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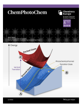
Teaching Photochemistry: Experimental Approaches and Digital Media



Claudia Bohrmann-Linde,*[a] Nico Meuter,[a] Diana Zeller,[a] and Michael W. Tausch[a]

In this paper we give an insight into results from our curricular innovation research which aims at integrating photochemistry in university and school curricula. We have been exploring experimental approaches and developing teaching materials for more than 20 years and most of our experiments and teaching materials have been digitalized and made available in German and English as open educational resources (OER) on our website. The addressed photochemical content can be connected to well-established subject content at school and university level chemistry, but their theoretical interpretation and the understanding of their applications go well beyond this. However, primarily they should motivate learners to, even after they leave school and university, continue to work on the investigation and development of sustainable processes and materials based on the use of (solar) light.

1. Introduction

Energy, climate, food, water and mobility – these topics are the big challenges for humankind in the 21st century, making it mandatory to gradually replace energy from fossil fuels by renewable energies. Among these, solar energy is definitely the most abundant and clean kind of energy. This is a major reason, although not the only reason, for including the study of photoprocesses in chemical education. The 2021 editorial of this journal's older sister, *Angew. Chem.*, is titled "Chemistry 2030: A Roadmap for a New Decade", and outlines a perspective for the development of chemistry during the ongoing decade. This perspective includes demands that became very clear and stringent in the year of the Covid-19 pandemic 2020. Prominent among these demands is "Rethinking chemistry innovation and education." J. Garcia-Martinez states "If we keep teaching chemistry like in the second industrial revolution, we will produce excellent chemists for a world that no longer exists".[1]

We strongly agree with this and consider this particularly true in terms of photochemistry. If school educators keep exclusively teaching the generation of colour as caused by light absorption only and if we focus on the dyes of the 19th century, we are not preparing students for the reality they are faced with outside school. Unlike 50 years ago, their everyday life is full of objects whose colour is generated by light emission and that contain functional dyes with special chemical, optical, and electronic properties.

Actually, light-involving phenomena are most suitable for the communication of core concepts of chemistry and related sciences (physics, biology, geography and information technology) in close combination with everyday experiences of students as well as with scientific research and innovative technological applications.

In this sense, we have been exploring experimental approaches and developing teaching materials for more than 20 years.[2–13] Some of them have been presented in about ten editions of the Central European Photochemistry Conference CECP in Bad Hofgastein (Austria), and most of our experiments and teaching materials have been digitalized and made available in German and English as open access on our website.[14] This is not only due to new teaching necessities during the pandemic, but also due to the fact that there is a need for digital teaching/learning materials that can be used for blended learning approaches and self-regulated learning via animations and explanatory videos. Animations in particular help students understand processes on the particle level because of their visualizations, integrated simulations help to explore the influence of parameters such as wavelength of the irradiating light or temperature on (photo)chemical reactions. Besides being a help to prepare for a lab class, videos also allow students to recall observations from the lab or can be shown in school settings where some of the needed apparatus may not be available.

The addressed photochemical contents can be connected to well-established subject contents of school and university level chemistry, but their theoretical interpretation and the understanding of their applications go well beyond this. However, primarily they should motivate learners to, even after they leave school and university, continue to work on the investigation and development of sustainable processes and materials based on the use of (solar) light. In this article, we give a selected overview of our repertoire, containing two groups of experiments and digital materials, each involving a

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central photoactive system, on the one hand the molecular switch spiropyran/merocyanine, and on the other hand the photoactive n-type semiconductor titanium dioxide. These experiments work with a relatively simple pair of isomers of organic molecules and the semiconductor TiO_2 respectively, whose structure and properties are taught at school. Therefore, they are more suitable for teaching basic concepts of photochemistry than the structurally more complicated photosensitive transition-metal-based complexes.[15,16] The basic concepts of photochemistry to be introduced in connection with the two case studies considered here are highlighted graphically in *italics* at the appropriate places in the following text.

2. Spiropyran/Merocyanine: A "Dream Couple" for Teaching Core Concepts

The isomers spiropyran and merocyanine can be considered as a dream couple because the system can be treated in various contexts in order to explore structure–property concepts, e.g. photochromism in solvents and matrices, the dependence of the chemical environment on absorption and emission, as well as the application in molecular logic gates.

2.1. Spiropyran/Merocyanine Photochromism in Nonpolar Solvents

In order to demonstrate and investigate the *photochromism* of a photoactive molecular switch and to address a considerable number of photochemical concepts, we use the non-hazardous and commercially available spiropyran (1,3,3-trimethylindolino-6′-nitrobenzopyrylospirane; SP), which has been known for more than 60 years.[17] One of us has been dealing with this compound for more than 30 years, and other authors have also reported in educational journals about experiments with spiropyran.[18–20] The experimental observations listed below can be carried out easily as microscale versions using solutions of approx. 20 mg SP in 10 mL toluene or xylene. The experiments are suitable for demonstrations in lectures, for chemistry lessons in classrooms and even for experiments at home.

- Colourless SP in toluene (or xylene) solution is converted rapidly within 1–2 seconds, independent of temperature, into its blue isomer merocyanine (ME) by irradiation with ultraviolet or violet ($\lambda = 400$ nm) light from an LED torch or even with sunlight (Figure 1).
- The disappearance of the blue colour, corresponding to the reverse reaction ME→SP, occurs at room temperature in the dark and in diffuse daylight within approx. 2 minutes.
- The reaction time of the reverse ME→SP reaction can be shortened to less than 5 seconds by immersing the test tube in 50 °C warm water.
- The reverse reaction can also be driven by irradiation with green or red light from an LED torch.

2.2. Spiropyran/Merocyanine Photochromism in a Nonpolar Solid Matrix

The immobilization of spiropyran in a polystyrene matrix can be realized, following the detailed instructions on the internet platform[14] (see QR-code in Figure 1, experiment 4). Using the obtained "intelligent foil", the following observations can be shown or investigated carrying out simple instant experiments.

