Hydrogen Generation

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Photocatalytic Water Reduction with Copper-Based Photosensitizers: A Noble-Metal-Free System**

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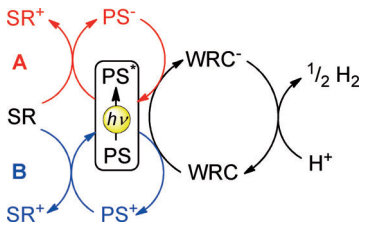
The provision of energy has been listed in the "Top Ten of global concerns" as the single most important issue to be faced to improve quality of life and ultimately to stop, or at least to mitigate, the environmental impact of human activities on the planet.[1] One way in which chemistry can be used to provide more sustainable and benign energy technologies is through the development of artificial photosynthesis systems, which allow for the conversion of the energy of sunlight into useful chemical energy by water splitting.[2] The resulting molecular hydrogen constitutes in principle a clean, renewable, and carbon-free energy source.[3]

Nowadays, typical photocatalytic systems for the reduction of protons to hydrogen consist of a suitable photosensitizer (PS), which absorbs the energy of light, a homogeneous or heterogeneous catalyst (water reduction catalyst; WRC), and a sacrificial electron donor (SR). Often the photosensitizer is the limiting component of the overall system. Hence, the development of novel photosensitizers represents a key issue for the advancement in this area. Since the 1970s, when the use of $[Ru(bipy)_3]^{2+}$ as a photosensitizer was first reported,[4] other ruthenium complexes,[5] and several other noble-metal-based systems, including rhenium,[6] platinum,[7] and iridium[8] systems, have been successfully used in this process. Less expensive noble-metal-free PS are comparatively scarce.[8f,9] The most popular noble-metal-free photosensitizers make use of organic dyes but show low activity and facile decomposition.[10] In addition, iron hydrogenase mimics,[11] biomimetic zinc(II) porphyrins,[12] and magnesium (chlorophyll A)[13] systems have been also investigated.

Based on our interest on the development of a completely noble-metal-free photocatalytic proton-reduction catalyst,[8b,c,14] we had the idea to use copper-based photosensitizers for this purpose. Notably, copper(I) complexes with polypyridine ligands show interesting emission properties and they are considered as active components in organic light-emitting diodes (OLEDs), light-emitting electrochemical cells (LECs), luminescence-based sensors, etc.[15]

In this context, we describe herein the synthesis and characterization of a series of cationic Cu^I complexes of the type $[Cu(\widehat{NN})(\widehat{PP})]^+$ and their function as active photosensitizers in the photocatalytic hydrogen generation from water under basic conditions. To the best of our knowledge, this is the first efficient noble-metal-free photocatalytic system for proton reduction using copper-based photosensitizers.

At the start of our investigations we tested around 15 different copper complexes as PSs in the presence of $[Fe_3(CO)_{12}]$ as a WRC and triethylamine as a sacrificial reductant (Scheme 1). To our delight, the complex [Cu(bathocuproine)(DPEphos)]PF_6 (**1**; Scheme 2) effectively promoted proton reduction in the presence of triethylamine (TEA) and $[Fe_3(CO)_{12}]$ with a turnover number (TON) of 477 (equiv of H/equiv of Cu) (Table 1 entry 1). Notably, all three components, PS, WRC, and SR, are necessary for hydrogen generation as in the absence of any of them, no activity was observed. Complex **1** has previously been reported to display interesting photoluminescence features and was synthesized according to the described procedure.[15a] Next, several



Scheme 1. Three-component system for the photocatalytic proton reduction. SR = sacrificial reductant, PS = photosensitizer, WRC = water reduction catalyst. Pathway A (red): reductive quenching cycle; Pathway B (blue): oxidative quenching cycle.

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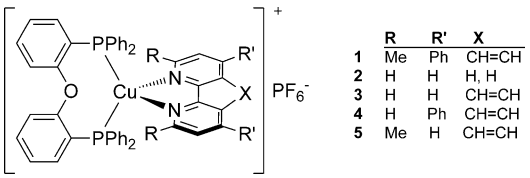


	R	R'	X
1	Me	Ph	CH=CH
2	H	H	H, H
3	H	H	CH=CH
4	H	Ph	CH=CH
5	Me	H	CH=CH

Scheme 2. Copper(I) complexes containing the ligand DPEphos (bis[2-(diphenylphosphino)phenyl]ether) and different NN ligands.

