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An Optic/Proton Dual-Controlled Fluorescence Switch based on Novel Photochromic Bithienylethene Derivatives

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A simple method for the synthesis of new bithienylethenes bearing a functional group on the cyclopentene moiety is developed. Three new photochromic compounds (**4a**, **4b**, **4c**) have been successfully synthesized through this simple method, and exhibit good photochromic properties with alternate irradiation of ultraviolet and visible light. Furthermore, the fluorescence of compound **4a**, which bears a quinoline unit on the cyclopentene, can be modulated via optic and proton dual inputs. Upon excitation by 320 nm light, **4a** emits a strong fluorescence at 404 nm. After irradiation with 254 nm light, the emission intensity is reduced due to the fluorescence resonance energy transfers (FRET) from quinoline unit to bithienylethene unit. Moreover, on addition of H^+, the fluorescence is quenched completely due to the protonation of the quinoline. In addition, both the FRET and protonation process are reversible, which indicates a potential application in molecular switches and logic gates.

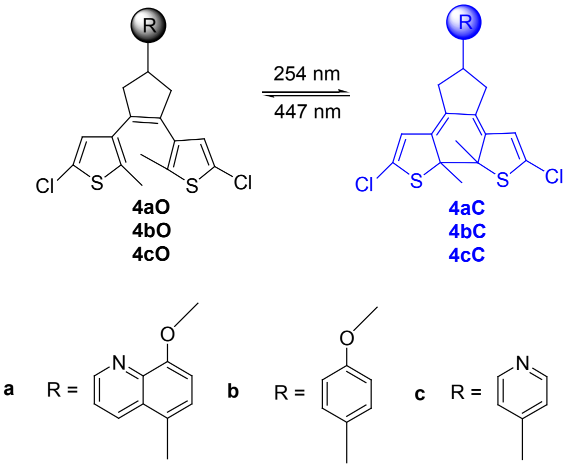
Keywords photochromism, diarylethenes, dual-control, fluorescence

Introduction

Photochromic compounds have attracted considerable attention in recent years[1-3] because of their potential application in optical data storage[4-6] and molecular switches.[7-9] Among all photochromic compounds, diarylethenes are regarded as the best candidates for such devices, owing to their excellent thermal stability, fatigue resistance, and rapid response.[10-12] During the past decades, many achievements on the modification of diarylethene family have been carried out, such as expanding the branched chain of the aryl,[13-17] and changing the center ethene bridge.[18-21] However, the modification of the perhydrogencyclopentene is rarely seen. In this paper, a simple route for the synthesis of several novel bithienylethenes bearing a functional group on the cyclopentene moiety with two simple initial materials is developed. The photochromism of diarylethenes **4a**, **4b** and **4c** are shown in Scheme 1.

Because of their extensively application in chemosensors[22,23] and biological imaging,[24-26] fluorescent photochromic diarylethenes are among the top study list of scientific researchers.[27,28] The regulation of the fluorescence in one molecule using multi-ways, such as proton, light and electron, is the ultimate aim of the scientists.[29-32] As we all know, 8-quinolinol derivatives are excellent fluorophores, and they can respond to the protons and metal ions, which are widely used in constructing fluorescent probes and chemosensors. The combination between 8-quinolinol derivatives and diarylethenes is promising in developing a dual-control fluorescent switch system. Herein, we synthesized a novel molecule diarylethene **4a** linked with a fluorophore 8-methoxyquinoline (8-MQ) on the cyclopentene, and its optic and proton dual-controlled switch properties were investigated.

Scheme 1 Photochromism of diarylethenes **4a**, **4b** and **4c**



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Experimental

General methods

5-Chloro-2-methyl-3-acetylthiophene (**1**) and 5-aldehyde-8-hydroxyquinoline were synthesized according to the literature.[33,34] Other reagents were commercially available and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer in $CDCl_3$ solutions using tetramethylsilane as the internal standard. High resolution mass spectra (HRMS) were recorded on a Waters LCT Premier XE spectrometer using standard conditions (ESI, 70 eV). UV-Vis absorption spectra were measured on a Varian Cary 500 UV-Vis spectrophotometer. Fluorescence emission spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer. The optical switch experiments were carried out using a photochemical reaction apparatus with a 200 W Hg lamp. Fluorescence quantum yields were recorded on FluoroMax-4 spectrofluorometer with a quanta-Φ integrating sphere (Horiba Jobin-Yvon).

