

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

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Abstract **Key words** photochemistry, homogeneous catalysis, copper, free radicals, radical reaction

Photoredox catalysis 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 modulability. 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 bisdiimine 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



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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).

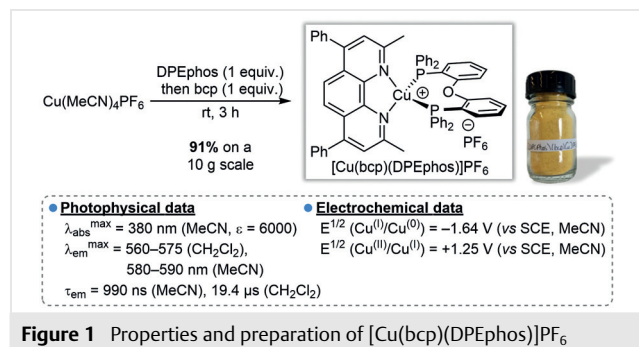


Figure 1 Properties and preparation of $[\text{Cu}(\text{bcp})(\text{DPEphos})]\text{PF}_6$

Photophysical and Electrochemical Properties

The geometry of $[\text{Cu}(\text{bcp})(\text{DPEphos})]\text{PF}_6$ in its solid state has been assessed by X-ray diffraction,⁵ the complex adopting the classical distorted tetrahedral geometry.⁴ In solution, it shows an absorption band centered around 380 nm and absorbs light up to 440 nm in a variety of organic solvents.^{6,7} Its emission spectrum is centered around 560–590 nm with an excited-state lifetime ranging from 990 ns in acetonitrile to 19.4 μs in dichloromethane. It exhibits a single reduction wave at -1.64 V vs SCE in acetonitrile using tetrabutylammonium hexafluorophosphate as support electrolyte, and an oxidation wave at $+1.25 \text{ V}$ vs SCE (Figure 1).⁸

Besides these photophysical and electrochemical properties, $[\text{Cu}(\text{bcp})(\text{DPEphos})]\text{PF}_6$ is also remarkably air and moisture stable, both in the solid state and in solution, with only minor amounts of the corresponding homoleptic complexes being observed upon irradiation at 420 nm in deoxygenated acetonitrile.⁸ All these properties have made $[\text{Cu}(\text{bcp})(\text{DPEphos})]^+$ appealing for many applications, its attractiveness being reinforced by its ease of synthesis via a simple ‘mix-and-stir’ procedure.

Complex Synthesis

The synthesis of this complex was first published in 2006 by the Nierengarten group, who prepared the tetrafluoroborate salt by simple treatment of $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ with a stoichiometric amount of bcp and DPEphos.⁶ Adapting this procedure, the Beller group then reported the synthesis of the analogous $[\text{Cu}(\text{bcp})(\text{DPEphos})]\text{PF}_6$ in 2013.⁷ $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ was sequentially treated with stoichiometric amounts of DPEphos and bcp in refluxing dichloromethane. The desired complex was obtained as a yellow solid in 85% yield after *n*-hexane-induced precipitation and an optional recrystallization from dichloromethane/*n*-hexane at

4°C . More recently, our groups have reported a more user-friendly modification proceeding at room temperature in a few hours and producing tens of grams with 91% yield after precipitation with diethyl ether.⁸ Traces of $[\text{Cu}(\text{bcp})_2]\text{PF}_6$ can be easily removed through recrystallization by slow diffusion of diethyl ether in a concentrated solution of complex in acetonitrile.

Applications in Organic Photoredox Catalysis

As mentioned above, copper photoredox catalysis has gained significant attention recently.¹ In this context, some contributions of our groups highlight the potential and attractiveness of $[\text{Cu}(\text{bcp})(\text{DPEphos})]\text{PF}_6$ as a photoredox catalyst and as an efficient and cheaper surrogate to commonly utilized iridium or ruthenium complexes.

It has been shown that this complex is able to activate, not only several $\text{C}(\text{sp}^2)\text{--X}$ bonds, but also $\text{C}(\text{sp}^3)\text{--X}$ ones (X being a bromide or an iodide) and thus dehalogenation of a wide range of aryl or alkyl bromides and iodides could be achieved under mild visible-light irradiation in the presence of Hünig’s base as a sacrificial electron donor (SED, 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).⁸ More sophisticated applications of $[\text{Cu}(\text{bcp})(\text{DPEphos})]\text{PF}_6$ such as domino radical cyclizations of aryl iodide tethered ynamides and cyanamides have also 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).⁹

