[Copper(phenanthroline)(bisisonitrile)]$^+$-Complexes for the Visible Light-Mediated Atom Transfer Radical Addition and Allylation Reactions.

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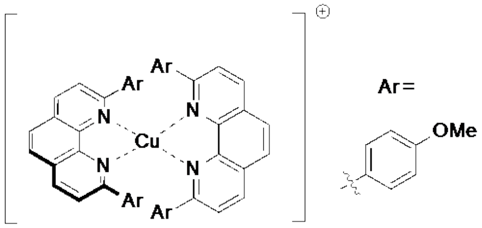
ABSTRACT: A series of heteroleptic [Cu(phenantroline)(bisisonitrile)]$^+$-complexes was synthesized and their structural, spectroscopic and electrochemical properties were investigated. The new copper(I) complexes were employed as photoredox-catalysts in the visible light-mediated atom transfer radical addition (ATRA). Especially [Cu(dpp)(binc)]BF_4 (**6a**-$\mathbf{BF_4}$) (dpp = 2,9-diphenyl-1,10-phenanthroline; binc = bis(2-isocyanophenyl) phenylphosphonate) proved to be highly active owing to an enhanced excited state lifetime compared to the commonly employed [Cu(dap)$_2$]Cl (**1-Cl**) (dap = 2,9-di(*p*-anisyl)-1,10-phenanthroline). Furthermore, the catalyst could be applied to allylation reactions with trimethylallylsilane under mild visible-light photoredox conditions.

KEYWORDS: copper, isonitrile, visible light photocatalysis, atom transfer radical addition, allylation.

INTRODUCTION

In the last years, visible-light mediated photoredox catalysis developed rapidly. Besides the search for new applications, the continuous design of highly active catalysts promotes this green technology. The most commonly employed visible-light photoredox catalysts are metal complexes based on ruthenium or iridium,[1] owing to their excellent stability and catalytic activity manifested in long life times of their excited states combined with suitable redox potentials to initiate electron transfer events with organic compounds. However, these metals are scarce in nature, and hence the use of copper complexes is an attractive alternative, since it is less expensive, safer and environmentally more benign. Nevertheless, there are only few reports on copper based photoactive complexes used for visible-light driven organic synthesis.[2]

In particular, the excited-state properties of copper(I) diimine complexes attracted attention since long. As a major drawback, such materials often suffer from short excited state lifetimes, caused by an excited-state reorganization from a tetrahedral to a square-planar complex geometry. The introduction of bulky substituents, e.g. in 2,9-position of the phenanthroline moiety, thus preventing such a structural relaxation that facilitates the non-radiative relaxation to the ground state, has been attempted to overcome this problem.[3] Accordingly, [Cu(dpp)$_2$]$^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) could be used for hydrogen production from water[4] as well as for the generation of aryl radicals derived from diaryliodonium salts under visible-light photoredox catalysis conditions.[5] Recently, we succeeded in the application of [Cu(dap)$_2$]$^+$ (**1**) (dap = 2,9-di(*p*-anisyl)-1,10-phenanthroline)[6] as photoredox catalyst (Figure 1), utilizing its oxidative quenching cycle for intermolecular atom transfer radical addition (ATRA) and allylation reactions under irradiation with green LEDs (λ = 530 nm) or even sunlight.[7]



[Cu(dap)$_2$]$^+$ (**1**)

Figure 1. [Cu(dap)$_2$]$^+$ (**1**) (dap: 2,9-di(*p*-anisyl)-1,10-phenanthroline).

Very recently, fluoroalkylsulfonyl chlorides were introduced as reagents for the [Cu(dap)$_2$]Cl (**1-Cl**) catalyzed visible light ATRA reaction.[8] Similar to ruthenium and iridium based photocatalysts, net CF_3Cl addition was observed by the reaction of triflyl chloride with heteroatom containing alkenes. In contrast, an inner sphere mechanism which suppresses SO_2 extrusion was described for inactivated alkenes, leading to the trifluoromethylsulfonylated products, pointing to special opportunities copper based photocatalysts might offer beyond acting as electron transfer reagents.[8b]

Nevertheless, with sub-microsecond (~ 300 ns) luminescence decay times,[5,6] these two copper complexes are disadvantageous with respect to their short excited-state lifetime compared to related ruthenium or iridium complexes, (e.g.: $[Ru(bpy)_3]^{2+}$ (bpy: 2,2'-bipyridyl): 1.1 μs[9a], $[Ir(dF(CF_3)ppy)_2(dtbbpy)]^+$ ($dF(CF_3)ppy$: 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine; dtbbpy: 4,4'-di-*tert*-butyl-2,2'-dipyridyl): 2.3 μs[9b]) which limits their application in photocatalysis.

