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PAPER

Multi-addressable molecular switches based on photochromic diarylethenes bearing a rhodamine unit

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Two novel diarylethene derivatives bearing a rhodamine unit have been successfully synthesized. Their unique multi-addressable switching characteristics as induced by chemical and optical dual inputs stimulation were observed using UV and FL measurements. The two diarylethenes showed excellent photochormism with alternating UV/vis light irradiation. Addition of trifluoroacetic acid (TFA) protonated the diarylethenes, which resulted in good photochromism and notable fluorescence change *via* the FRET mechanism. Subsequent addition of triethanolamine base would neutralize and return both their protonated open-ring and closed-ring isomers to their original forms. It was found that the diarylethene bearing a rhodamine unit linked by a benzhydrazide bridge group was more sensitive, efficient and reacted faster to protonation by TFA when compared to the benzamide bridged derivative. Furthermore, the benzhydrazide bridged diarylethene derivative was found to be selective towards Cr(III), Al(III), or Ca(II) with significant color and fluorescence changes.

Introduction

Recently, the regulation of fluorescent molecules, which can be converted from one state to another by external stimuli such as light, chemical reaction and electric signals, has attracted more and more attention due to their potential application in sensors,[1] switches,[2] high density optical data storage,[3] and logic gates.[4] In particular, many studies have been focused on the regulation of the fluorescence properties of photochromic compounds as a promising signaling mode for molecular switches. A lot of examples have been reported by Irie,[5] Branda,[6] Tian[7] and Feringa.[8] Among the various photochromic compounds, diarylethenes bearing two thiophene/benzothiophene rings are regarded as the best candidates for photonics applications such as optical memories[9] and photoswitches,[10] owing to their excellent thermal stability, remarkable fatigue resistance, highly efficient photo-isomerizations and rapid responses.[11] The 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 a digital code analogous to 'on' and 'off' states, respectively.[12] Moreover, photochromic compounds that can be reversibly converted between the open and closed ring states with different spectroscopic properties upon exposure to UV or visible light have been used to achieve a reversible, photoswitchable fluorescent system through addition of fluorescent dye and induction of fluorescence resonance energy transfer (FRET) from the fluorescent dye to the close-ring state of the photochromic compound.[13]

Rhodamine-based dyes have received increasing interest in the development of fluorescent probes due to their excellent photophysical properties such as high fluorescence quantum yields, large molar extinction coefficients, visible wavelength excitation[14] and chemosensors.[15] It is well-known that many derivatives of rhodamine in the colorless spirolactam (no fluorescence) form will become the red open-ring form (strong fluorescence) with emission in the visible region in the presence of protons or metal ions. Thus far, several rhodamine-based derivatives have been prepared as fluorescent probes for detecting Hg(II),[16] Cu(II),[17] Fe(II),[15e] Ag(I)[18] and Cr(III).[19] Given the advantages of diarylethenes and rhodamine dyes, a dual-control FRET system may be achieved by combining both moieties. FRET is a non-radiative physical process in which energy is transferred from an excited fluorophore group (donor) to a chromophore unit (acceptor) within a 1–10 nm range. However, such occurrence requires that the acceptor characteristic absorption band overlaps with the emission of the donor. The reports on photochromic diarylethene and fluorophores functionized to form FRET molecules are rare,[5b,20] and they mainly involve the use of perhydrogencyclopentenes that do not possess good thermal stability as control units. Although an example of perfluorocyclopentene as an acceptor has been reported, it did not show proton response.[5b] We have recently reported a proton and optical dual-control fluorescent switch based on perfluorocyclopentene–diarylethene bearing a rhodamine, which showed good fluorescent modulation and naked eye recognition properties.[21] However, the compound does not response to metal ions. We herein report the synthesis of two novel

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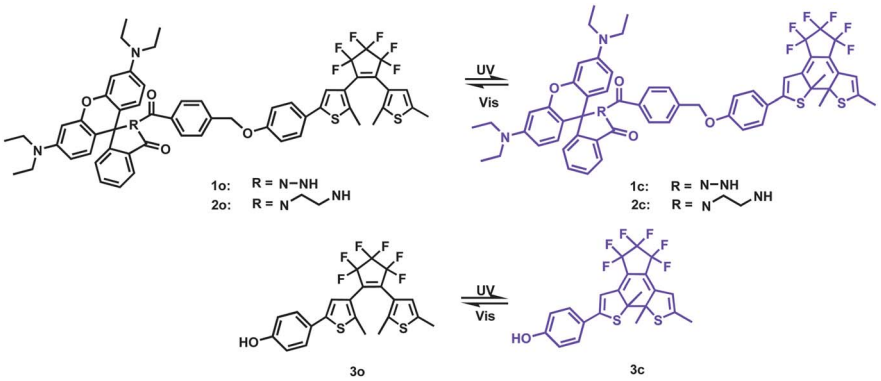


Scheme 1 Photochromism of compounds **1o–3o**.

fluoreophore–photochromic diarylethenes **1o** and **2o** containing photochromic perfluorocyclopentene and rhodamine B moieties (Scheme 1), as well as their proton and light dual-control responses. Moreover, diarylethene **1o** was found to also act as a reversible fluorescent probe for Cr(III), Al(III), or Ca(II).

Experimental

General methods

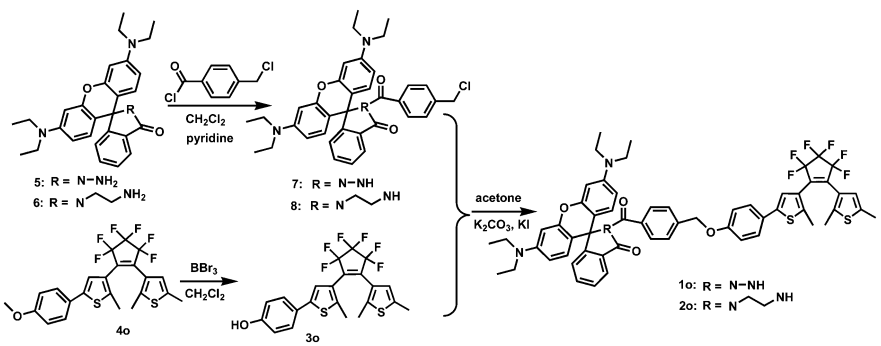
NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. IR spectra were recorded on a Bruker Vertex-70 spectrometer. Elemental analysis was carried out with a PE CHN 2400 analyzer. Melting point was measured using a WRS-1B melting point apparatus. Absorption spectra were measured using an Agilent 8453 UV/VIS spectrophotometer. 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. Fluorescence spectra were measured on a HITACHI 4500 fluorescence spectrophotometer. The fluorescence quantum yield in solution was measured using rhodamine ($\Phi = 0.89$ in ethanol) as a reference. All solvents used were of spectro-grade and purified by distillation prior to use. Expect for Mn(II), K(I), and Ba(II) (all of their counter ions were chloride ions), other tested metal ions were obtained by the dissolution of their respective metal nitrates (0.1 mmol) in distilled water (10 mL).

