Light Makes Smart - Photoactive Molecular Switches for Logic Gates

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Abstract This mini review presents a series of experiments in which light acts on two general phenomena: isomerization reactions and photoluminescence. The experiments described using the reversible photoactive molecular switch spiropyran/merocyanine, is suited to teach fundamental concepts of photochemistry as well as to introduce innovative applications related to smart materials, molecular motors and logic gates.

Keywords: molecular switch, photochromism, solvatochromism, AIE (aggregation induced emission), molecular logic gates, super resolution microscopy

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1. Introduction

Photoactive Molecular Switches for Basic Concepts: The Covid-19 pandemic has significantly reduced the use of real experiments in teaching, favouring their replacement by videos. However, chemistry still is and will remain an experimental discipline and real experimentation should be part of classroom teaching. Even the genius A. Einstein, who has developed the famous equation $E = mc^2$ exclusively by thinking in 1905, stated 50 years later that “A pretty experiment quite often is more precious than equations bred in the thinking retort”.

Convinced that light will become the most important form of sustainable energy in the 21st century, physical, chemical and biological processes involving light should get a key function in science education in schools and universities as soon as possible. Not only the scientists, engineers and technicians, but also the journalists, entrepreneurs and artists of tomorrow, as well as the entire upcoming young generation should be educated about the enormous possibilities offered by the technical use of light. On one hand, this involves the sustainable supply of electrical energy by photovoltaics and the production of synthetic fuels using solar light. On the other hand, photoprocesses concerning smart materials based on photoactive molecular switches are among the prominent topics in research and development of new materials with special opto-electronic and chemical properties [1,2,3,4,5]. Spiropyran based molecular switches in chemical education belong to the portfolio of the corresponding author for more than 25 years, and have also been covered by other authors [6,7,8,9,10]. In this article, we report on new experiments and photochemical concepts with the isomer pair spiropyran/merocyanine SP/ME. Before introducing the logic gates as the key feature of this article, we would like to sum up some contents from previous publications [11,12].

2. Switching Colour with Light

1,3,3-Trimethylindolino-6'-nitrobenzopyrylospirane SP, known for more than 60 years [13] is commercially available. We have included SP into an experimental kit which we make available via our internet portal [14] as a key chemical. Re-crystallized from ethanol, SP forms wine-red crystals. In darkness, this color persists over months, but rapidly turns yellow even under the light of a microscope as shown in Figure 1.

Figure 1. Spiropyran crystals under a light microscope. Top left, 50x magnification after crystallization, top right 150x magnification. Bottom left at 200x magnification after a few hours under daylight, bottom right at 100x magnification. The reddish color (top) gives way to a yellow-golden color (bottom) [15].
This chameleon-like color behaviour of the solid SP is due to the fact that during the re-crystallization from ethanol a very thin layer of wine-red merocyanine ME was formed on the surface which, when exposed to light, reverts to colorless SP. In fact, the X-ray analysis of the crystals shows that they consist almost exclusively of spiropyrane [15].

However, for classroom teaching, there are much easier options to demonstrate and investigate the photochromism, of the system SP/ME, i.e. its reversible colour change under light irradiation and in darkness. Following instant experiments can be performed again and again using the same solutions of SP or the “intelligent foil”, due to the fact that both can be stored in the dark for months.

**Photochromism in solution:** 10 mg of SP spiropyrene are dissolved in about 10 mL of toluene (or xylene) in a test tube with screw cap. The solution is then distributed to three test tubes with screw caps. Test tube no. 1 is kept at room temperature, No. 2 is heated in a water bath to about 60°C. No. 3 is cooled in a beaker to about 0°C using an ice-water mixture.

1. The test tube no. 1 is irradiated with violet light ($\lambda = 400$ nm) or UV-Light ($\lambda = 365$ nm) from an LED torch. Within 1-2 seconds the solution changes its color to blue (Figure 2). The blue coloration disappears within 20-30 s after the light has been switched off.
2. The irradiation is repeated with the heated sample in test tube No. 2. The coloration occurs again immediately; but the decoloration occurs considerably faster than in the test tube No. 1.
3. The cooled sample in test tube No. 3 also changes its color immediately after being irradiated. After switching the light off, the color persists for much longer than in samples No. 1 and No. 2. The bleaching process takes about 2 minutes.
4. If the blue solution from 3) is irradiated with green or red light from an LED torch ($\lambda = 530$ nm or $\lambda = 600$ nm) directly after being irradiated with violet or UV-light, then the color of the solution fades within about 10 s.