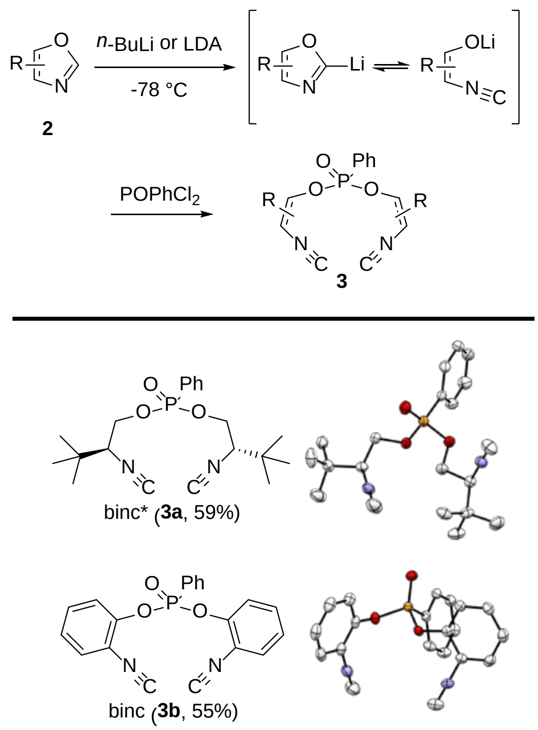
To increase the excited-state lifetime, specially designed copper(I)bisphenanthroline complexes utilizing cooperative steric hindrance were developed with reported excited state lifetimes in the range of one microsecond.[10] As an alternative approach, mixed ligand copper(I) complexes with a phenanthroline (NN) and a wide-bite-angle bidentate phosphine (PP) ligand have been proposed.[11] With reported room temperature lifetimes in the order of several microseconds (e.g. $[Cu(dmp)(DPEPhos)]^+$ (dmp: neocuproine, 2,9-dimethyl-1,10-phenanthroline; DPEPhos: bis(2-(diphenylphosphanyl)phenyl)ether): 14.3 μs[11c]), these complexes were extensively studied as sensitizers for the nobel-metal free photocatalytic water reduction.[12] Moreover, Collins and co-workers reported the visible-light mediated synthesis of helicenes and carbazoles,[13] using different $[Cu(NN)(PP)]^+$-complexes. Very recently, a remarkable study by Chen *et al.* appeared in which heteroleptic copper(I) complexes containing phenanthroline and a monoanionic *nido*-carborane-diphosphine ligand with excited-state lifetimes of 10-20 μs at ambient temperature were applied for photoinduced cross-dehydrogenative couplings.[14]

Following our interest[15] in photocatalysis and the further improvement and investigation of copper-complexes for visible-light photoredox catalysis,[7,8b] we were intrigued by a study of Mann *et al.*[16] that reports emission lifetimes up to milliseconds for specially designed heteroleptic copper(I) complexes having phenanthroline and monodentate isonitrile ligands. We envisioned that copper(I) phenanthroline complexes bearing chelating bis(isonitrile) ligands further impede structural reorganization upon irradiation and thus extend the lifetimes of the excited state, which might lead to improved photoredox catalysts. Here we report the synthesis and characterization of new heteroleptic $[Cu(phenanthroline)(bisisonitrile)]^+$-complexes. The new compounds have significantly improved photophysical characteristics and can be used under mild visible-light conditions for a variety of atom transfer radical additions (ATRAs) and allylation reactions with trimethylallylsilane, the latter being particularly challenging with previously known catalysts.

RESULTS AND DISCUSSION

Aiming at heteroleptic $[Cu(phenanthroline)(bisisonitrile)]^+$ complexes, bisisonitrile ligands **3a**[17] and **3b**[18] were synthesized, following the methodology introduced by us[17] by treating oxazoles with *n*-BuLi or LDA and trapping the resulting anion with phenylphosphonic dichloride (Scheme 1). Bisisonitrile **3b** was further characterized by X-ray analysis.[19] Its solid state structure revealed that both isonitrile moieties are already pre-oriented for the chelation of a metal. In contrast, in the X-ray structure[17a] of bis(isonitrile) **3a** both isonitriles point away from each other, thus coordination of **3a** to a metal center must be realized by rearrangement of the two diastereotopic isonitrile arms (Scheme 1). As counterparts, commercially available phenanthroline ligands **4a-c** and readily synthesized 2,9-di(p-anisyl)-1,10-phenanthroline[6,7a] (**4d**) were employed in this study (Chart 1).

Besides the known $[Cu(dap)_2]Cl$ (**1-Cl**) the novel heteroleptic copper(I)-complexes **6a-e** were investigated that were obtained in quantitative yield by reacting an equimolar solution of two different ligands in dichloromethane with $[Cu(MeCN)_4]BF_4$ (Scheme 2).[20] After precipitation in diethyl ether, the light-brown to brown colored complexes **6** could be stored for extended periods without any sign of decomposition.



[a] Synthesis of (bis((*S*)-2-isocyano-3,3-dimethylbutyl) phenylphosphonate) (binc*, **3a**) and (bis(2-isocyanophenyl) phenylphosphonate) (binc, **3b**) and their crystal structures. Conditions: Oxazole **2** (1.0 equiv.), n-BuLi (1.6 M in hexane, 1.05 equiv.), THF (0.4 M), −78 °C, 1.5 h; $POPhCl_2$ (0.53 equiv.), −78°C to rt, 2 h.

