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Acid/Alkali Gated Photochromism of Diarylethenes with Quinoline Derivatives

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Three new diarylethenes **1**—**3** combined with quinoline derivatives have been synthesized. Through controlled chemical condition of deprotonation/protonation, they presented some new irreversible photochromic phenomenons under UV/Vis light irradiation in chloroform solution. It was found that **1**—**3** had well photoisomerization upon UV/Vis light irradiation in neutral chloroform solution. Addition of acid to the solution of the ring-opening isomers of **1**—**3** produced **1oa**—**3oa**, which performed reversible photochromic behavior under UV/Vis light irradiation and reversed back to **1**—**3** under neutralizing with adding lewis base. However, addtion of base to neutral soluton of the ring-opening isomers of **1**—**3** produced **1ob**—**3ob**, which could not change to the deprotonated ring-closing isomers under UV light irradiation.

Keywords diarylethene, photochromism, quinoline, acid, alkali

Introduction

Photochromic diarylethene[1] has aroused much attention because of the reversible transformation between two isomers by different wavelength light irradiation. It could be used in many applications in optoelectronic devices, such as displays, switches and storages, because of its advantaged photochromic properties such as high fatigue resistance, high thermally irreversible properties, and various physical properties including absorbance, luminescence refractive index and so on.

Since the photochemical reaction is in generally proceed in proportion to the number of photons absorbed by the molecules, the memories or images recorded will be destroyed during storage under room light or after many readout operations. A method that is strongly desired but still inadequate for circumventing this problem is gated photochromic reactivity. Generally, it is hard to keep in an isomer under UV/Vis light irradiation. Addition of external stimulations, such as photon,[2] heat,[3] chemical reaction,[4] electric field,[5] *etc.*, to some kind of diarylethenes with special derivative structures will be able to achieve gated photochromic reactivity. Addition of acid/alkali is one of the most usually used chemical methods to control reversibility of isomerization of diarylethene.[6] So far, some works have been reported about providing gated photochromic reactivity. Lehn *et al.*[7] once reported that several diarylethenes with phenol and pyridine derivatives, exhibited proton-gated photochromic properities by deprotonation and reprotonation of the molecules. The substituents on heteroaromatics and heteroaromatic forms influence on the characteristics of diarylethenes. The diarylethene derivatives have many works reported, such as pyrrole,[8] thiazole,[9] indole,[10] oxazole,[11] imidazo phenathroline[12] and so on. Quinoline has been well known for its use in metallic complex materials.[13] Chen *et al.*[14] have reported a kind of diarylethene, which was combined with 3,4-bis(5-formyl-2-methylthien-3-yl)-2,5-dihydrothiophene and 8-hydroxy-2-methyl-quinoline and had excellent photoisomer under UV/Vis light irradiation under acid-base effect by the addition of trifluoroacetic acid or boron trifluoride diethyletherate.

If we can control the isomerization of diarylethene, the applied range of diarylethene will be more spacious. In this paper, we have synthesized three novel diarylethenes **1**—**3** (Scheme 1) combined with quinoline derivatives at the 5-position of thiophene ring of diarylethene. Deprotonation/protonation could control the irreversibility of photochromic isomerization of them. They presented irreversible photochromic properties under deprotonation condition and reversible behaviors under protonation/neutral condition.

