
TOWARDS ARTIFICIAL PHOTOSYNTHESIS: PROMOTING MICROSCALE PHOTOCHEMISTRY IN SCIENCE EDUCATION

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ABSTRACT

In order to simulate basic features of the natural cycle of photosynthesis and respiration, a model experiment called Photo-Blue-Bottle PBB has been developed. According to the title of this paper, the experiment will be presented and interpreted in accordance to basic contents from science education. An extended version of the PBB experiment also enables the evolution of hydrogen. This is a key step towards a prospective technological scenario with solar light driven production of “green fuels”. The concept of electronically excited state, the “heart of all photoprocesses” (N. J. Turro), will be completed by further teaching experiments and concepts concerning the up-to-date topic of photoactive molecular switches. [*African Journal of Chemical Education—AJCE 9(3), November 2019*]

INTRODUCTION

A fundamental demand on science education today is to communicate core principles of chemistry, physics, biology and computer sciences in close combination with everyday life experiences of students as well as in combination with convincing applications from modern science and technology. Photochemical and photophysical processes are par excellence suitable to fulfill this requirement. Therefore, research in science education is challenged to develop experiments, concepts and teaching materials which help to interpret and communicate photoprocesses in a manner that is exciting and understandable. Doing so, research in chemical education contributes in bridging the gap between the state of the art in advanced science and technology and science education in schools and universities (Figure 1).



Fig. 1: Internet platform “Chemistry with Light” provided by the Chemical Education Research Group from the University of Wuppertal [1]

The “big five” global challenges in the 21st century

In view of the “big five” global challenges in the 21st century that are related to the terms energy, food, water, climate and mobility, mankind has to replace energy from fossil fuels step by

step by renewable energies. Solar energy is definitely not only the most abundant one of them, but also the cleanest. Accordingly, the contribution of solar energy in the global energy mix is estimated to increase until the end of the 21st century to more than 60% [2]. In addition to photovoltaics and solar heat, artificial photosynthesis of “green fuels” is a promising option for exploiting the enormous supply of solar radiation on our planet. In regard to the topic light for green chemistry, there are mainly two different scenarios being discussed (Figure 2).

- One scenario intensively debated and investigated suggests carbon containing fuels, prepared by CO₂ sequestration and subsequent photocatalytic reductive conversion with water using solar light into carbon containing fuels such as methanol or hydrocarbons.
- A different route includes molecular hydrogen either as an intermediate or as the target. Indeed, hydrogen produced directly by solar irradiation is an excellent “green fuel”, that can be used in different ways to regain the energy stored.

