

Copper(I) Bis(diimine) Complexes with High Photooxidation Power: Reductive Quenching of the Excited State with a Benzimidazoline Sacrificial Donor

Lea Gimeno, Clemence Queffelec, Errol Blart, and Yann Pellegrin*

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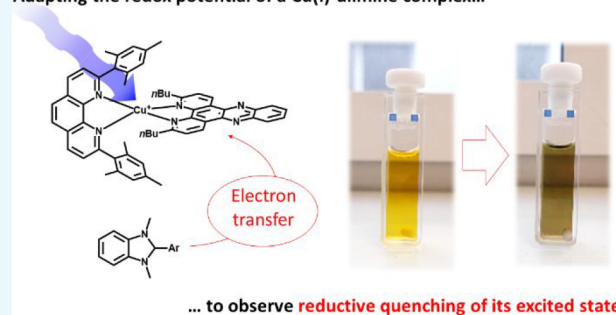
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ABSTRACT: The reductive quenching of photoexcited photosensitizers is a very efficient way to achieve challenging reduction reactions. In this process, the excited photosensitizer is reduced by a sacrificial electron donor. This mechanism is rarely observed with copper(I) bis(diimine) complexes, which are nevertheless acknowledged as very promising photosensitizers. This is due to the fact that they are very poor photooxidants and prove unable to react with common donors once promoted in their excited state. In this article, we evidence the rare reductive quenching cycle with two specially designed copper(I) complexes. These complexes exhibit improved photooxidation power thanks to an optimized coordination sphere made of strongly π -accepting ligands. Reductive quenching of the excited state of the latter complexes with a classical benzimidazoline sacrificial donor is monitored, and reduced complexes are accumulated during prolonged photolysis. Trials to utilize the photogenerated reductive power are presented.

Adapting the redox potential of a Cu(I)-diimine complex...



1. INTRODUCTION

Heavy-metal-based complexes are very useful photosensitizers because they are stable, feature long-lived excited states, luminescence in the visible, and have versatile redox properties in their excited state. However, heavy metals are rare and thus expensive and are potentially noxious. A lot of efforts is now devoted to developing earth-abundant photosensitizers.¹ Among them, copper(I) complexes have been abundantly used in the fields of lighting devices,² photovoltaics,³ solar fuel synthesis,⁴ and organic photochemistry.⁵ There are several copper(I) species which can act as photosensitizers, among them copper(I) bis(diimine) complexes (where diimines are, for example, phenanthroline ligands bearing bulky groups R in α of the nitrogen atoms). These complexes are particularly interesting because they are strongly colored in the visible (broad metal to ligand charge transfer (MLCT) spreading between 400 and 550 to 600 nm, depending on diimine ligand) and exhibit luminescence in the near-infrared and a significantly long lifetime of the excited state (from ca. 70 ns for $[\text{Cu}(\text{dmp})_2]^+$ to 3.26 μs for $[\text{Cu}(\text{dtbp})_2]^+$,⁶ where dmp and dtbp stand for 2,9-dimethyl-1,10-phenanthroline and 2,9-di-tert-butyl-1,10-phenanthroline, respectively).

As can be observed, the overall properties of copper(I) bis(diimine) complexes are strongly impacted by the diimine ligand and in particular by the nature of the bulky group R. Mostly, the diimine ligand is a phenanthroline derivative. It is mandatory to tether such a bulky group at positions 2 and 9 of

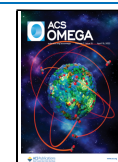
phenanthroline in order to observe long-lived, exploitable excited-state properties. Indeed, upon excitation in the MLCT, an electron shifts from copper-centered d orbitals to ligand-centered π^* empty orbitals. Thus, the copper complex transiently changes from a tetrahedral copper(I) complex to a square-planar copper(II) complex before returning to the ground state. This translates into a photoinduced flattening of the coordination sphere of the complex and opens several deactivation channels, leading to the premature quenching of the excited state. Preventing such flattening by grafting bulky groups R in α of the nitrogen atoms improves the lifetime of the excited state.⁷

Many complexes with different R groups on ligand L have been isolated and studied in the literature, and a few of them have been used as photosensitizers to drive photochemical reactions. In most cases, the excited state of the complexes was oxidatively quenched by an electron acceptor (either a catalyst or an organic reagent). Indeed, homoleptic copper(I) complexes are very potent reductants in their excited state, even outcompeting famous $[\text{Ru}(\text{bpy})_3]^{2+}$. Interestingly, there

