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Copper photosensitizers containing P^N ligands and their influence on photoactivity and stability

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Abstract: Driven by the intention to improve classic heteroleptic copper photosensitizers two novel Cu(I) complexes applying a heterobidentate P^N ligand were prepared. A combined photophysical, electrochemical and theoretical study gives insights into structureactivity-relationships and revealed an increased absorptivity. Both complexes were tested for the light-driven production of H₂.

The increasing use of sunlight represents a promising option which might contribute to solve the current energy challenge.^[1-3] Therefore, photocatalysis and the storage of solar energy in the form of chemical energy carriers are becoming more and more important.^[1-3] This also requires the design of efficient, inexpensive and sustainable photosensitizers for light harvesting.^[4,5] In addition, a suitable photosensitizer should possess a strong absorption, long-lived excited states, a reversible electrochemical behavior and a high stability which all need to be adjusted with the respect to their costs and activity.^[6] In this context, heteroleptic Cu(I) complexes of the general type [(P^P)Cu(N^N)]+, where N^N indicates a diimine and P^P a diphosphine ligand, are of particular interest.^[7-11] Starting with the pioneering work by McMillin et al. a rising number of (heteroleptic) copper photosensitizers (CuPS) were developed and successfully applied in intermolecular systems for the photocatalytic production of hydrogen from water.[7-10,12-18]

As a common feature of such heteroleptic Cu(I) complexes it has been recognized, that bulky and rigid diphosphine ligands with wide bite-angles are beneficial in order to obtain photophysical properties like long-lived triplet excited states and high quantum yields.^[7,8,19,20] DFT and spectroscopic studies revealed that the photophysical activity solely originates from the diimine ligand, as the electron density in the S₁ state is located on the diimine moiety compared to S₀.^[11,21] This often results in smaller extinction coefficients compared to classic homoleptic bis-diimine complexes [Cu(N^N)₂]⁺.^[10,14,15] In contrast, the diphosphine ligand predominantly ensures a maximum site occupancy and shields the system from exciplex quenching after light-induced excitation

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Supporting information for this article is given via a link at the end of the document. These includes experimental and synthetic details, crystallographic data, MS and NMR spectra as well as detailed results of the (TD-)DFT calculations.

to the S1 state, where a flattening distortion of the Cu(I) center occurs followed by the population of a triplet excited state.^[21,22] This excited state exhibits a long lifetime primarily due to the presence of the bulky diphosphine ligand.^[8,21] However, these diphosphines bind less strongly to the copper center, and hence, the formation of homoleptic bis-diimine complexes is thermodynamically favored.^[20,23,24,25] It was shown that the extent of dissociation mainly depends on the size and kind of the phosphine ligands as well as on the solvent.^[20,23,26] This dynamic ligand exchange represents one of the major drawbacks of current heteroleptic [(P^P)Cu(N^N)]⁺ photosensitizers. Therefore, it is of significant interest to enhance the complex stability and absorptivity. This might be realised by exchanging the diphosphine with a heterobidentate P^N ligand^[27,28] while maintaining favourable steric (e.g. rigidity) and electronic (e.g. nitrogen and phosphorus donor/acceptor ability) features important for photocatalytic applications.

Consequently, the synthesis of two novel Cu(I) complexes **1** and **2** (Figure 1) was successfully performed. The solid state structures, photophysical and electrochemical properties as well as the photocatalytic activities are presented and compared to the standard complex [(xant)Cu(bcp)]⁺ **3** (with xant = xantphos and bcp = bathocuproine). The experimental results are accompanied by DFT/TD-DFT (density functional theory/time-dependent DFT) calculations. Within this framework the electronic ground-state (S₀) and excited state structures (S₁, T₁), the electronic densities as well as associated properties were determined.

