



## Photoprocesses in Chemistry Education – Tracing Photochemical Reactions with a Digital Low-Cost Photometer

Malte Petersen<sup>1,†</sup>, Carolin Müller<sup>2,3,†</sup>, Manuel Wejner<sup>1</sup>, Sven Rau<sup>4</sup>,  
Benjamin Dietzek-Ivanšić<sup>2,3</sup>, Timm Wilke<sup>1,\*</sup>

<sup>1</sup>Friedrich Schiller University Jena, Institute for Inorganic and Analytical Chemistry, Chemistry Education Department, 07743 Jena, Germany, [timm.wilke@uni-jena.de](mailto:timm.wilke@uni-jena.de)

<sup>2</sup>Friedrich Schiller University Jena, Institute of Physical Chemistry and Abbe, Center of Photonics, 07743 Jena, Germany

<sup>3</sup>Leibniz Institute of Photonic Technology Jena, Department of Functional Interfaces, 07745 Jena, Germany

<sup>4</sup>Ulm University, Institute of Inorganic Chemistry I 89081 Ulm, Germany.

<sup>†</sup> These authors contributed equally to this work and should be regarded as equal authors.

### Abstract

*Chemical reactions with light are the basis of life on earth and currently highly relevant with regard to the climate debate. However, their importance is not yet adequately reflected in school education, and consideration in chemistry classes is often limited to narrow focal points, such as photovoltaics or light as a possible radical starter. To fill this gap to some extent, we propose the sustainable generation of hydrogen with sunlight as a valuable extension of the curricula. This area offers the potential to address students' interest in green chemistry and synergistically link several classical school chemistry contents with societal issues. Reactions driven by (solar) light are the main focus of the German transregional collaborative research center CATALIGHT. To pave way for a broad usage of abundant solar energy, CATALIGHT develops molecular light-driven chromophores and catalysts, and establishes concepts for their integration into soft matter matrices. In close cooperation between chemistry and chemistry didactics, central results are didactically reconstructed for school chemistry education. An important building block for understanding the scientific background is the tracking of photochemical processes. However, schools often lack the necessary equipment for quantitative analysis. For this reason, we developed a low-cost photometer module for the existing LabPi framework. This offers teachers accurate, inexpensive, and easy-to-use analytics and enables quantitative observation of diverse processes and reactions with light. In this paper, we demonstrate the analytical capabilities of the LabPi photometer using the photochemical hydrogenation of a ruthenium complex as an example, which is considered to have great potential for photocatalytic water splitting in research. Within this simple experiment, we will combine the UV light irradiation with a simultaneous measurement of the reaction progress over time. These results are easy to analyse and can be obtained by pupils within a few minutes.*

**Keywords:** chemistry education, photocatalysis, water-splitting, low-cost, photometer

### 1. Introduction

In 2019, about 80% of the world's energy was derived from fossil fuels [1]. Their use releases a large amount of carbon dioxide, which contributes to the greenhouse effect and accelerates climate change. In addition to this effect, the continued shrinking availability of these resources is creating increased pressure on all disciplines of science to develop alternative ways to provide energy. For these reasons, renewable energy sources will become increasingly important in the future and will have to replace conventional methods in the long run [2]. This development must be brought closer to the students and explained in school. If energy generation from sunlight is considered, it shows the greatest potential of all primary energy sources. The annual irradiated light energy amounts to about  $2,7 \times 10^7$  exajoules on average [3] and thus exceeds the annual energy demand of mankind - about 600 exajoules - many times over [1]. This resource can be used in various ways, but with sunlight, in addition to the extraction, the storage of energy must always be considered. In this context, the direct photochemical conversion and sustainable generation of hydrogen with sunlight is currently receiving high attention in science.



## 2. Chemistry Education

Despite this increasing importance of chemistry with light, the subject complex is not yet adequately reflected in schools. To fill this gap and to address students' interests („Fridays for Future“), the implementation of current research on photochemistry into chemistry education offers great didactic potential. Here, the transregional collaborative research center CATALIGHT [4] develops molecular light-driven chromophores and catalysts, and establishes concepts for their integration into soft matter matrices, providing an excellent starting point for integration into school. For this, central research results are didactically reconstructed for school chemistry in close cooperation between specialist in science and in chemistry education [5].

An important building block for the understanding of numerous photochemical processes is an accompanying photometric tracing of the reaction course. This is typically problematic at schools, where the necessary analytical equipment is often lacking due to cost constraints. This challenge can be addressed with low-cost measuring stations; in the following experiment, the quantitative determination is carried out by the photometer of the measuring system LabPi (Fig. 1) [6]. This enables schools to follow different photochemical reactions in a simple and inexpensive way.

In addition to the typical concentration determination of different solutions [7], this experiment shows that the photometer can also serve as a photon source for a light-driven reaction. For this purpose, the photochemical hydrogenation of the ruthenium complex  $[(tbbpy)_2Ru(dppz)]Cl_2^+$  (*tbbpy*: 4,4'-dimethyl-2,2'-bipyridine, *dppz*: dipyrido[3,2-a:2',3'-c]phenazine) [8] was reconstructed for chemistry education, which is a model compound for the photoactive center in light-driven molecular catalysts for hydrogen evolution [9].



