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Synthesis and Luminescence Studies of Hydrocarbon-Branched Tris-Cyclometallated Iridium (III) Complexes

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We synthesized the tris-cyclometallated iridium complexes containing the substituted styryl groups and their saturated analogs. As the styryl iridium complexes, $Ir(F\text{-}ppy\text{-}4\text{-}CH{=}CHC_6H_4R)_3$ *(where* $R = Me$, NMe_2, OMe*) were prepared via direct functionalization of the methyl groups in the ppy (2-phenylpyridine) ligand at the iridium complexes. The corresponding saturated analogs,* $Ir(F\text{-}ppy\text{-}4\text{-}CH_2CH_2C_6H_4R)_3$ *(where* $R = Me$, NMe_2*), were synthesized during the two step reactions of the* $IrCl_3 \cdot xH_2O$ *with* $F\text{-}ppy\text{-}4\text{-}CH{=}CHC_6H_4R$ *via* in situ *hydrogenation. Their photophysical properties were investigated both in solution and in film. The longer π-conjugation in the cyclometallating ligands leads to the bathochromic shift in photoluminescence of their iridium complexes. Among R groups, the* NMe_2 *end group had the strongest push-pull effect with the F group at the other end, and led to the effective control of the ILCT transition.*

Keywords Hydrocarbon-branched; iridium complex; OLED; phosphorescence

1. Introduction

Phosphorescent transition-metal complexes are being widely utilized in the light-emitting diodes (OLEDs) [1–3]. Among the transition metal complexes, the iridium complexes were known to have high efficiency, utilizing large population of the emitting triplet state by strong spin-orbit coupling induced by the metal center [4–9]. The cyclometallating ligands of the iridium complexes were reported to determine the major color of phosphorescence since the energy gaps between the HOMO and LUMO levels of the complexes can be controlled by variation of these ligands [10,11].

The oligomeric hydrocarbon compounds have been studied as macromolecular phosphors for such a purpose [12]. There were also several reports regarding the synthesis and photophysical properties of the iridium complexes containing hydrocarbon-branched cyclometallating ligands [13,14]. Furthermore, the iridium complexes with the hydrocarbon-branched ligands can make the solution-processed fabrication of OLEDs possible. Direct functionalization of the ligands in the iridium

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complexes was previously reported [13,14]. In these literatures, unsaturated tris-cyclometallated iridium(III) styryl complexes, Ir(ppy-4-CH=CHC$_6$H$_4$R)$_3$ and their saturated analogs, Ir(ppy-4-CH$_2$CH$_2$C$_6$H$_4$R)$_3$, were investigated and reported to exhibit green phosphorescence. The 'push-pull' effect between R and the pyridyl groups in the C^N ligand was also discussed with the (C^N)$_2$Ir(acac) systems where C^N represents the *para*-substituted styryl-pyridyl ligands [13].

Herein, we designed the new hydrocarbon-branched iridium complexes containing the 4′-F-ppy ligand backbone. We expected that the 4′-F-ppy backbone can induce emission of their complexes at shorter wavelengths than the unsubstituted ppy ligand. The complexes of the saturated and unsaturated hydrocarbon-branches were prepared via different synthetic routes. Their photophysical properties were compared, emphasizing the emission wavelength control and the long range push-pull effect between *p*-R groups and 4′-F-ppy moiety in the complexes. As R groups, −Me, −OMe and −NMe$_2$ groups were introduced in the styryl portion of the complexes. Photoluminescence (PL) of the complexes was investigated in both organic solutions and polymeric matrixes.

2. Experimental Section

All reactions were carried out under the dry argon atmosphere.

2.1. *Synthesis of Ligands*

Synthesis of 4-Me-4′-F-ppy. 4-methyl-4-fluorophenylpyridine ligand was obtained from the reaction of 2-chloro-4-methylpyridine with 4-fluorophenylboronic acid by the modified Suzuki coupling [15]. (yield: 60%)

Synthesis of F-ppy-4-CH=CHC$_6$H$_4$-R. 2-(4′-Fluorophenyl)-4-(4-methylstyryl) pyridine and 2-(4′-fluorophenyl)-4-*p*-R-pyridine ligand were obtained from the 4-Me-4′-F-ppy with the corresponding aldehydes, *p*-tolylaldehyde and 4-(dimethylamino)benzaldehyde, respectively [13,14]. (yield: 83%)