Results and Discussions

The already known phosphinooxazoline (phox) ligand was chosen as P^N ligand,^[27] which potentially fulfils the requirements for a suitable photosensitizer. Subsequently, the respective homo- and heteroleptic Cu(I) complexes 1 and 2 (Figure 1) were prepared following a modified synthesis procedure (see SI) starting from [Cu(MeCN)₄]PF₆ (MeCN = acetonitrile) as precursor.^[8,11] The homoleptic complex **1** was obtained in a onestep reaction of the copper precursor with two equivalents of the phox ligand in dichloromethane solution under inert conditions. Full conversion of the P^N ligand was already accomplished after a few minutes under reflux. This gives a first indication of an enhanced binding of the P^N ligand compared to the previously applied diphosphines, because full formation of the [(P^P)Cu(MeCN)₂]⁺ intermediate typically requires several hours.^[8,11] Then, the heteroleptic complex 2 was prepared by a one-pot two-step synthesis where the phox ligand is added first, followed by addition of the diimine ligand. However, in contrast to the synthesis of [(P^P)Cu(N^N)]⁺ complexes, the risk of formation of the homoleptic by-product [Cu(N^N)₂]⁺ is substantially minimized and almost independent from the reaction time of the first step. The pure complexes were obtained as vellow to orange crystalline solids in excellent to good yields of 87 % (1) and 54 % (2), respectively.

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Figure 1. General structure of the homo- and heteroleptic Cu(I) complexes 1 and 2 applied in this study.



Figure 2. Solid state structures (ORTEP representation) of complex 1 (left) and 2 (right) with thermal ellipsoids at a probability level of 50 %. Hydrogen atoms, counter anions and solvent molecules are omitted for clarity.

Single crystals suitable for X-ray crystallography were received either by slow diffusion of n-pentane in a saturated dichloromethane solution (for 1) or in ethanol (for 2). In both complexes the ligand environment displays a distorted tetrahedral geometry around the copper center (Figure 2). The angle between the two ligand planes, which are spanned through the chelating hetero atoms and the copper center, differs from 90° (Table 1 and Figure SI10). However, with 88.3° the deviation of the heteroleptic complex 2 is smaller than in 3 with 85.0°. This could be caused by the smaller size and less steric demand of the phox ligand in contrast to xantphos. Another reason for distortion is given by the quite small bite angle of phox in 2 (N3-Cu-P1: 88.97(12)°) compared to that of xant in 3 (P1-Cu-P2: 119.48(4)°), which strongly deviates from the ideal tetrahedral angle of 109.5° (Table 1 and SI2). The smaller binding angle is also reflected by a shorter Cu-P distance in 2 (e.g. Cu-P1: 220.44(15) pm) in comparison to 3 (e.g. Cu-P2: 230.48(10) pm). Furthermore, the coordinated phox ligand shows a strong twist in relation to the respective N-Cu-P plane (see visualization of DFT calculation in Figures SI4 and SI5). As a result, in the homoleptic complex 1 an interaction between the two phox ligands takes place, resulting in a considerably distorted geometry with an angle between the planes of 71.1°. The extent of distortion is also supported by the DFT calculation yielding in 76.1° (Table SI3). Further structural analysis of 1 and 2 also reveals a slight electronic effect. In 1, where the π-acceptor bcp is missing, the Cu-P bond lengths (Cu-P1: 226.40(8) and Cu-P2: 227.26(7) pm) are elongated compared to 2 (Cu-P1: 220.44(15) pm), which is again confirmed by DFT calculations where the Cu-P bonds are increased from 224.1 pm in 2 to 230.0 pm in 1 (for details see SI).

Table 1. Selected crystallographic bond lengths (pm) and angles (°) of the complexes 1-3. For atom labeling compare with Figure 2, further values are given in the SI. The respective CCDC reference numbers are 1561237 (1), 1561238 (2) and 1561239 (3).

