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Multichannel Digital Transmission in an Optical Network of Communicating Molecules

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Abstract: In present telecommunication networks, information transfer relies on the interplay of optical and electrical signals. Data are communicated optically but processed electronically. Methods to maintain the propagating signals solely at the optical level must be developed to overcome the transmission capacities and speed limits imposed by the electronic components. We have demonstrated that molecular switches can be used to gate optical signals in response to optical signals. We have realized a simple optical network consisting of three light sources, one cell containing a solution of three fluorescent molecules, one cell containing a solution of a three-state molecular switch and a detector. The light emitted by the three fluorophores is absorbed by the three states of the molecular switch. Using this simple operating principle, we have shown that multichannel digital transmission can be implemented on an ensemble of communicating molecules relying exclusively on the interplay of optical inputs and optical outputs.

Introduction

The growing demand for telecommunication and Internet applications continues to stimulate the development of optical networks for the faster transmission of larger volumes of data.[1] In these networks, bundles of optical fibers coupled to opto-electronic devices ensure the communication of optical signals over long distances. Present optical transport technology permits the transmission of hundreds of gigabits per second over hundreds of kilometers. The routes of the optical signals traveling through these networks are determined by switching devices in response to electrical stimulations. Unfortunately, the interplay of optical and electrical signals in these hybrid devices limits dramatically the transmission capacity and speed.[1,2] Only a tiny fraction of the huge bandwidth of optical fibers can be used.

In principle, hundreds of optical signals with closely spaced wavelengths can be transmitted through a single waveguide relying on current optical fiber technology.[1c] The propagating light beams do not interfere with each other and can be transported in parallel. The noninteracting properties of optical signals, however, do not apply to electrical signals. Only one electrical signal can be transported through a single electrical wire. Thus, even although optical fibers can transmit multiple data in parallel, optoelectronic switches process them more or less sequentially.[1b] The electronic portion of these devices simply cannot handle the immense parallelism potentially offered by optical signals. These intrinsic limitations will stop soon the rapid escalation of the photonic traffic supported in optical networks.[2] It is necessary to develop practical strategies to switch the propagating optical signals with optical, rather than electrical, stimulations.[3] Ultimately, the electronic element of present communication networks must be eliminated completely, all intervening signals must be optical and only optical effects must be exploited.

Molecular switches[4] are promising candidates for the realization of signal processing networks. Simple logic operations[5] have been implemented already at the molecular level by using chemical, electrical, and/or optical signals.[6-12] Furthermore, the miniaturized dimensions of these chemical systems have encouraged the design of prototypical devices incorporating

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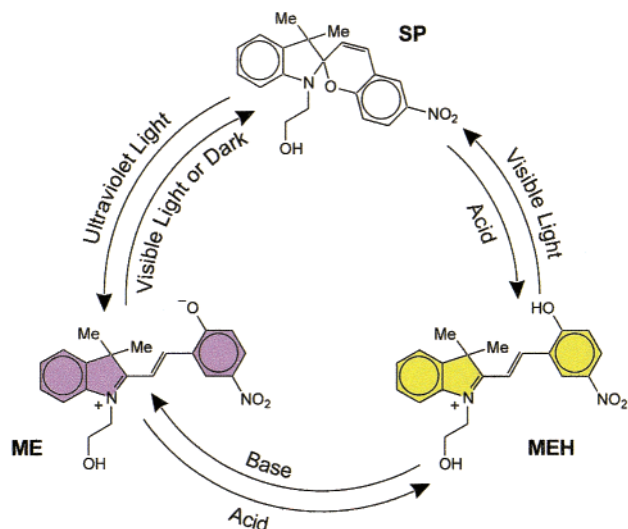
Figure 1. The switching cycle associated with the three states **SP**, **ME**, and **MEH**.

molecular components.[13,14] However, the lack of reliable strategies to communicate signals between individual molecules has prevented, so far, the integration of molecular switches into functioning circuits.[14e] Recently, we have developed a three-state molecular switch[15] and we have identified a simple mechanism for the intermolecular communication of optical signals.[16] The design of our switch is based on the reversible photoisomerization of a spiropyran derivative.[17] Ultraviolet light, visible light, and H^+ inputs induce the interconversion between the colorless spiropyran state **SP** (Figure 1) and the colored merocyanine forms **ME** and **MEH**. In this article, we demonstrate that the pronounced changes in absorption properties

