Phosphorescent Cuprous Complexes with N,O Ligands – Synthesis, Photoluminescence, and Electroluminescence

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Six heteroleptic cuprous complexes, $[\mathbf{L}^1\mathrm{Cu}(\mathrm{PPh}_3)_2](\mathrm{BF}_4)$ (1a), $[\mathbf{L}^1\mathrm{Cu}(\mathrm{DPEphos})](\mathrm{BF}_4)$ (1b), $[\mathbf{L}^2\mathrm{Cu}(\mathrm{PPh}_3)_2](\mathrm{BF}_4)$ (2a), $[\mathbf{L}^2\mathrm{Cu}(\mathrm{DPEphos})](\mathrm{BF}_4)$ (2b), $[\mathbf{L}^3\mathrm{Cu}(\mathrm{PPh}_3)_2](\mathrm{BF}_4)$ (3a), and $[\mathbf{L}^3\mathrm{Cu}(\mathrm{DPEphos})](\mathrm{BF}_4)$ (3b) (\mathbf{L}^1 = diphenyl(2-pyridyl)phosphane oxide, \mathbf{L}^2 = diphenyl(8-quinolyl)phosphane oxide, \mathbf{L}^3 = diphenyl(2-pyridylmethyl)phosphane oxide, DPEphos = bis[2-(diphenylphosphanyl)phenyl] ether}, were prepared and fully characterized. The electronic absorption spectra and quantum chemical calculations indicate that the lowest excited states of these complexes can be assigned to the metal-to-ligand charge transfer (MLCT) transition. In poly(methyl)

Introduction

Extensive efforts have been focused on N-heterocyclic Cu^I complexes for replacing phosphorescent transition metal complexes based on ruthenium or other noble metal ions in chemical sensors,^[1] probes of biological systems,^[2] and energy-conversion devices^[3] due to their advantages such as having abundant resources, low cost, and nontoxic properties. However, these tetrahedral cuprous complexes always undergo a significant geometry change going from the ground to excited state corresponding to a change from d¹⁰ to d⁹ as a result of MLCT transitions. The distortion of the excited state narrows the energy gap and increases the nonradiative decay of these Cu^I complexes.^[4] Compared to classical [Cu(N,N)₂]⁺ systems, mixed-ligand systems involving bulky phosphanes ([Cu(N,N)(P,P)]⁺) exhibit improved emission properties, because the bulky and strong π -acidic phosphane ligands will sterically inhibit the excited-state distortion as well as enhance the energy level of the excited states by stabilizing of the Cu^I species.^[5] In 2002, McMillin

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[c] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China methacrylate) (PMMA) films, these complexes exhibit bluegreen to orange emissions with long lifetimes ranging from 7.5 to 28.6 μ s. With wide energy-band gaps of 3.50 and 3.28 eV, complexes **3a** and **3b** emit efficiently in 20 wt.-% PMMA films with photoluminescence quantum efficiencies of 0.69 and 0.72, and emission maxima at 477 nm and 495 nm, respectively. Electroluminescent devices were fabricated with these N,O-based Cu^I complexes as emitters. The best device performance, with a peak current efficiency of 4.9 cd/A, was obtained for **3b**.

and co-workers reported the first example of a highly emissive mononuclear cuprous complex, $[Cu(dbp)(DPEphos)]^+$ (dbp = 2,9-di-n-butyl-1,10-phenanthroline), with an impressive quantum efficiency of $0.16^{[6]}$ ($0.26^{[3d]}$) in CH₂Cl₂ solution and $0.69^{[3a]}$ in an PMMA film. Recently, a series of Cu^I complexes combining two bis(phosphane) ligands $([Cu(P,P)_2]^+)$ was also found to exhibit strong emission bands in both solid state and organic light-emitting diodes (OLEDs).^[7]

Over the past few years, increasing attention has also been paid to luminescent Cu¹ complexes based on asymmetric N,P ligands. These complexes display some unexpected properties perhaps due to the asymmetric electronic character of their ligands. Recently, Peter et al. reported several dinuclear and mononuclear CuI complexes supported by [P,N,P]⁻ {bis[2-(diisobutylphosphanyl)phenyl]amide}^[8] and [P,N]⁻ (amidophosphane) ligands^[9] with unusually high quantum efficiencies, in the range of 0.16–0.70, in solution. More recently, our group and Tsukuda et al. reported a series of phosphorescent homo- and heteroleptic Cu^I complexes with asymmetric N.P ligands of 8-(diphenylphosphanyl)quinoline (dppq) and 2-methyl-8-(diphenylphosphanyl)quinoline.^[10,11] The Cu^I complexes based on these iminophosphane ligands exhibit higher electro- and photochemical stability than those based on traditional diimine or diphosphane ligands.^[11]

In the course of our studies on cuprous complexes with N,P ligands, we isolated an unexpected phosphorescent complex containing the oxidized N,P ligand, diphenyl(2-pyridyl)phosphane oxide. To the best of our knowledge, cu-

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FULL PAPER

prous complexes containing phosphane oxide coordinating ligands are few, and their luminescent properties have never been reported.^[12] The unexpected finding motivated us to systematically explore the effects of the electronic character of the ligands on the photophysical properties of cuprous complexes. Herein, we report the synthesis of phosphorescent cuprous complexes containing phosphane oxide coordinating ligands, and the applications of these complexes in OLEDs.

