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Digital Communication through Intermolecular Fluorescence Modulation

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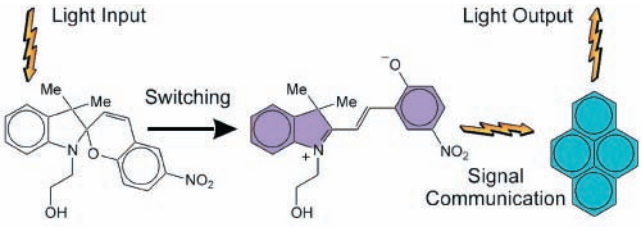
ABSTRACT



Ultraminiaturized processors incorporating molecular components can be developed only after devising efficient strategies to communicate signals at the molecular level. We have demonstrated that a three-state molecular switch responds to ultraviolet light, visible light, and H^+, attenuating the emission intensity of a fluorescent probe. Intermolecular communication is responsible for the transduction of three input signals into a single optical output. The behavior of the communicating ensemble of molecules corresponds to that of a logic circuit incorporating seven gates.

The urge for miniaturization is encouraging the design of molecule-based electronic devices.[1] Efficient strategies to embed organic molecules between electrodes continue to be developed,[2,3] and ultraminiaturized systems incorporating a single molecule as the active component have been fabricated already.[4] These hybrid devices can perform amplification, rectification, and switching operations analogous to those executed by their macroscopic counterparts. However, the inherent difficulty in establishing electrical communication between molecules limits the integration of molecule-based devices into complete electronic circuits.[1e] Practical procedures to process and transmit signals at the molecular level must be developed.

Mimicking the complex processes that ensure detection, elaboration, and propagation of environmental stimulations in living organisms[5] is an alternative and promising strategy

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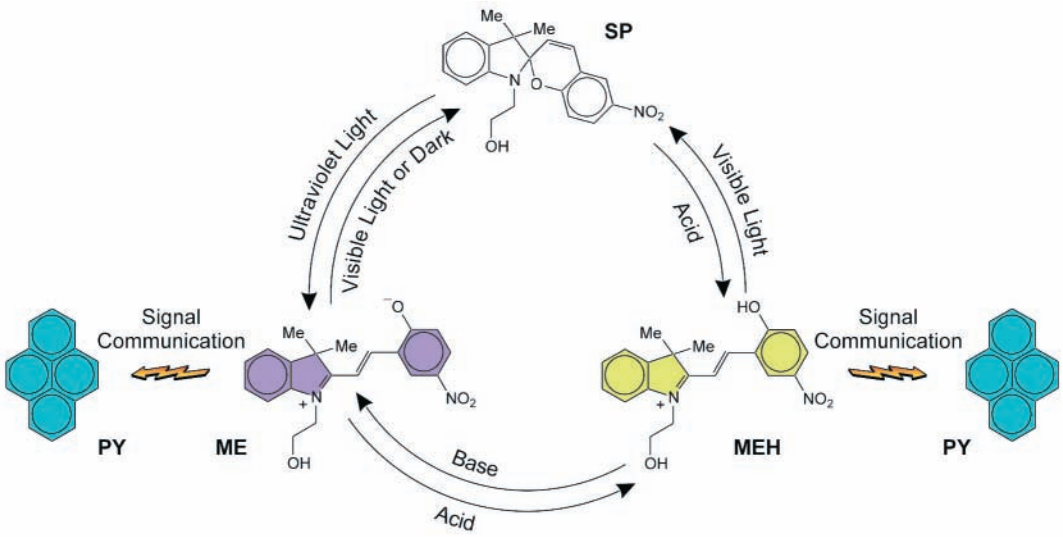

Figure 1. The switching cycle associated with the three states **SP**, **ME**, and **MEH** and the communication between **PY** and **ME** or **MEH**.

for the realization of molecular circuits. In our bodies, a concatenation of events at the molecular level is responsible for the communication of information from the environment to the brain.[6] A remarkable example is the complex mechanism of vision.[5] A molecule (retinal) present in certain eye pigments undergoes a pronounced geometrical change (*cis-trans* isomerization) upon absorption of light. This simple change in shape triggers a cascade of chemical signals. They are converted ultimately into an electrical signal (nerve impulse) that propagates up to the brain.