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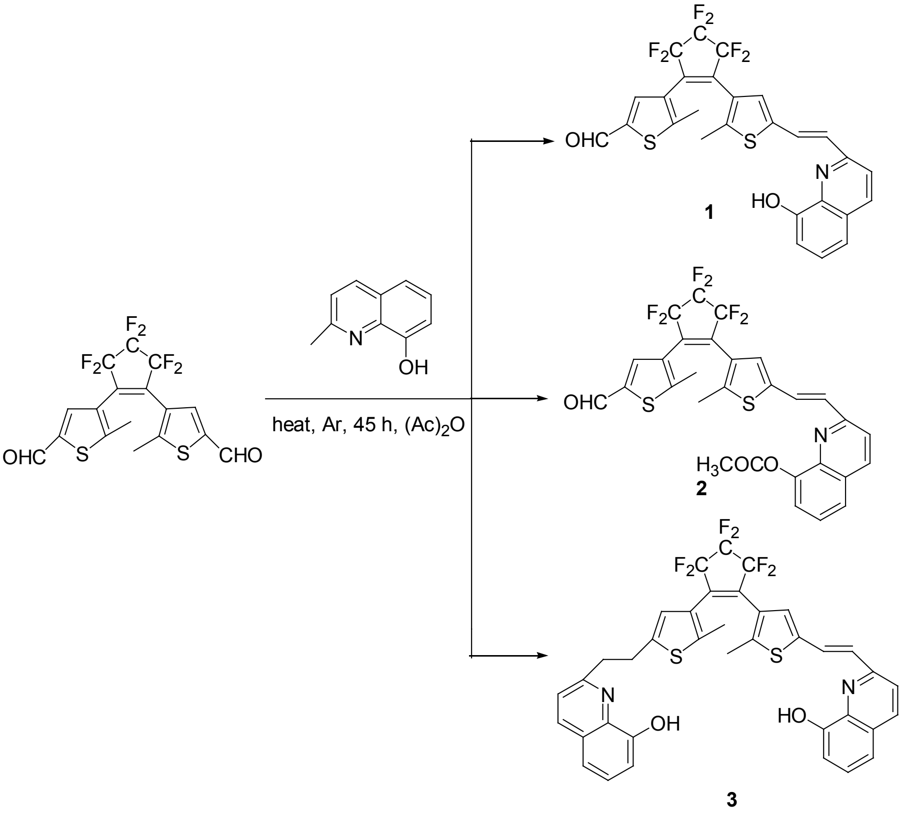
Scheme 1 Synthetic route of three kinds of diarylethene



Results and Discussion

The optical properties of **1**—**3** and 1,2-bis(2,5-methyl-3-thienly)-perfluorocyclopentene (DTE) in chloroform solution were summarized in Table 1. DTE has larger $E_{g,opt}$ and smaller $\lambda_{abs,max}$ because of the shorter π-conjugated chain. Similarly, **1** and **2** have larger $E_{g,opt}$ and smaller $\lambda_{abs,max}$ than **3**, too. As known, DTE, which does not have 8-hydroxyquinoline derivatives, is reversible in acid/neutral/basic solution. Nonetheless, the new three diarylethenes have some novel phenomena, respectively.

The UV/Vis absorption spectrum changes of **1**—**3** at room temperature were shown in Figure 1—Figure 6. The reacting products of the ring-opening isomers of **1** — **3** with trifluoroacetic acid are the protonated ring-opening isomers of **1**—**3** (**1oa**—**3oa**, Scheme 2). The mechanism is that N-group of 8-hydroxyquinoline in **1**—**3** will react with acid.[4a,7] The reacting products of the ring-opening isomers of **1** and **3** with sodium hydroxide were the deprotonated ring-opening isomers of **1** and **3** (**1ob** and **3ob**, Scheme 2), which could not transfer to the ring-closing isomers in chloroform solution. As known, hydroxide radical in **1** and **3** will react with sodium hydroxide. But the reaction mechanism of base and **2** is still unclear at present.

