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Synthesis and Spectral Investigations of a New Dyad with Spiropyran and Fluorescein Units: Toward Information Processing at the Single Molecular Level

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A new dyad **1** with two spiropyran units as the photochromic acceptors and one fluorescein unit as the fluorescent donor was synthesized and characterized. External inputs (ultraviolet light, visible light, and proton) induce the reversible changes of the structure and, concomitantly, the absorption spectrum of dyad **1** due to the presence of two spiropyran units. Only the absorption spectrum of the ME form of the spiropyran units in dyad **1** has large spectral overlap with the fluorescence spectrum of the fluorescein unit. Thus, the fluorescence intensity of dyad **1** is modulated by reversible conversion among the three states of the photochromic spiropyran units and the fluorescence resonance energy transfer (FRET) between the ME form and the fluorescein unit. Based on the fact that dyad **1** could "read out" three external input signals (ultraviolet light, visible ligh,t and proton) and "write" a compatible specific output signal (fluorescence intensity), dyad **1** described here can be considered to perform an integrated circuit function with one OR and one AND interconnected logic gates. The present results demonstrate an efficient strategy for elaborating and transmitting information at the single molecular level.

Introduction

The expectation of potential application in molecular devices, such as molecular wires, sensors, switches, logic gates, and signal nanoprocessors,[1] has been inspiring active investigations into designing and synthesizing functional molecules. Photochromic compounds are promising candidates due to their reversible structural interconversion in response to external optical, chemical, and thermal stimulation.[2] Among them, the system taking advantage of the interconversion between spiropyran (SP)[3] and merocyanine (ME) has been extensively investigated.[4]

Like photoinduced electron transfer, energy transfer is another mechanism for quenching the excited states of fluorophores. If the fluorescence intensity of the fluorophore can be regulated by the controlled energy transfer process in response to external signals, the corresponding molecular switch or logic gate can be designed.[5] One of the energy transfer mechanisms is fluorescence resonance energy transfer (FRET), for which the basic requirement is the certain degree of spectral overlap between the emission spectrum of the fluorophore and the absorption spectrum of the "quencher". The three states of spiropyran SP, ME, and MEH[6a] show different

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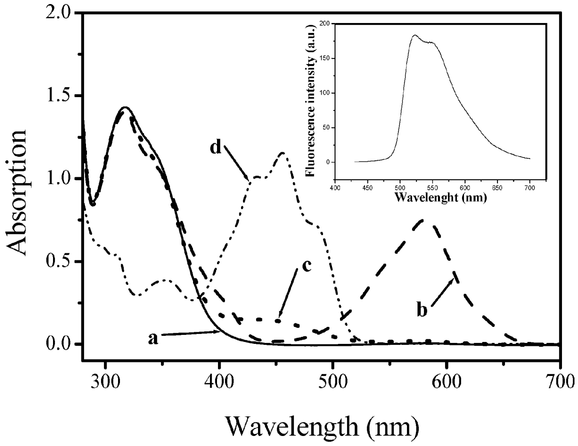

FIGURE 1. Absorption spectra of reference compound **10** (see Scheme 1) (1.0×10^{-4} M, 25 °C) (a) before and (b) after irradiation with ultraviolet light at 365 nm for 5 min and (c) after irradiation with ultraviolet light followed by the addition of 1 equiv of CF_3COOH in THF and (d) absorption spectra of the reference compound **9** (see Scheme 1) (5.0×10^{-5} M, THF, 25 °C). The inset curve is the emission spectrum of **9** in THF (5.0×10^{-5} M, 25 °C) excited at 430 nm. For the UV irradiation experiments, a 140-W high-pressure mercury lamp ($\lambda = 365$ nm) was held above the cuvettes containing solutions by about 3 cm.

absorption spectra, and thus it is possible to regulate the fluorescence intensity of a suitable fluorophore by irradiation of the solution containing both spiropyran and the fluorescent molecule. Indeed, *Raymo* and his colleagues[6] studied the "signal communication" between pyrene (naphthalene, anthracene, and tetracene) and spiropyran, and proposed the corresponding integrated logic gates and communication network. By attaching spiropyran covalently to porphyrin, Moore et al.[5a] studied the quenching process of the porphyrin excited states upon irradiation by ultraviolet light.

