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Lea Gimeno, Clemence Queffelec, Errol Blart, Yann Pellegrin. Copper(I) Bis(diimine) Complexes with High Photooxidation Power: Reductive Quenching of the Excited State with a Benzimidazoline Sacrificial Donor. ACS Omega, 2022, 7 (15), pp.13112-13119. <10.1021/acsomega.2c00531>. <hal-03690057>

HAL Id: hal-03690057

<https://hal.science/hal-03690057v1>

Submitted on 7 Jun 2022

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1 **Copper(I) bis(diimine) complexes with high photo-oxidation**
2 **power: reductive quenching of the excited state with**
3 **benzimidazoline sacrificial donor**

4
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9
10 **Abstract:** The reductive quenching of photo-excited photosensitizers is a very efficient way to
11 achieve challenging reduction reactions. In this process, the excited photosensitizer is reduced by a
12 sacrificial electron donor. This mechanism is rarely observed with copper(I)-bis(diimine) complexes
13 which are nevertheless acknowledged as very promising photosensitizers. This is due to the fact that
14 they are very poor photo-oxidants, and prove unable to react with common donors once promoted in
15 their excited state. In this contribution, we evidence the rare reductive quenching cycle with two
16 specially designed copper(I) complexes. These complexes exhibit improved photo-oxidation power,
17 thanks to an optimized coordination sphere made of strongly π -accepting ligands. Reductive quench-
18 ing of the excited state of the latter complexes with a classical benzimidazoline sacrificial donor is
19 monitored and reduced complexes are accumulated during prolonged photolysis. Trials to utilize the
20 photo-generated reductive power are presented.

21
22 **Keywords:** reductive quenching • copper(I) complexes • photochemistry • benzimidazoline • dipyr-
23 ridophenazine spacer

24
25 **1. Introduction**

26 Heavy metal based complexes are very useful photosensitizers because they are stable, feature
27 long lived excited states, luminescence in the visible, and versatile redox properties in their excited
28 state. However, heavy metals are rare and thus expensive, and are potentially noxious. A lot of efforts
29 are now devoted to developing Earth abundant photosensitizers.¹ Among them, copper(I) complexes
30 have been abundantly used in the fields of lighting devices,² photovoltaics,³ solar fuel synthesis⁴ and
31 organic photochemistry.⁵ There are several copper(I) species which can act as photosensitizers,

32 among them copper(I) bis(diimine) complexes (where diimines are for example phenanthroline lig-
33 ands bearing bulky groups R in α of the nitrogen atoms). Those complexes are particularly interesting
34 because they are strongly colored in the visible (broad metal to ligand charge transfer (MLCT) spread-
35 ing between 400 and 550 to 600 nm, depending on diimine ligand), they exhibit luminescence in the
36 near infrared and a significantly long lifetime of the excited state (from ca. 70 ns for $[\text{Cu}(\text{dmp})_2]^+$ to
37 $3.26 \mu\text{s}$ for $[\text{Cu}(\text{dtbp})_2]^+$,⁶ where dmp and dtbp respectfully stand for 2,9-dimethyl-1,10-phenanthro-
38 line and 2,9-di-tertbutyl-1,10-phenanthroline).

39 As can be observed, the overall properties of copper(I)-bis(diimine) complexes are strongly im-
40 pacted by the diimine ligand and in particular by the nature of the bulky group R. Mostly, the diimine
41 ligand is a phenanthroline derivative. It is mandatory to tether such bulky group in positions 2 and 9
42 of phenanthroline in order to observe long-lived, exploitable excited state properties. Indeed, upon
43 excitation in the MLCT, an electron shifts from copper centered d orbitals to ligand centered π^* empty
44 orbitals. Thus, the copper complex transiently changes from a tetrahedral copper(I) complex to a
45 square planar copper(II) complex before returning to the ground state. This translates into a photo-
46 induced flattening of the coordination sphere of the complex, and opens several deactivation channels
47 leading to the premature quenching of the excited state. Preventing such flattening by grafting bulky
48 groups R in α of the nitrogen atoms improves the lifetime of the excited state.⁷

49 Many complexes with different R groups on ligand L have been isolated and studied in the liter-
50 ature and a few of them have been used as photosensitizers to drive photochemical reactions. In most
51 cases, the excited state of the complexes was oxidatively quenched by an electron acceptor (either a
52 catalyst or an organic reagent). Indeed, homoleptic copper(I) complexes are very potent reductants in
53 their excited state, even outcompeting famous $[\text{Ru}(\text{bpy})_3]^{2+}$. Interestingly, there has been many less
54 reports where the excited state of a homoleptic copper(I) complex $[\text{CuL}_2]^{+*}$ is reductively quenched
55 by an electron donor.⁸ This is explained by the very weak oxidative power of $[\text{CuL}_2]^{+*}$, a common
56 feature of all traditional homoleptic copper(I) complexes.^{8a,8b,9}

57 Yet, implementing the reductive quenching of $[\text{CuL}_2]^{+*}$ would be an asset in the field of photo-
58 chemistry. Indeed, reduction of photo-excited complex $[\text{CuL}_2]^{+*}$ by an electron donor in solution
59 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 L = 2,9-diiso-
60 propyl-1,10-phenanthroline, designated as dipp in what follows).¹⁰ In addition, $[\text{Cu}(\text{L})(\text{L}^\bullet)]^0$ accu-
61 mulates in the mixture during irradiation (if the electron donor is irreversibly oxidized) thus facilitat-
62 ing collisional reactions with substrates or catalysts.

