



High light electroluminescence of novel Cu(I) complexes

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ABSTRACT

Three novel Cu(I) complexes, [Cu(DPEphos(NN))BF₄], where NN = 1-(4-5'-phenyl-1,3,4-oxadiazolylbenzyl)-2-pyridinylbenzimidazole (OXD-Pybm; L1) (**1**), 1-(4-carbazolylbutyl)-2-pyridinylbenzimidazole (Carl-Pybm; L2) (**2**), and 1-H-2-pyridinylbenzimidazole (HPybm; L3) (**3**), were synthesized. The photoluminescent (PL) properties of **1–3** and the electroluminescent (EL) properties of complexes **1** and **2** were systematically studied. The maximum brightness of **2**-based devices was 8669 cd/m², which should be the best among the reported Cu(I) complexes-based devices.

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1. Introduction

In order to realize the application of organic light-emitting diodes (OLEDs) in flat-panel displays, lighting sources, etc. The neutral metal complexes are commonly chosen as the active materials for OLEDs to avoid charge migration under the device electric field [1–10]. As a result, the performance of the OLEDs based on the charged luminescent metal complexes such as Ru(II) complexes [11,12] and Cu(I) complexes [13–17] were not widely studied. However, Cu(I) complexes [13–15], a new class of charged electrophosphorescent materials, possess many advantages such as relatively abundant resource and nontoxic property, which make these complexes very applicable in OLEDs. In 1999, Ma et al. [16] reported the first Cu(I) complex-based OLEDs with the spin-coated polynuclear Cu(I) complex as the active material. Lately, Che et al. [15] obtained highly efficient OLEDs based on mononuclear Cu(I) complex; the efficiency and the brightness of the devices are 11.3 cd/A and 2322 cd/m², respectively. To date, the performances of the Cu(I) complexes-based OLEDs have been greatly improved by several strategies, such as the introduction of novel ligands into Cu(I) complexes [15,17]. At the same time, it has been found that the sterically hindered spacers in electrophosphorescent materials might endow the OLEDs much better light-emitting properties, for example, the introduction of substitution groups into the second diimine ligands could improve the performances of the Cu(I) complexes-based OLEDs [13]. In this

paper, we synthesized three novel Cu(I) complexes [Cu(DPEphos)(OXD-Pybm)]BF₄ (**1**), [Cu(DPEphos)(Carl-Pybm)]BF₄ (**2**), and [Cu(DPEphos)(HPybm)]BF₄ (**3**) (where OXD-Pybm = 1-(4-5'-phenyl-1,3,4-oxadiazolylbenzyl)-2-pyridinylbenzimidazole, Carl-Pybm = 1-(4-carbazolylbutyl)-2-pyridinylbenzimidazole, HPybm = 1-H-2-pyridinylbenzimidazole, and DPEphos = bis(2-(diphenylphosphino)phenyl)ether) based on the studies mentioned above. It was found that complexes **1** and **2** were capable of being vacuum deposited to construct electroluminescent (EL) devices. Then, the photoluminescent (PL), the electrochemical, the thermal, and the EL properties of complexes **1** and **2** were systematically analyzed.