5-Aldehyde-8-methoxyquinoline (2a) To a stirred solution of 5-aldehyde-8-hydroxyquinoline (1.73 g, 10 mmol) in DMF (100 mL) at room temperature, K_2CO_3 (2.76 g) was successively added in batches. After refluxed for 1 h, MeI (1.56 g, 11 mmol) dissolved in DMF (50 mL) was dropwise added to the reaction mixture. Continued refluxing for 3 h, the reaction mixture was cooled, evaporated, and poured into water. The mixture was extracted with CH_2Cl_2 (50 mL×3), washed with water, and dried with anhydrous Na_2SO_4. After distillation of solvent, the residue was chromatographed on silicon using petroleum ether∶ethyl acetate (1∶1) as eluent. Compound **2a** was separated in 70% yield (1.31 g). m.p. 113—115 ℃; ^{1}H NMR δ: 4.20 (s, 3H), 7.17—9.69 (m, 5H), 10.18 (s, 1H).

Diketone (3a) To a stirred solution of **2a** (0.94 g, 5 mmol) in ethanol (40 mL) and NaOH aqueous solution (40 mL, 10%) was dropwise added the solution of 5-chloro-2-methyl-3-acetylthiophene (2.1 g, 15 mmol) in ethanol (50 mL) at 0 ℃, then stirred for 18 h at room temperature. After evaporated the solvent, the mixture was extracted with CH_2Cl_2 (50 mL×3), washed with water, and dried with anhydrous Na_2SO_4. After distillation of solvent, the residue was purified on a silica gel column using petroleum ether∶ethyl acetate (1∶2) as the eluent to obtain the target compound **3a** (0.906 g, 35%). m.p. 250—252 ℃; ^{1}H NMR δ: 8.93—7.00 (m, 5H), 7.18 (s, 2H), 4.72—4.64 (m, 1H), 4.07 (s, 3H), 3.32—3.19 (m, 4H), 2.49 (s, 6H); ^{13}C NMR δ: 193.47, 154.19, 148.89, 148.19, 140.39, 134.72, 131.68, 131.40, 127.30, 126.61, 125.50, 123.84, 121.69, 107.02, 55.94, 47.78, 35.96, 15.91; HRMS (ESI) calcd for $C_{25}H_{22}NOS_2Cl_2$ (M+H) 518.0418, found 518.0414.

Diketone (3b) Compound **3b** was prepared by an analogous method similar to that used for **3a** and obtained as a white solid in a yield of 40%. m.p. 100—102 ℃; ^{1}H NMR δ: 7.17 (s, 2H), 7.14 (d, J=8.7 Hz, 2H), 6.81 (d, J=8.7 Hz, 2H), 3.87—3.82 (m, 1H), 3.77 (s, 3H), 3.16—3.06 (m, 4H), 2.67 (s, 6H); ^{13}C NMR δ: 193.81, 158.25, 147.90, 135.56, 134.95, 128.32, 126.76, 125.30, 114.01, 55.24, 48.05, 36.00, 15.98; HRMS (ESI) calcd for $C_{22}H_{21}O_3S_2Cl_2$ (M + H) 467.0309, found 467.0303.

Diketone (3c) Compound **3c** was prepared by an analogous method similar to that used for **3a** and obtained as a white powder in a yield of 40%. m.p. 116—118 ℃; ^{1}H NMR δ: 8.53—8.49 (m, 2H), 7.22—7.18 (m, 2H), 7.17 (s, 2H), 3.97—3.90 (m, 1H), 3.27—3.07 (m, 4H), 2.59 (s, 6H); ^{13}C NMR δ: 192.58, 152.80, 150.06, 148.46, 134.46, 126.46, 125.63, 122.88, 46.64, 35.61, 16.06; HRMS (ESI) calcd for $C_{20}H_{18}NO_2S_2Cl_2$ (M+H) 438.0156, found 438.0165.

