Two Versatile Experiments for Teaching Photochemistry: Photon Upconversion by TTA and All Optical INHIBIT Logical Gate

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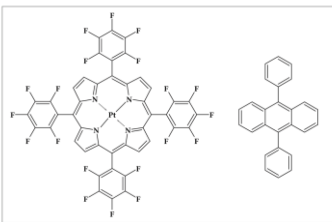
The two new experiments reported below address students and teachers at the tertiary educational level, that is students and teachers from colleges and universities. Experimental approaches at the secondary educational level in high schools have already been published. Appropriate introductory experiments concerning photoluminescence, photochromism, solvatochromism and molecular switches are available as follows:

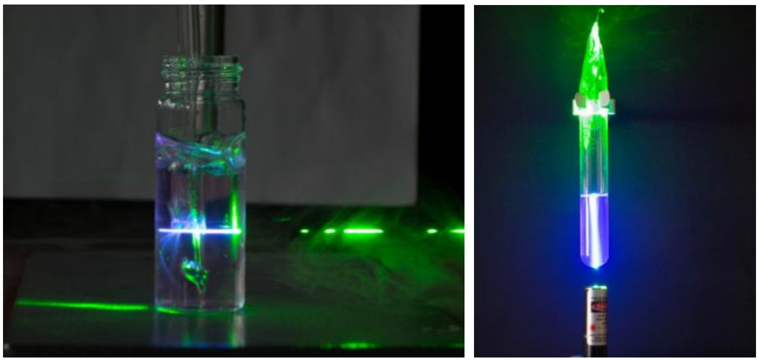
- M. W. Tausch, N. Meuter, S. Spinnen: "Photoprocesses in Chemical Education - Key Experiments for Core Concepts" **(2018)**, *Education Quimica*, DOI: 10.1016/j.eq.2017.03.003
- M. W. Tausch, R. Brunnert, C. Bohrmann-Linde, N. Meuter; N. Pereira Vaz, S. Spinnen, Y. Yurdanur: „Photons and Molecules - Basic Concepts of Photochemistry in Video Tutorials" EPA (European Photochemistry Association) Newsletter, Volume 96, p. 70-77 **(2019)**;
- M. W. Tausch et al. „Chemistry with Light - Innovative Didactics for Study and Teaching" Internet Platform **(2019)** https://chemiemitlicht.uni-wuppertal.de/

Upconversion by TTA

Experimental procedure: 0,5 mg of Diphenylanthracene DPA and 0,2 mg of 5,10,15,20-Tetrakis-(2,3,4,5,6-pentafluorophenyl) porphyrine-Pt(II) TPFPP-Pt(II) are dissolved in 15 mL of acetone. The solution shows a slight pink color and generates a weak red fluorescent trace if irradiated with the beam of a green laser pointer (power: about 10 mW). In order to make the



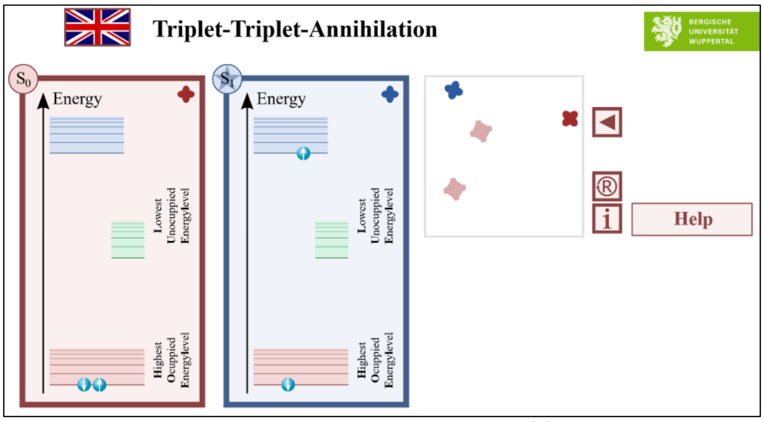
upconversion effect visible, oxygen has to be removed from the solution. This is easily achieved by flushing the solution with nitrongen. During this process the fluorescent trace insidet the solution changes from a weak red to strong blue color within one or two minutes. If the purging with nitrogen is stopped, the blue fluorescence stays for a maximum of roughly 2 to 3 minutes until sufficient oxygen has diffused back into the solution.
In order to get a long-lasting upconverting solution, the vial has to be hermetically sealed immediately after flushing the solution with nitrogen gas. The solution can then be stored for years within the sealed vial. It is suitable for hands-on demonstrations of the photon upconversion effect.