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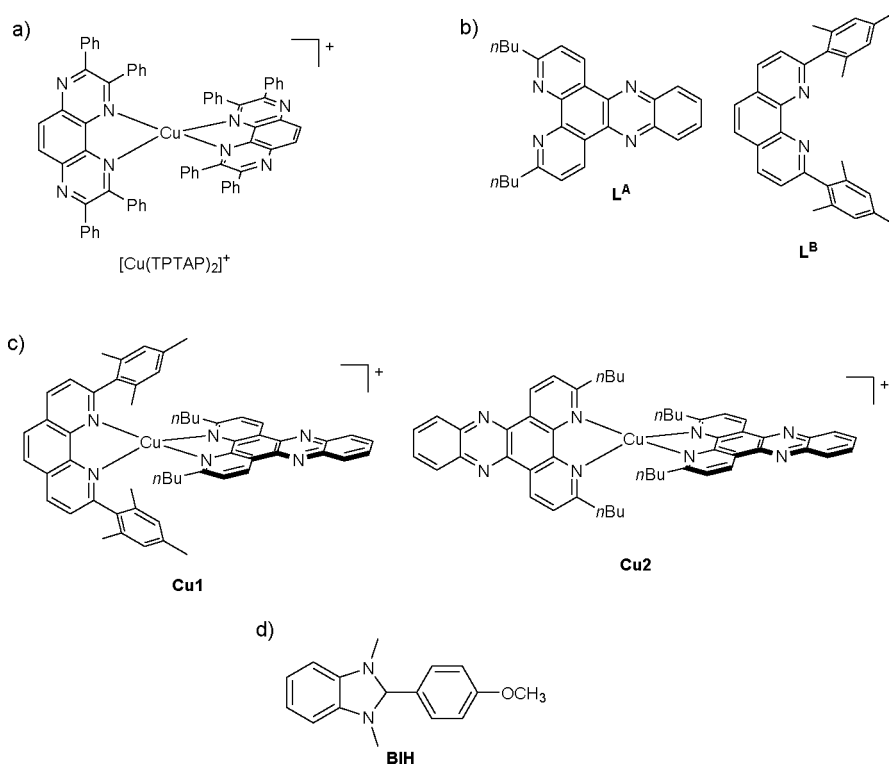


Figure 1. (a) Structure of complex $[\text{Cu}(\text{TPTAP})_2]^+$.^{8b} (b) Structure of ligands L^{A} and L^{B} . (c) Structures of complexes Cu1 and Cu2 . (d) Structure of BIH ($\text{BIH} = 1,3\text{-dimethyl-2-(4'-hydroxyphenyl)-2,3\text{-dihydro-1H-benzimidazole}$).

have been fewer reports where the excited state of a homoleptic copper(I) complex $[\text{CuL}_2]^*$ is reductively quenched by an electron donor.⁸ This is explained by the very weak oxidative power of $[\text{CuL}_2]^*$, a common feature of all traditional homoleptic copper(I) complexes.^{8a,b,9}

However, implementing the reductive quenching of $[\text{CuL}_2]^*$ would be an asset in the field of photochemistry. Indeed, the reduction of photoexcited complex $[\text{CuL}_2]^*$ by an electron donor in solution leads to $[\text{Cu}(\text{L})(\text{L}^{\bullet-})]^0$, which can be a very potent reductant (e.g., -1.65 V vs SCE for $\text{L} = 2,9\text{-diisopropyl-1,10-phenanthroline}$, designated as dipp in what follows).¹⁰ In addition, $[\text{Cu}(\text{L})(\text{L}^{\bullet-})]^0$ accumulates in the mixture during irradiation (if the electron donor is irreversibly oxidized), thus facilitating collisional reactions with substrates or catalysts.

Aiming at circumventing the low oxidation potential of $[\text{CuL}_2]^*$, attempts to increase $E([\text{CuL}_2]^*/[\text{Cu}(\text{L})(\text{L}^{\bullet-})]^0)$ have been made. From the Rehm and Weller equation,

$$E^* = E_{\text{red}} + E^{00} \quad (1)$$

where $E^* = E([\text{CuL}_2]^*/[\text{Cu}(\text{L})(\text{L}^{\bullet-})]^0)$, $E_{\text{red}} = E([\text{CuL}_2]^+ / [\text{Cu}(\text{L})(\text{L}^{\bullet-})]^0) + E^{00}$, and E^{00} is the energy of the excited state, E^* allows us to estimate the photooxidation power of $[\text{CuL}_2]^+$. One strategy to increase E^* consists of increasing E^{00} ,^{8c} and another consists of shifting E_{red} to a less-negative potential.^{8b,11} The LUMO of homoleptic copper(I) complexes $[\text{CuL}_2]^+$ is located on the phenanthroline ligands L ; therefore, tethering electron-withdrawing groups^{8b,12} or fusing aromatic cycles onto L ¹¹ leads to a stabilization of the LUMO and a shift of $E_{\text{red}}([\text{CuL}_2]^+)$ toward less-cathodic potentials. This strategy was successfully implemented by Cunningham et al. with complex $[\text{Cu}(\text{TPTAP})_2]^+$ (Figure 1a, TPTAP = 2,3,6,7-tetraphenyl-1,4,5,8-tetraazaphenanthrene).^{8b} In this case,

$E_{\text{red}}([\text{Cu}(\text{TPTAP})_2]^+) = \text{ca. } -0.9$ V vs SCE, which is considerably less cathodic than $E_{\text{red}}([\text{Cu}(\text{dipp})_2]^+) = -1.65$ V vs SCE, for example. Using eq 1, a spectacularly high oxidation potential of the excited state of $[\text{Cu}(\text{TPTAP})_2]^+$ of approximately 0.8 vs SCE was estimated. This value is comparable to E^* for $[\text{Ru}(\text{bpy})_3]^{2+}$ and significantly higher than E^* for most traditional homoleptic copper(I) complexes (for example, $E^* = 0.3$ V vs SCE for $[\text{Cu}(\text{dipp})_2]^+$). Conclusively, RQ was observed when $[\text{Cu}(\text{TPTAP})_2]^+$ was illuminated in the presence of diversely substituted ferrocene derivatives Fc' as electron donors. However, Fc'^+/Fc' is a reversible couple. Therefore, the reduced species $[\text{Cu}^{\text{I}}(\text{TPTAP}^{\bullet-})(\text{TPTAP})]^0$ quickly recombined with oxidized ferrocene Fc'^+ and could not accumulate in the photolyzed mixture.

