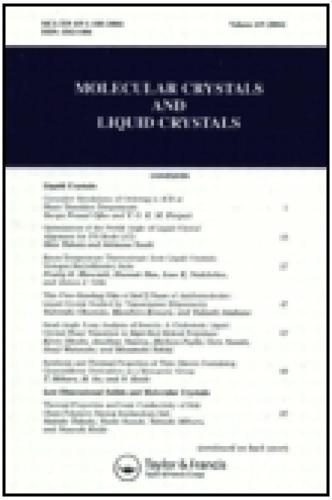


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

The Role of Ancillary Ligands in Iridium(III) Complexes for Blue OLEDs

Ho Wan Ham [a], In June Kim [a] & Young Sik Kim [a] [b]

[a] Department of Information Display, Hongik University, Seoul, Korea

[b] Department of Science, Hongik University, Seoul, Korea

To cite this article: Ho Wan Ham, In June Kim & Young Sik Kim (2009) The Role of Ancillary Ligands in Iridium(III) Complexes for Blue OLEDs, Molecular Crystals and Liquid Crystals, 505:1, 130/[368]-138/[376], DOI: 10.1080/15421400902945576

To link to this article: http://dx.doi.org/10.1080/15421400902945576

Mol. Cryst. Liq. Cryst., Vol. 505, pp. 130/[368]–138/[376], 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902945576

The Role of Ancillary Ligands in Iridium(III) Complexes for Blue OLEDs

Ho Wan Ham[1], **In June Kim**[1], **and Young Sik Kim**[1,2]
[1]Department of Information Display, Hongik University, Seoul, Korea
[2]Department of Science, Hongik University, Seoul, Korea

In this study, new deep blue emitting mixed ligand iridium(III) complexes comprising one cyclometalating, two phosphines trans to each other and two cis-ancillary ligands, such as $Ir\{(CF_3)_2Meppy\}(PPh_3)_2(H)(Cl)$, $[Ir\{(CF_3)_2Meppy\}(PPh_3)_2(H)(NCMe)]^+$ *and* $Ir\{(CF_3)_2Meppy\}(PPh_3)_2(H)(CN)$, $[(CF_3)_2Meppy = 2\text{-}(3',5'\text{-bis-trifluoromethylphenyl})\text{-}4\text{-methylpyridine}]$ *were synthesized and studied to tune the phosphorescence wavelength to the deep blue region and to enhance the luminescence efficiencies. We investigate the strong field capabilities of ancillary ligands to gain insight into the factors responsible for the emission color change and the different luminescence efficiencies. This work represents a strategy for the design of deep blue phosphorescent iridium complexes. The electron-withdrawing trifluoromethyl group substituted on the phenyl ring, the electron- donating methyl group on the pyridyl ring and the cyano strong field ancillary ligand increase HOMO-LUMO gap to achieve the hypsochromic shift in emission color. As a result, the maximum emission spectrum of* $Ir\{(CF_3)_2Meppy\}(PPh_3)_2(H)(Cl)$, $[Ir\{(CF_3)_2Meppy\}(PPh_3)_2(H)(NCMe)]^+$ *and* $Ir\{(CF_3)_2Meppy\}(PPh_3)_2(H)(CN)$ *were in the ranges of 436, 434 and 434 nm, respectively.*

Keywords: blue; iridium complex; mixed ligand; OLED; phosphorescence

1. INTRODUCTION

Since Tang and coworkers first reported organic light-emitting devices (OLED) with a multi-layer structure [1,2] materials and device fabrication have been extensively studied [3–5]. Luminescent materials are generally classified into two groups, either fluorescent or phosphorescent. OLEDs based on phosphorescent materials are able to improve

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2007-313-D00290).

Address correspondence to Young Sik Kim, Department of Information Display, Hongik University, Seoul, 121-791, Korea. E-mail: youngkim@wow.hongik.ac.kr

electroluminescence performance significantly because both singlet and triplet excitons can be used to harvest light emission. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach almost 100% [6]. 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 [7,8]. The spin-forbidden nature of radiative relaxation from the triplet excited state then becomes allowed, resulting in high phosphorescent efficiencies. Thus, heavy metal complexes can serve as efficient phosphors for OLEDs. Unfortunately, most of phosphorescent emitters have a long radiative lifetime, which leads to the 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 [9,10].