Synthesis

The synthetic route of diarylethenes **1o** and **2o** is shown in Scheme 2.

Synthesis of *N*-(rhodamine-B)lactam-(4-chloromethyl) benzohydrazide (7)

In a 150 mL flask, *N*-(rhodamine-B)hydrazide (**5**)[15c] (2.77 g, 6.07 mmol) was dissolved in anhydrous dichloromethane (90 mL) and then added to triethylamine with vigorous stirring in a cold water bath. A solution of 4-(chloromethyl)benzoyl chloride (2.30 g, 12.14 mmol) in anhydrous dichloromethane (10 mL) was added dropwise slowly to the chilled mixture with vigorous stirring and stirred for 10 h at room temperature. The reaction was quenched with water and the product was extracted with CH_2Cl_2. The organic layer was washed with saturated sodium bicarbonate and water, and then dried over $MgSO_4$, filtrated and evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane/acetic ether (4 : 1) as the eluent to obtain 2.08 g of **7** as a pink solid in 56% yield. M.p. 179–179.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.15 (t, 12H, $J = 6.6$ Hz, $-CH_3$), 3.31–3.36 (m, 8H, $-CH_2$), 4.53 (s, 2H, $-CH_2$), 6.30 (d, 2H, $J = 7.6$ Hz, –phenyl), 6.35 (s, 2H, –phenyl), 6.69 (d, 2H, $J = 8.2$ Hz, –phenyl), 7.16 (d, 2H, $J = 6.4$ Hz, –phenyl), 7.35 (s, 2H, phenyl–H), 7.51 (d, 2H, $J = 7.2$ Hz, –phenyl), 7.55 (d, 2H, $J = 7.6$ Hz, –phenyl), 7.98 (s, 1H, –NH); ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 13.07, 44.78, 45.86, 66.84, 98.09, 103.15, 104.84, 108.51, 124.06, 124.68, 128.42, 128.81, 129.76, 130.88, 132.88, 133.71,



Scheme 2 Synthetic route to compounds **1** and **2**.

141.46, 149.45, 151.89, 154.30, 165.63, 165.81; IR (ν, KBr, cm^{-1}): 819, 1078, 1094, 1119, 1151, 1220, 1266, 1305, 1330, 1356, 1375, 1401, 1426, 1467, 1547, 1615, 1634, 1722, 2971. Anal. calcd. for $C_{36}H_{37}ClN_4O_3$ (%): C, 70.98; H, 6.12; N, 9.2. Found: C, 71.21; H, 6.33; N, 9.02.

Synthesis of *N*-(rhodamine-B)lactam-ethyl-2-(4-chloromethyl) benzamide (8)

Compound **8** was prepared by a method similar to that used for **7**. Briefly, a solution of 4-(chloromethyl)benzoyl chloride (2.50 g, 13.23 mmol) in anhydrous dichloromethane (10 mL) was added dropwise slowly with vigorous stirring at 0 °C to a mixture of *N*-(rhodamine-B)lactam-1,2 -ethylenediamine (**6**)[15g] (3.1 g, 6.37 mmol) and triethylamine in anhydrous dichloromethane (90 mL). The reaction mixture was stirred for 10 h and then quenched with water. The product was extracted with CH_2Cl_2. The organic layer was washed with saturated sodium bicarbonate and water, then dried over $MgSO_4$, filtrated and evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane/acetic ether (4 : 1) as the eluent to obtain 3.24 g of **8** as a brown solid in 80% yield. M.p. 201–202 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.16 (t, 12H, $J = 7.8$ Hz, $-CH_3$), 3.20 (s, 2H, $-CH_2$), 3.30–3.35 (m, 8H, $-CH_2$), 3.44 (t, 2H, $-CH_2$), 4.62 (s, 2H, $-CH_2$), 6.26 (d, 2H, $J = 9.2$ Hz, –phenyl), 6.38 (s, 2H, –phenyl), 6.44 (d, 2H, $J = 8.8$ Hz, –phenyl), 7.08–7.10 (m, 1H, –phenyl), 7.45–7.50 (m, 4H, –phenyl), 7.91 (d, 2H, $J = 8.4$ Hz, –phenyl), 7.94 (d, 2H, $J = 2.8$ Hz, –phenyl), 8.40 (s, 1H, –NH); ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 12.60, 39.98, 41.95, 44.36, 45.31, 45.61, 66.01, 97.83, 104.59, 108.37, 122.91, 123.93, 127.68, 128.20, 128.60, 130.58, 132.88, 134.33, 140.31, 142.84, 149.01, 153.92, 166.41, 170.43; IR (ν, KBr, cm^{-1}): 816, 1119, 1152, 1219, 1265, 1302, 1329, 1356, 1400, 1425, 1467, 1514, 1546, 1614, 1634, 1665, 2972. Anal. calcd. for $C_{38}H_{41}ClN_4O_3$ (%): C, 71.63; H, 6.49; N, 8.79. Found: C, 71.35; H, 6.65; N, 8.53.

