Tetrahedron 68 (2012) 2267–2275

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Photochromism of new unsymmetrical isomeric diarylethenes bearing a pyridine group

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ARTICLE INFO

Article history:
Received 22 November 2011
Received in revised form 10 January 2012
Accepted 18 January 2012
Available online 24 January 2012

Keywords:
Diarylethene
Pyridine
Photochromism
Nitrogen atom position
Acidchromism

ABSTRACT

A new class of unsymmetrical isomeric diarylethenes bearing a terminal pyridine group was synthesized and their structures were determined by single-crystal X-ray diffraction analysis. The effects of the nitrogen atom position in the pyridine group on their properties including photochromism, acidchromism, and fluorescence were investigated systematically. Among the three isomeric derivatives, the cyclization quantum yield and the absorption maxima of the *ortho*-substituted diarylethene were the biggest, while the fluorescence quantum yield of the *para*-substituted diarylethene was the biggest. Furthermore, the three isomeric diarylethenes exhibited multi-addressable switching behaviors by the stimulation of acid/base and light. Addition of trifluoroacetic acid to solutions of these diarylethenes produced the protonated derivatives, which also showed excellent photochromic behaviors, but only the *para*-substituted diarylethene exhibited a notable color change of solution from crimson to violet. The results revealed that the effects of the nitrogen atom position in the terminal pyridine group played a very important role during the process of photoisomerization for these isomeric diarylethene derivatives.

1. Introduction

Organic photochromic systems have recently received increasing attention in materials science because of the widespread potential application in photonic devices. Various types of photochromic compounds, such as spirobenzopyrans,[1] azobenzenes,[2] fulgides,[3] and diarylethenes,[4] have hitherto been developed. Among such compounds, diarylethene derivatives are one of the most promising candidates for optoelectronic devices, such as optical memories and photoswitches, mainly due to the excellent thermal stability of the respective isomers, notable fatigue resistance, and high reactivity in the solid state.[5]

The six-membered pyridine ring has good aromaticity with the similar structure to the benzene ring.[6] The nitrogen atom of pyridine ring can easily occur to nucleophilicity substituted reaction resulted from its vigoroso electronegativity.[7] Additionally, pyridine bases have high biological activities, which are widely used as core components or modifiers of pharmaceutical products and agricultural chemicals.[8] Recently, diarylethenes bearing a pyridine group have attracted more and more attention, and the pyridine ring is regarded as side group connected with other aromatic rings, such as thiazolyl,[9] thiophene,[10] and benzothiophene.[11] These diarylethene derivatives exhibited some unusual characteristics, which could be potentially applied in photoswitches, the photomodulation of the chemical reactivity, and biochemistry. Recently, Piard et al. developed a ratiometric fluorescent photoswitch based on a diarylethene with two terminal pyridine rings linked with thiazolyl moieties.[9] Branda et al. reported a photocontrolled molecular switch based on a symmetrical dithienylethene bearing two terminal pyridine rings and found it could control biological organism and retain its photoswitching behavior in vivo.[10b] Furthermore, the pyridyl group can directly connect to perfluorocyclopentene ring. Our group explored a new class of unsymmetrical diarylethenes bearing a pyridine unit directly linked with the ethene moiety, which exhibited excellent photochromism even in the crystalline phase.[12] Diarylethenes bearing pyridine units could be used as fluorescent probes of recognizing ions due to the excellent coordinating ability of pyridyl with some specific ions.[13] For example, Yi et al. developed a multiresponsive fluorescence switch based on diarylethene and terpyridine units, which could serve as a detector for the biological process of metal ion transmembrane transport.[13a] Tian et al. prepared a new Iridium complex coordinating to the photochromic diarylethene, which showed excellent near-Infrared photochromic behaviors accompanied by efficient quenching of phosphorescence emission.[13b] All of the results reveal that diarylethenes bearing pyridine units have attracted much attention as highly promising candidates for optoelectronic devices due to their specific characteristics.

Generally, the photochromic behaviors of diarylethene derivatives can be effectively modified by suitable functionalization of the aromatic rings with different substituents.[14] Apart from the fact

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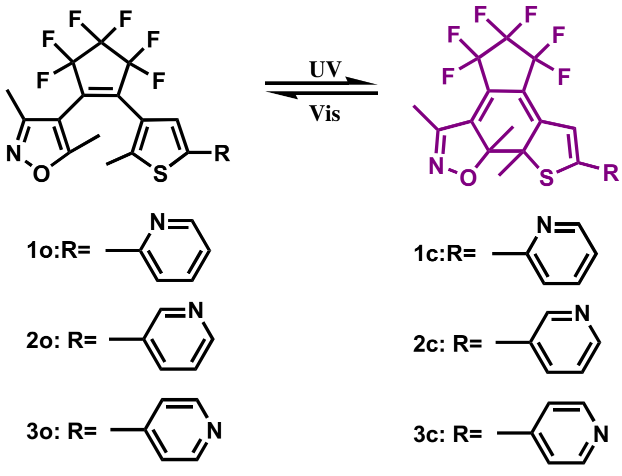
doi:10.1016/j.tet.2012.01.058

that the substituent effects have an important role to play in modifying the properties of diarylethenes, the position of the substituent can also affect their properties significantly, which can be used for the fine tuning of the optoelectronic behaviors of diarylethene derivatives. Although many reports concerning the substituent position effects on the photochromic properties have been hitherto reported, the results mainly emphasis on effects of a certain same substituent linked with the different position of the terminal benzene ring on their photochromic properties.[15] To the best of our knowledge, the nitrogen atom position effect of pyridine ring on the properties of diarylethenes has not been hitherto reported. In this study, we have explored a new class of unsymmetrical isomeric diarylethenes bearing both isoxazole and thiophene moieties with a terminal pyridine unit and mainly discussed the nitrogen atom position effect of pyridine ring on their physicochemical properties. The synthesized diarylethenes are 1-(3,5-dimethyl-4-isoxazolyl)-2-[2-methyl-5-(2-pyridyl)-3-thienyl] perfluorocyclopentene (**1o**), 1-(3,5-dimethyl-4-isoxazolyl)-2-[2-methyl-5-(3-pyridyl)-3-thienyl]perfluorocyclopentene (**2o**), and 1-(3,5-dimethyl-4-isoxazolyl)-2-[2-methyl-5-(4-pyridyl)-3-thienyl] perfluorocyclopentene (**3o**). All of these derivatives exhibited excellent photochromism in solution, in PMMA amorphous films, and even in their respective crystalline phase. The photochromic scheme of diarylethenes **1**–**3** is shown in Scheme 1.



