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## Room-Temperature Pure Blue-Emitting Phosphorescent Multinuclear Cu(I)-Based Emitters

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In this paper, we report two easily synthesized pure blue-emitting phosphorescent Cu(I)-based emitters. The phosphorescent nature of the blue emissions ( $\lambda_{em} = 442$  and  $450$  nm) has been identified by both theoretical calculations and experimental data. The blue emissions are the closest to pure blue light among phosphorescent Cu(I) complexes, and their photoluminescence characters are comparable with those of reported noble metal complexes. An electroluminescent device using one of the blue-emitting emitters is fabricated, and a maximum brightness of  $1140$  cd/m<sup>2</sup> is achieved.

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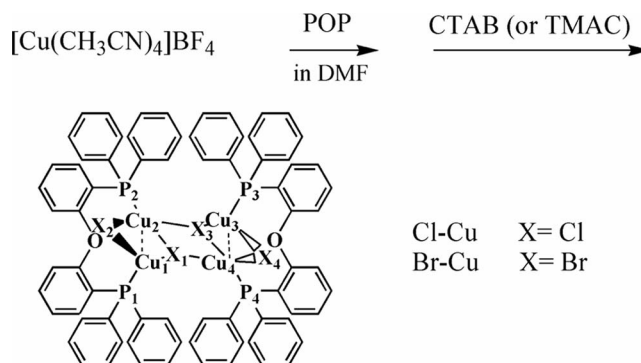
Since the first report of phosphorescent complex porphyrin platinum as a highly efficient emitter in organic light-emitting diodes (OLEDs), the scope and diversity of studies on transition-metal complexes have continued to expand at an exponential rate due to the potential advantage of achieving a maximum internal quantum efficiency of 100%.<sup>1</sup> In exploring the high efficiency phosphorescent emitters and moving toward materials with the required color gamut for full-color displays, many efforts have been devoted to develop tricolor-emitting phosphorescent materials.<sup>2</sup> However, the design and preparation of practicable pure blue-emitting phosphorescent emitters have been experiencing considerable challenges. This task is far more difficult than those for preparing green- and red-emitting complexes. Thanks to Chou and co-workers' constructive efforts on developing blue-emitting phosphorescent materials, deep-blue emitters based on iridium(III) complexes have been explored and proved to be excellent candidates for OLED application.<sup>3-5</sup> Nevertheless, it is still important for the realization of actual full-color display panels based on OLEDs to develop highly efficient and low cost pure blue-emitting phosphorescent emitters. Cu(I) complexes, as a class of electrophosphorescent materials, have recently attracted much more attention due to their advantages such as abundant resource and low cost in comparison with other heavy-metal complexes. To date, various phosphorescent Cu(I) complexes have been synthesized, and their emission properties have been qualitatively discussed.<sup>6-9</sup> Unfortunately, most of their emissions localize in the yellow-red region, which prevents Cu(I)-based emitters from actual utilizations in the fields of full-color display and so on.<sup>10-13</sup> Thus, one of the major problems facing phosphorescent Cu(I)-based emitters is the exploration of pure blue-emitting complexes.

In this paper, we report two easily synthesized pure blue-emitting phosphorescent Cu(I)-based emitters. The phosphorescent nature of the blue emissions has been identified by both theoretical calculations and experimental data. The blue emissions are the closest to pure blue light among phosphorescent Cu(I) complexes, and their photoluminescence (PL) characters are comparable with those of the reported noble metal complexes. Electroluminescent performances are also investigated.

### Experimental

**Synthesis.**—The molecular structures of the two emitters are shown in Scheme 1 and denoted as Cl-Cu and Br-Cu. Hexadecyl trimethylammonium bromide (CTAB), tetramethylammonium chloride (TMAC), and bis[2-(diphenylphosphino)phenyl]ether (POP) were purchased from Aldrich Chemical Co. *N,N*-Dimethylformamide (DMF) was purified by a standard procedure. Cu(CH<sub>3</sub>CN)BF<sub>4</sub> was prepared according to a procedure in Ref. 10.

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Scheme 1. Structural drawing of Cl-Cu and Br-Cu.

