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Highly Efficient Green Organic Light-Emitting Diodes Containing Luminescent Three-Coordinate Copper(I) Complexes

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Supporting Information

ABSTRACT: A series of highly emissive three-coordinate copper(I) complexes, (dtpb)$Cu^{I}X$ [X = Cl (**1**), Br (**2**), I (**3**); dtpb =1,2-bis(*o*-ditolylphosphino)benzene], were synthesized and investigated in prototype organic light-emitting diodes (OLEDs). **1**−**3** showed excellent photoluminescent performance in both degassed dichloromethane solutions [quantum yield (Φ) = 0.43−0.60; lifetime (τ) = 4.9−6.5 μs] and amorphous films (Φ = 0.57−0.71; τ = 3.2−6.1 μs). Conventional OLEDs containing **2** in the emitting layer exhibited bright green luminescence with a current efficiency of 65.3 cd/A and a maximum external quantum efficiency of 21.3%.

Much effort has been devoted to improving the external quantum efficiency (EQE, photons per electron) of organic light-emitting diodes (OLEDs). OLEDs doped with phosphorescent metal complexes, such as cyclometalated iridium(III) complexes, can exhibit high EQEs of >20%.[1] This value is much higher than the theoretical limit of 5% for fluorescent OLEDs. Over the past two decades, phosphorescent and delayed-fluorescent tetrahedral copper(I) complexes containing two bidentate ligands (bisimine and/or bisphosphine ligands) have received increasing attention as dopants because of the low cost and stable supply of copper metal.[2,4b] However, tetrahedral copper(I) complexes tend to display weak emission because of excited-state distortion, which accelerates nonradiative decay of the emissive excited state. According to earlier studies,[3] the use of sterically congested ligands affords a rigid environment around the copper center in the complexes, leading to effective suppression of the nonradiative processes caused by (i) Jahn−Teller distortion of emissive excited states with metal-to-ligand charge transfer (MLCT) character, (ii) ligand dissociation in the excited state, and (iii) solvent-induced exciplex formation. Recently, Harkins and Peters reported $\{(PNP)Cu^{I}\}_2$, a highly emissive bimetallic copper(I) complex wherein two tetrahedral Cu^{I} units are bridged by the amido groups of the rigid, bulky PNP ligand [PNP^{-} = bis(2-diisobutylphosphinophenyl)amido].[4a] An optimized EQE of 16.1% was achieved for vapor-deposited OLEDs containing the analogous complex $\{(PNP\text{-}^{t}Bu)Cu^{I}\}_2$ [$PNP\text{-}^{t}Bu^{-}$ = bis(2-diisobutylphosphino-4-*tert*-butylphenyl)amido].[4b]

Herein we describe the synthesis and photophysical properties of (dtpb)$Cu^{I}X$ [X = Cl (**1**), Br (**2**), I(**3**)], a simple three-coordinate copper(I) system containing a chelating bisphosphine ligand [dtpb =1,2-bis(*o*-ditolylphosphino)benzene], and the use of these complexes as dopants in OLEDs. A vapor-deposited OLED doped with **2** exhibited a maximum EQE of 21.3%.

The bidentate bisphosphine ligand dtpb was synthesized by addition of 2-methylphenylmagnesium bromide to 1,2-bis(dichlorophosphino)benzene in THF at 0 °C under argon.[5] Complexes **1**−**3** were prepared in 75−95% yield by mixing a suspension of CuX (X = Cl for **1**, Br for **2**, I for **3**) in dichloromethane with 1 equiv of dtpb. Single crystals of **1**−**3** suitable for X-ray analysis were obtained by layering of Et_2O on the surface of solutions of the complexes in $CHCl_3$ (for **1**) or CH_2Cl_2 (for **2** and **3**).