Synthesis of 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(4-hydroxylphenyl)-3-thien yl]perfluorocyclopentene (3o)

To a stirred solution of 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(4-methoxylphenyl)-3-thienyl] perfluorocyclopentene[22] (**4o**) (1.0 g; 2 mmol) in anhydrous dichloromethane (60 mL) at −78 °C, a 1M BBr_3 solution in dichloromethane (4.5 mL; 4.5 mmol) was added dropwise under an argon atmosphere. Stirring was continued for 3 h at −78 °C, and the mixture was stirred for 3–4 days at room temperature. The reaction mixture was quenched with water and extracted with ether. The organic layer was washed with brine, then dried over $MgSO_4$, filtrated and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/acetic ether (1 : 2) as the eluent and 0.8 g of **3o** was obtained as a brown oil in 82% yield. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.852 (s, 3H, $-CH_3$), 1.89 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.74 (s, 1H, –thienyl), 6.84 (d, 2H, $J = 0.8$ Hz, –phenyl), 7.13 (s,1H, –thienyl), 7.42 (d, 2H, $J = 3.6$ Hz, –phenyl); ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 13.54, 15.16, 115.86, 121.36, 122.10, 124.66, 125.86, 126.40, 127.12, 133.34, 137.73, 139.84, 140.17, 141.32, 141.87, 155.56; IR (ν, KBr, cm^{-1}): 828, 890, 949, 987, 1018, 1050, 1116, 1135, 1174, 1190, 1272, 1337, 1437, 1474, 1515, 1555, 1610, 1722. Anal. calcd. for $C_{22}H_{16}F_6OS_2$ (%): C, 55.69; H, 3.4. Found: C, 55.84; H, 3.16.

Synthesis of 1-(2,5-dimethyl-3-thienyl)-2-{2-methyl-5-[4-*N*-(rhodamine-B)lactam-(4-oxymethyl)benzhydrazide-yl]phenyl-3-thienyl}perfluorocyclopentene (1o)

A mixture of compound **7** (0.728 g, 1.3 mmol), compound **3o** (0.615 g, 1.27 mmol), K_2CO_3 (4g) and KI (0.5 g) in dried acetone (120 mL) was refluxed for 24 h. The reaction mixture was subsequently washed with water and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, filtered and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/acetic ether (2 : 1) as the eluent, and 0.5 g of **1o** was obtained as a brown solid in 38% yield. M.p. 159.5–160 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.26 (t, 12H, $J = 7.2$ Hz, $-CH_3$), 1.83 (s, 3H, $-CH_3$), 1.87 (s, 3H, $-CH_3$), 2.42 (s, 3H, $-CH_3$), 3.33 (d, 8H, $J = 4.4$ Hz, $-CH_2$), 5.09 (s, 2H, $-CH_2$), 6.31(d, 2H, $J = 8.8$ Hz, –phenyl), 6.36 (d, 2H, $J = 12.4$ Hz, –phenyl), 6.70 (d, 2H, $J = 4.8$ Hz, –phenyl), 6.73 (s, 1H, –thienyl), 6.90 (d, 2H, $J = 4.2$ Hz, –phenyl), 7.13 (s, 1H, –thienyl), 7.16 (d, 2H, $J = 3.8$ Hz, –phenyl), 7.39 (d, 2H, $J = 3.6$ Hz, –phenyl), 7.42 (d, 2H, $J = 4.0$ Hz, –phenyl), 7.53 (d, 2H, $J = 3.8$ Hz, –phenyl), 7.59 (d, 2H, $J = 4.0$ Hz, –phenyl), 7.90 (s, 1H, –NH); ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 13.54, 14.38, 15.13, 44.32, 60.40, 69.38, 97.59, 104.42, 108.22, 115.30, 121.51, 123.59, 124.20, 124.64, 124.65, 125.88, 126.73, 127.86, 128.38, 129.30, 132.22, 133.23, 137.50, 139.77, 140.22, 141.74, 148.95, 151.44, 153.83, 163.20, 165.31, 171.16; IR (ν, KBr, cm^{-1}): 821, 986, 1017, 1049, 1119, 1222, 1269, 1516, 1634, 1718, 2973, 3275, 3330, 3395, 3435, 3468, 3500, 3525, 3562, 3584, 3622. Anal. calcd. for $C_{58}H_{52}F_6N_4O_4S_2$ (%): C, 66.52; H, 5.01; N, 5.35. Found: C, 67.04; H, 5.13; N, 5.19.

Synthesis of 1-(2,5-dimethyl-3-thienyl)-2-{2-methyl-5-[4-*N*-(rhodamine-B)lactam-ethyl-2-(4-oxymethyl)benzamide-yl] phenyl-3-thienyl}perfluorocyclopentene (2o)

A mixture of compound **8** (0.5 g, 0.79 mmol), compound **3o** (0.39 g, 0.82 mmol), K_2CO_3 (4 g) and KI (0.15 g) in dried acetone (60 mL) was refluxed for 24 h. The mixture was subsequently washed with water and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, filtered and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/acetic ether (2 : 1) as the eluent, and 0.64 g of **2o** was obtained as a brown solid in 75% yield. M.p. 93–94 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.16 (t, 12H, $J = 7.0$ Hz, $-CH_3$), 1.88 (s, 3H, $-CH_3$), 1.91 (s, 3H, $-CH_3$), 2.41 (s, 3H, $-CH_3$), 3.20 (s, 2H, $-CH_2$), 3.28–3.37 (m, 8H, $-CH_2$), 3.34 (d, 2H, $J = 4$ Hz, $-CH_2$), 5.15 (s, 2H, $-CH_2$), 6.26 (d, 2H, $J = 8.8$ Hz, –phenyl), 6.38 (d, 2H, $J = 1.2$ Hz, –phenyl), 6.45 (d, 2H, $J = 8.8$ Hz, –phenyl), 6.74 (s, 1H, –thienyl), 6.97 (d, 2H, $J = 8.0$ Hz, –phenyl), 7.08–7.11 (m, 1H, –phenyl), 7.15 (s, 1H, –thienyl), 7.45–7.48 (m, 4H, –phenyl), 7.52 (d, 2H, $J = 8.0$ Hz, –phenyl), 7.94 (d, 3H, $J = 7.6$ Hz, –phenyl), 8.39 (s, 1H, –NH); ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 12.61, 14.46, 15.20, 39.94, 42.08, 44.38, 66.00, 69.55, 97.68, 104.41, 108,27, 115.36, 121.43, 122.91, 123.96, 124.63, 126.94, 127.22, 127.59, 127.95, 128.24, 128.43, 130.13, 130.29, 132.95, 133.93, 137.75, 139.89, 148.93, 153.29,

153.94, 158.36, 166.63, 170.47; IR (ν, KBr, cm^{-1}): 821, 986, 1017, 1047, 1118, 1220, 1270, 1514, 1634, 1668, 2970, 3464, 3335, 3351, 3392, 3409, 3425, 3465, 3492, 3535, 3596. Anal. calcd. for $C_{60}H_{56}F_6N_4O_4S_2$ (%): C, 67.02; H, 5.25; N, 5.21. Found: C, 67.23; H, 5.01; N, 5.42.