1,2-Bis(2-methyl-5-chloro-3-thienyl)-4-(8-methoxyl-5-quinolyl)cyclopentene (4a) 5 mL THF and 173 mg Zn powder were put into a two-neck Schlenk tube under a nitrogen atmosphere. 0.62 mL $TiCl_4$ (5.3 mmol) was added very cautiously by a glass syringe under 0 ℃. The solution turned yellow and was refluxed for 3 h. After that was cooled in an ice bath, **3a** (0.223 g, 0.44 mmol) was added in portions. Then the mixture was refluxed overnight, subsequently quenched with 10% K_2CO_3 (20 mL), filtered, and the filtrate was extracted with diethyl ether (20 mL×3). The combined organic phase was washed with H_2O (50 mL), saturated NaCl solution (50 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The product was purified by column chromatography using petroleum ether∶ethyl acetate (1∶2) as the eluent to obtain the target compound **4a** (50 mg, 24%). ^{1}H NMR δ: 8.96 (dd, J=4.1, 1.5 Hz, 1H), 8.44 (dd, J=8.6, 1.4 Hz, 1H), 7.48 (dd, J=8.6, 4.1 Hz, 1H), 7.43 (d, J=8.1 Hz, 1H), 7.01 (d, J=8.1 Hz, 1H), 6.61 (s, 2H), 4.29—4.21 (m, 1H), 4.09 (s, 3H), 3.32—2.95 (m, 4H), 1.94 (s, 6H); ^{13}C NMR δ: 154.07, 148.75, 146.28, 134.21, 133.84, 133.33, 133.27, 131.90, 127.53, 126.48, 125.64, 123.24, 121.36, 107.00, 55.96, 45.51, 37.38, 14.29; HRMS (ESI) calcd for $C_{25}H_{22}NOS_2Cl_2$ (M+H) 486.0520, found 486.0511.

1,2-Bis(2-methyl-5-chloro-3-thienyl)-4-(*p*-methoxyl-phenyl)cyclopentene (4b) Compound **4b** was prepared by an analogous method similar to that used for **4a** and obtained as a colorless solid in a yield of 90%. ^{1}H NMR δ: 7.23 (d, J=8.6 Hz, 2H), 6.87 (d, J=8.6 Hz, 2H), 6.60 (s, 2H), 3.80 (s, 3H), 3.66—3.56 (m, 1H), 3.14—2.83 (m, 4H), 1.92 (s, 6H); ^{13}C NMR δ: 157.99, 138.27, 134.46, 133.64, 133.36, 127.69, 126.59, 125.40, 113.92, 55.32, 46.36, 41.83, 14.29; HRMS (ESI) calcd for $C_{22}H_{21}OS_2Cl_2$ (M+H) 435.0411, found 435.0413.

1,2-Bis(2-methyl-5-chloro-3-thienyl)-4-(pyridyl)-cyclopentene (4c) Compound **4c** was prepared by an analogous method similar to that used for **4a** and obtained as a colorless solid in a yield of 60%. ^{1}H NMR δ: 8.56—8.52 (m, 2H), 7.23—7.20 (m, 2H), 6.60 (s, 2H), 3.67—3.57 (m, 1H), 3.21—2.85 (m, 4H), 1.92 (s, 6H); ^{13}C NMR δ: 155.34, 149.79, 134.00, 133.86, 132.98, 126.39, 125.73, 122.27, 45.30, 41.65, 14.31; HRMS

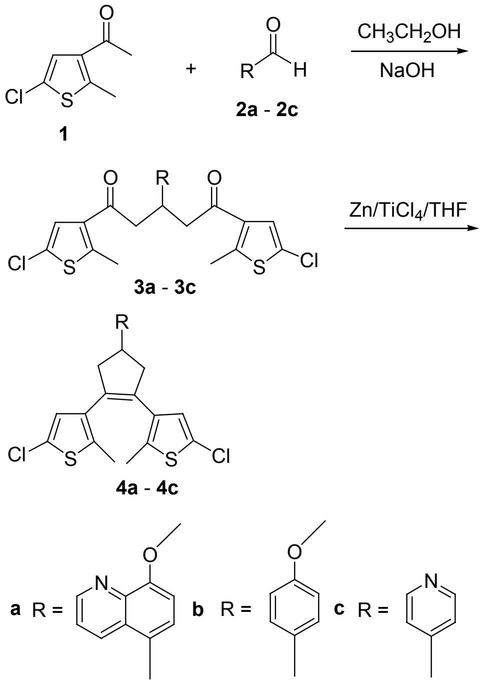
(ESI) calcd for $C_{20}H_{18}NS_2Cl_2$ (M+H) 406.0258, found 406.0258.

Results and Discussion

Synthesis and characterization

In this work, three new photochromic diarylethenes with functional groups on the cycloethenes were prepared by a simple method and their photochromic behaviors were investigated in detail. The synthetic route used to obtain diarylethene **4** is shown in Scheme 2. 5-Chloro-2-methyl-3-acetylthiophene (**1**) was synthesized according to the literature method. Aldehyde **2a** was prepared by the methylation of 5-aldehyde-8-hydroxyquinoline with MeI. The diketone compound **3** was synthesized from compound **1** and the corresponding aldehyde **2** in the presence of NaOH in ethanol. According to a common McMurry reaction, cyclization of these diketones in the presence of Zn and $TiCl_4$ in anhydrous THF gave the corresponding target bithienylethenes **4a**, **4b** and **4c**. The products were purified by silica-gel-column chromatography. In this way, novel diarylethenes with multi-modifiable sites in both aryl and cyclopentene moieties can be easily synthesized, acquiring only two steps. All of the target compounds were characterized by ^{1}H NMR, ^{13}C NMR spectroscopes and HRMS.