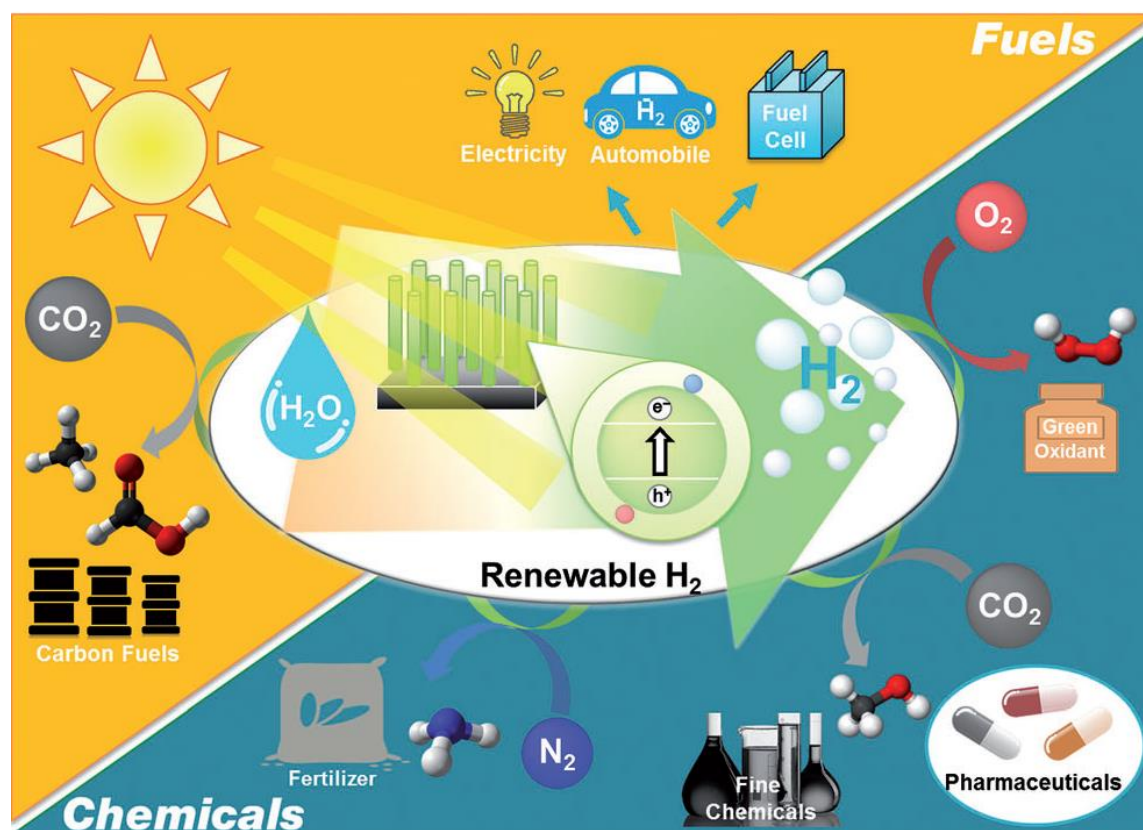


Fig. 2: “Artificial photosynthesis for sustainable fuel and chemical production” - title and chart from *Angew. Chem. Int. Ed.* [3]

Microscale Chemistry - versatility and sustainability in chemical education

With respect to the philosophy of Microscale Chemistry, chemical education is challenged to focus on the basic principles of green chemistry and to exploit the advantages of sustainable microscale-sized experiments. In this sense, the topic of artificial photosynthesis and adequate experiments using small reaction containers, harmless chemicals, and inexpensive LED-torches or sunlight are not only scientifically relevant but also highly motivating for young people. Teaching experiments for artificial photosynthesis should mimic and point out bio-inspired strategies of natural photosynthesis. First of all, they have to illustrate the reaction type of a light driven endergonic reduction providing for clearly observable and coherently interpretable phenomena. Accordingly, science educators should feel guided by A. Einstein’s statement elaborated in 1955:

“A pretty experiment quite often is more precious than twenty equations bred in the thinking retort.”

A “pretty” experiment

The experiment proposed here is called Photo-Blue-Bottle PBB. The reason for this is the production of a blue compound by irradiation of the PBB solution (Fig. 3). This is caused by the endergonic, light driven reduction of a colorless substrate to a blue reduced species. However, the reaction occurs only with the aid of a visible light absorbing photocatalyst (see chemicals below). The reduction, as well as the re-oxidation of the reduced species with oxygen from air, realized by shaking the vial, are visualized as color changes from yellow to blue and vice versa. The phenomenological cycles yellow-blue-yellow (reduction-oxidation cycles) can be repeated more than 20 times, using just 3 mL of the PBB solution in a 10 mL vial, as is shown in Figure 3.



Fig. 3: Basic version of the Photo-Blue-Bottle experiments; irradiation and shaking of the PBB solution as Screenshots from video-supplements provided via Ref. [4]

In order to prepare the *PBB-solution*, dissolve:

- 1 g of EDTA (ethylene-diaminetetraacetic acid disodium salt, Merck/Sigma-Aldrich, CAS No. 6381-92-6),
- 561 mg of ethylviologen (1,1'-Diethyl-4,4'-bipyridinium dibromide, Merck/Sigma-Aldrich, CAS No. 53721-12-3), and

- 15 mg of proflavine (3,6-Diaminoacridine-hemisulfate, Merck/Sigma-Aldrich, CAS No. 1811-28-5)

in 500 mL of distilled water. The yellow solution should be stored in a brown glass flask with screw cap. The solution remains stable and usable for several months in such a container and suffices for at least 15 groups of students if they use microscale equipment.

A simplified explanation for the color cycles in the PBB experiment can be given by the coupled reaction cycles depicted in Figure 4. The color of the PBB solution changes from yellow (caused by PF^+) to deep blue (caused by EV^+) by irradiation. If oxygen is introduced into the blue solution (for instance by shaking the vial), EV^+ is re-oxidized into the colorless EV^{2+} . The endergonic reduction of an ethylviologen dication EV^{2+} to a monocation EV^+ is photocatalyzed by proflavine PF^+ .

