Photocatalysis

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Optimization of Hydrogen-Evolving Photochemical Molecular Devices**

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Abstract: *A molecular photocatalyst consisting of a Ru^{II} photocenter, a tetrapyridophenazine bridging ligand, and a PtX_2 ($X = Cl$ or I) moiety as the catalytic center functions as a stable system for light-driven hydrogen production. The catalytic activity of this photochemical molecular device (PMD) is significantly enhanced by exchanging the terminal chlorides at the Pt center for iodide ligands. Ultrafast transient absorption spectroscopy shows that the intramolecular photophysics are not affected by this change. Additionally, the general catalytic behavior, that is, instant hydrogen formation, a constant turnover frequency, and stability are maintained. Unlike as observed for the Pd analogue, the presence of excess halide does not affect the hydrogen generation capacity of the PMD. The highly improved catalytic efficiency is explained by an increased electron density at the Pt catalytic center, this is confirmed by DFT studies.*

Emission-free solar energy is widely seen as an attractive alternative to fossil fuels, and photovoltaic cells have been under investigation for many decades. However, a disadvantage of photovoltaic cells and indeed of other renewable energy sources, such as wind and wave energy, is the effective storage of excessively produced energy. As a result there is a growing interest in the design of new catalytic systems that can store energy locally. Besides electrocatalytic approaches,[1–3] metal oxide semiconductors have demonstrated their capability to directly convert visible light into chemical energy (hydrogen).[4] Even though such heterogeneous systems exhibit promising properties, such as high H_2-production rates[5,6] or self-healing ability,[7] detailed mechanistic investigations of the processes occurring in the solid phase remain challenging. In addition, molecular photocatalytic systems have been developed. Many studies focus on multicomponent systems, which are based on an intermolecular electron transfer from a molecular photosensitizer through an electron relay towards a catalytic unit, where subsequently the molecular hydrogen is formed. The first systems of that type were developed from the late 1977s onwards, applying $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) as the photosensitizer, $[Rh(bpy)_3]^{3+}$ or methyl viologene as the electron relay, and in situ formed Pt nanoparticles as catalytically active centers.[8] Recent approaches showed that nanoparticles of earth-abundant-metals (e.g. Fe or Ni) can also serve as the catalytically active centers, however a decreased catalytic activity and a lower stability of the nanoparticles during catalysis is observed in comparison to Pt.[9] In addition to metal-nanoparticle-based systems homogeneous (intermolecular) systems are known, for example, applying cyclopentadienyl Rh^{III} complexes as a catalyst for the reduction of protons.[10] Furthermore also noble-metal-free systems using heteroleptic Cu^{I} complexes as photosensitizers instead of $[Ru(bpy)_3]^{2+}$ in combination with $[Fe_3(CO)_{12}]$ as the reducing catalyst can efficiently produce molecular hydrogen from water.[11] Besides these intermolecular approaches, intramolecular photocatalysts can also effectively produce hydrogen from aqueous solution under visible-light irradiation.[12,13] These so called photochemical molecular devices (PMDs) combine the photocenter, the electron relay, and the catalytic center in one single molecule and offer the potential for a specific modification of the single modules to optimize the PMD's efficiency and stability during catalysis. A particular example of this approach, which has been investigated in great detail,[14] is shown in Figure 1.

It has become clear, however, that the design and optimization of such a PMD is by no means straight forward and it is surprising that, while extensive effort has been taken in the variation of the bridging[15] or peripheral ligands,[16,17] the structural features of the attached catalytic center have not been addressed in detail. In particular, since data obtained

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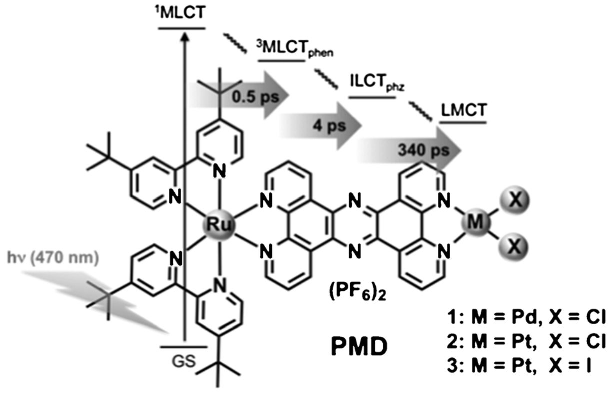

