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Photochromism of novel isomeric diarylethenes with benzofuran and pyridine moieties



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ABSTRACT

A new class of isomeric diarylethenes with benzofuran and pyridine moieties was synthesized to investigate the effects of the position of the nitrogen atom in pyridine moiety on their photochromism, acidichromism, and fluorescence. The six-membered pyridine moiety was connected directly to the central cyclopentene ring as an aryl moiety and participated in the photoisomerization reaction in both solution and solid media. These isomeric diarylethenes exhibited multi-addressable switching behavior by the stimulation of acid/base and light. Addition of trifluoroacetic acid to the solutions of these excellent photochromism and notable acidichromism, and the different nitrogen atom position resulted in distinguishable absorption spectra and color changes. The results revealed that the effects of the nitrogen atom position in pyridine moiety played a very important role during the photoisomerization process of these isomeric diarylethenes.

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1. Introduction

In the last few decades, many photochromic molecules have been developed in order to investigate their photoelectrical properties aimed at finding more promising optical memory media and photo-optical switching devices [1-4]. Among such compounds, photochromic diarylethenes are of special concern because of their excellent thermal stability of the respective isomers, notable fatigue resistance, and high reactivity in the solid state [5-8].

The pyridine ring has attracted much attention because of its unique nucleophilicity and reactivity [9]. Some examples of diarylethenes with pyridine groups have been previously explored. In these diarylethene systems, pyridine groups are mainly connected by two ways: one way is that the pyridine ring connects with other aromatic moieties as a side substituent [10–12], and the other is that pyridine ring directly connects with the ethene moiety as a heteroaryl moiety to participate in photoisomerization reaction [13–15]. Moreover, some pyridine derivatives can be used to detect metal ions or synthesize complexes [16–18]. Recently, multiple responsive switching systems have attracted more and more attention based on modulating the photochromism of diary-lethenes [19–21]. Diarylethenes with a pyridine group are good candidates for the multiple responsive switching systems because of their sensitive response of hydrogen and metal ions [22-25]. For example, Tian and co-workers demonstrated that near-Infrared photochromic diarylethene Iridium (III) complex exhibited excellent near-infrared photochromic behavior accompanied by efficient quenching of phosphorescence emission [20]. Ordronneau et al. reported several new rhenium and ruthenium complexes coordinating to the photochromic diarylethene, which could be modulated by linear and nonlinear optical properties [22]. Yi et al. developed a multiresponsive fluorescence switch as a detector for the biological process of metal ion transmembrane transport based on a diarylethene with terpyridine units [23]. In our previous work we reported a multiple responsive diarylethene with a pyridine unit and found it could be simultaneously modulated by light and chemical stimuli [24]. The valuable achievements have contributed to a broad understanding of the specific photochromic characteristics of diarylethenes with pyridine units.

In general, the substituent position effects have a vital role to modify the optoelectronic behavior of diarylethene derivatives [26–28]. Although many publications concerning the substituent position effects on the photochromic properties have been hitherto reported, the results mainly focus on effects of a certain substituent attached at different positions of the terminal benzene ring on their photochromic properties [29–31]. Previously, we have reported the nitrogen atom position effect of pyridine ring on the properties of diarylethenes [32–34]. The results revealed that the nitrogen atom





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position of pyridine ring had a significant effect on the photochromism of these diarylethenes, although the pyridine ring didn't directly participate in photoisomerization reaction. To the best of our knowledge, the nitrogen atom position effect of a pyridine ring directly linked with the ethene moiety of a diarylethene derivative has not been hitherto reported. Therefore, we designed a series of new unsymmetrical isomeric diarylethenes with both benzofuran and pyridine moieties to investigate the nitrogen atom position effect of pyridine ring on the properties of these derivatives in this work. The photoisomerization of diarylethenes with nitrogen atom at *ortho-, meta-*, and *para*-position of the methylpyridyl moiety (1– 3) along with a diarylethene with a benzene moiety as a reference compound (4) is illustrated in Fig. 1.

