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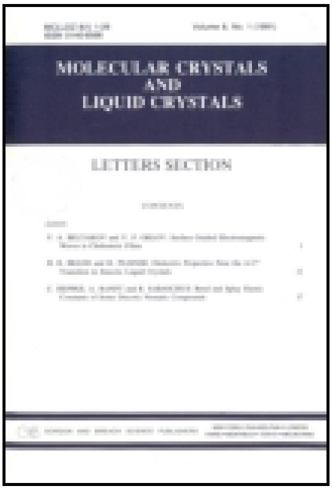

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Dual Emission from Organic Light-Emitting Diodes Using Deep Red Novel Phosphorescent Iridium(III) Complexes

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Dual Emission from Organic Light-Emitting Diodes Using Deep Red Novel Phosphorescent Iridium(III) Complexes

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A new phosphorescent Iridium complex, Ir(TMP-TT)$_2$(acac) was synthesized for organic light-emitting diodes (OLEDs). The ligand, TMP-TT, was synthesized by Suzuki coupling reaction, and Ir(TMP-TT)$_2$(acac) was synthesized by Nonoyama reaction. The UV-Visible absorption peak and shoulders of Ir(TMP-TT)$_2$(acac) were measured to be at 366, 420, 490 nm and its photoluminescence (PL) emission spectrums showed blue light-emission peaked 440 nm at 366 nm of UV absorption red light-emission peaked 638 nm at 490nm of UV absorption in chloroform solvent. Optoelectronic properties of device with the structure of ITO / PEDOT (40 nm) / TFB (30 nm) / RH-02 : Ir(TMP-TT)$_2$(acac) (30 nm : 10%) / Bphen (40 nm) / Liq / Al was measured. The relative intensity of the dual wavelength emissions at 540 nm and 638 nm varied with applying voltage. This study shows that Ir(TMP-TT)$_2$(acac) can be a strong dopant candidate for the white light-emitting OLEDs.

Keywords Ir(TMP-TT)$_2$(acac); yellow light-emitting; dual wavelength emitting; iridium(III) complex

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention in scientific and industrial utilization due to their merits in low operating voltage, wide range of self-emissive materials, high contrast, fast response time, wide-viewing angle, ultrathin structure and light weight [1–2]. In particular, heavy metal ions, such as Pt(III), Ru(III), and Ir(III) have been employed for the synthesis of high emission phosphorescent materials to utilize for the solar-cells and the OLEDs [3–4]. White organic light-emitting diodes (WOLEDs) can be applied to the backlights of liquid-crystal display (LCD), large area solid-state lighting and other type full color flat-panel display [5–7]. In order to achieve full range white color back light panels, triple emission layers from red, green and blue emitter are necesary [8–9]. However, this method usually results in processing complexity, high operational voltages, and undesired spectral variations due to a recombination zone shift. Alternatively, WOLEDs can be achieved by two complementary color emission such as blue emissive materials are mixed with yellow or orange color emission dyes [10–13].

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This method has advantages such as low material cost and simple fabrication process with reliability [14–15]. For these reasons, there exist a continuing need and innovative opportunity for the development of highly efficient yellow dopant materials for various OLED display applications [16–17].

In this work, we designed and synthesized a new deep red phosphorescent Iridium complex, Ir(TMP-TT)$_2$(acac), that emitted dual wavelengths in an adequate device configuration for the yellow OLEDs. In order to achieve yellow light emission with high device performance, device using Ir(TMP-TT)$_2$(acac) as a dopant was fabricated with a green host.