Results and Discussion

Synthesis and Characterization

We synthesized six mixed-ligand Cu^I complexes of the type $[Cu(N,O)(P,P)](BF_4)$, where N,O is diphenyl(2-pyridyl)phosphane oxide (L¹), diphenyl(8-quinolyl)phosphane oxide (L^2) or diphenyl(2-pyridylmethyl)phosphane oxide (L^3) , and P,P is DPEphos or a pair of PPh₃ ligands. The structures of the complexes are shown in Scheme 1. Complex 1a was first obtained as a byproduct when we attempted to prepare the N,P Cu^I complex. In the following studies, all complexes were directly synthesized from the oxidized N,P ligands (N,O), in which ligand L² was easily synthesized by the reaction of 8-(diphenylphosphanyl)quinoline with excess H_2O_2 in tetrahydrofuran (thf) at room temperature. The mixed-ligand complexes were obtained from two displacement reactions of $[Cu(CH_3CN)_4](BF_4)$. Crystals of the complexes were obtained through slow concentration and diffusion of solvents in moderate yields ranging from 47.2 to 86.6%, and characterized by ¹H NMR, ³¹P NMR spectroscopy, and elemental analysis.

Significant upfield shifts are observed for the signal of the α -H atom of the pyridine or quinoline ring in all complexes compared to those of the free ligands in the ¹H NMR spectra, implying electron donation from the Cu ion and the phosphane auxiliary ligands to the N,O ligands. For instance, **1a** and **1b** exhibit signals at $\delta = 8.44$ and 8.27 ppm, whereas L¹ displays a signal at $\delta = 8.83$ ppm. In comparison with [Cu(dppq)(DPEphos)]⁺,^[11] **2b** has almost the same signal for the α -H atom, but signals for other protons of the quinoline ring are shifted downfield due to the lower electron-donating ability of $-OPPh_2$ to the adjacent quinoline ring than that of $-PPh_2$. Additionally, signals in the upfield region for **3a** and **3b** indicate a higher electron density relative to **1a** and **1b**, which is attributed to the introduction of an electron-donating methylene unit.

In the course of our studies on cuprous complexes with N,P ligands, we noticed that significant ligand exchange or redistribution reactions sometimes occur. For instance, the homoleptic species $[Cu(dppq)_2](BF_4)$ has been observed in CDCl₃ solution alongside $[Cu(dppq)(PPh_3)_2](BF_4)$ in a ratio of 0.07:1, according to ¹H NMR spectra. However, signals for the homoleptic species have not been found in the ¹H NMR spectra of these N,O-based complexes probably due to their less crowded coordination environment.

Description of the Structures

The X-ray crystal structures of all N,O complexes have been determined. Selected bond lengths and angles are listed in Table 1, and views of the structures of the complexes showing the atom numbering appear in Figures 1, 2, 3, 4, 5, and 6.

The central copper atoms in all of the complexes are surrounded by one O and one N atom from the N,O ligands and two P atoms from phosphane ligands in a distorted tetrahedral geometry. The metallacycles consisting of the Cu, O, N, P, and one or two C atoms of the N,O ligands are found in either a half-chair or a boat conformation. The former is found in complexs **1a** and **1b** where the O atoms are out of the Cu–N–C–P near-plane. The latter conformation is seen in **2a** and **2b**, where the N and P atoms are out of the Cu–O–C–C near-plane, and in **3a** and **3b**, where the Cu and sp³ C atoms are out of the O–P–N–C(sp²) plane.^[13]

There are two independent molecules of **1a** in the asymmetric unit of the crystal lattice. The largest deviations from ideal tetrahedral geometry (109.4°) are seen in the N–Cu–O bond angles [83.98(11)° for **1a** and 86.36(9)° for **1b**] due to the rigidity of L¹. With PPh₃ as the auxiliary ligand, **1a** has a larger P–Cu–P bond angle and longer Cu–N and Cu–P bonds than **1b**, which has a DPEphos auxiliary ligand, implying more steric congestion in **1a**. Similar changes in the P–Cu–P bond angle and the Cu–N and Cu–P bond lengths have also been found in other complexes described here and in [Cu(N,N)(P,P)]⁺ systems reported previously.^[6,14,15] The sum of the internal angles of the five-membered metallacycles of Cu–O–P(1)–C(5)–N and Cu–O–P(1)–C(1)–N are



Scheme 1. Molecular structures of the Cu^I complexes.