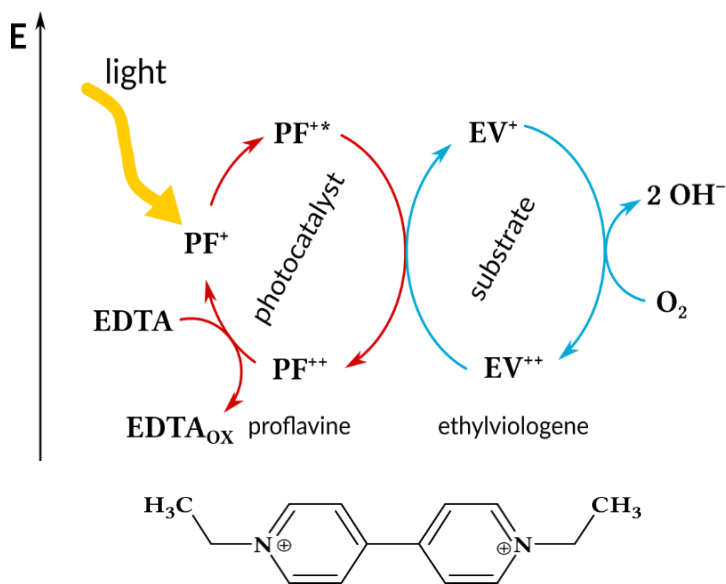
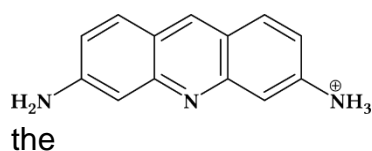


Fig 4: Coupled reaction cycles in the PBB experiment (top).



Formula of the substrate ethylviologen EV^{2+} and the photocatalyst proflavine PF^+ (below).

The excited state of the proflavine monocation PF^{+*} initially generated by blue light absorption ($\lambda_{\text{max}} = 445 \text{ nm}$) acts as reducing agent for EV^{2+} , oxidizing itself to PF^{2+} in the process. The photocatalyst monocation PF^+ is regenerated from PF^{2+} by electron capture from the sacrificial donor EDTA. Consequently, EDTA is irreversibly consumed during irradiation, whereas proflavine goes through many reaction cycles, that is photocatalytic oxidation-reduction cycles, without being consumed. (Note that the concentration of proflavine in the PBB solution is approximately only 1% of the concentration of ethylviologen).

In order to understand why the PBB experiment works as described above, the redox potentials of the involved redox pairs have to be considered (Figure 5).

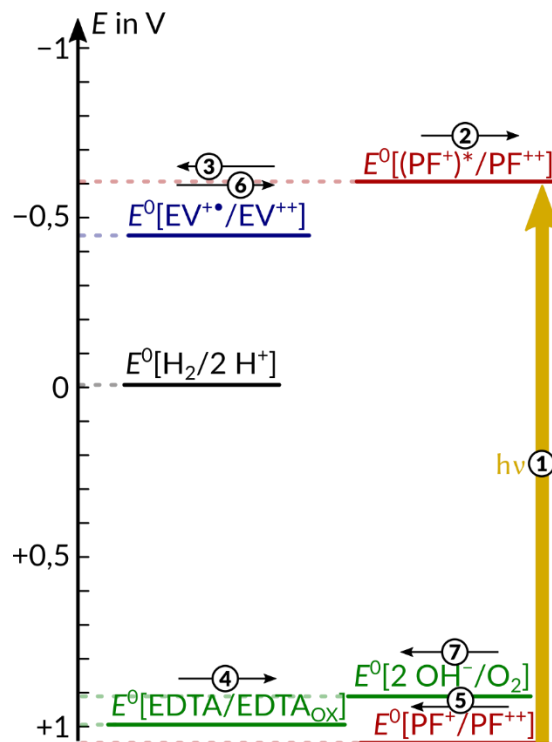


Fig. 5: Redox potentials of redox pairs in the PBB experiment

Since $E^0(\text{EV}^+/\text{EV}^{2+}) = -0,48 \text{ V}$, a redox pair with $E^0 < -0,48 \text{ V}$ is needed for the reduction process $\text{EV}^{2+} \rightarrow \text{EV}^+$. This becomes available after the electronic excitation $\text{PF}^+ \rightarrow \text{PF}^{+*}$, because