- Optical information visible as blue colouration on the foil can be written by irradiation with a violet ($\lambda = 400$ nm) LED torch or with sunlight.
- The information can be erased within a couple of seconds by heating up the foil in hot water.
- Keeping the foil at low temperature (for example in the fridge) in darkness, the information can be stored for hours and days.
- The blue zones of the foil can be selectively erased, rewriting a new information in to the blue zone using a green laser pointer or a green LED torch.

Just like the experiments using the solution of SP in nonpolar solvents, the "intelligent foil" is also suitable for demonstrating and investigating the photochromism of the SP/ME system. In the beginners' classroom and in the early stages of chemical education, this term should be interpreted only

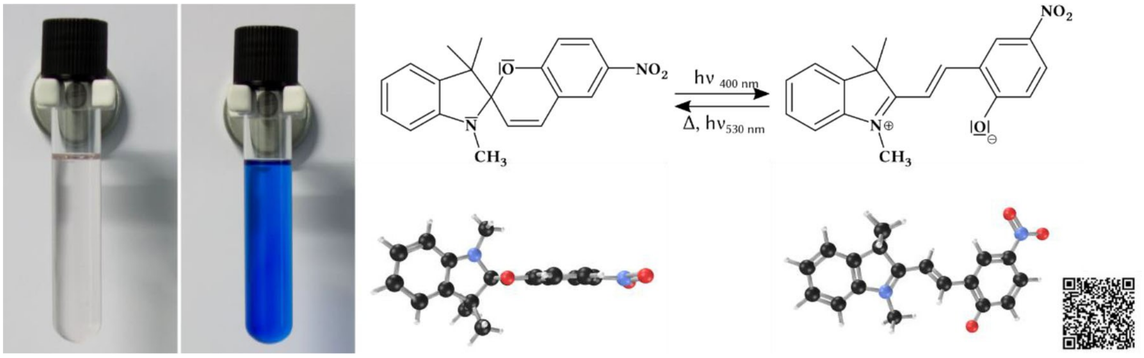


Figure 1. Colours in toluene or xylene solution of spiropyran SP ($C_{19}H_{18}O_3N_2$) and merocyanine ME ($C_{19}H_{18}O_3N_2$); reversible isomerization and molecular models; adapted from the source provided in [14] with permission.

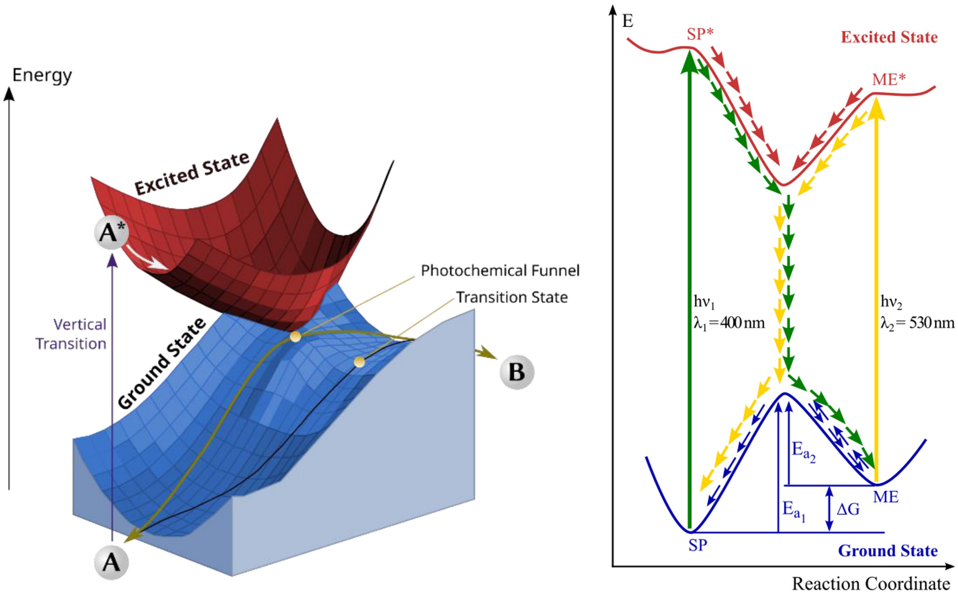
from the phenomenological point of view, in the sense that chemical reactions (in this case the reactions SP$\rightarrow$ME and ME$\rightarrow$SP) can be energetically driven either by light or by heat, and that light of different colours can induce different chemical reactions. The selective light-induced erasing of the information written on the "intelligent foil" works best when the foil is kept at low temperature. This is a good example of the general possibility of *remote control* of light-induced processes.

Further on in higher level secondary education at schools and colleges the formulas from Figure 1 should be used to explain *the relationship between the molecular structure, the light absorption and the colour* of a compound. While in the nonplanar SP molecule the π-electron delocalisation is interrupted at the sp^3-hybridised spiro-centre, it extends across the entire framework of the ME molecule. An explanation of the colour change during the isomerization SP$\rightarrow$ME is given in an understandable way by the video "Light turns On and Off – A photoactive molecular switch" available at the website listed in Ref. [14] (see the QR-code in Figure 3a).

However, even in higher secondary education, it is not recommended to deal with the mechanism of the electrocyclic ring-opening and ring-closure reaction between SP and ME. Instead, the experimental proof with SP in nonpolar solvents and in the nonpolar polystyrene matrix mentioned above should be used to communicate *the fundamental difference between a photochemical reaction and a thermal reaction at molecular level.* For this purpose, energy diagrams as shown in Figure 2 are suitable. At this point we would like to emphasize that according to N. J. Turro's paradigm of the "*excited states of molecules*" as "*the heart of all photoprocesses*",[21] should be taught as a key concept already at high school level. An approach for doing so using examples of photoluminescence has been reported in Ref. [10]. The energy hypersurface diagram (Figure 2a) clearly shows some special features, e.g. the vertical transition corresponding to the *Franck-Condon principle* and *photochemical funnel* corresponding to the conical intersection of the hypersurfaces.

Unlike Figure 2a), the *energy profile diagram* Figure 2b contains an abscissa. It represents the reaction coordinate that concerns changes of nuclear geometry during the reaction. It corresponds to the usual energy diagrams used in teaching at high school and in undergraduate courses at university. The blue curve describes the energetic pathway of a *thermal reaction that always occurs exclusively in the ground state.* Dealing with this diagram, students should understand that the *energetic pathway of a photochemical reaction always includes the electronically excited state* of the reacting system and the corresponding energy profile curve.