A typical synthetic procedure for Cl-Cu and Br-Cu is described as follows: 2 mmol of Cu(CH<sub>3</sub>CN)BF<sub>4</sub> and 1 mmol of POP were dissolved in 10 mL of DMF and stirred at room temperature for 0.5 h, and then 2.2 mmol of CTAB (or TMAC) was added into the mixture and stirred for another 1 h. The crude product was collected by filtration and washed with ethanol and then ether. The obtained product was recrystallized by vapor diffusion of diethyl ether into a dichloromethane solution of the product. The identification of the product was carried out by NMR spectra, elemental analysis, and single-crystal X-ray diffraction.

Cl-Cu: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.34–7.28 (m, 28H), 7.18–7.14 (m, 8H), 7.04–6.98 (m, 20H). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ + 1.3(s) (br s, *W*<sub>1/2</sub> = 325 Hz). Anal. calcd. for C<sub>36</sub>H<sub>28</sub>Cl<sub>2</sub>Cu<sub>2</sub>OP<sub>2</sub>: C, 58.70%; H, 3.83%. Found: C, 58.56%; H, 3.91%.

Br-Cu: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.32–7.27 (m, 28H), 7.12–7.08 (m, 8H), 7.03–6.97 (m, 20H). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ + 1.3(s) (br s, *W*<sub>1/2</sub> = 325 Hz). Anal. calcd. for C<sub>36</sub>H<sub>28</sub>Br<sub>2</sub>Cu<sub>2</sub>OP<sub>2</sub>: C, 52.38%; H, 3.42%. Found: C, 52.44%; H, 3.49%.

The data above were further confirmed by single-crystal diffraction. The crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre (CCDC) with the deposition number CCDC-722589.

**Measurement.**—<sup>1</sup>H NMR (500 MHz) and <sup>31</sup>P NMR (202 MHz) spectra were recorded on a Bruker AVANCE-500 NMR spectrometer. A luminescent lifetime was obtained with a 266 nm light generated from a fourth-harmonic-generator pump, which used the pulsed Nd:yttrium aluminum garnet (YAG) laser as the excitation source. The Nd:YAG laser possessed a linewidth of 1.0 cm<sup>-1</sup>, a pulse duration of 10 ns, and a repetition frequency of 10 Hz. A Rhodamine 6G dye pumped by the same Nd:YAG laser was used as the frequency-selective excitation source. Elemental analysis was

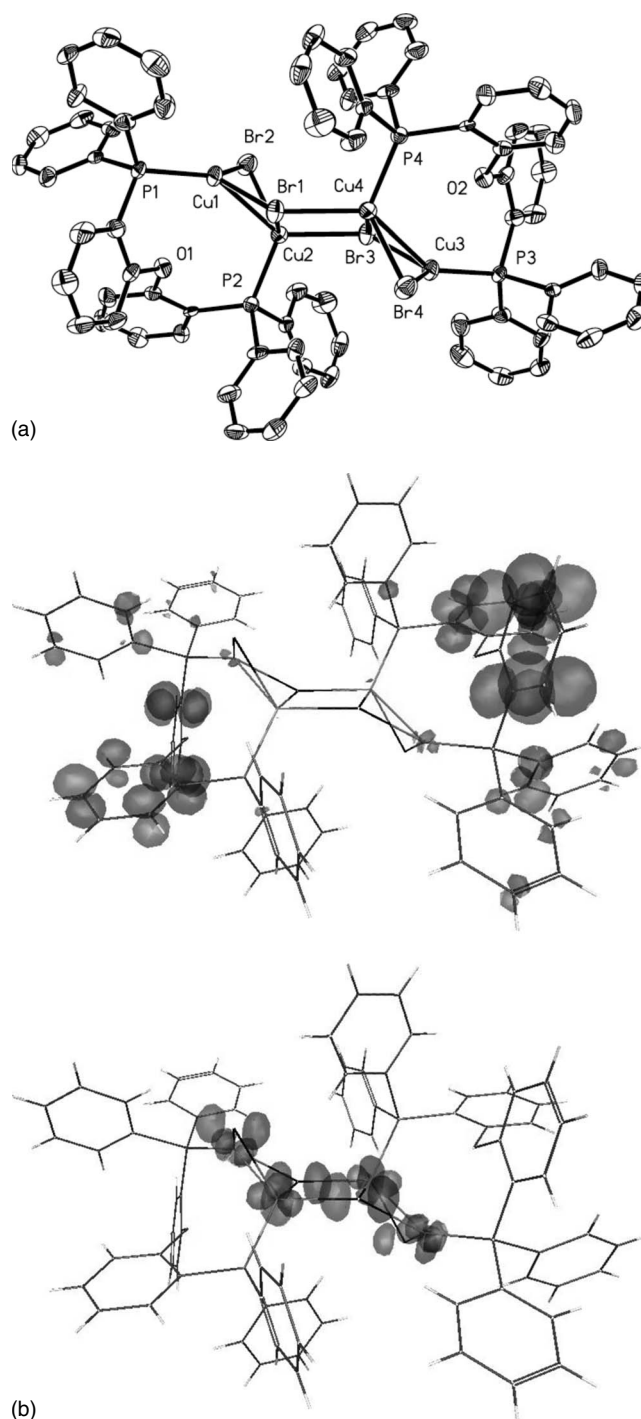
performed on a Carlo Erba 1106 elemental analyzer. All the PL spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. UV/visible absorption spectra were recorded using a Shimadzu UV-3101PC spectrophotometer. Electrochemical data were collected with a CHI660C electrochemical workstation. All measurements were carried out in the air at room temperature without being specified. Density functional theory calculation was done by PC GAMESS using RB3LYP/SBKJC.