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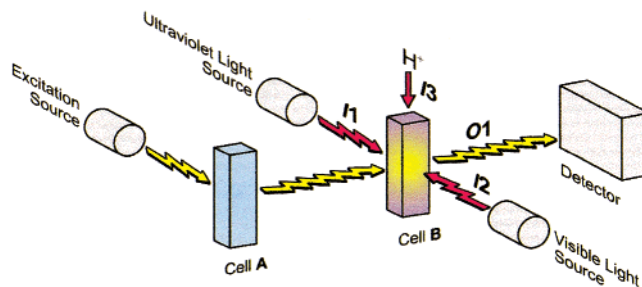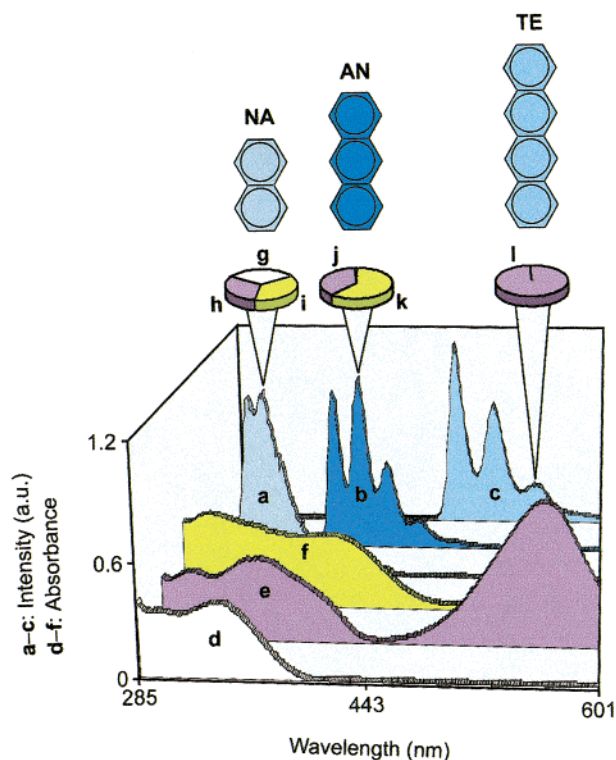
Figure 2. The optical network employed to implement digital transmission on an ensemble of communicating molecules.

associated with these chemical transformations can be exploited to switch optical signals.

Results and Discussion

The simple optical network shown in Figure 2 was assembled in the sample compartment of a commercial emission spectrometer. An optical signal (yellow arrows) travels from the excitation source to the detector passing through two quartz cells. Cell **A** contains a solution of fluorescent molecules that absorb the incident radiation and reemit light at longer wavelengths. The light emitted in the direction perpendicular to the exciting beam is communicated to cell **B**. This cell contains a solution of the three-state molecular switch illustrated in Figure 1. The interconversion between **SP**, **ME**, and **MEH** is induced by addressing cell **B** with three input signals (red arrows). They are ultraviolet light (*I1*), visible light (*I2*), and H^+ (*I3*). These inputs modulate the amount of light absorbed by the solution in cell **B** and, ultimately, determine the intensity of the final optical output (*O1*) that reaches the detector.

The fluorescent molecules selected for this investigation are naphthalene (**NA**), anthracene (**AN**), and tetracene (**TE**). Their emission spectra (**a**, **b**, and **c** in Figure 3) were recorded by placing a MeCN solution of the fluorophore in cell **A** and pure MeCN in cell **B**. The absorption spectra (**d**, **e**, and **f** in Figure 3) of the three states of the molecular switch are significantly different in the range of wavelengths where **NA**, **AN**, and **TE** emit. The absorbances of **SP**, **ME**, and **MEH** at wavelengths corresponding to selected emission maxima of **NA**, **AN**, and **TE** are compared in the pie charts of Figure 3. The **NA** emission at 335 nm can be absorbed equally by **SP**, **ME**, and **MEH** (**g**, **h**, and **i** in Figure 3). The **AN** emission at 401 nm can be absorbed only by **ME** and **MEH** (**j** and **k** in Figure 3). The **TE** emission at 544 nm can be absorbed only by **ME** (**l** in Figure 3). These observations anticipate that (1) **NA** can communicate with all three states of the molecular switch, (2) **AN** can communicate with **ME** and **MEH**, but not with **SP**, and (3) **TE** can communicate with **ME**, but not with **SP** and **MEH**.

