



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

Homoleptic vs. Heteroleptic Orange Light-Emitting Iridium Complexes Chelated with Benzothiazole Derivatives

Hye Joo Lee^a & Yunkyoung Ha^a

^a Department of Information Display Engineering, Hongik University, Seoul, 121-791, Korea

Published online: 16 Dec 2013.

To cite this article: Hye Joo Lee & Yunkyoung Ha (2013) Homoleptic vs. Heteroleptic Orange Light-Emitting Iridium Complexes Chelated with Benzothiazole Derivatives, *Molecular Crystals and Liquid Crystals*, 584:1, 53-59, DOI: [10.1080/15421406.2013.849434](https://doi.org/10.1080/15421406.2013.849434)

To link to this article: <http://dx.doi.org/10.1080/15421406.2013.849434>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Homoleptic vs. Heteroleptic Orange Light-Emitting Iridium Complexes Chelated with Benzothiazole Derivatives

HYE JOO LEE AND YUNKYOUNG HA*

Department of Information Display Engineering, Hongik University, Seoul
121-791, Korea

The homoleptic and heteroleptic iridium(III) complexes exhibiting orange phosphorescence were investigated to compare their emission colors, luminance efficiency, and stability. The homoleptic iridium complexes, Ir(pbt-R)₃, were prepared from the reaction of the iridium(III) precursor and phenylbenzothiazole derivatives. The heteroleptic ones containing the anions of 4-methyl-2,3-diphenylquinoline (4-Me-dpq) and 2-phenylbenzothiazole (pbt) as ligands, Ir(pbt-OMe)₂(4-Me-2,3-dpq) and Ir(4-Me-2,3-dpq)₂(pbt-OMe), were synthesized via the chloro-bridged iridium dimer. We investigated photoabsorption and photoluminescence (PL) properties of the iridium complexes and studied their bandgaps with cyclic voltammetry (CV). Orange phosphorescence with the PL maxima of 530–620 nm was observed with these complexes, and the bandgaps between their highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) were correlated with CV data. The electro-luminescence (EL) study of these complexes was not possible due to lack of sublimability. The light-emitting mechanisms regarding the phosphorescence colors were discussed.

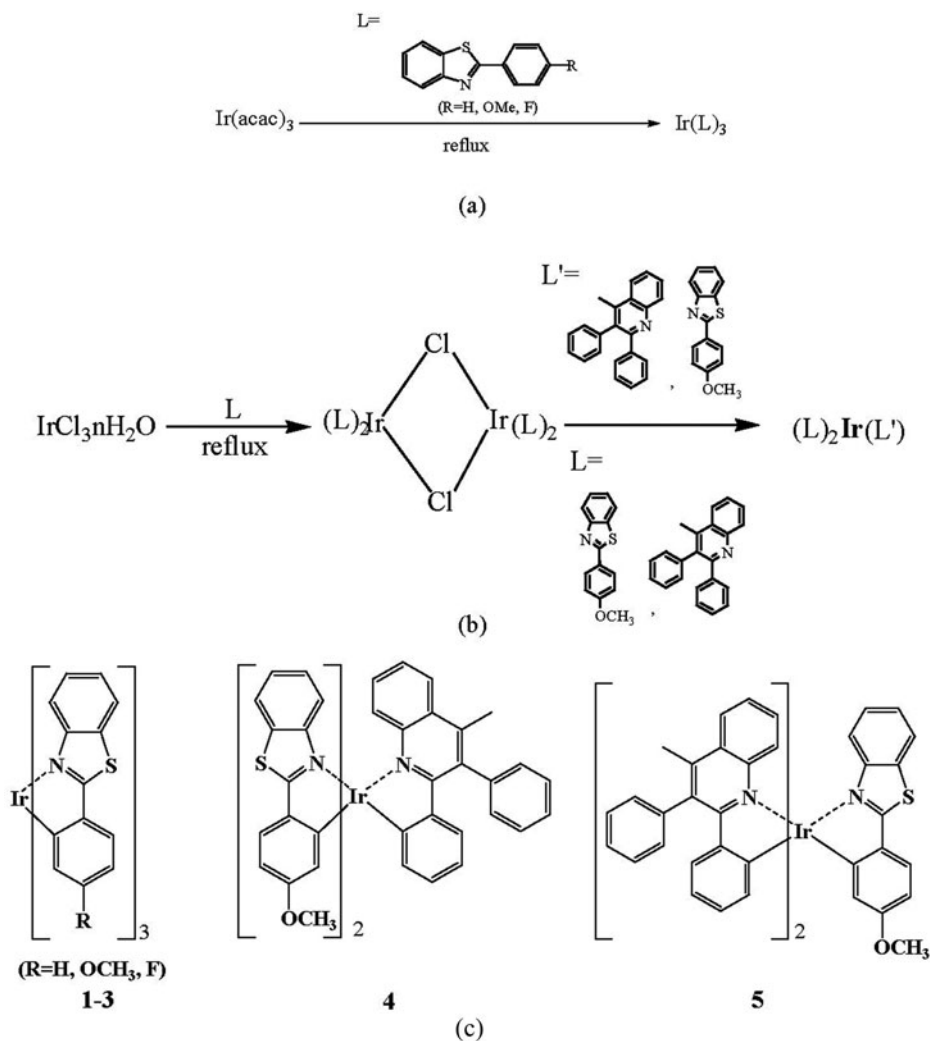
Keywords Heteroleptic iridium complexes; homoleptic iridium complexes; phenylbenzothiazole derivatives; phosphorescence; orange emission