Note that some key terms from photochemistry such as vibrational relaxation, photochemical funnel, conical intersection, and photosteady state have not yet been used. In fact, this didactically reduced explanation follows the teaching principle, according to which new technical terms should be introduced only when they are absolutely required by the observed phenomena. Such further phenomena as well as the concept of *photosteady state* can be introduced by the video "Unequal Equilibria – Thermodynamic equilibrium *vs.* photosteady state" (see the QR-code in Figure 3a). Going further, the interactive animation from QR-code b in Figure 3b can be used to explore the photosteady state. With this animation the reversible isomerization reaction can be simulated. The system reaching the photosteady state can be explored by manipulating temperatures and wavelengths of irradiation.



a) b)

Figure 2. Energetic pathways for reversible isomerization reactions represented as trajectories between and on energy hypersurfaces (a) and as energy profile curves (b); adapted from the source in [14] with permission.

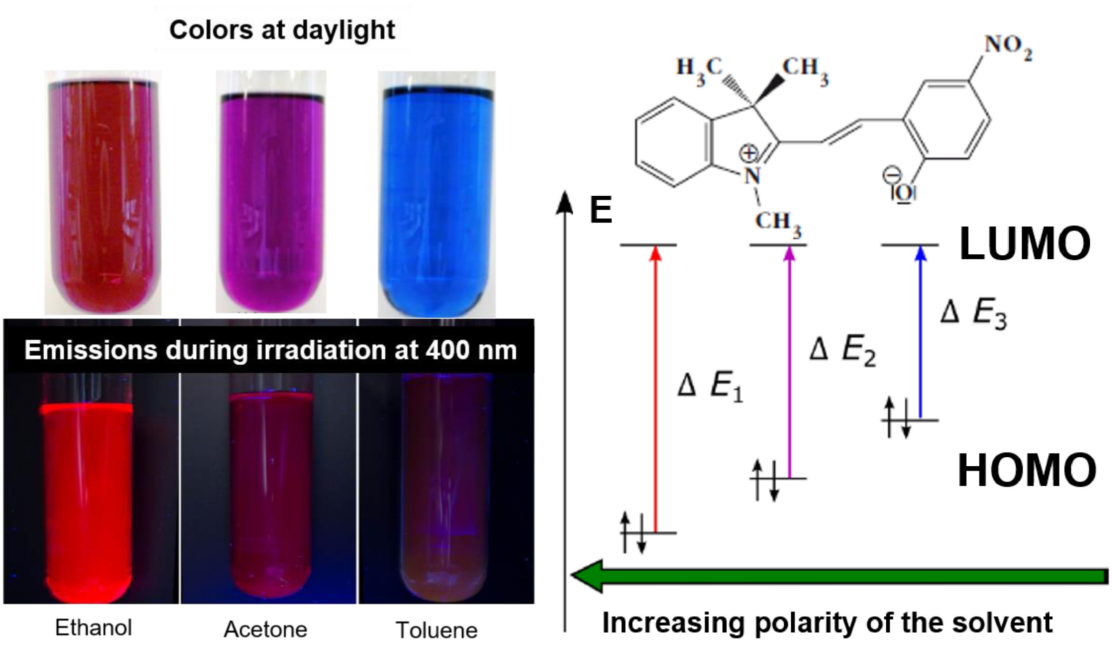
a) b)

Figure 3. Screenshots from the video “Unequal Equilibria - Thermodynamic equilibrium *vs.* photosteady state” (a) and from the Animation “photosteady State” (b); both available from the source provided in [14]. Images used with permission.

2.3. Absorption and Emission of Merocyanine in Different Molecular Environments

Surprising observations can be obtained when the properties of the molecular switch SP/ME are investigated in solvents of different polarities. In this respect, the couple SP/ME provides an excellent textbook example for demonstrating and communicating the *influence of the nano-environment of photoactive molecules on their properties*. The experimental observations are as follows (Figure 4).

- Merocyanine ME generated by the irradiation of spiropyran shows a very pronounced *negative solvatochromism*, that is a hypsochromic shift of the absorption maximum with increasing polarity of the solvent molecules. It is clearly visible in the series toluene, acetone, ethanol (Figure 4a, top).
- With increasing polarity of the solvent molecules, an increasingly strong red fluorescence of the solution can be observed (Figure 4a, bottom). This is caused by *aggregation induced emission* (AIE; see explanation below).
- Unlike the blue colour in toluene solution, the red colour of the ethanol solution does not disappear in the dark or in daylight, i.e. ME is *thermodynamically more stable* than SP in a strong polar molecular environment that is capable of H bridging.
- At this point it should be mentioned that even in the nonpolar environment of rigid polystyrene, that is in the “intelligent foil”, ME exhibits a red fluorescence, which is completely different from ME in the toluene solution. This is caused by the *restriction of intramolecular mobility* (RIM) in the solid matrix.



a) b)

Figure 4. Colours generated by merocyanine ME by absorption and by emission of light (a) and explanation of the negative solvatochromism of merocyanine ME (b); reprinted from the doctoral thesis of S. Spinnen (2018), available from the source in [14], reproduced with permission.

At this point it is clear that for the explanation of the phenomena enumerated above also the radiative and non-radiative deactivation pathways of excited states i.e. *fluorescence, phosphorescence, vibrational relaxation* and *aggregation induced emission* (AIE), as well as the influence of *intermolecular interactions* between the photoactive species and the molecular environment must be dealt with. The videos "Underground Minigolf – Colour by light emission" and "A chemical chameleon – Molecular environment and solvatochromism" on our website[14] (see QR-code in Figure 3a) serve as a basis for this. The essential idea for the justification of the negative solvatochromism used in the video is shown by Figure 4b.

2.4. Spiropyran/Merocyanine in Molecular Logic Gates

When SP is dissolved in ethylene glycol and acidified, during irradiation with violet or UV light a third species MEH^+ is formed which has to be additionally considered. The following experiment uses the system $SP/ME/MEH^+$.