2. Results and discussion

2.1. General methods

NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with CDCl₃ as solvents and tetramethylsilane as an internal standard. Infrared spectra (IR) were carried out on a Bruker Vertex-70 spectrometer. Fluorescence spectra were measured on a Hitachi 4600 fluorescence spectrophotometer. Melting points were measured on a WRS-1B melting point apparatus. UV–Vis absorption spectra were measured using an Agilent 8453 UV–Vis spectrometer. Photoconversion ratios in the photostationary state were measured using an Agilent 1100 HPLC chromatographic analyzer. Photo-irradiation was carried out with an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. Lights of appropriate wavelengths were isolated by different light filters. All solvents used were of spectrograde and were purified by distillation prior to use. All other reagents were obtained



Fig. 1. Photochromism of diarylethenes 1-4.

from J&K Scientific LTD without further purification. All reactions were monitored by thin-layer chromatography carried out on 0.20–0.25 mm silica gel plates (GF-254). Column chromatography was performed on silica gel (300–400 mesh). Dissolved ultrasonically 10 mg of diarylethene sample and 100 mg PMMA into 1.0 mL chloroform, the diarylethene/PMMA film was prepared by spincoating on the surface of quartz substrate.

2.2. Synthesis

The synthetic route to prepare diarylethenes **10–40** is shown in Fig. 2. The mono-substituted (2-methyl-3-benzofuranyl)per-fluorocyclopentene (**6**) was synthesized by the reported method using 3-bromo-2-methylbenzofuran (**5**) as raw material [35,36]. Compounds **7a–d** were lithiated and then separately coupled with **6** to give diarylethenes **10–40**, respectively. The structures of **10–40** were confirmed by elemental analysis, NMR, and IR spectroscopy.

2.2.1. (2-Methyl-3-benzofuranyl)perfluorocyclopentene (6)

To a stirred THF solution (80.00 mL) of compound 5 (3.17 g, 15.00 mmol) was added dropwise a 2.4 mol L^{-1} *n*-BuLi/hexane solution (8.90 mL, 16.50 mmol) at 195 K under nitrogen atmosphere. Stirring was continued for 30 min at 195 K, octafluorocyclopentene (C₅F₈) (2.30 mL, 16.50 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 1.0 mol L^{-1} aqueous HCl and water. The organic layer dried over anhydrous MgSO₄, filtered and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to give 4.25 g 6 as pale yellow liquid in 87% yield. IR (v, KBr, cm⁻¹): 564, 744, 800, 972, 1041, 1130, 1205, 1282, 1456, 1601, 1700, 2970, 3676; ¹H NMR (400 MHz, CDCl₃): δ 2.02 (s, 3H, -CH₃), 7.20-7.25 (m, 2H, benzofuran-H), 7.29-7.34 (m, 1H, benzofuran-H), 7.43-7.45 (m, 1H, benzofuran-H); ¹³C NMR (100 MHz, CDCl₃): δ 13.8, 111.2, 122.6, 124.9, 126.2, 129.0, 133.4, 154.3, 154.4; MS (ESI+): m/z calcd for C₁₄H₇F₇O [M + H]⁺ 325.1; found 325.0.

2.2.2. 1-(2-Methyl-3-benzofuranyl)-2-(2-methyl-3-pyridyl) perfluorocyclopentene (**10**)