Figure 1. Structure of the photochemical molecular device (PMD): compounds **1**, **2**, and **3**, based on Ru and Pd/Pt moieties. Light-induced dynamics based on the initial excitation of the Ru photocenter in acetonitrile (assignment of excited states is based on literature:[33] GS = ground state, MLCT = metal-to-ligand charge transfer, ILCT = Intra-ligand charge transfer, LMCT = ligand-to-metal charge transfer). The time constants are depicted representatively for photocatalyst **3**.

from intermolecular systems suggest that the rate-determining step in the photocatalytic process may be hydrogen generation at the catalytic center.[18] Therefore, apart from continuing studies to improve the electron transfer between the chromophore and the catalytic center, more attention needs to be paid to the optimization of the hydrogen-producing catalytic center itself. In addition Pd-based catalytic centers tend to be instable and they may create colloidal particles, which although they may be involved in the photocatalytic process[19–21] are essentially the result of decomposition of the photocatalytic assembly and limit the efficiency of the catalytic process. For the assembly shown in Figure 1 and in other examples in the literature, $PdCl_2$ is used as a photocatalytic center since it tends to yield higher turnover numbers (TONs), defined as the number of hydrogen molecules generated per molecule of catalyst, than $PtCl_2$ even though the $PtCl_2$ metal center is more stable.[20,22–24]

To date the difference in TONs obtained by Pd- and Pt-based catalytic centers is considerable. While compound **1** ($[Ru(tbbpy)_2(tpphz)PdCl_2](PF_6)_2$; tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine and tpphz = tetrapyrido[3,2-a:2′,3′-c:3′′,2′′-h:2′′′,3′′′-j]phenazine, Figure 1), containing a $PdCl_2$ unit as catalytic center, yields a maximum TON of 238,[25] for compound **2** containing a $PtCl_2$ unit, a considerably lower catalytic activity with maximum TONs of less than 10 is obtained.[20] However, the catalytic activity of **2** compares well with other molecular photocatalysts for hydrogen production containing Pt as catalytic center.[26–28]

Herein it is shown that by replacing the $PtCl_2$ catalytic center in **2** by a PtI_2 center (to give **3**) the maximal TON obtained is increased by a factor of almost 40, from 7 to 276. In addition, increased long-term stability is observed for the iodide analogue in terms of a relative constant turnover frequency (TOF) within the first 46 h of catalysis. The higher activity can be explained by the increased electron density at the Pt center because of the softer nature of the iodide ligand. It is also shown that by increasing the intensity of the excitation light a further enhancement of the catalytic activity can be obtained, leading to an increase in the TON to 465.

Compound **3** was prepared using the methodology reported for the $PdCl_2$ analogue,[14] by the reaction of the ruthenium precursor $[Ru(tbbpy)_2(tpphz)](PF_6)_2$ with *cis*-$[Pt(dmso)_2I_2]$[29] (dmso = dimethylsulfoxide) in good yield. The structure proposed is confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (see Supporting Information) and is in good agreement with reported data for compounds **1** and **2**.[20,30]

The capacity of compound **3** as catalyst for light-driven hydrogen evolution was investigated and compared to that of compounds **1** and **2**. These studies were carried out in GC vials containing an acetonitrile/water mixture using trimethylamine (TEA) as a sacrificial agent. Full experimental details are given in the Supporting Information.

The TON and TOF values obtained for compound **3** over 46 h of irradiation (LED 470 nm) are shown in Figure 2. With longer irradiation times the TOF decreases slightly until the maximum amount of produced hydrogen with a TON of 276 is reached after 70 h (see Tables S1 and S2). This means an overall increase of the maximal TON by factor of almost 40 compared to compound **2**.