Table 1.	Selected	bond	lengths	[Å]	and	angles	[°]	for	1a,	1b,	2a,	2b ,	3a,	and	3 b	
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	1a	1b	2a	2b	3a	3b
Cu–N	2.059(3)	2.044(3)	2.146(3)	2.129(3)	2.113(3)	2.065(2)
Cu–O	2.199(2)	2.171(2)	2.105(2)	2.117(2)	2.148(2)	2.230(2)
Cu-P(2)	2.2621(10)	2.2120(9)	2.2364(9)	2.2376(9)	2.2734(9)	2.2466(7)
Cu-P(3)	2.2390(10)	2.2611(9)	2.2906(9)	2.2787(9)	2.2595(9)	2.2657(7)
O-Cu-N	83.98(11)	86.36(9)	94.46(9)	97.22(10)	96.98(10)	93.22(8)
N-Cu-P(2)	114.01(8)	130.02(8)	116.04(8)	120.17(8)	106.47(8)	116.39(6)
O-Cu-P(2)	99.59(7)	109.68(6)	115.16(6)	114.47(7)	104.36(7)	116.50(5)
N-Cu-P(3)	121.34(8)	106.92(8)	103.17(7)	103.77(8)	108.07(8)	118.14(6)
O-Cu-P(3)	113.77(7)	104.64(6)	95.51(6)	102.59(7)	110.38(7)	94.19(5)
P(2)-Cu-P(3)	116.71(4)	113.46(3)	126.39(3)	115.74(3)	126.58(4)	114.22(2)
Σ metallacycle	537.07	534.98	689.04	686.46	688.83	675.01



Figure 1. Crystal structure of the cation of 1a with thermal ellipsoids at 30% probability. Solvent molecules, the anion, and H atoms are omitted for clarity.



Figure 2. Crystal structure of the cation of 1b with thermal ellipsoids at 30% probability. Solvent molecules, the anion, and H atoms are omitted for clarity.

537.07 and 534.98° for **1a** and **1b**, respectively, which are slightly smaller than the value for a regular pentagon (540°), indicating the near coplanarity of the metallacycles.

Figure 3. Crystal structure of the cation of 2a with thermal ellipsoids at 30% probability. The anion and H atoms are omitted for clarity.

The Cu–N bond for **2b** [2.129(3) Å] is 0.043 Å longer than that in the [Cu(dppq)(DPEphos)]⁺ cation.^[11] However, the average Cu–P bond for **2b** (2.258 Å) is 0.017 Å shorter



Figure 4. Crystal structure of the cation of 2b with thermal ellipsoids at 30% probability. Solvent molecules, the anion, and H atoms are omitted for clarity.



Figure 5. Crystal structure of the cation of 3a with thermal ellipsoids at 30% probability. Solvent molecules, the anion, and H atoms are omitted for clarity.

than that in the analogous N,P complex, indicating that the N,O ligand is sterically less crowded than the corresponding N,P ligand. The sum of the internal angles of the metallacycle Cu–N–C(9)–C(8)–P(1)–O is 689.04 and 686.46° for complexes **2a** and **2b**, respectively, indicating significant distortion of the six-membered metallacycles.

Complexes based on L^3 tend towards ideal tetrahedral geometry compared to the complexes based on L^1 . For example, the N–Cu–O bond angle of **3b** (93.22°) is 6.85°



Figure 6. Crystal structure of the cation of 3b with thermal ellipsoids at 30% probability. Solvent molecules, the anion, and H atoms are omitted for clarity.

closer to the ideal tetrahedral value of 109.4° than that of **1b**. Furthermore, cuprous complexes based on L^3 show larger P–Cu–P bond angles and longer bonds than those in L^1 -based complexes, suggesting that the coordination sphere of the central copper atoms is more congested for the complexes based on L^3 . For example, the P–Cu–P bond angle for **3a** (126.58°) is 9.87° larger than that in **1a**. The Cu–N bond length in **3a** is 2.113(3) Å, which is 0.054 Å longer than that in **1a**, and the average Cu–P bond length in **3a** is 2.267 Å, which is 0.0159 Å longer than that in **1a**. The sums of the internal angles of the Cu–N–C(5)–C(6)–P(1)–O six-membered metallacycles are 688.83 and 675.01° for **3a** and **3b**, respectively, which are markedly different from the value of a regular hexagon (720°).

Photophysical Properties

The electronic absorption spectra of the Cu^I complexes in CH₂Cl₂ are shown in Figure 7. The intense UV absorption bands at 256–259 nm for 1a, 1b, 3a, and 3b and 267– 274 nm for **2a** and **2b** are ascribed to the π - π * absorption bands of the N,O ligands. In addition to the high-energy absorption bands, weak, broad, low-energy shoulder bands are observed at around 355 nm for 1a and 1b, and around 385 nm for 2a and 2b, in agreement with the yellow color of these four complexes. These low-lying bands are attributed to the MLCT transitions involving the N-heterocyclic unit and the Cu^I ion, which are always observed in diimine (N,N) and iminophosphane (N,P) Cu^I complexes.^[3f,6,11] However, the MLCT band was not detected in the colorless complexes 3a and 3b. To rationalize the feature qualitatively, DFT calculations were performed on 3b by using 6-31+G** coupled to the LanL2DZ basis set. As shown in



Figure 7. UV/Vis spectra of 1–6 in CH_2Cl_2 ($c \approx 10^{-5}$ M); inset: UV/Vis spectra in the low energy band.

