

# Monomolecular Logic: “Half-Adder” Based on Multistate/Multifunctional Photochromic Spiropyrans

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Integration of relatively simple logic gates into high-level circuits (e.g., half-adder) is highly important not only for the potential application in molecular level devices but also for the understanding of complex mechanisms of some important biological processes. In this report, we demonstrate a novel kind of theoretical “monomolecular” half-adder based on multistate/multifunctional photochromic spiropyran for the first time. Spiropyran molecule (SP1) can be transformed to MC1, MC1·Fe<sup>3+</sup> and SP1<sup>+</sup> under the appropriate actions of I1 (UV light) and I2 (ferric ion). The intrinsic network of the transformations among the four states (SP1, MC1, MC1·Fe<sup>3+</sup>, and SP1<sup>+</sup>) reveals the distinct and interesting properties. The behaviors of the absorption changes at 420 and 520 nm correspond to those of an “AND” gate and an “XOR” gate, respectively. Since the absorption changes at both 420 and 520 nm are based on the entity of a single molecule of spiropyran (e.g., SP1) and under the same external inputs, the AND and XOR gates can be “operated” in parallel. Therefore, the absorption spectral variations of the solution of spiropyran in response to UV light irradiation and ferric ion mimic the function of a “half-adder” that can perform simple arithmetic addition.

## Introduction

Motivated by the urge for miniaturization of electronic devices, in recent years, researchers have been intensively investigating molecule-based electronic devices, such as molecular wires,<sup>1</sup> molecular rectifiers,<sup>2</sup> and molecular transistors.<sup>3</sup> Significant progress has been achieved in this field thanks to the development of nanoscience and nanotechnology (e.g., SPM techniques).<sup>4</sup> However, the fabrication of highly complex integrated circuits at the molecular level is still the crucial requirement for future nanoprocessors and molecular computers, and it remains a great challenge.<sup>5</sup>

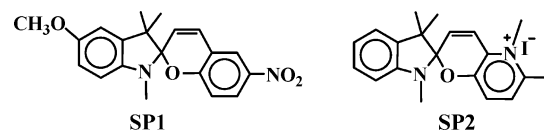
Meanwhile, a potential approach to molecular switches and logic devices (AND, NOT, OR, XOR, etc.)<sup>6</sup> has been demonstrated through the detectable spectroscopic changes within molecular or supramolecular systems upon chemical, electrical, or optical inputs. The operating mechanisms of these molecular switches and logic gates are based on acid/base reactions, conformation changes, photoinduced electron and energy transfer mechanisms, photoinduced isomerizations, redox processes, and supramolecular chemistry, different from those ruling conventional electronics. Most importantly, with these mechanisms, efficient approaches for the signal communication between molecular switches and logic gates can be developed. In this regard, several new combinational logic gates for information processing and communication at the molecular level employing the reversible interconversions of photochromic spiropyran upon external light or chemical stimulations have been recently described.<sup>6b,7</sup>

Rational integration of relatively simple logic gates into high-level circuits (e.g., “half-adder” which, as the basis of electronic

calculators and computer machines, require two binary inputs and two binary outputs to perform simple arithmetic addition) is highly important not only for the potential application in molecular electronics, but also for the understanding of complex mechanisms of important biological processes. To the best of our knowledge, there are only a few reports dealing with half-adder.<sup>8</sup> Monomolecular half-adder is very attractive since possible mutual interferences due to the intermolecular interactions can be avoided, and thus, signal processing and communication would become more reliable. Up to now, only two examples of monomolecular half-adder based on the properties of spectroscopically pumped and probed excited states have been described.<sup>8b</sup> In this report, we describe for the first time a new monomolecular half-adder based on multistate/multifunctional photochromic spiropyran.