To a stirred anhydrous THF (40 mL) solution of compound 7a (0.69 g, 4.00 mmol) was added dropwise a 2.4 mol L^{-1} *n*-BuLi/ hexane solution (1.67 mL, 4.00 mmol) at 195 K under argon atmosphere. After 30 min, THF (10 mL) containing compound 6 (1.43 g, 4.40 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 guenched by water. The product was extracted with ether. The combined organic layers was dried over MgSO₄, filtered and concentrated. 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 0.12 g diarylethene 10 as a pale red solid in 30% yield. mp 69-70 °C; IR (v, KBr, cm⁻¹): 785, 843, 879, 992, 1067, 1125, 1140, 1156, 1195, 1250, 1278, 1317, 1342, 1401, 1455, 1648, 3131, 3436; ¹H NMR (400 MHz, CDCl₃): δ 2.10 (s, 3H, -CH₃), 2.22 (s, 3H, -CH₃), 7.22-7.29 (m, 3H, benzofuran–H, pyridine–H), 7.39 (d, 1H, J = 8.0 Hz, benzofuran—H), 7.46 (d, 1H, J = 7.6 Hz, benzofuran—H), 7.70 (d, 1H, J = 8.0 Hz, pyridine–H), 8.51–8.52 (m, 1H, pyridine–H); ¹³C NMR (100 MHz, CDCl₃): δ 13.4, 22.8, 104.4, 111.2, 119.7, 120.8, 123.1, 123.6, 124.7, 126.3, 136.8, 150.4, 154.2, 155.5, 156.7; Calcd for C₂₀H₁₃F₆NO (%): Calcd C, 60.46; H, 3.30; N, 3.53. Found C, 60.57; H, 3.35; N, 3.51.



Fig. 2. Synthetic route for diarylethenes 10-40.

2.2.3. 1-(2-Methyl-3-benzofuranyl)-2-(3-methyl-2-pyridyl) perfluorocyclopentene (**20**)

Diarylethene **20** was prepared according to the method used for diarylethene **10** from 3-bromo-4-methylpyridine (**7b**). The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate ($\nu/\nu = 6/1$) as the eluent to give 0.34 g **20** as a pale red solid in 8% yield. mp 98–99 °C; IR (ν , KBr, cm⁻¹): 795, 844, 878, 989, 1081, 1129, 1193, 1249, 1269, 1282, 1321, 1338, 1400, 1455, 3133, 3468; ¹H NMR (400 MHz, CDCl₃): δ 1.95 (s, 3H, –CH₃), 2.13 (s, 3H, –CH₃), 7.20–7.26 (m, 3H, benzofuran–H, pyridine–H), 7.36–7.42 (m, 2H, benzofuran–H), 7.51 (d, 1H, J = 7.6 Hz, pyridine–H), 8.61 (d, 1H, J = 4.4 Hz, pyridine–H); ¹³C NMR (100 MHz, CDCl₃): δ 1.32, 18.3, 104.4, 111.0, 120.1, 123.6, 124.1, 124.5, 126.4, 133.4, 138.5, 147.3, 147.7, 154.1, 156.7; Calcd for C₂₀H₁₃F₆NO (%): Calcd C, 60.46; H, 3.30; N, 3.53. Found C, 60.54; H, 3.37; N, 3.59.

2.2.4. 1-(2-Methyl-3-benzofuranyl)-2-(4-methyl-3-pyridyl) perfluorocyclopentene (**30**)

Diarylethene **30** was prepared according to the method used for diarylethene **10** from 3-bromo-2-methylpyridine (**7c**). The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate ($\nu/\nu = 6/1$) as the eluent to give 0.47 g **30** as a pale red solid in 21% yield. mp 71–72 °C; IR (ν , KBr, cm⁻¹): 797, 843, 870, 982, 1061, 1080, 1126, 1195, 1272, 1323, 1400, 1457, 1651, 3119, 3447; ¹H NMR (400 MHz, CDCl₃): δ 2.01 (s, 3H, – CH₃), 2.12 (s, 3H, –CH₃), 6.06 (d, 1H, J = 5.2 Hz, pyridine–H), 7.22–7.29 (m, 2H, benzofuran–H), 7.39 (d, 1H, J = 7.6 Hz, benzofuran–H), 7.47 (d, 1H, J = 8.4 Hz, benzofuran–H), 8.46 (d, 1H, J = 5.6 Hz, pyridine–H), 8.56 (s, 1H, pyridine–H); ¹³C NMR (100 MHz, CDCl₃): δ 13.4, 19.3, 104.3, 111.2, 119.7, 123.7, 124.3, 124.7, 125.5, 126.3, 146.3, 149.3, 150.7, 154.1, 155.7; Calcd for C₂₀H₁₃F₆NO (%): Calcd C, 60.46; H, 3.30; N, 3.53. Found C, 60.53; H, 3.33; N, 3.58.