Fluorescein is the most widely used fluorophore for labeling and sensing biomolecules[7] due to its high extinction coefficient, high fluorescence quantum yield, and the fact that its excitation wavelength lies in the visible-wavelength range. As shown in the inset curve of Figure 1, fluorescein shows the emission in the range of 500−650 nm, and hence the overlap between its fluorescence spectrum and the absorption spectrum of ME is significantly large (see Figure 1), as compared to that between porphyrin and pyrene.[5a,6] By contrast, there is almost no overlap between the fluorescence spectrum of fluorescein and the absorption spectra of SP and MEH (see Figure 1). Consequently, for the fluorescein−spiropyran system the corresponding fluorescence "*on/off*" ratio as well as the "output" ratio (signal-to-noise ratio) can be enhanced. Besides, fluorescein shows strong absorption around 430 nm, at which SP, ME, and MEH have very weak absorption. Thus, excitation of fluorescein at 430 nm will perturb none of the three states of spiropyran (SP, ME, and MEH). With these thoughts in mind, we started the studies of the photoswitching behavior of SP units in the presence of the fluorescein unit. Here we report the synthesis and spectral studies of a well-defined dyad **1** with both spiropyran and fluorescein units (SP-Flu-SP, see Scheme 1). By considering the ease of synthesis, two SP units are covalently attached to the fluorescein unit in dyad **1**. The results demonstrate that the fluorescence intensity of the fluorescein unit can be controlled by alternating ultraviolet light, visible light, and proton stimulations, which implies that this SP-Flu-SP dyad can lend itself to be an efficient molecular design for processing and communicating information at the single molecular level. For comparable studies, the intermolecular communicating behavior of the mixture solution of a fluorescein derivative (compound **9**, see Scheme 1) and a SP molecule (compound **10**, see Scheme 1) (in a molar ratio of 2:1) were also investigated.

Results and Discussion

Synthesis. The preparation of dyad **1** was depicted in Scheme 1. Condensation of 4-methoxyphenylhydrazine hydrochloride **2** with methyl isopropyl ketone afforded Fisher's base **3**, which was demethylated with boron tribromide to yield Fisher's base **4**.[8] Fisher's base **4** was then methylated with methyl iodide to give the intermediate salt **5**. The condensation of **5** with 5-nitrosalicylaldehyde led to spiropyran **6** in good yield.[8] Fluorescein derivative **8** was prepared from fluorescein disodium **7** according to the reference.[9] Finally, reaction of **8** with spiropyran **6** in DMF at room temperature in the presence of anhydrous K_2CO_3 gave the target compound **1** in 42.7% yield after separation with column chromatography.

The reference compounds **9** and **10** were prepared in ways similar to those for compounds **8** and **6**, respectively.

Absorption Spectra. As for the spiropyran reported by Raymo et al.,[6] the reference compound **10** also shows the reversible interconversion among the corresponding SP, ME, and MEH states upon irradiation of ultraviolet and visible light and addition of acid. Similar phenomena were observed for the mixed solution of reference compounds **9** and **10** (in a molar ratio of 1:2).

Figure 2 shows the absorption spectrum of dyad **1** and those of the solution after treatment with ultraviolet light and acid in THF. The absorption peaks at 430, 450, and 485 nm are essentially identical with those observed for reference compound **9** (Figure 1). As shown in Figure 2, the absorption spectra of dyad **1** before irradiation by ultraviolet light are essentially a simple addition of the spectra of the fluoroscein and nitrospiropyran chromophores (for their absorption spectra, see Figure 1), and thus there is no significant electronic interactions between fluorescein and nitrospiropyran units of dyad **1** in the ground state. After the THF solution of dyad **1** was