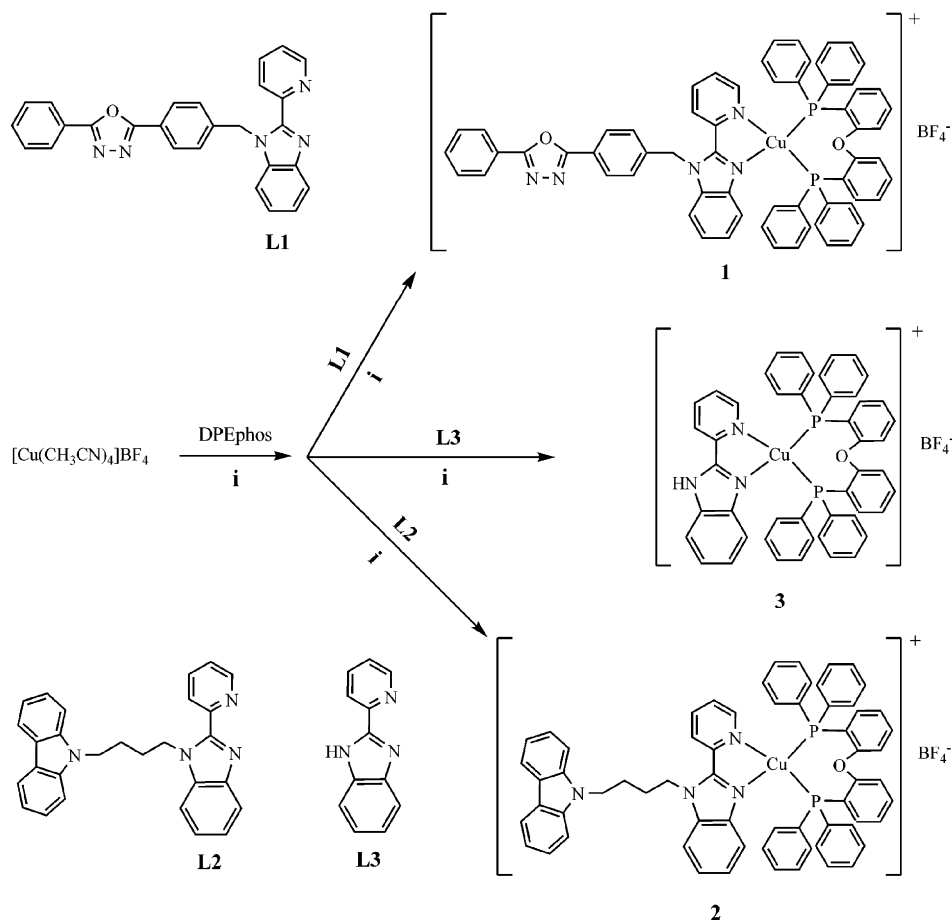
2. Experimental details

2.1. Materials

All starting chemicals and charge-transporting materials used in the process of the OLEDs fabrication: 4,4',4''-tris[3-methylphenylphenylamino]triphenylamine (m-MTDATA), 4,7-diphenyl-1,10-phenanthroline (Bphen), 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB), 4,4'-dicarbazolyl-1,1'-biphenyl (CBP), tris(8-hydroxy-quinoline)aluminum (Alq₃), and LiF were commercially available and used without further purification. The organic precursor of 2-4'-methylbenzyl-5-benzoyloxadiazole [18], the ligands of 1-(4-carbazolylbutyl)-2-pyridinylbenzimidazole (L1) [19], 1-(4-5'-phenyl-1,3,4-oxadiazolylbenzyl)-2-pyridinylbenzimidazole (L2) [20], and the corresponding Cu(I) complexes [21] were prepared according to the modified procedures. The synthetic route to complexes **1–3** is presented in Scheme 1, and

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Scheme 1. Synthetic Route to Complexes 1–3. (i) dichloromethane, RT, 1 h.

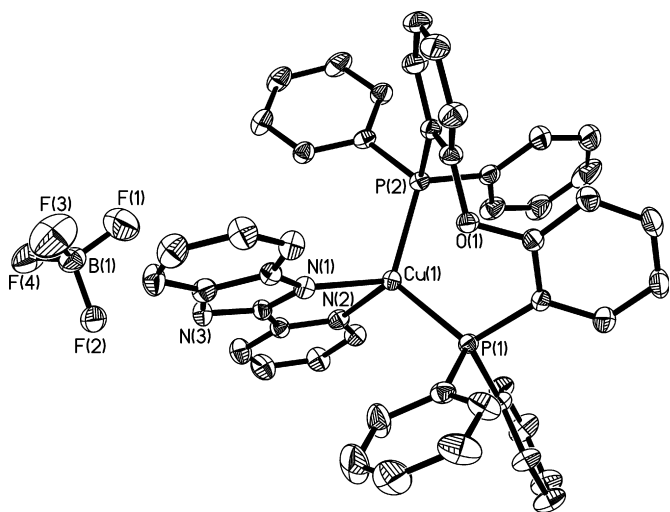


Fig. 1. ORTEP drawing of crystal **3** with displacement ellipsoids at the 20% probability level.

the ORTEP drawing of crystal **3** is presented in Fig. 1, as the coordination model for the synthesized Cu(I) complexes. All reactions and manipulations were carried out under N_2 with the use of standard inert atmosphere and Schlenk techniques. Solvents used for synthesis were dried by standard procedures and stored under N_2 . Solvents used in luminescent and electrochemical studies were of spectroscopic and anhydrous grades, respectively.

2.1.1. Synthesis of 2-(4-bromomethylphenyl)-5-phenyl-1,3,4-oxadiazole

To the solution of 13.20 g (0.097 mol) benzohydrazide, 9.80 g (0.097 mol) triethylamine, and 150 mL chloroform, 15.00 g (0.097 mol) 4-methylbenzoyl chloride was added dropwise at room temperature (RT). The resulting mixture was stirred for 1 h and then filtered. The collected solid was washed with water and methanol to give 23.43 g (yield 95%) product of *N'*-benzoyl-4-methylbenzohydrazide. A mixture of 20.00 g *N'*-benzoyl-4-methylbenzohydrazide and 250 mL $POCl_3$ in a 500 mL flask was refluxed under nitrogen for 5 h. The excessive $POCl_3$ was then distilled out and the residue was poured into water. The crude solid product was collected by filtration and purified by recrystallization from chloroform/methanol to give 15.80 g 2-4'-tolyl-5-phenyl-1,3,4-oxadiazole as needle-like crystals (85%). A mixture of 14.16 g (0.06 mol) 2-4'-tolyl-5-phenyl-1,3,4-oxadiazole, 11.68 g (0.066 mol) *N*-bromosuccinimide, 0.13 g benzoyl peroxide, and 200 mL CCl_4 in a 500 mL flask was refluxed for 5 h. The mixture was filtered while it was still hot. The solid was washed with hot chloroform. The residual solid was recrystallized from tetrahydrofuran/methanol to give 8.00 g of product as white needle-like crystals (40%). 1H NMR ($CDCl_3$, 500 MHz): 4.570 (2H, s), 7.334 (2H, d, $J = 8$), 7.534–7.552 (3H, m), 8.026 (2H, d, $J = 8$), 8.133 (2H, d, $J = 8$). Anal. Calcd. for $C_{15}H_{11}BrN_2O$: C, 57.16; H, 3.52; N, 8.89. Found: C, 57.04; H, 3.70; N, 8.96; and IR (in KBr) ν/cm^{-1} : 631, 1610, and 3018.