Scheme 1. Photochromism of diarylethenes **1**–**3**.

2. Experiment

2.1. General methods

Melting point was taken on a WRS-1B melting point apparatus. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Infrared spectra (IR) were recorded on a Bruker Vertex-70 spectrometer. Elemental analysis was measured with an elemental analyzer labeled the PE CHN 2400 analyzer. Fluorescent spectra were measured using a Hitachi F-4500 fluorimeter. Absorption spectra were measured using an Agilent 8453 UV/vis spectrophotometer. Photoirradiation was carried out using an SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 Visible lamp. The required wavelength was isolated by the use of the appropriate filters. The quantum yields of cyclization/cycloreversion were determined by comparing the reaction yield with the known yield of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane.[5c] Dissolved ultrasonically 10 mg of diarylethene sample and 100 mg PMMA into 1.0 mL chloroform, the film was prepared by spin-coating on the surface of quartz substrate.

Suitable crystals **1o**–**3o** were obtained by slow evaporation of the mixture solutions containing chloroform and hexane. All the measurements were made on a Bruker SMART APEX II CCD diffractometer using a MULTI scan technique at room temperature using Mo Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 by full-matrix least-squares techniques using SHELXTL-97 program. All nonhydrogen atoms were refined anisotropically. Crystallographic data for the structures of diarylethenes **1o**–**3o** have been deposited with in the Cambridge Crystallographic Data Centre as supplemental publication CCDC 846204 for **1o**, CCDC 846205 for **2o**, and CCDC 846206 for **3o**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk; fax: +44 0 1223 336033).

2.2. Synthesis

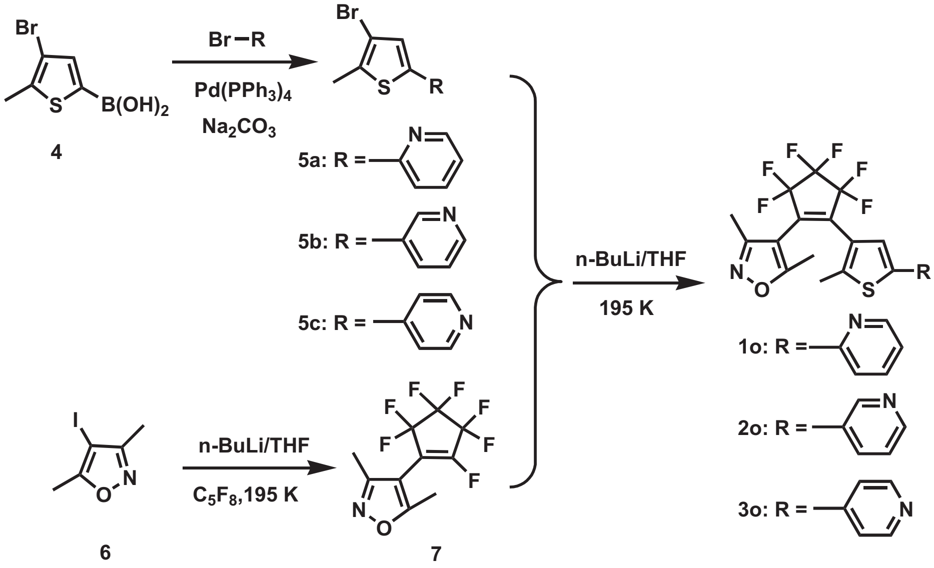
The synthetic route used to obtain diarylethenes **1o**–**3o** is shown in Scheme 2. Suzuki coupling of three bromopyridine derivatives with a thiophene boronic acid gave the pyridylthiophene derivatives **5a**–**c**. The mono-substituted (3,5-dimethyl-4-isoxazolyl)perfluorocyclopentene (**7**) was synthesized by the similar reported method using 3,5-dimethyl-4-iodoisoxazole (**6**) as raw material.[16] Finally, compounds **5a**–**c** were lithiated and then separately coupled with compound **7** to give diarylethenes **1o**–**3o**, respectively. The structures of **1o**–**3o** were confirmed by elemental analysis, NMR, and IR.

2.2.1. 3-Bromo-2-methyl-5-(2-pyridyl)thiophene (***5a***). Compound **5a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid[17] (3.10 g, 14.00 mmol) with 2-bromopyridine (2.20 g, 14.00 mmol) in the presence of $Pd(PPh_3)_4$ (0.27 g, 0.23 mmol) and Na_2CO_3 (6.36 g, 60.00 mmol) in THF (80 mL containing 10% water) for 15 h at 343 K. The reaction was allowed to slowly cool to the room temperature. After being extracted with ether, the organic layer was dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on SiO_2 using hexane as the eluent and 3.00 g of **5a** obtained as a pale yellow solid in 83% yield. Mp 71–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, $-CH_3$), 7.13–7.16 (m, 1H, pyridine–H), 7.36 (s, 1H, thiophene–H), 7.55 (d, J=8.0 Hz, 1H, pyridine–H), 7.65–7.69(m, 1H, pyridine–H), 8.53 (d, J=8.0 Hz, 1H, pyridine–H); IR (ν, KBr, cm^{-1}): 732, 771, 882, 1012, 1094, 1158, 1288, 1327, 1481, 1628, 3458.

2.2.2. 3-Bromo-2-methyl-5-(3-pyridyl)thiophene (***5b***). Compound **5b** was prepared by a method similar to that used for **5a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether/ethyl acetate (v/v=8/1) as an eluent to give 2.60 g **5b** as a pale yellow solid in 72% yield. Mp 39–40 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, $-CH_3$), 7.16 (s, 1H, thiophene–H), 7.29–7.32 (m, 1H, pyridine–H), 7.77(d, J=8.0 Hz, 1H, pyridine–H), 8.51(d, J=8.0 Hz, 1H, pyridine–H), 8.78 (s, 1H, pyridine–H); IR (ν, KBr, cm^{-1}): 703, 797, 946, 1017, 1124, 1164, 1320, 1454, 1489, 1614, 3437.

2.2.3. 3-Bromo-2-methyl-5-(4-pyridyl)thiophene (***5c***). Compound **5c** was prepared by a method similar to that used for **5a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether/ethyl acetate (v/v=6/1) as an eluent to give 2.82 g **5c** as a pale yellow solid in 78% yield. Mp 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, $-CH_3$), 7.30 (s, 1H, thiophene–H), 7.37 (d, 2H, J=8.0 Hz, pyridine–H), 8.58(d, J=8.0 Hz, 2H, pyridine–H); IR (ν, KBr, cm^{-1}): 714, 810, 864, 1011, 1163, 1220, 1323, 1458, 1495, 1597, 3431.

