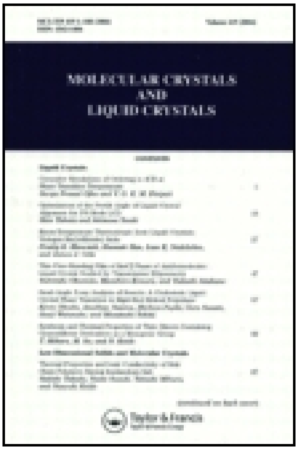

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Previously, we studied the luminescence characteristics of Ir(ppy)$_2$(F$_2$-ppy) and Ir(ppy)$_2$(piq-F), which are heteroleptic iridium complexes involving two kinds of ligands, where F$_2$-ppy, ppy and piq-F represent 2-(2,4-difluoro-phenyl)-pyridine, 2-phenylpyridine and 1-(4′-fluoroyphenyl)isoquinoline, respectively. Photoluminescence (PL) spectrum of Ir(ppy)$_2$(F$_2$-ppy) showed an emission peak at 495 nm in bluish green area. Ir(ppy)$_2$(piq-F) showed two peaks at 513 nm and 600 nm in the PL spectrum. In order to make a white phosphorescent emitter for OLED, we herein designed a heteroleptic iridium complex containing three different ligands. We thought that reaction of F$_2$-ppy, ppy and piq-F ligands all together with Ir(acac)$_3$ might lead to Ir(F$_2$-ppy)(ppy)(piq-F) among the mixture, displaying red and bluish green emission simultaneously. Ir(F$_2$-ppy)(ppy)(piq-F) and other double-heteroleptic complex mixture are prepared from various concentration combination of ligands. The heteroleptic iridium complex mixture displays a variety of emission color, depending upon the combination ratio of ligands in the iridium complex synthesis. UV-vis absorption and photoluminescence (PL) spectra of the mixtures are analyzed and compared with the double-heteroleptic complexes. The white-yellow emission is observed when the mole ratio of ligands is 5:1:3 for F$_2$-ppy, ppy and piq-F, respectively.

Keywords: Ir(F$_2$-ppy)(ppy)(piq-F) and other mixture; heteroleptic Ir(III) complex; white dopant; phosphorescence; DFT; OLED

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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]. Along with this development, a variety of luminescence dopants have been intensively designed and investigated. OLEDs based on phosphorescent emitters can significantly improve electroluminescence performance because both singlet and triplet excitons can be harvested for light emission. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach 100% [5].

In the meantime, bright white light sources have drawn attention. Various methods of producing white light have been demonstrated from polymer and/or small-molecule organic devices [6–10]. To obtain white light efficiently with good color purity, complicated fabrication technologies have often been necessary [11,12]. A simple approach for making efficient white electroluminescent devices is thus required urgently [13].

Herein, we conceive that one phosphorescent material may emit white light. In our earlier result, PL spectrum of a heteroleptic complex, $Ir(ppy)_2(piq\text{-}F)$ showed two peaks at 516 nm and 600 nm while $Ir(ppy)_3$ and $Ir(piq\text{-}F)_3$ are reported as green and red emitter materials, respectively [14]. Our previous study also showed that PL spectrum of $Ir(ppy)_2(F_2\text{-}ppy)$ exhibited one broad peak at 494 nm while $Ir(F_2\text{-}ppy)_3$ emitted at 470 nm [15]. Therefore, we thought that the triple-heteroleptic complex, $Ir(F_2\text{-}ppy)(ppy)(piq\text{-}F)$, might display bluish green and red emission simultaneously. Thus, the investigation on the synthesis and characteristics of the triple-heteroleptic complex was performed in this study.

