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## An Ester-Substituted Iridium Complex for Efficient Vacuum-Processed Organic Light-Emitting Diodes

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Lighting and display applications account for about 19% (Western world 15%) of worldwide electricity consumption. To develop a sustainable world, not only shall we require renewable energy sources but also devices with low energy consumption. In this regard, organic light-emitting devices (OLEDs) are very promising for light production for lighting or display applications. In this area, dopants based on cyclometalated iridium complexes have been the material of choice to date as a result of their excellent photophysical properties.

Since the seminal work by Watts and co-workers,<sup>[1]</sup> the emission wavelength of cyclometalated iridium complexes has been tuned by introducing donor and/or acceptor substituents on the ligands. These studies have led to phenylpyridine-based iridium complexes with emission colors ranging from sky-blue to yellow-orange. However, despite this approach being well known, it has not been solely used for tuning the emission to wavelength higher than 600 nm. To obtain emission at such wavelengths, the common strategies are based on an extension of the aromatic delocalization in the ligand through the attachment or fusion of extra aromatic groups either on the pyridine or the phenyl<sup>[2]</sup> moiety or on interligand energy transfer.<sup>[3]</sup> In the latter case, emitting ancillary ligands with low band-gaps are introduced into the complex, whereas in the former case, the main ligand is often based on benzothienylpyridine or phenylquinoline. Complexes with extended aromatic ligands have quantum yields of 0.1 to 0.6 and radiative lifetime ranging from microseconds to tens of microseconds. Such long radiative lifetimes can lead to triplet–triplet annihilation at high loadings of the complex in the device, decreasing the performances of the OLED despite using materials with good photoluminescence properties.<sup>[4]</sup>

With this in hand, it looked promising to seek for red-emitting iridium complexes with shorter radiative lifetimes to de-

velop efficient OLEDs. To observed an emission maximum higher than 600 nm, we used an ester substituent on the pyridine. Such an acceptor group in the *para* position with respect to the nitrogen atom of the pyridine is expected to strongly stabilize the LUMO level of the iridium complex and only slightly stabilize the HOMO level. Overall, it will lead to a reduced HOMO–LUMO gap and the complex will emit red light. More specifically, we chose an ester group owing to the straightforward preparation of the ligand and possibility to further graft polymer or extra electroactive groups on the complex. Herein, we show that by using an ester as a strong acceptor substituent, OLEDs with an efficiency reaching those of the very good devices reported to date can be achieved.<sup>[2]</sup>

**N958** was synthesized by reacting the dimer iridium(III) complex  $[\{\text{Ir}(\text{methyl-2-phenyl-4-carboxypyridine})_2(\text{Cl})\}_2]$  with acetylacetonate (acac) anion freshly prepared by refluxing acetylacetone and tetrabutylammonium hydroxide in dichloromethane. This two-step strategy was necessary to avoid the hydrolysis of the ester groups on the phenylpyridine ligand during the formation of the **N958** complex, which was finally obtained as a red powder (see Supporting Information). The full <sup>1</sup>H and <sup>13</sup>C NMR spectra of the **N958** complex show the expected resonance patterns for a symmetrical heteroleptic complex with 10 (two of them overlap) and 16 resonance signals (Supporting Information), respectively. The structure was further confirmed by mass spectrometry with peaks observed at 739.12 corresponding to  $[\text{M}+\text{Na}]^+$  and at 617.46 corresponding to the loss of the acac ancillary ligand.

Single crystals of **N958** suitable for X-ray analysis were obtained (Figure 1). The complex **N958** crystallizes in space group *C2/c* with four independent molecules within the cell. The molecule lies on a crystallographic twofold axis (site .2.) and shows perfect *C*<sub>2</sub> molecular symmetry.

The cyclic voltammogram of the complex measured in acetonitrile solution shows a reversible couple at 0.52 V (vs ferrocene (Fc)) due to the oxidation of the iridium(III) center to iridium(IV), and reversible reduction waves at –1.92 and –2.08 V (vs Fc) assigned to the subsequent reduction of the two main ligands. As expected, introduction of an acceptor group on the pyridine ring leads to a significant stabilization of the LUMO level of the molecule and less significant stabilization of the HOMO level.

