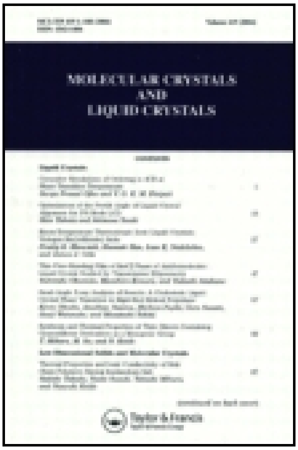

Molecular Crystals and Liquid Crystals

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

New Red Phosphorescent Heteroleptic Tris-Cyclometalated Iridium Complex with 1-phenylisoquinoline and 2,4-diphenylquinoline

Seung Chan Lee [a] & Young Sik Kim [a b]

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

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

Version of record first published: 10 Nov 2009

To cite this article: Seung Chan Lee & Young Sik Kim (2009): New Red Phosphorescent Heteroleptic Tris-Cyclometalated Iridium Complex with 1-phenylisoquinoline and 2,4-diphenylquinoline, Molecular Crystals and Liquid Crystals, 513:1, 236-245

To link to this article: http://dx.doi.org/10.1080/15421400903212000

Mol. Cryst. Liq. Cryst., Vol. 513, pp. 236–245, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903212000

New Red Phosphorescent Heteroleptic Tris-Cyclometalated Iridium Complex with 1-phenylisoquinoline and 2,4-diphenylquinoline

Seung Chan Lee[1] **and Young Sik Kim**[1,2]
[1]Department of Information Display, Hongik University, Seoul, Korea
[2]Department of Science, Hongik University, Seoul, Korea

The synthesis and photophysical study of efficient phosphorescent iridium(III) complexes having two different (C^N) ligands are reported. In order to improve luminescence efficiency by avoiding triplet–triplet (T-T) annihilation, a heteroleptic iridium complex, Ir(dpq)$_2$(piq), is designed and prepared, where dpq and piq represent 2,4-diphenylquinoline and 1-phenylquinoline, respectively. Dpq and piq ligands can act as a source of energy. When Ir(dpq)$_2$(piq) is placed in the lowest excited state, the excitation energy is neither quenched nor deactivated but quickly transferred intermolecularly from two dpq ligands to one luminescent piq ligand. Such transfer can occur because the triplet energy level of dpq is higher than that of piq and light is emitted mainly from the piq ligand in the end. Thus, Ir(dpq)$_2$ (piq) shows strong photoluminescence from piq ligands. To analyze this luminescent mechanism, we calculated these complexes theoretically using a computational method.

Keywords: heteroleptic tris-cyclometalated iridium(III) complex; Ir(dpq)$_2$(piq); oLED

INTRODUCTION

In the years since Tang and coworkers 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, fluorescent and phosphorescent. OLEDs based on phosphorescent materials are known to improve electroluminescence performance significantly

---

This work was supported by Seoul R&BD Program (10555).

Address correspondence to Prof. Young Sik Kim, Department of Information Display Hongik University Sangsu-dong, Mapo-gu, Seoul 121-791, Korea (ROK). E-mail: youngkim@wow.hongik.ac.kr

because both singlet and triplet excitons can be used to harvest light emission. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach 100% [6]. The heavy metal complexes, particularly those containing Pt and Ir, can induce the 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 spin-allowed, resulting in high phosphorescence efficiencies. Thus, heavy metal complexes can serve as efficient phosphors in OLEDs.

Unfortunately, most of phosphorescent emitters have a long radiative 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 [9,10]. Lamansky *et al.* [3] reported that a series of bis-cyclometalated iridium complexes with β-diketonato ancillary ligands such as $Ir(ppy)_2$ (acac) gave a wide range of emission colors with high phosphorescence yields comparable to those of tris-cyclometalated homoleptic iridium complexes. However, Tsuboyama *et al.* [10] show that complexes with acetylacetonate ligands tend to thermally decompose at relatively low temperatures. These results indicate that iridium complexes having three (C^N) ligands are thermally more stable than the acetylacetonate complexes.

