CHEMISTRY
A EUROPEAN JOURNAL

ChemPubSoc
Europe

DOI: 10.1002/chem.201302091

A Noble-Metal-Free System for Photocatalytic Hydrogen Production from Water

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Abstract: A series of heteroleptic copper(I) complexes with bidentate $\widehat{PP}$ and $\widehat{NN}$ chelate ligands was prepared and successfully applied as photosensitizers in the light-driven production of hydrogen, by using $[Fe_3(CO)_{12}]$ as a water-reduction catalyst (WRC). These systems efficiently reduces protons from water/THF/triethylamine mixtures, in which the amine serves as a sacrificial electron donor (SR). Turnover numbers (for H) up to 1330 were obtained with these fully noble-metal-free systems. The new complexes were electrochemically and photophysically characterized. They exhibited a correlation between the lifetimes of the MLCT excited state and their efficiency as photosensitizers in proton-reduction systems. Within these experiments, considerably long excited-state lifetimes of up to 54 μs were observed. Quenching studies with the SR, in the presence and absence of the WRC, showed that intramolecular deactivation was more efficient in the former case, thus suggesting the predominance of an oxidative quenching pathway.

Keywords: copper · homogeneous catalysis · hydrogen · photochemistry · sustainable chemistry

Introduction

In the search for sustainable and abundant energy sources as alternatives to the current fossil-fuel-based paradigm, sunlight appears to be the most appealing candidate because it bathes the Earth with an amount of energy that is about 10000 times larger than the amount that is required by human technologies.[1] Although photovoltaic devices directly convert solar energy into electricity, the latter cannot be efficiently stored as such and the systems can only operate during the daytime. To circumvent these drawbacks, efficient ways of storing this energy in suitable secondary energy carriers are desirable.[2]

Starting in the 1930s, when it was suggested that hydrogen derived from water splitting could be used as fuel for transportation, the idea of changing the energy scheme of oil-dependence into a "hydrogen economy"[3] is coming to maturity. Although the infrastructure for a hydrogen-based energy system is still under development,[4] it is foreseeable that, for hydrogen to succeed as an energy commodity, it should be produced in a sustainable, economical, and environmentally friendly manner, for which artificial photosynthesis is a feasible way to go.[5] The concept of artificial photosynthesis encircles those processes, biomimetic or not, in which solar energy is harvested and stored in the form of chemical bonds of highly energetic molecules, known as solar fuels.[6]

Currently, most homogeneous proton-reduction reactions are carried out by using three-component systems that consist of a light-harvesting chromophore or photosensitizer (PS), a water-reduction catalyst (WRC), and an electron donor or sacrificial reductant (SR).[7] Arguably, the photosensitizer can be considered as the bottleneck of the whole system. Since the beginning of this research field in the 1970s,[8] ruthenium complexes have played a key role,[9] although a plethora of compounds based on other noble metals, including iridium,[10] platinum,[11] and rhenium,[12] have also been successfully employed. In contrast, efficient noble-metal-free photosensitizers are still rare. Biomimetic iron-,[13] zinc-,[14] and magnesium-based[15] systems have been thoroughly investigated, albeit the reported activities are still low.

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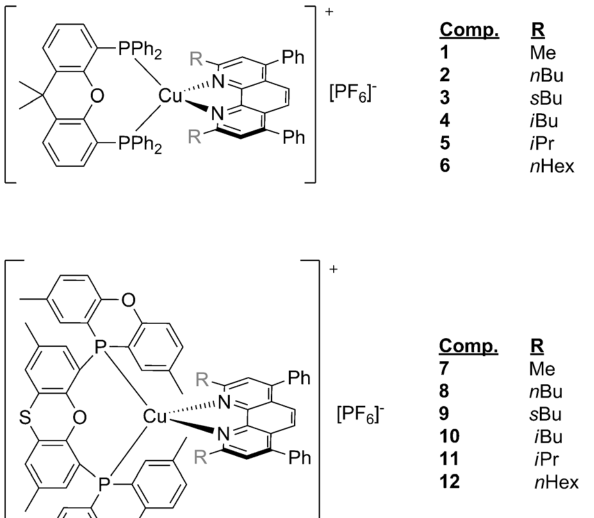
Supporting information for this article, including experimental information on the synthesis and characterization of the copper complexes, general conditions and detailed information on the photophysical, electrochemical, and X-ray measurements and the photocatalytic reaction conditions, is available on the WWW under http://dx.doi.org/10.1002/chem.201302091.