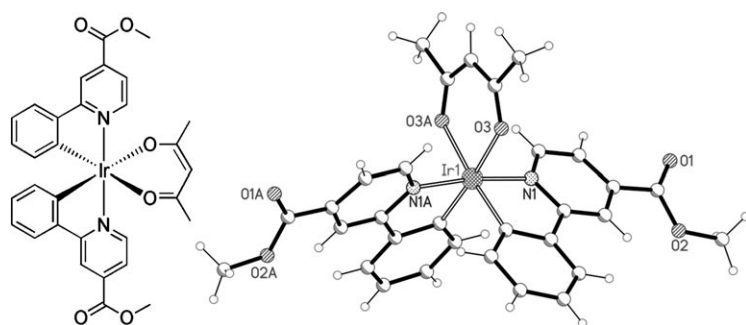
UV/Vis absorption spectra measured in acetonitrile solution at 298 K display bands in the UV (at 264, 320, and 370 nm) and the visible region (at 422 and 500 nm, the latter extending up to 580 nm in the visible) as a result of intraligand ( $\pi$ – $\pi^*$ ) and metal-to-ligand charge-transfer (MLCT) transitions, respectively (Figure 2). When excited at 298 K within the  $\pi$ – $\pi^*$  and MLCT absorption bands, the acetonitrile solution of **N958** shows a

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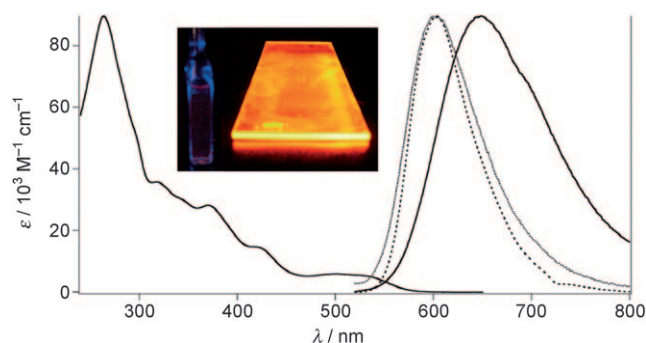
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**Figure 1.** Chemical structure and X-ray crystal structure of **N958**.



**Figure 2.** Absorption (solid line, left) and emission (solid line, right) spectra of **N958** ( $10^{-5}$  M) in acetonitrile. Dotted line: emission of PMMA:0.7 wt% **N958** film; dashed line: device emission. The insert shows a photo of the **N958** solution and of the PMMA film excited at 365 nm.

red emission centered at 648 nm. The photoluminescence quantum yield is low (0.02) in deaerated acetonitrile at room temperature. The lifetime of the excited state under these conditions is 80 ns. As the polarity of the solvent is decreased, the maximum emission shifts to lower wavelength and the lifetime of the excited state and the photoluminescence quantum yield both increase, as a less polar environment destabilizes the charge-transfer state (Table 1).

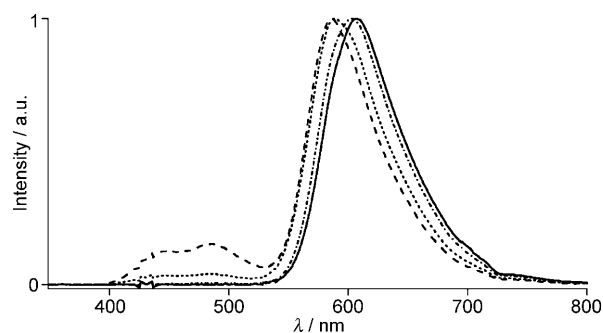
Using a set-up with an integrated sphere, the same phenomenon was observed in poly(methyl methacrylate) (PMMA) films containing **N958** at various concentrations. The emission spectrum of a solid-state film prepared by dissolving 0.7 wt% **N958** complex in a PMMA matrix shows bright orange-red lu-

