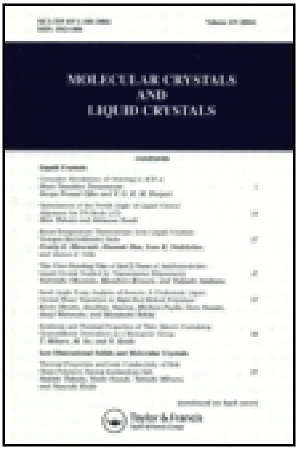

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Red Organic Light-Emitting Diode Using the Heteroleptic Tris-Cyclometalated Iridium Complex

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A novel red phosphorescent heteroleptic tris-cyclometalated iridium complex, $Ir(ppy)_2(dpq)$ based on 2-phenylpyridine (ppy) and 2,4-diphenylquinoline (dpq) ligand was synthesized and characterized for application in organic light-emitting diodes (OLEDs). The heteroleptic tris-cyclometalated iridium complex leads to a significant improvement in luminescence efficiency by cascade exciton transfer and the avoidance of triplet-triplet (T-T) annihilation. A ppy ligand with triplet state energies intermediate between that of the host and the emitting ligand can be successfully employed as "sensitizing ligand" allowing for efficient energy transfer from the host to the emitting ligand. A maximum luminance efficiency of $\eta_c = 14.06\,cd/A$ was achieved at a current density of $J = 20.94\,mA/cm^2$. At a higher current density of $J = 100\,mA/cm^2$, an efficiency of $\eta_c = 10.77\,cd/A$ was obtained.

Keywords: electroluminescence; heteroleptic tris-cyclometalated iridium complex; organic light-emitting diode; red phosphorescence

1. INTRODUCTION

Since organic light-emitting devices (OLED) were developed in 1987 [1,2], materials for the devices and device fabrication have been extensively studied [3,4]. In association with device research, design and synthesis of luminescence dopants have been intensively studied. Luminescent materials are generally classified into two groups: fluorescent and phosphorescent. OLEDs based on phosphorescent emitters can significantly improve electroluminescence performance, because

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Address correspondence to Young Sik Kim, Department of Science, Hongik University, Seoul 121-791, Korea. E-mail: youngkim@hongik.ac.kr both singlet and triplet excitons can be harvested for light emission. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach 100% [5]. The heavy metal complexes, particularly those containing Pt and Ir, can induce intersystem crossing by strong spin-orbit coupling, leading to the mixing of the singlet and triplet excited states [6,7]. The spin-forbidden nature of radiative relaxation from the triplet excited state then becomes spin-allowed, resulting in high phosphorescence efficiencies. Thus, heavy metal complexes can serve as efficient phosphors in OLEDs.

Unfortunately, however, most phosphorescent emitters have a long lifetime, which leads to dominant triplet-triplet (T-T) annihilation at high current. The occurrence of T-T annihilation decreases the performance of a phosphorescent material, particularly its maximum brightness and luminescence efficiency at high currents [8,9]. In order to improve the luminescence efficiency by avoiding T-T annihilation, a metal complex having a different species of plural ligands has been proposed [10–12]. When a metal complex having three ligands including one luminescent ligand is placed in an excited state, the excited energy is transferred from two other ligands to one luminescent ligand, thus producing a monochromatic luminescent color.

In this paper, we report a highly efficient red phosphorescent OLED containing a heteroleptic Ir complex which shows improved luminescence and current-tolerant efficiency characteristics due to the introduction of a phenylpyridine (ppy) ligand as a "sensitizing ligand" which enables efficient energy transfer. The purpose of the present study is to design a high-efficiency heteroleptic Ir(III) complex having different species of ligands, producing a complex suitable for red OLED devices.

2. EXPERIMENTAL DETAILS

2.1. Synthesis and Characterization

The cyclometalated Ir(III) μ-chloro-bridged dimer, $(C^\wedge N)_2Ir(\mu\text{-}Cl)_2Ir(C^\wedge N)$ was synthesized by the method reported by Nonoyama with slight modification. Heteroleptic complexes were measured by Gas Chromatography – Mass Spectrometry (GC/MS) using the DIP method on a Varian 3800GC/1200L single quadruple mass in dilute CH_2Cl_2 at room temperature. The synthesis method is shown in Figure 1.