Results and discussion

Photochromism of diarylethenes 1–3

Diarylethenes **1–3** showed reversible color and absorption spectral changes upon alternating irradiation with UV and visible light (Fig. 1). As shown in Fig. 1A, within 3 min after irradiation with light of 297 nm, changes can be observed in the absorption spectra of compound **1o** as induced by photoirradiation at room temperature in methanol ($C = 2.0 \times 10^{-5}$ mol L^{-1}). The absorption maximum of compound **1o** was observed at 273 nm ($\varepsilon = 4.74 \times 10^4$ L mol^{-1} cm^{-1}). Upon irradiation with 297 nm light, the colorless solution of **1o** turned purple due to the appearance of a new visible absorption band centered at 550 nm ($\varepsilon = 7.84 \times 10^3$ L mol^{-1} cm^{-1}) attributable to the closed-ring form of compound **1**. On the other hand, the purple solution became colorless upon irradiation with visible light ($\lambda > 450$ nm) for 2 min, indicating that **1c** returned to its initial form **1o** and a clear isosbestic point was observed at 316 nm. The spectral change of diarylethene **2o** was similar to that of diarylethene **1o** as shown in Fig. 1B. The absorption maximum of **2o** was observed at 275 nm ($\varepsilon = 4.73 \times 10^4$ L mol^{-1} cm^{-1}) and the absorption maximum of **2c** was observed at 551 nm ($\varepsilon = 7.40 \times 10^3$ L mol^{-1} cm^{-1}) in methanol at room temperature. In order to clarify the difference before and after the introduction of the rhodamine dye moiety into the diarylethene, the photochromism of the precursor diarylethene **3** was measured under the same conditions. The changes in the absorption spectra of **3** induced by photoirradiation at room temperature in methanol are shown in Fig. 1C. In the methanol solution, the absorption maximum of compound **3o** was observed at 294 nm ($\varepsilon = 2.72 \times 10^4$ L mol^{-1} cm^{-1}). Upon irradiation with 297 nm light, the color of the methanol solution turned purple, in which the absorption maximum was observed at 552 nm ($\varepsilon = 1.01 \times 10^4$ L mol^{-1} cm^{-1}). The photochromic properties of compounds **1** and **3** are slightly different. Whereas diarylethene **1** exhibited a larger molar coefficient in the open-ring form than that of diarylethene **3**, the close-ring form of **1** exhibited a smaller molar coefficient compared with **3**. However, the previously reported rhodamine B linked derivative has a larger molar coefficient than the diarylethene monomer in the close-ring form.[21] The reason could be that the terminal group linked to diarylethene was too long, which slightly lowered the degree of molecular conjugation. The fact is that various functional substituents have notable effects on the photochromic features of diarylethenes. Similar substitution effects on the photochromic properties of diarylethene derivatives have been reported in our previous studies.[23] Fig. 1D indicates the color changes of diarylethenes **1–3** in methanol upon alternating irradiation with UV and visible light.

Cyclic modulation of proton-control photochromism

The room temperature emission spectra of diarylethenes **1o** and **2o** ($C = 2.0 \times 10^{-5}$ mol L^{-1}) in methanol solutions excited at 520 nm after TFA addition are shown in Fig. 2. The rhodamine derivatives undergo equilibrium between the colorless spirolactam form and the pink open-ring form. The two forms feature completely different spectrophotometric properties when

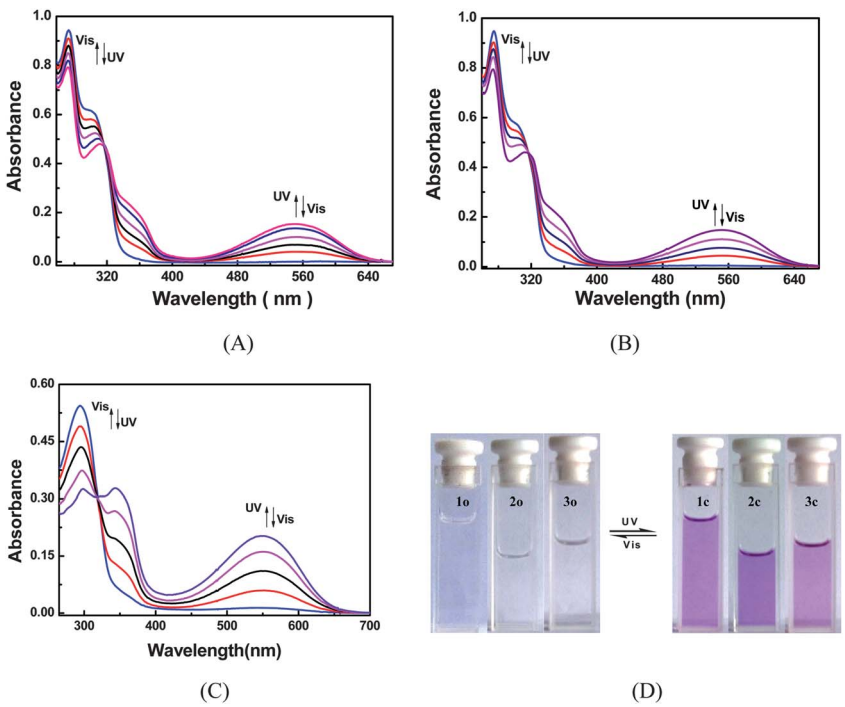


Fig. 1 Changes in absorption spectra and color of diarylethenes **1–3** in methanol ($C = 2.0 \times 10^{-5}$ mol L^{-1}) at room temperature: (A) spectral changes for **1**, (B) spectral changes for **2**, (C) spectral changes for **3**, and (D) color changes for diarylethenes **1–3**.