Figure 8, the electron density in the highest occupied molecular orbital (HOMO) is mainly associated with the Cu^I center and the Cu–P σ -bonding orbital, whereas that of the lowest unoccupied molecular orbital (LUMO) is localized on the π -antibonding orbital of the pyridine ring. This implies that the lowest excited state of the complex **3b** is also attributed to the MLCT transition. The undetectable MLCT band for **3b** may be obscured by the strong π - π * absorption band nearby.

The energy-band gaps, estimated by the edge of the absorption bands, increase in the series $[L^3Cu(PP)]^+ > [L^1Cu(PP)]^+ > [L^2Cu(PP)]^+$ (Figure 7), relating to the π electron-accepting ability of the N-heterocycle on the N,O ligands. The energy-band gap of 2.56 eV for **2b** is narrower than that of $[Cu(dppq)(DPEphos)]^+$ (2.93 eV),^[11] because the incorporation of the electron-withdrawing $-OPPh_2$ group^[16] decreases the electron density of the quinoline ring and thus makes it easier to be reduced. The introduction of the electron-donating methylene group between the pyridine ring and the $-OPPh_2$ group^[16] increases the electron density of the pyridine ring and enhances the energy-band gaps from 3.06 and 2.93 eV for **1a** and **1b** to 3.50 and 3.28 eV for **3a** and **3b**, respectively. According to the DFT calculations, **3b** shows a significantly higher LUMO energy level (-0.14685 Hartree) and a close HOMO energy level (-0.28709 Hartree) relative to those of [Cu(NN)(PP)]⁺ systems [e.g. the analogous 2-(2'-pyridyl)benzimidazolylbenzene complex^[15]].

In degassed CH₂Cl₂, complexes **3a** and **3b** emit with maxima at 556 and 558 nm, respectively, while emission maxima of 589 and 581 nm are observed for 1a and 1b, respectively (Table 2). The blueshift of the emission maxima is associated with the introduction of the electron-donating methylene unit to the pyridine rings in 3a and 3b. Meanwhile, the quantum efficiencies (ϕ) and lifetimes (τ) increase from 0.0005 (1.12 µs) and 0.0005 (1.05 µs) for 1a and 1b to 0.037 (2.15 µs) and 0.023 (1.71 µs) for 3a and 3b, respectively, due to the enlarged energy gap that decreases the nonradiative rate constant of the Cu^I complexes (energygap law). In addition, the complexes comprising the PPh₃ auxiliary ligand (1a and 3a) have longer lifetimes and higher quantum efficiencies relative to the complexes with the DPEphos auxiliary ligand (1b and 3b), which is different to observations in classical mixed-ligand (phenanthroline)Cu^I complexes^[6] and consistent with a previous report of biquinoline systems.^[3f] Emissions for 2a and 2b in degassed CH₂Cl₂ are too weak to be detected, owing to the narrow energy-band gaps that increase the nonradiative pathways.

The photophysical data in PMMA films with concentrations of 20 wt.-% are listed in Table 2. In a rigid matrix, the Cu^I complexes showed emission blueshifts of tens of



Figure 8. Calculated electron density of the HOMO (left) and LUMO (right) for 3b.

Complex	Solution (in degassed CH	Film (20 y	Film (20 wt% in PMMA)					
1	Abs. $[nm]^{[a]}$, $(\lg \varepsilon)$	λ [nm]	τ [µs] ^[b]	\varPhi [%]	λ [nm]	τ [μs] ^[c]	´Φ [%]	
1a	258 (4.5), 347 (3.2)	589	1.12	0.05	521	8.3	11.8	
1b	256 (4.4), 358 (3.4)	581	1.05	0.05	527	7.5	12.7	
2a	267 (4.5), 375 (2.9)		[d]		565	28.6	6.4	
2b	274 (4.4), 395 (3.0)		[d]		573	14.9	6.4	
3a	259 (4.5)	556	2.15	3.70	477	24.6	69.3	
3b	258 (4.3)	558	1.71	2.26	495	18.6	71.9	

[a] $c \approx 10-5 \text{ M}$ in CH₂Cl₂. [b] Fitted by single exponential. [c] Fitted by two exponentials, a pre-exponential weighted average lifetime (τ_{ave}) was used and calculated by the equation $\tau_{ave} = \Sigma(A_i \tau_i / \Sigma A_i)$, where A_i is the pre-exponential for the lifetime τ_i . [d] Too weak to be detected.