2.1.1. *Synthesis of the dpq Ligand*

dpq ligands were obtained from the Friedlander Reaction, using 2-aminobenzophenone (10.0 mmol) with acetophenone (10.0 mmol) in

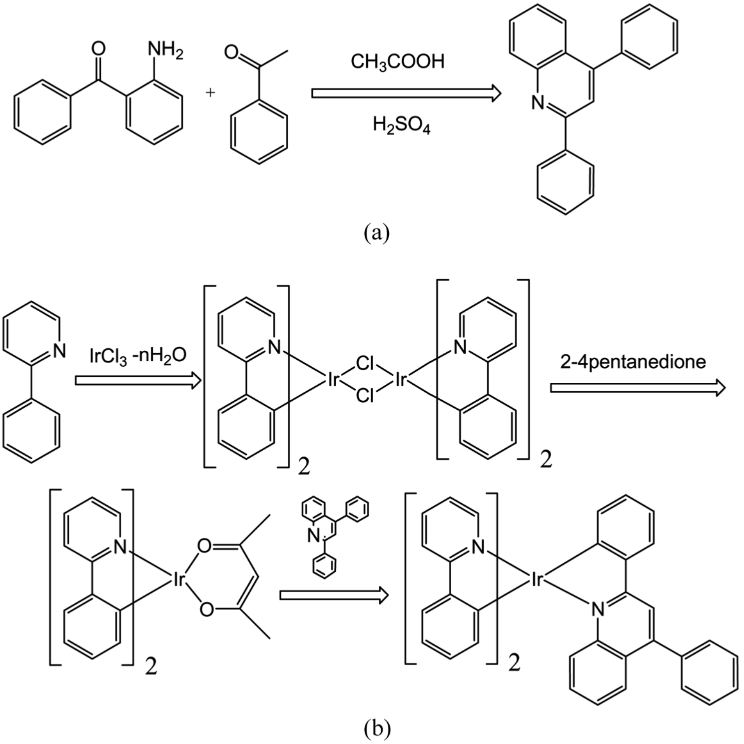

FIGURE 1 (a) Synthesis of C^N Ligands. (b) Synthesis of heteroleptic tris-cyclometalated iridium(III) complex.

30 ml of glacial acetic acid according to the procedure described Figure 1(a).

2.1.2. *Synthesis of Ir(ppy)$_2$(acac)*

To a flask containing $IrCl_3 \cdot H_2O$ (1.49 g, 5 mmol) and a cyclometalating ligand (C^N = ppy 12.5 mmol (2.5 eq)) we added a 3:1 mixture of 2-ethoxyethanol and water. The mixture was refluxed for 15 hr and cooled to room temperature. The solution mixture was slowly evaporated to obtain the crude product $(C^\wedge N)_2Ir(\mu\text{-}Cl)_2Ir(C^\wedge N)_2$. The yellow solid was filtered and washed with ethanol. This chloride-bridged dimer (2 mmol) was then placed in a 50 ml two-neck flask filled with 2-ethoxyethanol (30 mL). 2,4-pentanedione (0.68 ml, d = 0.975, 6.8 mmol (3.4 eq)) was added and the reaction mixture was refluxed for 2 hr at 135°C. The solution was cooled to room temperature and poured into 30 ml of 2N HCl. The yellow solid was filtered and washed with water, followed by purification by silica gel column chromatography by using CH_2Cl_2 to afford a dark yellow powder.

$Ir(ppy)_2(acac)$: Yield (0.614 g, 51%).

