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Bright electrophosphorescent devices based on sterically hindered spacer-containing Cu(I) complex

Zhenjun Si[a], Jiang Li[b], Bin Li[a,*], Shiyong Liu[b,*], Wenlian Li[a]

[a]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, and Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun 130033, PR China*
[b]*State Key Laboratory of Integrated Optoelectronics, Jilin University, Changchun 130023, PR China*

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Abstract

A Cu(I) complex, [Cu(Dppp)(DPEphos)]BF_4 (Dppp = 2,3-diphenyl-pyrazino[2,3-f][1,10]phenanthroline, DPEphos = Bis[2-(diphenylphosphino)phenyl]ether), is synthesized and used as the dopant in bright electrophosphorescent devices with the general structure ITO/*m*-MTDATA (30 nm)/NPB (20 nm)/CBP: × wt% [Cu(Dppp)(DPEphos)]BF_4 (30 nm)/Bphen (20 nm)/Alq_3 (20 nm)/LiF (0.8 nm)/ Al (200 nm). These devices exhibit a maximum brightness of 4483 cd/m^2 and a peak efficiency of 3.4 cd/A. Compared with previously reported similar devices based on Cu(I) complexes, the brightness of the devices presented in this article is the best. Meanwhile, 2% [Cu(Dppp)(DPEphos)]BF_4-based devices exhibit white light-emitting properties with CIE coordinates of (0.32. 0.35) at 10 V.

PACS: 78.55; 85.60.P; 79.60.B

Keywords: OLEDs; Electrophosphorescence; Cu(I) complex

1. Introduction

The application of heavy metal complexes into electroluminescent (EL) devices has been extensively studied since the utilization of the triplet excitations was reported by Forrest et al. [1]. All of these studies indicate that strong spin–orbital coupling of central ions results in the mixing of singlet–triplet state, and the full utilization of both singlet and triplet excitons can achieve an internal quantum efficiency of 100% theoretically [2,3]. Besides, Cu(I) complexes, as a new class of electrophosphorescent materials, have recently attracted much more attention due to their advantages such as abundant resource, low cost, and nontoxic property compared to other heavy metal complexes [4–8]. In 1999, Ma et al. [9] reported the low efficient OLEDs based on poly-nuclear Cu(I) complexes by spin coating. The low efficiency may be attributed to the phase segregation, which is unavoidable during the solution process. Up to now, the performances of the Cu(I)-complexes-based OLEDs have been greatly improved by several strategies, such as introduction of novel ligands into Cu(I) complexes [10,11] and optimization of the device structure [12]. It has been found that the sterically hindered spacers in electrophosphorescent materials might endow the OLEDs much better light-emitting properties. For example, Wang et al. [13] reported that the introduction of substitution groups into the second diimine ligands could improve the performances of the Cu(I)-complexes-based OLEDs .

In this paper, we demonstrate the bright OLEDs by employing [Cu(Dppp)(DPEphos)]BF_4 (Dppp = 2,3-diphenyl-pyrazino[2,3-f][1,10]phenanthroline, DPEphos = Bis[2-(diphenylphosphino)phenyl]ether) as the dopant in emissive layer. The peak current efficiency of 3.4 cd/A and the maximum brightness of 4483 cd/m^2 were obtained, respectively. The key performance parameters of these OLEDs are listed in Table 1.

*Corresponding authors. Fax: +86 0431 86176935.
E-mail addresses: lib020@ciomp.ac.cn (B. Li), syliu@mail.jlu.edu.cn (S. Liu).

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Table 1
The key performance characteristics of the OLEDs based on $[Cu(Dppp)(DPEphos)]BF_4$

Concentration (wt%)	B_{max}[a] (cd/m^2)	η[b] (cd/A)	η[c] (cd/A)	η[d] (cd/A)
2	4189	1.14	0.88	1.33
6	4483	2.94	1.41	2.94
10	4123	3.33	1.40	3.40
15	1361	1.88	0.67	1.93

[a]Maximum luminance.
[b]Current efficiency at 1 mA/cm^2.
[c]Current efficiency at 100 mA/cm^2.
[d]Maximum current efficiency.

