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A proton and optic dual-control molecular switch based on photochromic diarylethene bearing a rhodamine unit

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ABSTRACT

A novel fluorescent switch based on rhodamine B and photochromic diarylethene, 1-[2-methyl-5-(4-methoxylphenyl)-3-thienyl]-2-[2-methyl-5-(4-rhodamine B hydrazine-Schiff base-phenyl)-3-thienyl]perfluorocyclopentene (**1**), has been successfully synthesized through the condensation of rhodamine B hydrazine and 1-[2-methyl-5-(4-methoxylphenyl)-3-thienyl]-2-[2-methyl-5-(4-formylphenyl)-3-thienyl] perfluorocyclopentene. UV and FL measurements reveal that the compound exhibits good photochromic properties responsive to proton and optic dual inputs. Upon irradiation with 297 nm light, the colorless solution of compound **1** turns blue, while the blue solution becomes colorless after irradiated with visible light ($\lambda>450$ nm). Furthermore, upon an addition of H^+, the fluorescence resonance energy transfers from the rhodamine unit (FRET donor) to the closed-ring diarylethene unit (FRET acceptor), although no energy transfer occurs when the diarylethene is in the open-ring form. The emission intensity of the rhodamine can be modulated with proton and UV/vis light and molecular-level signal communication has been constructed, indicating high potentials of the compound in molecular switches or naked eye recognition systems.

1. Introduction

Recently, photochromic compounds have attracted more and more attention due to their unique characteristics in simulating functional electronic components. Open-ring and closed-ring isomers of photochromic compounds, corresponding to colorless and colored modes when stimulated with UV/vis light, can represent '0' and '1' of digital codes homologous to 'on' and 'off' states, respectively.[1] Among various photochromic compounds, diarylethenes bearing two thiophene/benzothiophene rings are regarded as the best candidates for photonics applications, such as optical memories[2] and photoswitches,[3] owing to their excellent thermal stability, remarkable fatigue resistance, and rapid response.[4] In the field of photochromic complex molecular systems, integrating several switchable groups within a single molecule to form molecular switches is especially attractive. In this regard, various approaches to switching systems based on diarylethenes have been proposed in recent years.[5]

Because of their high fluorescence quantum yields, large molar extinction coefficients, and visible wavelength excitation, rhodamine dyes are widely employed to construct fluorescent probes[6] and chemosensors.[7] Rhodamine derivatives can undergo equilibrium between a colorless spirolactam (no fluorescence) form and a red open-ring form (strong fluorescence) when protons or metal ions are bound to the host compound. In view of virtue of diarylethenes and rhodamine, their combination is promising in developing a dual-control fluorescence resonance energy transfer (FRET) system. FRET is a typical process where fluorescence energy transfers from an excited fluorophore group (donor) to another chromophore unit (acceptor) via a link distance of 1–10 nm. Such occurrence, however, requires that the acceptor characteristic absorption band overlaps the emission of the donor. Therefore, reports about photochromic diarylethene and fluorophore functionalized to form FRET molecular are still lacking. Zheng et al. reported a dual-control perhydrogencyclopentene–diarylethene switching molecule using rhodamine as a fluorophore donor and the closed-ring form of diarylethene as an acceptor, and, however, the stability and fatigue resistance were found to be unsatisfactory.[8] Similarly, Tian et al. employed perhydrogencyclopentene as a control molecule and a naphthyl moiety as a fluorescence donor to construct a multistimulus that responded to UV irradiation, proton, and copper ions.[9] Giordano et al. studied a series of photochromic FRET molecules based on perfluorocyclopentene as acceptors and naphthyl fluorophore derivatives as donors, but only found them to possess no proton and light control response, presumably because naphthyl fluorophore has no proton capture capability.[10]

Herein we synthesize a novel proton and optic dual-control fluorescent switch containing photochromic perfluorocyclopentene and rhodamine B moieties, 1-[2-methyl-5-(4-methoxylphenyl)-3-thienyl]-2-[2-methyl-5-(4-rhodamine B hydrazine-Schiff base-phenyl)-3-thienyl]perfluorocyclopentene (**1**), and explore its proton and light dual-control responses.

