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Structure activated copper photosensitizers for photocatalytic water reduction

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Abstract: A series of phenanthroline-based ligands have been synthesized and their influence as bidentate N ligands in heteroleptic [Cu(P^P)(N^N)]+ photosensitizers in light driven water reduction has been studied. In this noble-metal free Cu-Fe-based photocatalytic water reduction system, the structural effects of these N ligands have been explored, including the steric and electronic effects in the 2, 9 and 4, 7 substituent positions of phenanthroline. Ligands were prepared that showed an increase in hydrogen generation, up to 1388 turnover numbers (TON$_{Cu}$) was observed. All new complexes were electrochemically and photophysically characterized. This report provides the first demonstration that the fluorine effect in N ligand increased the photochemical transfer ability of copper complexes.

Introduction

The development of technologies for the application of sustainable and abundant energy sources remains one of the most important issues of our modern society.[1] In this respect, the use of sunlight for the production of hydrogen from water is a highly desirable option. As the resulting H$_2$ is not carbon based, it could indeed constitute an environmentally benign source of chemical energy.[2] Commonly, approaches focus on the hydrogen half reaction in a first step applying three component photocatalytic systems, consisting of a suitable photosensitizer (PS), a water reduction catalyst (WRC) and a sacrificial electron donor (SR). A key component constitutes the PS; it´s electron transfer efficiency and lifetime of the excited state are crucial regarding costs, productivity and feasibility of hydrogen generation. Since the 1970´s, noble-metal-based complexes including ruthenium,[3] platinum,[4] iridium[5] and rhenium[6] have been successfully employed as PS. However, the high price and toxicity of a number of these metals limit their potential application. In contrast, reports on noble metal-free photosensitizers, e.g., organic dyes[7], biomimetic zinc[8] and magnesium porphyrins

(chlorophyll A)[9] are comparatively scarce due to their low efficiencies and fast photodegradation.

Previously, we reported the successful application of a series of heteroleptic copper (I) complexes possessing the general formula [Cu(N^N)(P^P)]PF$_6$, as photosensitizers.[10] Our recent mechanistic studies demonstrated that the dominant species observed in solution was the heteroleptic complex [Cu(P^P)(N^N)]PF$_6$.[11] Indeed, this was found to be the active PS species, rather than the homoleptic species, [Cu(N^N)$_2$]+ (or [Cu(P^P)$_2$]+), that was only formed initially in very low quantities and, its growth over time was correlated to the reaction rate decay. During optimization studies, the necessity of appropriate ligands in the 2, 9 and 4, 7 positions of the 1, 10-phenanthroline ligand (N^N) for a successful H$_2$ generation became obvious. Especially, substitution in the 2, 9-position was found to have a high impact on rates and catalyst longevities. For example, by switching from n-butyl to sec-butyl and to isobutyl, the PS activity was strongly influenced and TON´s ($_{Cu}$) of 954, 1330 and 224, respectively, were obtained.[10b] Thus, the importance and the influence of the steric hindrance were preliminary demonstrated. Moreover, it was established that without substituents in the 4, 7 positions no H$_2$ generation was detected. However, besides phenyl groups no other groups had tested so far. Considering the importance of these key positions in the CuPS, further investigations have now been performed.

A variety of phenanthroline derivatives containing different substituents in their 2, 9 and 4, 7 positions were synthesized. Using these ligands, the in situ generated heteroleptic copper complexes [Cu(P^P)(N^N)]PF$_6$ (P^P = xantphos (I) and thixantphos (II)) have been tested in the photocatalytic water reduction (Figure 1).[11] In addition, the resulting PS have been photophysically characterized.
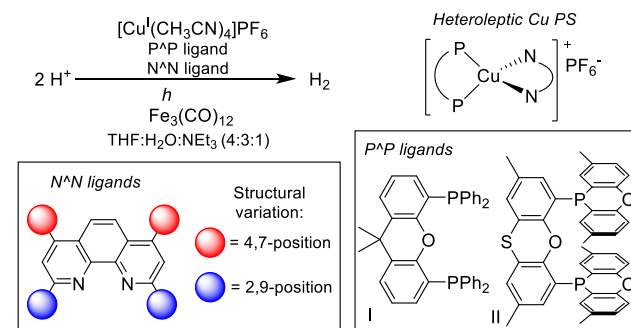
Figure 1. Photocatalytic proton reduction applying in situ generated heteroleptic copper PS and triirondodecacarbonyl as WRC.