the redox potential of the photocatalyst changes dramatically by electronic excitation from $E^0(\text{PF}^+)/\text{PF}^{2+} = +1,1 \text{ V}$ to $E^0(\text{PF}^+)/\text{PF}^{2+}* = -0,6 \text{ V}$ (see the yellow arrow in Figure 5). The electronic excitation by absorption of a photon is actually always the very first elementary process of every light driven reaction or multistep cascade of reactions. The numbered redox reactions in Figure 5 correspond to the reactions taking place in the coupled cycles shown in Figure 4. It should be emphasized that except for the initial electronic excitation **1**, all other elementary processes consist of a reduction/oxidation pair. These are the pairs **2/3**, **5/4**, and **7/6** highlighted in Figure 5.

Obviously, there are some *similarities* between the *reaction cycles* in the PBB experiment and the *natural cycles* of photosynthesis and respiration:

- the carbon cycle in natural photosynthesis and respiration is similar to the ethylviologen cycle in the PBB experiment,
- the photocatalyst in the experiment works like chlorophylls and other pigments in green leaves,
- the photocatalytic active species are colored, they absorb visible light,
- all reactions occur in aqueous solution,
- oxygen from the air is the oxidizing agent in both cases, and
- light is the driving force for the endergonic reduction.

However, no evidence has been given that the photoreduced substrate is an energy storage system similar to the sugar produced in natural photosynthesis. So we felt compelled to develop another suitable experiment that can be used to determine whether energy is converted and stored in the system or not. The question was how to design such an experiment.

The breaking through idea was, to take into consideration the *Nernst* equation for the couple of the substrate $\text{EV}^+/\text{EV}^{2+}$. In general, the redox potential should become more negative,

if the concentration ratio of the reduced species in a redox pair increases. Consequently, the experiment was designed like a photoelectrochemical measuring device connected to a digital voltmeter as indicated in Figure 6.

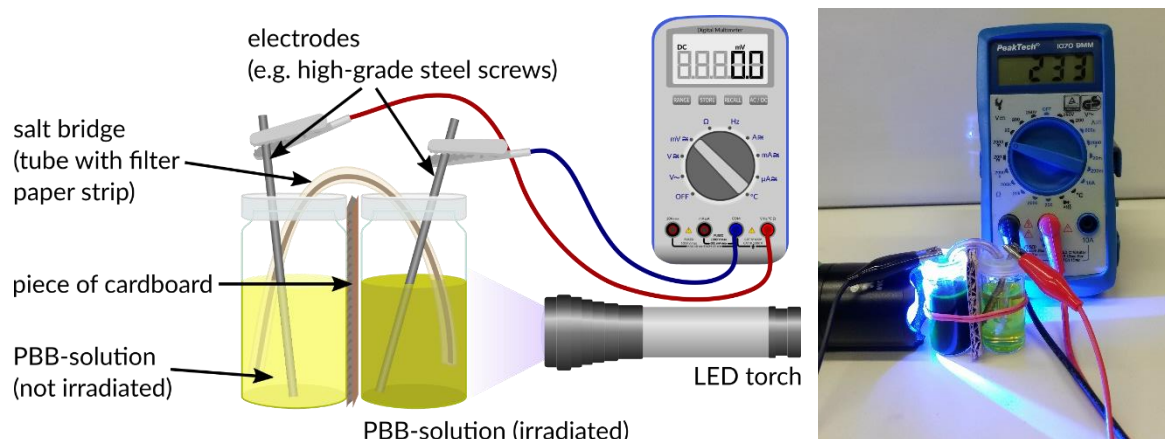


Fig. 6: Scheme and photo of a concentration cell with PBB solution; a video-supplement is provided via Ref. [4]

Indeed, simultaneously with the blue coloration a voltage is generated and increases up to 300 mV and more. Even after the lamp is switched off, neither the color nor the voltage changes. But it falls down and the color turns back to yellow, if air or oxygen is introduced. That's the evidence that in the PBB-experiment light energy is converted into chemical energy and stored in the reduced substrate. Actually this system works like a “solar rechargeable battery”, like a “solar accumulator”.

Nevertheless, it's still unsatisfactory, that the reduced species EV^+ from the PBB experiment is not a veritable green fuel as glucose or other sugars from natural photosynthesis. How can we come closer to nature? Can we produce a veritable green fuel such as hydrogen using the PBB experiment?