2.2.4. (3,5-Dimethyl-4-isoxazolyl)perfluorocyclopentene (***7***). To a stirred THF solution (80 mL) of compound **6** (3.62 g, 20.10 mmol)



Scheme 2. Synthetic route for diarylethenes **1o**–**3o**.

was added dropwise a 2.5 M *n*-BuLi/hexane solution (8.80 mL, 22 mmol) at 195 K under nitrogen atmosphere. Stirring was continued for 30 min at 195 K, octafluorocyclopentene (C_5F_8) (2.80 mL, 20.50 mmol) was slowly added and the reaction mixture was stirred for 2 h at this low temperature. The reaction was quenched by water. After being extracted with ether, the organic layer was washed with 1 M aqueous HCl and water. The organic layer dried over anhydrous $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to give 2.80 g compound **7** as pale yellow liquid in 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H, −CH$_3$), 2.43 (s, 3H, −CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7, 12.2, 99.9, 158.5, 170.6.

*2.2.5. 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(2-pyridyl)-3-thienyl]perfluorocyclopentene (**1o**).* To a stirred anhydrous THF (80 mL) of compound **5a** (0.63 g, 2.50 mmol) was added dropwise a 2.5 M *n*-BuLi/hexane solution (1.00 mL, 2.50 mmol) at 195 K under argon atmosphere. After 30 min, 15 mL THF containing compound **7** (0.70 g, 2.50 mmol) was added and the reaction mixture was stirred for 2 h at this low temperature. The reaction was allowed to slowly warm to the room temperature and quenched by water. The product was extracted with ether, dried with $MgSO_4$, filtrated, and evaporated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v=4/1) as the eluent to give 0.34 g diarylethene **1o** as a pale yellow solid in 31% yield. Mp 88–89 °C; calcd for $C_{20}H_{14}F_6N_2OS$: calcd C, 54.05; H, 3.18; N, 6.30. Found C, 54.42; H, 3.04; N, 6.18; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3H, −CH$_3$), 2.29(s, 3H, −CH$_3$), 3.59 (s, 3H, −CH$_3$), 6.93 (s, 1H, pyrrole–H), 7.18 (t, 1H, *J*=8.0 Hz, pyridine–H), 7.49 (s, 1H, thiophene–H), 7.62 (d, 1H, pyridine–H), 7.71 (t, 1H, *J*=8.0 Hz, pyridine–H), 8.55 (d, 1H, pyridine–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 14.7, 105.6, 109.9, 112.7, 115.9, 118.5, 118.7, 122.3, 124.0, 126.0, 135.9, 136.7, 143.0, 143.2, 149.6, 151.5; IR (ν, KBr, cm^{-1}): 743, 774, 810, 894, 989, 1068, 1128, 1196, 1272, 1344, 1432, 1488, 1588, 1642, 3405.

*2.2.6. 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(3-pyridyl)-3-thienyl]perfluorocyclopentene (**2o**).* Diarylethene **2o** was prepared by a method similar to that used for diarylethene **1o** using 3-bromo-5-(3-pyridyl)-2-methylthiophene (**5b**) instead of **5a**. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v=3/1) as the eluent to give 0.47 g **2o** as a pale yellow solid in 43% yield. Mp 160–161 °C; calcd for $C_{20}H_{14}F_6N_2OS$: Calcd C, 54.05; H, 3.18; N, 6.30. Found C, 53.89; H, 3.26; N, 6.41; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79 (s, 3H, −CH$_3$), 1.99(s, 3H, −CH$_3$), 3.61 (s, 3H, −CH$_3$), 6.91 (s, 1H, pyrrole–H), 7.29 (s, 1H, thiophene–H), 7.34 (t, 1H, *J*=8.0 Hz, pyridine–H), 7.82 (d, 1H, *J*=8.0 Hz, pyridine–H), 8.54 (d, 1H, *J*=8.0 Hz, pyridine–H) 8.80 (t, 1H, *J*=8.0 Hz pyridine–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 14.5, 33.0, 105.7, 112.7, 118.7, 123.7, 123.9, 126.3, 128.8, 129.3, 130.8, 132.7, 135.8, 138.6, 146.6, 148.8; IR (ν, KBr, cm^{-1}): 698, 747, 804, 847, 893, 945, 989, 1065, 1128, 1192, 1276, 1341, 1424, 1493, 1594, 1657, 2921, 3677.

*2.2.7. 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(4-pyridyl)-3-thienyl]perfluorocyclopentene (**3o**).* Diarylethene **3o** was prepared by a method similar to that used for diarylethene **1o** using 3-bromo-5-(4-pyridyl)-2-methylthiophene (**5c**) instead of **5a**. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v=3/1) as the eluent to give 0.50 g **3o** as a pale yellow solid in 48% yield. Mp 153–154 °C; calcd for $C_{20}H_{14}F_6N_2OS$: calcd C, 54.05; H, 3.18; N, 6.30. Found C, 54.36; H, 3.09; N, 6.14; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.78 (s, 3H, −CH$_3$), 2.04(s, 3H, −CH$_3$), 3.61 (s, 3H, −CH$_3$), 6.90 (s, 1H, pyrrole–H), 7.41 (d, 2H, *J*=8.0 Hz, pyridine–H), 7.44 (s, 1H, thiophene–H), 8.61 (d, 2H, *J*=8.0 Hz, pyridine–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 14.6, 33.0, 105.7, 109.7, 112.6, 118.7, 119.4, 125.0, 126.5, 135.8, 139.3, 140.2, 142.7, 150.5; IR (ν, KBr, cm^{-1}): 749, 812, 844, 895, 989, 1067, 1135, 1198, 1276, 1318, 1346, 1430, 1500, 1594, 1653, 2924, 3030, 3416.

