

## Memory Effects Based on Intermolecular Photoinduced Proton Transfer

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**Abstract:** We have identified a strategy to communicate a chemical signal between two independent molecular components. One of them is a photoactive merocyanine that switches to a spiropyran, releasing a proton, when stimulated with visible light. The other is a 4,4'-pyridylpyridinium monocation that captures the released proton, producing an electroactive 4,4'-bipyridinium dication. Under the irradiation conditions employed, the photoinduced transformation requires ca. 15 min to reach a photostationary state. In the dark, the ensemble of communicating molecules reequilibrates to the original state in ca. 5 days. These processes can be monitored following the photoinduced enhancement and thermal decay, respectively, of the current for the mono-electronic reduction of the 4,4'-bipyridinium dication. The pronounced difference in time scale for the current enhancement and decay steps can be exploited to implement a memory element with a bit retention time of 11 h. A bit of information can be written optically in the chemical system and it can be read electrically and nondestructively. The memory can be reset, extending its permanence in the dark beyond the bit retention time. A binary logic analysis of the signal transduction operated by the communicating molecules reveals the characteristic behavior of sequential logic operators, which are the basic components of digital memories.

### Introduction

The human nervous system processes and stores information relying on a concatenation of events at the molecular level.<sup>1</sup> For example, the complex mechanism of vision bases its ability to convert optical inputs into electrical outputs on efficient chemical transduction.<sup>1</sup> A sophisticated chemical processor, the retina, converts images into nerve impulses and transmits the visual information from the eye to the brain through the communication of chemical signals.

Molecular switches<sup>2,3</sup> can convert chemical, electrical, and optical inputs into detectable outputs according to specific transduction protocols.<sup>4</sup> Although these rudimentary processors remain far from the high level of sophistication of the human nervous system, they can also elaborate multiple inputs and outputs relying on chemical mechanisms. They can even

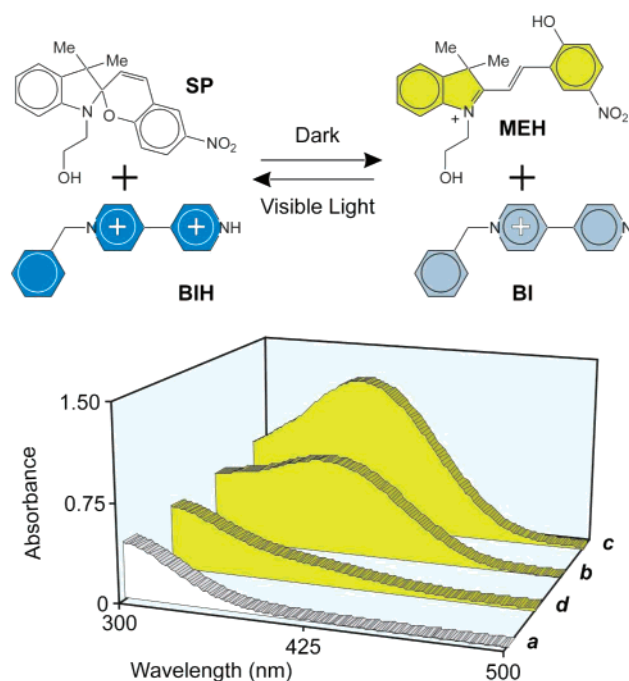
reproduce AND, NOT, OR operations<sup>5</sup> and simple combinational logic functions equivalent to those executed by conventional logic gates and digital circuits.<sup>4,6–22</sup> In addition, molecular memories able to store binary digits are also starting to emerge.<sup>23,24</sup>

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Most of the molecular logic gates reported so far perform a single transduction step.<sup>4–22</sup> The initial inputs reaching a molecular switch are converted into the final outputs by the very same chemical species. The lack of reliable strategies to exchange signals between independent molecular components has limited the development of multistep transduction mechanisms.<sup>4e</sup> The identification of design criteria to implement intermolecular communication in multimolecular ensembles will translate into the possibility of emulating the concatenation of events responsible for information transfer in the central nervous system. In principle, these chemical strategies can lead to the development of innovative operating mechanisms and materials for data processing, storage, and communication. Here, we illustrate a simple mechanism to exchange chemical signals between two independent molecular components. One of them is a photoactive spiroopyran.<sup>25</sup> The other is an electroactive 4,4'-bipyridinium derivative.<sup>26</sup> We demonstrate that the chemical communication established between them mediates the transduction of the optical input of one molecular component into the electrical output of the other.