The potential application of copper(I) complexes with polypyridine ligands as photosensitizers has been long overlooked, although their photo- and electrochemical properties are widely known, having found successful use in organic light-emitting diodes (OLEDs), light-emitting electrochemical cells (LECs), sensors, dye-sensitized solar cells (DSSCs), etc.[16] In an early communication, the group of Sauvage reported the use of homoleptic copper(I) complexes with bipyridyl ligands for the photochemical reduction of water by using platinum (supported on titanium dioxide) as a WRC, with, in the best case, an overall turnover number of 80 moles of H_2 per mole of copper.[17]

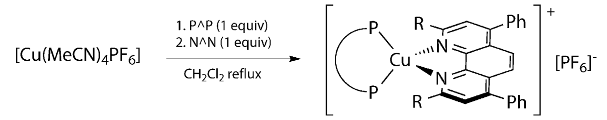
In a recent communication, we reported the successful use of a series of heteroleptic copper(I) complexes with the general formula $[Cu(\widehat{NN})(\widehat{PP})]PF_6$ as photosensitizers in photocatalytic proton-reduction systems with TON_H up to 804 by using $[Fe_3(CO)_{12}]$ as the water-reduction catalyst.[18] Herein, we report an improved system in which turnover numbers ($TON_H = n\text{H}/n\text{Cu}$, or the number of equivalents of H^+ that are reduced by one equivalent of copper) of up to 1330 were obtained. Selected complexes were characterized by using photophysical and electrochemical methods and some insights into the reaction mechanism were gained. This system is, to the best of our knowledge, the most efficient noble-metal-free homogeneous system for the photocatalytic reduction of protons reported to date.

Results and Discussion

Synthesis and structural characterization of the copper photosensitizers: All of the copper(I) complexes (Scheme 1) were synthesized from $[Cu(MeCN)_4]PF_6$ by using a straightforward one-pot tandem ligand-substitution method, according to a previously reported procedure (Scheme 2).[18] The complexes were obtained as yellow-to-orange solids that were stable to ambient conditions (air and moisture).



Scheme 1. General structure of the copper(I) photosensitizers in this work.



Scheme 2. General synthetic procedure of copper complexes **1**–**12**.

X-ray diffraction analysis of complexes **4** and **6** (Figure 1) revealed a distorted tetrahedral geometry around the metal center, as previously observed for this kind of compounds.[16b] This distortion mainly arises from the considerable differences in the bite angles of the bidentate $\widehat{PP}$ and $\widehat{NN}$ ligands (for complex **4**: N1-Cu-N2 80.04(7)°, P1-Cu-P2 118.70(2)°) and also from interligand interactions. This distortion is clearly reflected in the difference between the angles that are formed by the plane of the $\widehat{NN}$ ligand with each of the phosphorus atoms: In the isobutyl derivative (**4**), these angles are 91.97° and −130.02°, whereas, in the *n*-hexyl analogue (**6**), these angles are 78.66° and −60.84°. In the former case (**4**), this huge difference renders one side of