1			2		3
Cu-N1	209.4(2)	Cu-N1	207.5(4)	Cu-N1	206.5(3)
Cu-P1	226.40(8)	Cu-N2	205.0(4)	Cu-N2	209.9(3)
Cu-N2	207.0(2)	Cu-N3	207.5(4)	Cu-P1	230.48(10)
Cu-P2	227.26(7)	Cu-P1	220.44(15)	Cu-P2	224.25(10)
N1-Cu-P1	86.38(6)	N1-Cu-N2	80.38(17)	N1-Cu-N2	80.41(10)
N2-Cu-P2	86.98(7)	N3-Cu-P1	88.97(12)	P1-Cu-P2	119.68(4)
P1-Cu-P2	120.65(3)	N2-Cu-P1	134.42(14)	N2-Cu-P1	128.84(8)
plane angle	71.1 ^[a]	plane angle	88.3 ^[a]	plane angle	85.0 ^[a]

[a] calculated angle between the two ligand planes

The cyclic voltammogram of **2** in acetonitrile exhibits a reversible reduction wave at -2.02 V vs. Fc/Fc⁺ and two quasireversible oxidation processes (Figure 3). These findings are in accordance with related Cu(I) complexes.^[8,11,25] The reduction potential of **1** (-2.27 V) is 250 mV more anodic than that of **2** (-2.02 V), whereas the oxidation of both complexes occurs around 0.38 - 0.56 V. The additional redox event at -0.92 V appears only after the previous reduction of **1** (Figure SI19) and can be therefore assigned to a newly formed side-product. Comparison of **2** with **3** reveals that the reduction potentials of these two heteroleptic complexes are almost the same (Table 2). This is due to the fact that the reversible one-electron reduction is assigned to the reduction of the diimine ligand,^[8,25] which is identical in **2** and **3**.

Furthermore, the small other redox-wave at approx. -2.1 V of **2**, can be attributed to the progressive build-up of the homoleptic species **1** upon redox cycling.^[24,25] However, from previous experiments with related heteroleptic [(P^P)Cu(N^N)]⁺ complexes it is known, that the equilibrium (K_{eq}) between hetero- and homoleptic Cu(I) complexes is comparably low in acetonitrile.^[20] Hence, no or only little formation of the homoleptic [Cu(P^N)₂]⁺ and [Cu(N^N)₂]⁺ species is expected as long as the complexes are not electro- or photochemically oxidized.^[20,24,25]



Figure 3. Cyclic voltammograms of 1 (black) and 2 (grey) in acetonitrile solution referenced vs. the ferrocene/ferrocenium (Fc/Fc⁺) couple. Conditions: scan rate of 100 mVs⁻¹, 0.1 M Bu₄NPF₆ as supporting electrolyte. The arrow indicates the scan direction.

A comparison of the absorption spectra (Figure 4) of 1 and 2 in acetonitrile solution reveals clear differences between both complexes. The spectrum of 2 possesses bands at 280 and 450 nm, which are assigned to ligand-centered and metal-to-ligand charge transfer (MLCT) transitions, respectively.^[10,14,21] Instead, in **1** the ligand centered π - π * transitions are blue-shifted and the MLCT transitions occur only as broad shoulder of the firstmentioned. Further, the molar extinction coefficient of complex 1 is significantly lower than of 2 (Table 2) as also approved by TD-DFT calculations with lower oscillator strengths (cf. Figure SI11 and further transition energies in Table SI4). This highlights the importance of the diimine ligand on the absorptivity of the resulting CuPS. Intrinsic basis bonding analysis (IBBA) of the TD-DFT calculation shows, that the HOMO of 2, which has the highest orbital contributions in the lowest-lying excitations, is predominantly located on the copper center (54 %) as well as on the phosphorous (15 %) and the nitrogen (7 %) atom of the phox ligand (see Table SI6). A closer inspection on the orbital contributions of the acceptor orbitals of 2 revealed that the LUMO and LUMO+1 are mainly located on the bcp scaffold (Table SI5 and Figure SI15). Furthermore, the respective transitions to the LUMO possess the largest oscillator strength in the visible range as also obtained for related CuPS containing a bcp and xant ligand or derivatives thereof.^[21] However, there are also small contributions originating from the phox ligand which are located at 419 and 441 nm (compare Table SI5) as obtained by TD-DFT calculation. This additional participation of the P^N ligand in the absorption of visible light increases the molar extinction coefficient of 2 by about 40 % compared to 3. However, the contribution of the phox ligand to the light absorption process is significantly lower than of the bcp ligand. Hence, the absorption of 1 is considerably decreased in relation to that of 2. In order to examine the effects of the P^N ligand on the ability of these novel Cu(I) complexes to function as photosensitizers they were tested in the light-driven hydrogen production.

