First Application of a Water-Soluble Matrix-Stabilized Palladium Nanoparticle Catalyst for Photocatalytic Hydrogen Generation with High Activity and Stability

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Abstract: Pd@(BiPy-PEG-OMe) is a catalyst comprised of palladium nanoparticles (Pd-NPs) stabilized and made water soluble by 2,2'-bipyridine-end-functionalized polyethylene glycol monomethyl ether. It has been used in the past for nitrile hydrogenation. In this work, we prove that it is also very active for photocatalytic hydrogen generation, which might be true for more catalysts of its kind and worth further investigation. Using the inexpensive photosensitizer Eosin Y, high turnover numbers (TONs) of over 4.500 are achieved for the evolution of molecular hydrogen from pure water under visible light irradiation. Replacing Eosin Y, which showed only a short lifetime under experimental conditions (i.e. few hours) by a novel osmium-based metal complex, which is also characterized by its crystal structure, the longevity of the system can be boosted to over one and a half months with a maximum TON of 1500. Combining excellent yield and stability is a clear goal for further research.

Introduction

In the last years, a very quickly growing area of research has been the utilization of sunlight to generate various fuels. One of the different ways developed to this end is the conversion of solar energy into chemical energy stored in the hydrogen molecule, which can be burned as fuel directly, used in fuel cells or further converted to a vast number of more complex useful chemicals. Ideally, the protons to be reduced into molecular hydrogen gas would be supplied by water, a naturally abundant and environmentally friendly solvent.

The foundation for this line of research was laid in the late 1970s by Lehn and Sauvage et al. with a system utilizing a sacrificial donor, a ruthenium dye as photosensitizer capable of absorbing visible light, an electron relay and a colloidal platinum catalyst active in the hydrogen evolution reaction (HER).[1] Ideally, a coupling with an oxygen evolving reaction (OER) supplying the needed electrons would overcome the need for an additional donor, but except for alternative non-oxygenic water splitting schemes, two fitting half-systems have not yet been found. The

following findings will also present a pure HER system with a typical amine donor.

In the early days of HER discoveries, nanoscience was not a topic named as such, but it is well known that the old field of colloidal chemistry was always using particles on a nanometer scale. As such, the original colloidal platinum catalyst was already an example for a system using heterogeneous nanoparticles. Later developments would eliminate the need for an electron relay by choosing dyes and catalysts with better matched redox potentials. Dyes were replaced with ones using more abundant metals,[2],[3] for sustainability and cost reasons. These metal complexes are usually chosen for solubility and stability as well as the possibility to fine-tune the electronic properties, but simple two-component nanocrystals can also be used as photosensitizers.[4] On the catalyst side, there are many examples for water soluble compounds capable of the HER,[5],[6] in these cases also using earth-abundant metals. These homogeneous catalysts offer the advantages of being easier to study and control, as many factors like surface effects and light diffraction do not have to be taken into account. However, heterogeneous HER catalysts are at least equally, if not more popular, with especially TiO_2 modifications dominating the field.[7]

In recent years also composite materials for photo- or electrocatalysis have been an upcoming topic of research. Especially in the field of electrocatalysis, coordination polymers[8] and stabilized nanoparticles[9] in polymer electrodes have become increasingly interesting. Composite materials based on graphene, metal free or doped with different metals, show a high potential in the field of photocatalysis.[10][11] A very detailed review about graphene composites and their application for solar water splitting was published by Yuan et al.[12] The clear advantage of using for example nanostructured photoelectrodes or surface-grafted nanoparticles is the ability to fine-tune many different properties of the catalyst at once as desired.

However, many of the chosen examples have a clear disadvantage: due to solubility or stability reasons, they do not work in pure water. A system with an organic solvent as necessary component is surely less sustainable or "green" as a purely water-based one. Overall, to our knowledge there is currently no HER system capable of fulfilling all the mentioned demands: earth-abundant and inexpensive materials, a clearly understandable mechanism, longevity, usability in pure water and, maybe above all, high turnover numbers for hydrogen production.

