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A Switch in a Cage with a Memory

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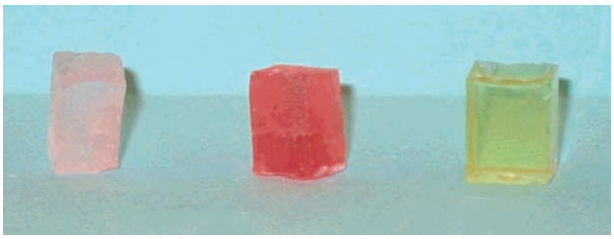
ABSTRACT



Chemical and optical stimulations control the interconversion of a three-state molecular switch trapped inside a silica monolith. The resulting absorbance changes in the visible region can be exploited to reproduce a sequential logic operator with one optical input and one optical output. This strategy to transfer operating principles for digital processing from bulk solutions to rigid materials can lead to the development of chemical logic gates based on functional solid components.

The power of chemical synthesis to deliver compounds with tailored properties, engineered shapes, and subnanometer dimensions is encouraging the identification of molecular strategies for digital processing.[1] Indeed, molecules can be designed to execute the three basic logic operations (AND, NOT, OR) and simple combinations of them (EOR, INH, NAND, NOR, XNOR, XOR) relying on the interplay of chemical, electrical, and/or optical signals.[2−10] Under the influence of appropriate input stimulations, these chemical systems switch from one form to another producing a change in a detectable output. The application of simple logic conventions allows the encoding of binary digits in the inputs and outputs, offering the opportunity to reproduce the

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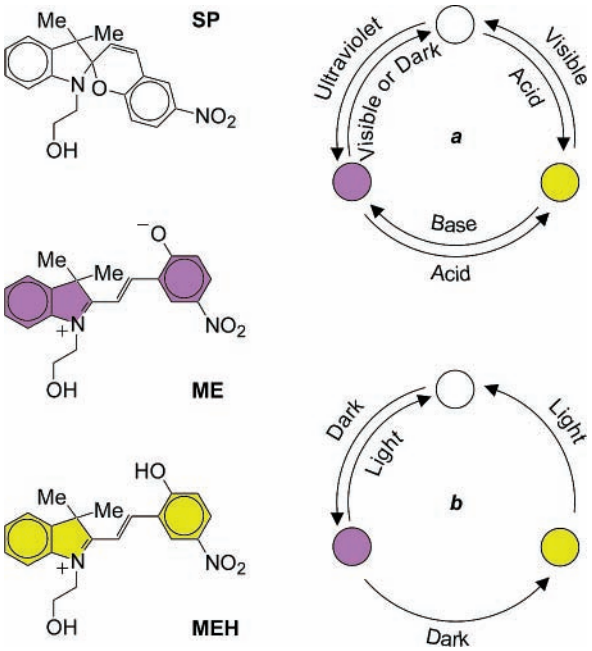

Figure 1. The switching cycle associated with the interconversion of the three states **SP**, **ME**, and **MEH** in acetonitrile (***a***) and inside a silica cage (***b***).

functions of digital circuits with molecules. However, most of these chemical logic gates are operated in solution. The next step in this fascinating research area must be the identification of reliable procedures to reproduce their operating principles with solid materials. Only then, device configurations for digital processing based on functional molecular components can start to be envisaged.

In a search for innovative strategies to implement logic functions at the molecular level, we developed a three-state molecular switch and studied its behavior in acetonitrile (***a*** in Figure 1).[9a,g] Our design is based on the established photoisomerization of spiropyrans.[11] We demonstrated that ultraviolet, visible, and H^+ stimulations control the interconversion of the three states of the switch, producing

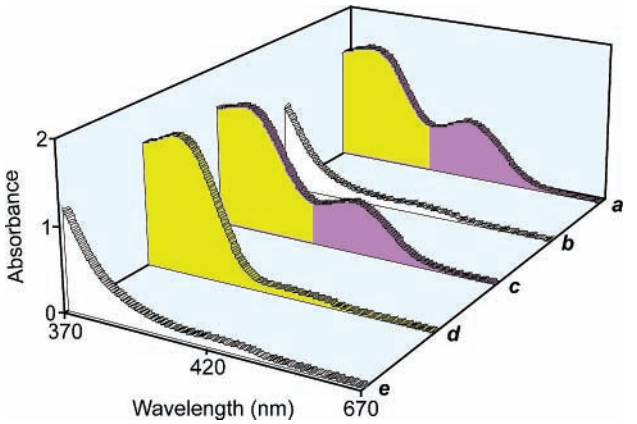

Figure 2. Absorption spectra of a doped silica monolith before (***a***) and after (***b***) visible irradiation, followed by storage in the dark for 1 d (***c***), exposure to hydrochloric acid vapors for 1 h in the dark (***d***), and visible irradiation (***e***).

significant absorbance changes at two distinct wavelengths in the visible region. Following these operating principles, we reproduced the logic function associated with a combinational logic circuit with three inputs and two outputs. In this paper, we show that (1) our molecular switch can be encaged and operated within rigid matrixes and (2) the resulting solids can be employed to implement simple logic operations.

