ORGANIC
LETTERS

2001
Vol. 3, No. 22
3475−3478

Signal Communication between Molecular Switches

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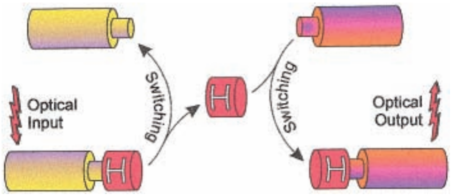
Received July 26, 2001

ABSTRACT



Efficient strategies for the communication of signals between molecules must be identified for the development of molecule-based nanoprocessors. We have demonstrated that photoinduced proton transfer can be exploited to implement intermolecular digital transmission. Light inputs operate a three-state molecular switch inducing the transfer of a proton to or from a two-state molecular switch. The signal transduction protocol of the two communicating molecular switches is equivalent to that of a sequential logic circuit incorporating three logic gates.

The communication of signals at the molecular level ensures the transfer of information from the environment to our brain.[1] A remarkable example is the complex mechanism of vision. Optical inputs reach the eye pigments, inducing the isomerization of a simple molecule called retinal. The change in molecular shape produces a sequence of chemical signals that are converted into an electrical output. This final signal is communicated to the brain.

The principles ruling neurotransmission[2] are related conceptually to the elaboration of binary data in microprocessor systems.[3] Computers transduce binary inputs into binary outputs through sequences of logic operations that are implemented on sophisticated electronic circuits. The dimensions of the communicating components of these circuits continue to be reduced at an exponential rate.[4] Their miniaturization permits the assembly of ultradensely integrated circuits and faster processors. It is becoming apparent, however, that intrinsic limitations associated with conventional silicon-based devices will prevent their miniaturization down to the nanoscale.[4] Alternative materials for the nanoscaled components of future information storage and elaboration devices must be developed. Molecules and chemical systems are an obvious and promising choice.[5,6] The functions of simple electronic devices have been replicated already using organic films and even single molecules.[6] However, the integration of these molecule-based devices into functioning circuits remains more than a challenge. The major limitation is that methods to communicate signals between molecules are not available. A potential strategy to implement signal communication at the molecular level is that of mimicking the complex mechanisms that ensure information transfer in living organisms. These processes are

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10.1021/ol016502e CCC: $20.00

all based on chemical assemblies, and trying to reproduce their operating principles with artificial systems is a promising alternative to the problematic fabrication of nanoscaled electronic circuits.

Molecules undergoing reversible transformations in response to chemical, electrical, and/or optical stimulations are often termed molecular switches.[7] The photoinduced isomerization of certain spiropyran derivatives, for example, has been widely exploited to design photochromic switches.[8] In some instances, simple logic operations have been implemented on similar chemical systems.[9−12]

However, methods to communicate signals between molecular switches have not been identified yet. Recently, we have developed a three-state molecular switch that responds to ultraviolet light, visible light, and H^+ inputs, producing optical outputs.[13] We have then developed a simple strategy to communicate intermolecularly the two optical outputs to compatible fluorophores.[14] In this Letter, we show how the communication of chemical signals between two independent molecular switches can be established, exploiting photoinduced proton-transfer processes.

The reversible interconversion between the orange azopyridine **AZ** (Figure 1) and the red-purple **AZH** can be followed by absorption spectroscopy. The spectrum of **AZ** (**a** in Figure 1) shows a strong absorption band at 422 nm. After the addition of 10 equiv of CF_3CO_2H, **AZ** switches completely to the protonated form **AZH**. Consistently, the absorption band of **AZ** at 422 nm disappears (**b** in Figure 1) and a new band for **AZH** is observed at 556 nm instead. After the addition of 10 equiv of Et_3N, the protonated form **AZH** switches back to **AZ** and the absorption band at 422 nm is restored (**c** in Figure 1).