**Electroluminescence devices.**—Electroluminescence (EL) devices were fabricated by the conventional vacuum deposition method. The devices were made on an indium–tin oxide (ITO) film ( $15 \Omega/\text{cm}^2$ ) with a  $4 \text{ mm}^2$  round-patterned area. The organic materials for the EL devices were vacuum deposited in turn onto the ITO films at chamber pressures of less than  $3 \times 10^{-4}$  Pa; then aluminum was deposited over a LiF layer as the cathode. The emissive layer was formed by codeposition of the emissive dopant, Br–Cu, and the host material.

### Results and Discussion

**Single-crystal structure of Br–Cu.**—Figure 1 shows the Oak Ridge thermal ellipsoid plot (ORTEP) diagram of Br–Cu, and key parameters of Br–Cu are summarized in Table I. The X-ray crystallographic study on Br–Cu reveals that each copper atom is ligated to a coordinated P atom. Two Br–Cu  $\cdots$  Cu–Br centers are bridged by two Br atoms to form a double dinuclear structure with a four-membered coplanar  $\text{Cu}_2\text{Br}_2$  ring at the center plus two distorted  $\text{Cu}_2\text{Br}_2$  tetrahedra at the opposite sides of the coplanar four-membered ring. The bond angle of C–O–C ( $119.6^\circ$ ) is largely different from the usual one; the long Cu  $\cdots$  Cu coordination center should be responsible for the POP structure distortion. In Br–Cu, the Cu  $\cdots$  Cu distance ( $2.62 \text{ \AA}$ ) is shorter than the sum of the van der Waals radii of copper ( $2.8 \text{ \AA}$ ), which indicates an interaction between two copper atoms and is believed to be a critical factor for bright luminescence.<sup>14–17</sup> Thus, the O atom in POP should act as a medium that connects the two coordination P atoms by offering proper room for the Cu  $\cdots$  Cu coordination center.