- A solution of SP in ethylene glycol, $c(SP)=10^{-3}$ mol/L, was acidified with trichloroethanoic acid TCE, $c(TCE)=5\cdot10^{-2}$ mol/L, placed in a Petri dish, and completely irradiated by UV light ($\lambda=365$ nm). It shows a red fluorescence emission at $\lambda=615$ nm (Figure 5, left).

Simultaneously, three small areas were irradiated with blue light ($\lambda=450$ nm) for 4 seconds (Figure 5, middle). After switching off the blue light it can be seen that the fluorescence on the three small surfaces is extinguished (Figure 5, right). It takes approx. 10 seconds until the entire surface fluoresces red again.

According to the characteristics of molecular logics[22] this is a model for *an all-optical INHIBIT logic gate*. Typical for the INHIBIT logic gate is that the second input cancels the effect of the first input (see the truth table in Figure 6). In this case, the reversible reactions shown in Figure 6 occur, when input 1 and input 2 are activated. Input 1 switches the non-fluorescent SP to ME, which is simultaneously protonated to red fluorescent MEH^+. Input 2 reverses the isomerization and deprotonation to SP.

Taking into account that other logic gates (AND-, OR-, NOR-XOR-, and Half Adder-Gate) have also been realized, we consider such molecular mimicking of logic gates suitable to teach some important contents of photochemistry and information technology in an interdisciplinary way.

It should be mentioned that the experiment described above, in which a fluorescent state is switched ON and OFF remotely controlled exclusively by light, can be considered as a model for the RESOLFT concept developed by Stefan Hell.[23] While in Hell's Nobel Prize-winning STED (*stimulated emission depletion*) concept, fluorescence is switched ON and OFF using only one species of molecules, the RESOLFT concept includes more than one species. He first wanted to test the concept on *cis-trans* isomerization and explained his naming of the method as follows: "I called it RESOLFT, for '*reversible saturable/switchable optically linear (fluorescence) transitions*', simply because I could not have called it STED anymore. There is no stimulated emission in there, which is why I had to give it a different name. The strength is not only that one can obtain high resolution at low light levels. Notably, one can use inexpensive lasers, continuous-wave (CW) lasers, and/or spread out the light over a large field of view, because one does not need such intense light to switch the molecules." In fact, in the model

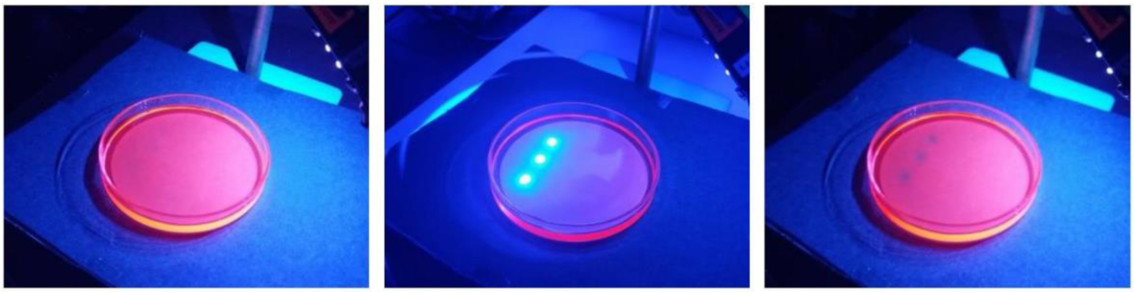


Figure 5. Experimental observations obtained with the system $SP/ME/MEH^+$; reprinted from the doctoral theses of S. Spinnen (2018) and Nico Meuter (2018), available at the source provided in [14], reproduced with permission.

INHIBIT-Gate		
Input 1 ($\lambda_{365\,nm}$)	Input 2 ($\lambda_{400\,nm}$)	Output ($EM_{632\,nm}$)
0	0	0
1	0	1
0	1	0
1	1	0

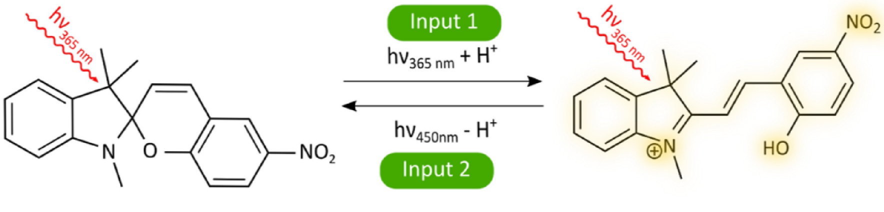


Figure 6. Truth table and reaction scheme for the all-optical INHIBIT logic gate with the system $SP/ME/MEH^+$; reprinted from the doctoral thesis of S. Spinnen (2018), available from the source provided in [14], reproduced with permission.

experiment described above light intensities of less than one Watt/cm^2 from LED to turn fluorescence ON and OFF are used.

As it is typical of models, this model *teaching experiment* also contains important differences to real super-resolution microscopes according to the STED or RESOLFT concept. Nevertheless, the results presented above and the digital materials from our website[14] partially developed in collaboration with the group of Klaus Schaper in Düsseldorf[24] prove its didactic potential in teaching innovative contents of photochemistry.

3. Titanium Dioxide: A Multi-talent for Teaching Photochemistry

Titanium dioxide is a didactically versatile substance which can be used in teaching photochemistry due to its chemical and physical properties and the fact that it is inexpensive and easy to handle. Investigation and teaching concepts on the two main topics in this part of the article, *solar cells* with TiO_2 and *photocatalysis* with TiO_2, have been reported by us and other authors in Refs. [3, 4, 8, 25, 26, 27]. Here we complement earlier work with new experimental variations and digital media.

Students dealing with titanium dioxide in the experiments described below use titanium dioxide suspensions, thus in a non-respirable kind of dosage. The titanium dioxide used in the experiments was Hombikat UV100 or P25, which both contain anatase titanium dioxide.