 Table 2. Summary of the photophysical and electrochemical properties of the complexes 1-2 and of the reference 3 in acetonitrile solution at room temperature.

complex	λ_{abs} [nm]	є аьь, _{max} [M ⁻¹ cm ⁻¹]	E _{ox} [V] ^[a]	E _{red} [V] ^[a]
1	400 sh	1.450 [c]	+0.56 ^[b]	-2.27
2	408	7.300	+0.38 ^[b] +0.52 ^[b]	-2.02
3 ^[d]	389	5.700	+0.93	-2.05

[a] in acetonitrile vs. Fc/Fc+, [b] quasireversible oxidation, [c] ϵ at 400 nm, [d] taken from ref. [8].



Figure 4. UV/vis absorption spectrum of 1 (black solid) and 2 (grey dashed) in acetonitrile. The enlargement represents the range of the metal-to-ligand charge transfer transitions.

The photocatalytic reduction of protons to hydrogen was chosen to study the influence of the P^N ligand on the photocatalytic activity. Therefore, a fully noble-metal-free system composed of [Fe₃(CO)₁₂] as WRC, triethylamine (TEA) as SR and the Cu(I) complexes was used.^[7,8,11] Previously developed standard conditions, i.e. a solvent mixture of THF/TEA/H₂O in the ratio 4:3:1, were applied (for further details see Table 3 and the SI).^[7,8,11] Both complexes 1 and 2 show a low, but fairly constant production of H₂ within 24 h (Figure 5). The development of the respective turnover numbers over time is presented in the supporting information (see Figure SI22). The catalytic behavior might be explained by the reduced ability of 1 and 2 to undergo electron transfer from the SR compared to 3 (see excited-state redox potentials below and Figure SI18). Another reason are the adverse effects of the smaller steric demand and low rigidity of the phox ligand on the excited state properties (see Figures SI16 and SI17). The resulting sensitivity to fast exciplex-quenching also reduces the turnover numbers compared to 3. However, the additional contribution of the phox ligand to MLCT transitions as well as the increased stability of 1 and 2 are of high importance in order to develop a sustainable catalytic system in the future. A further elucidation of this issue is currently ongoing in our laboratories.



Figure 5. Hydrogen evolution curves for the photocatalytic reduction of protons using the copper photosensitizers (ca. 3.5 μ mol) 1 (black solid) and 2 (grey dashed) with [Fe₃(CO)₁₂] (ca. 5.0 μ mol) as water reduction catalyst (for experimental details see SI).

In addition to the investigation of the different MLCT transitions and of the involved ligands therein, the analysis of the extent of

distortion of the ligands through photoexcitation is of high interest. Calculation of the singlet and triplet excited states at full TD-DFT level of theory reveals a significant change of the dihedral angle between the planes,^[29,30] e.g. of the homoleptic CuPS $[Cu(phen)_2]^{2+}$ and $[Cu(dmp)_2]^{2+}$ (dmp = 2,9-Me₂phen) from 90° (S_0) to 41.7° (T_1) and 67.4° (T_1) , respectively.^[31] As a consequence of this large distortion the triplet excited states can be efficiently quenched by solvent molecules.^[10,14] A reduced distortion and a shielding through the diphosphine ligand was found for [(DPEphos)Cu(dmp)]⁺ (DPEphos bis[2-= (diphenylphosphino) phenyl]ether) with a change from 82.5° (S₀) to 69.0° (S₁) and 70.2° (T₁),^[32] resulting in a considerably evolution of H₂.^[7,8,11,18] In contrast, the angles between the planes of 1 and 2 in the excited states were obtained by TDDFT calculation to be 60.6° (59.6° in T₁) and 50.9° (55.4° in T₁), respectively (see Table SI7 and Figure SI17). These smaller values indicate, that the phox ligand lacks the high steric demand of the DPEphos or xant ligand.^[21] Thus, the copper center is more prone to nucleophilic attack, and hence, fast exciplex quenching. This might explain the absence of emission at room temperature in solution and the relatively weak evolution of hydrogen.