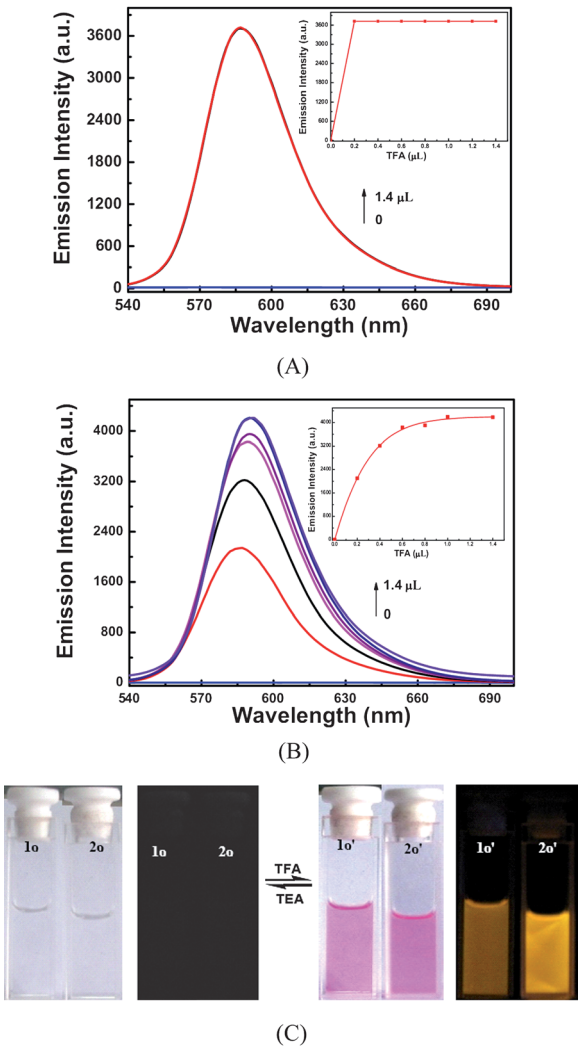


Fig. 2 Changes in fluorescence and color of diarylethenes **1o** and **2o** in methanol ($C = 2.0 \times 10^{-5}$ mol L^{-1}) induced by the addition of TFA when excited at 520 nm at room temperature: (A) emission spectral changes for **1o**, (B) emission spectral changes for **2o**, and (C) changes in graphs of color and fluorescence for **1o** and **2o**. Inset shows the emission intensity changes of **1o** (A) and **2o** (B) as a function of the addition of TFA.

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 and absorption. Therefore, the emission intensity of diarylethenes **1o** and **2o** can be tuned with protons. Initially, methanol solutions of diarylethenes **1o** and **2o** were non-fluorescent with excitation at 520 nm, but became increasingly fluorescent at about 588 nm as TFA was gradually added and their corresponding open-ring amide forms were formed. Furthermore, the fluorescent emission of **1o** increased when more than 0.2 μL TFA ($C = 1.34 \times 10^{-3}$ mol L^{-1}) was added, but no increase was observed for **2o** with increasing amounts of TFA beyond 1.0 μL. The result indicates that diarylethene **1o** is more proton sensitive than **2o**. As the fluorescence intensity reaches the maximum, the fluorescent quantum yields of **1o** and **2o** were determined as 0.34 and 0.52, respectively, using rhodamine B ($\Phi = 0.89$ in ethanol) as a reference.[18,24] The gradual back addition of 1.0 μL TEA ($C = 3.56 \times 10^{-3}$ mol L^{-1}) regenerates the spirolactam form of rhodamine, while the fluorescent intensity decreases as the original emission spectra recover. In general, addition of TFA to the colorless methanol solutions of **1o** and **2o** would turn the solutions pink with strong fluorescence as the open-ring **1o′** and **2o′** forms were generated. Subsequent quenching by the addition of TEA would return the pink solutions to colorless.

The curves of fluorescent intensity as a function of time in the presence of 1.0 μL TFA ($C = 1.34 \times 10^{-3}$ mol L^{-1}) in methanol are shown in Fig. 3. Upon addition of TFA, the fluorescent intensity of **1o** immediately reached the maximum, suggesting that its fluorescence intensity in response to protons was independent to time. However, the fluorescence intensity of **2o** increased gradually with increasing time and the maximum was reached after 55 min. This indicated that the response to protons

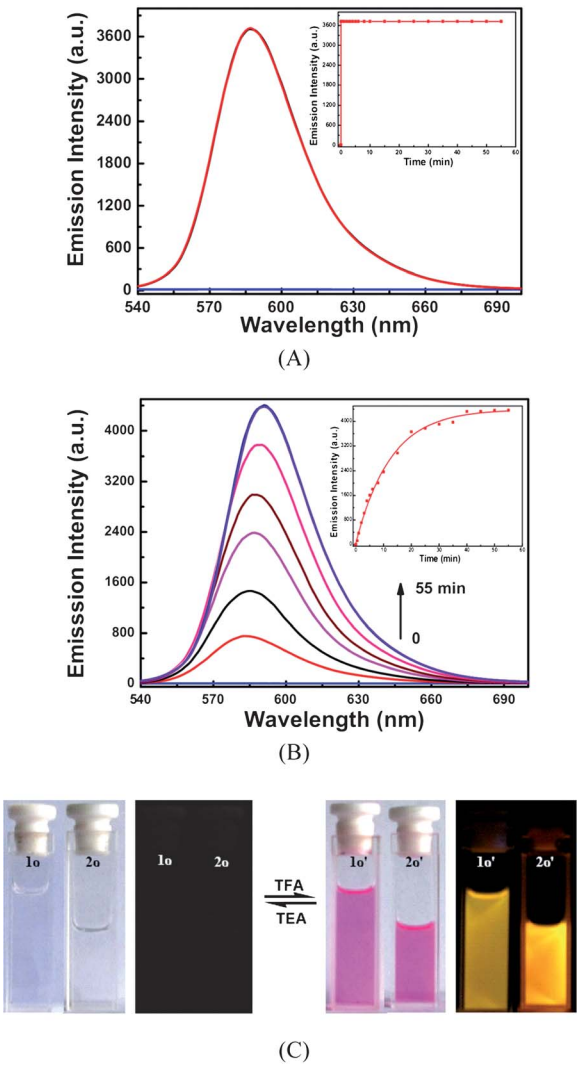


Fig. 3 Changes in fluorescence and color of diarylethenes **1o** and **2o** ($C = 2.0 \times 10^{-5}$ mol L^{-1}) with time in the presence of TFA ($C = 1.34 \times 10^{-3}$ mol L^{-1}) in methanol when excited at 520 nm at room temperature: (A) emission spectral changes for **1o**, (B) emission spectral changes for **2o**, and (C) changes in graphs of color and fluorescence for **1o** and **2o**. Inset shows the emission intensity changes of **1o** (A) and **2o** (B) as a function of time.

