Making photocatalysis comparable using a modular and characterized open source photoreactor

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Abstract

Reproducibility and comparability of photocatalytic experiments are still challenging, owing to the large number of experimental parameters and their comprehensive documentation. To overcome this limitation, a modular, adaptable, and extensible photoreactor platform is reported, which enables experiments under well-characterized, reproducible conditions. Comparability is ensured by comprehensive photonic characterization with chemical actinometry and radiometry and open documentation of the incident photon fluxes in the reaction vessels for different setups as well as the homogeneity of irradiation in multi-reactor setups. Comprehensive documentation minimizes the need of repeated photonic characterization when modifying the setups. Experimental reproducibility within and across experiments was evaluated with studies of photocatalytic systems for hydrogen evolution, emphasizing the validity of the concept.

Introduction

Increasing atmospheric CO2 concentrations and global warming are stark reminders for the need to develop sustainable, carbon-neutral energy schemes.[1][2] Solar irradiation provides by far the most promising sustainable energy source. This is evident when comparing the annual solar energy influx on earth (ca. 10^6 PWh) with the current global annual energy demand (ca. 17 PWh).[3] However, while the amount of solar energy is immense, its global harvesting is restricted by geographic issues as well as diurnal and seasonal cycles.[4] Conversion of abundant solar energy into storable fuels is therefore a key challenge for energy technologies. In particular, visible light-driven photochemistry is a versatile approach to store solar energy as fuels; in addition, photochemical concepts can also be used for organic synthesis, e.g. to access value-added chemicals, such as pharmaceuticals.[5–7] Efforts of storing solar energy by light-driven chemistry can be traced back to the 18th century, where solar photochemical experiments were simply performed by placing the reaction vessel in direct sunlight.[8] However, complexity challenges related to photochemistry, photophysics and reaction engineering, have thus far limited progress in the field, and particular in the technological deployment of photochemical conversions in industry. However, recent progress in irradiation sources (LED technology) and reaction systems.[9] combined with a raised awareness of climate change has led to increasing interest in (sun)light-driven chemistry, both in academia and industry.[10] In addition,
photochemistry is a prime example of green chemistry, adding further environmental interest in this concept.\textsuperscript{10}

With focus on the use of solar light, photocatalytic water splitting into hydrogen and oxygen has received widespread attention.\textsuperscript{11–15} This principle opens new pathways to virtually unlimited amounts of hydrogen as secondary energy carrier with high gravimetric energy density.\textsuperscript{16} However, the reaction system, including light source, photocatalyst, and photoreactor type, can be quite different across different research groups, currently limiting a wide-spread application of this promising process.

At this point, ensuring reproducibility and comparability of photocatalytic experiments in general remains a challenge that is not solved yet.\textsuperscript{17} Since research on light-driven reactions involves a broad range of experimental parameters that require consideration, an experimental platform that ensures comparability and reproducibility across different laboratories and chemical systems is required. This contribution aims at filling this gap with a modular, documented and characterized photoreactor platform presented in this study.

Challenges in achieving reproducibility and comparability

Reproducibility of experiments from the scientific literature is of fundamental importance in chemistry. However, more often than desired, many researchers experience difficulties reproducing reported results which can even comprise their own results.\textsuperscript{18} The basis for reproducibility is the knowledge of parameters that influence the performance of a chemical reaction, including the reaction system, \textit{i.e.} the sum of all components in the reaction such as the reactive components, solvent, concentrations or partial pressures. More technical aspects such as reaction temperature, continuous or discontinuous operation mode, morphologies of heterogeneous components and reactor design are further parameters that can significantly influence the observed activity of a chemical system. For light-driven reactions, guiding light to the photochemically active species represents an additional aspect whose importance cannot be underestimated. The amount of available photons or the photon flux for the reaction within a reaction compartment is influenced by various parameters like the properties of the light source, the geometrical arrangement of light source with respect to the reactor, the reactor material, etc. (technical parameters).\textsuperscript{19} This adds an additional parameter space to the already large list of molecular parameters that influence the performance of a photoinduced chemical reaction. Molecular parameters cover e.g. the absorption spectra of photoactive as well as photoinactive species, scattering coefficients of heterogeneous matter as well as the underlying reaction network. These molecular photophysical properties are inherently interlinked with the technical parameters of the reaction setup. It is obvious that the extensive set of relevant parameters raises challenges to comparability.\textsuperscript{17} Only if the influencing factors are known, they can be adjusted purposefully to ensure comparability. Even for thermal reactions, identification of the relevant parameters can be a challenging task.

Commercial and Open Source photoreactors

To improve comparability of experimental results for light-driven reactions, various experimental platforms have been published recently.\textsuperscript{20–23} To minimize the impact of the extensive parameter space, various concepts were reported that define the arrangement of the light source and the reactor through the use of commercially available or Open Source photoreactors. The term “standardization” is frequently related to such experimental platforms but should be interpreted with care. The purpose of such a standardization must be very clear to avoid misguided application of experimental platforms for different applications. For instance, a standardized platform for screening the effect of reaction conditions might only be suitable to a limited extend when applied for the development of new synthesis routes. Different chemical systems frequently require larger changes to the experimental setup to address the properties of different chemical species.

Consequently, ensuring comparability across different chemical systems and experimental platforms is more valuable in research than sole standardization for certain tasks. Ensuring
comparability requires two main steps: first, experimental conditions must be thoroughly defined prior to conducting the experiments. Second, the experimental conditions need to be reported in a very comprehensive manner. Only when such comprehensible datasets are freely and easily accessible, experimental results can be compared or even joined to an even more comprehensive larger dataset that allows global analysis to gain overarching insights.