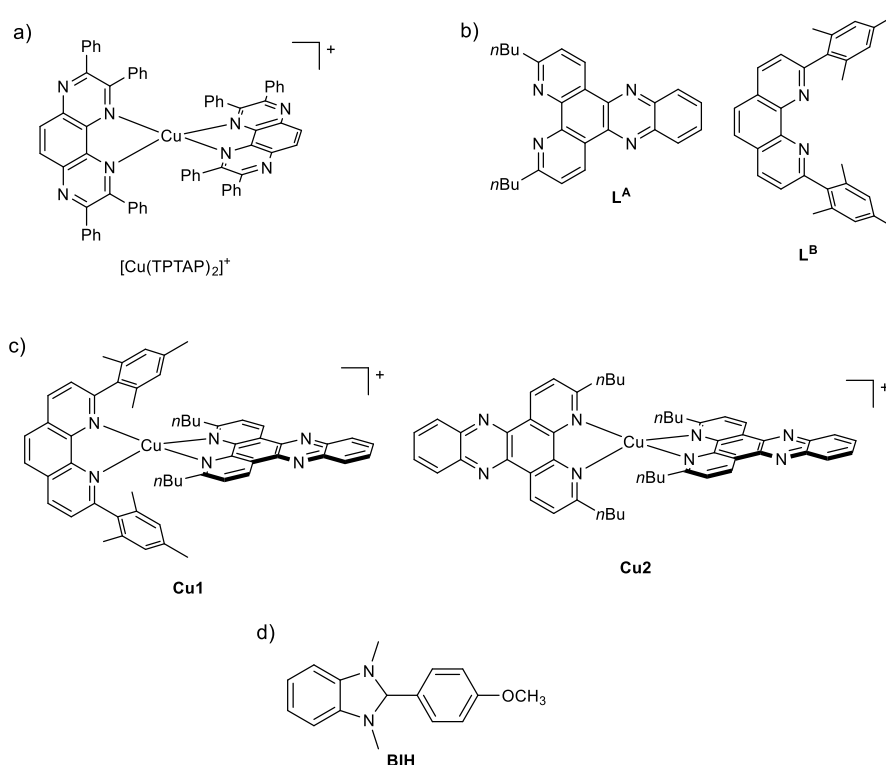
63 Aiming at circumventing the low oxidation potential of $[\text{CuL}_2]^{+*}$, attempts to increase
64 $E([\text{CuL}_2]^{+*}/[\text{Cu}(\text{L})(\text{L}^\bullet)]^0)$ have been made. From the Rehm and Weller equation:

65
66

67

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

68 (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
 69 of the excited state). E^* allows to estimate the photo-oxidation power. One strategy to increase E^*
 70 consists in increasing E^{00} ,^{8c} another in shifting E_{red} to less negative potential.^{8b,11} The LUMO of
 71 homoleptic copper(I) complexes $[\text{CuL}_2]^+$ is located on the phenanthroline ligands L; therefore tether-
 72 ing electron withdrawing groups^{8b,12} of fusing aromatic cycles onto L¹¹ leads to a stabilization of the
 73 LUMO and a shift of $E_{\text{red}}([\text{CuL}_2]^+)$ towards less cathodic potentials. This strategy was successfully
 74 implemented by Cunningham et al. with complex $[\text{Cu}(\text{TPTAP})_2]^+$ (Figure 1a, TPTAP = 2,3,6,7-Tetra-
 75 phenyl-1,4,5,8-tetraazaphenanthrene).^{8b} In this case, $E_{\text{red}}([\text{Cu}(\text{TPTAP})_2]^+) = \text{ca. } -0.9 \text{ V vs. SCE}$ which
 76 is considerably less cathodic than $E_{\text{red}}([\text{Cu}(\text{dipp})_2]^+) = -1.65 \text{ V vs. SCE}$ for example. Using equation
 77 1, a spectacularly high oxidation potential of the excited state of $[\text{Cu}(\text{TPTAP})_2]^+$ of approximately
 78 0.8 vs. SCE was estimated. This value is comparable to E^* for $[\text{Ru}(\text{bpy})_3]^{2+}$ and significantly higher
 79 than E^* for most traditional homoleptic copper(I) complexes (for example, $E^* = 0.3 \text{ V vs. SCE}$ for
 80 $[\text{Cu}(\text{dipp})_2]^+$). Conclusively, RQ was observed when $[\text{Cu}(\text{TPTAP})_2]^+$ was illuminated in presence of
 81 diversely substituted ferrocene derivatives Fc' as electron donors. However, Fc'^+/Fc' are reversible
 82 couples. Therefore the reduced species $[\text{Cu}^{\text{I}}(\text{TPTAP}^{\bullet-})(\text{TPTAP})]^0$ quickly recombined with oxidized
 83 ferrocene Fc'^+ and could not be accumulated in the photolyzed mixture.