The aim of the present work is to design copper(I) complexes with high E^* (at least 0.8 V vs SCE) by tuning their reduction potential and to observe the productive reductive quenching of their excited state by a sacrificial donor, namely, a species which is irreversibly oxidized by the photoexcited complexes. Inspired by Cunningham's work, we prepared two copper(I) complexes bearing the electron-depleted ligand 3,6-di-*n*-butyl-dipyrido[3,2-*a*:2',3'-*c*]phenazine (L^{A} , Figure 1b) whose synthesis was reported earlier by us.¹¹ Ligand L^{A} is a derivative of famous dppz ,¹³ ($\text{dppz} = \text{dipyrido}[3,2\text{-}a:2',3'\text{-}c]\text{phenazine}$) functionalized in α of the chelating nitrogen atoms by *n*-butyl chains to promote the excited-state properties of the corresponding copper(I) complex. The reduction potentials of such ligands and associated coordination complexes are known to be shifted toward less-negative potentials compared to plain phenanthroline. This guarantees that $E^*([\text{Cu}(\text{L}^{\text{A}})_2]^+)$ will be more positive and that RQ with a given sacrificial donor will be encouraged.

We investigated two complexes: heteroleptic $[\text{Cu}(\text{L}^{\text{A}})(\text{L}^{\text{B}})]^+$ and homoleptic $[\text{Cu}(\text{L}^{\text{A}})_2]^+$ (**Cu1** and **Cu2**, respectively; Figure 1c) bearing one and two ligands L^{A} , respectively. Heteroleptic copper(bis-diimine) complexes are usually not kinetically stable because the coordination sphere around Cu(I) is very labile. Here, we nevertheless managed to isolate stable **Cu1** using Schmittel's strategy, also known as the HETPHEN concept (HETPHEN = HETeroleptic PHENanthroline complexes).¹⁴ This concept relies on the use of very bulky ligands such as 2,9-dimesityl-1,10-phenanthroline (L^{B}). L^{B} bears two mesityl groups at positions 2 and 9, and the important steric bulk around the coordinating cavity prevents the formation of homoleptic $[\text{Cu}(\text{L}^{\text{B}})_2]^+$, leading rather to $[\text{Cu}(\text{L}^{\text{B}})(\text{solvent})_n]^+$. The latter can readily react with a less-encumbered ligand such as L^{A} leading to **Cu1**.

Concerning the choice of the sacrificial donor, we focused on benzimidazolines such as **BIH**¹⁵ (Figure 1d, here **BIH** = 1,3-dimethyl-2-(4'-hydroxyphenyl)-2,3-dihydro-1H-benzimidazole). These organic molecules are well-known reductants,¹⁶ their oxidation potential can be easily tuned,^{8d,15} and they have been abundantly used as sacrificial donors in photochemistry.^{4f,i,17} Importantly, they are irreversibly oxidized to stable benzimidazolium species in the presence of a base such as triethylamine (TEA) following the steps described in Figure S1, as commonly observed for benzimidazoline donors when oxidized in a basic medium.¹⁵

We report in this article the synthesis and characterization of **Cu1** and **Cu2** in THF. We evidence the occurrence of the reductive quenching of the excited states of **Cu1** and **Cu2** in the presence of **BIH** and the accumulation of their reduced states during photolysis.

2. MATERIALS AND METHODS

General. Chemicals were purchased from Sigma-Aldrich or Alfa Aesar and used as received. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with Merck 5735 Kieselgel 60F₂₅₄. Column chromatography was carried out with Merck 5735 Kieselgel 60F (0.040–0.063 mm mesh). ¹H spectra were recorded on an Avance 300 UltraShield Bruker instrument. Chemical shifts for ¹H NMR spectra are referenced relative to residual protium in the deuterated solvent ($\delta = 7.26$ ppm for CDCl_3). NMR spectra were recorded at room temperature, chemical shifts are written in ppm, and coupling constants are given in Hz. High-resolution mass spectra (HR-MS) were obtained either by electrospray ionization coupled with a high-resolution ion trap orbitrap (LTQ-Orbitrap, ThermoFisher Scientific) or by MALDI-TOF-TOF (Autoflex III, Bruker) working in ion-positive or ion-negative mode. Electrochemical measurements were made under an argon atmosphere in CH_2Cl_2 with 0.1 M Bu_4NPF_6 . Cyclic voltammetry experiments were performed by using an Autolab PGSTAT 302N potentiostat/galvanostat. A standard three-electrode electrochemical cell was used. Potentials were referenced to a saturated calomel electrode (SCE) as an internal reference. All potentials are quoted relative to SCE. The working electrode was a glassy carbon disk, and the auxiliary electrode was a Pt wire. In all of the experiments, the scan rate was 100 $\text{mV}\cdot\text{s}^{-1}$. UV–visible absorption spectra were recorded on an Analytik Jena Specord 210 Plus double-beam spectrophotometer using 1 cm path length cells. Emission spectra were recorded on a Fluoromax-4 Horiba Scientific spectrofluorimeter (1 cm quartz cells). Luminescence decays were recorded with a DeltaFlex Time

Correlated Single Photon Counting (TCSPC) system (Horiba Scientific) equipped with a DD-440L DeltaDiode laser (440 ± 9 nm, 60 ps pulse width at 20 MHz) and a PPD-850 detector (250–850 nm) on degassed dichloromethane and THF solutions.

