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## Organic Light-Emitting Diodes

VIP

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## Multifunctional Iridium Complexes Based on Carbazole Modules as Highly Efficient Electrophosphors\*\*

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Since the seminal work on organic green-light-emitting diodes using fac-[Ir(ppy)<sub>3</sub>] (Hppy=2-phenylpyridine),<sup>[1]</sup> intensive research effort has been directed towards the development of efficient phosphorescent materials for potential use in full-color flat-panel-display technology.<sup>[2]</sup> Although the emission efficiency and the color of Ir-based organic light-emitting diodes (OLEDs) can be tuned by structural modifications of the ligand chromophores,<sup>[3]</sup> the performance of the device is greatly influenced by the charge balance between the electrons and holes from opposite electrodes. It is highly

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desirable that the designed phosphor shows improved chargebalancing features and permits a complete transfer of energy between the host and the dopant in the device. Interestingly, small-molecule IrIII complexes derived from hole-transporting (HT) carbazole units have not been reported to date. Many carbazole derivatives are known to transport predominantly positive charge carriers in organic systems. For example, poly(9-vinylcarbazole) (PVK) is often described as being a unipolar hole transporter whereas 4,4'-N,N'-dicarbazolebiphenyl (CBP) is recognized to have a more bipolar transport character.<sup>[4]</sup> Typically, purely organic carbazolebased compounds are high-mobility HT materials with a tunable and high triplet energy level, and they are widely used as the host materials for electrophosphors emitting different colors.<sup>[5]</sup> The integration of HT carbazole modules and emissive Ir complexes seems to be a wise choice for vacuum-evaporated OLED materials with multicomponent molecules, which are essential for more efficient charge transport in the electroluminescence process. [6] We report here two robust IrIII triplet emitters of green light that are based on the rigid 2-[3-(N-arylcarbazolyl)]pyridine system and possess the dual functions of light emission and hole transportation, and also show improved charge-transporting properties and morphological stability.

The green-light-emitting multifunctional metal chelates 1 and 2 can be synthesized in moderate to good yields by a onestep cyclometalation of  $L^1$  and  $L^2$  with  $[Ir(acac)_3]$  (acac = acetylacetone) in refluxing glycerol (Figure 1 a). [3f] Purification of the mixture by preparative thin-layer chromatography (TLC) on silica gel furnished homoleptic fac-[Ir(X-Cz-py)<sub>3</sub>] (X = H, 1; X = F, 2; Cz = carbazolyl, py = pyridyl) as air-stable yellow powders in high purity. Their 1D <sup>1</sup>H NMR spectra are consistent with a facial geometry around the Ir center, which was also confirmed by a single-crystal X-ray analysis of 1 (Figure 1b).<sup>[7]</sup> Both **1** and **2** show excellent thermal stability, with their onset decomposition temperatures  $(T_d)$  greater than 420 °C, as revealed by thermogravimetric analysis (TGA, Table 1), and with 1 being thermally much more stable than 2 and fac-[Ir(ppy)<sub>3</sub>] (423 °C). Furthermore, both of them can be vacuum-evaporated without decomposition and show good film-forming qualities.

The nature of the X group on the carbazole ring does not have a great influence on the absorption and photoluminescence (PL) spectra of 1 and 2 (Table 1). The first two bands appear to be ligand-based transitions that closely resemble the spectra of the free ligands ( $\lambda_{abs}$ : ca. 252 and 297 nm). Somewhat weaker bands are observed at lower energies in the visible region which correspond to electronic excitations to the allowed and spin-forbidden metal-to-ligand charge-transfer states (<sup>1</sup>MLCT and <sup>3</sup>MLCT, respectively). These assignments were supported by DFT calculations on 1, which show that the highest occupied molecular orbitals (HOMOs) are derived from the out-of-phase combinations of the Ir "t<sub>2g</sub>" set of d orbitals and the  $\pi$  orbitals of the three Ir-bonded phenyl rings of the three N-C bidenate ligands. In each of the first three HOMOs, the Ir(d) orbitals make an approximate 20% contribution, with the N(amine)  $p_{\pi}$  orbitals also contributing to the HOMOs. The lowest unoccupied molecular orbitals (LUMOs) are the  $\pi^*$  orbitals of the three pyridine rings. Both