2.1.2. Synthesis of 9-4'-bromobutylcarbazole

To 100 mL anhydrous *N,N*-dimethylformamide (DMF) in a 250 mL flask, 0.74 g (0.020 mol) NaH and 3.34 g (0.020 mol) of

9-H-carbazole were added. The solution became clear after 1 h, and 3.0 mL (0.022 mol) 1,4-dibromobutane was added dropwise. The reaction mixture was stirred for another 6 h and then poured into 300 mL cold water; the organic components were extracted with CH_2Cl_2 (3×50 mL). The organic phase was washed with water and dried over anhydrous sodium sulfate. After the solvent was removed by rotary evaporation, the residue was purified by silica gel column chromatography with petroleum ether and acetic acid ethyl ester ($v/v = 10:1$) to yield 3.00 g white needle-like crystal. ^1H NMR (CDCl_3 , 500 MHz) δ [ppm]: 1.91 (m, 2H), 2.05 (m, 2H), 3.37 (t, 2H), 4.34 (t, 2H), 7.23 (m, 2H), 7.38 (d, 2H, $J = 8.0$ Hz), 7.46 (t, 2H), 8.09 (d, 2H, $J = 8.0$ Hz). Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{BrN}$: C, 63.59; H, 5.34; N, 4.63. Found: C, 63.45; H, 5.28; N, 4.74. IR (in KBr), ν/cm^{-1} : 3048, 2935, 2858, 1587, 1450, and 1370.

2.1.3. Synthesis of L1

To 100 mL stirring anhydrous DMF in a 250 mL flask, 0.37 g (0.010 mol) NaH and 1.95 g (0.010 mol) 2-pyridinylbenzimidazole were added; 3.45 g (0.011 mol) 2-(4-bromomethylphenyl)-5-phenyl-1,3,4-oxadiazole was added when the solution became clear. The mixture was stirred continuously for 24 h and then poured into 300 mL cold water. The resulting white powder was collected by filtering and purified by silica gel column chromatography with petroleum ether and acetic acid ethyl ester ($v/v = 10:1$) to yield 2.10 g yellow powder (60%). ^1H NMR (CDCl_3 , 500 MHz) δ [ppm]: 6.299 (2H, s), 7.364 (6H, m), 7.553 (3H, m), 7.875 (1H, t, $J = 8$), 7.909 (1H, d, $J = 8$), 8.045 (2H, d, $J = 8$), 8.115 (2H, d, $J = 6.5$), 8.469 (1H, d, $J = 7.5$), 8.629 (1H, d, $J = 3.5$). Anal. Calcd. for $\text{C}_{27}\text{H}_{19}\text{N}_5\text{O}$: C, 75.51; H, 4.46; N, 16.31. Found: C, 75.60; H, 4.52; N, 16.20. IR (in KBr), ν/cm^{-1} : 1446, 1549, and 1770.

2.1.4. Synthesis of L2

The procedure is similar to that of L1. Yield: 55%. ^1H NMR (CDCl_3 , 500 MHz) δ [ppm]: 2.016 (4H, m, $J = 6.5$), 4.340 (2H, t, $J = 6.5$), 4.846 (2H, t, $J = 6.5$), 7.240–7.343 (8H, m), 7.448–7.477 (2H, m), 7.828–7.888 (2H, m), 8.114 (2H, d, $J = 7.5$), 8.408 (1H, d, $J = 8$), 8.560 (1H, d, $J = 4$). Anal. Calcd. for $\text{C}_{28}\text{H}_{24}\text{N}_4$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.89; H, 6.00; N, 13.11. IR (in KBr), ν/cm^{-1} : 3046, 2924, 1584, 1446, and 1390.