Organic molecules undergoing reversible transformations under the influence of appropriate stimulations can be designed and synthesized.[1d] These systems are often termed molecular switches,[7] and some of them can perform simple logic operations.[8−10] The photoinduced isomerization of certain spiropyran derivatives, for example, has been exploited to design photochromic switches.[11] Recently, we developed a spiropyran-based three-state molecular switch[12,13] that responds to light and chemical stimulations, producing optical signals. In this Letter, we demonstrate that our molecular switch can communicate intermolecular signals to a fluorescent probe.[14]

Ultraviolet light, visible light, and H^+ (input signals) induce the interconversion between the spiropyran state **SP** (Figure 1) and the merocyanine forms **ME** and **MEH**.[12] The absorption properties of the three states **SP**, **ME**, and **MEH** are significantly different. The colorless **SP** does not absorb light at wavelengths greater than 400 nm. The colored forms **ME** and **MEH** have intense absorption bands (output signals) in the visible region. These output signals can be *communicated* to a compatible fluorophore. The fundamental requirement is a certain degree of overlap between the absorption bands of the molecular switch and the emission bands of the fluorescent probe.[15]

The emission spectrum of pyrene **PY** (**a** in Figure 2) was recorded in MeCN after excitation at 336 nm. In the presence

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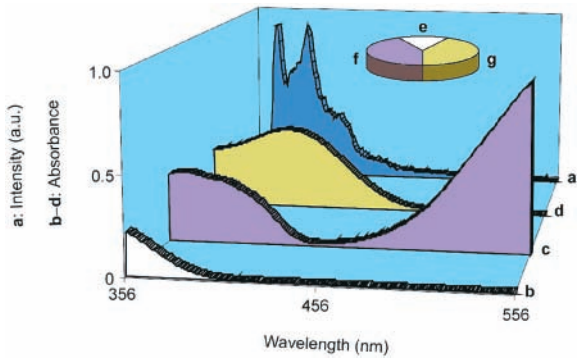

Figure 2. (**a**) Emission spectrum of **PY** (1×10^{-4} M, MeCN, 25 °C, $\lambda_{exc} = 336$ nm). Absorption spectra of **SP** (1×10^{-4} M, MeCN, 25 °C) (**b**) before and (**c**) after irradiation with ultraviolet light and (**d**) after irradiation with ultraviolet light followed by the addition of 1 equiv of CF_3CO_2H. Absorbance of (**e**) **SP**, (**f**) **ME**, and (**g**) **MEH** at 373 nm.

of the molecular switch, the fluorescence intensity of **PY** decreases. This change is a result of two concomitant effects. The molecular switch absorbs the exciting light (coabsorption) and the emitted light (reabsorption). However, the contribution of only one of these two factors varies upon switching. The absorbance at the excitation wavelength of a MeCN solution of **PY** increases by ca. 17% in the presence of equimolar amounts of **SP**. The absorbance does not change after switching from **SP** to **ME** or **MEH**. Thus, the coabsorption effect remains constant during the switching process. On the contrary, the absorption properties of **SP**, **ME**, and **MEH** (**b**, **c**, and **d** in Figure 2) are different in the region where **PY** emits. For example, the absorbance of **SP** (**e** in Figure 2) is smaller than those of **ME** and **MEH** (**f** and **g** in Figure 2) at 373 nm. This wavelength corresponds to one of the two emission maxima of **PY**. Thus, the reabsorption efficiency of **SP** is significantly smaller than those of **ME** and **MEH**, which are, instead, equivalent at this particular wavelength.

Ultraviolet light, visible light, and H^+ inputs do not affect the fluorescence intensity of **PY** when the three-state molecular switch is absent.[16] In the presence of equimolar amounts of **SP**, the emission intensity decreases to ca. 60% (**a** in Figure 3). Upon irradiation with ultraviolet light,[17] **SP** switches to **ME** (Figure 1), increasing the reabsorption efficiency. As a result, the fluorescence intensity of **PY** drops to ca. 50% (**b** in Figure 3). Upon irradiation with visible

(16) The fluorescence intensity of **PY** (1×10^{-4} M, MeCN, 25 °C, $\lambda_{exc} = 336$ nm) was measured before and after (1) irradiation for 5 min at 254 nm, (2) irradiation for 15 min at 524 nm, and (3) irradiation for 5 min at 254 nm followed by the addition of 1 equiv of CF_3CO_2H. In all cases, the emission intensity remained constant.

(17) 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 84:16. 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.

