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Enhanced electrophosphorescence of copper complex based devices by codoping an iridium complex

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Evidently enhanced electrophosphorescence of [Cu(bis[2-(diphenylphosphino)phenyl] ether)(6,7-dicyanodipyrido [2,2-d:2′,3′-f] quinoxaline)] BF$_4$ (Cu^I complex) by codoping bis[(4,6-difluorophenyl)-pyridinato-N, C^2](picolinato)Ir(III) (FIrpic) into the same host, 4,4′-N,N′-dicarbazole-biphenyl, was demonstrated. The device codoped with 8 wt % FIrpic and 2 wt % Cu^I complex shows a maximum current efficiency and power efficiency of 26.6 cd/A and 17.8 lm/W, respectively, which were increased by factors of 2.6 and 2.1 compared with the 2 wt % Cu^I complex monodoped device. The improvements of the devices were testified to the efficient energy transfer from FIrpic to the Cu^I complex. The detail of the energy transfer mechanism between the two phosphors was also proposed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2719238]

In the past two decades, yellow emission organic light-emitting devices (OLEDs) attached considerable attention[1–4] because it is a complementary color for blue to achieve white light emission.[5–7] Unlike fluorescent materials that can only make use of singlet excitons, phosphorescent materials can harvest both singlet and triplet excitons and make the potential of reaching a maximum internal efficiency of 100%.[8] Recently, electrophosphorescence based on Cu^I complexes were demonstrated.[9–12] However, the properties of these devices are unsuitable for commercial applications. Thus, it is desirable to find an effective method to improve the performances of these devices.

The concepts of phosphor sensitized fluorescence[13] and phosphor sensitized phosphorescence[14] by codoping two dopants into the same host as the emitting layer (EML) for improving the performances of the devices have been reported. The improvements of the devices were ascribed to the resonant energy transfer from the phosphorescent sensitizer to the other dopant. In this letter, [Cu(bis2-(diphenylphosphino)phenyl] ether)(6,7-dicyanodipyrido [2,2-d:2′,3′-f] quinoxaline)] BF$_4$ (Cu^I complex) and bis[(4,6-difluorophenyl)-pyridinato-N, C^2] (picolinato)Ir(III) (FIrpic) are codoped into the same host, 4,4′-N,N′-dicarbazole-biphenyl (CBP), as the EML. Efficient energy transfer from FIrpic to the Cu^I complex is demonstrated, which leads to dramatically improved performances of the codoped devices.

Figure 1 illustrates the molecular structures of FIrpic and the Cu^I complex, and shows the schematic energy diagram of the devices. The data of the highest occupied molecular orbital and the lowest unoccupied molecular orbital levers come from literatures.[11,15,16] Electroluminescent (EL) devices were fabricated by vapor-depositing organic layers onto a precleaned indium tin oxide glass substrate with a sheet resistance of 15 Ω/sq in vacuum chamber at

$3×10^{-4}$ Pa. The deposition process started with a 40 nm thick N,N′-diphenyl-N,N′-bis(1-naphthyl)(1,1′-biphenyl)-4,4′-diamine (NPB) as hole-transporting layer, a 30 nm thick FIrpic and the Cu^I complex codoped CBP as emitting layer, a 40 nm thick 2,2′,2″-(1,3,5-benzenetriyl)tris-[1-phenyl-1H-benzimidazole] as exciton-blocking and electron-transporting layer, and finally a LiF and Al composite cathode. Details of the fabrication process and the property measurement of the devices were the same as reported elsewhere.[11]

Figure 2 shows the EL spectra of the 2 and 4 wt % Cu^I complex based devices with different doping concentrations of FIrpic at a voltage of 6 V. We can note that there is a small fraction emission of NPB in the 2 wt % Cu^I complex monodoped device, which may result from interlayer energy transfer from CBP or recombination of the injected electrons with holes in the NPB layer. As the concentration of FIrpic increases, the emission of FIrpic with the peak at about 472 nm increases relative to the Cu^I complex with the peak
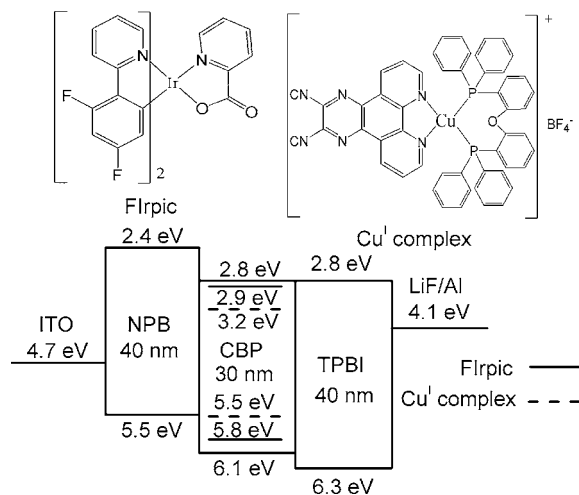

FIG. 1. Molecular structures of the materials and the energy diagram of the codoped devices.