2. EXPERIMENTAL SECTION

2.1. Synthesis and Characterization

All reagents were purchased from Aldrich Co. except Ir(III) trichloride hydrate ($IrCl_3 \cdot H_2O$) which was purchased from Strem Co. and used without further purification. All reactions were carried out under a nitrogen or argon atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230-Mesh, Merck Co). Mass spectra were determined on JEOL, JMS-AX505WA, HP 5890 Series II Hewlett-Packard 5890 A (capillary column) at Seoul National University, Korea.

2.1.1. Synthesis of Ligands (L = F_2-ppy, piq-F)

Phenylisoquinoline ligand, piq-F was obtained from the reaction of 1-chloroisoquinoline with the corresponding substituted phenylboronic acids by Suzuki coupling. Phenylpyridine ligand, F_2-ppy was obtained from the reaction of 2-chloropyridine with the corresponding substituted phenylboronic acids by Suzuki coupling, either.

Synthesis of piq-F. 1-chloroisoquinoline (0.899 g, 5.5 mmol), 4-fluorophenylboronic acid (0.699 g, 5 mmol) and tetrakistriphenylphosphine palladium(0) (0.196 g, 0.17 mmol) were placed in the mixture of toluene (20 ml), ethanol (10 ml) and 2 N sodium carbonate aqueous solution (20 ml). The reaction mixture was heated to reflux for 15 h at 135°C. The mixture was cooled to room temperature and extracted with 20 ml of ethyl acetate. The organic fraction were dried over anhydrous $MgSO_4$, filtered and pumped dry. The residue was chromatographed on a silica gel column with ethyl acetate/hexane (1:7). The product were collected and dried in vacuum to yields a white powder with 64% yield.

Ligands F_2-ppy was prepared from the reaction of 2-chloropyridine with 4-fluorophenylboronic acid by a similar procedure, respectively.

piq-F: Yield 0.72 g (64%), ***F_2-ppy***: Yield 0.59 g (61.5%)

2.1.2. Synthesis of Complexes.

Synthesis of Triple Heteroleptic Ir(III) Complex and the other Mixtures. General Procedure. Ir(F_2-ppy)(ppy)(piq-F) mixture was prepared from the reaction of $Ir(acac)_3$ with the various ratio of the three different ($C^\wedge N$) ligands by a reported procedure [16].

Iridium Complex with Three Different Ligand Mixture. $Ir(acac)_3$ (489 mg, 1.0 mmol) was reacted with F_2-ppy, ppy and piq-F in 20 ml of glycerol and refluxed for 12 h. After cooling, 20 ml of 1 N HCl solution was added and the resulting precipitate was filtered off. The residue was purified by a silica gel chromatography using CH_2Cl_2. The product was obtained as a bright orange powder. FAB/MS: Ir(F_2-ppy)(ppy)(piq-F) calcd. 758.81; found 759; Ir$(ppy)_2$(F_2-ppy) calcd. 690.76; found 691; Ir$(F_2\text{-ppy})_2$(ppy) calcd. 726.74; found 727; Ir$(ppy)_2$ (piq-F) calcd. 722.83; found 723.

3:1:2 ligand ratio, F_2-ppy (327 mg, 1.71 mmol), ppy (0.081 ml, 0.57 mmol) and piq-F (254 mg, 1.14 mmol)-iridium complex mixture: Yield 258 mg (34%).

3:1:3 ligand ratio, F_2-ppy (281 mg, 1.47 mmol), ppy (0.067 ml, 0.49 mmol) and piq-F (328 mg, 1.47 mmol)-iridium complex mixture: Yield 395 mg (52%).

5:1:3 ligand ratio, F_2-ppy (363 mg, 1.9 mmol), ppy (0.054 ml, 0.38 mmol) and piq-F (254 mg, 1.14 mmol)-iridium complex mixture: Yield 311 mg (41%).