3.1. TiO_2 in Different Types of Photogalvanic Cells

Since *photogalvanic* cells are similar to galvanic cells, which are among the standard experiments carried out in chemistry classrooms worldwide, we have been dealing with this type of cells for more than 20 years. In our chemistry lab, where students carry out experiments and evaluate them with the help of digital media, the so-called *2-pot-cell* and the *1-pot-cell* have proven to be particularly useful. We have reported on this and on further developments shown in Figure 7, in Refs. [3], [8] and [12].

Detailed information on the preparation of photoelectrodes from conductive glass and TiO_2 as well as the assembly of the different cells can be found on our website[14] (see the QR-code in Figure 3a). Experiments carried out in the order of the sequence from Figure 7 enable the learners to explore and understand the *elementary processes in the conversion of light into electrical energy* (voltage and current flow), which can be developed step by step.

Investigations with the 2-pot-cell provide the following observations:

- In principle, the 2-pot cell has the same set-up as the Daniell cell: two half cells with different solutions, different electrodes and a salt bridge.
- The irradiated TiO_2-photoelectrode is always the negative pole of the cell.
- The cell only provides a voltage and an electrical current if the white TiO_2 photoelectrode is irradiated with violet or ultraviolet light of wavelengths below $\lambda = 388$ nm.
- Photo-induced open-circuit voltages up to 600 mV and short-circuit currents less than 0.06 mA can be achieved under constant illumination.
- Variations of the set-up reveal that the photoinduced voltage increases with smaller distance between the light source and the photoelectrode and depends on the intensity and the spectrum of the light used for illumination.
- After about 20 min of irradiation under short-circuit conditions, very small amounts Br_2 can be detected in the irradiated donor half-cell containing KBr(aq) and H_2 at the Pt-electrode in the acceptor half-cell containing HCl(aq).

These observed phenomena allow students to draw conclusions about the operating principle of the cell. The phenomena suggest that the redox reactions taking place in the two half cells consist of an oxidation of bromide anions at the TiO_2 electrode and a reduction of hydrogen cations at the Pt-electrode: $Br^- \rightarrow e^- + {}^1/_2\ Br_2$ and $H^+ + e^- \rightarrow {}^1/_2\ H_2$. Despite the very low efficiency in converting light into electrical energy, the 2-pot cell has a great advantage for teaching and learning. The following key steps can be easily understood using the animation indicated in Figure 8a: (i) the *light-induced charge separation* by *photoexcitation of electrons* from the valence band to the conduction band in the TiO_2 -nanoparticle, leading to the formation of *electron/hole pairs*, e^-/h^+, (ii) the diffusion

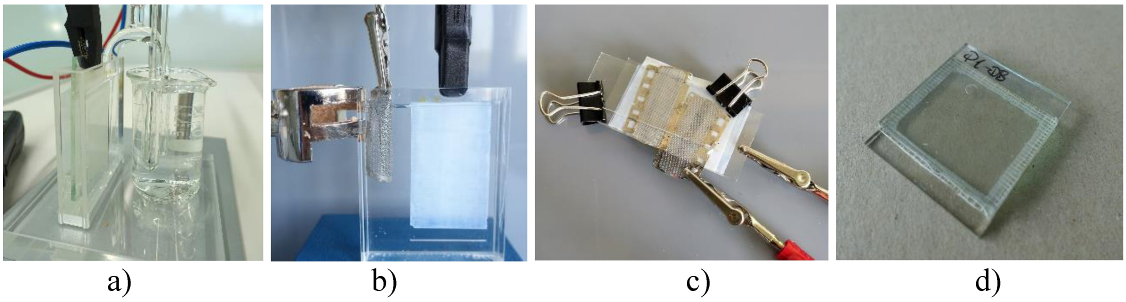
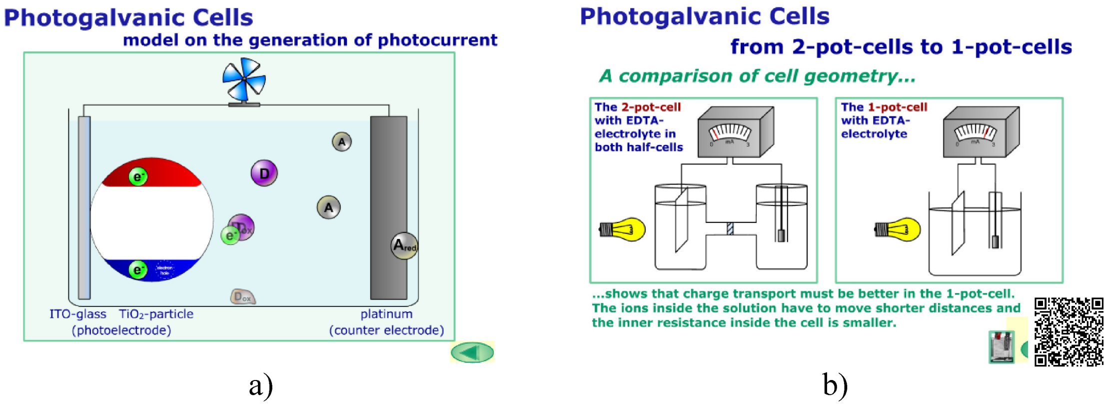

a) b) c) d)

Figure 7. Photogalvanic cells with TiO_2: 2-pot-cell (a), 1-pot-cell (b), compact cell (c), and transparent cell (d); pictures taken by D. Zeller, reproduced with permission.



Photogalvanic Cells
model on the generation of photocurrent

Photogalvanic Cells
from 2-pot-cells to 1-pot-cells
A comparison of cell geometry...

...shows that charge transport must be better in the 1-pot-cell. The ions inside the solution have to move shorter distances and the inner resistance inside the cell is smaller.

Figure 8. Generation of photocurrent in a photogalvanic cell (a) and comparison of cell geometries from 2-pot- and 1-pot-cells (b); Screenshots from model animations at the source provided in [14], reproduced with permission.

of photoexcited electrons, e^-, and holes, h^+, in opposite directions to generate a photo-induced current, (iii) compensation of the electron deficit in the semiconductor by oxidation of bromide ions, (iv) flow of photoelectrons through the outer circuit, and (v) reduction of hydrogen ions at the counter electrode. In the 2-pot-cell the bromide ions represent the *sacrificial donor* that is irreversibly oxidized.

