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Optic and proton dual-control of the fluorescence of Rhodamine based on photochromic diarylethene: mimicking the performance of an integrated logic gate

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ABSTRACT

A proton and optic dual-responsive fluorescence switch dyad which contains Rhodamine and photochromic diarylethene has been designed and an integrated logic circuit at the molecular level has been proposed.

Regulation of molecular fluorescence through external stimuli such as light, chemical, and electronic signals attracts much attention due to potential application in sensors,[1–3] switches,[4–6] high density optical data storage,[7] and logic gates.[8–11] In particular, the regulation of fluorescence properties based on the photochromic compounds has been studied extensively. The energy transfer (ET) from the fluorescent dye to one of the isomers of the photochromic switch is a powerful tool to modulate the fluorescence. A lot of examples have been reported by Irie,[12–14] Branda,[15] Tian,[16,17] and Feringa.[18] Furthermore, in order to construct multi-functional logic system, development of smart system in which the fluorescence can be tuned by several signals is much more important.[19,20]

Among various photochromic compounds, diarylethene has received much attention owing to the thermally irreversibility, excellent fatigue resistance, highly efficient photo-isomerizations and rapid response.[21] Upon irradiation by ultraviolet light, the colorless opened-form isomers can transfer to closed-form accompanied with the appearance of the new absorption. The absorption spectra of the closed-form depend on the substitutions of thiophene rings.[21] Thus, it is possible to regulate the emission intensity of the fluorophore through the optical stimuli when its emission spectrum overlaps the absorption spectrum of the diarylethene in closed-form, which functions as an ET acceptor.

Rencently, Rhodamine-based dyes have received increasing interest because they have several advantages: large molar extinction coefficients, high fluorescence quantum yields, and visible wavelength excitation.[22] In addition, the Rhodamine chromorphore has two distinct conformations: colorless spirocyclic form and red ring-open form. Commonly, the colorless spirocyclic forms turn to the open-ring forms when they are interacted with protons or metal ions accompanied with emission in visible region. Thus it is possible to modulate the fluorescence intensity of the Rhodamine by the chemical inputs.[23–25] In this Letter, we have designed and synthesized a dyad with covalently bonded Rhodamine and diarylethene. Rhodamnie existed in ring-open form shows emission in the range of 540–700 nm which has a certain overlap with the absorption of diarylethene in closed form whereas there is not in open form. Thus, the energy transfer process from Rhodamine unit (ET donor) to diarylethene unit (ET acceptor) will be regulated by the light.[26–28] Moreover, the emission intensity of the Rhodamine unit will be also modulated by the proton. Based on these results, an integrated digital circuit is proposed.

The synthetic route of the dyad is illustrated in Scheme 1. Compound **2**[29] and Rhodamine derivative **5**[30] were obtained according to described methods. Compound **3** was prepared by coupling *p*-bromoanisole to the bis(boronic ester) which obtained from compound **2** through Suzuki reaction.[31] Treatment of compound **3** with an excess amount of boron tribromide afforded **4** quantitatively, which subsequently reacted with compound **5** in DMF at 60 °C in the presence of anhydrous K_2CO_3 to give dyad **1** in good yield.

The photochromic behavior of the dyad **1** was studied by UV–vis absorption spectra and ^{1}H NMR. As shown in Figure 1, dyad **1** shows strong absorption in the UV region indicating that the diarylethene unit is in the opened form.[21] After irradiating the solution of dyad **1** in acetonitrile at 312 nm for 1.5 min, the colorless solution turned purple and new absorption bands centered at 360 nm and 518 nm were observed, indicating the formation of the closed form of the diarylethene moiety.[21] The process of photocyclization reaction was also monitored by ^{1}H NMR. After 90 min of irradiation, the photostationary state was reached and about 71% of the opened form (1O) converted to the closed form (1C). In the ^{1}H NMR spectrum of dyad **1**, a new peak appeared at upfield