2. Experimental Details

2.1. *Synthesis*

The synthetic pathway of Ir(TMP-TT)$_2$(acac) was shown in Fig. 1. 2-bromo-4-(trifluoromethyl)pyridine and dithieno[3,2-*b*:2′,3′-*d*]thiophen-2-ylboronic acid were obtained from Matrix Scientific and TCI, respectively. Iridium(III) chloride hydrate and Acetylacetone were purchased from Aldrich. These chemicals used without further purification. 2-(dithieno[3,2-*b*:2′,3′-*d*]thiophen-2-yl)-4-(trifluoromethyl)-pyridine (TMP-TT, I) was obtained from the reaction of 2-bromo-4-(trifluoromethyl)pyridine with dithieno[3,2-*b*:2′,3′-*d*]thiophen-2-ylboronic acid by Suzuki coupling. 2-bromo-4-(trifluoromethyl)pyridine (2.0 g, 8.85 mmol), dithieno[3,2-*b*:2′,3′-*d*]thiophen-2-ylboronic acid (2.4 g, 9.99 mmol), Aliquat336(1.785 ml, 3.54 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.409 g, 0.354 mmol) were placed in a mixture of tetrahydrofuran (160 ml), and 2N sodium carbonate aqueous solution (100 ml). The reaction mixture was heated to reflux for 6 hours at 360 K. The reaction mixture was washed with ethanol and water several times and dried in vacuum to yield light-yellow solid product with 69.5% yield. The cyclometalated iridium(III) μ-chloride-bridged dimer, [(TMP-TT)$_2$Ir(μ-Cl)]$_2$ (II) was prepared using a slight modification of the Nonoyama reaction. Iridium(III) chloride hydrate (1.49 g, 5 mmol) and TMP-TT (2.0 g, 5.858 mmol) was added a 3 : 1 mixture of 2-ethoxyethanol and water (80 ml). The mixture was refluxed for overnight at 398 K and cooled to room temperature. The solution was cooled to room temperature, and the precipitate was collected and washed with water and hexane several times to afford brown powder (compound II, yield : 41.3%). And then, acetylacetone (0.27 g, 2.72 mmol), sodium carbonate (0.16 g, 1.51 mmol), and compound II (2.2 g, 0.61 mmol) were dissolved in 2-ethoxyethanol (60 ml) and refluxed under nitrogen atmosphere for overnight at 408 K. After cooling to room temperature, the crude reaction product was poured onto water, extracted with dichloromethane, and concentrated under vacuum. The product was purified by column chromatography (silica gel, CH_2Cl_2) to obtain a dark-brown powder with yield of 78%. ^{1}H-NMR (500 MHz,

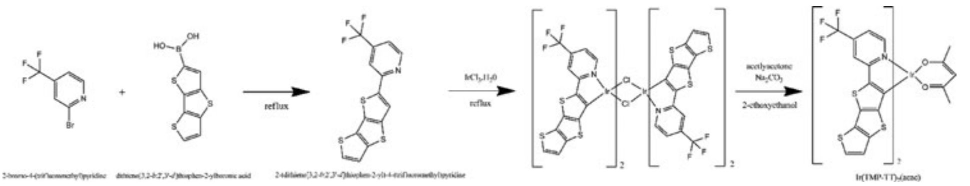

Figure 1. The synthetic pathway of Ir(TMP-TT)$_2$(acac).

Acetone-d6) d (ppm) 8.816 (d, 2H, pyridine), 8.349 (d, 2H, pyridine), 7.704 (d, 2H, pyridine), 7.597 (d, 2H, thiophene), 7.306 (d, 2H, thiophene). 2.077(s, 2H, methyl); ^{13}C-NMR (125 MHz, Acetone-d6) d (ppm) 179.71, 152.30, 149.75, 147.74, 142.76, 141.47, 137.28, 131.20, 125.35, 125.26, 124.43, 123.71, 122.10, 119.95, 21.84.

2.2. Fabrication of Device and Measurement

The device with the structure of ITO / PEDOT (40 nm) / TFB (30 nm) / RH-02 : Ir(TMP-TT)$_2$(acac) (30 nm : 10%) / Bphen (40 nm) / Liq / Al was fabricated. PEDOT and TFB were spin-coated on indium tin oxide (ITO) substrate and emission layer (EML, Ir(TMP-TT)$_2$(acac) doped in RH-02) was vacuum deposited on on top of HTL films. Liq and Bphen deposition was followed. The rates of spin-coating were 500 rpm for 3 seconds, and 2000~4000 rpm for 30 seconds. And the deposition rates were 1.0~1.1 Å/sec for Bphen and Liq, 0.1 Å /sec for lithium quinolate (Liq) and 10 Å/sec for aluminum (Al) cathode. Figure 2 shows the Highest occupied molecular orbital(HOMO) and Lowest occupied molecular orbital(LUMO) energy levels of materials used in fabricating the device in this study. The EL emission spectra were measured using Perkin Elmer LS-55 and device performance was recorded on Keithley 236 and CHROMA METER CS-100A instruments.