3. Results and discussion

3.1. Photochromism of diarylethenes in solution and solid medium

The photochromic behaviors of diarylethenes **1o**–**3o** induced by photoirradiation at room temperature were measured both in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA films (10%, w/w). The changes in the absorption spectra of diarylethene **1** and the color of diarylethenes **1o**–**3o** in hexane induced by alternating irradiation with UV and visible light are shown in Fig. 1. Diarylethene **1o** exhibited a sharp absorption peak at 303 nm in hexane, which aroused from π–π^* transition.[18] Upon irradiation with 297 nm

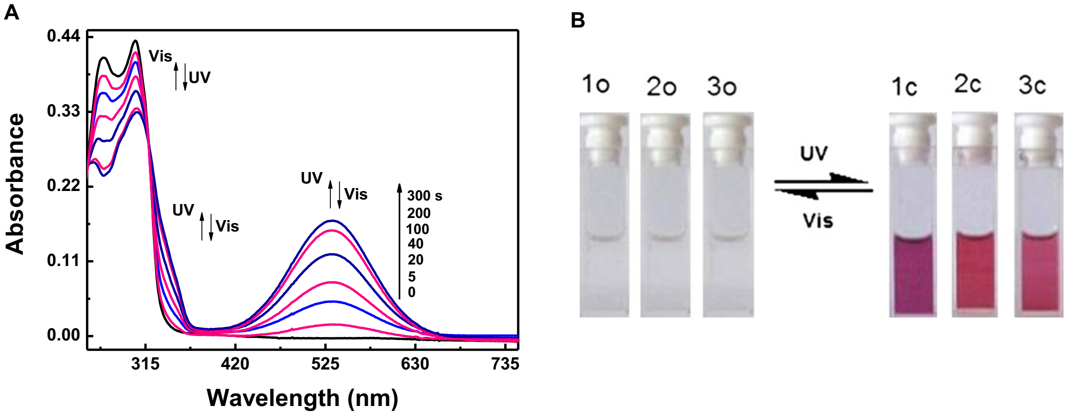


Fig. 1. Absorption spectral changes of diarylethene **1** (A) and color changes of diarylethenes **1**–**3** (B) upon alternating irradiation with UV and visible light in hexane (2.0×10^{-5} mol L^{-1}) at room temperature.

light, a new visible absorption band centered at 534 nm emerged while the original peak at 303 nm decreased due to the formation of the closed-ring isomer **1c**. This could be seen with the naked eye, as the colorless solution of **1o** turned purple red. Alternatively, the purple red solution could be bleached completely to colorless upon irradiation with visible light ($\lambda>450$ nm), indicating that **1c** returned to the initial state **1o**. As with compound **1**, diarylethenes **2** and **3** also exhibited notable photochromism in hexane. Upon irradiation with 297 nm light, absorption bands in the visible region appeared and the colorless solutions **2o** and **3o** turned crimson (Fig. 1B) due to cyclization reactions resulting in the formation of the closed-ring isomers **2c** and **3c**, which their absorption maxima were appeared at 519 and 521 nm, respectively. Both of the crimson-colored solutions **2c** and **3c** could be decolorized by irradiation with visible light of wavelength greater than 450 nm, suggesting return to the open-ring isomers **2o** and **3o**. In the photostationary state, the isosbestic points for diarylethenes **1**–**3** in hexane were observed at 318, 299, and 313 nm, respectively. The photoconversion ratios from open- to closed-ring isomers of the three derivatives in the photostationary state were analyzed by HPLC in hexane. As shown in Fig. 2, the photoconversion ratios of diarylethenes **1**–**3** were 80% for **1**, 75% for **2**, and 79% for **3**. Compared to the reported analogous derivative, namely 1-(3,5-dimethyl-4-isoxazolyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**DIMPTP**),[16] the photoconversion ratios of the three isomeric diarylethenes were notably increased when arrived at the photostationary state in solution. But they were much lower than that of diarylethenes bearing a pyrrole moiety.[19] In PMMA films, diarylethenes **1**–**3** also showed similar photochromism to that in hexane. The changes in the absorption spectra of diarylethene **1** and the color changes of diarylethenes **1**–**3** are shown in Fig. 3. Upon irradiation with 297 nm UV light, the colorless diarylethene **1o**/PMMA film turned violet, of which the absorption maximum was observed at 544 nm; while the colors of other two diarylethene/PMMA films changed from colorless to purple red with the appearance of a new broad absorption band centered at 531 nm for **2** and 532 nm for **3** due to the formation of the closed-ring isomers **2c** and **3c**. All colored diarylethene/PMMA films could be bleached completely by irradiating of visible light with appropriate wavelength. Compared with that in solution, the absorption maxima of the closed-ring isomers **1c**–**3c** exhibited an evidently bathochromic shift in their respective PMMA film. The red shifts of the absorption maxima of **1c**–**3c** were 10 nm for **1c**, 12 nm for **2c**, and 11 nm for **3c**. This red shift phenomenon may be attributed to the polar effect of the polymer matrix in amorphous polymer state as observed for the majority of the reported diarylethenes.[15d,20]

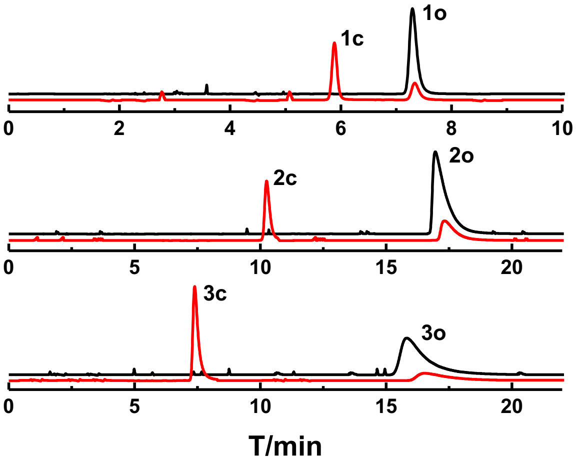


Fig. 2. The photoconversion ratios of diarylethenes **1**–**3** at photostationary state in hexane analyzed by HPLC method.

The photochromic features of diarylethenes **1**–**3** in hexane and in PMMA films are summarized in Table 1. These data revealed that the position of the nitrogen atom in the terminal pyridine unit had a significant effect on the photochromic properties of these diarylethene derivatives, such as the absorption maxima, molar absorption coefficients, and quantum yields of cyclization/cycloreversion. Among the three isomeric compounds, the absorption maxima of the open- and closed-ring isomers of diarylethene **1** were at the longest wavelength both in hexane and in a PMMA film. When the nitrogen atom was located at the *meta*- or *para*-position of the terminal pyridine unit, the absorption maxima of other two isomeric diarylethenes had notably decreased in both hexane and PMMA films. The molar absorption coefficients increased in the order of *para*-<*ortho*-<*meta*-substitution by the nitrogen atom in pyridine ring for the closed-ring isomers. Among the closed-ring isomers **1c**–**3c**, the molar absorption coefficient of the *para*-substituted derivative **3c** is the smallest; while that of the *meta*-substituted derivative **2c** is the biggest. For the open-ring isomers **1o**–**3o**, the molar absorption coefficient of **1o** is the smallest and that of **2o** is the biggest. The cyclization and cycloreversion quantum yields of diarylethene **1** were 0.47 and 0.10, respectively. When the nitrogen atom was located at the *meta*- or *para*-position of the terminal pyridine unit, the cyclization quantums of other two isomeric diarylethenes decreased significantly and their values were almost equal to each other ($\Phi_{o\text{-}c,2}=0.37$ and $\Phi_{o\text{-}c,3}=0.36$). The cycloreversion quantum yields increased in the order of *meta*-<*ortho*-<*para*-substitution by the nitrogen atom in