Introduction

For the past decade, organic light-emitting diodes (OLEDs) based on phosphorescence materials have drawn great interest due to their applications in low cost, more efficient flat-panel displays and solid-state lighting [1–2]. In particular, cyclometalated iridium complexes, which have relatively short excited-state lifetime, high phosphorescence efficiency and flexible color tunability, are regarded as the most promising phosphors in organic light-emitting devices [3–5]. Recently, the orange light-emitting iridium complexes beside the three primary color emitting materials have drawing attention since they can be used in combination with blue emitters to fabricate two-component white OLEDs, which has definitely become one of the most important directions of OLED studies [6–8].

Herein, our interest is to design and synthesis orange phosphorescent iridium complexes having high luminescence yields and excellent device performance for white OLED applications. For such purpose, we introduced 2-phenylbenzothiazole (pbt) derivatives as

*Address correspondence to Prof. Yunkyoung Ha, Department of Information Display Engineering, Hongik University, Sangsu-dong, Mapo-gu, Seoul 121-791, Korea (ROK). Tel.: (+82)2-320-1490; Fax: (+82)2-3142-0335. E-mail: ykha@hongik.ac.kr



Scheme 1.

main ligands in the iridium complexes. The *para*-position of the phenyl moiety in the ligands in the complexes was substituted with the functional groups having different electronegativities. Thus, we synthesized the homoleptic iridium complexes of *pbt-R* ($\text{R} = \text{H}, \text{OMe}, \text{F}$), **1–3** (Scheme 1) and also prepared the heteroleptic complexes, **4–5**, with the anions of *pbt-OMe* and 4-methyl-2,3-diphenylquinoline (4-Me-dpq) as the ligands. The photophysical and electrochemical properties of the homoleptic and heteroleptic iridium complexes were investigated and compared.

Experimental

Synthesis of Ligands

2-(4-fluorophenyl)benzothiazole (pbt-F). 2-(4-fluorophenyl)-benzothiazole were synthesized according to the literature method [9]. Yield: 76 %

4-Methyl-2,3-diphenylquinoline (4-Me-2,3-dpq). 4-methyl-2,3-diphenylquinoline was obtained according to Friedlander reaction with the corresponding precursors, 2-aminoacetophenone (1.35 g, 10.0 mmol) and deoxybenzoin (1.96 g, 10.0 mmol) [10–11]. Yield: 75 %

Synthesis of Iridium Complexes

Ir(pbt-R)₃ (*R*=H, OMe, F). (1–3). Each complex was prepared from the reaction of Ir(acac)₃ with the respective pbt-R ligand according to the reported procedure [12]. Ir(acac)₃ (1.22 g, 2.5 mmol) and pbt-R (2.07 g, 10 mmol) were dissolved in 50 ml of ethylene glycol and the mixture was refluxed for 24 hr. After cooling, 1N HCl solution was added and the resulting precipitate was filtered off. The residue was purified by silica gel chromatography by using CH₂Cl₂.