Herein we report two basic systems using Pd-nanoparticles (NPs) stabilized by water-soluble functionalized polyethylene glycol (PEG), combining hence the advantage of homogeneous and heterogeneous catalysis. While the noble metal palladium is still used, a number of other desirable properties are achieved that should prove them as a solid platform for further refinement. One system works in pure water due to the PEG matrix. To our knowledge, this is the first work using these kinds of compounds

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for molecular hydrogen generation as opposed to organic synthesis. One system uses an osmium-based photosensitizer to achieve constant hydrogen production over months; the other uses Eosin Y, an inexpensive and nontoxic dye that has been used in many other systems[13], for an excellent hydrogen evolution rate and amount.

Results and Discussion

Pd-NPs surrounded by various matrices to improve both stability and solubility are currently of high interest as catalysts for organic synthesis, as the possibility of using water as a solvent provides the opportunity for them to be used in green chemistry.[14] Pd-NPs of an average size of 2.1 nm and stabilized by an 2,2'-bipyridine-functionalized polyethylene glycol monomethyl ether (PEG-OMe) matrix (Pd@BiPy-PEG-OMe) (**1**), as shown in Figure 1, with a Pd content of 2.0 wt% have been synthesized, characterized and applied for the catalytic hydrogenation of various nitriles to amides in water.[15] Herein **1** has been used to photocatalytically generate hydrogen, following suggested catalytic cycles depicted in Figure 2.
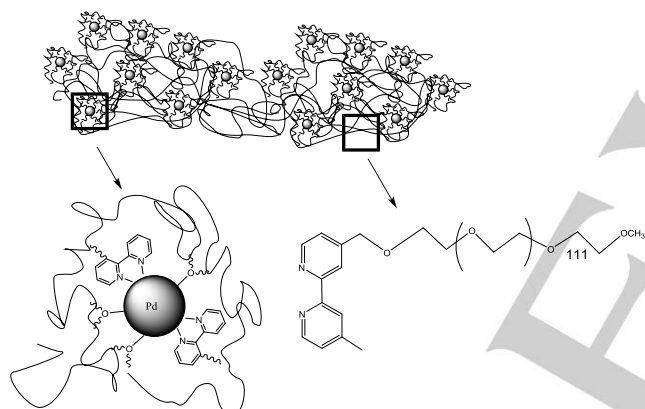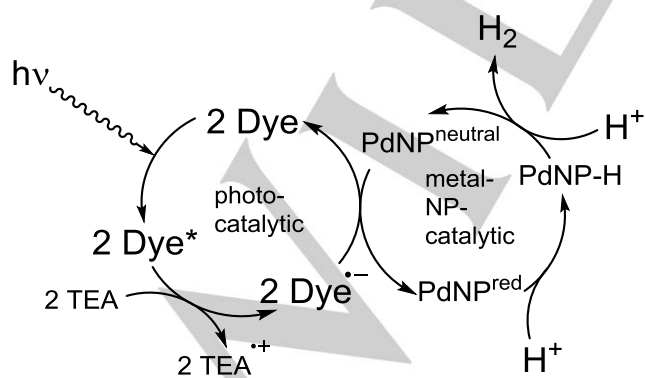

Figure 1. Schematic drawing of **1**.

Figure 2. Suggested catalytic cycles operative in Pd-NPs-based photocatalytic H$_2$ generation.

For the following reactions, the same general setup was used. Solvent in all cases but the first was a 10% solution of triethylamine (TEA) in pure water (all experiments with Eosin Y) or a 1:1 (v:v) water and acetonitrile solvent mixture (most other experiments), in which both dye and catalyst were completely dissolved in various concentrations. The solution was degassed using the freeze-pump-thaw method. Irradiation was done with a white-light LED lamp, hydrogen detected and measured with gas chromatography. Using the thus obtained volume of H$_2$ gas in the headspace, a turn-over-number (TON) was calculated with respect to the amount of Pd atoms exposed to the reaction solution; this is also the amount used to give molar ratios. More details on measurements and exact TON calculation are available in the supporting information.