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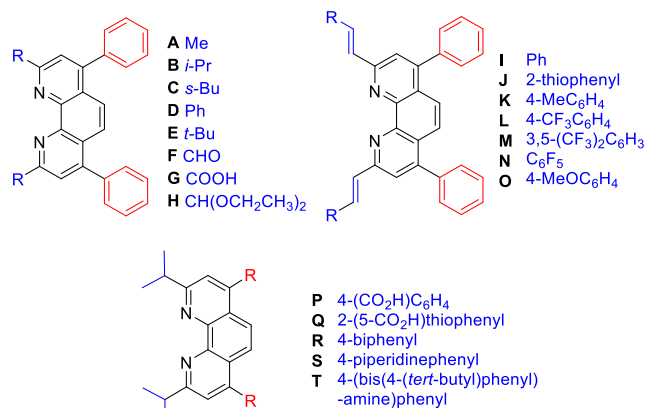
Figure 2. Synthesized 1, 10-phenanthroline derivatives with variations in 2, 9 and 4, 7 positions.

A Me
B i-Pr
C s-Bu
D Ph
E t-Bu
F CHO
G COOH
H CH(OCH$_2$CH$_3$)$_2$

I Ph
J 2-thiophenyl
K 4-MeC$_6$H$_4$
L 4-CF$_3$C$_6$H$_4$
M 3,5-(CF$_3$)$_2$C$_6$H$_3$
N C$_6$F$_5$
O 4-MeOC$_6$H$_4$

P 4-(CO$_2$H)C$_6$H$_4$
Q 2-(5-CO$_2$H)thiophenyl
R 4-biphenyl
S 4-piperidinephenyl
T 4-(bis(4-(*tert*-butyl)phenyl)
   -amine)phenyl

Results and Discussion

In addition to sp^3 substituents in the 2,9 positions, e.g., Me, *i*-Pr, *s*-Bu and *t*-Bu (ligands **A**-**C**, **E**), we were also interested in the potential effect of sp^2 carbon centers. Thus, we synthesized the respective N^N ligands containing phenyl (**D**), aldehyde (**F**) and carboxyl (**G**) groups, as well as a range of aryl vinyl moieties (ligands **I**-**O**) in 2,9 positions with Ph in the 4, 7 positions. Alternatively, ligands bearing different aromatic moieties in the 4, 7 positions (**P**-**T**) with *i*-Pr groups in the 2, 9 positions were prepared. The synthesis methods were varied depending on the desired structures. Ligands **B**-**E** were prepared by reaction of 4,7-diphenyl-1,10-phenanthroline with the corresponding organolithium reagent,[12] while ligands **F** and **G** were obtained by oxidation of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (**A**).[13] Further, ligand **H** was prepared starting from **F** by reaction with triethylorthoacetate.[14] The aryl vinyl phenanthrolines **I**-**O** were synthesized by aldol condensation of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline and aromatic aldehydes catalyzed by acetic anhydride.[15] Ligands **P** and **Q** were synthesized by reaction of 4,7-bis(4-bromophenyl)-1,10-phenanthroline and 4,7-bis(5-bromothiophen-2-yl)-1,10-phenanthroline, respectively, with isopropyl lithium and subsequent quenching by CO$_2$.[16] Ligand **R** was prepared by reaction of 4,7-di ([1, 1'-biphenyl]-4-yl)-1, 10-phenanthroline with isopropyl lithium. Finally, ligands **S** and **T** were synthesized by N alkylation catalyzed by Pd$_2$(dba)$_3$/xantphos between 4,7-bis (4-bromophenyl)-1,10-phenanthroline and piperidine or bis (4-(tert-butyl)phenyl)amine and subsequent treatment with isopropyl lithium.[12, 17] See SI for full details.