## Results and Discussion

**Absorption Spectroscopy.** The spiroopyran SP (Figure 1) switches to the protonated merocyanine MEH upon acidification.<sup>20a</sup> The transformation of the colorless SP into the yellow-green MEH is accompanied by the appearance of an absorption band in the visible region. Upon irradiation with visible light, MEH releases a proton, switching back to the colorless form SP, and its characteristic absorption band disappears. This reversible process can be exploited to control the interconversion between the base BI and its conjugated acid BIH. Indeed, the absorption spectra (a–c in Figure 1) of an



**Figure 1.** Absorption spectra ( $1 \times 10^{-4}$  M, MeCN, 25 °C) of an equimolar solution of SP and BIH at initial time (a), after 1 day (b) and 5 days (c) in the dark, and after the subsequent visible irradiation for 15 min (d).

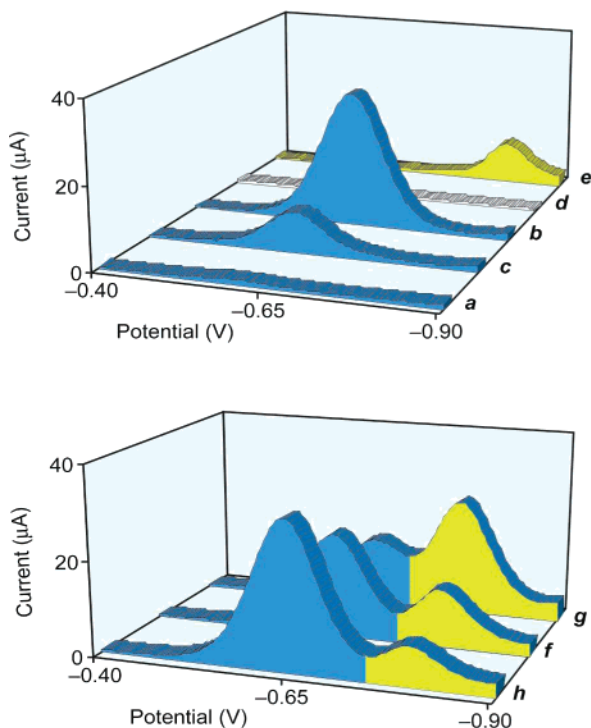
equimolar solution of SP and BIH maintained in the dark show the gradual appearance of the absorption band of MEH at 401 nm. Instead, no changes can be observed when the 1,1'-dibenzyl-4,4'-bipyridinium dication is used in place of BIH, under otherwise identical conditions. These observations indicate that the evolution of the absorption spectrum is a result of proton transfer from BIH to SP. A stationary state is reached in ca. 5 days. At this point, the ratio between SP and MEH is ca. 30:70. Upon irradiation with visible light, MEH releases its proton, inducing the interconversion of BI into BIH. Consistently, the absorption band of MEH fades (spectrum d in Figure 1). At the photostationary state, the ratio between SP and MEH is ca. 90:10. Thus, an optical input (visible light) induces the interconversion of MEH into SP, sending a chemical signal (proton transfer) to BI and encouraging the formation of BIH.

**Differential Pulse Voltammetry.** The monocation BI switches to the dication BIH upon addition of acid. This process is accompanied by the appearance of a peak at  $-0.64$  V in the differential pulse voltammogram (traces a and b in Figure 2). It corresponds to the mono-electronic reduction of the 4,4'-bipyridinium core of BIH and does not change upon visible irradiation. The protonated form BIH reverts to BI after the addition of a base. Consistently, the current at  $-0.64$  V decreases significantly (trace c in Figure 2).

