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Long-Lived and Efficient Emission from Mononuclear Amidophosphine Complexes of Copper

Alexander J. M. Miller, Jillian L. Dempsey, and Jonas C. Peters*

Division of Chemistry and Chemical Engineering, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

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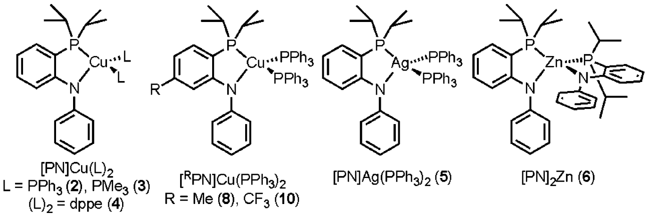
A number of structurally unusual, monomeric amidophosphine complexes of copper exhibit luminescence properties that are unprecedented for monocopper systems in solution at room temperature. The complexes exhibit lifetimes as long as 150 μs in benzene and quantum efficiencies in the range of $0.16 < \phi < 0.70$.

Highly luminescent transition metal complexes are widely studied[1] due to broad interest in their use for such applications as biological imaging,[2] photochemical catalysis,[3] and light-driven fuel production.[4] Copper luminophores[5] have been investigated as relatively inexpensive, biologically relevant[6] replacements for more ubiquitous Pt and Ru emitters. The most thoroughly studied Cu emitters are monomers supported by modified polypyridine and phenanthroline ligands, but these complexes often suffer from low quantum efficiencies and short luminescence lifetimes.[6] Using tertiary phosphine and substituted-phenanthroline ligands in concert, McMillin and co-workers have demonstrated that bulky bidentate phosphines inhibit exciplex quenching, providing unusually long lifetimes and rather good quantum efficiency ($\tau = 16$ μs, $\phi = 0.16$ in solution at 298 K).[7] Simple phosphine complexes of copper halides have also been reported,[8] and the effect of bulky diphosphine ligands on such complexes has recently been investigated.[9] While these complexes can be highly emissive in the solid state or in low-temperature solvent glasses, they display only faint, short-lived emission in solution at ambient temperatures.

Scheme 1



Our group recently reported an amide-bridged dicopper complex, $\{(PNP)Cu^I\}_2$ ($[PNP]^- =$ bis(2-(diisopropylphosphino)phenyl)amide), that featured both long-lived and highly efficient emission ($\tau = 10.9(4)$ μs, $\phi = 0.67(4)$ in THF at 298 K).[10] Isostructural complexes—with thioether donors in place of the phosphines[11] and with a phosphide bridging ligand in place of the amide[12]—show essentially no luminescence. The unusual luminescence behavior of $\{(PNP)Cu^I\}_2$ thus motivated us to study related amidophosphine Cu systems.

We now report the synthesis and characterization of a set of *monomeric* amidophosphine complexes of copper (general type [^{R}PN]Cu(L)$_2$), silver, and zinc (Scheme 1). All of these compounds are luminescent, but the Cu complexes are unique in their high quantum efficiency (ranging $0.16 < \phi < 0.70$), unusually long lifetimes (16−150 μs), and variable emission maxima (∼500−550 nm) in benzene at 298 K.

The amidophosphine [PN] ligands used herein can be readily prepared by nucleophilic attack of LiP^{i}Pr$_2$ on fluorine-substituted diarylamine precursors. The simplest such substrate, 1-fluoro-diphenylamine, provides [PN]Li (**1**; see Supporting Information for details). A related ligand containing phenyl rather than isopropyl substituents at phosphorus

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* To whom correspondence should be addressed. E-mail: jonas.peters@gmail.com.

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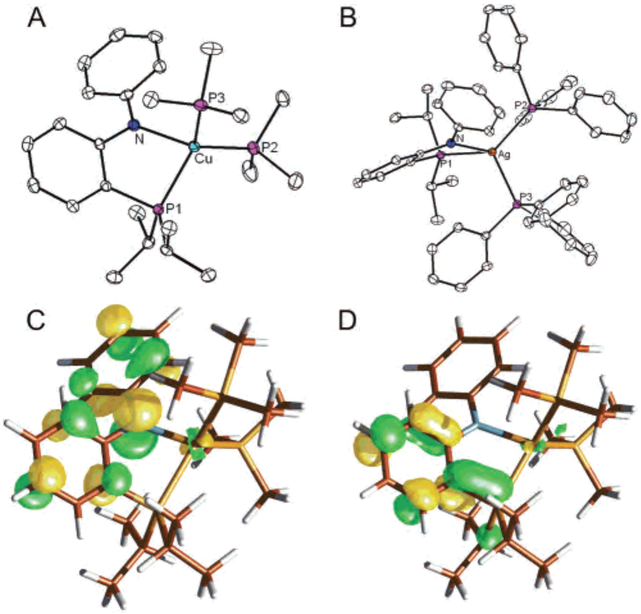