2. Experiment

2.1. Preparation of Dppp

Ligand Dppp was conveniently synthesized by the condensation of 5,6-diamino-1,10-phenanthroline and benzyl [14]. Benzyl (0.420 g, 2.0 mmol) and 5,6-diamino-1,10-phenanthroline (0.420 g, 2.0 mmol) were added into 50 mL flask containing 10 mL glacialacetic acid. The mixture was refluxed and stirred under nitrogen for 10 h. After cooling to room temperature (RT), the mixture was poured into 60 mL water and stirred for another 0.5 h. The pale solid was collected by filtration and successively washed with 10 mL diluted aqueous ammonia and 50 mL water, and finally dried in vacuum, yielding 0.53 g (ca. 70%).

2.2. Preparation of $[Cu(Dppp)(DPEphos)]BF_4$

Complex $[Cu(Dppp)(DPEphos)]BF_4$ was prepared from $[Cu(NCCH_3)_4]BF_4$, DPEphos, and Dppp in CH_2Cl_2 [15]. A mixture of $[Cu(NCCH_3)_4]BF_4$ (0.063 g, 0.25 mmol) and bis[2-(diphenylphosphino)phenyl]ether (0.108 g, 0.20 mmol) in 20 mL of dichloromethane was stirred at RT for 2 h and then treated with a solution of Dppp monohydrate (0.0768 g, 0.20 mmol) in 5 mL of dichloromethane. This reaction mixture was stirred for another 1 h and filtered, the and solvent was distilled out, yielding 0.75 g (ca. 70%). The yellow powder of this complex was purified by vacuum sublimation and used to fabricate EL devices.

2.3. Fabrication of the devices

The chemical structure of $[Cu(Dppp)(DPEphos)]BF_4$ and the energy diagram of EL devices are depicted in Fig. 1. The general device structure is indium tin oxide (ITO)/4,4′,4″-tris [3-methylphenylphenylamino] triphenylamine (*m*-MTDATA) (30 nm)/*N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB) (20 nm)/CBP: × wt% $[Cu(Dppp)(DPEphos)]BF_4$ (30 nm)/4,7-diphenyl-1,10-phenanthroline (Bphen) (20 nm)/tris(8-hydroxyquinoline)aluminum (Alq_3) (20 nm)/LiF (0.8 nm)/Al (200 nm), where *m*-MTDATA is used as the hole-injection layer, NPB is the hole-transporting and electron-blocking layer, and Bphen and Alq_3 are employed as the exciton-blocking layer and the electron-transporting layer, respectively. CBP doped with $[Cu(Dppp)(DPEphos)]BF_4$ is chosen as the light-emitting layer. All layers in the diodes are deposited by a resistive heating method. The pressure of the chamber is below 3×10^{-4} Pa. The shadow masks are used to define the electrode areas and to make eight 4 mm^2 devices per substrate.