a) 
$$X$$

$$X = H(L^{1})$$

$$X = F(L^{2})$$

$$fac-[Ir(X-Cz-py)_{3}]$$

$$X = H(1)$$

$$X = F(2)$$

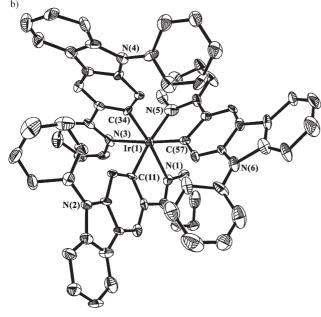


Figure 1. a) Synthesis of 1 and 2; b) ORTEP plot of 1, with the hydrogen atoms omitted for clarity.

Table 1: Photophysical, electrochemical, and thermal data for 1 and 2.

	Absorption <sup>[a]</sup>	Emission		E <sub>1/2</sub> [V] <sup>[d]</sup>	E <sub>1/2</sub> [V] <sup>[e]</sup>	HOMO [eV]	LUMO [eV]	T <sub>d</sub> [°C] <sup>[f]</sup>
	$\lambda_{abs}$ [nm]	$\lambda_{\scriptscriptstyle{em}}[nm]^{\scriptscriptstyle{[b]}}$	$ au_{ extsf{P}}  [\mu  extsf{s}]^{ extsf{c}]}$		. ,		. ,	
1	291 sh (4.69), 316 (4.69), 398 sh (0.20)	515 (0.43)	0.46	0.07	-2.56	-4.87	-2.24	477
2	281 sh (4.89), 315 (4.85), 400 sh (0.16)	514 (0.33)	0.54	0.13	-2.49	-4.93	-2.31	421

[a] In degassed CH<sub>2</sub>Cl<sub>2</sub> at 293 K; log $\varepsilon$  values are shown in parentheses; sh=shoulder. [b]  $\Phi_P$  values are shown in parentheses versus fac-[Ir(ppy)<sub>3</sub>] ( $\Phi_P$ =0.40),  $\lambda_{ex}$ =380 nm. [c] Triplet lifetimes at 293 K. [d] 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>, versus the ferrocene/ferrocinium (Fc/Fc<sup>+</sup>) couple. [e] 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> in THF, versus Fc/Fc<sup>+</sup> couple. [f] At a heating rate of 20 °C min<sup>-1</sup> under N<sub>2</sub>.

complexes emit strong phosphorescence ( $\lambda_{\rm em}$  ca. 514 nm, Stokes shifts ca. 200 nm) at room temperature in CH<sub>2</sub>Cl<sub>2</sub>. The triplet energy levels ( $T_1$ : ca. 2.41 eV) of the two complexes are very similar and also similar to that of *fac*-[Ir(ppy)<sub>3</sub>] (2.43 eV).<sup>[1a]</sup> The phosphorescence quantum yields

 $Φ_P$  in CH<sub>2</sub>Cl<sub>2</sub> of these triplet emitters of green light are approximately 0.33–0.43 relative to a fac-[Ir(ppy)<sub>3</sub>] standard ( $Φ_P$  = 0.40).<sup>[8]</sup> The triplet lifetimes  $τ_P$  are very short at 0.46–0.54 μs for **1** and **2** in the solid state. Accordingly, the triplet radiative lifetimes ( $τ_r$ ) deduced from  $τ_r$ = $τ_P/Φ_P$  are 1.07–1.64 μs, which are shorter than that of fac-[Ir(ppy)<sub>3</sub>] (ca. 4.75 μs)<sup>[3f]</sup> and other Ir<sup>III</sup> complexes.<sup>[3]</sup>

