

## Reductive Quenching with copper(I) diimine complexes thanks to a new chemical design of phenanthrolines

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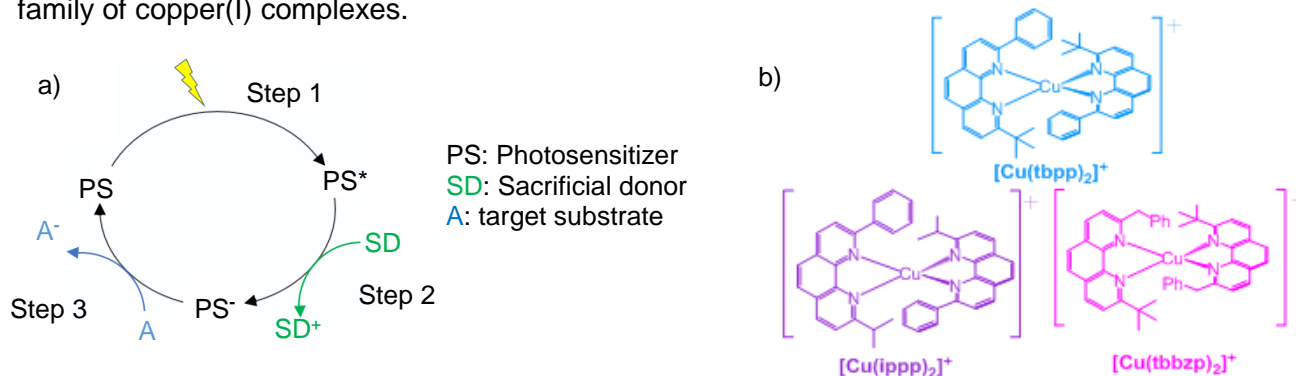
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Reductive quenching is the best way to do recalcitrant reduction reactions. Using light, we will excite a photosensitizer (PS) into its excited state (PS<sup>\*</sup>) (**step 1** fig. 1a). The key step is the reduction of PS<sup>\*</sup> by a sacrificial electron donor (**step 2**). Copper(I) bis(diimine) complexes have the particularity to have a very strong reduction potential (for example [Cu(dpp)<sub>2</sub>]<sup>+</sup> and [Cu(dipp)<sub>2</sub>]<sup>+</sup> exhibit respectively -2.10 and -2.21 V vs Fc<sup>+0</sup> for the couple PS/PS<sup>-[1]</sup>) paving the way towards a cheap and efficient way to drive difficult reduction reactions with light. For now, copper diimine complexes are poor oxidant at the excited state so **step 2** is thermodynamically impossible.

To make **step 2** possible, we aim at increasing the photooxidation potential of copper(I) – bis(diimine) complexes (E<sub>ox</sub><sup>\*</sup>) by a new chemical design of phenanthrolines. We first worked on the excited state energy of the complexes which will directly impact E<sub>ox</sub><sup>\*</sup> by increasing the steric bulk around copper(I) coordination cage. However, increasing too much the steric bulk around copper(I) raises stability issues. Molecular engineering guided us to break the symmetry of the ligand, phenanthroline was namely substituted in position 2 by a bulky aliphatic group (to increase E<sub>ox</sub><sup>\*</sup>) and position 9 by an aromatic group (to stabilize the coordination sphere by intramolecular π stacking). Thus, we designed three new complexes [Cu(iPPP)<sub>2</sub>]<sup>+</sup>, [Cu(tbpp)<sub>2</sub>]<sup>+</sup> and [Cu(tbbzp)<sub>2</sub>]<sup>+</sup> (fig. 1b). We studied the impact of the ramified alkyl groups (using both isopropyl and tertbutyl) as well as the effect of a spacer between phenanthroline and the aromatic ring (CH<sub>2</sub> vs. direct bonding) on electrochemical and optical properties of the complexes. Following this strategy we managed to increase E<sub>ox</sub><sup>\*</sup> by 100 mV for those three complexes. This presentation will focus on the synthesis, optoelectronic characterizations, stability studies and **reductive quenching trials** of this new family of copper(I) complexes.



**Figure 1:** a) Reductive quenching mechanism. b) Copper(I) complexes with non symmetric ligands