Since for light driven reactions photons must be considered as a reagent, the challenge for comparability lies in the knowledge of the photon flux available to the photoactive species. Even more precisely, the photon flux absorbed by the photoactive species should be known. The absorbed photon flux strongly depends on the technical and molecular parameters. Consideration of this aspect requires a comprehensive photonic characterization of the experimental platforms and would pave the way towards comparability of experimental results. Radiometry and actinometry are the methods of choice in this case. Radiometry yields insights into the radiation field mostly outside of the actual reactor but can also be used to calculate the photon fluxes insight reactors. Complementary to this, chemical actinometry can be used to measure the photon flux available insight the reactor. Characterization of the experimental platform has to be repeated every time when components that influence the radiation field are changed, i.e., light source, reactor, geometric arrangement, etc.

Modularity and photonic characterization as key for reproducibility and comparability

An experimental platform that is standardized in the narrow sense of the term is not desirable when aiming for comparability since optimal reaction conditions can only be provided to some but not for all of the chemical systems under investigation. Consequently, an experimental platform that offers a high flexibility to address the different demands of the chemical systems while still ensuring comparability is required. To meet this demand, modularization together with a comprehensive photonic characterization were used to develop a new experimental platform. This way, it becomes possible to fulfill the demands of different chemical systems. Knowledge of the incident photon flux as key parameter governing the activity of a light-driven system enables comparisons. As third pillar, the experimental platform together with the characterization results are published as Open Source and Data. During the development, the following design criteria were considered:

1) easy handling in laboratories,
2) simple extensibility also in the future,
3) easy and fast adaption to new demands,
4) cost-effective and simple manufacturing,
5) simple control of the whole platform through a system that offers
   a. the possibility to integrate and control active equipment such as pumps and stirrers,
   b. the possibility to integrate sensors and analytics,
   c. the possibility to further automate the platform e.g., through a software interface,
6) applicability for screening purposes and case studies and
7) comprehensive photonic and reaction engineering characterization.

These design criteria were met by close collaboration with experimentalists, the use of 3D-printing for manufacturing, the development of parts that can be widely reused for different purposes, the use of affordable high-level electronic components for controlling the equipment and the development of the controller software in a high-level programming language. Characterization of the platform was conducted in parallel and iteratively contributed to the optimization of individual parts of the platform.

Modular photoreactor platform

The development of the photoreactor platform was based on 4 major categories of modules: i) controller module, ii) corpus and holders, iii) irradiation modules and iv) peripheral modules. A
The 3D-printed parts were manufactured out of commercially available thermoplastic polymers such as polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS). The material PLA is particularly suitable due to its uncomplicated handling, it can be printed without problems with all available 3D printers that work according to the principle of fused deposition modelling (FDM). Nonetheless, the use of PLA is not suited for elevated temperatures due to its relatively low glass transition temperature of 61°C (Raise 3D Premium). The good mechanical properties such as high impact resistance, toughness, and rigidity and its stability at higher temperatures with a glass temperature of 98°C (Raise 3D Premium) render ABS an attractive alternative to PLA to ensure high stability even at elevated reactor temperatures. It should also be noted that the colour of the printed filament has a significant influence on the wavelength-dependent reflectivity of the chamber and should therefore be chosen with care (see SI).

**Controller module**

The control unit is the core module for controlling active components, e.g. LEDs or pumps, and logging of sensor data, e.g. temperature or pressure. To enable a high flexibility with respect to the extension of the reactor platform, a Raspberry Pi computer together with Tinkerforge microcontroller were chosen. This combination was deliberately chosen despite the relatively high cost compared to e.g. Arduino microcontrollers for the two following reasons:

i) The Raspberry Pi can run independent of other hardware, either as a desktop computer with monitor, input devices and network connection or headless without additional periphery except for the Tinkerforge modules. Compared to the sole use of microcontroller, individual adaption of the controller module can be realized in a more convenient way and often with a higher programming level. This allows also simple interfacing with machine learning software or online data management concepts.

ii) The Tinkerforge platform offers a multitude of so called “Bricks” and “Bricklets” with different functionalities, e.g., temperature and light intensity sensors, analog and digital in and out hardware, input devices, displays, etc. This portfolio allows easy and straight forward extension of the basic functionalities since the extensions can be installed by plug and play on the controller. The wide

![Figure 1: Schematic overview of the controller and its functionality.](image-url)
range of available functionalities also reduces the need to create own electronic functions. Furthermore, programming can be realized with high level programming languages such as Python, LabVIEW or even Matlab. A simple viewer allows also limited direct control of the Bricks and Bricklets without additional programming. The Tinkerforge devices can either be used with a desktop computer and a USB connection or with a Raspberry Pi HAT (Hardware Attached on Top). The first use case allows convenient programming on a desktop computer, while the second use case enables standalone operation.

The controller module offers several interfaces, i) two HDMI ports, ii) four USB ports, iii) Tinkerforge Hat Brick with 8 interfaces and iv) a network port. Figure 1 gives a schematic overview of the controller module and its functionality. The controller interfaces and its electronic setup are depicted in Figure 2. Pictures of currently available modules which can be connected to the controller module are shown in Figure 3.

By default, PWM Bricklets are installed on the controller unit that are used to control the stirrer and the fan modules (see below). The controller module also hosts the electronics that are used to drive LEDs. The LED drivers are connected to a PWM channel, enabling operation with constant electric current (350 mA, 500 mA and 700 mA) as well as pulsed operation with frequencies up to 1 kHz and different duty cycles. Furthermore, it is possible to directly control a conventional lab power supply KORAD Ka3005P as driver for LEDs with high electrical currents or voltages connect to a USB port.

The software for the controller module was developed in Python and enables easy extension of the controller module also on the software side. Registration of modules is realized with simple config files that contain information on the installed modules and their standard settings. With these information, the software automatically generates the graphical user interface (GUI) on a touchscreen module that is always installed on the controller. This touchscreen is the main human interface device to control all connected modules. As indicated above, direct control with the Raspberry Pi is also possible but not considered as main use case.
Corpus and reaction vessel holder modules

These modules represent the base modules in and at which other modules can be installed. The corpus itself has a modular structure. Figure 4 shows schematically which modules can be used with the different components of the corpus.