**Bandgaps of Cl–Cu and Br–Cu.**—The absorption and excitation spectra of Cl–Cu and Br–Cu, as well as the absorption of ligand POP, are shown in Fig. 2. It is observed that POP exhibits strong absorption in the UV region, up to 325 nm, while the two Cu(I) complexes, Cl–Cu and Br–Cu, present weak spectral bands ending at  $\sim 400$  nm. According to the previous report, these newly generated absorption bands are ascribed to the absorptions of metal-to-ligand charge transfer (MLCT) states mixed with halogen-to-ligand charge transfer (XLCT) states.<sup>8</sup> To further understand the electronic structure of the emitters, density functional theory calculation is carried out for Br–Cu, which reveals that the electron density in the highest occupied molecular orbital (HOMO) is distributed over the copper and Br atoms, while that in the lowest unoccupied molecular orbital (LUMO) is localized on the ligand, POP, as shown as the insets of Fig. 1. Thus, the lowest excited state of Br–Cu is confirmed to be a mixture of MLCT and XLCT states. Tsuboyama's report, a series of luminescent halogen-bridged Cu(I) complexes based on a chelating ligand of 1,2-bis(diphenylphosphino)benzene (dppb) is reported.<sup>8</sup> Both their molecular structures and electronic natures are quite similar to Cl–Cu and Br–Cu, but the emission energies of Cu(I) complexes based on dppb ( $492\text{--}533 \text{ nm}$ ) are much lower than those of Cl–Cu and Br–Cu, indicating that ligand  $\pi^*$  plays an important role in controlling the  $^3(\text{M} + \text{X})\text{LCT}$  emission energy. Aiming at high energy emission from halogen-bridged phosphorescent Cu(I) complexes, the  $\pi^*$  of the phosphorous ligand should be lifted to meet the wide energy gap requirement. Considering that the molecular structures of dppb and POP (shown below) are quite similar to each other, we conclude that the introduction of an O atom facilitates the mentioned POP structural distortion and decreases the conjugation system in POP, leading to POP's higher  $\pi^*$  and, consequently, to the wide bandgaps of Cl–Cu and Br–Cu. Moreover, the



**Figure 1.** (a) ORTEP diagram of Br–Cu. (b) LUMO (up) and HOMO (down) of Br–Cu.

bandgap of Cl–Cu is smaller than that of Br–Cu, which is consistent with the order of the ligand field strength of halides in the complexes ( $\text{Br}^- < \text{Cl}^-$ ). The MLCT [ $d^{10}(\text{Cu}) \rightarrow \pi^*(\text{POP})$ ] excited state is affected by the nature of halides directly bound to copper atoms. In a tetrahedral crystal field, the d orbitals split into two groups, with an energy difference of  $\Delta_{\text{tet}}$  where the lower energy orbitals are  $d_z^2$  and  $d_{x^2-y^2}$  and the higher energy orbitals are  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$ . Considering that the ligand field strength of  $\text{Cl}^-$  is stronger than that of  $\text{Br}^-$ , the  $\Delta_{\text{tet}}$  in Cl–Cu is thus bigger than that in Br–Cu; correspondingly, the energy levels of  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  in Cl–Cu are

Table I. Key geometric parameters of Br-Cu.

	Distance (Å)		Angles (°)		Angles (°)
Br(1)-Cu(1)	2.446	Cu(1)-Br(1)-Cu(4)	127.5	P(2)-Cu(2)-Cu(1)	113.6
Br(1)-Cu(4)	2.504	Cu(1)-Br(1)-Cu(2)	62.4	Br(2)-Cu(2)-Cu(1)	55.0
Br(1)-Cu(2)	2.608	Cu(4)-Br(1)-Cu(2)	81.5	Br(3)-Cu(2)-Cu(1)	135.6
Br(2)-Cu(1)	2.364	Cu(1)-Br(2)-Cu(2)	65.3	Br(1)-Cu(2)-Cu(1)	55.8
Br(2)-Cu(2)	2.489	P(2)-Cu(2)-Br(2)	118.7	P(1)-Cu(1)-Br(2)	132.4
Cu(2)-P(2)	2.212	P(2)-Cu(2)-Br(3)	110.2	P(1)-Cu(1)-Br(1)	114.8
Cu(2)-Br(3)	2.504	Br(2)-Cu(2)-Br(3)	108.5	Br(2)-Cu(1)-Br(1)	112.4
Cu(2)-Cu(1)	2.621	P(2)-Cu(2)-Br(1)	115.7	P(1)-Cu(1)-Cu(2)	144.9
Cu(1)-P(1)	2.186	Br(2)-Cu(2)-Br(1)	103.3	Br(2)-Cu(1)-Cu(2)	59.6
		Br(3)-Cu(2)-Br(1)	98.5	Br(1)-Cu(1)-Cu(2)	61.8

higher than those in Br-Cu. Considering the electronic transition type of (M + X)LCT, it is expected that the excitation energy of Cl-Cu is smaller than that of Br-Cu, leading to Br-Cu's larger MLCT energy and, therefore, a larger bandgap.