Scheme 1. Synthesis of bisisonitrile ligands 3.[a]

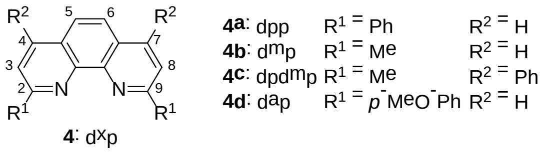
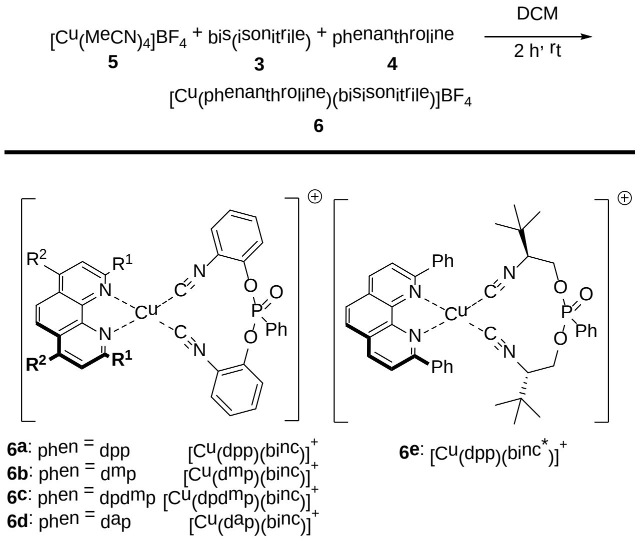


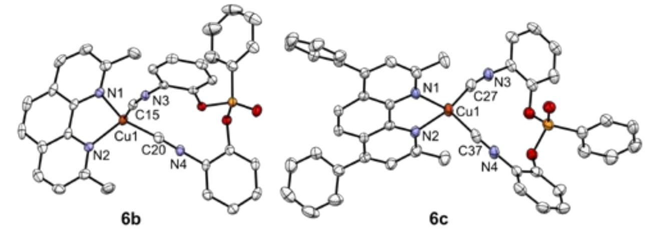
Chart 1. 2,9-diphenyl-1,10-phenanthroline (dpp, 4a); 2,9-dimethyl-1,10-phenanthroline (dmp, 4b); 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (dpdmp, 4c); 2,9-di(*p*-anisyl)-1,10-phenanthroline (dap, 4d).

Single crystals suitable for X-ray analysis of **6b**[19] and **6c**[19] were obtained by vapor diffusion of diethyl ether into dichloromethane solution, which revealed a tetrahedral coordination set up by the two different ligands around Cu(I) with little distortion (Table 1). While the bond distances of Cu to either the phenanthroline or the bisisonitrile ligands are almost the same and in the expected range, the bite angle of the bisisonitrile ligands in both copper complexes are significantly larger (101° and 103°) than the bite angle of a phenanthroline ligand (81-82° in agreement with other literature reports.[11c,14,16]) This should result in increased steric interactions between both ligands upon planarization, which corroborates our hypothesis that the lifetime of the excited state in Cu(I) complexes can be increased by substituting one phenanthroline by one bisisonitrile ligand.



Scheme 2. Preparation of the [Cu(phenanthroline)(bisisonitrile)]$^+$-complexes 6a-e.

Table 1. X-ray structures of [Cu(dmp)(binc)]$^+$ (6b) and [Cu(dpdmp)(binc)]$^+$ (6c).



bond angle [deg]			
N1-Cu1-N2	81.9	N1-Cu1-N2	80.8
C15-Cu1-C20	101.2	C27-Cu1-C37	103.1
Cu1-C15-N3	164.2	Cu1-C27-N3	166.8
Cu1-C20-N4	161.3	Cu1-C37-N4	166.5
dieder angle [deg]			
N1Cu1N2/C15Cu1C20	80.0	N1Cu1N2/C15Cu1C20	84.2
bond length [Å]			
Cu1-N1	2.045	Cu1-N1	2.066
Cu1-N2	2.053	Cu1-N2	2.050
Cu1-C15	1.903	Cu1-C27	1.912
Cu1-C20	1.910	Cu1-C37	1.906

The UV-Vis absorption spectrum of [Cu(dpp)(binc)]$^+$ (**6a**) (Figure 2) displays below 350 nm intense absorptions (e.g. ε(299nm) = $3.9\cdot10^4$ mol dm^3 cm^{-1}), which are assigned to $\pi \rightarrow \pi^*$ transitions of the ligands. At longer wavelengths, a much weaker tail (ε(450 nm) = $5\cdot10^2$ mol dm^3 cm^{-1}) is observed, which is attributed to metal-to-ligand charge-transfer (MLCT) transitions involving an occupied 3d orbital of the copper ion and an empty π^* orbital of the dpp ligand (singlet-singlet d $\rightarrow \pi^*$ transitions). This analysis is in line with other Cu(I) complexes with phenathroline ligands,[11a,21] moreover, the MLCT character of the lowest singlet excited state in [Cu(dpp)(binc)]$^+$ (**6a**) is also supported by the results of TD-DFT calculations (Figure 5).

