

Amorphous iridium complexes for electrophosphorescent light emitting devices[†]

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Iridium complexes with fluorene-modified phenylpyridine ligands are resistant to crystallization and can be used in the fabrication of single layer light emitting diodes.

Phosphorescent metal complexes that can be incorporated into organic light emitting diodes^{1,2} (OLEDs) are under intense investigation in academic and industrial laboratories.^{3,4} This interest arises from the potential to increase device efficiency, relative to devices containing all-organic emissive materials.⁵ It is generally accepted that charge recombination statistics in organic LEDs lead to a theoretical maximum efficiency of 25%.⁶ It should be noted that the 25% limitation for maximum efficiency in organic materials, while widely quoted in literature, does not necessarily hold under all circumstances.^{7,8} Nevertheless, phosphorescent emitters with heavy metal ions allow for circumvention of this limitation if the excitons generated by hole–electron recombination reside at a site where efficient spin-orbit coupling leads to efficient singlet–triplet mixing.⁹

Highly efficient LEDs with multilayer structure have been constructed with tris(2-phenylpyridine) $Ir(III)^{10}$ (1) as a dopant in 4,4'-N,N'-dicarbazolebiphenyl host as the emissive layer.^{5a} Recent work shows that it is possible to tune the frequency of emission from the complex by modifying the phenylpyridine ligand.¹¹ Additional efforts show that it is possible to reduce self-quenching by the introduction of bulky groups on the basic phenylpyridine ligand.¹² In the cases discussed above, devices were prepared by vapor-depositing techniques.

Ideally, one would like to fabricate efficient LEDs by casting the electroemissive layer directly from solution and simultaneously limiting the number of layers between electrodes. Indeed, devices that use a blend of **1** with poly(vinylcarbazole) have been demonstrated.¹³ The use of conjugated polymers doped with lanthanide emitters has also been reported.¹⁴

It occurred to us that *single* component iridium-containing devices could be fabricated if the complex was designed to allow for hole and electron transport. Additionally, molecular attributes¹⁵ would have to be incorporated such that the bulk material would be resistant to crystallization¹⁶ and able to form thin films directly from solution, despite modest dimensions.^{15c} In this communication, we report the synthesis, characterization, and preliminary device performance of complexes **2–4**. Oligofluorene-type moieties were included as part of the ligand framework to facilitate charge transport across the bulk. Of additional interest is the effect of ligand structure on the solid-state quantum efficiency. Compounds **2–4** provide a progression of steric protection around the metal center and make it possible to examine the effect of ligand substitution patterns on the bulk morphology and solid state phosphorescence.¹⁷

The ligand frameworks were prepared by taking advantage of Suzuki coupling protocols.¹⁸ As an example, we note that

† Electronic supplementary information (ESI) available: experimental details, synthetic and spectroscopic data. See http://www.rsc.org/suppdata/ cc/b2/b200957a/



treating 2,5-dibromopyridine with two equivalents of 9,9-dihexyl-2-pinacolatoboranefluorene¹⁹ in the presence of Pd(dppf)Cl₂ (dppf = 1,1'-bis(diphenylphosphino)ferrocene) affords 2,5-bis(2'-(9',9'-dihexylfluorene)pyridine in 50% yield. Compound **4** is obtained by refluxing a glycerol solution containing six equivalents of 2,5-bis(2'-(9',9'-dihexylfluorene)pyridine and Ir(acac)₃. Similar protocols are used to generate compounds **2** and **3**. Materials used in the optical and morphological studies, and device fabrication, were purified by multiple silica gel chromatographic separations and tested for purity by HPLC.