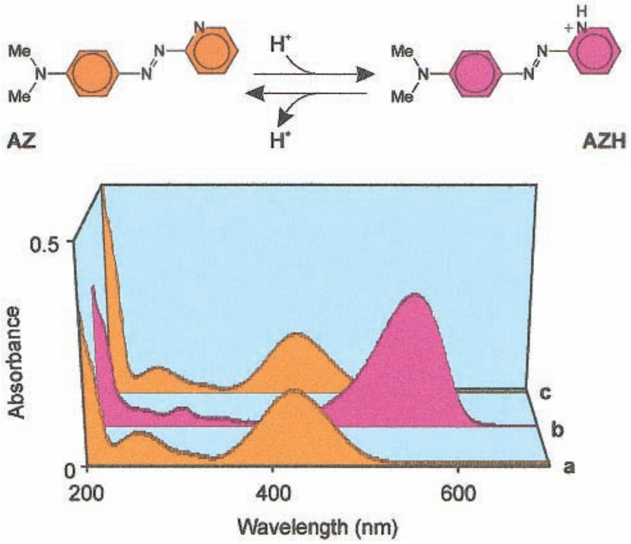

Figure 1. The reversible interconversion between the two states **AZ** and **AZH**. Absorption spectra of (**a**) a MeCN solution of **AZ** (1×10^{-4} M, 25 °C) and of the same solution after the consecutive additions of (**b**) 10 equiv of CF_3CO_2H and (**c**) 10 equiv of Et_3N.

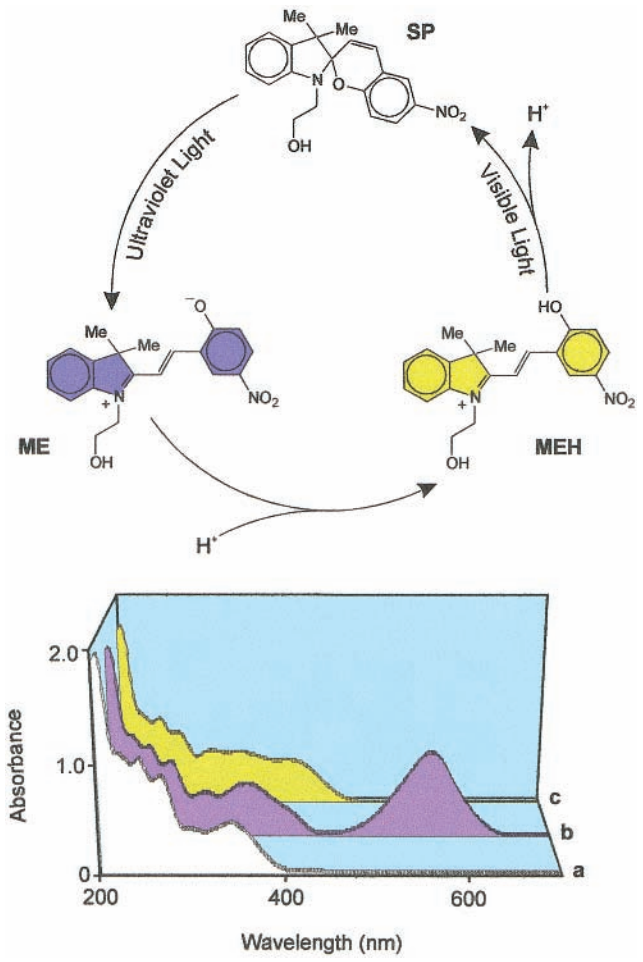

Figure 2. The reversible interconversion between the three states **SP**, **ME**, and **MEH**. Absorption spectra of a MeCN solution of **SP** (1×10^{-4} M, 25 °C) (**a**) before and (**b**) after irradiation with ultraviolet light and (**c**) after irradiation with ultraviolet light followed by the addition of 1 equiv of CF_3CO_2H.