2.2.5. 1-(2-Methyl-3-benzofuranyl)-2-(2-methylphenyl) perfluorocyclopentene (**40**)

Diarylethene **40** was prepared according to the method used for diarylethene **10** from 2-bromotoluene (**7d**). The crude product was

purified by column chromatography on silica gel using petroleum ether as the eluent to give 0.86 g **40** as a pale yellow solid in 54% yield. mp 82–83 °C; IR (ν , KBr, cm⁻¹): 764, 835, 865, 985, 1074, 1126, 1171, 1193, 1249, 1270, 1316, 1336, 1400, 1454, 1608, 1652, 3138, 3433; ¹H NMR (400 MHz, CDCl₃): δ 1.97 (s, 3H, –CH₃), 2.06 (s, 3H, –CH₃), 7.09–7.11 (m, 1H, phenyl–H), 7.20–7.27 (m, 4H, benzofuran–H, phenyl–H), 7.35–7.38 (m, 2H, benzofuran–H), 7.51 (d, 1H, J = 7.6 Hz, phenyl–H); ¹³C NMR (100 MHz, CDCl₃): δ 13.4, 19.6, 104.7, 111.0, 120.0, 123.5, 124.4, 126.1, 126.7, 127.2, 128.9, 129.9, 130.9, 136.9, 154.1, 155.7; Calcd for C₂₁H₁₄F₆O (%): Calcd C, 63.64; H, 3.56. Found C, 63.73; H, 3.61.

3. Results and discussion

3.1. Photochromism of diarylethenes

The photochromic behavior of diarylethenes 1–4 induced by photoirradiation at room temperature were measured in both hexane (5.0 \times 10⁻⁵ mol L⁻¹) and PMMA films (10%, w/w). The absorption spectral changes of 1 and the color changes of 1–4 upon alternating irradiation with UV and visible light in hexane at room temperature are shown in Fig. 3. The absorption band of the openring isomer **10** appeared at 242 nm in hexane, which arose from a $\pi - \pi^*$ transition [37]. Upon irradiation with 297 nm UV light, the colorless solution of 10 turned into orange red and produced a new visible absorption band centered at 496 nm due to the formation of the closed-ring isomer 1c. Alternatively, the orange red solution could be bleached completely upon irradiation with visible light $(\lambda > 450 \text{ nm})$, indicating that **1c** returned to the initial state **1o**. The coloration/decoloration cycle could be repeated more than 20 times and a clear isosbestic point was observed at 263 nm, indicating a reversible two-component photochromic reaction scheme [38]. Diarylethenes **2**–**4** exhibited similar photochromism to that observed for 1 in hexane solution. Upon irradiation with 297 nm UV light, absorption bands in the visible region appeared and the colorless solutions 20-40 turned orange red due to the formation of the closed-ring isomers 2c-4c (Fig. 3). Their absorption maxima were observed at 493 nm for 2, 491 nm for 3, and 489 nm for 4. All



Fig. 3. Absorption spectral changes of diarylethene **1** (A) and color changes of diarylethenes **1–4** (B) upon alternating irradiation with UV and visible light in hexane $(5.0 \times 10^{-5} \text{ mol/L})$ at room temperature.

of the orange red solutions 2c-4c could be decolorized by irradiation with visible light of wavelength longer than 450 nm. In the photostationary state, the isosbestic points of 2-4 in hexane were observed at 264, 264, and 263 nm, respectively. In addition, the photoconversion ratios from open-ring to closed-ring isomers of 1-4 in the photostationary state in hexane were measured by HPLC analysis. As shown in Fig. 4, the photoconversion ratios of