On discussing these results, students can develop the following hypothesis: (i) a faster kinetics of the charge transfer from the dissolved sacrificial donor to the TiO_2 particles, (ii) a larger surface of the Pt electrode, and (iii) an optimized geometry of the cell should improve the performance parameters.

Optimizations via the 1-pot-cell led to the photogalvanic compact cell, in which filter paper impregnated with EDTA in aqueous solution is used, and to the transparent cell with a micro dispersion of nano-TiO_2 and a gel electrolyte of polyvinylalcohol and EDTA in PVA gel (Figure 7).

Experiments with the more compact photogalvanic 1-pot-cell (Figure 8b) containing a platinized Ni-foil (razor foil) as low-cost Pt-electrode and EDTA as sacrificial donor and the only electrolyte in the cell can be carried out analogously to those with the 2-pot-cell, leading to the following results:

- Compared to the 2-pot-cell, the 1-pot-cell yields moderately higher photo-induced voltages (0.9–1.1 V), but considerably higher photo-induced currents (~2 mA).
- A small motor can be started and powered for some time under constant irradiation of the photoelectrode.
- Like the 2-pot cell, the 1-pot cell is only photoactive during irradiation with violet or ultraviolet light from LED torches, but not with green or red light.
- However, compact cells can be powered by sunlight (see video on [14]).

These improvements confirm all three parts of the hypothesis from above. Nevertheless, all photogalvanic cells considered so far still have a crucial disadvantage: The sacrificial donor is irreversibly consumed. With each generated electron/hole pair and diffusion of the electron into the external circuit, a particle of the sacrificial donor is irreversibly oxidized. Therefore, a further improvement would be achieved if a constantly self-regenerating electron donor could be employed. This is realized in the dye-sensitized *photoelectrochemical cell* demonstrated by G. P. Smestad and M. Grätzel,[28] where the redox mediator, $2I^-/I_2$, is used. At the photoelectrode, iodide ions are oxidized and, at the same time, iodide ions are regenerated at the ITO-counter electrode by the reduction of iodine molecules. After having tested various materials for low-cost materials as counter electrodes we have found graphite foils to work most effectively. Only in the case of the transparent cell (see Figure 7d), both electrodes must of course be made of conductive glass.

3.2. TiO_2 in Dye-Sensitized Photoelectrochemical and Photovoltaic Cells

For a technical application as alternative photovoltaic cells are a second disadvantage needs to be discussed, that is the relatively large *energy band gap* of TiO_2 ($E_g = 3.2$ eV). In order to convert ambient solar light into electric energy a *photosensitizer* has to be used. Suitable photosensitizers for the use in TiO_2-based cells in schools have to meet with the following requirements:

- they should absorb in a large range of the visible region of the electromagnetic spectrum,
- they should be water-soluble or soluble in other solvents typically used in school chemistry,
- their molecules should contain functional groups that can chemically bind to TiO_2,
- the position of the LUMO should be higher than that of the conduction band of the semiconductor, so electron transfer can take place, and
- they should be stable against photodegradation as well as degradation by oxygen and humidity.

In the past,[28,3] anthocyanin dyes have been proposed as suitable sensitizers for school purposes. Anthocyanin dyes are natural products in petals of flowers and in many fruits. They are readily available throughout the year, e.g. in frozen raspberries, easy to handle and generally effective to show the principle of sensitization. One drawback though, is their shortlived stability when irradiated with light, especially in the presence of TiO_2. Depending on the light source, it comes to a visible degradation of the dye, yielding in lower voltages within a school lesson. In fact, TiO_2 is a *photocatalyst* and promotes the *photodegradation* of anthocyanin dyes.[4] After a few irradiation cycles an anthocyanin-sensitized photoelectrode is obviously bleached by degradation of the dye.

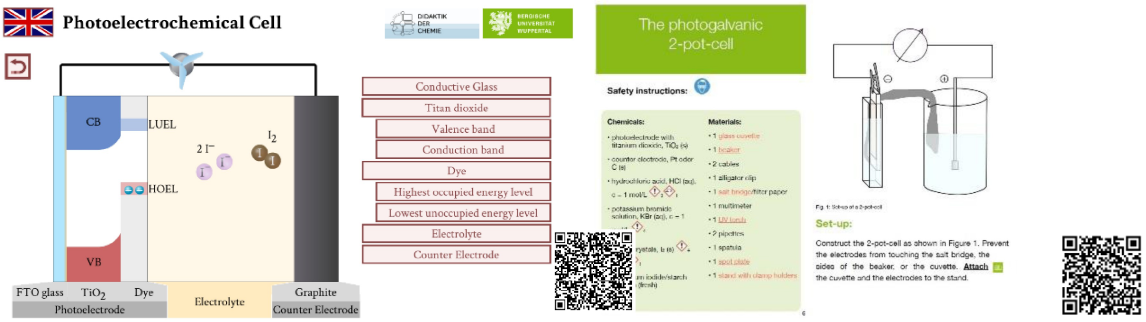
With respect to availability and occurrence in the students' everyday lives we have tested a number of different food colourants as well as spices such as saffron and turmeric. Especially saffron proved to work as a suitable dye for the use as alternative sensitizer for TiO_2. The dye crocin is mainly responsible for the yellow colour of saffron. It is a carotene derivative with disaccharide substituents, which cause the dye to be highly water-soluble. The animation as well as the e-book from Figure 9 contains among many other aspects, the formulas of anthocyanin and crocin molecules and information about their mode of binding to TiO_2, and on their photostability.

The experimental section in Ref. [8] presents a sequence of lab experiments useful for the preparation of dye sensitized photoelectrodes (Figure 10), their absorbing properties, their stabilities and, finally, the performances of dye-sensitized photoelectrochemical cells.