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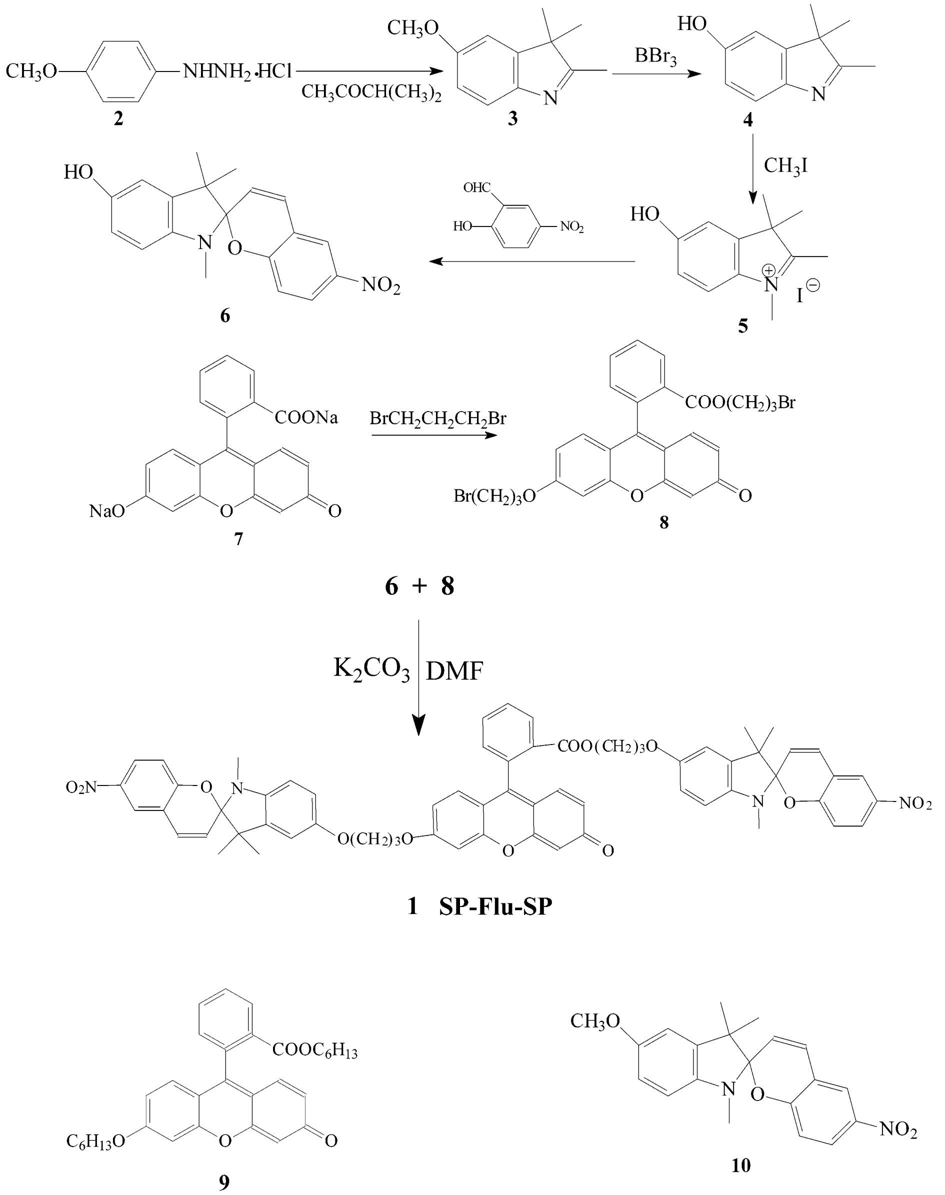
SCHEME 1. Synthetic Scheme for Dyad 1 (SP-Flu-SP) and Chemical Structures of Reference Compounds 9 and 10



irradiated with ultraviolet light at 365 nm, the main absorption bands of the fluorescein unit were still unchanged, but the characteristic absorption band of the ME form with a maximum at 580 nm emerged. This indicates the formation of the corresponding ME form by reference to the absorption spectrum of compound **10** upon irradiation under the same conditions. Upon addition of 2 equiv of CF_3COOH, the absorption band at 580 nm disappeared due to the complete transformation of ME to MEH. The initial absorption was recovered after irradiation of the above solution, which had been treated with UV light and acid, with visible light ($\lambda > 460$ nm) (not shown).

Fluorescence Spectra. Figure 3 shows the fluorescence spectra of the solution of dyad **1** in THF under several different conditions with excitation wavelength at 430 nm. Before irradiation with ultraviolet light, it showed a broad emission band in the range of 500−650 nm with the maximum around 550 nm (curve a, Figure 3). Upon irradiation with ultraviolet light for 5 min, the intensity of the fluorescence band around 550 nm decreased to 45% of that of the initial solution (curve b, Figure 3). This fluorescence intensity reduction is significantly large compared to that of the porphyrin−spiropyran dyad.[5a] Besides, a new emission band with maxima at ~650 nm appeared. Ultraviolet light irradiation induced the formation of the ME moiety in dyad **1**, which quenched the excited state of the fluorescein unit through fluorescence resonance energy transfer. Energy transfer from the excited fluorescein state to ME produced the excited ME state, which should be responsible for the appearance of this new emission band. A control experiment with reference compound **10** confirms this conclusion: no significant fluorescence emission was observed upon excitation of the SP form of reference compound **10**. After irradiation of the THF solution of **10** with ultraviolet light at 365 nm for 5 min, the corresponding ME form was produced. This solution

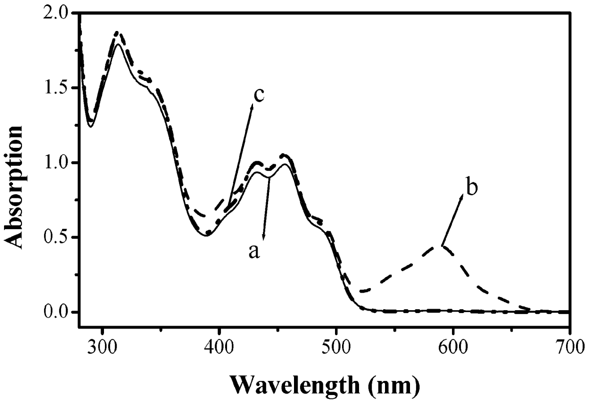


FIGURE 2. Absorption spectra of dyad **1** (5.0×10^{-5} M, THF, 25°C) (a) before and (b) after irradiation with ultraviolet light for 5 min and (c) after irradiation with ultraviolet light followed by addition of 2 equiv of CF_3COOH in THF. For the UV irradiation experiment, a 140-W high-pressure mercury lamp ($\lambda = 365$ nm) was held above the cuvette containing the solution by about 3 cm.

