

## Phosphorescence of red Os ( fptz ) 2 ( P Ph 2 Me ) 2 doped organic light-emitting devices with n and p hosts

Tswen-Hsin Liu, Shih-Feng Hsu, Meng-Hung Ho, Chi-Hung Liao, Yao-Shan Wu, Chin H. Chen, Yung-Liang Tung, Pei-Chi Wu, and Yun Chi

Citation: *Applied Physics Letters* **88**, 063508 (2006); doi: 10.1063/1.2172405

View online: <http://dx.doi.org/10.1063/1.2172405>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/88/6?ver=pdfcov>

Published by the *AIP Publishing*

---

### Articles you may be interested in

High spontaneous polarization in Pb Ti O 3 – Bi Me O 3 systems with enhanced tetragonality

*Appl. Phys. Lett.* **91**, 171907 (2007); 10.1063/1.2794742

Cumulative contributions of 3 s – n p ( n 3 ) transitions in comparing O atom densities in low-pressure Ar – O 2 and He – O 2 glow discharges

*Appl. Phys. Lett.* **89**, 171501 (2006); 10.1063/1.2364464

Electronic structures and spectroscopic properties of nitrido-osmium(VI) complexes with acetylide ligands [ Os N ( C C R ) 4 ] R H , C H 3 , and Ph by density functional theory calculation

*J. Chem. Phys.* **124**, 144309 (2006); 10.1063/1.2189220

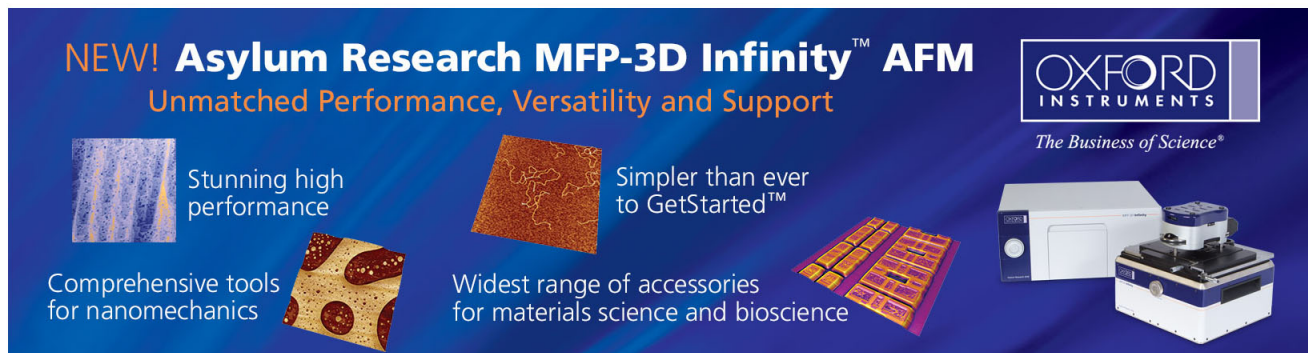
Theoretical study of the effects of F to Cl chemical substitution on the electronic structure and the luminescence properties of Cs 2 Ge F 6 : Os 4 + and Cs 2 Zr Cl 6 : Os 4 + materials

*J. Chem. Phys.* **124**, 124315 (2006); 10.1063/1.2180772

Classification of transition temperature behavior in ferroelectric Pb Ti O 3 – Bi ( Me Me ) O 3 solid solutions

*J. Appl. Phys.* **99**, 024106 (2006); 10.1063/1.2163986

---



**NEW! Asylum Research MFP-3D Infinity™ AFM**  
Unmatched Performance, Versatility and Support

**OXFORD INSTRUMENTS**  
*The Business of Science®*

Stunning high performance

Simpler than ever to GetStarted™

Comprehensive tools for nanomechanics

Widest range of accessories for materials science and bioscience

*Asylum Research*

## Phosphorescence of red Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> doped organic light-emitting devices with *n* and *p* hosts