Until now, greater success has been achieved in the development of green and red emitters in fluorescent and phosphorescent displays. However purely blue-emitting complex dopants are rarely found. Hence, the current effort of researchers has been focused on the syntheses of blue-emitting iridium complexes. Some phosphorescent blue emitter materials have been synthesized and reported; 2-phenylpyridine (ppy) with some electro-withdrawing groups added to the phenyl ring (fluoro, cyano group and others) or electro-donating groups to the pyridyl ring (methyl group and others) had especially good blue emission characteristics [11,12].

In this study, new deep blue emitting mixed ligand iridium(III) complexes comprising one cyclometalating, two phosphines trans to each other and two *cis*-ancillary ligands, such as $Ir\{(CF_3)_2Meppy\}(PPh_3)_2(H)(Cl)$, $[Ir\{(CF_3)_2Meppy\}(PPh_3)_2(H)(NCMe)]^+$, and $Ir\{(CF_3)_2Meppy\}(PPh_3)_2(H)(CN)$, [$(CF_3)_2Meppy$ = 2-(3′,5′-bis-trifluoromethylphenyl)-4-methylpyridine] were synthesized and studied to tune the phosphorescence wavelength to deep blue region and to enhance the luminescence efficiencies. To analyze the color tuning by the effects of trans ligands to $(CF_3)_2Meppy$ ligand on the luminescent property, we have measured UV-absorption and photoluminescence (PL) spectra of these iridium complexes.

2. EXPERIMENTAL DETAILS

2.1. Synthesis

All reagents were purchased from Aldrich 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).

2.1.1. Synthesis of Ligand: $(CF_3)_2$Meppy

$(CF_3)_2$Meppy was obtained from the reaction of 2-chloro-4-methylpyridine with the corresponding 3,5-bis(trifluoromethyl)phenylboronic acid by Suzuki coupling. 2-Chloro-4-methylpyridine (0.438 ml, 5 mmol), 3,5-bis(trifluoromethyl)phenylboronic acid (1.29 g, 5 mmol) and tetrakis(triphenylphospine)palladium(0) (0.196 g, 0.17 mmol) were dissolved in 20 ml of toluene, 10 ml of ethanol and 20 ml of 2N sodium carbonate aqueous solution. The mixture was refluxed at 110°C under a nitrogen atmosphere for 8 hr. The mixture was cooled to room temperature and extracted with 20 ml of ethyl acetate. The organic fraction was dried over anhydrous $MgSO_4$, filtered off and dried under vacuum. The residue was purified by silica gel chromatography by using ethyl acetate/hexane (1:3). The product was collected and dried under vacuum.

$(CF_3)_2$Meppy – Yield 60%, bright orange oil, MW: 302.25.

2.1.2. Synthesis of Complex: Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(Cl)

Chloro(1,5-cyclooctadiene)iridium(I) dimer $[Ir(COD)Cl]_2$ (0.1 g, 0.15 mmol), triphenylphosphine (PPh_3) (0.16 g, 0.6 mmol) and $(CF_3)_2$Meppy (0.092 g, 0.3 mmol) were dissolved in 10 ml of 2-ethoxyethanol in a 50 ml flask. The mixture was refluxed at 110°C under a nitrogen atmosphere for 6 hr and then cooled to room temperature. The product portion was collected and washed with 20 ml of methanol, recrystallized in chloroform/n-hexane, and dried under vacuum.

Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(Cl) – Yield 78%, yellowish crystal.

2.1.3. Synthesis of Complex: [Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(NCMe)](OTf)

Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(Cl) (0.1 g, 0.1 mmol), silver trifluoromethane sulfonate (AgOTf) (0.026 g, 0.1 mmol) and anhydrous acetonitrile (MeCN) (1 ml, 20 mmol) were dissolved in 10 ml of chloroform in a 50 ml flask. The mixture was stirred under a nitrogen atmosphere for 2 hr at normal temperature. After 2 hr stirring, the white powder of AgCl was removed by filtration and 20 mmol of MeCN was added into the product solution and stirred under a nitrogen atmosphere for an additional 2 hr at normal temperature. 20 ml of n-hexane was added to yield yellowish crystals and residue was collected, washed with methanol, and dried under vacuum.

[Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(NCMe)](OTf) – Yield 65%, yellowish crystal.

2.1.4. Synthesis of Complex: Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(CN)

[Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(CN)](OTf) (0.1 g, 0.08 mmol) and tetrabutylammonium cyanide (0.027 g, 0.1 mmol) were dissolved in 10 ml of methylene chloride in a 50 ml flask. The mixture was stirred under a nitrogen atmosphere for 6 hr at normal temperature. After 6 hr stirring, 20 ml of n-hexane was added to yield a yellowish crystal and residue was collected, washed with methanol, and dried under vacuum.

Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(CN) – Yield 73%, yellowish crystal.

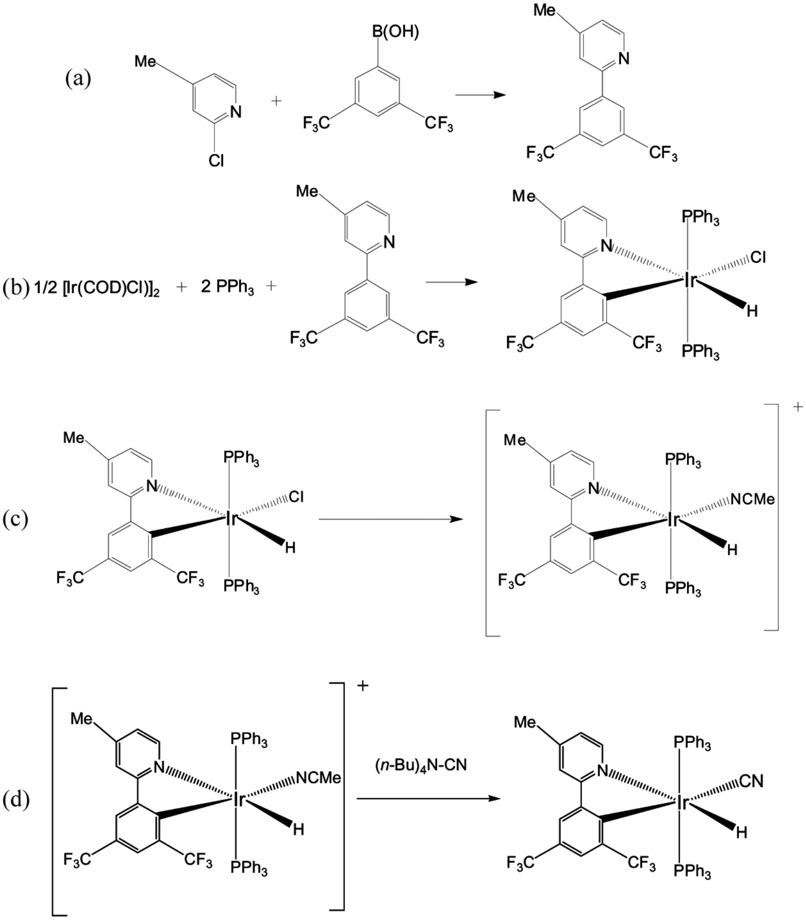
2.2. Optical Measurements

The UV-Vis absorption spectra were measured on Hewlett Packard 8425A spectrometer. The PL spectra were obtained on Perkin Elmer LS 55 spectrometer. UV-Vis and PL spectra of complexes were measured in CH_2Cl_2.

3. RESULTS AND DISCUSSION

The colors of phosphorescent complexes used in OLEDs are tuned by the variation of both cyclometalating and ancillary ligands. Several small molecular and polymeric blue emitting phosphorescent complexes have been reported, but the realization of highly efficient deep blue emission is still remains a challenge. For the common 2-phenylpyridine (ppy) cyclometalating ligand, the highest occupied molecular orbital (HOMO) is localized on phenyl π and iridium 5d orbitals, while the lowest unoccupied molecular orbital (LUMO) is localized on the π^* orbitals of the pyridyl ring. To achieve deep blue emission: (1) substitution of CF_3 groups on the 3′,5′-position of phenyl ring of the ppy ligand as an electron withdrawing group to stabilize the HOMO and increase HOMO-LUMO gap, (2) addition of electron-donating methyl groups on the 4-position of the pyridyl ring of the ppy ligand to destabilize the LUMO and increase HOMO-LUMO gap and (3) changing ancillary ligands coordinated to the iridium atom into phosphine and cyano groups. Both phosphine and cyano groups are known as very strong field ligands, and their inclusion in the coordination sphere can increase the HOMO-LUMO gap to achieve the hypsochromic shift in the emission color.

The ligands, $(CF_3)_2$Meppy, were prepared by Suzuki coupling, as illustrated in Scheme 1(a). The final iridium complexes were obtained via several steps. In the first step, $[Ir(COD)Cl]_2$, PPh_3 and $(CF_3)_2$



SCHEME 1 (a) Synthesis of $(CF_3)_2$Meppy ligand; (b) Synthesis of Iridium complex of Ir$\{(CF_3)_2$Meppy$\}(PPh_3)_2$(H)(Cl); (c) Synthesis of Iridium complex of $[$Ir$\{(CF_3)_2$Meppy$\}(PPh_3)_2$(H)(NCMe)$]^+$; (d) Synthesis of Iridium complex of Ir$\{(CF_3)_2$Meppy$\}(PPh_3)_2$(H)(CN).