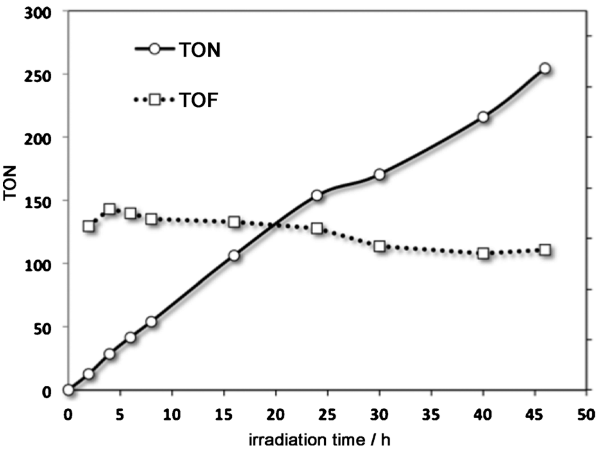

Figure 2. Turnover numbers (TONs) and turnover frequencies (TOFs) of compound **3** (c = 70 μM) in 2 mL of a catalytic mixture (6:3:1 v/v/v CH_3CN/TEA/H_2O; TEA = triethylamine) under continuous LED irradiation (λ = 470 nm, 30–40 mW cm^{-2}).

A possible reason for this significant increase of the catalytic activity by exchanging the terminal chloride ligands with iodide might be changes in either the intramolecular electron-transfer processes or the catalytic mechanism at the platinum center. To address these options, steady-state and transient absorption spectroscopy were applied. As shown in Figure 3, there are no significant differences observed in the steady state UV/Vis spectra of compounds **2** and **3** in acetonitrile. However, **3** shows an absorption maximum at 360 nm, which is not present for **2** and can be assigned to π–π* transitions located on the phenazine unit of the tpphz ligand.[31,32]

The photoinduced processes in the ps range of compound **3** were investigated by using transient absorption spectrosco-

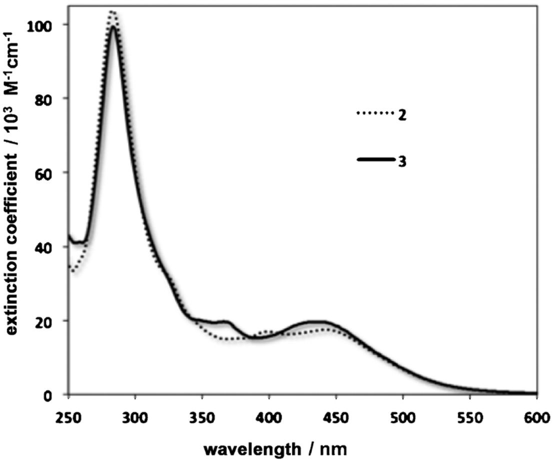

Figure 3. Steady state UV/Vis absorption spectra of compounds **3** (solid line) and **2** (dashed line) in CH_3CN ($c_{\text{photocatalyst}} = 1\times10^{-5}$ M).

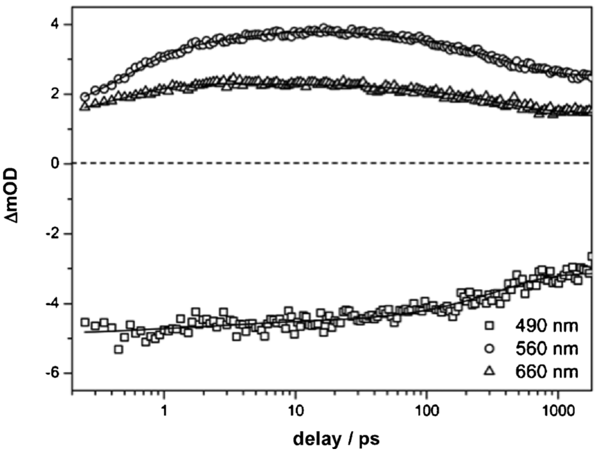

Figure 4. Photoinduced kinetics (data and fit) of compound **3** in air equilibrated acetonitrile at selected probe wavelengths upon excitation at 470 nm.

py (Figure 4, for experimental details see Supporting Information). The positive excited state absorption (ESA) feature at wavelengths longer than 520 nm grows in intensity during the first 50 ps. Between 50 and 1000 ps the signal amplitude decays to reach a constant value, which is roughly 75 % of the original maximum amplitude. The remaining signal corresponds to the presence of a long-lived species. A global fit of the data results in three characteristic time constants and an additional term corresponding to the long-lived species formed. This behavior is in agreement with the closely related species **1** and **2** in which a stepwise photoinduced electron transfer from the ruthenium photocenter to the catalytically active palladium or platinum center is observed (Figure 1).[20,32,33]