The second complex investigated was [Ir^{III}(ppy)$_2$(bpy)](PF$_6$) (**2**), (Figure 3), while the molecular structure of **2** is shown in Figure 4. It is also a common photosensitizer for these kinds of reactions.[16],[17] The initial experiment already produced a promising TON of over 360, with hydrogen production ceasing after only 1 h of reaction time. This was suspected to be due to decomposition of the metal complex, so more **2** was added to the reaction mixture. Upon further irradiation, H$_2$ production resumed, proving that the photosensitizer was the limiting factor (Figure 3).

In this and the following graphs, connection lines are added only for visual clarity, not meant to indicate a linear behavior.
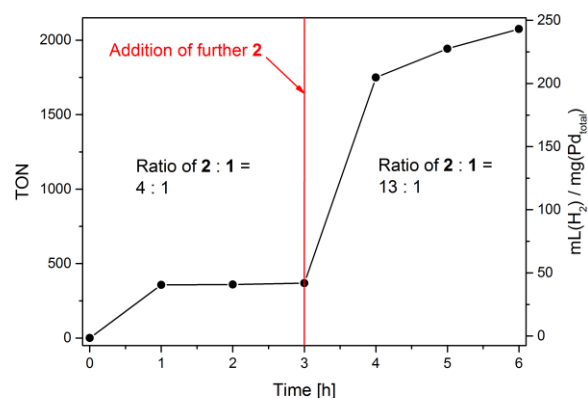

Figure 3. Hydrogen generation with catalyst **1** and photosensitizer **2** in a 1:1 water and acetonitrile mixture containing 10% TEA. Irradiation performed with a white light LED. Second stoichiometric ratio calculated under the assumption that all of the initially present **2** had been bleached after 3 h.

Different molar ratios between **2** and **1** were tested and the TON measured after 1 h. The results are summarized in Figure 4.

As one can see, increasing the ratio to higher than 20-40:1 is not advantageous, with the highest TON achieved just under 2000.
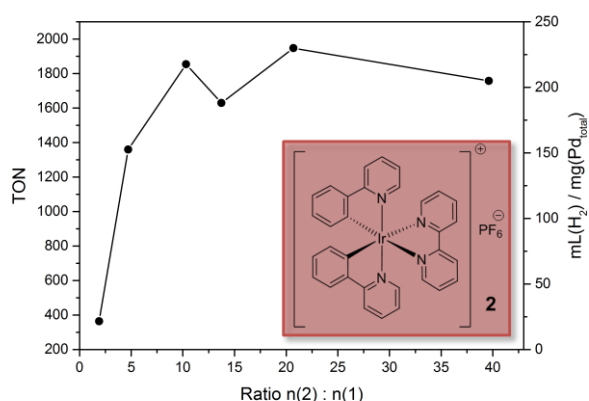
Figure 4. Optimization of the **2**:**1** molar ratio

The actual palladium content of the catalyst is ultimately rather low, so using the catalyst in general should be acceptable from a green chemistry standpoint if it worked well enough; however, the dye needed to be replaced with one containing no noble metals.

Eosin Y (**3**) (see Figure 6 for structure) is a common dye used in photocatalytic hydrogen generation reactions, containing no metals at all, as well as being nontoxic and inexpensive. During initial tests with a **3** to **1** molar ratio of 40, promising results were obtained with hydrogen gas formed in good TONs.

However, the question arose if the measurement method could be prone to errors due to the fact that even though for each measurement the headspace was pumped off, hydrogen would still remain dissolved in solution. This could affect the reaction either negatively (due to the possibility of a back reaction in equilibrium) or positively (due to the presence of a reducing atmosphere, eliminating quenching or other efficiency reducing effects from trace oxygen left after Argon purging). Therefore, two experiments were performed with the same conditions and the usual method of pumping off the entire headspace for GC analysis; however, in one case, the solution was then purged with additional Argon gas after each measurement. Surprisingly, these experiments gave almost the same results, suggesting that pumping off the headspace eliminated enough hydrogen from the system that further hydrogen removal with Argon made no difference. Another experiment was therefore conducted with no measurements made during irradiation at all, only after two hours, the previously observed stopping point of hydrogen evolution, which also coincided with a color change of the solution, to a typical green associated with bromide loss from the dye.[18] In another surprise, this led to a vastly increased TON. The results of these experiments are summed up in Figure 5.

