

# High performance hybrid white OLEDs based on new platinum complexes and new blue fluorescence host

Anurach Poloek,<sup>a,b,c</sup> Chieh Wang,<sup>b,d</sup> Chiao-Wen Lin,<sup>b</sup> Chin-Ti Chen,<sup>\*b</sup> and Chao-Tsen Chen,<sup>\*a</sup>

<sup>a</sup>Department of Chemistry, National Taiwan University, Taipei, Taiwan 10617, R. O. C.

<sup>b</sup>Institute of Chemistry, Academia Sinica, Taipei, Taiwan 11529, R. O. C.

<sup>c</sup>Nano Science and Technology Program, TIGP, Academia Sinica, Taipei, Taiwan 11529, R. O. C.

<sup>d</sup>Department of Chemistry, National Chiao Tung University, Hsinchu, Taiwan 300, R.O.C.

## ABSTRACT

A new series of platinum complexes containing 4-hydroxy-1,5-naphthyridine derivative with different substituents such as methyl, dimethyl, phenyl, phenoxy, dimethyl amine, piperidine, morpholine, phenoxazine or carbazole unit as the primary ligand and 2-(2,4-difluorophenyl)pyridine as the secondary ligand were synthesized and characterized. Single crystal X-ray diffraction studies of **FPtOPhND**, **FPtCzND** and **FPtdmaND** showed trans-coordinated in distorted square-planar geometry. Their photophysical properties and electrochemical properties were examined. All platinum complexes in these series exhibited dual emissions not only in solution but also in solid state thin film. Employing CBP or 4P-NPD as host material, high efficiency monochromatic and high quality hybrid white organic light emitting diodes (WOLEDs) were achieved with the single platinum complex dopant device, a relatively simple device configuration.

**Keywords:** hybrid white OLEDs, platinum complex, high CRI, phosphorescence.

## 1. INTRODUCTION

In the past few decades, white organic light-emitting diodes (WOLEDs) have drawn increasing attention because of their potential applications in full color flat-panel displays and solid-state lighting.<sup>1,2</sup> In order to achieve white light emission, two or three emitters are generally required in device configuration. Particularly, three phosphorescent dopants (red, green, blue) have been employed to realize high efficiency and high quality WOLEDs.<sup>3,4</sup> Nonetheless, such a strategy leads to the complicated structure and difficulty getting of color balance. In addition, blue phosphorescent emitters still suffer from the lack of stability. To simplify WOLED fabrication, utilizing only two complementary phosphorescent emitters, either blue and yellow or blue and orange,<sup>5-8</sup> is a reasonable alternative to achieve white EL. In order to achieve stable WOLEDs and yet having easy fabrication, fluorescence (F)-phosphorescence (P) hybrid WOLEDs have been demonstrated before.<sup>9</sup> Recently, the hybrid of blue fluorescence and yellow<sup>10,11</sup> or orange<sup>12,13</sup> phosphorescence has attracted much attention in generating white EL with long stability and simplified device structure. However, most of such hybrid WOLEDs have been based on iridium complex phosphorescent dopant. Although F-P hybrid WOLEDs with iridium complexes exhibit relatively high EL efficiency, insufficient CRI less than 80 is always the results. To improve the quality (i.e., CRI) of F-P hybrid WOLED with a simple device configuration, platinum complex is a better choice than iridium complex because square planar molecule geometry of platinum complex can facilitate molecular aggregate and excimer formation that exhibits red-shifted emission different from the complex itself. Such emission feature of platinum complex easily broadens the EL spectra and high quality virtual sunlight often can be achieved.

Herein, we report the synthesis, and characterization, as well as photophysical and electrochemical properties of a new series of heteroleptic platinum complexes bearing 4-hydroxy-1,5-naphthyridine derivatives<sup>14</sup> and 2-(2,4-difluorophenyl)pyridine (F)<sup>15</sup> as the mixed ligand (Figure 1). With conventional 4,4'-N,N'-dicarbazolebiphenyl (CBP) or the new 4P-NPD as the host material, application of FPtXND for OLEDs showing monochromatic color or hybrid white EL has been extensively explored.