is more rapid for diarylethene **1o** than **2o**. This may be attributed to the different length of the bridge-bond bearing two N atoms. The distance between the two N atoms of the benzamide bridge-bond (**2o**) is longer than that of the benzhydrazide bridge-bond, resulting in the slower responsive rate of a spirolactam opening process when rhodamine was protonated under acidic conditions. Fig. 3C shows the color and fluorescence changes of diarylethenes **1o** and **2o** with alternating addition of TFA and TEA. As expected, the colorless solutions of **1o** and **2o** turned pink with strong fluorescence as TFA was added and the open-ring forms **1o′** and **2o′** were generated, and then became colorless after quenching with TEA. The reversible modulation of the fluorescent emission intensity of diarylethenes **1** and **2** with alternating additions of TFA and TEA is shown in Fig. 4. The switchable fluorescent cycles of both **1** and **2** could be repeated at least 10 times with no degradation observed. This suggested that the fatigue resistances of these perfluorocyclopentene derivatives are significantly enhanced in comparison to the perhydrogen-cyclopentene derivatives,[20a] which were considered as promising candidates for fluorescent modulation switches.[25]

Cyclic modulation of optical-control photochromism

Since diarylethene derivatives usually afford different color changes upon alternating irradiation with UV/vis light, the combination of diarylethene with a chemo-responsive dye offers a promising approach to the design of optical molecular switches.[20,21a] We have also studied the spectral modulation of compounds **1o′** and **2o′** (**1o** and **2o** in the presence of TFA) using UV/vis light and FL techniques. Fig. 5 shows the fluorescent changes of compound **1o′** and **2o′** upon alternating irradiation with UV/vis light in methanol at room temperature. As is shown in Fig. 5A, a visible color change from colorless to pink can be clearly observed due to the formation of the open-ring amide form **1o′** or **2o′** whose absorption maximum was observed at 558 nm after addition of TFA (1.0 μL, $C = 1.34 \times 10^{-3}$ mol L^{-1}) into the solution containing diarylethene **1o** or **2o**. Upon irradiation with UV light, the color of their respective solutions turned from pink to purple due to the formation of the closed-ring diarylethene **1c′** or **2c′**, whose absorption maximum was still centered at 558 nm because of an overlap of the visible absorption bands between the closed-ring diarylethene and the rhodamine moiety.

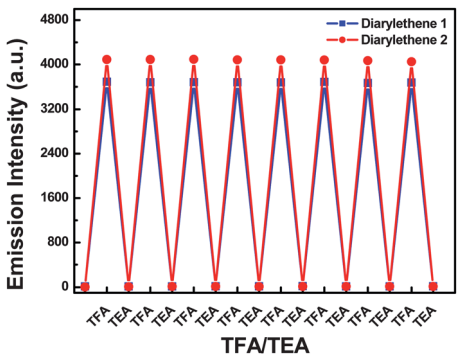


Fig. 4 Fluorescent switch cycles of diarylethenes **1o** and **2o** ($C = 2.0 \times 10^{-5}$ mol L^{-1}) induced by alternating additions of TFA and TEA in methanol when excited at 520 nm at room temperature.

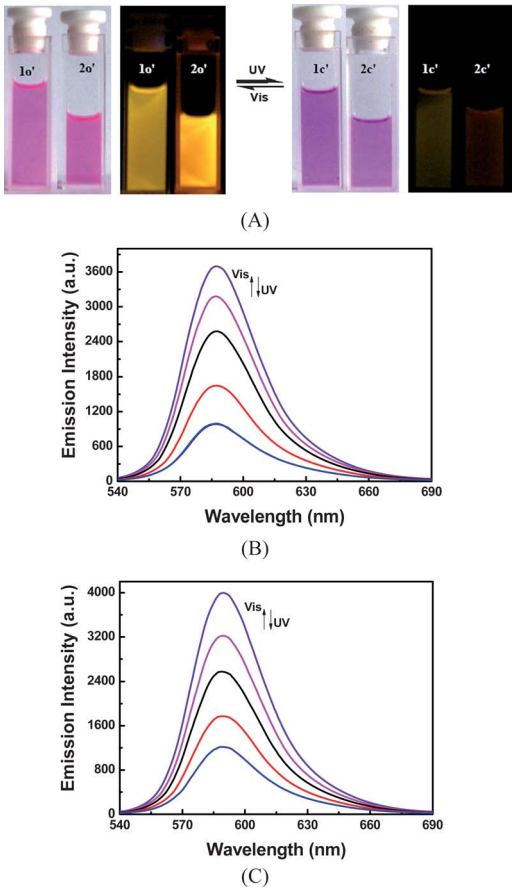


Fig. 5 Changes in color and fluorescence of diarylethenes **1o′** and **2o′** ($C = 2.0 \times 10^{-5}$ mol L^{-1}) upon alternating irradiation with UV/vis light in methanol when excited at 520 nm at room temperature: (A) Changes in graphs of color and fluorescence for **1′** and **2′**, (B) emission spectral changes for **1o′**, and (C) emission spectral changes for **2o′**.