Luminescence of [Cu(dpp)(binc)]$^+$ (**6a**) was studied in poly(methyl methacrylate) (PMMA). At ambient temperature the complex shows a broad unstructured emission spectrum centered at λ_{em} = 560 nm, with a quantum yield Φ_{PL} of 3 %, accompanied by a decay time τ of 17 µs, which is higher compared to [Cu(dap)$_2$]$^+$ (**1**) (τ = 560 ns in PMMA)[22] by a factor of about 30. Notably, **6a** shows only a very weak emission in dichloromethane, being most likely a result of the greatly prolonged radiative lifetime (570 µs in PMMA, *vide infra*) of **6a** that make non-radiative relaxation the dominating process in solution.[23]

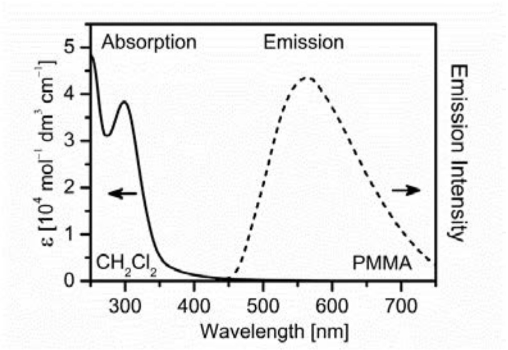


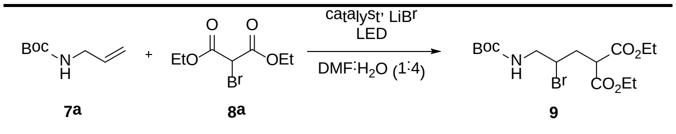
Figure 2. Electronic absorption and luminescence spectra of [Cu(dpp)(binc)]BF$_4$ (**6a-BF$_4$**) at ambient temperature. Absorption spectrum was recorded in CH$_2$Cl$_2$ and emission was measured in poly(methyl methacrylate) (PMMA) respectively. The emission quantum yield Φ_{PL} and lifetime τ (mean lifetime resulting from a biexponential fit of the measured transient) are 3 % and 17 µs, respectively.

Electrochemical measurements reveal the reversible redox behavior at 0.69 V (vs SCE) for the Cu(I)/Cu(II) couple in

[Cu(dpp)(binc)]$^+$ (**6a**). Considering this and the spectroscopic data,[24] a reduction potential Cu(I)*/Cu(II) of –1.88 V (vs SCE) could be appraised. Both values are higher compared to [Cu(dap)$_2$]$^+$ (**1**) (0.62 and -1.43 V vs SCE),[6] and especially the latter in combination with the long decay time makes **6a** promising for applications in photoredoxcatalysis.

Having addressed the synthesis and characterization of the complexes, as well as the spectroscopic and electrochemical properties of [Cu(dpp)(binc)]$^+$ (**6a**), we started to investigate their catalytic activity for visible-light mediated photoredoxcatalysis. As model system we choose the visible-light induced atom transfer radical addition (ATRA) between *N*-boc-allylamine (**7a**) and diethyl-2-bromomalonate (**8a**), for which we previously demonstrated that [Cu(dap)$_2$]$^+$ (**1**) is a capable catalyst upon irradiation at 530 nm (Table 2, entry 1).[7a] Employing only half the catalyst amount (0.5 mol%) of [Cu(dpp)(binc)]BF$_4$ (**6a-BF$_4$**) under otherwise identical conditions gave 87% of the ATRA-product **9** after 20 h, however, shortening the reaction time resulted in a significant decrease of yield (entry 3). Further optimization indicated that the reaction proceeds faster upon irradiation at 455 nm (blue LED), which reduces the reaction time to 7.5 h (entry 4), while also under these conditions [Cu(dap)$_2$]$^+$ (**1**) gave inferior results (entry 2). It should be noted that the absorption spectra of [Cu(dap)$_2$]$^+$ (**1**) and [Cu(dpp)(binc)]$^+$ (**6a**) are very similar (see supporting information) with slightly larger extinction coefficients found for **1** both at 455 and 530 nm. Thus, the higher activity of **6a** with respect to **1** is not a reflection of a more efficient absorption of light but rather of the greatly extended life time of its excited state. No conversion in the presence of **6a-BF$_4$** was observed in the dark (entry 5), and further control experiments omitting catalyst or ligands did not lead to appreciable conversion (entries 6 and 7). As reported for dap **4d**[7a], employing the dpp **4a** alone promotes the reaction, but to a lesser extent than [Cu(dpp)(binc)]BF$_4$ (**6a-BF$_4$**) (entry 8). The bisisonitrile ligand **3b**, however, shows no significant catalytic effect (entry 9).