To improve luminescence efficiency by avoiding T-T annihilation, a metal complex having a different species of plural ligands has been proposed [11,12]. The metal complex has been designed to transfer the energy of excitons smoothly between ligands placed in excited states. More specifically, when a metal complex having one luminescent ligand among three is placed in the lowest excited state, the excited energy is transferred from the other two ligands to one luminescent ligand [13,14]. Furthermore, it is expected that the use of one luminescent ligand decreases the probability of energy transition between spatially adjacent molecules, leading to the decrease of quenching or energy deactivation.

Herein, we report an efficient red phosphorescent emitter having different ligands, $Ir(dpq)_2(piq)$. Previously, $Ir(piq)_2(acac)$ and Ir $(dpq)_2(acac)$ were known to have high phosphorescence efficiencies in electroluminescent (EL) emissions near 622 nm and 614 nm respectively, because they exhibit metal-to-ligand charge transfer (MLCT) excited states [15,16] The purpose of the present study is to design a high efficiency heteroleptic Ir(III) complex having different species of ligands suitable for red OLED devices. In addition to high phosphorescence efficiency, the phosphorescent mechanism of the Ir(III) complexes having different ligands is compared with that of homoleptic Ir(III) complexes having the same species of ligands.

EXPERIMENTAL

Synthesis

1. *Synthesis and Characterization*

All reagents were purchased from Aldrich 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). The synthesis method is shown in Figure 1.

1.1. *Synthesis of Ligand: Dpq and Piq*

Synthesis of dpq. Dpq ligands were obtained from the Friedlander Reaction [17,18] Concentrated sulfuric acid 1.0 ml was added to a solution of 1.972 g (10.0 mmol) of 2-aminobenzophenone and 1.169 g (10.0 mmol) of acetophenone (for dpq) in 30 ml of glacial acetic acid. The solution was heated to reflux for 4 hr. The reaction mixture was then cooled and dripped slowly with stirring into an ice cold solution

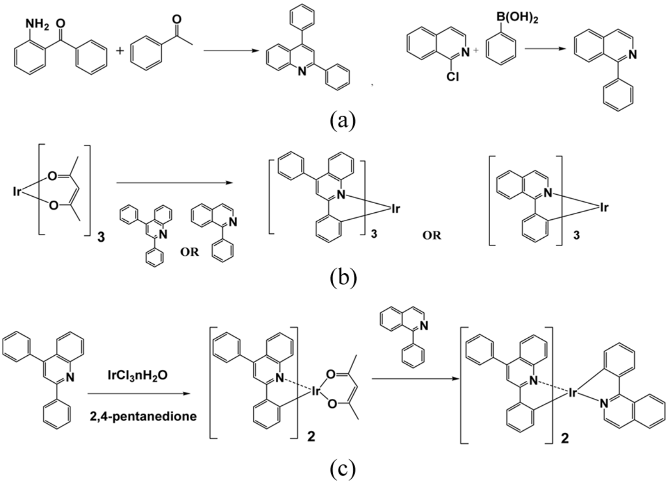

FIGURE 1 (a) Synthesis of C^N Ligands. (b) Synthesis of homoleptic Iridium (III) complexes containing one kind of C^N ligand. (c) Synthesis of heteroleptic Iridium(III) complexes containing two different kinds of C^N ligands.

of 15 ml of concentrated ammonium hydroxide in 40 ml of water. The resultant yellow precipitate was filtered, washed with water, and dissolved in dichloromethane (CH_2Cl_2). The organic fraction was separated and dried over anhydrous $MgSO_4$, and pumped dry. The solid was chromatographed on a silica gel column with dichloromethane.

Synthesis of piq. 0.899 g of 1-chloroisoquinoline (5.5 mmol), 0.699 g of phenylboronic acid (5 mmol) and 0.196 g of tetrakistriphenylphospine palladium(0) (0.17 mmol) were placed in 20 ml of toluene, 10 ml of ethanol and 20 ml of 2 N sodium carbonate aqueous solution. The mixture was heated to reflux for 15 hr. 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) [19].