A green laser beam triggers a blue fluorescent trace in the TTA solution

Teaching recommendations: In photoluminescence processes photons are commonly down converted. The energy of incident photons is partially dissipated as heat by vibrational relaxations within molecules. As a consequence, the color of the light emitted by fluorescence is red shifted compared to the color of the exciting radiation (*Stokes* shift). This can be explained convincingly by means of the concept of electronically excited states of molecules including their vibrational levels. While teaching photoluminescence, it's recommended to introduce this theoretical concept by first investigating the photon down conversion via fluorescence and phosphorescence (see experiments in online publications mentioned above).
Doing so, students will be surprised when seeing that green light is converted into blue light by fluorescence. In fact, the observation from

the TTA-experiment disagrees with the established theoretical concept. Therefore, the logical contradiction between the theoretical prediction and the experimental observation requires a credible explanation for the anti-*Stokes* behavior of the setup in our TTA experiment. In order to facilitate this explanation, we provide a model animation.



Screenshot from the model animation available at https://chemiemitlicht.uni-wuppertal.de/en/models-animations/triplet-triplet-annihilation.html

The interactive animation shows and describes step by step the TTA mechanism from the absorption of a "green" photon by the platinum complex (the triplet sensitizer) until the emission of an upconverted "blue" photon by diphenylanthracene (the fluorophore).

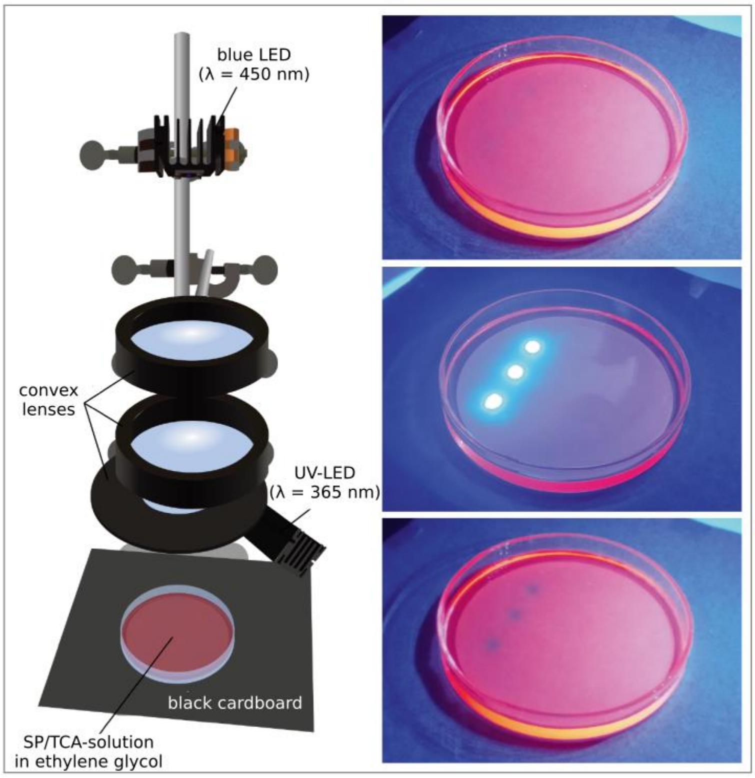
Corresponding key terminology: photoluminescence, fluorescence, phosphorescence, upconversion, triplet-triplet-annihilation, energy transfer, Stokes shift, model animation

All Optical INHIBIT Logical Gate

INHIBIT-Gate		
Input 1 ($\lambda_{365\ nm}$)	Input 2 ($\lambda_{450\ nm}$)	Output ($EM_{615\ nm}$)
0	0	0
1	0	1
0	1	0
1	1	0

Experimental procedure a): A solution of spiropyrane SP in ethylene glycol, acidified with trichloroacetic acid TCA, [c(SP) = 10^{-3} mol/L, c(TCE) = $5{\cdot}10^{-2}$ mol/L] is placed in a Petri dish and irradiated on the whole surface with a strong LED-UV-light-source (λ = 365 nm). The solution exhibits a fairly strong red fluorescence. This emission at λ = 615 nm is generated by the protonated species of merocyanine MCH^{+}, and represents the ON signal (input 1) of the INHIBIT gate.

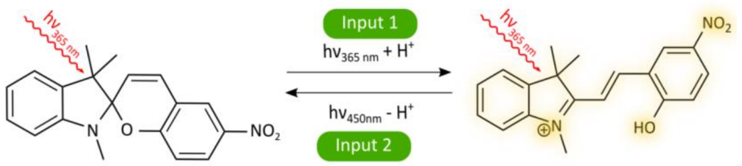
It persists during the whole experiment.