Scheme 2 Synthetic route for the target compounds



Photochromism of compound 4

Diarylethene **4** can undergo a reversible photochromic reaction in MeCN upon alternating irradiation with UV and visible light. Changes in the absorption spectra of compound **4a** induced by photo irradiation at room temperature in MeCN ($C=2.5\times10^{-5}$ mol•L^{-1}) are shown in Figure 1a. The maximum absorption of compound **4aO** is observed at 243 nm. Upon irradiation with 254 nm light, the colorless solution of **4a** gradually turns yellow due to the appearance of a new visible absorption band centered at 447 nm, which is attributed to the formation of the closed-ring form **4aC**. The photo-stationary state is attained after about 7 min. Alternatively, the yellow solution could be bleached to colorless upon irradiation with visible light ($\lambda>$440 nm), indicating that **4aC** returned to the initial state **4aO**. Similarly, the colorless solutions of **4b** and **4c** can turn yellow on irradiation with 254 nm UV light, and the color can also disappear upon irradiation with the same visible light ($\lambda>$ 440 nm). The corresponding spectra are shown in

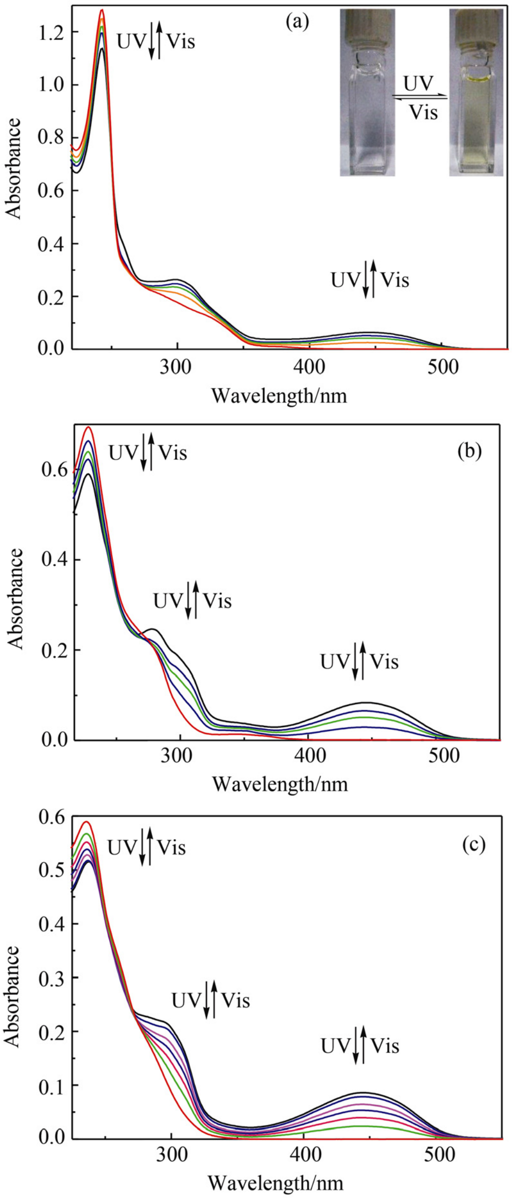


Figure 1 Changes in the absorption spectra of compounds **4a** (a), **4b** (b) and **4c** (c) in MeCN at room temperature (2.5×10^{-5} mol•L^{-1}). Inset (a): color change of compound **4a** upon alternating irradiation with UV/Vis light in MeCN.

Figure 1b and Figure 1c.

The thermal stability of these diarylethenes was also investigated. Putting the solutions of diarylethenes **4a**, **4b** and **4c** in MeCN at room temperature in the dark for more than one week, no changes in their colors and spectra were observed. Moreover, The cyclization and cycloreversion quantum yield of these compounds were measured. The photochromic properties of diarylethenes **4a**, **4b** and **4c** are summarized in Table 1. From these data, it can be seen that the photochromic features (including the absorption maxima, molar absorption coefficients, and quantum yields) of these diarylethenes are different, which indicates that the different functional groups on the cyclopentene moiety will affect the photochromic properities, and the further work is in progress. Because the diarylethene **4a** can emit a strong fluorescence upon excitation with 320 nm light, we put emphasis on the switchable fluorescence properties of **4a** below.

