Catalysis Science & Technology

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal

Check for updates

Cite this: DOI: 10.1039/d1cy01209f

Received 6th July 2021,
Accepted 13th July 2021

DOI: 10.1039/d1cy01209f

rsc.li/catalysis

Dehalogenation reaction photocatalyzed by homoleptic copper(I) complexes associated with strongly reductive sacrificial donors†

Lea Gimeno, Clémence Queffélec, * Kevin Mall Haidaraly,
Errol Blart and Yann Pellegrin *

In order to perform challenging reduction reactions with light, at low cost and low toxicity, we aim at using for the first time a reductive quenching cycle with a simple, strongly colored homoleptic copper(I) complex $[Cu(dipp)_2]^+$ (dipp = 2,9-diisopropyl-1,10-phenanthroline). Complexes of this family being weak photo-oxidants, we specifically designed and synthesized powerful, recyclable sacrificial electron donors D. We demonstrate that, during irradiation with LED light in the presence of D, the strong reductant $[Cu(dipp)_2]^0$ is efficiently photo-generated. Further, we present the first photochemical reaction using photo-generated $[Cu(dipp)_2]^0$ and evidence that the kinetics of the overall reaction are strongly affected by the oxidation potential of the sacrificial donor $E(D^+/D)$. Adapting the thermodynamics of sacrificial donors D and $[Cu(dipp)_2]^+$ has thus allowed us to unlock a brand new concept, giving access to cheap, non-toxic solar light-generated very strong reductive power.

Introduction

Organic photochemistry is a very active research field where light is used to drive challenging reactions (involving, in particular, reactive radicals) under mild, green and sustainable conditions, with a high tolerance towards functional groups.[1,2] Most of the time, the addition of a photosensitizer PS in the reaction mixture is necessary. While heavy metal (*e.g.* ruthenium or iridium) based complexes are frequently used as a PS, copper(I) complexes are playing a more and more important role in modern photochemistry as cheaper, less noxious and efficient photosensitizers.[3–5] In the context of organic photochemistry, there are mainly two sorts of Cu(I) complexes: homoleptic complexes of the general formula $[Cu^I(NN)_2]^+$ (PS_{Cu}) and heteroleptic ones of the general formula $[Cu^I(PP)(NN)]^+$ ($PS_{Cu'}$) where NN is a sterically burdened chelating diimine ligand and PP is a bulky bisphosphine ligand.[6] Both sorts of complexes are abundantly used in the frame of oxidative quenching-based processes[7] because they exhibit very strong photoreductive power (*e.g.* −1.43 V *vs.* SCE for $[Cu(dap)_2]^+$ (ref. 8 and 9) and −1.44 for $Cu(Xantphos)(dmp)^+$)[10] and can react with a variety of electron acceptors, once they are in their excited state.

Conversely, Cu(I) complexes are less used in the frame of reductive quenching-based processes.[7] Several examples of photochemical cycles involving the reductive quenching of the excited state of heteroleptic Cu(I) complexes can be found in the literature.[11–15] In those examples, RQ was advantageously used to generate the reduced state $[Cu^I(PP)(NN^{•-})]^0$ in the presence of an electron donor (*e.g.* triethylamine). This reduced species is a very strong reductant (from *ca.* −1.6 V to −1.8 V *vs.* SCE)[13,16,17] and is better than or comparable to many ruthenium and iridium PS under the same conditions (*e.g.* −1.3 V *vs.* SCE for $[Ru(bpy)_3]_2^+$ (ref. 18) and −1.4 V *vs.* SCE for $[Ir(dFCF_3ppy)_2(bpy)]^+$).[19]

RQ with homoleptic Cu(I) complexes (PS_{Cu}) would also present many advantages for the following reasons: they feature very negative reduction potentials like the heteroleptic parent complexes, making them equally potent reductants after RQ (*e.g.* −1.6 V *vs.* SCE for $[Cu(dipp)_2]^+$ where dipp stands for 2,9-diisopropyl-1,10-phenanthroline). Second, they exhibit a broad absorption band in the visible region, where usual efficient $PS_{Cu'}$ are less efficient light collectors (Fig. S1†) although significant progress has been made to red-shift their absorption spectrum.[20–23] Third, $[Cu(NN)_2]^+$ complexes are easy to prepare and more stable in the long term than the $[Cu(PP)(NN)]^+$ ones.[24,25] Finally, the excited state of PS_{Cu} is sufficiently long-lived[26] to ensure reactivity with a donor D.

