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Highly efficient and color-tuning electrophosphorescent devices based on Cu^I complex

Guangbo Che, Zisheng Su, Wenlian Li,[a] Bei Chu, and Mingtao Li
Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16-Dong NanHu Road, Changchun 130033, People's Republic of China and Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Zhizhi Hu and Zhiqiang Zhang
Organic Photoelectronic Materials and Technology Development Center, Anshan University of Science and Technology, Anshan 114000, People's Republic of China

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Highly efficient electrophosphorescence from organic light-emitting devices based on a Cu^I complex, [Cu(DPEphos)(Dicnq)]BF$_4$ (DPEphos=bis[2-(diphenylphosphino)phenyl]ether and Dicnq=6,7-Dicyanodipyrido[2,2-*d*:2′,3′-*f*] quinoxaline), doped into 4,4′-*N*,*N*′-dicarbazole-biphenyl is demonstrated. The performances of these devices fabricated by vacuum vapor deposition technique are among the best reported for devices incorporating Cu^I complexes as emitters. A low turn-on voltage of 4 V, a maximum current efficiency up to 11.3 cd/A, and a peak brightness of 2322 cd/m^2 were achieved, respectively. The phosphorescent operating mechanism of organic light-emitting devices based on Cu^I complex was discussed. Electroluminescent colors can be tuned ranging from green-yellow to orange-red region, and its band tail at longer wavelength can cover near infrared. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2345826]

Phosphorescent materials based on heavy metal complexes have been extensively used to fabricate highly efficient electroluminescent (EL) devices since the utilization of the triplet excitations in organic light-emitting devices (OLEDs) was proposed several years ago.[1] In phosphorescent complexes, singlet-triplet state mixing was generated owing to strong spin-orbital coupling of transition metal ions, thus both singlet and triplet excitons can be fully utilized leading to an internal quantum efficiency of 100% theoretically.[2–4] Recently, Cu^I complexes as a new class of electrophosphorescent materials have attracted much attention due to their advantages including abundant resource, low cost, and nontoxic property compared to noble metal complexes, e.g., Re^I,[5,6] Os^{II},[7] Ir^{III},[3,8–10] Pt^{II},[2,11] and Rh^I.[12] Ma *et al.* and Jia *et al.* fabricated the EL devices based on polynuclear Cu^I complexes by spin coating, but the performances of those devices should be further improved.[13,14] The low efficiencies were presumably attributed to the relatively long excited-state lifetime of those Cu^I complexes or to the emissive layer fabricating method. Zhang *et al.* demonstrated an improved efficiency of OLEDs by using a mononuclear Cu^I complex as an emitter which exhibits a short excited-state lifetime.[15]

In this letter, we describe highly efficient EL devices based on a Cu^I complex, [Cu(DPEphos)(Dicnq)]BF$_4$ (CuDD), in which DPEphos and Dicnq stand for bis[2-(diphenylphosphino)phenyl] ether and 7-dicyanodipyrido [2,2-*d*:2′,3′-*f*]quinoxaline, respectively. Vacuum vapor deposition instead of spin coating was chosen to fabricate devices since CuDD is sufficiently stable to be sublimed. The emissive color can be tuned by varying the Cu-complex content in the host 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) from green-yellow to orange-red region, and the band tail at longer wavelength can even cover near infrared zone. A low driving bias of 4 V, a maximum efficiency up to 11.3 cd/A, and a peak brightness of 2322 cd/m^2 were gained, respectively. Comparing with previously reported devices fabricated from Cu^I complexes, performances of devices based on our new Cu complex were considerably improved.

Ligand Dicnq is conveniently synthesized by the condensation of 1,10-phenanthroline-5,6-dione and diaminomaleonitrils,[16] and complex CuDD was prepared from [Cu(NCCH$_3$)$_4$]BF$_4$, DPEphos, and Dicnq in CH$_2$Cl$_2$ at room temperature (RT).[17] Crystals of this complex were obtained by slow vapor diffusion of diethylether into the resulting solution and were used to fabricate devices. Chemical structure of CuDD and configuration of EL devices are depicted in Fig. 1.