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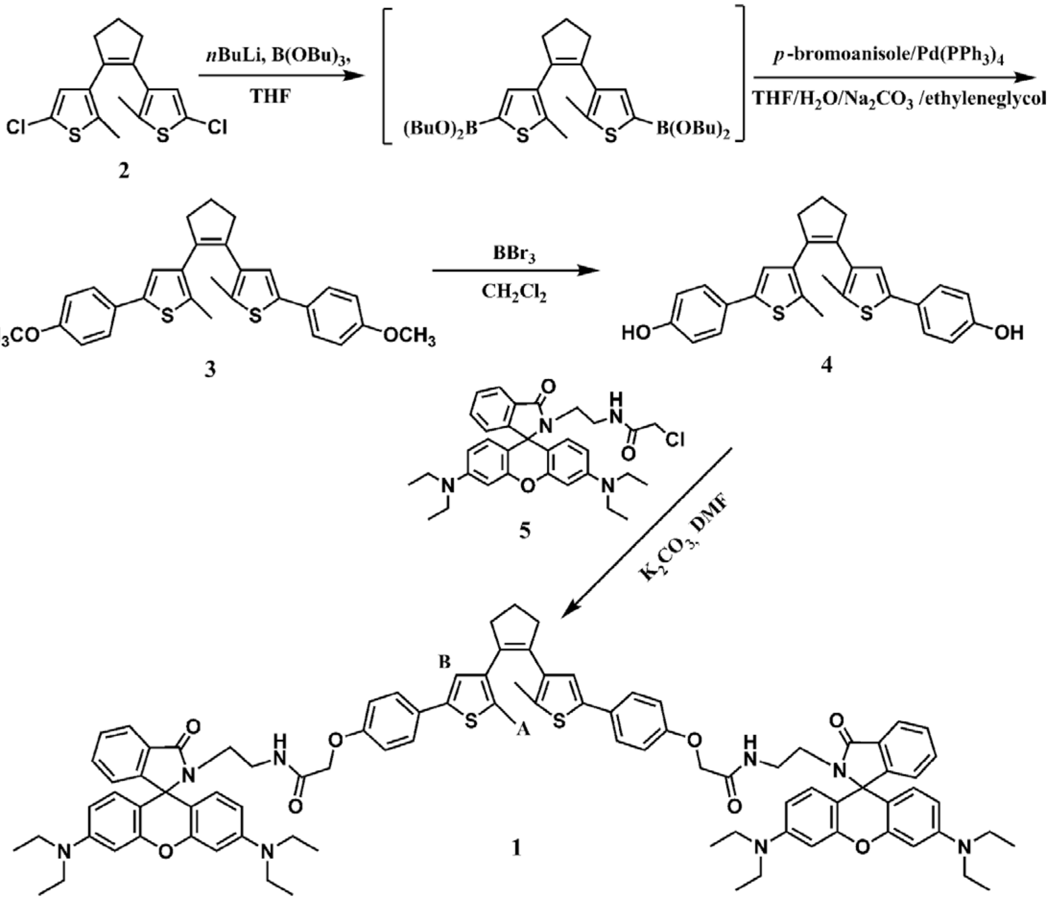


Scheme 1. Synthetic route for dyad **1**.

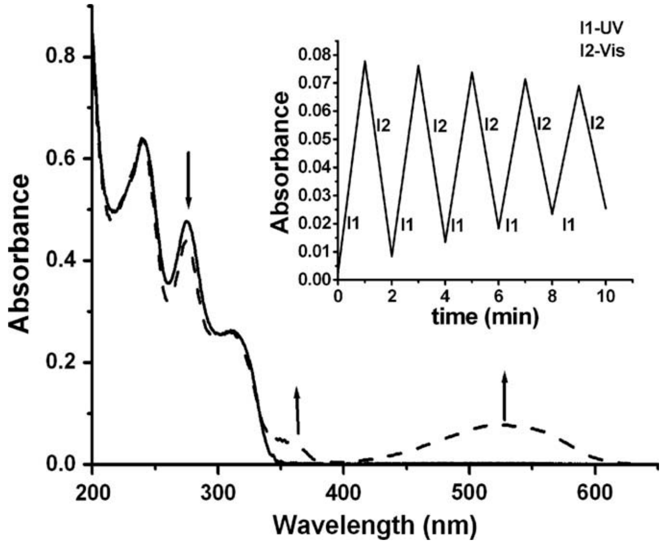


Figure 1. Absorption spectra of dyad **1** (5×10^{-6} M, CH_3CN, 25 °C) before (solid line) and after (dashed line) irradiation with light of 312 nm for 1.5 min. Inset: The absorption at 518 nm during alternate irradiation at 312 nm and visible light ($\lambda > 400$ nm) for 1.5 min.