Table 1: Results for the photocatalytic proton reduction using Cu^{I} PS in the presence of $[Fe_3(CO)_{12}]$ as WRC and TEA as SR. Screening of nitrogen ligands.

Entry[a]	Complex (PS)	*t* [h]	Vol. H_2 [mL]	TON (Cu)[b]
1	**1**	24	20	477
2	**2**	5	<1	–
3	**3**	21	<1	–
4	**4**	24	<1	–
5	**5**	21	1.8	42

[a] Reaction conditions: Cu PS (ca. 3.5 μmol), $[Fe_3(CO)_{12}]$ (ca. 5 μmol), THF/TEA/H_2O (4:1:1, 10 mL), pH 11.5, 25 °C, Xe light irradiation (output 1.5 W), without light filter, gas evolution measured quantitatively by automatic gas burettes, gas analysis by GC. All given values are the averages of at least two experiments. Reaction times were taken when no further gas evolution was observed. The results differ between 1 to 20% except for volumes <10 mL (up to 40%); [b] TON(Cu) = *n*(H)/*n*(Cu).

analogues with simple variations on the dinitrogen ligand scaffold (**2**–**5**) were also synthesized and tested. However, their use led to a significant decrease of activity (see Table 1). The better performance of the bathocuproine complex (**1**) compared with the other bipyridine analogues might be explained by the improved steric and electronic factors, which are necessary to get long-lived metal-to-ligand charge-transfer (MLCT) excited states. The methyl groups located at the 2- and 9-positions should not only hamper the expansion of the coordination sphere of the metal center, thus preventing exciplex quenching,[16] but also should favor the tetrahedral geometry as opposed to the preferred square-planar geometry in the formal Cu^{II} MLCT excited state, thus slowing nonradiative decay. This effect, as pointed out by Riesgo et al.,[17] is due to an increase in the energy gap between the Cu d orbitals and the ligand π* orbitals in the destabilized emissive state. Moreover, the presence of electronegative phenyl substituents and the extended aromaticity of the phenanthroline backbone provide π* states of decreased energy and hence should facilitate the MLCT, d10π*0→ d9π*1.[17]

The absorption and fluorescence spectra of **1** are similar to those of ruthenium[5] and iridium[8g] complexes with pyridine ligands (see Figure 1). The absorption spectrum exhibits strong bands in the UV region and a moderate band in the near UV region at about 400 nm, which results most probably from a MLCT excited state. The luminescence peaks at 580 nm and the quantum yield in THF is 13%. The lifetime of the MLCT excited state is 6.9 μs and demonstrates that the nonradiative decay is indeed slow and does not interfere with photocatalytic electron-transfer processes.