The colorless spiropyran state **SP** (Figure 2) isomerizes to the purple merocyanine form **ME** upon irradiation with ultraviolet light.[15] This process is accompanied by the

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appearance of a band at 563 nm in the absorption spectrum (**a** and **b** in Figure 2). The photogenerated base **ME** switches completely to the yellow-green **MEH** after the addition of 1 equiv of CF_3CO_2H. Consistently, the absorption band of **ME** at 563 nm disappears (**c** in Figure 2) and a new band for **MEH** is observed at 401 nm instead. Upon irradiation with visible light,[16] the protonated merocyanine form **MEH** switches completely back to **SP**, releasing H^+.

Ultraviolet and visible light stimulations induce the interconversion between the three states **SP**, **ME**, and **MEH**, controlling the uptake and release of H^+. When the three-state molecular switch and the two state-molecular switch are combined in solution, the photoregulation of the concentration of H^+ can be exploited to modulate the switching between the two states **AZ** and **AZH** (Figure 3). The photogenerated base **ME** can deprotonate the acid **AZH**, promoting the formation of **AZ**. The acid **MEH** can protonate the base **AZ** upon irradiation with visible light, inducing the formation of **AZH**.

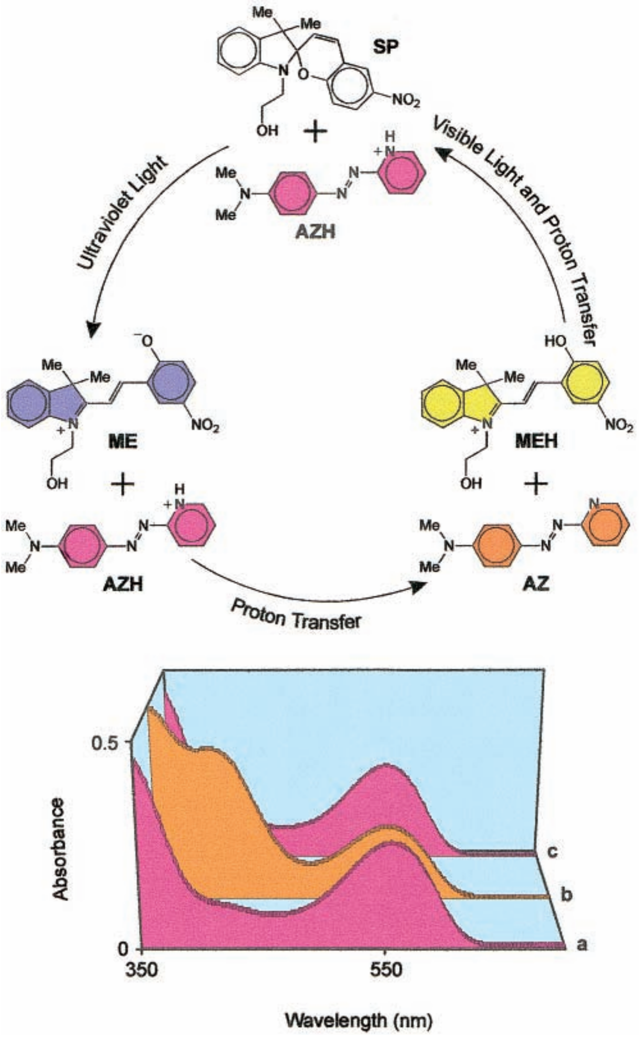

Figure 3. The photoinduced proton transfer between the three-state molecular switch and the two-state molecular switch. Absorption spectra of an equimolar MeCN solution of **SP**, **AZ**, and CF_3CO_2H (1×10^{-4} M, 25 °C) (**a**) before and (**b**) after irradiation with ultraviolet light and (**c**) after the subsequent irradiation with visible light.