\*Correspondence: Email: [chintchen@gate.sinica.edu.tw](mailto:chintchen@gate.sinica.edu.tw); Tel: +886-2-2789-8542; Fax: +88-2-2783-1237

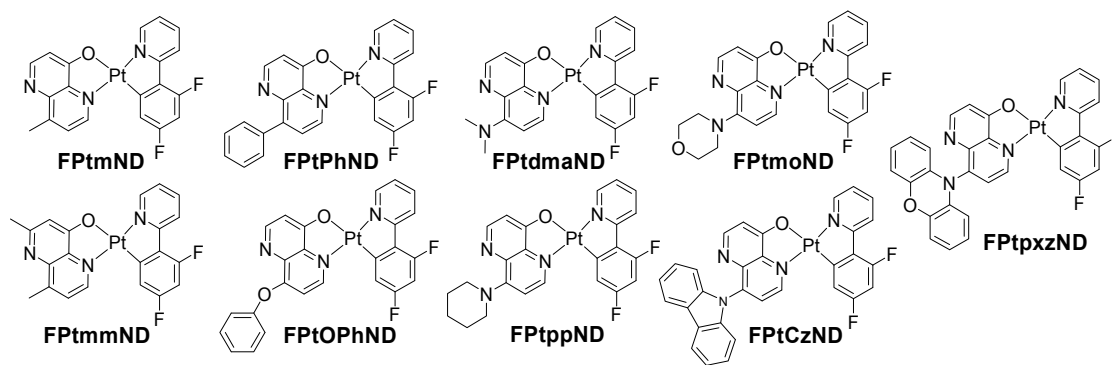


Figure 1. Chemical structures of FPtXND.

## 2. RESULTS AND DISCUSSION

### 2.1 Synthesis

The new heteroleptic platinum complexes were prepared in two steps as shown in Figure 2. It involved the cyclometallation of  $K_2PtCl_4$  with 2-(2,4-difluorophenyl)pyridine (**F**) to form the Pt  $\mu$ -dichloro-bridged dimer (**FPtCl**)<sub>2</sub>. The subsequent reaction of (**FPtCl**)<sub>2</sub> with **XND** ligand yielded heteroleptic platinum complexes.

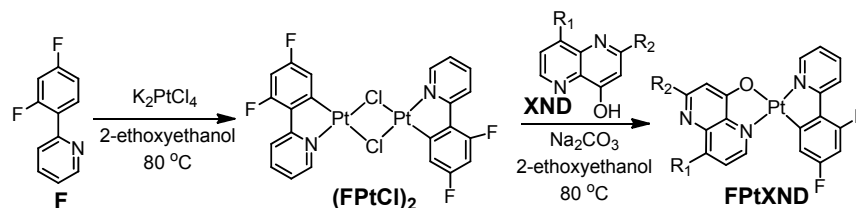


Figure 2. Synthesis method of FPtXND.

### 2.2 Single crystal structure x-ray analysis

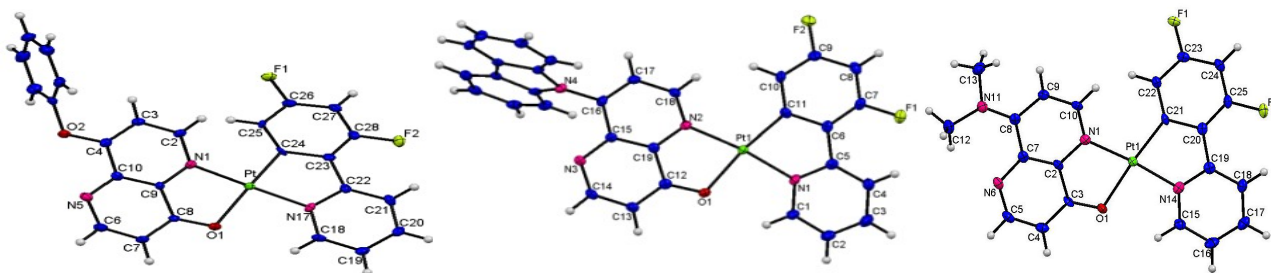


Figure 3. ORTEP diagram of **FPtOPhND** (left), **FPtCzND** (center) and **FPtdmaND** (right) with thermal ellipsoids shown at the 50% probability level.

Single crystals of **FPtOPhND**, **FPtCzND** and **FPtdmaND** were grown from dichloromethane/methanol solution and determined by single-crystal X-ray diffraction. Figure 3 shows the ORTEP diagram of **FPtOPhND**, **FPtCzND** and **FPtdmaND**. Each platinum atom in all three platinum complexes exhibits a distorted square planar geometry with the coordinating nitrogen atom of **F** and **XND** ligands in *trans* conformation. In the crystal packing, each platinum complex form pair wise stacking with Pt-Pt distance of 3.540, 3.169 and 5.869 Å for **FPtOPhND**, **FPtCzND** and **FPtdmaND**, respectively. **FPtOPhND** and **FPtCzND** show a short Pt-Pt distance, a clear indication of EL originated from the

dimer/aggregate of the platinum complexes. **FPtdmaND** displays a longer Pt-Pt distance, suggestive of moderate contact interaction between two platinum complexes.