3. Results and Discussion

3.1. Photophysical Properties

Figure 3 shows the UV–visible absorption and PL emission spectrum of the iridium complex in chloroform solution at room temperature. The strong Ir(TMP-TT)$_2$(acac) absorption spectrum exhibited a peak at 366 nm which can be assigned to the spin-allowed $^1\pi$–π^* transition from the cyclo-metalated ligand TMP-TT. The broad absorption bands at 410 nm

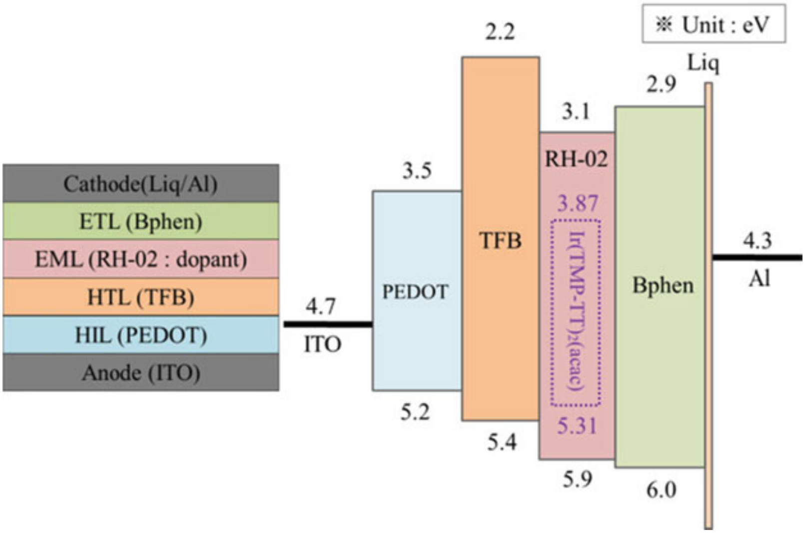

Figure 2. The structure of device and energy band-gap of materials used in the device.

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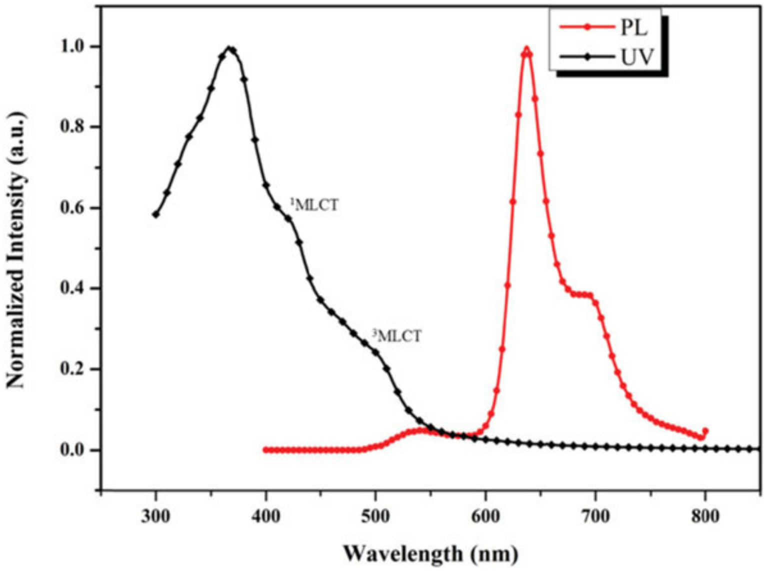

Figure 3. UV–visible absorption, and photoluminescence spectrum of Ir(TMP-TT)$_2$(acac) in CHCl$_3$ solution.