Meppy ligand are synthesized, as illustrated in Scheme 1(b). At the second step, the chlorine legends of Ir$\{(CF_3)_2$Meppy$\}(PPh_3)_2$(H)(Cl) are replaced with MeCN legends by a precipitation reaction of Ag and Cl ions, as illustrated in Scheme 1(c). In the third step, the MeCN ligand is substituted with a CN ligand, as illustrated in Scheme 1(d). The overall reaction yields were about $60 \sim 78\%$, respectively.

The solution UV–Vis absorption complexes were measured as shown in Figure 1. The interesting characteristic of the MLCT absorption

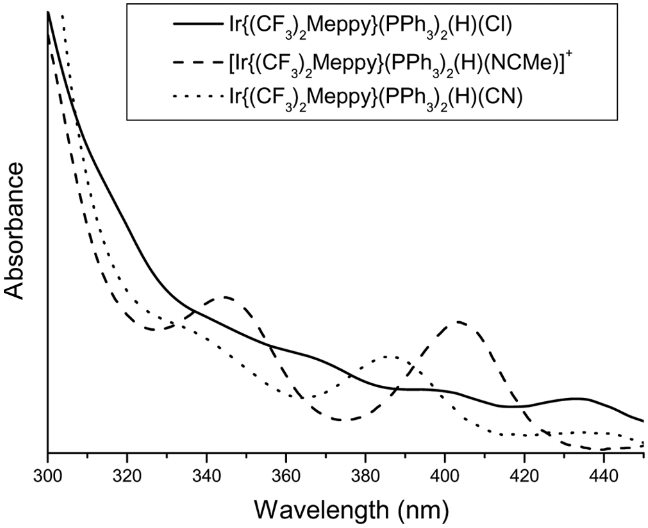


FIGURE 1 UV-Vis absorption spectra of Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(Cl), [Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(MeCN)]$^+$ and Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(CN) in CH_2Cl_2 solution of room temperature.

spectra for [Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(NCMe)]$^+$ is that it resembles that of Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(CN). Both ^{1}MLCT and ^{3}MLCT peaks are observed for these complexes. MLCT absorption peaks of [Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(NCMe)]$^+$ are observed at 345 and 403 nm, while MLCT absorption peaks of Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(CN) are observed at 337 and 385 nm. On the other hand, absorption peaks of Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(Cl) are observed at 365, 405 and 433 nm. This can be explained by the strong field ancillary ligand such as CN^- that lowered the HOMO energy level more than did the weak field ancillary ligand Cl^-. Ancillary ligands alter the MLCT energy mainly by changing the HOMO energy level. The HOMO energy level may then be lowered by strong-field ancillary ligands, which causes a large d-orbital energy splitting. It is also likely that strong-field ancillary ligands lengthen the bond lengths of Ir–C (ppy) trans to the ancillary ligand to lower the energy levels of the dπ-orbitals of the metal as strong-field ligands are known to show a high trans effect. The medium field ancillary ligand MeCN is located between these. CF_3 groups, substituted on the 3′,5′-position of phenyl ring as electron withdrawing groups, tune the MLCT absorption peak to bluish. In addition, the methyl group substituted on the 4-position of pyridyl ring as an electron donating group strongly affected LUMO and raised the LUMO energy and increased the energy gap.

The PL spectra of iridium complexes are shown in Figure 2, the maximum emission spectra of Ir{(CF$_3$)$_2$Meppy}(PPh$_3$)$_2$(H)(Cl), [Ir{(CF$_3$)$_2$Meppy}(PPh$_3$)$_2$(H)(NCMe)]$^+$ and Ir{(CF$_3$)$_2$Meppy}(PPh$_3$)$_2$(H)(CN) were 436, 434, and 434 nm, respectively. Knowing that d orbitals of iridium are involved in the HOMO of C$^\wedge$N complexes such as Ir(C$^\wedge$N)$_3$ and Ir(C$^\wedge$N)$_2$LL′, one could expect the HOMO energy level to be lowered by strong field ligands more than by weak field ligands. Table 1 summarizes the photoluminescence data for iridium complexes. A significantly longer wavelength emission band is measured for the complex that contains a chlorine ligand trans to the carbon of the C$^\wedge$N ligand, whereas the emission band is measured at much shorter wavelengths for all other complexes with a strong field ligand such as CN$^-$. The trans and axial ligand PPh$_3$ is not involved in the HOMO of iridium complexes. The effects of CF$_3$ groups in phenyl ring on luminescence wavelength are clearly shown in comparison with the study of Ir(F$_2$Meppy)(PPh$_3$)$_2$(H)(CN) [13]. The complex with (CF$_3$)$_2$ Meppy ligand has an about 5 nm blue-shifted emission band compared to the complex with F$_2$Meppy ligand.