The electrochemical data of Cl-Cu and Br-Cu also prove their wide energy gaps. As for Cl-Cu, the HOMO is calculated to be  $-5.98$  eV and the LUMO is calculated to be  $-2.95$  eV. As for Br-Cu, the corresponding values are  $-6.07$  and  $-2.97$  eV, respectively. Clearly, their LUMO energy level values are quite similar to each other due to the same  $\pi^*$ (POP). The higher HOMO energy level value of Cl-Cu compared to that of Br-Cu confirms that the narrower bandgap of Cl-Cu is indeed caused by the stronger ligand field strength of Cl<sup>-</sup>. The HOMO and LUMO energy level values of Cl-Cu and Br-Cu are much lower than previously reported.<sup>18</sup> It is assumed that both the relatively strong halogen ligand field and the interaction between copper atoms may be responsible for the low energy levels. The energy gaps are so wide that commonly used hosts for phosphorescent emitters in OLED, such as *N,N'*-dicarbazolyl-3,5-benzene, *N,N'*-di-1-naphthyl-*N,N'*-diphenylbenzidine, and poly(vinyl carbazole), are not suitable to serve as hosts for Cl-Cu and Br-Cu. To obtain blue electrophosphorescent emissions from Cl-Cu and Br-Cu, corresponding host materials with wide energy gaps and high triplet energies should be explored.

*PL properties.*— As shown in Fig. 3, Cl-Cu and Br-Cu exhibit MLCT-characterized emission spectra peaking at 450 and 442 nm, respectively. Unlike emitters based on Ir(III) and Pt(II) complexes, which exhibit multiple emission peaks, Cl-Cu and Br-Cu demon-

strate Gaussian bandgap emission spectra with full widths at half-maximum (fwhms) of 82 and 78 nm, respectively. The blue emissions are quite close to the standard blue light, which is defined by Commission Internationale de l'Eclairage (CIE) as the emission with  $\lambda = 435.8$  nm, making them useful for fabricating the blue-emitting OLEDs.

Cl-Cu and Br-Cu exhibit biexponential decay patterns with long-lived average lifetimes of  $\tau = 8.3$  and  $7.9$   $\mu$ s in solid state at 298 K. Taking the density functional calculation into account, their emissions are thus attributed to the spin-forbidden <sup>3</sup>(M + X)LCT excited states, indicating the presence of a triplet phosphorescent character. Their PL quantum yields in solid state are determined to be 0.51 and 0.47, which are among the highest efficient phosphorescent emitters, making Cl-Cu and Br-Cu promising candidates in the field of full-color display. In our previous report, emitters with long excited-state lifetimes showed sensitivity toward O<sub>2</sub>, which is known as an efficient triplet quencher.<sup>19</sup> The insets of Fig. 3 show that Cl-Cu and Br-Cu decrease their luminescent intensities in O<sub>2</sub> atmosphere compared with those in N<sub>2</sub> atmosphere, which confirms the existence of triplet excited states. Despite the decreased emission intensities, PL band shapes and emission peaks change little in O<sub>2</sub> atmosphere, suggesting that there is only one emissive center in each Cu(I) complex, namely, the <sup>3</sup>(M + X)LCT excited state. Thus, we conclude that the blue emissions are phosphorescence emissions. The luminescence decreases in O<sub>2</sub> atmosphere are no more than 10% of their initial intensities, indicating that the blue emissions are

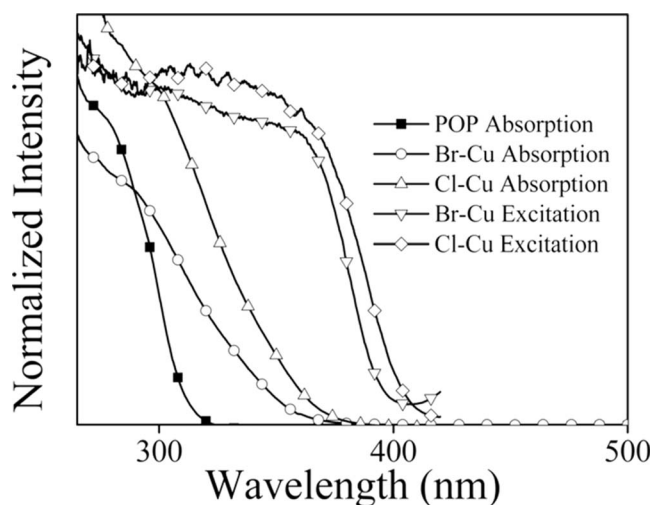


Figure 2. Absorption spectra of Cl-Cu, Br-Cu, and POP in DMF with a concentration of  $1 \times 10^{-5}$  mol/L as well as excitation spectra of Cl-Cu and Br-Cu in solid state.