2.2. *Synthesis of Complexes*

Synthesis of Ir(F-ppy-4-CH=CHC$_6$H$_4$-R)$_3$. Ir(4-Me-4′-F-ppy)$_3$ was prepared according to the literature preparation [16]. And then, these crudes were reacted with the corresponding aldehydes, *p*-tolualdehyde, 4-(dimethylamino)benzaldehyde and 4-methoxybenzaldehyde, respectively [13,14]. (yield: 68%)

Ir(F-ppy-4-CH=CHC$_6$H$_4$Me)$_3$ FAB-MS: calculated 1057.2, found 1057.
Ir(F-ppy-4-CH=CHC$_6$H$_4$NMe$_2$)$_3$ FAB-MS: calculated 1144.4, found 1144.
Ir(F-ppy-4-CH=CHC$_6$H$_4$OMe)$_3$ FAB-MS: calculated 1105.2, found 1105.

Synthesis of Ir(F-ppy-4-CH$_2$CH$_2$C$_6$H$_4$-R)$_3$. Ir(F-ppy-4-CH$_2$CH$_2$C$_6$H$_4$-R)$_3$ were obtained from the crude dimer (F-ppy-4-CH=CHC$_6$H$_4$-R)$_2$Ir(μ-Cl)$_2$Ir(F-ppy-4-CH=CHC$_6$H$_4$-R)$_2$ with the corresponding styryl ligands, F-ppy-4-CH=CHC$_6$H$_4$-R (2.5 mmol) [17]. (yield: 44%)

Ir(F-ppy-4-CH$_2$CH$_2$C$_6$H$_4$CH$_3$)$_3$ FAB-MS: calculated 1063.3, found 1063.
Ir(F-ppy-4-CH$_2$CH$_2$C$_6$H$_4$NMe$_2$)$_3$ FAB-MS: calculated 1150.4, found 1150.

2.2. *Optical Measurements*

UV-Vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. PL spectra were measured on a Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of the iridium complexes were measured in a 10^{-5} M dilute CH_2Cl_2 solution and in a PMMA film. The PMMA film was fabricated by the spin-coating onto the glass substrate with 10 wt% Ir complexes of PMMA in 1,2-dichloroethane solution followed by solvent evaporation.

3. Results and Discussion

The intraligand charge transfer (ILCT) properties in the unsaturated styryl iridium complexes can be enhanced with the electron-donating end group (−Me, $-NMe_2$, −OMe) of the styryl moiety via the π linker. The effective charge transfer from the styryl end group to the pyridine acceptor might lead to the bathochromic shift, compared with the saturated complex analogs. Furthermore, addition of the electron-withdrawing group such as F to the phenyl ring in the complex might effectively induce the electron density from the pyridine ring to the phenyl ring. Thus, the new tris-cyclometallated Iridium complexes containing the modified F-ppy-4-styryl derivatives were designed and synthesized. To investigate the π-conjugation effects of the hydrocarbon-branches at the ligand, the saturated hydrocarbon-branched iridium complexes were also prepared for comparison. The discontinuity of the π-conjugation of the ligand in the complex make ILCT prohibited, inducing the hypsochromic shift of the emission by the complex.

The unsaturated and saturated hydrocarbon-branched iridium complexes were obtained according to the literature [13]. The ligands (L), F-ppy-4-CH=CHC_6H_4-R, were synthesized via two steps. The precursor, the 4-Me-4′-F-ppy, was prepared according to the modified Suzuki coupling method, as illustrated in Figure 1(a). The styryl susbstituted ppy ligands, F-ppy-4-CH=CHC_6H_4-R, was obtained from the reaction of the 4-Me-4′-F-ppy with the corresponding aldehyde. The unsaturated complexes were formed from the reaction of $Ir(4\text{-}Me\text{-}4'\text{-}F\text{-}ppy)_3$ with the corresponding aldehyde at the room temperature via direct functionalization of the methyl group in the ligands [13]. The saturated styryl complexes were prepared from the two-step reactions of the iridium precursor with their corresponding free ligands at 200°C via *in situ* ligand hydrogenation [14]. The overall synthetic scheme is shown in of Figure 1.

