

Improving OLEDs by Doping With Phosphorescent Organometallic Complexes

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Organic light-emitting diodes (OLEDs) are emerging as a leading display technology in comparison with liquid crystal displays (LCD). Relative to LCDs, OLEDs are lighter, have a wider viewing angle, and can be made into flexible displays.¹ However, one of the disadvantages of OLEDs is their low external quantum efficiency of 1.6%.² External quantum efficiency (η_{ext}) is defined as the number of photons emitted from the device for every electron injected into the device.³ Inorganic LEDs, such as AlGaInP, can have external quantum efficiencies up to 50%, but are expensive to manufacture.⁴ To be competitive with inorganic LEDs, OLEDs need to have an efficiency of 20%.¹

Organic polymer based LEDs emit light from the recombination of singlet excitons, which account for about 25% of the excited state population.⁵ Improved efficiencies can be obtained by doping the OLED with third row transition metal complexes that phosphoresce efficiently due to the large spin orbit coupling that allow transitions from triplet to singlet states.⁶ By tuning the ligand sets, phosphorescent dyes with d^6 metals, such as Re^I , Os^{II} , and Ir^{III} , have increased the efficiencies of OLEDs and the doped OLEDs can emit over the entire visible spectrum.⁷

Rhenium based yellow-red phosphorescent dyes have been limited in efficiency by triplet-triplet annihilation, which limits the desired phosphorescence.⁸ Triplet-triplet annihilation can be limited by improving the charge transfer from the host polymer to the dopant.⁹ Adding redox centers based on oxadiazazole or carbazole (Fig. 1) to a Re^I complex with chelating diimines, such as (2-pyridinylbenzoimidazole)- $\text{Re}(\text{CO})_3\text{Br}$, (Pybm), can improve the overlap of the orbitals between the host polymer and the dye leading to better transfer of excitons to the dye, therefore improving external device efficiency to 1.2%.

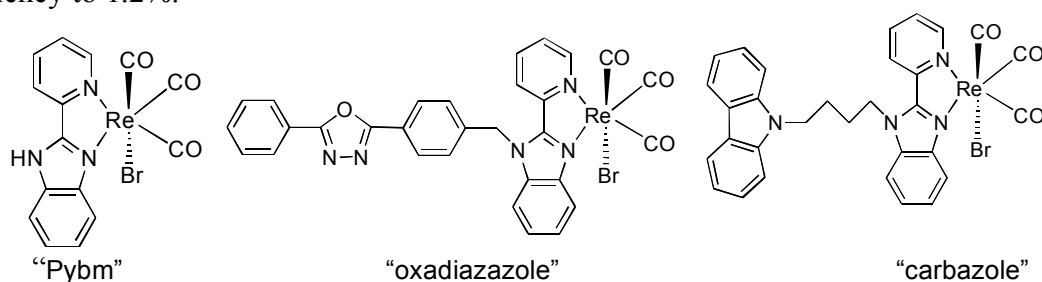


Fig. 1

Diimine complexes of Os^{II} have also been examined for use as red dyes in OLEDs, as osmium compounds tend to be more robust than their rhenium analogs.¹⁰ Several organometallic compounds (Fig. 2) were synthesized to study the effect of the

electron donating and withdrawing properties of ligands on the external quantum efficiency and emission spectrum of Os^{II} compounds. 2-(2'-pyridyl)-benzoxazole (pboz) has a lower energy π^* orbital as compared to the diimines, bipyridine and phenanthroline. Further substitution of pboz to 5-*tert*-butyl-2-(2'-pyridyl)benzoxazole (tbpboz), resulted in the device with the higher external efficiency, 2.8%.¹¹

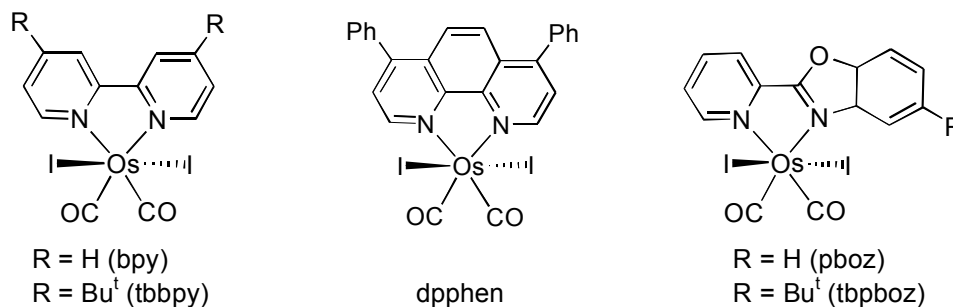


Fig. 2

Highly efficient blue emissions from an OLED are still elusive due to the low electron affinities of most polymers. The low electron affinities make electron injection into the polymer difficult.¹² Ir^{III} complexes that include strong field ligands such as phosphine and cyano groups have a large HOMO-LUMO gap, allowing for emission in the deep blue region.¹³ The 4-position of the pyridyl ring of $[(2-(4',6'-\text{difluorophenyl})\text{-pyridine})_2\text{Ir}(\text{PPh}_3)\text{CN}]$ was substituted to study the connection between the excited states and the photophysical behavior of Ir^{III} complexes (Fig. 3).¹⁴ Methyl substitution in the 4-position of the pyridyl ring lead to the highest efficiency device ($\eta_{\text{ext}} = 2.0$). The high η_{ext} was attributed to the electron donating ability of the methyl group.

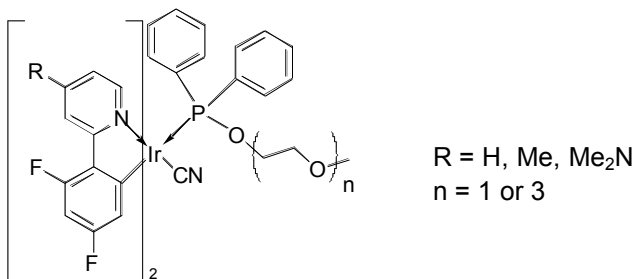


Fig. 3

While internal quantum efficiencies are high, improving device design needs to be studied before phosphorescent OLEDs match the efficiency of inorganic LEDs. The long term stability of phosphorescent OLEDs also must be further studied.

References

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