Figure 1. (A) Displacement ellipsoid representation (50%) of [PN]Cu(PMe$_3$)$_2$ (**3**), hydrogen atoms omitted: Cu−P1 2.2744(5) Å, Cu−N 2.086(1) Å, Cu−P2 2.2331(5) Å, Cu−P3 2.2690(5) Å, N−Cu−P1 82.54(4)°. (B) Displacement ellipsoid representation (50%) of [PN]Ag(PPh$_3$)$_2$ (**9**), hydrogen atoms omitted: Ag−N 2.369(1) Å, Ag−P1 2.4881(4) Å, Ag−P2 2.4919(4) Å, Ag−P3 2.5028(4) Å, N−Ag−P1 76.40(3)°. (C) The HOMO of **3**, as determined by DFT (5% Cu; 2% P; 36% N; 57% C). (D) The LUMO of **3**.

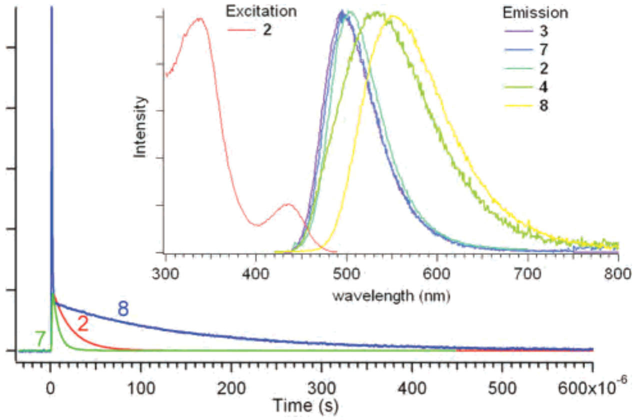

Figure 2. Luminescence decay traces of [^{Me}PN]Cu(PPh$_3$)$_2$ (**7**, green), [PN]Cu(PPh$_3$)$_2$ (**2**, red), and [^{CF3}PN]Cu(PPh$_3$)$_2$ (**8**, blue) in C$_6$H$_6$; λ_{ex} = 430 nm. Inset: Excitation spectrum of **2** and normalized emission spectra.

Table 1. Photophysical Comparison of Cu Complexes at 298 K

complex	solvent	λ_{abs} (nm)	λ_{em} (nm)	ϕ_{em}^{a}	τ (μs)
1	Et$_2$O	411	480	0.16	0.012(1)
2	C$_6$H$_6$	434	504	0.56	20.2(1)
3	C$_6$H$_6$	427	497	0.21	22.3(7)
4	C$_6$H$_6$	423	534	0.32	16.3(3)
7	C$_6$H$_6$	433	498	0.70	6.7(1)
8	C$_6$H$_6$	444	552	0.16	150(3)
[dbpCuPOP]$^+$	CH$_2$Cl$_2$	378	560	0.16	16.1^b
[dmpCudppe]$^+$	CH$_2$Cl$_2$	400	630	0.010	1.33^b
CuI(dppb)PPh$_3$	Me−THF	~380	550	0.01	<1^c

[a] Quantum yields from this work are reported with confidence of ± 5 on the last significant figure. [b] Data reported in CH$_2$Cl$_2$. [c] Data reported in 2-methyl-tetrahydrofuran. dbp = 2,9-di-*n*-butyl-1,10-phenanthroline; dmp = 2,9-dimethyl-1,10-phenanthroline; POP = bis[2-(diphenylphosphino)-phenyl]ether; dppb = 1,2-bis[diphenylphosphino]benzene.

has been reported by Liang.[13] [PN]Li exhibits blue luminescence when irradiated with a UV lamp and features an optical spectrum with transitions at 411, 354, and 286 nm. Addition of diethyl ether solutions of [PN]Li to a stirring suspension of CuBr·Me$_2$S and the appropriate tertiary phosphine readily affords bright yellow Cu complexes [PN]-Cu(L)$_2$ [**2**, L = PPh$_3$; **3**, L = PMe$_3$; **4**, (L)$_2$ = dppe, 1,2-bis(diphenylphosphino)ethane]. The expected monomeric, pseudotetrahedral structures were confirmed by X-ray diffraction (XRD) analysis. The structure of **3** is shown in Figure 1A, while related structural data for **2** are provided in the Supporting Information.[14] Cyclic voltammetry of **2** shows a reversible peak at −270 mV vs Fc/Fc$^+$ (Figure S2).