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2. Results and discussion

2.1. Photochromism of compound 1

Diarylethene **1** can undergo a reversible photochromism reaction in DMSO upon alternating irradiation with UV and visible light (Scheme 1). Changes in the absorption spectra of compound **1** induced by photoirradiation at room temperature in DMSO (C=2.0×10^{-5} mol/L) are shown in Fig. 1. The absorption maximum of compound **1O′** (see Scheme 1) is observed at 276 nm (ε=4.12×10^{4} L mol^{-1} cm^{-1}). Upon irradiation with 297 nm light, the colorless solution of **1O′** turns blue due to the appearance of a new visible absorption band centered at 618 nm (ε=1.11×10^{4} L mol^{-1} cm^{-1}) attributable to the formation of the closed-ring form **1C**. After irradiation for 30 min under UV light, a photostationary state (PSS) is reached and about 66% of the open-ring form (**1O′**) is converted to the closed-ring form (**1C′**) as evidenced by ^{1}H NMR results. For open-ring **1O′**, a peak at 3.83 ppm is assigned to the ^{1}H resonance of $-OCH_3$. After the formation of PSS, a noticeable new peak at 3.86 (H signal shift of $-OCH_3$) appears, indicative of the formation of a new closed-ring compound **1C′**. On the other hand, the blue solution turns colorless upon irradiation with visible light (λ>450 nm) for 2 min, indicating that **1C′** returns to its initial form **1O′**, and a clear isosbestic point is observed at 364 nm. Such coloration–decoloration cycles can be repeated more than 50 times. In order to clarify the difference before and after the introduction of the rhodamine dye moiety into the diarylethene, compound **2** (Scheme 1) was studied under the same measurement conditions. As revealed in Fig. 2, the absorption maximum in the open- and closed-ring forms are 314 (ε=1.78×10^{4} L mol^{-1} cm^{-1}) and 618 nm (ε=9.68×10^{3} L mol^{-1} cm^{-1}), respectively, while a clear isosbestic point is observed at 348 nm. Apparent differences exist between the photochromic properties of compounds **1** and **2**. Diarylethene **1** exhibits a larger molar coefficient in either the open- or closed-ring forms than those of **2**, while displays a smaller absorption maximum in the open-ring form than that of **2**. This observation could be attributed to the substituent effect induced by the rhodamine unit. Similar substitution effects on the photochromic properties of diarylethene derivatives have been reported in our previous studies.[11]

2.2. Photon-control photochromism of compound 1

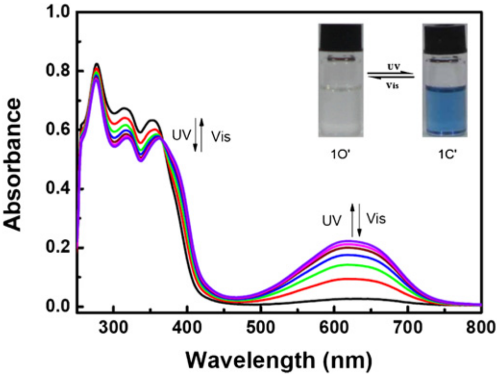


Fig. 1. Changes in the absorption spectra of compound **1** in DMSO at room temperature (C=2.0×10^{-5} mol/L). Inset: color change of compound **1** upon alternating irradiation with UV/vis light in DMSO.

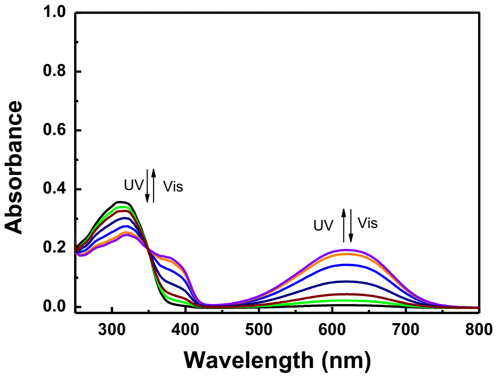
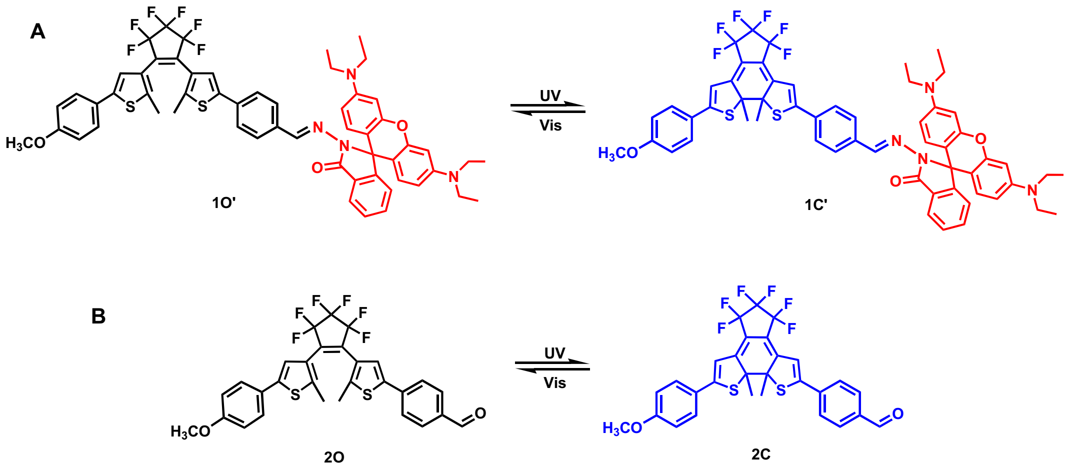