However, reports of RQ processes involving PS_{Cu} are extremely rare compared to $PS_{Cu'}$ because the excited state of homoleptic copper(I) complexes is a weak photo-oxidant,

---

CEISAM, UMR 6230, Université de Nantes, CNRS, 2 chemin de la Houssinière, Nantes F-44000, France. E-mail: clemence.queffelec@univ-nantes.fr, yann.pellegrin@univ-nantes.fr

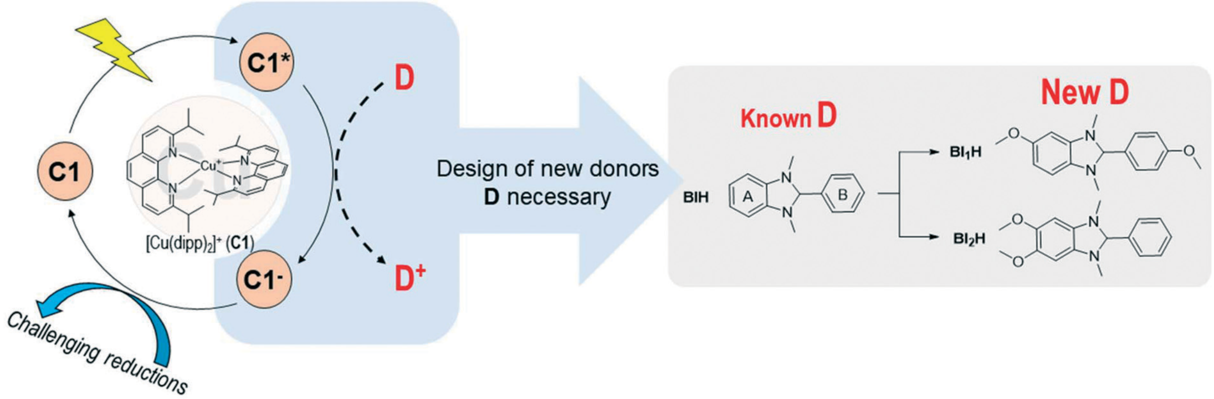
† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1cy01209f

making them unable to react with usual electron donors.[27–29] Efforts have been made to increase the photo-oxidizing strength of PS_{Cu} (quantitatively described by $E(PS^*_{Cu}/PS_{Cu^-})$) by shifting the reduction potential $E(PS_{Cu}/PS_{Cu^-})$ to less negative values. This strategy proved to be efficient to implement RQ but the reductive power of PS_{Cu^-} was sacrificed. Another more recent strategy is based on increasing the energy of the excited state. Improvements of $E(PS^*_{Cu}/PS_{Cu^-})$ are reported without altering $E(PS_{Cu}/PS_{Cu^-})$. A different, complementary approach is to shift the oxidation potential of the electron donor D to less positive values. This method was successfully used by McMillin *et al.*[30,31] Several ferrocene derivatives featuring very low oxidation potentials were used as a D in the presence of $[Cu(dipp)_2]^+$ or $[Cu(dpp)_2]^+$ (where dpp stands for 2,9-diphenyl-1,10-phenanthroline) as a PS_{Cu}. A minimum experimental driving force of 300 meV for RQ to occur between PS^*_{Cu} and D was determined on this occasion. However, the ferrocenium/ferrocene couples are reversible and a fast charge recombination takes place between D^+ and PS_{Cu^-}, preventing the accumulation of the latter and to manage a reduction reaction with a substrate. Trials involving $[Cu(dpp)_2]^+$ with irreversible electron donors (dithionite and dihydroxyquinone) were unsuccessful owing to their oxidation potential being too positive with respect to $E(PS^*_{Cu}/PS_{Cu^-})$.[32] It thus appears relevant to develop electron donors D such that D is irreversibly oxidized and $E(D^+/D)$ is shifted at a very low anodic potential. RQ can be basically described as a photo-induced electron transfer process from D to PS^*_{Cu}. The thermodynamics of the reaction thus depend on both species. In order to refine our objectives, we focus on implementing RQ with a simple homoleptic complex $[Cu(dipp)_2]^+$ (hereafter named C1). The latter was chosen because it features a very negative reduction potential (*ca.* −1.6 V *vs.* SCE)[17,33] and one of the most intense absorption band in the visible region, for a homoleptic copper(I) complex (ε_{455nm} = *ca.* 6700 M^{-1} cm^{-1}, Fig. S1†). Additionally, C1 is stable, with a long excited state lifetime (200 ns in degassed THF).[17] Knowing that for C1, the photo-oxidation potential $E(C1^*/C1^-)$ is equal to 0.46 V *vs.* SCE in THF, and the relevant target D should exhibit an irreversible oxidation step at $E(D^+/D)$ = 0.16 V *vs.* SCE at least.

Benzimidazoline donors, epitomized by famous BIH (Scheme 1), fulfill almost all required parameters. However, $E(BIH^+/BIH)$ is too positive to allow RQ with common homoleptic complexes.[34] The potential of benzimidazoline donors can, however, be efficiently tuned by chemical engineering. Jin-Pei Chen *et al.*[35] successfully demonstrated that $E(BIH^+/BIH)$ could be substantially lowered when electron donating groups are tethered either to cycles A or B (Scheme 1). Aiming at implementing RQ involving C1 and a benzimidazoline donor, we thus prepared new BI_1H and BI_2H donors with multiple electron-rich methoxy groups grafted on cycles A and B of the BIH molecular skeleton (Scheme 1).

In this contribution, we focus on the design of new donors D based on a benzimidazoline molecular frame such that RQ with benchmark C1 is thermodynamically possible. We implement for the first time reductive quenching of the excited state of a strongly colored homoleptic copper(I) complex, by using specifically designed benzimidazoline donors and mild light sources. A very powerful and cheap reductant $[Cu(dipp)(dipp^{\bullet-})]^0$ is photo-generated and accumulated in the photolyzed medium, and this unprecedented process is used to achieve a challenging reduction reaction in the field of organic photochemistry.