FULL PAPER

W. Sun, Q. Zhang, L. Qin, Y. Cheng, Z. Xie, C. Lu, L. Wang

nanometers (54–79 nm), much higher quantum efficiencies and longer lifetimes (up to 28.6 μ s) relative to the liquid phase.^[3f,11] The quantum efficiencies of 0.69 for **3a** and 0.72 for **3b** are amongst the highest found for cuprous complexes^[3a,3f,17] and significantly higher than those of **1a**, **1b**, **2a**, and **2b**. Furthermore, an absence of concentration quenching was observed in the complexes based on L³. For example, **3b** has an efficiency of 0.71 and an emission maximum of 501 nm in its neat film, similar to those in 20 wt.-% PMMA film. This may be associated with the bulky phosphane auxiliary ligand and –OPPh₂ that can effectively separate the π -electron acceptors (i.e. N-heterocycles) from each other and therefore avoid the nonradiative intermolecular energy transfer.

Electrophosphorescent Properties Characterization

Multilayer OLEDs with the configuration of indium tin oxide/poly(3,4-ethylenedioxythiophene)/emitting layer (≈ 50 nm)/bathocuproine (BCP) (20 nm)/Alq₃ (40 nm)/LiF (1 nm)/Al (≈ 100 nm) were fabricated to evaluate the electrophosphorescent properties of the cuprous complexes, as shown in Figure 9. The host materials utilized here include poly(9-vinylcarbazole) (PVK) that can match the phosphorescent materials with high energy-band gaps^[3a,18] and 3,6-bis(carbazol-9-yl)-*N*-[4-(carbazol-9-yl)phenyl]carbazole (TCCz) that is suitable for phosphorescent materials with low energy-band gaps.^[3f,19] The performance data of the OLEDs are listed in Table 3.

Table 3. Turn-on voltage ($V_{\rm T}$), current efficiency ($\eta_{\rm c}$), maximum brightness ($B_{\rm max}$), and emission wavelength ($\lambda_{\rm max}$) of the OLEDs.

Emitting layer	V _T [V]	$\eta_{c}^{[a]}$ [cd/A]	$\eta_{c}^{[b]}$ [cd/A]	$B_{\rm max}$ [cd/m ²]	λ_{\max} [nm]
PVK:1a	8.7	0.39	0.30	211 (19.3 V)	535
PVK:1b	6.1	0.72	0.55	403 (13 V)	548
PVK:2a	9.3	0.32	0.22	124 (20.9 V)	620
PVK:2b	7.9	0.63	0.42	119 (16.7 V)	628
PVK:3a	9.3	0.33	0.23	124 (18.9 V)	522
PVK:3b	7.7	0.84	0.58	370 (14.9 V)	540
TCCz:1b	6.1	0.95	0.84	1502 (13.5 V)	541
TCCz:2b	8.5	1.57	1.08	846 (15.9 V)	612
TCCz:3b	8.7	0.29	0.26	508 (18.1 V)	609
3b	7.9	4.9	1.7	164 (12 V)	542

[a] Measured at 1 mA/cm². [b] Measured at 10 mA/cm².

Contrary to those of $[Cu(N,N)(P,P)]^+$ systems, ^[3a,3f] the electroluminescent (EL) spectra of the complexes based on L^2 or L^3 have large redshifts ($\approx 50 \text{ nm}$) in PVK compared to their photoluminescent (PL) spectra in PMMA films, as shown in Figure 10. The reason for this is not very clear but could be related to the flexible six-membered ring of (N-C-C-P-O-Cu), which may vibrate under the electric field and cause a decrease in the excited-state energy.^[17] Although the complexes with the PPh₃ auxiliary ligand have almost the same quantum efficiencies in PMMA film compared to the complexes based on DPEphos, the devices based on the former displayed lower performances. A similar result has been observed previously by our group and has been ascribed to the ligand dissociation reactions in solutions.^[3f] It is likely that an undetectable ligand-dissociation reaction still occurs in these mixed-ligand systems in CH₂Cl₂.



Figure 10. EL and PL spectra of 3b.

With TCCz as the host material, the device performance of the complexes **1b** and **2b** are significantly improved in comparison with those with PVK. For instance, the current efficiency at 1.0 mA/cm² and the maximum brightness for **1b** increases from 0.72 to 0.95 cd/A and from 403 to 1502 cd/m², respectively. The improved performance of the devices based on TCCz may be attributed to the improved distribution of the cuprous complexes in TCCz than in PVK.^[3f] The blueshifted EL spectra give further evidence for the lower aggregation level of the emitter in TCCz.



Figure 9. Device architecture (left) and molecular structures of the OLED materials (right).