Figure 3: Available modules: a Controller, b LED module, c master extension (4 ports), d pressure sensor extension, e stirrer module, f reactor temperature readout, g ambient temperature readout, h tempering extension, i membrane pump module.
Corpus: This module is the base module that is always required. Its functional principle and setup is depicted in Figure 5. It consists of two walls with slots, in which sample holder can be installed. Different reactor holders can be installed at a defined (adjustable) distance and irradiated from the bottom with an irradiation module. This modular cassette can be inserted between the side walls, closing the corpus from below and thus acts as a bottom wall of the corpus. Instead of an irradiation module, different peripheral modules can be installed in the bottom as well. The modularity of the reactor also enables the exchange of the side walls with LED modules to enable irradiation from the sides. A third wall is equipped with an opening. Here, a fan can be installed to temper the inner volume of the corpus. A fourth wall is used to close the reactor. It is equipped with an opening which works as exhaust for the ventilation air, either for operation with or without the tempering module. The reactor can be closed from above using a modular top cover, which can also be used as a sample holder. The modular setup of the reactor corpus also enables radiometric studies of the reactor, ensuring an easy assessment of changes in photon fluxes when individual reactor components are changed or modified. The design of the corpus enables easy scale-up of the irradiation chamber to either hold more samples for screening or larger lab-scale reaction vessels within the corpus. Corpuses with the dimensions of 90x90x100 mm, 90x90x140 mm and 130x130x130 mm are already in use.
**Holders:** Depending on the camber dimensions, a variety of holders can be used to place 1 to 18 GC-vials with volumes from 5 to 8 mL in the corpus module. Correct positioning of the vials can be enforced by using an additional alignment ring holder. The irradiation module can also be used as a Schlenk tube holder, when installed upside down. The Schlenk tube is then additionally fixed from above with an extension for the top cover. The reactor holders are shown Figure 6.

![Figure 6: Overview of holder modules and 90x90x90 mm corpus: a and b holder and alignment rings for GC vials in 90x90x140 mm corpus and c holder for Schlenk flasks.](image)

**Irradiation modules**

Irradiation modules allow the direct installation of self-made light sources or the connection of light sources from commercial manufacturers to the corpus. Irradiation modules are available either for irradiation from the bottom or the sides. For all light sources, eventually required cooling equipment such as heat sinks and/or fans are installed outside the corpus to avoid any additional heat spreading in the irradiation chamber. Currently, the following irradiation modules were developed.

**LED modules:** Narrow banded high-power LEDs with peak emission wavelengths of 365 nm, 385 nm, 405 nm, 450 nm, 530 nm are currently in use. In addition, a RGBA module which consists of four high

![Figure 7: Photographs and CAD Models of a the LED module and b the corpus with sidewise irradiation.](image)
power LEDs at peak emission wavelengths of 623 nm (red), 523 nm (green), 460 nm (blue) and 590 nm (amber) can be used. This enables switching between desired wavelengths while experiments are running without the need to exchange modules. The modularity of the corpus not only allows the use of the described LED modules as bottom part of the chamber but enables the use of the side parts as irradiation modules as well which is shown in Figure 7.

**Adaptor for Ashai Spectra Max-350:** This extension couples the Ashai Spectra Max-350 irradiation source to the corpus using a RLQL80-1 collimator lens and a RLQ-BH downward illumination unit depicted in Figure 8. The irradiation source can be used with either bandpass filters or a monochromator, studies on the impact of irradiation with different wavelengths become possible.

![Figure 8: a Ashai downward illumination unit RLQ-BH for collimator lens RLQL80-1 (Asahi Spectra Co., Ltd., Japan), b 3D-printed holder for RLQ-BH and c CAD model illustrating the fixation of the holder to the irradiation module.](image_url)

**Adaptor for Thorlabs LED with collimator:** This extension enables the use of commercially available lamps for irradiation. Thorlabs LEDs can be screwed into the collimator and fixed in the adapter using M3 screws as shown in Figure 9.

![Figure 9 a Side view of the Thorlabs adapter module for the installation of a Thorlabs collimator (b) and a Thorlabs LED (c). d Top view of the irradiation module with installed Thorlabs collimator and e CAD models of the adapter.](image_url)
Peripheral modules

All peripheral modules can be used as standalone modules or together with other modules. To enable reactor tempering, a module containing a temperature measurement device must be combined with the tempering module and a fan to ensure air circulation through the reactor. A schematic overview over the modules and possible new functionalities through a combination of those is shown Figure 10.

**Ambient-, surface- and reactor temperature modules:** The temperature can be measured at various positions. A typical setup includes measurements of the ambient, reactor and chamber temperature. The ambient temperature module does not require any additional thermocouple and is simply placed at a suited position. Reactor and chamber temperature are measured with type K thermocouples that can be installed at the required positions. Type K thermocouples are available for various applications so that e.g., surface temperatures or the temperature in the reactor can be measured. The latter one can be used together with a PTFE adapter (1/8” to ND13) to seal the reaction vessel.

**Stirring module:** This module can be inserted into the bottom of the corpus instead of a LED module. It consists of an electric fan that is equipped with neodymium magnets and controllable by a PWM signal. The module enables mixing in the reactors independently of a laboratory magnetic stirrer.

**Fans:** Depending on the tempering requirements, a fan can be installed for constant flow of fresh air into the irradiation chamber.