A solution of the two molecular switches was prepared by mixing equimolar amounts of **SP**, **AZ**, and CF_3CO_2H. In the presence of H^+, **AZ** switches to **AZH**. Consistently, the absorption spectrum (**a** in Figure 3) shows the characteristic band of **AZH** at 556 nm. The absorbance of this band indicates a ratio between **AZH** and **AZ** of 80:20.[17] Upon irradiation with ultraviolet light,[15,18] **SP** switches to **ME**. The photogenerated base **ME** deprotonates the acid **AZH** inducing the formation of **MEH** and **AZ**. Consistently, the absorption spectrum (**b** in Figure 3) shows an increase in the absorbance at 401 nm for **MEH** and a decrease in the absorbance at 556 nm for **AZH**. The ratio between **AZH** and **AZ** is now 60:40. Upon irradiation with visible light,[16,18] **MEH** switches to **SP** releasing H^+ and inducing the conversion of **AZ** into **AZH**. As a result, the original absorbance for the band at 556 nm is restored (**c** in Figure 3). Thus, the alternation of ultraviolet and visible light stimulations controls the interconversion between the two states **AZ** and **AZH**, switching the absorbance at 556 nm between two values. The data points **a**−**g** in Figure 4 illustrate this effect for three consecutive switching cycles.

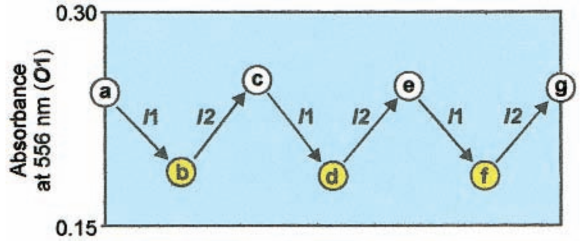

Figure 4. Changes in the absorbance at 556 nm (***O*1**) of an equimolar solution of **SP**, **AZ**, and CF_3CO_2H (1×10^{-4} M, 25 °C) upon irradiation with ultraviolet light (***I*1**) and irradiation with visible light (***I*2**).

The behavior of the two communicating molecular switches can be analyzed with the aid of binary logic.[3] Two input signals operate the three-state molecular switch. They are ultraviolet light (***I*1**) and visible light (***I*2**). In response to these optical inputs, the three-state molecular switch com-