Table 2. Optimization and control experiment for the visible-light mediated ATRA between boc-allylamine (7a) and diethyl-bromomalonate (8a).[a]



entry	catalyst (mol%)	λ [nm]	time [h]	yield (%)
1[b]	[Cu(dap)$_2$]Cl (**1-Cl**) (1.0)	530	24	75
2	[Cu(dap)$_2$]Cl/BF$_4$ (**1-Cl** or **BF$_4$**) (0.5)	455	7.5	45 / 46
3	[Cu(dpp)(binc)]BF$_4$ (**6a-BF$_4$**) (0.5)	530	7.5 / 20	30 / 87
4	[Cu(dpp)(binc)]BF$_4$ (**6a-BF$_4$**) (0.5)	455	7.5 / 20	88 / 89
5	[Cu(dpp)(binc)]BF$_4$ (**6a-BF$_4$**) (1.0)	–	20	n.r.
6	no catalyst	455	20	3
7	CuBF$_4$ (1.0)	455	7.5	2
8	dpp (**4a**) (0.5)	455	7.5	45
9	binc (**3b**) (0.5)	455	7.5	5
10	[Cu(dmp)(binc)]BF$_4$ (**6b-BF$_4$**) (0.5)	455	7.5	13
11	[Cu(dpdmp)(binc)]BF$_4$ (**6c-BF$_4$**) (0.5)	455	7.5	12
12	[Cu(dap)(binc)]BF$_4$ (**6d-BF$_4$**) (0.5)	455	7.5	78
13	[Cu(dpp)(binc*)]BF$_4$ (**6e-BF$_4$**) (0.5)	455	7.5	88[c]

[a] Conditions: *tert*-butyl allylcarbamate (157 mg, 1.0 equiv., 1.0 mmol), diethyl 2-bromomalonate (0.34 ml, 2.0 equiv., 2.0 mmol), LiBr (174 mg, 2.0 equiv., 2.0 mmol), catalyst, DMF:H$_2$O (1:4) 1 ml, LED-Stick, freeze-pump-thaw (3x), rt; n.r.= no reaction; [b] see ref. [7a]; [c] $[\alpha]_D^{20}$ 0 ° (c = 1 g/100 ml, CHCl$_3$)

Subsequently, we applied the heteroleptic [Cu(phenanthroline)(bisisonitrile)]BF$_4$ complexes **6b-6e** to this reaction using the optimized conditions from entry 3. While the yield was slightly reduced employing dap **4d** as NN-ligand (**6d-BF$_4$**, entry 12), the crucial role of the aryl moiety in 2,9-position of the phenanthroline can clearly be seen by comparing the low yields of product that were obtained with complexes **6b-BF$_4$** and **6c-BF$_4$** (entries 10 and 11). In contrast, the exchange of binc **3b** with its more flexible, chiral version binc* **3a** did not affect the catalytic performance. No asymmetric induction was observed in this reaction (entry 12), albeit **3a** had been proven to be a capable chiral promoter in iron complexes.[17a]

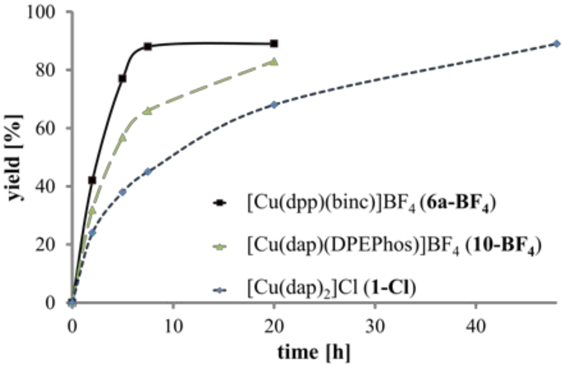


Figure 3. Kinetic study of the visible-light mediated ATRA between boc-allylamine (**7a**) and diethyl-bromomalonate (**8a**). Conditions: *tert*-butyl allylcarbamate (157 mg, 1.0 equiv., 1.0 mmol), diethyl 2-bromomalonate (0.34 ml, 2.0 equiv., 2.0 mmol), LiBr (174 mg, 2.0 equiv., 2.0 mmol), catalyst (0.5

mol%), DMF:H_2O (1:4) 1 ml, LED-Stick (455 nm), freeze-pump-thaw (3x), rt, 7.5 h.

The higher activity of the heteroleptic complex [Cu(dpp)(binc)]BF_4 (**6a-BF$_4$**) compared to the homoleptic copper [Cu(dap)$_2$]Cl (**1-Cl**) was further confirmed by a kinetic study of the title reaction (Figure 3). For comparison, we tested [Cu(dap)(DPEPhos)]BF_4 (DPEPhos: 2,2'-oxybis(2,1-phenylene)bis(diphenylphosphine) (**10-BF$_4$**) for this model reaction to quantify the effect of the bisphosphine vs. the bisisonitrile substitution. Mixed ligand [Cu(phenanthroline)(bisphosphine)]$^+$-complexes have excited state lifetimes of several microseconds and promote photocatalytic reactions effectively.[12,13] Indeed, [Cu(dap)(DPEPhos)]BF_4 (**10-BF$_4$**) is more active than [Cu(dap)$_2$]Cl (**1-Cl**), but did not reach the rate measured for [Cu(dpp)(binc)]BF_4 (**6a-BF$_4$**).

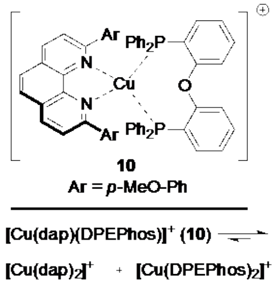
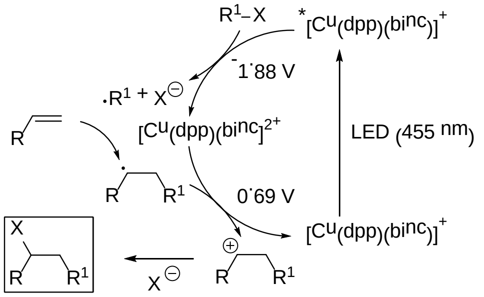


Figure 4. [Cu(dap)(DPEPhos)]$^+$ (**10**) in equilibrium with its homoleptic representatives in solution.