Fig. 2. Changes in the absorption spectra of compound **2** in DMSO at room temperature (C=2.0×10^{-5} mol/L).

Rhodamine derivatives undergo equilibrium between the colorless spirolactam form and the red open-ring form. The two forms feature completely different spectrophotomatric properties when protons or metal ions are bound to the host compounds: the spirolactam form is non-fluorescent and non-absorbing, while the open-ring form has strong fluorescent emission. The emission intensity of compound **1** can thus be tuned with proton, and the emission spectra of **1** (C=2.0×10^{-5} mol/L) are shown in Fig. 3A with excitation at 520 nm in DMSO after alternating additions of trifluoroacetic acid (TFA) and triethylamine (TEA). Initially the **1O′** DMSO solution is non-fluorescent with excitation at 520 nm. Upon addition of TFA gradually (0.1 μL each time) up to 30 equiv (~1.0 μL), the color of the **1O′** solution becomes red progressively and an obvious increase is found in fluorescent emission for **1O** at about 586 nm, due to the formation of the open-ring amide form of **1O**,



Scheme 1. Photochromism of diarylethenes **1** (A) and **2** (B).

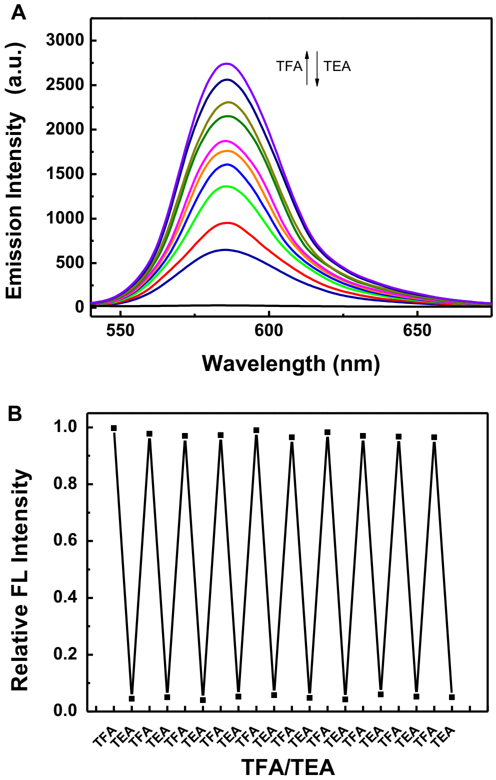


Fig. 3. Fluorescent changes (A) and switch cycles (B) of compound **1** (C=2.0×10^{-5} mol/L) induced by alternating additions of TFA and TEA in DMSO excited at 520 nm and detected at 586 nm at room temperature.

whose characteristic absorption is centered at 565 nm. Its absorption intensity increases with increasing amount of TFA. As the absorption intensity reaches the maximum, the fluorescence intensity also peaks with a fluorescent quantum yield of 0.103 using anthracene as a reference.[12] The gradual back addition of TEA up to 50 equiv (~3.0 μL) regenerates the spirolactam form of rhodamine (see Fig. 4 for changes in the absorption spectra upon alternating addition of TFA and TEA, where the addition amount of the latter is more than that of the former), while the fluorescent intensity decreases as the original emission spectra recover simultaneously. Shown in Fig. 3B is the reversible modulation of the fluorescent emission intensity of compound **1** with alternating additions of TFA and TEA; the results indicate that the fluorescent switch cycles can be repeated many times with only a slight degradation observed. The results also suggest that the stability and fatigue resistance of perfluorocyclopentene–diarylethene have been improved markedly compared with a perhydrogencyclopentene–diarylethene molecular switch.[8]

