Journal of
Nanoscience and Nanotechnology
Vol. 13, 8007–8010, 2013

Pure Red Phosphorescent Organic Light-Emitting Diodes Made of Iridium(III) Complex with Thiophene-Quinoline Ligand

Jong Min Lim[1], Ji-Young Kwon[2], Fei Xu[1], Hee Un Kim[1], and Do-Hoon Hwang[1,*]

[1] *Department of Chemistry, and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Republic of Korea*
[2] *Department of Applied Chemistry, Kumoh National Institute of Technology, Kumi 730-701, Republic of Korea*

A cyclometalated iridium(III) complex, bis(2-thiophen-2-yl-quinolinato)(acetoacetonate)iridium(III) [$(tq)_2$Ir(III)(acac)] was synthesized for use in phosphorescent organic light-emitting diodes. The photophysical and electrochemical properties of the iridium(III) complex were characterized by UV-visible absorption, photoluminescence, and cyclic voltammetry. The maximum UV-visible absorption of $(tq)_2$Ir(acac) was observed at 289 nm. $(Tq)_2$Ir(acac) in dichloromethane showed its maximum photoluminescence (PL) emission at 629 nm. The optical band gap energy of $(tq)_2$Ir(III)(acac) was measured to be 2.11 eV, and the HOMO energy level of $(tq)_2$Ir(III)(acac) was calculated to be −5.08 eV. The T_1 state of $(tq)_2$Ir(III)(acac), calculated from the PL emission maximum (2.01 eV), was well matched with the T_1 level of CBP (2.6 eV). The phosphorescent organic light-emitting diode with a configuration of ITO/PEDOT:PSS/α-NPD/TCTA/CBP:$(tq)_2$Ir(III)(acac)(8 wt%)/BCP/Alq_3/LiF/Al was fabricated and characterized. Light emission from the device was observed at a low turn-on voltage of 4.3 V. The device showed a maximum brightness of 24,000 cd/m^2 at 16.3 V and an external quantum efficiency of 11.1% with a Commission Internationale de l'Eclairage (CIE) coordinate of (0.690, 0.310).

Keywords: Red Phosphorescent Organic Light-Emitting Diode, Iridium Complex.

1. INTRODUCTION

Recently many electrophosphorescent materials have been actively investigated to overcome the quantum-efficiency limit of fluorescence, because these materials can theoretically generate emission with 100% quantum efficiency using both triplet and singlet excitons.[1–4] By using triplet emitters with heavy metal cores and various organic ligands, strong spin-orbital coupling leads to enhanced mixing of singlets and triplets, which in turn, induces efficient intersystem crossing to overcome the internal quantum yield.[5–8] Many phosphorescent materials containing various heavy metals such as Ru(II),[9,10] Rh(III),[11–14] Re(I),[15] Ir(III),[16] and Pt(II,IV)[17–20] have been extensively developed to demonstrate red, green, and blue electrophosphorescent emission. In particular, cyclometalated iridium(III) complexes show strong electrophosphorescent emission with a high quantum efficiency.

Tsuboyama[21] and Colombo[21] investigated the optical properties of the iridium(III) complexes, iridium(III) bis(2-(2′-benzothienyl)pyridinato)(acetylacetonate) [$(thp)_2$Ir(III)(acac)] and iridium(III) bis(2-(2′-phenylpyridinato))(acetylacetonate) [$(ppy)_2$Ir(III)(acac)], respectively. On comparison, the UV absorption spectra of the two complexes were observed to be very similar; however, the difference in photoluminescence emissions were ca. 50 nm (562 nm for ($(thp)_2$Ir(III)(acac) and 516 nm for $(ppy)_2$Ir(III)(acac)). This demonstrated that a cyclometalated iridium(III) complex containing a thiophene moiety could have a longer emission wavelength than a phenyl group because the thiophene group has a better electron donating ability. Consequently, quinoline could also give better red-shifted emission than a pyridine ligand. Iridium(III)bis(2-(2′-phenylquinolyl))(acetylacetonate) [$(pq)_2$Ir(acac)] showed a maximum PL emission at 597 nm, which is more red-shifted than that for $(ppy)_2$Ir(III)(acac) (516 nm).[22]

Huang et al. reported the synthesis of quinoline-thiophene-based cyclometalated iridium(III) complex, bis(2-thiophen-2-yl-quinolinato)(acetoacetonate)iridium(III) [$(tq)_2$Ir(III)(acac)],[23] but detailed device results were not provided in the report. In this study, we independently

---

[*] Author to whom correspondence should be addressed.