Photocatalytic hydrogen production

The heteroleptic copper (I) complexes were obtained by a previously developed in situ method.[11] This allows for the application of optimized ratios of each ligand and copper precursor. The photocatalytic production of H$_2$ was performed for each PS with Fe$_3$(CO)$_{12}$ as WRC and triethylamine as SR in a 4:3:1 (v:v:v) mixture of THF:Et$_3$N:water (Table **1**). Noteworthy, the in situ generated complexes showed the same activity as the molecularly-defined isolated CuPS.[10] Comparing the different

CuPS structures and their productivities in the photocatalytic proton reduction the following was established:

Firstly, the application of thiaxantphos (**II**) resulted in higher or at least equal productivity compared to the respective xantphos containing complexes (Entries 1- 4, 9 and 10). This effect can be attributed to the large planar structure at phosphorous in thiaxantphos and therefore less steric hindrance to the N^N ligand. In contrast, xantphos (**I**) contains rotatable phenyl groups which can interact with substituents in the 2,9-positions of the phenanthroline derivatives. For this reason the thiaxantphos derivative **II** was preferably employed for the subsequent test reactions.

Secondly, comparing the influence of substituents in the 2,9 positions of the N^N ligand an increased bulkiness is beneficial for productivity. This was exemplarily shown for methyl and iso-propyl groups (Entries 2, 4, and 6). On the other hand, a decrease occurred switching from *s*-Bu to phenyl (Entries 6 and 8). In general, the steric bulk of different substituents can be represented by Charton steric parameters. The relationship between the productivity and bulkiness of substituents in the CuPS is provided by diagram in Figure **3**. The volcano plot shows that there is an optimal steric parameter for the CuPS in photocatalytic proton reduction. Furthermore, aldehyde or carboxylic acid moieties in the 2,9-positions completely deactivate the photosensitizer (entries 11 and 12). This may be due to an inhibition of the original coordination of the metal centre to the N^N ligand by competition with oxygen containing functionalities. In contrast, introduction of closely related acetal group resulted in almost the same productivity as the methyl group (Entry 14).

Thirdly, the results applying ligands **I**-**O** (Entries 15-22) illustrate a fine balance between electronic and steric effects is essential. In order to get a rational understanding of electronic effects, the groups attached to the trans olefin was varied (ligands **I**-**O**). This variation is far enough away from the metal centre to not drastically alter the steric environment and so only electronic effects can be measured. By substitution of the phenyl group by thiophene an increase of TON was observed (Entries 15-17). A further increase in the electron withdrawing was achieved by the introduction of a CF$_3$ group and perfluorinated phenyl groups (Entries 19, 21). However, the introduction of two CF$_3$ groups in meta positions lead to decreased TON (Entry 20). In this case, a steric effect likely hampers the PS activity. In contrast, the introduction of electron donating substituents like Me and OMe in the para position resulted either in almost unchanged or lower productivities, respectively (Entries 18 and 22). The influence of various substituents, on the productivity is summarized in Figure **4**. The advantages of strongly electron withdrawing groups can be attributed to a stable excited state, which improves the electron transport efficiency to the water reduction catalyst.

Fourthly, substituents in 4,7 positions also have a significant influence. So far only CuPS containing phenyl groups in these positions were active in the photocatalytic proton reduction. The introduction of a carboxylic acid group into the para position of phenyl had almost no influence. Changing the substituents in the para-position of the phenyl groups from carboxylic acid to phenyl resulted in a slightly decreased TON (Entry 28). However, in this position, piperidine and bis(4-(tert-butyl)phenyl)amine, which were often used as electron donor group in organic dye, lead to a significant decrease of the productivity (Entries 30 and 32). Even more surprising was the substitution of phenyl by thiophene, leading to deactivation of the PS (Entries 23-26). The most probable reason for the latter might be the destabilization of the excited state of CuPS by the good electronic conductivity of the thiophene group.