The EL devices based on CuDD were fabricated as follows: 4, 4′,4″-tris[2-naphthyl(phenyl)amino] triphenylamine and *N*,*N*′-di-1-naphthyl-*N*,*N*-diphenyl-benzidine (NPB) were used as the hole-injection material and hole transporter. These two layers were deposited in sequence on indium-tin-oxide substrate with a resistance of 20 Ω/sq. Deposition of an emissive layer of CuDD doped in CBP film with mass ratios of 2%–25% followed. A layer of 2,2′,2″-(1,3,5-benzenetriyl)tris-[1-phenyl-1H-benzimidazole] to serve as the hole blocker and the electron transporter and LiF/Al as the complex cathode were then deposited. The pressure in the chamber is below 2×10^{-4} Pa. Deposition rates and thicknesses of layers were monitored by an oscillating quartz monitor. Photoluminescence (PL), EL spectra, and Commission Internationale de I'Eclairage (CIE) coordinates were measured with a Hitachi MPF-4 fluorescence spectrophotometer. The data of brightness-current-voltage (*B-I-V*) were measured with a 3645 dc power supply combined with a 1980A spot photometer. All measurements were

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[a] Author to whom correspondence should be addressed; electronic mail: wllioel@yahoo.com.cn

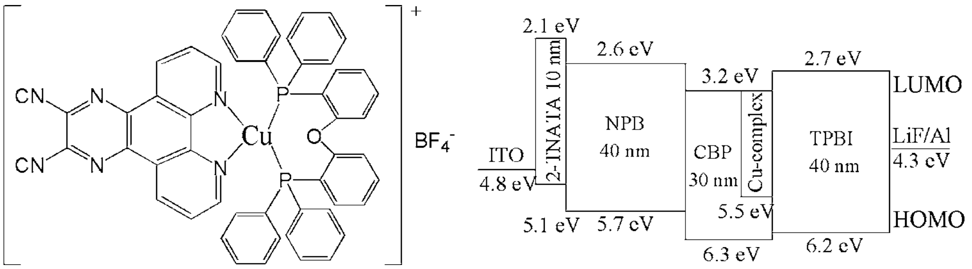

FIG. 1. Chemical structure of Cu^I complex (left) and energy diagram of OLED (right).

carried out in air at RT. Emission spectrum of Cu complex in CH_2Cl_2 glass at 77 K was performed under excitation of a Nd:YAG (yttrium aluminum garnet) pulsed laser. Absorption spectra were measured with a Shimadzu UV-3101PC UV-Vis-NIR scanning spectrophotometer. The excited-state lifetimes of PL were determined by a system equipped with a TDS 3052 digital phosphor oscilloscope pulsed Nd:YAG laser with a THG 355 nm output.

Different from other most phosphorescent complexes, no emission from CuDD in solid state or in solution was observed at RT. Only weak PL emission of Cu complex in CBP films at RT or in CH_2Cl_2 glass at 77 K was determined. Absorption spectrum of CuDD in CH_2Cl_2, PL spectra of CuDD doped into CBP films with different concentrations at RT, and PL spectrum of CBP were displayed in Fig. 2. The broad metal to ligand charge transfer absorption band of Cu complex centered at 420 nm overlaps the PL spectrum of CBP insufficiently, indicating that Förster energy transfer is not the dominant mechanism here. It is interesting that the PL colors of CuDD doped into CBP films showed a strong dependence on doping levels, i.e., as the CuDD concentration in CBP increases from 2% to 25%, there is a remarkable redshift of 52 nm shown in Fig. 2. There exists emission from CBP at lower concentration ($\leqslant 6\%$) due to incomplete energy transfer. As the doping concentration increases up to 10%, the emission from CBP disappeared, indicating that complete energy transfer from host CBP to guest CuDD was realized. However, emission from CBP appeared again at a concentration of 25% arising from the saturation of phosphorescence sites, as illustrated in Fig. 2.

Figure 3 plots the dependence of EL spectra on doping concentrations in CBP. Obviously, with increasing doping level, EL bands also exhibit a redshifting trend similar to that of PL spectra, although the peak positions of EL and PL spectra are different. Color-tuning EL emissions can be observed from green-yellow to orange-red region as the doping concentration increases from 2% to 25%. The reason for PL and EL spectral shift was presumably attributed to strong polarization effect.[18] Complete quenching of EL emission from CBP occurred at a concentration of 6%, which is much lower than that in PL emission, suggesting that charge trapping is the dominant process rather than Förster energy transfer in our devices. The energy diagram of EL device provides further support, as illustrated in Fig. 1. The highest occupied molecular orbital energy level (5.5 eV) of CuDD is higher than that of CBP (6.3 eV), which meets the requirement for efficient charge trapping followed by recombination on phosphorescent molecules.[19] Furthermore, as the concentration increases up to 25%, blue emission from NPB was found. This was likely due to the interlayer energy transfer from CBP to NPB as a result of saturation of the emission sites at high doping concentrations.