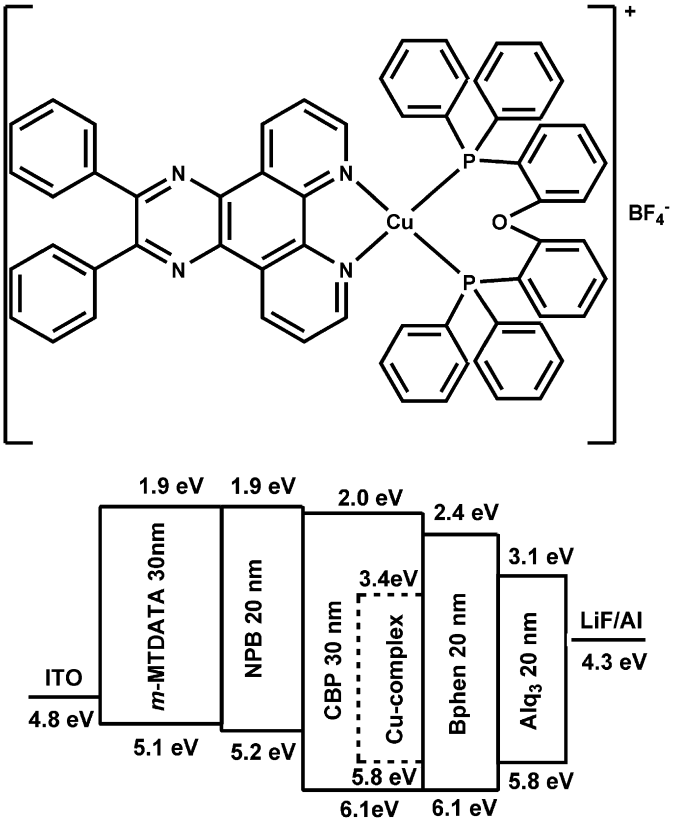

Fig. 1. Chemical structure of $[Cu(Dppp)(DPEphos)]BF_4$ (upside) and the energy diagram of EL devices are depicted (underside).

2.4. Measurement

Absorption and emission spectra were recorded on Shimadzu Model 3100 spectrometer and Hitachi Spectrophotometer model F-4500, respectively. The EL spectra and Commission Internationale de L'Eclairage (CIE) coordinates of the devices are measured by a PR650 spectrometer under ambient conditions. The excited-state lifetime of $[Cu(Dppp)(DPEphos)]BF_4$ powder of 0.27 μs is detected by a system equipped with a TDS 3052 digital phosphor oscilloscope pulsed Nd:YAG laser with a THG 355 nm output. Cyclic voltammetry measurements were conducted on a voltammetric analyzer (CH Instruments, Model 620B) with a polished Pt plate as the working

electrode, Pt mesh as the counter electrode, and a commercially available saturated calomel electrode as the reference electrode, at a scan rate of 0.1 V/s. The supporting electrolyte is 0.1 mol/L tetrabutylammonium hexafluorophosphate in CH_3CN. Prior to each electrochemical measurement, the solution was purged with nitrogen for ~10–15 min to remove the dissolved O_2 gas. All measurements are carried out at RT.

3. Results and discussion

The absorption spectra and photoluminescent (PL) spectra of neat CBP and [Cu(Dppp)(DPEphos)]BF_4 films are presented in Fig. 2. The absorption band ranging from 240 to 400 nm is attributed to the spin-allowed ligand-centered transitions with comparison to the absorption spectra of Dppp and DPEphos. The absorption band extending into the visible region from 400 to 500 nm is tentatively assigned to the metal-to-ligand charge transfer (MLCT) [$d\pi(Re)\rightarrow\pi^*$(ligand)] transitions. The PL spectrum of [Cu(Dppp)(DPEphos)]BF_4 film exhibits a broad band centered at 565 nm, which is attributed to the ^{3}MLCT emission. The PL spectrum of CBP film centered at 380 nm largely overlaps with the MLCT absorption spectrum of [Cu(Dppp)(DPEphos)]BF_4 film, which demonstrates that Förster energy transfer probably exists during the process of UV or electrical excitation.

Fig. 3 plots the dependence of EL spectra on doping concentrations in CBP. The EL emission centered at 420 nm, which might originate from CBP, almost disappears when the doping concentration rises up to 15%. The other emission band centered at ca. 570 nm are tentatively ascribed to the ^{3}MLCT emission of [Cu(Dppp)(DPEphos)]BF_4, which shows red-shift with the increasing of the doping concentration from 2 to 15%. This red-shift should be explained by the interaction of the dopant molecules at higher doping concentration [10]. As shown in Fig. 4, 2% [Cu(Dppp)(DPEphos)]BF_4-based devices emit white light with the CIE coordinates of (0.32, 0.35) at 10 V, with a brightness of 512 cd/m^2 and a current efficiency of 1.0 cd/A, indicating that [Cu(Dppp)(DPEphos)]BF_4 holds the potential application in white OLEDs.