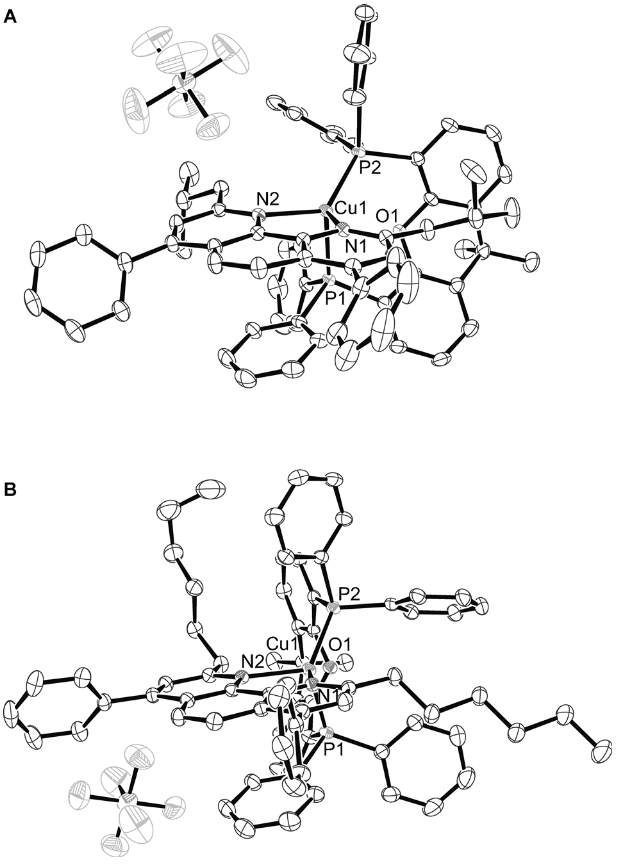


Figure 1. Solid-state molecular structures (ORTEPs) of complexes **4**·$(CH_2Cl_2)_{3.8}$ (A) and **6**·$(CH_2Cl_2)_{2.3}$ (B), as determined by X-ray crystallography. Displacement ellipsoids are set at 50 % probability. Hydrogen atoms and solvent molecules are omitted for clarity.[19]

the molecule more "open", which means that the copper atom is more exposed to a possible nucleophilic attack. This result is an example of the so-called "rocking distortion" of tetrahedral towards trigonal-pyramidal coordination geometries,[16e] in which the P1 atom occupies the apical position and the P2 atom occupies an equatorial position. This effect is less pronounced in the latter case (**6**) and could (among other factors) account for the differences in their photocatalytic performance, as discussed below.

Whereas the phenanthroline moiety remains structurally unaltered upon coordination, the diphosphine scaffold suffers considerable distortion. In free 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos), the angle between the planes that contain the two aromatic rings (those that are connected by the oxygen atom) is only 18.2° (for the X-ray structure of the ligand, see the Supporting Information, Figure SI1). Conversely, in complex **4**, this interplanar angle is 36.9°, whereas, in complex **6**, it is 30.3°. This result again reflects the higher steric demand of the isobutyl substituents on the $\widehat{NN}$ ligand in comparison with the *n*-hexyl chains.

In spite of these structural distortions, which could also arise from crystal-packing effects, NMR analysis of all of the complexes (^{1}H, ^{13}C, and ^{31}P NMR) shows relatively simple patterns, which is more in agreement with C_{2v} symmetry. These observations suggest a fluxional behavior in solution (at room temperature), which makes, for instance, both phosphorus atoms equivalent on the NMR timescale.

Photophysical studies: Electronic absorption and photoluminescence spectra were measured for a representative selection of copper photosensitizers, namely complexes **1**, **2**, **3**, **7**, **8**, and **9**. The corresponding data are summarized in Table 1. As observed for other Cu^I complexes of the general formula $[Cu(\widehat{NN})(\widehat{PP})]^+$, the absorption bands that are attributed to low-lying MLCT (metal-to-ligand-charge-transfer) transitions occur at higher energies than those of the homoleptic $[Cu(\widehat{NN})_2]^+$ complexes.[16a,e] These bands (located at about 390 nm) showed no significant shifts on changing either the diphosphine scaffold or the substituents at the 2,9-positions of the phenanthroline ligand (Figure 2), from which it can be concluded that the ground-state orbital energies are comparable in all the cases. Absorption and emission spectra of the different copper photosensitizers were also measured in MeCN (see the Supporting Information, Figure SI8), which showed, in general, only a small solvent effect.[20]

Table 1. Electronic absorption and luminescence data for different $[Cu(\widehat{NN})(\widehat{PP})]PF_6$ complexes in degassed THF at room temperature.