Photolysis Procedures. A classical 4 mL UV–vis quartz cuvette (1 cm path length) was charged with a small stirring bar, ca. 0.35 mg of a copper complex (ca. 0.35 μmol), and 3 mL of analytical-grade THF. The mixture was degassed by argon bubbling for 15 min, after which a Teflon cap was fit on the cuvette, thus protecting it from ambient air. Then ca. 20 mg of **BIH** (80 μmol) was quickly added, and the solution was further degassed for 1 min. The obtained solution was then irradiated under one blue LED light for a few minutes. Every minute, the irradiation was stopped and a UV–vis spectrum was taken. The distance from the light source irradiation to the cuvette was 0.3 cm without the use of any filters.

For the photoreduction of 4-bromobenzophenone (**Bz-Br**), an oven-dried vial was charged with **BIH** (0.2 mmol) and 4-bromobenzophenone (0.10 mmol). The vial was sealed with a rubber septum and purged with argon. Then tetrahydrofuran (THF, 3 mL) and freshly distilled triethylamine (TEA) (400 μL , 2.9 mmol) were added, and the mixture was degassed for 10 min. **Cu2** (5 mg, 0.005 mmol) was next added, and the mixture was degassed again for 5 min. Then the reaction mixture was stirred under the radiation from one blue LED (purchased from Farnell, 450 nm, 25 lm, 75 mW) for 3 h. The distance from the light source irradiation to the vial was 0.3 cm without the use of any filters. The conversion was then estimated using gas chromatography. Those measurements were made on a Hewlett-Packard HP 5 ($l = 30$ m, i.d. = 0.32 mm, film thickness = 0.25 mm) equipped with an FID detector (N_2 as the carrier gas (1.6 $\text{mL}\cdot\text{min}^{-1}$); temperature program: 80 °C for 1 min and then 15 °C· min^{-1} to 320 °C). **Bz-Br** was purchased from Sigma-Aldrich.

Synthesis. Ligands $\text{L}^{\text{A}11}$ and $\text{L}^{\text{B}18}$ and complex **Cu2**¹¹ were prepared as previously reported.

Complex Cu1. L^{B} (23.4 mg, 56 μmol) is dissolved in dichloromethane (10 mL). The mixture is thoroughly degassed by argon bubbling and $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ is added quickly (21 mg, 56 μmol). The colorless solution turns yellow. After 5 min, a degassed solution of L^{A} (20 mg, 51 μmol , 10 mL dichloromethane) is added via syringe to the mixture over 5 min. The deep-orange mixture is left at room temperature for 30 min. The clear solution is then evaporated under reduced pressure. The orange residue is purified by thin layer chromatography on silica (with a gradient of petroleum ether/dichloromethane (100% petroleum ether to 100% dichloromethane). The orange fraction is collected and reprecipitated in toluene, affording a pure sample of **Cu1**.

Yield: 35 mg (68%). ¹H NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 9.64$ – 9.61 (2H, d, $J = 8.4$ Hz), 8.78 – 8.75 (2H, d, $J = 8.1$ Hz), 8.46 – 8.43 (2H, dd, $J = 6.6$ Hz, $J' = 3.3$ Hz), 8.29 (2H, s), 8.05 – 8.01 (2H, dd, $J = 6.6$ Hz, $J' = 3.3$ Hz), 7.81 – 7.78 (2H, d, $J = 8.4$ Hz), 7.71 – 7.68 (2H, d, $J = 8.4$ Hz), 6.18 (4H, s), 2.41 – 2.36 (4H, m), 1.73 (6H, s), 1.60 (12H, s + broad water peak), 1.23 – 1.19 (4H, m), 0.90 – 0.82 (4H, m), 0.72 – 0.67 (6H, m) ppm. The NMR spectrum is provided in Figure S2. ¹³C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 163.1$, 161.1 , 154.9 , 149.8 , 148.1 , 142.7 , 141.3 , 139.6 , 138.2 , 138.1 , 137.3 , 136.4 , 134.8 , 134.2 , 131.5 , 129.7 , 128.5 , 128.3 , 127.5 , 127.4 , 126.5 , 124.2 , 39.2 , 30.3 , 22.6 , 20.7 , 20.1 , 13.9 ppm. HRMS (MALDI)

Table 1. Optical and Electrochemical Parameters for Cu1 and Cu2^a

	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\cdot\text{cm}^{-1}$) ^b	$\lambda_{\text{em}}/\text{nm}$ ^b	$\tau_{\text{em}}/\text{ns}$	E^{00}/eV ^b	cyclic voltammetry		square wave voltammetry			
					$E_{1/2\text{ox}}/\text{V}$ ($\Delta E/\text{mV}$) ^c	$E_{1/2\text{red}}/\text{V}$ ($\Delta E/\text{mV}$) ^c	E_{ox}/V ^{c,d}	$E_{\text{red}}^1/\text{V}$ ^{c,d}	$E_{\text{red}}^2/\text{V}$ ^{c,d}	E^*/V vs SCE
Cu1	455 (4500)	730	47.7 ^b (53.2) ^c	1.98	1.04 (100)	-1.23 (120)	1.04	-1.30		0.68
Cu2	455 (9200)	720	14.0 ^b (55.5) ^{c,11}	2.03	1.14 (120)	-1.16 (230)	1.12	-1.17 (sh)	-1.21	0.86