and 490 nm were assigned to the spin-allowed metal-to-ligand (^{1}MLCT) transition and the spin-forbidden metal-to-ligand (^{3}MLCT) transition, respectively. The Ir(TMP-TT)$_2$(acac) give out a light caused by ^{3}MLCT energy transition from LUMO to HOMO, The ^{3}MLCT absorption bands of Ir(TMP-TT)$_2$(acac) ranged near 490 nm, exhibiting good spectral overlap with the PL emission band (540 nm) of RH-02. In particular, TMP-TT has ligand–centered (LC) emission band at near 482 nm. Both ^{3}MLCT and LC absorptions provided opportunity for green and deep red emission of Ir(TMP-TT)$_2$(acac). The partial spectral overlap between RH-02 and Iridium complex indicated that the Főrster from ligand centered energy transfer or Dexter energy transfer from ^{3}MLCT from the host to the iridium complex dopants and emission from the host were possible. The maximum PL emission of Ir(TMP-TT)$_2$(acac) was observed at 638 nm at room temperature. The cross point of the ^{3}MLCT absorption and PL emission spectrum was assigned to correspond to the first triplet excited energy (T$_1$) level.

3.2. *Electroluminescent Properties*

The EL spectra of the device measured at 8.0 V was observed as shown in the Figure 4(a). Device exhibited EL emission peaks at 545 nm, and 638 nm. The energy transfer from the RH-02 host to the Ir(TMP-TT)$_2$(acac) dopant emitter in the EML of the device is dependent on the overlap of emission and absorption peaks of host and guest and the effective confinement of charge carriers and excitons. Figure 4(b) represented Commission Internationale de I'Eclairage (CIE$_{xy}$) of chromaticity of device with applied voltage, respectively. As shown in Figure 5(b), the variation of CIE$_{xy}$ coordinates of device was considerable from (0.545, 0.454) at 4 V to (0.475, 0.479) at 10 V. The EL spectra showed that green emitting peak was increased as the applying voltage was increased and orange emission of device was gradually shifted to yellowish green with increasing applied voltage. This phenomena means that the increase of applied voltages make a energy transfer from lower energy of

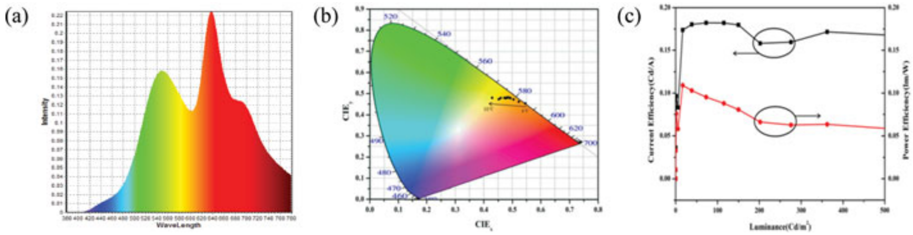

Figure 4. (a) EL spectra of Ir(TMP-TT)$_2$(acac) (10% doped in RH-02) device, (b) 1931 CIE chromaticity diagram exhibiting variation of chromaticity of device with increase of applied voltage, and (c) Current and Power efficiency versus Luminance of device.

red light emission(638 nm, ^{3}MLCT energy level) to higher energy of green light emission(545 nm, ligand centered energy level). As the applied voltages increase, the light color of the Ir(TMP-TT)$_2$(acac) shifted to short wavelength due to the stronger ligand centered energy transfer. Thus, It presents that the emitting color of the device can be controlled by applied voltage. The maximum luminance of 181.7 cd/m^2 was observed at 8.0 V. Figure 4(c) showed current efficiency (cd/A) and power efficiency (lm/W) with luminance variation of device. Maximum current efficiency and power efficiency were measured to be 0.057 cd/A at 6.0 V(152.43 mA/cm^2) and 0.311 lm/W at 5.5V (104.17 mA/cm^2), respectively.