Tswen-Hsin Liu,<sup>a)</sup> Shih-Feng Hsu,<sup>b)</sup> Meng-Hung Ho,<sup>b)</sup> Chi-Hung Liao,<sup>b)</sup> Yao-Shan Wu,<sup>b)</sup> and Chin H. Chen<sup>c)</sup>

Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China, and AU Optronics Corporation, Hsinchu 300, Taiwan, Republic of China

Yung-Liang Tung, Pei-Chi Wu, and Yun Chi

Department of Chemistry, National Tsing Hua University, Hsinchu 300, Taiwan, Republic of China

(Received 14 March 2005; accepted 19 December 2005; published online 8 February 2006)

We have applied a sterically-hindered red phosphorescent dopant Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> [fptz=3-trifluoromethyl-5-(2-pyridyl)-1,2,4-triazole, PPh<sub>2</sub>Me=phosphine ligand] in *p*-type 4,4'-*N,N'*-dicarbazole-biphenyl or *n*-type *bis*(2-methyl-8-quinolinolato)(*p*-phenylphenolato) aluminum host and found that the latter produced higher luminance efficiency at lower doping concentration. We present a model to rationalize this phenomenon in which the *n*-type host impedes hole transport, which leads to narrower recombination zone near the hole transport layer/emission layer interface than the *p*-type host, hence, more effective recombination. © 2006 American Institute of Physics. [DOI: 10.1063/1.2172405]

One of the key developments in the advance of modern organic light-emitting devices (OLEDs) technology is the discovery of electrophosphorescence which lifts the upper limit of the internal quantum efficiency of the usual fluorescent dopant-based devices from 25% to nearly 100%.<sup>1,2</sup> To ensure effective proximity for complete energy transfer, the dopant concentration in phosphorescent OLEDs is always higher than that of the fluorescent OLEDs.<sup>3-5</sup> A short-distance Dexter Energy transfer ( $\sim 10 \text{ \AA}$ ) between the phosphorescent host and dopant has been often used to rationalize this phenomenon.<sup>6</sup> Nevertheless, a high doping concentration of phosphorescent dopants can also provide better overlap of ligand  $\pi$  orbitals, which will promote the direct recombination of electron-hole pairs on dopants.<sup>7</sup> In this case, the role of the host will not be the dominant excitation energy source as in the energy transfer model, rather a mere medium for carrier transport.

In this study, we used a highly sterically hindered red phosphorescent dye Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> [fptz=3-trifluoromethyl-5-(2-pyridyl)-1,2,4-triazole, PPh<sub>2</sub>Me=phosphine ligand] as the dopant together with a *p*-type host 4,4'-*N,N'*-Dicarbazole-biphenyl (CBP) or *n*-type host *bis*(2-methyl-8-quinolinolato)(*p*-phenylphenolato) aluminum (BALq) for our emission layer. By studying the electroluminescence (EL) characteristics of the dopant in the hosts of different charge transport natures, we expect to provide more insights about the relationship between phosphorescent dopant and host and attempt to elucidate the emissive mechanism.

The structure, purity, chemical, energy levels, and optical properties of Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> has been verified and disclosed in other publication.<sup>8</sup> Figure 1 depicts the absorption and luminance spectrum of Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> in

CH<sub>2</sub>Cl<sub>2</sub>. The strong absorption in the UV region are assigned to the spin-allowed  $^1\pi\pi^*$  transition of fptz ligands, owing to their spectral similarity to the free fptz anion. The next lower energy absorption can be ascribed to a typical spin-allowed metal to ligand charge transfer ( $^1\text{MLCT}$ ) transition, while two absorption bands extending into visible region are associated with the spin-orbit coupling enhanced  $^3\pi\pi^*$  and  $^3\text{MLCT}$  transitions. Further luminance properties (*vide infra*) support  $^3\text{MLCT}$  to be in the lowest triplet state with peak wavelength at 540 nm.