Fig. 4. The photoconversion ratios of diarylethenes **1–4** in the photostationary state in hexane by HPLC analysis.

diarylethenes **1–4** were calculated with the value of 49% for **1**. 37% for **2**, 43% for **3**, and 17% for **4**. Compared to the diarylethene with a benzene moiety (4), the photoconversion ratios of the three isomeric diarylethenes with a pyridine (1-3) were notably increased in hexane. In PMMA films, diarylethenes 1-4 also showed similar photochromism as observed in hexane. The absorption spectral changes of **1** and the color changes of diarylethenes 1–4 are shown in Fig. 5. Upon irradiation with 297 nm UV light, the colorless diarylethene 10/PMMA film turned orange red with a new visible absorption band at 499 nm due to the formation of the closed-ring isomer 1c. The other three films changed from colorless to orange red for 2, purple red for 3, and orange red for 4. In PMMA films, the absorption maxima of 2c-4c were observed at 501 nm, 516 nm, and 497 nm, respectively. All colored diarylethene/PMMA films could be bleached completely by irradiating of visible light with appropriate wavelength. Compared with those in solution, the absorption maxima of the closed-ring isomers 1c-4c exhibited an evidently bathochromic shift in PMMA films. The red shifts of the absorption maxima of 1c-4c were 3 nm for 1c, 8 nm for 2c, 25 nm for 3c, and 8 nm for 4c. This red shift phenomenon may be attributed to the polar effect of the polymer matrix in the amorphous polymer state as observed for the majority of the reported diarylethenes [28,39,40].

The photochromic properties of diarylethenes **1–4** in hexane and PMMA films are summarized in Table 1. The data indicated that



Fig. 5. Absorption spectral changes of diarylethene **1** (A) and the color changes of diarylethenes **1–4** (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 **1–4** in hexane $(5.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ and PMMA films (10%, w/w).

Compd	$\lambda_{o,max}/Nm^{a}$ ($\epsilon/L mol^{-1} cm^{-1}$)		$\lambda_{c,max}/Nm^{b}$ ($\epsilon/L mol^{-1} cm^{-1}$)		Φ^{c}		PR ^d (%)
	Hexane	PMMA film	Hexane	PMMA film	$\Phi_{\rm o-c}$	$\Phi_{\rm c-0}$	
1	$242~(1.27\times10^4)$	243	$496~(7.12\times10^3)$	499	0.13	0.31	49
2	$240~(1.03 \times 10^4)$	243	493 (6.86×10^3)	501	0.10	0.32	37
3	$241~(1.38 \times 10^4)$	243	$491~(5.42 \times 10^3)$	516	0.077	0.27	43
4	$242~(1.40\times10^4)$	244	$489~(1.54 \times 10^4)$	497	0.11	0.20	17

^a Absorption maxima of open-ring isomers.

^b Absorption maxima of closed-ring isomers.

 $^{\rm c}$ Quantum yields of cyclization reaction ($\Phi_{\rm o-c})$ and cycloreversion reaction ($\phi_{\rm c-o})$, respectively.

^d Photoconversion ratio at PSS in hexane.