Table 1 Absorption parameters and photochromic reactivity of diarylethenes **4a**, **4b** and **4c** in MeCN (2.5×10^{-5} mol•L^{-1})

Compd	$\lambda_{\mathrm{o,max}}{}^{a}$/nm [$\varepsilon$/(L•mol^{-1}•cm^{-1})]	$\lambda_{\mathrm{c,max}}{}^{b}$/nm [$\varepsilon$/(L•mol^{-1}•cm^{-1})]	Φ^{c}		Conversion at PSS
			Φo-c	Φc-o	
4a	243 (5.13×10^{4})	448 (3.94×10^{3})	0.17	0.12	61%
4b	228 (2.78×10^{4})	446 (4.94×10^{3})	0.20	0.11	68%
4c	236 (2.36×10^{4})	445 (4.77×10^{3})	0.24	0.09	72%

[a] Absorption maxima of open-ring isomers. [b] Absorption maxima of closed-ring isomers. [c] Quantum yields of cyclization reaction (Φo-c) and cycloreversion reaction (Φc-o), respectively.

Optic fluorescence switch of compound 4a

8-Quinolinol derivatives, which are excellent fluorophores, are widely used in OLED and electroluminescence. 8-MQ is strongly fluorescent because of the existing of the methoxy group preventing the intramolecular proton transfer process in the excited state compared with 8-hydroxyquinoline.[10] The fluorescence spectra of the diarylethene **4a** in MeCN at room temperature are shown in Figure 2a. In MeCN, diarylethene **4a** exhibited strong emission intensity at 404 nm when excited at 320 nm. After irradiation with 254 nm UV light, the fluorescence intensity of **4a** decreased enormously due to the formation of ring-closed isomer as a fluorescence quencher. It can also be seen in the inset that the absorption band of ring-closed form **4aC** is well overlapped with the emission band of the quinoline fluorophore, which may lead to an efficient FRET process. FRET is a typical fluorescence energy transfer process from an excited fluorophore (donor) to another chromophore unit (acceptor) which required that the characteristic absorption band of the acceptor overlapped with the emission of the donor via a link distance of 1—10 nm.[31,35,36] In our work, the emission band (350—500 nm) of quinoline fluorophore in the open-ring state has certain overlap with the absorption band (400—500 nm) of the closed-ring isomer of diarylethene **4a**, and the FRET process can occur. As a result, the fluorescence intensity of quinoline was quenched to 15% by the larger π-conjugation system of the ring-closed isomer. Furthermore, we measured the fluorescence quantum yields, and the absolute quantum yields of **4aO** and **4aC** were 0.28 and 0.03, respectively, which were coincident with the FRET process. The fatigue resistance of **4a** was also investigated in air at room temperature. Solution of **4a** in MeCN was alternately irradiated with UV (λ=254 nm) and visible light (λ>440 nm). As shown in Figure 2b, bithienylethene **4a** was rather stable in the fluorescence emission spectra at photo-stationary state towards photochemical deposition.

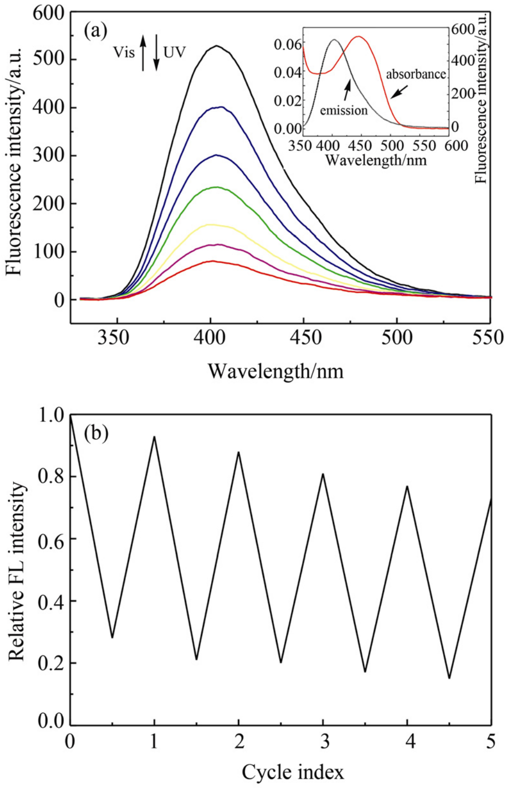


Figure 2 Fluorescent changes (a) and switch cycles (b) of compound **4a** upon alternate irradiation with UV/Vis light in MeCN (2.5×10^{-5} mol•L^{-1}) at room temperature. Inset: the overlapping between the absorbance spectrum of the ring-closed form of **4a** and the emission spectrum of quinoline fluorophore.