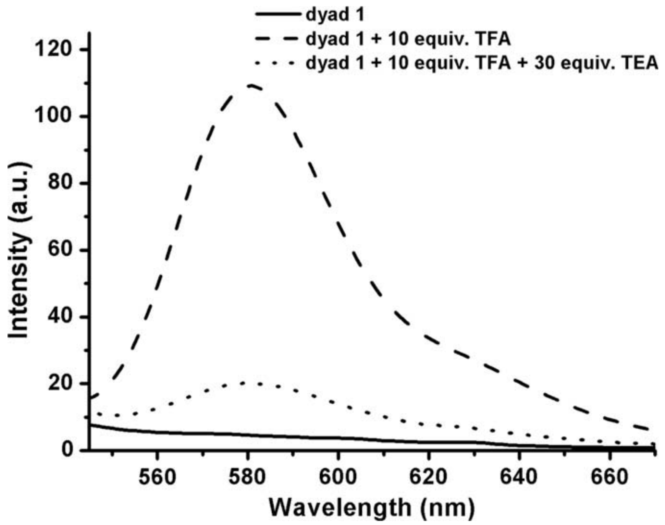
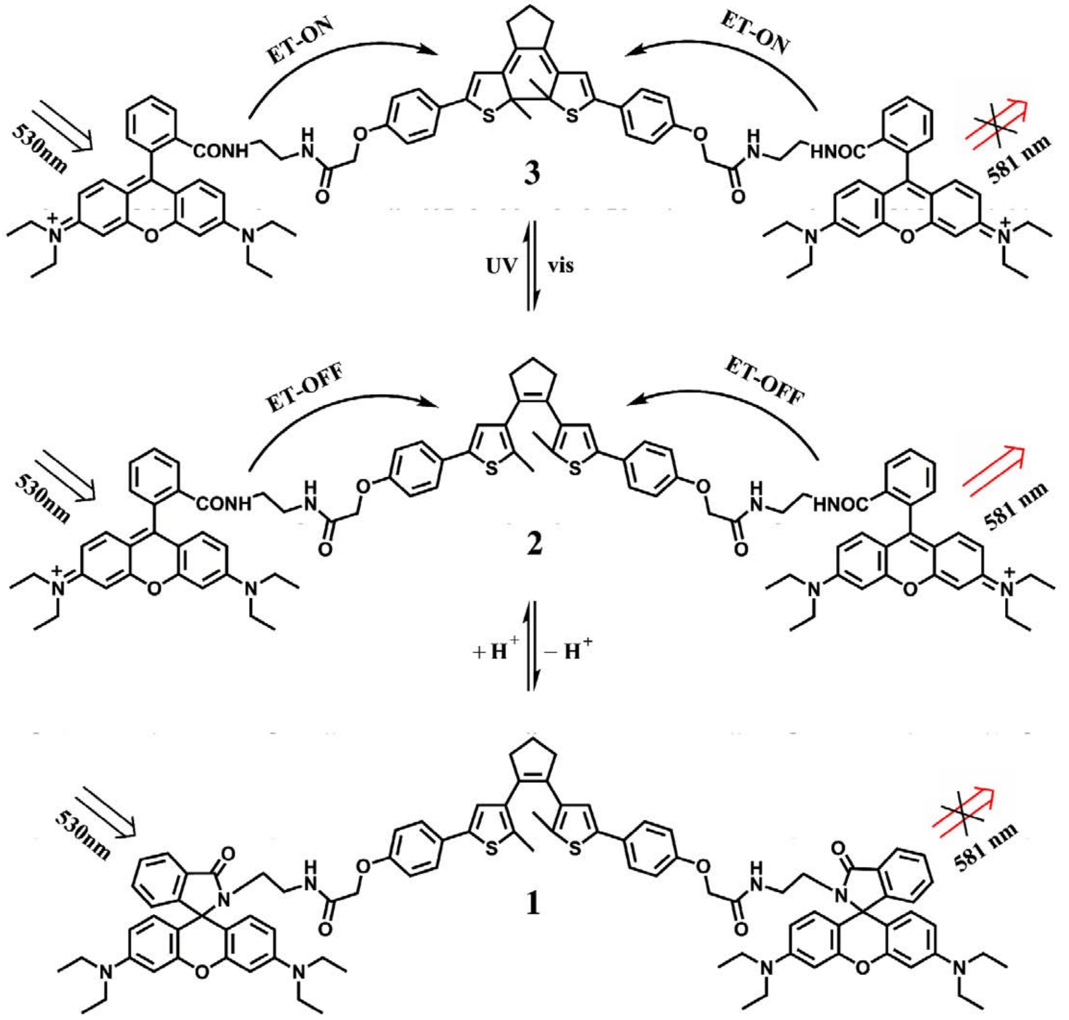


Figure 2. Emission spectra of dyad **1** (5×10^{-6} M, CH_3CN, 25 °C) in the presence of 10 equiv of TFA (5×10^{-3} M, CH_3CN), and 10 equiv of TFA + 30 equiv of TEA (5×10^{-3} M, CH_3CN) excited at 530 nm.

