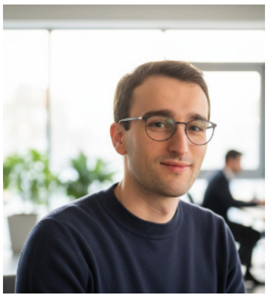


Exploiting Powerful Photo-generated Species from Homoleptic Copper(I) Complexes via a Reductive Quenching Mechanism: Mechanistic Study and Scope

**N. Oppé,[1]* O. Baffroy,[1] V. Maurel,[2] Frédéric Robert,[3] C. Queffélec,[1]
E.Blart,[1] and Y. Pellegrin,[1]**

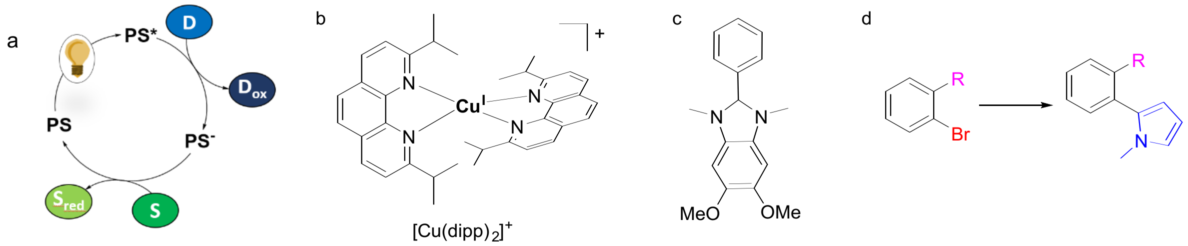
[1] Laboratoire CEISAM, Université de Nantes, 44000 Nantes, France
[2] CEA-Grenoble, 38000 Grenoble, France
[3] Institut des Sciences Moléculaires, Université de Bordeaux, 33405 Talence, France

E-mail: nicolas.oppe@univ-nantes.fr

Photo-driven reactions have been widely explored since recent years and represent a very powerful tool in organic synthesis. In a previous contribution,[1] we have reported a reductive quenching cycle with a simple, strongly colored homoleptic copper(I) complex $[Cu(dipp)_2]^+$ (Scheme 1a and 1b, dipp = 2,9-diisopropyl-1,10-phenanthroline) as photosensitizer (PS). Complexes of this family being weak photo-oxidants,[2] we specifically designed and synthesized a recyclable sacrificial electron donor D based on a benzimidazoline molecular skeleton (Scheme 1c). We have demonstrated that, during irradiation with blue LED in presence of D, the strong reductant $[Cu(dipp)_2]^{(0)}$ was efficiently photo-generated and we used this strong reductive power to realize the dehalogenation of aryl halides.

Building on this result, we optimized the reaction conditions, increased the scope of the possible photo-induced reactions, and aimed at better understanding the mechanism underlying the photo-induced transformations.

In order to confirm the supposed mechanism pathway of photo-dehalogenation, we performed different tests (EPR, radical trap experiments, on/off cycles, deuteration). All the results point towards the involvement of a hydrogen atom transfer step (HAT). On the other hand, we focused on the possibility to exploit the reactivity of $[Cu(dipp)_2]^{(0)}$ to successfully achieve cross-couplings between 2 partners as shown in Scheme 1d. All the results highlight the relevance of implementing reductive quenching of the excited state of homoleptic Cu(I) complexes in organic photochemistry.



Scheme 1: (a) Illustration of the reductive quenching cycle. Structures of (b) $[Cu(dipp)_2]^+$ and (c) the benzimidazoline donor used in this study and (d) possible coupling reaction with aryl halides

References

[1] Gimeno, L.; Queffélec, C.; Mall Haidaraly, K.; Blart, E.; Pellegrin, Y. *Catal. Sci. Technol.* **2021**, *11*, 6041-6047.
[2] Gushurst, A. K. I.; McMillin, D. R.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *Inorg. Chem.* **1989**, *28*, 4070-4072.; Cunningham, K. L.; McMillin, D. R. *Inorg. Chem.* **1998**, *37*, 16, 4114–4119.