Ir(pbt)₃ : An orange powder (Yield: 49 %). ¹H NMR (400MHz, DMSO): δ 8.17–7.45 (m, 24H, aromatic C–H).

Ir(pbt-OMe)₃ : An orange powder (Yield: 49 %). ¹H NMR (400MHz, DMSO): δ 8.12–6.51 (m, 24H, aromatic C–H) 3.51 (s, 6H).

Ir(pbt-F)₃ : An orange powder (Yield: 49 %). ¹H NMR (400MHz, DMSO): δ 8.26–6.04 (m, 21H, aromatic C–H).

Ir(pbt-OMe)₂(4-Me-2,3-dpq). (4). The cyclometalated Ir(III) μ -chloro-bridged dimer, (4-Me-2,3-dpq)₂Ir(μ -Cl)₂Ir(4-Me-2,3-dpq)₂ (1.9 mmol), was first prepared according to the Nonoyama method. [13] In the second step, the resulting dimer and 4-Me-2,3-dpq ligands (6.5 mmol) were mixed with Na₂CO₃ (500 mg) in 2-ethoxyethanol (30 mL). The mixture was refluxed for 2 h and the red solid was filtered after cooling. Ir(4-Me-2,3-dpq)₂(pbt-OMe) were purified by chromatography on silica gel column with dichloromethane and recrystallization. An orange powder was obtained. (Yield: 49 %) FAB-MS: calculated 967; found 673 (M⁺-4-Me-2,3-dpq). ¹H NMR (400MHz, DMSO): δ 8.35–6.20 (m, 27H, aromatic C-H) 3.52 (s, 6H) 2.50 (s, 3H).

Ir(4-Me-2,3-dpq)₂(pbt-OMe). (5). The complexes were prepared from the reaction of 4-Me-2,3-dpq with IrCl₃·H₂O and then treated with the pbt-OMe (2-phenylbeonzothiazole derivative), similar to the procedure described above. A red powder was obtained. (Yield 65 %) FAB-MS: calculated 1021; found 781(M⁺-pbt-OMe). ¹H NMR(DMSO) (δ, ppm): 8.35~6.00 (m, aromatic C-H, 33H); 3.48 (s, 3H); 2.50 (s, 6H).

Measurements

UV-Vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. PL spectra were measured on an Aminco-Bowman Series 2 luminescence. The UV-Vis and PL spectra of the iridium complexes were measured in 10⁻⁴ M dilute CH₂Cl₂ solution. Cyclic voltammograms were obtained at scan rate of 100 mV/s with Electrochemical Analyzer of CH Instruments, and tetrabutylammonium hexafluorophosphate was added as an electrolyte in CH₂Cl₂ solution.

Results and Discussion

The synthesis of the ligands, F-pbt and 4-Me-2,3-dpq, was straightforward, according to the procedures reported previously [9–11]. The other ligands were purchased and used