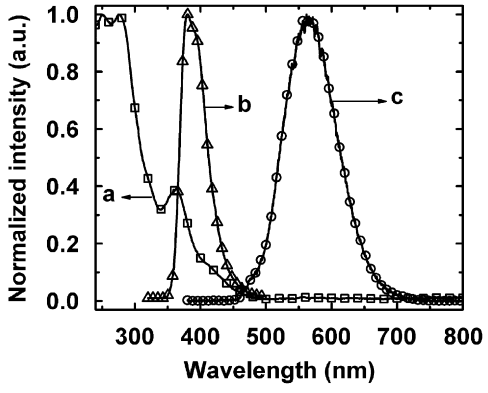

Fig. 2. Normalized absorption spectrum of Cu complex in CH_2Cl_2 solution (a), PL spectra of neat CBP (b), and [Cu(Dppp)(DPEphos)]BF_4 (c) films.

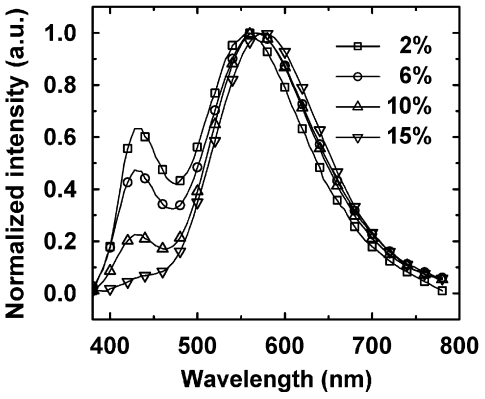

Fig. 3. Normalized EL spectra of devices based on [Cu(Dppp)(DPEphos)]BF_4 with various doping levels at 5 V.

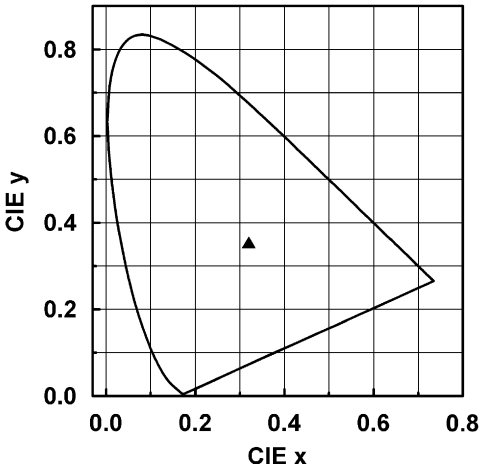

Fig. 4. White CIE coordinates of 2% [Cu(Dppp)(DPEphos)]BF_4-based OLEDs at 10 V.

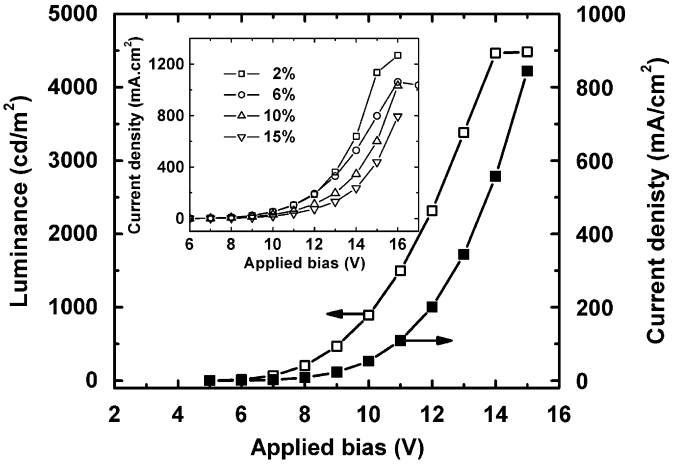

Fig. 5. *J–L–V* characteristics of 6 wt% [Cu(Dppp)(DPEphos)]BF_4-doped devices. Inset: *J–V* characteristics of the devices based on the various doping concentrations.

