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High efficiency *mer*-iridium complexes for organic light-emitting diodes†

Cheng-Hsien Yang, Kai-Hung Fang, Chun-Hung Chen and I-Wen Sun*

National Cheng Kung University, Department of Chemistry, No. 1, Ta-Hsueh Road, Tainan, Taiwan 701, Republic of China. E-mail: iwsun@mail.ncku.edu.tw; Fax: +886 6274 0552; Tel: +886 6275 7575 -65355

Received (in Cambridge, UK) 11th May 2004, Accepted 16th July 2004
First published as an Advance Article on the web 23rd August 2004

We have developed a new process at high vacuum (5 × 10^{-5} Torr) and high temperature (300 °C) to produce meridional iridium complexes from the dimer; interestingly, *mer*-Ir(m-ppy)$_3$ overthrows the concept of poor efficiency and shows excellent efficiency which is almost equal to that of *fac*-Ir(ppy)$_3$, *fac*-Ir(m-ppy)$_3$ and (ppy)$_2$Ir(acac).

In the past decade, great progress has been made in organic light-emitting diodes (OLEDs).[1–3] Electroluminescence from small molecules based on light-emitting diodes figures in the history of flat panel display. Recently, highly efficient OLEDs using phosphorescent dyes such as 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine platinum (PtOEP), iridium(III) *fac*-tris(2-phenylpyridinato-*N*,$C^{2'}$) (Ir(ppy)$_3$), iridium(III) bis(2-phenylpyridinato-*N*,$C^{2'}$)acetylacetonate ((ppy)$_2$Ir(acac)), and their derivatives have been reported.[4–10] Both *fac*-Ir(ppy)$_3$ and (ppy)$_2$-Ir(acac) exhibit green emission with high external quantum efficiency. By employing triplet-based phosphorescent dye in OLEDs, where both singlet and triplet excited states participate, the external quantum efficiency can reach as high as 8 ~ 15%.[11,12]

Most of the previous investigations have been focused on the facial type of iridium complexes because of their structure symmetry and photophysics properties. The photophysics of *mer*-Ir(ppy)$_3$ is different from that of *fac*-Ir(ppy)$_3$; it shows a marked red shift and band broadening in the photoluminescence (PL) and electroluminescence (EL) spectra.[13] Similar to *mer*-Ir(ppy)$_3$, it was expected that iridium(III) *mer*-tris(2-phenyl-4-methylpyridinato-*N*,$C^{2'}$) (*mer*-Ir(m-ppy)$_3$) would show a similar red shift in its PL and EL spectra. Interestingly, we have found that *mer*-Ir(m-ppy)$_3$ in fact results in a blue shift with respect to *fac*-Ir(ppy)$_3$ and produces a fairly pure green emission. In this communication, we report our results on the preparation of meridional iridium complexes for phosphorescent OLEDs.

Chemical structures of the iridium complexes, *fac*-Ir(ppy)$_3$, *fac*-Ir(m-ppy)$_3$, *mer*-Ir(ppy)$_3$ and *mer*-Ir(m-ppy)$_3$ are shown in Fig. 1. (ppy)$_2$Ir(acac) was prepared from the 2-phenylpyridine ligand by treatment with iridium trichloride to form a dimer, [C^N$_2$Ir(μ-Cl)$_2$IrC^N$_2$], followed by reaction with acetylacetone in the presence of sodium carbonate.[14] *fac*-Ir(ppy)$_3$ was prepared from the complex, (ppy)$_2$Ir(acac), followed by reaction with 2-phenylpyridine in glycerol. *fac*-Ir(m-ppy)$_3$ was prepared by the same process. All procedures involving Ir(III) species were carried out under nitrogen gas atmosphere. *mer*-Ir(ppy)$_3$ and *mer*-Ir(m-ppy)$_3$ were prepared from train sublimation of the dimer, [C^N$_2$Ir(μ-Cl)$_2$IrC^N$_2$]. All these materials were characterized by ^{1}H and ^{13}C NMR as well as mass spectrometry.