(1.85 ppm) assigned to the methyl group (H_a) of 1C[32] and the thiophene C–H (H_b) signal shift to the upfield (7.09 ppm for 1O, 6.60 ppm for 1C) which indicates the lose of the aromatic character of the thienyl moiety[33] (see Supplementary data). Upon irradiation of visible light ($\lambda > 400$ nm), the absorption band in the visible region almost completely disappeared which indicates the photochromic process is reversible. The inset of Figure 1 shows the change of absorption at 518 nm during alternate irradiation by ultraviolet light ($\lambda = 312$ nm) and visible light ($\lambda > 400$ nm). It indicates the dyad **1** can undergo several ring opening-closing cycles with slight fatigue in the absorption spectrum.



Scheme 2. The dual-mode fluorescence switching principle of dyad **1** with four external stimuli: UV light (λ = 312 nm), visible light (λ > 400 nm), TFA and TEA.

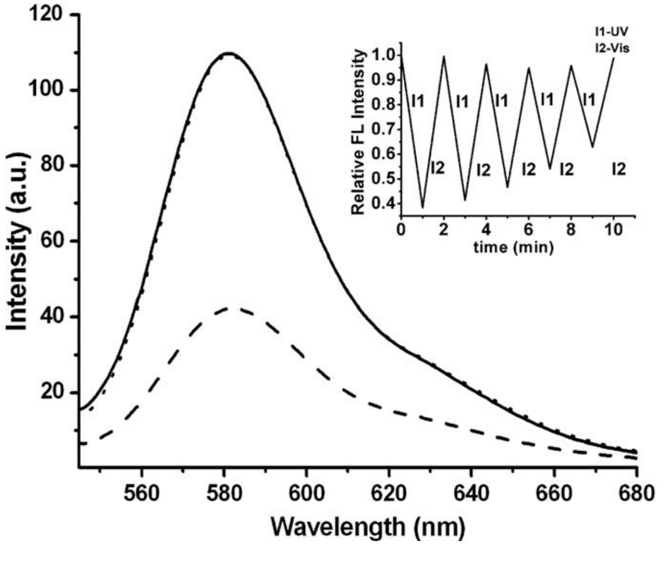


Figure 3. Emission spectra of dyad **1** (5×10^{-6} M, CH_3CN, 25 °C) in the presence of 10 equiv of TFA (5×10^{-3} M, CH_3CN) (solid line), irradiation with ultraviolet light (λ = 312 nm) for 1.5 min (dashed line) and irradiation with visible light (λ > 400 nm) for 1.5 min (dotted line). Inset: Reversible modulation of the emission intensity of dyad **1** (5×10^{-6} M, CH_3CN, 25 °C) in the presence of 10 equiv of TFA (5×10^{-3} M, CH_3CN) with the ultraviolet (I1) and visible light (I2), the excitation wavelength is 530 nm.

As expected, the emission intensity of the Rhodamine unit in dyad **1** can be tuned by chemical signals. Figure 2 shows the emission spectra of dyad **1** with excitation at 530 nm in CH_3CN upon addition of trifluroacetic acid (TFA) and triethylamine (TEA). Initially, the solution of dyad **1** in CH_3CN was nonfluorescent by excitation at 530 nm. Upon addition of 10 equiv of TFA, the color of the solution of dyad **1** became purple progressively and a broad emission band in the range of 540–680 nm with the maximum at 581 nm appeared due to the formation of the strongly fluorescent ring-opened Rhodamine. With addition of excess TEA to the solution, the Rhodamine unit switched to spirocyclic form and the intensity of the fluorescence at 581 nm decreased to 18% of that of the solution in acidic condition after reaching to the stationary state.