Figure 2 shows our experimental results of the device structure: indium tin oxide (75 nm)/copper phthalocyanine (CuPc) (15 nm)/1,4-*bis*[*N*-(1-naphthyl)-*N'*-phenylamino]biphenyl-4,4' diamine (NPB), (60 nm)/host: *x*% Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> (40 nm)/BALq (15 nm)/tris(8-hydroxyquinolato)aluminum (Alq<sub>3</sub>), (20 nm)/LiF (1 nm)/Al(200 nm). The CuPc, NPB, BALq, and Alq<sub>3</sub> were used as the hole injection, hole transport, hole blocking material,<sup>9</sup> and electron transport material, respec-

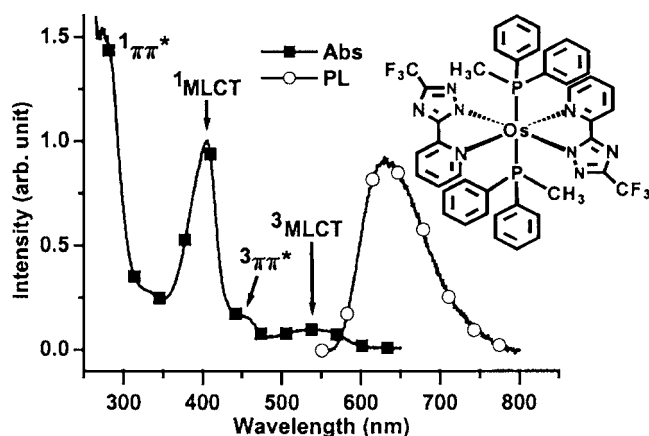


FIG. 1. UV-visible absorption (■) and normalized emission spectrum (○) of Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Inset: molecular structure of Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub>.

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: peteliu@auo.com

<sup>b)</sup> Also at: Department of Applied Chemistry.

<sup>c)</sup> Also at: Display Institute.

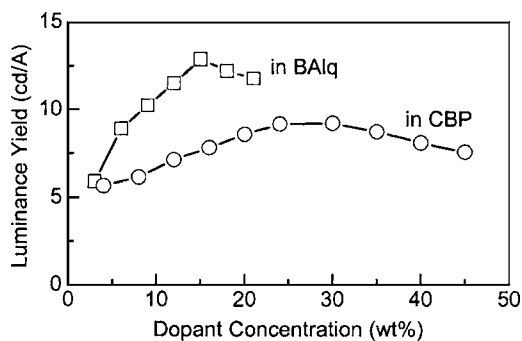


FIG. 2. Efficiency dependency on  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  concentration in CBP ( $\square$ ) and BAQ ( $\circ$ ) hosts.

tively. It is apparent from Fig. 2 that when  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  is doped in CBP (device A),  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  has the property of resistance to concentration quenching and the sustaining of its EL luminance efficiency ( $>8.5$  cd/A) over a wide range of doping concentration from 20% to 35%. However, when doped in *n*-type BAQ (device B), the luminance efficiency can reach as high as 12.8 cd/A at the current density of 20 mA/cm<sup>2</sup>, which is obviously higher than that with CBP as the host. Furthermore, a much lowered doping concentration of 15% is required for reaching the maximum luminance efficiency when using BAQ as the host as compared to that of 30% in CBP. In terms of color and operation voltage, both devices show a Commission Internationale d'Éclairage (CIE) coordinates of (0.65, 0.35), but the operation voltage of the CBP-based device is approximately 1 V lower than that of the BAQ-based device.

The photoluminescence spectra of BAQ and CBP under room and low temperature are illustrated in Fig. 3. By looking at Fig. 3, there appears a small shoulder under low temperature at 430–580 nm which is the triplet energy peak of CBP in addition to the singlet energy peak at  $\sim 360$  nm which will blue shift under low temperature.<sup>5,9</sup> Moreover, the

