[Cu(bcp)(DPEphos)]\(^+\): A Versatile and Efficient Copper-Based Photoredox Catalyst and Photosensitizer

Samuel Oger\(^a\)
Hajar Baguia\(^a\)
Tuan-Anh Phan\(^b\)
Titouan Teunens\(^b\)
Jérôme Beaudelot\(^a,b\)
Cécile Moucheron\(^*\)
Gwilherm Evano\(^*\)

\(^a\) Laboratoire de Chimie Organique, Université Libre de Bruxelles (ULB), Avenue F. D. Roosevelt 50, CP160/06, 1050 Brussels, Belgium
Gwilherm.Evano@ulb.be
\(^b\) Laboratoire de Chimie Organique et Photochimie, Service de Chimie et PhysicoChimie Organiques, Université Libre de Bruxelles (ULB), Avenue F. D. Roosevelt 50, CP160/06, 1050 Brussels, Belgium
Cecile.Moucheron@ulb.ac.be

Abstract

Photochemistry has had a strong impact in many areas of chemistry, notably in organic synthesis,\(^1\) or for clean-energy production.\(^2\) A simple glance at the homogeneous photoredox catalysts available reveals that, in addition to organic dyes, this field is largely dominated by photoactive noble-metal complexes; mostly containing Ru(II) or Ir(III), which poses major problems in terms of availability, cost, and industrial applications. While they have been used for decades,\(^3\) photoactive Cu(I) complexes have emerged over the last ten years as reliable alternatives and are attracting a great deal of interest in terms of availability, cost, and modularity. However, they are still far from being ideal, since most of these complexes suffer from limited absorption in the visible region and lower stability in solution compared to traditional photosensitizers.

While achieving the desired photophysical/chemical properties with homoleptic bisdiamine Cu(I) complexes has proven to be challenging, heteroleptic Cu(I) complexes, combining diimine and diphosphine ligands, have been found to be quite attractive and efficient. Their photophysical and electrochemical properties are directly linked to those two distinct ligands; while the diphosphine moiety mainly allows to adjust the HOMO energy level, the diimine ligand controls the LUMO of the Cu(I) complex. A judicious choice of the two ligands chelated to the Cu(I) ion therefore allows a fine tuning of both the optical and electrochemical properties.\(^4\) Among this family of heteroleptic copper complexes, one combining a bathocuproine (bcp) and a bis[2-(diphenylphosphino)phenyl] ether (DPEphos), has been shown to be particularly versatile and efficient. [Cu(bcp)(DPEphos)]\(^+\) is indeed characterized by high molar...
absorption coefficients of metal-to-ligand charge-transfer (MLCT) transitions, a long-lived excited state, high emission quantum yields and a good stability in solution (Figure 1).

**Photophysical and Electrochemical Properties**

The geometry of [Cu(bcp)(DPEphos)]PF₆ in its solid state has been assessed by X-ray diffraction, the complex adopting the classical distorted tetrahedric geometry. In solution, it shows an absorption band centered around 380 nm and absorbs light up to 440 nm in a variety of organic solvents. Its emission spectrum is centered around 560–590 nm and absorbs light up to 440 nm in a variety of organic solvents, used in excess, could be efficiently arylated upon similar conditions and without significant competing reduction (Table 1, A). Alkyl and aryl radicals generated under these conditions could also be trapped by tethered alkenes to afford indolines, dihydrofurans, indanes, pyrrolidines, or cyclopentanes through a 5-exo-trig radical cyclization (Table 1, B). Alternatively, a range of pyrroles and electron-rich arenes, used in excess, could be efficiently arylated upon similar conditions and without significant competing reduction (Table 1, C). More sophisticated applications of [Cu(bcp)(DPEphos)]PF₆ such as domino radical cyclizations have been reported. A 5-exo-dig/6-endo-trig radical-cyclization cascade from such acyclic precursors afforded complex polycyclic scaffolds, among which natural/biologically relevant products such as luotonin A, rosettacin, and deoxyvascinone were obtained in a few steps and high efficiency (Table 1, D).

From a mechanistic point of view and based on various mechanistic studies, all these reactions are thought to involve a rare and underexplored Cu(I)/Cu(I)*/Cu(II) catalytic cycle in which the copper complex activated by light irradiation is first reduced by a SED, generating a strongly reducing Cu(0) complex that is able to reduce the alkyl or aryl halide, regenerating the Cu(I) complex and releasing the alkyl or aryl radical species (Scheme 1, black pathway). As an important note, the putative Cu(0) intermediate complex can be seen as a monodentated Cu(I) complex in which the unpaired electron is actually centered on the bcp ligand, and absorbs light up to 440 nm in a variety of organic solvents, used in excess, could be efficiently arylated upon similar conditions and without significant competing reduction (Table 1, C). More sophisticated applications of [Cu(bcp)(DPEphos)]PF₆ such as domino radical cyclizations have been reported. A 5-exo-dig/6-endo-trig radical-cyclization cascade from such acyclic precursors afforded complex polycyclic scaffolds, among which natural/biologically relevant products such as luotonin A, rosettacin, and deoxyvascinone were obtained in a few steps and high efficiency (Table 1, D).