**Tempering module:** This module can be installed for tempering of the inner volume of the corpus and with this the reactor vessels. This module consists of a fan, a thermoelectric temperature control unit and a thermal hose. The temperature control unit can either cool or heat the reactor. The pre-tempered air is circulated through the reactor by a fan and is subsequently recycled through the thermal hose. This allows efficient temperature control of the system with temperature differences to the room temperature of around -16 K to more than +35 K. Within this temperature range, the controller keeps the temperature constant within ± 1 K of the set temperature.

![Figure 10: Assembly and functionality of the tempered modular photoreactor, a thermal hose for air recycling, b tempering module, c irradiation chamber, d variable irradiation module.](image)

**Pressure sensor module:** This module can be used to record the pressure in the reaction vessel.
Membrane pump: This module operates a KFN FEM 1.09 KP.55RC diaphragm dosing pump for continuous reactor setups. The pump is chemically resistant and can be operated with flow rates of 10 to 110 mL min⁻¹.

Master Extension Modul: This module enables the installation of up to four additional modules by providing additional Bricklet ports.

Photonic Characterization

The experimental platform was photonically characterized by chemical actinometry and multidimensional radiometry. The raw data can be found on Zenodo and evaluated with the tools published on GitHub. Using the ferrioxalate actinometer and a 365 nm LED (LST1-01G01-UV01-00) at a current of 500 mA, a mean photon flux per vial of $q_{\text{vial}} = 89 \text{ nmol s}^{-1}$ was determined by recording a time series, when using an 8-vial holder at a distance of 7 cm from the radiation source (Figure 11). For the experiments with the 365 nm LED all printable components were manufactured using orange PLA (Raise 3D premium). Since for the UV region all examined filaments show a relatively low and comparable reflectance (see SI) the obtained photon fluxes can also be applied to chambers printed using white and black PLA. In comparative measurements to determine the spatial homogeneity of the irradiation at 120 s and 240 s, mean photon fluxes of $87 \pm 5 \text{ nmol s}^{-1}$ were recorded, respectively. It should be noted that the outlier at position 7 at 240 s was not included in the calculation of the mean photon flux. The lower conversion of the said outlier in vial 7 resulted from a missing stirring bar, through which the application limits of the ferrioxalate actinometer were surpassed. The deviation within a series of measurements is about 6%, which is within the expected experimental error. The average photon fluxes of the measurements for spatial homogeneity also agree very well with the averaged photon flux of the time series.

Photon fluxes were also determined by chemical actinometry for the 4-sample holder equipped with 4 vials and the 1-sample holder equipped with one vial. An average photon flux of $157 \text{ nmol s}^{-1}$ per vial could be determined for the 4-sample holder. For the vial in the 1-sample holder, an average photon flux of $168 \text{ nmol s}^{-1}$ was measured.

![Figure 11: Photon flux determined by chemical actinometry for the 1-vial holder, 4-vial holder and 8-vial holder at a distance of 7 cm for the irradiation source. Deviations at 10 s for the timeseries resulted from conversions below 1 %](image-url)
Complementary to the actinometric determination of the photon fluxes, photon fluxes were determined for the 365 nm LED with 2D radiometry following a three-step scheme (see SI) for the 8-vial holder, positioned at a distance of 7 cm from the radiation source (Figure 12). The calculation of the photon fluxes is based on the radiometric measurements shown in A photon flux of \( q_{\text{vial}} = 92 \text{ nmol s}^{-1} \) corresponding to a total absorbed photon flux of \( q_{\text{tot}} = 733 \text{ nmol} \cdot \text{s}^{-1} \) was determined. The emitted photon flux of the 365 nm LED was determined to be \( q_{\text{emit}} = 2854 \text{ nmol} \cdot \text{s}^{-1} \). The complete setup

\[\text{Figure 12: Radiometric scans for the setup with an 8-vials holder. The first row always represents the radiometric scan and the second row shows the reactor setup.} \ a \ \text{365 nm LED module,} b \ \text{LED module installed in the corpus,} c \ \text{empty vials installed in the setup,} d \ \text{vials filled with methyl orange installed in the setup.}\]
(corpus, holder, methylorange solution filled vials) absorbed a photon flux of $q_{\text{setup}} = 2387$ nmol s$^{-1}$. About 31% of the photons available in the corpus can be absorbed by the reaction solution.

The radiometric scans can be converted to maps of the absorbed fraction of the light (Figure 13), indicating efficient light absorption when the vials are filled with highly concentrated methyl orange solution.

Photon fluxes were determined as a function of the number of vials by radiometry and chemical actinometry. Radiometric photon fluxes of $q_{\text{vial}} = 92$ nmol s$^{-1}$, 167 nmol s$^{-1}$ and 168 nmol s$^{-1}$ were determined for the 8-vial holder, the 4-vial holder and the 1-vial holder, respectively (Table 1).

The comparison of the vial holders clearly shows that the horizontal placement of the vial has a significant influence on the absorbed photon flux $q_{\text{vial}}$. For the 8-vial holder an about 83% higher photon flux is calculated compared to the 1-vial holder (Figure SI-10 (left)). However, when the total absorbed photon flux of all vials is compared, (Figure SI-10 (right)), 168 nmol per s were measured for the 1-vial holder, 668 nmol s$^{-1}$ for the 4-vial holder, and 736 nmol s$^{-1}$ for the 8-vial holder. In total, the 8-vial holder absorbs a more than 4 times higher photon flux than the 1-vial holder. Results from chemical actinometry were found to be in good agreement with radiometry.