Synthesis of Double-Heteroleptic Ir(III) Complexes. General Procedure. Cyclometalated Ir(III) μ-chloro-bridged dimers of the general formula, $(L)_2Ir(\mu\text{-}Cl)_2Ir(L)_2$, where L represents the cyclometalated phenylpyridine or phenylisoquinoline derivatives, were synthesized according to the method reported by Nonoyama with slight modification [17]. Further reaction with 2,4-pentadione (acac) gave $Ir(ppy)_2acac$.

$Ir(ppy)_2acac$ (0.600 g, 1 mmol) and a cyclometalating ligand (piq-F, or F_2-ppy = 2.3 mmol) were dissolved in 20 ml of glycerol in 50 ml flask. The reaction mixture was refluxed for 10 h at 210°C. The resulting mixture was poured into 30 ml of 2 N HCl to give the crude solid. Column chromatography on silica followed by recrystallization in CH_2Cl_2/CH_3OH yielded the red powder of the desired Ir complexes.

Ir(ppy)$_2$(F$_2$-ppy): Yield 0.470 g (68%), ***Ir(ppy)$_2$(piq-F):*** Yield 0.448 g (62%).

2.2. Photoluminescence Measurement

UV-vis absorption spectra were measured on Hewlett Packard 8425 A spectrometer. The PL spectra were measured on Perkin Elmer LS 50B spectrometer. UV-vis and PL spectra of iridium complexes were measured with 10^{-5} M dilute solution in CH_2Cl_2.

2.3. Theoretical Calculation

The ground and low-lying excited electronic states in the Ir(III) complexes were calculated using the Gaussian 98 package [18]. The highest occupied molecular orbital (HOMO) energy level and the energy gap between HOMO and the lowest unoccupied molecular orbital (LUMO) of the F2-ppy, ppy ligand, and piq-F were compared. The Hartree-Fock (HF) with the 3-21G(d) basis set and the B3LYP with the 6-31G(d) basis set were used for the geometry optimization and the energy level calculation of the ground state of these ligands, respectively.

The ground electronic states in the ligands were calculated using the Gaussian 98 package. The Hatree-Fork (HF) method with 3-21G

(d) basis set and B3LYP method with the 6-31G (d) basis set were used for the geometry optimization and the energy level calculation of the ground state of the ligands, respectively [18].

3. RESULTS AND DISCUSSION

The triple-heteroleptic Ir(III) complex mixed with the other Ir(III) complexes were prepared from the reaction of Ir(acac)$_3$ with various ratio of ligands, as shown in Figure 1. The resulting iridium complexes were obtained as a mixture due to several possible combinations of ligands upon complexation with the Ir center. The separation of these mixtures by column chromatography has not been successful till now since the polarity of the complexes in the mixtures are very similar. Thus, the iridium complexes isolated as a mixture were investigated as obtained. The mixture consisted of the triple-heteroleptic complex (Ir(F$_2$-ppy)(ppy)(piq-F)), the double-heteroleptic complexes (Ir(ppy)$_2$(F$_2$-ppy), Ir(F$_2$-ppy)$_2$(ppy), Ir(ppy)$_2$(piq-F), Ir(piq-F)$_2$(ppy), Ir(F$_2$-ppy)$_2$(piq-F) and Ir(piq-F)$_2$(F$_2$-ppy)) and the less likely homoleptic complexes (Ir(ppy)$_3$, Ir(F$_2$-ppy)$_3$ and Ir(piq-F)$_3$). The presence of each complex was confirmed by FAB/MS of the product mixture. In order to obtain the white light emitting materials, several mole ratio