1.2. *Synthesis of Heteroleptic Ir(III) Complex: Ir(Dpq)$_2$(Piq)*

Cyclometalated Ir(III) μ-chloro-bridged dimers of the general formula, $(dpq)_2Ir(\mu\text{-}Cl)_2Ir(dpq)_2$, were synthesized by the method reported by Nonoyama with slight modification [20]. $IrCl_3 \cdot H_2O$ (1.490 g, 5 mmol) and H_2O (10 ml) were added to a solution of dpq (3.51 g, 12.5 mmol) in 2-ethoxyethanol (30 ml). The mixture was refluxed at 120°C under argon for 12 hr and then cooled to room temperature. The solution mixture was slowly evaporated under vacuum to obtain the crude product $(dpq)_2Ir(\mu\text{-}Cl)_2Ir(dpq)_2$. The resultant precipitate was dissolved in dichloromethane and was filtered chromatographically on a silica gel column with dichloromethane. The product portion was collected and dried in vacuum. $(dpq)_2Ir(\mu\text{-}Cl)_2$ $Ir(dpq)_2$ (0.959 g, 0.24 mmol) and 2,4-pentanedione (0.07 ml, $d = 0.975$, 0.84 mmol) were mixed with Na_2CO_3 (250 mg) in 2-ethoxyethanol (30 ml). The mixture was refluxed for 2 hr.

The solution was cooled to room temperature and the yellow solid was filtered. $Ir(ppy)_2(acac)$ was obtained after the chromatographing on a silica gel column with dichloromethane to yield a bright red powder. $Ir(dpq)_2(acac)$ (845.14 mg, 1 mmol) and piq ligand (2 mmol) were dissolved in 20 ml of glycerol and refluxed for 10 hr. After cooling, 20 ml of 1 N HCl solution was added and the resulting precipitate was filtered off. The residue was purified by silica gel chromatography using CH_2Cl_2.

1.3. *Synthesis of Homoleptic Ir(III) Complex: Ir(Dpq)$_3$, Ir(Piq)$_3$*

These complexes were prepared from $Ir(acac)_3$ and the corresponding ligand by a reported procedure [9]. $Ir(acac)_3$ (245 mg, 0.5 mmol) and dpq (or piq) (2 mmol) were dissolved in 20 ml of glycerol and refluxed for 12 hr. After cooling, 20 ml of 1 N HCl solution was added and the resulting precipitate was filtered off. The residue was purified by silica gel chromatography using CH_2Cl_2.

UV-Absorption and Photoluminescence (PL) Measurement

UV-Vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. The PL spectra were obtained on a Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of $Ir(dpq)_3$, $Ir(piq)_3$, $Ir(dpq)_2(piq)$ were measured with a 10^{-5} M dilute solution in CH_2Cl_2.

Theoretical Calculation

Calculations on the electronic ground states of dpq, piq ligands, $Ir(dpq)_2(piq)$ were carried out using the B3LYP density functional theory (DFT) and compared with those of $Ir(dpq)_3$ and $Ir(piq)_3$. LANL2DZ [21] and 6–31G(d) [22] basis sets were employed for Ir and the other atoms, respectively. For the calculated ground state geometries, the electronic structure is examined in terms of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). The electronic populations on the central atom were calculated to show the significant admixture of ligand π character with the amount of metal 5d character in the occupied molecular orbitals related to those MLCT transitions. To obtain the vertical excitation energies of the low-lying singlet and triplet excited states of the complexes, time-dependent density functional theory (TD-DFT) calculations using the B3LYP functional was performed at the respective ground-state geometry, where the basis set of ligands was changed to $6–31 + G(d)$. Typically, the lowest 10 triplet and 10 singlet roots of the nonhermitian eigenvalue equations were obtained to get the vertical excitation energies and compared with the absorption spectra to examine each peak. The ground-state B3LYP and excited-state TD-DFT calculations were carried out using Gaussian 98 [23]. We noted that our results pertain only to the ground state geometry. If there are significant geometry changes in the excited state, the luminescence properties of complex could change significantly from the presented results [24].