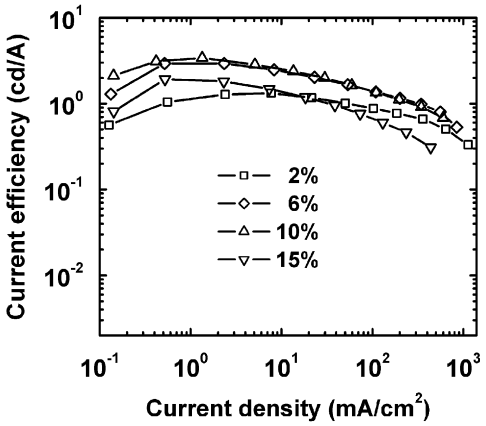

Fig. 6. Current efficiency of the OLEDs based on [Cu(Dppp)(DPEphos)]BF_4 as a function of current density.

Fig. 5 shows the current density–luminance–voltage (*J–L–V*) characteristics of a 6 wt% [Cu(Dppp)(DPEphos)]BF_4-doped CBP device. A maximum brightness of 4483 cd/cm^2 at 15 V and a maximum efficiency of 2.93 cd/A at 7 V are achieved, indicating that employment of sterically hindered groups containing diimine compounds as the second ligand of Cu(I) complexes is helpful to improve the device performances. Shown in the inset of Fig. 5 is the effect of doping concentration on the *J–V* characteristics of the EL devices. By increasing the doping concentration of [Cu(Dppp)(DPEphos)]BF_4 from 2 to 15%, the current density monotonously decreases at the same driving voltage, indicating that the dopant molecules can lower the carrier-transporting mobility in the CBP layer, which is in accordance with the energy level diagram of the device presented in Fig. 1. The highest occupied molecular orbital (HOMO) (5.8 eV) and the lowest unoccupied molecular orbital (LUMO) (3.4 eV) levels of [Cu(Dppp)(DPEphos)]BF_4 are located between the HOMO (6.1 eV) and LUMO (2.0 eV) levels of CBP, which meets the requirement for efficient carriers trapping [16]. So both the holes and the electrons transported into the CBP layer can be trapped directly by [Cu(Dppp)(DPEphos)]BF_4 molecules and recombine with the counter charge carriers.

The efficiency versus current density characteristics of devices based on [Cu(Dppp)(DPEphos)]BF_4 are presented in Fig. 6. It is found that a 10% doped device offers the highest EL efficiency of 3.4 cd/A at 0.42 mA/cm^2, which would be further enhanced by optimization of the device structure. As can be seen, the efficiency increases slowly at first with the increase of the current density, and the peak efficiency of these devices appears at ~0.5 mA/cm^2, suggesting that the effect of triplet–triplet annihilation on efficiency is neglectable at a low current density range, which is partly due to the shorter lifetime and the sterically hindered spacer of phenyl groups in the phosphor molecules. The triplet–triplet annihilation induced by the light-emitting site saturation should respond to the decreasing efficiency at high current density. The optimum concentration of the device is 10%, which is much higher than that of the device based on the fluorescence materials, indicating that Dexter transfer should occur during the EL process.

4. Conclusion

In summary, [Cu(Dppp)(DPEphos)]BF_4 is successively synthesized and applied as the phosphorescent dopant in a CBP emissive layer to construct a series of OLEDs. It is experimentally found that the brightness of 6 wt% [Cu(Dppp)(DPEphos)]BF_4-based devices is 4483 cd/m^2, which is the highest value for the OLEDs-based Cu(I) complexes so far. Efficient charge trapping should be mainly responsible for such an outstanding brightness. The CIE coordinates of the 2% doped devices indicate that the OLEDs based on [Cu(Dppp)(DPEphos)]BF_4 and suitable host materials probably result in highly pure white light emission.

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