Additionally, for ligands **P** to **T**, the same trend achieving higher TONs by application of thiaxantphos (**II**) compared to xantphos (**I**) has been obtained (Entries 23, 25, 27, 29, 31).

Table 1. Photocatalytic H_2 production with copper-based photosensitizers by in-situ method in the presence of $[Fe_3(CO)_{12}]$ as WRC and TEA as SR.[a]

Entry	N^N Ligand	P^P ligand[b]	Time(h)[c]	Vol.H_2 (mL)	TON_{Cu}[d]
1	**A**	I	27	33.0	770
2	**A**	II	6	40.7	950
3	**B**	I	17	54.0	1260
4	**B**	II	11	59.5	1388
5	**C**	I	24	54.3	1267
6	**C**	II	11	56.2	1312
7	**D**	I	7	2.7	63
8	**D**	II	6	4.6	107
9	**E**	I	10	9.8	229
10	**E**	II	7	5.6	131
11	**F**	I	4	0.2	-
12	**G**	I	4	0.1	-
13	**H**	I	19	24.3	567
14	**H**	II	7	40.0	934
15	**I**	I	7	5.6	90
16	**I**	II	12	20.3	330
17	**J**	II	11	29.0	470
18	**K**	II	11	19.4	320
19	**L**	II	11	40.6	660
20	**M**	II	7	13.4	220
21	**N**	II	11	27.8	500
22	**O**	II	9	15.7	257
23	**P**	I	20	43.8	1020
24	**P**	II	9	57.0	1330
25	**Q**	I	4	0.8	-
26	**Q**	II	4	0.8	-
27	**R**	I	43	38.9	908
28	**R**	II	6	44.3	1034
29	**S**	I	20	15.1	352
30	**S**	II	9	17.1	399
31	**T**	I	10	16.2	378
32	**T**	II	7	18.1	423

[a] Reaction conditions: N^N ligand (3.5 µmol), P^P ligand (3.5 µmol), $Cu(MeCN)_4PF_6$ (3.5 µmol), $[Fe_3(CO)_{12}]$ (5 µmol) (Among them ligand G-M (5.0 µmol), P^P ligand (5 µmol), $Cu(MeCN)_4PF_6$ (5 µmol)), 10 mL THF/TEA/H_2O(4:3:1), 25 °C, Xe-light irradiation (output 1.5 W), without light filter, gas evolution quantitatively measured via manual gas burettes, gas analysis via GC. All given values are the averages of at least two experiments. The results differ between 1 and 18%. [b] See figure 1, I = xantphos, II = thixantphos derivative. [c] Time until no further H_2 evolution was observed. [d] TON_{Cu} = nH/nCu rounded to nearest 10.
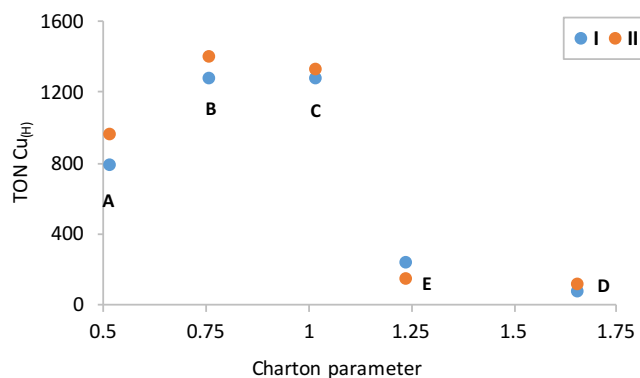

Figure 3. Charton parameters and productivities of CuPS containing ligands **A**-**E**. Charton parameters taken from ref 18a.
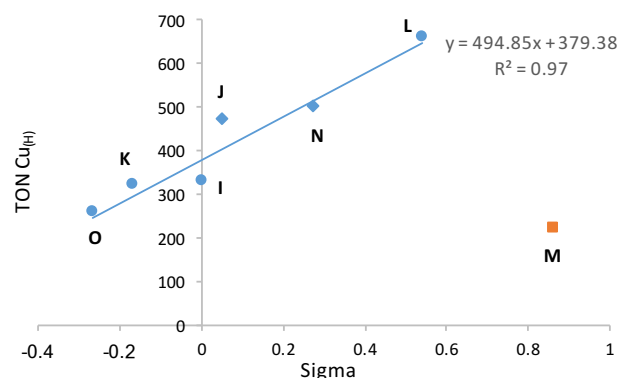

Figure 4. Hammett plot for the productivity of CuPS containing ligands **I**-**O** (Entries 16-22) Hammett values taken from ref 18b. Estimated values used for **M** (3,5-CF_3, σ_m doubled), **J** (2-thiophenyl, as σ_p) and **N** (C_6F_5, as σ_p).