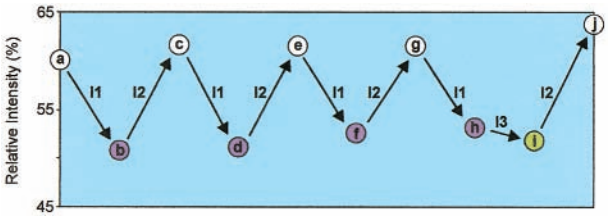

Figure 3. Changes in the fluorescence intensity at 373 nm of an equimolar solution of **PY** and **SP** (1×10^{-4} M, MeCN, 25 °C, $\lambda_{exc} = 336$ nm) upon (**I1**) irradiation with ultraviolet light, (**I2**) irradiation with visible light, and (**I3**) addition of CF_3CO_2H. The intensity is reported relative to that of pure **PY**.

light,[18] **ME** switches completely back to **SP** (Figure 1) and the emission intensity returns to its original value (**c** in Figure 3). Thus, sequences of alternating ultraviolet and visible light inputs regulate the fluorescence intensity of **PY**. The data points **a**−**g** in Figure 3 illustrate this effect for three consecutive switching cycles. The subsequent irradiation with ultraviolet light produces again **ME** and the associated decrease in fluorescence intensity (**h** in Figure 3). At this point, the addition of CF_3CO_2H converts **ME** into **MEH** (Figure 1). The reabsorption efficiency is maintained and the emission intensity of **PY** remains at ca. 50% (**i** in Figure 3). Upon irradiation with visible light, **MEH** switches completely to **SP** (Figure 1) and the fluorescence intensity of **PY** returns to its initial value (**j** in Figure 3).

Binary logic[19] can be used to describe the behavior of the communicating ensemble of molecules. The input signals are **I1** (ultraviolet light), **I2** (visible light), and **I3** (H^+). The output signal is **O1**, the emission band at 373 nm of **PY**.[20] Each signal can be either *off* or *on* and can be represented by a binary digit (Table 1).[21] Thus, the communicating molecules transduce a string of three input data (**I1**, **I2**, and

Table 1. Truth Table for the Communicating Ensemble of Molecules Where 0 or 1 Indicates That the Corresponding Signal Is *Off* or *On*

input data			output data[a]
ultraviolet light (**I1**)	visible light (**I2**)	H^+ (**I3**)	emission at 373 nm (**O1**)
0	0	0	1
0	0	1	0
0	1	0	1
1	0	0	0
0	1	1	1
1	0	1	0
1	1	0	0
1	1	1	0

[a] The value of **O1** reported for input strings with **I1** or **I2** equal to 1 was determined immediately after, rather than during, the application of the light input. The value of **O1** reported for input strings with **I1** and **I2** equal to 1 was determined immediately ater, rather than during, the simultaneous irradiation of the sample for 15 min at 254 and 524 nm using two independent light sources.

I3) into a single output digit (**O1**). For example, the input string is 000 when the three input signals are all *off*. Under these conditions, the molecular switch is in state **SP**, the reabsorption efficiency is low, and the relative emission intensity of **PY** is ca. 60%. As a result, the output signal **O1** is *on* and the output digit is 1. When **I1** and **I3** are *on* and **I2** is *off*, the input string is 101. Under these conditions (ultraviolet light and H^+), the molecular switch is in state **MEH**, the reabsorption efficiency is high, and the relative emission intensity of **PY** is ca. 50%. Thus, the output signal **O1** is *off* and the output digit is 0.

The combinational logic circuit equivalent to the truth table of the communicating ensemble of molecules is illustrated in Figure 4. In this circuit, the input data **I1**, **I2**, and **I3** are transduced into the output data **O1** through three AND operators, three NOT operators, and one OR operator. *In total, seven interconnected logic gates are required to reproduce the operations executed by two communicating molecules.*

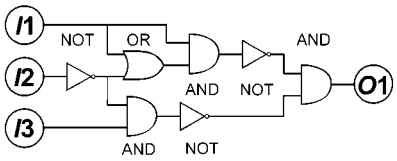

Figure 4. The logic circuit equivalent to the communicating ensemble of molecules transduces the inputs **I1**, **I2**, and **I3** into the output **O1** through AND, NOT, and OR operations.

The communication of signals at the molecular level ensures the transmission of information in living organisms. The extension of this paradigm to artificial systems is a promising alternative to the problematic miniaturization of conventional electronic devices down to the nanoscale. The working principles of future information storage and elaboration devices might be similar to those governing neurotransmission rather than being surrogates of those ruling present computers. Our results demonstrate that the communication of signals between appropriately designed molecules is possible. These findings might be the first steps toward the realization of nanoprocessors formed by arrays of communicating molecular switches.

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(21) The output signal **O1** is *off* when the relative emission intensity at 373 nm is ca. 50%. It is *on* when the relative intensity is ca. 60%. The ratio between these two values is 1.2 and is smaller than that between the two switching voltage levels of most electronic devices, which is at least 2.5. If necessary, however, this ratio can be optimized adjusting the molecular design of the communicating components.