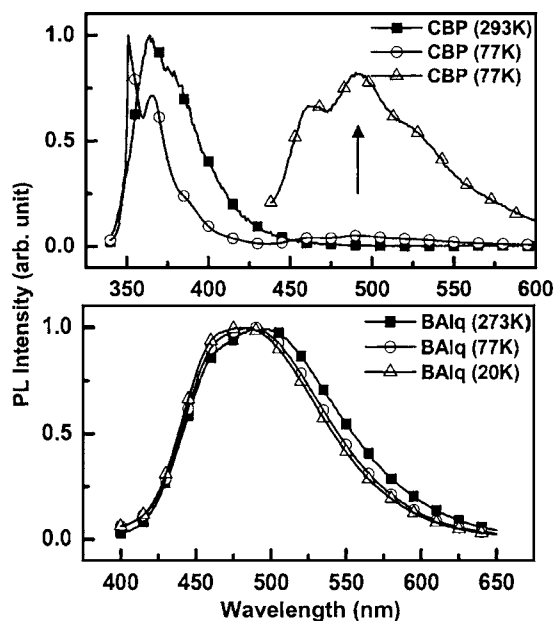


FIG. 3. The photoluminescent spectra of CBP (top figure) and BAQ (bottom figure) under room and low temperatures. CBP: 293 K ( $\blacksquare$ ), 77 K ( $\circ$ ), amplified phosphorescent signals at 77 K ( $\triangle$ ); BAQ: 293 K ( $\blacksquare$ ), 77 K ( $\circ$ ), 22 K ( $\triangle$ ).

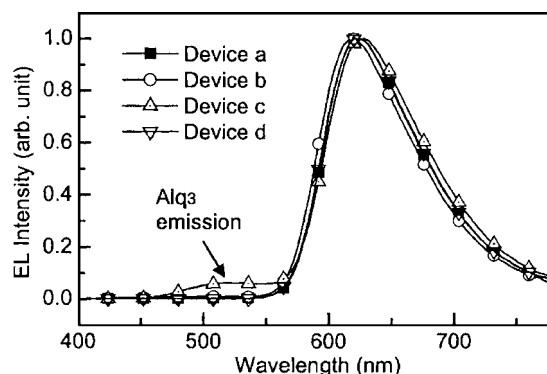


FIG. 4. EL spectra of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  doped devices driven at 20 mA/cm<sup>2</sup>. The spectrum of CBP-based device without hole-blocking layer (device D) reveals Alq<sub>3</sub> emission at  $\sim 520$  nm.

fluorescent spectrum of CBP overlaps with the two spin-allowed absorption transitions of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  at 290 and 400 nm. According to the energy transfer model, the 25% singlet energy of CBPs excitons could effectively transform into the singlet energy of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$ , which then generates phosphorescence via internal system crossing process. Not only that, the triplet energy of CBPs excitons is higher than the transition energy due to <sup>3</sup>MLCT in  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$ . Therefore, the triplet energy of CBPs excitons can successfully transform into that of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  as well. On the other hand, the situation is totally different in the case of BAQ. First, the fluorescent spectrum of BAQ at 490 nm has shown poor overlap with the spin-allowed singlet transition of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$ . Second, the photoluminescent spectra of BAQ under room and low temperatures seem to be identical (even at 22 K). We believe this is attributed to the very weak triplet energy of BAQ, which gives signal that is undetectable by the instrument. If this is the case, the energy transfer from the host to dopant mentioned previously will not be applicable to explain the observation depicted in Fig. 2 since CBP obviously has higher probability to undergo energy transfer but inconsequently has lower luminance efficiency.

In order to clarify the emission mechanism of doped OLEDs, we have designed the devices without hole blocking layer (devices C and D). The hole-blocking layer of 15 nm BAQ was removed and replaced by Alq<sub>3</sub> of the same thickness. The doping concentrations for both devices are optimized for achieving the highest luminance efficiency. The EL spectra and detailed EL performance of the devices are shown in Fig. 4 and Table I, respectively.