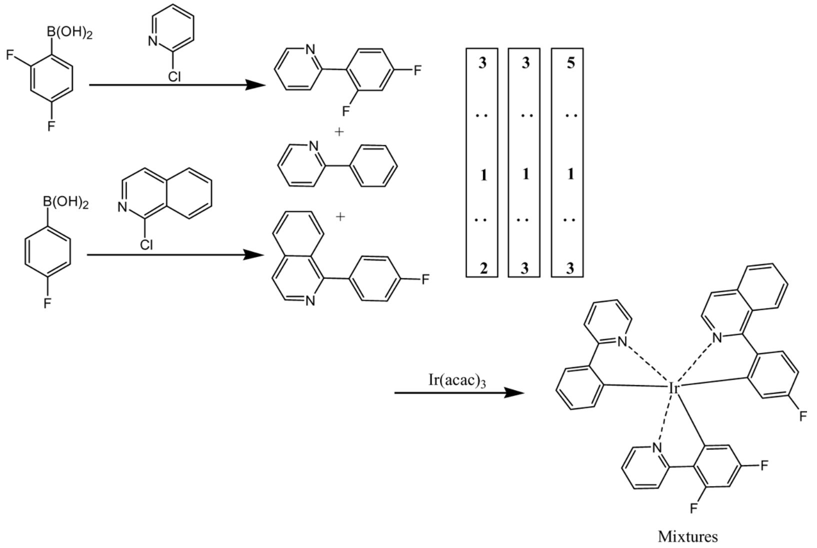

FIGURE 1 Synthesis of the ligands and tris heteroleptic iridium complexes mixtures.

combinations of ligands were attempted in the iridium complex synthesis. The mole ratios of ligands employed were 3:1:2, 3:1:3 and 5:1:3 for F_2-ppy: ppy: piq-F, respectively. The ligand ppy was introduced in a smaller amount compared to F_2-ppy and piq-F since the white-light usually requires the bluish-green and red light combination rather than green emission.

We thought that the heteroleptic iridium complex can absorb the energy through all of the ligands involved. We also expect that emission can occur at two or more wavelengths, resulting in white emission. UV-vis absorption spectra of the mixture were investigated in 10^{-5} M CH_2Cl_2 at room temperature. Among these combinations of ligand ratios, mole ratio of 5:1:3 or F_2-ppy: ppy: piq-F in the iridium complex synthesis showed the whitest emission. Thus, the discussion on UV-vis absorption spectra of the mixture is stated mainly about 5:1:3 mixture with the Ir center. Figure 2 shows the absorption spectrum of the triple-heteroleptic mixture and this spectrum is compared with those of the double-heteroleptic mixture and $Ir(ppy)_3$. The UV-vis spectra of $Ir(ppy)_2(F_2\text{-ppy})$ and $Ir(ppy)_2(\text{piq-F})$ are blue-shifted and red-shifted, respectively, compared with that of $Ir(ppy)_3$. Blue-shifted UV-vis spectrum of $Ir(ppy)_2(F_2\text{-ppy})$ can be explained by the interaction of the molecular orbitals between F_2-ppy and ppy portions, and red-shifted UV-vis spectrum of $Ir(ppy)_2(\text{piq-F})$ is explained by the previous result that MLCT absorption occurs mainly at the piq-F ligand. This study reveals that MLCT absorption of the triple-heteroleptic complex mixture occurs at ppy as well as at piq-F ligands as

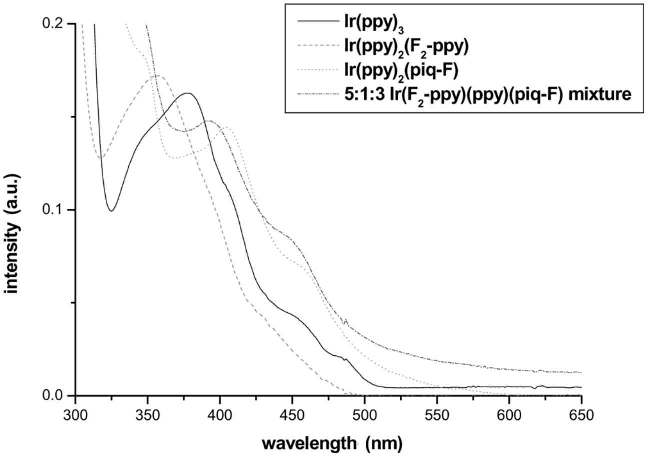

FIGURE 2 Comparison of the HOMO and LUMO energy levels of ligands.

shown in Fig. 2. To further support the argument, the theoretical calculations are performed on ligands. Energy levels of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of F_2-ppy, ppy, and piq-F ligands are calculated by the ab initio method as shown in Figure 3. Because F_2-ppy, ppy and piq-F ligands have a similar HOMO levels at -6.251 eV, -6.119 eV and -5.942 eV, respectively, absorption can occur at the ppy and piq-F ligands.