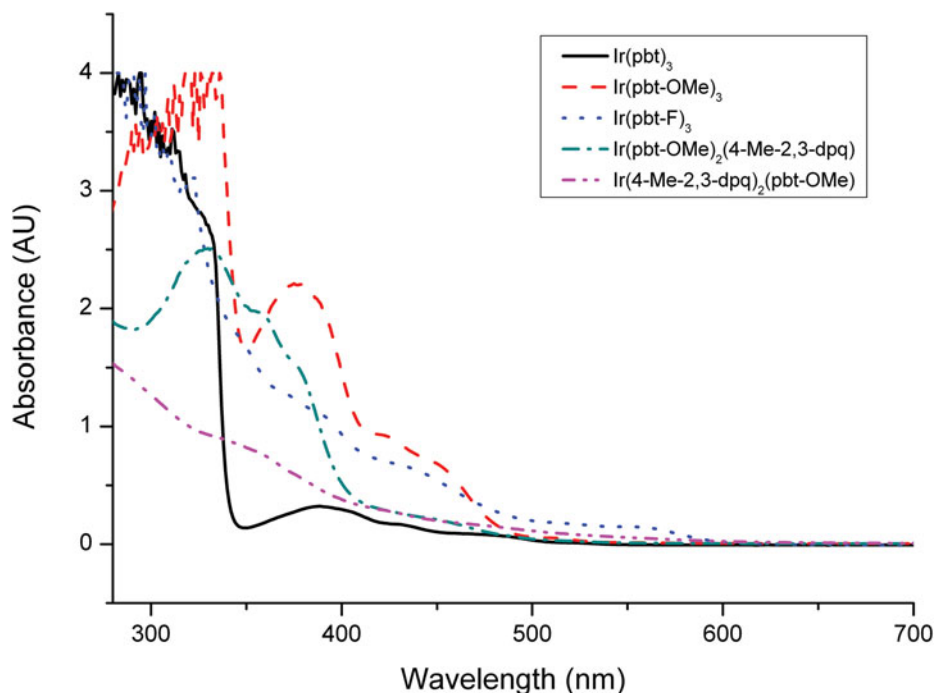


Figure 1. UV-Vis absorption spectra of iridium complexes in a 10^{-4} M CH_2Cl_2 solution.

directly. The homoleptic iridium complexes, $\text{Ir}(\text{pbt-R})_3$, were prepared from the one-pot reaction of the corresponding main ligand with $\text{Ir}(\text{acac})_3$ [12]. The heteroleptic iridium complexes were synthesized via two steps, as reported by Nonoyama [13]. The overall synthetic schemes are illustrated in Scheme 1.

The UV-Vis absorption spectra of the complexes in CH_2Cl_2 are shown in Fig. 1. The absorption spectra of iridium complexes have strong absorption bands appearing at the ultraviolet region of the spectrum between 280 and 330 nm. These bands were assigned to the spin-allowed $^1\pi \rightarrow \pi^*$ transitions of the ligands. The $^1\pi - \pi^*$ bands are accompanied by weaker and lower energy features extending into the visible region from 350 to 500 nm. These absorption are assigned to a spin-allowed metal charge transfer ($^1\text{MLCT}$) band, and the weaker absorption bands at the longer wavelengths can be attributed to the spin-forbidden $^3\text{MLCT}$ and spin-orbit coupling enhanced $^3\pi - \pi^*$ transition. The intensities of the MLCT and $^3\pi - \pi^*$ transition bands are varied, depending on the chelating ligands. These intensities are generally attributed to mixing of the charge-transfer transitions with high lying spin-allowed transitions on the chelating ligand [14].

The PL spectra of the Ir complexes in CH_2Cl_2 solution are shown in Fig. 2. The homoleptic complexes, $\text{Ir}(\text{pbt})_3$, $\text{Ir}(\text{pbt-OMe})_3$ and $\text{Ir}(\text{pbt-F})_3$, showed the PL peaks at 550, 534, and 528 nm, respectively. $\text{Ir}(\text{pbt-OMe})_2(4\text{-Me-2,3-dpq})$ and $\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{pbt-OMe})$ exhibited the emission maxima at 554 and 627 nm, respectively. Unexpectedly, the PL spectra of the homoleptic iridium complexes were not influenced by the substituent characteristics of the chelating ligands since both electron-withdrawing F and electron-donating OMe substituents led the emission of their complexes to shorter wavelengths than those of the unsubstituted $\text{Ir}(\text{pbt-H})_3$. On the other hand, the heteroleptic iridium complexes have drastic contrasts, depending on the species and number of the chelating