## Results and Discussion

**Absorption Spectral Studies of Spiropyran under the Actions of Ferric Ion and Light Irradiation.** As reported by Buncel and Raymo et al.,<sup>9,10</sup> under UV light irradiation, the spiropyran molecule (SP1) was photoswitched to its open merocyanine form (MC1) (Scheme 1) with the appearance of a



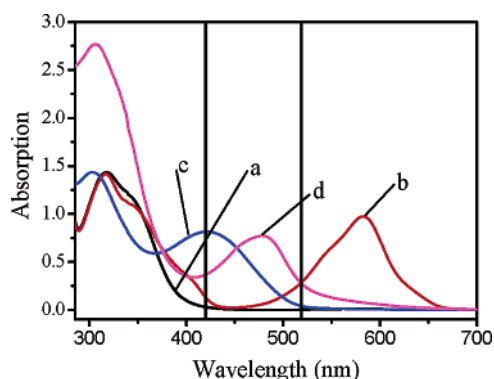
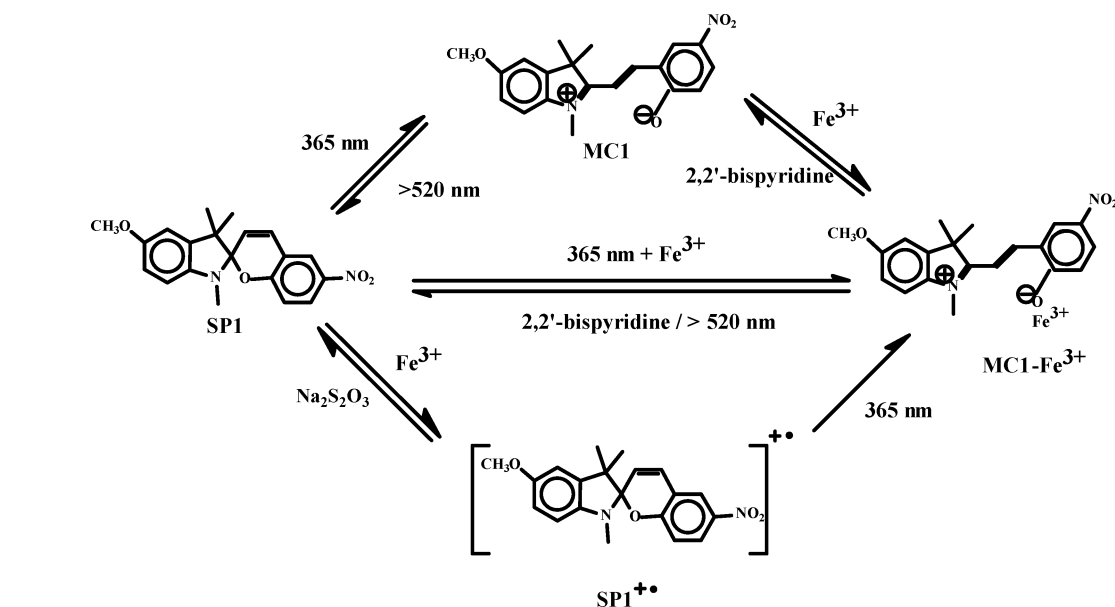
characteristic absorption band with  $\lambda_{\text{max}} = 580$  nm (curve b in Figure 1). It was reported that addition of some metal ions ( $M^{n+}$ ) to the solution of MC1 can induce the hypsochromic shift of the absorption band due to the formation of MC1· $M^{n+}$ .<sup>10</sup> Such spectral changes were found to be dependent on the nature and quantities of the metal ions employed, and usually only the rather broad bands were obtained. In our experiments, it was discov-

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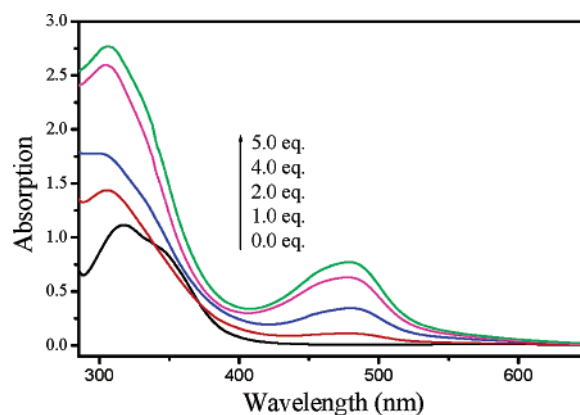
## SCHEME 1 Intrinsic Interconversion Network of the Four States of SP1.