2.1.3. ***Synthesis of Heteroleptic Ir(III) Complexes***

$Ir(ppy)_2$(acac) (0.600 g, 1 mmol) and a dpq ligand [2.3 mmol (2.3 eq)] were dissolved in 20 mL of glycerol in a 50 ml flask. The mixture was refluxed for 10 hr at 210□. The reaction mixture was poured into 30 ml of 2N HCl to give the crude solid. Column chromatography on silica followed by recrystallization in methylene chloride/hexanes yielded an orange powder of the hetero Ir complex.

$Ir(ppy)_2(dpq)$: Yield (0.148 g, 19%) GC/MS: calcd.780.95; found 781.38.

2.2. Optical Measurements

UV-Vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. Photoluminescence (PL) spectra were measured on a Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of iridium complexes were measured in a 10-5 M dilute CH_2Cl_2 solution.

2.3. Device Fabrication

Figure 2 shows the chemical structures of synthesized red Ir complexes, $Ir(ppy)_2(dpq)$ and $Ir(dpq)_3$. The device configuration used in this study is shown below. An OLED was fabricated by high vacuum (5×10^{-7} Torr) thermal deposition of organic materials onto the surface of an indium tin oxide (ITO, 30 Ω/□, 80 nm) coated glass substrate. The ITO glass was chemically cleaned using acetone, methanol, distilled water and isopropyl alcohol. The organic materials were deposited in the following sequence: 40 nm of 2-TNATA and 20 nm of NPB were applied as a hole injection layer (HIL) and a hole transporting layer (HTL), respectively, followed by a 30 nm thick emissive layer (EML) of Ir complexes doped in CBP. The doping rate was 10%. A 30 nm thick layer of Alq_3 and 1 nm thick layer of Liq were deposited as an electron transporting layer (ETL) and as an electron injection layer (EIL), respectively. Finally, 100 nm of Al was deposited as a cathode. The molecular structure of other materials for HIL, HTL, host and ETL are found in the literature [13]. After fabrication, the current density–voltage (J-V) characteristics of the OLEDs were measured with a source measure unit (Keithley 236) and the luminescence and CIE chromaticity coordinates of the fabricated devices were measured using a chromameter (MINOLTA CS-100A). All measurements

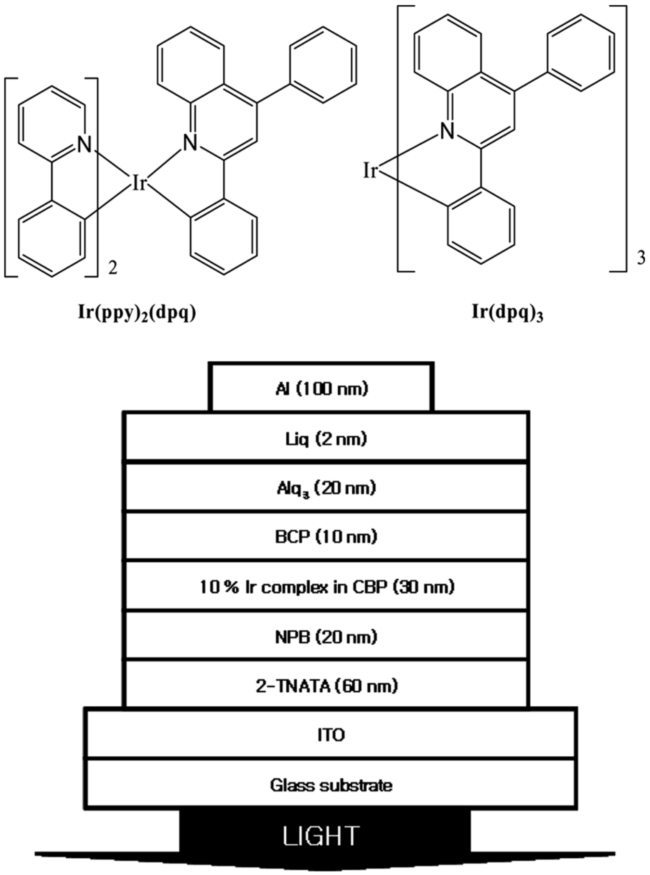

FIGURE 2 Molecular structures of Ir complexes and configuration of OLED used in this study.

were performed in ambient conditions under a DC voltage bias. The active area of the OLED was 0.09 cm^2.