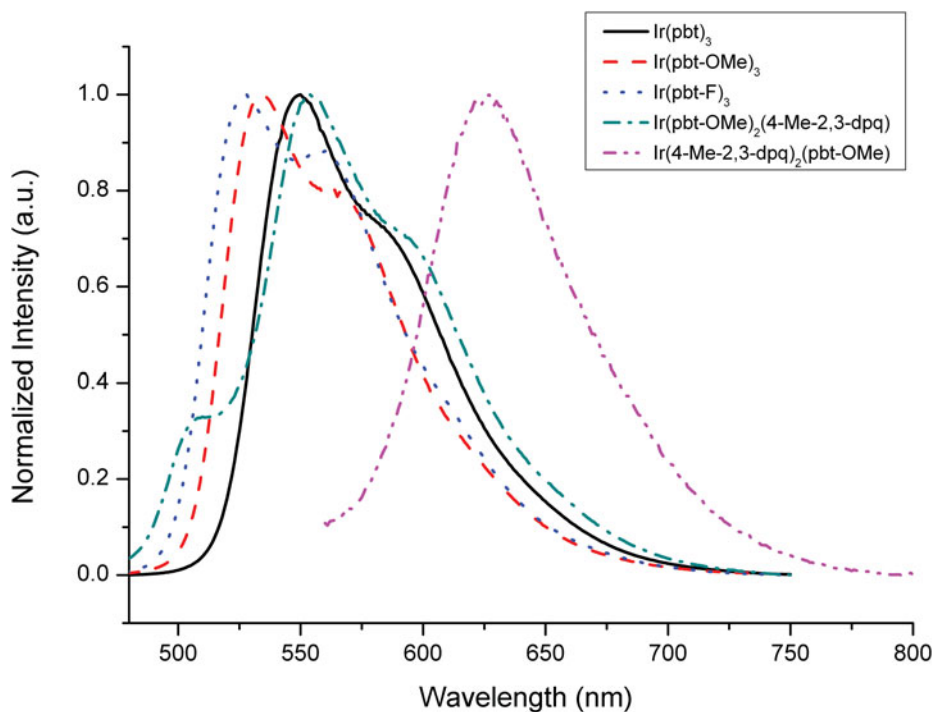


Figure 2. PL spectra of the iridium complexes in a 10^{-4} M CH_2Cl_2 solution.

ligands. The anion of 4-Me-2,3-dpq was reported to lead its iridium complexes to red phosphorescence around 600 nm [11]. $\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{pbt-OMe})$ which contains two 4-Me-2,3-dpq ligands showed a bathochromic shift, resulting in the emission at 627 nm, while $\text{Ir}(\text{pbt-OMe})_2(4\text{-Me-2,3-dpq})$ which has only one 4-Me-2,3-dpq ligand exhibited the PL maxima at 554 nm near those of the homoleptic complexes. We attribute the red-shifted emission by $\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{pbt-OMe})$ to inter-ligand energy transfer (ILET) from pbt-OMe ligand to 4-Me-2,3-dpq ligands. The energy which the pbt-OMe ligand absorbs might be transferred and contributed to the emission by 4-Me-2,3-dpq ligands which have a smaller energy gap, resulting in a bathochromic shift in PL of their complex. ILET has been reported to occur between the ligands of the large and small energy gaps, according to the literatures recently published [3, 15].

We investigated the electrochemical properties of the Ir complexes by the cyclic voltammetry (CV) as shown in Table 1, which reveal their positions of the HOMO/LUMO [16–17]. The oxidation potentials which indicate the HOMOs of $\text{Ir}(\text{pbt})_3$, $\text{Ir}(\text{pbt-OMe})_3$, $\text{Ir}(\text{pbt-F})_3$, $\text{Ir}(\text{pbt-OMe})_2(4\text{-Me-2,3-dpq})$ and $\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{pbt-OMe})$ were reversible at 0.50–0.75 V relative to an internal ferrocenium/ferrocene reference (Fc^+/Fc), respectively. The LUMOs of the complexes were not observed within the electrochemical windows of the solvents and thus estimated from their respective absorption spectra. They were calculated to be between -0.76 and -2.37 eV, according to optical-edge estimation [17]. The resulting ΔE s ($E_{\text{ox}} - E_{\text{red}}$) of the complexes were well correlated with their tendencies of PL maxima.

The electroluminescence (EL) of these complexes prepared in this study was attempted, but the vacuum sublimation of the complexes to fabricate the light-emitting device was not

Table 1. Physical parameters for the complexes

Ir complex	$\lambda_{\text{em}}/\text{nm}^{\text{a}}$	$E_{\text{ox}}/\text{V}^{\text{b}}$	HOMO /eV ^c	LUMO /eV ^d	$\Delta E/\text{eV}^{\text{d}}$
Ir(pbt) ₃	550	0.50	−4.30	−1.11	3.19
Ir(pbt-OMe) ₃	534	0.52	−4.28	−1.01	3.27
Ir(pbt-F) ₃	528	0.74	−4.06	−0.76	3.30
Ir(pbt-OMe) ₂ (4-Me-2,3-dpq)	554	0.75	−5.55	−2.37	3.18
Ir(4-Me-2,3-dpq) ₂ (pbt-OMe)	627	0.60	−4.20	−1.26	2.94

^aMeasured in CH₂Cl₂ solution.^bscan rate: 100 mV/s, Electrolyte: tetrabutylammonium hexafluorophosphate. The potentials are quoted against the internal ferrocene standard.^cDeduced from the equation HOMO = −4.8 − E_{ox} .^dCalculated from the optical edge $\Delta E = \text{LUMO} - \text{HOMO}$.

successful so far. We now try to fabricate devices of these orange phosphorescent complexes by the solution process to investigate the EL performance of the complexes.