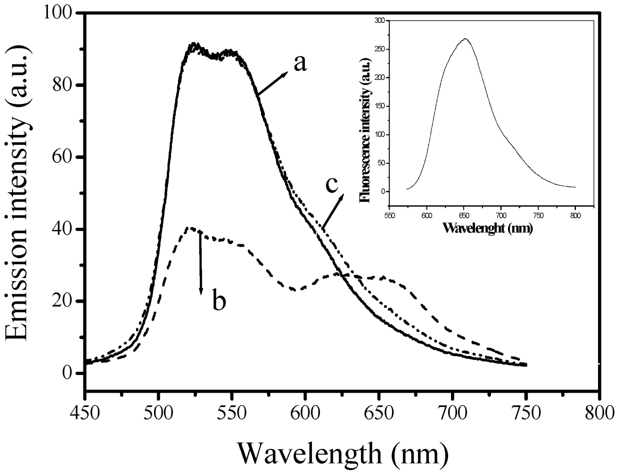


FIGURE 3. Emission spectra of dyad **1** (5.0×10^{-5} M, THF, 25 °C) excited at 430 nm (a) before and (b) after irradiation with ultraviolet light for 5 min and (c) after irradiation with ultraviolet light followed by addition of 2 equiv of CF_3COOH. The inset curve is the emission spectrum of the ME form of compound **10** (1.0×10^{-4} M in THF, 25 °C, after irradiation with ultraviolet light for 5 min) excited at 563 nm. For the UV irradiation experiments, a 140-W high-pressure mercury lamp ($\lambda = 365$ nm) was held above the cuvettes containing solutions by about 3 cm.

displayed a fluorescence band with the maximum at 650 nm after excited at 563 nm (Figure 3, inset curve). After addition of 2 equiv of CF_3COOH to the solution of dyad **1** after UV light irradiation, the fluorescence intensity of the solution was restored to its initial value (curve c, Figure 3). Irradiation with visible light for 5 min on the solution of dyad **1** just after treatment with ultraviolet light irradiation showed a similar effect as the case where treatment with ultraviolet light irradiation was followed by addition of acid.

This fluorescence intensity alteration can be repeated consecutively. As an example, Figure 4A illustrates this effect of the fluorescence intensity of the fluorescein unit at 550 nm for several switching cycles. Control experiments indicated that both light irradiation and addition of acid did not affect the fluorescence intensity of reference compound **9** as shown in Figure 4B.

The above fluorescence modulation observed for dyad **1** can be explained with the switching cycles starting and ending with SP-Flu-SP as showed in Scheme 2. There should exist seven states of dyad **1** due to the partial conversion between SP and ME on exposure to ultraviolet light.[10] Since changes of the fluorescence intensity are the sole result of irradiation with ultraviolet light, we simplify them to the three extreme states (see Scheme 2) to interpret the mechanism clearly. Upon irradiation with ultraviolet light, the SP moieties in dyad **1** are converted to ME units [formation of ME-Flu-ME (SP)], which quench the excited state of the fluorescein unit, and as a result, the fluorescence intensity of the fluorescein unit is reduced to about 45% of the initial value. Upon addition of 2 equiv of CF_3COOH, the ME units are transformed to the MEH unit [formation of MEH-Flu-MEH (SP)], whose absorption spectrum has almost no overlap with the fluorescent spectrum of the fluorescein unit. Thus, effective energy transfer cannot take place, and consequently the fluorescence intensity of the fluorescein unit returns to its initial value. On the other hand, upon irradiation of the solution of ME-Flu-ME (SP) with visible light, the fluorescence intensity also returns to its initial value as a result of the complete conversion from ME-Flu-ME (SP) to SP-Flu-SP. Thus, alternating ultraviolet light, visible light, and proton inputs can regulate the fluorescence intensity of the fluorescein unit.

For comparative studies, similar experiments were performed for the mixtures of reference compounds **9** and **10** (in a molar ratio of 1:2) (Figure 5). Before ultraviolet light irradiation, the solution showed a broad and featureless emission band with the maximum around 550 nm. After irradiation of the solution at 365 nm for 5 min, the fluorescence intensity was reduced by about 13%, which should be due to the quenching of the excited state of the fluorescein unit by the corresponding ME form generated from the SP form of **10** upon ultraviolet light irradiation. Similar to what is described above for dyad **1**, the fluorescence intensity of the solution returned to its initial value upon addition of 2 equiv of CF_3COOH or upon irradiation with visible light. As compared to dyad **1**, the fluorescence intensity reduction for the mixed solution of **9** and **10** is less significant. This may be interpreted as follows: According to the Förster theory,[11] the energy transfer efficiency is strongly dependent on the donor−acceptor distance. The donor and acceptor units in dyad **1** are much closer to each other than those in the case of the mixed solution of **9** and **10** (intermolecular). Thus, the intermolecular energy transfer is not as effective as that for the intramolecular case. In addition, the emission band ascribed to the ME form was not obvious for the mixed solution. This also may be due to the ineffective energy transfer from the excited state of fluorescein to the ME form of **10**. As a result, only a rather limited amount of the ME form of **10** was excited. The excited state of the ME form may be easily deactivated by the surrounding solvents, so that the emission around 650 nm due to the excited state of the ME form was too weak to be observed.

