

# Copper Coordination Compounds as Highly Emissive Dopants in Organic LEDs

Noel Chang

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Light-emitting diode (LED) have great technological and commercial importance owing to their low power consumption, light weight, and ability to self-illuminate.<sup>1</sup> Current generation LEDs use inorganic semiconductors such as gallium nitride as the emissive layers. Flexible organic semiconductors, usually polymers with highly conjugated  $\pi$ -system, are attractive candidates for the next generation of LED displays. Although these polymers are highly fluorescent ( $S_1 \rightarrow S_0$ ), they lack a phosphorescence ( $T_1 \rightarrow S_0$ ) or intersystem crossing pathway ( $T_1 \rightarrow S_1$ ) competitive with nonradiative relaxation. Because singlet ( $S_1$ ) and triplet ( $T_1$ ) excitons form with a 1:3 ratio, purely organic LEDs have a theoretical quantum efficiency limit of 25%.<sup>2</sup> In order to exceed this limit, a way to convert both singlet and triplet excitons into light must be developed.

A common strategy to harvest excitons of both spin states is to dope the organic polymer with phosphorescent dyes.<sup>1,3</sup> These dyes are usually coordination compounds of a third-row metal such as iridium, rhenium, or osmium, whose spin-orbit coupling allows intersystem crossing followed by efficient phosphorescence. Presently, the most promising candidates are iridium(III) phenylpyridine complexes, which are reported to have up to 29% external quantum efficiency (EQE = photon output vs. electron input) in an OLED device.<sup>4,5</sup> However, these third-row metals are expensive, motivating effort to seek a lower-cost alternative.

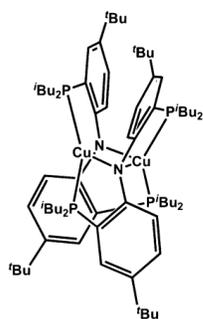


Figure 1:  $[\text{Cu}(\text{PNP})]_2$  complex, **1**

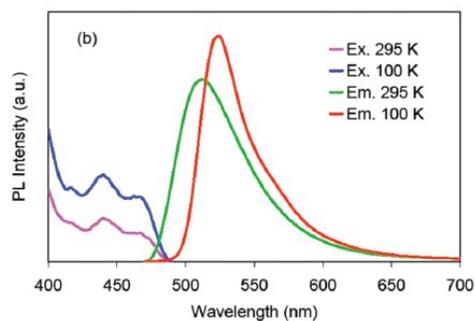


Figure 2: Absorption/emission spectrum of **1**

In 2005, Jonas and co-workers reported a new class of dimeric copper diphosphino-amine compounds ( $[\text{Cu}(\text{PNP})]_2$ , *Figure 1*) that may fulfill this role. First synthesized to model electron transfer reaction in  $\text{Cu}_A$  site of cytochrome *c* oxidase, these complexes are highly emissive with quantum yields ( $\Phi$ ) up to 65%.<sup>6,7</sup> Luminescence of copper(I) compounds is common yet inefficient ( $\Phi < 1\%$ ).<sup>8,9</sup> Recently, some of the more emissive Cu(I) compounds have been tested in OLED device with promising results.<sup>10,11</sup> To understand the atypical emissive properties of  $[\text{Cu}(\text{PNP})]_2$  and its candidacy as a new class of emissive dopant in OLEDs, the redox behavior, photophysical properties, and electroluminescence properties of representative compound **1** have been investigated.

The emission band (*Figure 2*) of **1** at 100 K is red-shifted from that at room temperature (where  $\lambda_{\text{max}} = 512$  nm), where the absorption spectrum is unchanged.<sup>12</sup> Time gated emission spectroscopy demonstrates that there are two excited states, one a singlet ( $S_1$ ) and one a triplet ( $T_1$ ), which are in thermal equilibrium with one another. At room temperature, **1** is excited to a mixture of utilizes both  $S_1$  and  $T_1$  states but emits exclusively through the  $S_1 \rightarrow S_0$  fluorescence pathway.

The origin of the compound's unusually high (65%) quantum yield can be explained by its redox properties. K-edge x-ray absorption spectroscopy (XAS) of **1** reveals that, for oxidation by both one- and two-electrons, the oxidation states of the two copper centers remain relatively unchanged.<sup>13</sup> Instead, the bridging amides are oxidized in these reactions. The non-innocent nature of the ligands means that the excited state structure of the  $\text{Cu}_2\text{N}_2$  core is minimally distorted from the ground state geometry; this structural invariance leads to a higher quantum yield by eliminating non-radiative pathways such as vibrational relaxation during structural reorganization.<sup>6,14</sup>

An OLED device fabricated from the organic semiconductor CBP (4,4'-N,N'-dicarbazole-biphenyl) doped with 0.02 wt.% **1** achieves molecular emission and an external quantum efficiency of 10.9% at 1 mA/cm<sup>2</sup> (compared to a typical value of ~10% for 6-8 wt.% loading of Ir(III) compounds).<sup>5</sup> The internal quantum efficiency (IQE = EQE/device efficiency) has been estimated to be 55-73%, suggesting that both triplet and singlet excitons are harvested by the device.

Cyclic voltammetry of the holes-only device gives an insight into the exciton formation mechanism.<sup>12</sup> During the reverse sweep after the initial hole injection, charges are not retracted even at high voltage and over a long time. In successive sweeps, onset of charge injection shifts to higher voltage, indicating that **1** traps holes deeply. A complimentary EPR study of the full OLED device shows that the triplet excitons in the electron transport layer are removed upon the addition of **1**. These observations indicate that most electron-hole recombinations take place directly on the dopant. This way to harvest excitons is more efficient than an alternative pathway in which the excitons form in the polymer matrix then subsequently excite the dopant.<sup>1</sup>

The success of OLEDs doped with the  $[\text{Cu}(\text{PNP})]_2$  have demonstrated that third row metal complexes are not required to efficiently harvest both singlet and triplet excitons. By developing improved copper-based dopants, an inexpensive OLED device could achieve external quantum efficiency suitable for commercial applications.

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