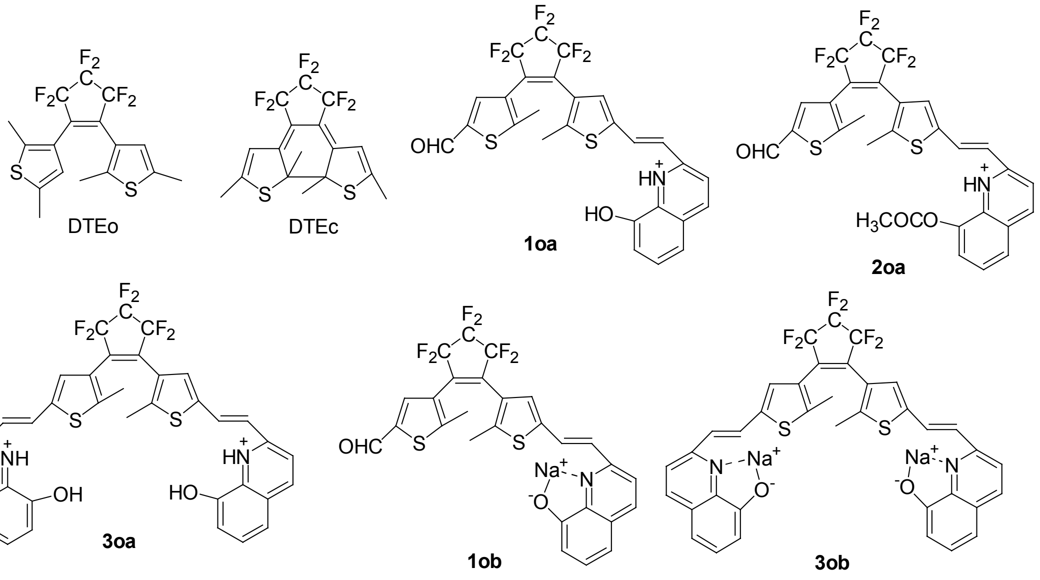
The reversibility of **3** with UV/Vis light irradiation in chemical condition of deprotonation/protonation was summarized in Scheme 3. **3o**, **3c**, **3oa**, **3ca**, **3ob** and **3cb** were researched by irradiation with ultraviolet light or visible light, acidification with trifluoroacetic acid chloroform solution (0.1 mol•L^{-1}) and alkalization with sodium hydroxide in methanol (0.1 mol•L^{-1}). The protonation and deprotonation effects on **3** were reversible. **3o** and **3c**, **3oa** and **3ca** were reversible under UV/Vis light irradiation. Only **3ob** and **3cb** were directional transform: **3cb** isomer could change to **3ob** upon Vis

Table 1 Maximum absorption spectrum ($\lambda_{abs,max}$, nm), maximum fluorescence spectrum ($\lambda_{f,max}$, nm), fluorescence quantum yield (Φ_f, %) , optical energy band-gap ($E_{g,opt}$, eV) for **1**—**3** and DTE in chloroform solution