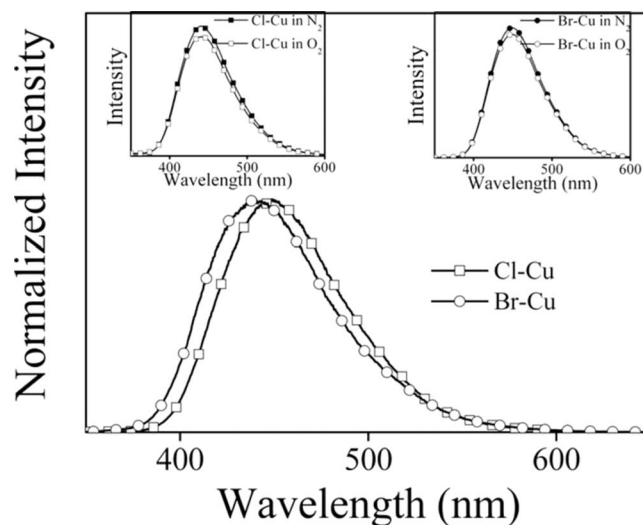


Figure 3. Emission spectra of Cl-Cu and Br-Cu in solid state with  $\lambda_{\text{ex}} = 365$  nm. The insets demonstrate emission spectra in N<sub>2</sub> and O<sub>2</sub> atmosphere.

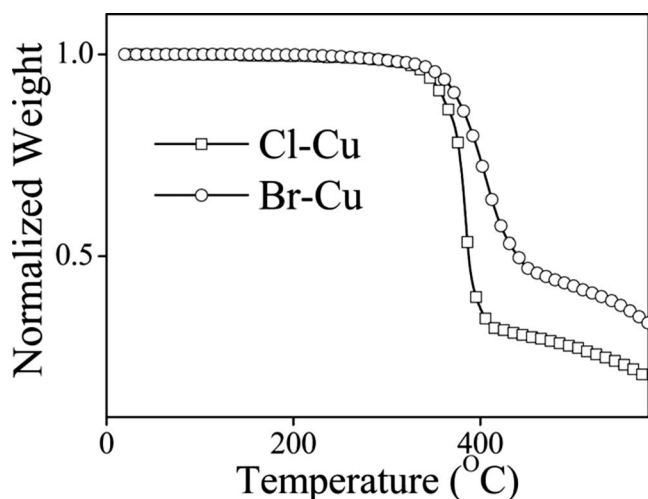


Figure 4. Thermal gravity analysis of Cl-Cu and Br-Cu.

largely immune to O<sub>2</sub> quenching. The low sensitivity of Cl-Cu and Br-Cu makes them convenient for use in actual applications.

**Thermal stability.**—As shown in Fig. 4, Cl-Cu and Br-Cu show high thermal stability by exhibiting high decomposition temperatures of 358 and 373°C, respectively, indicating that they are thermally stable enough for the construction of organic EL devices by vacuum evaporation. Both the good thermal stability and the high PL quantum yields of the two emitters make them promising candidates for pure blue electrophosphorescent emitters in OLEDs.