However, TCCz is not a suitable host material for **3b**. As shown in Figure 10, the device based on a TCCz:3b emitting layer exhibited multiple emissions with the maximum at 609 nm, which is not from 3b but probably from the exciplexes. DFT calculations reveal that 3b has a relatively high LUMO level, while the LUMO level of TCCz is estimated to be 0.45 eV lower than that of PVK, judging from the cyclic voltammetry and absorption edge data. It may make the cuprous complex a less than an ideal center for electron direct-trapping in TCCz. In fact, the low current efficiency $(0.8 \text{ cd/A at } 1.0 \text{ mA/cm}^2)$ and the impurities seen in the EL spectrum (Figure 10) suggest that **3b** has poor ability for charge capture even in PVK. For comparison, pure 3b was used as the emitting layer in this device configuration. Unsurprisingly, the undoped device achieved an improved current efficiency of 4.9 cd/A at 1.0 mA/cm² with an EL spectrum almost identical to the PL spectrum of **3b** in CH₂Cl₂. We believe the EL performance of this complex can be further improved by optimizing the device configurations.

Conclusions

We report the synthesis and characterization of six mixed-ligand Cu^I complexes based on three N,O ligands. All of the complexes are easily prepared and stable in air. Similar to other mixed-ligands Cu^I complexes, they show the characteristic MLCT transition demonstrated by the electronic absorption spectra and DFT calculations. Their emissive colors depend on the electron-accepting ability of the N-heterocyclic unit in the N,O ligands. High PL efficiencies of about 0.70, without concentration quenching, were observed in these complexes (**3a** and **3b**) based on the ligand diphenyl(2-pyridylmethyl)phosphane oxide with a high π^* level, implying that the cuprous complexes containing coordinated oxygen atoms are as effective phosphorescent emitters as the classical heteroleptic [Cu(N,N)(P,P)]⁺ systems.

Experimental Section

General Considerations: The compounds [Cu(CH₃CN)₄](BF₄),^[20] diphenyl(2-pyridyl)phosphane oxide (L¹),^[21] diphenyl(2-pyridylmethyl)phosphane oxide (L³),^[22] and 8-(diphenylphosphanyl)quinoline^[23] were synthesized according to literature procedures. All other chemicals were of reagent grade and used without further purification. All solvents were dried and distilled by standard methods. ¹H NMR, with TMS as internal reference, and ³¹P NMR spectra, with 85% H₃PO₄ as external reference were measured with a Bruker AV300 NMR spectrometer at room temperature. Elemental analyses were performed with a BioRad elemental analysis system. The UV/Vis and PL spectra were measured at room temperature with Perkin-Elmer Lambda 45 UV/Vis and Horiba Jobin-Yvon FluoroMax-4 spectrometers, respectively. The solution PL quantum efficiencies were measured and calculated by a relative method using $[Ru(bpy)_3](PF_6)_2$ ($\Phi = 0.042$ in degassed water) as the standard.^[24] The film samples were prepared by spin-coating a mixture of the Cu^I complex (20 wt.-%) and PMMA (80 wt.-%) in CH₂Cl₂ onto a quartz glass slide. The spectra were measured with the FluoroMax-4 spectrometer equipped with an integrating sphere and



background-corrected by subtracting the spectrum obtained using a blank substrate, and subsequently corrected for the wavelength sensitivity of the fluorimeter and the spectra response of the sphere.^[25] The film PL quantum efficiency was determined according to the method outlined by de Mello.^[26] The luminescence-decay measurements were performed with the time-correlated single-photon counting (TCSPC) upgrade on the FluoroMax-4 spectrometer with a FluoroHub module. The lifetimes of solution samples were measured by TCSPC mode in conjunction with a nanoLED pulsed source (372 nm). The lifetimes of the PMMA film samples were measured by multi-channel scaling mode in conjunction with a spectraLED pulsed source (373 nm). Signals were collected with a FluoroHub module and analyzed by the DAS6 Decay Analysis software (HORIBA Jobin–Yvon).

Synthesis of the Ligand and the Cuprous Complexes

Synthesis of Diphenyl(8-quinolyl)phosphane Oxide (L²): To 8-(diphenylphosphanyl)quinoline (0.60 g, 1.92 mmol) in thf (12 mL) was added an excess of 30% H₂O₂ at room temperature. The reaction mixture was stirred for 0.5 h. The solution was poured into water (ca. 30 mL) and extracted into CH₂Cl₂. The organic extract was dried with sodium sulfate, filtered, and concentrated to afford a yellow solid, which was purified by column chromatography to give L². Yield: 0.45 g (71.4%). ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 7.36–7.50 (m, 7 H, Ar and quin-H3), 7.66 (m, 1 H, quin-H6), 7.80–7.87 (m, 4 H, Ar), 8.05 (d, ³J_{H,H} = 8.1 Hz, 1 H, quin-H5), 8.19 (d, ³J_{H,H} = 8.4 Hz, 1 H, quin-H4), 8.40 (dd, ³J_{H,H} = 8.1 Hz, 1 H, quin-H7), 8.75 (dd, ³J_{H,H} = 4.2 Hz, 1 H, quin-H2) ppm.