Alternatively, their color and the absorption spectra could return to their original states upon irradiation with appropriate visible light. Under acidic conditions, compound **1o′** showed a strong fluorescent emission at 587 nm (excitation at 520 nm) ascribed to the formation of the open-ring rhodamine amide. Upon exposure to UV light (297 nm), its fluorescence intensity decreased dramatically along with the photochromism from open-ring isomer to closed-ring isomer. The fluorescence intensity gradually increased upon irradiation with visible light ($\lambda > 450$ nm). Compound **2o′** displayed a similar fluorescent property. Its fluorescent peak was observed at 589 nm when excited at 520 nm. At the photostationary state, the emission intensity of compounds **1c′** and **2c′** was quenched to 27% and 31% of their original intensity, respectively (Fig. 5B and C). The results indicated that the emission intensities of **1o′** and **2o′** could be modulated effectively and they underwent reversible photochromism upon alternating irradiation with UV/vis light. The color and fluorescence changes of compounds **1′** and **2′** are also shown in Fig. 5A. Upon irradiation with UV light, the pink solutions of **1o′** and **2o′** exhibited very weak fluorescence in methanol as the closed-ring forms **1c′** and **2c′** were generated. Subsequently, their fluorescences recovered to the original states after visible light irradiation. It should be noted that the residual

fluorescence of diarylethenes **1c′** and **2c′** may be attributed to incomplete cyclization reaction and the existence of parallel conformations.[11d] Such fluorescence quenching is possibly a result of the intramolecular fluorescence resonance energy transfer from the open-ring rhodamine amide unit to the closed-ring isomer of diarylethene, since FRET is a typical process where fluorescence energy transfers from an excited fluorophore (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 with the emission of the donor.[5b,26] Since the emission band (550–650 nm) of rhodamine in the open-ring state has certain overlap with the absorption band (450–650 nm) of the closed-ring isomer of diarylethene, the FRET process can occur. Subsequent irradiation with visible light (λ > 450 nm) regenerates the open-ring isomer of diarylethene and recovers the original emission spectrum.

Fluorescent response to ions

Many examples of metal ions selective fluorescent probes based on rhodamine B have been reported. Samanta *et al.* reported di(2-ethylsulfanylethyl)amine as a receptor moiety in organic solvents.[27] Liu *et al.* synthesized two fluorescent probes with selectivity for Fe(III) and Cr(III).[28] Kewei *et al.* investigated a rhodamine derivative containing 8-hydroxyquinoline group with selectively for Cr(III) over other metal cations.[15b] The design of these molecular structures has mainly focused on introducing N, S and O atoms to the rhodamine spriolactam neighborhood, which can recognize Cr(III) ion *via* colorimetric or fluorescent changes of the non-bonded pair of electrons. Most of these fluorescence probes are conventional probes that respond irreversibly to certain events or nondynamically to environmental stimuli. Thus, further development of novel photocontrollable and multiresponsive fluorescent probes may be very important in cellular imaging as powerful tools for elucidating the physiological dynamics in living cells. The reported reversible fluorescent probes lack protons and ions control response.[29] Although one reported example exhibits ion response, it has no proton control response.[29c] Modulation of fluorescence to compound **1o** is reversible upon addition of Cr(III). Diarylethene **1o** showed no fluorescence due to the spirocyclic form of rhodamine. Fig. 6 shows the fluorescence changes of diarylethene **1o** upon addition of Cr(III). An increase in fluorescence intensity at 587 nm was observed for compound **1o** when Cr(III) concentration was increased from 0 to 7.5 equivalents, then plateaued (Fig. 6A inset). From Fig. 6B, it can be seen that the colorless diarylethene **1o** solution turned to pink and exhibited strong fluorescence after addition of Cr(III). This suggested that diarylethene **1** could be used as an off–on fluorescent probe for Cr(III). Moreover, the results indicate that the fluorescence enhancement of compound **1o** in the presence of Cr(III) involves the spirocycle-open mechanism, in which the spirolactam form of rhodamine B (non-fluorescence) transforms to its ring-opened amide form (strong fluorescence). After irradiation with UV light, the fluorescence was quenched to 30% of its original intensity ascribed to the formation of the closed-ring **1c** and the occurrence of FRET. Subsequent irradiation with visible light regenerated the open-ring form of diarylethene and recovered the original emission spectrum. Furthermore, the modulation of emission intensity of

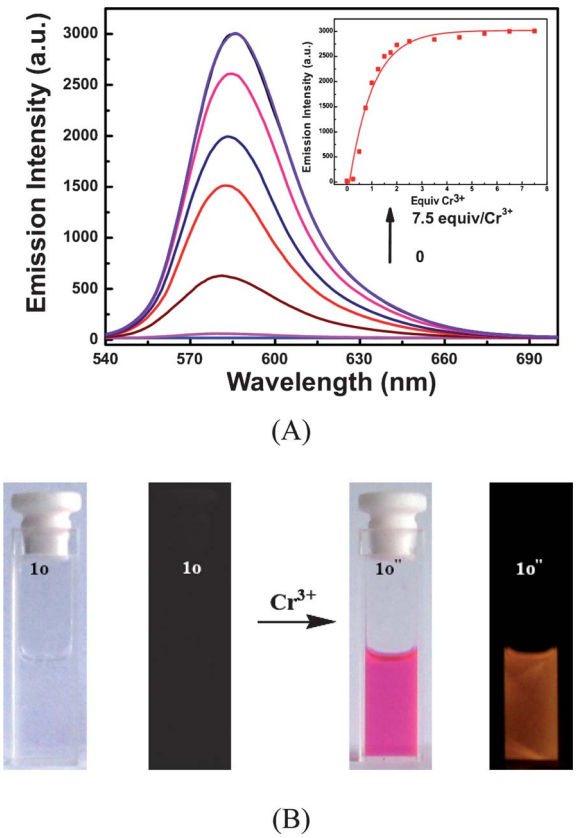


Fig. 6 Changes in fluorescence and color of diarylethene **1o** with response to Cr(III) when excited at 520 nm in methanol: (A) emission spectral changes for **1o**, (B) changes in graphs of color and fluorescence for **1o**. Inset shows the effect of Cr(III) concentration on emission intensity of **1o** at 587 nm.

compound **1** after Cr(III) binding is reversible by alternating irradiation with UV/vis and the fluorescent switch cycles can be repeated more than 10 times.