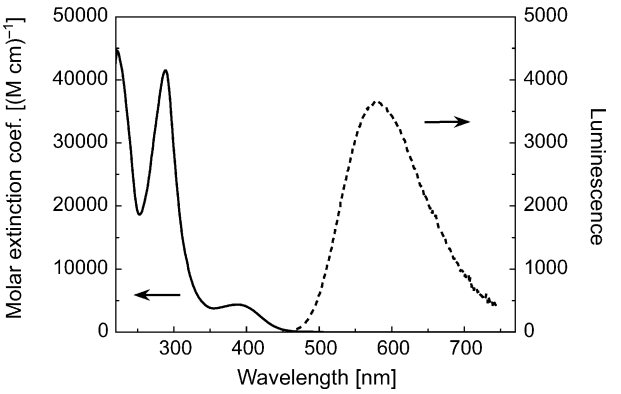
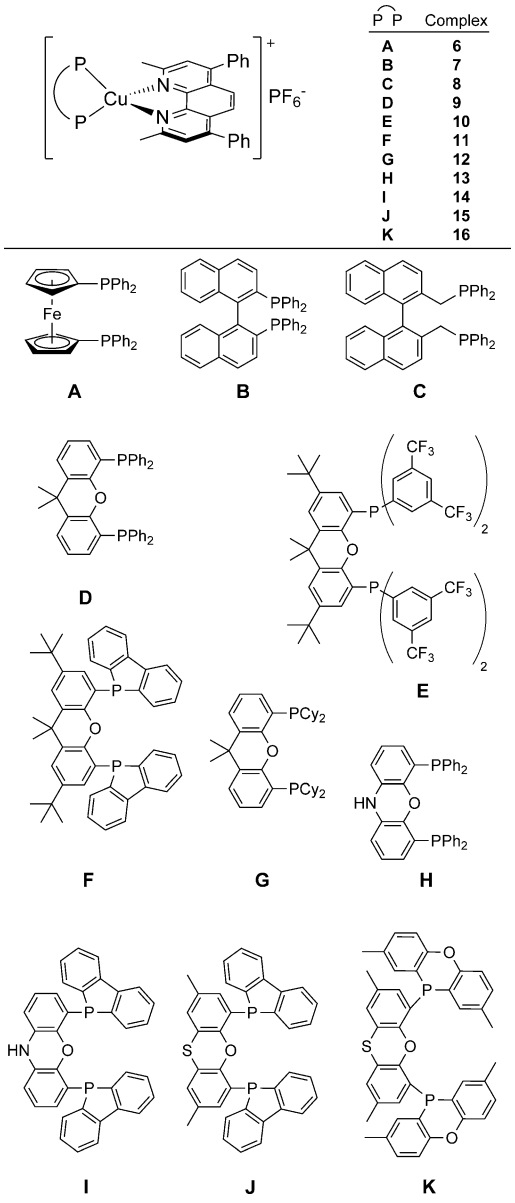


Figure 1. Absorption and luminescence spectra of complex (**1**) in THF.

With bathocuproine established as a suitable $\widehat{NN}$ ligand in the copper complex, we next looked for an optimized $\widehat{PP}$ ligand for our system. Hence, several Cu^{I} complexes with different chelating diphosphines were synthesized, characterized, and their catalytic activity for hydrogen generation was assessed with different WRCs.

We screened a range of different diphosphine scaffolds, such as dppf, binap, naphos, and xantphos (**A**–**D**, Scheme 3), and observed that the replacement of the DPEphos ligand by the more-rigid xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) confers to the corresponding complex (**9**) not only enhanced stability but also improved luminescence performance (for the UV spectrum of **9** see the Supporting Information, Figure S6).[15d] Based on this observation, we took xantphos as the lead structure when choosing other diphosphine ligands to screen (**E**–**K**; complexes **10**–**16**; Scheme 3).

The results obtained for proton reduction with this new series of complexes are presented in Table 2. Although for the complexes containing dppf and binap, no and low activity, respectively, were achieved, with naphos a much higher TON was observed (Table 2, entries 1–3). Moreover, complex **9**, containing the ligand xantphos, (Table 2, entry 4) displayed a higher activity than the DPEphos analogue (**1**). This result is presumably due to the fact that by making the $\widehat{PP}$ ligand more rigid (with a larger bite-angle) it is possible to raise the energy of the CT state, therefore partially inhibiting the nonradiative quenching, and yielding longer lifetimes.[15b] Further tuning of the steric and electronic properties of the $\widehat{PP}$ ligands showed no improvement mainly because of the inherent difficulty of separately assessing both properties (Table 2, entries 5–9). Nevertheless, when complex **15**, containing the ligand DBP-thixantphos (**J**),[18] which is electron-enriched compared to xantphos with practically the same bite-angle, was used, a higher activity was observed (Table 2, entry 10). Only complex **16** showed better activity (Table 2, entry 11), with almost the same TON being reached in a much shorter time. Under our reaction conditions the catalytic performance of the Cu-based system was better than those of the well-known photosensitizers $[Ru(bipy)_3]Cl_2$ and $[Ir(bipy)(ppy)_2]PF_6$ (Table 2, entries 12 and 13). The Ru-based system showed very low efficiency while the Ir-based one gave relatively good results, as we also previously reported.[14a]



Scheme 3. Copper(I) complexes containing bathocuproine (2,9-dimethyl-4,7-diphenyl-1-10-phenantroline) and different $\widehat{PP}$ ligands.