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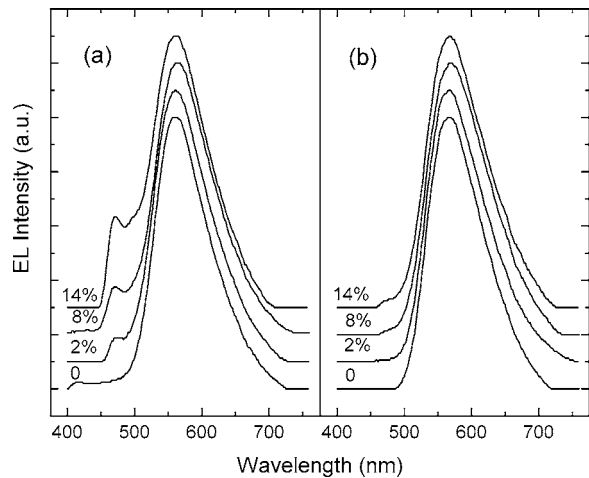
FIG. 2. EL spectra of the 2 wt % (a) and 4 wt % (b) Cu^I complex based devices with different doping concentrations of FIrpic at 6 V.

FIG. 3. Current efficiency and power efficiency vs current density of the 8 wt % FIrpic and 2 wt % Cu^I complex codoped device.

at about 562 nm. Meanwhile, the emission of NPB disappeared, suggesting that all the energy of CBP is transfer to the dopants. However, even with 14 wt % FIrpic, the emission of FIrpic is weaker compared with the Cu^I complex. Similar trend is found in the 4 wt % Cu^I complex based devices except the even weaker emission of FIrpic and the redshifted emission of the Cu^I complex to 568 nm due to the dipole-dipole interaction between the Cu^I complex molecules.[11,12]

The EL performances of the devices are summarized in Table I. It can be found that the performances of the codoped devices, i.e., the current efficiency, the power efficiency, and the maximum luminance, are improved significantly compared with the Cu^I complex monodoped devices. As the doping concentration of FIrpic increases, the efficiencies of the 2 and 4 wt % Cu^I complex based devices increase at first, and then slightly decrease with further increased doping concentration. In the 2 wt % Cu^I complex based devices, a maximum current efficiency and power efficiency of 26.6 cd/A and 16.7 lm/W are found at 0.13 mA/cm^2 when the doping concentration of FIrpic is 8 wt %. The efficiencies are increased by factors of 2.6 and 2.1, respectively, compared with the 2 wt % Cu^I complex monodoped device which shows a maximum current efficiency and power efficiency of 10.3 cd/A and 7.8 lm/W. The decrease of efficiencies at high current density in the codoped devices is more significant than the monodoped one, as shown in Fig. 3, which is
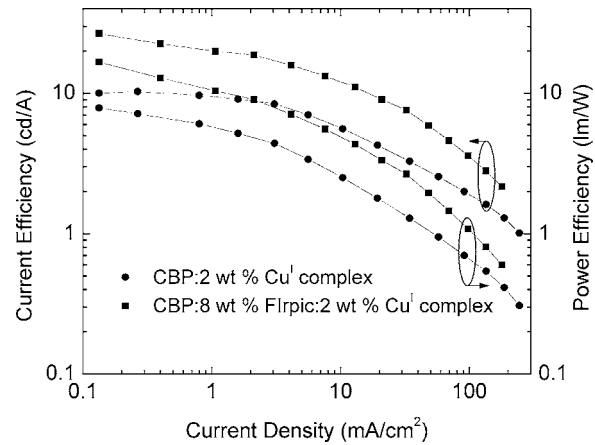
attributed to the more significant triplet-triplet annihilation.[17] However, the current efficiency and power efficiency of the codoped device are higher than the monodoped one in the whole current range, and the current efficiency and power efficiency are remaining 2.1 and 1.9 times to the monodoped ones at 20 mA/cm^2. In the 4 wt % Cu^I complex based devices, the highest efficiencies are found when the doping concentration of FIrpic is 2 wt %, and the improvements of the efficiencies are less significant. The improvements would decrease with further increased doping concentration of the Cu^I complex (not shown here). It is common that in the doped device, higher doping concentration would lead to aggregate-induced quenching and hence decreases the efficiency of the devices.[18] Thus, we believe that in our codoped system, higher concentration of any dopant or the total one would lead to increased aggregate-induced efficiency decrease.

To further understand the mechanisms of the improvements of the device properties, photoluminescence transient decays in the 50 nm CBP:Cu^I complex (2 wt %), CBP:FIrpic (8 wt %), and CBP:FIrpic:Cu^I complex (8 wt %,2 wt %) films were investigated. The transient decays were measured with a spectrometer (Spex 1403), a photomultiplier, and a boxcar averager, and the samples were excited by Neodymium-doped yttrium aluminum garnet laser at a wavelength of 355 nm with 10 ns pulse width. The time rates of decay of FIrpic and the Cu^I complex in the films were taken from their photoluminescent emissions centered

TABLE I. EL performances of the devices.