In addition, the TD-DFT results do not provide information on the oscillator strength of the triplet excited states since the spin-orbit coupling effects are not included in current TD-DFT results.

RESULTS AND DISCUSSION

In order to improve the luminescence efficiency by avoiding T-T annihilation, new phosphorescent iridium complexes having a different species of plural ligands were designed for the application in OLEDs. The iridium complexes prepared herein can be classified into two groups. The first group includes the iridium complexes having two different C^N ligand structures (heteroleptic complexes) such as Ir(dpq)$_2$(piq), and the second one includes the iridium complexes having only one kind of C^N ligand (homoleptic complexes) such as Ir(dpq)$_3$ and Ir(piq)$_3$.

The HOMO and LUMO energy levels of the ground state of Ir(dpq)$_3$ and Ir(piq)$_3$ ligands are shown in Figure 2. Comparing HOMO and LUMO energy levels of the piq complex with those of the dpq complex, we confirmed that the LUMO energy level of the piq complex falls between the HOMO and LUMO energy levels of the dpq complex. However, the HOMO energy level falls below that of the dpq complex. In homoleptic complex cases, luminescence efficiency may decrease because of the saturated quenching effect caused by energy transfer between the same species of ligands. Therefore, we have prepared and characterized heteroleptic Ir(III) complexes having two dpq ligands and one piq as the luminescent ligand.

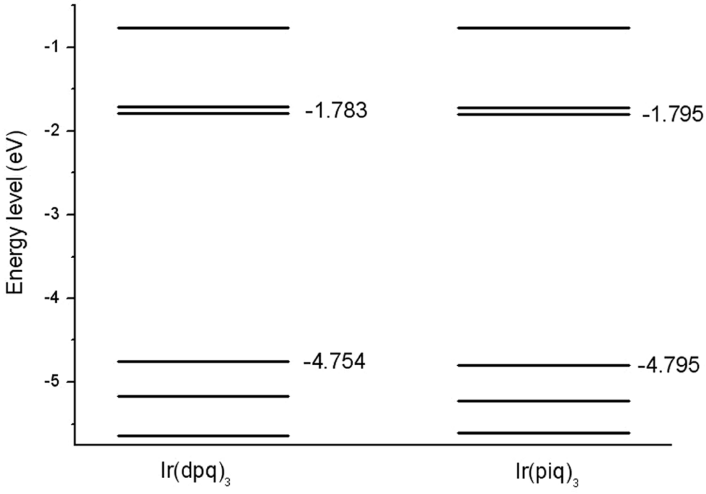

FIGURE 2 HOMO and LUMO energy levels of Ir(dpq)$_3$ and Ir(piq)$_3$ complexes.

These complexes exhibit more red-shifting emission peaks than Ir(dpq)$_3$ and have higher luminescence efficiency than that of the homoleptic Ir(III) complexes, Ir(dpq)$_3$ and Ir(piq)$_3$.

The synthesis of heteroleptic complexes was straightforward, according to the procedure reported by Nonoyama with slight modification, and its scheme is shown in Figure 1. The final yields of the hetero-complexes were usually 62–79%. The second group, homo-complexes, was prepared from the reaction of Ir(acac)$_3$ with the corresponding C^N ligands, dpq and piq, as shown together in Figure 1.

The UV-vis absorption spectra of heteroleptic and homoleptic Ir(III) complexes are shown in Figure 3. The overall profile of the absorption spectrum is red-shifted as the dpq ligand was replaced with piq ligands. Both ^{1}MLCT and ^{3}MLCT peaks are observed for these complexes, *vide infra*. The high degree of spin-orbit coupling is evident, reflected in the comparison of oscillator strength for the two MLCT peaks. Figure 3 shows the absorption spectra of the Ir(dpq)$_3$, Ir(piq)$_3$ and Ir(dpq)$_2$(piq) in 10^{-5} M CH_2Cl_2 at room temperature. The absorption peaks of Ir(dpq)$_3$ are located at 410, 460, 490, 510, and 560 nm. The absorption bands below 410 nm can be assigned to the spin-allowed $^1\pi$-π^* transition, the band around 460 nm to a spin-allowed ^{1}MLCT band, and the bands around 460 and 490 nm to