Entry	Complex	Absorption		Emission			
		λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]	λ_{max} [nm]	Φ_{abs}[a]	τ_0 [µs][b]	$\tau_{cat.}$ [ns][c]
1	**1**	389	5701.9	569	0.08	(6.4±0.1)	180
2	**2**	389	5838.5	565	0.27	(15.6±0.1)	130
3	**3**	387	4848.9	546	0.75	(54.1±0.6)	440
4	**7**	386	5432.7	545	0.05	(16.3±0.1)	90
5	**8**	389	4810.2	535	0.34	(40.3±0.4)	180
6	**9**	386	4215.6	518	0.52	(51.2±0.5)	82

[a] The quantum yield was measured at an optical density of about 0.1 (error: about 10%). [b] The lifetimes were measured in dilute solution with an optical density of about 0.1, 0.02 mM (388 nm). [c] The lifetime was measured under comparable catalytic conditions: 0.35 mM copper PS, 0.5 mM $[Fe_3(CO)_{12}]$ (reduction catalyst), in a mixture of THF/triethylamine/water (4:1:1).

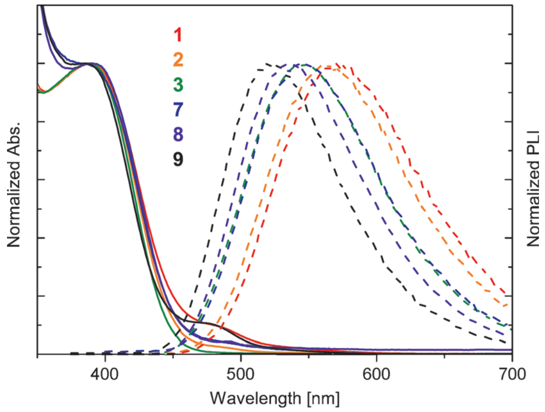


Figure 2. Normalized absorption (solid lines) and emission spectra (photoluminescence intensity (PLI), dashed lines) for different copper(I) photosensitizers. Measurements were made in THF at room temperature.

An interesting feature in some of the absorption spectra is the growth of a small band in the proximity of 480 nm, which probably arises from the formation of the homoleptic complexes,[21] $[Cu(\widehat{NN})_2]PF_6$, owing to the ligand-redistribution equilibrium in solution, as observed previously for this kind of system.[16e] It is important to note that this band is more prominent for complex **9**, which has the most sterically demanding $\widehat{NN}$ ligand, thus enabling more-effective ligand dissociation and redistribution.

Strong room-temperature photoluminescence is exhibited by all of the complexes, which is caused by the deactivation of the MLCT excited states (Figure 2 and Table 1). A comparison of the emission maxima (λ_{max}) reveals the same systematic trend upon changing the alkyl substituents at the 2,9-positions of the $\widehat{NN}$ ligands in both series of complexes **1**–**3** and **7**–**9**. Increasing the bulkiness at the 2,9-positions of the $\widehat{NN}$ scaffold results in a blue-shift of the emission bands (Δ**1**–**3**=23 nm and Δ**7**–**9**=27 nm), which means higher-energy emissive states and a smaller energy difference between the absorption and emission maxima. This kind of hypsochromic ligand effect, as previously observed in homoleptic[20,22] and heteroleptic[16a,e] cuprous phenanthroline derivatives, reflects the effectiveness with which the Jahn–Teller (flattening) distortion of the initially populated Franck-Condon excited state is hindered. Because the energy of the MLCT state depends on the dihedral angle between the ligands and the potential-energy surface presents a local maximum at 90°, conservation of the tetrahedral geometry results in a larger energy gap between the ground and excited states and, hence, higher emission energies.[22]