We trapped the spiropyran **SP**[12] inside a silica monolith relying on sol−gel processes.[13,14] The absorption spectrum (***a*** in Figure 2) of a doped monolith, prepared under neutral conditions in the dark,[15] reveals two bands at 403 and 520 nm. They correspond to the merocyanine forms **MEH** and **ME**, respectively. Upon either ultraviolet[16] or visible[17] irradiation, **MEH** and **ME** switch to **SP** and the corresponding absorption bands disappear (**b** in Figure 2). The colorless state **SP** reverts to the colored forms **MEH** and **ME**, if the doped monolith is stored in the dark for 1 d. Consistently, the bands at 403 and 520 nm can be observed again in the absorption spectrum (***c*** in Figure 2).[18] The exposure of a doped monolith to vapors of hydrochloric acid[19] results in

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(12) This compound can be synthesized in three steps starting from 2,3,3-trimethyl-3*H*-indole with an overall yield of ca. 50% (see ref 9g).

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(15) A mixture of $(EtO)_4Si$, EtOH, and H_2O (1:3:4, v/v/v) was heated under reflux for 1 h. An aliquot of this mixture (3 mL) was combined with a DMSO solution of **SP** (1×10^{-3} M, 0.5 mL). The resulting solution was stored in a polystyrene cuvette with a perforated cap at ambient temperature in the dark. A transparent and rigid monolith was obtained after 21 d.

(16) The doped monolith was irradiated at 254 nm for 120 min with a Mineralight UVGL-25 lamp.

(17) The doped monolith was irradiated at 524 nm for 15 min with a Cole-Parmer Fiber Optic Illuminator 9745−00.

the protonation of the *p*-nitrophenolate fragment of **ME**. Indeed, the absorption spectrum (***d*** in Figure 2) recorded at this point shows only the band at 403 nm for **MEH**. This band disappears (***e*** in Figure 2) after visible irradiation,[17] as the colored **MEH** switches to the colorless **SP**.

The switching behavior emerged from the analysis of the doped monoliths is markedly different from that observed in acetonitrile. In this solvent (***a*** in Figure 1), **SP** switches to **ME** upon ultraviolet irradiation and **ME** reverts to **SP** either in the dark or under visible illumination. Inside a silica cage (***b*** in Figure 1), **SP** switches to **ME** in the dark and **ME** is partially converted into **MEH** by the water molecules trapped in the monolith. Upon either ultraviolet or visible irradiation, **ME** and **MEH** revert to **SP**.

The different behavior in the two media prompted us to examine the interconversion of our molecular switch in the same solvent mixture [EtOH/H_2O/DMSO (36:48:16, v/v/v)] employed for the preparation of the doped monoliths.[15] Under these conditions, the changes in the absorption spectrum parallel those observed for the doped monoliths. Presumably, the environment around the molecular switch in this particular combination of solvents and that surrounding the dopant in a silica cage are remarkably similar. In both instances, the polar medium stabilizes the zwitterionic form **ME** relative to **SP**, encouraging the thermal isomerization from **SP** to **ME**. Furthermore, the protic media promote the protonation of **ME** and its partial transformation into **MEH**.

The spectroscopic analysis of the doped monoliths revealed that the absorbance at 520 nm can be modulated by alternating visible irradiation and storage in the dark (***a***−***c*** in Figure 2). Thus, the magnitude of an optical output (***O***) can be regulated by turning on and off an optical input (***I***). The data points ***a***−***g*** in Figure 3 (top) show the change of ***O*** for three consecutive switching cycles. When ***I*** is turned off, ***O*** increases from ca. 5 (***a***) to 100% (***b***) in 1 d. When ***I*** is turned on, ***O*** returns to ca. 5% (***c***) in 15 min only. The pronounced difference in time scale of the two processes is evident from the absorbance evolution during the first switching cycle (Figure 3, bottom).

The relatively slow enhancement of the absorbance in the dark implies that ***O*** can have a delayed digital response to a change in ***I*** from on to off. For example, ***O*** switches from a binary value of *0* to *1* only after 12 h from the moment ***I*** is turned off (Figure 3, ***a***, bottom), if a positive logic convention and an arbitrary absorbance threshold at 0.8 are applied.[20] During this interval of time, ***O*** retains the binary value imposed by the previous state of ***I***. Afterward, the current state of ***I*** defines the binary value of ***O***. This intriguing behavior is equivalent to that of *sequential* logic circuits,[21]