Single-crystal X-ray diffraction studies of **1**−**3** revealed monomeric three-coordinate structures. The molecular structure of **2** is shown in Figure 1 as an example. The coordination geometries of the copper centers in **1**−**3** are trigonal-planar; the sum of the angles around the Cu(I) center are 359.66, 359.37, and 359.43°, respectively. The *o*-methyl groups of dtpb are required for the formation of three-coordinate complexes because 1,2-bis(diphenylphosphino)benzene (dppb), which lacks methyl groups, forms only the halogen-bridged binuclear copper complexes $[Cu(\mu\text{-}X)dppb]_2$ with CuX.[2h] This is probably because the Cu_2X_2 diamond core in $[Cu(\mu\text{-}X)dtpb]_2$ would be highly unstable as a result of steric hindrance of the *o*-methyl groups located on the sides of the metal centers, causing the unusual monomeric three-coordinate structures to be produced. The introduction of a bulky substituent on the ligand appears to be necessary to produce three-coordinate copper complexes. Recently, emissive three-coordinate cooper(I) complexes with bulky anions (monodentate amide ligands or N-heterocyclic carbene ligands with bulky substituents) have been reported.[6] The Cu−P distances (2.2442−2.2768 Å) in **1**−**3** are almost equal to those in $[Cu(\mu\text{-}X)dppb]_2$, indicating that the chelating ability of dtpb is similar to that of dppb.

The absorption and emission spectra of dtpb and copper(I) complexes **1**−**3** are shown in Figure 2. The absorption spectrum of dtpb exhibits a broad, intense band at 289 nm ($\varepsilon = 1.92 \times 10^4$ M^{-1} cm^{-1}), which is characteristic of an arylphosphine compound. This band is assigned to a mixed transition of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$; the former is the transition of an electron from the lone-pair orbital on phosphorus to an empty antibonding π^* orbital on

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a phenyl ring, and the latter are transitions localized on a tolyl or phenylene ring or those from a tolyl ring to a phenylene ring.[7] Complexes **1**−**3** show more complicated spectra than dtpb; the spectra possess a broad band with a maximum at 300−303 nm [$\varepsilon = (1.13-1.28) \times 10^4\ M^{-1}\ cm^{-1}$] and a shoulder at ∼370 nm. These two absorption bands are assigned to a mixed transition of $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ and an $X \rightarrow \pi^*$(dtpb) transition (X = Cl, Br, I), respectively, analogous to those in related tetrahedral copper complexes.[2h,8]

The photoluminescence properties of complexes **1**−**3** are presented in Table 1. While solutions of dtpb do not luminesce at 293 K, complexes **1**−**3** emit intense green phosphorescence in degassed CH_2Cl_2 solutions at 293 K with phosphorescence quantum yields (Φ) of 0.43, 0.47, and 0.60, respectively. The phosphorescence lifetimes (τ) of the three complexes were measured after laser excitation at 355 nm; the phosphorescence decay profiles are illustrated in the inset of Figure 2, from which τ values of 4.9, 5.4, and 6.5 μs were calculated for **1**−**3**, respectively. The emission maxima (λ_{max}) of **1**−**3** show the order **3** < **2** < **1**, suggesting that λ_{max} is affected by the ligand-field strength ($I^- < Br^- < Cl^-$). Presumably the electronic nature of the triplet excited state of **1**−**3** is influenced to some extent by $X^- \rightarrow \pi^*$(dtpb) charge-transfer transitions.

The electrochemical properties of these complexes were investigated by cyclic voltammetry (CV). Irreversible oxidation waves at 407, 432, 468, and 443 mV vs Fc^+/Fc for dtpb and **1**−**3**, respectively, were observed. This result suggests that orbitals of the Cu(I) atom and those of the halogen atom partially contribute to the highest occupied molecular orbitals (HOMOs) of **1**−**3**.

Natural transition orbital (NTO) analysis revealed that these transitions can be described as single hole/electron pairs and reproduce over 95% of the change in electron density upon excitation. The hole (approximately HOMO) and electron [approximately the lowest unoccupied molecular orbital (LUMO)] distributions for the lowest triplet state of **2** at the T_1 optimized geometry are shown in Figure 3A. The hole distribution of **2** is essentially halogen-based but also includes the orbitals with σ character between the Cu(I) and P atoms; the contributions from the Br, Cu, and P atoms to the hole distribution are 16, 28, and 31%, respectively. The electron distribution is largely confined to the *o*-phenylene group in the dtpb ligand. Excited-state calculations carried out for **1**−**3** indicated that phosphorescence results from the transitions $(\sigma + X) \rightarrow \pi^*$. Another notable feature of **2** is that there is little structural change between the ground and excited states. Furthermore, the singlet−triplet energy gaps are very small (2.63−4.51 kcal/mol) in all of the optimized structures, as shown in Figure 3B.