Synthesis of $[Cu(L^1)(PPh_3)_2](BF_4)$ (1a): Under nitrogen, $[Cu(CH_3CN)_4](BF_4)$ (0.157 g, 0.5 mmol) and PPh₃ (0.263 g, 1.0 mmol) were dissolved in CH₂Cl₂ (8 mL) and stirred for 1 h. L¹ (0.139 g, 0.5 mmol) was added to the solution, and the mixture was stirred for 5 h. The solution was filtered, and the solvents were removed. The same procedure was applied in the synthesis of the complexes **1b**, **2a**, **2b**, **3a**, and **3b**. Recrystallization of the residue from CH₂Cl₂ and methanol (MeOH) gave yellow-green crystals of **1a**. Yield: 0.27 g (56.7%). ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 7.09–7.18 (m, 26 H, Ar), 7.27–7.36 (m, 12 H, Ar), 7.55 (m, 2 H, Ar), 7.70 (m, 1 H, Py-H5), 7.82 (m, 1 H, Py-H4), 8.29 (m, 1 H, Py-H3), 8.44 (m, 1 H, Py-H6) ppm. ³¹P NMR: δ = –34.25 (s, PPh₃), 0.69 (s, PO) ppm. C₅₃H₄₄BCuF₄NOP₃·0.2CH₂Cl₂ (970.0): calcd. C 65.79, H 4.61, N 1.44; found C 65.85, H 4.32, N 1.48.

Synthesis of [Cu(L¹)(DPEphos)](BF₄) (1b): Recrystallization of the residue from CH₂Cl₂ and MeOH gave yellow-green crystals of **1b**. Yield: 0.28 g (57.9%). ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 6.72 (m, 2 H, Ar), 6.96 (t, ³*J*_{H,H} = 7.5 Hz, 6 H, Ar), 7.05 (m, 6 H, Ar), 7.16–7.35 (m, 22 H, Ar), 7.49 (m, 3 H, Py-H5 and Ar), 7.81 (t, ³*J*_{H,H} = 6.6 Hz, 1 H, Py-H4), 8.20 (d, ³*J*_{H,H} = 4.8 Hz, 1 H, Py-H3), 8.27 (m, 1 H, Py-H6) ppm. ³¹P NMR: δ = -48.00 (s, DPEphos), 0.91 (s, PO) ppm. C₅₃H₄₂BCuF₄NO₂P₃ (967.2): calcd. C 65.75, H 4.37, N 1.45; found C 65.94, H 4.00, N 1.44.

Synthesis of [Cu(L²)(PPh₃)₂](BF₄) (2a): Recrystallization of the residue from MeOH gave yellow crystals of **2a**. Yield: 0.30 g (61.2%). ¹H NMR (300 MHz, CDCl₃, 298 K): $\delta = 6.97-7.41$ (m, 40 H, Ar), 7.51 (m, 2 H, quin-H3 and H6), 7.64 (t, ³*J*_{H,H} = 6.3 Hz, 1 H, quin-H5), 8.38 (d, ³*J*_{H,H} = 7.5 Hz, 1 H, quin-H4), 8.59 (m, 2 H, quin-H2 and H7) ppm. ³¹P NMR: $\delta = -34.97$ (s, PPh₃), 6.28 (s, PO) ppm. C₅₇H₄₆BCuF₄NOP₃ (1003.2): calcd. C 68.17, H 4.61, N 1.39; found C 67.77, H 4.61, N 1.53.

Synthesis of $[Cu(L^2)(DPEphos)](BF_4)$ (2b): Recrystallization of the residue from MeOH gave yellow crystals of 2b. Yield: 0.24 g

FULL PAPER

Table 4. Crystallographic data for compounds 1a, 1b, 2a, 2b, 3a, and 3b.

	1a	1b	2a	2b	3a	3b
Empirical formula Formula mass	$C_{109}H_{93}B_2Cl_7Cu_2F_8N_2O_2P_6$ 2197.52	C ₅₆ H ₄₈ BCuF ₄ NO ₃ P ₃ 1002.19	C ₅₇ H ₄₆ BCuF ₄ NOP ₃ 1004.21	C _{58.5} H ₅₀ BCuF ₄ NO _{3.5} P ₃ 1066.26	C ₅₅ H ₅₀ BCuF ₄ NO ₂ P ₃ 1000.22	C ₅₅ H ₄₈ BCuF ₄ NO ₃ P ₃ 1014.20
Crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic	orthorhombic
Space group	C2/c	ΡĪ	PĪ	PĪ	$P2_1/c$	$Pna2_1$
a [Å]	57.114(3)	12.7999(8)	12.3447(9)	12.2697(8)	12.8052(10)	33.5515(14)
b [Å]	12.7707(6)	14.0967(8)	13.1441(10)	14.1003(9)	22.1640(13)	9.2554(4)
c [Å]	27.2789(12)	14.3565(8)	16.4044(13)	15.6564(10)	17.9279(11)	15.6499(7)
a [°]	90	72.3360(10)	73.6520(10)	103.0970(10)	90	90
β [°]	91.1270(10)	75.0550(10)	83.6310(10)	97.4870(10)	95.555(5)	90
γ [°]	90	88.6640(10)	72.6630(10)	93.7190(10)	90	90
V[Å ³]	19892.9(15)	2380.6(2)	2437.1(3)	2603.2(3)	5064.3(6)	4859.8(4)
Z	8	2	2	2	4	4
D _{calcd.} [gcm ⁻³]	1.467	1.398	1.368	1.360	1.312	1.386
Abs. coefficient [mm ⁻¹]	0.780	0.621	0.604	0.573	0.582	0.609
Final R indices						
$[I > 2\sigma(I)]$:						
R1, wR2	0.0576, 0.1156	0.0545, 0.1549	0.0505, 0.1285	0.0581, 0.1580	0.0647, 0.1813	0.0346, 0.0809
R indices (all						
data):						
R1, wR2	0.1048, 0.1277	0.0713, 0.1642	0.0635, 0.1384	0.0761, 0.1724	0.0894, 0.2069	0.0384, 0.0830
GOF	0.997	1.003	1.015	1.015	1.057	1.016