**Figure 1.** UV-visible absorption spectra of SP1 ( $1.0 \times 10^{-4}$  M, 25 °C) in THF (a) before and (b) after irradiation with ultraviolet light, (c) simultaneously or consecutively upon addition of 5 equiv of  $\text{Fe}(\text{ClO}_4)_3$  and irradiation with ultraviolet light, and (d) only upon addition of 5 equiv of  $\text{Fe}(\text{ClO}_4)_3$ .

ered that addition of  $\text{Fe}(\text{ClO}_4)_3$  to the solution of MC1 led to the emergence of a new absorption band with  $\lambda_{\text{max}} = 420$  nm (curve c in Figure 1) with the concomitant disappearance of the characteristic absorption band ascribed to MC1. This new absorption with  $\lambda_{\text{max}} = 420$  nm was ascribed to the complex  $\text{MC1} \cdot \text{Fe}^{3+}$ , as reported previously.<sup>7f</sup>

In agreement with the reports of Buncel et al.,<sup>10</sup> after coordination with ferric ion, the thermal stability of the open form of spiropyrans was greatly enhanced, but the complex  $\text{MC1} \cdot \text{Fe}^{3+}$  was so stable that the solution of  $\text{MC1} \cdot \text{Fe}^{3+}$  did not exhibit photochromism upon irradiation of visible light ( $\lambda > 460$  nm) and even in the presence of  $\text{Na}_2\text{S}_2\text{O}_3$  at room temperature. Such a unique property of  $\text{MC1} \cdot \text{Fe}^{3+}$  made the complete conversion of SP1 to  $\text{MC1} \cdot \text{Fe}^{3+}$  possible. It should be noted that the transformation of SP1 into MC1 could be performed only partially in the absence of ferric ion under the same conditions. The ferric ion in complex  $\text{MC1} \cdot \text{Fe}^{3+}$  could be released by addition of 3 equiv of 2,2'-bipyridine (vs  $\text{Fe}^{3+}$ ), a strong chelate ligand, and the free MC1 could be switched back to SP1 upon further visible light irradiation (see Supporting Information). The release of  $\text{Fe}^{3+}$  from complex  $\text{MC1} \cdot \text{Fe}^{3+}$  also confirmed the coordination of  $\text{Fe}^{3+}$  with MC1 in complex  $\text{MC1} \cdot \text{Fe}^{3+}$ , as discussed above. Since the complex of 2,2'-bipyridine and  $\text{Fe}^{3+}$  showed absorption in the range of 400–600 nm, which

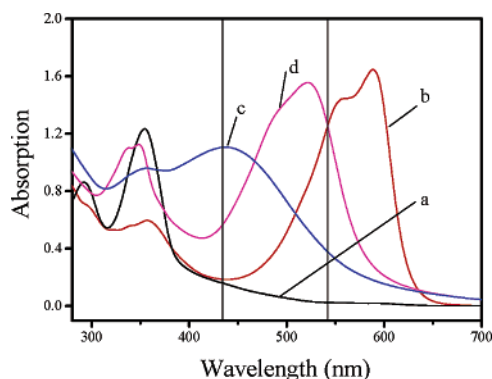


**Figure 2.** UV-visible absorption spectral changes of SP1 ( $1.0 \times 10^{-4}$  M, 25 °C) in THF upon addition of 1.0, 2.0, 4.0, and 5.0 equiv (vs SP1) of  $\text{Fe}(\text{ClO}_4)_3$ .

made it difficult to precisely “read” the spectral changes purely due to the actions of UV light irradiation and  $\text{Fe}^{3+}$ , it would be better to remove the complex of 2,2'-bipyridine and  $\text{Fe}^{3+}$  from the solution before the experiments are recycled.