The lower activity of **10-BF4** could be a consequence of the known[25] tendency of heteroleptic copper(I) complexes combining biphosphine with sterically more demanding phenanthroline ligands to form equilibria with their homoleptic representatives in solution that was also observed by NMR for **10** (Figure 4). In contrast, NMR studies revealed a low susceptibility of **6a** to undergo ligand exchange. In conclusion, [Cu(dpp)(binc)]BF_4 (**6a-BF$_4$**) was identified as the most active catalyst, and especially outperforming the up to now best copper catalyst for ATRA reactions [Cu(dap)$_2$]Cl (**1-Cl**) by a factor of at least two, which we attribute to the increased lifetime as well as to the higher reduction potential of its excited state.

The data obtained suggest a mechanistic picture for [*Cu(dpp)(binc)]$^+$ (**6a**) (Scheme 3) that is in agreement with the previously reported mechanism for copper(I)-catalyzed ATRA reactions under visible light irradiation.[16,17] The excited catalyst species transfers an electron to the ATRA reagent following the oxidative quenching cycle. The generated radical adds to the alkene, forming an intermediate which transfers its electron to the Cu(II) species to regenerate the catalyst in a thermodynamically favored process.[26]

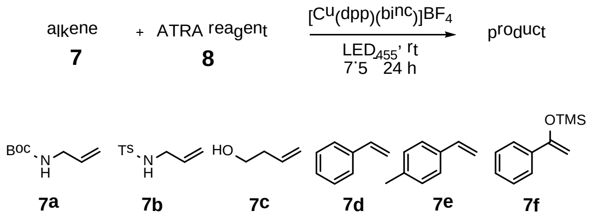


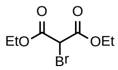
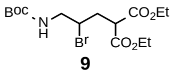
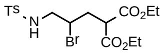
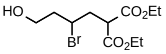
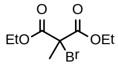
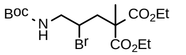
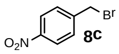
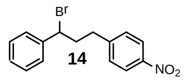
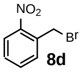
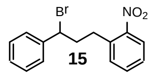
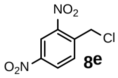
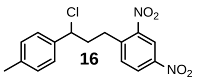
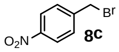
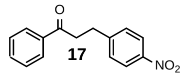
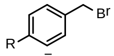
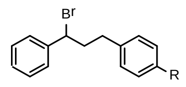
Scheme 3. Mechanistic concept of the Cu(I) catalyzed ATRA under visible-light photocatalysis.

The scope of ATRA reactions catalyzed by [Cu(dpp)(binc)]BF_4 (**6a-BF$_4$**) was evaluated next. The addition of bromomalonate **8a** to different olefins **7a-c** proceeded smoothly with the exception of the sterically more hindered diethyl-2-bromo-2-methylmalonate (**8b**) (Table 3, entries 1-4). Nitro substituted benzylhalides (**8c-e**) cleanly reacted with styrenes **7d,e** or silylenol ether **7f** giving rise to the ATRA products **14-17** in repectable yields (entries 5-8), although steric hindrance in the benzylhalide has a detrimental effect (**8d**, entry 6). Attempts to utilize 4-cyano (**8f**) (entry 9) or 4-methylsulfonyl-benzyl bromide (**8g**) (entry 10) resulted in no conversion of the starting material. The higher reduction potential of the benzyl bromides with less electron withdrawing groups ($E_{1/2}$ = -0.95 V for **8c**, -1.39 V for **8f** and -1.43 V for **8g**; vs SCE in MeCN) apparently prevented the turnover with these substrates, although based on the estimated reduction potential of **6a** (vide supra) we had assumed that this catalyst should be able to activate these substrates.

While the utilization of allyltrimethylsilanes under visible-light photoredox conditions was impressively shown in trifluoromethylation reactions,[27] its use in allylation reactions of organohalides remains challenging. In our previous report we could demonstrate the reaction of allyltributyltin with organohalides under visible light photoredoxcatalyzed conditions, but our attempts using allyltrimethylsilane as ecologically more viable alternative, was met with success only in one example.[7a] We questioned, whether the new copper(I) catalysts could engage in this barley investigated process.

Table 3. Visible-light induced ATRA reactions with [Cu(dpp)(binc)]BF_4 (6a-BF$_4$) as photoredox catalyst



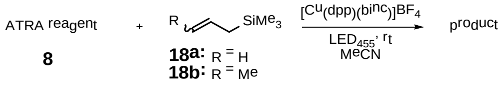
entry	ATRA reagent	alkene	product	yield (%)
1	 8a	**7a**	 9	88
2		**7b**	 11	68
3		**7c**	 12	80
4	 8b	**7a**	 13	29
5	 8c	**7d**	 14	80
6	 8d	**7d**	 15	42
7	 8e	**7e**	 16	70
8	 8c	**7f**	 17	85
9	 8f R = CN	**7d**		n.r.
10	8g R = SO$_2$Me			n.r.