Proton controlled fluorescence switch of compound 4a

On account of the existing of the N atom in 8-MQ, **4a** is responsive to the acid and base. Addition of 1 equiv. trifluoromethanesulfonic acid (TFMSA) to **4a** in MeCN solution, the maximum absorption shifts from 243 to 256 nm. Meanwhile, the absorbance in the region of the 8-MQ absorption band (270—320 nm) decreases substantially, and a new absorption band is observed at *ca*. 379 nm. All the above changes are attributed to the protonation of 8-MQ. Moreover, the absorption curve can be recovered with the addition of equal equiv. triethylamine (TEA) (Figure 3).

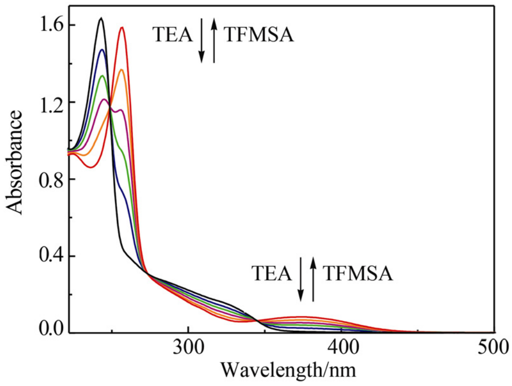


Figure 3 Absorption changes of compound **4aO** (2.5×10^{-5} mol•L^{-1}) in MeCN upon alternating addition with TFMSA and TEA.

The emission intensity of compound **4a** can also be tuned with proton. The emission spectra of **4a** with excitation at 320 nm in MeCN solution after alternating additions of TFMSA and TEA are shown in Figure 4a. On addition of TFMSA gradually (0.2 equiv. each time) up to 1 equiv., the strong fluorescence was quenched completely because of the protonation of the fluorophore. The gradual back addition of TEA regenerated the unprotonated form of 8-MQ, while the fluorescence intensity was restored to its initial state. Figure 4b also shows the reversible modulation of the fluorescence emission intensity of compound **4a** with alternating additions of TFMSA and TEA, which indicates that the acid/base-controlled fluorescent switch cycles between **4aO** and **4aO'** are fully reversible and can be repeated many times in the same solution without appreciable reduction in fluorescence intensity.

One should be noted that the photochromic behavior of **4a** is not disturbed upon the addition of TFMSA. After irradiation with UV light, the protonated **4a** can still undergo photocyclization, and shows the reversible change when irradiated with visible light (Figure 5). Accompanied by the changes of the absorption curve, the solution alters its color from colorless to yellow.

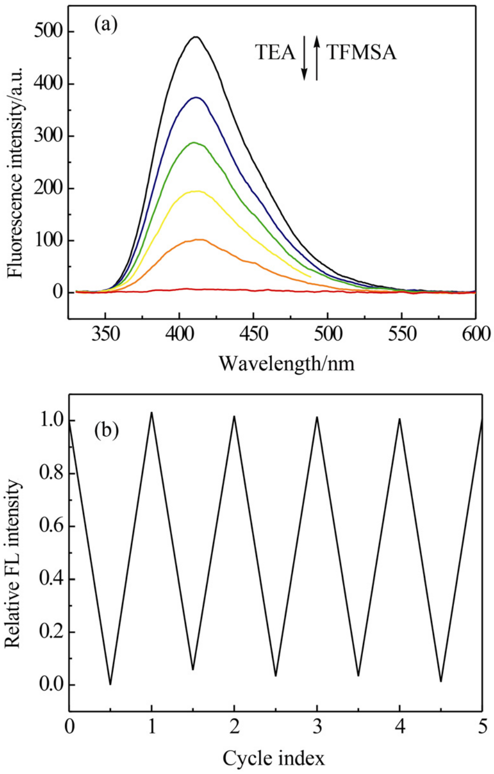


Figure 4 Fluorescent changes (a) and switch cycles (b) of compound **4a** (2.5×10^{-5} mol•L^{-1}) induced by alternate additions of TFMSA and TEA in MeCN excited at 320 nm at room temperature.