The intermolecular communication between the three fluorophores and the three states of the molecular switch was explored by filling cell **A** with an equimolar MeCN solution of **NA**, **AN**, and **TE** and cell **B** with a MeCN solution of **SP**. The three fluorophores were excited selectively by irradiating cell **A** with three consecutive monochromatic beams at 275, 357, and 441 nm. These sequential stimulations induce the emission of **NA** at 335 nm (**NA** channel), **AN** at 401 nm (**AN** channel), and **TE** at 544 nm (**TE** channel), respectively. After each excitation step, the intensity of the optical output *O1* was recorded at the wavelength of the stimulated channel. Then,

Figure 3. Emission spectra of (**a**) **NA** ($\lambda_{exc.}$ = 275 nm), (**b**) **AN** ($\lambda_{exc.}$ = 357 nm), and (**c**) **TE** ($\lambda_{exc.}$ = 441 nm) recorded using the configuration illustrated in Figure 2 by placing the fluorescent solution (1 × 10⁻⁵ M, MeCN) in cell **A** and pure MeCN in cell **B**. Absorption spectra of **SP** (1 × 10⁻⁴ M, MeCN) (**d**) before and (**e**) after irradiation with ultraviolet light and (**f**) after irradiation with ultraviolet light followed by the addition of 1 equiv of CF₃CO₂H. Absorbance of (**g**) **SP**, (**h**) **ME**, and (**i**) **MEH** at 335 nm, of (**j**) **ME** and (**k**) **MEH** at 401 nm, and of (**l**) **ME** at 544 nm.

the interconversion of the molecular switch was induced addressing cell **B** with the input signals *I1*, *I2*, and/or *I3* and the intensity of *O1* for the three channels was recorded again in three consecutive runs. Following this experimental protocol, the changes in the relative intensities of the three output channels were monitored for nine consecutive switching steps (**a**–**j** in Figure 4).