It stands to reason therefore that the presence of hydrogen evolved from and staying in the system is purely positive, and total removal for each measurement would therefore give lower TONs.
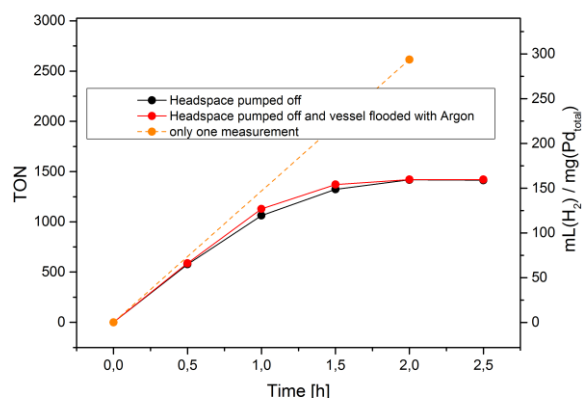

Figure 5. Different H$_2$ measurement methods with Eosin Y as photosensitizer

The system using **3** as sensitizer was then varied to find optimized conditions.
Different donors instead of TEA were tested, leading ultimately to the conclusion that TEA was the most optimal one to use. The pH value was changed to see how the outcome would be affected. It was found that the highest TON values were obtained by not lowering the pH off its initial 12 from the TEA solution. Finally, the molar ratio between 3 and 1 was optimized to an ideal ratio of 120:1.

These conditions were then employed in the original laboratory setup to determine the highest possible TON number with the white-light irradiation method. For this experiment, each data point was acquired by irradiating a new sample of the same mixture of compounds for a certain time and then measuring just once. Despite the above results showing a molar ratio of 120:1 between **3** and **1** being ideal, in the changed irradiation conditions, 100:1 proved superior. The excellent result of this system is shown in Figure 6.
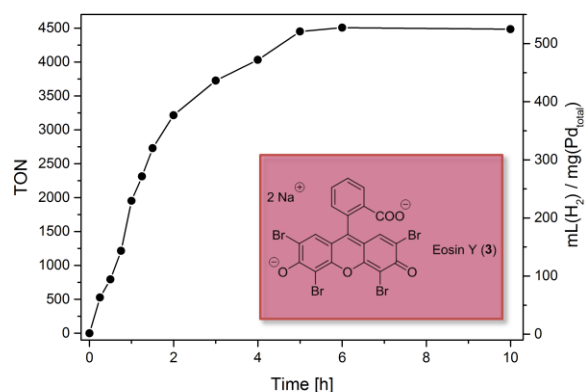

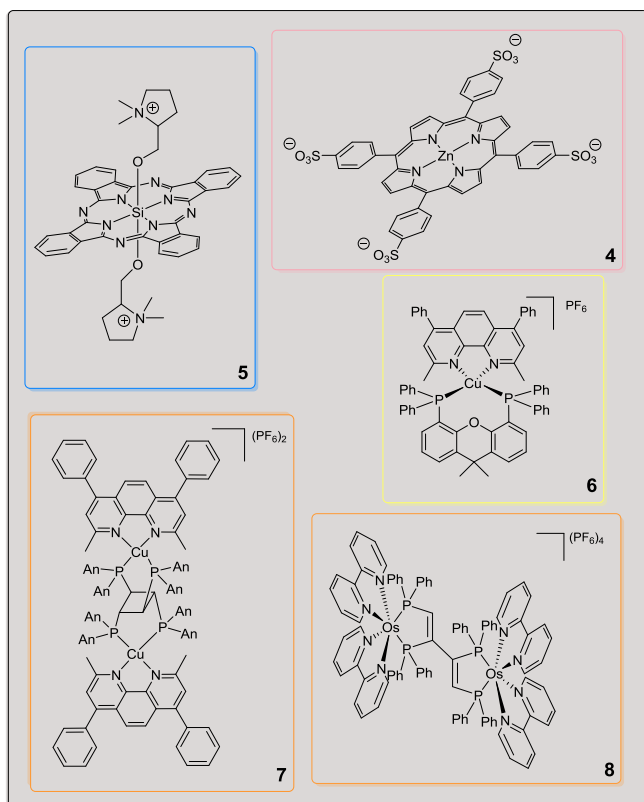**Figure 6.** TON curve using Eosin Y (**3**) as photosensitizer

Figure 7. Photosensitizers investigated for stability.