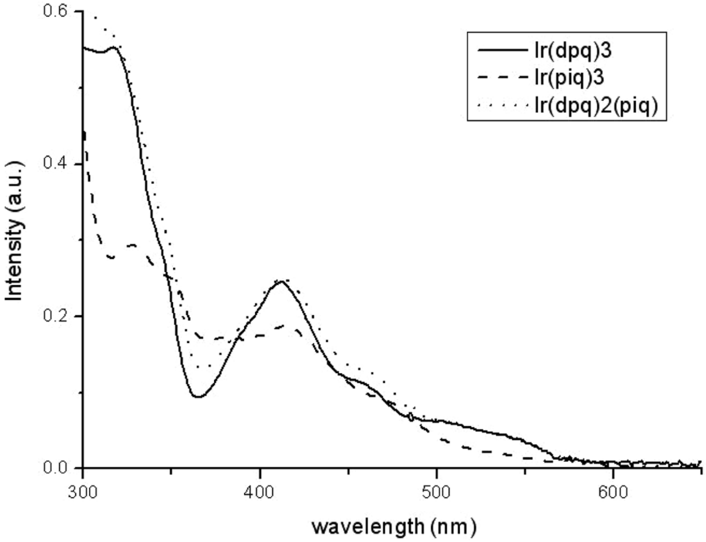

FIGURE 3 UV-vis absorption spectra of Ir(dpq)$_3$, Ir(piq)$_3$, and Ir(dpq)$_2$(piq) in 10^{-5} M CH_2Cl_2.

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 the HOMOs. The MLCT absorption peaks of Ir(piq)$_3$ have very similar ^{1}MLCT and ^{3}MLCT energies at 460 nm and 510 nm, respectively. The overall profile of the absorption spectrum and the peak position of the MLCT absorption of the heteroleptic Ir(dpq)$_2$(piq) are very similar to those of Ir(dpq)$_3$. This provides the evidence that MLCT absorption of the heteroleptic Ir(dpq)$_2$(piq) occurs mainly at the dpq ligand. Also, the MLCT characteristic of Ir(dpq)$_2$(-piq) is stronger than that of the homoleptic Ir(III) complexes because the absorption intensities of Ir(dpq)$_2$(piq) are higher than those of Ir(dpq)$_3$.

The PL spectra of the homoleptic and heteroleptic complexes on CH$_2$Cl$_2$ are shown in Figure 4. The PL spectra of Ir(dpq)$_3$ show the maximum emission peak band at 609 nm, while Ir(piq)$_3$ and Ir(dpq)$_2$ (piq) show maximum emission peaks at 617 nm and 625 nm, respectively. We confirmed that the heteroleptic complex Ir(dpq)$_2$(piq) has a red-shifted emission peak compared to those of Ir(dpq)$_3$ and Ir(piq)$_3$ by emitting from the excited state of piq. This is because the LUMO energy level of Ir(piq)$_3$ is lower than that of Ir(dpq)$_3$. Thus the absorption energy of the dpq ligands can transfer to the piq ligand. Therefore, in the case of the emission mechanism of Ir(dpq)$_2$(piq), emission occurs mostly at the piq ligand site. Also, two dpq ligands of Ir(dpq)$_2$(piq)