This observation indicates that the ultrafast photoinduced electron-transfer processes are not affected by the exchange of the terminal Pt bound anions. We therefore considered the potential changes in the catalytic mechanism occurring at the platinum center. The kinetic processes during the light-driven hydrogen production of the photocatalysts **2** and **3** were compared. In spite of the fact that **3** shows a significantly increased catalytic activity its underlying photocatalytic behavior is in line with that observed for **2**. Importantly, both catalysts show an instant hydrogen formation and a relatively constant TOF until the maximum TON is reached (catalytic activity of **3** is shown in Figure 2). In that respect **2** and **3** behave completely differently to the Pd analogue **1**, which shows an induction period of 2 h and a quite unstable TOF varying between 2.4 h^{-1} and 15.0 h^{-1}.[20] These observations indicate that the catalytic mechanism taking place at the catalytic metal center is similar for **2** and **3**.

To further confirm this assumption a 2000-fold excess of TBAX (TBA = tetra-*n*-butylammonium, X = Cl or I) was added to the catalytic mixture containing **3**. This test is applied to detect a potential dissociation of the terminal anion under catalytic conditions. This is an important issue as the addition of extra chloride led to a complete loss of catalytic activity for **1**, whereas no deactivation was observed for **2**.[20] To test for a potential iodide dissociation during catalysis, two experiments were carried out, in a first one a 2000-fold excess of TBACl was added to the catalytic mixture containing photocatalyst **3** and in the second experiment TBAI was added under similar conditions. Importantly, no negative effect on the activity of **3** was observed upon addition of extra chloride or iodide, demonstrating that no iodide dissociation occurs during catalysis (see Table S3).

Recent studies on related photocatalysts, for example, photocatalyst **1**, demonstrated the decomposition of the catalytic metal center by the formation colloidal metal particles, which might contribute to the catalytic hydrogen formation.[19,20] To test for the formation of metal colloids the mercury test was applied, however it turned out that this test is not applicable for compound **3**[*].

Both, the catalytic behavior of **3** and the TBAX halide-addition experiments support the hypothesis that the dominant catalytic reaction mechanism is similar to that of **2**. Sakai and co-workers recently reported for structurally related hydrogen evolving photocatalysts, that the d_{z^2} orbital of the Pt center plays a major role in the bond formation with the proton source (water).[34] Based on the different ligand properties, that is, iodo ligands are stronger π donors than chloride we assumed an increased electron density at the Pt core. This increased electron density could potentially accelerate the initial catalytic step, which is the Pt−H−OH bond formation. To further investigate the effect of the iodido ligands on the electron density at the catalytic Pt center the charge distribution at the catalytic center of **3** was calculated and compared to **2**. DFT calculations indicate that there is a decrease of the positive charge on Pt (by about 0.25) going from **2** to **3** (see Figure S7 and Table S6). This electron density comes essentially from the iodide atoms as can be seen comparing the charges on chloride and iodide, that is, 2 ×

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[*] Preliminary ^{1}H NMR investigations on **3** showed that the dinuclear catalyst reacts with elemental mercury in the dark prior to any catalytic testing (see Figure S6). Nevertheless, even under presence of elemental mercury there is still a significant activity observed for **3**. Thus, a contribution of colloidal platinum to the photocatalytic hydrogen evolution is rather unlikely (see Figure S5 and Table S5).

(charge iodide minus charge chloride) = 0.27. A similar result was obtained by ^{195}Pt NMR spectroscopy investigations on related [(bpy)PtX$_2$] (X = Cl or I) complexes showing an increase in electron density (more negative chemical shift values) at the Pt nucleus induced by the softer iodide ligand compared to chloride.[35,36] In addition, electrochemical investigations were carried out to test whether the increased electron density at the Pt center, induced by the iodide ligands, is also expressed by a corresponding change of the reduction potential of the Pt center. However, no significant difference in the reduction potentials was observed comparing photocatalyst **2** and **3** (see Figure S9 and S10).