While the systems using Eosin Y as photosensitizer lead to high TONs, a clear dead end for further development with this kind of dye is their longevity. Therefore, different photosensitizers were investigated as possible replacements (Figure 7).

The zinc-centered water-soluble Zinc(II)-tetrakis(4-sulfonatophenyl)porphyrin (ZnTPPS^{4-}, **4**) has been used as a single electron donor compound in photocatalytic reactions before,[19] as well as been investigated for hydrogen generation in our group with surprising activity even without a catalyst.[20] Additionally, while it will still bleach after overnight irradiation, it is more stable than Eosin Y and might be a good starting point for further, even more stable derivatisations. However, no hydrogen evolution was observed using the standard conditions. As it has been shown that on its own with an electron donor, ZnTPPS^{4-} does evolve hydrogen from water, the sensitizer must have some interaction with the catalyst, but is probably not enough to supply both electrons needed for free hydrogen generation.

Another compound previously investigated by our workgroup is bis[(1-methylpyrrolidin-2-yl)methoxy] [phthalocyaninato] silicon (SiPc, **5**), a silicon phthalocyanine made water soluble through ionic axial ligands.[21],[22] It was shown that under red-light irradiation with an electron donor present, a stable radical anion forms. This species should theoretically be able to serve as an electron donor for a single-electron-transfer (SET) to the catalyst. However, using the standard conditions, no hydrogen was detected and said radical anion was accumulated, proving that

the SET is not possible. Reactions with **4** and **5** were conducted in pure water, but for the following sensitizers, the solvent mixture had to be changed back to a 1:1 mixture of water and acetonitrile for solubility reasons.

[Cu^I(bathocuproine)(xantphos)](PF$_6$) (**6**), was tested as it had previously along with other copper-based dyes been reported as lasting for up to three days in the right conditions, a vast improvement over the two hours of the most efficient Eosin Y systems.[23],[24] Using **6** in this system did not lead to hydrogen evolution. It was however observed that the originally yellow solution turned colorless after overnight irradiation and black particles precipitated. This led to speculation about agglomeration of the nanoparticles caused by the xanthphos ligand. To prove this hypothesis, the free ligand was added to a solution otherwise identical to the ones used for the successful hydrogen evolution experiments. This prevented hydrogen evolution completely. It can therefore be reasoned that free phosphine in the solution will cause the Pd-NPs to agglomerate.

Thus, further investigation was done with sensitizers featuring more stable metal-phosphorus bonds, like in [Cu$_2$(o-MeO-dppcb)(bathocuproine)$_2$](PF$_6$)$_2$ (**7**), where the preparation of this new complex will be published elsewhere. In a system using this sensitizer, hydrogen evolution was detected, but only a single time after one hour of irradiation, giving a TON of 276. It is possible that the central tetraphos-ligand was still not bound stably enough to the copper ions.

We synthesized a new Osmium-tetraphos-based photosensitizer of the formula [Os$_2$(bpy)$_4$(dppbd)](PF$_6$)$_4$ (**8**) (see SI) which exhibited a surprisingly high stability (i.e. multiple days) in the course of the photocatalytic reaction at the expense of the catalytic activity. The TON curve for this experiment is shown in Figure 8.
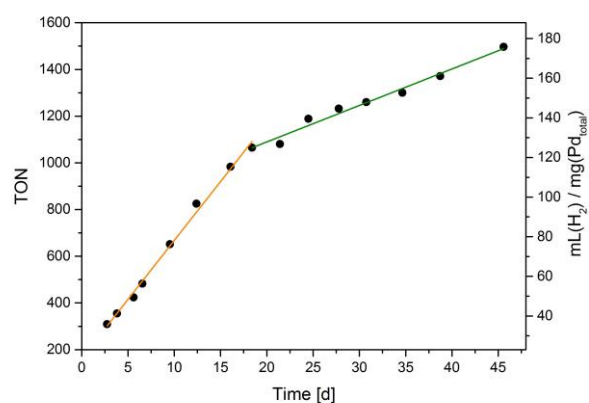