Knowledge on the efficiency of guiding photons to the reaction solution can be used to transfer knowledge of the irradiation field from a setup with a certain light source to the same setup with a light source of e.g. different wavelength and radiant power. The efficiency of irradiation of the reactor $\xi_{\text{irr}}$ can be determined according to (1)

$$\xi_{\text{irr}} = \frac{q_{\text{tot}}}{q_{\text{emit}}}$$

with the photon flux absorbed under full absorption $q_{\text{tot}}$ and the photon flux emitted by the light source $q_{\text{emit}}$. This efficiency can also be calculated for a single vial with the photon flux absorbed in one vial $q_{\text{vial}}$:

$$\xi_{\text{vial}} = \frac{q_{\text{vial}}}{q_{\text{emit}}}$$

A similar trend as for the photon flux can also be observed for $\xi_{\text{vial}}$ as a function of the number of vials. The radiometrically determined irradiation efficiencies per vial $\xi_{\text{vial}}$ (Figure SI-13 (left)), are 3.2%, 5.8% and 5.9% for the 8-vial holder, the 4-vial holder and the 1-vial holder, respectively. Thus, an increase of about 83% can be observed. The total $\xi_{\text{irr}}$, however, is only 5.9% for the 1-vial holder and increases to 23.2% and 25.6% for the 4-vial holder and the 8-vial holder, respectively. This is shown in (Figure SI-13 (right)). Thus, a fourfold increase from the 1-vial holder to the 8-vial holder can also be observed for $\xi_{\text{irr}}$.

To compare different reaction systems, the absorbed photon flux should be normalized to the volume. For the three holder setups introduced above, this is illustrated in (Figure SI-12). This volumetric photon flux $q_{\text{vol}}$ will be used for the comparison of the case studies below.
Table 1: Photon flux determined by actinometry and radiometry for different vial holders for a 365 nm LED with 130 ° beam angle operated with a constant electrical current of 500 mA.

| method  | holder | $q_{tot}$ / nmol s$^{-1}$ | $\xi_{irr}$ / % | $q_{vial}$ / nmol s$^{-1}$ | $\xi_{vial}$ / % | $V_{vial}$ / mL | $q_{vol}$ / nmol s$^{-1}$ mL$^{-1}$ |
|---------|--------|---------------------------|-----------------|-----------------------------|-----------------|----------------|----------------------------------|
| radiometry | 1      | 168                       | 5.9             | 168                         | 5.9             | 3              | 56                               |
|          | 4      | 667                       | 23.4            | 167                         | 5.8             | 3              | 56                               |
|          | 8      | 732                       | 25.7            | 92                          | 3.2             | 3              | 31                               |
| actinometry | 1     | 168                       | 6.1             | 168                         | 6.1             | 3              | 56                               |
|          | 4      | 629                       | 22.4            | 157                         | 5.6             | 3              | 52                               |
|          | 8      | 710                       | 25.6            | 89                          | 3.2             | 3              | 31                               |

The influence of the vertical distance of the holder to the radiation source $d_{vert}$ for the 8-vial holder is shown in Table 2. The distance is measured from the holder to the radiation source. An increasing distance leads to an increasing photon flux per vial. By increasing the vertical distance from 5 cm to 9 cm, $q_{vol}$ can be increased from 29 to 34 nmol s$^{-1}$ mL$^{-1}$, corresponding to $\xi_{irr}$ ranging from 24.4 % to 28.4 %, respectively.

Table 2: Photon flux measured by radiometry in dependency of the position relative to the radiation source for the 8-vial holder and a 365 nm LED with 130 ° beam angle operated with a constant electrical current of 500 mA.

| $d_{vert}$ / cm | $q_{tot}$ / nmol s$^{-1}$ | $\xi_{irr}$ / % | $q_{vial}$ / nmol s$^{-1}$ | $\xi_{vial}$ / % | $V_{vial}$ / mL | $q_{vol}$ / nmol s$^{-1}$ mL$^{-1}$ |
|----------------|---------------------------|-----------------|-----------------------------|-----------------|----------------|----------------------------------|
| 5              | 696                       | 24.4            | 87                          | 3.0             | 3              | 29                               |
| 7              | 732                       | 25.7            | 92                          | 3.2             | 3              | 31                               |
| 9              | 811                       | 28.4            | 101                         | 3.6             | 3              | 34                               |

The results of the photonic characterization of the systems used for the case studies are summarized in Table 3. In dependence of the used setup and light source, the volumetric photon flux lies between 32 and 399 nmol s$^{-1}$ mL$^{-1}$ resulting in a more than 12-fold difference in the available volumetric photon flux between the setups used for the case studies. It is obvious that relatively small changes of the used setup like changes in the reaction vessels, volume, relative positioning to the radiation source or the use of different radiation sources can have a large impact on the absorbed volumetric photon fluxes. Thus, a valid comparison of different systems is only possible with a sufficient photonic characterization of the setup, underlining the importance of a sufficient photonic characterization.

Table 3: Photonic characterization of the setups used for the case studies with 3 LEDs: 1 (LED Engin, LZ1-00DB00, $\lambda_{P} = 460$ nm, $\Theta_{0.9} = 90^\circ$) the case studies for this LED were performed in 8 mL WICOM WIC 41600/333 clear glass screw neck vials (ND13) GC-vials, 2 (New Energy, LST1-01F06-RYL1-00, $\lambda_{P} = 455$ nm, $\Theta_{0.9} = 120^\circ$) and 3 (LED Engin, LZ4-40B208-0000, $\lambda_{P} = 453$ nm, $\Theta_{0.9} = 120^\circ$) used for case studies. The case studies for the 453 nm and 455 nm LED were performed in 4 mL LABSOLUTE 7613421 clear glass screw neck vials (ND13) GC-Vials.