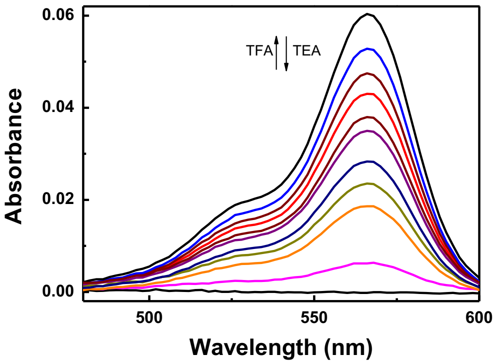


Fig. 4. Changes in the absorption spectra of compound **1O** in DMSO (C=2.0×10^{-5} mol/L) with alternating additions of TFA and TEA at room temperature.

2.3. Optic-control photochromism of compound 1

Diarylethene derivates usually afford different color changes upon alternating irradiation with UV/vis light. Because of these features, the combination of diarylethene with a chemo-responsive dye offers a promising approach to the design of optical molecular switches.[8,9] In this study, we record spectral modulation of compound **1O** (**1O′** in the presence of TFA) using UV/vis light and FL techniques. Fig. 5A depicts the fluorescent changes of compound **1O** (C=2.0×10^{-5} mol/L, the addition quantity of TFA is 30 equiv (~1.0 μL)) with excitation at 520 nm in DMSO under alternating irradiation with UV/vis light. The results show that the fluorescent emission of **1O** can also be modulated reversibly and undergo reversible photochromism upon alternating irradiation with UV/vis light. Under acidic condition, **1O** exhibits a strong fluorescent emission at 586 nm ascribed to the formation of the open-ring rhodamine amide. The emission intensity is greatly dependent on the status of the diarylethene whether in the open- or closed-ring forms. When the photocyclization reaction is carried out on the diarylethene unit upon irradiation with UV light, the formation of the closed-ring form results in decreased emission intensity at 586 nm with the increasing UV irradiation time. After reaching the photostationary state, the emission intensity of **1C** is quenched to only ~ 17% of its original intensity and the FRET efficiency is close to 100%.[10,13] Such fluorescence quenching is likely due to the intramolecular fluorescence resonance energy transfer from the open-ring rhodamine amide unit to the closed-ring diarylethene unit, since FRET is a typical process where fluorescence energy transfers

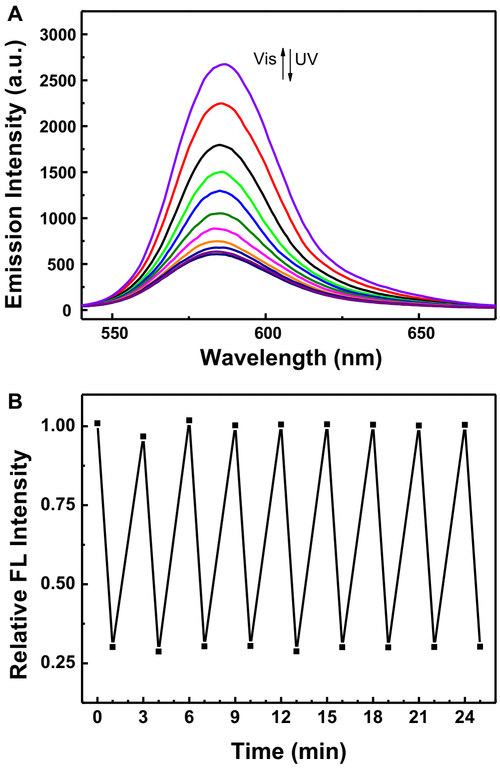


Fig. 5. Fluorescent changes (A) and switch cycles (B) of compound **1** (C=2.0×10^{-5} mol/L) in the presence of 30 equiv (~1.0 μL) of TFA upon alternating irradiation with 297 nm ultraviolet light and visible light (λ>400 nm), in DMSO excited at 520 nm and detected at 586 nm at room temperature.