Photophysical studies

For a deeper insight of the effect of structure on the productivity of the CuPS, UV-vis absorption and photoluminescence spectra were recorded. For these measurements, ligands **B**, **H**, **I**, **J**, **L**, **O**, **P**, **Q**, **R**, **S** and phosphine **II** were selected.

The copper photosensitizers were self-assembled by our in situ method.[11] The corresponding data are summarized in Table **2**. All complexes showed absorption in the UV region with a typical absorption band around 380 nm (Figure **5**) contributing to a MLCT transition from a copper d-orbital to the π* of the N^N ligands.[19] A small band in the proximity of 450 nm was found, which probably arises from the formation of the homoleptic complex, $[Cu(N^N)_2]PF_6$ due to the ligand redistribution in solution that has been previously described for these kind of systems.[20] Compared to the other complexes, Cu(**J**)(**II**) complex containing thiophene showed a more efficient absorption peak from 350nm

to 450nm, as thiophene is a good chromogenesis group.[21] In addition, CuPS containing ligands **I**, **J**, **L** and **O** possessed a significantly stronger absorption ability (Figure 5). This might be due to the elongated conjugated π-system formed by the aryl or thiophene, the vinyl group and the phenanthroline derivative. The comparison of the absorption maxima wavelengths revealed that increasing the degree of conjugated π-system of the N^N scaffold resulted either in a blue- (ligands **L**, **O**, **R**; table **2**, entries 5, 6, 8), red-(ligand **P**, Entry 7) or no significant shift (Ligand **J**, Entry 4) of the absorption bands of the respective CuPS compared to the ligands **B** and **H** (Entries 1 and 2).

The emission spectra of selected photosensitizers are shown in Figure **6**. The maximum emission wavelengths are located around 450 nm. A comparison of the emission maxima (λ_{max}) reveals the same systematic trend upon changing the aryl or thiophene substituents at the 2,9-positions of the N^N ligands in both series of complexes **I-O**. Electron withdrawing groups at the 2,9-positions of the N^N scaffold results in a blue-shift of the emission bands ($\triangle$**J-L**=28 nm), which means higher energy emissive states and a smaller energy difference between the absorption and emission maxima. The photoluminescence intensity of copper complex containing ligand **L** is much higher than those containing ligands **I** and **J**. This can be attributed to the effect of fluorine, being a strong electron withdrawing group which can enhance the photoluminescence intensity.[22] Compared to the other complexes, carboxylic acid containing ligand **P** showed a significant red-shift of the emission band. This is probably a result of the strong electron withdrawing property of the carboxylic acid group. Although CuPS bearing ligand **Q** showed more visible light absorption compared to ligand **P**, its luminescence is almost totally lost. A transient fluorescence test confirmed that by applying ligand **Q**, the lifetime of CuPS is decreased to 200 ns, which is much less than 2 µs for Cu(**P**)(II) (see supporting information).