Efficient sacrificial donors D should be colorless (in order not to interfere with light collection by C1) and exhibit an oxidation at a sufficiently low potential $E(D^+/D)$ to allow photo-induced electron transfer from D to C1*, and the oxidation must be irreversible to avoid counter-productive charge recombination between D^+ and $C1^-$. Indeed, McMillin *et al.* successfully evidenced RQ between C1* and ferrocene donors[30,31] but the reversibility of the ferrocenium/ferrocene couples prevented $C1^-$ from accumulating and using its strong reductive power in further reactions. However, this work permitted to determine that a minimum driving force of 300 meV is necessary to drive RQ. Knowing that for C1, the



Scheme 1 Illustration of the strategy developed in this contribution: to implement for the first time reductive quenching of the excited state of homoleptic copper(I) complexes by using benzimidazoline donors.

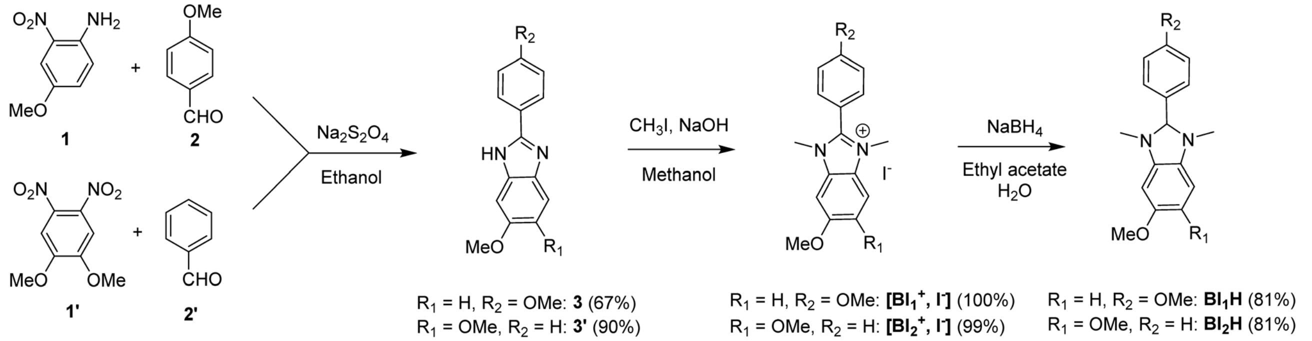
photo-oxidation potential $E(C1^*/C1^-)$ is equal to 0.46 V *vs.* SCE in THF, and the relevant target D should exhibit $E(D^+/D)$ = 0.16 V *vs.* SCE at least. Benzimidazoline donors, epitomized by famous BIH (Scheme 1), fulfill all required parameters but their oxidation potential must be adapted to the low photo-oxidation power of C1. Jin-Pei Chen *et al.*[35] successfully demonstrated that $E(BIH^+/BIH)$ could be substantially lowered when electron donating groups are tethered either to cycles A or B (Scheme 1). Aiming at implementing RQ involving C1 and a benzimidazoline donor, we thus prepared new BI_1H and BI_2H donors with multiple electron rich-methoxy groups grafted on cycles A and B of the BIH molecular skeleton (Scheme 1). BI_1H was synthesized using the procedure developed by Jin-Pei Cheng *et al.*,[35] using dithionite as a reductant agent and *para*-anisaldehyde. The same strategy was envisioned in the case of BI_2H. However, in order to save unnecessary synthesis steps, we started with 4,5-dimethoxy-1,2-dinitrobenzene (**1′**) (easily obtained on a gram scale[36] instead of 4,5-dimethoxynitroaniline), under the same above experimental conditions, with dithionite and benzaldehyde (**2′**). Rewardingly, after 7 days of reaction, the desired benzimidazole derivative (**3′**) was isolated with 90% yield. Both precursors **3** and **3′** could be obtained on a gram scale starting with 5 g of **1** or **1′**. Then, the imidazole nitrogen atoms were methylated in the presence of methyl iodide and target compounds (BI_1H and BI_2H) were finally obtained as colorless powders, by reduction of $[BI_1^+,I^-]$ or $[BI_2^+,I^-]$ with $NaBH_4$, respectively, (Scheme 2 and detailed procedures in the ESI†).

The synthesis of BI_1H and BI_2H thus proceeded smoothly: it is reproducible, scalable, does not require to isolate unstable species nor drastic conditions for the reduction of the nitro groups, and the overall yield of the synthesis (72% over 3 steps for BI_2H and 55% for BI_1H) is satisfying.

Both BI_1H and BI_2H are stable as powders (shelf stability: several months). ^1H NMR studies of BI_1H and BI_2H in aerated deuterated THF (Fig. S2 and S3†) revealed mild degradation of BI_mH after 20 hours (*ca.* 10%) under ambient conditions. A fine precipitate was observed, collected and identified as BI_1^+ (counter-anion undetermined) and BI_2^+ (counter-anion undetermined), probably resulting from the O_2-promoted oxidation of corresponding benzimidazolines. Importantly, no degradation was monitored for at least 3 hours, namely the duration of the photolysis trials.