Figure 8. TON curve using **8** as sensitizer

As shown in Figure 8, the photocatalytic system produced hydrogen for more than one month. It is interesting to note that after 15-20 days, the slope of the graph (Figure 8) decreased, indicating a slower H$_2$ production. Overall, the TON does not exceed 1500 by much, which is obviously worse than the very high numbers reached when using Eosin Y as sensitizer.

However, the stability of **8** under the chosen experimental conditions is unprecedented. Apart from the behavioral change after 15-20 days, both catalyst and sensitizer seem capable of maintaining their activity for a very long time.

In order to elucidate the nature of the observed activity changes occurring during the reaction with photosensitizer **8**, a TEM investigation was carried out. To this purpose, two drops of the catalytic solution (*i.e.* after 45 days) were deposited onto a holey carbon grid and the volatile compounds evaporated at room temperature. In Figure 9, a representative TEM micrograph is shown.
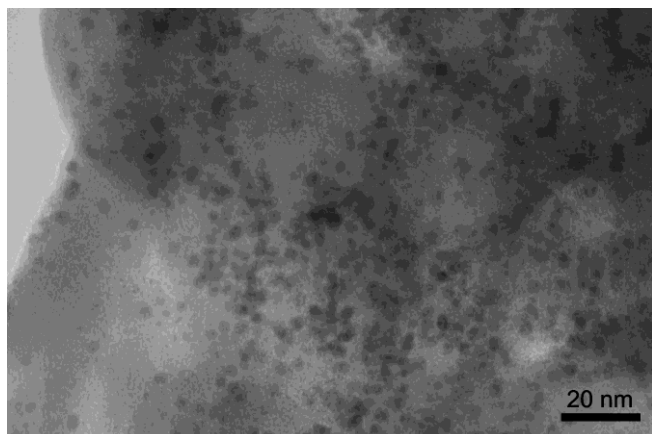

Figure 9. TEM micrograph of the catalytic solution using **8** as photosensitizer.

The observed Pd-NPs showed some aggregation, while the original Pd-size (*i.e.* as-synthesized, 2.1 nm) did only slightly increase to 2.5-3.0 nm. Hence, an increase of the Pd-aggregation led to the accessibility of a lower number of active sites exposed to the solution and consequently the catalytic activity decreased.

Since there are many different experimental setups and only very few similar systems, we are aware of the fact that a comparison with literature values is rather difficult. However, a couple of similar systems, reported in the literature, might be suitable for comparison and are given below. Modified [Ir(ppy)$_2$(bpy)]$^+$ photosensitizers in combination with platinum nanoparticles and TEA/TEOA as sacrificial donors have been used for hydrogen production and reached values of 49 mL(H$_2$)/mg(Pt)[25] and 615 mL(H$_2$)/mg(Pt)[26], respectively, using in situ generated non-stabilized Pt-NPs. Furthermore, THF as an organic solvent was necessary. Another comparable system comprising classic [Ru(bpy)$_3$]$^{2+}$ photosensitizer, ascorbic acid as sacrificial donor and Pt-NPs stabilized with different polymers reached a hydrogen production of up to 25 mL(H$_2$)/mg(Pt) under optimized conditions with no need of an organic solvent.[27]

Conclusions

We have successfully proven that Pd-nanoparticles of an average size of 2.1 nm and stabilized by 2,2'-bipyridine-end functionalized polyethylene glycol (**1**) could easily be applied in typical hydrogen evolution catalysis instead, yielding good results. **1** was successfully applied in combination with Eosin Y (**3**) and a new binuclear Os-tetraphos complex (**8**) as photosensitizer and triethylamine as electron donor to produce hydrogen from water. The surface atom related TON values obtained were 4500 (**3**) and 1500 (**8**). Unlike **3**, **8** proved to be very stable under photocatalytic conditions (*i.e.* 45 days (**8**) vs 6 h (**3**)). The molecular structure of **8** gave rational hints for its observed photocatalytic stability. The combination of **1** and **8** (long living photosensitizer) made it possible to test **1** under exceptionally long experimental conditions (45 days) and to prove that the PEGylated Pd-nanoparticles increased only slightly in size under real photocatalytic conditions, making them ideal candidates to conduct the catalytic reaction homogeneously. This stability outperforms colloidal platinum catalysts as well as comparable molecular Os−Pd-dyads.[26],[28],[29]