The spiroopyran SP switches to MEH after the addition of acid and storage in the dark. This process is accompanied by the appearance of a peak at  $-0.79$  V in the differential pulse voltammogram (traces d and e in Figure 2). It corresponds to the reduction of the indolium fragment of the protonated form MEH. Under visible irradiation, MEH switches to SP and, consistently, this peak fades.

The thermal interconversion of SP and BIH into MEH and BI (Figure 1) as well as the opposite photoinduced transformation can be monitored electrochemically by probing the voltammetric response of BIH and/or MEH. Indeed, the differential

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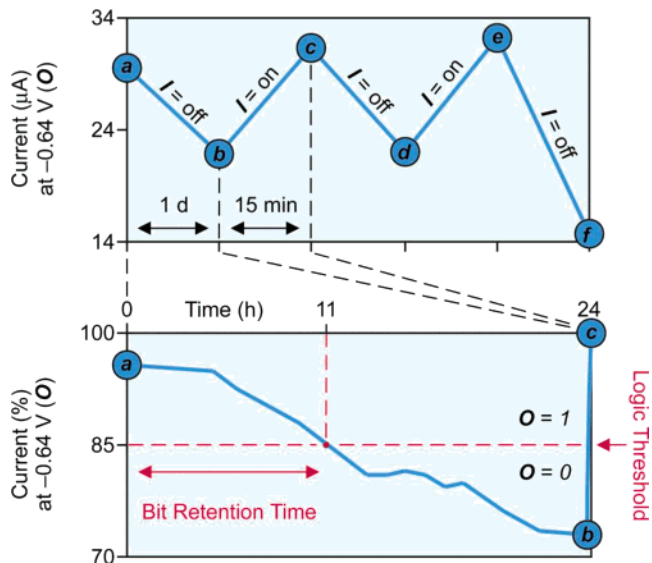


**Figure 2.** Differential pulse voltammograms ( $1 \times 10^{-3}$  M, 0.1 M Bu<sub>4</sub>-NPF<sub>6</sub>, MeCN, 25 °C, scan rate = 20 mV s<sup>-1</sup>, pulse height = 50 mV, V vs Ag/Ag<sup>+</sup>) of BI before (a) and after (b) the addition of 4 equiv of CF<sub>3</sub>-CO<sub>2</sub>H; of BIH after the addition of 0.5 equiv of Et<sub>3</sub>N (c); of SP before (d) and after (e) the addition of 1 equiv of CF<sub>3</sub>CO<sub>2</sub>H and storage in the dark for 1 day; and of an equimolar solution of SP and BIH after 1 day (f) and 3 days (g) in the dark and after the subsequent visible irradiation for 15 min (h).

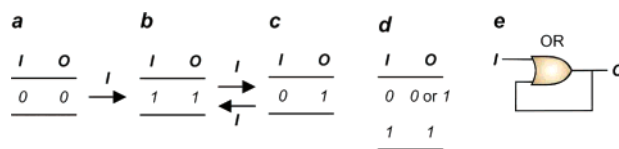
pulse voltammogram of an equimolar solution of SP and BIH reveals two peaks at -0.64 and -0.79 V after ca. 1 day in the dark (trace f in Figure 2). They correspond to the reduction of BIH and MEH, respectively (traces b and e in Figure 2). The presence of MEH confirms that proton transfer from BIH to SP has occurred. The process, however, is relatively slow and a stationary state is reached only after ca. 5 days in the dark. During this time, the concentration of BIH decreases while that of MEH increases. Consistently, the peak at -0.64 fades while that at -0.79 V grows (trace g in Figure 2). Upon irradiation with visible light, MEH releases its proton, inducing the interconversion of BI into BIH. The increase in concentration of BIH is accompanied by the growth of the peak at -0.64 V (trace h in Figure 2). Similarly, the decrease in concentration of MEH translates into a drop in current at -0.79 V.