3.3. TiO_2 in Heterogeneous Photocatalysis

Owing to its physical, chemical, toxicological, economical, and accessibility characteristics, anatase TiO_2 is typically the semiconductor of choice when teaching the concept of *heterogeneous photocatalysis*. For school experiments, the same formulations of nano-TiO_2, as in the experiments described above can be used. At higher secondary education level, it should be taught that thermodynamically difficult or even endergonic redox reactions can be photocatalytically driven. In this process, the electron/hole pairs generated in the TiO_2 nano-particles after light absorption actively participate in electron transfer processes with molecules from the environment. In the photogalvanic cell this partially takes place when the hole in the semiconductor is stuffed by a donor particle such as bromide ions or EDTA molecules. In photocatalytic processes the semiconductor facilitates the electron transfer from a donor to an acceptor, without undergoing itself any net change. An animation showing the elementary processes in the photocatalytic model reaction from Figure 11a) is available on our website[14] (see QR-code in Figure 11).

We have profitably used the negative aspect of the rapid photobleaching of the anthocyanin-sensitized TiO_2 photoelectrodes (see section above) to develop experiments on the photocatalytic oxidation of organic compounds.[4] In order to prepare a thin layer of dye-sensitized photocatalytic TiO_2, we



The photogalvanic 2-pot-cell

Safety instructions:

Chemicals:
- photoelectrode with titanium dioxide, TiO_2 (s)
- counter electrode, Pt oder C (s)
- hydrochloric acid, HCl (aq), c = 1 mol/L
- potassium bromide solution, KBr (aq), c = 1
- rystals, I_2 (s)
- m iodide/starch (fresh)

Materials:
- 1 glass cuvette
- 1 beaker
- 2 cables
- 1 alligator clip
- 1 salt bridge/filter paper
- 1 multimeter
- 1 UV torch
- 2 pipettes
- 1 spatula
- 1 spot plate
- 1 stand with clamp holders

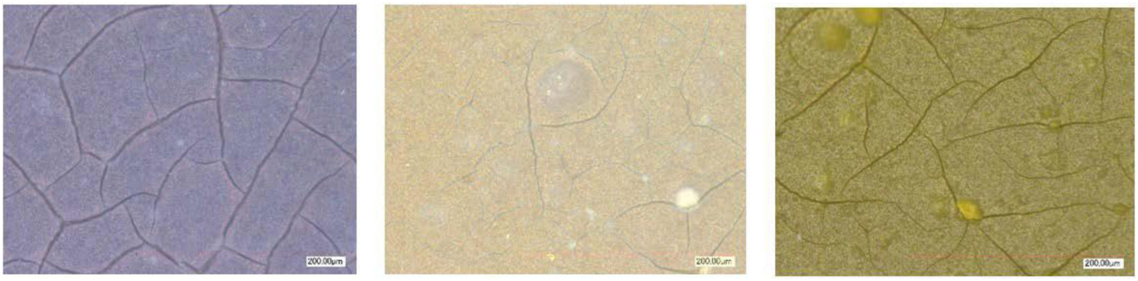
Fig. 1: Set-up of a 2-pot-cell

Set-up:

Construct the 2-pot-cell as shown in Figure 1. Prevent the electrodes from touching the salt bridge, the sides of the beaker, or the cuvette. **Attach** the cuvette and the electrodes to the stand.

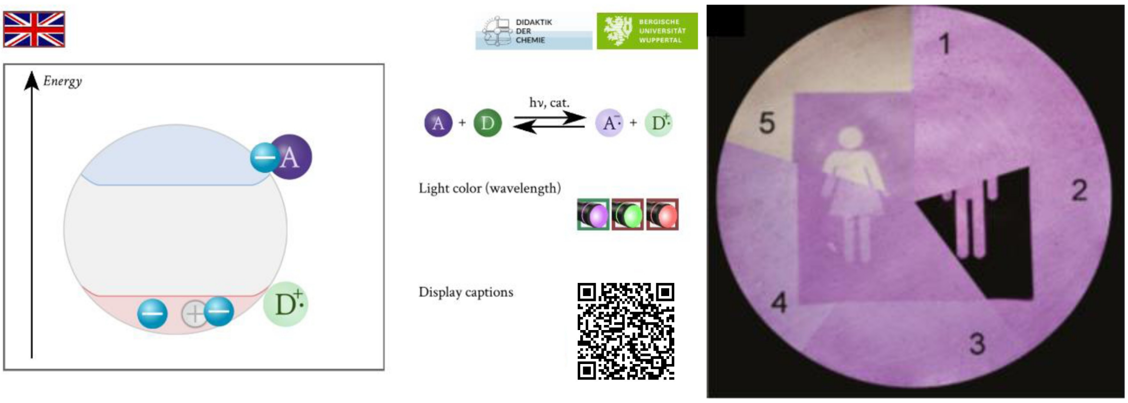
a) b)

Figure 9. General Information on dye-sensitized photoelectrochemical cells and animation of the current flow (a) ;[14] screenshot from the e-book "Solar cells with titanium dioxide",[12] reproduced with permission under terms of the CC-BY license, copyright 2020, The Authors, published by Science and Education Publishing.



a) b) c)

Figure 10. Light microscope images (1 000 x) of TiO_2 surfaces on photoelectrodes, sensitized with a) raspberry juice, b) saffron solution, and c) with crocin solution (Keyence VHD-1000X); pictures taken by D. Zeller, reproduced with permission.



a) b)

Figure 11. Working principle of photocatalytic redox reactions on TiO_2 (a) and collage of filter papers before and after photocatalytic oxidative bleaching of anthocyanin (b); a) reproduced with permission from the source provided in [14] with permission; b) Reproduced with permission from Ref. [4], copyright (2011), American Chemical Society.

have brushed a slurry of nanocrystalline TiO_2 (anatase) on pieces of regular laboratory filter paper. After drying with a hair dryer, the coated filter papers were sensitized by dipping them in juice extracted from frozen raspberries. Irradiation of such samples with light from different lamps, at different distances, with and without masks lead to results as those shown in Figure 11b. The following results can be obtained:

- The completely bleached zone 5 in Figure 11b) was obtained after only 5 min of irradiation with a 300 W Ultra-Vitalux lamp at a distance of 30 cm.
- The bleaching occurs in the presence of air and humidity, and it is irreversible.
- Using a green or red laser pointer, photocatalytic writing is possible so that the message can be read with the naked eye.
- A control experiment without TiO_2 shows that bleaching takes place much slower when there is no TiO_2 on the irradiated filter paper.