Conditions: entries 1-4: alkene (1.0 mmol, 1.0 equiv.), ATRA reagent (2.0 mmol, 2.0 equiv.), LiBr (2.0 mmol, 2.0 equiv.), [Cu(dpp)(binc)]BF$_4$ (**6a-BF$_4$**) (0.5 mol%), DMF/H$_2$O mixture (0.2 ml / 0.8 ml), blue LED (455 nm), freeze-pump-thaw (3x), rt; entries 5-10: benzyl halide (1.0 mmol, 1.0 equiv.), alkene (5.0 mmol, 5.0 equiv.), Cu(dpp)(binc)BF$_4$ (**6a-BF$_4$**) (1.0 mol%), MeCN (1.0 ml), blue LED (455 nm), freeze-pump-thaw (3x), rt.

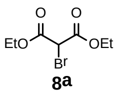
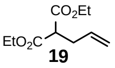
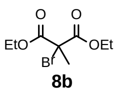
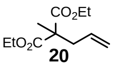
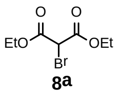
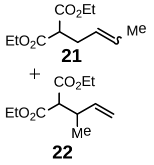
Indeed, we found that 0.5 mol% [Cu(dpp)(binc)]BF$_4$ (**6a-BF$_4$**), 3 equivalents of allyltrimethylsilane (**18a**) in MeCN and irradiation with blue LED for 24 h furnishes the allylated product **19** in 64% yield (Table 4, entry 1). The necessity of both, catalyst and irradiation with visible light was shown by control experiments (entry 2-3). An even higher yield could be obtained for the 2-methyl substituted malonate **8b** (entry 4). Furthermore, we successfully applied 2-butenyltrimethylsilane (**18b**) in this reaction (entry 5), which gave rise to a 84:16 mixture of the linear and the branched isomer **21** and **22** in good yield.

Again, we assume an oxidative quenching cycle, in which the copper catalyst acts as electron shuttle. After irradiation, the excited Cu(I) catalyst **6a** is transformed to its Cu(II) species generating the reactive radical from the organohalide. Upon forming the product, a trimethylsilylradical is released which re-oxidizes the catalyst (Scheme 4).[26]

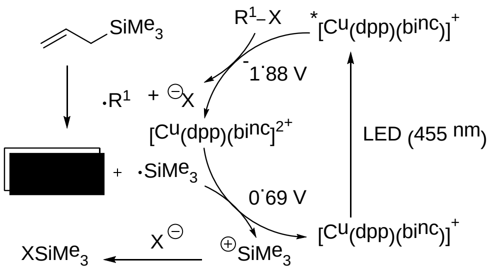
Table 4. Visible-light mediated allylation of organohalides with allyltrimethylsilan and [Cu(dpp)(binc)]BF$_4$ (6a-BF$_4$) as photoredox catalyst.[a]



8
18a: R = H
18b: R = Me

Entry	ATRA reagent	Allylsilane	Product	Yield [%]
1[b]	 8a	**18a**	 19	64
2[c]				n.r.
3[d]				n.r.
4	 8b	**18a**	 20	82
5	 8a	**18b**	 21 + 22 21 : 22 = 84 : 16	80

a) Conditions: halide (0.5 mmol, 1.0 equiv.), allyltrimethylsilane (1.5 mmol, 3.0 equiv.), [Cu(dpp)(binc)]BF$_4$ (**6a-BF$_4$**) (1.0 mol%), MeCN (1.0 ml), blue LED (455 nm), freeze-pump-thaw (3x), rt. b) 0.5 mol% [Cu(dpp)(binc)]BF$_4$ (**6a-BF$_4$**); c) dark reaction; d) without catalyst.



Scheme 4. Proposed mechanism for the visible-light mediated allylation of organohalides with [Cu(dpp)(binc)]BF$_4$ (6a-BF$_4$) as photoredox catalyst.

To gain a deeper understanding of the radiative processes of [Cu(dpp)(binc)]$^+$ (**6a**), we determined the radiative rate $k^r = \Phi_{PL}/\tau \approx 1.8\cdot10^3$ s^{-1} from the measured values $\Phi_{PL} = 3\%$ and $\tau = 17$ µs (Figure 2), which corresponds to a radiative lifetime of $\tau^r = 1/k^r \approx 570$ µs. This large value points to a forbidden character of the emission. The emission decay profile recorded for **6a** in PMMA (Supporting Information) is distinctly non-monoexponential. In particular, significant relaxation processes occurring in the timescale of a few microseconds, e.g. with a time constant of 3.7 µs, dominate the decay behavior and lead to a substantial shortening of the mean excited state lifetime. The latter processes can be assigned to bimolecular quenching processes such as energy transfer and triplet-triplet annihilation, which for extremely long-lived excited states can be effective even at small concentrations. Therefore, the intrinsic radiative rate k^r for **6a** is probably even smaller than the estimate of $1.8\cdot10^3\ s^{-1}$ (consequntly $\tau^r > 570\ \mu s$) based on the mean decay time. Thus, the emitting state is assigned to the lowest triplet state T_1 and the emission of [Cu(dpp)(binc)]$^+$ (**6a**) at ambient temperature represents $T_1 \rightarrow S_0$ phosphorescence. Such an assignment of the emitting state as a triplet state T_1 is, at first glance, surprising, since the ambient temperature emission of numerous copper(I) complexes with phenanthroline-type ligands was demonstrated to represent thermally activated delayed fluorescence (TADF).[11a,21f,28] The latter process involves an emission from the lowest excited singlet state S_1, which is thermally populated from the long-lived triplet state T_1. Since the $S_1 \rightarrow S_0$ transition is spin allowed, the TADF decay times (radiative) of such materials are usually in the order of few to several microseconds, i.e. the TADF lifetimes are much shorter than 570 μs determined for [Cu(dpp)(binc)]$^+$ (**6a**). This discrepancy can be rationalized by a relatively high energy separation between the lowest triplet and singlet excited states $\Delta E(S_1\text{-}T_1)$.