### 2.3 Photophysical properties

The absorption spectra of FPtXND are displayed in Fig 4. FPtXND showed two major absorption bands. The strong absorption band at  $\leq 300$  nm are derived from  $\pi-\pi^*$  local electronic transition of the ligands. The weak absorption bands around 300-450 nm have relatively small extinction coefficients and are assigned to electronic transitions of mixed singlet metal-to-ligand charge transfer ( $^1\text{MLCT}$ ) and triplet metal-to-ligand charge transfer ( $^3\text{MLCT}$ ). **FPtdmaND**, **FPtppND**, and **FPtmoND** show stronger absorbance in the long wavelength region ( $\geq 375$  nm), which are attributed to the contribution of intraligand charge transfer (ILCT) due to the strong electron-donating aliphatic amine substituent.

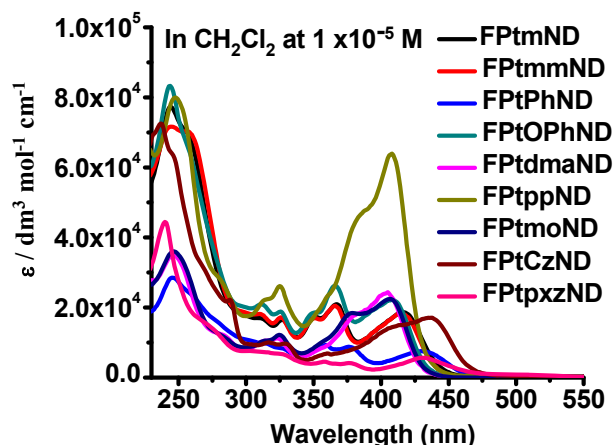


Figure 4. UV-Vis absorption spectra of FPtXND in  $\text{CH}_2\text{Cl}_2$  at a concentration of  $1 \times 10^{-5}$  M.

The emission behaviors of these platinum complexes were recorded both in solution and solid state (Figure 5). In  $\text{CH}_2\text{Cl}_2$  solution ( $2 \times 10^{-5}$  M), **FPtmND**, **FPtmmND**, **FPtPhND**, **FPtOPhND**, **FPtdmaND**, **FPtppND**, **FPtmoND**, **FPtCzND** and **FPtpxzND** displayed photoluminescence at 550, 550, 597, 555, 537, 545, 542, 573 and 537 nm, respectively. In solid thin film, all platinum complexes exhibited more red-shifted emission. These two different emission bands can be attributed to the isolated platinum complex at shorter wavelength and its aggregated forms at longer wavelength, respectively. The PL quantum yields ( $\Phi_{PL}$ ) of FPtXND were measured in degassed dilute solution of  $\text{CH}_2\text{Cl}_2$  by the optical dilute method with  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  in acetonitrile ( $\Phi_{PL} = 0.062$ ) as the reference. The platinum complexes show  $\Phi_{PL}$  of 0.13, 0.09, 0.22, 0.21, 0.17, 0.08, 0.23, 0.15 and 0.04 for **FPtmND**, **FPtmmND**, **FPtPhND**, **FPtOPhND**, **FPtdmaND**, **FPtppND**, **FPtmoND**, **FPtCzND** and **FPtpxzND**, respectively.

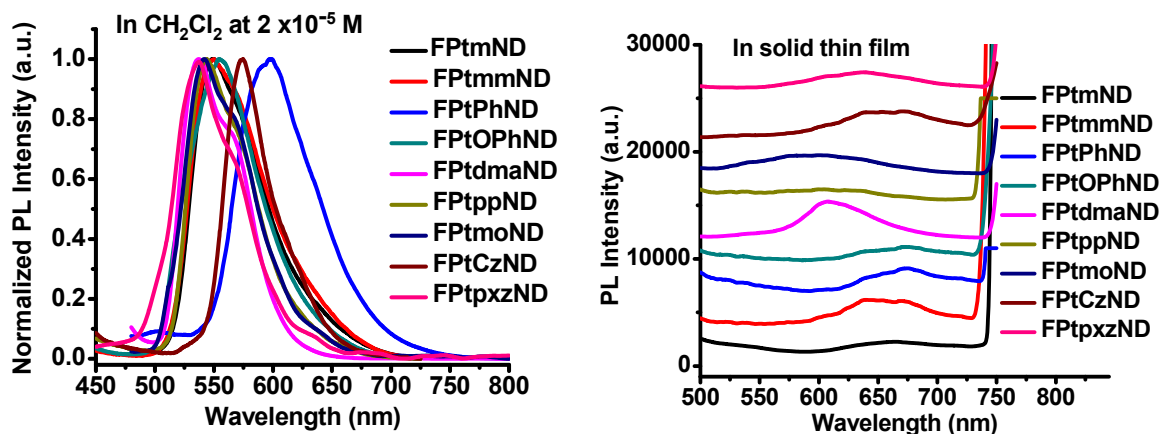


Figure 5. Normalized solution PL spectra of FPtXND in  $\text{CH}_2\text{Cl}_2$  at  $2 \times 10^{-5}$  M (left) and the PL spectra of the thin film.

