

Intramolecular Energy Transfer in Heteroleptic Red Phosphorescent Organic Light Emitting Diodes

Jun Yeob Lee,^{*1} Sung Hyun Kim,^{1,2} Jyongsik Jang²

¹Department of Polymer Science and Engineering, Dankook University, Seoul, Korea

²School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea
leej17@dankook.ac.kr

Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have been studied intensively for the last decades due to their high light-emitting efficiency. However, charge trapping effect in red phosphorescent dopant limits the performances of red PHOLEDs due to high driving voltage. One way to minimize charge trapping effect in red PHOLEDs is to add another dopant which has an intermediate bandgap between host and dopant materials 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 50 % by cascade energy transfer from carbazole type host to Ir(ppy)₃ and then to red dopant materials. However, the energy transfer was not complete and green emission from Ir(ppy)₃ 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 phenylisoquinoline (piq) and phenylpyridine (ppy) in one molecule was studied. Light emission mechanism was investigated and electroluminescence behavior of red PHOLEDs with piq and ppy ligands was also reported.

Experimental

Device configuration of ITO(150 nm)/NPB(50 nm)/EML(30 nm)/Balq(5 nm)/Alq₃(25 nm)/LiF(1 nm)/Al(200 nm) was used. 4,4'-N,N'-dicarbazole biphenyl(CBP) 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 and N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine(NPB) was used as a hole injection and hole transport material. Host material was (4,4'-N,N'-dicarbazole)biphenyl(CBP) and four phosphorescent materials were dopants for the emitting layer. Biphenoxy-bis(8-hydroxy-3-methylquinoline) aluminum(Balq) was a hole blocking material and the electron transport layer(ETL) was tris(8-hydroxyquinoline)aluminum(Alq₃). LiF/Al double layer was used as a cathode system. Glass substrates were cleaned with acetone and isopropyl alcohol in an ultrasonic bath and they were dried at 120 °C for 2 hr before use. The ITO glass was exposed to UV-ozone for 10 min for surface treatment and 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 were evaporated at a thickness of 30 nm and doping concentration was 10 %. Balq thickness was 5 nm and Alq was formed 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 lids. Device performances of PHOLEDs were measured with PR 650 spectrometer.

Results and discussion

Chemical structures of phosphorescent dopant materials we used in this work are shown in Fig. 1. Ir(piq)₃ was used as a conventional red dopant material and Ir(ppy)₃ was a standard green dopant material. Phenylpyridine-bis(1-phenylisoquinoline) iridium(Ir(piq)₂ppy) and 1-phenylisoquinoline-bis(phenylpyridine) iridium(Ir(piq)(ppy)₂) 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. Ppy was used as a high energy ligand unit and piq was introduced as a low energy ligand unit because piq 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(ppy)₃ showed a sharp triplet emission peak at 494 nm and a vibrational peak at 535 nm at 77 K, whereas broad emission peak at 516 nm without any clear shoulder was obtained from triplet emission of Ir(ppy)₃ at room temperature. Compared with Ir(ppy)₃, Ir(piq)₃ 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(ppy)₃ and Ir(piq)₃ are known to be originated from metal ligand charge transfer(MLCT) state of ppy and piq and these results coincide with results reported in other works. Compared with Ir(ppy)₃ and Ir(piq)₃, Ir(piq)₂ppy and Ir(piq)(ppy)₂ have both piq and ppy ligand and it is expected that they will show emission from both ppy and piq. However, the two mixed ligand dopant materials showed emission only from piq ligand. PL spectra of mixed ligand dopant materials at 77 K and room temperature were almost the same as those of Ir(piq)₃. PL emission from ppy ligand was not detected in two dopant materials containing both ppy and piq ligand. This result can be explained by intramolecular energy transfer from ppy ligand to piq ligand within the molecule. Both ppy and piq ligands absorb UV-Vis light and are excited to MLCT excited state, but MLCT state of ppy is higher than that of piq, leading to energy transfer from ppy to piq within the molecule. No emission from ppy indicates complete energy transfer from ppy MLCT state to piq MLCT state. Higher triplet energy gap of ppy(2.4 eV) than that of piq(2.0 eV) supports efficient triplet energy transfer from ppy to piq. Slight bathochromic shift observed in heteroleptic phosphorescent dopants is due to less steric hindrance in ppy modified dopants. Piq ligand is distorted in Ir(piq)₃ structure because of steric hindrance of bulky piq unit, resulting in hypsochromic shift of emission spectrum.

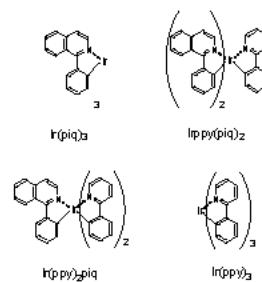


Figure 1. Chemical structures of heteroleptic red dopants.

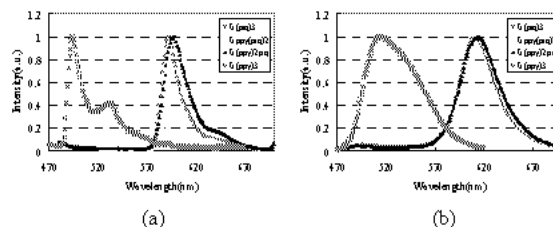


Figure 2. PL spectra of heteroleptic red dopants.

Conclusions

In conclusion, intramolecular energy transfer was effectively induced by replacing one or two piq ligands with ppy ligand in Ir(piq)₃. Pure red color could be obtained in mixed ligand dopant materials containing both ppy and piq ligands. Light-emitting efficiency could also be improved by more than 20% due to efficient energy transfer from ppy ligand to piq ligand. In addition, deposition temperature of mixed ligand dopant materials could also be lowered by using small ppy ligand instead of bulky piq ligand.

References

- [1] Y. Kawamura, S. Yanagida, S. R. Forrest, *J. Appl. Phys.* **2002**, *92*, 87.