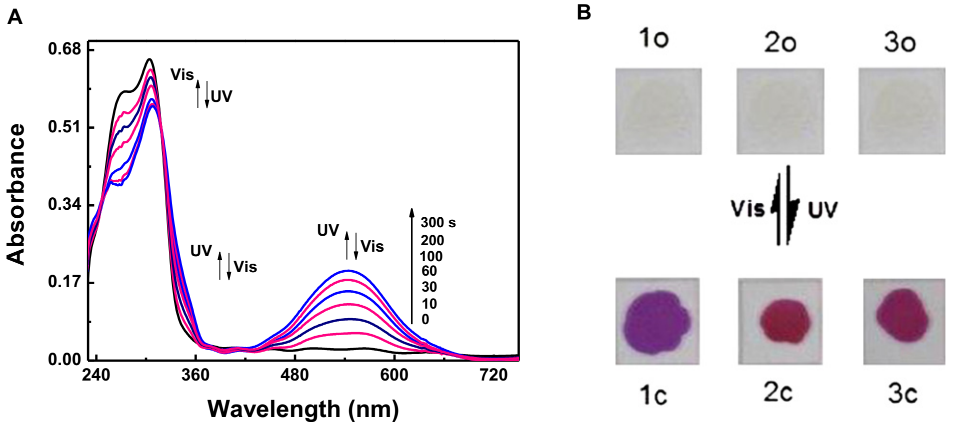


Fig. 3. Absorption spectral changes of diarylethene **1** (A) and color changes of diarylethenes **1**–**3** (B) upon alternating irradiation with UV and visible light in PMMA films (10%, w/w) at room temperature.

Table 1
Absorption parameters and photochromic reactivity of diarylethenes **1**–**3** in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA films (10%, w/w)

Compound	$\lambda_{o,max}$/nm[a] (ε/L mol^{-1} cm^{-1})		$\lambda_{c,max}$/nm[b] (ε/L mol^{-1} cm^{-1})		Φ[c]		Conversion at PSS in hexane
	Hexane	PMMA film	Hexane	PMMA film	$\Phi_{o\text{-}c}$	$\Phi_{c\text{-}o}$	
1	303 (2.13×10^4)	304	534 (1.06×10^4)	544	0.47	0.10	80%
2	269 (2.53×10^4)	276	519 (1.33×10^4)	531	0.37	0.080	75%
3	272 (2.17×10^4)	278	521 (9.99×10^3)	532	0.36	0.11	79%

[a] Absorption maxima of open-ring isomers.

[b] Absorption maxima of closed-ring isomers.

[c] Quantum yields of cyclization reaction ($\Phi_{o\text{-}c}$) and cycloreversion reaction ($\Phi_{c\text{-}o}$), respectively.

pyridine ring. Compared to the analogous diarylethene **DIMPTP**,[16] diarylethenes **1**–**3** had bigger molar absorption coefficients and cyclization quantum yields as well as smaller cycloreversion quantum yields. The result indicated that the terminal pyridine ring could be effective to enhance the cyclization quantum yield and suppress the cycloreversion quantum yield.

So far, the thermal stability and fatigue resistance of diarylethenes have been extensively reported.[21] Especially, the fatigue-resistant property, i.e., how many times photocyclization and photocycloreversion reaction cycles could be repeated without loss of performance, was a very important factor for practical applications in optical devices.[21,22] On the one hand, the thermal stabilities of the open- and closed-ring isomers of diarylethenes **1**–**3** were tested in hexane at room temperature and at 341 K, respectively. Storing these solutions in hexane at room temperature in the dark and then exposing them to air for more than 1000 h, no changes in their colors and spectra were observed. Moreover, no decomposition was detected when the three isomeric diarylethenes were exposed to air for more than one month. At 341 K, diarylethenes **1**–**3** also exhibited good thermal stabilities for more than 8 h. After refluxing more than 8 h in hexane in the dark, no changes in their absorption spectra were observed and no any decomposition was detected by NMR method. On the other hand, the fatigue resistances of diarylethenes **1**–**3** were examined both in hexane and in PMMA films by alternating irradiation with UV and visible light in air at room temperature, as shown in Fig. 4. In hexane, the coloration and decoloration cycles of diarylethenes **1**–**3** could be repeated more than 50 times with only ca. 4% degradation of **1c**, 12% degradation of **2c**, and 19% degradation of **3c**. In PMMA films, they also exhibit good photochromism with only ca. 14% degradation of **1c**, 19% degradation of **2c**, and 25% degradation of **3c** after 200 repeated cycles. Therefore, the fatigue resistance of

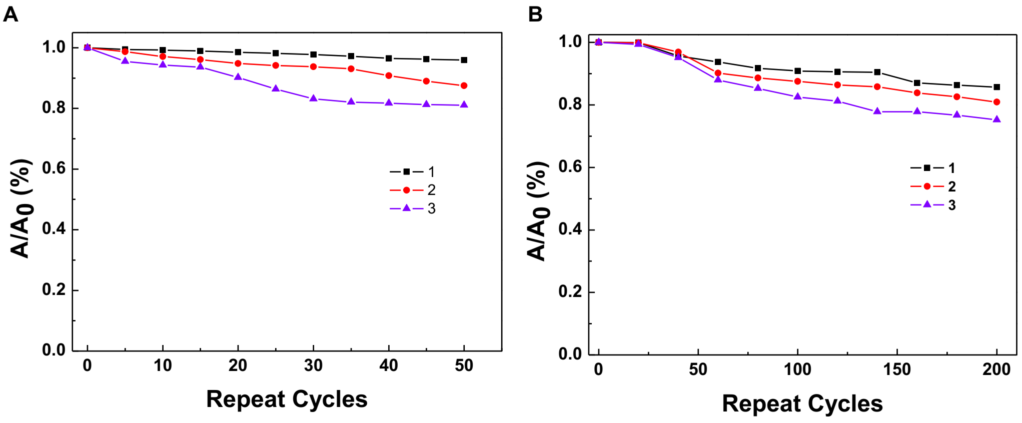


Fig. 4. Fatigue resistances of diarylethenes **1**–**3** in hexane (A) and in PMMA films (B) in air atmosphere at room temperature. Initial absorptance of the sample was fixed to 1.0.