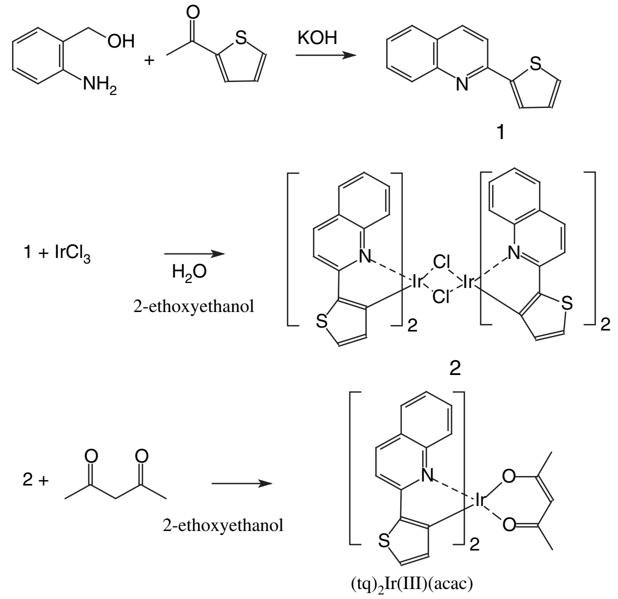

Fig. 1. Synthetic route to $(tq)_2Ir(acac)$.

synthesized the $[(tq)_2Ir(III)(acac)]$ and evaluated its luminescent properties as a red dopant for electrophosphorescent devices. The synthetic route and chemical structure of the $[(tq)_2Ir(III)(acac)]$ are shown in Figure 1.

2. EXPERIMENTAL DETAILS

2.1. Materials

2-Aminobenzylalcohol and 2-acetylthiophene were purchased from Aldrich. 2-Ethoxyethanol and potassium hydroxide were purchased from JUNSEI. Iridium(III) chloride was purchased from Alfa Aesar and 2,4-pentanedione was purchased from ACROS. All chemicals were used without further purification.

2.2. Measurements

Elemental analysis was performed using an EA 1110 Fisons analyzer. UV-visible and PL emission spectra were recorded using a Jasco V-530 and a Spex Fluorolog-3 spectrofluorometer. The film thickness was measured with a TENCOR AlphaStep 500 Surface Profiler. OLED devices were fabricated on glass substrates coated with indium-tin oxide (ITO). EL spectra of the devices were obtained using a Minolta CS-1000. Current–voltage–luminance (I–V–L) characteristics were recorded simultaneously with the measurement of the EL intensity by attaching the photospectrometer to a Keithley 238 and a Minolta LS-100 luminance detector. All measurements were carried out at room temperature under ambient atmosphere.

2.3. Synthesis of the Iridium Complex

2.3.1. Synthesis of 2-Thiophen-2-yl-Quinoline (1)

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.13 (t, 1 H), 7.45 (m, 2 H), 7.70 (m, 4 H), 8.03 (d, 1 H), 8.09 (d, 1 H); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 117.47, 125.78, 125.95, 127.02, 127.36, 127.98, 128.48, 129.05, 129.69, 136.48, 145.19, 147.90, 152.14.