Ultraviolet light (*I1*) and visible light (*I2*) inputs induce the switching between **SP** and **ME** (Figure 1) in cell **B**. These two states absorb equally at 335 nm (**g** and **h** in Figure 3). As a result, their interconversion does not affect the intensity of *O1* for the **NA** channel (**a**–**h** in Figure 4 top). The colorless state **SP** does not absorb at 401 and 544 nm, while the colored form **ME** absorbs strongly at these wavelengths (**j** and **l** in Figure 3). Consistently, the switching from **SP** to **ME**, induced by the input *I1*, reduces the intensities of *O1* for the **AN** and **TE** channels (**a** and **b** in Figure 4 center and bottom). The original values of *O1* are restored for both channels (**b** and **c** in Figure 4 center and bottom) after the switching from **ME** back to **SP** induced by the input of *I2*. Thus, the alternation of the optical inputs *I1* and *I2* switches the optical output *O1* for the **AN** and **TE** channels between two values. The data points **a**–**g** in Figure 4 (center and bottom) illustrate this effect for three consecutive switching cycles. The subsequent irradiation with ultraviolet light (*I1*) produces again **ME** and the associated decrease in the intensity of *O1* for the **AN** and **TE** channels. At this point, the addition of 1 equiv of CF₃CO₂H (*I3*) to cell **B** converts **ME** into **MEH** (Figure 1). The resulting state **MEH** absorbs at
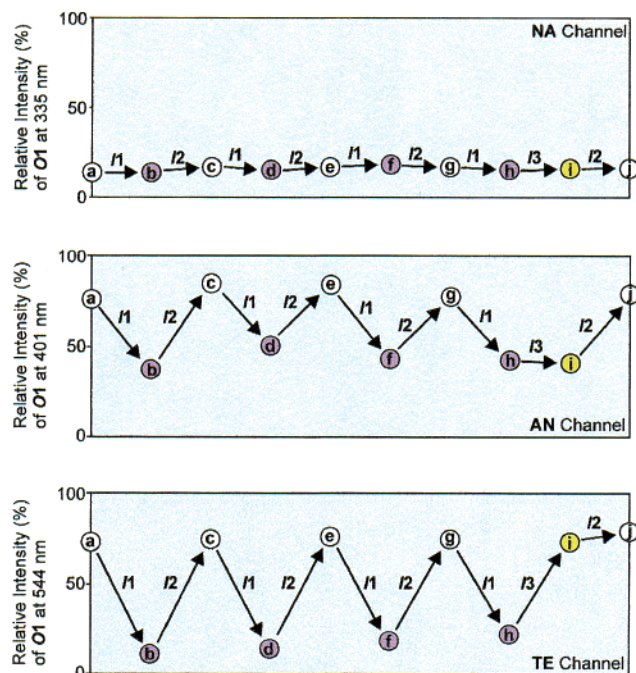
Figure 4. Changes in the relative intensities of *O1* for the **NA**, **AN**, and **TE** channels. The intensities of *O1* are reported relative to those of the emission bands in **a**, **b**, and **c** of Figure 3. They were recorded with the configuration illustrated in Figure 2 by placing an equimolar solution of **NA**, **AN**, and **TE** (1 × 10⁻⁵ M, MeCN) in cell **A** and a solution of **SP** (1 × 10⁻⁴ M, MeCN) in cell **B**. Cell **A** was excited at 275, 357, and 441 nm in three consecutive runs. Cell **B** was addressed with ultraviolet light (*I1*), visible light (*I2*), and H⁺ (*I3*).

401 nm (**k** in Figure 3), but not at 544 nm. As a result, the intensity of *O1* for the **AN** channel remains constant (**h** and **i** in Figure 4 center), while that for the **TE** channel returns to the original value (**h** and **i** in Figure 4 bottom). The subsequent irradiation of cell **B** with visible light (*I2*) induces the interconversion of **MEH** into **SP** (Figure 1). The result is a change in the absorbance of cell **B** at 401 nm, but not at 544 nm. Thus, the intensity of the **AN** channel returns to its initial value (**i** and **j** in Figure 4 center) while that of the **TE** channel remains constant (**i** and **j** in Figure 4 bottom).

In the simple optical network of Figure 2, the three input signals *I1*, *I2*, and *I3* (red arrows) modulate the optical output *O1* (yellow arrows). This switching protocol can be described with the aid of binary logic.[5] The three inputs *I1*, *I2*, and *I3* can be either *off* or *on* and each of them can be represented by a binary digit (*0* or *1*). Similarly, the output *O1* can be considered *off* when its relative intensity is below 50% and *on* when it is above. Thus, the communicating ensemble of molecules converts an input string of four digits (*I1*, *I2*, and *I3*) into a single output data (*O1*) for each channel (Table 1). For example, the input string is *010* when the ultraviolet light source is *off* (*I1* = *0*), the visible light source is *on* (*I2* = *1*), and the H⁺ input is *off* (*I3* = *0*). Under these conditions, the molecular switch is in state **SP**. This state absorbs the emission of **NA** at 335 nm (**NA** channel = *off*), but not that of **AN** at 401 nm (**AN** channel = *on*) and that of **TE** at 401 nm (**TE** channel = *on*). As a result, the output data *O1* corresponding to the input string *010* is *0* for the **NA** channel, *1* for the **AN** channel, and *1* for the **TE** channel. A similar analysis can be extended to all of the eight possible combinations of input strings (Table 1). In the case of the **NA** channel, the output *O1* is always