Conclusions

We have synthesized and characterized the homoleptic and heteroleptic iridium complexes chelated with the anions of phenylbenzothiazoles having the substituents of different electronegativities. Surprisingly, the substituent, R, was found to have little influence on photoluminescence of the orange phosphorescent homoleptic complexes, Ir(pbt-R)₃. On the other hand, the heteroleptic iridium complexes, Ir(OMe-pbt)₂(4-Me-2,3-dpq) and Ir(4-Me-2,3-dpq)₂(OMe-pbt), exhibited quite contrasting luminescence properties. While Ir(OMe-pbt)₂(4-Me-2,3-dpq) showed the emission maxima at 554 nm, similar to the homoleptic ones, Ir(4-Me-2,3-dpq)₂(OMe-pbt) which contain two red-emitting 4-Me-2,3-dpq ligands underwent ILET to display red phosphorescence at 627 nm. The electrochemical measurement of these complexes supported their luminescence characteristics. The orange light-emitting iridium complexes developed in this study are now under investigation as candidates for the possible application to orange phosphors for white OLEDs.

Acknowledgment

This research was supported by the Korea Research Foundation (NO. 2011- 0003765).

References

- [1] Tang, C. W., & Vanslyke, S. A. (1987). *Appl. Phys. Lett.*, *16*, 913.
- [2] D'Andrade, B. W., & Forrest, S. R. (2004). *Adv. Mater.*, *16*, 1585.
- [3] You, Y., & Park, S. Y. (2009). *Dalton Trans.*, 1267.
- [4] Chen, K., Yang, C.-H., Chi, Y., Liu, C.-S., Chang, C.-H., Chen, C.-C., Wu, C.-C., Chung, M.-W., Cheng, Y.-M., Lee, G.-H., & Chou, P.-T. (2010). *Chem. Eur. J.*, *16*, 4315.
- [5] Li, J., & Liu, D. (2009). *J. Mater. Chem.*, *17*, 7584.
- [6] Reneke, S., Lindner, F., Schwartz, G., Seidler, N., Walzer, K., Lüssem, B., & Leo, K. (2009) *Nature*, *459*, 234.
- [7] Sasabe, H., Takamatsu, J., Watanabe, S., & Kido, J. (2010). *Adv. Mater.*, *22*, 5003.
- [8] Seo, J. H., Park, H.-R., Kim, Y. K., & Ha, Y. (2011). *J. Nanosci. Nanotechnol.*, *11*, 7198.
- [9] Zhang, L., Li, B., Shi, L., & Li, W. (2009). *Optical Mater.*, *31*, 905.

- [10] Wu, F. I., Su, H. J., Shu, C. F., Luo, L., Diau, W. F., Cheng, C. H., Duan, J. P., & Lee, G. H. (2005). *Mater. J. Chem.*, *15*, 1035.
- [11] Park, G. Y., & Ha, Y. (2008). *Syn. Metals.*, *158*, 120.
- [12] Lee, S. J., Park, K.-M., Yang, K., & Kang, Y. (2009). *Inorg. Chem.*, *48*, 1030.
- [13] Nonoyama, M. (1975). *Organomet. Chem.*, *86*, 263.
- [14] Holmes, R. J., D'Andrade, B. W., Forrest, S. R., Ren, X., Li, J., & Thompson, M. E. (2003). *Appl. Phys. Lett.*, *83*, 3813.
- [15] Park, H.-R., & Ha, Y. (2012). *J. Nanosci. Nanotechnol.*, *12*, 1365.
- [16] Thomas, K. R. J., Velusamy, M., Lin, J. T., Chien, C., Tao, Y., Wen, Y. S., Hu, Y., & Chou, P. (2005). *Inorg. Chem.*, *44*, 5677.
- [17] Zhao, Q., Jiang, C., Shi, M., Li, F., Yi, T., Cao Y., & Huang, C. (2006). *Organometallics*, *25*, 3631.