## 2.4 Thermal and electrochemical properties

The thermal stabilities of these platinum complexes were examined by thermogravimetric analysis (TGA) under nitrogen atmosphere (Table 1). Platinum complexes in these series have high thermal stabilities ( $\Delta T_{5\%}$ ) in a range of 304–392 °C, sufficiently high for OLED fabrication by vacuum-thermal-decomposition process.

Table 1. The thermal properties and energy level of FPtXND.

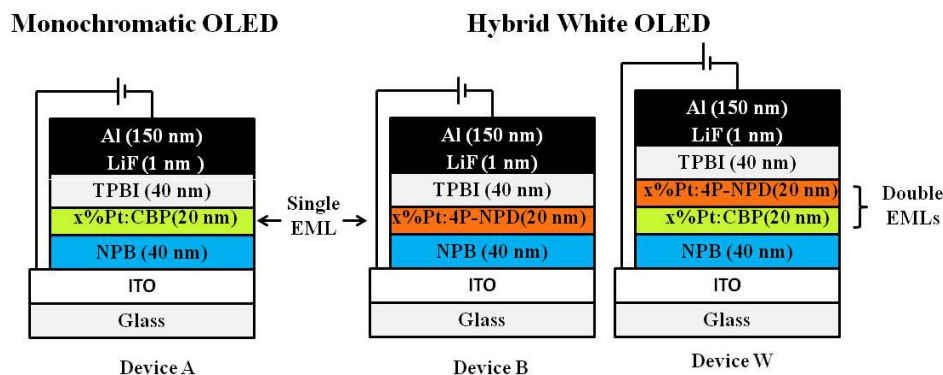
Complex	$E_{\text{HOMO}}$ (eV) <sup>a</sup>	$E_{\text{LUMO}}$ (eV)	$\lambda_{\text{onset}}$ (nm)	$E_g$ (eV)	$\Delta T_{5\%}$ <sup>b</sup> (°C)
FPtmND	-5.18	-2.40	448	2.78	332
FPtmmND	-5.20	-2.41	445	2.79	304
FPtPhND	-5.32	-2.68	470	2.64	313
FPtOPhND	-5.16	-2.33	438	2.83	319
FPtdmaND	-5.11	-2.24	432	2.87	318
FPtppND	-5.11	-2.26	435	2.85	351
FPtmoND	-5.18	-2.34	437	2.84	357
FPtCzND	-5.25	-2.63	473	2.62	392
FPtpxzND	-5.22	-2.65	483	2.57	356

<sup>a</sup>The energy level of HOMO was determined from the onset oxidation based on the reference level of ferrocene (4.8 V below the vacuum level). <sup>b</sup> $\Delta T_{5\%}$  is the temperature of 5% weight-reduction.

## 2.5 Electroluminescence

### Monochromatic OLEDs

Fig. 6 shows the device configurations and the molecular structures of relevant compounds used in OLEDs of this work. Five platinum complexes, FPtmND, FPtmmND, FPtOPhND, FPtppND and FPtCzND, were selected to fabricate OLEDs with multilayer structures. Device A was first fabricated with configuration of ITO/NPB (40 nm)/5 wt% Pt:CBP(20 nm)/TPBI(40 nm)/LiF(1 nm)/Al(150 nm) where NPB (4,4'-bis[N-(1-naphthyl)-N-phenylamino]-biphenyl) was used as hole-transporting layer (HTL), whilst CBP was used as host material and TPBI was used as electron-transporting layer (ETL). The dopant concentration was carried out at 5 wt% in CBP host.



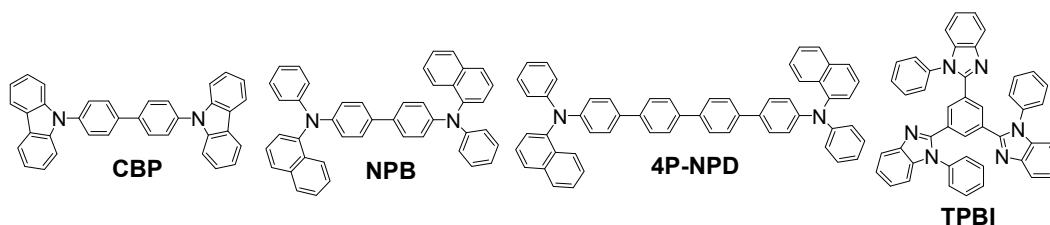


Figure 6 Device configurations and the molecular structures of the relevant compounds used in these devices.