2.1.5. Synthesis of 1

In 10 mL of dichloromethane, 0.539 g (0.001 mol) DPEphos and 0.314 g (0.001 mol) $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ were dissolved and was stirred for 1 h. After 0.429 g (0.001 mol) **L1** was added, the solvent was stirred for another 1 h. The solvent was removed in a water bath under reduced pressure. And the product was recrystallized two times by dissolving in dichloromethane and then precipitating by adding ether. The final yield depended on the ullage in the recrystallization process, and was about 50%. Anal. Calcd. for $\text{C}_{63}\text{H}_{47}\text{BCuF}_4\text{N}_5\text{O}_2\text{P}_2$: C, 67.66; H, 4.24; N, 6.26. Found: C, 67.41; H, 4.44; N, 6.12. IR (in KBr), ν/cm^{-1} : 1695, 1550, 1430, 1384, and 1060.

2.1.6. Synthesis of 2 and 3

The procedures are similar to that of (**1**). Yield: ~50%. Anal. Calcd. for $\text{C}_{64}\text{H}_{52}\text{BCuF}_4\text{N}_4\text{OP}_2$ (**2**): C, 69.54; H, 4.74; N, 5.07. Found: C, 69.26; H, 4.56; N, 4.93. IR (in KBr), ν/cm^{-1} : 1462, 1432, 1214, and 1092. Anal. Calcd. for $\text{C}_{48}\text{H}_{37}\text{BCuF}_4\text{N}_3\text{OP}_2$ (**3**): C, 65.21; H, 4.22; N, 4.75. Found: C, 64.97; H, 4.04; N, 4.48. IR (in KBr), ν/cm^{-1} : 1592, 1566, 1216, and 1097.

2.2. Measurements

A suitable amount of sample for emission studies was dissolved in the appropriate solvent to make the concentration

reach 10^{-5} mol/L and the absorbance of the solution was measured. Such a concentration provided enough material for data acquisition but excluded self-quenching processes. The corrected PL spectra of the powder samples were collected by a Hitachi Spectrophotometer model F-4500. Thermogravimetric (TGA) analysis was performed on ~2 mg of samples using a PerkinElmer Thermal analyzer. The samples were dried under vacuum at 56.5°C before being heated from 40 to 605°C at the heating rate of $10.0^\circ\text{C}/\text{min}$. A 10 mL/min flow of dry nitrogen was used to purge the sample at all times. 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 (SCE) as the reference electrode, at a scan rate of 0.1 V/s. The voltammograms were recorded using CH_3CN sample solutions with $\sim 10^{-3}$ M of corresponding Cu(I) complex and 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Prior to each electrochemical measurement, the solution was purged with nitrogen for ~10–15 min to remove the dissolved oxygen. The Origin 7.0 program by OriginLab Corporation was used for curve-fitting analysis.

2.3. Fabrication of EL devices

Prepatterned ITO substrates with a resistivity $< 30\ \Omega$ and an effective individual device area of 4 mm^2 were cleaned by sonication in detergent solution, water, and ethanol sequentially. After being blown dry with nitrogen, the ITO substrates were treated with oxygen plasma for 1 min before being loaded into the vacuum chamber. All the layers in the diodes were deposited by a resistive heating method. The pressure of the chamber was below 3×10^{-4} Pa and 0.8 nm LiF was deposited as the electron-injection layer, which was capped with 200 nm of Al used as cathode. The EL spectra and Commission Internationale de L'Eclairage coordinates of the devices were measured by a PR650 spectrometer, and the key parameters of the OLEDs based on **1** and **2** are listed in Table 1. All measurements were carried out at RT under ambient conditions.

3. Result and discussion

3.1. Thermal analysis

TGA was performed on complexes **1–3** in N_2 atmosphere to investigate their stable characteristics, and the TGA traces of **1–3** are presented in Fig. 2. The decomposition temperatures of **1**, **2**, and **3** are 322, 354, and 297°C , respectively, which should be attributed to the loss of the BF_4^- anion. The diimine ligands of L2

Table 1
Key parameters of the OLEDs based on **1** and **2**

Concentration	Devices based on 1					Devices based on 2				
	η_{max}^a	η^b	η^c	λ_{max}^d	B_{max}^e	η_{max}^a	η^b	η^c	λ_{max}^d	B_{max}^e
1	2.23	1.82	1.46	568	5543	1.38	1.27	1.33	448	8669
7	2.80	2.05	1.31	572	4905	1.79	1.49	1.72	508	5105
15	2.68	1.88	1.20	570	4567	2.18	1.74	2.05	528	2913
25	2.40	1.73	1.09	568	4138	1.48	0.64	1.38	556	423

^a Maximum current efficiency (cd/A).

^b Current efficiency at $10\text{ mA}/\text{cm}^2$ (cd/A).

^c Current efficiency at $100\text{ mA}/\text{cm}^2$ (cd/A).

^d Maximum EL emission wavelength at 9 V (nm).

^e Maximum brightness (cd/m^2).