3. RESULTS AND DISCUSSION

In order to improve the luminescence efficiency by cascade exciton energy transfer, a new phosphorescent heteroleptic iridium complex, Ir(ppy)$_2$(dpq) having a different species of plural ligands was designed for application in OLEDs. For the homoleptic complex cases, luminescence efficiency may be decreased because of the saturated quenching effect caused by the energy transfer between the same species of

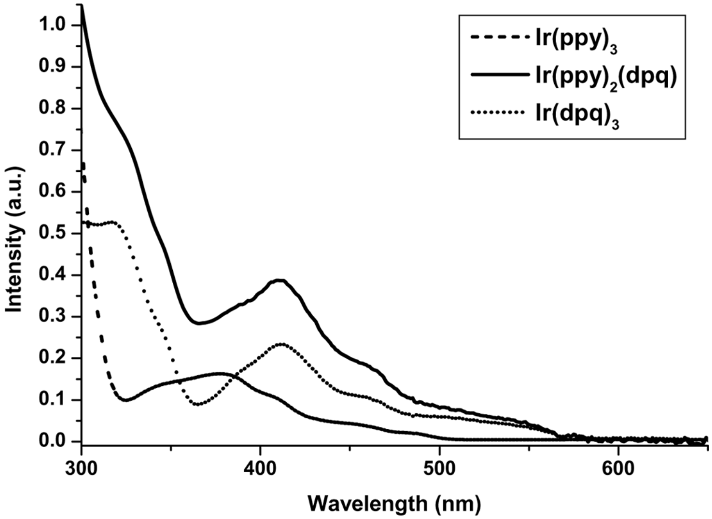

FIGURE 3 UV-Vis. absorption spectra of Ir(ppy)$_3$, Ir(dpq)$_3$ and Ir(ppy)$_2$(dpq).

ligands. Therefore, we have prepared and characterized heteroleptic Ir(III) complex having two ppy ligands and one dpq as a luminescent ligand. This heteroleptic complex exhibits a more reddish emission peak and has highly efficient electrical characteristics. Figure 3 shows the absorption spectra of Ir(ppy)$_3$, Ir(dpq)$_3$ and Ir(ppy)$_2$(dpq) in 10^{-5} M CH_2Cl_2 at room temperature. The absorption peaks of Ir(ppy)$_3$ are located at 380, 410, 460 and 490 nm. The absorption bands below 380 nm can be assigned to the spin-allowed $^1\pi - \pi^*$ transition, the band around 410 nm to a spin-allowed ^{1}MLCT band, and the bands around 460 and 490 nm to a spin-forbidden ^{3}MLCT band. MLCT absorption is allowed by the strong mixing of the π character of the ligand and the 5d character of the centric metal in HOMOs. The MLCT absorption peaks of Ir(dpq)$_3$ are observed at 460, 510 and 560 nm. The overall profile of the absorption spectrum and the peak position of the MLCT absorption of the heteroleptic Ir(ppy)$_2$(dpq) are very similar to those of Ir(dpq)$_3$. This provides evidence that MLCT absorption of the heteroleptic Ir(ppy)$_2$(dpq) occurs mainly at the dpq ligand.

The PL spectra of the homoleptic and heteroleptic complexes on CH_2Cl_2 are shown in Figure 4. Ir(ppy)$_2$(dpq) and Ir(dpq)$_3$ showed maximum emissions at 618 and 603 nm, respectively, while Ir(ppy)$_3$ exhibited maximum emission at 513 nm.