Table 1. Photophysical properties of <b>N958</b> in various media at 298 K.					
Medium	$\lambda_{\max}$ [nm] <sup>[a]</sup>	$\tau$ [ns] <sup>[a]</sup>	QY <sup>[b]</sup>	$k_r$ [ $10^{-5}$ s <sup>-1</sup> ] <sup>[c]</sup>	$k_{nr}$ [ $10^{-5}$ s <sup>-1</sup> ] <sup>[d]</sup>
CH <sub>2</sub> Cl <sub>2</sub> /hexane <sup>[e]</sup>	625	296	0.10	3.4	30.4
CH <sub>2</sub> Cl <sub>2</sub>	632	136	0.04	2.9	70.6
acetonitrile	648	80	0.02	2.5	122.5
PMMA (1 wt %)	603	385	0.33 <sup>[f]</sup>	8.6	17.4
PMMA (2 wt %)	605	359	0.38 <sup>[f]</sup>	10.6	17.3
PMMA (10 wt %)	620	258	0.13 <sup>[f]</sup>	5.0	33.6

[a] From excitation of deaerated solutions at 400 nm. [b] Photoluminescence quantum yield. [c] Radiative constant. [d] Non-radiative constant. [e] 60:40 v/v. [f] Using a set-up with an integrated sphere.

minescence with a maximum emission at 601 nm (Figure 2). As the amount of dopant increases, a red shift of the emission as well as decreases in the quantum yield and the lifetime of the excited state occur (Table 1). This behavior means that the dopant itself modifies substantially the polarity in the film.<sup>[5]</sup> As expected from the energy-gap law, as the charge-transfer state is stabilized and the emission is red-shifted, the non-radiative constant increases. At an optimum concentration, the radiative lifetime of the complex is as short as 1  $\mu$ s.

Thermal vapor deposition was employed to fabricate standard organic light-emitting diodes using **N958** in the following architecture: ITO/CuPc/NPB/**N958**:BCP/BCP/Alq3/LiF/Al (ITO=indium tin oxide, CuPc=copper phthalocyanine, NPB=*N,N'*-di(1-naphthyl)-*N,N'*-diphenylbenzidine, BCP=2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, Alq3=[tris(8-hydroxyquinoline)aluminum]). CuPc, NPB, Alq3, and LiF were used as the hole-injection, hole-transport, electron-transport, and electron-injection layers, respectively. Doping with **N958** ranged from 1 to 12 wt%. Electroluminescence spectra at various doping levels are shown in Figure 3 and the corresponding device properties are listed in Table 2.



**Figure 3.** Electroluminescence spectra of BCP devices at various concentrations of **N958**: 1 wt% (----); 3 wt% (.....); 9 wt% (-.-.-); 12 wt% (—).

Table 2. Properties of a BCP-based device at various concentrations of <b>N958</b> dopant and a comparison with known compounds.				
<b>N958</b> [wt %] in BCP	$\lambda_{\max}$ [nm]	EQE [%]	Power efficacy [lmW <sup>-1</sup> ]	Luminance at 9 V [cd m <sup>-2</sup> ]
1	586	5.6	8.1	650
3	589	4.7	7.0	540
6	603	9.2	13.0	1500
9	604	9.8	13.3	1740
12	607	9.8	11.2	1680
[Btp <sub>2</sub> Ir(acac)] <sup>[6]</sup>	600	7.0	4.6	n.a. <sup>[a]</sup>
Ir-G1 <sup>[2f]</sup>	640	11.65	3.65	≈ 250 <sup>[b]</sup>
Ir4F5Mpiq <sup>[2d]</sup>	607	15.5	12.4	n.a. <sup>[c]</sup>

[a] Not available at 9 V. Values reported: 6.5 cd m<sup>-2</sup> at 0.1 mA cm<sup>-2</sup> and 6800 cd m<sup>-2</sup> at 690 mA cm<sup>-2</sup>. [b] Estimated from graph. [c] Non available at 9 V. Value reported is over 10 000 cd m<sup>-2</sup> at about 8 V

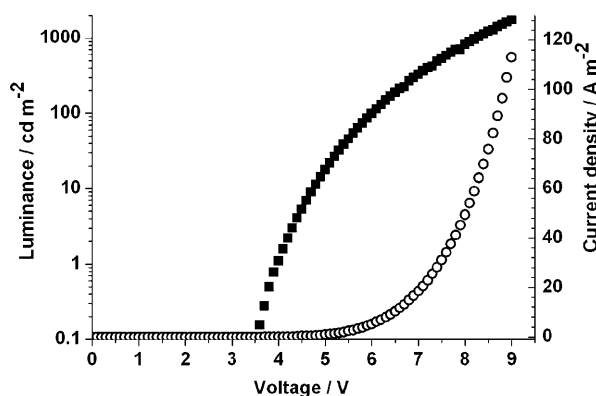
As the concentration of the dopant increases, the blue component of the emission spectra originating from the matrix decreases and completely disappears at high concentrations (9–10 wt% **N958**). Additionally, the emission maximum is shifted to the red in line with what is observed in the PMMA thin film, indicating that again the dopant modifies substantially the polarity of the BCP film.