Table 2. Electronic absorption and luminescence data for different [Cu(N^N)(P^P)]PF$_6$ complexes in degassed CH$_2$Cl$_2$ at room temperature.[a]

Entry	Cu(N^N)(P^P)	Abs λmax (nm)	Abs ε(M⁻¹cm⁻¹)	Em λmax (nm)	Φ
1	Cu(**B**)(**II**)	389	1628.6	446	0.13
2	Cu(**H**)(**II**)	387	2571.4	414	0.07
3	Cu(**I**)(**II**)	-	-	440	-
4	Cu(**J**)(**II**)	388	27414.3	462	0.02
5	Cu(**L**)(**II**)	371	30085.7	434	0.27
6	Cu(**O**)(**II**)	376	16828.6	452	0.08
7	Cu(**P**)(**II**)	394	6142.9	550	0.07
8	Cu(**Q**)(**II**)	392	4514.3	525	0.01
9	Cu(**R**)(**II**)	379	4257.1	467	0.37
10	Cu(**S**)(**II**)	-	-	455	-

[a] conditions: N^N ligand (1.75 µmol), P^P ligand (1.75 µmol), Cu(MeCN)$_4$PF$_6$ (1.75µmol) formed copper photosensitizers by in-situ method in CH$_2$Cl$_2$, then move to 50mL Volumetric flask.

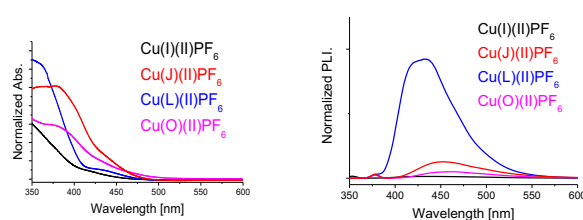Figure 5. Normalized absorption and Emission spectra for Cu (**I**)(**II**)PF$_6$, Cu(**J**)(**II**)PF$_6$, Cu(**L**)(**II**)PF$_6$, Cu(**O**)(**II**)PF$_6$. Measurements made in CH$_2$Cl$_2$ at room temperature.
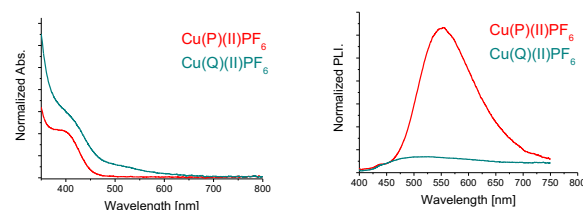

Figure 6. Normalized absorption and Emission spectra for Cu(**P**)(**II**)PF$_6$, Cu(**Q**)(**II**)PF$_6$. Measurements made in CH$_2$Cl$_2$ at room temperature.

Electrochemical studies

Cyclic voltamograms of copper complexes containing phenanthroline ligands **I**, **J**, **L**, **B**, **O**, **R** and phosphine ligand **II** were recorded in THF solution (Figure 7). Upon reduction, all of the complexes display comparable behaviour, with a reversible single-electron-reduction couple, which is associated with a reduction of the phenanthroline ligand, thus forming [Cu^{II}(N^N)$^{\cdot-}$(P^P)]$^+$. This behaviour is known from previous studies of related [Cu(N^N)$_2$]$^+$ complexes.[23] Comparing the reduction potentials of complexes **I** (-1.63V) and **J** (-1.74V versus Fc/Fc$^+$) or **L** (-1.60V) and **O** (-1.70V versus Fc/Fc$^+$), a shift of about 90 mV or 100 mV is observed, thus indicating an influence of the substitution pattern at the 2,9-positions of the phenanthroline scaffold that correlates with Hammett parameters. Complexes **B** and **R** also indicate an influence of the substitution pattern at the 4,7-positions. They all appear at more negative potentials than the reduction peak of the WRC. However, so far no correlation between CV results and the productivity in proton reduction could be detected.
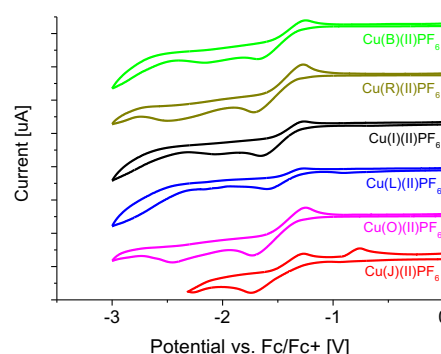

Figure 7. Cyclic voltammograms of complexes Cu(**I**)(**II**)PF$_6$, Cu(**J**)(**II**) PF$_6$, Cu(**L**)(**II**) PF$_6$, Cu(**B**)(**II**) PF$_6$, Cu(**O**)(**II**) PF$_6$, Cu(**R**)(**II**) PF$_6$ in THF solution. All potentials are referenced to the Fc/Fc$^+$ couple.