SP1 is a moderate electron donor, as indicated by its oxidation potential ( $E_{\text{ox}}^{1/2} = 0.96$  V vs SCE; see Supporting Information). Addition of 5 equiv of  $\text{Fe}(\text{ClO}_4)_3$  to the solution of SP1 led to a new absorption band with  $\lambda_{\text{max}} = 480$  nm (curve d in Figure 1), which should be attributed to the formation of the radical cation of SP1 ( $\text{SP1}^{+\bullet}$ ). Control experiments provided further evidences for the above assumption: (1) when the solution of SP1 after addition of 5 equiv of  $\text{Fe}(\text{ClO}_4)_3$  was further treated with 5 equiv of  $\text{Na}_2\text{S}_2\text{O}_3$ , the absorption band with  $\lambda_{\text{max}} = 480$  nm disappeared, and the original absorption spectrum was restored; (2) if an aqueous solution of  $\text{K}_3\text{Fe}(\text{CN})_6$  was added to the solution of SP1 that had been treated by  $\text{Fe}(\text{ClO}_4)_3$ , dark-blue precipitates appeared immediately, indicating the presence of ferrous ion in the mixture solution. The formation of ferrous ion should be owing to the reduction of ferric ion by SP1, and as a result, SP1 was oxidized to  $\text{SP1}^{+\bullet}$ .<sup>11</sup> The strength of this absorption band was dependent on the quantities of  $\text{Fe}(\text{ClO}_4)_3$  added to the solution, as shown in Figure 2.

SP1 can be transformed to MC1,  $\text{MC1} \cdot \text{Fe}^{3+}$ , and  $\text{SP1}^{+\bullet}$  under the appropriate actions of UV light and ferric ion, as detailed



**Figure 3.** UV-visible absorption spectra of SP2 ( $1.0 \times 10^{-4}$  M, 25 °C) in THF (a) before and (b) after irradiation with ultraviolet light, (c) simultaneously or consecutively upon addition of 5.0 equiv of  $\text{Fe}(\text{ClO}_4)_3$  and irradiation with ultraviolet light, and (d) only upon addition of 5.0 equiv of  $\text{Fe}(\text{ClO}_4)_3$ .

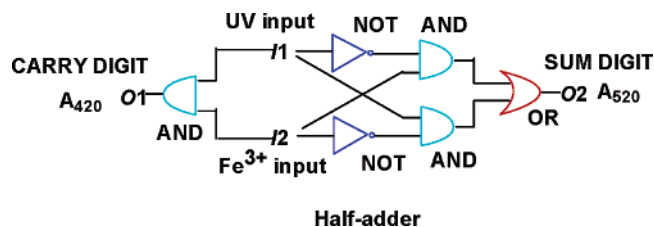
**TABLE 1: Equivalent Truth Table for the “AND” Gate**

I1 (UV)	I2 ( $\text{Fe}^{3+}$ )	AND O1 ( $A_{420}$ )
0	0	0 (low, <0.60)
1	0	0 (low, <0.60)
0	1	0 (low, <0.60)
1	1	1 (high, >0.60)

above. Scheme 1 demonstrates the interconversions among the four states of SP1. In addition to SP1, other spiropyran derivatives with different substituents of the benzene ring or with a *N*-methylpyridinium group instead of benzene, such as SP2 were also investigated under the same conditions (Figure 3). Interestingly, it was found that they all showed similar spectral changes in response to UV light and ferric ion, although the corresponding absorption bands were slightly different from those of SP1.