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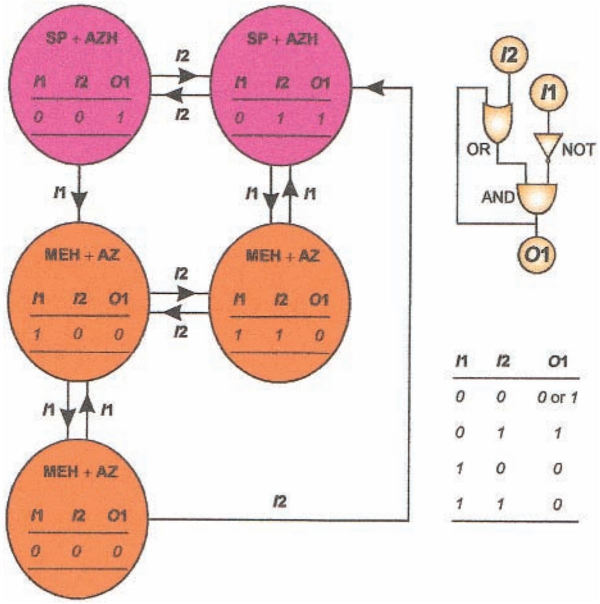
municates a chemical signal (proton transfer) to the two-state molecular switch. The two-state molecular switch transduces the received chemical signal into an optical output (***O*1**) that is the absorption band at 556 nm.[19] The two input signals ***I*1** and ***I*2** can be either *off* or *on*. Similarly, the output signal ***O*1** can be considered *off* when the absorbance at 556 nm is below 0.20 and *on* when it is above.[20] Binary digits (*0* or *1*) can be used to represent the two levels (*off* or *on*) of each signal. The truth table in Figure 5 lists the four possible combinations of two-digit input strings and the corresponding one-digit output. The output digit ***O*1** for the input strings *01*, *10*, and *11* can take only one value. In fact, the input string *01* is transduced into a *1*, and the input strings *10* and *11* are converted into *0*. The output digit ***O*1** for the input string *00*, instead, can be either *0* or *1*. The sequence of events leading to the input string *00* determines the value of the output. The diagram in Figure 5 illustrates this effect. The five ovals represent the five three-digit input/output strings. The transformation of one oval into any of the other four is achieved in one or two steps, changing the values of ***I*1** and/or ***I*2**. In two instances (red-purple ovals), the two-state molecular switch is in state **AZH** and the output signal is *on* (***O*1** = *1*). In the other three cases (orange ovals), the two-state molecular switch is in state **AZ** and the output signal is *off* (***O*1** = *0*). The strings *000* (bottom left) and *001* (top left) correspond to the first entry of the truth table. They share the same input digits but differ in the output value. The string *000* (bottom left) can be obtained only from the string *100* (center left) varying the value of ***I*1**. Similarly, the string *001* (top left) can be accessed only from the string *011* (top right) varying the value of ***I*2**. In both transformations, the output digit remains unchanged. Thus, the value of ***O*1** in the *parent* string is memorized and maintained in the *daughter* string when both inputs become *0*. This memory effect is the fundamental operating principle of sequential logic circuits, which are used extensively to assemble the memory elements of modern microprocessors.[3] The sequential logic circuit equivalent to the truth table of the two communicating molecular switches is illustrated in Figure 5. In this circuit, the input data ***I*1** and ***I*2** are combined through NOT, OR, and AND operators. The output of the AND gate ***O*1** is also an input of the OR gate and controls, together with ***I*1** and ***I*2**, the signal transduction behavior.



I1	I2	O1
0	0	0 or 1
0	1	1
1	0	0
1	1	0

Figure 5. Truth table and logic circuit equivalent to the two communicating molecular switches and the interconversion between the five three-digit strings of input (***I*1** and ***I*2**) and output (***O*1**) data.

These results demonstrate that signal communication between molecular switches is possible. Photoinduced proton-transfer processes can be exploited to implement digital transmission at the molecular level. This simple strategy will lead to the development of arrays of communicating molecular switches for information storage and elaboration at the nanoscale.

Acknowledgment. We thank the University of Miami for financial support.

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(15) The solution was irradiated for 5 min at 254 nm using a Mineralight UVGL-25 lamp. During irradiation, the ratio between **SP** and **ME** changed from the initial 100:0 to a stationary 60:40. These values were derived from the absorbance measured at 563 nm, using the molar extinction coefficient of the merocyanine form of the parent compound 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′(2*H*)-indole]. Sakuragi, M.; Aoki, K.; Tamaki, T.; Ichimura, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 74−79.

(16) The solution was irradiated for 15 min at 524 nm using a Cole-Parmer fiber optic illuminator 9745-00.

(17) The ratio between the two states was derived from the absorbance measured at 556 nm, using the molar extinction coefficient of **AZH** determined from the absorption spectrum **b** in Figure 1.

(18) The absorption spectrum of **AZ** (1×10^{-4} M, MeCN, 25 °C), recorded with and without CF_3CO_2H (10 equiv), remains unchanged after ultraviolet light or visible light irradiation. These observations indicate that both irradiation conditions do not affect the two states **AZ** and **AZH**.

(19) For a related example of the interplay between optical inputs and optical outputs, see: Miller, S. E.; Lukas, A. S.; Marsh, E.; Bushard, P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 7802−7810.

(20) The absorbance at 556 nm was determined immediately after, rather than during, the application of the light inputs ***I*1** and/or ***I*2**. Two independent light sources and an irradiation time of 15 min were used when the simultaneous application of both inputs was required.