Cyclic voltammetry experiments were conducted for BI_1H and BI_2H in dry THF (cyclic voltammograms are shown in Fig. S4 and S5†). The forward scans feature in both cases an intense oxidation wave associated with $BI_mH \rightarrow BI_mH^+$. A less intense cathodic wave appears on the reverse scan, indicating the partial reversibility of the BI_mH^+/BI_mH couple. In the presence of one equivalent of triethylamine (TEA), the cathodic waves disappear (Fig. S4 and S5†). Indeed, oxidation of BI_mH into $BI_mH^{\bullet+}$ is then followed by deprotonation of the latter into $BI_m^\bullet$, a strongly reductive species (Fig. S6†). Assigning a reliable potential value for an irreversible process is not straightforward. Following Nicewicz and Vullev's lead,[37,38] we choose to quantify $E(BI_mH^+/BI_mH)$ under our conditions as the half-peak potential $E_{p/2}$ in the absence of TEA (Table 1), considering that the CE character of BI_mH oxidation in basic medium distorts the oxidation waves. Edge potentials E_e (where the faradaic current starts to grow, indicating the beginning of the donors' electroactivity) are also given. As expected, the values of $E_{p/2}$ for both BI_1H and, in particular, BI_2H are significantly less positive than the case of benchmark BIH due to the electron donating effect of the methoxy groups (Table 1; Fig. S4 and S5†). BI_2H notably features a remarkably low $E_{p/2}$ value of 0.13 V *vs.* SCE, which is strongly shifted towards less positive potentials by *ca.* 300 mV compared to that of previously published benzimidazoline donors.[35]

We next monitored the evolution of the UV–Vis spectrum of C1 in THF, in the presence of benzimidazoline donors and triethylamine, under irradiation with a blue LED. For both BI_1H and BI_2H, the solution darkened and a fine powder precipitated. Light scattering prevents suitable UV-vis spectra from being recorded and the same experiment is thus performed in acetonitrile where photolyzed solutions remained transparent. Under those conditions, a broad band at 575 nm quickly appears (Fig. S8 and S9†) which is in good agreement with the spectrum of $C1^-$ obtained by reductive spectro-electrochemistry (Fig. S10†). We thus assigned the monitored spectral changes to the photo-induced formation of $C1^-$, proving that C1* is reductively quenched by BI_1H and BI_2H despite the rather weak estimated driving force for BI_1H



Scheme 2 Synthesis of BI_1H and BI_2H sacrificial donors.

Table 1 Electrochemical data and deduced driving forces for electron transfer in the frame of RQ. Potentials are given *vs.* SCE. Cyclic voltammetry has been conducted in THF with 0.1 M tetrabutylammonium hexafluorophosphate

	$E_{p/2}(BI_mH^+/BI_mH)$	$E_e(BI_mH^+/BI_mH)$	ΔG_{RQ} (eV)[a]
BI_1H	0.38	0.2	−0.08
BI_2H	0.13	0.0	−0.33

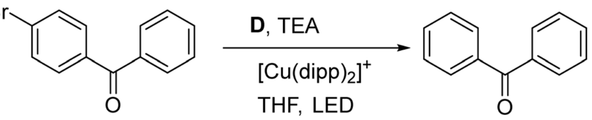
[a] Calculated using the equation $\Delta GRQ = -F\cdot[E(C1^*/C1^-) - E_{p/2}(BI_mH^+/BI_mH)]$ with $E(C1^*/C1^-) = 0.46$ V *vs.* SCE. $E(C1^*/C1^-)$ estimated with the Rehm and Weller equation $E(C1^*/C1^-) = E(C1/C1^-) + E_{00}$, where $E(C1/C1^-) = -1.65$ V *vs.* SCE (Fig. S7†) and $E_{00} = 2.11$ eV.[17]

(Table 1). Stern–Volmer analysis (Fig. S11†) allowed the estimation of the rate constants for RQ at $k_{RQ} = 4.4 \times 10^7$ and 1.4×10^8 s^{-1} M^{-1} when the quencher is BI_1H and BI_2H, respectively. RQ is faster with BI_2H than with BI_1H thanks to the improved driving force for the electron transfer (Table 1). Nevertheless, the kinetics are sluggish compared to that of the case of a heteroleptic copper(I) complex in the presence of BIH.[25] In the latter situation, however, the Gibbs free energy for the electron transfer is much larger than in our case, and it is known that RQ with copper(I) complexes is particularly demanding from the thermodynamic point of view because of the large reorganization energy which is expected in the transformation from C1* to $C1^-$.[32]

Achieving reductive quenching of C1* with an irreversible electron donor not only allows the generation of the strong reductant $C1^-$ but also permits the accumulation of the latter in the photolyzed medium, opening a new avenue towards the photo-assisted reduction of challenging substrates. This encouraged us to implement a photochemical reaction involving the BI_mH/C1 couple in a demanding reductive process. We selected the photo-assisted dehalogenation of aromatic compounds which is known to be challenging,[13,39] paving the way towards fruitful aryl radical chemistry.[15,39,40]