**Potential “AND” and “XOR” Logic Gates Based on the Spectral Properties of SP1.** The above interconversions among SP1, MC1,  $\text{MC1}\cdot\text{Fe}^{3+}$ , and  $\text{SP1}^{+*}$  can be described with binary logic.<sup>12</sup> The input signals are UV light (365 nm, I1) and ferric ion ( $\text{Fe}^{3+}$ , I2). The presence of MC1,  $\text{MC1}\cdot\text{Fe}^{3+}$ , and  $\text{SP1}^{+*}$  can be characterized by the corresponding typical absorption bands. The absorption band with  $\lambda_{\text{max}} = 420$  nm (due to  $\text{MC1}\cdot\text{Fe}^{3+}$ ) can be considered as one of the output signals (O1): O1 = 0 when the absorbance at 420 nm is low (<0.60); O1 = 1 when the absorbance at 420 nm is high (>0.60). As mentioned above,  $\text{MC1}\cdot\text{Fe}^{3+}$  was formed in solution only under the simultaneous actions of UV light (I1) and  $\text{Fe}^{3+}$  (I2), namely, only when I1 = 1 and I2 = 1, the output signal O1 is 1. Otherwise, O1 is 0. Consequently, the absorption changes at 420 nm upon the external inputs of UV light (I1) and  $\text{Fe}^{3+}$  (I2) can be interpreted as an “AND” gate (see Table 1).

The absorption spectra of MC1 and  $\text{MC1}\cdot\text{Fe}^{3+}$  are overlapped to some extent (see curves b and d in Figure 1). At their spectral intersection point (520 nm), the absorbance of the solution was relatively high because of the formations of either MC1 or  $\text{SP1}^{+*}$  since both SP1 and  $\text{MC1}\cdot\text{Fe}^{3+}$  have rather weak absorption at 520 nm. The absorbance at 520 nm was selected as another output signal (O2): O2 = 0, when the absorbance is low (<0.15) at 520 nm; O2 = 1 when the absorbance is high (>0.15) at 520 nm. The separate actions of UV light and  $\text{Fe}^{3+}$  led to the formations of MC1 and  $\text{SP1}^{+*}$ , respectively, and as a result, the absorbance at 520 nm is high (O2 = 1). The original solution (curve a in Figure 1, without the actions of both UV light and  $\text{Fe}^{3+}$ ) did not absorb at 520 nm, and thus, O2 = 0. Interestingly, under the consecutive actions of UV light and  $\text{Fe}^{3+}$ , SP1 was transformed to  $\text{MC1}\cdot\text{Fe}^{3+}$ , and as a result, the absorbance at



**Figure 4.** The corresponding physical electronic symbols of the 2-input logic half-adder circuit.

**TABLE 2: Equivalent Truth Table for the “XOR” Gate**

I1 (UV)	I2 ( $\text{Fe}^{3+}$ )	XOR O2 ( $A_{520}$ )
0	0	0 (low, <0.15)
1	0	1 (high, >0.15)
0	1	1 (high, >0.15)
1	1	0 (low, <0.15)

**TABLE 3: Truth Table for the “Half-Adder” Circuit**

I1 (UV)	I2 ( $\text{Fe}^{3+}$ )	added number	
		carry digit output O1 ( $A_{420}$ )	sum digit output O2 ( $A_{520}$ )
00	00	0 (low, <0.60)	0 (low, <0.15)
01	00	0 (low, <0.60)	1 (high, >0.15)
00	01	0 (low, <0.60)	1 (high, >0.15)
01	01	1 (high, >0.60)	0 (low, <0.15)

520 nm of the solution became low (O2 = 0). Similarly, these absorption changes at 520 nm in response to the actions of UV light and ferric ion can be interpreted as an “XOR” gate (see Table 2).