**Photochromism and fluorescence in solid matrix:**
The immobilization of spiropyrene in a polystyrene matrix can be realized, following the QR-code from Figure 2. If the “intelligent foil” obtained by the described procedure is kept dark (for instance in an envelope) it lasts for months. It is ideal for demonstrating the phenomena of photochromism and fluorescence.

- Actually, the isomerization $\text{SP} \rightarrow \text{ME}$ of colorless spiropyrene to blue merocyanine (see equation in Figure 2) equally be performed by irradiation the solution with violet (or UV) light from an LED torch (Figure 3a) or with sunlight.
- The reverse isomerization $\text{ME} \rightarrow \text{SP}$ occurs by irradiation with green (or red) light (Figure 3b); it can also be powered very quickly by simply immersing it into warm water at 60 °C.
- Unlike as in toluene solution, blue merocyanine immobilized in the polystyrene matrix of the “intelligent foil” exhibits a bright red fluorescence (Figure 3c).
- Keeping the foil at low temperature (for example in the fridge) in darkness, the information in blue can be stored for hours and days.

The difference in color between the two isomers SP and ME is initially due to the different molecular structures (Figure 2).

![Figure 2. Colors in toluene or xylene solution of spiropyrene SP (C$_{19}$H$_{18}$O$_3$N$_2$) and merocyanine ME (C$_{19}$H$_{18}$O$_3$N$_2$); reversible isomerization and molecular models [15]](image)

![Figure 3. Writing (a) and erasing (b) on the “intelligent foil”; while merocyanine dissolved in toluene doesn’t fluoresce, it shows a red fluorescence when it is immobilized in polystyrene (c)](image)
In the SP molecule, the bond delocalization is interrupted at the sp³-hybridised spiro-centre. Therefore, the indole- and the benzopyrane-part form two mutually perpendicular planes. In contrast, the two molecular parts of the ME molecule are coplanar, and consequently the bond delocalization extends across the entire molecule (Figure 4). This causes a significant reduction in the HOMO-LUMO gap and consequently a strong bathochromic shift in light absorption (see Figure 5). From this point of view, the experiments on the photochromism of the SP/ME system are well suited to teaching the relationship between molecular structure and macroscopic properties.

For science education at high school and college level the experiments described above should be also used for emphasizing the fundamental difference between a photochemical reaction and a thermal reaction. In this sense the concept of ground state GS and excited state ES of molecules in combination with the energy profile curves can be used (see Figure 6).

The abscissa in this diagram represents the reaction coordinate that concerns changes of nuclear geometry during the reaction. The ordinate represents the energy of the reacting system. The different reaction pathways indicated in Figure 6 by arrows are extensively commented in another issue of this journal in detail [10]. The essential insight from the energy diagram should be that thermal reactions occur exclusively in the GS of molecules, while photochemical reactions always include the ES. This explains all the experimental observations described above at different temperatures and different wavelengths.

But what is the theoretical explanation for the huge difference in the fluorescence behaviour of SP in solution and in solid matrix (see Figure 3c)?

### 3. Checking Polarity with Light

In order to elucidate the influence of the nano-environment more precisely, solutions of merocyanine ME in different solvents have to be investigated.
Figure 7. Colors of ME dissolved in different solvents (from left to right): toluene, tetrahydrofurane, chloroform, acetone, acetonitrile, dimethylsulfoxide, ethanol methanol, and ethylene glycol [16]

| Farbeindruck (Komplementärfarbe) | Wellenlänge λ [nm] | Energie E [eV] |
|----------------------------------|--------------------|---------------|
|                                  | 400                | 3,1           |
|                                  | 450                | 2,8           |
|                                  | 500                | 2,5           |
|                                  | 550                | 2,3           |
|                                  | 600                | 2,1           |
|                                  | 650                | 1,9           |
|                                  | 700                | 1,8           |