The steric effects of the ligands also have a profound influence on the excited-state dynamics of the corresponding complexes, as reflected in the lifetime (τ_0) of the emissive MLCT state and in the quantum yield (Φ_{abs}), thus exhibiting unprecedentedly high values of up to 54.1 μs and 74.5 %, respectively (for complex **3**; Table 1, entry 3). These high values are more astonishing considering the fact that the measurements were performed in THF, which, as a Lewis base, can typically act as an additional ligand.[23]

These results reflect the effective shielding of the metal core that is imparted by the bulky ligands. For both properties, τ_0 and Φ_{abs}, the same trend is observed within series of complexes **1**–**3** and **7**–**9** (that is: **1** < **2** < **3** and **7** < **8** < **9**) and, not surprisingly, it is derived from the ability with which the flattening distortion of the cupric excited state is inhibited (perfectly correlated with the bulkiness of the substituents: Me < *n*Bu < *s*Bu). Under catalytic conditions (with a higher concentration of PS and in the presence of TEA and water), much shorter lifetimes (τ_{cat}, Table 1) were observed (see below).

Upon excitation, the formally 3d^9 metal center tends to adopt a pseudo-square-planar geometry with two open coordination positions in which one or two solvent molecules can coordinate to form an exciplex intermediate.[23] This species has a smaller energy gap to the ground state and, consequently, the non-radiative decay pathway is favored; thus, short lifetimes of the MLCT state are observed.[24] Effective inhibition of this process, as in our case, leads to long-lived excited states (with high-energy levels), along with high quantum yields. The experimentally measured lifetimes (τ_0) and quantum yields (Φ_{abs}, Table 1) were used to calculate the radiative (k_r) and non-radiative rate constants (k_{nr}) of the MLCT excited states (see the Supporting Information, Table SI1).[25] The obtained k_r values are typical of heteroleptic copper complexes with phenanthroline and diphosphine ligands.[21] Conversely, the obtained k_{nr} values are up to three orders of magnitude smaller than those for homoleptic phenanthroline complexes,[26] which indicates that the non-radiative decay is much slower and accounts for the relative long lifetimes of the excited states, thus fulfilling one of the prerequisites for a complex to be a successful photosensitizer for solar-energy-conversion systems.

Electrochemical studies: For complexes **1**, **3**, and **7**, cyclic and differential pulse voltammograms were recorded in MeCN solution (Figure 3 and Table 2). Upon reduction, all of the complexes display comparable behavior, with a reversible single-electron-reduction couple. This peak is associated with a reduction of the phenanthroline ligand and, thus, with the formation of $[Cu^{II}(\widehat{NN})^{\bullet-}(\widehat{PP})]^+$. This behavior is known from previous studies of related $[Cu(N\hat{}N)_2]^+$ complexes.[21] Comparing the reduction potentials of complexes **1** (−2.05 V) and **3** (−2.12 V versus Fc/Fc$^+$), a shift of about 70 mV is observed, thus indicating an influence of the substitution pattern at the 2- and 9-positions of the phenanthroline scaffold. In contrast, the influence of different phosphine ligands is negligible, as shown by complexes **1** and **7**, which only display a small difference of 30 mV between their metal-based oxidation potentials (0.93 and 0.90 V versus Fc/Fc$^+$, respectively). Moreover, for complex **7**, a second oxidation peak can be observed, in which the phosphine ligand is oxidized, presumably at the sulfur atom. Besides this peak, the substitution pattern in complex **3** causes an oxidation potential that is 90 mV higher than that of complex **1**.