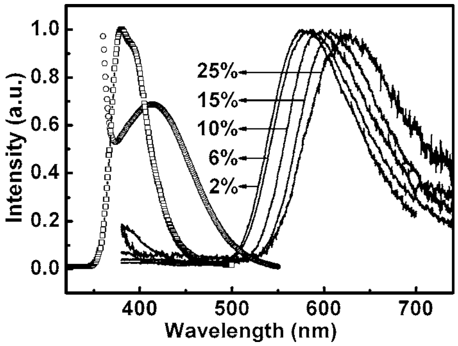

FIG. 2. Normalized absorption spectrum of Cu complex in CH_2Cl_2 (○), PL spectra of neat CBP film (□), and CuDD-doped CBP films with various contents under excitation of 355 nm UV light.

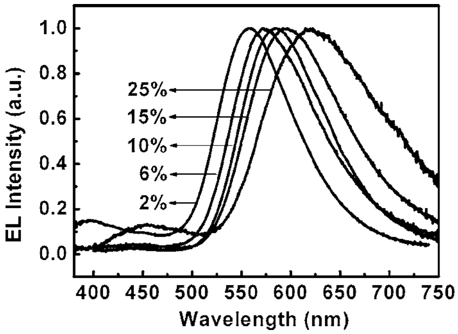

FIG. 3. Normalized EL spectra of devices based on CuDD with various doping levels at 6 V.

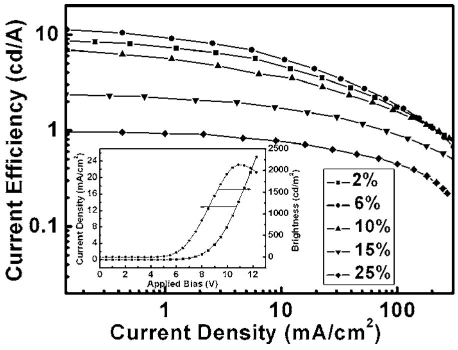

FIG. 4. Dependence of current efficiency (η_c) on current density (J) of EL devices based on CuDD doped into CBP. Inset: V-I-B plots of EL device fabricated from 6% CuDD in CBP.

Figure 4 shows the efficiency-current density (η_c-J)

TABLE I. EL performances of OLEDs with various Cu-complex concentrations.

Doping concentration (x%)	Turn-on voltage (V)	η_c at 0.14 mA/cm^2 (cd/A)	η_c at 1.0 mA/cm^2 (cd/A)	η_c at 100 mA/cm^2 (cd/A)	λ_{max} of EL (nm)	Maximum brightness (cd/m^2)
2	4.5	8.5	7.4	1.7	558	2268
6	4.0	11.3	9.2	1.9	572	2132
10	4.0	6.9	5.8	1.6	585	2322
15	4.5	2.4	2.2	0.9	592	1586
25	5.5	1.0	0.9	0.5	615	618

characteristics of devices based on CuDD with different concentrations. Key properties of these devices are summarized in Table I. Thanks to the relatively short lifetime of CuDD (4.26 μs), which is a favorable feature for improving performance of OLEDs,[20] all devices exhibit a very slow decrease of current efficiency with increasing current density, indicating that the saturation of the phosphorescence sites is not severe. Similar to other phosphorescent EL devices, the efficiency of devices based on CuDD shows a strong dependence on doping concentration. By comparison, the device with 6% CuDD-doped CBP shows a maximum current efficiency of 11.3 cd/A and a peak brightness as high as 2132 cd/m^2 with a very low turn-on voltage at 4 V (inset of Fig. 4). Most importantly, the efficiencies of this device are still kept at a high level at high current density. Besides the relatively short lifetime of CuDD, we assume that charged carrier trap effect is another important factor to improve the EL efficiency by reducing the energy loss during energy transfer.

In conclusion, we have demonstrated highly efficient electrophosphorescent devices using a Cu^{I} complex as an emitter. By adjusting CuDD dopant concentration, color-tuning EL emissions were obtained from green-yellow to orange-red region. Vacuum vapor deposition technique, short excited-state lifetime of Cu^{I} complex, and efficient charge trapping followed by recombination on emissive layer come into effect to result in significant improvements in device performance. The present results indicate that some materials with no emission at RT in solid or in solution can also provide excellent EL performance, and this work paves the way in developing efficient and economical phosphorescent materials.

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