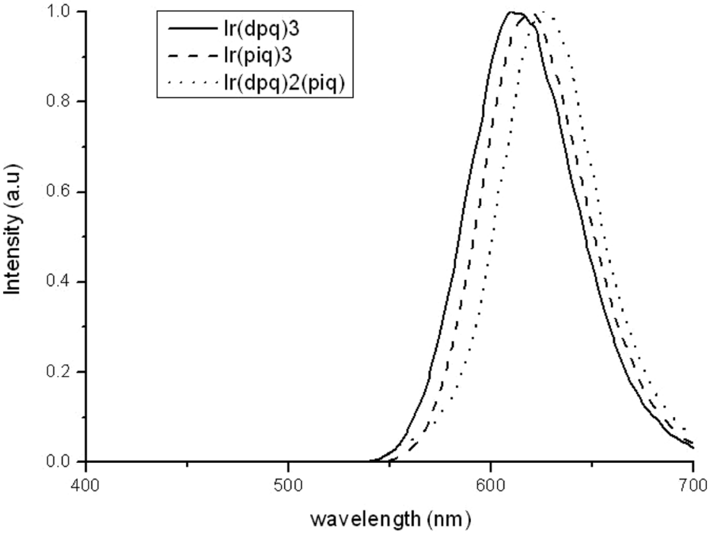

FIGURE 4 PL spectra of Ir(dpq)$_3$, Ir(piq)$_3$, and Ir(dpq)$_2$(piq).

having electron donating characteristics increases the t_2 energy level of the central metal atom, and decreases the energy gap of Ir(dpq)$_2$(piq). In result, the piq ligand emitting peak of Ir(dpq)$_2$(piq) represents more red shifted emission wavelength than that of Ir(piq)$_3$.

CONCLUSIONS

In summary, we report the detailed syntheses and photophysical properties of phosphorescent iridium(III) complexes having a different species of plural (C^N) ligands to improve the luminescence efficiency by avoiding T-T annihilation. We synthesized iridium complexes such as Ir(dpq)$_2$(piq) and studied their photophysical properties for the application in OLEDs. As a result, lower LUMO levels of the piq group enable energy transfer from the dpq group. Thus, Ir(dpq)$_2$(piq) emits red light at 625 nm, receiving absorption energy from the dpq group. Therefore, Ir(dpq)$_2$(piq) provides a high efficiency luminescence and a red emission color originating from piq ligand.

REFERENCES

[1] Tang, C. W. & Van Slyke, 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). *Syth. 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. (1999). *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] Rho, H. H., Lee, Y. H., Park, Y. H., Park, G. Y., Ha, Y. K., & Kim, Y. S. (2006). *Jpn. J. Appl. Phys.*, *45*, 563.
[12] Park, Y. H. & Kim, Y. S. (2007). *Thin Solid Film*, *515*, 5084.
[13] Park, Y. H., Park, G. Y., & Kim, Y. S. (2007). *Mol. Cryst. Liq. Cryst.*, *462*, 197.
[14] Park, G. Y., Kim, Y. S., & Ha, Y. K. (2007). *Curr. Appl. Phys.*, *7*, 390.
[15] 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.
[16] Wu, F. I., Su, H. J., Shu, C. F., Luo, L., Diau, W. G., Cheng, C. H., Duan, J. P., & Lee, G. H. (2003). *J. Mater. Chem.*, *15*, 1035.
[17] Imai, Y., Johnson, E. F., Katto, T., Kurihara, M., & Sittle, J. K. (1975). *J. Polym. Sci. Polym. Chem. Ed.*, *13*, 2233.

[18] Zhang, X., Fan, X., Wang, J., & Li, Y. (2004). *J. Chin. Chem. Soc.*, *51*, 1339.
[19] Su, Y., Huang, H., Li, C., Chien, C., Tao, Y., Chou, P., Datta, S., & Liu, R. (2003). *Adv. Mater.*, *15*, 884.
[20] Nonoyama, M. (1974). *Bull. Chem. Soc. Jpn.*, *47*, 767.
[21] Hay, P. J. & Wadt, W. R. (1985). *J. Chem. Phys.*, *82*, 270.
[22] Hehre, W. J., Ditchfield, R., & Pople, J. A. (1972). *J. Chem. Phys.*, *56*, 2257.
[23] Frisch, M. J. *et al*. (1988). *Gaussian 98, Revision A. 9, Gaussian, Inc.*, Pittsburgh, PA.
[24] Lee, Y. H. & Kim, Y. S. (2007). *Curr. Appl. Phys.*, *7*, 5004.