It can be seen that as the concentration of the dopant increases, the external quantum efficiency (EQE) and the power efficacy increase (Table 2). In a first approximation, the EQE is defined according to Equation (1), where  $b$  denotes the recombination efficiency (equal to 1 for two ohmic contacts)<sup>[7]</sup>,  $\phi$  is the fraction of excitons that decay radiatively, and  $n$  is the refractive index of the glass substrate and is equal to 1.5 (the factor  $1/2n^2$  accounts for the coupling of light out of the device).

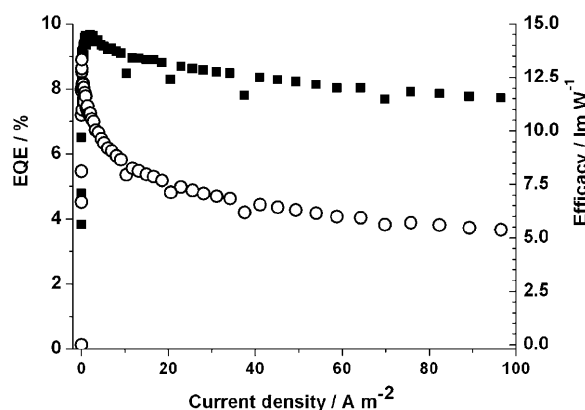
$$\text{EQE} = b\phi/2n^2 \quad (1)$$

As the **N958** complex can efficiently harvest both singlet and triplet excitons,  $\phi$  should resemble the photoluminescence efficiency in the solid state. Using the maximum photoluminescence quantum efficiency obtained in PMMA matrix, for a qualitative understanding, the EQE calculated from Equation (1) would be 8.4, which is rather close to what is experimentally observed as the maximum EQE. Note that in the PMMA film, the photoluminescence quantum efficiency decreases with increasing **N958** concentration, and the optimum concentration of emitter to matrix can differ considerably from PMMA to the BCP matrix.

Plots of luminance and current density versus voltage and of external quantum efficiency and efficacy versus luminance for the 9 wt% doped device are shown in Figure 4 and Figure 5, respectively. The entire device is 114-nm thick between the two electrodes. The luminance and the density of current achieve  $1740 \text{ cd m}^{-2}$  and  $113 \text{ A m}^{-2}$ , respectively, with a turn-on voltage at 3.5 V. The external quantum efficiency and the power conversion efficiency reach a maximum of 9.8% at 5.4 V and  $13.3 \text{ lm W}^{-1}$  at 4.1 V, respectively. At  $100 \text{ cd m}^{-2}$ , values of 9.3% and  $9.4 \text{ lm W}^{-1}$  are achieved. The electroluminescence



**Figure 4.** Luminance (■) and current density (○) versus applied bias voltage of the **N958**-based OLED.



**Figure 5.** External quantum efficiency (■) and efficacy (○) versus luminance of the **N958**-based OLED.

spectrum shows an orange emission centered at 603 nm with a half-bandwidth of 74 nm.

In conclusion, by introducing a single ester moiety as the acceptor group on the pyridine of the main ligand, that is, without relying on extending the aromatic delocalization or on interligand energy transfer, the maximum emission wavelength of the iridium complex **N958** either in solution or as a thin film or device is higher than 600 nm. Moreover, the radiative lifetime of the complex as a thin film is short. Despite being at the low end of red-emitting iridium complexes for the photoluminescence quantum yield, as a dopant **N958** is a fairly good orange-red-emitting iridium complex leading to devices with enhanced brightness and good color purity and with excellent external quantum efficiencies close to 10%. Additionally, this work shows that the adequate figure of merit is the photoluminescence quantum yield obtained from the thin-film configuration and not that obtained from solution, as is generally the case.

## Experimental Section

Experimental procedures, characterizations, and crystal structure tables are available in the Supporting Information.

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