Figure 7 display EL spectra and performance data for Device A. Device A with dopant **FPtmND**, **FPtmmND**, **FPtOPhND**, **FPtppND** at 5 wt% dopant concentration exhibited greenish yellow EL emission ( $\lambda_{\max}^{\text{EL}}$  around 543~551 nm), which are similar to their PL of the isolated platinum complex in solution, whereas **FPtCzND** displayed an orange EL with  $\lambda_{\max}^{\text{PL}}$  at 574 nm. The EL efficiencies are given in the Table 2.

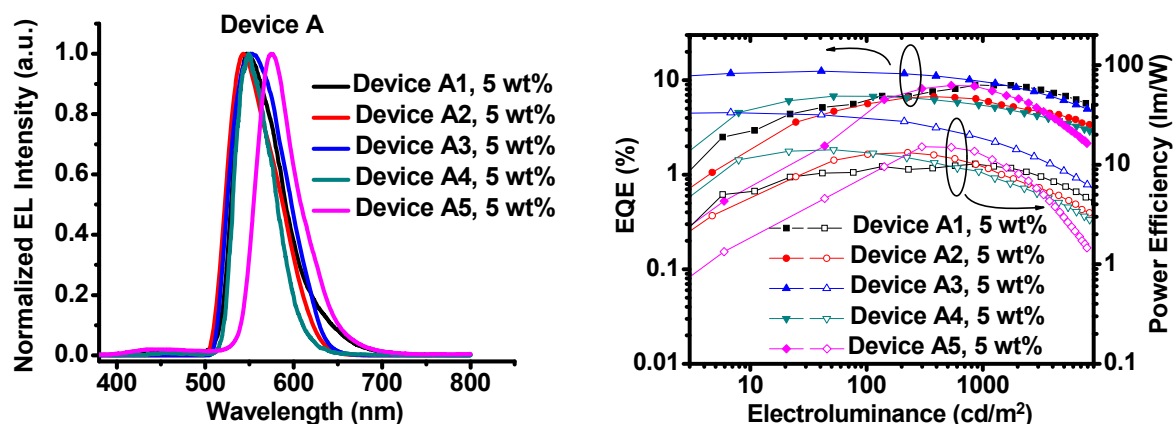


Figure 7 Normalized EL spectra of Device A with different platinum complexes at 5 wt% (left) and their external quantum efficiency (EQE) and power efficiency as a function of electroluminescence (right).

### Hybrid white OLEDs

Hybrid white OLEDs were fabricated with relatively simple configurations, in which platinum complexes were directly doped into 4P-NPD host. **FPtmND** and **FPtOPhND** were selected for evaluation of WOLED performance. Device B with configuration of ITO/NPB/4P-NPD: 8% FPtXND (20 nm)/TPBI (40 nm)/LiF(1 nm)/Al (150 nm). With 4P-NPD as host material, Device B exhibited different EL profiles from the Device A hosted by CBP. Two strong emissions were observed, containing (i) The blue emission ( $\lambda_{\max}^{\text{EL}}$  around 441~468 nm) (ii) The orange red board emission spectrum ( $\lambda_{\max}^{\text{EL}}$  around 603~608 nm). These two different emission bands can be attributed to the deep blue fluorescence 4P-NPD emission and excimer/aggregate emission from platinum complex, which was achieved from the diffusive triplet transfer to platinum complex. Device B with 8 wt% **FPtmND** displayed white EL ( $\text{CIE}_{x,y}$  (0.39, 0.29)), showing maximum external quantum efficiency of 5.9%, current efficiency of  $11.0 \text{ cd A}^{-1}$ , power efficiency of  $6.2 \text{ lm W}^{-1}$  and a maximum CRI of 83. Device B with 8 wt% **FPtOPhND** also displayed white EL ( $\text{CIE}_{x,y}$  (0.42, 0.34)) with the peak EL efficiency of 6.0%,  $10.5 \text{ cd A}^{-1}$  and  $4.7 \text{ lm W}^{-1}$  and a CRI of 79.