Cyclic voltammetric studies show that both 1 and 2 undergo a reversible one-electron oxidation of the Ircarbazolyl ring system ( $E_{1/2}^{\text{ox}}$  0.07, **1**; 0.13 V, **2**). The attachment of electron-withdrawing F substituents in 2 causes the oxidation to occur at a more anodic potential, which would have a major impact on the device properties (see below). Both 1 and 2 were oxidized at less-positive potentials than fac- $[Ir(ppy)_3]$ , thus indicating a greater propensity for **1** and **2** to lose an electron. [3k,5b] Cathodic sweeps in THF reveal an irreversible wave at -2.49 to -2.56 V. There is subtle changes in the HOMO and LUMO levels arising from the presence of different X groups in 1 and 2, and we were able to tune the HOMO level without influencing the triplet energy of these Ir phosphors. The HOMO levels are significantly elevated (-4.87, 1; -4.93 eV, 2) relative to those of fac- $[Ir(ppy)_3]$ (-5.50 eV).[3k,5b] This finding indicates that they have a lower ionization potential (IP) than fac-[Ir(ppy)3], thus leading to a better HT ability in 1 and 2 which favors the transport of holes. The LUMO levels of 1 and 2 are comparable to that of the widely used electron-transporting/hole-blocking 2-(4biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole

(-2.4 eV). Our complexes show  $T_1$  levels well below the level of those of the CBP host (2.56 eV) which prevents reverse energy transfer from the guest back to the host, and confines triplet excitons to the guest molecules.

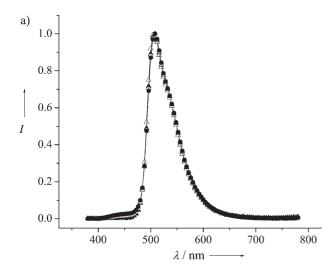
The optoelectronic properties of both Ir<sup>III</sup> complexes were characterized, and efficient OLEDs I and II were fabricated using 1 and 2, respectively, as phosphorescent dopant emitters in a four-layer structure of ITO/NPB (40 nm)/6% 1 or 2 in

 $(20 \text{ nm})/BCP \quad (8 \text{ nm})/Alq_3$ (20 nm)/Mg:Ag (200 nm) (ITO =indium tin oxide, NPB = 4.4'-bis[N-(1-naphthyl)-N-phenylamino]bi-BCP = 2,9-dimethyl-4,7phenyl, diphenyl-1,10-phenanthroline,  $Alq_3 = tris(8-hydroxyquinoline)$ ). CBP acts as the host material for the electrophosphor and NPB as a hole-transport layer. A thin holeblocking barrier layer of BCP inserted between the CBP and the electron-transporting Alq3 was necessary to confine excitons within the luminescent zone and hence maintain high efficiencies. The electroluminescence (EL) spectra consist only of a green phosphor emission

without any residual emission from the host and/or adjacent layers, even at high drive currents—an indication of complete energy and/or charge transfer from the host exciton to the phosphor upon electrical excitation. The EL spectra and Commission Internationale de L'Eclairage (CIE) coordinates

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for the devices exhibited no significant change on variation of the current and operating bias voltages from 5 V to 12 V (Figure 2a), and both of the devices I and II show a sharp EL peak at 508 nm. The turn-on voltages (defined as the bias at a



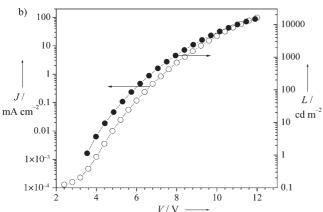


Figure 2. a) The EL spectra of device I at 5 (△), 8 (▲), 10 (○), and 12 V (♠) and b) current–voltage–luminance (*J-V-L*) characteristics for device I

brightness of 1 cd m $^{-2}$ ) are 4.4 and 4.8 V for devices **I** and **II**, respectively, with the CIE color coordinates being (0.24, 0.63) and (0.27, 0.60), which correspond to the bright green region of the chromaticity diagram. There is a close resemblance between the EL and PL spectra in each case.