The UV-Vis absorption spectra of the complexes in CH_2Cl_2 are shown in Figure 2. The ILCT absorption by the longer π-conjugation in the unsaturated styryl complexes are observed between 300 and 350 nm. For comparison, the strong absorption bands between 250 and 300 nm by the saturated complexes are assigned to the spin-allowed $^1\pi$-π^* transition of the styryl ligands in the complexes, which support the relatively high energy absorption due to discontinuity of π-conjugation. The ILCT transition was not observed in saturated complexes due to discontinuity of the π linker, as expected. It is also noted that 'push-pull' effects between NMe_2 end group in the pyridine ring and F end group in the phenyl moiety become conspicuous from the absorption peaks around 400 and 420 nm in $Ir(F\text{-}ppy\text{-}CH{=}CHC_6H_4NMe_2)_3$ and $Ir(F\text{-}ppy\text{-}CH_2CH_2C_6H_4NMe_2)_3$, respectively. The complexes containing the Me and OMe end group did not have absorption peaks around in this region. The weaker absorption bands at the longer wavelengths can

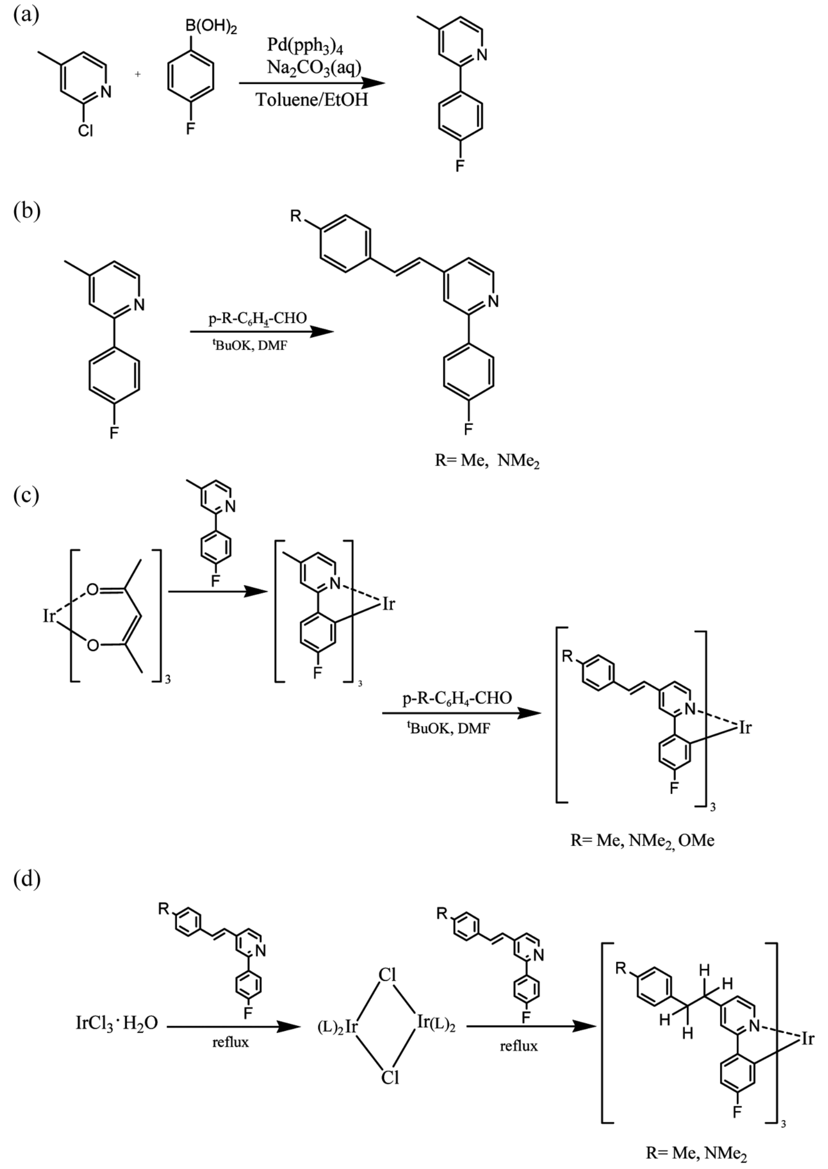

Figure 1. (a) Synthesis of the 4-Me-4′-F-ppy, (b) Synthesis of the F-ppy-4-CH=CHC_6H_4-R, (c) Synthesis of the unsaturated styryl Ir complexes, Ir(F-ppy-4-CH=CHC_6H_4-R$)_3$, (d) Synthesis of the saturated styryl Ir complexes, Ir(F-ppy-4-$CH_2CH_2C_6H_4$-R$)_3$.

be attributed to the spin-forbidden ^{3}MLCT and spin-orbit coupling enhanced $^3\pi$-π^* transition. The formally spin-forbidden ^{3}MLCT gains the intensity by mixing with the higher-lying ^{1}MLCT transition through the strong spin-orbit coupling on the iridium center.