The idea for an attempt to realize that, looks like this: Try to *collect* electrons from the reduced species EV^+ in the reaction pot containing the PBB solution, *transfer* them via an exterior electric conductor to a Pt-electrode immersed into an hydrochloric acid solution in a second pot and *connect* the two pots with a salt bridge (Figure 7).

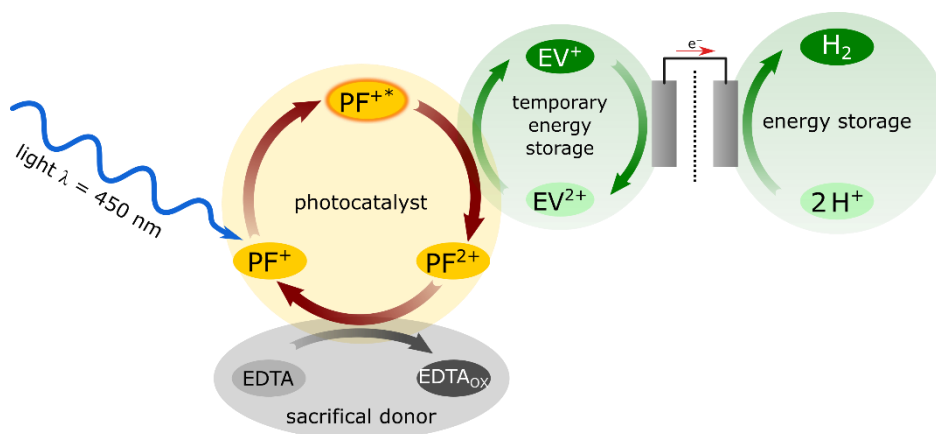


Fig. 7: Concept of a 2-pot photogalvanic cell for hydrogen production via PBB

In contrast to the PBB versions mentioned above, this 2-pot-photogalvanic cell is an open system because the produced hydrogen gas escapes the reaction mixture.

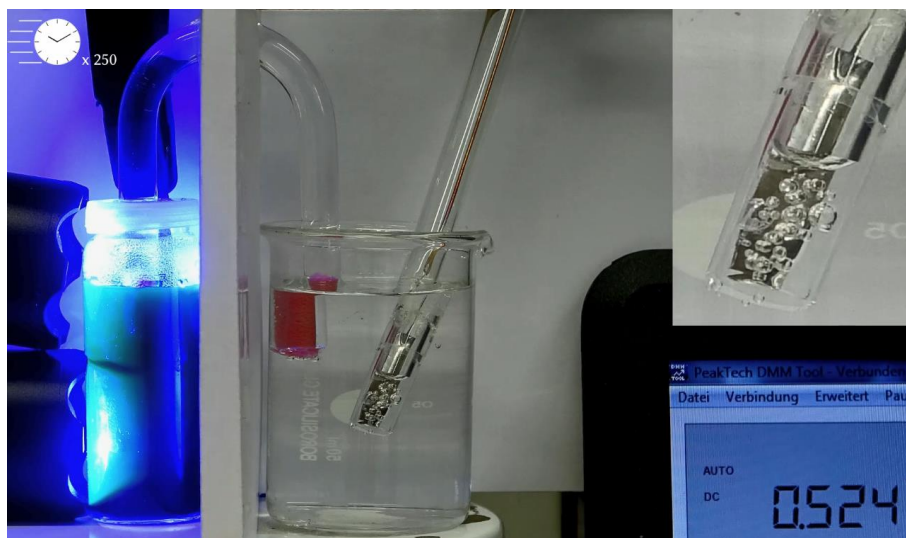


Fig. 8: The 2-pot-photogalvanic cell using PBB solution; video-supplements showing hydrogen evolution and hydrogen-oxygen explosion test are provided via Ref. [4]

By using the setup shown in Figure 8, 0.2 mL of hydrogen could be generated within 30 minutes. Although it is not much, it is enough to perform a hydrogen-oxygen explosion test.

Compared to former published versions of the PBB experiment [5, 6], the microscale design as well as the hydrogen production refine and enhance the suitability of this “pretty” experiment for teaching chemistry with light.

How much theory is necessary?