diarylethene **1** was the strongest and that of diarylethene **3** was the weakest in both solution and solid medium among the three isomeric compounds. The result revealed that the fatigue resistance of diarylethenes **1**–**3** in PMMA films was much better than that in hexane as observed for the reported diarylethenes bearing a thiazole ring.[23]

3.2. Photochromism of diarylethenes in the crystalline phase

To gain a deeper understanding of the relationship between the conformation and the photochromism of these isomeric diarylethene derivatives in the crystalline phase, the structural confirmations of diarylethenes **1o**–**3o** were provided by X-ray crystallographic analysis. The X-ray crystallographic analysis data are listed in Table S1. Their ORTEP drawings and photochromism induced by alternating irradiation with UV and visible light in the crystalline phase are shown in Fig. 5. For diarylethene **1o**, the molecule crystallizes with an appropriate C_2 symmetry with the photoactive *anti*-parallel conformation in the crystalline phase, which can be expected to undergo photocyclization.[24] The dihedral angles between the hexafluorocyclopentene ring and the two adjacent heteroaryl rings was 48.3° for O1/N1/C16–C18 and 51.3° for S1/C6–C9, and that between the thiophene ring and the linked pyridine ring was 19.5°. The intermolecular distance between the two photoactive C atoms (C9···C18) was 3.500 Å, which was close enough to perform the cyclization reaction.[24,25] The corresponding data of other two diarylethenes are summarized in Table S2. For diarylethene **2o**, the molecule crystallizes with an appropriate C_2 symmetry with the photoactive *anti*-parallel conformation in the crystalline phase and the distance between the two reactive C atoms (C9···C18) is 3.647 Å. There are two independent molecules in the asymmetric unit of diarylethene **3o** and each of them adopts an *anti*-parallel conformation in the crystalline phase. The distances between the potentially photoactive C atoms (C9···C18 and C29···C37) in each molecule were 3.635 Å and 3.643 Å, respectively.

From the data, it could be concluded that all molecules of crystals **1o**–**3o** were fixed in an *anti*-parallel mode in the crystalline phase and the distances of the two reactive C atoms were less than 4.2 Å. So they could be expected to undergo photochromism in the single crystalline phase. As a matter of fact, the crystals of **1o**–**3o** underwent excellent photochromism in accordance with the expected ring closure upon irradiation with UV light, as shown in Fig. 5E. Upon irradiation with 297 nm light, these colorless crystals of **1o**–**3o** turned to purple red quickly due to the formation of the closed-ring isomers **1c**–**3c**. When the colored crystals were dissolved separately in hexane, an intense absorption band was appeared at the same wavelength as that of their respective closed-ring isomer in solution. Alternatively, the colored crystals returned to colorless upon irradiation with the appropriate visible light. Furthermore, these crystals exhibited remarkable fatigue-resistance greater than 200 cyclization/cycloreversion repeated cycles and their closed-ring isomers remained stable for more than a half year in the dark at room temperature. As such, they could be potentially used for the promising candidates for certain

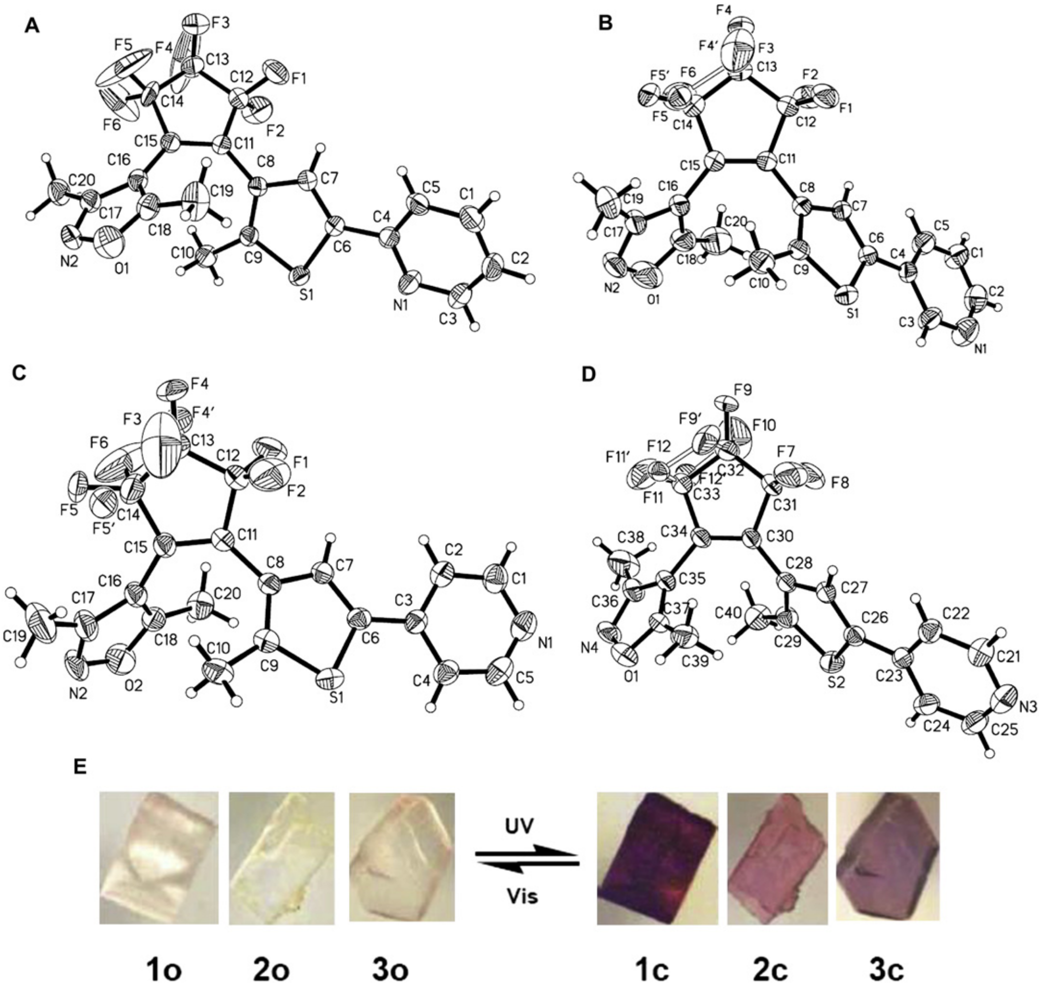


Fig. 5. ORTEP drawings of crystals **1o**–**3o** and their color changes by photoirradiation in the single crystalline phase: (A) ORTEP drawing of **1o**; (B) ORTEP drawing of **2o**; (C) ORTEP drawing of **3o**–I; (D) ORTEP drawing of **3o**–II; (E) color changes for crystals **1**–**3**.