To improve the EL performance and CRI, devices with double EMLs were further fabricated, in which the platinum complex was doped into both CBP and 4P-NPD host materials. Device W with configuration of ITO/NPB (40 nm)/CBP: 5% FPtXND (20 nm)/4P-NPD: 8% FPtXND (20 nm)/TPBI (40 nm)/LiF(1 nm)/Al (150 nm) was constructed. The EL spectra of Device W and efficiencies are shown in Figure 8 and Table 2. Device W1 with **FPtmND** exhibited warm white EL,  $\text{CIE}_{x,y}$  (0.44, 0.47), displaying the peak efficiencies of 9.3%,  $24.1 \text{ cd A}^{-1}$  and  $9.6 \text{ lm W}^{-1}$  and a CRI of 86. For Device W2 with **FPtOPhND**, CRI increased to 90 as compared to its white EL with the single EML-type device and maximum EL efficiency elevated to 11.9%,  $29.0 \text{ cd/A}$ ,  $12.1 \text{ lm/W}$ , respectively. Interestingly, the EL spectra of Device

W2 displayed nearly pure white light  $CIE_{x,y}$  (0.36, 0.37) due to much stronger blue fluorescence EL and broader EL from both **FPtOPhND** and its excimer/aggregate.

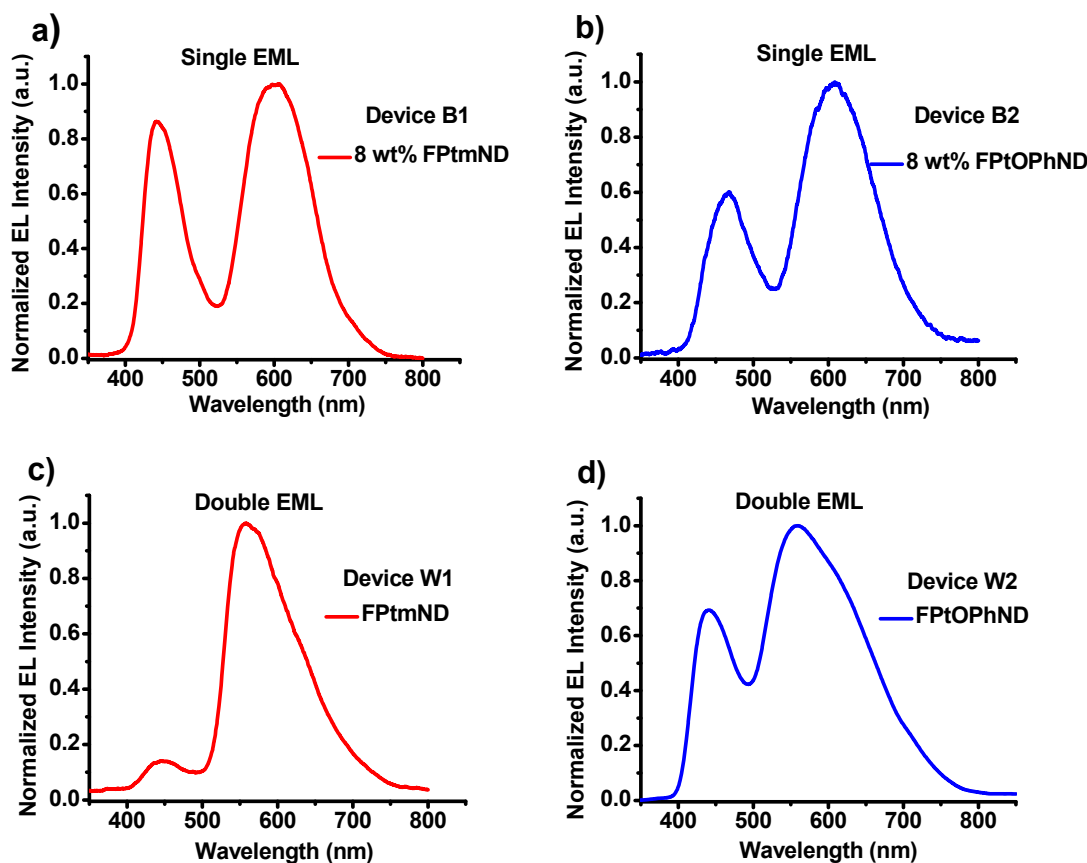


Figure 8 Normalized hybrid white EL spectra of single EML WOLED of **FPtmND** (a), **FPtOPhND** (b) and Normalized hybrid white EL spectra of double EML WOLED of **FPtmND** (c), **FPtOPhND** (d).