84

85 **Figure 1.** a) structure of complex $[\text{Cu}(\text{TPTAP})_2]^+$.^{8b} b) Structure of ligands L^{A} and L^{B} . c) Structures
 86 of complexes Cu1 and Cu2 . d) Structure of BIH ($\text{BIH} = 1,3\text{-Dimethyl-2-(4'-hydroxyphenyl)-2,3-}$
 87 $\text{dihydro-1H-benzimidazole}$).

88

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

100 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**
101 and **Cu2** respectively, Figure 1c) bearing respectively one and two ligands **L^A**. Heteroleptic cop-
102 per(bis-diimine) complexes are usually not kinetically stable because the coordination sphere around
103 Cu(I) is very labile. Here, we managed nevertheless to isolate stable **Cu1** using Schmittel's strategy,
104 also known as HETPHEN concept (HETPHEN = HETeroleptic PHENanthroline complexes).¹⁴ This
105 concept relies on the use of very bulky ligands such as 2,9-dimesityl-1,10-phenanthroline (**L^B**). **L^B**
106 bears two mesityl groups in positions 2 and 9 and the important steric bulk around the coordinating
107 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
108 latter can readily react with a less encumbered ligand such as **L^A** leading to **Cu1**.

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

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

119

120 2. Materials and Methods

121 **General:** chemicals were purchased from Sigma-Aldrich or Alfa Aesar and used as received.
122 Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735
123 Kieselgel 60F₂₅₄. Column chromatography was carried out either with Merck 5735 Kieselgel 60F

124 (0.040-0.063 mm mesh). ^1H spectra were recorded on an *AVANCE 300 UltraShield BRUKER*. Chem-
125 ical shifts for ^1H NMR spectra are referenced relative to residual protium in the deuterated solvent (δ
126 = 7.26 ppm for CDCl_3). NMR spectra were recorded at room temperature, chemical shifts are written
127 in ppm and coupling constants in Hz. High-resolution mass (HR-MS) spectra were obtained either by
128 electrospray ionization coupled with high resolution ion trap orbitrap (LTQ-Orbitrap, ThermoFisher
129 Scientific,) or by MALDI-TOF-TOF (Autoflex III, Bruker), working in ion-positive or ion-negative
130 mode. Electrochemical measurements were made under an argon atmosphere in CH_2Cl_2 with 0.1 M
131 Bu_4NPF_6 . Cyclic voltammetry experiments were performed by using an Autolab PGSTAT 302N po-
132 tentiostat/galvanostat. A standard three-electrode electrochemical cell was used. Potentials were ref-
133 erenced to a saturated calomel electrode (SCE) as internal reference. All potentials are quoted relative
134 to SCE. The working electrode was a glassy carbon disk and the auxiliary electrode was a Pt wire. In
135 all the experiments the scan rate was $100 \text{ mV}\cdot\text{s}^{-1}$. UV-visible absorption spectra were recorded on an
136 Analytik Jena Specord 210 Plus double beam spectrophotometer, using 1 cm path length cells. Emis-
137 sion spectra were recorded on a Fluoromax-4 Horiba Scientific spectrofluorimeter (1 cm quartz cells).
138 Luminescence decays were recorded with a DeltaFlex Time Correlated Single Photon Counting
139 (TCSPC) system (Horiba Scientific) equipped with a DeltaDiode laser DD-440L ($440 \pm 9 \text{ nm}$, 60 ps
140 pulse width at 20 MHz) and PPD-850 detector (250-850 nm) on degassed dichloromethane and THF
141 solutions.

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

150 For photoreduction of 4-bromobenzophenone (**Bz-Br**): an oven-dried vial was charged with **BIH**
151 (0.2 mmol) and 4-bromobenzophenone (0.10 mmol). The vial was sealed with a rubber septum and
152 purged with Argon. Then tetrahydrofuran (THF, 3 mL) and freshly distilled triethylamine (TEA) (400
153 μL , 2.9 mmol) were added and the mixture was degassed for 10 min. **Cu2** (5 mg, 0.005 mmol) was
154 next added and the mixture was degassed again for 5 min. Then the reaction mixture was stirred under
155 one blue LED (purchased from Farnell, 450 nm, 25 lumens, 75 mW) irradiation for 3 h. The distance
156 from light source irradiation to the vial was 0.3 cm without the use of any filters. The conversion was
157 then estimated using gas chromatography. Those measurements were performed on a Hewlett Pack-
158 ard HP 5 (l = 30 m, i.d. = 0.32 mm, film thickness = 0.25 mm), equipped with a FID detector (N_2 as

159 carrier gas (1.6 mL.min⁻¹); temperature program: 80 °C for 1 min then 15 °C.min⁻¹ to 320 °C). **Bz-Br**
160 was purchased from Sigma-Aldrich.