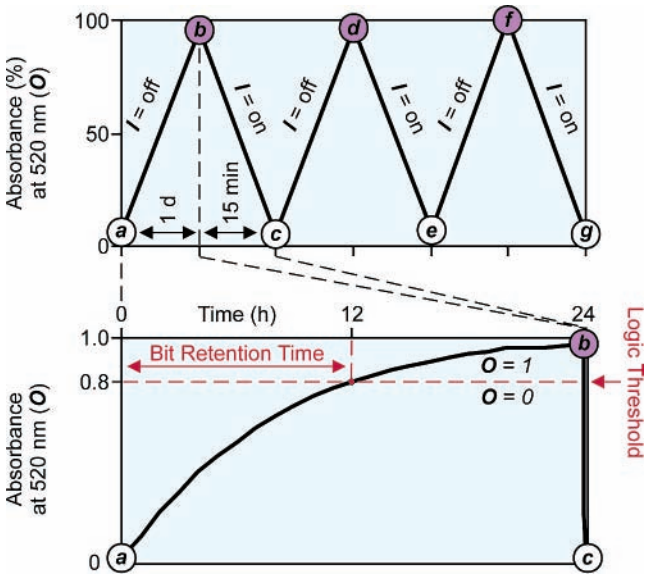

Figure 3. (Top) Changes in the absorbance output (***O***) at 520 nm under the influence of a visible light input (***I***) for three consecutive switching cycles (***a***−***g***). (Bottom) Time profile of ***O*** for the first switching cycle (***a***−***c***).

whose outputs are dictated by the interplay of past and present inputs in contrast to *combinational* logic circuits which are not sensitive to their history.

The sequential logic behavior of a doped monolith can be appreciated from the analysis of the binary strings in ***a***−***c*** in Figure 4.[22] After storage of a doped monolith in the dark

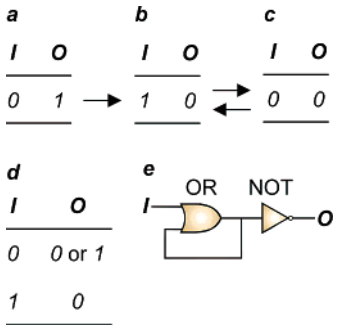

Figure 4. Binary strings accompanying the writing of a bit (***a*** and ***b***), its irreversible storage within the bit retention time (***c***), the corresponding truth table (***d***), and sequential logic operator (***e***).

(***I*** = *0*) beyond the bit retention time, the absorbance is above the logic threshold (***O*** = *1*) and the corresponding binary string is *0 1* (***a*** in Figure 4). If the light is turned on (***I*** = *1*), the absorbance drops below the logic threshold (***O*** = *0*) and the binary string changes to *1 0* (***b*** in Figure 4). After the

(18) After ultraviolet irradiation and storage in the dark, the original absorbances at 430 and 520 nm are not restored. Presumably, these irradiation conditions encourage the partial degradation of the molecular switch.

(19) The doped monolith was maintained for 1 h in a sealed chamber saturated with hydrochloric acid vapors.

(20) Binary digits can be encoded in ***O*** by comparing its absorbance value with that of the logic threshold. Under a positive logic convention, ***O*** is *0* when its absorbance is below the threshold. ***O*** is *1* when its absorbance is at or above the threshold.

(21) Mitchell, R. J. *Microprocessor Systems: An Introduction*; Macmillan: London, 1995.

(22) Binary digits can be encoded in ***I*** by assigning a *0* to its off state and a *1* to its on state.

light is turned off ($\boldsymbol{I} = 0$), a low absorbance output ($\boldsymbol{O} = 0$) is retained for 12 h and the binary string is now *0 0* (***c*** in Figure 4). When the light is turned on again ($\boldsymbol{I} = 1$) within the bit retention time, the output remains low ($\boldsymbol{O} = 0$) and the binary string changes to *1 0* (***b*** in Figure 4). After listing all these binary strings in a truth table (***d*** in Figure 4), we note that ***O*** can be *0* or *1* when ***I*** is *0*. Under these conditions, the value of the input alone is not sufficient to determine that of the output. It is the history of the system that controls the value of ***O*** when ***I*** is *0*. This logic behavior is equivalent to that of a sequential logic circuit in which the output of an OR gate becomes one of the two inputs of the same operator as well as the input of a NOT gate (***e*** in Figure 4). It is important to note also that the transformation of the mother string ***a*** into the daughter string ***b*** is irreversible within the bit retention time. It is impossible to reset the value of ***O*** from *0* to *1* within this interval of time.

In summary, we have demonstrated that our three-state molecular switch can be operated inside a silica monolith with chemical and optical inputs. The controlled interconversion of the three states within the rigid matrix produces significant absorbance changes in the visible region. In particular, the absorbance at 520 nm can be modulated turning on and off a visible input. However, the photoinduced absorbance decay is much faster than the thermal absorbance raise. The pronounced difference in time scale between the two processes offers the opportunity to implement an all-optical memory element with a bit retention time of 12 h. An optical input "writes" a bit of information in the doped monolith. The encaged molecular switch "memorizes" the binary digit for a relatively long time and an optical output "reads" the information stored. Finally, the memory can be reset maintaining the doped monolith in dark beyond the bit retention time. Our findings demonstrate that mechanisms to reproduce logic functions with molecular switches in solution can be adapted to operate rigid materials. This strategy is certainly not limited to our spiropyran. It can be extended to the many other operating principles for digital processing that have been already identified in solution. Thus, our approach will presumably stimulate the development of a new generation of functional solids able to process and store binary information.

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