Fig. 2 shows the PL spectra of the iridium complexes. The PL spectrum of *fac*-Ir(ppy)$_3$ in CH$_2$Cl$_2$ shows an emission band at 525 nm. In comparison to *fac*-Ir(ppy)$_3$, (ppy)$_2$Ir(acac) and *mer*-Ir(ppy)$_3$ exhibit a bathochromic shift at 530.6 and 535.2 nm, respectively, whereas *fac*-Ir(m-ppy)$_3$ and *mer*-Ir(m-ppy)$_3$ exhibit a hypsochromic shift at 515 and 513.4 nm, respectively. These data indicate that when we introduce a methyl group to the *para* position of 2-phenylpyridine, these iridium complexes will show the blue shift effect. The emission band of *mer*-Ir(ppy)$_3$ is broad, indicating that the color purity is not excellent. Interestingly *mer*-Ir(m-ppy)$_3$ shows a better color purity. According to the data of ^{1}H and ^{13}C NMR, the chemical equivalence of *mer*-Ir(m-ppy)$_3$ is better than *mer*-Ir(ppy)$_3$, notedly. This result may improve the photophysics properties of *mer*-Ir(m-ppy)$_3$ and thus it could show better efficiency for OLEDs. The blue shift of *mer*-Ir(m-ppy)$_3$ and red shift of *mer*-Ir(ppy)$_3$ indicate that the emission color is tunable according to the position of the substitution in the meridional type iridium complexes.

Devices were fabricated by high vacuum (10^{-6} Torr) thermal evaporation on pre-cleaned indium-tin-oxide (ITO) glass substrate

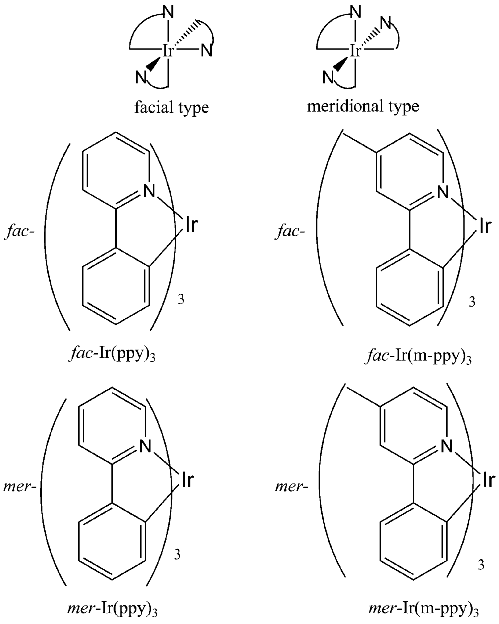

Fig. 1 Chemical structure of iridium complexes.

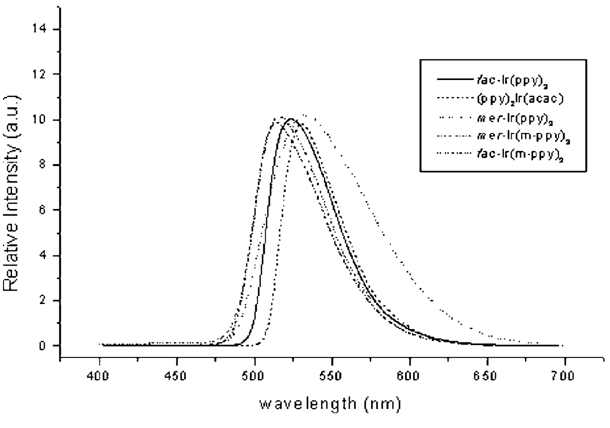

Fig. 2 PL spectra of iridium complexes in CH$_2$Cl$_2$.

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b4/b406958g/

DOI: 10.1039/b406958g

Table 1 Electrophosphorescence and photophosphorescence data for iridium complexes[a]

Compound	Brightness (cd m^{-2})	Luminance efficiency (cd A^{-1})	Power efficiency (lm W^{-1})	Voltage (V)	CIE	EL (nm)	PL (nm)	FWHM (nm)
fac-Ir(ppy)$_3$	A-4987	24.94	8.08	9.7				
	B-9831	19.66	5.28	11.7	$x = 0.35$	516	525	49.3
	C-16744	16.74	3.93	13.4	$y = 0.60$	537		
	D-28298	14.15	2.94	15.1				
fac-Ir(m-ppy)$_3$	A-4405	22.03	7.29	9.5				
	B-9762	20.46	5.79	11.1	$x = 0.31$	511	515	53.5
	C-19653	19.74	5.17	12.0	$y = 0.62$	541		
	D-37385	18.41	4.28	13.5				
(ppy)$_2$Ir(acac)	A-4391	22.00	7.93	8.7				
	B-10681	21.36	6.71	10.0	$x = 0.33$	524	530.6	43.6
	C-21198	21.20	5.84	11.4	$y = 0.60$	552		
	D-42801	21.40	5.06	13.3				
mer-Ir(ppy)$_3$	A-3061	15.31	5.28	9.1				
	B-6409	12.82	3.80	10.6	$x = 0.42$	564	535.2	79
	C-11854	11.85	3.13	11.9	$y = 0.50$			
	D-20813	10.41	2.40	13.6				
mer-Ir(m-ppy)$_3$	A-4315	21.58	6.92	9.8				
	B-9711	19.42	5.50	11.1	$x = 0.31$	508	513.4	50.4
	C-18315	18.32	4.68	12.3	$y = 0.59$	538		
	D-35249	17.62	4.01	13.8				