161 **Synthesis:** ligands **L^A**,¹¹ **L^B**,¹⁸ and complex **Cu2**¹¹ were prepared as previously reported.

162 **Complex Cu1:** **L^B** (23.4 mg, 56 μmol) is dissolved in dichloromethane (10 mL). The mixture is
163 thoroughly degassed by argon bubbling and Cu(CH₃CN)₄PF₆ is added quickly (21 mg, 56 μmol). The
164 colourless solution turns yellow. After 5 min, a degassed solution of **L^A** (20 mg, 51 μmol, 10 mL
165 dichloromethane) is syringed in the mixture over 5 min. The deep orange mixture is left at room
166 temperature for 30 min. The clear solution is then evaporated under reduced pressure. The orange
167 residue is purified by thin layer chromatography on silica (with a gradient of petroleum ether/di-
168 chloromethane (100% petroleum ether to 100% dichloromethane). The orange fraction is collected
169 and re-precipitated in toluene, affording a pure sample of **Cu1**.

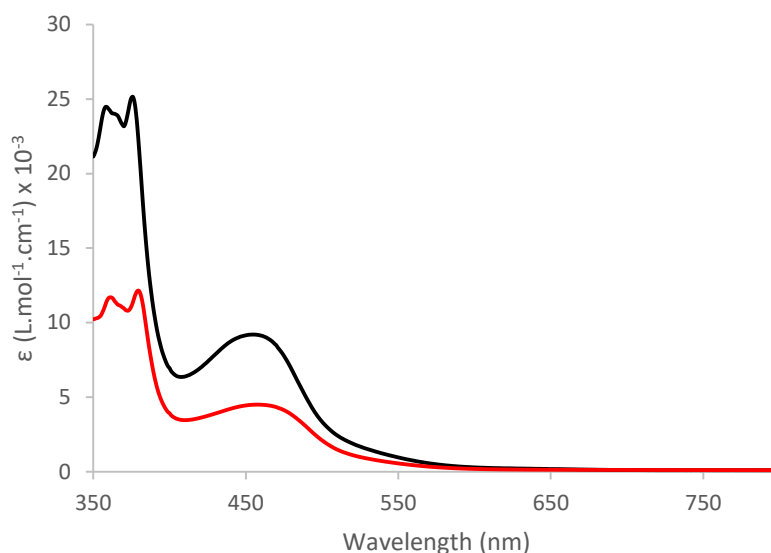
170 Yield: 35 mg (68%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 9.64-9.61 (2H, d, *J* = 8.4 Hz), 8.78-
171 8.75 (2H, d, *J* = 8.1 Hz), 8.46-8.43 (2H, dd, *J* = 6.6 Hz, *J*' = 3.3 Hz), 8.29 (2H, s), 8.05-8.01 (2H, dd,
172 *J* = 6.6 Hz, *J*' = 3.3 Hz), 7.81-7.78 (2H, d, *J* = 8.4 Hz), 7.71-7.68 (2H, d, *J* = 8.4 Hz), 6.18 (4H, s),
173 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,
174 m), 0.72-0.67 (6H, m) ppm. NMR spectrum provided in Figure S2. ¹³C NMR (75 MHz, CDCl₃,
175 25 °C): δ = 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,
176 134.2, 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.
177 HRMS (MALDI) *m/z*: [M+H]⁺ calculated for C₅₆H₅₄CuN₆: 873.3706; found: 873.3696. Δ = 1.1 ppm.

178

179 3. Results

180 3.1. Optical Properties

181 **Cu1** and **Cu2** exhibit the usual properties of all copper(I) complexes and are summarized in
182 Table 1. The visible part of the absorption spectrum is dominated by a broad metal to ligand charge
183 transfer transition (MLCT) with a maximum absorption wavelength λ_{abs} of 455 nm in THF for both
184 **Cu1** and **Cu2** (Figure 2). The extinction coefficient for the MLCT of **Cu1** (4500 L.mol⁻¹.cm⁻¹) is
185 roughly half the one of **Cu2** (9200 L.mol⁻¹.cm⁻¹). This is due the different dipole moments of **Cu1**
186 and **Cu2**. Indeed, **L^A** is a diimine ligand with an extended π-conjugated system increasing the dipole
187 moment of the complex and thus raising the probability of the MLCT dipolar transition. Since there
188 are two ligands **L^A** in **Cu2** *versus* only one in **Cu1**, the dipole moment of **Cu2** is larger than the one
189 of **Cu1**, thus rationalizing the different extinction coefficients of the two complexes. Conversely, the
190 mesityl groups on **L^B** contribute to decrease the dipole moment,¹⁹ and likely contribute to the overall
191 weak extinction coefficient of the MLCT of **Cu1**. The set of sharp transitions at 360 and 380 nm on
192 both spectra corresponds to a complex mixture of phenazine centered transitions and high energy
193 MLCT transitions, as previously demonstrated by quantum calculations on **Cu2**.¹¹



194
 195 **Figure 2.** UV-Vis absorption spectra of **Cu1** (red line) and **Cu2** (black line) in THF.