From Fig. 4, the Alq<sub>3</sub> emission at  $\sim 520$  nm can be observed besides the  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  emission at 624 nm for the CBP-based device without hole-blocking layer, therefore, the CIE coordinates of device C were blueshifted to (0.63, 0.36). Significant drop in luminance efficiency to 2.4 cd/A can be seen as well from Table I for the CBP-based device without hole-blocking layer and the operation voltage is  $\sim 2$  V lower than that of the device with hole-blocking layer. But these phenomena do not exist in the case of BAQ-based devices. The luminance efficiency of device D is well above 12 cd/A at 20 mA/cm<sup>2</sup> and the color saturation remains unchanged at CIE=(0.65, 0.34) due to no Alq<sub>3</sub> emission was observed. The operation voltages of the BAQ-based devices are very similar. Based on these evidences, it is clearly shown that the removal of the hole-blocking layer

TABLE I. EL performance of Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> doped devices driven at 20 mA/cm<sup>2</sup>.

Device	A	B	C	D
Host	CBP	BAIq	CBP	BAIq
Dopant (wt %)	30	15	30	15
HBL	BAIq	BAIq	None	None
Voltage (V)	7.8	8.7	5.9	9.0
Luminance (cd/m <sup>2</sup> )	1832	2575	474	2416
Luminance Yield (cd/A)	9.2	12.8	2.4	12.1
<i>x</i>	0.65	0.65	0.63	0.65
CIE 1931 <i>y</i>	0.34	0.35	0.35	0.34
Power efficiency (lm/W)	3.6	4.7	1.3	4.2
EQE (%)	8.9	11.1	2.4	11.6

will cause the holes to diffuse/drift into Alq<sub>3</sub>/cathode without recombining radiatively in the emission layer and the formed triplet excitons also have a chance to diffuse into Alq<sub>3</sub> layer, which will then transfer to the irradiative Alq<sub>3</sub> triplet energy level. On the contrary, the removal of the hole-blocking layer did not have much impact on the efficiency of the BAIq-based device since the recombination zone is narrower and near the hole transport/emission layer interface.

We conclude that the direct recombination of electron-hole pairs on dopants may be the dominate electroluminescent mechanism in red Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> doped devices. Our rationalization is that the *n*-type host will impede hole transport, which leads to a narrow recombination zone near the hole transport layer/emission layer interface. The con-

finement of the holes leads to narrow recombination zone, hence, more effective recombination. On the contrary, the *p*-type host will assist holes to transport deeper in the emission layer, which makes less restrain for carrier recombination. As the result, reactivity of recombination is reduced in the emission layer, hence lower efficiency.

This work was supported by the Ministry of Education under a Grant from the PPAEU (No. 91-E-FA04-2-4-B) and the National Science Council of Taiwan, Republic of China. The authors thank e-Ray Optoelectronics Technology Co., Ltd., Chungli, Taiwan for generously supplying most of the OLED materials used in this study.

- <sup>1</sup>M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature (London)* **395**, 151 (1998).
- <sup>2</sup>A. Köhler, J. S. Wilson, and R. H. Friend, *Adv. Mater. (Weinheim, Ger.)* **14**, 701 (2002).
- <sup>3</sup>M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **75**, 4 (1999).
- <sup>4</sup>C. Adachi, M. A. Baldo, S. R. Forrest, S. Lamansky, M. E. Thompson, and R. C. Kwong, *Appl. Phys. Lett.* **78**, 1622 (2001).
- <sup>5</sup>C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **79**, 2082 (2001).
- <sup>6</sup>M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals* (Oxford University Press, Oxford, 1982).
- <sup>7</sup>K. Yamashita, J. Futenma, T. Mori, and T. Mizutani, *Synth. Met.* **111**, 87 (2000).
- <sup>8</sup>Y. L. Tung, P. C. Wu, C. S. Liu, Y. Chi, J. K. Yu, Y. H. Hu, P. T. Chou, S. M. Peng, G. H. Lee, Y. Tao, A. J. Carty, C. F. Shu, and F. I. Wu, *Organometallics* **23**, 3745 (2004).
- <sup>9</sup>M. A. Baldo and S. R. Forrest, *Phys. Rev. B* **62**, 10958 (2000).