| LED | holder | $d_{vert}$ / cm | c / mA | $q_{tot}$ / nmol s$^{-1}$ | $\xi_{irr}$ / % | $q_{vial}$ / nmol s$^{-1}$ | $\xi_{vial}$ / % | $V_{vial}$ / mL | $q_{vol}$ / nmol s$^{-1}$ mL$^{-1}$ |
|-----|--------|----------------|--------|--------------------------|-----------------|-----------------------------|-----------------|----------------|----------------------------------|
| 1   | 8      | 8             | 10     | 700                      | 1001            | 31.4                        | 126             | 3.9            | 4                                | 32                               |
| 2   | 8      | 8             | 7      | 290                      | 891             | 41.5                        | 111             | 5.2            | 2                                | 56                               |
| 3   | 8      | 8             | 7      | 960                      | 6380            | 33.6                        | 797             | 4.2            | 2                                | 399                              |
| 3   | 8      | 8             | 7      | 200                      | 1820            | 32.4                        | 227             | 4.0            | 3                                | 76                               |
| 3   | 4      | 2             | 7      | 200                      | 718             | 12.8                        | 359             | 6.4            | 3                                | 120                              |
| 3   | 4      | 2             | 7      | 400                      | 1440            | 15.1                        | 721             | 7.6            | 3                                | 240                              |
Case studies

A direct conversion of sunlight into chemical fuels is one of the great current challenges. Light-driven hydrogen evolution is a promising approach to achieve a renewable and emission-free energy cycle.[34] Water is utilized as feedstock and with a suitable catalyst under solar irradiation, the water is split into hydrogen and oxygen. The hydrogen then can be stored, which could compensate for diurnal and seasonal fluctuations of the sun light. If the hydrogen is then combusted again, the only waste product produced is water. Most of the concepts developed for light-driven hydrogen evolution reaction (HER) are somehow derived from natural photosynthesis and combining specialized units for light-absorption and as catalytic centers.[34,35]

Hydrogen evolution reaction with molecular molybdenum sulfide catalysts

Promising earth abundant HER catalysts are amorphous molybdenum sulfides.[36,37] In 2018, the potential of this cluster was investigated in homogeneous light-driven HER catalysis and showed promising activity towards hydrogen evolution, while mechanistic details of HER were investigated in later studies. [36–39]

![Figure 14: Reaction scheme for the three-component system for the light-induced hydrogen evolution reaction using 1 ascorbic acid as electron donor, 2 [Mo₆S₆]²⁺ as catalyst and 3 Ru(bpy)₃]²⁺ as photosensitizer.](image-url)
We investigated the HER with \([\text{Ru}(\text{bpy})_3](\text{PF}_6)_2\) as photosensitizer, ascorbic acid as sacrificial electron donor and \(\text{Na}_2[\text{Mo}_3\text{S}_{13}] \times 5\text{H}_2\text{O}\) or \((\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}] \times 2\text{H}_2\text{O}\) as catalysts in different methanol/water mixtures and varying pH according to a published and adapted procedure (Figure 14). Depending on solvent mixtures and pH, different activities of the systems were observed (see Figure 15). While at pH 6 in MeOH/H\text{2O} 1:2 an average turnover number of 1454 with a standard deviation of 9 % between trials and a standard deviation of 7 % to 12 % within trials were determined, increasing the methanol content to MeOH/H\text{2O} 1:1 resulted in an average TON of 5103 with a standard deviation of 3.8 % between trials and 3 % to 4 % within trials. In these experiments we utilized a 460 nm LED (LZ1-00DB00) in the setup resulting in a \(q_{\text{vol}}\) of 32 nmol s\(^{-1}\) mL\(^{-1}\) (see Table 3). However, TONs obtained are not

Figure 15: Results of reproducibility tests for \(c([\text{Mo}_3]) = 0.3 \, \mu \text{M}, c([\text{Ru}(\text{bpy})_3](\text{PF}_6)_2) = 20 \, \mu \text{M}, c(\text{ascorbic acid}) = 0.1 \, \text{M}, \text{irradiation time} = 6 \, \text{h}\) in different solvent mixtures and pH. Top: MeOH/H\text{2O} 1:2, pH 6, 460 nm; Middle: MeOH/H\text{2O} 1:1, pH 6, 460 nm; Bottom: blue bars: MeOH/H\text{2O} 9:1, pH 4, 455 nm, no stirring; orange bar: 453 nm LED; green bar: with stirring. Left: average results for different trials; right: individual results for different positions in the setup.
identical to the published results which report in the MeOH/H₂O 1:1 mixture TON = 3950 with a standard deviation of 3-4 % while irradiating at 470 nm in a different photoreactor setup operating at 40 mW cm⁻² photocurrent.⁴⁰ The main difference might be the choice of wavelength at a potentially lower photocurrent combined with the absorption properties of the photosensitizer.

When increasing the methanol content to MeOH/H₂O 9:1, lowering the pH to 4, and using a 455 nm LED (qvol = 56 nmol s⁻¹ mL⁻¹) as well as performing the reaction without stirring resulted in an average TON of around 16,633 with standard deviation 2 % between trials and of 4 % to 7 % for each trial was observed.

By changing to a more powerful LED 453 nm (qvol = 399 nmol s⁻¹ mL⁻¹) in this irradiation setup we increased the HER performance in the MeOH/H₂O 9:1 system by 68 %, reaching an average TON of 27,920 with a standard deviation of 4 % over 8 samples (Figure 15). The more than 6-fold higher photon flux increased hydrogen evolution activity by merely 21 %, compared to previously published results which we will discuss in the following.⁴⁰ Typically, the here applied catalysis reaction sample has a transmission of 71.7 % and 71.4 % at 455 nm and 453 nm respectively (Abs = 0.144 – 0.146). Therefore, no full absorbance can be ensured as compared to the radiometric measurements and a significant fraction of photons remains unused under the applied catalytic conditions. Interestingly, performing the reaction under stirring decreased the activity by 29 % resulting in an average TON of 19,864 with a standard deviation of 9 % over 8 samples which may arise from mass transport effects (Figure 15).

In summary, variations of reaction conditions at the same solvent ratio and pH can induce changes in observed catalysis performance between 21 % to 68 % which underlines that not only irradiation, but also mass transport and other factors such as concentrations and (photo)stability of reagents can cap the activity in this system,⁴⁰,⁴¹ emphasizing the need for a comprehensive documentation of the experimental procedure along with the need for further investigations.