196
 197 Upon excitation in the MLCT, a weak and broad emission band can be observed in the near
 198 infrared at ca. 730 and 720 nm for **Cu1** and **Cu2** respectively (Figure S3). The energies of the lowest
 199 lying excited singlet state for **Cu1** and **Cu2** were determined from the emission spectra using the
 200 tangent method^{10,20} and are comparable for both complexes. The emission quantum yields are weak
 201 (< 0.1%) and the emission lifetimes are rather short (Table 1). This observation was made before on
 202 other copper(I) complexes studied in THF.¹⁰ Such behavior is due to different very efficient deacti-
 203 vation channels competing with the radiative decay. First of all, the use of THF favors exciplex
 204 quenching.²¹ This process consists in the nucleophilic attack of the excited state of the complex by
 205 Lewis bases. Here, THF acts as a Lewis base through the non-bonding doublets on the oxygen atom
 206 and deteriorates the emission properties of **Cu1** and **Cu2**. The deleterious impact of THF on the
 207 emission properties is demonstrated by comparing the steady state emission spectra and emission
 208 decays recorded in dichloromethane and THF (Table 1 and Figures S4 to S7): indeed, the lumines-
 209 cence intensities and emission lifetimes are both smaller in THF compared to dichloromethane for
 210 **Cu1** and **Cu2** (for absorption matched solutions in both solvents). Interestingly, **Cu2** seems to be
 211 much more affected than **Cu1** by the solvent. The emission lifetime of **Cu2** is indeed weaker than in
 212 dichloromethane, while the emission of **Cu1** is a lot less affected. This could be due to the mesityl
 213 groups in **L^B**, better shielding **Cu1** vs. nucleophilic attacks from THF. Finally, internal conversion
 214 from populated excited states to lower lying dark states is possible too as previously observed on
 215 **Cu2**.^{11,22}

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 217
 218

220 **Table 1.** Optical and electrochemical parameters for **Cu1** and **Cu2**.

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

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

226

227

3.2. Electrochemical Properties

228 The electrochemical behavior of **Cu1** and **Cu2** was analyzed by cyclic and square wave voltam-
 229 metries (Figures S8-S11). The voltammograms are strongly distorted when recorded in THF vs. di-
 230 chloromethane (see for example the cyclovoltammogram of the same sample of **Cu2** recorded in THF
 231 and in dichloromethane, Figures S9 and S12). For example, the oxidation wave assigned to the
 232 $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple appears curiously irreversible, although it is well known that the oxidation of
 233 bis(imine) copper(I) complexes is pseudo reversible in dichloromethane and acetonitrile.²³ Increasing
 234 the sweep rate did not affect the shape of the signal. We thus characterized the electrochemical be-
 235 havior of **Cu1** and **Cu2** in dichloromethane.

236 In the anodic part of the voltammogram, the reversible wave associated to the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple
 237 can be monitored at 1.02 and 1.12 V vs. SCE for **Cu1** and **Cu2** respectively. These values are in
 238 accordance with previously published work on copper(I) complexes where the metal ion is coordi-
 239 nated by two (identical or not) phenanthroline ligands.^{8b,10,18,23-24} The slightly higher oxidation poten-
 240 tial of **Cu2** vs. **Cu1** is likely due to the stronger π -accepting character of L^{A} vs. L^{B} . In the cathodic
 241 part, well-defined ligand-centered reduction waves are monitored for **Cu1** and **Cu2** at -1.28 and -1.21
 242 V vs. SCE. Those reduction waves can be safely assigned to a L^{A} centered reduction step for both
 243 **Cu1** and **Cu2**, leading to a species which can be formally written $[\text{Cu}(\text{L}^{\text{A}\bullet-})(\text{L}^{\text{B}})]^0$. The reduction of
 244 copper(I) complexes bearing classical bulky phenanthroline ligands like neocuproine or 2,9-diisopro-
 245 pyl-1,10-phenanthroline, are usually reduced at much more negative potential, ruling out the possi-
 246 bility that the reduction wave of **Cu1** could correspond to $\text{L}^{\text{B}\bullet-}$ formation.