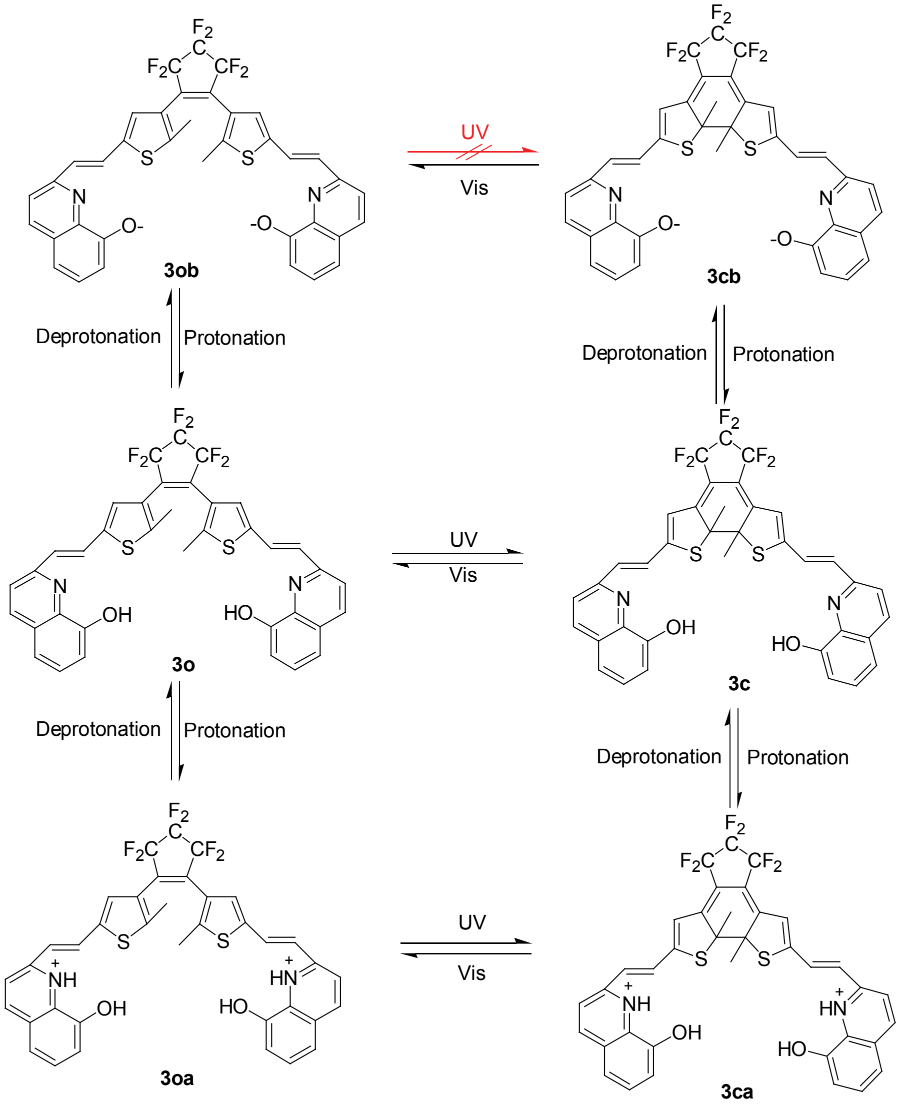
	$\lambda_{abs,max}$ (ε)	$\lambda_{f,max}$ [a]	Φ_f [b]	$E_{g,opt}$ [c]
DTEo[d]	346 (4.0×10^4)	402	0.92	3.31
DTEc[d]	502 (2.2×10^4)			2.14
1o	364 (2.9×10^4)	424	1.27	2.95
1c	625 (1.0×10^4)			1.55
2o	365 (3.0×10^4)	423	1.35	2.99
2c	583 (1.3×10^4)			1.68
3o	370 (4.0×10^4)	408, 437	0.0761	2.92
3c	650 (1.9×10^4)			1.61

[a] Exciting wave-length is 365 nm; fluorescence emission spectrum of the ring-closing isomers is almost undetectable or very weak, so the fluorescence quantum yield of the ring-closing isomers is not listed. [b] Fluorescence quantum yield is detected by a Horiba Jobinyvon Fluorolog spectrometer. [c] $E_{g,opt} = 1240/\lambda_{edge}$ (eV), λ_{edge} is the absorption edge wavelength in solution. [d] Structures of DTEo and DTEc were showed in Scheme 2.

Scheme 2 Structures of DTEo, DTEc, **1oa**—**3oa**, **1ob** and **3ob**



Scheme 3 Schematic diagram of light-operated isomerization of **3** under chemical condition of deprotonation/protonation in chloroform solution



light irradiation; but **3ob** could not transform to **3cb** upon UV light irradiation. The mechanisms of the reversibility of **1** and **2** with UV/Vis light irradiation in chemical condition of deprotonation/protonation were similar, too.