Emission can be possible from F_2-ppy and piq-F portion in the complex mixture since they have lower LUMOs than ppy. Emission from ppy portion is also possible due to the short lifetime of the ppy excited state. The photoluminescence spectra of heteroleptic Ir(III) complexes are shown in Figure 4, reflecting our assumption. In Fig. 4(a), the emission peaks of 3:1:2 mixture are observed at 494 and 593 nm. For comparison, PL spectrum of $Ir(ppy)_2(F_2\text{-ppy})$ exhibited the broad band around 495 nm, being shifted 18 nm to a blue region compared to the peak by $Ir(ppy)_3$ at 513 nm.

Figure 4(b) shows that 3:1:3 mixture and $Ir(ppy)_2$(piq-F) have the similar PL spectra. The PL spectrum of 3:1:3 mixture shows the emission bands at 593 and 494 nm while PL spectrum of $Ir(ppy)_2$(piq-F) shows the emission bands at 600 and 514 nm. In $Ir(ppy)_2$(piq-F), the

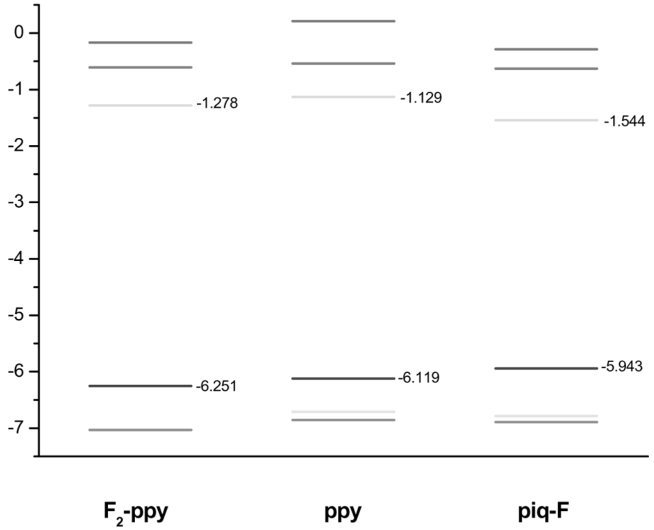

FIGURE 3 UV-vis absorption spectra of the homo and heteroleptic iridium complexes in 10^{-5} M CH_2Cl_2 at room temperature for $Ir(ppy)_3$, $Ir(ppy)_2$ (F_2-ppy) and $Ir(ppy)_2$(piq-F).

