

# Photoprocesses in chemistry education – Tracing photochemical reactions with a digital low-cost photometer

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## Introduction

Renewable energy sources will become increasingly important in the future and will have to replace conventional methods in the long run due to the limited resources of those. If energy generation from sunlight is considered, it shows the greatest potential of all primary energy sources. 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. 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.

## Chemistry Education

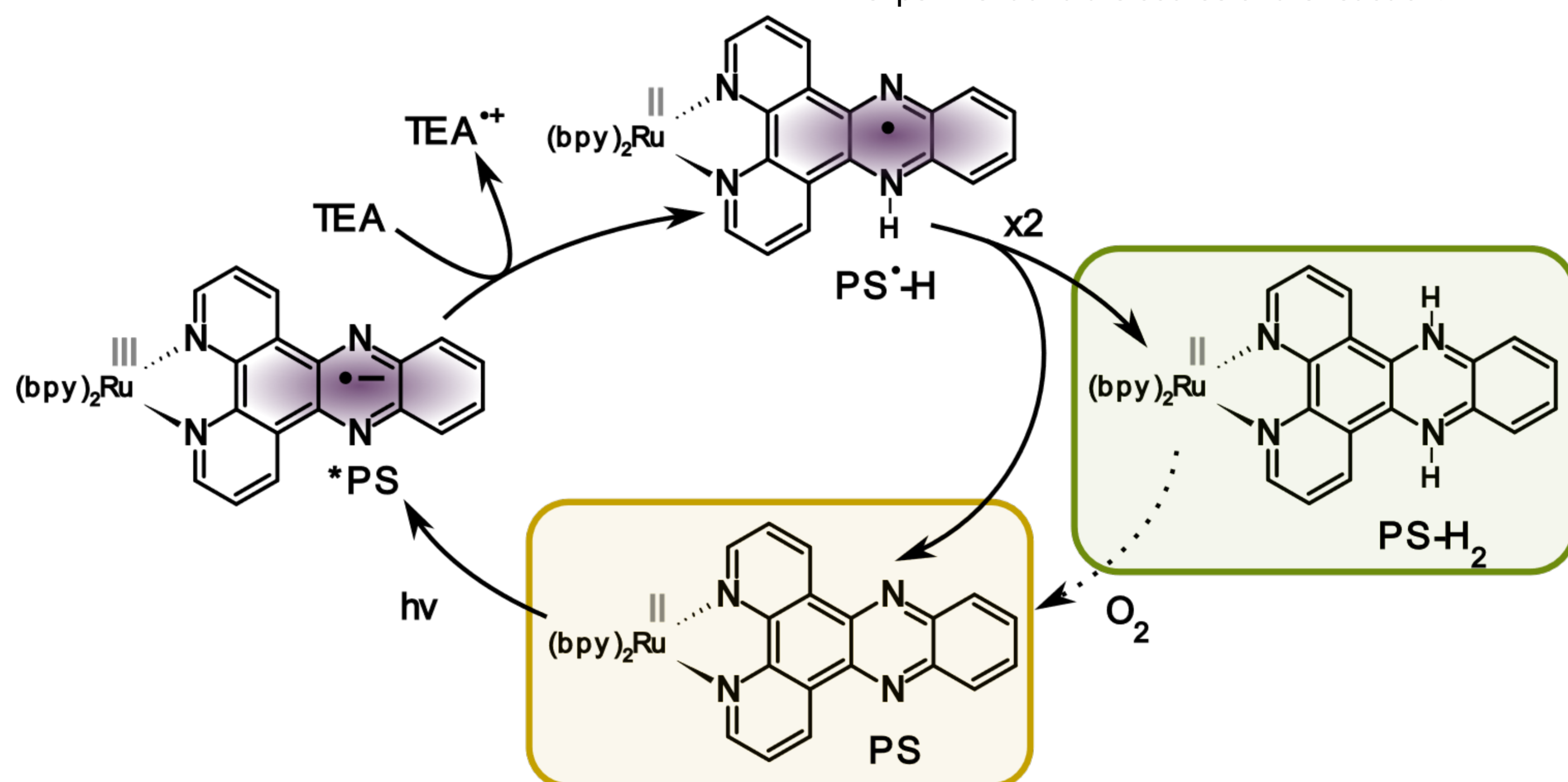
An important building block for the understanding of numerous photochemical processes is an accompanying photometric tracing of the reaction course. This is typically problematic at schools, where the necessary analytical equipment is often lacking due to cost constraints. This challenge can be addressed 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) [1]. This enables schools to follow different photochemical reactions in a simple and inexpensive way. In addition to the typical concentration determination of different solutions [2], 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  $[(\text{tbbpy})_2\text{Ru}(\text{dppz})]\text{Cl}_2^+$  (tbbpy: 4,4'-dimethyl-2,2'-bipyridine, dppz: dipyrdo[3,2-a:2',3'-c]phenazine) [3] was reconstructed for chemistry education, which is a model compound for the photoactive center in light-driven molecular catalysts for hydrogen evolution [4].