Our observations demonstrate that visible light promotes the transfer of a proton from one molecular component to the other, producing an increase in current at -0.64 V. Overall, an optical input (*I*) is transduced into an electrical output (*O*) as a result of the intermolecular communication of a chemical signal (proton transfer). The points a–e in Figure 3 (top) illustrate the influence of *I* on the intensity of *O* for two consecutive switching cycles. When *I* is turned off, *O* decreases from the photostationary value of ca. 31 µA (points a, c, and e) to ca. 22 µA (points b and d) in 1 day and to ca. 15 µA (point f) at the thermal equilibrium. When *I* is turned on again, *O* returns to the photostationary value (points c and e) in 15 min.

**Sequential Logic Analysis.** The time profile of the current for part of the first switching cycle (Figure 3, bottom) reveals



**Figure 3.** (Top) Changes in the current output (*O*) at -0.64 V under the influence of visible light inputs (*I*) for two consecutive switching cycles (a–e) and value of the current at the thermal equilibrium (f). (Bottom) Time profile of *O* for part of the first switching cycle (a–c).



**Figure 4.** Binary strings accompanying the irreversible optical writing of a bit (a–c) and the corresponding truth table (d) and sequential logic operator (e).

that *O* decreases from ca. 100% (point a) to ca. 70% (point b) after 1 day in the dark. It returns to its original value (point c) in only 15 min under visible irradiation. The large difference between the time scales of the two processes can be exploited to implement the memory effect characteristic of sequential logic circuits.<sup>5</sup> First, a logic threshold for *O* can be fixed arbitrarily at 85%. Then, binary digits can be encoded in *O* by applying a positive logic convention. When the current is equal to or greater than 85%, *O* is 1. When the current is below the threshold, *O* is 0. Applying a similar logic convention, binary digits can be encoded in *I* also. When the visible light source is off, *I* is 0. When the visible light source is on, *I* is 1. It follows that turning *I* from 0 to 1 switches *O* from 0 to 1. Thus, a binary 1 can be written optically in the chemical system. The communicating molecular components memorize the change imposed by visible light and retain the bit of information for at least 11 h in the dark. During this time, the binary value of *O* can be read nondestructively by measuring the current at -0.64 V. The information can be erased and the memory reset, maintaining the communicating molecular switches in the dark beyond the bit retention time.

The binary strings in panels a–c of Figure 4 illustrate the sequence of events associated with the switching processes. After equilibration of a solution of SP and BIH in the dark (*I* = 0), the current is low (*O* = 0) and the corresponding binary string is 0 0 (panel a). If the light is turned on (*I* = 1), the current raises to a high value (*O* = 1) and the binary string changes to 1 1 (panel b). After the light is turned off (*I* = 0), the high output is retained (*O* = 1) for 11 h and the binary string is now 0 1 (panel c). When the light is turned on again



( $I = 1$ ) within the bit retention time, the output remains high ( $O = 1$ ) and the binary string changes to 1 1 (panel b). After listing all these binary strings in a truth table (panel d), 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 sequence of events that controls the value of  $O$  when  $I$  is 0. In the daughter string (panel c),  $O$  is 1 because it was 1 in the mother string (panel b). 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 (panel e). 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 1 to 0 within this interval of time.

## Conclusions

Our results demonstrate that the communication of a chemical signal between two independent molecular components can transduce an optical input into an electrical output. This strategy can be exploited to implement a chemical equivalent to a conventional memory element.<sup>5</sup> A bit of information can be written optically in the ensemble of communicating molecules and read nondestructively by probing a current output within the bit retention time. The operating principles of our rudimentary molecular memory are more similar to the chemical mechanisms ruling the transfer of information in the central nervous system than to the physical strategies ensuring the storage of data in electronic devices. Our simple mechanism is conceptually analogous to the complex retinal processes that ensure the conversion of light into nerve impulses. In both instances, the exchange of chemical information between independent molecular components mediates the transduction of optical into electrical signals. Perhaps, a new generation of materials and design criteria for information technology will evolve from these innovative chemical approaches to data processing, storage, and communication.