As recent studies by Reisner et al. on a photo-hydrogen-evolving system, consisting of Eosin Y as an organic dye and a [NiFeSe] hydrogenase-based catalyst, revealed a pronounced effect of the light intensity of the irradiation source on the catalytic performance, studies were carried out to investigate, if a similar effect exists for **3**.[37]

For technical reasons, the light intensity dependent experiments were not performed in GC vials (5 mL), but in a Schlenk tube (23 mL), which was equipped with one, two, or four LED arrays ($\lambda = 470$ nm, 30–40 mW cm^{-2}) to modulate the light intensity (see Figure S8). As shown in Figure 5, photocatalytic experiments carried out in a Schlenk tube equipped with two LED arrays result in an overall TON of 275, which is close to the value obtained in GC vials (276). However it must be noted that the endpoint of catalysis is reached after just 48 h of irradiation, meaning an increase of the overall TOF from 3.9 h^{-1} (GC vials) to 5.7 h^{-1} (Schlenk tube). This effect can be explained by the different geometry of the reaction vessel.[38] Upon the addition of two additional LED arrays two major effects were observed. First, the maximum TON rises from 275 to 465 and second, the obtained overall TOF (9.9 h^{-1}) is significantly enhanced. Accordingly, both values, the maximum TON (188) and the overall TOF (2.9 h^{-1}), decrease when only one LED array is used as the irradiation source. To further exploit the photocatalytic potential for compound **3** further studies with more-intense irradiation sources are planned.

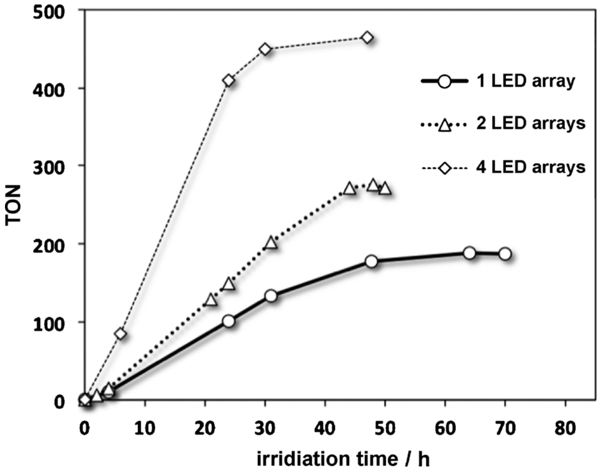

Figure 5. Turnover numbers (TONs) of **3** ($c = 70$ μM) in 8 mL of a catalytic mixture (6:3:1 v/v/v CH_3CN/TEA/H_2O) in a Schlenk tube equipped with one, two, or four LED arrays as the irradiation source ($\lambda = 470$ nm, 30–40 mW cm^{-2}).

In summary we show that the exchange of the halide ligands of the catalytic platinum center in a molecular photocatalyst changes neither the intramolecular photophysics nor the principal catalytic behavior in the photocatalytic hydrogen production. Both catalysts **2** and **3** show no induction period and a constant TOF during catalysis. However, the exchange of chloride by iodide leads to significant increase of catalytic activity. These observations support studies carried out by Sakai and co-workers, who highlighted the importance of the d_{z^2} orbital of the Pt center for the generation of Pt–H intermediates.[34] As the introduction of iodide ligands increases the electron density at the Pt center and therefore stabilizes such an intermediate, this is likely to lead to increased TON values.

To date the nature of the bridging ligand[19,24,25] and/or the peripheral ligands at the photocenter[17] have been considered as the main components of molecular photocatalysts that can be modified to achieve optimized catalytic behavior and this will always involve changes in the photophysical properties of the systems studied. Therefore, the outcomes of the present study are striking, as upon a very simple change in the composition of the catalytic center the catalytic efficiency increases by a factor of almost 40, while the photoinduced intramolecular processes observed in the PtI$_2$ containing compound **3** are not different from those found for compound **2** based on PtCl$_2$. This shows for the first time that significant improvements in the photocatalytic behavior of intramolecular assemblies can be obtained by targeted co-ligand optimization of the catalytic metal center and without the need for a modification of the photophysical properties. This is a completely new starting point in the continuing efforts to optimize the photocatalytic properties of such supramolecular assemblies and suggests that as observed for intermolecular systems the rate determining step could be based on the catalytic center.

Keywords: electron density · hydrogen production · iodide ligands · photocatalysis · platinum

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