This is because the triplet energy level of Ir(ppy)$_3$ is higher than that of Ir(dpq)$_3$ and because the energy transfer time from ppy to dpq within ns time scale is shorter than the radiative lifetime of

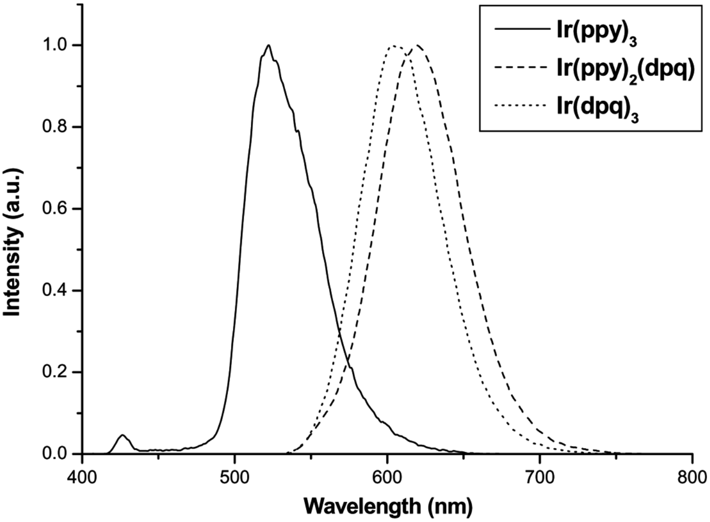

FIGURE 4 PL spectra of Ir(ppy)$_3$, Ir(dpq)$_3$, and Ir(ppy)$_2$(dpq).

Ir(ppy)$_3$ and Ir(dpq)$_3$ which are 0.8 μs and 0.98 μs, respectively. Thus, Ir(ppy)$_2$(dpq) is placed in the excited state, the excitation energy is quickly inter-ligand energy transferred from two ppy ligands to one luminescent dpq ligand. It allow a monochromatic luminescent color. However, for the PL spectra of Ir(ppy)$_2$(4-Me-2,3-dpq) showed the green emission mainly from the MLCT state of ppy. This is because the radiative lifetime of Ir(4-Me-2,3-dpq)$_3$ is longer than of that of Ir(ppy)$_3$ and inter-ligand energy transfer time from the ppy MLCT state to the 4-Me-2,3-dpq MLCT state [14]. This suggests that the heteroleptic Ir(ppy)$_2$(dpq) shows a significant red shifted phosphorescence due to lower steric hindrance in ppy moieties compared with Ir(dpq)$_3$.

In order to confirm pure red emission in the device, the EL spectra of Ir(ppy)$_2$(dpq) and Ir(dpq)$_2$(acac) were determined, and are shown in Figure 5. The main EL peak of the device at 606 nm is blue-shifted 10–12 nm from the PL peaks of the Ir(ppy)$_2$(dpq). This is because the steric hindrance is increased in amorphous solid film. A weak shoulder peak at around 685 nm was considered to represent the ligand-centered $^3\pi - \pi^*$ excited state exhibiting vibronic progressions [9]. The main EL peak of the device did not change with various applied voltages from 4 V to 14 V.

The devices with Ir(ppy)$_2$(dpq) showed a high efficient electrical characteristics. Their performances was compared to that of Ir(dpq)$_2$ (acac) and summarized in Table 1. The EL spectra of Ir(ppy)$_2$(dpq) and Ir(dpq)$_2$(acac) have a maximum at a similar wavelength of

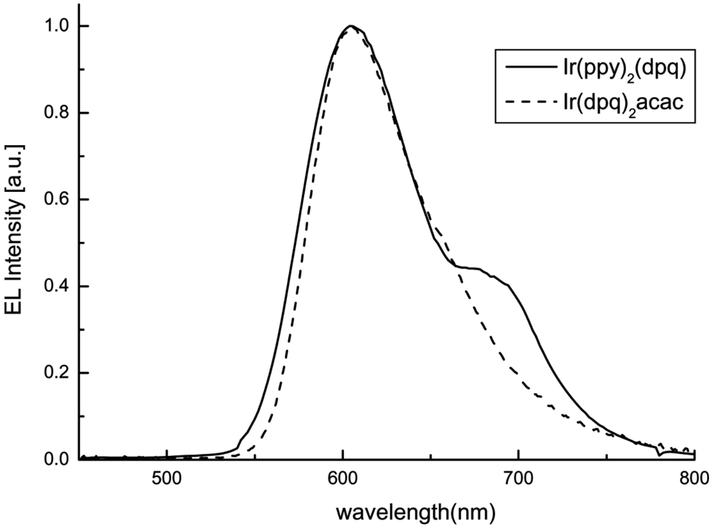

FIGURE 5 Emission spectrum of OLED using Ir(ppy)$_2$(dpq) as red dopants at 12 V.