[a] For each parameter, the data in different rows correspond to those measured at different current density: [A]: 20 mA cm^{-2}, [B]: 50 mA cm^{-2}, [C]: 100 mA cm^{-2}, [D]: 200 mA cm^{-2}.

with the following structures: ITO/NPB (50 nm)/CBP : 6% dopant (30 nm)/BCP (10 nm)/AlQ$_3$ (30 nm)/Al. With a base pressure of $\sim 1 \times 10^{-6}$ Torr, the organic and metal cathode layers were grown successively. In this device, 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB) acted as a hole transport layer, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a hole blocking layer, tris-(8-hydroxyquinoline)aluminium(III) (AlQ$_3$) as an electron transport layer, 4,4′-bis(*N*-carbazolyl)biphenyl (CBP) as the host material, and iridium complexes as the dopant. The corresponding CIE (Commission International de L'Eclairage) chromaticity coordinates are $x = 0.35$, $y = 0.60$ for *fac*-Ir(ppy)$_3$, $x = 0.35$, $y = 0.60$ for *fac*-Ir(ppy)$_3$, $x = 0.31$, $y = 0.62$ for *fac*-Ir(m-ppy)$_3$, $x = 0.33$, $y = 0.60$ for (ppy)$_2$Ir(acac), $x = 0.42$, $y = 0.50$ for *mer*-Ir(ppy)$_3$ and $x = 0.31$, $y = 0.59$ for *mer*-Ir(m-ppy)$_3$. All five devices show green to yellow-green emissions, and *mer*-Ir(ppy)$_3$ shows the same tendency in PL spectrum data.

Electrophosphorescence data for the iridium complexes are summarized in Table 1.

The peak wavelength of the EL spectrum for the devices using *fac*-Ir(ppy)$_3$, *fac*-Ir(m-ppy)$_3$, (ppy)$_2$Ir(acac), *mer*-Ir(ppy)$_3$ and *mer*-Ir(m-ppy)$_3$, was 516, 511, 524, 564 and 508 nm, respectively. The EL spectrum for each device was almost coincident with the corresponding PL spectrum. Although *fac*-Ir(ppy)$_3$ shows the best luminance efficiency and power efficiency at low current density, (ppy)$_2$Ir(acac) exhibits the best brightness, luminance efficiency and power efficiency at a high current density. Similar to the demonstration of last year,[13,15] *mer*-Ir(ppy)$_3$ shows the yellow-green emission and poor performance among these complexes. Although *mer*-Ir(m-ppy)$_3$ is meridional type, its photophysics properties are different from *mer*-Ir(ppy)$_3$. *mer*-Ir(m-ppy)$_3$ shows the best brightness of 35249 cd m^{-2}, luminance efficiency of 17.62 cd A^{-1} and power efficiency 4.01 lm W^{-1} at a high current density of $J = 200$ mA cm^{-2}, which are almost the same as for *fac*-Ir(ppy)$_3$, *fac*-Ir(m-ppy)$_3$ and (ppy)$_2$Ir(acac). We speculate that when we introduced a methyl group to the *para* position of 2-phenylpyridine, the MLCT energy level of the iridium complex decreased. Then, energy transfer from the host to the *mer*-Ir(m-ppy)$_3$ occurs more efficiently than to the *mer*-Ir(ppy)$_3$.

In conclusion, we have developed a simple procedure to prepare novel iridium complexes with 2-phenyl-4-methylpyridine ligands. Marvellously, *mer*-Ir(m-ppy)$_3$ shows excellent performance comparable to *fac*-Ir(ppy)$_3$, *fac*-Ir(m-ppy)$_3$ and (ppy)$_2$Ir(acac). This result opens up a new direction in developing novel emitters for OLEDs.

This work was supported by the National Science Council of the Republic of China, Taiwan.

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