^aAll potentials are given vs saturated calomel electrode (SCE). $E_{1/2} = (E^{\text{p,a}} + E^{\text{p,c}})/2$; $\Delta E = |E^{\text{p,a}} - E^{\text{p,c}}|$, where $E^{\text{p,a}}$ and $E^{\text{p,c}}$ are the anodic and cathodic peak potentials for a given electrochemical wave. Solutions were purged from oxygen by argon bubbling. E^{00} was determined by the tangent method (Figure S2). E^* was calculated with eq 1 using square voltammetry data. ^bIn THF. ^cIn dichloromethane. ^dDetermined by square wave voltammetry.

m/z : $[M + H]^+$ calculated for $\text{C}_{56}\text{H}_{54}\text{CuN}_6$: 873.3706; found: 873.3696. $\Delta = 1.1$ ppm.

3. RESULTS

3.1. Optical Properties. Cu1 and Cu2 exhibit the usual properties of all copper(I) complexes and are summarized in Table 1. The visible part of the absorption spectrum is dominated by a broad metal-to-ligand charge-transfer transition (MLCT) with a maximum absorption wavelength λ_{abs} of 455 nm in THF for both Cu1 and Cu2 (Figure 2). The

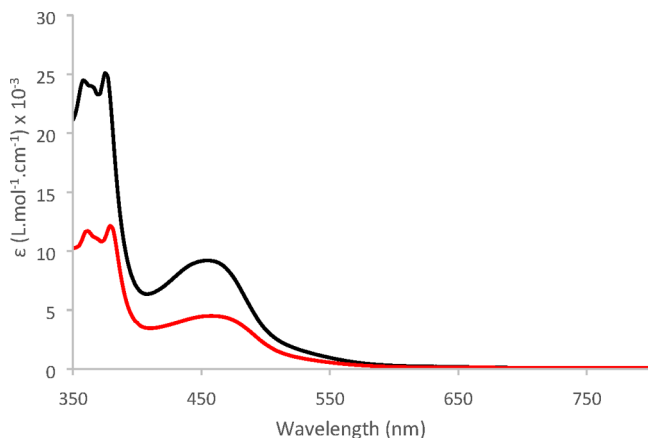


Figure 2. UV-vis absorption spectra of Cu1 (red line) and Cu2 (black line) in THF.

extinction coefficient for the MLCT of Cu1 ($4500 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) is roughly half that of Cu2 ($9200 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). This is due to the different dipole moments of Cu1 and Cu2. Indeed, L^A is a diimine ligand with an extended π -conjugated system that increases the dipole moment of the complex and thus raises the probability of the MLCT dipolar transition. Since there are two ligands L^A in Cu2 versus only one in Cu1, the dipole moment of Cu2 is larger than that of Cu1, thus rationalizing the different extinction coefficients of the two complexes. Conversely, the mesityl groups on L^B contribute to decrease the dipole moment¹⁹ and likely contribute to the overall weak extinction coefficient of the MLCT of Cu1. The set of sharp transitions at 360 and 380 nm on both spectra corresponds to a complex mixture of phenazine-centered transitions and high-energy MLCT transitions, as previously demonstrated by quantum calculations on Cu2.¹¹

Upon excitation in the MLCT, a weak and broad emission band can be observed in the near-infrared at ca. 730 and 720 nm for Cu1 and Cu2, respectively (Figure S3). The energies of the lowest-lying excited singlet states for Cu1 and Cu2 were determined from the emission spectra using the tangent

method^{10,20} and are comparable for both complexes. The emission quantum yields are weak ($<0.1\%$), and the emission lifetimes are rather short (Table 1). This observation was made previously for other copper(I) complexes studied in THF.¹⁰ Such behavior is due to different, very efficient deactivation channels competing with the radiative decay. First, the use of THF favors exciplex quenching.²¹ This process consists of the nucleophilic attack of the excited state of the complex by Lewis bases. Here, THF acts as a Lewis base through the nonbonding doublets on the oxygen atom and deteriorates the emission properties of Cu1 and Cu2. The deleterious impact of THF on the emission properties is demonstrated by comparing the steady-state emission spectra and emission decays recorded in dichloromethane and THF (Table 1 and Figures S4 to S7): indeed, the luminescence intensities and emission lifetimes are both smaller in THF than in dichloromethane for Cu1 and Cu2 (for absorption-matched solutions in both solvents). Interestingly, Cu2 seems to be much more affected than Cu1 by the solvent. The emission lifetime of Cu2 is indeed weaker than in dichloromethane, while the emission of Cu1 is a lot less affected. This could be due to the mesityl groups in L^B which are better-shielding Cu1 vs nucleophilic attacks from THF. Finally, the internal conversion from populated excited states to lower-lying dark states is also possible, as previously observed on Cu2.^{11,22}

3.2. Electrochemical Properties. The electrochemical behavior of Cu1 and Cu2 was analyzed by cyclic and square wave voltammeteries (Figures S8–S11). The voltammograms are strongly distorted when recorded in THF vs dichloromethane. (See, for example, the cyclic voltammogram of the same sample of Cu2 recorded in THF and in dichloromethane, Figures S9 and S12.) For example, the oxidation wave assigned to the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple appears to be curiously irreversible, although it is well known that the oxidation of bis(imine) copper(I) complexes is pseudoreversible in dichloromethane and acetonitrile.²³ Increasing the sweep rate did not affect the shape of the signal. We thus characterized the electrochemical behavior of Cu1 and Cu2 in dichloromethane.