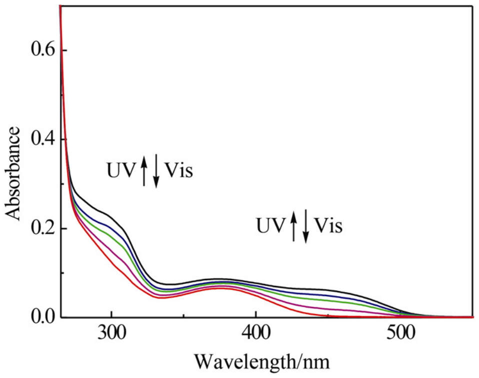


Figure 5 Absorption changes of compound **4a** in the presence of 1 equiv. of TFMSA (2.5×10^{-5} mol•L^{-1}) in MeCN upon alternating irradiation with 254 nm ultra-violet light and visible light ($\lambda>440$ nm).

Logic gate operation of compound 4a

Owing to the connection with the fluorophore 8-methoxyquinoline, **4a** displays strong fluorescence intensity at 404 nm when excited at 320 nm. After irradiation with 254 nm UV light, the fluorescence intensity was decreased because of the formation of ring-closed isomer. Also, on addition of H^{+}, the fluorescence was quenched completely due to the protonation of the quinoline. The structure and fluorescence changes are shown in Figure 6. This special spectroscopic behavior and the chemical reversibility of the UV/Vis and acid/base switching can be used to obtain an INHIBIT logic gate, using the 254 nm UV light (I1) and the base TEA (I2) as the inputs, and fluorescent emission signals (ΔF_{404}) as the data outputs. An INHIBIT logic gate is a two-input AND gate with one input carrying a NOT gate.[37] We set non-fluorescent **4aO'** as the initial state, and the output is "1" when the fluorescence intensity is more than 50% of **4aO**. Without irradiation of UV light (I1=0) and addition of TEA (I2=0), **4aO'** did not emit

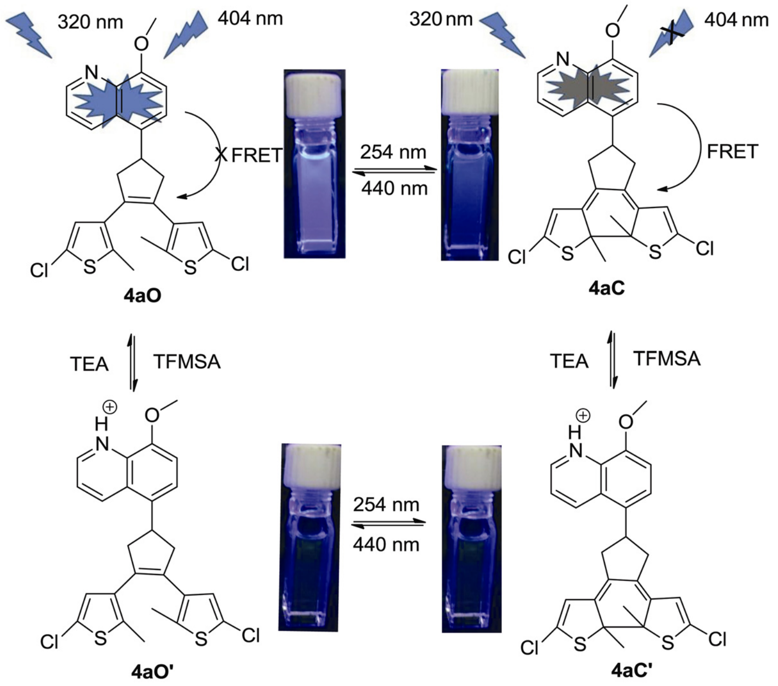
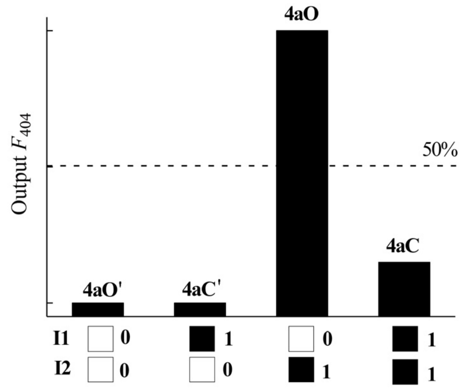


Figure 6 Structure and fluorescence changes by the optic and proton dual stimuli.