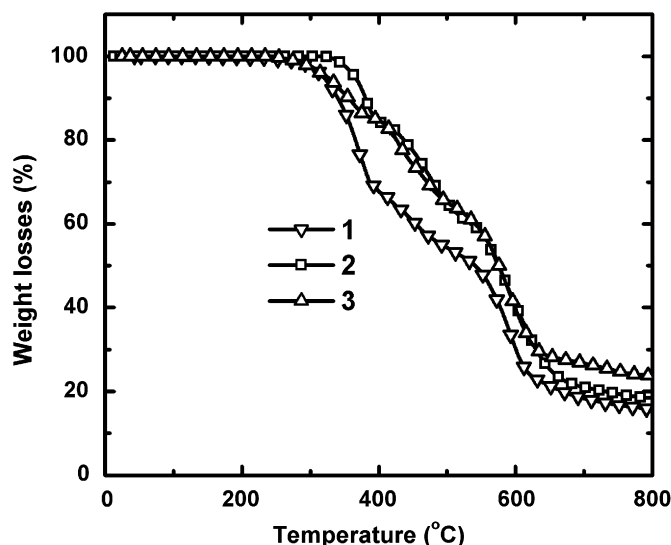


Fig. 2. TGA traces for 1–3.

and L3 probably began to decompose gradually when the temperature was up to 415 and 398 °C, respectively, and there was no obvious temperature sign for the decomposition of L1. As far as the ligand of DPEphos is concerned, the decomposition temperature is about 550 °C. All Cu(I) complexes totally decomposed when they are heated up to 600 °C. Therefore, both **1** and **2** are stable enough to be sublimated to construct OLEDs devices at ~300 °C.

3.2. Electrochemistry

Cyclic voltammograms of complexes **1–3** are shown in Fig. 3 and exhibit irreversible metal-centered oxidation and ligand-based reduction in CH₃CN solution. Complex **1** shows irreversible anodic waves at $E_{1/2} = +0.80$ V with an onset oxidation potential of +0.72 V vs. SCE, and irreversible cathodic waves at $E_{1/2} = -1.62$ V with an onset reduction potential of -1.57 V vs. SCE. The anodic waves were associated with a Cu(I)-based oxidation process ($\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$), and the cathodic waves with the ligand-based reduction process ($[\text{Cu}(\text{L})]/[\text{Cu}(\text{L}^{\cdot-})]$). Complex **2** shows a similar redox behavior. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are calculated from the onset oxidation ($E_{\text{onset}}(\text{Ox})$) and reduction ($E_{\text{onset}}(\text{Red})$) potentials by the following formula: $E_{\text{HOMO}} = -4.74 - E_{\text{onset}}(\text{Ox})$ (-4.74 V for SCE with respect to the zero vacuum level [22] and $E_{\text{onset}}(\text{Ox}) = +0.78$ V for **2** and $E_{\text{LUMO}} = -4.74 - E_{\text{onset}}(\text{Red})$ ($E_{\text{onset}}(\text{Red}) = -1.54$ V for **2**). These calculations give the HOMO and LUMO energy levels to be -5.46 and -5.52 and -3.17 and -3.20 eV for **1** and **2**, respectively. The gaps between the LUMO and the HOMO energy levels of **1** and **2** were thus derived to be 2.29 and 2.32 eV, respectively.

3.3. Photophysical properties

Fig. 4 shows the UV–vis absorption spectra of complexes **1–3** in dichloromethane. For both **1** and **2**, the dominant absorption bands in the 250–360 nm region were assigned to an admixture of the intraligand ($\pi \rightarrow \pi^*(\text{L})$) transitions of DPEphos and the HPybm derivatives. These assignments are based on the absorption spectra of the free ligands and similar Cu(I) complexes [15]. These bands are also accompanied by lower-energy features extending into the visible region from 360 to 470 nm, which are tentatively assigned to the metal to ligand charge-transfer $d\pi(\text{Cu}) \rightarrow \pi^*(\text{N}-\text{N})$ (MLCT) transitions. It is obvious that all of the

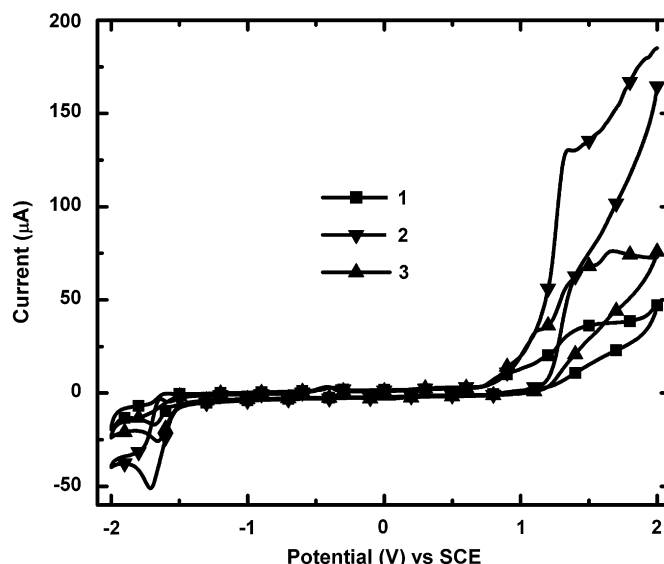


Fig. 3. Cyclic voltammograms of complexes **1–3** measured in CH₃CN (vs. SCE) at a scan rate of 0.1 V/s. A polished Pt plate and a Pt mesh were used as the working electrode and the counter electrode, respectively. TBAH was taken as the supporting electrolyte.