(47.2%). ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 6.64–7.31 (m, 38 H, Ar), 7.49 (td, ³*J*_{H,H} = 7.2 Hz, 2 H, quin-H3 and H6), 7.62 (m, 1 H, quin-H5), 8.37 (d, ³*J*_{H,H} = 7.5 Hz, 1 H, quin-H4), 8.47 (d, ³*J*_{H,H} = 8.4 Hz, 1 H, quin-H7), 8.58 (d, ³*J*_{H,H} = 8.4 Hz, 1 H, quin-H2) ppm. ³¹P NMR: δ = -48.29 (s, DPEphos), 6.78 (s, PO) ppm. C₅₇H₄₄BCuF₄NO₂P₃ (1017.2): calcd. C 67.23, H 4.36, N 1.38; found C 66.96, H 4.36, N 1.24.

Synthesis of [Cu(L³)(PPh₃)₂](BF₄) (3a): Recrystallization of the residue from MeOH gave colorless crystals of **3a**. Yield: 0.35 g (72.3%). ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 3.75 (d, ²*J*_{H,H} = -13.8 Hz, 2 H, CH₂), 6.83 (m, 1 H, Py-H3), 7.09–7.14 (m, 24 H, Ar), 7.31–7.46 (m, 12 H, Ar), 7.61–7.72 (m, 5 H, Ar and Py-H5), 7.89 (d, ³*J*_{H,H} = 7.8 Hz, 1 H, Py-H4), 7.98 (d, ³*J*_{H,H} = 4.8 Hz, 1 H, Py-H6) ppm. ³¹P NMR: δ = -2.51 (s, PPh₃), 36.42 (s, PO) ppm. C₅₄H₄₆BCuF₄NOP₃·CH₃OH (999.2): calcd. C 66.04, H 5.04, N 1.40; found C 65.84, H 4.82, N 1.24.

Synthesis of [Cu(L³)(DPEphos)](BF₄) (3b): Recrystallization of the residue from MeOH gave colorless crystals of **3b**. Yield: 0.30 g (61.2%). ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 3.77 (d, ²J_{H,H} = -13.8 Hz, 2 H, CH₂), 6.77 (m, 3 H, Py-H3 and Ar), 6.91–7.02 (m, 5 H, Ar), 7.18–7.49 (m, 31 H, Ar), 7.69 (t, ³J_{H,H} = 7.5 Hz, 1 H, Py-H5), 7.82 (d, ³J_{H,H} = 7.5 Hz, 1 H, Py-H4), 8.02 (d, ³J_{H,H} = 4.5 Hz, 1 H, Py-H6) ppm. ³¹P NMR: δ = -17.02 (s, DPEphos), 37.09 (s, PO) ppm. C₅₄H₄₄BCuF₄NO₂P₃·CH₃OH (1013.2): calcd. C 65.13, H 4.77, N 1.38; found C 65.30, H 4.41, N 1.12.

X-ray Crystallographic Studies: Data from selected crystals were collected with a Bruker Smart APEX diffractometer with a CCD detector, graphite monochromator, and Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The intensity data were recorded in the ω -scan mode (187 K). Lorentz and polarization factors were used to correct the raw intensity data, and absorption corrections were performed by using the SADABS^[27] program. The crystal structure was solved by using the SHELXTL program and refined by using full-matrix least squares.^[28] All non-hydrogen atoms were refined anistropically. The positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions. Details of crystal and structure refinement are shown in Table 4. CCDC-765391, -765392, -765393, and -765397, -765398, and -765399 contain the

supplementary crystallographic data for complexes 1a, 1b, 3b, 3a, 2b, and 2a, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http:// www.ccdc.cam.ac.uk/data request/cif.

Density Functional Calculations: DFT calculations were performed by using the GAUSSIAN 03 software package^[29] using a spin-restricted formalism at the B3LYP level. 6-31+G** was used to optimize the molecular geometry as a basis set for all elements, and Los Alamos ECP plus DZ (LANL2DZ) was used additionally for Cu. The HOMO and LUMO energies were determined by using minimized singlet geometries to approximate the ground states.

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