Figure 8. Relationship between the perceived color, the wavelength and color of the absorbed light, and the energetic depression of the HOMO in ME molecules solved in ethanol, acetone and toluene; HBE (Höchste Besetzte Energiestufe is the German abbreviation for HOMO, and NUE (Niedrigste Unbesetzte Energiestufe) for LUMO [15,16]

Figure 9. Colours of merocyanine solutions in ethanol, acetone and toluene (left), related absorption maxima (centre), and AIE-fluorescence of merocyanine solutions in different solvents by irradiation with violet or UV light (right)
4. Designing Molecular Logic Gates with Light

In a tutorial review, J. Andreasson and U. Pischel paraphrase molecular logic as a “continuously developing multidisciplinary field that is driven by the beguiling idea of processing information contained in photonic, electrochemical, and chemical signals with the help of molecules and their inherent chemical transformations” [18]. They expect future applications of molecular logic in switchable catalysis, biomolecular recognition, or theranostics.

According to the linking rules of Boolean Algebra based on zeros and ones, the molecular species involved in a molecular logic gate should fulfill the following requirements: i) easily distinguishable properties, e.g. different absorption or emission of light, ii) easy to produce and destroy, e.g. by irradiation with different wavelengths or addition of acids and bases, and iii) thermally stable enough for the output signal to be read out.

**AND-gate with SP, ME and MEH**: If the wine-red solution of merocyanine ME in ethylene glycol (see sections above) is irradiated with green light ($\lambda = 530$ nm), the solution becomes colourless, but it turns yellow, if it is acidified with a solution of trichloroacetic acid TCA (Figure 10).

This behaviour of the system SP/ME/MEH system makes it possible to design the AND-gate shown in Figure 11. It starts from a solution of SP in ethylene glycol ($c(\text{SP}) = 5 \times 10^{-4}$ mol/L). The targeted output is an absorption at 440 nm, i.e. the yellow color of the solution. It is only realized when both inputs are activated, i.e. set to "1". Input 1 is activated by irradiation at 365 nm, and input 2 by acidifying with TCA solution ($c(\text{TCA}) = 10^{-2}$ mol/L). This leads to the formation of the required protonated species MEH$, which can be deprotonated by adding solution of triethanolamine TEA ($c(\text{TEA}) = 10^{-2}$ mol/L).

Using spiropyran SP as the starting chemical, ethylene glycol as solvent, LED-torches as light sources, the acid TCA and the base TEA, other molecular logic gates have also been realized, i.e. the OR-, NOR-, XOR- and Adder-Gate) [16]. When experimenting with such molecular logic gates, contents of (photo) chemistry and information technology can be taught in an interdisciplinary way.

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**Figure 10.** Colours of the System SP/ME/MEH$^+$ by irradiation at 367 nm (a), without any irradiation (b), and by simultaneous irradiation at 367 nm and 450 nm; truth table of a logic AND gate.

| AND-Gate | Input 1 ($\lambda_{365}$ nm) | Input 2 ($H^+$) | Output (Abs$^{440}$ nm) |
|----------|--------------------------|----------------|------------------------|
| 0        | 0                        | 0              | 0                      |
| 1        | 0                        | 0              | 0                      |
| 0        | 1                        | 0              | 0                      |
| 1        | 1                        | 1              | 1                      |
All-optical INHIBIT logic gate (see setup in Figure 12): A solution of spiropyran SP in ethylene glycol, \( c(\text{SP}) = 10^{-3} \text{ mol/L} \), weakly acidified with 2-3 drops of trichloroacetic solution TCA, \( c(\text{TCA}) = 5 \times 10^{-2} \text{ mol/L} \), is irradiated continuously on the whole surface in a Petri dish with UV light (\( \lambda = 365 \text{ nm} \)) from source (2) in Figure 12. This is the ON signal for a red fluorescence emission at \( \lambda = 615 \text{ nm} \) (Figure 12a). Blue light (\( \lambda = 450 \text{ nm} \)) from source (1), which is focused for 4 seconds via a vertically mounted lens system onto three small areas, is used as the OFF signal (Figure 12b). Immediately after the blue OFF signal is switched off, it can be seen that the fluorescence on the three small surfaces is deleted (Figure 12c). It takes approx. 10 seconds until the entire surface glows red again.