For the above studies, the quantitative estimates were not performed for the following reasons: (1) since irradiation was not carried out during the recording of the

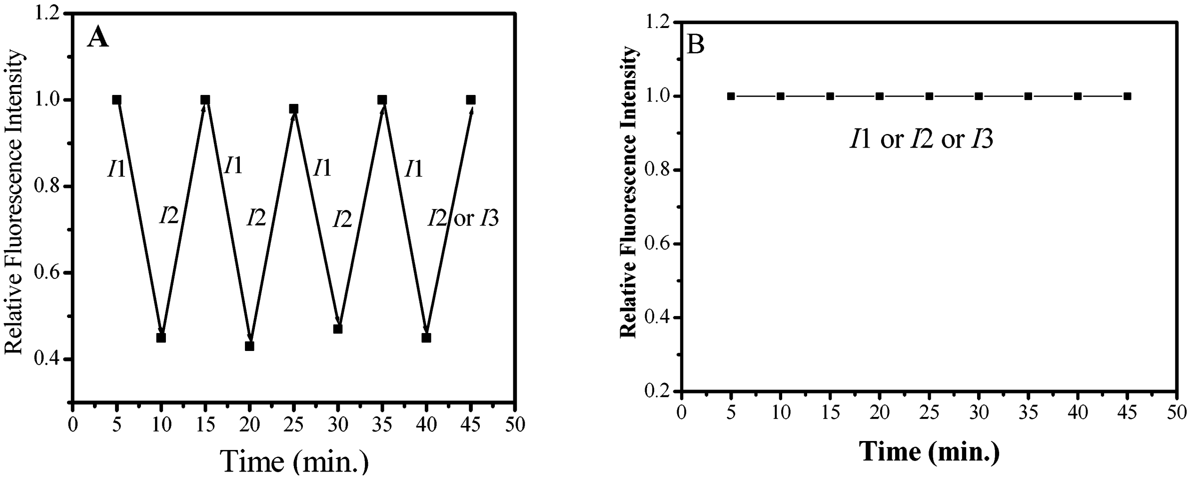
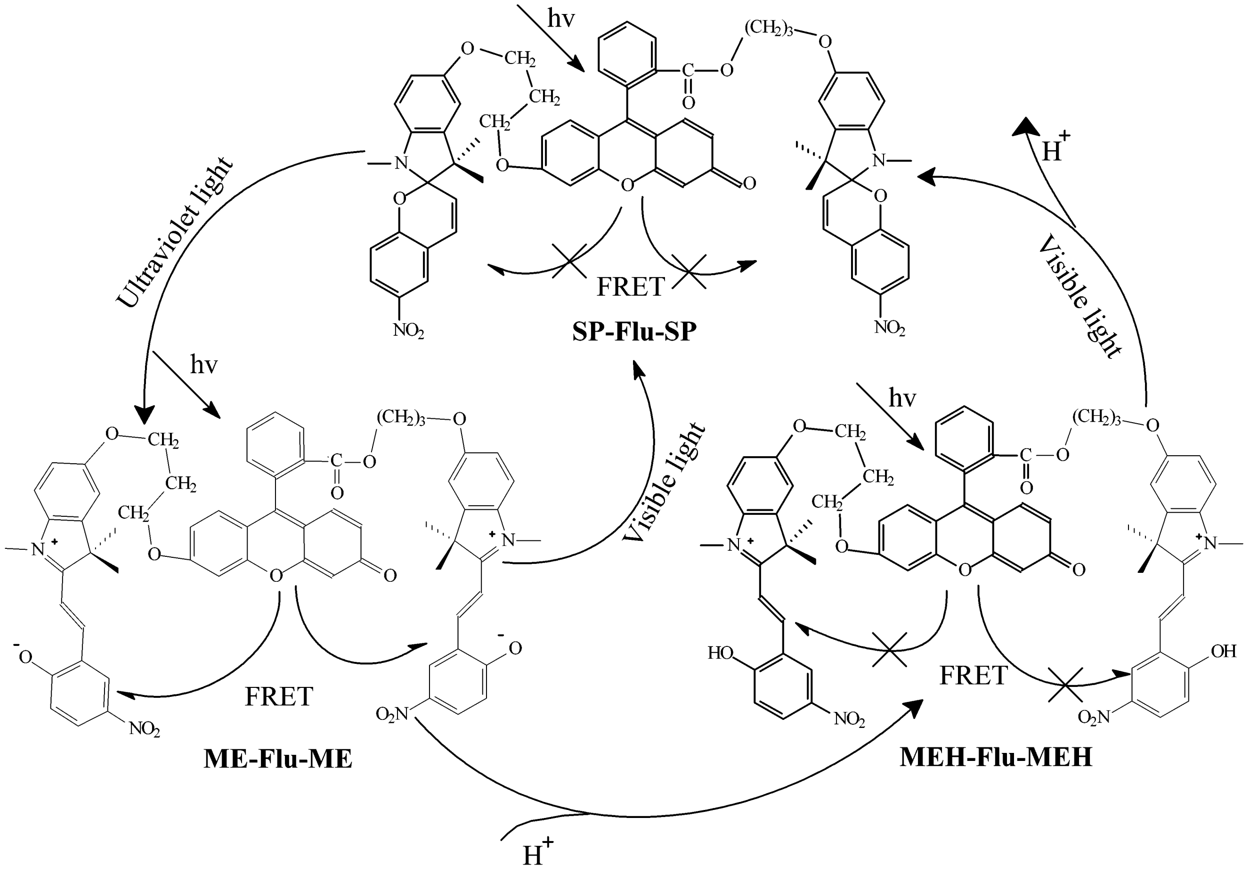