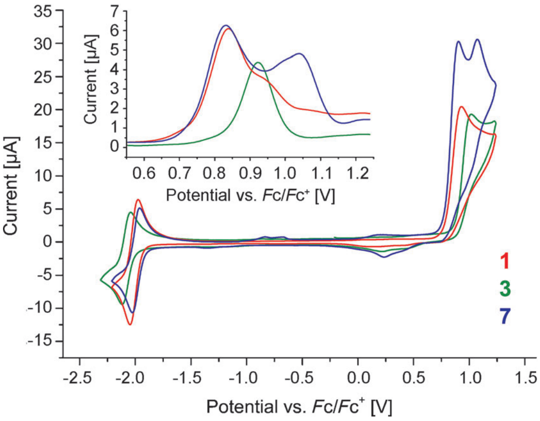


Figure 3. Cyclic voltammograms of complexes **1** (red), **3** (green), and **7** (blue) in MeCN solution. All potentials are referenced to the Fc/Fc$^+$ couple. Inset: Oxidative differential pulse voltammograms (DPVs). Scan rate: 100 mV s^{-1}, supporting electrolyte: 0.1 M $[Bu_4N]PF_6$, Ag/AgCl/LiCl$_{sat.}$ reference electrode, glassy carbon working electrode, platinum counter electrode, temperature: 25 °C.

Table 2. Electrochemical data of selected complexes in MeCN.[a]

Entry	Complex	E_{ox} [V]	E_{red} [V]	ΔE_{ox-red} [V]
1	**1**	+0.93	−2.05	2.98
2	**3**	+1.02	−2.12	3.14
3	**7**	+0.90 (+1.08)[b]	−2.03	2.93 (3.11)[b]

[a] The measurements were carried out in dry MeCN under an argon atmosphere with 0.1 M $[Bu_4N]PF_6$ as a supporting electrolyte. Peak potentials are versus Fc/Fc$^+$ (for potentials versus NHE and Ag/AgCl see the Supporting Information, Table SI2)

Because differences in the electronic inductive effects between the alkyl groups cannot be invoked, the shift in the oxidation potentials should be attributed to the larger steric effect of the *sec*-butyl group (in **3**) compared to the methyl group (in **1**), thus more-effectively preventing the structure-flattening that is associated with the oxidation of Cu^I to Cu^{II} and, hence, stabilizing the cuprous state.[16b,21,27] Conversely, the effect of the 2,9-substitution pattern cannot be observed in the absorption spectra (Figure 2), because the spectra are not influenced by structural changes that occur after the MLCT process.[21]

It is important to mention that, as previously reported for $[Cu(\widehat{NN})_2]^+$ complexes,[21] the oxidation process is not totally reversible (Figure 3), because ΔE_{ox-red} also incorporates energy changes that are associated with structural modifications (Jahn–Teller distortion and coordination number). For the same reason, a direct correlation between the emission energies and the reduction potentials (expected for d^6 metal complexes) is not observed.[28]

Nevertheless, the reduction and oxidation potentials of the excited states can be calculated from their corrected emission energies; that is, instead of the emission maxima, the values that are obtained from the intersection of the normalized absorption and emission spectra of a photosensitizer are used for the calculations.[25]

For example, upon light absorption, complex **1** displays E_{ox} and E_{red} potentials (vs. NHE) of +1.28 and −1.10 V respectively, which indicates that it is able to undergo electron transfer with both the WRC (oxidative quenching) and the SR (reductive quenching). For details, see the Supporting Information, Figure SI10.

Photocatalytic hydrogen production: In a recent communication, we reported the first effective application of heteroleptic $[Cu(\widehat{NN})(\widehat{PP})]PF_6$ complexes as photosensitizers in the photocatalytic water-reduction reaction by using the readily available complex $[Fe_3(CO)_{12}]$ as a water-reduction catalyst and triethylamine as a sacrificial reductant.[18] At that time, we realized that complexes that contained either xantphos or thixantphos $\widehat{PP}$ ligands (Scheme 1), along with the bathocuproine $\widehat{NN}$ moiety, displayed the highest activities, with TON_Hs of up to 886 and 874 (nH/nCu) for complexes **1** and **7**, respectively, under optimized conditions.

With that precedent in hand, the synthesis of several new tailored copper complexes was undertaken, by systematically changing the steric bulkiness of the substituents proximal to the nitrogen atoms (at the 2- and 9-positions) of the phenanthroline ligand (complexes **1**–**12**, Scheme 1). Once in hand, these complexes were tested in the water-reduction system. Most of them showed excellent activities with TON_Hs of up to 1330 at room temperature with $[Fe_3(CO)_{12}]$ as a WRC and triethylamine (TEA) as a SR (Table 3). Typical hydrogen-evolution curves for selected photosensitizers are shown in Figure 4.