In ethylene glycol solution the red fluorescence of MCH^+ is switched ON by irradiation at 365 nm, and the fluorescence is locally switched OFF by irradiation at 450 nm

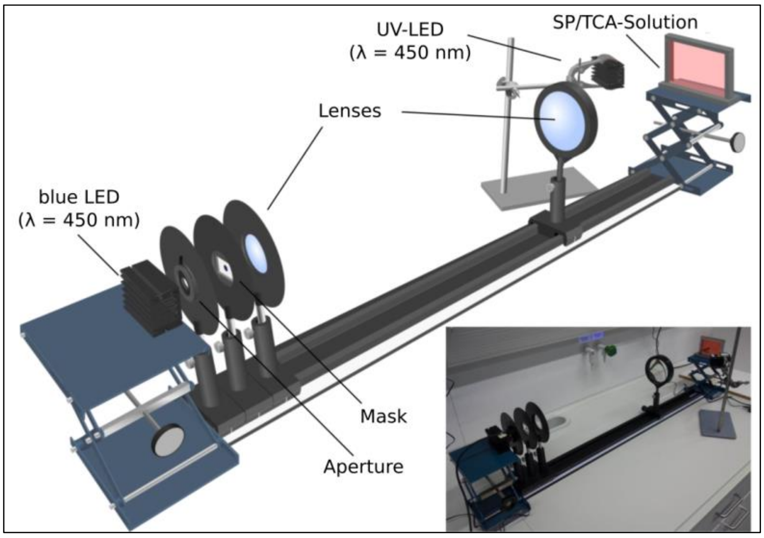
The OFF signal (input 2) consists of irradiation with blue light (λ = 450 nm). It is focused on three small circular points using a vertically arranged device made of three LEDs and a system of lenses as seen above. Irradiation with blue light for four seconds leads to a complete quenching of the fluorescence. This can be convincingly observed immediately after switching off the 450 nm LEDs. It takes approx. 10 seconds until the whole surface in the Petri dish fluoresces again.

The reversible processes are summarized in the following scheme:



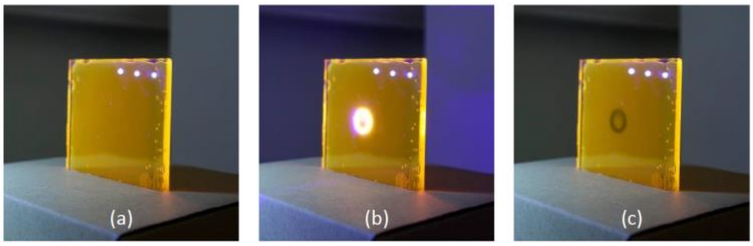
Spiropyrane SP *Protonated Merocyanine MCH^+*

Experimental procedure b): Using samples of spiropyrane SP and trichloroacetic acid TCA in a matrix of polymethylmethacryate PMMA, applied as thin film on a plate of glass, the all optical INHIBIT experiment can be carried out using the following horizontal set up.



Horizontal setup for demonstration of an all optical INHIBIT logical gate

In this case the ON signal (input 1, irradiation at λ = 365 nm) induces a yellow-orange fluorescence, and the OFF signal (input 2, irradiation at λ = 450 nm) quenches the fluorescence. Operating similarly as in procedure a), the following pictures have been obtained.



In a PMMA matrix the yellow fluorescence of MCH^{+} *is switched ON by irradiation at 365 nm, and the fluorescence is locally switched OFF by irradiation at 450 nm*

Teaching comments: The non-fluorescent region on the sample (c) brings to mind the doughnut-like non-fluorescent region applied in the STED nanoscopy method invented and developed by Stefan Hell [S. W. Hell, "Nanoscopy with Focused Light", Nobel Lecture, *Angew. Chem. Int. Ed. 2015*, 54,8054 –8066]. Due to the fact, that the fluorescence of different molecular species (SP and MCH^+) is remotely switched ON and OFF using focused light, our experiment can be considered as a model for the STED-related RESOLFT concept. With reference to *Z/E (cis-trans)* isomers, S. Hell justifies the denotation RESOLFT in the cited paper above 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."

Actually, in our all optical INHIBIT gate continuous waves from inexpensive LEDs (< 1 W/cm^2) are used for switching the fluorescence ON and OFF. But like any other model experiment it is far away from the real super resolution micro- and nanoscopy. However, it is suitable for teaching applications of molecular switches and for demonstrating the principle of the RESOLFT method used in nanoscopy.

Corresponding key terminology: molecular switch, all optical INHIBIT logical gate, model experiment, RESOLFT concept, nanoscopy