In the anodic part of the voltammogram, the reversible wave associated with the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple can be monitored at 1.02 and 1.12 V vs SCE for Cu1 and Cu2, respectively. These values are in accordance with previously published work on copper(I) complexes where the metal ion is coordinated by two (identical or not) phenanthroline ligands.^{8b,10,18,23,24} The slightly higher oxidation potential of Cu2 vs Cu1 is likely due to the stronger π -accepting character of L^A vs L^B . In the cathodic part, well-defined ligand-centered reduction waves are monitored for Cu1 and Cu2 at -1.28 and -1.21 V vs SCE. Those reduction waves can be safely assigned to an L^A -centered reduction step for both Cu1 and Cu2, leading to a

species which can be formally written as $[\text{Cu}(\text{L}^{\text{A}\bullet-})(\text{L}^{\text{B}})]^0$. The reduction of copper(I) complexes bearing classical bulky phenanthroline ligands such as neocuproine or 2,9-diisopropyl-1,10-phenanthroline are usually reduced at a much more negative potential, ruling out the possibility that the reduction wave of **Cu1** could correspond to $\text{L}^{\text{B}\bullet-}$ formation.

For **Cu1**, the reduction and oxidation waves have similar sizes as expected for two one-electron electrochemical processes, but for **Cu2**, the reduction wave is anomalously large ($\Delta E = 230$ mV) and is approximately twice as large as the oxidation wave (whereas both oxidation and reduction processes feature on average the same current intensities for **Cu1**). This is due to the fact that **Cu2** bears two ligands L^{A} coordinated to one copper(I) center and that both ligands are reduced at similar potentials. As a matter of fact, square wave voltammograms in dichloromethane (Figure S11) in the cathodic region show that two peaks have merged in a broad deformed one. The first reduction process (E_{red}^1 , Table 1) appears as a shoulder at -1.17 V vs SCE, and the second process (E_{red}^2) appears at -1.21 V vs SCE, corresponding to the formation of $[\text{Cu}(\text{L}^{\text{A}\bullet-})(\text{L}^{\text{A}})]^0$ and $[\text{Cu}(\text{L}^{\text{A}\bullet-})_2]^-$, respectively. Consistently, the area under the cathodic peak is twice as large as the area under the anodic peak. The fact that both ligands L^{A} in the same copper complex can be reduced at similar potentials shows that there is limited electronic communication between them. Importantly, this means that the driving forces which must be wielded to reach monoreduced **Cu1**⁻ and bis-reduced **Cu2**²⁻ are very similar, paving the way for charge photoaccumulation upon excitation.

3.3. Photolysis Experiments. With all of the collected electrochemical and optical data, the oxidation and reduction potentials of **Cu1** and **Cu2** in their excited states can be estimated using the Rehm and Weller equation (Table 1). Both **Cu1** and **Cu2** can *a priori* be reduced by BIH ($E(\text{BIH}^+/\text{BIH}) = 0.28$ V vs SCE)^{17a} upon excitation because both feature respectable driving forces of -0.40 and -0.58 eV, respectively, for this reductive quenching process.

We thus performed preliminary photochemical trials where degassed solutions of **Cu1** and **Cu2** in THF are irradiated under 450 nm LED light in the presence of electron donors, and we monitored the evolution of the photolyzed medium by UV-vis spectroscopy.

No spectral evolution was noticed when solutions of **Cu1** or **Cu2** were irradiated in the presence of classical sacrificial electron donor triethylamine ($E(\text{TEA}^+/\text{TEA}) \approx 0.7$ V vs SCE)²⁵ despite an encouraging driving force of -0.16 eV for **Cu2**. This means that no reductive quenching step is taking place under these conditions. More important driving forces are required, probably to overcome the large reorganization energy that is supposed to take place upon reductive quenching.

When the sacrificial donor is BIH in the presence of TEA, photolyzed solutions darken very quickly after the beginning of the irradiation. As mentioned above, TEA is essential to ensure that BIH is irreversibly oxidized and that charge recombination is thus limited (Figure S1). However, the precipitation of a fine powder during irradiation prevented the recording of consistent UV-vis spectra because of strong light scattering. The powder was identified as **BI**⁺ by NMR. The precipitation of **BI**⁺ and the darkening of the solutions are, however, qualitative pieces of evidence that reductive quenching is taking place.