For **1** in Figure 1, the ring-opening isomer of **1** (**1o**, the black line, $\lambda_{max}=364$ nm) and the ring-closing isomer of **1** (**1c**, the green line, $\lambda_{max}=625$ nm) could be transformed to each other upon UV/Vis light irradiation. Adding trifluoroacetic acid (in chloroform solution, 0.1 mol•L^{-1}) to **1o** would produce a new absorption band (the orange line, $\lambda_{max}=420$ nm), which was red-shifted to the absorption band of **1o** and deceased in intensity. Upon irradiation of **1oa** with 420 nm light, the propornated ring-closing isomer of **1** (**1ca**, $\lambda_{max}=650$ nm) would be obtained whose absorption band also was red-shifted to the band of **1c**. The addition of acid to the organic photochromic materials, such as spirooxazine, would change the color of solution and the band of absorption spectrum in solution, which had been investigated by Fan *et al.*[15] Oppositely, the addition of sodium hydroxide (in methanol, 0.1 mol•L^{-1}) to the chloroform neutral solution of **1o** produced **1ob**, whose absorption band (the yellow line, $\lambda_{max}=332$ nm), compared to the absorption spectra of **1o** (the black line, $\lambda_{max}=364$ nm) in chloroform solution was blue-shifted. Upon 365 nm light irradiation, the 332 nm peak of the yellow line would reduce in intensity, but there was not any new band in the 600—700 nm range. It suggested that **1ob** could not transform to the deprotonated ring-closing isomer of **1** (**1cb**) under 365 nm light irradiation.

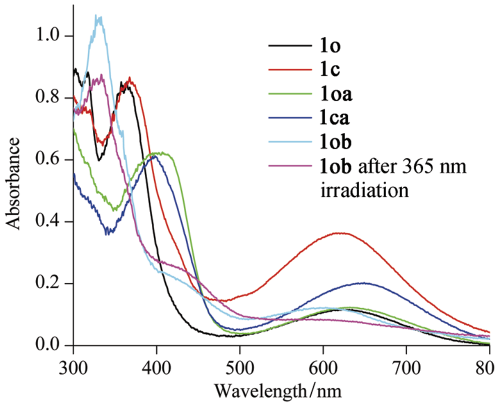


Figure 1 The visible absorption spectrum changes of **1** (2.5×10^{-5} mol•L^{-1}, $CHCl_3$). Absorption spectra of **1o** (black), **1c** (green), **1oa** (orange), **1ca** (blue), **1ob** (yellow) and the ring-opened isomer of **1** with addition of base (red) upon 365 nm light irradiation.

Addition of base to **1c** produced **1cb**, whose bands would decrease in the range of 500—800 nm and almost did not change in the range of 300—400 nm in intensity under visible light (>500 nm) irradiation (Figure 2). It suggested that **1cb** could isomerize to **1ob** under visible light irradiation.

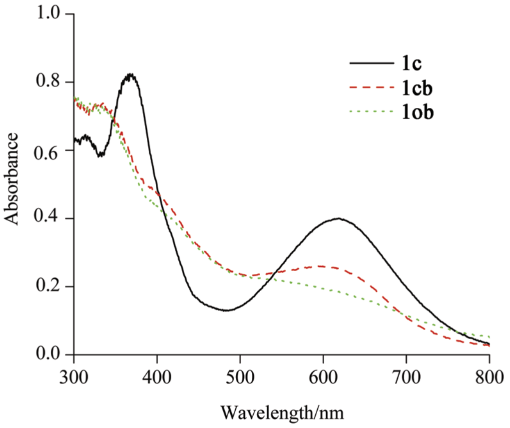


Figure 2 The visible absorption spectrum changes of **1** (2.5×10^{-5} mol•L^{-1}, $CHCl_3$) with visible light (⩾500 nm) irradiation. Absorption spectra of **1c** (solid), **1cb** (dash) and **1ob** (dot).

Generally, the absorption changes in the range of 300—400 nm from the ring-closed form to the ring-opened form were a little, the main change was decreased in the range of 500—700 nm. In the Figure 2, we could see certain decrease change from **1cb** to **1ob** in the range of 500—700 nm. Of course, the main change was not so obvious as compound **2** and compound **3** in the Figure 4 and Figure 6. The reason might be the change speed of compound **1** from **1cb** to **1ob**. Comparing Figure 2 and Figure 4, we could get that addition of base to compound **1** made the absorption in the range of 500—700 nm decrease a lot; but for compound **2**, decrease a little. This result implied that **1cb** was not very stable in the solution. Furthermore, addition of base to compound **1** was operated in the dark condition, which ruled out the influence of light irradiation. As known, most kinds of diarylethene were P-type compounds, whose two isomers were thermally stable. But **1cb** was T-type compound, which would have certain decrease in the room temperature and dark condition. As a result, **1cb** decreased in intensity because of the transform from **1cb** to **1ob** under dark condition, so the absorption change under visible light irradiation was not so remarkable, but there existed certain change from **1cb** to **1ob** under visible light irradiation. Obviously, the visible light could make the change from **1cb** to **1ob**.

