Intramolecular Energy Transfer in Heteroleptic Red Phosphorescent Organic Light Emitting Diodes

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Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have been studied extensively for the last decade due to their high light-emitting efficiency. However, charge trapping effect in red phosphorescent dopant limits the performance of red PHOLEDs due to its high doping concentration. One way to minimize charge trapping effect is to add another dopant which has an intermediate bandgap between host and dopant material to induce efficient energy transfer from host to dopant. Forrest et al. reported doubly doped PHOLEDs with green and red dopant materials in the same emitting layer.[1] Quantum efficiency of the doubly doped device could be improved by 20% by cascade energy transfer from carbazole type host to Ir(piq), and then to red dopant materials. However, the energy transfer was not complete and green emission from Ir(piq) was observed.

In this work, phosphorescent dopant materials which can induce intramolecular energy transfer were developed and light emission in red phosphorescent dopant material with mixed ligands of phenylacridinolone (paq) and phenylpyridinone (ppq) in one molecule was studied. Light emission mechanism was investigated and electroluminescence behavior of red PHOLEDs with ppq and pq ligands was also reported.

Experimental

Device configuration of ITO(150 nm)/NPB(50 nm)/EMML(30 nm)/Baalg(5 nm)/Alq(x25 nm)/LiF(1 nm)/Al(100 nm) was used. 4,4’-N,N’-dicyanobenzene (DCB) was used as a host for light-emitting layer (EML) and doping concentration was 10%. ITO glass was used as a substrate for the device, N,N’-dicyanobenzene (DCB) and 4,4’-N,N’-dicyanobenzene (DCB) and four phosphorescent materials were dopants for the emitting layer (ppq (4%), paq (4%), q(4%) and Alq). A hole blocking material and the electron transport layer (ETL) was triis(hydroxyphenyl)aminole acid (TAP). LiF/Al double layer was used as a cathode system. Glass substrate was cleaned with acetone and isopropyl alcohol in an ultrasonic bath and they were dried at 120 °C for 2 h before use. The ITO glass was exposed to UV-ozone for 15 min for cleaning. After deposition of the EML, the glass substrate was transferred to the evaporation chamber. NPB was evaporated at a thickness of 50 nm as a hole transport layer and phosphorescent light-emitting layer was evaporated at a thickness of 30 nm and doping concentration was 10%. ITO thickness was 5 nm and Al was evaporated at a thickness of 25 nm. LiF thickness was 1 nm and Al was evaporated at a thickness of 200 nm. After cathode deposition, the devices were encapsulated with glass lid. Device performances of PHOLEDs were measured with a FE-6500 spectrometer.

Results and Discussion

Chemical structures of phosphorescent dopant materials used in this work are shown in Fig. 1. Ir(piq) was used as a conventional red dopant material and Ir(pq) was a standard green dopant material. Phenylpyridinone-based (phenylpyridinone) trichloro (Ir(pq)Cl3=ppq) and 1-phenylpyridinone-based (phenylpyridinone) trichloro (Ir(pq)Cl3=ppq) were developed as materials with mixed ligands within the molecule. Many phosphorescent dopant materials have been developed, but no material was reported with different main ligands in one dopant material. Two main ligands with different energy levels were introduced in the molecular backbone in this work and it is expected that intramolecular energy transfer from a high energy ligand to a low energy ligand would be induced. Doped samples were used as a high energy ligand and pq was introduced as a low energy ligand unit because pq produces pure red color.

Fig. 2 shows photoluminescence (PL) spectra of four dopant materials used in this experiment. PL spectra were obtained at 77 K and room temperature. Ir(piq) showed a sharp triplet emission peak at 494 nm, and a vibrational peak at 535 nm at 77 K, which was broad emission peak at 516 nm without any clear shoulder was obtained from triplet emission of Ir(pq) at room temperature. Compared with Ir(piq), Ir(pq) showed a triplet emission peak at 593 nm at 77 K and broad emission peak at 615 nm at room temperature. The light emission from Ir(piq) and Ir(pq) are known to be origin from metal ligand charge transfer (MLCT) state of ppq and pq and these results coincide with results reported in other works. Compared with Ir(piq) and Ir(pq), Ir(pq)ppq and Ir(qppq) have both ppq and pq ligand and it is expected that they will show emission from both ppq and pq. However, the two mixed ligand dopant materials showed emission only from pq ligand. PL spectra of mixed ligand dopant materials at 77 K and room temperature were almost the same as those of Ir(pq), and no emission from ppq ligand was not detected in two dopant materials containing both ppq and pq ligand. This result can be explained by intramolecular energy transfer from pq ligand to ppq ligand within the molecule. Both ppq and pq ligands absorb UV-Vis light and are excited to MLCT excited state, but MLCT state of ppq is higher than that of pq, leading to energy transfer from ppq to pq within the molecule. No emission from pq indicates complete energy transfer from ppq MLCT state to pq MLCT state. Higher triplet energy gap of ppq (4 eV) than that of pq (2 eV) supports efficient triplet energy transfer from ppq to pq. Slight bathochromic shift observed in heteroleptic phosphorescent dopants is due to less steric hindrance in ppq modified dopants. Pq ligand is distorted in Ir(pq) structure because of steric hindrance of bulky pq unit, resulting in hypochromic shift of emission spectrum.

Figure 1. Chemical structures of heteroleptic red dopants.

Figure 2. PL spectra of heteroleptic red dopants.

Conclusions

In conclusion, intramolecular energy transfer was effectively induced by replacing one of two ligands with ppq ligand in Ir(qppq). Pure red color could be obtained in mixed ligand dopant materials containing both ppq and pq ligands. Light-emitting efficiency could also be improved by more than 20% due to efficient energy transfer from ppq ligand to pq ligand. In addition, deposition temperature of mixed ligand dopant materials could also be lowered by using small ppq ligand instead of bulky pq ligand.

References


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