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Communication

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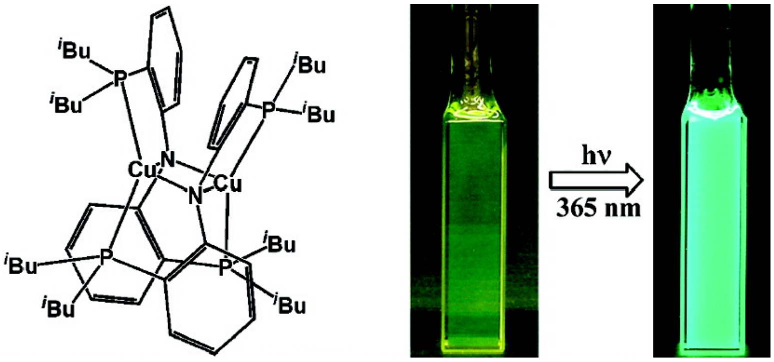

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COMMUNICATIONS

A Highly Emissive Cu_2N_2 Diamond Core Complex Supported by a $[PNP]^-$ Ligand

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Photoluminescent complexes have garnered much attention because of their possible utilization in electrochemical devices, as sensors and biological imaging agents, and in solar energy conversion schemes.[1] In this context, polypyridine-supported Cu(I) systems show promising features, including the availability of low-lying charge-transfer (CT) excited states and the relatively low cost of copper in comparison to other transition metal luminophores. However, their tendency to display weak emission and short-lived excited states is problematic.[2] McMillin has underscored these collective points,[3] and his group recently reported a fascinating mononuclear complex, $[Cu(dmp)(POP)]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline; POP = bis[2-(diphenylphosphino)phenyl]-ether), that exhibits both a relatively high quantum yield and long-lived excited state as compared to other polypyridine−Cu(I) systems.[4] Incorporation of a tightly bound bis(phosphine) chelate appears to create a rigid environment around the copper center that (i) suppresses solvent-induced exciplex formation due to steric factors and (ii) limits problematic ligand dissociation from the excited state.

Herein we describe an amido-bridged bimetallic copper system, $\{(PNP)Cu^I\}_2$ (**2**), derived from a chelating bis(phosphine)amide ligand ($[PNP]^-$ = bis(2-(diisobutylphosphino)phenyl)amide). This species is an exceptional luminophore in its own right. Aside from the absence of supporting polypyridine ligands, its combined quantum yield ($\phi > 0.65$) and lifetime ($\tau > 10\ \mu s$), in combination with its dinuclear structure and redox behavior, are without precedent. The synthesis of **2** was motivated by our recent elucidation of the dinuclear, thioether-supported Cu_2N_2 complex $\{(SNS)Cu^I\}_2$ ($[SNS]^-$ = bis(2-*tert*-butylsulfanylphenyl)amide).[5] $\{(SNS)Cu^I\}_2$ exhibits a reversible $1e^-$ oxidation to form a mixed-valence $[\{(SNS)Cu^{1.5}\}_2]^+$ complex, and electrochemical and XRD studies establish minimal structural reorganization between these two redox partners. While $\{(SNS)Cu^I\}_2$ is negligibly emissive at 298 K, its phosphine congener **2** emits strongly in solution and in the solid state when irradiated by visible light.

The required tridentate PNP−H ligand, **1**, was synthesized by addition of ^nBuLi to bis(2,2′-difluorophenyl)amine in THF followed by the addition of lithium diisobutylphosphide.[6] Heating this mixture at 45 °C for 4 days and subsequent passage of the crude product through silica gel afforded amine **1** as a spectroscopically pure viscous oil (75% yield). Deprotonation with ^nBuLi affords [PNP][Li], [**1**]Li, in good yield. Related bis(phosphino)amido ligands were first introduced by Fryzuk and have received the attention of several groups more recently.[6−8] [**1**]Li reacts rapidly with $CuBr{\cdot}Me_2S$ in diethyl ether to generate a luminescent yellow solution. The neutral, diamagnetic copper complex **2** can be subsequently isolated in pure form by crystallization (92%). Alternatively, complex **2** can be generated in good yield by the addition of $\{(2,4,6\text{-}Me_3C_6H_2)Cu\}$[9] to free amine **1**, producing mesitylene upon metalation.