Similarly, for **2** in Figure 3, the ring-opening isomer of **2** (**2o**, the black line, $\lambda_{max}=365$ nm) and the ring-closing isomer of **2** (**2c**, the green line, $\lambda_{max}=583$ nm), the protonated ring-opening isomer of **2** (**2oa**, the orange line, $\lambda_{max}=415$ nm) and the protonated ring-closing isomer of **2** (**2ca**, the blue line, $\lambda_{max}=640$ nm) could severally change to each other under UV/Vis light irradiation. The absorption spectra of **2oa** and **2ca** were red-shifted to those of **2o** and **2c**, respectively. Relatively, the absorption spectrum of **2ob** (the yellow line) had a maximum absorption peak at 335 nm, which was blue-shifted compared to that of **2o**. Upon exposing to 365 nm light, the 335 nm peak dropped down in intensity and no new absorption band was detected in the 500—800 nm range. This result indicated that the degradation of **2ob** might take place marginally and **2ob** could not change to the deprotonated ring-closing isomer of **2** (**2cb**) under 365 nm light irradiation. Addition of base to **2c** produced **2cb**, whose bands would decrease in the range of 300—800 nm in intensity (Figure 4). It suggested that **2cb** might simultaneously be degraded and have partly isomerized to **2ob** under light irradiation.

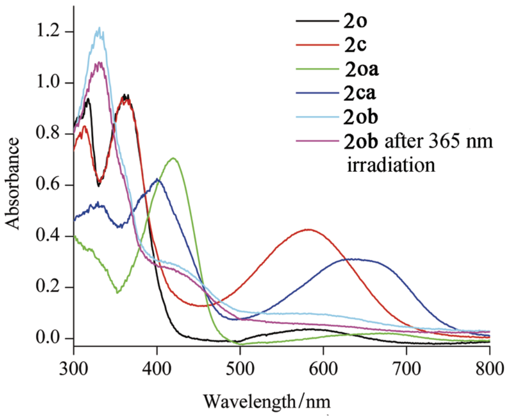


Figure 3 The visible absorption spectrum changes of **2** (2.7×10^{-5} mol•L^{-1}, CHCl$_3$). Absorption spectra of **2o** (black), **2c** (green), **2oa** (orange), **2ca** (blue), **2ob** (yellow) and the ring-opened isomer of **2** with addition of base (red) upon 365 nm light irradiation.

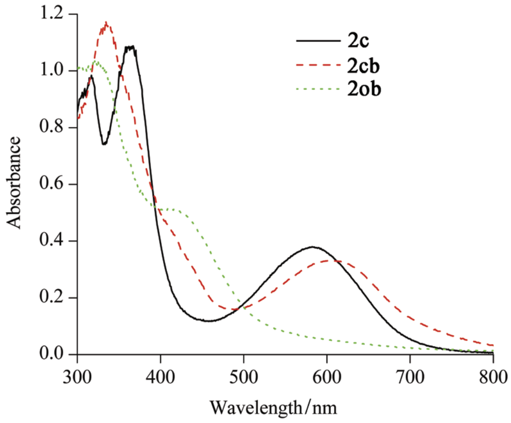


Figure 4 The visible absorption spectrum changes of **2** (2.7×10^{-5} mol•L^{-1}, CHCl$_3$) with visible light (≥500 nm) irradiation. Absorption spectra of **2c** (solid), **2cb** (dash) and **2ob** (dot).