The fluorescence intensity of the dyad **1** can also be regulated reversibly by the alternation of ultraviolet and visible light stimuli. The emission spectrum of dyad **1** in CH_3CN under acidic condition recorded the transformation. After acidification, it appeared a broad emission band in the range of 540–680 nm with the maximum around 581 nm ascribed to the formation of the ring-opened amide form of Rhodamine (Fig. 3 solid line). The luminescence of dyad **1** in acidic condition greatly depends on the state of the diaylethene photoswitch. In the open form, the Rhodamine in acidic condition displayed strong fluorescence at 581 nm when excited at 530 nm. When the photocyclization reaction was carried out by irradiating the dyad **1** with ultraviolet light, the emission intensity around 581 nm decreased to 38% of that of initial state (Fig. 3

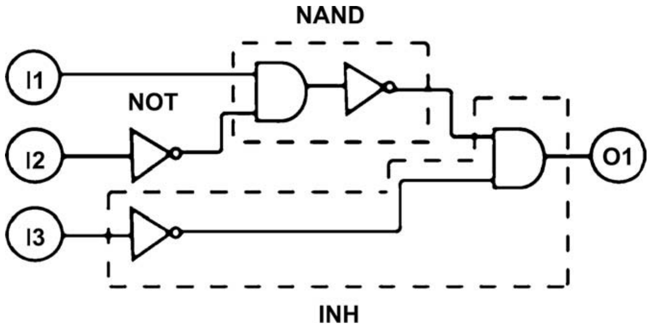


Figure 4. The combinational logic circuits equivalent to the truth table gave in Table 1.

Table 1
Truth table for all possible strings of three binary-input data and the corresponding output digit (combinational logic circuits corresponding to the truth table is given in Fig. 4)

Input			Output[a]
I1 (UV)	I2 (vis)	I3 (TEA)	λ_{em} = 581 (nm)
0	0	0	1
1	0	0	0
0	1	0	1
0	0	1	0
1	1	0	1
1	0	1	0
0	1	1	0
1	1	1	0

[a] At 581 nm, the emission intensity below 40% of the original value is defined as 0, otherwise defined as 1.

dashed line) due to the closed form formation of the diarylethene moiety. Upon irradiation with visible light, 1C switched back to 1O almost completely, the emission intensity returned to the original value (Fig. 3 dotted line). This fluorescence quenching maybe due to the intramolecular energy transfer from the excited Rhodamine unit to the closed diarylethene moiety because the spectral overlap between the emission band of the Rhodamine unit and the enhanced absorption band of the closed diarylethene moiety in dyad **1** (see Supplementary data).[26–28] In addition, this emission change was not observed when mixing the compound **3** and **5** (molar ratio of 1:2) in acidic condition in CH_3CN upon ultraviolet light irradiation (see Supplementary data), so the trivial or radiative energy transfer can be ignored. It is obvious that the modulation of the emission intensity of the Rhodamine unit by alternate ultraviolet and visible light is fully reversible and it can be cycled in several times (inset of Fig. 3).

As shown above, the emission intensity of the Rhodamine could be modulated by the chemical and light stimuli independently. The dual-mode fluorescence switching principle of dyad **1** is summarized in Scheme 2.

The dependence of the fluorescence of dyad **1** on the external stimuli: ultraviolet, visible light, and chemical signals can be described with the aid of binary logic.[34–36] The dyad **1** in acidic condition which exhibited strong fluorescence was regarded as the initial state. The three inputs signals are I1 (ultraviolet light), I2 (visible light), and I3 (TEA). The output signal is O1 (the emission band at 581 nm). The input signals I1, I2 and I3 can be either off or on. Similarly, the output signal can be considered off when the relative emission intensity at 581 nm is below 40% of the original value and on when it is 100%. The binary digits (0 or 1) can be explored to represent the two levels (off and on).

Thus, the dyad **1** can read a string of three inputs and write a unique fluorescence output. For example, when the input string is 100, corresponding to the I1, I2 and I3 are on, off, off, respectively. Under these conditions, the dyad **1** is in state 3 and the fluorescence of the Rhodamine unit is quenched. Hence, the output signal is off. If the I1, I2 and I3 are all off, the input string is 000. Under these conditions, the dyad **1** is in state 2 and the relative intensity of the fluorescence is 100%. Thus, the output signal O1 is on and the output digit is 1. All the possible strings of the three inputs are listed in Table 1 and the combinational logic circuits equivalent to the truth table is illustrated in Figure 4.

In conclusion, a novel dyad **1** with proton-sensitive and photochromic components has been synthesized and characterized. The emission intensity of the dyad **1** can be regulated by chemical and optical stimuli. Based on the fact, an integrated digital circuit with three external input signals and one fluorescence output signal was constructed and the information transmission at the single molecular level was realized.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.01.093.

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