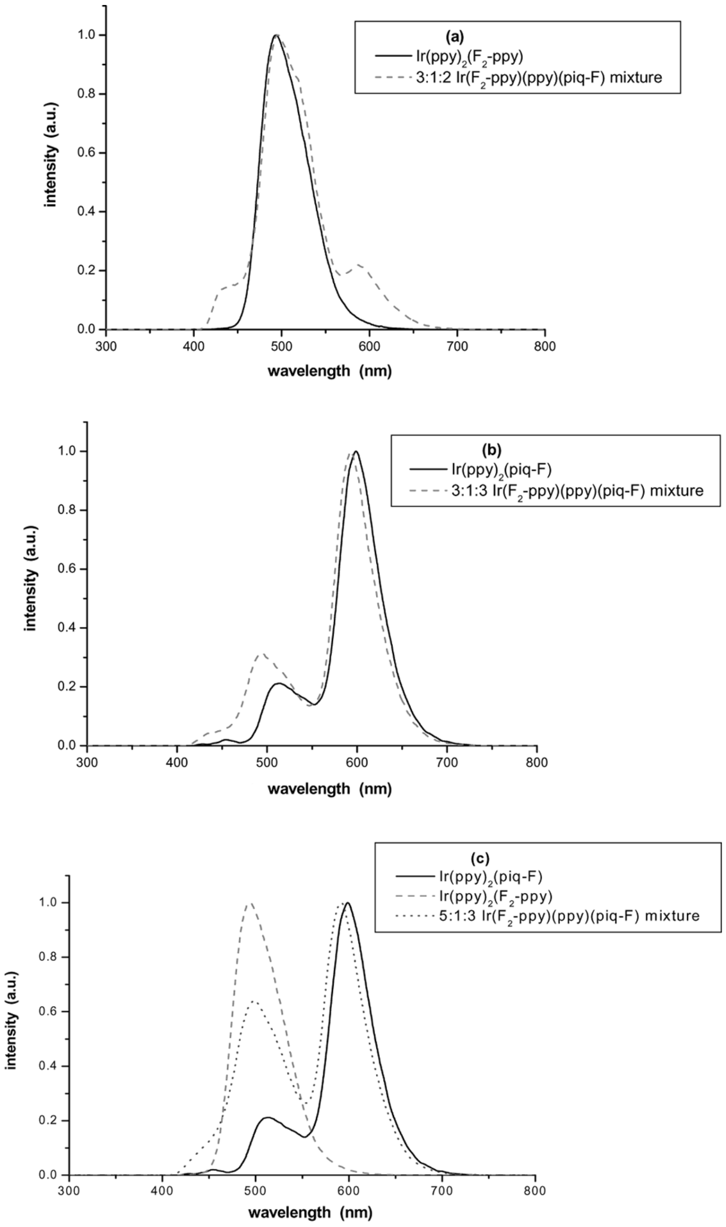

FIGURE 4 Phosphorescence spectra of tris heteroleptic iridium complexes: (a) Ir(ppy)$_2$(F$_2$-ppy) and Ir(F$_2$-ppy)(ppy)(piq-F) mixture, (b) Ir(ppy)$_2$(piq-F) and Ir(F$_2$-ppy)(ppy)(piq-F) mixture, (c) Ir(ppy)$_2$(F$_2$-ppy), Ir(ppy)$_2$(piq-F) and Ir(F$_2$-ppy)(ppy)(piq-F) mixture.

excited electrons in ppy portion can either transferred to the LUMO of piq-F ligand or relaxed to the LUMO of ppy ligand, leading to orange emission from piq-F portion or green emission from ppy portion, respectively. Both of the complexes exhibited the highest peak at red-emtting wavelength with the shoulder at green or bluish green region. The PL spectrum of 3:1:3 mixture around 593 nm shows blue shift compared to the emission of Ir(ppy)$_2$(piq-F) due to the presence of F$_2$-ppy ligand in the Ir complex mixture. The shoulder around 510 nm which was observed in the PL spectrum of Ir(ppy)$_2$(F$_2$-ppy) is also found in that of 3:1:3 mixture. Thus, in the 3:1:3 mixture, Ir(ppy)$_2$(piq-F) and/or Ir(piq-F)$_2$(ppy) are supposed to be produced mainly.

The PL spectrum of 5:1:3 mixture is compared with that of Ir(ppy)$_2$(F$_2$-ppy) and that of Ir(ppy)2(piq-F) as shown in Fig. 4(c). The PL spectrum of 5:1:3 mixture shows the combined characteristics of Ir(ppy)$_2$(F$_2$-ppy) and Ir(ppy)$_2$(piq-F) spectra. Thus, it is considered either that Ir(ppy)$_2$(F$_2$-ppy) and Ir(ppy)$_2$(piq-F) are produced or that Ir(F$_2$-ppy)(ppy)(piq-F) is formed. In the latter case, PL spectrum of Ir(F$_2$-ppy)(ppy)(piq-F) can exhibit PL characteristics shown possibly with both the double-heteroleptic mixtures. FAB/MS revealed that the triple-heteroleptic complex is in fact formed. The emission of 5:1:3 mixture shows the whitest emission with the peak combination at 494 and 593 nm.