Conclusions

In summary, we have synthesized a range of new copper complexes containing several new phenanthroline-based ligands by an in situ method. The complexes have been tested as photosensitizers in light driven proton reduction from water and characterized by spectroscopic, photo-physical and electrochemical techniques. The effect of the steric features of the N^N ligands were investigated by varying substituents in the 2,9 and 4,7 positions. Interestingly, the 2,9 positions are very sensitive to steric bulk, and electron withdrawing groups in this position increased the productivity. For 4,7-positions phenyl groups are of fundamental importance. Analysis of the photo-physical properties revealed a strong emission in solution. The copper PS exhibited a significant hydrogen generation ability if applied together with an iron-based WRC. A maximum turnover number (TON$_{Cu}$) of 1388 was achieved in this noble metal free system.

Experimental Section

Materials and Synthesis. All reagents and solvents were commercially available and used as received without further purification.

Synthesis of ligands **B-E**. N^N ligands B-E were synthesized according to a literature procedure.[12]

Synthesis of ligand **F**. A stirred solution containing 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (0.5 g, 1.4 mmol) and selenium dioxide (0.375 g, 3.4 mmol) in 10 mL of dioxane was heated at 80 °C in a sealed tube under an argon atmosphere for 2 h. After the reaction was finished the, mixture turned dark orange. Filtration, concentration and purification of the orange organic phase by crystallization at 4 °C gave yellow solid, yield 85 %.[13]

Synthesis of ligand **G**. A mixture containing ligand F (0.2 g, 0.52mmol) and 10 mL of hydrogen peroxide was stirred at 80 °C for 8 h. Filtration, concentration and purification of the orange organic phase by crystallization gave yellow solid, yield 80 %.[13]

Synthesis of ligand **H**. A stirred mixture of ligand F (0.2 g, 0.52mmol), p-toluene sulfonic acid, 10 mL ethanol and 15 mL the triethylorthoacetate were refluxed at 100 °C for 8 h under an argon atmosphere. Filtration, concentration and purification of the orange residue by flash column chromatography (1:4 EA/PE) give light yellow solid, yield 87 %.[14]

Synthesis of ligand **I-O**. The N^N ligands (I-O) were synthesized according to a literature procedure.[15] A mixture of BCP and arylcarboxaldehyde or thiophene-2-carbaldehyde (6 equiv) in acetic anhydride was refluxed for 5-16 h. The cooled reaction mixture was poured into menthol/water to give a solid. The solid precipitate was filtered off, solved in dichloromenthane and extracted with water in a separating funnel. The organic phase was washed with deionized water, dried over anhydrous magnesium sulphate and evaporated. The resulting yellow and brown solids were found to be stable under air and moisture and were obtained in moderate yields (50-68 %).

Synthesis of ligand **P** and ligand **Q**. The N^N ligands P and Q were synthesized according to a literature procedure.[16]

Synthesis of ligand **R**. A mixture of 4,7-di([1,1'-biphenyl]-4-yl)-1,10-phenanthroline (0.2 g, 0.41 mmol) and 5 mL of dry ether was stirred in a sealed tube under an argon atmosphere, and isopropyl lithium (1.3 mL, 2.05 mmol) was added at 0 °C. The resulting suspension was further stirred at o °C for 30 min then at room temperature for 12 h. The reaction was quenched with water (10 mL) Then, the mixture was extracted with EtOAc (4×10 mL) and dried over MgSO$_4$.. Filtration, concentration and purification of the orange residue by flash column chromatography (1:4 EA/PE) gave a pale yellow solid, yield 56 %.[12]