from an excited fluorophore group (donor) to another chromophore unit (acceptor) via a link distance of 1–10 nm. The process requires that the characteristic absorption band of the acceptor overlaps the emission of the donor.[10,14] Because the emission band (550–650 nm) of rhodamine in the open-ring state has certain overlap with the absorption band (550–750 nm) of the closed-ring form of diarylethene, the FRET process occurs. Subsequent back irradiation with visible light (λ>450 nm) regenerates the open-ring form of diarylethene and recovers the original emission spectra. Furthermore, the modulation of the emission intensity of **1O** upon alternating irradiation with UV/vis is reversible and the fluorescent switch cycles can be repeated several times as shown in Fig. 5B. Compound **1O** is also found to have good stability and fatigue resistance. Absorption changes of compound **1O** are illustrated in Fig. 6 corresponding to the repeated irradiation. Due to the appearance of a new visible absorption band centered at 618 nm, the red solution of **1O** turns blue upon irradiation with 297 nm light. The blue solution changes back to red upon irradiation with visible light (λ>450 nm), indicating that **1C** has returned to the initial state of **1O**.

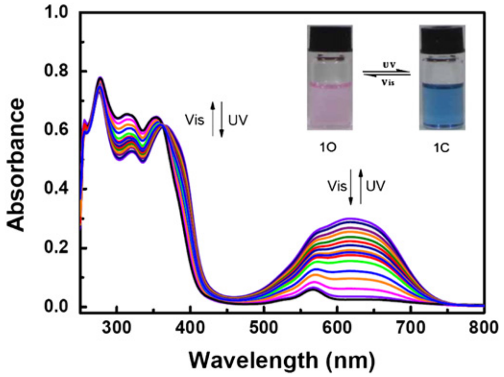


Fig. 6. Absorption changes of compound **1O** (**1O′** in the presence of 30 equiv (~1.0 μL) of TFA, $C=2.0\times10^{-5}$ mol/L) in DMSO upon alternating irradiation with 297 nm ultraviolet light and visible light (λ>400 nm). Inset: color change of **1O** upon alternating irradiation with UV/vis light in DMSO.

2.4. Logic circuit with compound 1

If compound **1O′** in acidic condition is regarded as the initial state, the fluorescence changes of compound **1** can be combined as a molecular switch with three inducing inputs: I1 (297 nm UV light), I2 (450 nm visible light), and I3 (TEA). The responding output signal is the emission at 586 nm. The output is off when the fluorescent intensity at 586 nm is quenched to 17% of the original value, with the original value signaling on. The molecular switch in compound **1** can read a string of three inputs and give a specific output. For example, when the input string 001 is corresponding to off, off, and on in I1, I2, and I3, respectively, the output of compound **1** is off and the fluorescence is quenched. Similarly, when the string is 010, 000, 100, 101, 110, 111, and 011, the output is 1, 1, 0, 0, 1, 0, and 0, respectively. The corresponding fluorescent and molecular structure change schematics are shown in Fig. 7. Upon an addition of H^+ to compound **1O′**, the molecule exhibits strong red fluorescence at 586 nm when excited at 520 nm, which is ascribed to the characteristics of the open-ring rhodamine amide. The subsequent irradiation with 297 nm UV light weakens the fluorescence sharply, owing mainly to the formation of the closed-ring diarylethene and thus resulting in fluorescence transfers from the dye donor to the closed-ring diarylethene acceptor. In other words, the emission intensity of the compound can be modulated with proton and UV/vis light with good stability and fatigue resistance. At the same time, the color change responsive to both light and chemical inputs is desired to be visible to naked eye. For example, upon irradiation with 297 nm UV light, the colorless open-ring isomer **1O′** induces a ring-closure reaction and evolves into the blue color of the closed-ring isomer **1C′**. The blue solution returns to colorless upon irradiation with visible light because **1C′** goes back to the initial state **1O′**. Furthermore, upon addition of H^+, the colorless **1O′** solution becomes red due to the formation of the open-ring amide **1O**, and the subsequent irradiation with UV light yields the blue **1C** solution,