Further investigation is necessary to optimize the Pd catalyst and further increase its high hydrogen yield. Also, the longevity of the osmium dye is unprecedented for homogeneous catalysis and a way needs to be found to optimize this photocatalytic system for hydrogen production from water.

Experimental Section

All chemicals and solvents were purchased from commercial sources in reagent quality and used without further purification. Water was purified with a Milli-Q system (Millipore, Bedford, MA, USA).

Synthetic details/appropriate references for all new and previously reported compounds **1**−**8** are provided in the Supporting Information, pages 15−18. Characterisation data (NMR spectra, mass spectral/-elemental analysis data) for any new compounds are also given.

Depending on the deployed chromophore either pure water or a 1:1 (v:v) mixture of water and acetonitrile was used. The experiments were conducted with different setups:

TEM analysis was carried out on a TEM PHILIPS CM 12 instrument, equipped with an OLYMPUS Megaview G2 camera and using an accelerating voltage of 100 keV. A suitable sample for the analysis was prepared by depositing a drop of the catalytic solution on a holey film of a 300 MESH Cu grid, followed by evaporation of the volatile compounds at room temperature.

X-Ray Diffraction (XRD): Measurements were conducted with a Bruker D8 Quest PHOTON 100 diffractometer (Mo-Kα-tube, multi layered optics, CMOS detector). Bruker Apex II was utilised for data collection. For cell refinements, data reduction, and empirical absorption corrections Bruker SAINT-V 8.34A and Bruker SADABS-2014/5 were used, respectively. Structural refining was performed with the program SHELXL-2014/7. For graphic representations the program ShelXle Version 4.3.0 was utilised.

Further details regarding the different reaction setups, exact amounts of compounds used in each reaction as well as individual results, and the calculation of turnover numbers are found in the Supporting Information. CCDC-1561073–1561074 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data%5Frequest/cif.