Table 2: Results for the photocatalytic proton reduction using Cu^{I} PS in the presence of $[Fe_3(CO)_{12}]$ as WRC and TEA as SR. Screening of phosphine ligands.

Entry[a]	Complex (PS)	t [h]	Vol. H_2 [mL]	TON (Cu)[b]
1	**6**	5	<1	–
2	**7**	20	2.2	52
3	**8**	18	28	646
4	**9**	27	33	781
5	**10**	5	<1	–
6	**11**	23	17	397
7	**12**	10	3.6	85
8	**13**	8	<1	–
9	**14**	50	6.4	150
10	**15**	18	34	797
11	**16**	6	34	804
12	$[Ru(bipy)_3]Cl_2$	12	2.5	58
13	$[Ir(bipy)(ppy)_2]PF_6$	15	25	576

[a] Reaction conditions: Cu PS (ca. 3.5 μmol), $[Fe_3(CO)_{12}]$ (ca. 5 μmol), THF/TEA/H_2O (4:1:1, 10 mL), pH 11.5, 25 °C, Xe light irradiation (output 1.5 W), without light filter, gas evolution measured quantitatively by automatic gas burettes, gas analysis by GC. All given values are the averages of at least two experiments. Reaction times were taken when no further gas evolution was observed. The results differ between 1 to 20% except for volumes <10 mL (up to 40%), [b] TON (Cu) $= n(H)/n(Cu)$.

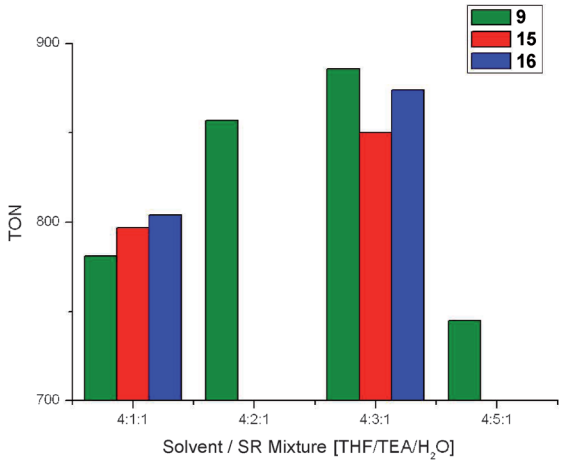


Figure 2. Highest productivities (TON) observed for light-driven proton reduction in the presence of a variety of solvent/SR mixtures for complexes **9**, **15**, and, **16** (as PS) after different reaction times (provided in the Supporting Information, Table 1). Cu PS (3.5 μmol), $[Fe_3(CO)_{12}]$ (5.0 μmol), THF/TEA/H_2O (10 mL), 25 °C, Xe light irradiation (output 1.5 W), without light filter.

To optimize the reaction conditions for this novel system we used complex **9** as the model PS. First, we investigated the effect of changing the concentration of PS with a fixed amount of WRC (see the Supporting Information, Figure S2). The best compromise between activity and reaction time was found for a concentration of 2.5×10^{-4} M of PS for which an average TON of 930 (equiv of H/equiv of Cu) was obtained. Reactions run at lower concentrations require longer reaction times (i.e. the time required until no further gas evolution is observed), whereas larger amounts of PS had a detrimental effect on the activity.

The optimal ratio for the solvent/SR/water mixture was also investigated (Figure 2). Best results were obtained when a mixture of THF/TEA/H_2O with a volumetric composition of 4:3:1 was used. With the optimized conditions a turnover number of 804 (equiv of H/equiv of Cu) in 6 h was obtained when **16** was used as the PS. Alternative SRs to TEA (i.e. ascorbic acid and triethanolamine) were also tried and K_2PtCl_6 was tried as the as the WRC. Notably, also under these conditions hydrogen generation is observed, thus demonstrating the general applicability of the Cu PS. However, the use of either ascorbic acid or triethanolamine led to a decrease in the activity compared to the optimized system described above. By using $[HNEt_3][HFe_3(CO)_{11}]$ as the WRC we observed the same behavior as with $[Fe_3(CO)_{12}]$. The addition of the electron-deficient tris(3,5-bis(trifluoromethyl)phenyl)phosphine, which had a positive influence in the

Ir PS/Fe WRC system,[8b] led only to a slightly decreased TON.