We attempted to reproduce the same photolysis experiment in the absence of TEA with BIH only. Likewise, photolyzed solutions darken very quickly after the beginning of the irradiation. The coloration persisted for a sufficiently long time to allow the recording of absorption spectra of the photolyzed mixtures (Figure 3). After only 1 min of irradiation at 450 nm,

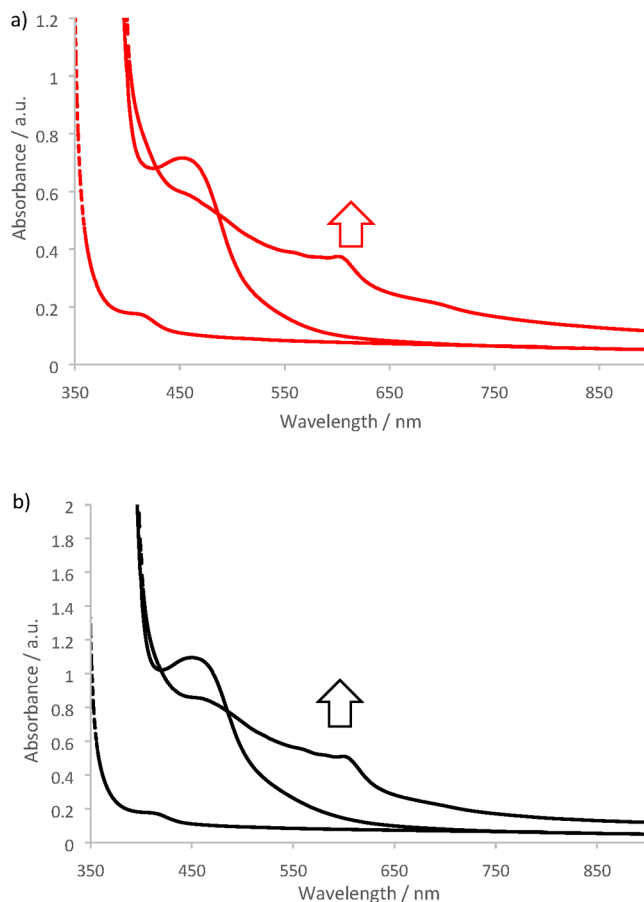


Figure 3. (a) UV-vis spectra of a photolyzed mixture of **Cu1** and **BIH** in THF. (b) UV-vis spectra of a photolyzed mixture of **Cu2** and **BIH** in THF. Solid lines: UV-vis spectra before photolysis. Dashed lines: UV-vis spectra after photolysis. Dotted lines: UV-vis spectra of **BIH** alone in THF at the same concentration (25 mM).

a broad absorption band with a maximum at around 605 nm rises for both **Cu1** and **Cu2**. This band is typical of reduced phenazine spacers (Figure S13 and comments)²⁶ and can be safely assigned to $[\text{Cu}(\text{L}^{\text{A}\bullet-})(\text{L}^{\text{B}})]^0$ (**Cu1**⁻) and $[\text{Cu}(\text{L}^{\text{A}\bullet-})(\text{L}^{\text{A}})]^0$ (**Cu2**⁻). The formation of the reduced forms of **Cu1** and **Cu2** upon irradiation in the presence of BIH conclusively points to a reductive quenching of the excited states of both complexes by the benzimidazole sacrificial donor. When irradiation is stopped, the solution returns to its initial orange color, although a significant loss of MLCT was observed, pointing to some instability of the complexes during irradiation. This instability could be due to the well-known lability of the coordination sphere of the complexes.²⁷

As mentioned above, **Cu2** can be twice reduced at close potentials. Interestingly, it has been proven several times that the phenazine spacer was electronically decoupled from the dipyrrolyl chelate.²⁸ Thus, $[\text{Cu}(\text{L}^{\text{A}\bullet-})(\text{L}^{\text{A}})]^0$ could be formally considered to be a $[\text{Cu}(\text{L})(\text{L}^{\text{A}})]^+$ moiety (where L is a sterically challenged phen ligand such as 2,9-di-*n*-butyl-1,10-

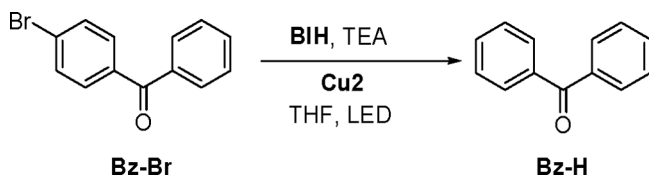
phenanthroline) linked to an isolated reduced phenazine spacer. As such, reduced complex Cu2^- could in principle be excited a second time and could be involved in a second reductive quenching with BIH , leading to doubly reduced Cu2^{2-} . If we assume that E^{00} remains similar for Cu2 and Cu2^- , then we can apply eq 1:

$$E^*(\text{Cu2}^-) = E_{\text{red}}^2 + E^{00} = \text{ca. } 0.8 \text{ V vs SCE}$$

Reductive quenching of $(\text{Cu2}^-)^*$ by BIH would thus be thermodynamically allowed. However, photolyzed mixtures of Cu1 (where such photoaccumulation is not thermodynamically possible) and Cu2 show virtually identical spectral features, and prolonged irradiation did not result in any further spectral change for Cu1 or Cu2 . Thus, under our conditions, it is very unlikely that a double photoinduced reduction of Cu2 takes place. The excited state of Cu2^- is probably very quickly quenched by energy transfer toward low-lying (L^{A^*})-centered states.

3.4. Photoinduced Reduction Trials. We then attempted to utilize the implemented reductive quenching of the designed copper(I) complexes in the presence of BIH to perform the reductive dehalogenation of 4-bromobenzophenone (Bz-Br). This was recently successfully used as a benchmark reaction to test the efficacy of reductive quenching with copper^{5b,8d} and iridium complexes (Scheme 1).^{17f} In particular, we demon-

Scheme 1. Reductive Photodehalogenation of Bz-Br via Reductive Quenching of Cu2's Excited State in the Presence of BIH



strated the efficient reduction of Bz-Br to Bz-H (benzophenone) when a mixture of $[\text{Cu}(\text{dipp})_2]^+$, Bz-Br , and chemically engineered benzimidazoline derivative BI_2H (Figure S14) is irradiated in the visible region.