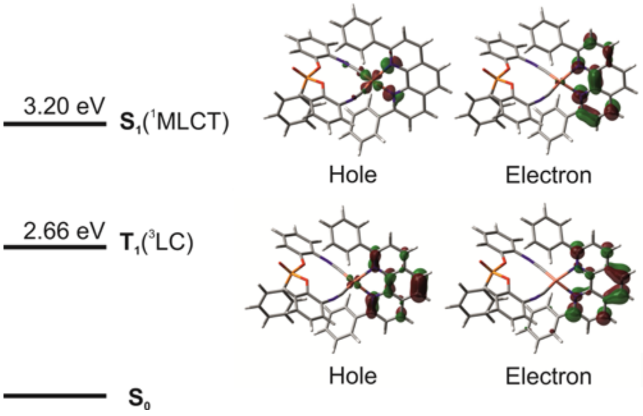


Figure 5. Energy level diagram of the lowest energy excited states of [Cu(dpp)(binc)]$^+$ (**6a**) resulting from the TD-DFT calculations and natural transition orbitals for the lowest excited singlet (S_1) and triplet (T_1) states. Results obtained for the ground-state molecular geometry.

Indeed TD-DFT calculations predict the S_1 state (= ^{1}MLCT) at 3.20 eV and the T_1 state, being a ligand-centered (^{3}LC) excited state localized mainly at the dpp ligand, at 2.66 eV (Figure 5). Thus, the calculated energy difference $\Delta E(S_1\text{-}T_1) = 0.54$ eV, being much larger than the singlet-triplet splitting typically found (0.05 – 0.2 eV) for compounds showing TADF at ambient temperature, is not adequate for efficient S_1 population at 300 K. Accordingly, the excited state behavior of Cu(dpp)(binc)$^+$ (**6a**), in particular luminescence as well as light-induced energy/charge-transfer reactions, is related to the T_1 properties of this compound.

CONCLUSION

In conclusion, we showed the synthesis and characterization of a series of new, bench-stable heteroleptic copper-(phenanthroline)(bisisonitrile)$^+$-complexes. Referring its applicability in visible light-mediated photoredox catalysis we analyzed the spectroscopic and electrochemical properties of [Cu(dpp)(binc)]BF_4 (**6a-BF$_4$**). The correlation between its enhanced excited state lifetime compared to the known [Cu(dap)$_2$]Cl (**1-Cl**) and its catalytic activity could be investigated by a kinetic study. The new complex showed excellent activity in the visible light-mediated atom transfer radical addition as well as in the so far scarcely investigated allylation with trimethylallylsilane under mild visible light conditions.

ASSOCIATED CONTENT

Experimental details. Compound characterization. Electrochemical measurements. X-ray data. NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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

Funding Sources

The authors thank the DFG (GRK 1626, Photocatalysis) and the German Ministry of Education and Research (BMBF) for financial support.

ACKNOWLEDGMENT

We thank Sabine Stempfhuber and Michael Bodensteiner, Universität Regensburg, for carrying out the X-ray crystal structure analysis of **4b**, **6b** and **6c**.

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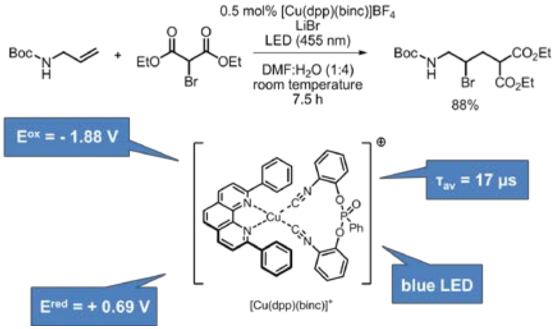
0.5 mol% [Cu(dpp)(binc)]BF$_4$
LiBr
LED (455 nm)
DMF:H$_2$O (1:4)
room temperature
7.5 h
Boc
N
H
+
EtO
OEt
Br
CO$_2$Et
Br
CO$_2$Et
88%
E^{ox} = - 1.88 V
τ$_{av}$ = 17 µs
blue LED
E^{red} = + 0.69 V
[Cu(dpp)(binc)]$^+$