**Monomolecular Half-Adder Based on Multistate/Multifunctional Spiropyrans.** The intrinsic network of the transformations of SP1 among the four states (SP1, MC1,  $\text{MC1}\cdot\text{Fe}^{3+}$ , and  $\text{SP1}^{+*}$ ) led to the absorption changes of the solution at 420 and 520 nm, and these spectral properties were interpreted as the “AND” and “XOR” gates, respectively, as described above. These absorption changes were based on the entity of a single molecule of spiropyran under the same inputs (UV light, I1;  $\text{Fe}^{3+}$ , I2), and thus, the “AND” and “XOR” gates can be “operated” in parallel. Therefore, the spectral variations of the solution of spiropyran, due to the interconversions among the four states of spiropyran (SP1, MC1,  $\text{MC1}\cdot\text{Fe}^{3+}$ , and  $\text{SP1}^{+*}$ ) as shown in Scheme 1, can be used to mimic the function of a half-adder. This can be represented by conventional electronic symbols (Figure 4). As illustrated in Table 3, the first binary number is coded for by the presence (01) or absence (00) of UV light (365 nm, I1) input signal. The second binary number is coded for by the presence (01) or absence (00) of  $\text{Fe}^{3+}$  (I2) input signal. The sum digit is coded for by the absorbance output at 520 nm (O2) when high (1) or low (0). The carry digit is coded for by the absorbance output at 420 nm (O1) when high (1) or low (0). The truth table demonstrates the binary additions: 00 + 00 = 00, 00 + 01 = 01, and 01 + 01 = 10. In the universally recognizable decimal number system, these operations become 0 + 0 = 0, 0 + 1 = 1, 1 + 0 = 1, and 1 + 1 = 2.

This new monomolecular half-adder has the following features which we like to emphasize: (1) due to their facile synthesis, the spiropyran molecules can be accessible in large quantities, which makes it possible to construct inexpensive, throw-away devices in the future; (2) the two input signals, one of which is optical (UV light at 365 nm) and the other chemical ( $\text{Fe}^{3+}$ ), can be executed simultaneously or consecutively without any dependency and any annihilation problems in wireless mode; (3) for the present half-adder, the transmission of

chemical and optical input signals into one type of optical output signals was performed without the requirement for complex and specific modulation techniques.

## Conclusion

The spiropyran can be transformed into four states, each of which shows a characteristic absorption spectrum, under the actions of UV light irradiation and ferric ion. These spectral changes mimic the functions of an "AND" gate and an "XOR" gate. Most importantly, these two gates can be operated in parallel, and thus, a novel potential "monomolecular" half-adder based on multistate/multifunctional photochromic spiropyrans is demonstrated for the first time. This new half-adder is based on the entity of a single molecule of spiropyran, which has been extensively studied.<sup>13</sup> Hence, this report opens up the possibility of designing and optimizing the structures of photochromic spiropyrans and other systems<sup>13</sup> for molecular computing in the future. Further investigations in this field are underway.

## Experimental Section

Compounds SP1 and SP2 were synthesized according to the reported procedures.<sup>14</sup> The purity of these two compounds was checked by elemental analysis. THF was dried over Na/benzophenone before use.

Absorption spectra were measured with a Hitachi (model U-3010) UV-vis spectrophotometer. The ultraviolet light irradiation experiments were performed under N<sub>2</sub> atmosphere with a 140-W high-pressure mercury lamp at 365 nm.

Differential pulse voltammetric experiments were performed on an EGDG PAR 370 system at a scan rate of 100 mV in THF using Bu<sub>4</sub>NPF<sub>6</sub> as electrolyte, platinum as counter and work electrodes, and SCE as reference electrode.

**Supporting Information Available:** Characterization data for SP1 and SP2, differential pulse voltammograms of the THF solutions of SP1 and that of SP1 after consecutive treatment with UV light and Fe(ClO<sub>4</sub>)<sub>2</sub>, and the absorption spectra of the SP1 solution under the different condition. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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