247 For **Cu1**, the reduction and oxidation waves have similar sizes as expected for two one-electron
 248 electrochemical processes. But for **Cu2**, the reduction wave is anomalously large ($\Delta E = 230 \text{ mV}$) and

249 is approximately twice larger than the oxidation wave (whereas both oxidation and reduction pro-
250 cesses feature on average the same current intensities for **Cu1**). This is due to the fact that **Cu2** bears
251 two ligands **L^A** coordinated to one copper(I) center, and that both ligands are reduced at similar po-
252 tentials. As a matter of fact, square wave voltammograms in dichloromethane (Figure S11) in the
253 cathodic region show that two peaks have merged in a broad deformed one. The first reduction pro-
254 cess (E_{red}^1 , Table 1) appears as a shoulder at -1.17 V vs. SCE and the second (E_{red}^2) at -1.21 V vs.
255 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,
256 the area under the cathodic peak is twice as large as the area under the anodic peak. The fact that both
257 ligands **L^A** in the same copper complex can be reduced at similar potentials shows that there is a
258 limited electronic communication between them. Importantly, this means that the driving forces
259 which must be wielded to reach mono-reduced **Cu1⁻** and bis-reduced **Cu2²⁻** are very similar, paving
260 the way towards charge photo-accumulation upon excitation.

261

262 3.3. Photolysis Experiments

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

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

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

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

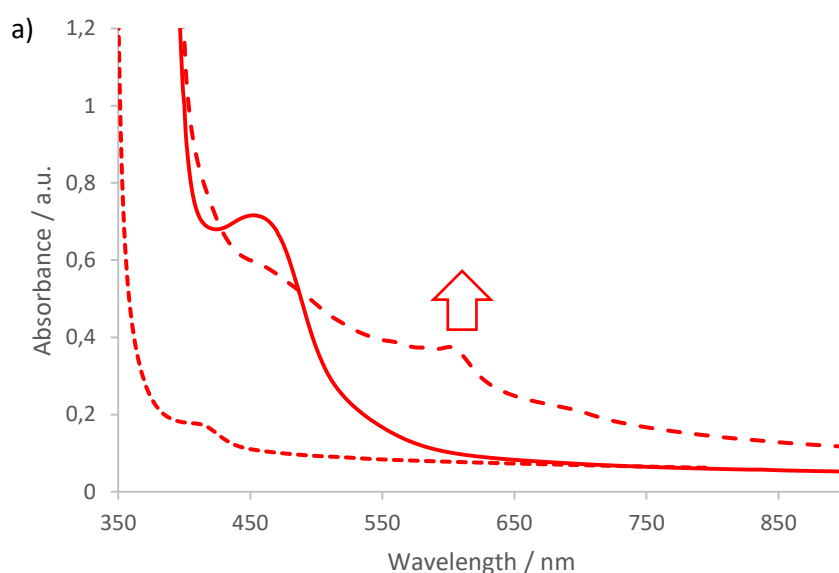
283 We attempted to reproduce the same photolysis experiment in absence of TEA with **BIH** only.
284 Likewise, photolyzed solutions darken very quickly after the beginning of the irradiation. The color-
285 ation persisted for a sufficiently long time to allow recording absorption spectra of the photolyzed
286 mixtures (Figure 3). After only one minute of irradiation at 450 nm, a broad absorption band with a
287 maximum around 605 nm rises for both **Cu1** and **Cu2**. This band is typical of reduced phenazine
288 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
289 $[\text{Cu}(\text{L}^{\text{A}\bullet})(\text{L}^{\text{A}})]^0$ (**Cu2**⁻). The formation of the reduced forms of **Cu1** and **Cu2** upon irradiation in
290 presence of **BIH** conclusively points to a reductive quenching of the excited states of both complexes
291 by the benzimidazoline sacrificial donor. When irradiation is stopped, the solution returns to its initial
292 orange color, although a significant loss of MLCT was observed pointing to some instability of the
293 complexes during irradiation. This instability could be due to the well-known lability of the coordi-
294 nation sphere of the complexes.²⁷

295 As mentioned above, **Cu2** can be twice reduced at close potentials. Interestingly, it has been
296 proven several times that the phenazine spacer was electronically decoupled from the dipyrrolyl che-
297 late.²⁸ Thus, $[\text{Cu}(\text{L}^{\text{A}\bullet})(\text{L}^{\text{A}})]^0$ could be formally considered as a $[\text{Cu}(\text{L})(\text{L}^{\text{A}})]^+$ moiety (where **L** is a
298 sterically challenged phen ligand like e.g. 2,9-di-*n*butyl-1,10-phenanthroline) linked to an isolated
299 reduced phenazine spacer. As such, the reduced complex **Cu2**⁻ could in principle be excited a second
300 time, and be involved in a second reductive quenching with **BIH** leading to doubly reduced **Cu2**²⁻. If
301 we assume that E^{00} remains similar for **Cu2** and **Cu2**⁻, we can apply equation 1:

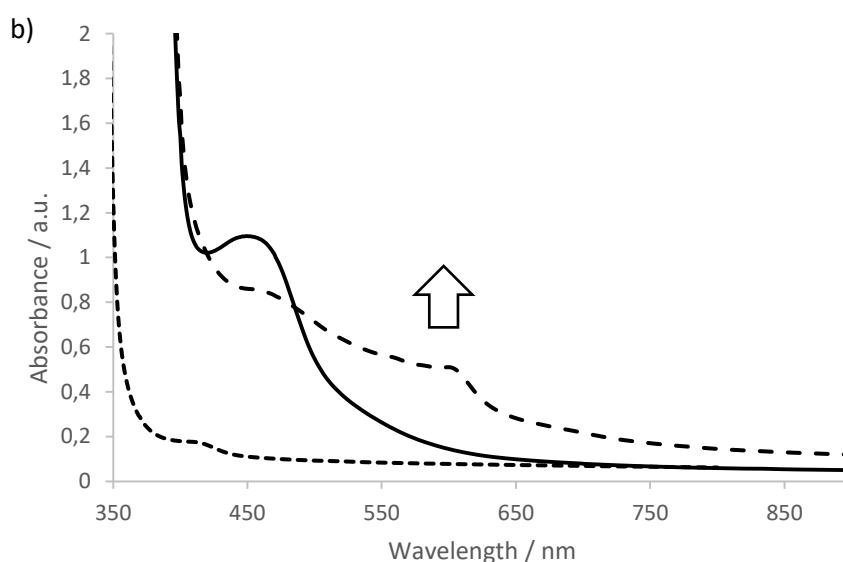
$$302 \quad E^*(\text{Cu2}^-) = E_{\text{red}}^2 + E^{00} = \text{ca. } 0.8 \text{ V vs. SCE.}$$

303 Reductive quenching of $(\text{Cu2}^-)^*$ by **BIH** would thus be thermodynamically allowed. However,
304 photolyzed mixtures of **Cu1** (where such photo-accumulation is not thermodynamically possible) and
305 **Cu2** show virtually identical spectral features and prolonged irradiation did not result in any further
306 spectral change for **Cu1** nor **Cu2**. Thus, in our conditions, it is very unlikely that a double photo-
307 induced reduction of **Cu2** take place. The excited state of **Cu2**⁻ is probably very quickly quenched by
308 energy transfer towards low lying $(\text{L}^{\text{A}\bullet})^-$ -centered states.

309



310



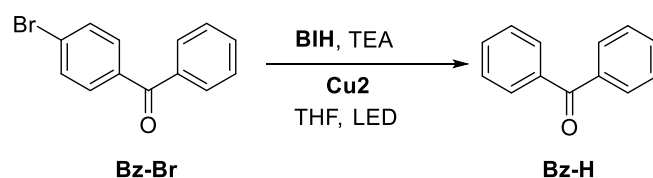
311

312 **Figure 3.** (a) UV-Vis spectra of a photolyzed mixture of **Cu1** and **BIH** in THF; (b) UV-Vis spectra
 313 of a photolyzed mixture of **Cu2** and **BIH** in THF. Plain lines: UV-Vis spectra before photolysis.
 314 Dashed lines: UV-Vis spectra after photolysis. Dotted lines: UV-Vis spectra of **BIH** alone in THF at
 315 the same concentration (25 mM).

316

317 3.4. Photo-Induced Reduction Trials

318 We then attempted to utilize the implemented reductive quenching of the designed copper(I)
 319 complexes in presence of **BIH**, to perform the reductive dehalogenation of 4-bromobenzophenone
 320 (**Bz-Br**). This was recently successfully used as a benchmark reaction to test the efficacy of reductive
 321 quenching with copper^{5b,8d} and iridium complexes (scheme 1).^{17f} In particular, we demonstrated the
 322 efficient reduction of **Bz-Br** into **Bz-H** (benzophenone) when a mixture of [Cu(dipp)₂]⁺, **Bz-Br** and
 323 a chemically engineered benzimidazoline derivative **BI₂H** (Figure S14) is irradiated in the visible.



324

325 **Scheme 1.** Reductive photo-dehalogenation of **Bz-Br** via reductive quenching of **Cu2**'s excited state
 326 in presence of **BIH**.

327

328 A degassed mixture of **Bz-Br** with 2 equivalent of **BIH**, an excess of TEA and 5 mol% **Cu2**
 329 in THF was irradiated for 3 hours under 450 nm LED light. **Cu2** was chosen over **Cu1** for this ex-
 330 periment because it is the best photo-oxidant. Immediately after the beginning of the irradiation, the
 331 solution darkened and the color was maintained during the whole photolysis duration, demonstrating
 332 that reductive quenching of the excited state of **Cu2** was taking place. However, there was virtually
 333 no conversion of **Bz-Br** into **Bz-H** after 3 hours of light soaking. We reproduced the same experiment
 334 with **BI₂H** instead of **BIH**, leading to a marginally improved conversion of 8%, proving that the
 335 reduction of **Bz-Br** is only slightly influenced by the nature of the sacrificial donor.