The photoluminescence (PL) spectra of the unsaturated iridium complexes in 10^{-5} M CH_2Cl_2 solution show the emission peaks at 468, 492 and 490 nm for Ir(F-ppy-4-CH=CHC_6H_4-R$)_3$ where R is Me, NMe_2 and OMe, respectively. These

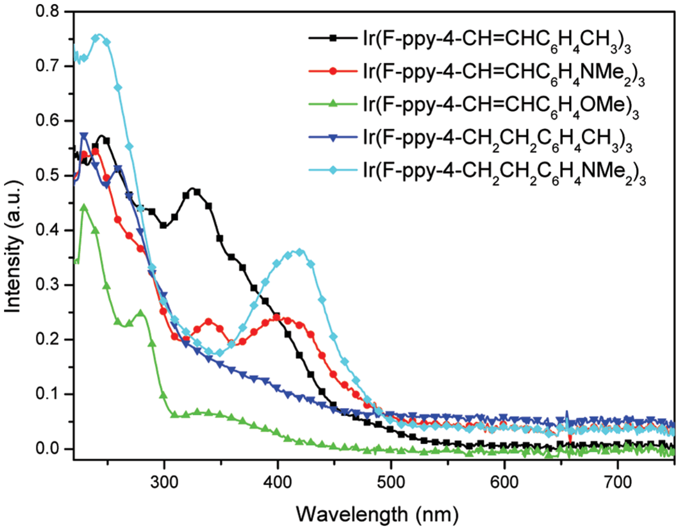

Figure 2. UV-vis absorption spectra of Ir(F-ppy-4-CH=CHC_6H_4-R$)_3$ and Ir(F-ppy-4-$CH_2CH_2C_6H_4$-R$)_3$ in 10^{-5} M CH_2Cl_2 solution.

PL maxima are slightly shifted bathochromically with respect to those of the corresponding free ligands shown in Figure 3 because the electron-withdrawing effect of F-ppy backbone in the ligands increases upon their coordination to the iridium center. On the other hand, the emission spectra of the saturated complexes, Ir(F-ppy-$CH_2CH_2C_6H_4$R$)_3$ where R = Me and NMe_2, exhibit the emission around 453 and 425 nm, respectively, shifted toward the shorter wavelengths due to discontinuity of π linker. Similar spectroscopic phenomena were reported in the emission

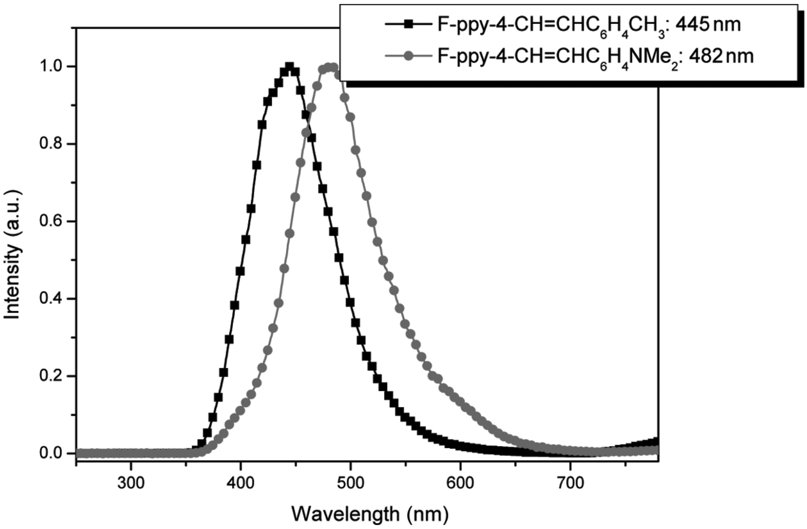

Figure 3. PL spectra of the free stryl ligands, F-ppy-4-CH=CHC_6H_4-R in 10^{-5} M CH_2Cl_2 solution.

spectra of Ir(ppy-4-CH=CHC_6H_4-OMe)$_3$ (526 nm) and Ir(ppy-4-$CH_2CH_2C_6H_4$-OMe)$_3$ (490 nm) [13]. It is also noteworthy that involvement of the electron-withdrawing group, F, to the phenyl ring of the complex in our study changes the electron balance between the pyridine and phenyl ring, resulting in hypsochromic shift in PL, compared with the results of unsubstituted Ir(ppy-4-CH=CHC_6H_4-OMe)$_3$.