Table 1. Truth Table for the **NA**, **AN**, and **TE** Channels

input data[a]			output data[a]		
ultraviolet light	visible light	H⁺	**NA** channel[b]	**AN** channel[c]	**TE** channel[d]
I1	*I2*	*I3*	*O1*	*O1*	*O1*
0	*0*	*0*	*0*	*1*	*1*
0	*0*	*1*	*0*	*0*	*1*
0	*1*	*0*	*0*	*1*	*1*
1	*0*	*0*	*0*	*0*	*0*
0	*1*	*1*	*0*	*1*	*1*
1	*0*	*1*	*0*	*0*	*1*
1	*1*	*0*	*0*	*0*	*0*
1	*1*	*1*	*0*	*0*	*1*

[a] A *0* indicates that the corresponding signal is *off*. A *1* indicates that the corresponding signal is *on*. [b] Emission intensity at 335 nm (λ_{exc} = 275 nm). [c] Emission intensity at 401 nm (λ_{exc} = 357 nm). [d] Emission intensity at 544 nm (λ_{exc} = 441 nm).
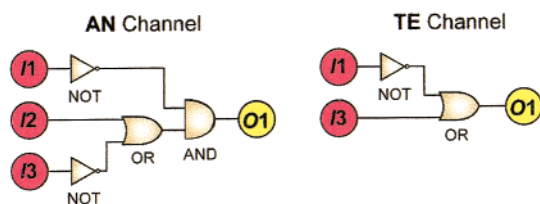

Figure 5. The combinational logic circuits equivalent to the **AN** and **TE** channels convert the input *I1*, *I2*, and *I3* into the output *O1* through AND, NOT, and OR operations.

off (**a**−**j** in Figure 4 top) and the eight input strings are all transduced into a *0*. In the case of the **AN** channel, the output *O1* is *on* (**a** in Figure 4 center) when the molecular switch is state **SP**. Only the three input strings *000*, *010*, and *011* satisfy these conditions and are transduced into a *1*. The other five input strings are all converted into a *0*. In the case of the **TE** channel, the output *O1* is *on* (**a** and **i** in Figure 4 bottom) when the molecular switch is in state **SP** or **MEH**. The six input strings *000*, *001*, *010*, *011*, *101*, and *111* satisfy these conditions and are transduced into a *1*. The other two input strings are converted into a *0*.

The combinational logic circuits[5] equivalent to the transduction protocols of the **AN** and **TE** channels are illustrated in Figure 5. The three inputs *I1*, *I2*, and *I3* (red in Figures 2 and 5) modulate the output *O1* (yellow in Figures 2 and 5) of the **AN** channel through one AND, one OR, and two NOT operators. Only the two inputs *I1* and *I3* control the output *O1* of the **TE** channel through one NOT and one OR gate. The input *I2* has no influence on the output of this channel (Table 1). Similarly, the output of the **NA** channel is not affected by any of the three inputs. This particular channel is always *off* and *O1* is always equal to *0*.

Experimental Section

The spiropyran derivative **SP** was synthesized following a published procedure.[15] The fluorescent probes **NA**, **AN**, and **TE** were purchased from Aldrich and used as received. MeCN was purchased from EM Science and distilled over CaH_2 under N_2. The optical network shown in Figure 2 was assembled in the sample compartment of an emission spectrometer (Varian Cary Eclipse). Cell **B** was irradiated for 5 min at 254 nm (Mineralight UVGL-25 lamp) or for 15 min at 524 nm (Cole-Parmer Fiber Optic Illuminator 9745-00). When the simultaneous irradiation of cell **B** with ultraviolet and visible light was required, the same light sources and wavelengths were employed with an irradiation time of 15 min. The emission intensity was measured immediately after, rather than during, the application of the light inputs.

Conclusions

We have demonstrated that optical signals can be communicated between complementary molecules and that complex logic operations can be performed by using molecule-based systems. Our molecular switch can modulate the intensity of a traveling optical signal in response to optical and chemical stimulations. This gating mechanism does not at all require the participation of undesired electrical signals. In addition, the wavelength dependence of the switching protocol permits the control of three independent optical channels with a single switch. This simple operating principle to gate *optical signals* with *optical signals* might lead to the development of all-optical switches based on molecular components. First, however, the switching mechanism, timescale, and fatigue resistance must be assessed and methods to avoid the unpractical use of chemical inputs and volatile organic solvents must be identified.