In summary, the standard deviations in these trials range from 4 % to 12 %. Photonic characterization yielded standard deviations of 6 %. Larger deviations of the actual experimental results in these case studies are also linked to the experimental analysis method which includes manual injection of a head space volume into the GC, as well as manual sample preparation with a pipetting standard error of 0.3 %.

**Hydrogen evolution reaction with Co(dmg)₂ClPy**

The proton reduction electrocatalyst [Co(dmg)₂ClPy] (4)⁴² (Figure 16) was successfully introduced in the scope of photocatalytic proton reduction from aqueous solutions by Eisenberg and coworkers in

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**Figure 16**: Reaction scheme for the three-component system for the light-induced hydrogen evolution reaction using 3 [Ru(bpy)₃]²⁺ as photosensitizer, 4 [Co(dmg)₂ClPy] as catalyst and 5 N,N-Dimethyl-p-toluidine (DMT) as electron donor.
In 2008, a series of multicomponent photocatalytic systems comprising 4, a photosensitizer and a sacrificial donor were investigated. In 2018 Lu et al. combined 4 with the widely used [Ru(bpy)₃]²⁺ (3) as photosensitizer and N,N-Dimethyl-p-toluidine (DMT) (5) as electron donor to compare different Ru-based light harvesters. The three-component system (3-5) yielded a turnover number of 376 after six hours of irradiation with visible light (450 nm). In the present case study, this hybrid system was used to investigate the reproducibility of the photocatalytic results in the modular photoreactor.

For first photocatalytic experiments with eight samples, an average turnover number of 6.14 was determined with a standard deviation of 3 to 5% within each trial and a standard deviation of 5% between the trials (see Figure 17). Using a 453 nm LED for irradiation a qvol of 76 nmol s⁻¹ mL⁻¹ was calculated based on radiometric measurements. For further investigations on the effect of the incident photon flux, two reaction vials were placed oppositely to each other in a four-sample holder and irradiated for 30 minutes with different intensities (qvol = 120 nmol s⁻¹ mL⁻¹ and 240 nmol s⁻¹ mL⁻¹, see Table 3). The results are shown in Figure 17. For stock solution 1 (stock solution 2 in brackets) the low photon flux resulted in an average turnover number of 6.50 ± 2% (6.03 ± 0.6%) between the trials; for the high photon flux an average TON of 9.42 ± 3% (8.58 ± 1%) was registered. Due to preparation inaccuracies, the averaged turnover numbers of stock solution 2 are about 8% lower than those of stock solution 1.

In the case of the four-sample holder, the different photon fluxes (difference of about 100%) do not lead to a similar increase of the averaged turnover numbers (difference of 42% (stock solution 1) and 45% (stock solution 2)). Furthermore, the higher volumetric photon flux available in the four-sample holder compared to the eight-sample holder (about 58%) is also not reflected by the similar averaged turnover numbers.

The case study shows a good reproducibility within experiments conducted in parallel as well as between different trials. Despite a low observed turnover number, the hydrogen evolution during half-hour irradiation is quite rapid (about 30 µL H₂ in 2 mL headspace), thus small random mutations can easily lead to deviations inside and between the measurements. There is a big gap between literature and the present study with respect to the catalytic turnover. After half-hour irradiation (450 nm), the reported turnover number (280) is significantly higher than the one, achieved herein (about 6 to 9). However, it is noted that the TONs reported in the literature might be miscalculated: our own calculations with experimental data presented by Lu et al. (V = 5 mL, ccat = 77.5 µM, nH₂ = 9.4 µmol) yielded a TON of about 24. This value is in better agreement with our measurements, since the reported radiant power reaching the reaction vessel and the radiant power calculated for one vessel in our setup using the 8-vial sample holder are in good agreement as well. The reported LED irradiance of 122 mW cm⁻² and the irradiated area 0.8 cm⁻² indicate a radiant power of 98 mW corresponding to 369 nmol s⁻¹ reaching the reaction vessel. Therefore, a volumetric photon flux of 74 nmol s⁻¹ mL⁻¹ can be calculated for the reported setup, which is very similar to our setup with 76 nmol s⁻¹ mL⁻¹. The investigated three-component system (3-5) is found to be poor in the scope of photocatalytic proton reduction and also lacks robustness. Despite this, the low activity results in a high sensitivity towards experimental errors, especially for short experiments. An issue that was not observed with the photoreactor platform, emphasizing the advantages of a well-defined experimental setup.
Discussion

The case studies confirm a very good reproducibility of the catalytic experiments, being in good agreement with the photonic characterization. The practical need for adaptations of the experimental setup leads to changes of the incident photon flux that directly influence the photocatalytic activity. For instance, using 8 instead of 1 vials almost halved the photon flux per vial, variations of the distance between LED and vial cause differences of more than 10% and the use of different types of LEDs resulted in changes of the photon flux by an order of magnitude (see Table 1 to Table 3). Thus, parameter studies on non-photonic parameters can be falsified.

Comprehensive characterization of the modular photoreactor platform overcomes this issue. Open documentation minimizes the need for repeated actinometric and/or radiometric measurements since characteristic figures, e.g. $\xi_{\text{vial}}$, allow exchange of modules without the need of new measurements. Given that the new module is sufficiently characterized, e.g. the emitted photon flux of a different LED is known, the characteristic figures can be used to consider modifications. Knowledge of normalized photon fluxes ($q_{\text{vial}}$ or $q_{\text{vol}}$) allows for comparison between different setup, as demonstrated for trials with different positions and vials in the case studies.