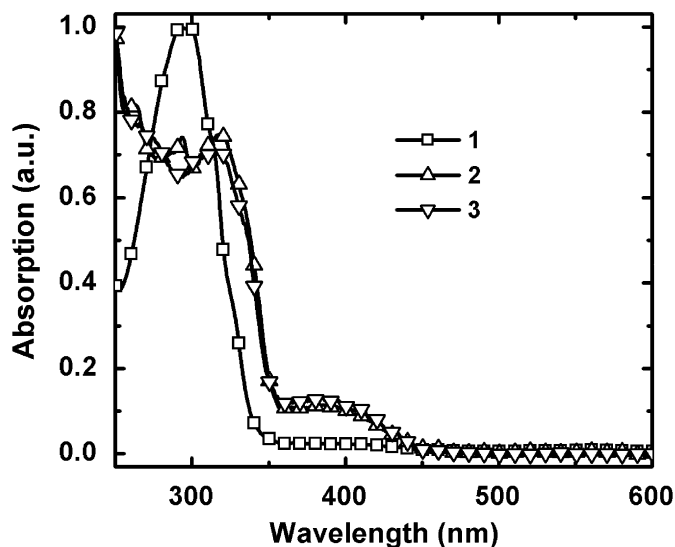


Fig. 4. UV–vis absorption spectra of **1–3** in CH₂Cl₂ solution at the concentration of 10^{-5} mol/L.

MLCT absorption bands of these Cu(I) complexes, except that of **1**, which is relatively weak, are similar to those of the previously reported Cu(I) complexes [13,15] and show little difference from each other. Fig. 5 exhibits the emission spectra of complexes **1–3** in dichloromethane. The ³MLCT transitions bands with the maximum value at 552 nm for **1**, 521 nm for **2**, and 532 nm for **3** imply that the substituted groups influence the energy levels of the excited states of the Cu(I) complexes, and the influence should be as follows: the energy levels of the Cu(I) complexes could be heightened by the hole-transporting group (Car1) and lowered by the electron-transporting group (OXD).

3.4. EL properties

The OLEDs utilizing complexes **1** and **2** as dopants in the CBP emissive layer were fabricated with the structure of ITO/*m*-

MTDATA(30 nm)/NPB(20 nm)/dopant: CBP(× wt%, 30 nm)/Bphen(20 nm)/Alq₃(20 nm)/LiF(0.8 nm)/Al(200 nm) [23]. *m*-MTDATA is used as the hole-injection layer, NPB as the hole-transporting and electron-blocking layer, and Bphen and Alq₃ as the exciton-blocking layer and the electron-transporting layer, respectively. Carrier recombination occurring in the CBP layer is necessary to generate CBP excitons. The Bath layer with a LUMO level of −2.4 eV and the NPB layer with a HOMO level of −5.2 eV pave the

ways for electrons and holes to transport from Alq₃ (LUMO level = −3.1 eV) and *m*-MTDATA (HOMO = −5.1 eV) to the CBP layer (HOMO = −5.5 eV, and LUMO = −2.0 eV). As the PL spectrum of CBP centered at 380 nm shows large spectral overlap with the MLCT absorption bands of complexes **1** and **2**, there should be efficient Föster type of energy transfer in the constructed light-emitting devices.

Fig. 6 shows the EL spectra for the devices based on **1** (a) and **2** (b) at the applied voltage of 9 V. For the EL devices based on **1**, the EL emission bands centered at 410, 426, and 572 nm should originate from CBP, NPB, and **1**, respectively. The decrease of the emission from CBP at higher doping concentrations for these EL devices indicates the efficient energy transferring from the host material of CBP to the dopant of **1**. As far as the EL devices based on **2** are concerned, the EL spectra are mainly dominated by the emission from NPB with the maximum emission wavelength (λ_{max}) of 448 nm at lower doping concentrations (1 wt%), as the doping concentration is up to 25 wt%, the λ_{max} appears at 556 nm with a shoulder peak at 448 nm, suggesting that the emission color of the devices can be changed by changing the doping concentration. As presented in Fig. 7, the maximum brightness achieved from the devices based on 1 wt% **1** and 7 wt% **2** reached 5543 cd/m² at 16 V and 8669 cd/m² at 14 V, respectively. These values are much higher than the previous reported devices based on Cu(I) complexes.