FIGURE 4. (A) Reversible modulation of the fluorescence intensity of the fluorescein unit at 550 nm for dyad **1** (5.0×10^{-5} M, THF, 25 °C) excited at 430 nm. (B) The relative fluorescence intensity of the reference compound **9** at 550 nm under the action of three external inputs; the excitation wavelength is 430 nm. The three inputs *I*1, *I*2, and *I*3 are UV light, visible light, and proton, respectively.

SCHEME 2 The Reversible Switching Cycle for Dyad 1 under the Action of Three External Inputs: UV Light, Visible Light, and Proton



fluorescent spectra, thermal reversion to the closed SP form may occur before and during the collection of the fluorescent spectra; (2) since both the SP and ME forms of the spiropyran units and the fluorescein unit absorb at 365 nm, irradiation at this wavelength causes only photostationary equilibrium of the two forms (SP and ME) of spiropyran units, rather than driving the system totally to one form; and (3) the overlap of the fluorescence bands of the ME form and fluorescein unit partially offsets the fluorescence quenching of the fluorescein moiety in the same wavelength region as mentioned above.

Analysis of the Information Transmission Pattern. The dependence of the fluorescent spectra of dyad **1** on the external stimulations—ultraviolet light, visible light, and proton—mimics the function of an integrated

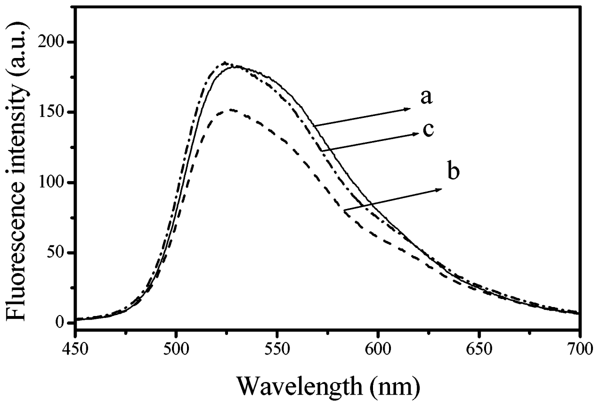


FIGURE 5. Fluorescence spectra of the mixture of **9** and **10** excited at 430 nm (5.0×10^{-5} M for **9**, 1.0×10^{-4} M for **10**, THF, 25 °C) (a) before and (b) after irradiation with ultraviolet light for 5 min and (c) after irradiation with ultraviolet light followed by addition of 2 equiv of CF_3COOH. For the UV irradiation experiment, a 140-W high-pressure mercury lamp (λ = 365 nm) was held above the cuvette containing the solution by about 3 cm.

logic gate.[1g–j,12] This behavior can be analyzed with the aid of binary logic.[13] The three input signals are *I*1 (ultraviolet light), *I*2 (visible light), and *I*3 (proton). The output signal is *O*1, the emission band at 550 nm of the fluorescein unit. Each signal can be either *off* or *on* and can be represented by a binary digit. Consequently, dyad **1** reads a string of three binary inputs and writes a specific output. For example, when the three input stimulations *I*1, *I*2, and *I*3 are *on*, *off*, and *off*, respectively, the input string is 100. Under these conditions, dyad **1** exists as the ME-Flu-ME (SP) form in solution, which has strong absorption bands in the visible range with a maximum at 580 nm. As a result, the excited state of the fluorescein unit is quenched and the fluorescence intensity is reduced. Hence, the output signal is *off*. And the output digit is 0. If both *I*1 and *I*3 are *on*, and *I*2 is *off*, the input string is 101. Under these conditions, dyad **1** is in the MEH-Flu-MEH (SP) state, which shows no absorption bands at wavelengths longer than 500 nm. Accordingly, the fluorescence intensity of the fluorescein unit returns to its initial value. Thus the output signal is *on*, and the digit is 1. All the possible strings of three binary inputs data and the corresponding output digit are included in the truth table as showed in Figure 6. The two entries in the truth table where both *I*1 and *I*2 are 1 imply that the sample is simultaneously irradiated by UV and visible light.