2.3.2. Synthesis of Bis(2-Thiophen-2-yl-Quinolinato)(Acetylacetonate)Iridium(III) [(tq)$_2$Ir(III)(acac)]

^{1}H-NMR: (400 MHz, $CDCl_3$, δ): 1.60 (s, 6H), 4.83 (s, 1 H), 6.25 (s, 2 H), 7.10 (d, 4 H), 7.40 (m, 4 H), 7.68 (m, 4 H), 7.98 (d, 2 H), 8.36 (d, 2 H); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 29.98, 100.81, 156.93, 124.76, 125.77, 127.79, 128.79, 130.81, 134.34, 138.37, 139.38, 149.96, 153.48, 167.09, 185.73 Anal. Calcd for $C_{31}H_{23}IrN_2O_2S_2$(%): C, 52.30; H, 3.26; N, 3.94; S, 9.01. Found (%): C, 51.89; H, 3.16; N, 3.85; S, 8.77.

2.4. Fabrication of the EL Device

A phosphorescent OLED was fabricated to evaluate the synthesized iridium complex. The device was constructed with a configuration of ITO/PEDOT-PSS/α-NPD/TCTA/CBP:iridium(III) complex (8 wt%)/BCP/Alq_3/LiF/Al. Indium-tin-oxide (ITO) was used as a transparent anode; PEDOT:PSS, as a hole injection layer; α-NPD, as a hole transport layer; TCTA, as a hole transport layer or electron blocking layer; CBP, as a host; $(tq)_2Ir(III)(acac)$, as a triplet emitter; BCP, as a hole blocking layer; Alq_3, as an electron transport layer; and LiF/Al, as the compound cathode.

3. RESULTS AND DISCUSSION

3.1. Optical Properties

UV-visible absorption and PL emission spectra of $(tq)_2Ir(III)(acac)$ were measured in dichloromethane. The UV-visible spectrum of the Ir complex, including the 2-thiophene-2-quinolinato moiety, is presented in Figure 2. The strongest absorption band, caused by the $^1\pi$–π^* transition of the ligand attached to Ir(III), was observed at 289 nm. The medium band, shown at 352 nm, is from the spin-allowed singlet metal-to-ligand charge transfer (^{1}MLCT). The weakest band of around 500 nm is caused by the spin-forbidden triplet metal-to-ligand charge transfer (^{3}MLCT). The strong spin orbital coupling of Ir supports an absorbance in the triplet energy-transfer region of around 500 nm. The PL spectrum of the iridium(III) complex shows its emission maximum at 616 nm with full width at half maximum (FWHM) (45 nm) as shown in Figure 2.

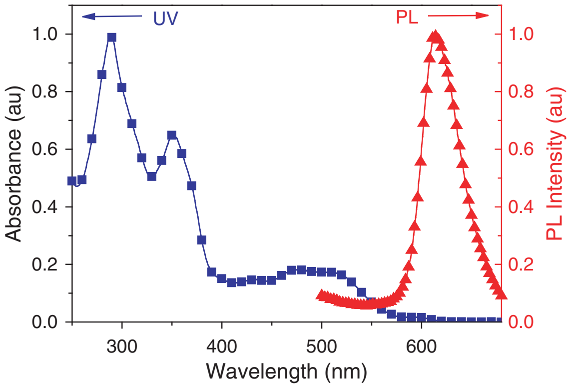

Fig. 2. UV-visible absorption and PL spectra of $(tq)_2Ir(III)(acac)$ in CH_2Cl_2.

3.2. Electrochemical Properties

The electrochemical analysis was performed using cyclic voltammetry (CV) to determine the band gap energy, and the HOMO and LUMO energy levels of $(tq)_2Ir(III)(acac)$. According to the literature, the HOMO level can be estimated from the onset oxidation potential using the following equation:

$$E_{\mathrm{HOMO}}\ (\mathrm{eV}) = -(E_{\mathrm{ox,\,onset}} + E_{1/2\mathrm{Ferr}}) \qquad (1)$$