fluorescence (Output=0, form **4aO'**). If the UV light was turned on (I1=1) while the whole system remained in the acid condition (I2=0), the fluorescence at 404 nm was still off (Output=0, form **4aC'**). On another occasion, keeping off the UV light (I1=0) and adding 1 equiv. of TEA into the system (I2=1), the emission at 404 nm increased significantly to show a highly fluorescent state (output=1, form **4aO**). Finally, we both turned on the UV light (I1=1) and added 1 equiv. of TEA consequently (I2=1), the fluorescence dropped below the standard again (output=0, form **4aC**). This leads to a UV irradiation and protonation modified INHIBIT logic gate. The output (ΔF_{404}) and the truth table for the INHIBIT gate are exhibited in Figure 7. Because of the full reversibility of the photoisomerization and protonation/deprotonation processes, the current INHIBIT gate can operate repeatedly.



I1 254 nm	I2 TEA	Output ΔF_{404}	Molecule structure
0	0	0 (low, 0)	**4aO'**
1	0	0 (low, 0)	**4aC'**
0	1	1 (high, 100%)	**4aO**
1	1	0 (low, 15%)	**4aC**

Figure 7 Output (ΔF_{404}) and the truth table for the INHIBIT gate. The dashed line indicates the detection limit (50%).

Fluorescence changes in the film

In order to have a better application in practice, we also studied the fluorescent properties in polymeric matrices of diarylethene **4a**. Compound **4a** (2 mg) and poly(methyl methacrylate) (PMMA) was dissolved in chloroform (2 mL), and thin film was obtained by spin-coating the solution onto a quartz plate with a spin rate of 1000—2000 r/min. Compound **4a** displayed high fluorescence intensity at 390 nm in PMMA film when excited at 245 nm, which is 14 nm blue-shifted than the emission in MeCN solution. This difference from the fluorescence in MeCN solution may be attributed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state. While upon irradiation with 254 nm UV light, fluorescence intensity of **4a** in PMMA decreases, which is similar to that in MeCN solution (Figure 8a), indicating that the photochromic properties of **4a** are conserved in the solid state. Dipping the film in the TFA atmosphere for 2 min, the fluorescence exhibits significant quenching (Figure 8b), and the fluorescence recovers when dipped in the TEA atmosphere, which are also corresponding to the changes in MeCN solution. All the phenomena above promise a possible application in photo-switchable devices.

Conclusions

In summary, we have synthesized a series of novel

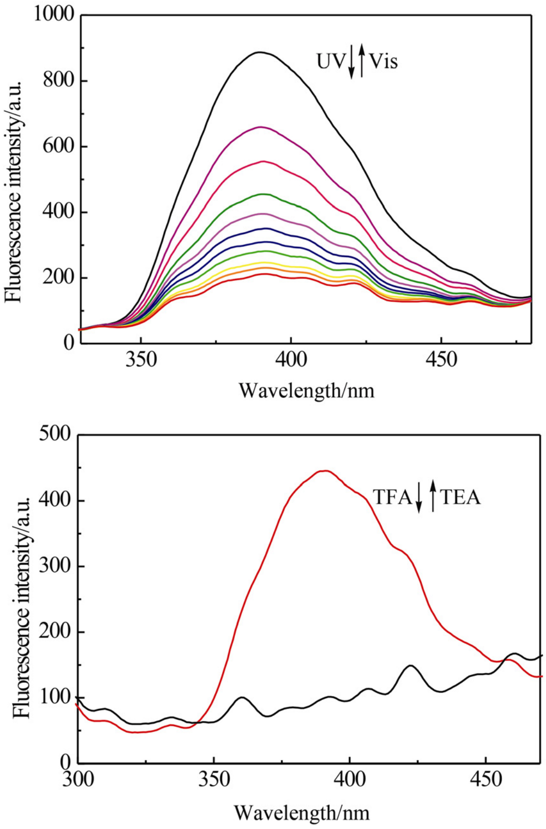


Figure 8 Fluorescence emission spectra changes of **4a** doped in PMMA with the irradiation of alternant 254 nm UV and visible light (a) and putting in the TFA/TEA atmosphere (b).

photochromic molecules using a simple method, which exhibit good photochromic properties. The high fluorescence of diarylethene **4a** can be reversibly controlled by both UV/Vis light and protonation/deprotonation. In this way, we have successfully realized the dual-control of a fluorescent molecule, which can be used to construct an INHIBIT logic gate. Moreover, the photochromic and fluorescence behaviors of **4a** doped in the PMMA film are similar to that in the solution, which indicates a potential application in devices. Further investigations of applications in devices are currently in progress.

Acknowledgement

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