As a result, the PL spectrum of Ir{(CF$_3$)$_2$Meppy}(PPh$_3$)$_2$(H)(CN) shows a significant blue shifted phosphorescence emission due to the

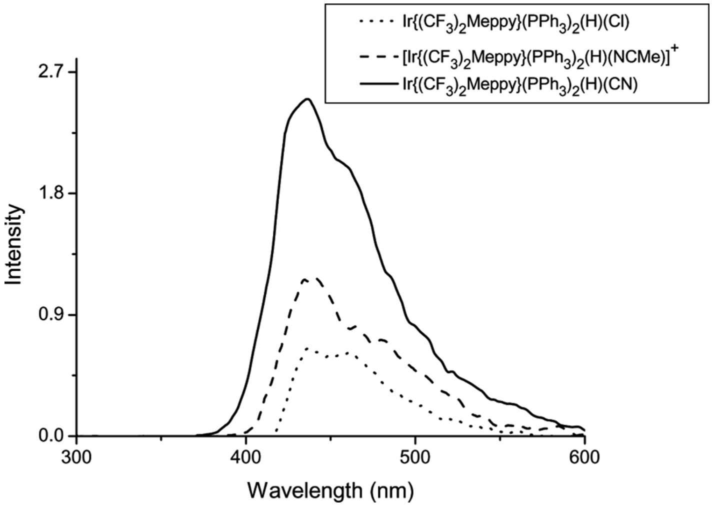


FIGURE 2 PL spectrum of Ir{(CF$_3$)$_2$Meppy}(PPh$_3$)$_2$(H)(Cl), [Ir{(CF$_3$)$_2$Meppy}(PPh$_3$)$_2$(H)(NCMe)]$^+$ and Ir{(CF$_3$)$_2$Meppy}(PPh$_3$)$_2$(H)(CN) in CH$_2$Cl$_2$ solution of room temperature.

TABLE 1 UV-Vis Absorption and Photoluminescence Data of Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(Cl), [Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(NCMe)]$^+$ and Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(CN)

Complex	$\lambda_{abs.}$ (nm)	$\lambda_{em.}$ (nm)
Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(Cl)	365, 435	436, 462
[Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(NCMe)]$^+$	345, 403	434, 463
Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(CN)	337, 385	434, 460

substitution of CF_3 groups in the phenyl ring that pulls the HOMO level of iridium complexes, and the added methyl group in the pyridyl ring that pulls up the LUMO level of iridium complex, and the strong field ancillary, it helps enlarge HOMO-LUMO energy gap to achieve the hypsochromic shift in emission color.

4. CONCLUSIONS

We synthesized and measured optical properties of Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(Cl), [Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(NCMe)]$^+$ and Ir{$(CF_3)_2$-Meppy}$(PPh_3)_2$(H)(CN) in order to find a new blue emitting material for the application in OLEDs by tuning the ancillary ligand and modified emit ligand. The PL spectra of Ir{$(CF_3)_2$Meppy}$(PPh_3)_2$(H)(CN) shows a significant blue shifted phosphorescence due to replacing chlorine with CN, MeCN ligand. We suggest that the Ir{$(CF_3)_2$-Meppy}$(PPh_3)_2$(H)(CN) might serve as a good radiation characteristic blue dopant for new phosphorescent OLED materials.

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., Kwak, M. Y., Kim, B. O., Kwon, O. K., Kim, Y. K., You, B. R., Kim, T. W., & Kim, Y. S. (2002). *Jpn. J. Appl. Phys.*, *41*, 1523.

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

[6] 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.

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

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

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

[10] 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.

[11] Park, N. G., Choi, G. C., Lee, Y. H., & Kim, Y. S. (2006). *Curr. Appl. Phys.*, *6*, 620.

[12] Takizawa, S., Nishida, J., Tsuzuki, T., Tokito, S., & Yamashita, Y. (2007). *Inorg. Chem.*, *46*, 4308.

[13] Eum, M. S., Chin, C. S., Kim, S. Y., Kim, C., Kang, S. K., Hur, N. H., Seo, J. H., Kim, G. Y., & Kim, Y. K. (2008). *Inorg. Chem.*, *47*, 6289.