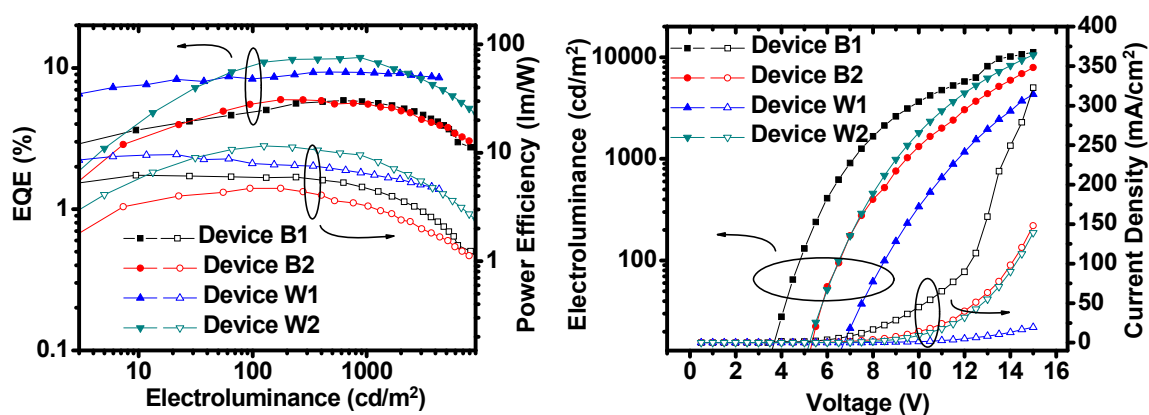


Figure 9 External quantum efficiency (EQE) and power efficiency as a function of electroluminescence of Device B and W (left). Luminance-voltage and Current density-voltage characteristics of Device B and W.

Table 2. Device performances

Device	Phosphorescence dopant	EQE <sup>a</sup> (%)	CE <sup>a</sup> (cdA <sup>-1</sup> )	PE <sup>a</sup> (lmW <sup>-1</sup> )	L <sub>max</sub> (cdm <sup>-2</sup> ), Voltage (V)	λ <sub>max</sub> (nm)	CIE <sup>b</sup> (x,y)	CRI <sup>c</sup>
A1	FPtmND	7.8 (8.9)	29.2 (33.9)	9.6 (10.1)	9153, 15	548	(0.42, 0.56)	–
A2	FPtmmND	6.6 (6.7)	27.4 (27.8)	11.8 (13.2)	12816, 15	543	(0.39, 0.60)	–
A3	FPtOPhND	10.8 (12.4)	43.7 (44.8)	22.5 (33.3)	25448, 15	551	(0.42, 0.57)	–
A4	FPtppND	6.0 (6.8)	25.8 (29.1)	9.7 (14.1)	11658, 15	549	(0.39, 0.60)	–
A5	FPtCzND	8.7 (8.8)	28.3 (28.6)	15.0 (15.1)	7886, 15	574	(0.51, 0.47)	–
B1	FPtmND	5.8 (5.9)	10.8 (11.0)	5.0 (6.2)	11188, 15	443 603	(0.39, 0.29)	83
B2	FPtOPhND	5.6 (6.0)	10.0 (10.5)	3.7 (4.7)	7929, 15	468 608	(0.42, 0.34)	79
W1	FPtmND	9.2 (9.3)	24.0 (24.1)	7.2 (9.6)	4316 15	444 558	(0.44, 0.47)	86
W2	FPtOPhND	11.6 (11.8)	25.5 (25.9)	9.9 (11.6)	10523, 15	441 560	(0.36, 0.37)	90

<sup>a</sup> The data for external quantum efficiency (EQE), current efficiency (CE), and power efficiency (PE) obtained at 500 cd/m<sup>2</sup>. The data in the parentheses are the maximum values; <sup>b</sup> Commission Internationale d' Eclairage chromaticity coordinates at 7-10 V; <sup>c</sup> Color rendering index.

## ACKNOWLEDGMENT

This research was support in part by the National Science Council of Taiwan (NSC 101-2113-M-001-004-MY2).