Absorption spectra for these three complexes feature similar peaks around 430 (ϵ = 2000−2500 M^{-1} cm^{-1}) and 350 nm (ϵ = 10 000−15 000 M^{-1} cm^{-1}), along with more complicated higher-energy transitions (Figure S3). Complexes **2**−**4** glow bright green under visible light, both in the solid state and in solution. Excitation into any absorption band leads to sharp, featureless emission peaks at 298 K: 504 nm for **2**, 497 nm for **3**, and 534 nm for **4** (Figure 2). The quantum efficiency of each complex in benzene solution at 298 K was assessed with excitation at 430 and 350 nm.[15−17] Quantum yields of the present complexes vary widely depending on the auxiliary ligand, from ϕ = 0.56 for **2** to ϕ = 0.21 for **3** (see Table 1). Such high solution quantum efficiency is unique among monomeric Cu systems,[18] as underscored in Table 1. When more polar solvents such as diethyl ether or THF are employed, the luminescence efficiency is significantly attenuated, typically by ~50%.

Complexes **2**, **3**, and **4** show long luminescence lifetimes in benzene solutions: 20.2(1) μs for **2** (Figure 2), 22.3(7) μs for **3**, and 16.3(3) μs for **4**. The lifetimes in Et$_2$O were virtually identical to those in benzene. We observe that the luminescence decay of PMe$_3$ adduct **3** has two components, with a small spike indicating the decay of a shorter-lived species (<10 ns; see Supporting Information).

In order to tune the emission frequency, we prepared two [PN] ligands with donating and withdrawing groups on the arene backbone. Methyl- and trifluoromethyl-substituted [^{Me}PN]Li (**5**) and [^{CF3}PN]Li (**6**) were chosen for ease of synthesis and were prepared analogously to **1**, with subsequent metalation in the presence of 2 equiv of PPh$_3$ yielding [^{Me}PN]Cu(PPh$_3$)$_2$ (**7**) and [^{CF3}PN]Cu(PPh$_3$)$_2$ (**8**). Methyl-substitution does not greatly perturb the optical spectrum

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(13) Liang, L.-C.; Lee, W.-Y.; Hung, C.-H. *Inorg. Chem.* **2003**, *42*, 5471−5473.

(14) An XRD study of **4** confirmed an overall connectivity related to **2** and **3**. The structure, however, suffered from severe twinning.

(15) The reducing power of excited-state complex **2*** is estimated by taking the difference between E^{00} (2.65 eV, the emission/excitation crossover point) and the ground state Cu$^{II/I}$ couple, predicting a hypothetical reduction potential of −2.9 V. A quenching experiment was undertaken and a Stern−Volmer plot (Figure S1) shows linear dependence of luminescence decay rate vs concentration of quencher, indicating a diffusion-controlled electron-transfer process. See Supporting Information for experimental details.

(16) [Ru(bpy)$_3$][PF$_6$]$_2$ standard: Wallace, W. L.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 1350−1357.

(17) Quinine sulfate standard: Demas, J. N.; Crosby, G. A. *J. Chem. Phys.* **1971**, *75*, 991−1024.

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when compared to **2** (Figure S4), and only a 6 nm blue-shift is observed for its emission maximum (Figure 2). Complex **7** emits significantly brighter than **2**, with $\phi = 0.70$, and a concomitantly shorter luminescence lifetime of 6.7(1) μs.

Relative to **2**, CF_3 substitution on the ligand backbone imparts a 10 nm red-shift in the optical spectrum ($\lambda_{abs} = 444$ nm, Figure S4) for **8**, which is matched by a 48 nm red-shift in the emission maximum (Figure 2). The quantum efficiency of **8** in benzene at 298 K, with $\phi = 0.16$, presents a substantial decrease compared to PPh_3 adducts **2** and **7**. Polycrystalline **8** displays structured emission at 77 K and broad emission at 298 K that closely resembles the room-temperature solution data (Figure S16).[19] Most interesting, however, is a dramatic increase in the measured luminescence lifetime, to 150(3) μs (Figure 2). As for the PMe_3 adduct **3**, there is a two-component decay profile, with a much more pronounced short-lived (<10 ns) species.[20] These decay profiles appear to reflect independent singlet/triplet emission pathways.[21] The triplet excited-state species is nearly an order of magnitude longer-lived than dbpCu(POP),[7] and is to our knowledge the longest-lived monomeric Cu emitter presently known in solution at ambient temperature.