We chose to start with 4-bromo-benzophenone Bzp-Br as a substrate ($E_{p/2} = -1.62$ V *vs.* SCE, Fig. S12†) and investigate the photogeneration of plain benzophenone Bzp-H in degassed THF and in the presence of C1, TEA and benzimidazoline donors with visible light, under the same conditions described by Michelet *et al.* (blue LED, 450 nm).[13] The photolyzed mixture is regularly monitored by gas chromatography. Knowing that copper(I) complexes are strong photo-reductants, we first confirmed that C1 was unable to reduce Bzp-Br *via* the well-known oxidative quenching process (Table 2, entry 1). On the other hand, when a mixture of C1, TEA, BI_1H and Bzp-Br was irradiated (entry 2) the solution darkened and a fine white powder precipitated. The conversion gradually increases with time to reach a final value of 95% after 3 hours of irradiation. The precipitate and the filtrate were separated by centrifugation. ^1H NMR of the filtrate confirms that all Bzp-Br has been consumed and the signals of Bzp-H are clearly observed, while the precipitate is identified as $[BI_1^+, Br^-]$ by ^1H NMR (Fig. S13†). When the same experiment is conducted with BI_2H instead of BI_1H (entry 3), the kinetics of the reaction are spectacularly improved: GC monitoring reveals a conversion of 99% after only 30 minutes of light soaking (for comparison with BI_1H after 30 min, the conversion is 42%). Analysis results of the filtrate reveals the spectral features of Bzp-H (Fig. S14†). This improvement is likely due to the larger driving force of the reductive quenching of C1* by BI_2H. Importantly, when light is masked, the conversion stops and

Table 2 Results of the photochemical experiments. Reaction conditions: C1 = 5 mol%, [TEA] = 0.95 M in THF, 0.1 mmol Bzp-Br, and 1 or 2 eq. of D. All counter-anions for the complexes are PF_6^-

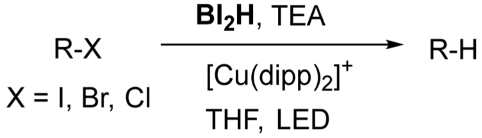


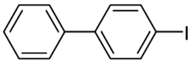
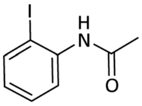
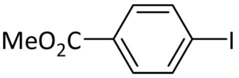
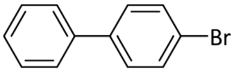
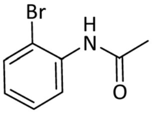
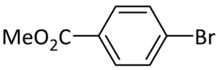
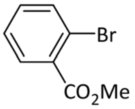
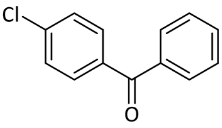
Entry	Catalyst	Donor (D)	Light	Time (*h*)	Conversion (yield)[a]
1	$[Cu(dipp)_2]^+$, C1	None	Blue LED	3	0%
2	$[Cu(dipp)_2]^+$, C1	BI_1H	Blue LED	3	95% (89%)
3	$[Cu(dipp)_2]^+$, C1	BI_2H	Blue LED	0.5	99% (93%)
4	$[Cu(dipp)_2]^+$, C1	BI_2H	None	3	0%
5	None	BI_2H	Blue LED	3	0%
6	$Cu(CH_3CN)_4PF_6$	BI_2H	Blue LED	3	0%
7	$[Cu(dipp)_2]^+$, C1	HE	Blue LED	3	16%
8	$[Cu(dipp)_2]^+$, C1	DmFc	Blue LED	3	0%
9	$[Cu(Xantphos)(dmp)_2]^+$, C2	BI_2H	Blue LED	3	85% (80%)
10	$[Cu(dipp)_2]^+$, C1	BI_2H	Green LED	3	75% (73%)
11	$[Cu(Xantphos)(dmp)_2]^+$, C2	BI_2H	Green LED	3	23% (n.d.)[b]
12	$[Cu(dipp)_2]^+$, C1	BI_2H	Simulated solar light	3	84% (80%)
13	$Ru(bpy)_3PF_6$[c]	BI_2H	Blue LED	3	73% (55%)[d]
14	$[Cu(dipp)_2]^+$, C1[c]	BI_2H	Blue LED	0.5	99% (88%)
15	$[Cu(dipp)_2]^+$, C1	BI_2H[e]	Blue LED	3	82% (66%)

[a] NMR yield with *p*-anisaldehyde as the internal standard. [b] Not determined. [c] Reaction performed in acetonitrile. [d] Yield obtained after purification by preparative TLC. [e] Reaction performed with one equivalent of D.