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Application in Artificial Photosynthesis

This heteroleptic copper complex has also been shown to be promising in artificial photosynthesis. In this context, Cu(I) complexes have been investigated as potential photosensitizers to absorb light in order to induce an electron transfer from a SED to a catalyst (Cat) that accumulates electrons to then either reduce protons or CO₂ (Scheme 1, green path).

In 2013, the Beller group reported that \([\text{Cu(bcp)(DPEphos)}]\)PF₆ is an efficient photosensitizer 7 that, when combined with \([\text{Fe₃(CO)₁₂}]\), is able to produce dihydrogen efficiently under visible-light irradiation. They showed in 2016 that in situ generated heteroleptic Cu(I) complexes are superior in producing large amounts of hydrogen. \(^{10}\) \([\text{Cu(bcp)(DPEphos)}]\)PF₆, was formed in situ in 73% yield under the reaction conditions, had one of the highest turnover

### Table 1 Applications of \([\text{Cu(bcp)(DPEphos)}]\)\(^{+}\)

<table>
<thead>
<tr>
<th>Application</th>
<th>Reaction Conditions</th>
<th>Products</th>
<th>Turnover Numbers (TON)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Photoinduced radical dehalogenation of alkyl and aryl halides</td>
<td>([\text{Cu(bcp)(DPEphos)}])PF₆ (5 mol%)</td>
<td>(\text{Alk-X} \rightarrow \text{Alk-H})</td>
<td>TONCu = 1090</td>
<td>Electron-rich/poor (hetero)aryl bromides and chlorides, wide variety of hetero- and carbocycles obtained</td>
</tr>
<tr>
<td>(B) Photoinduced radical 5-exo-trig cyclization of alkene-tethered aryl and alkyl halides</td>
<td>([\text{Cu(bcp)(DPEphos)}])PF₆ (10 mol%)</td>
<td>(\text{Alk-X} \rightarrow \text{Alk-H})</td>
<td>TONCu = 0.05</td>
<td>Electron-rich/poor (hetero)aryl iodides</td>
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<tr>
<td>(C) Direct radical arylation of pyrroles and electron-rich arenes with aryl halides</td>
<td>([\text{Cu(bcp)(DPEphos)}])PF₆ (10 mol%)</td>
<td>(\text{Alk-X} \rightarrow \text{Alk-H})</td>
<td>TONCu = 477</td>
<td>Electron-rich/poor aryl bromides, electron-poor aryl chlorides</td>
</tr>
<tr>
<td>(D) Photoinduced radical 5-exo-dig/6-endodig cyclization of acti-vated alkynes</td>
<td>([\text{Cu(bcp)(DPEphos)}])PF₆ (5 mol%)</td>
<td>(\text{Alk-X} \rightarrow \text{Alk-H})</td>
<td>TONCu = 85%</td>
<td>Electron-rich/alkyl bromides and aryl chlorides</td>
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<td>(E) Dihydrogen photoproduction</td>
<td>([\text{Cu(bcp)(DPEphos)}])PF₆ (0.35 mM)</td>
<td>(\text{H}_2 \rightarrow \text{H}_2)</td>
<td>TONCu = 365 nm</td>
<td>High turn-over numbers (TON)</td>
</tr>
<tr>
<td>(F) CO₂ photoreduction</td>
<td>([\text{Cu(bcp)(DPEphos)}])PF₆ (0.35 mM)</td>
<td>(\text{CO}_2 \rightarrow \text{CO}_2)</td>
<td>TONCu = 0.05</td>
<td>Highest TON among the photocatalytic systems using Fe complexes as catalyst</td>
</tr>
<tr>
<td>(G) UV photodetection</td>
<td>([\text{Cu(bcp)(DPEphos)}])PF₆ (0.35 mM)</td>
<td>(\text{H}_2 \rightarrow \text{H}_2)</td>
<td>TONCu = 365 nm</td>
<td>High photosresponse for UV photodetection</td>
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numbers of over 1000 for the photoinduced proton reduction system (Table 1, E).

Following the more recent trend of photocatalytic CO₂ reduction, three studies have been carried out with [Cu(bcp)(DPEphos)]PF₆ as a photosensitizer. In all three systems, it was shown to be one of the most efficient photosensitizers in combination with Fe(II) catalysts (Table 1, F). Quenching studies carried out with 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benz[d]imidazole (BIH) as a sacrificial reductant showed that the reaction was initiated by the reductive quenching of the excited photosensitizer, supporting a Cu(I)/Cu(I)/Cu(0) catalytic cycle.

Application as a UV-Photodetector

[Cu(bcp)(DPEphos)]BF₄ was also investigated in 2011 in a visible-blind UV photodetector device (Table 1, G), which displayed a high peak response of 186 mA/W under illumination with a 365 nm UV light source and a higher selectivity for the UV spectrum compared to previously developed devices.

Conclusion and Outlook

In conclusion, as light-mediated processes are becoming more and more investigated because of their sustainability and relevance, a strong and increasing demand for non-noble metal photocatalysts has emerged. Among them, heteroleptic Cu(I) complexes such as [Cu(bcp)(DPEphos)]⁺ have proven to be valuable alternatives to ruthenium- and iridium-based photocatalysts and have been shown to be efficient in a range of processes, paving the way for the development of related diimine-diphosphine Cu(I) complexes and further development.