$\lambda_{max} = 606$ and 605 nm, respectively. This indicates that the EL of Ir(ppy)$_2$(dpq) originated from the emitting dpq ligand. The maximum luminescence of the device was 54,740 cd/m^2 ($J = 231$ mA/cm^2) at the applied voltage of 13 V. Figure 6 shows the luminescence efficiency of 14.06 cd/A ($J = 20.94$ mA/cm^2) for the devices with Ir(ppy)$_2$(dpq) and 11.61 cd/A ($J = 1.59$ mA/cm^2) for the Ir(dpq)$_2$(acac) device. The efficiency of Ir(ppy)$_2$(dpq) at a current density of 300 mA/cm^2 was maintained at 48.08% (7.30 cd/A) of its maximum efficiency. In generally, the performance of the OLEDs was considered to be severely affected by T-T annihilation as the applied current increased. Thus, the luminescence efficiency decreased substantially with increased current [15]. From the luminescence and luminescence efficiency

TABLE 1 Electroluminescence Characteristics of Heteroleptic Iridium Complexes

Red dopant	Max. luminance [cd/m^2] at 14 V	Max. luminous efficiency (cd/A)	λ_{max}	CIE	Turn-on voltage (V)
Ir(dpq)$_2$(acac)	17,457	11.61	605 nm	(0.61, 0.37)	7.1
Ir(ppy)$_2$(dpq)	54,740	14.06	606 nm	(0.62, 0.39)	3

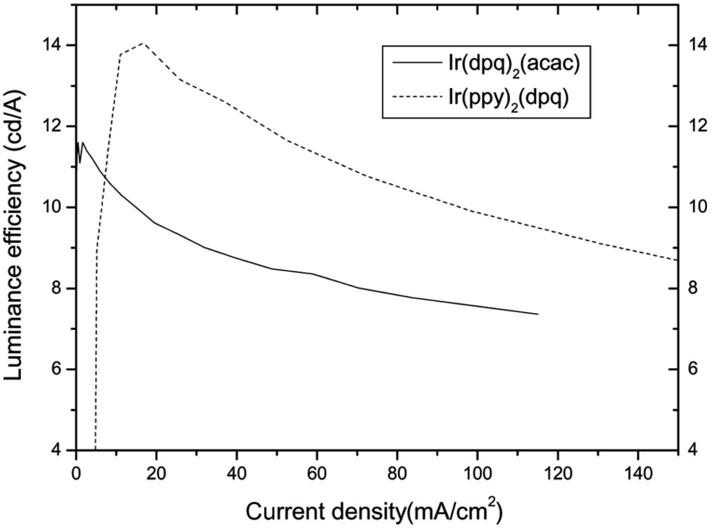

FIGURE 6 Luminous efficiency curve as increasing the current density of OLED.

characteristics, it is apparent that the devices containing the Ir(ppy)$_2$(dpq) exhibit high efficient electrical characteristics based on cascade exciton energy transfer. The triplet energy levels of ppy ligand are intermediate between that of the host and the emitting ligand, works as cascade to easily energy transfer from the host to the luminescent ligand as shown in Figure 7.