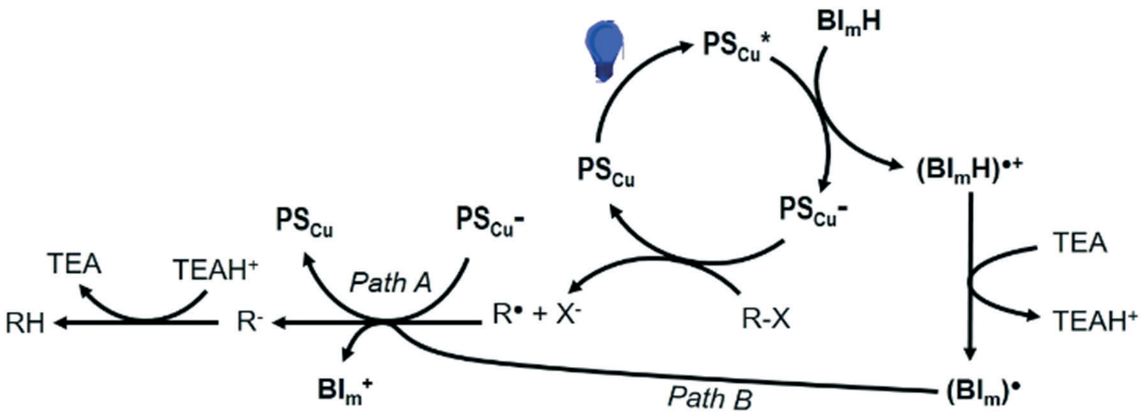
restarts when light is restored, ensuring that the reaction is not photo-initiated. Control experiments confirmed that no reaction occurred in the absence of light or C1, and that plain Cu$^+$ was (photo)catalytically inactive (entries 4, 5 and 6, respectively). In the absence of BI$_2$H, no reaction occurred proving that TEA (entry 1) cannot play the role of a sacrificial donor. A traditional donor Hantzsch ester (HE) (entry 7) showed very little efficiency compared to BI$_1$H and BI$_2$H because its oxidation potential is too positive to allow RQ with C1*. Decamethylferrocene (dmFc) is so far the only reported donor able to reduce C1* because E(dmFc$^+$/dmFc) is sufficiently low.[30,31] Yet, attempts with DmFc as a D did not work (entry 8) because dmFc$^+$/dmFc is a reversible couple, and fast recombination between C1$^-$ and dmFc$^+$ prevents accumulation of C1$^-$. Significantly, when C1 is replaced by the heteroleptic complex [Cu(xantphos)(dmp)]$^+$ (C2, Fig. S1†), the reaction is slowed down because the heteroleptic complex is less sensitive to visible light ($\varepsilon_{450\text{nm}} \approx 100$ L mol^{-1} cm^{-1}, Fig. S1†) (entry 9). This is more blatant when the dehalogenation reaction is driven with a longer wavelength light source (green LED at 550 nm). While the reaction is still successful when the photocatalyst is C1 (entry 9), it is significantly impeded when C1 is replaced by C2 (entry 11). C1 still features significant absorbance at this wavelength ($\varepsilon_{550\text{nm}} \approx 230$ L mol^{-1} cm^{-1}) compared to C2 ($\varepsilon_{550\text{nm}} \approx 10$ L mol^{-1} cm^{-1}, Fig. S1†), rationalizing the different performances of the two photosensitizers. Finally, under simulated solar light (entry 12), the reaction performed with C1 was successful. Rewardingly, C1 outperforms the classical [Ru(bpy)$_3$]$^{2+}$ complex used as a PS under the same conditions (entries 13 and 14) proving the relevance of using homoleptic copper complexes to drive challenging reduction reactions. Furthermore, we tested the reaction with only one equivalent of BI$_2$H. The reaction is still very efficient (entry 15) but slower than the case when two equivalents were used (entry 3). At the end of each run, we could simply recover [BI$_1^+$, Br$^-$] and [BI$_2^+$, Br$^-$] by filtration of the photolyzed solution. In the case where only one equivalent of BI$_2$H was used (entry 15), 70 μmol of [BI$_2^+$, Br$^-$] was collected showing that 70% of the initial loading of the donor can be restored. We could regenerate BI$_1$H and BI$_2$H from the corresponding collected benzimidazolium by treatment with NaBH$_4$ under mild

Table 3 Scope of the photochemical experiments. Reaction conditions: C1 = 5 mol%, [TEA] = 0.95 M in THF, 0.2 mmol BI$_2$H, 0.1 mmol R–X



Entry	R–X	Time	Conversion (yield)
1		3 h	73% (72%)[a]
2		30 min	99% (96%)[a]
3		1 h	99% (89%)[b]
4		3 h	5% (n.d.)[c]
5		3 h	20% (n.d.)[c]
6		3 h	50% (n.d.)[c]
7		3 h	55% (46%)[b]
8		3 h	3% (n.d.)[c]

[a] NMR yield with *p*-anisaldehyde as the internal standard. [b] GC yield with hexadecane as the internal standard. [c] Not determined.



Scheme 3 Supposed mechanism for the photo-induced dehalogenation reaction of R–X.

conditions, and re-use the compounds in new photochemical reactions.[41] No alteration of the photoconversion efficiencies was noted while using recycled BI_1H or BI_2H. The fact that the sacrificial donor can be easily regenerated by a cheap chemical is a strong advantage of this photochemical cycle and demonstrates the overall renewability of this BIH-based photochemical reaction. It is worth noting that the ketone functional group of Bzp-Br was untouched during the photolysis, proving the selectivity of the photochemical process. At the end of each run, no elemental copper was observed in the photolyzed mixtures.