## Experimental Section

**General Methods.** Chemicals were purchased from Acros Organics or Aldrich and were used as received. MeCN was distilled over CaH<sub>2</sub>. The spiroiran SP was synthesized according to a literature procedure.<sup>20a</sup>

Aluminum plates coated with silica gel 60 F<sub>254</sub> (Merck 5554/7) were used for thin-layer chromatography (TLC). Melting points (mp) were determined with an Electrothermal 9100 and are uncorrected. Fast atom bombardment mass spectra (FABMS) were recorded with a VG Mass Lab Trio-2 by use of a 3-nitrobenzyl alcohol matrix. Nuclear magnetic resonance (NMR) spectra were determined with either a Bruker DPX 300 or a Bruker Avance 500. Absorption spectra were recorded with a Varian Cary 100 Bio. Sample irradiation was performed with a Cole-Parmer fiber optic illuminator 9745-00 coupled to a band-pass filter (360–650 nm). Differential pulse voltammograms were recorded with a CH Instruments 610A connected to a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag<sup>+</sup> reference electrode.

**1-Benzyl-4-(4'-pyridyl)pyridinium Hexafluorophosphate (BI).** The temperature of a solution of 4,4'-bipyridine (1.00 g, 6 mmol) in PhMe (4 mL) was raised to the boiling point. Then benzyl bromide (0.76 mL, 6 mmol) was added dropwise over 5 min. The resulting mixture was maintained under reflux for a further 2 h. After cooling to ambient temperature, the mixture was filtered and the solid residue was washed with Et<sub>2</sub>O (8 mL) and dissolved in H<sub>2</sub>O (15 mL). After the addition of NH<sub>4</sub>PF<sub>6</sub> (3 g) and stirring for 30 min at ambient temperature, the mixture was filtered. The solid residue was washed with H<sub>2</sub>O (5 mL) and crystallized from EtOH (6 mL) to give BI (1.42 g, 56%) as a white solid. mp = 147 °C; FABMS  $m/z$  = 247 [M - PF<sub>6</sub>]<sup>+</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>CN)  $\delta$  = 8.85–8.81 (4H, m), 8.30 (2H, d,  $J$  = 7 Hz), 7.77 (2H, d,  $J$  = 6 Hz), 7.51–7.46 (5H, m), 5.74 (2H, s); <sup>13</sup>C NMR (CD<sub>3</sub>CN)  $\delta$  = 155.71, 152.24, 146.01, 142.27, 133.99, 131.06, 130.56, 130.25, 127.37, 122.95, 62.52.

**1-Benzyl-1'H-4,4'-bipyridinium Bis(hexafluorophosphate) (BIH).** A solution of BI (50 mg, 0.1 mmol) and CF<sub>3</sub>CO<sub>2</sub>H (0.1 mL, 1.0 mmol) in MeCN (5 mL) was stirred at ambient temperature for 2 h. After the addition of NH<sub>4</sub>PF<sub>6</sub> (0.2 g), the solution was stirred for 30 min at ambient temperature. After the evaporation of the solvent, the solid residue was washed with H<sub>2</sub>O (10 mL) and dried to give BIH (27 mg, 40%) as a white solid. mp = 142 °C; FABMS  $m/z$  = 248 [M - 2PF<sub>6</sub>]<sup>+</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>CN)  $\delta$  = 8.96 (2H, d,  $J$  = 7 Hz), 8.91 (2H, d,  $J$  = 7 Hz), 8.38–8.25 (4H, m), 7.51 (5H, s), 5.82 (2H, s); <sup>13</sup>C NMR (CD<sub>3</sub>CN)  $\delta$  = 152.76, 152.40, 146.92, 144.55, 133.95, 131.53, 131.02, 130.71, 128.91, 127.84, 66.13.

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