Conclusions

The developed highly modular photoreactor was successfully used for different photocatalytic hydrogen evolution systems, proving reproducibility and comparability. Adaptability and extensibility
of the photoreactor enables the use of different reaction vessels, positioning of the reaction vessel relative to the radiation source and the use of different radiation source, while a thorough photonic characterization ensures comparability even for the changed setups. By design an intuitive use of the platform is given, preventing user errors. Comprehensive and open documentation of the photoreactor construction as well as the photonic characterization ensures reproducibility and lays the foundation for its widespread use in photochemical laboratories. The use of relatively inexpensive and photonically characterized radiation sources such as high-power LEDs and the use of 3D printing for the fabrication of most reactor components results in affordable cost.

Reproducibility and the comparability of photocatalytic experiments are inherently linked to a comprehensive photonic characterization of the studied systems. The photonic characterization of different systems by using complementary methods such as chemical actinometry and radiometry provides highly reliable results for incident and absorbed photon fluxes. This knowledge allows comparison of experimental results between different setups and a simple transfer in case of modifications of the setup, minimizing the need for repeated photonic characterization.

The modular, documented, characterized and Open Source photoreactor platform presented in this contribution is an initial step to overcome the experimental challenges of research on light-driven reactions. It is envisioned that a wide adaption will lead to ongoing improvements and the development of new modules, that will be shared with the research community together with a comprehensive characterization in the available repositories.

**Electronic Supplementary Information**

Electronic supplementary information (ESI) available: Description of experimental procedures and details of photonic characterization.

All CAD drawings of the modular reactor platform, assembly descriptions and the Python code for the controller are available on GitHub https://github.com/photonZfeed/modularPhotoreactor and as a stable version in the Zenodo repository https://doi.org/10.5281/10.5281/zenodo.5615742. Raw data of the characterization can be found on Zenodo https://doi.org/10.5281/10.5281/10.5281/zenodo.5614942 and evaluated with the tools published on GitHub.[32]

**Experimental Section**

**Actinometry**

Chemical actinometry was performed using the ferrioxalate actinometer based on the method of Hatchard and Parker and following the procedure of Wriedt et al.[27,46,47] Actinometric experiments were performed in 4 mL GC vials under constant stirring. The vials were each filled with 3 mL of a 0.016 M K$_3$Fe(C$_2$O$_4$)$_3$ solution in 0.05 M H$_2$SO$_4$. A 365 nm LED (LST1-01G01-UV01-00, $I = 0.5$ A) operated at constant current was used for the actinometric experiments. (see SI for more details).

**Radiometry**

2D radiometry was performed according to the method of Sender.[9] Full surface 2D scans were performed for all used radiation sources. 2D scans of all reactor setups with installed radiation sources were performed using a reduced scan surface adjusted to the radiation field. The obtained incident radiant powers of the different sole radiation sources were calibrated and this calibration was applied to all other measurements of the radiation sources installed in the reactor setup. The absorbed photon fluxes were determined using a 3-step-procedure (see SI).
Hydrogen evolution reaction with molecular molybdenum sulfide catalysts

Sample preparation was carried out according to a published and adapted procedure and is further specified in SI.[40] For each trial 8 solutions consisting of [Ru(bpy)3](PF6)2 (20 µM), ascorbic acid (100 mM) and [Mo3S13]2− (0.3 µM) in different mixtures of methanol/water were irradiated simultaneously for 6 hours at room temperature (fan controlled). Afterwards, evolved hydrogen was quantified using head space gas chromatography analysis. Turnover numbers were calculated from the number of hydrogen molecules produced per molecule [Mo3S13]2−.

Photocatalytic experiments in methanol/water 1:1 and 1:2 were carried out in 8 mL WICOM WIC 41600/333 clear glass screw neck vials (ND13) GC vials with 4 mL of catalysis solution at pH 6 under stirring utilizing Na3[Mo3S13] x 5H2O as catalyst. As LED emitter a 460 nm LED operating at an electrical current of 0.7 A was used as light source equipped in the 90x90x140 mm corpus. The sample holder was placed in position 10 with an additional alignment ring holder in position 6.

Photocatalytic experiments in methanol/water 9:1 were carried out in 4 mL LABSOLUTE 7613421 clear glass screw neck vials (ND13) GC vials with 2 mL of catalysis solution at pH 4 without and under stirring utilizing (NH4)2[Mo3S13] x 2H2O as catalyst. As LED emitter a 455 nm LED operating at an electrical current of 0.29 A as well as a 453 nm LED operating at an electrical current of 0.95 A were used as light sources equipped in the 90x90x100 mm corpus. The sample holder was placed in position 7 with an additional alignment ring holder in position 6.

Hydrogen evolution reaction with (Co(dmg)ClPy) catalysts

The CH3CN reaction samples (3 mL) were prepared in LABSOLUTE clear glass screw neck vials (ND13, total volume 4 mL) under an N2 atmosphere with the following concentrations, according to literature:[45] [Co(dmg)2ClPy] = 78 µM; [Ru(bpy)3]2+ = 5 µM; [DMT] = 5.5 mM; [H2O] = 2.2 mM. The CH3CN reaction samples (3 mL) were prepared in LABSOLUTE 7613421 clear glass screw neck vials (ND13, total volume 4 mL) under an N2 atmosphere with the following concentrations, according to literature:[45] [Co(dmg)2ClPy] = 78 µM; [Ru(bpy)3]2+ = 5 µM; [DMT] = 5.5 mM; [H2O] = 2.2 mM. CH3CN, H2O and DMT were degassed with an N2 or Ar flow before use. The sealed samples were stored in the dark until they were placed in the reactor and subsequently irradiated for 30 minutes with the 453 nm LED operating with a constant current of 0.2 A (or 0.4 A) and under vigorous stirring in the 90x90x100 mm corpus. The sample holder was placed in position 7 with an additional alignment ring holder in position 6. Samples (200 µL) for hydrogen quantification were drawn from the headspace and measured by GC-TCD.

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