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[1] M. Kirch, J.-M. Lehn, J.-P. Sauvage, *Helv. Chim. Acta* **1979**, *62*, 1345.
[2] W. Krüger, J.-H. Fuhrhop, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 131.
[3] J. R. Darwent, P. Douglas, A. Harriman, G. Porter, M.-C. Richoux, *Coordination Chemistry Reviews* **1982**, *44*, 83.
[4] Z. Han, F. Qiu, R. Eisenberg, P. L. Holland, T. D. Krauss, *Science (New York, N.Y.)* **2012**, *338*, 1321.
[5] J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson, S. Bernhard, *J. Am. Chem. Soc.* **2005**, *127*, 7502.
[6] P. Du, K. Knowles, R. Eisenberg, *J. Am. Chem. Soc.* **2008**, *130*, 12576.
[7] F. E. Osterloh, *Chemical Society reviews* **2013**, *42*, 2294.
[8] H. Jia, Y. Yao, Y. Gao, D. Lu, P. Du, *Chemical communications (Cambridge, England)* **2016**, *52*, 13483.
[9] D. Mullangi, V. Dhavale, S. Shalini, S. Nandi, S. Collins, T. Woo, S. Kurungot, R. Vaidhyanathan, *Adv. Energy Mater.* **2016**, *6*, 1600110.
[10] N. Zhang, M.-Q. Yang, S. Liu, Y. Sun, Y.-J. Xu, *Chemical reviews* **2015**, *115*, 10307.
[11] M.-Q. Yang, N. Zhang, Y. Wang, Y.-J. Xu, *Journal of Catalysis* **2017**, *346*, 21.
[12] L. Yuan, C. Han, M.-Q. Yang, Y.-J. Xu, *International Reviews in Physical Chemistry* **2016**, *35*, 1.
[13] T. Lazarides, T. McCormick, P. Du, G. Luo, B. Lindley, R. Eisenberg, *Journal of the American Chemical Society* **2009**, *131*, 9192.
[14] S. Doherty, J. G. Knight, T. Backhouse, E. Abood, H. Alshaikh, I. J. S. Fairlamb, R. A. Bourne, T. W. Chamberlain, R. Stones, *Green Chem* **2017**, *19*, 1635.
[15] W. Oberhauser, M. Bartoli, G. Petrucci, D. Bandelli, M. Frediani, L. Capozzoli, C. Cepek, S. Bhardwaj, L. Rosi, *Journal of Molecular Catalysis A: Chemical* **2015**, *410*, 26.
[16] F. Gartner, B. Sundararaju, A.-E. Surkus, A. Boddien, B. Loges, H. Junge, P. H. Dixneuf, M. Beller, *Angewandte Chemie (International ed. in English)* **2009**, *48*, 9962.
[17] X.-W. Song, Y. Meng, C.-L. Zhang, C.-B. Ma, C.-N. Chen, *Inorganic Chemistry Communications* **2017**, *76*, 52.
[18] M. A. Mahmoud, G. Weng, *Catalysis Communications* **2013**, *38*, 63.
[19] Y. Amao, R. Abe, S. Shiotani, *Journal of Photochemistry and Photobiology A: Chemistry* **2015**, *313*, 149.
[20] S. Salzl, M. Ertl, G. Knor, *Physical chemistry chemical physics : PCCP* **2017**, *19*, 8141.
[21] C. Uslan, B. Şebnem Sesalan, *Inorganica Chimica Acta* **2013**, *394*, 353.
[22] C. Uslan, K. T. Oppelt, L. M. Reith, B. S. Sesalan, G. Knor, *Chemical communications (Cambridge, England)* **2013**, *49*, 8108.
[23] S.-P. Luo, E. Mejia, A. Friedrich, A. Pazidis, H. Junge, A.-E. Surkus, R. Jackstell, S. Denurra, S. Gladiali, S. Lochbrunner et al., *Angewandte Chemie (International ed. in English)* **2013**, *52*, 419.
[24] N.-Y. Chen, L.-M. Xia, A. J. J. Lennox, Y.-Y. Sun, H. Chen, H.-M. Jin, H. Junge, Q.-A. Wu, J.-H. Jia, M. Beller et al., *Chemistry (Weinheim an der Bergstrasse, Germany)* **2017**, *23*, 3631.
[25] Y.-J. Yuan, J.-Y. Zhang, Z.-T. Yu, J.-Y. Feng, W.-J. Luo, J.-H. Ye, Z.-G. Zou, *Inorganic chemistry* **2012**, *51*, 4123.
[26] S.-C. Yang, G. Chang, G.-J. Yang, Y.-J. Wang, B. Fang, *Catal. Sci. Technol.* **2015**, *5*, 228.
[27] H. Lin, D. Liu, J. Long, Z. Zhang, H. Zhuang, Y. Zheng, X. Wang, *Physical chemistry chemical physics : PCCP* **2015**, *17*, 10726.
[28] C. M. Strabler, S. Sinn, R. Pehn, J. Pann, J. Dutzler, W. Viertl, J. Prock, K. Ehrmann, A. Weninger, H. Kopacka et al., *Faraday discussions* **2017**, *198*, 211.
[29] J. Prock, C. Strabler, W. Viertl, H. Kopacka, D. Obendorf, T. Müller, E. Tordin, S. Salzl, G. Knör, M. Mauro et al., *Dalton transactions (Cambridge, England : 2003)* **2015**, *44*, 20936.

Entry for the Table of Contents

Layout 2:

ARTICLE

Author(s), Corresponding Author(s)*

Page No. – Page No.

Title

Palladium nanoparticles of 2.1 nm in size, stabilized by 2.2'-bipyridine-end-functionalized polyethylene glycol monomethyl ether in combination with a suitable photosensitizer showed either excellent productivity (TON of 4500) or longevity (45 days) in the photocatalytic hydrogen generation from water.