336

337 With these experimental results in hand, we propose the following rationale. Upon photo-excita-
 338 tion, **Cu2*** is reduced by **BIH** (or **BI₂H**) leading to the formation of **Cu2⁻** and **BIH^{•+}** (**BI₂H^{•+}**). **Cu2⁻**
 339 is thermodynamically unlikely to reduced **Bz-Br** ($E(\text{Bz-Br}/\text{Bz-Br}^-) = -1.62\text{V vs. SCE}$)^{8d} because
 340 $E(\text{Cu2}/\text{Cu2}^-)$ is not sufficiently negative. Indeed, $E^*(\text{Cu2})$ was significantly improved by coordinat-
 341 ing electron poor ligands to copper(I) but $E(\text{Cu2}/\text{Cu2}^-)$ was sacrificed. On the other hand, **BIH^{•+}**
 342 (**BI₂H^{•+}**) is quickly deprotonated in presence of TEA leading to **BI[•]** (**BI₂[•]**) which is a strong reductant
 343 (ca. -1.6 V vs. SCE).¹⁵ Summarily, the reductive quenching of the excited state of **Cu2** by **BIH** (**BI₂H**)
 344 leads to two reductants with only one photon. In the present case, **BI[•]** is apparently not sufficiently
 345 reductive to react with **Bz-Br** (since there is no conversion for the photochemical reaction). **BI₂[•]** is
 346 slightly more reductive than **BI[•]** thanks to the additional methoxy groups tethered to the structure
 347 (Figure S14), which could account for the slight improvement of the conversion when **BI₂H** is used
 348 as sacrificial donor.

349 Moreover, those results have an important fallout on our previous work. As mentioned above,
 350 we recently demonstrated that irradiating a mixture of **Bz-Br**, $[\text{Cu}(\text{dipp})_2]^+$ and **BI₂H** lead to the ef-
 351 ficient photo-reduction of **Bz-Br** into **Bz-H** (93% yield in 30 mn irradiation). However, we were
 352 unable to determine whether **Bz-Br** was reduced by photoproducted $[\text{Cu}(\text{dipp})(\text{dipp}^\bullet)]^0$ or **BI₂[•]**. In the
 353 present work, we demonstrate that **BI₂[•]** (and incidentally **BI[•]** too) is unable to efficiently reduce **Bz-
 354 Br**. Stronger reductants are necessary to reduce such challenging substrates, such as homoleptic cop-
 355 per(I) complexes with more negative reduction potentials than $E(\text{Cu2}/\text{Cu2}^-)$.

356 Given the results obtained with **Cu2**, we did not perform further trials with **Cu1** which shows
357 very similar properties.

358

359 **5. Conclusions**

360 We reported the synthesis and characterization of two copper(I) complexes **Cu1** and **Cu2** show-
361 ing enhanced photo-oxidative power. This task was realized by using electron poor, phenazine-fused
362 ligands, which allowed to significantly shift the reduction potential of both complexes to less negative
363 values and subsequently increased the reduction potential of the excited state of each complex
364 $E(\text{Cu1}^*/\text{Cu1}^-)$ and $E(\text{Cu2}^*/\text{Cu2}^-)$. **Cu1** and **Cu2** were therefore able to oxidize a common benzim-
365 idazoline sacrificial reductant **BIH** under blue light irradiation. In other words, **Cu1** and **Cu2** were
366 involved in a reductive quenching cycle, a very rare photochemical process with copper(I)-
367 bis(diimine) complexes. The challenging photo-induced reduction of an aryl bromide via reductive
368 quenching was then attempted but proved unsuccessful because reduced complexes are insufficiently
369 reductive to react with such substrates.

370

371 **Supplementary Materials:** Figure S1: Series of electron transfers following one electron oxidation
372 of benzimidazolines. Figure S2: NMR spectra of **Cu1**. Figure S3: emission spectra of complex **Cu1**
373 (red line) and **Cu2** (black line) in THF, Figures S3-S5: Steady state emission spectra in THF. Figures
374 S6-S7: luminescence decays. Figures S7: Luminescence decays of solutions of **Cu2** recorded by TC-
375 SPC in degassed dichloromethane (grey line) and THF (black line). Figures S8-S12: Cyclovoltam-
376 mograms and square wave voltammograms of **Cu1** and **Cu2**. Figure S13: spectroelectrochemistry.
377 Figure S14: structure of **BI₂H**.

378

379 **Funding:** this research was funded by ANR, grant number ANR-16-CE07-0012-01.

380

381 **Conflicts of Interest:** the authors declare no conflict of interest.

382

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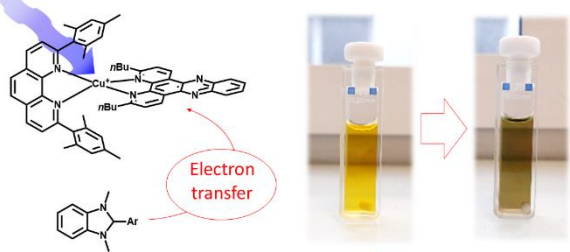
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... to observe **reductive quenching of its excited state**