E_{HOMO} represents the HOMO energy level of a specific chemical species, $E_{\mathrm{ox,onset}}$ is the onset potential of that species, and $E_{1/2,\,\mathrm{Ferr}}$ is the half oxidation potential of ferrocene. The energy levels of the LUMO and the HOMO-LUMO energy gap can be determined from spectroscopic and electrochemical data. The optical band gap of the molecule could be determined from the onset shown in the UV-PL spectra. CV data indicated that the onset oxidation potential ($E_{\mathrm{ox,\,onset}}$) of $(tq)_2Ir(III)(acac)$ was 0.35 eV. From the oxidation onset and the half oxidation potential of ferrocene (4.73 eV), the HOMO energy level of $(tq)_2Ir(III)(acac)$ was calculated to be −5.08 eV. The optical band gap energy of $(tq)_2Ir(III)(acac)$ was measured to be 2.11 eV (586 nm). These frontier orbital levels closely correspond to the energy levels for CBP (HOMO: −6.0 eV, LUMO: −2.9 eV), so the electronic-structure requirements for the OLED device could be satisfied. In addition, the T_1 state of $(tq)_2Ir(III)(acac)$, calculated from the PL emission maximum (2.01 eV), was well matched with the T_1 level of CBP (2.6 eV),[24] and this allows electrons to be transferred from CBP to $(tq)_2Ir(III)(acac)$.

3.3. EL Properties of the Fabricated Device

To investigate the light-emitting properties of the Ir(III) complex, phosphorescent OLEDs were fabricated with a configuration of ITO/PEDOT:PSS/α-NPD/TCTA/CBP:$(tq)_2Ir(III)(acac)$(8 wt%)/BCP/Alq_3/LiF/Al, as shown in Figure 3.

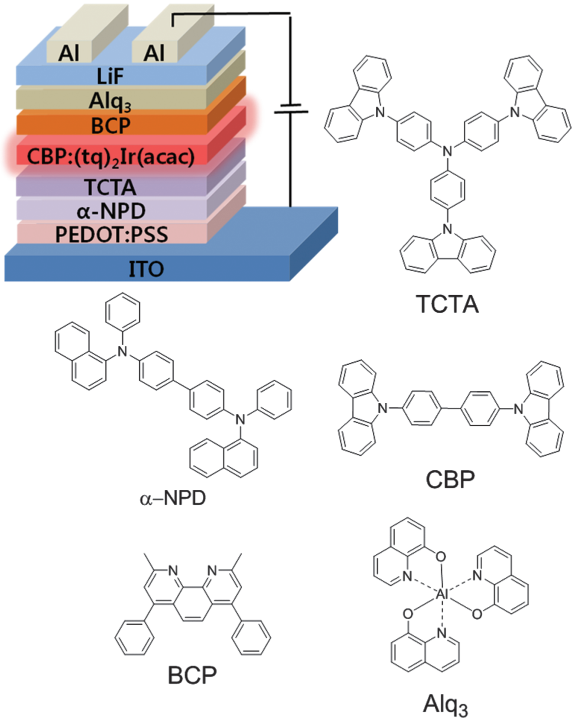

Fig. 3. The fabricated EL device structure and the materials used for each layer of the device.

The electroluminescent (EL) spectra of the fabricated device at different currents were measured to determine the spectral stability of the device. As shown in Figure 4, no significant spectral change was observed in the current range of 100 μA to 1 mA. The fabricated phosphorescent OLED showed very narrow FWHM (46 nm) as well as very good color purity as a red emitter. The fabricated device doped with 8 wt% of $(tq)_2Ir(III)(acac)$ showed the Commission Internationale de l'Eclairage (CIE) coordinate of (0.690, 0.310). This is close to that of standard red (0.670, 0.330).