Repeatedly, teachers and students get afraid when they try to anticipate the theoretical background necessary for teaching photochemistry. But when you actually look at what is needed to begin understanding photochemistry, is just the following simple concept at the level of a paradigm, i.e. a pattern of thinking:

“The ‘photo’ part of molecular photochemistry is a historical prefix and is now too restrictive. It is now clear that electronically excited states of molecules are the heart of all photoprocesses. The excited state is in fact an electronic isomer of the ground state”.

This paradigm has been formulated by N. J. Turro in 1978 [7]. Actually, it is suitable for the explanation of all photoprocesses in a didactically reduced, but scientifically consistent approximation. In general, the excited state A^* emerges from an electronic excitation of a molecule by absorption of a photon (Figure 9).

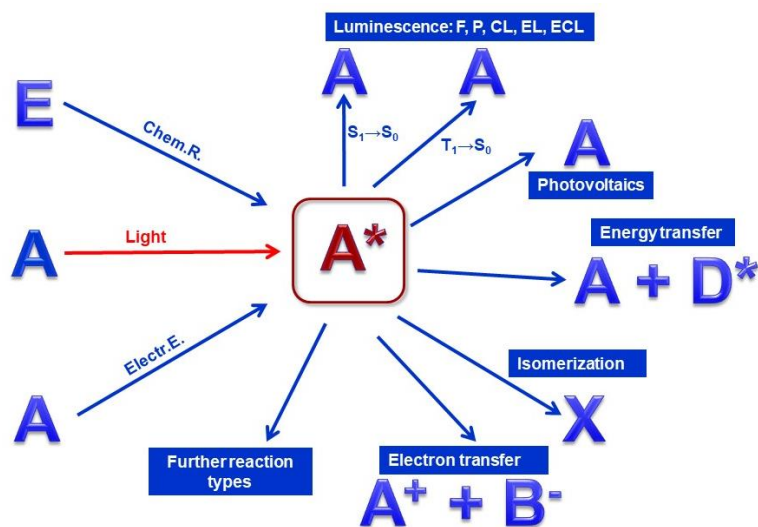


Fig. 9: Generation of the excited state A^* and deactivation routes without and with chemical reaction

But according to Turro's statement, the excited state A^* , is not necessarily generated by light irradiation, it can also emerge from an exergonic chemical reaction as well as by supplying of electrical energy. Actually, A^* can deactivate or react in very different ways too. So we get a veritable "zoo" of photoprocesses stretching across different types of luminescence, photovoltaics, energy transfer, isomerization and redox reactions (Figure 9).

A molecular switch for fascinating photochemistry

Compounds that undergo reversible isomerization reactions by irradiation with light of different wavelengths belong to the class of photoactive molecular switches. The isomerization is, in general, accompanied by changes of macroscopic properties. The commercially available spiropyrane (Figure 10) can really be considered a dream compound for chemical education as starting material for a variety of microscale experiments.