optoelectronic devices such as high density three-dimensional optical recording media, optical switches, or color displays.[21,24,26]

3.3. Acidchromism of diarylethenes

Here, the multiple switching behaviors of diarylethenes **1**–**3** were discussed by the stimulation of acid/base and light. Fig. 6 illustrates the structural and color changes between **1**–**3** and **4**–**6** in acetonitrile solution (2.0×10^{-5} mol L^{-1}). Addition of trifluoroacetic acid in acetonitrile solution (1.0 μL, 6.8×10^{-3} mol L^{-1}) to the solutions of **1o**–**3o** produced the protonated diarylethenes **4o**–**6o**, whose absorption maxima bathochromic shifted from 303 nm to 338 nm for **4o** ($\varepsilon=1.48\times10^{4}$ L mol^{-1} cm^{-1}), from 270 nm to 295 nm for **5o** ($\varepsilon=1.75\times10^{4}$ L mol^{-1} cm^{-1}), and from 284 nm to 341 nm for **6o** ($\varepsilon=2.11\times10^{4}$ L mol^{-1} cm^{-1}). The protonated **4o**–**6o** could return to the initial state **1o**–**3o** by neutralization with triethylamine base (2.0 μL, 3.6×10^{-3} mol L^{-1}). Diarylethenes **4o**–**6o** also exhibited notable photochromism by photoirradiation. Upon irradiation with UV light, the colorless solutions containing **4o**–**6o** separately turned the closed-ring isomers **4c**–**6c** with different colors, whose absorption maxima in the visible region were observed at 538 nm for **4c** ($\varepsilon=1.08\times10^{4}$ L mol^{-1} cm^{-1}), 529 nm for **5c** ($\varepsilon=1.04\times10^{4}$ L mol^{-1} cm^{-1}), and 546 nm for **6c** ($\varepsilon=8.26\times10^{3}$ L mol^{-1} cm^{-1}). Similarly, a reversible transformation between the colored diarylethenes **1c**–**3c** and **4c**–**6c** could be performed by the stimulation of acid/base. As depicted in Fig. 7, addition of trifluoroacetic acid to the solution of **3c** produced the protonated **6c** whose absorption maximum shifted from 528 to 546 nm, and this process was accompanied by a notable color change of solution from crimson to violet. This phenomenon is consistent with that of reported diarylethenes bearing a pyridine ring.[27] However, for diarylethenes **1c** and **2c**, no changes in their absorption maxima and colors were observed under the same experimental condition. The result revealed that the nitrogen atom position in the terminal pyridine ring had a significant effect on the acidchromism of these isomeric diarylethene derivatives.

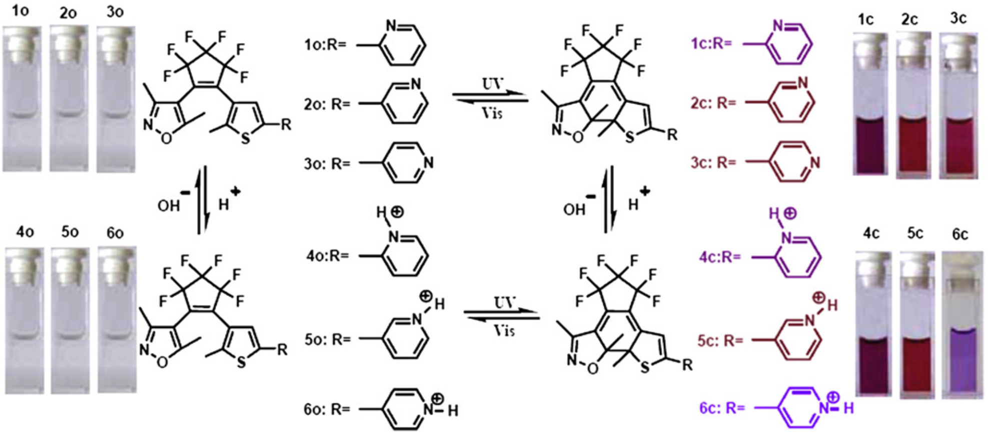


Fig. 6. The structural and color changes between diarylethenes **1**–**3** and diarylethenes **4**–**6** in acetonitrile (2.0×10^{-5} mol L^{-1}).

3.4. Fluorescence of diarylethenes

The fluorescence properties of diarylethenes **1o**–**3o** both in solution (5.0×10^{-5} mol L^{-1}) and in PMMA films (10%, w/w) were measured at room temperature. As shown in Fig. 8, the emission peaks of the diarylethenes **1o**–**3o** were observed at 399, 403, and 394 nm when excited at 290 nm in hexane, and were observed at 412, 418, and 403 nm when excited at 310 nm in PMMA films. As have been observed for most of the reported diarylethenes,[28] the emission peaks of diarylethenes **1o**–**3o** showed an evident hypsochromic shift in PMMA films with values of 13 nm for **1o**, 15 nm for **2o**, and 9 nm for **3o** when compared with that in hexane. Among diarylethenes **1o**–**3o**, the emission intensity of diarylethene **2o** was the weakest and that of **3o** was the strongest both in hexane and in a PMMA film. By using anthracene as the reference, the fluorescence quantum yields of diarylethenes **1o**–**3o** were determined to be 0.0129, 0.0139, and 0.0368, respectively. The result suggested that the fluorescence quantum yield could be significantly enhanced when the nitrogen atom was located at the *para*-position of the terminal pyridine unit. Compared to the analogous diarylethene **DIMPTP** ($\Phi_{f,DIMPTP}=0.0094$),[16] diarylethenes **1**–**3** had much bigger fluorescence quantum yields, indicating that the terminal pyridine ring could be effective to enhance the fluorescence quantum yield as compared a terminal benzene ring.

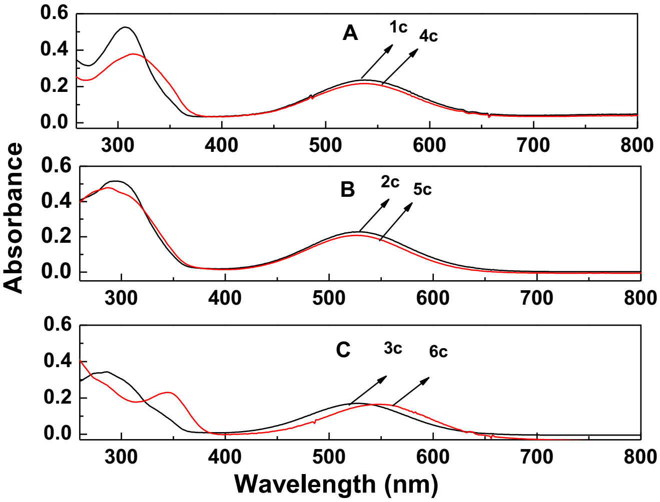


Fig. 7. The absorption changes of diarylethenes **1**–**3** with addition of acid in the photostationary state: (A) **1**; (B) **2**; (C) **3**.