The current–voltage–luminance (I–V–L) characteristic of the device was plotted in Figure 5 along with the current

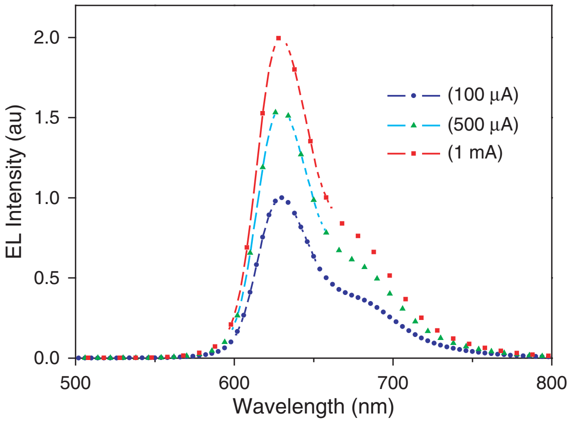

Fig. 4. EL spectra of the fabricated devices at different currents.

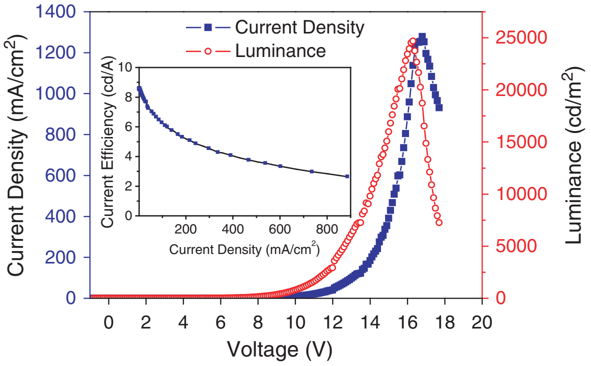

Fig. 5. *I–V–L* characteristics of the device and current efficiency versus current density of the device (inset).

Table I. Electrophosphorescence data for the device doped with 8 wt% Ir complex.

Complex	η_{ext} (%)	η_c (cd/A)	$V_{\text{turn-on}}$ (V)^a	Luminance (cd/m^2)^b	λ_{EL} (nm)	CIE (x, y)
$(tq)_2Ir(acac)$	11.1	8.6	4.3	24,673	629	(0.690, 0.310)

Notes: ^{a}This term was denoted as a bias at a brightness of 1 cd/m^2. ^{b}The maximum luminance of the device at 16.3 V.

efficiency curve shown in the inset. As in the case of most phosphorescent devices, a continual reduction in the efficiency was observed at a high current density, and this was caused by the collision between the triplet spins with long lifetime and field-induced exciton dissociation. The turn-on voltage (defined as a bias at a brightness of 1 cd/m^2) was 4.3 V. For the device, a maximum brightness of 24,673 cd/m^2 at 16.3 V was achieved, and the peak current efficiency was 8.6 cd/A at 1.5 mA/cm^2. The external quantum efficiency of the device was 11.1% at 2.6 mA/cm^2. The performance of the fabricated phosphorescent OLED is summarized in Table I.

4. CONCLUSIONS

In summary, we designed and synthesized a $(tq)_2Ir(III)$ (acac) complex that emits pure red light. Efficient and pure red organic phosphorescent devices using the iridium complex were fabricated and characterized. The results demonstrate that the iridium complex with the quinoline-thiophene ligand could produce pure red phosphorescence with a narrow FWHM.

Acknowledgments: This work was supported by the industrial strategic technology development program (No. 10039141, Development of core technologies for organic materials applicable to OLED lighting with high color rendering index) funded by the Ministry of Knowledge Economy (MKE, Korea), and a National Research Foundation (NRF) grant funded by the Korean government (MEST) (No. 2011-0011122).