**Fig. 1:** *Left:* Image of the LabPi photometer with the measuring chamber closed. *Right:* Image of the LabPi photometer with the measuring chamber open and view of the holder for the cuvette.

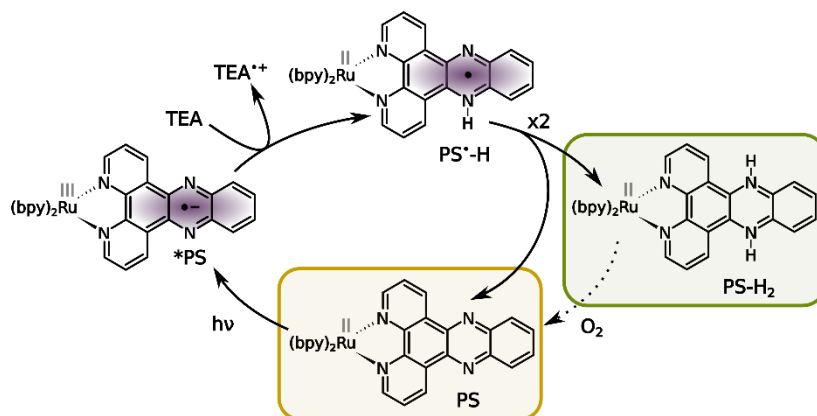
## 3. Scientific Background

Until now,  $[Ru(tbbpy)_3]^{2+}$  is a popular building block utilized in artificial photosynthetic systems due to their chemical and photochemical stability, redox activity, and long-lived excited states [10]. A key property of such photosensitizers is the ability to drive the accumulation of charges at a catalytic center (intra- or intermolecular). Since, many light-driven catalytic processes, such as proton or  $CO_2$  reduction, are based on multielectron and -proton processes, Ru(II) complexes that can store at least two reducing equivalents came into focus of research over the last decades. A typical approach to meet these requirements is  $\pi$ -extension of a bpy (2,2'-bipyridine) ligand, yielding complexes of the type  $[(tbbpy)_2Ru^{II}(L)]^{2+}$ , where L is a planar, aromatic ligand that bears non-coordinating heteroatoms [11-14]. In particular, the *dppz* chromophore emerged as promising lead structure for many other  $\pi$ -extended ligands [11-15].

During light-illumination in the presence of sacrificial electron donor (e.g., triethylamine or triethanolamine),  $[(tbbpy)_2Ru^{II}(dppz)]Cl_2^+$  (**PS**) and structurally related systems accumulate two electrons and protons, i.e., hydrogen, on the *dppz*-type ligand by proton-coupled electron transfer (PCET) steps. Upon photoexcitation of **PS** between 350 and 500 nm, i.e., in the metal-to-ligand charge-transfer ( $^1MLCT$ ) absorption band (spin-allowed singlet-singlet transitions), electron density is shifted from the metal-centered valence d- to vacant  $\pi$ -orbitals on the ligand spheres. This charge-transfer excitation causes a low-energy hole on the metal and excess electron density on the ligands. The so formed singlet-state usually undergoes rapid inter-system crossing (ISC) giving rise to  $^3MLCT$  states. This  $^3MLCT$  state can act as both a reductant and an oxidant, which is primarily determined by the reduction/oxidation potential of the  $^3MLCT$  state compared to them of electron donors/acceptors. Herein, triethylamine (TEA) is employed as electron donor, to reductively quench the formally oxidized Ru-center of the photoexcited complex  $*[(bpy)_2Ru^{III}(dppz^{\cdot-})]^{2+}$  (**\*PS**), to form  $[(bpy)_2Ru^{II}(dppz^{\cdot-})]Cl$  (**PS $^{\cdot-}$** ).