Another possible reason for the reduced photocatalytic activity is the lability of the oxazoline C_{aryl} - $C_{oxazoline}$ and phosphine C_{aryl} - P_{PPh2} joints. In addition to the steric constraints due to the small bite angle, the six-membered phox-Cu chelate ring gets twisted in the S₁ state in both, complex **1** and **2** (see Figs. SI16 and SI17). Especially in **1**, the strong geometrical changes lead to a more distinct definition of a *trans*-position. Hence, the Cu-N bond opposite to the more powerful acceptor atom gets weakened which leads to a difference in Cu-N bond lengths of 20.6 pm (Cu-N1: 195.9 pm, Cu-N2: 216.5 pm). In complex **2** this effect is less pronounced and the deviations between the Cu-N1 and Cu-N2 distances is only about 4.8 pm.

In combination with the catalytic experiments the ability of the new CuPS to undergo electron transfer with the water reduction catalyst (WRC) and the sacrificial reductant (SR) is estimated by the calculation of the excited state redox potentials.^[33] For 1 these can be determined to +0.15 V and -1.86 V (Table SI9), which only renders the reduction of the WRC [HFe₃(CO)₁₁]⁻ (-1.64 V *vs.* Fc/Fc⁺) possible, whereas the electron transfer from the SR triethylamine (+0.46 V *vs.* Fc/Fc⁺) is not likely.^[8] This also holds true for complex **2**, where the excited state redox potentials are predicted as +0.20 V and -1.84 V *vs.* Fc/Fc⁺. Therefore, both **1** and **2** appear to be potent photoreductants, where an electron can be transferred from the CuPS to the WRC after light excitation. Unfortunately, **1** and **2** are not able to act as photooxidant, which is in contrast to complex **3**.

Table 3. Overview of the photocatalytic hydrogen production using 1-3 as photosensitizers. $^{\left[a\right] }$

complex	V _{24h} [mL]	V _{corr} [mL] ^[b]	TON _{H,Cu} ^[c]
1	4.8	2.3	53
2	5.2	2.5	58
3 ^[d]	39.7	37.0	862

[a] Conditions: CuPS (ca. 3.5 μ mol), [Fe₃(CO)₁₂] (ca. 5.0 μ mol), THF/TEA/H₂O (4:3:1, 10 mL), 25°C, Xe light irradiation (output 1.5 W) without light filter, 24 h

[b] V_{24h} corrected by a blank volume of 2.5 mL (entry 1) or 2.7 mL (entries 2 and 3) [c] TON_{H,Cu} = n(H) / n(CuPS) with $V_{m,H2,25^{\circ}C}$ = 24.48 mL/mmol., [d] taken from ref. ^[8] for comparison.

Conclusions

First insights in the effect of exchanging a classic diphosphine P^P by a heterobidentate P^N ligand on the photophysical and catalytic properties of the resulting Cu(I) complexes are presented. The employed phox ligand leads to an increase in absorptivity and a bathochromic shift of the main MLCT absorption compared to the heteroleptic reference complex [(bcp)Cu(xant)]⁺. With regard to the photocatalytic hydrogen production an increased stability could be observed, enabling a catalytic activity of more than 24 h. However, further P^N ligands with more steric demand and an increased rigidity have to be tested, as this renders the major drawback of the current system.

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Keywords: copper complexes • heterobidentate P^N ligands • photocatalysis • hydrogen • photophysics • DFT calculations

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