Fig. 8 presents the characteristic of EL efficiency vs. current density of the devices based on **1** (a) and **2** (b). It is found that

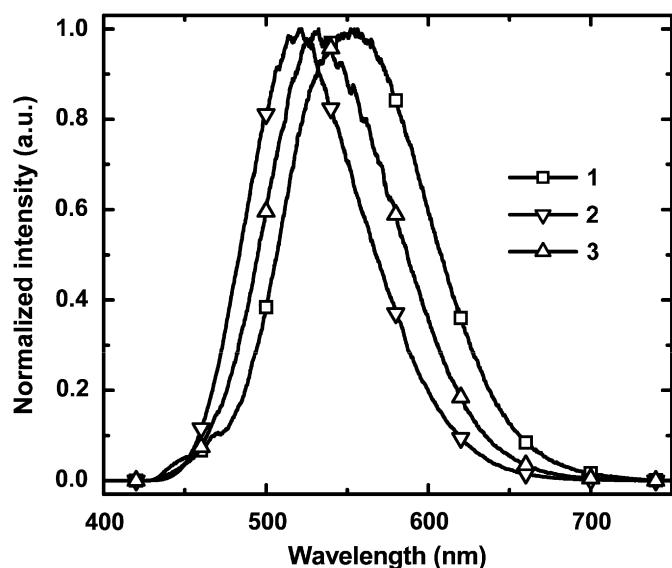


Fig. 5. Emission spectra of the powder samples of **1**–**3**.

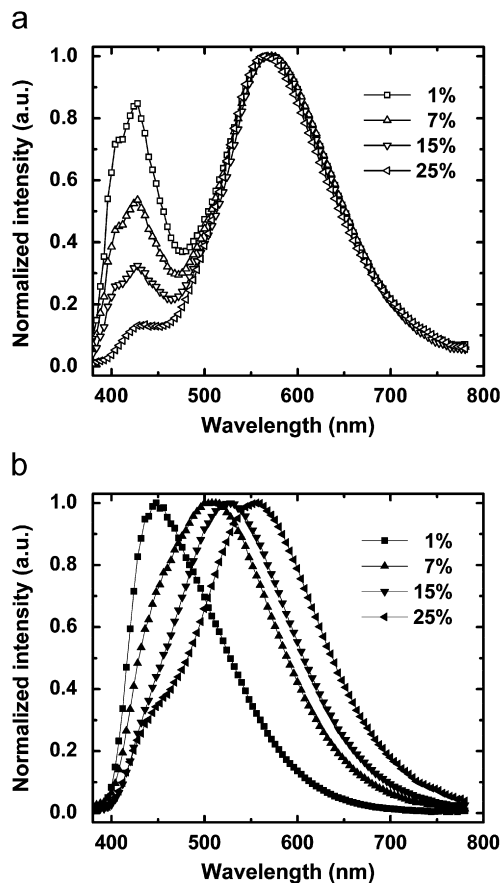


Fig. 6. EL spectra of the OLEDs based on **1** (a) and **2** (b) at 9 V.

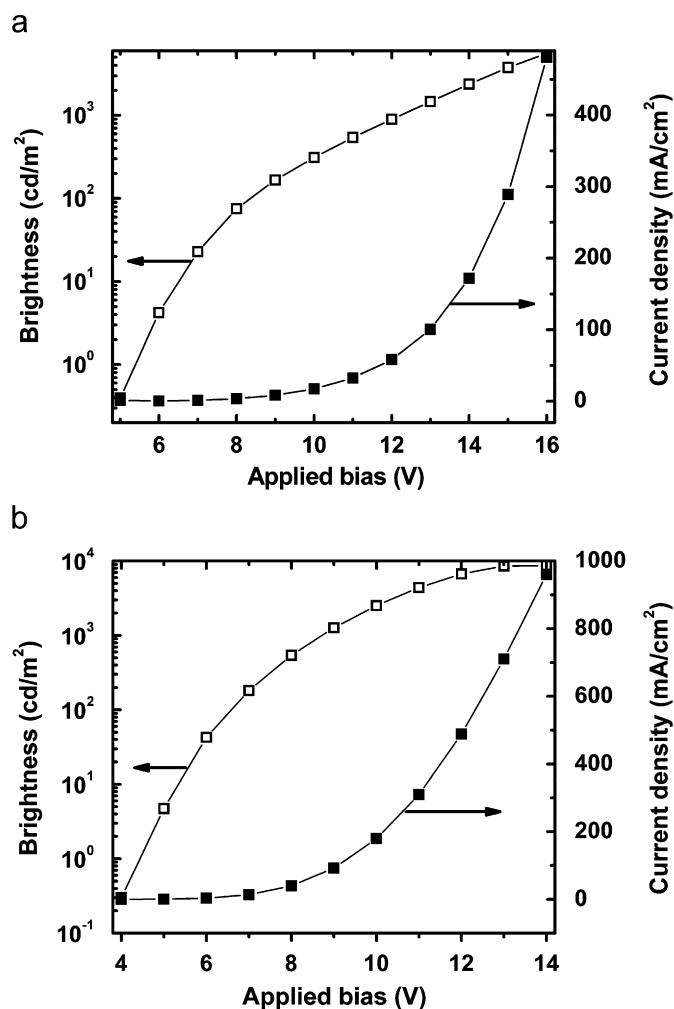


Fig. 7. *L*–*I*–*V* characteristics of the OLEDs based on **1** (a) and **2** (b), respectively.