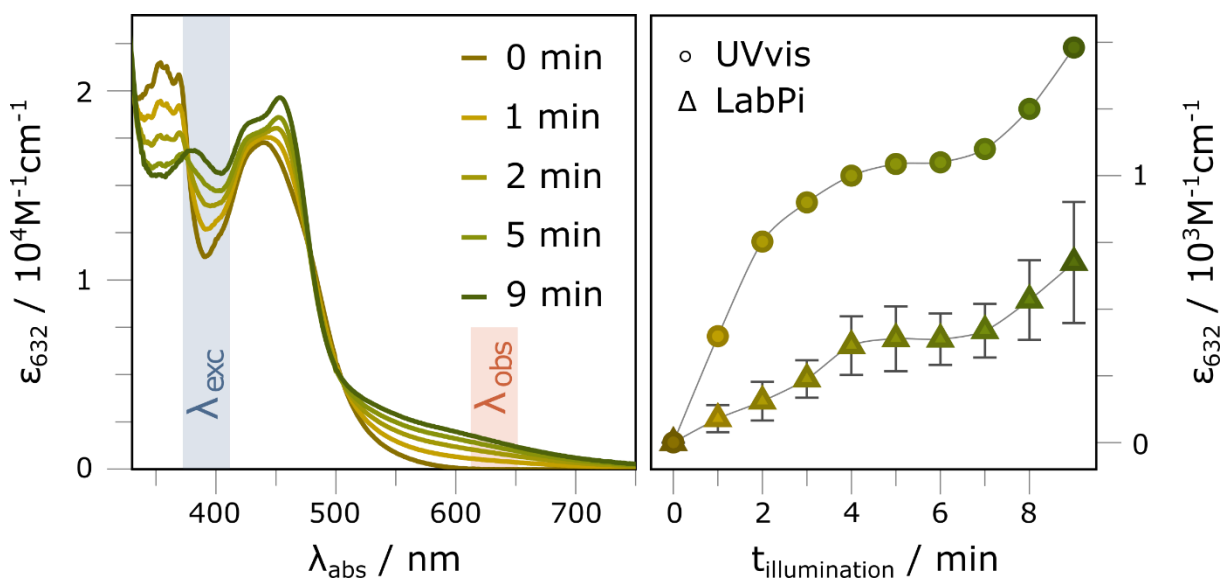
Moreover, upon the oxidation of TEA protons are released that cause a protonation of  $\text{PS}^{\cdot-}$ , forming  $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{dppzH}^+)]\text{Cl}_2^+$  ( $\text{PS}^{\cdot-\text{H}}$ ). This charge compensation was found to be essential to allow a second electron transfer to occur on the same molecular unit as the first one, *i.e.*, the **dppz** ligand [12,16]. In turn, completion of a second reductive quenching cycle, or disproportionation of  $\text{PS}^{\cdot-\text{H}}$  yields the formation of a two-fold reduced and protonated species, namely  $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{dppzH}_2)]\text{Cl}_2$  ( $\text{PS}^{\cdot-\text{H}_2}$ ). The formation of that species causes new arising **dppzH<sub>2</sub>**-centered  $\pi\pi^*$  absorption features at around 600 nm, which is manifested in a color change of the solution from yellow to green [12,16,17].



**Fig. 2:** Mechanism of the light-driven hydrogenation of **PS** (yellow), forming **PS-H<sub>2</sub>**. (green) *via* **\*PS** and **PS<sup>•-</sup>H**. For the sake of clarity, the chloride anions are not shown.

#### 4. Experimental Series

For use in school, a first simplification of the experimental setting was tested. A minimal amount of chromophore **PS** (synthesized in the laboratory) is placed in a UV-transparent plastic cuvette (Brand,  $d = 1$  cm) and successively mixed with 0.5 mL dem. Water, 2 mL acetonitrile (Sigma Aldrich, 99.9%, "ACN") and 0.5 mL triethylamine (Sigma Aldrich, 99%, "TEA"). The measurement and irradiation is performed in the photometer of the LabPi and is carried out in a nine-fold interval of 60-second illumination of the sample by the UV LED ( $\lambda = 392$  nm) and acquisition of the measured values after a 10-second irradiation by the red LED ( $\lambda = 632$  nm). The absorbance coefficient is determined from the absorbance calculated in this way and standardized to the concentration  $\text{PS} = 20 \mu\text{M}$  and plotted against time (Fig. 3). Compared to the recording of the reaction course by the research spectrometer, the values recorded by the LabPi are lower. However, this is due to the cost factor as well as the modified reaction conditions, under oxygen exclusion vs. oxygen atmosphere. The experiment showed that the students can be provided with a device that is suitable for tracking the experiment and the course of the reaction.







**Fig. 3:** *Left:* Monitoring of the light-driven formation of PS-H<sub>2</sub> (green) from PS (yellow, 20 μM) upon LED-illumination at 455 nm (5 mW) in the presence of 1.0 M triethylamine by means of UVvis absorption spectroscopy. *Right:* Increase of absorption at 632 nm in the course of the photoreaction corresponding to the data as shown on the left side and collected using the LabPi (LED-illumination at 392 nm, c(PS) = 20 μM, c(TEA) = 1.2 M).

## 5. Conclusion & Outlook

This proof-of-concept offers an initial opportunity to make the experiments carried out in CATALIGHT accessible to schools. Within the context of a sustainable hydrogen generation with sunlight, students' interests can be addressed and synergistically linked to classical school topic such as catalysis, energetic considerations and redox reactions. The concept presented here offers the potential to apply an analytical procedure not represented in schools and a transfer to other experiments seems possible. In further experiments, the electron donor TEA shall be replaced by TEOA or ascorbic acid for a lower hazard potential.

## 6. Acknowledgments

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## 7. Conflict of Interest

The authors Manuel Wejner and Timm Wilke have affiliations with the organization iTUBS mbH which distributes the measuring system LabPi for educational institutions and training laboratories at cost price. No profits were generated.

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