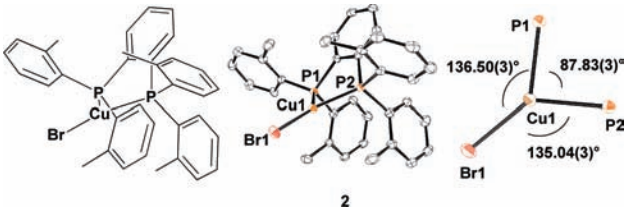

Figure 1. (left) Molecular structure of **2**. (center) ORTEP view of **2**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms have been omitted for clarity. (right) Core structure of **2**.

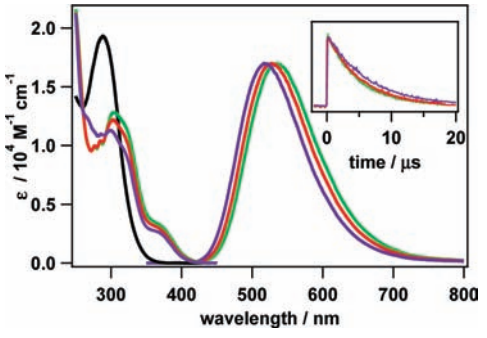

Figure 2. Absorption and corrected emission spectra of dtpb (black), **1** (green), **2** (red), and **3** (purple). The inset shows the observed decay profiles of the phosphorescence from **1**−**3** after excitation at 355 nm at 293 K.

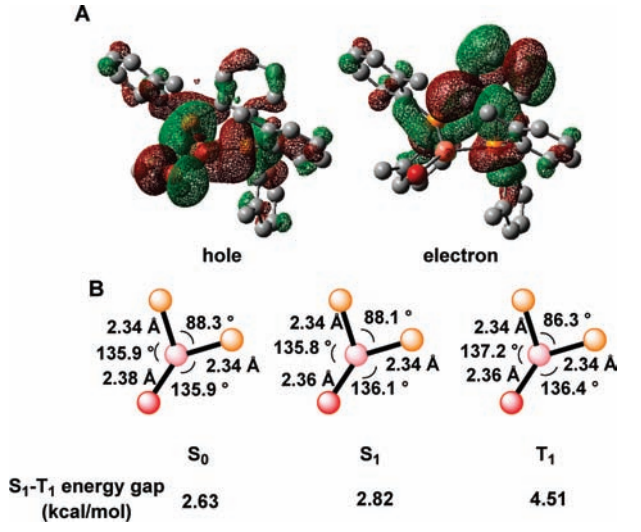

Figure 3. (A) NTO pairs for the lowest triplet excited state of **2** at the T_1 optimized geometry. (B) Optimized core structures of **2** in the ground state (S_0) and the singlet (S_1) and triplet (T_1) excited states and the energy gap between the S_1 and T_1 levels in each optimized structure.

Table 1. Photophysical Data for 1−3 at 293 K

	emission in CH_2Cl_2			emission in mCP (containing 10% complexes)		
complex	λ_{max} (nm)[a]	Φ_{PL}[b]	τ (μs)[c]	λ_{max} (nm)	Φ_{PL}	τ (μs)[d]
1	534	0.43	4.9	520	0.68	6.1 (4.6)
2	527	0.47	5.4	514	0.71	5.5 (3.9)
3	517	0.60	6.5	504	0.57	3.2 (1.4)

[a] PL maximum. [b] Absolute PL quantum yield. [c] PL lifetime. [d] PL lifetime is composed of two components. The faster component is shown in parentheses.