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

## Scientific Background

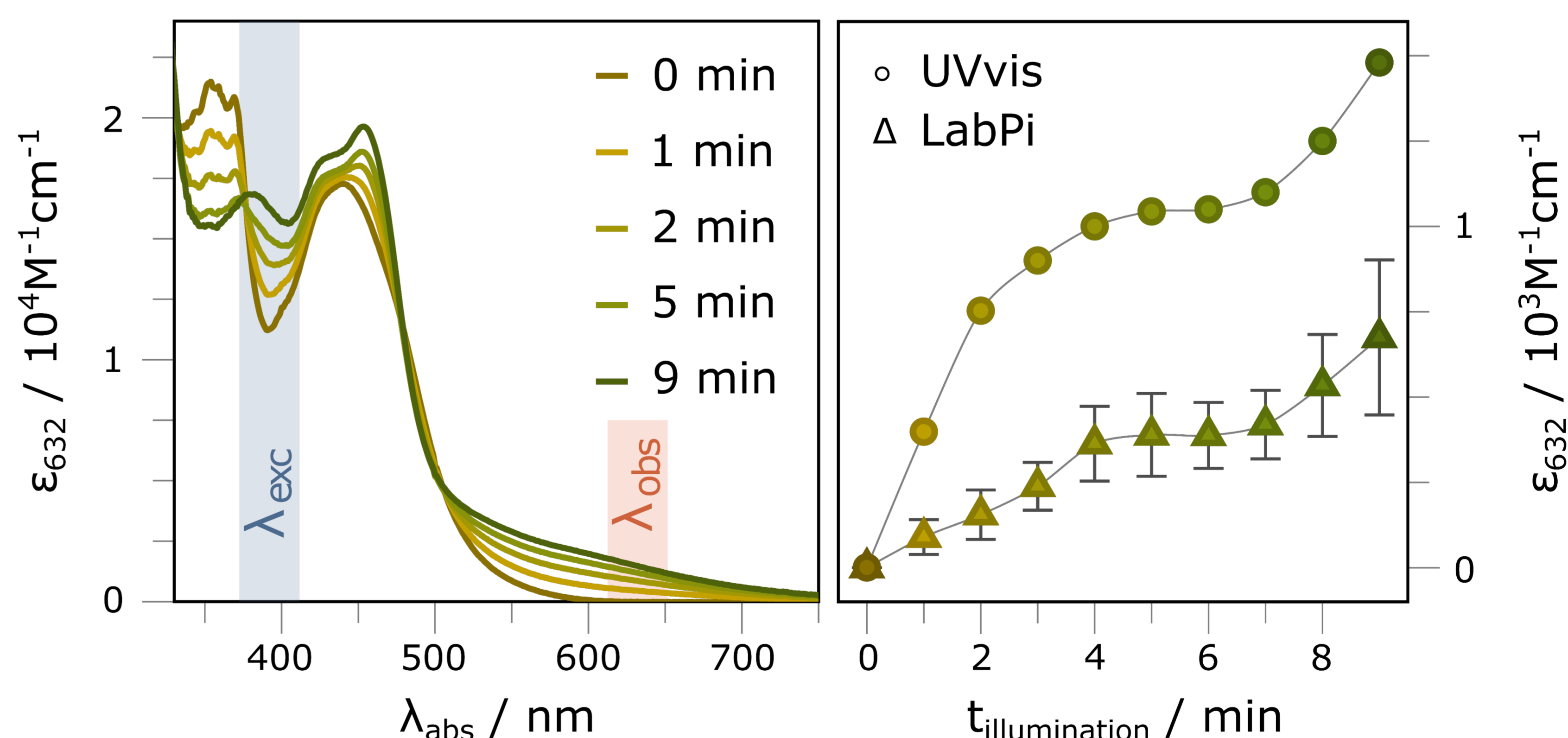
During light-illumination in the presence of sacrificial electron donor triethylamine (TEA),  $[(\text{tbbpy})_2\text{Ru}(\text{dppz})]\text{Cl}_2^+$  (PS) and structurally related systems accumulate two electrons and protons, i.e., hydrogen, on the dppz-type ligand by proton-coupled electron transfer (PCET) steps. Herein, triethylamine (TEA) is employed as electron donor, to reductively quench the formally oxidized Ru-center of the photoexcited complex  $^*[(\text{bpy})_2\text{Ru}(\text{dppz}^{\bullet})]^{2+}$  ( $^*\text{PS}$ ). Moreover, upon the oxidation of TEA protons are released that cause a protonation of  $\text{PS}^*$ , forming  $[(\text{bpy})_2\text{Ru}(\text{dppzH}^{\bullet})]\text{Cl}_2$  ( $\text{PS}^{\bullet}\text{H}$ ). 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 [5,6]. In turn, completion of a second reductive quenching cycle, or disproportionation of  $\text{PS}^{\bullet}\text{H}$  yields the formation of a two-fold reduced and protonated species, namely  $[(\text{bpy})_2\text{Ru}(\text{dppzH}_2)]\text{Cl}_2$  ( $\text{PS}^{\bullet}\text{H}_2$ ). The formation of that species causes new arising dppzH<sub>2</sub>-centered  $\pi\pi^*$  absorption features at around 600 nm (Fig. 3), which is manifested in a color change of the solution from yellow to green [5,6,7]. Fig. 2 summarizes the mechanism.



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

## Experiment & Results

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 and successively mixed with 0.5 mL dem. Water, 2 mL acetonitrile (ACN) and 0.5 mL triethylamine (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 transmission at 392 nm in solvent mixture alone and with the complex (20  $\mu\text{M}$ ) prior to illumination and plotted versus time and standardized to the concentration 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  $\mu\text{M}$ ) 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  $\mu\text{M}$ , c(TEA) = 1.2 M).

## References

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All authors would like to thank the Deutsche Forschungsgemeinschaft (Transregio SFB TRR 234 CATALIGHT, projects A1 and Ö1).



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