A comparison of the gas-evolution curves in Figure 4 clearly reveals the effects of both the diphosphine and phenanthroline ligands. On the one hand, changing the diphosphine scaffold influences the kinetics of the catalytic reaction, which is more rapid with the complexes that contain thixantphos derivatives (**1**–**6**) than with complexes which contain xantphos derivatives (**7**–**12**). This effect can be attributed to a faster electron-transfer rate from the excited PS to the WRC (see below). On the other hand, the systematic change in the steric features of the phenanthroline ligands affects the thermodynamic properties of the excited complex (see above), thereby hampering the non-radiative decay by increasing the energy gap between the Cu d orbitals and the ligand π* orbitals in the emissive states.[26]

Table 3. Results of photocatalytic water-reduction reactions by using copper(I) catalysts as the PS in the presence of $[Fe_3(CO)_{12}]$ as the WRC and TEA as the SR.[a]

Entry	Complex	T [h]	Volume H_2 [mL]	TON_H[b]
1	**1**	24	37	862
2	**2**	40	41	954
3	**3**	60	57	1330
4	**4**	45	9.6	224
5	**5**	24	54	1270
6	**6**	65	17	400
7	**7**	8	37	873
8	**8**	6	46	1085
9	**9**	6	54	1251
10	**10**	10	44	1029
11	**11**	6	49	1147
12	**12**	6	43	1005

[a] Reaction conditions: copper PS (3.5 μmol), $[Fe_3(CO)_{12}]$ (5 μmol), 10 mL THF/TEA/water (4:3:1), 25 °C, Xe-light irradiation (output: 1.5 W), without a light filter. Gas evolution was quantitatively measured by using automatic gas burettes; gas analysis was performed by using GC. The values are the averages of at least two experiments. The results differ between 1 and 17 %. [b] $TON_H = nH/nCu$.

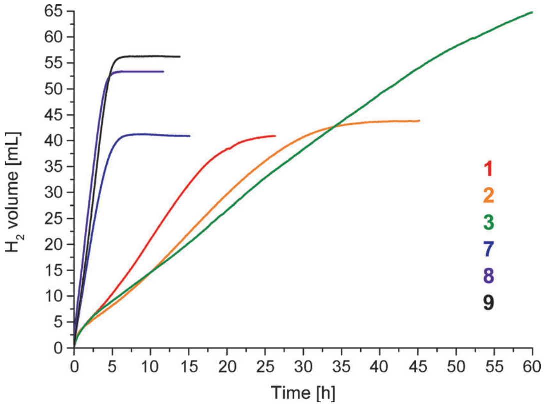


Figure 4. Typical hydrogen-evolution curves for the photocatalytic reduction of water by using a copper(I) PS in the presence of $[Fe_3(CO)_{12}]$ as a WRC and TEA as a SR. For the reaction conditions, see Table 3.

In both series of complexes, that is, **1**–**6** and **7**–**12**, the obtained TON_Hs (Table 3) were found to be dependent on the bulkiness of the alkyl residues at the 2,9-positions. This dependence correlates nicely with the same effect that was observed on the lifetimes of the excited complexes (τ_0, Table 1). Thus, it appears clear that long-lived MLCT states are beneficial for the activity of the catalysts. However, although a rough correlation is observed (Figure 5), a direct dependence could not be concluded.