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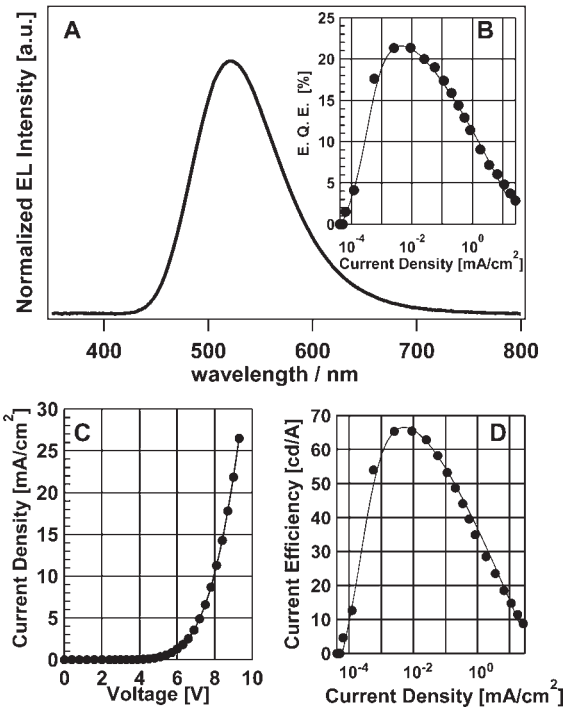

Figure 4. Properties of an OLED containing **2** as a dopant: (A) EL spectrum; (B) dependence of EQE on current density; (C) $I-V$ characteristics; (D) dependence of current efficiency on current density.

Barakat observed Jahn−Teller distortion from Y- to T-shaped geometry in the triplet excited state of trigonal planar Au(I) complexes containing three monophosphine ligands ($[Au(PR_3)_3]^+$).[9] Our calculations predicted that the Cu(I) complex $[Cu(PMe_3)_3]^+$ with a structure similar to that of $[Au(PMe_3)_3]^+$ should undergo comparable distortion in the excited state.[10] The contribution of MLCT character to the excited state is necessary for excited-state distortion in the Au(I) and Cu(I) complexes. Although there is 28% MLCT character in the triplet excited state of complex **2**, the distortion is markedly small, as shown in Figure 3. Presumably the bisphosphine ligand largely prevents Jahn−Teller distortion in the three-coordinate Cu(I) complexes. The small distortion of the excited states of **2** is assumed to reduce the rate of nonradiative decay, leading to a high Φ.

As described above, complexes **1**−**3** exhibit strong phosphorescence in dichloromethane solution. Prior to preparation of OLEDs, the phosphorescence from evaporated amorphous films containing **1**−**3** was investigated using layers of 1,3-bis(carbazol-9-yl)benzene (mCP) doped with 10% **1**−**3** with a thickness of 50 nm deposited onto a quartz plate. The amorphous films exhibited Φ values of 0.57−0.71 and τ values of 3.2−6.1 μs (Table 1). On the basis of the PL data for the doped samples, complex **2** was selected for use as a dopant in an OLED. Except for **2**, the materials used to make the device are commercially available. A bottom-emitting device with a three-layer structure of ITO (110 nm)/TAPC (30 nm)/mCP + 10% **2** (25 nm)/3TPYMB (50 nm)/LiF (0.5 nm)/Al (100 nm), where TAPC is di-[4-(*N*,*N*-ditolylamino)phenyl]cyclohexane and 3TPYMB is tris[2,4,6-trimethyl-3-(pyridine-3-yl)phenyl]borane, was fabricated. The electroluminescence (EL) of **2** (λ_{max} = 517 nm) is in good agreement with the PL data, as shown in Figure 4A and Table 1. The current−voltage ($I-V$) characteristics of the device containing **2** indicate a turn-on voltage of 2.7 V (Figure 4C). A maximum current efficiency of 65.3 cd/A was achieved at 0.01 mA/cm^2, which corresponds to a maximum EQE of 21.3% (Figure 4B,D). This efficiency is comparable to that of cyclometalated iridium(III)-based devices, which currently set the standard for efficiency. The present work suggests that three-coordinate copper(I) complexes are promising EL materials in terms of efficiency and thermal stability. Detailed studies of the photophysics of these three-coordinate copper complexes are in progress.

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data (CIF), synthetic details, time-dependent density functional theory calculations, and a table of experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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