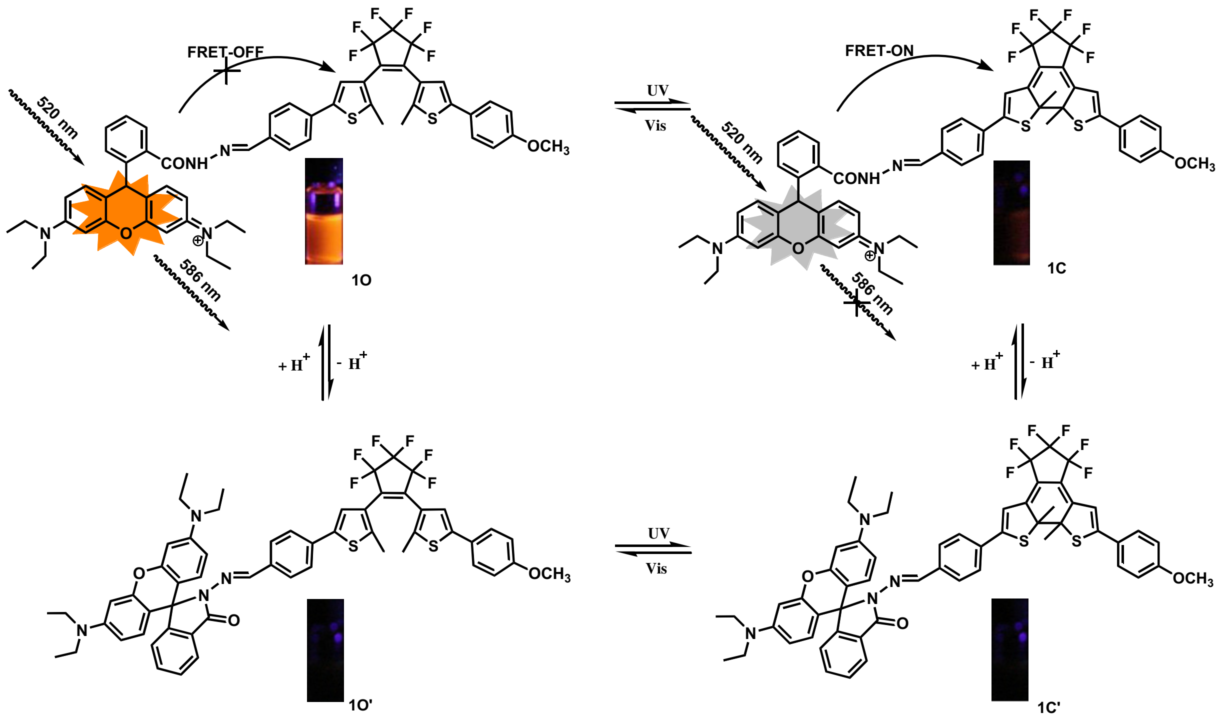
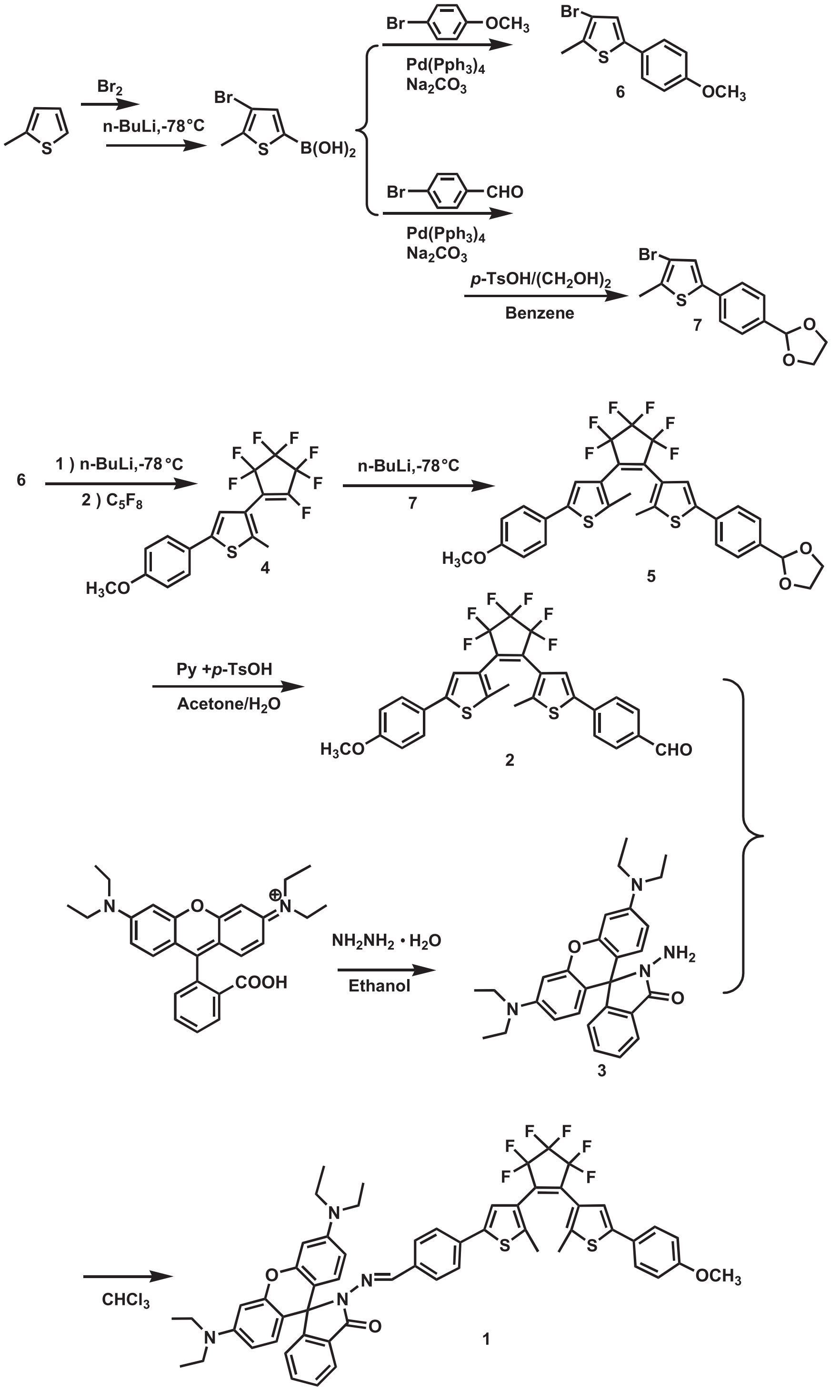