References and Notes

1. M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature* 395, 151 (**1998**).
2. D. H. Hwang, M. J. Park, J. Ho. Eom, H. K. Shim, S. Lee, N. C. Yang, D. Lian, M. C. Suh, and B. D. Chin, *J. Nanosci. Nanotechnol.* 8, 4649 (**2008**).
3. J. H. Choi, C. H. Jung, J. Y. Kwon, H. J. Cho, J. H. Lee, J. I. Lee, H. Y. Chu, and D. H. Hwang, *Synth. Met.* 159, 1517 (**2009**).
4. J. H. Eom, D. Mi, M. J. Park, H. J. Cho, J. Lee, J. I. Lee, H. Y. Chu, H. K. Shim, and D. H. Hwang, *J. Nanosci. Nanotechnol.* 9, 7029 (**2009**).
5. M. J. Park, J. Kwak, J. Lee, I. H. Jung, H. Kong, C. Lee, D. H. Hwang, and H. K. Shim, *Macromolecules* 43, 1379 (**2010**).
6. M. E. Thompson, P. E. Burrows, and S. R. Forrest, *Curr. Opin. Solid State Mater. Sci.* 4, 369 (**1999**).
7. J. H. Seo, H. M. Kim, E. Y. Choi, D. H. Choi, J. H. Park, K. H. Lee, S. S. Yoon, and Y. K. Kim, *J. Nanosci. Nanotechnol.* 11, 1373 (**2011**).
8. J. Kavitha, S. Y. Chang, Y. Chi, J. K. Yu, Y. H. Hu, P. T. Chou, S. M. Peng, G. H. Lee, Y. T. Tao, C. H. Chien, and A. J. Carty, *Adv. Funct. Mater.* 15, 223 (**2005**).
9. P. Reveco, R. H. Schmehl, W. R. Cherry, F. R. Fronczek, and J. Selbin, *Inorg. Chem.* 24, 4078 (**1985**).
10. P. Reveco, J. H. Medley, A. R. Garber, N. S. Bhacca, and J. Selbin, *Inorg. Chem.* 24, 1096 (**1985**).
11. F. Barigelletti, D. Sandrini, M. Maestri, V. Balzani, A. Zelewsky, L. Chassot, P. Jolliet, and U. Maeder, *Inorg. Chem.* 27, 3644 (**1988**).
12. S. Sprouse, K. A. King, P. J. Spellane, and R. J. Watts, *J. Am. Chem. Soc.* 106, 6647 (**1984**).
13. Y. Ohsawa, S. Sprouse, K. A. King, M. K. DeArmond, K. W. Hanck, and R. J. Watts, *J. Phys. Chem.* 91, 1047 (**1987**).
14. M. G. Colombo, T. C. Brunold, T. Riedener, H. U. Gudel, M. Fortsch, and H. Burgi, *Inorg. Chem.* 33, 545 (**1994**).
15. P. Spellane, R. J. Watts, and A. Vogler, *Inorg. Chem.* 32, 5633 (**1993**).
16. K. Dedeian, P. I. Djurovich, F. O. Garces, G. Carlson, and R. J. Watts, *Inorg. Chem.* 30, 1685 (**1991**).
17. M. Gianini, A. Forster, P. Haag, A. von Zelewsky, and H. Stoeckli-Evans, *Inorg. Chem.* 35, 4889 (**1996**).
18. C. C. Deuschel and A. Zelewsky, *Inorg. Chem.* 26, 3354 (**1987**).
19. P. Jolliet, M. Gianini, A. Zelewsky, G. Bernardinelli, and H. S. Evans, *Inorg. Chem.* 35, 4883 (**1996**).
20. M. Gianini, A. Zelewsky, and H. S. Evans, *Inorg. Chem.* 36, 6094 (**1997**).
21. A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, and K. Ueno, *J. Am. Chem. Soc.* 125, 12971 (**2003**).
22. S. Lamansky, D. Murphy, F. A. Razzaq, R. Kwong, I. Tsyba, M. Bortz, R. Bau, and M. E. Thompson, *Inorg. Chem.* 40, 1704 (**2001**).
23. Q. Zhao, C. Y. Jiang, M. Shi, F. Y. Li, T. Yi, Y. Cao, and C. H. Huang, *Organometallics* 25, 3631 (**2006**).
24. P. Leriche, P. Frère, A. Cravino, O. Alévêque, and J. Roncali, *J. Org. Chem.* 72 , 8332 (**2007**).

Received: 1 May 2012. Accepted: 20 December 2012.