## REFERENCES

- [1] Kim, S., Kwon, H.-J., Lee, S., Shim, H., Chun, Y., Choi, W., Kwack, J., Han, D., Song, M., Kim, S., Mohammadi, S., Kee, I., Lee, S. Y., "Low-Power Flexible Organic Light-Emitting Diode Display Device." *Adv. Mater.* 23, 3511-35162 (2011).
- [2] D'Andrade, B. W., Forrest, S. R., "White Organic Light-Emitting Devices for Solid-State Lighting." *Adv. Mater.* 16, 1585-1595 (2004).
- [3] Reineke, S., Lindner, F., Schwartz, G., Seidler, N., Walzer, K., Lüssem, B., Leo, K., "White organic light-emitting diodes with fluorescent tube efficiency." *Nature.* 459, 234-238 (2009).
- [4] Sasabe, H., Takamatsu, J.-I., Motoyama, T., Watanabe, S., Wagenblast, G., Langer, N., Molt, O., Fuchs, E., Lennartz, C., Kido, J., "High-Efficiency Blue and White Organic Light-Emitting Devices Incorporating a Blue Iridium Carbene Complex." *Adv. Mater.* 22, 5003-5007 (2010).
- [5] Yu, X.-M., Zhou, G.-J., Lam, C.-S., Wong, W.-Y., Zhu, X.-L., Sun, J.-X., Wong, M., Kwok, H.-S., "A yellow-emitting iridium complex for use in phosphorescent multiple-emissive-layer white organic light-emitting diodes with high color quality and efficiency." *J. Organomet. Chem.* 693, 1518-1527 (2008).
- [6] Lai, S.-L., Tong, W.-Y., Kui, S. C. F., Chan, M.-Y., Kwok, C.-C., Che, C.-M., "High Efficiency White Organic Light-Emitting Devices Incorporating Yellow Phosphorescent Platinum(II) Complex and Composite Blue Host." *Adv. Funct. Mater.* 23, 5168-5176 (2013).
- [7] Wang, R., Liu, D., Zhang, R., Deng, L., Li, J. "Solution-processable iridium complexes for efficient orange-red and white organic light-emitting diodes." *J. Mater. Chem.* 22, 1411-1417 (2012).

- [8] Chang, C.-H., Ho, C.-L., Chang, Y.-S., Lien, I.-C., Lin, C.-H., Yang, Y.-W., Liao, J.-L., Chi, Y., "Blue-emitting Ir(III) phosphors with 2-pyridyl triazolates chromophores and fabrication of sky blue- and white-emitting OLEDs." *J. Mater. Chem. C* 1, 2639-2647 (2013).
- [9] Sun, Y., Giebink, N. C., Kannol, H., Ma, B., Thompson, M. E., Forrest, S. R., "Management of singlet and triplet excitons for efficient white organic light-emitting devices." *Nature*. 440, 908-912 (2006).
- [10] Hung, W.-Y., Chi, L.-C., Chen, W.-J., Chen, Y.-M., Chou, S.-H., Wong, K.-T., "A new benzimidazole/carbazole hybrid bipolar material for highly efficient deep-blue electrofluorescence, yellow-green electrophosphorescence, and two-color-based white OLEDs." *J. Mater. Chem.* 20, 10113-10119 (2010).
- [11] Hofmann, S., Furno, M., Lussem, B., Leo, K., Gather, M. C., "Investigation of triplet harvesting and outcoupling efficiency in highly efficient two-color hybrid white organic light-emitting diodes." *Phys. Status Solidi A*. 210, 1467-1475 (2013).
- [12] Wan, J., Zheng, C.-J., Fung, M.-K., Liu, X.-K., Lee, C.-S., Zhang, X.-H., "Multifunctional electron-transporting indolizine derivatives for highly efficient blue fluorescence, orange phosphorescence host and two-color based white OLEDs." *J. Mater. Chem.* 22, 4502-4510 (2012).
- [13] Ye, J., Zheng, C.-J., Ou, X.-M., Zhang, X.-H., Fung, M.-K., Lee, C.-S., "Management of Singlet and Triplet Excitons in a Single Emission Layer: A Simple Approach for a High-Efficiency Fluorescence/Phosphorescence Hybrid White Organic Light-Emitting Device." *Adv. Mater.* 24, 3410-3414 (2012).
- [14] Liao, S.-H., Shiu, J.-R., Liu, S.-W., Yeh, S.-J., Chen, Y.-H., Chen, C.-T., Chow, T. J., Wu, C.-I., "Hydroxynaphthyridine-Derived Group III Metal Chelates: Wide Band Gap and Deep Blue Analogues of Green Alq<sub>3</sub> (Tris(8-hydroxyquinolate)aluminum) and Their Versatile Applications for Organic Light-Emitting Diodes." *J. Am. Chem. Soc.* 131, 763-777 (2009).
- [15] You, Y., Park, S. Y., "Inter-Ligand Energy Transfer and Related Emission Change in the Cyclometalated Heteroleptic Iridium Complex: Facile and Efficient Color Tuning over the Whole Visible Range by the Ancillary Ligand Structure." *J. Am. Chem. Soc.* 127, 12438-12439 (2005).
- [16] Poloek, A., Chen, C.-T., Chen, C.-T., "High performance hybrid white and multi-colour electroluminescence from a new host material for a heteroleptic naphthyridinolate platinum complex dopant." *J. Mater. Chem. C* 2, 1376-1380 (2014).