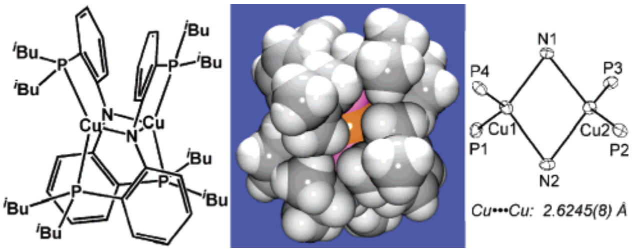

Figure 1. Left: Molecular representation of **2**. Center: Space-filling representation of **2** from crystal coordinates. Right: Displacement ellipsoid representations (50%) of the core atoms of **2**. See Supporting Information for complete details.

Complex **2** is characterized by a single resonance in its ^{31}P NMR spectrum (−33.9 ppm), and XRD analysis establishes the dimeric structure represented in Figure 1. A short Cu•••Cu bond distance of 2.6245(8) Å is observed that is similar in length to the Cu•••Cu distance reported for $\{(SNS)Cu^I\}_2$.[5] The P−Cu−P angles of 132.93(5)° and 137.69(5)° are significantly smaller than the S−Cu−S angles in $\{(SNS)Cu^I\}_2$ (av 153°). As a result, the copper centers are less severely distorted from a tetrahedral geometry than in $\{(SNS)Cu^I\}_2$, which more closely approximates a *cis*-divacant octahedron at each copper site. These geometrical differences presumably arise from the different steric requirements of the thioether $[SNS]^-$ and diisobutylphosphine $[PNP]^-$ ligands.

Electrochemical analysis of **2** in CH_2Cl_2 (Fc^+/Fc, 0.3 M $[^nBu_4N][PF_6]$, 250 mV/s, Fc = ferrocene) reveals two reversible waves, one centered at −550 mV and the other at 300 mV. An irreversible wave is encountered at higher potential (E_{pa} = 860 mV).[10] The event at −550 mV is assigned to a reversible $Cu^{1.5}Cu^{1.5}/Cu^1Cu^1$ redox process by analogy to the $\{(SNS)Cu^I\}_2$ system. The $Cu^{1.5}Cu^{1.5}/Cu^1Cu^1$ event is cathodically shifted for **2** in comparison to $\{(SNS)Cu^I\}_2$ (by ca. 160 mV) because of its stronger phosphine donors. The second *reversible* wave observed for **2** ($E_{1/2}$ = 300 mV) is noteworthy and is distinct from $\{(SNS)Cu^I\}_2$, for which only an *irreversible* redox process is observed at similar potential (E_{pa} = 560 mV).[5] Incorporation of the phosphine donors appears to stabilize an unusual second oxidation event in **2**, at least on the time scale of the electrochemical experiment (250 mV/s). While it is tempting to assign this second wave to a $Cu^2Cu^2/Cu^{1.5}Cu^{1.5}$ redox process, at this stage it is equally plausible to suggest that a ligand-centered oxidation process is operative.[11,12]

The absorption spectra for ligand **1** and complex **2** are shown in Figure 2A, and the corrected emission and excitation spectrum for **2** (298 K in cyclohexane) is also shown in part B.[13] The optical spectrum of **2** is typical for Cu(I). MLCT bands at 23 800 and 22 300 cm^{-1} give rise to its yellow color. Its emission spectrum, collected by excitation into its lowest energy absorption band (λ_{ex} = 440 nm, ∼22 700 cm^{-1}), shows a λ_{max} at 20 000 cm^{-1}. Its

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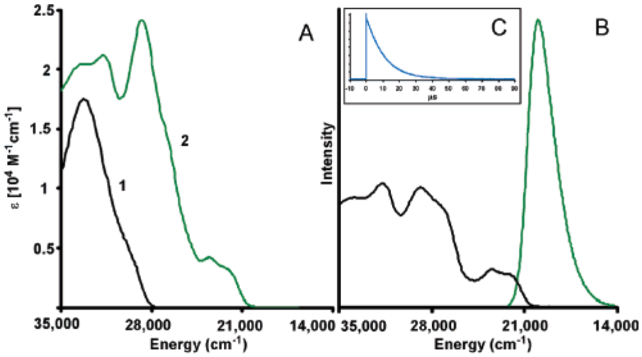

Figure 2. (A) Absorption spectra for **1** and **2** in cyclohexane. (B) Corrected emission spectrum (green, $\lambda_{ex} = 440$ nm) and excitation spectrum (black, $\lambda_{em} = 560$ nm) of **2** in cyclohexane. (C) Luminescence decay measurement of **2** in cyclohexane (laser pulse at $t = 0$ μs, $\lambda_{ex} = 440$ nm, $\lambda_{em} = 510$ nm).

corresponding excitation profile is also shown ($\lambda_{em} = 560$ nm, $\sim$17 900 cm^{-1}).