Input			Output
*I*1	*I*2	*I*3	*O*1
0	0	0	1
0	0	1	1
0	1	0	1
1	0	0	0
0	1	1	1
1	0	1	1
1	1	0	0
1	1	1	1

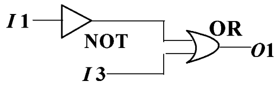


FIGURE 6. Truth table (up) for all the possible strings of three binary inputs data and the corresponding output digit, and the combinational logic circuit (below) corresponding to the truth table. *I*1, *I*2, *I*3, and *O*1 are ultraviolet light, visible light, proton, and the fluorescence of fluorescein unit at 550 nm. The output signal (*O*1) is *off* when the relative emission intensity at 550 nm is about 45% (relative to the initial value), and it is *on* when the relative intensity is 100%.

The combinational logic circuit equivalent to the truth table is also shown in Figure 6. It can be seen from the truth table (Figure 6) that *I*2 has no influence on *O*1, and thus the combinational logic circuit includes only the two inputs: *I*1 and *I*3. Then inputs *I*1 and *I*3 were transmitted into the output *O*1 through one OR operation and one AND logic operation in this circuit.

Besides the intensity reduction of the fluorescein fluorescence upon UV light irradiation of the solution of dyad **1**, a new broad emission band around 650 nm appears due to the absorption−energy transfer−emission (AETE)[14] process from the excited fluorescein unit to the ME forms. This emission band can be regarded as another output signal (*O*2). Compared with that of the fluorescein unit of dyad **1** in the SP-Flu-SP state (Scheme 2), this emission band is relatively weak.

Conclusion

Since the absorption spectrum of the ME form of spiropyran matches very well with the fluorescence spectrum of fluorescein, a new dyad **1** with two SP units and one fluorescein unit was designed for studies of the information transmission at the single molecular level. The fluorescence of this new dyad can be modulated by three inputs: ultraviolet light, visible light, and proton based on the resonance energy transfer mechanism. Thus, new dyad **1** can “read out” three external input signals and “write” a compatible specific output signal. This behavior corresponds to an integrated circuit with one OR and one AND logic gates. It should be noted that the communicating components are covalently linked, and as a result the energy transfer is more effective than

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(10) The two SP units are not symmetrically attached to the fluorescein unit in dyad **1**. Thus, under the action of UV light irradiation and acid, there exist seven possible states for dyad **1**: SP-Flu-SP, ME-Flu-SP, MEH-Flu-SP, SP-Flu-ME, SP-Flu-MEH, ME-Flu-ME, and MEH-Flu-MEH.

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that of the intermolecular case. These results will be useful for further molecular design of new dyads that will mimic the function of the complex logic gates. Searching for a new fluorophore whose emission spectrum has a large overlap with the absorption spectra of both ME and MEH forms (but, still the spectrum overlap of the fluorophore with the ME form is different from that with the MEH form) should have priority in our future work.

Experimental Section

1′,3′-Dihydro-5′-hydroxyl-1′,3′,3′-trimethyl-6-nitrospiro-[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (Compound 6). 6 was prepared from 4-methoxyphenylhydrazine hydrochloride according to ref 8. Mp > 280 °C; MS (EI) m/z 338 (M^+). Anal. Calcd for $C_{19}H_{18}N_2O_4$: C, 67.45; H, 5.36; N, 8.28. Found: C, 67.19; H, 5.48; N, 7.98.