Additionally, we fabricated the PMMA (poly(methylmethacrylate)) film of the complexes studied herein, and investigated their PL characteristics. The hydrocarbon-branched iridium complexes can be compatible with polymers and thus may be applied as emitting materials for the polymer light-emitting device (PLED). Moreover, sterically bulky hydrocarbon branches may help to prevent the T-T annihilation of the phosphors. PMMA is chosen as a host because its non-emitting property within the visible range could provide the PL of the iridium complexes only [18]. In Figure 4, the overall PL spectra of the PMMA films for tris-cyclometallated styryl complexes were bathocromically shifted relative to their solution PLs. Previously, Guerchais, *et al.* reported the PL of the tris-cylcometallated iridium styryl complexes containing the ppy backones and compared them with those of their saturated analogs [13]. In his study, the temperature effect on their PLs was also elaborated. He claimed that presence of the extended π-conjugation and/or strong intramolecular donor-acceptor interaction into the ligand of the complex induced a strong red shift upon the temperature variation from 298 to 77 K. The emission mechanism of the complexes in our study in the rigid PMMA film can be thought similar to that occurred at 77 K. The rigidity of the PMMA film could make the ILCT character of the styryl moiety dominant, and the bathochromic shift of the film could be explained by this increased ILCT. Meanwhile, the motional relaxation of the styryl moiety in solution at the higher temperatures may make ILCT character weaker and limit the contribution of the π-conjugation to the emission of their complexes.

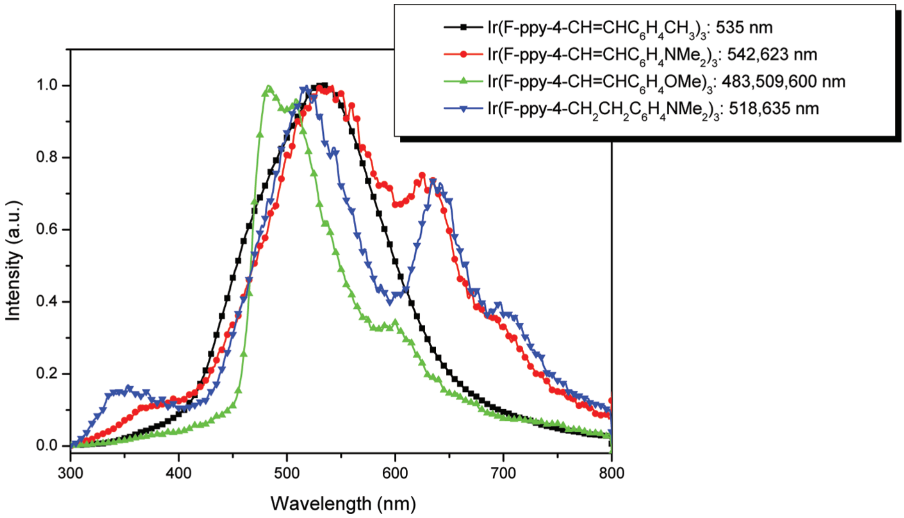

Figure 4. PL spectra of Ir(F-ppy-4-CH=CHC_6H_4-R)$_3$ and Ir(F-ppy-4-$CH_2CH_2C_6H_4$-R)$_3$ on the PMMA films.