Fig. 7. Schematics of molecular structures and fluorescence changes with proton and optic stimuli.

which further changes to red upon back irradiation with visible light. These observations demonstrate that the compound has great potentials as a molecular switch.[15]

3. Conclusion

In the current paper, we have synthesized a novel fluorescent molecular switch, 1-[2-methyl-5-(4-methoxylphenyl)-3-thienyl]-2-[2-methyl-5-(4-rhodamine B hydrazine-Schiff base-phenyl)-3-thienyl]perfluorocyclopentene (**1**), using rhodamine B as a fluorophore and perfluorodiarylethene as a photochromic group. The compound exhibits good photochromic, and proton and optic dual-control properties. The fluorescent emission intensity of compound **1** can be modulated with proton and UV/vis light stimuli, and the fluorescent switch cycles can be repeated many times. A molecular-level signal communication system is constructed using three external inputs and one optical output. These results demonstrate that compound **1** has great potentials as a molecular switch and



Scheme 2. Synthetic route to compound **1**.

a naked eye recognition system in virtue of its color changes upon light or proton stimuli.

4. Experimental

4.1. General methods

NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer using CDCl$_3$ as a solvent and tetramethylsilane as an internal standard. UV/vis spectra were recorded on a Perkin–Elmer Lambda 900 spectrometer. Photoirradiation was carried out using an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. Lights of appropriate wavelengths were isolated using different light filters. Luminescence spectra were measured on a HITACHI 4500 fluorescence spectrophotometer. The luminescence quantum yield in solution was measured using anthracene (Φ=0.27 in DMSO) as a reference. All solvents used were of spectro-grade and purified by distillation prior to use.

4.2. Synthesis

The rhodamine-based perfluorodiarylethene derivative, 1-[2-methyl-5-(4-methoxylphenyl)-3-thienyl]-2-[2-methyl-5-(4-rhodamine B hydrazine-Schiff base-phenyl)-3-thienyl]perfluorocyclopentene (**1**), was synthesized from rhodamine B hydrazide and perfluorodiarylethene in 75% yield. Compound **1** and other intermediate products were confirmed structurally by ^{1}H and ^{13}C NMR spectroscopy. Their synthetic route is summarized in Scheme 2 and experimental details were carried out as follows.