In these demonstrations, anthocyanin serves both as a sensitizer and as the target species to be photodegraded. This occurs because of (i) the ability of the dye to covalently bind to the TiO_2 nanoparticles, (ii) the relative size of the energy gap, E_g between the HOMO and LUMO, and (iii) the position of the LUMO relative to the conduction band of the semiconductor (see QR-code in Figure 9).

The general mechanism for the *oxidative photocatalytic degradation* of an adsorbed dye D in the presence of oxygen O_2 contains three key steps consisting of the electronic excitation of the dye molecule, the electron-transfer from the LUMO of the dye molecule into the conduction band CB of the TiO_2 nano-particle, and the formation of an oxidizing species such as the superoxide anion radical [Eq. (1–3)]:

$$D + h\nu \rightarrow D^* \qquad (1)$$

$$D^* + TiO_2 \rightarrow D^{\bullet +} + TiO_2^{\cdot -} \qquad (2)$$

$$TiO_2^{\bullet -} + O_2 \rightarrow TiO_2 + O_2^{\cdot -} \qquad (3)$$

The superoxide anion radical $O_2^{\bullet -}$ is further reduced, ultimately to H_2O, with simultaneous further oxidation of the adsorbed dye monocation radical D^{++} [Eq. (4–5)]:

$$O_2^{\bullet -} + 2H^+ + e^- \rightarrow H_2O + \ 0.5\ O_2 \qquad (4)$$

$$D^{\bullet +} \rightarrow D^{++} + e^- \qquad (5)$$

This way dye D quickly becomes irreversibly photooxidized (i.e., bleached). Note that Equations (1)–(5) represent only an extreme simplification of the elementary processes occurring on the TiO_2 surface. However, they include the key steps from the animation from Figure 11, use standard notation in education and take into account the fundamental processes discussed in the literature, e.g. in the review article.[29] In this article, the photoinduced oxidation and reduction reactions at TiO_2 are given by examples and explained mechanistically.

For teaching purposes, these different types of redox reactions can be investigated using the dye methylene blue, MB. Bleaching experiments with MB are very suitable because they are easy to perform and provide clear observations. They can be carried out in a very simple set-up irradiating suspensions of nano-TiO_2 with a 200-W halogen lamp and cooling with a water-filled PE bag. If the irradiation is performed with two UV-LED torches ($\lambda = 365$ nm) as shown in Figure 12a, no cooling is necessary.

The irradiation of 10 mL of a blue suspension with $c(MB) = 2\cdot10^{-5}$ mol/L and 30 mg of TiO_2 (anatase) in a thin-walled test tube yields the following (curious) observations:

- If nitrogen is introduced into the suspension during irradiation, the solution becomes completely bleached within 5 minutes.
- However, when air or oxygen is introduced into the bleached suspension, blue colouring occurs quickly again.
- If oxygen is introduced into the suspension during irradiation, it takes much longer (more than 15 minutes) for the bleaching to become visible.

Figure 12. Experimental set-up for the photocatalytic bleaching of methylene blue (a) and self-made solar reactor for overall oxidation of organic compounds (b); picture b) by M. Tausch (2001) reproduced with permission.

- In this case, however, bleaching cannot be reversed by introducing hydrogen or any other reducing gas.
- The TiO_2 filtered out of the bleached suspension, and added to a potassium iodide solution immediately leads to the formation of molecular iodine.

Bleaching under nitrogen gassing is based on the reversible *reduction of MB* to colourless leuko-methylene blue MBH_2. Accompanying this, oxygen atoms from water molecules or from the OH groups from the surface of the TiO_2 particles get oxidized. The resulting oxygen molecules as well as the peroxo-groups remain on the surface of the TiO_2 particles. Therefore, the TiO_2 used in the experiment (in contrast to fresh TiO_2) has an oxidizing effect on iodide ions. The slow bleaching process during irradiation under oxygen gassing is due to the gradual and irreversible *oxidation of MB*, with destruction of the molecule chromophore. This bleaching is similar to the above discussed bleaching of anthocyanin on TiO_2 coated filter papers (Figure 11b).

For technical applications, the *oxidative degradation* of persistent organochlorine compounds is primarily relevant for the decontamination of wastewater, e.g. from industrial plants and hospitals.[20] In this sense, model experiments can also be carried out for teaching purposes. With the self-built solar reactor shown in Figure 12b (a parabolic TV-antenna dish covered with aluminium foil and a two-necked flask at the focal point), even persistent organochlorine compounds such as tetrachloroethylene can be mineralized under air gassing up to carbon dioxide and chloride ions following Equation (6).

$$C_2Cl_4 + 2H_2O + O_2 \rightarrow 2CO_2 + 4H^+ + 4Cl^- \quad (6)$$

The products are detectable by common school methods: Turbidity of a barium hydroxide solution when introducing the gas from the photoreactor, pH measurement in the irradiated suspension, and precipitation when treating the filtrate from the photoreactor with a silver nitrate solution. Experiments like this are suitable to encourage students to get involved in school research projects.

4. Conclusions

Repeatedly the editorials of this journal asked the question "What should we teach students about photochemistry?" In this report we address several topics and concepts as well as a variety of digital media regarding "*what* to teach" and also give some hints about "*how* to teach". Our aim is to teach core concepts of photochemistry in a sustainable way on the basis of clearly observable and coherently interpretable phenomena.

Accordingly, as science educators, we feel guided by A. Einstein's aphorism that "a pretty experiment quite often is more precious than twenty equations bred in the thinking retort". The experiments and digital media presented in this article are intended to show *how* simple devices and harmless chemicals can nevertheless be used to produce convincing phenomena for teaching contents and concepts of photochemistry. This is *what* we have to teach - not only in photochemistry courses, but also in general chemistry courses and even in school chemistry.

In this article, we only gave a selected insight into our repertoire, focusing on two groups of experiments and digital materials, involving the molecular switch spiropyran/merocyanine on the one hand and on the other hand the photoactive n-type semiconductor titanium dioxide as central photoactive systems. More details on the described work and on further experiments have been published and can be found in Refs. [2-14].

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Conflict of Interest

The authors declare no conflict of interest.

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