Under the optimized conditions and to gain more information about the substrates that could be activated under these conditions, we then studied the scope and limitation of the light-mediated, $Cu(dipp)_2^+$-catalyzed reduction of a series of aryl halides possessing various substituents on the backbone. Reduction of various aryl iodides was first evaluated and found to proceed very rapidly in all cases (less than 1 h; Table 3, entries 2 and 3). Reduction of 4-iodobiphenyl was slower (Table 3, entry 1) likely because it is less activated than 2-iodoacetanilide or 4-iodomethylbenzoate. Corresponding deiodinated arenes were obtained in good to excellent yields regardless of the substituents on the molecular skeleton of the aryl iodide. The reduction of aryl bromides is more challenging and debromination reactions proceeded more slowly as expected, because the C–Br bond cleavage kinetics are slower upon aryl bromide reduction.[42] While the reaction yield was very satisfactory in the case of Bzp-Br (Table 2), the conversions and yields dropped for 4-bromomethylbenzoate (Table 3, entries 6 and 7). Conversions are particularly poor for 4-bromo biphenyl and 2-bromo acetanilide (entries 4 and 5) because the substrates were not sufficiently activated.[13] Finally, almost no conversion was monitored for 4-chlorobenzophenone (Table 3, entry 8), even when the irradiation time was prolonged to 12 h. This is likely due to the very challenging C–Cl cleavage kinetic rate upon reduction.[42] Importantly, no conversion was monitored for all substrates in the absence of C1, except in the case of 4-iodomethylbenzoate. A conversion of 45% was observed after 3 h of irradiation, which is significantly less efficient and more sluggish than in the presence of C1.

Based on the gathered experimental facts and on previous studies on a similar reaction,[13] we propose the following mechanism (Scheme 3): photogenerated C1* is efficiently reduced into $C1^-$ either by BI_1H or BI_2H. Bzp-Br is then reduced by $C1^-$ into $Bzp^•$ and Br^- thus regenerating C1. Meanwhile, BI_m-$H^{•+}$ is deprotonated by TEA yielding $BI_m^•$, which is also a strong reductant ($E_{p/2}$ ($BI_2^+/BI_2^•$) = −1.7 V *vs.* SCE, Fig. S15†). $Bzp^•$ is then eventually reduced into a carbanion Bzp^- either by $C1^-$ (path A) or $BI_m^•$ (path B), affording Bzp-H after protonation. We note that $BI_m^•$ could compete with $C1^-$ to also reduce Bzp-Br. However, the fact that the reaction is considerably less efficient when $[Ru(bpy)_3]^{2+}$ is used as a photosensitizer instead of C1 points to the fact that $C1^-$ is very active in the reduction of the substrates, being a better reductant than $[Ru(bpy)_3]^+$ by more than 300 mV. Further work is ongoing to decipher the full mechanism associated with this completely new photochemical cycle.

In summary, we synthesized in a few efficient steps new benzimidazoline donors BI_1H and BI_2H exhibiting very strong reductive power. We used them as sacrificial donors in a photochemical cycle and for the first time we were able to monitor the productive reductive quenching of the excited state of a simple and cheap colored homoleptic copper(I) complex C1. Using only mild light sources, the strong reductant $C1^-$ was photo-generated in the presence of BI_1H and BI_2H, performing a more efficient challenging photo-assisted dehalogenation reaction than that of classical photosensitizers. Importantly, the photo-oxidation of the designed benzimidazoline donors is well controlled and they can be easily regenerated. A preliminary scope study revealed that the photochemical process is compatible with many substrates. This work paves the way towards virtually waste-free demanding reduction reactions, driven only by solar energy, with a cheap and essentially non noxious, highly colored homoleptic copper(I) complex.

Funding sources

The authors wish to thank the ANR (PERCO program no. ANR-16-CE07-0012-01) for financial support.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

References

1 N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075–10166.

2 M. H. Shaw, J. Twilton and D. W. C. MacMillan, *J. Org. Chem.*, 2016, **81**, 6898–6926.

3 S. Engl and O. Reiser, *ACS Catal.*, 2020, **10**, 9899–9906.

4 A. C. Hernandez-Perez and S. K. Collins, *Acc. Chem. Res.*, 2016, **49**, 1557–1565.

5 R. Giereth, M. Obermeier, L. Forschner, M. Karnahl, M. Schwalbe and S. Tschierlei, *ChemPhotoChem*, 2021, **5**, 644–653.

6 A. Hossain, A. Bhattacharyya and O. Reiser, *Science*, 2019, **364**, eaav9713.

7 B. M. Hockin, C. Li, N. Robertson and E. Zysman-Colman, *Catal. Sci. Technol.*, 2019, **9**, 889–915.

8 J.-M. Kern and J.-P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 1987, 546–548.

9 M. Pirtsch, S. Paria, T. Matsuno, H. Isobe and O. Reiser, *Chem. – Eur. J.*, 2012, **18**, 7336–7340.

10 Y. Zhang, M. Heberle, M. Wächtler, M. Karnahl and B. Dietzek, *RSC Adv.*, 2016, **6**, 105801–105805.

11 B. Wang, D. P. Shelar, X.-Z. Han, T.-T. Li, X. Guan, W. Lu, K. Liu, Y. Chen, W.-F. Fu and C.-M. Che, *Chem. – Eur. J.*, 2015, **21**, 1184–1190.