Approximatively, for **3** (Figure 5), the ring-opening isomer of **3** (**3o**, the black line, $\lambda_{\max}$=370 nm) and the ring-closing isomer of **3** (**3c**, the green line, $\lambda_{\max}$=650 nm), the protonated ring-opening isomer of **3** (**3oa**, the orange line, $\lambda_{\max}$=402 nm) and the protonated ring-closing isomer of **3** (**3ca**, the blue line, $\lambda_{\max}$=720 nm) were severally reversible upon UV/Vis light irradiation. But the absorption spectrum of **3ob** (the yellow line, $\lambda_{\max}$=334 nm) was decreased a little in intensity and no new increase was detected in the 500—800 nm range under 365 nm light irradiation, too. It implied that **3ob** might degrade niggardly and could not change to the deprotonated ring-closing isomer of **3** (**3cb**) under 365 nm light irradiation. **3cb** ($\lambda_{\max}$=350 nm, 651 nm), which was synthesized by **3c** addition with base, would be blue-shifted and decease in the range of 500—800 nm in intensity (Figure 6). It was possibly degraded and had partly isomerized to **3ob** under light irradiation. It would generate a little flocculent precipitate after visible light irradiation for a long time, the reason had not been found out yet.

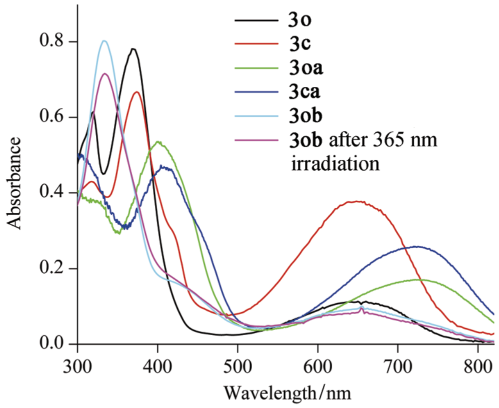


Figure 5 The visible absorption spectrum changes of **3** (2.0×10^{-5} mol•L^{-1}, CHCl$_3$). Absorption spectra of **3o** (black), **3c** (green), **3oa** (orange), **3ca** (blue), **3ob** (yellow) and the ring-opened isomer of **3** with addition of base (red) upon 365 nm light irradiation.

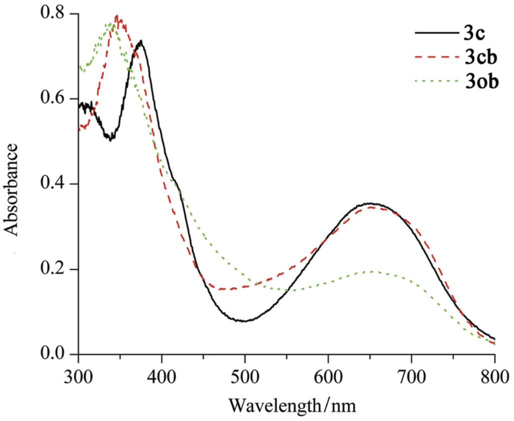


Figure 6 The visible absorption spectrum changes of **3cb** (2.0×10^{-5} mol•L^{-1}, CHCl$_3$) with visible light (≥500 nm) irradiation. Absorption spectra of **3c** (solid), **3cb** (dash) and **3ob** (dot).

Incorporating perfluorocyclopentene and quinoline compounds, three diarylethenes that exhibited acid/alkalis gated photochromic reactivity have been successfully obtained. It was worthwhile to note that after deprotonation of **1c**—**3c** and then upon visible light (≥500 nm) irradiation, the resulted **1cb**—**3cb** could convert to **1ob**—**3ob**, which kept unchanged after UV light irradiation. However, after addition of acid to the solutions of **1ob**—**3ob**, they would change to **1o**—**3o** or **1oa**—**3oa**, which had well reversibility of photochromic reaction.

