (for greenish-blue and red) were formed by co-deposition of the host material, CDBP, with the phosphorescent material, (CF$_3$ppy)$_2$Ir(pic) or (btp)$_2$Ir(acac). A 5-nm-thick BAIq layer was inserted as the exciton-blocking layer between the emissive layers. The EL spectra was measured with a spectroradiometer (Minolta CS-1000) and luminance was measured with a luminance meter (Minolta LS-110). A source meter (Keithley 2400) connected to a microcomputer (Epson LJirect) was used to operate the devices. External quantum efficiencies were calculated from the luminance, current density, and EL spectrum, assuming a Lambertian distribution.

3. Results and Discussion

3.1. Blue phosphorescence in an FIrpic-based device

The EL spectrum of a blue phosphorescent device based on FIrpic is shown in Fig. 3. The emission peak was located at 472 nm with a sub-peak at 500 nm. The CIE coordinates were (0.17, 0.34), which were similar to those previously reported.\textsuperscript{8} Figure 4 shows luminance versus the applied voltage for devices with CDBP or CBP as the host. Although the turn-on voltage for light emission slightly increased when CDBP
Fig. 3. EL spectrum of blue emission from a blue OLED with CDBP host.

Fig. 4. Luminance vs. applied voltage for blue OLEDs with either BCP or CDBP as the host.

was used as the host, the luminance reached 20000 cd/m² at an applied voltage of 15.5 V.

The external quantum efficiencies of the devices are shown as a function of current density in Fig. 5. The device with CBP exhibited a maximum efficiency of 5.1%, which is comparable to that (5.7%) reported in a similar device by the Princeton University group. In contrast, the device with CDBP exhibited greatly improved efficiency: the maximum external quantum efficiency was 10.4% at 0.1 mA/cm²,

indicating internal quantum efficiency of approximately 52%. This efficiency was almost twice that of the device with CBP. The power efficiency was 10.5 lm/W and the current efficiency was 20.4 cd/A. These efficiencies are very high compared to other reported values for blue OLEDs. In both devices, a gradual decrease of the external quantum efficiency was observed at high current density, which could be due to triplet-triplet annihilation. The improved efficiency can be explained in terms of the alignments of the triplet energies of organic materials used in the devices. The triplet energies of CDBP, CBP, and Flrpic measured at 77 K were 3.0, 2.6, and 2.7 eV, respectively. As we expected, the triplet energy of CDBP was much higher than that of CBP (2.6 eV) or Flrpic (2.7 eV), indicating that the introduction of the two methyl groups into the biphenyl moiety of CBP was an effective way to increase the triplet energy. From the energy-level alignments we can speculate that there was a very efficient energy transfer from the CDBP triplet states to the Flrpic triplet states and excellent triplet energy confinement on the Flrpic molecules.
Figure 6 shows the transient photoluminescence decay of a 3% Flrpic-doped CDBP thin film and a 3% Flrpic-doped CBP thin film, both measured at a wavelength of 474 nm at room temperature. The CBP thin film exhibited a complicated non-exponential decay curve, which we attributed to the exothermic energy transfer from Flrpic to CBP and the endothermic energy transfer to Flrpic.\(^8\) The CDBP thin film on the other hand clearly revealed a mono-exponential decay curve and a relatively long lifetime of 1.4 \(\mu\)s. Using triplet energies measured at 77 K, we show the energy-level alignment of the Flrpic, CDBP, and CBP schematically in Fig. 7. The transient photoluminescence observation clearly indicates that the triplet energy transfer from Flrpic to CDBP was completely suppressed and the energy was confined on Flrpic because the CDBP had a higher triplet energy than Flrpic. This efficient confinement of triplet energy must be the reason for the efficient phosphorescence from the Flrpic triplet. Thus, the high triplet energy of the host material is extremely important.

Fig. 7. Alignment of triplet energy levels for Flrpic, CDBP, and CBP.

with regard to the emission efficiency of blue phosphorescence.

3.2. White phosphorescence in a device with two emissive layers

The turn-on voltage for light emission (1 cd/m\(^2\)) in a white phosphorescent device was approximately 4 V. The EL spectrum of the white phosphorescent device was strongly influenced by the thicknesses of the greenish-blue and red emissive layers, and the doping concentration of each phosphorescent material. The optimal doping concentration for the greenish-blue and red phosphorescent materials was determined from the efficiency of each single-emissive-layer device; 1 wt% for (CF\(_3\)ppy\(_2\))Ir(pic) and 3 wt% for (btp)\(_2\)Ir(acac). Figure 8 shows the EL spectra of the optimized white light emitting device for different luminance values. The spectra contained two main peaks located at 472 and 620 nm, which are ascribed to the light emission from (CF\(_3\)ppy\(_2\))Ir(pic) of the greenish-blue emissive layer and that from (btp)\(_2\)Ir(acac) of the red emissive layer. Generally, the EL spectrum of a white light-emitting device with multiple emissive layers changes with luminance intensity; that is, with the current density and applied voltage.
However, our white light emitting device showed only a slight change in the spectrum over a wide range from 17.9 to 3590 cd/m². This indicates that the BA1q layer inserted between the greenish-blue and red emissive layers retarded the flow of holes from the greenish-blue emissive layer to the red emissive layer, and prevented the excitons generated in the greenish-blue emissive layer from diffusing into the red emissive layer. Actually, the device without the BA1q layer revealed a larger change. The CIE coordinates were close to (0.35, 0.36) on a straight line between those of the greenish-blue and red devices, and close to ideal white light with the CIE coordinates of (0.33, 0.33). The luminance reached 18000 cd/m² at an applied voltage of 14.5 V.

The maximum external quantum efficiency was 11% for the greenish-blue device and 8% for the red phosphorescent device. The efficiency for greenish-blue is the highest among the reported values in this wavelength region⁸, whereas the one for red was comparable to that reported previously.⁷ The red phosphorescence was not influenced by the host material, possibly because the triplet energy of the (btp)²Ir(acac) might have been lower than that of CBP. The external quantum efficiency and power efficiency of the white light emitting device are shown as a function of current density in Fig. 9. The maximum external quantum efficiency was 12% at 0.01 mA/cm², indicating an internal quantum efficiency of 60% if we assume an out-coupling efficiency of 20%. The corresponding luminous efficiency was 18 cd/A, and the power efficiency was 10 lm/W. Even at a luminance of 100 cd/m², the external quantum efficiency remained high (10%). These efficiencies are very high compared with the reported values for other white light emitting devices.¹¹,¹⁹,²² The highly efficient white emission can be explained in terms of the enhanced greenish-blue emission efficiency which we attribute to the high triplet energy of CDBP. Transient photoluminescence experiments for the (CF₃ppy)₂Ir(pic)-doped CDBP film revealed a single exponential decay with a lifetime of 3.0 µs. This indicates that the triplet excitons on the (CF₃ppy)₂Ir(pic) molecules were effectively confined, leading to highly efficient phosphorescence, as was the case for Flrpic.
4. Summary

We have described an improvement in the emission efficiency of Flpic-based blue emitting devices and white phosphorescent devices which was enabled through use of a new host material with a high triplet energy. The high efficiency can be explained by the strong confinement of the triplet energy on blue and greenish-blue phosphorescent molecules in the emissive layer. The host material selection is extremely important for improving high-energy light emission efficiency, such as for blue and greenish-blue. Our results also indicate that these phosphorescent materials are promising for developing highly efficient OLEDs.

References