The intensity of the emission from the excited state of **2**, ***2**, is quite striking to the eye, even at room temperature in relatively polar donor solvents such as tetrahydrofuran (THF). This property is consistent with the unusually high quantum yield we measured for **2** at 298 K: $\phi = 0.68(2)$ in cyclohexane and $\phi = 0.67(4)$ in THF. These quantum yields were determined by established methods using a fluorescein standard ($\phi = 0.90$ in 0.1 N NaOH).[14] It was also of interest to determine the excited-state lifetime of ***2**, measured as 10.2(2) μs in cyclohexane (see inset in Figure 2) and 10.9(4) μs in THF. These lifetimes were determined by a monoexponential fit to raw decay data collected at 510 nm upon excitation at 460 nm.[13] Complex **2** is thus a highly efficient luminophore, with a lifetime similar to that McMillin reported for mononuclear [Cu(dmp)(POP)]$^+$ and a quantum yield that is ca. four times greater. We also note that diffusion-limited excited-state electron transfer ($k_Q = 1.2 \times 10^{10}$ M^{-1} s^{-1}) has been demonstrated by time-resolved quenching experiments using 2,6-dichloroquinone (see Supporting Information).[15]

Emissive dinuclear copper systems have been reported previously, but these species typically feature much shorter excited-state lifetimes. Perhaps most structurally related to **2** is the neutral complex {[DPT]Cu^I}$_2$ (DPT = 1,3-triphenyltriazine anion), which features a Cu···Cu distance of 2.451(8) Å.[16] This neutral d$^{10}-$d^{10} system exhibits a fluorescence maximum at 570 nm and a lifetime of only 2.23 ns at 77 K,[17a] approximately 3 orders of magnitude shorter than that of **2**. Other Cu$^I_2$ luminophores that have been described are typically supported by polypyridine-type ligands and have rather long Cu···Cu distances.[17b] Quantum yields for these systems are small in magnitude by comparison to their well-studied, substituted Cu(phen)$_2^+$ analogues.

The unusual emission properties exhibited by **2** may be due to several factors. Foremost among these may be the relatively low structural reorganization between **2** and ***2**. This assertion is at least consistent with the relatively narrow full width at half-maximum of its emission band shown in Figure 2B (2400 cm^{-1}), which can be converted to an estimate of the total reorganization energy λ = 2600 cm^{-1}. Also, steric protection afforded by the bulky [PNP]$^-$ ligand, in addition to the absence of a net cationic charge for **2**, removes the possibility of anion binding and likely renders the excited-state complex resistant to donor solvent ligation. Each of these factors can otherwise contribute to undesirable exciplex quenching. Lewis acidic Cu(I) cations, such as Cu(phen)$_2^+$ systems, suffer from exciplex quenching because of solvent and/or counteranion binding in the excited state.[3] The space-filling model of **2** shown in Figure 1 reveals just how effectively the copper sites are shrouded by the surrounding phosphine ligand framework.

As a final point of interest, we note that a value for $E^{00} = 2.6$ eV can be estimated from the intersection of the emission and excitation profiles of **2**. Subtracting this value from the reversible Cu$^{1.5}$Cu$^{1.5}$/Cu^{1}Cu^1 redox couple provides an estimated value of -3.2 V (vs Fc$^+$/Fc) for the excited-state reduction potential of ***2**. It is possible that ***2** will prove to be a potent photoreductant/photosensitizer,[18] and given the presence of two reversible redox couples within this bimetallic copper system, there may be an opportunity to photochemically drive multielectron reaction processes.[19]

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Supporting Information Available: X-ray crystallographic files (CIF), complete synthetic details, electrochemistry, spectroscopy, and tables of experimental data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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