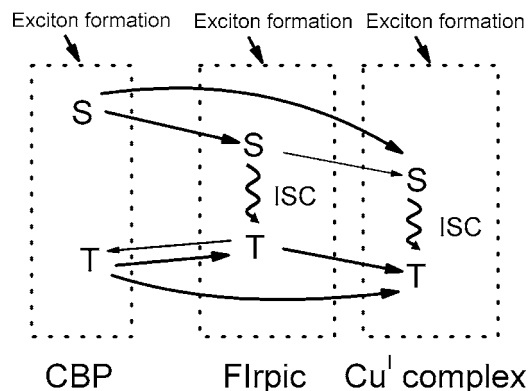| Mixing ratio			Maximum efficiency		At 20 mA/cm^2		
Cu^I complex (wt %)	FIrpic (wt %)	Turn on voltage (V)	Current efficiency (cd/A)	Power efficiency (lm/W)	Current efficiency (cd/A)	Power efficiency (lm/W)	Maximum luminance (cd/m^2)
2	0	3.2	10.3	7.8	4.2	1.7	2468
2	2	3.9	15.1	8.6	6.1	2.0	2870
2	8	3.7	26.6	16.7	9.1	3.3	3883
2	14	3.7	14.3	7.8	6.2	2.0	3851
4	0	3.2	12.6	8.8	5.0	1.9	2439
4	2	3.6	17.8	11.1	8.1	3.1	4050
4	8	4.1	15.0	8.6	5.7	1.9	3753
4	14	4.3	10.2	5.3	4.9	1.7	3093

FIG. 4. Proposed energy transfer mechanisms in the codoped system.

at 470 and 552 nm, respectively. The lifetimes were fitted by second and third orders for the monodoped and codoped films, respectively, according to literature.[19] The lifetime of FIrpic in the CBP:FIrpic film is 1.44 μs, which is similar to previous report.[20] Whereas, the lifetime of FIrpic in the codoped films decreases to 0.41 μs. While the lifetime of the Cu[I] complex increases from 0.41 μs in the CBP:Cu[I] complex film to 1.15 μs in the codoped film. Combining with the findings in the EL spectra, we can deduce that the improvements are attributed to the efficient energy transfer from FIrpic to the Cu[I] complex, and the emission of FIrpic is quenched primarily through energy transfer to the Cu[I] complex.

Figure 4 proposes the energy transfer mechanisms in the codoped system. Under the electrical field, excitons are formed on CBP with the singlet-to-triplet formation ratio of 1/3. On the other hand, excitons can be formed directly on the phosphors after they trapped the injected holes and electrons. The singlets of CBP can be directly transferred to the singlets of FIrpic and the Cu[I] complex through Förster energy transfer mechanism, while the triplets of CBP can be directly transferred to the triplets of FIrpic and the Cu[I] complex through Dexter energy transfer mechanism. The singlets of the two phosphors, including transferred from CBP and formatted directly in themselves, may rapid transfer to their triplets through intersystem crossing (ISC) due to strong spin orbit coupling. Due to efficient ISC of FIrpic, energy transfer from the singlets of FIrpic to the Cu[I] complex is minor and hence can be ignored. As reported previously,[21] the triplet energy of FIrpic is 0.1 eV higher than CBP; thus, there are three pathways to relax FIrpic triplets, i.e., radiate to its ground states, transfer back to the CBP triplets, and transfer to the Cu[I] complex triplets. Lower emission intensity of FIrpic in the EL spectra indicates that the fraction of the radiation of FIrpic is small. The shorter excited lifetime of the Cu[I] complex (0.41 μs) compared with FIrpic (1.44 μs) restricts back energy transfer from FIrpic to CBP but facilitates energy transfer from FIrpic to the Cu[I] complex. Thus, in principle, nearly all the excitons are transferred to the triplet states of the Cu[I] complex. Differing from the phosphor sensitized fluorescent dye system which has some excitons loss ways, this system avoids all the possible loss of the excitons, which would lead to higher device efficiencies.

In summary, we demonstrated that the EL performances of the devices based on the Cu[I] complex can be significantly improved by codoping FIrpic into CBP as the EML. The maximum current efficiency and power efficiency of the 8 wt % FIrpic and 2 wt % Cu[I] complex codoped device were increased by factors of 2.6 and 2.1 compared with the 2 wt % Cu[I] complex monodoped device, respectively. The improvements are attributed to the efficient energy transfer from FIrpic to the Cu[I] complex. The improved yellow emission has the potential use in constructing white OLEDs, and the phosphor sensitized phosphorescence concept has the potential use in improving the performances of the phosphorescence OLEDs.

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