To estimate the contribution of the WRC to the quenching processes, we also measured the lifetime of complex **1** under catalytic conditions in THF with TEA and water (4:1:1) but without the WRC. In this case, the obtained lifetime is 730 ns, which is much shorter than in the dilute THF solution (τ_0, Table 1). This difference results from the in-

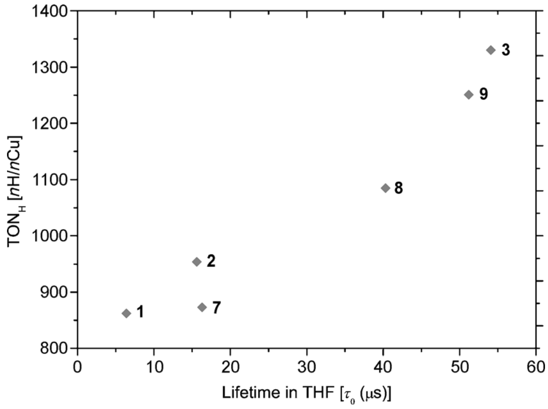
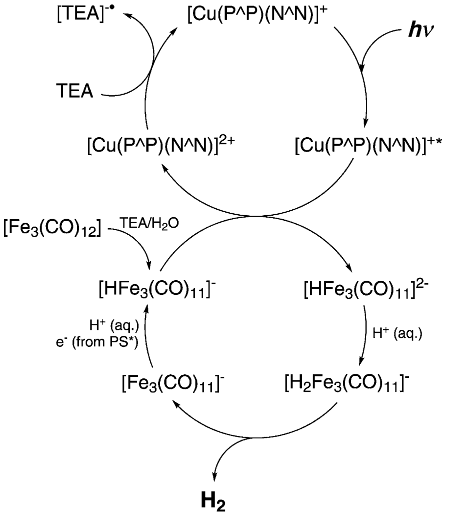


Figure 5. Plot of the turnover numbers (TON_Hs) for the photocatalytic reduction of water versus the lifetimes (in THF) of the corresponding photosensitizers. Reaction conditions are given in Table 3.

creased concentration of the photosensitizer, which enhances the number of molecular collisions and the corresponding quenching processes. In addition, exciplex quenching may occur, owing to the presence of water and TEA.[23] However, quenching by the WRC in the catalytic system (180 ns) is four-times more effective than all of the other decay channels put together ($\tau_{cat.}$, Table 1). Because good photocatalytic performance can only be achieved if effective electron transfer takes place, we suggest that electron-transfer processes contribute to the quenching. In this case, it is plausible to assume that oxidative quenching owing to the WRC is the dominant electron-transfer pathway. With this observation in mind and taking into account our previous mechanistic investigations on an analogous system that used Ir-based photosensitizers,[10b,29] we propose the reaction mechanism as shown in Scheme 3.



Scheme 3. Proposed reaction mechanism for the photocatalytic production of hydrogen by using complexes **1**–**12** ($[Cu(\widehat{PP})(\widehat{NN})]^+$) as the photosensitizer (PS), $[Fe_3(CO)_{12}]$ as a water-reduction catalyst (WRC), and triethylamine (TEA) as a sacrificial reductant (SR).

Conclusion

In summary, we have reported a noble-metal-free system that is capable of reducing protons from water by using light as the primary energy source, thereby resulting in the efficient generation of molecular hydrogen at room temperature. This three-component system includes a copper-based photosensitizer, an iron-based water-reduction catalyst, and triethylamine as a sacrificial reductant. The new heteroleptic copper complexes introduced herein were fully characterized by using spectroscopic, X-ray, photophysical, and electrochemical techniques. Notably, they displayed strong luminescence with extremely long lifetimes of the excited states and high stability towards atmospheric conditions. Thanks to their modularity and ease of synthesis, the effect of the steric features of the ligands was investigated and the correlation with the optical properties and catalytic activities of the complexes was assessed. This new molecular system represents, to the best of our knowledge, the most efficient noble-metal-free method for the homogeneous photocatalytic production of H_2 from water.

Acknowledgements

Thanks to Dr. A. Spannenberg and Dr. H.-J. Drexler for performing the crystallographic measurements and to Dr. N. Rockstroh for proofreading of the manuscript. Financial support by the BMBF through the program “Spitzenforschung und Innovation in den neuen Ländern” is gratefully acknowledged.

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Received: May 31, 2013