For comparison to the Cu complexes, **1** was added to AgOTf in the presence of 2 equiv of PPh_3 in diethyl ether, affording golden-yellow $[PN]Ag(PPh_3)_2$ (**9**). An XRD study showed an analogous geometry to copper complex **2** (Figure 1B). Compound **9** is a rare example of a mononuclear silver amide complex. While its absorption spectrum is similar to those of **2** and **3**, its emission spectrum exhibits a much broader peak at 544 nm, suggesting loss of energy via structural reorganization. The luminescence is extremely attenuated relative to the corresponding Cu complexes ($\phi = 0.0010$), and it has a lifetime that is likewise much shorter (125(5) ns). Metathesis of 2 equiv of **1** with $ZnCl_2$, followed by filtration and crystallization, provided yellow $[PN]_2Zn$ (**10**). Excitation at either absorption feature ($\lambda_{abs} = 324$, 390 nm) led to aquamarine blue emission centered at 475 nm that was substantially less efficient and shorter lived than for the Cu complexes ($\phi = 0.088$, $\tau < 10$ ns).

Copper appears critical to accessing the interesting long-lived triplet excited state, and in the absence of Cu only fluorescence is observed. We tentatively suggest that an intraligand charge transfer (ILCT) transition is present in *all* of the compounds **1**−**10**. Excitation from the N lone pair to arene π^* is consistent with the calculated HOMO and LUMO of **3**, where substantial N lone-pair character (mixed with nonbonding arene π character) is present in the HOMO, and a predominantly π^* orbital is depicted in the LUMO (Figure 1C,D).[22,23] Emission from this transition is manifested as short-lived fluorescence for non-copper-containing species **1**, **5**, **6**, and **10**. The more interesting Cu emitters (**2**, **3**, **4**, **7**, and **8**) seem to display both singlet and triplet emissions, indicative of additional luminescence processes.[24]

Perhaps the simplest description of the observed Cu phosphorescence is MLCT from a Cu d orbital to the arene π^* orbital. This explanation is inconsistent with the following data, however. First, only minor differences are observed in the absorption spectra of Cu and Ag complexes **2** and **5** (Figure S5)—rather than the often-striking shift in MLCT transition energy caused by moving to a 4d element.[25] Additionally, there is minimal solvent dependence on the ground-state absorption spectrum of **2** (Figure S7), while significant solvent dependence is often observed in well-defined MLCT systems.[26] Further, MLCT states generally have large Stokes shifts, but the complexes here all have anomalously small Stokes shifts for MLCT.

Finally, the Cu complexes do not appear to be quenched by a five-coordinate exciplex, as is typical for MLCT.[5] If exciplex quenching played a significant role, the differences in steric bulk between **2**, **3**, and **4** might be expected to have a more significant effect on the phosphorescence lifetime. Electronic effects seem to play a more important role when comparing **2**, **7**, and **8**, as the sterically similar (but electronically diverse) complexes have quite different lifetimes and quantum efficiencies. Given these data, we speculate that the Cu phosphorescence is derived from good orbital overlap and energetic matching between the Cu d manifold and the ligand π^* system, which allows facile intersystem crossing to a Cu-stabilized triplet, which is inaccessible in the other complexes.

In summary, we have reported the synthesis and luminescence properties of a new series of amidophosphine complexes of copper, silver, and zinc. While all of the [PN]-containing complexes are emissive, the combination of arylamido and phosphine donors engenders the copper species with emission properties that are distinct relative to previously studied classes of copper emitters.

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Supporting Information Available: Experimental procedures, spectra, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Similar emission from crystalline and solution samples is consistent with an unchanged structure in solution.

(20) The decay profile of **8** was highly reproducible in repeated data collection on independently crystallized, analytically pure samples.

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(22) The calculation for **3** was performed using the hybrid DFT functional B3LYP/LACVP** as implemented in the Jaguar 6.5 program package (see Supporting Information).

(23) The HOMO-1 and HOMO-2 orbitals feature appreciably more Cu d character: HOMO-1 (45% Cu; 13% P; 21% N; 20% C). HOMO-2 (46% Cu; 23% P; 15% N; 26% C).

(24) The presence of both triplet and singlet excited states is not uncommon. In a particularly similar case, a d^0 metal shows both charge transfer (LMCT) and N lone pair to arene π^* excited states: Da Re, R. E.; Jantunen, K. C.; Golden, J. T.; Kiplinger, J. L.; Morris, D. E. *J. Am. Chem. Soc.* **2005**, *127*, 682−689.

(25) McMillin, D. R. In *Physical Methods in Bioinorganic Chemistry: Spectroscopy and Magnetism*; Que, L., Jr., Ed.; University Science Books: Sausalito, CA, 2000; pp 25−27.

(26) See, for example, Timpson, C. J.; Bignozzi, C. A.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *J. Phys. Chem.* **1996**, *100*, 2915−2925.