A degassed mixture of Bz-Br with 2 equiv of BIH , excess TEA, and 5 mol % Cu2 in THF was irradiated for 3 h under 450 nm LED light. Cu2 was chosen over Cu1 for this experiment because it is the best photooxidant. Immediately after the beginning of the irradiation, the solution darkened and the color was maintained during the entire duration of the photolysis, demonstrating that reductive quenching of the excited state of Cu2 was taking place. However, there was virtually no conversion of Bz-Br to Bz-H after 3 h of light soaking. We reproduced the same experiment with BI_2H instead of BIH , leading to a marginally improved conversion of 8%, proving that the reduction of Bz-Br is only slightly influenced by the nature of the sacrificial donor.

With these experimental results in hand, we propose the following rationale. Upon photoexcitation, Cu2^* is reduced by BIH (or BI_2H), leading to the formation of Cu2^- and $\text{BIH}^{*\cdot}$ ($\text{BI}_2\text{H}^{*\cdot}$). Cu2^- is thermodynamically unlikely to lead to reduced Bz-Br ($E(\text{Bz-Br}/\text{Bz-Br}^-) = -1.62 \text{ V vs SCE}$)^{8d} because $E(\text{Cu2}/\text{Cu2}^-)$ is not sufficiently negative. Indeed, $E^*(\text{Cu2})$ was significantly improved by coordinating electron-poor ligands to copper(I), but $E(\text{Cu2}/\text{Cu2}^-)$ was sacrificed. On the other hand, $\text{BIH}^{*\cdot}$ ($\text{BI}_2\text{H}^{*\cdot}$) is quickly deprotonated in

the presence of TEA, leading to BI^\bullet (BI_2^\bullet), which is a strong reductant (ca. -1.6 V vs SCE).¹⁵ Summarily, the reductive quenching of the excited state of Cu2 by BIH (BI_2H) leads to two reductants with only one photon. In the present case, BI^\bullet is apparently not sufficiently reductive to react with Bz-Br (since there is no conversion for the photochemical reaction). BI_2^\bullet is slightly more reductive than BI^\bullet thanks to the additional methoxy groups tethered to the structure (Figure S14), which could account for the slight improvement in the conversion when BI_2H is used as a sacrificial donor.

Moreover, those results have important implications for our previous work. As mentioned above, we recently demonstrated that irradiating a mixture of Bz-Br , $[\text{Cu}(\text{dipp})_2]^+$, and BI_2H leads to the efficient photoreduction of Bz-Br to Bz-H (93% yield after 30 min of irradiation). However, we were unable to determine whether Bz-Br was reduced by photoproducted $[\text{Cu}(\text{dipp})(\text{dipp}^\bullet)]^0$ or BI_2^\bullet . In the present work, we demonstrate that BI_2^\bullet (and incidentally BI^\bullet also) is unable to efficiently reduce Bz-Br . Stronger reductants are necessary to reduce such challenging substrates, such as homoleptic copper(I) complexes with more negative reduction potentials than $E(\text{Cu2}/\text{Cu2}^-)$.

Given the results obtained with Cu2 , we did not perform further trials with Cu1 , which has very similar properties.

5. CONCLUSIONS

We reported the synthesis and characterization of two copper(I) complexes Cu1 and Cu2 showing enhanced photooxidative power. This task was realized by using electron-poor, phenazine-fused ligands, which allowed us to significantly shift the reduction potential of both complexes to less-negative values and subsequently increased the reduction potential of the excited state of each complex $E(\text{Cu1}^*/\text{Cu1}^-)$ and $E(\text{Cu2}^*/\text{Cu2}^-)$. Cu1 and Cu2 were therefore able to oxidize a common benzimidazoline sacrificial reductant BIH under blue light irradiation. In other words, Cu1 and Cu2 were involved in a reductive quenching cycle, a very rare photochemical process with copper(I) bis(diimine) complexes. The challenging photoinduced reduction of an aryl bromide via reductive quenching was then attempted but proved unsuccessful because reduced complexes are insufficiently reductive to react with such substrates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c00531>.

Series of electron transfers following the one-electron oxidation of benzimidazolines; NMR spectra of Cu1 ; emission spectra of Cu1 and Cu2 complexes in THF; steady-state emission spectra in THF; luminescence decays; cyclovoltammograms and square wave voltammograms of Cu1 and Cu2 ; spectroelectrochemistry; and structure of BI_2H (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Yann Pellegrin – CEISAM UMR6230, Nantes University, Nantes F 44000, France; orcid.org/0000-0003-0006-0815; Email: yann.pellegrin@univ-nantes.fr

Authors

Lea Gimeno – CEISAM UMR6230, Nantes University, Nantes F 44000, France

Clémence Queffelec – CEISAM UMR6230, Nantes University, Nantes F 44000, France; orcid.org/0000-0001-9794-7441

Errol Blart – CEISAM UMR6230, Nantes University, Nantes F 44000, France

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsomega.2c00531>

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Notes

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