9-(*o*-(3′-Bromopropyl)carboxyphenyl)-6-(3′-bromopropoxy)-3-xanthanone (Compound 8). To a solution of uranine (2.00 g, 5.32 mmol) in DMF (60 mL) was added 1,3-dibromopropane (5 mL) and anhydrous K_2CO_3 (7.35 g, 53.2 mmol). Then, the mixture was stirred at room temperature overnight before 200 mL of H_2O was added. The aqueous solution was extracted with dichloromethane (3 × 100 mL), and the combined extracts were washed with H_2O (2 × 50 mL) and saturated aqueous NaCl (20 mL), dried ($MgSO_4$), and concentrated in vacuo. After column chromatography on silica gel with ethyl acetate/petroleum (60−90 °C) (1:4, v/v) as eluant, **8** was obtained as red crystals (2.60 g) in 85% yield. Mp 107−108 °C. FTIR (KBr): 1721, 1642 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.89 (m, 2H), 2.40 (m, 2H), 3.11 (t, 2H, J = 6.5 Hz), 3.61 (t, 2H, J = 6.2 Hz), 4.14 (t, 2H, J = 5.6 Hz), 4.25 (t, 2H, J = 5.7 Hz), 6.51 (s, 1H), 6.58 (d, 1H, J = 9.2 Hz), 6.77 (d, 1H, J = 9.2 Hz), 6.90 (m, 2H), 7.00 (s, 1H), 7.32 (d, 1H, J = 7.6 Hz), 7.74 (m, 2H), 8.25 (d, 1H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$): δ 28.7, 29.3, 31.1, 31.6, 63.2, 66.1, 100.9, 105.6, 113.9, 114.8, 117.5, 128.9, 129.5, 129.7, 130.1, 130.2, 130.3, 131.2, 132.7, 133.9, 150.9, 154.3, 158.7, 163.4, 165.0, 184.9. EI MS: m/z 574 (M^+). Anal. Calcd for $C_{26}H_{22}O_5Br_2$: C, 54.38; H, 3.86. Found: C, 54.23; H, 3.87.

Dyad 1. To a solution of **8** (0.28 g, 0.49 mmol) in DMF (20 mL) was added **6** (0.33 g, 0.98 mmol) and anhydrous K_2CO_3 (1.35 g, 9.80 mmol). Then the mixture was stirred at room temperature for 2 days before 150 mL of H_2O was added. The aqueous solution was extracted with dichloromethane (3 × 70 mL), and the combined extracts were washed with H_2O (2 × 40 mL) and saturated aqueous NaCl (20 mL), dried ($MgSO_4$), and concentrated in vacuo. After column chromatography on silica gel with ethyl acetate/petroleum (60−90 °C) (3:2, v/v) as eluant, dyad **1** was obtained as yellow powder (0.22 g) in 42% yield. Mp 159−160 °C. FTIR (KBr): 1721, 1642, 1481 1338 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.19 (s, 6H), 1.28 (s, 6H), 1.82 (m, 2H), 2.33 (m, 2H), 2.70 (s, 3H), 2.71 (s, 3H), 3.71 (t, 2H, J = 5.6 Hz), 4.17 (m, 6H), 5.85 (d, 2H, J = 10.2 Hz), 6.47 (d, 2H, J = 10.2 Hz), 6.56 (d, 1H, J = 9.8 Hz), 6.63 (s, 1H), 6.76 (m, 7H), 6.90 (m, 4H), 6.99 (s, 1H), 7.32 (d, 1H, J = 7.7 Hz), 7.75 (m, 2H), 8.02 (m, 4H), 8.29 (d, 1H, J = 7.7 Hz). ^{13}C NMR ($CDCl_3$): δ 20.3, 26.2, 28.9, 29.6, 30.1, 52.8, 63.0, 64.9, 65.1, 65.9, 101.4, 106.3, 107.2, 107.5, 107.6, 110.5, 112.4, 112.7, 114.1, 115.3, 115.8, 118.1, 119.1, 121.8, 121.9, 123.1, 126.2, 128.6, 129.3, 130.1, 130.4, 130.6, 130.9, 131.8, 133.1, 134.7, 138.1, 138.2, 141.3, 142.4, 142.6, 153.5, 153.6, 154.6, 159.2, 160.2, 163.8, 165.8, 185.9. MALDI-TOF-MS: m/z 1089.2. Anal. Calcd for $C_{64}H_{56}N_4O_{13}$: C, 70.58; H, 5.18; N, 5.14. Found: C, 70.44; H, 5.08; N, 4.99.

1′,3′-Dihydro-5′-methoxy-1′,3′,3′-trimethyl-6-nitrospiro-[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (Compound 10).[15] **10** was prepared similarly as for compound **6** in 27% yield. Mp 149−150 °C. FTIR (KBr): 2957, 1482, 1336 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.21 (s, 3H), 1.29 (s, 3H), 2.71 (s, 3H), 3.82 (s, 3H), 5.88 (d, 1H, J = 10.3 Hz), 6.48 (d, 1H, J = 10.3 Hz), 6.76 (m, 3H), 6.94 (d, 1H, J = 9.8 Hz), 8.04 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 19.9, 25.8, 29.2, 52.4, 55.9, 106.8, 107.2, 109.6, 111.5, 115.5, 119.1, 121.6, 122.7, 125.9, 128.2, 137.8, 140.9, 141.9, 154.2, 159.9. EI MS: m/z 352 (M^+). Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.20; H, 5.55; N, 7.80.

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Supporting Information Available: General experimental methods; conditions for light irradiation experiments; characterization data for reference compound **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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