3. CONCLUSION

In summary, we reported detailed synthesis and photophysical properties of the heteroleptic iridium(III) complexes containing three different ligands in order to produce a white phosphorescent emitter for OLED. Ir(F$_2$-ppy)(ppy)(piq-F) and other double-heteroleptic mixture were prepared from various concentration combination of ligands. Their UV-vis absorption spectra were investigated to find the absorption mechanism. All the ligand portions in the Ir complexes were found to be involved in light absorption. Theoretical calculations on ligands were also performed to support the absorption mechanism. The heteroleptic iridium complex mixture displayed a variety of emission color, depending upon the combination ratio of ligands in the iridium complex synthesis. The PL spectra of 5:1:3 mixture showed two emission peaks at 494 and 593 nm with similar intensities. Bluish emission observed at 494 nm was assigned to be overlapping luminescence from F$_2$-ppy and ppy portions in the Ir complex mixture. On the other hand, orange-red emission at 593 nm can be explained by a different mechanism. Some excitation energy in the excited states can quickly undergo the intramolecular transfer from ppy and/or F$_2$-ppy portion to piq-F portion having the lowest LUMO levels, showing the orange-red luminescence.

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] (a) Park, N. G. (2002). *Jpn. J. Appl. Phys.*, *41*, 1523;
(b) Park, N. G., Lee, J. E., Park, Y. H., & Kim, Y. S. (2004). *Syth. 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] Chao, C. I. & Chen, S. A. (1998). *Appl. Phys. Lett.*, *73*, 426.

[7] Granstrom, M. & Inganas, O. (1996). *Appl. Phys. Lett.*, *68*, 147.

[8] Tasch, S., List, E. J. W., Ekström, O., Graupner, W., Leising, G., Schlichting, P., Rohr, U., Geerts, Y., Scherf, U., & Müllen, K. (1997). *Appl. Phys. Lett.*, *71*, 2883.

[9] Berggren, M., Gustafsson, G., Inganäs, O., Andersson, M. R., Hfertberg, T., & Wennerstrom, O. J. (1994). *Appl. Phys.*, *76*, 7530.

[10] Jordan, R. H., Dodabalapur, A., Strukel, M. J., & Miller, T. M. (1996). *Appl. Phys. Lett.*, *68*, 1192.

[11] Kido, J., Kimura, M., & Nagai, K. (1995). *Science*, *267*, 1332.

[12] Strukelj, M., Jordan, R. H., & Dodabalapur, A. (1996). *J. Am. Chem. Soc.*, *118*, 1213.

[13] Liu, Y., Guo, J., Zhang, H., & Wang, Y. (2002). *Angew. Chem. Int. Ed.*, *41*, 1.

[14] Tsuboyama, A., Iwawaki, H., Furugori, M., Mukaide, T., Kamatani, J., Igawa, S., Moriyama, T., Miura, S., Takiguchi, T., Okada, S., Hoshino, M., & Ueno, K. (2003). *J. Am. Chem. Soc.*, *125*, 12971.

[15] 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.

[16] Henson, N. J., Hay, P. J., & Redondo, A. (2000). *J. Phys. Chem. A.*, *104*, 2423.

[17] Nomoyama, M.J. (1975). *Organomet. Chem.*, *86*, 263.

[18] Frisch, M. J. *et al.* (1988). *Gaussian 98, Revision A.9*, Gaussian, Inc.: Pittsburgh, PA.