The typical characteristic for the INHIBIT logic gate is that the second input cancels the effect of the first input (see the truth table in Figure 13). In this case, the reversible reactions shown in Figure 13 occur when input 1 and input 2 are activated. Actually, this all-optical logic gate shows some additional advantages: i) the volume of the working sample remains constant, ii) the conversions between chemical species run quickly, iii) the “reset” command is not necessary because the gate automatically reaches the initial OFF state, and iv) a selectable section of a fluorescent surface can be switched OFF from luminescence for a couple of seconds.

Basically, this experiment realizes the operating principle of the RESOLFT concept (reversible saturable / switchable optically linear fluorescence transitions) developed by Stefan Hell. He stated in his Nobel lecture [19]:

“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.”

It has to be added, that in Hell’s Nobel Prize-winning STED (stimulated emission depletion) concept, fluorescence is switched ON and OFF using only one species of molecules, and especially for switching OFF their fluorescence very powerful lasers are needed. This is due to the very short lifetime of the fluorescent species (several nanoseconds).

Actually, in our model experiment on the RESOLFT concept described above, no lasers are needed, light intensities of less than one Watt/cm\(^2\) from LEDs are sufficient to switch ON and OFF remote-controlled the fluorescence. By mounting the experimental setup consisting of LEDs, lenses and sample horizontally and immobilizing spiropyran SP acidified with trichloroacetic TCA in a matrix of polymethylmetacrylate PMMA, we finally managed to turn OFF the fluorescence on a "doughnut" shaped zone (Figure 14). This is an additional approach to the RESOLFT method, even if only in a formal sense.
Figure 13. Reversible molecular rearrangements and truth table in the all-optical INHIBIT logic gate based on spiropyran.

Of course, the model experiments shown in Figure 12 and Figure 14 exhibit a big difference to Hell’s STED and RESOLFT methods. The selectable areas on which the fluorescence can be switched OFF in the setup from Figure 12 are much larger, i.e., in the magnitude of square millimeters, whereas in Hell’s super resolution microscopy methods, the fluorescence can be selected and switched ON and OFF in areas on the order of square micro- and nanometers. They became the basis of micro- and nanoscopy, which makes it possible to study protein molecules in vivo [19] and therefore help to achieve new breakthroughs in medicine.

Figure 14. RESOLFT model experiment with SP/TCA in a thin film matrix of PMMA on a sheet of glass.

5. Key Terminology, Digital Materials and Teaching Recommendations

The contents and corresponding key terminology to be taught with the help of the experiments highlighted in this report are indicated in italics. Our digital materials in various formats provided on the platform [14] can be used equally in on-site teaching as well as in teaching@distance or hybrid teaching. Parts of them have been developed to overcome the disruption in education at schools and universities caused by the global COVID-19 pandemic. Even before the pandemic, we produced tutorial videos showing experiments with spiropyran and developing key terminology on molecular switches [20]. For example, the phenomenon of solvatochromism is demonstrated and elucidated in the tutorial video indicated in Figure 15.

Figure 15. Screenshot from the tutorial video “A Chemical Chameleon” on solvatochromism.

During the pandemic, animations were developed to allow interactive exploration of reaction pathways of photochemical and thermal reactions at the molecular model level (Figure 16). This animation is also suitable for highlighting the difference between thermodynamic equilibrium and the photosteady state.

Figure 16. Screenshot from the animation “Photostedy State.”
Our most important teaching recommendation is: don’t fail to motivate the learners with live conducted experiments for the "fantastic world of photochemistry". The digital media can be used to prepare and evaluate live experiments or to critically examine the concepts and models propagated in them. However, videos, animations and other digital media should never replace real live experiments - except in the case of enforced teaching@distance as it was the case in the years 2020 and 2021.

Regarding the use of the experiments and materials in this article, we recommend a coherent adaptation to the respective educational level of the learners. Even in the early lessons, students should learn that chemical reactions can be driven by light and that light of different colours can cause different reactions. They should also experience that one and the same substance generates different colours when dissolved in different solvents. While the teaching of the mentioned phenomena is sufficient in the lower grades, the theoretical concepts and models should also be taught in the upper grades of high school and college. Doing so, light, the most sustainable, cleanest and abundantly available form of energy on our planet, is given the necessary importance in the education of our young generation.

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