The emission maxima of Ir(F-ppy-4-CH=$CHC_6H_4NMe_2)_3$ are observed at 542 and 623 nm, and those of Ir(F-ppy-4-CH=$CHC_6H_4OMe)_3$ occur at 509 and 600 nm, while Ir(F-ppy-4-CH=$CHC_6H_4Me)_3$ show broad emission with the maxima at 535 nm. These PLs were blue-shifted due to the F substitutent of the ppy ligand in the complex, compared to those of the complexes containing the unsubstituted ppy ligand. The saturated complex, Ir(4-F-ppy-$CH_2CH_2C_6H_4NMe_2)_3$ exhibits the emission maxima at 518 and 635 nm. Interestingly, the solid PLs of the styryl complexes containing NMe_2 group show similar emission patterns regardless of the presence of the π linker. It might be ascribed to the strong push effect by NMe_2 to the complex in both cases.

4. Conclusion

The tris-cyclometallated iridium complexes containing the substituted styryl groups and their saturated analogs were prepared and their luminescence properties of the iridium complexes were investigated. In the UV-vis spectral patterns of the iridium complexes, the absorption around 350 nm was assigned to the ILCT by the extended π-conjugation of the styryl moiety. Furthermore, the strong push-pull effect between the NMe_2 and F end groups led to the effective control of the ILCT transition, extending the absorption of the complexes up to 400 nm. The PLs in both the solution and the film of these unsaturated styryl complexes were bathochromically shifted with respect to those of their saturated analogs, as expected from the elongation of π-conjugation. Involvement of the electron withdrawing group, F, to the phenyl ring in the complex, led to the hypsochromic shift in PL, compared with the complexes without F substituents. In the PMMA film, the emission spectra of the branched iridium complexes were broad and red-shifted presumably due to their rigid environment.

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References

[1] Lowry, M. S. & Bernhard, S. (2006). *Chem. Eur. J.*, *12*, 7970.
[2] Kohler, A. Wilson, J. S., & Friend, R. H. (2002). *Adv. Mater.*, *14*, 701.
[3] 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.
[4] Baldo, B. A., O'Brian, D. F., You, Y., Shoustikov, A., Sibley, S., Thompson, M. E., & Forrest, S. R. (1998). *Nature*, *395*, 151.
[5] Baldo, B. A., Lamansky, S., Burrows, P. E., Thompson, M. E., & Forrest, S. R. (1999). *Appl. Phys. Lett.*, *75*, 4.
[6] Baldo, M. A., Thompson, M. E., & Forrest, S. R. (2000). *Nature*, *403*, 750.
[7] Ikai, M., Tokito, S., Sakamoto, Y., Suzuki, T., & Taga, Y. (2001). *Appl. Phys. Lett.*, *79*, 156.
[8] Chen, F. C., Yang, Y., Thompson, M. E., & Kido, J. (2002). *Appl. Phys. Lett.*, *80*, 2308.
[9] You, Y., Kim, K. S., Ahn, T. K., Kim, D., Park, S. Y., & Park, S. Y. (2007). *J. Phys. Chem. C.*, *111*, 4052.

[10] Yeh, S. J., Wu, M. F., Chen, C. T., Song, Y. H., Chi, Y., Ho, M. H., Hsu, S. F., & Chen, C. H. (2005). *Ads. Mater.*, *17*, 285.

[11] Li, J., Djurovich, P. I., Alleyne, B. D., Tsyba, I., Ho, N. N., Bau, R., & Thompson, M. E. (2004). *Polyhedron*, *23*, 419.

[12] Qin, T., Zhou, G., Scheiber, H., Bauer, R. E., Baumgarten, M., Anson, C. E., List, E. J. W., & Mullen, K. (2008). *Angew. Chem.*, *120*, 8416.

[13] Lepeltier, M., Bozec, H. L., Guerchais, V., Lee, T. K., & Lo, K. K. (2005). *Organometallics*, *24*, 6069.

[14] Lepeltier, M., Lee, T. K., Lo, K. K., Toupet, L., Bozec, H. L., & Guerchais, V. (2007). *Eur. J. Inorg. Chem.*, 2734.

[15] Park, G. Y., Seo, J. H., Kim, Y. K., Kim, Y. S., & Ha, Y. (2007). *J. Kor. Phys. Soc.*, *50*, 1729.

[16] King, K. A., Spellane, P. J., & Watts, R. J. (1985). *J. Am. Chem. Soc.*, *107*, 1431.

[17] Nonoyama, M. (1975). *J. Oranomet. Chem.*, *86*, 263.

[18] Lee, J., Chu, H. Y., Kim, S. H., Do, L. M., Zyung, T., & Hwang, D. H. (2003). *Opt. Mater.*, *21*, 205.