4. Conclusion

We demonstrated the OLEDs which showed dual emission of green (545 nm) and red (638 nm) using red-phosphorescence iridium complex hosted by RH-02. The emission was gradually shifted orange to yellow with increasing applied voltage. Device using Ir(TMP-TT)$_2$(acac) as a dopant of emitting layer was measured. Maximum luminance of device was measured to be 181.7 cd/m^2(at 8.0 V). Maximum current and power efficiency were observed to be 0.057 cd/A at 6 V(152.43 mA/cm^2) and 0.311 lm/W at 5.5V (104.17 mA/cm^2), respectively. The device emitted warm white light corresponding to CIE$_{xy}$ coordinates of (0.545, 0.454) at 4.0 V, (0.503, 0.473) at 5.0 V, (0.486, 0.482) at 6.0 V, (0.480, 0.481) at 7.0 V, (0.475, 0.479) at 8.0 V, respect tively. As the applied voltage was increased, orange emission of device was gradually shifted to near yellow. Therefore, it was concluded that Ir(TMP-TT)$_2$(acac) can be a strong candidate dopant for WOLEDs.

Acknowledgment

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References

[1] Reineke, S., Lindner, F., Schwartz, G., Seidler, N., Walzer, K., Lussem, B., & Leo, K. (2009). *Nature*, *459*, 234.
[2] D'Andrade, B. W., & Forrest, S. R. (2004). *Adv. Mater.*, *16*, 1585.
[3] Chi, Y., & Chou, P. T., (2007). *Chem. Soc. Rev.*, *36*, 1421.
[4] Kavitha, J., Chang, S. Y., Chi, Y., Yu, J. K., Hu, Y. H., Chou, P. T., Peng, S. M., Lee, G.-H., Tao, Y. T., Chien, C.-H., & Carty, A. J. (2005). *Adv. Funct. Mater.*, *15*, 223.

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[5] Lim, S. H., Ryu, G. Y., Kim, G. Y., Seo, J. H., Kim, Y. K., & Shin, D. M. (2008). *Mol. Cryst. Liq. Cryst.*, *491*, 40.

[6] Lee, H. K., Seo, J. H., Kim, J. H., Koo, J. R., Lee, K. H., Yoon, S. S., & Kim, Y. K. (2006). *JKPS*, *49*, 1052.

[7] Xiaoa, J., Yaob, Y., Denga, Z., Wangb, X., & Lianga, C. J. (2007). *J. Lumin.*, *122*, 639.

[8] Ryu, G. Y., Seo, J. H., Park, J. H., Lee, S. G., Lim, S. H., Shin, D. M., & Kim, Y. K. (2009). *Mol. Cryst. Liq. Cryst.*, *499*, 75.

[9] Lin, M. F., Wang, L., Wong, W. K., Cheah, K. W., TAM, H. L., Lee, M. T., Ho, M. H., & Chen, C. H. (2007). *Appl. Phys. Lett.*, *91*, 073517.

[10] Sasabe, H., Takamatsu, J. I., Motoyama, T., Watanabe, S., Wagenblast, G., Langer, N., Molt, O., Fuchs, E., Lennartz, C., & Kido, J. (2010). *Adv. Mater.*, *22*, 5003.

[11] Park, J. S., Yu, J. H., Jeon, W. S., Son, Y. H., Kulshreshtha, C., & Kwon, J. H. (2011). *J. Inf. Disp.*, *12*, 51.

[12] Son, Y. H., Park, Mi. J., Kim, Y. J., Yang, J. H., Park, J. S., & Kwon, J. H. (2013). *Org. Electron. 14*, 1183.

[13] Kim, Y. J., Son, Y. H., & Kwon, J. H. (2013). *J. Inf. Disp.*, *14*, 109.

[14] Ryu, G. Y., Shin, S. E., Seo, J. H., Park, J. S., Chang, H. M., Shin, S., Kim, Y. K., & Shin, D. M. (2011). *J. Nanosci. Nanotechno.*, *11*, 4430.

[15] Wang, Q., Ding, J., Ma, D., Cheng, Y., Wang, L., Jing, X., & Wang, F. (2009). *Adv. Funct. Mater.*, *19*, 84.

[16] Yu, X. M., Zhou, G. J., Lam, C. S., Wong, W. Y., Zhu, X. L., Sun, J. X., Wong, M., & Kwonk, H. S. (2008). *J. Organomet. Chem.*, *693*, 1518.

[17] Choy, W. C. H., Wu, Y. S., Chen, C. H., & Cheah, K. W. (2005). *Appl. Phys. A.*, *81*, 517.

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