It is worth mentioning, that the proton reduction also takes place, although at a lower rate, that is 688 TON after 65 h for complex **9**, in the absence of UV light by application of a 395 nm cut-off filter (see the Supporting Information, Table S1, entry 7). On the other hand, under these conditions the system shows an enhanced stability of up to three days.

To obtain mechanistic insights into the action of the Cu-based PS we measured the lifetime of **1** in a 4:1:1 mixture of THF/TEA/H_2O in the presence and absence of 0.5 mM of $[Fe_3(CO)_{12}]$. With TEA in the absence of WRC the decay time of the luminescence is 200 ns, thus reflecting the quenching rate by TEA and thereby most probably the electron-transfer rate. If the WRC is also added, the decay time of the luminescence reduces further to 100 ns. This finding shows that the presence of the WRC provides a second quenching pathway that is equally fast as the reductive electron transfer and the total quenching rate is twice as high. We assign this second pathway to the oxidative electron transfer from the sensitizer to the WRC. In both cases the strongly accelerated luminescence decay compared to that in pure THF (6.9 μs, see above) indicates that after optical excitation electron transfer occurs with a high efficiency. In addition, CV measurements of the reduction potential of the Cu PS **9** (−1.54 V vs. Ag/AgCl/$LiCl_{sat}$) show the general feasibility to reduce the WRC (see the Supporting Information, Figure S7).

The deactivation of the catalytic system is expected to be due either to the decomposition of the photosensitizer, decomposition of $[Fe_3(CO)_{12}]$,[14b] or by reaction with the decomposition products of TEA.[4b] Deactivation resulting from changes in the pH of the reaction mixture can be ruled out since the pH remains almost constant (from initial 11.5 to ca. 11.4 after reaction for example, with **16**; Table 2, entry 11).

In summary, we have developed a completely noble-metal-free molecular-defined system for the photocatalytic reduction of protons from water at room temperature. Our novel system makes use of Cu^I complexes as photosensitizers and $[Fe_3(CO)_{12}]$ as a water reduction catalyst in the presence of TEA as a sacrificial reductant. It should be noted that the new copper-based photosensitizers are relatively inexpensive, readily available from commercial sources, and stable to ambient conditions making them an attractive alternative to the widely used iridium (and other noble-metal-based) PS systems. Owing to the obvious possibilities of tuning the properties of the copper center with related ligands (carbenes, other P- and N-ligands) as well as potential heterogenization of the systems further improvements can be anticipated. Finally, it should be noted that these systems are also of interest for other applications (OLEDs, LEC, etc.) because of their photochemical behaviour.

Experimental Section

All catalytic experiments were carried out under an argon atmosphere with exclusion of air. THF, TEA, and doubly distilled water were degassed and purified by standard laboratory methods prior to use. The catalyst precursors were purchased from commercial suppliers and used as received. Copper(I) complexes (**1**–**16**) were synthesized according to a literature procedure (see the Supporting information).[15a] The diphosphine ligands were either purchased or synthesized following the reported procedures.[18,19] The amount of gas liberated was measured by an automatic gas burette. Details on the equipment and the experimental set-up have been published elsewhere.[8b] The relative composition of the evolved gas was determined by GC (gas chromatograph HP 6890N, carboxen 1000, TCD, external calibration). The light source was a 300W Xe lamp.

Typical procedure for light-driven water reduction: A double-walled thermostatically controlled reaction vessel was evacuated and purged with argon. The copper photosensitizer and $[Fe_3(CO)_{12}]$ were added as solids. The corresponding solvent mixture (THF/TEA/H_2O) was added and the temperature of the system was fixed at 25 °C before switching on the light source. The reaction mixture 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 20 % except for volumes of less than 10 mL (up to 40 %).

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