High selectivity is essential for an excellent chemosensor. In order to investigate the selectivity of diarylethene, metal ions including alkali, alkaline earth, and transition-metal ions were added into the diarylethene **1** methanol solution under the same

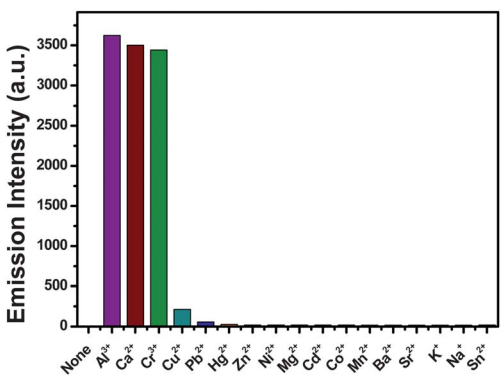


Fig. 7 Emission intensity of diarylethene **1o** at 587 nm when excited at 520 nm in methanol ($C = 2.0 \times 10^{-5}$ mol L^{-1}) in the presence of respective metal cations (25 equiv).

experimental condition. As shown in Fig. 7, the fluorescence intensity of compound **1o** increased significantly after the addition of Cr(III), Al(III), or Ca(II). Its fluorescence intensity was almost not influenced by the addition of 25 equiv of Cu(II), Pb(II), Hg(II), Zn(II), Ni(II), Mg(II), Cd(II), Co(II), Mn(II), Ba(II), Sr(II), Sn(II), K(I) and Na(I). Our results indicate that compound **1** was selective towards Cr(III) over other competing cations, except Ca(II) and Al(III). As with the reported rhodamine-based spirolactam chemosensors,[15b,h,30] the fluorescence enhancement of the diarylethene **1o** induced by the selective cations may be attributed to the spirolactam ring-opening mechanism of the rhodamine moiety. However, no change in the fluorescence intensity of compound **2o** was observed with any of these ions. This may be attributed to the longer distance between the two N atoms of the diaminoethyl bridge-bond in diarylethene **2o** that made binding to metal ions impossible. The chelating of diarylethenes bearing a rhodamine moiety with metal ions is possibley *via* the hetero-atom such as O, N, S, *etc*, which is in agreement with previously reported publications.[15b,30] The different chelating ability of the derivative with different metal ions is responsible for the selective detection of diarylethenes **1o** and **2o**.

Application of diarylethenes 1 and 2 in logic circuit

We have demonstrated that the emission intensity of diarylethenes bearing a rhodamine unit could be modulated by either chemical or light stimuli. The multi-mode fluorescence switching principle of diarylethenes **1** and **2** are summarized in Scheme 3. As an example, the fluorescence of diarylethene **1** by an external stimuli (UV/vis light and chemical signals) can be described with the aid of binary logic as follows.[29e,31] Diarylethene **1** in acidic condition is regarded as the initial state, its fluorescence changes can be combined as a molecular switch with three inducing inputs: I1 (297 nm UV light), I2 (450 nm visible light), and I3 (TEA). When the relative emission intensity at 587 nm is under 50% of the original value, the output signal can be regarded as off, but on when it is 100%. Hence, we can use the binary digits (1 or 0) instead of the two levels (off and on). The compounds **1** and **2** can read a string of three inputs and write one output. Using compound **1** as an example, when the input string is 000, corresponding to the I1, I2, I3 are all off. Under these conditions, compound **1** is in the state of compound **1o′** and the relative fluorescence intensity 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 exhibited in Fig. 8.

Conclusion

Two new fluorescent molecular switch diarylethene derivatives were successfully synthesized by using rhodamine B as a fluorophore and perfluorodiarylethene as a photochromic group. They have multi-state response to both light and chemical inputs, which result in different fluorescent emission under sequential alternating UV/vis light irradiation and protonation/deprotonation. Moreover, their fluorescence emission intensities can be modulated by proton and UV/vis light stimuli. Our results demonstrated that information transmission at the single molecular level could be realized using a multi-addressable photoswitching system based on functional photochromic diarylethene compounds.

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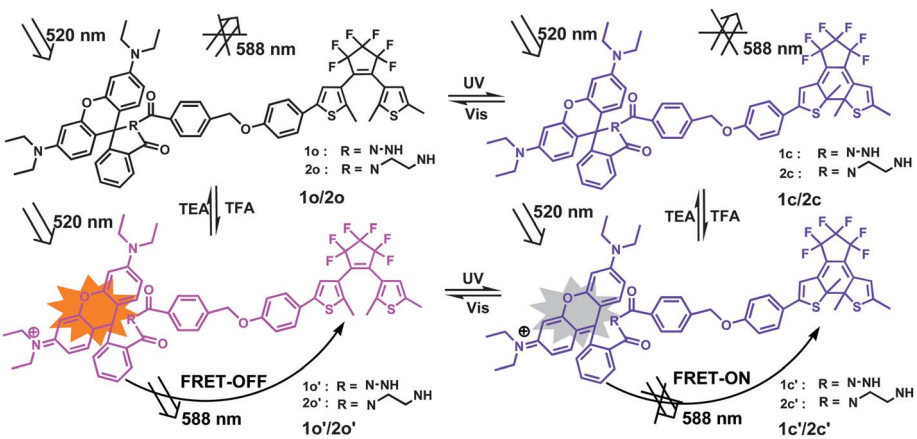
Table 1 Truth table for all possible strings of three binary-input data and the corresponding output digit

Input			Output[a]
I1 (UV)	I2 (vis)	I3 (TEA)	(Emission intensity at 587 nm)
0	0	0	1
0	0	1	0
0	1	0	1
1	0	0	0
0	1	1	0
1	0	1	0
1	1	0	0
1	1	1	0

[a] At 587 nm, the emission intensity below 50% of the original value is defined as 0, otherwise defined as 1.



Scheme 3 The fluorescence switching principle of compounds **1** and **2** with proton and optic stimuli.

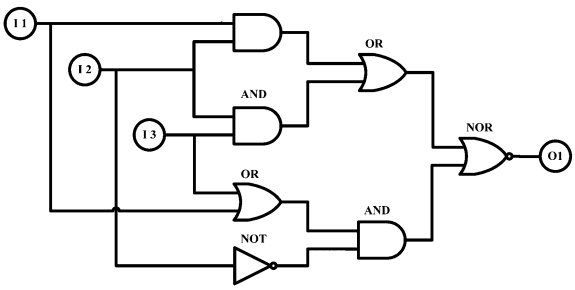


Fig. 8 The combinational logic circuits equivalent to the truth table given in Table 1: I1 (297 nm UV light), I2 (450 nm visible light), I3 (TEA), and O1 (in acidic condition).

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