4.3. Synthesis of compound 1

To a stirred solution of 1-[2-methyl-5-(4-methoxylphenyl)-3-thienyl]-2-[2-methyl-5-(4-formylphenyl)-3-thienyl]perfluorocyclo pentene (**2**, 0.80 g) and rhodamine B hydrazine (**3**, 0.65 g) in 80 mL of chloroform, a few drops of acetic acid were added to catalyze the reaction at room temperature and under a nitrogen atmosphere. After stirring for 10 min, the reaction mixture was heated to 85 °C and refluxed for 72 h; it was then allowed to warm to room temperature. The mixture solution was subsequently washed with dilute NaOH solution and extracted with CHCl$_3$, and the organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, v/v=1/6) to give pure product 1.05 g in 75% yield. Mp 170–171 °C. ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 1.15 (t, 12H, J=6.0 Hz), 1.91 (s, 3H), 1.95 (s, 3H), 3.29–3.35 (q, 8H, J=8.0 Hz), 3.83 (s, 3H), 6.23–6.26 (m, 2H), 6.44–6.53 (m, 4H), 6.89 (s, 1H), 6.91 (s, 1H), 7.12 (s, 1H), 7.14 (s, 1H), 7.24 (s, 1H), 7.42–7.55 (m, 8H), 7.99 (d, 1H, J=8.0 Hz), 8.72 (s, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz), δ (ppm): 12.62, 14.40, 14.50, 44.32, 55.38, 66.24, 97.97, 106.30, 108.04, 114.41, 121.29, 122.79, 123.34, 123.93, 125.30, 125.65, 126.20, 126.93, 128.03, 128.30, 129.63, 133.29, 134.25, 141.71, 142.21, 146.68, 148.98, 151.56, 153.30, 159.55, 164.87. MS (ESI) m/z 1017.2 (M+H).

4.4. Synthesis of compound 2

Compound **2** was synthesized according to a similar method in our previous report.[11f,16] Mp 141–142 °C. ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 1.95 (s, 3H), 2.00 (s, 3H), 3.83 (s, 3H), 6.90 (s,1H), 6.92 (s,1H), 7.15 (s,1H), 7.45 (t, 3H, J=8 Hz), 7.69 (d, 2H, J=8 Hz), 7.89 (d, 2H, J=8 Hz), 10.00 (s, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz), δ (ppm): 14.47, 14.46, 55.39, 114.44, 116.20, 121.20, 124.54, 125.17, 125.58, 125.80, 126.09, 126.49, 126.95, 127.27, 128.73, 129.97, 130.50, 135.44, 136.94, 138.93, 140.25, 140.49, 142.44, 143.37, 159.62, 191.24. MS (ESI) m/z 578.4 (M+H).

4.5. Synthesis of compound 3

Compound **3** was synthesized according to the reference.[7b,17] In a 250 mL flask equipped with a condenser and a stirrer, rhodamine B (3.00 g) was dissolved in 150 mL of ethanol. Hydrazine hydrate (85%, 7.0 mL) dissolved in 10 mL of ethanol was added dropwise with vigorous stirring at room temperature. After the addition, the stirred mixture was refluxed for 4 h, while the solution color changed from dark purple to light orange. The mixture was then cooled and ethanol was removed under reduced pressure. To the mixture was slowly added HCl (1.00 M) in the flask to generate a clear red solution. Subsequently, NaOH (1.00 M) was introduced slowly with stirring until the pH of the solution reached 9–10. The resulting precipitate was filtered, washed with water, and then dried in vacuum. A product of compound **3** (2.22 g) was obtained as a pink solid in 73% yield. Mp 176–177 °C. ^{1}H NMR (CDCl$_3$, 400 MHz), δ (ppm): 1.09 (t, 12H, J=6.8 Hz), 3.24–3.29 (q, 8H, J=6.7 Hz), 3.53 (s, 2H), 6.22 (d, 2H, J=8.0 Hz), 6.34–6.40 (m, 4H), 7.03(d, 1H, J=8.0 Hz), 7.38 (t, 2H, J=4.0 Hz), 7.86 (d, 1H, J=4.0 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz), δ (ppm): 12.62, 44.37, 65.91, 98.00, 104.63, 108.05, 122.99, 123.83, 128.09, 130.06, 132.49, 148.90, 151.57, 153.86, 166.14. MS (ESI) m/z 456.3 (M+H).

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