The solution absorption and emission of compounds 2–4 in the visible region are summarised in Table 1. The bands corresponding to the ligand ${}^{1}(\pi \rightarrow \pi^{*})$ are the most intense. ²⁰ These become increasingly red-shifted as the conjugation length of the ligand increases, from 330 nm, for 2, to 375 nm for 4. For each compound, one observes weaker transitions redshifted from the ${}^{1}(\pi \rightarrow \pi^{*})$ band, corresponding to excitation to ${}^{1}MLCT$, ${}^{3}MLCT$ and ${}^{3}(\pi \rightarrow \pi^{*})$ states (Table 1).^{20*a,e*} Observation of the ${}^{3}MLCT$ and ${}^{3}(\pi \rightarrow \pi^{*})$ bands confirms strong spin orbital coupling. Emission maxima are observed at 545, 550, and 595 nm for 2, 3, and 4, respectively.

The solution photoluminescence efficiencies were determined using quinoline bisulfate in 0.1 N H₂SO₄ as a standard.²¹ Quantum efficiencies of all the complexes were determined in a degassed solution of toluene, and the complexes were excited at

Table 1 Physical properties of 2, 3, and 4

	Solution QE (%)	$\Phi_{ m SSPL}~(\%)^a$	Absorbance/nm ^b	Emission/ nm ^b
2	59	1.3 ± 1	330, 412, 449, 470	545
3	61	1.7 ± 0.5	345, 401, 449, 470	550
4	63	11.2 ± 1	375, 441, 513	595
^a All films were spun from toluene. ^b In toluene.				

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the ${}^{1}(\pi \rightarrow \pi^{*})$ transition. Table 1 contains the values for the three iridium complexes.

DSC analysis shows that complexes 2–4 are amorphous solids upon removal of the solvent (Fig. 1). All DSC data were taken at a scanning rate of 10 °C min⁻¹. The ligand framework influences the glass transition temperature and the stability of the amorphous state. Complexes 2 and 3 show only glass transitions at 98 and 110 °C, respectively. The heating trace of complex 4 shows a glass transition at 83 °C, followed by crystallization at 130 °C, a solid–solid state transition and melting at 203 °C. For this set of compounds, the molecules with smaller ligands give rise to higher glass transition temperatures and are more resistant to crystallization. AFM studies show that, for all cases, casting from toluene results in smooth films, with an average mean roughness of *ca*. 0.3 nm.

Solid state fluorescence efficiencies (Φ_{SSPL}) were determined using an integrating sphere according to published protocols (Table 1).²² All films were spun cast onto a quartz substrate from 1% toluene solutions. For these measurements the complexes were excited at 365 nm. An efficiency of $1.3 \pm 1\%$ was determined for 2. While low, this efficiency should be compared against that of 1, for which no emission could be detected under our experimental conditions. It should be noted that efforts to obtain smooth films of 1 failed – only opaque polycrystalline samples formed. For compound 3, $\Phi_{\text{SSPL}} = 1.7 \pm 0.5\%$. Complex 4, which has two fluorene units *ortho* on the pyridine ring, has a Φ_{SSPL} of $11 \pm 1\%$. It is seen that increasing the bulk around the iridium center prevents self-quenching.

Device performance was tested with a general LED architecture of ITO (indium tin oxide)/PEDOT²³/Ir complex (1000 Å)/Ca (900 Å)/Ag (1000 Å). Modest efficiencies were observed of 0.1 cd/A, 0.04 cd/A, and 0.07 cd/A for complexes **2**, **3**, and **4**, respectively. The quantum efficiencies for all devices are 0.1%. Devices manufactured without the use of PEDOT were on average 50% lower in efficiency than devices with PEDOT. In all cases, the electroluminescence and the phosphorescence spectra were identical.

In summary, we have shown that iridium complexes supported by phenylpyridine ligands with fluorene groups give rise to amorphous solids. The extent of conjugation can be used to tune emission color, and the ligand environment controls solid state fluorescence quenching. From a practical perspective, it is noteworthy that smooth films can be obtained by



Fig. 1 DSC scans of 2-4: (a) crystallization; (b) melting.

casting these complexes directly from solution and that these films operate as the emissive layer within an LED configuration. Further optimization of LED performance is expected upon blending conjugated polymers with the iridium complexes and by better engineering of the device structure.

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- 23 PEDOT is polyethylenedioxythiophene-polystyrenesulfonic acid which is used to improve device performance of OLEDs.