12 A. Call, C. Casadevall, F. Acuña-Parés, A. Casitas and J. Lloret-Fillol, *Chem. Sci.*, 2017, **8**, 4739–4749.

13 B. Michelet, C. Deldaele, S. Kajouj, C. Moucheron and G. Evano, *Org. Lett.*, 2017, **19**, 3576–3579.

14 A. Nitelet, D. Thevenet, B. Schiavi, C. Hardouin, J. Fournier, R. Tamion, X. Pannecoucke, P. Jubault and T. Poisson, *Chem. – Eur. J.*, 2019, **25**, 3262–3266.

15 H. Baguia, C. Deldaele, E. Romero, B. Michelet and G. Evano, *Synthesis*, 2018, **50**, 3022–3030.

16 O. Green, B. A. Gandhi and J. N. Burstyn, *Inorg. Chem.*, 2009, **48**, 5704–5714.

17 S. Garakyaraghi, P. D. Crapps, C. E. McCusker and F. N. Castellano, *Inorg. Chem.*, 2016, **55**, 10628–10636.

18 S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini and V. Balzani, in *Photochemistry and Photophysics of Coordination Compounds I*, ed. V. Balzani and S. Campagna, Springer, Berlin, Heidelberg, 2007, pp. 117–214.

19 D. Hanss, J. C. Freys, G. Bernardinelli and O. S. Wenger, *Eur. J. Inorg. Chem.*, 2009, **2009**, 4850–4859.

20 B. J. McCullough, B. J. Neyhouse, B. R. Schrage, D. T. Reed, A. J. Osinski, C. J. Ziegler and T. A. White, *Inorg. Chem.*, 2018, **57**, 2865–2875.

21 M. Sandroni, M. Kayanuma, M. Rebarz, H. Akdas-Kilig, Y. Pellegrin, E. Blart, H. L. Bozec, C. Daniel and F. Odobel, *Dalton Trans.*, 2013, **42**, 14628–14638.

22 H. Takeda, Y. Monma, H. Sugiyama, H. Uekusa and O. Ishitani, *Front. Chem.*, 2019, **7**, 418.

23 S.-P. Luo, N.-Y. Chen, Y.-Y. Sun, L.-M. Xia, Z.-C. Wu, H. Junge, M. Beller and Q.-A. Wu, *Dyes Pigm.*, 2016, **134**, 580–585.

24 A. J. J. Lennox, S. Fischer, M. Jurrat, S.-P. Luo, N. Rockstroh, H. Junge, R. Ludwig and M. Beller, *Chem. – Eur. J.*, 2016, **22**, 1233–1238.

25 Y. Sakaguchi, A. Call, M. Cibian, K. Yamauchi and K. Sakai, *Chem. Commun.*, 2019, **55**, 8552–8555.

26 M. S. Lazorski and F. N. Castellano, *Polyhedron*, 2014, **82**, 57–70.

27 S. Paria and O. Reiser, *ChemCatChem*, 2014, **6**, 2477–2483.

28 C. Sandoval-Pauker, G. Molina-Aguirre and B. Pinter, *Polyhedron*, 2021, **199**, 115105.

29 N. Armaroli, G. Accorsi, F. Cardinali and A. Listorti, in *Photochemistry and Photophysics of Coordination Compounds I*, ed. V. Balzani and S. Campagna, Springer, Berlin, Heidelberg, 2007, pp. 69–115.

30 K. L. Cunningham and D. R. McMillin, *Inorg. Chem.*, 1998, **37**, 4114–4119.

31 K. L. Cunningham, C. R. Hecker and D. R. McMillin, *Inorg. Chim. Acta*, 1996, **242**, 143–147.

32 A. K. I. Gushurst, D. R. McMillin, C. O. Dietrich-Buchecker and J. P. Sauvage, *Inorg. Chem.*, 1989, **28**, 4070–4072.

33 M. K. Eggleston, D. R. McMillin, K. S. Koenig and A. J. Pallenberg, *Inorg. Chem.*, 1997, **36**, 172–176.

34 A. Rosas-Hernández, C. Steinlechner, H. Junge and M. Beller, *Green Chem.*, 2017, **19**, 2356–2360.

35 X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang and J.-P. Cheng, *J. Am. Chem. Soc.*, 2008, **130**, 2501–2516.

36 T. J. Collins, R. D. Powell, C. Slebodnick and E. S. Uffelman, *J. Am. Chem. Soc.*, 1991, **113**, 8419–8425.

37 H. G. Roth, N. A. Romero and D. A. Nicewicz, *Synlett*, 2016, **27**, 714–723.

38 E. M. Espinoza, J. A. Clark, J. Soliman, J. B. Derr, M. Morales and V. I. Vullev, *J. Electrochem. Soc.*, 2019, **166**, H3175.

39 J.-H. Shon, D. Kim, M. D. Rathnayake, S. Sittel, J. Weaver and T. S. Teets, *Chem. Sci.*, 2021, **12**, 4069–4078.

40 R. S. Shaikh, S. J. S. Düsel and B. König, *ACS Catal.*, 2016, **6**, 8410–8414.

41 S. Rohrbach, R. S. Shah, T. Tuttle and J. A. Murphy, *Angew. Chem., Int. Ed.*, 2019, **58**, 11454–11458.

42 C. Costentin, M. Robert and J.-M. Savéant, *J. Am. Chem. Soc.*, 2004, **126**, 16051–16057.