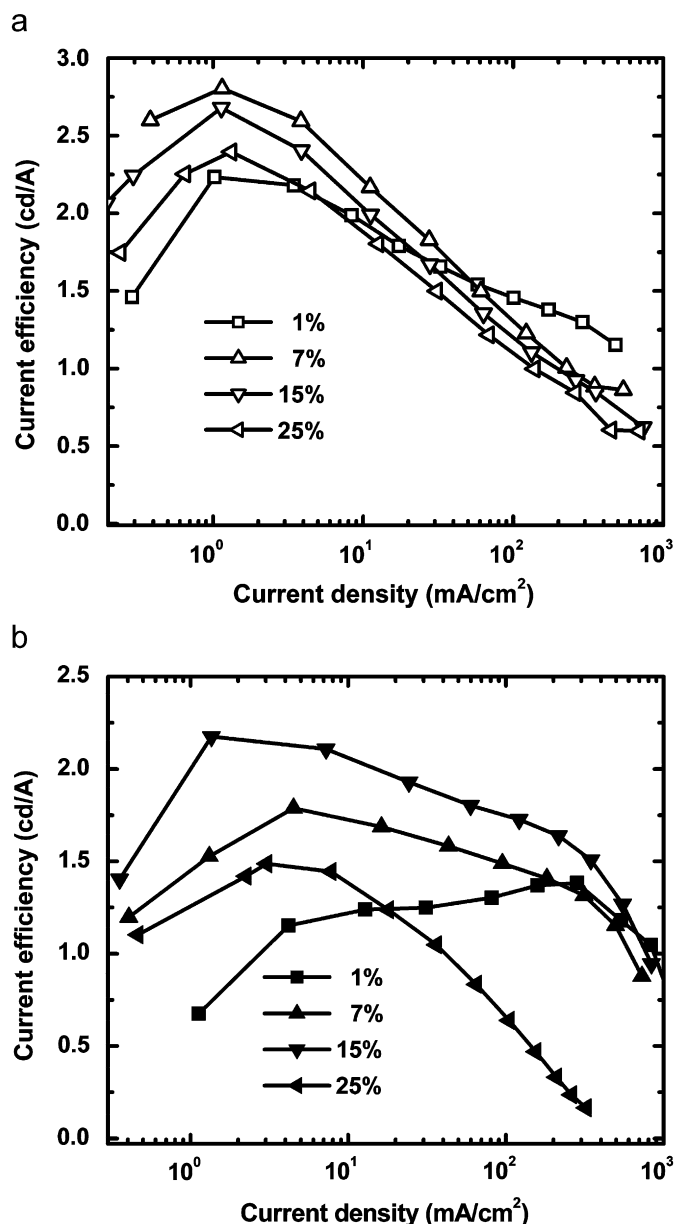


Fig. 8. Current efficiency of the OLEDs based on 1 (a) and 2 (b) as a function of current density.

7 wt% **1**- and 15 wt% **2**-doped devices offer the peak EL efficiency of 2.8 cd/A at 1.1 mA/cm² and 2.2 cd/A at 1.4 mA/cm², respectively. These optimum concentrations are much higher than those of the devices based on the fluorescence materials, indicating that Dexter transfer should occur during the EL process [24]. The efficiency of both types of devices increases slowly at first with the increase in current density, suggesting that the effect of *T*–*T* annihilation on efficiency is negligible at low current density range due to the existence of the sterically hindered spacer of phenyl groups in **1** and **2** and the shorter lifetimes (1.2 μs for **1** and 2.1 μs for **2**). The *T*–*T* annihilation induced by the light-emitting site saturation should be responsible for the fast decrease of the EL efficiency at higher current density. As a result, the optimum

current density of both types of devices is about 1.0 mA/cm² or much higher, which is one magnitude order higher than that of the traditional electrophosphorescent devices.

4. Conclusions

Three novel Cu(I) complexes **1**–**3** are successfully synthesized according to molecular engineering. Moreover, the color-tunable EL devices based on **1** and **2** are fabricated by thermal sublimation under vacuum due to their higher decomposition temperature, and their photo- and the electroluminescent properties of them are systematically studied. The maximum brightness of 7 wt% **2**-based devices was 8669 cd/m², which should be the best among the reported Cu(I) complexes-based devices. It is also found that the optimum current density of both types of devices is one magnitude order higher than that of the traditional electrophosphorescent devices, indicating that Cu(I) complexes possess great potential application in commercial OLEDs.

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