Diarylethenes **1**–**3** exhibited an excellent fluorescent switch on changing from the open-ring isomers to closed-ring isomers by photoirradiation both in hexane and in PMMA films. When irradiated by UV light, the photocyclization reaction was carried out and the emission intensity of **1o**–**3o** quenched evidently due to the formation of the non-fluorescent closed-ring isomers **1c**–**3c**. The back irradiation by appropriate wavelength visible light

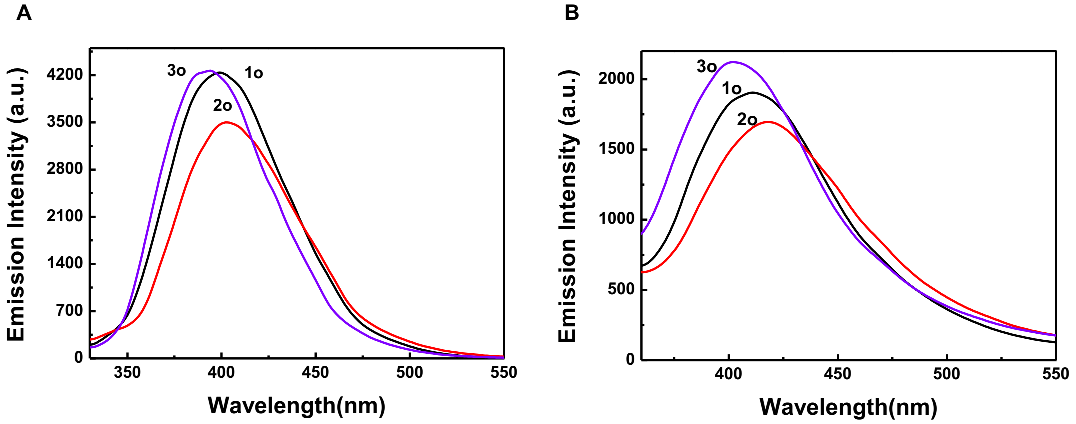


Fig. 8. Emission spectra of diarylethenes **1**–**3** in hexane (5.0×10^{-5} mol L^{-1}) when excited at 290 nm (A) and in PMMA films (10%, w/w) when excited at 310 nm (B) at room temperature.

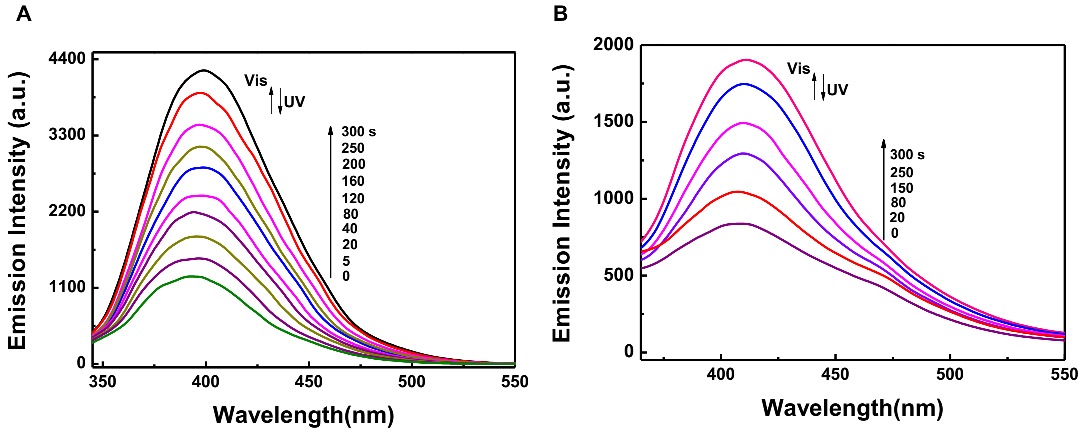


Fig. 9. Emission intensity changes of diarylethene **1** upon irradiation with UV and visible light at room temperature: (A) in hexane (5.0×10^{-5} mol L^{-1}), excited at 290 nm; (B) in a PMMA film (10%, w/w), excited at 310 nm.

regenerated their open-ring isomers and recovered their original emission intensity. Fig. 9 shows the fluorescent changes of diarylethene **1** by photoirradiation in hexane and in a PMMA film. When arrived at the photostationary state, the emission intensity of **1o** was quenched to ca. 30% in hexane and 33% in a PMMA film. Just like diarylethene **1o**, the emission intensities of diarylethenes **2** and **3** were quenched to ca. 28% for **2o** and 39% for **3o** in hexane, and those in PMMA films were quenched to ca. 29% for **2o** and 44% for **3o** when arrived at the photostationary state. The residues of fluorescence for diarylethenes **1**–**3** in the photostationary state may be attributed to the incomplete cyclization reaction and the existence of parallel conformations.[15d,20c] For practical applications in optoelectronic devices, it is very important that photochromic diarylethenes can function as an effective fluorescent switch in a solid state, such as PMMA film. Moreover, the fluorescent switching efficiencies of the three isomeric diarylethenes were significantly enhanced both in hexane and in PMMA films as compared to some reported dithienylethenes derivatives.[15d,20c] Therefore, these diarylethenes can be potentially suitable for using as optical memory with fluorescence readout method or a fluorescent photoswitch.[29]

4. Conclusion

Three new isomeric diarylethenes bearing a terminal pyridine group were synthesized to investigate the effects of nitrogen atom position on their multiple switching behaviors by the stimulation of acid/base and light. Each of the compounds showed notable photochromism in solution, in PMMA films, as well as in the crystalline phase. The isomeric diarylethenes also performed a reversible isomerization by acid/base stimuli, and all of them functioned as a fluorescence switch in both solution and solid medium. The behaviors of the three isomeric derivatives were notably different from each other, which might be attributed to the effects of nitrogen atom position in the terminal pyridine group. The results will be helpful in understanding the new type of the substituent position effect on the tunable behaviors of isomeric diarylethenes bearing a terminal pyridine unit.

Acknowledgements

This work was supported by Program for the NSFC of China (20962008, 21162011), the Project of Jiangxi Academic and Technological leader (2009DD00100), National Natural Science Foundation of Jiangxi Province (2009GZH0034, 2010GZH0040), and the Science Funds of the Education Office of Jiangxi, China (GJJ09646, GJJ11026).

Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.01.058.

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