From a mechanistic point of view and based on various mechanistic studies, all these reactions are thought to involve a rare and underexplored $\text{Cu}(\text{I})/\text{Cu}(\text{I}^*)/\text{Cu}(\text{0})$ catalytic cycle in which the copper complex activated by light irradiation is first reduced by a SED, generating a strongly reducing $\text{Cu}(\text{0})$ complex that is able to reduce the alkyl or aryl halide, regenerating the $\text{Cu}(\text{I})$ complex and releasing the alkyl or aryl radical species (Scheme 1, black pathway).⁸ As an important note, the putative $\text{Cu}(\text{0})$ intermediate complex can be seen as a monoreduced $\text{Cu}(\text{I})$ complex in which the unpaired electron is actually centered on the bcp ligand, which does not involve a change in geometry of the copper complex, a major problem associated to the more classical $\text{Cu}(\text{I})/\text{Cu}(\text{I}^*)/\text{Cu}(\text{II})$ catalytic cycle.

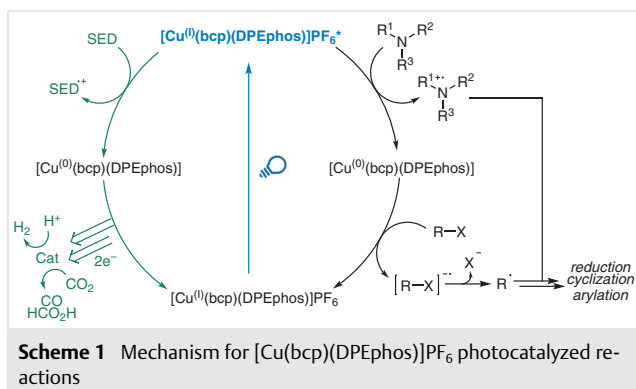
Table 1 Applications of [Cu(bcp)(DPEphos)]⁺

<p>(A) Photoinduced radical dehalogenation of alkyl and aryl halides⁸</p> <ul style="list-style-type: none"> ✓ electron-rich/poor (hetero)aryl iodides ✓ electron-poor aryl bromides ✓ vinyl and alkyl iodides, alkyl bromides ✗ aryl chlorides ✗ electron-rich aryl bromides 	
<p>(B) Photoinduced radical 5-exo-trig cyclization of alkene-tethered aryl and alkyl halides⁵</p> <ul style="list-style-type: none"> ✓ electron-rich and electron-poor aryl and alkyl halides ✓ wide variety of hetero- and carbocycles obtained 	
<p>(C) Direct radical arylation of pyrroles and electron-rich arenes with aryl halides⁸</p> <ul style="list-style-type: none"> ✓ electron-rich/poor (hetero)aryl iodides ✓ electron-poor aryl bromides ✓ catalytic amount of sacrificial reductant ✗ excess of pyrrole or arene required ✗ long reaction time ✗ electron-rich aryl bromides and aryl chlorides 	
<p>(D) Photoinduced radical 5-exo-dig/6-endo-dig cyclization cascade of activated alkynes⁹</p> <ul style="list-style-type: none"> ✓ tri- to pentacyclic natural scaffolds built in a single step ✓ total syntheses of 3 natural products in few steps. 	
<p>(E) Dihydrogen photoproduction^{7,10}</p> <ul style="list-style-type: none"> ✓ high turn-over numbers (TON) ✓ <i>in situ</i> method ✗ photosensitizer degradation during the photocatalytic process 	
<p>(F) CO₂ photoreduction^{5,11}</p> <ul style="list-style-type: none"> ✓ highest TON among the photocatalytic systems using Fe complexes as catalyst ✓ monoreduced species from the photosensitizer to the thermodynamically favorable catalyst ✓ <i>in situ</i> procedure 	
<p>(G) UV photodetection¹²</p> <ul style="list-style-type: none"> ✓ high photoresponse for UV photodetection ✓ good selectivity UV light vs visible light 	

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 [Cu(bcp)(DPEphos)]PF₆ is an efficient photosensitizer⁷ that, when combined with [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 [Cu(bcp)(DPEphos)]PF₆, was formed *in situ* in 73% yield under the reaction conditions, had one of the highest turnover



numbers of over 1000 for the photoinduced proton reduction system (Table 1, E).

Following the more recent trend of photocatalytic CO_2 reduction, three studies have been carried out with $[\text{Cu}(\text{bcp})(\text{DPEphos})]\text{PF}_6$ 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).^{5,11} Quenching studies carried out with 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[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

$[\text{Cu}(\text{bcp})(\text{DPEphos})]\text{BF}_4$ was also investigated in 2011 in a visible-blind UV photodetector device (Table 1, G),¹² 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 $[\text{Cu}(\text{bcp})(\text{DPEphos})]^+$ 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.

Conflict of Interest

The authors declare no conflict of interest.

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