**EL devices.**—EL devices were fabricated using Br-Cu as the dopant with a general device structure of ITO/*m*-MTDATA (30 nm)/ $\alpha$ -NPD (30 nm)/CzSi:Br-Cu (30 nm)/BPhen (20 nm)/AIQ (20 nm)/LiF (1 nm)/Al, as shown in Fig. 5, where AIQ, BPhen, CzSi,  $\alpha$ -NPD, and *m*-MTDATA present tri(8-hydroxyquinolato)aluminum, 4,7-diphenyl-1,10-phenanthroline, 9-(4-*tert*-butylphenyl)-3,6-bis(triphenylsilyl)-9*H*-carbazole,  $\alpha$ -naphthylphenylbiphenyl diamine, and 4,4',4''-tris(3-methylphenylphenylamino)-triphenylamine, respectively. CzSi served as the host due to its high triplet state energy of 3.02 eV.<sup>5</sup> As shown in Fig. 5, Br-Cu exhibits a similar EL spectrum with its PL spectrum, peaking at 453 nm upon a low dopant concentration of 2 wt % in

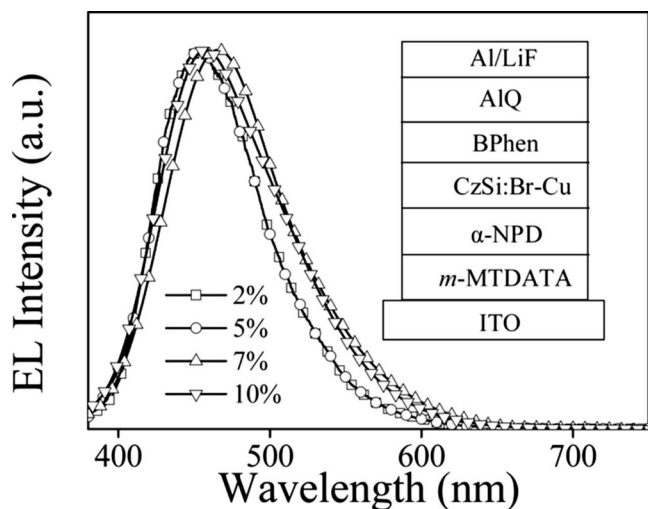


Figure 5. EL device structure and EL spectra upon various dopant concentrations.

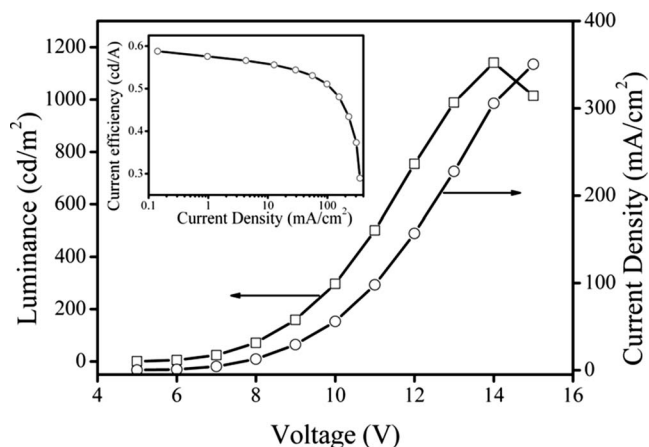


Figure 6. Plots of luminance and current density vs voltage. Inset: Plot of current efficiency vs current density.

CzSi, and no other emission peak is detected, suggesting that Br-Cu is a highly efficient trap for excitons. Upon the dopant concentration increase from 2 to 10 wt %, the EL spectrum redshifts to a longer wavelength of 467 nm, along with the enlarged fwhm from 80 to 92 nm. The optimal EL device with a dopant concentration of 10 wt % affords a maximum current efficiency of 0.59 cd/A with a luminance of 1 cd/m<sup>2</sup>. At concentrations of more than 10 wt %, however, device efficiency tends to decrease because of self-quenching. As shown in Fig. 6, the onset voltage of the optimal EL device is as low as 5 V. Luminance and current density increase with the increase of voltage, and a maximum brightness of 1140 cd/m<sup>2</sup> is achieved at the voltage of 14 V. After them the brightness decreases to 1000 cd/m<sup>2</sup>, indicating that the redundant injected charge carriers tend to quench the <sup>3</sup>(M + X)LCT excited state due to its long excited-state lifetime.

## Conclusion

We have obtained pure blue phosphorescent emissions originating from Cu(I) complexes at room temperature, for which the phosphorescent nature has been identified by both theoretical calculations and experimental data. The blue emissions are the closest to pure blue light among phosphorescent Cu(I) complexes, and their PL characters are comparable with those of reported noble metal complexes. An electroluminescent device using Br-Cu is fabricated, and a maximum brightness of 1140 cd/m<sup>2</sup> is achieved.

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