Phosphors 1 and 2 show outstanding EL performance, presumably because of the short  $\tau_P$  value and good hole-transporting properties of carbazole, which may help diminish the quenching of the triplet exciton. Figure 2b shows the current density-voltage-luminance (J-V-L) curve of device I. Complex 1 was shown to be a more efficient electrophosphor than 2, which suggests that the F substituents are rather unimportant here in relieving intermolecular interactions in the Ir complex, as is commonly the case in  $[Ir(C-N)_3]$ -type compounds with simpler ligands. Moreover, since 2 has a  $T_1$  lifetime comparable to that of 1, its poor EL performance may be attributed to its lower  $\Phi_P$  value relative to that of 1. The difference in the efficiency for 1 and 2 are also a

consequence of the lower  $E_{1/2}^{\text{ox}}$  value of **1**. As the HOMO of **1** is positioned higher in energy than that of 2 (relative to the CBP level of 6.3 eV), the efficiency of recombination by sequential charge trapping is increased in 1. The performance parameters of device I (maximum external quantum efficiency ( $\eta_{ext}$ ): 11.6% photons/electron, luminance efficiency  $(\eta_L)$ : 38 cd A<sup>-1</sup>, power efficiency  $(\eta_P)$ : 24 Lm W<sup>-1</sup>) clearly outweigh those of a prototypical green-light-emitting device of ITO/NPB/fac-[Ir(ppy)<sub>3</sub>]:CBP/BCP/Alq<sub>3</sub>/Mg:Ag (maximum  $\eta_{ext}$ : 7.5%,  $\eta_L$ : 26 cd  $A^{-1}$ ,  $\eta_P$ : 19 Lm  $W^{-1}$ ) in a device of similar structure, and this represents a tremendous improvement of about 55% in the  $\eta_{ext}\,value.^{[1a]}$  The maximum luminance of device I is 14730 cd m<sup>-2</sup> at 12 V, with the full width at half maximum (fwhm) only 56 nm at 8 V. With 2 as the dopant, device II has a maximum brightness of 19360 cd m<sup>-2</sup> and a luminance efficiency of approximately  $22 \text{ cd } A^{-1}$ , which corresponds to a  $\eta_{ext}$  value of 6.7% and a  $\eta_P$  value of approximately 13 Lm W<sup>-1</sup>. We can surmise that it is probably the carbazolyl moiety that brings about a more balanced electron and hole recombination in the host matrix of CBP, and/or that the rigid carbazole spacers play a crucial role in alleviating the self-quenching of the [Ir(X-Cz-py)<sub>3</sub>] luminophores, and consequently increase the emission efficiency. Typical efficiency roll-off at higher currents, attributable to a combination of triplet-triplet annihilation and fieldinduced quenching effects, is also observed here, but at the reference luminance of 100 cd m<sup>-2</sup> (6.5 V) the efficiencies remain high at 10.6%,  $35 \text{ cd A}^{-1}$ , and  $17 \text{ Lm W}^{-1}$  for device **I**. These values correspond to a loss of only 8% from the maximum  $\eta_{\text{ext}}$  value. Likewise, a loss of 7% was noted in the  $\eta_{ext}$  value for device II. Although the performance of these devices has yet to be optimized, it is our intention to highlight the potential merits of this prominent class of carbazole-based Ir phosphors in high-efficiency OLED applications.

In summary, we have reported some triplet-harvesting carbazolyl-substituted multicomponent iridium complexes, and this approach can offer advantages in terms of lowering the first IP, facilitating hole transport, and enhancing EL efficiencies relative to the prototypical *fac*-[Ir(ppy)<sub>3</sub>]. Given the ease of synthesis and performance advantages inherent to these carbazole-based phosphors, extension of the system to other emission colors warrants further examination.

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