Synthesis of ligand **S**. Step 1: A stirred solution of 4,7-bis(4-bromophenyl)-1,10-phenanthroline (0.3 g, 0.61 mmol), Pd$_2$(dba)$_3$ (52.8 mg, 0,06 mmol), xantphos (54 mg, 0.12 mmol), t-BuOK (0.32 g, 3.66 mmol) and piperidine (0.24 g, 3.66 mmol) in 10 mL of toluene (dry) were refluxed at 120 °C for 24 h. Filtration, concentratio and purification of the orange residue by flash column chromatography (EA) gave an orange solid (4,7-bis(4-(piperidin-1-yl)phenyl)-1,10-phenanthroline), yield 82%. Step 2: A mixture of 4,7-bis(4-(piperidin-1-yl)phenyl)-1,10-phenanthroline (0.2 g, 0.4 mmol) and 5 mL of dry ether were stirred in a sealed tube under an argon atmosphere and isopropyl lithium (1.2 mL, 2.0mmol) was added at 0 °C. The resulting suspension was stirred for 30 min at 0 °C and for 12 h at room temperature. The reaction was quenched with water (10 mL) and the mixture was extracted with EtOAc (4×10 mL) and dried over MgSO$_4$. Filtration, concentration and purification of the orange residue by flash column chromatography (1:4 EA/PE) gave an orange solid. The yields were 42 % for ligand **S**. [12, 17]

Synthesis of ligand **T**. Using the same method of synthesis of ligand **S**, the yield of ligand **T** was 34 %.

Photocatalytic proton reduction. A double-walled thermostatically controlled reaction vessel is evacuated and purged with argon. The N^N ligands, P^P ligands, Cu(MeCN)$_4$PF$_6$ and [Fe$_3$(CO)$_{12}$] are added as solids. The corresponding solvent mixture (THF/TEA/H$_2$O, 4:3:1) is added and the system is taken to 25 °C before switching on the light source. It is then stirred at 25 °C until no further gas evolution is observed. All given values are the averages of at least two experiments. The results differ between 1 and 19 % except for volumes < 10 mL (up to 45 %).

Photoluminescence Spectroscopy. General Methods. Absorption spectra were recorded using a 50 Conc (VARIAN) UV-vis spectrometer. Luminescence spectra were measured with a spectrofluorometer (F-4600, 5J2-004, HITACHI). The luminescence quantum yields were determined relative to quinine bisulfate (Aladdin. Co) in 0.1 M sulfuric acid (Aladdin. Co) as quantum yield standard (Φ = 0.53).

Electrochemical Measurements. General Methods. All studies were performed at room temperature in dried THF p. A. (VWR) under Argon atmosphere with 0.1 M Tetrabutylammoniumhexafluorophosphat: ([Bu4N]PF$_6$) as conducting salt using an Autolab (PGSTAT 128N, Metrohm). Working electrode was a glassy carbon disk electrode (d=2 mm), the counter electrode a Pt-electrode and the reference electrode an Ag/AgNO$_3$ sat. All the potentials were measured with regard to this reference system and were checked by using the ferrocen/ferrocenium internal reference system. The cyclic voltammetry scans were done two times at a scan rate of 100 mVs^{-1}. Concentrations of 0.1 mM analyte were used for the measurements.

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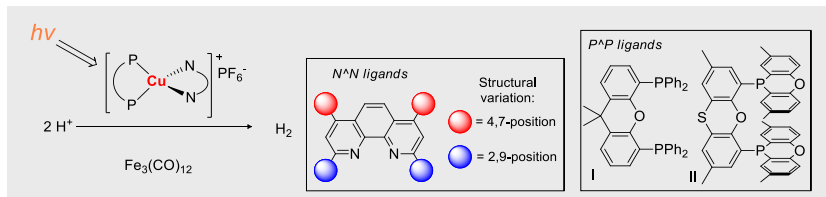
A series of phenanthroline-based ligands have been synthesized and their heteroleptic [Cu(P^P)(N^N)]⁺ photosensitizers in light driven Cu-Fe-based water reduction has been studied. In this noble-metal free system, the structural effects of these N ligands have been explored, including the steric and electronic effects in the 2, 9 and 4, 7 substituent positions of phenanthroline. This report provides the first demonstration that the fluorine effect in N ligand increased the copper.