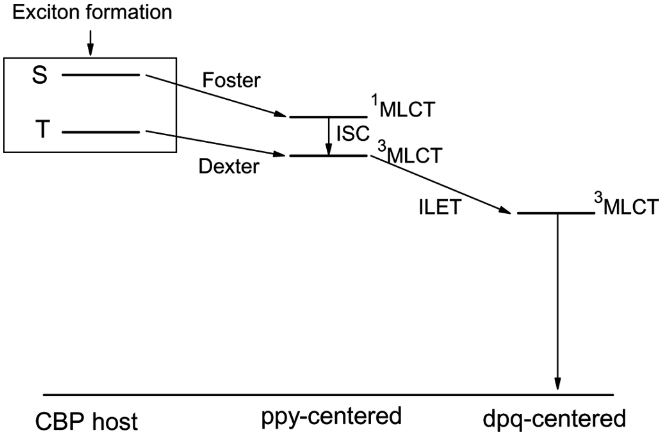

FIGURE 7 Energy level diagram of CBP host, ppy ligand and dpq ligand.

4. CONCLUSIONS

We have fabricated highly efficient red phosphorescent organic light-emitting diodes employing a new heteroleptic Ir complex, Ir(ppy)$_2$(dpq), and studied their electrical and optical characteristics. It was suggested that the cascade exciton transfer from two ppy ligands to one luminescent dpq ligand could suppress T-T annihilation and saturation of the ligand excited states by decreasing the number of the luminescent ligands, leading to better performance of the device at high currents. From the luminescence and luminescence efficiency characteristics of the devices containing the Ir(ppy)$_2$(dpq), we showed that the ppy ligand with triplet state energies intermediate between that of the host and the emitting ligand can be successfully employed as a "sensitizing ligand" allowing for efficient energy transfer from the host to the dopant. The resulting device exhibits highly efficient electrical characteristics due to cascade exciton energy transfer.

REFERENCES

[1] Tang, C. W. & VanSlyke, S. A. (1987). *Appl. Phys. Lett.*, *51*, 913.

[2] Baldo, M. A., Thompson, M. E., & Forrest, S. R. (2000). *Nature*, *403*, 750.

[3] Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Lee, H. E., Adachi, C., Burrow, P. E., Forrest, S. R., & Thompson, M. E. (2001). *J. Am. Chem. Soc.*, *123*, 4304.

[4] Park, N. G., Lee, J. E., Park, Y. H., & Kim, Y. S. (2004). *Synth. Met.*, *145*, 279.

[5] Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Kwong, R., Tsyba, I., Bortz, M., Mui, B., Bau, R., & Thompson, M. E. (2001). *Inorg. Chem.*, *40*, 1704.

[6] Baldo, M. A., Thompson, M. E., & Forrest, S. R. (1999). *Pure Appl. Chem.*, *71*, 2095.

[7] Brooks, J., Babaya, T., Lamansky, S., Djurovich, P., Tsyba, I., Bau, R., & Thompson, M. E. (2002). *Inorg. Chem.*, *41*, 3055.

[8] Kohler, A., Wilson, J. S., & Friend, R. H. (2002). *Adv. Mater.*, *14*, 701.

[9] Tamayo, A. B., Alleyne, B. D., Djurovich, P. I., Lamansky, S., Tsyba, I., Ho, N. N., Bau, R., & Thompson, M. E. (2003). *J. Am. Chem. Soc.*, *125*, 7377.

[10] Tsuboyama, A., Mizutani, H., Okada, S., Takiguchi, T., Miura, S., Noguchi, K., Moriyama, T., Igawa, S., Kamatani, J., & Furugori, M. (2003). *US Patent Appl. Pub.* 0054198.

[11] Park, Y. H. & Kim, Y. S. (2007). *Thin Solid Films*, *515*, 5084.

[12] Seo, J. H., Lee, S. C., Kim, Y. H., & Kim, Y. K. (2007). *Mol. Cryst. Liq. Cryst.*, *471*, 305.

[13] Rayabarapu, D. K., Paulose, B. M. J. S., Duan, J. P., & Cheng, C. H. (2005). *Adv. Mater.*, *17*, 349.

[14] Ahn, S. Y., Ko, M. J., & Ha, Y. K. (2008). *Journal of Physics and Chemistry of Solids*, *69*, 1320.

[15] Su, Y. J., Huang, H. L., Li, C. L., Chien, C. H., Tao, Y. T., Chou, P. T., Datta, S., & Liu, R. S. (2003). *Adv. Mater.*, *15*, 884.