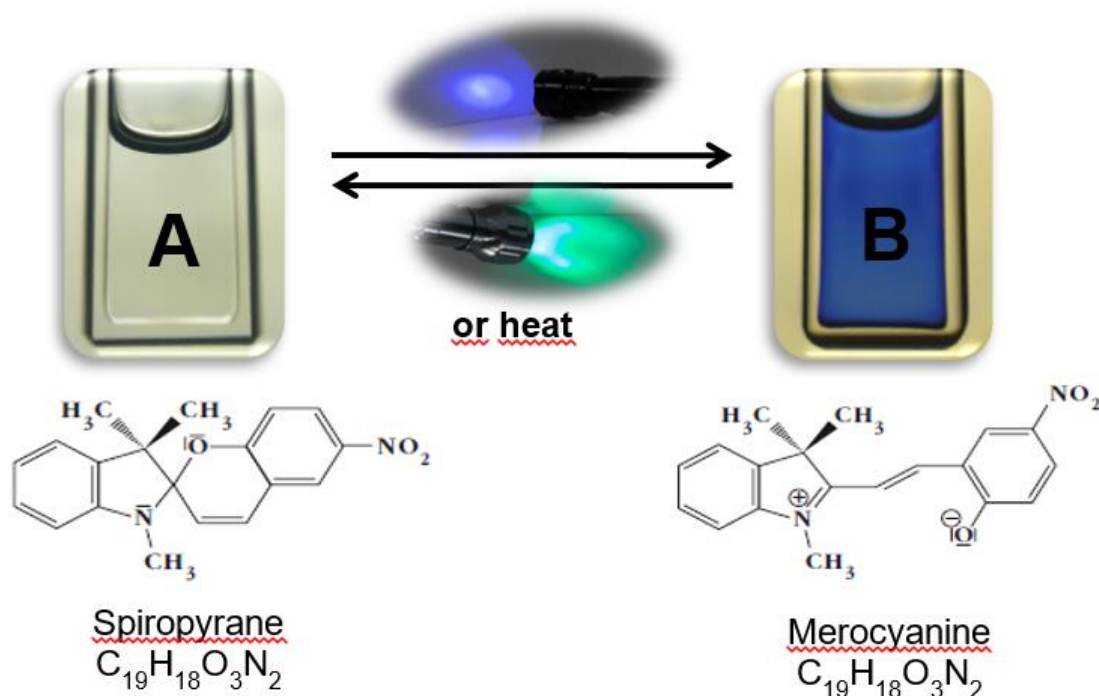


Fig. 10: Molecular switch spiropyrane/merocyanine

Experiments using the isomer pair spiropyrane/merocyanine in different nano-environments (solvents and/or rigid matrices) at different temperatures and with different light sources (different wavelengths) serve for introducing, expanding and differentiating basic concepts of general chemistry and photochemistry, for instance:

- the phenomenon and the concept of a photoactive molecular switch, that is switching a property ON and OFF by remotely controlling it using light only,
- the relation between the molecular structure and the color generated by a compound,
- the relation between the molecular structure and the reactivity of a compound by irradiation at a given wavelength,
- the different reaction pathways of a photochemical reaction in contrast to a thermal reaction,

- the temperature-dependence of the reaction rate of a photochemical reaction in contrast to that of a thermal reaction,
- the phenomena and concepts of photochromism and solvatochromism,
- the functional principle of logic gates
- the phenomenon and concept of aggregation induced fluorescence,
- similarities and differences between the thermodynamic (chemical) equilibrium and the photosteady (photostationary) state,
- the conceptual design of devices that work as optical logic gates following the rules of Boolean Algebra.

Even though the paradigm of excited state of molecules, the “heart” of all photoprocesses, is basically the only additional theory needed to teach all these contents at a reasonable level for high school and college, further theoretical background as well as the connection to common contents of general chemistry are given in recently published papers [7-8].

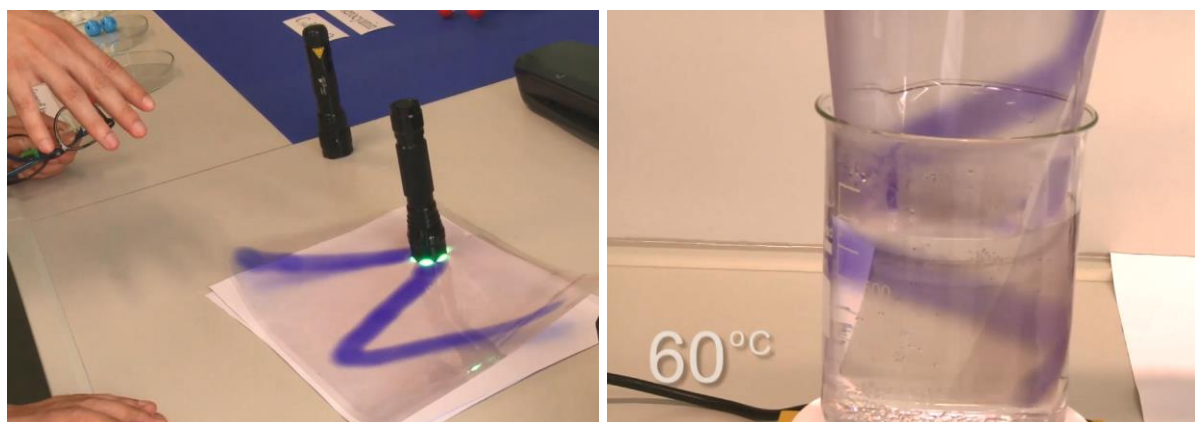


Fig. 11: Writing and erasing on the “intelligent” foil containing the molecular switch spiropyran/merocyanine; short videos are provided via Ref. [4]

Several tutorials and model animations concerning experiments with the molecular switch spiropyran/ as well as the concepts enumerated above, are provided on the internet platform [1].

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