Experimental

^{1}H NMR spectra were recorded at 300 MHz with TMS as an internal reference and $CDCl_3$ as solvent on a JOEL JNM-ECA300 spectrometer. MS spectra were recorded in methanol with an ESI-MS Esquire-LC spectrometer. UV/Vis absorption spectra were measured with a Shimadzu UV-2100S UV-Visible recording spectrophotometer. An SHG-200 Mejiro precision ultraviolet irradiate equipment, a PLC-SXE 300 Xenon lamp with different wavelength filters and an infrared lamp were used as light sources for photochromic reactions. Fluorescence spectra were recorded by a Hitachi F4500 spectrometer with a setting of 5 nm grating slit and 700 V amplifier of the photomultiplier, and a Horiba Jobinyvon Fluorolog spectrometer with a setting of 1 nm grating slit at room temperature. 1,2-Bis(2-methyl-3-thienly-5-formyl)-perfluorocyclopentene was synthesized by our laboratory. Other chemicals for synthesis were purchased from commercial suppliers. Column chromatography was performed on silica gel (zcx-2, 200—300 mesh). All solvents in analytical or chemical grade were purified from standard procedures.

The synthetic methodologies of 1-[2-methyl-3-thienly-5-(8-hydroxy-2-methylquinoline-2,2'-bithiophene)]-2-(2-methyl-3-thienly-5-formyl)-perfluorocyclopentene (**1**), 1-[2-methyl-3-thienly-5-(8-acetate-2-methylquinoline-2,2'-bithiophene)]-2-(2-methyl-3-thienly-5-formyl)-perfluorocyclopentene (**2**) and 1,2-bis[2-methyl-3-thienly-5-(8-hydroxy-2-methylquinoline-2,2'-bithiophene)]-perfluorocyclopentene (**3**) have been depicted in Scheme 1. They were prepared according to the previously reported method.[14] 1,2-bis(2-methyl-3-thienly-5-formyl)-perfluorocyclopentene (450 mg, 1.35 mmol) and 2-methyl-8-hydroxyquinoline (429 mg, 2.70 mmol) were stirred in acetic anhydride (30 mL) at 135 ℃ under Ar gas protection for 45 h. The product was then poured into cold water (50 mL). The mixed solution was stirred at room temperature for 5 min. The products were extracted with dichloromethane (160 mL) and the organic phase was dried with anhydrous Na_2SO_4. After evaporation of the solvent, the targets **1**—**3** were separated with petroleum/acetone (3/1, *V*/*V*) as extract. Compound **1**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.86 (s, CHO, 1H), 8.14 (d, J=9 Hz, 1H), 7.76 (s, 2H), 7.60 (d, J=8 Hz, 1H), 7.46—7.51 (m, 3H), 7.03—7.19 (m, 2H), 2.55 (s, 3H), 2.13 (s, 6H). MS (ESI) calcd for $C_{27}H_{17}O_2S_2NF_6$ $[M+H]^+$ 565.5, found 566.9. Compound **2**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.86 (s, CHO, 1H), 8.13 (d, J=8 Hz, 1H), 7.79 (s, 2H), 7.72 (d, J=10 Hz, 1H), 7.42—7.55 (m, 3H), 7.02—7.19 (m, 2H), 2.13 (s, 6H). MS (ESI) calcd for $C_{29}H_{19}O_3S_2NF_6$ $[M+H]^+$ 607.5865, found 608.9. Compound **3**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.16 (d, J=7 Hz, 2H), 7.66—7.79 (m, 4H), 7.43—7.54 (m, 6H), 6.99—7.19 (m, 4H), 2.01 (s, 6H). MS (ESI) calcd for $C_{37}H_{24}O_2S_2N_2F_6$ $[M+H]^+$ 706.7191, found 707.4.

Conclusions

In summary, we have successfully synthesized three novel diarylethenes combined with quinoline derivatives and demonstrated that the quinoline derivatives with alkyl groups attached to the thiophene heterocycles of diarylethenes, could undergo a gated photochromic reaction. The quinoline substituent attached to the 5-position of thiophene heterocycles could react with acid/alkali and influence on the reversibility of photochromic reaction. Compounds **1**—**3** could carry out good photochromic ring-closing reaction with addition of base.

Ackowlegement

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