the pyridine moiety and its nitrogen position had a significant effect on the photochromic properties of these diarylethenes, such as molar absorption coefficients, cyclization quantum yields, and cycloreversion quantum yields. For the three isomeric derivatives (1–3), the molar absorption coefficients of the open-ring isomers increased in the order of *meta- < ortho- < para-substitution* by the nitrogen atom in methylpyridyl moiety; however, those of the closed-ring isomers increased in the order of para- < meta- < orthosubstitution by the nitrogen atom in methylpyridyl moiety. The nitrogen atom position in pyridine ring had no significant effect on the absorption maxima of both the open-ring and closed-ring isomers of **1–3**. In hexane, the absorption maxima only changed slightly both for their open-ring and closed-ring isomers when the position of nitrogen atom was changed. In PMMA films, no changes in the absorption maxima of the open-ring isomers 10-30 were observed, but were observed for the closed-ring isomers 1c-3c. The absorption maximum of **3c** is at the longest wavelength and resulted in the appearance of purple red color in its PMMA film. Compared to the diarylethene with a benzene moiety (4c), the absorption maxima of the three isomeric diarylethenes with a pyridine (1c-3c) exhibited a bathochromic shift in both solution and PMMA films, but their molar absorption coefficients were notably decreased in hexane. The cyclization quantum yields increased in order of **3** (0.077) < 2 (0.10) < 1 (0.13), whereas the



Fig. 6. Fatigue resistance of diarylethenes 1-4 in hexane (A) and in PMMA films (B) in air atmosphere at room temperature. Initial absorptance of the sample was fixed to 1.0.

cycloreversion quantum yields decreased in order of 2 (0.32) > 1(0.31) > 3 (0.27). Consequently, the *ortho*-substituted derivative 1 has the largest cyclization quantum yield, and the *para*-substituted derivative 3 has the smallest quantum yields of cyclization and cycloreversion. Compared to 4, no significant changes in the cyclization quantum yields of 1-3 were observed, but were observed for their cycloreversion quantum yields. The cycloreversion quantum yields of 1-3 were larger than that of 4, indicating that the pyridine moiety could effectively enhance the cycloreversion quantum yield. Compared to the diarylethenes with a pyridine substituent [32-34], the cyclization quantum yields of diarylethenes 1-3 decreased and their cycloreversion quantum yields increased notably. This may be ascribed to the higher aromatic stabilization energy of the six-membered pyridine ring resulting in the lower cyclization quantum yield [14].

The thermal stability of the open-ring and closed-ring isomers of **1–4** was tested in hexane at room temperature and at 341 K. Storing these solutions in hexane at room temperature in darkness and then exposing them to air for more than 100 h, no changes in the UV/vis spectra of diarylethenes 1-4 were observed. When these hexane solutions were heated under reflux (341 K) for more than 2 h in darkness, no decomposition was detected by UV/vis spectroscopy. The fatigue resistance is a very important factor for practical applications in optical devices [41,42]. Upon alternating irradiation with UV and visible light in air at room temperature, the fatigue resistance of **1–4** was examined in both hexane and PMMA films, and the result is depicted in Fig. 6. In hexane, the coloration and decoloration cycles of diarylethenes **1–4** could be repeated more than 100 times with ca. 62% degradation of 1c. 13% degradation of 2c, 74% degradation of 3c, and 29% degradation of 4c. In PMMA films, they also exhibit favorable photochromism with ca. 61% degradation of 1c, 6% degradation of 2c, 39% degradation of 3c, and 43% degradation of 4c after 100 repeated cycles. Therefore, the fatigue resistance of diarylethene 2 was the best in both solution and PMMA films. The degradation of the absorption intensity may be ascribed to the undesirable side reactions resulting in generation of photo-inactive byproducts [41]. Compared to the diarylethenes with a pyridine substituent [32–34], the fatigue resistance of diarylethenes 1-3 became much weaker when the six-membered pyridine ring was directly connected with the ethene moiety as a heteroaryl moiety to participate in photoisomerization reaction [14].

3.2. Acidichromism of diarylethenes

It is a hot topic to develop multiple responsive switching diarylethenes. The derivatives integrate several switchable functions into a single molecule in order to miniaturize the components of machinery and electronics down to the molecular level [43,44]. Here, the multiple switching behaviors of diarylethenes 1-3 were studied by the stimulation of acid/base and light. The structural changes of diarylethene 1 and color changes of diarylethenes 1-3 in hexane $(5.0 \times 10^{-5} \text{ mol L}^{-1})$ were illustrated in Fig. 7. Addition of trifluoroacetic acid in hexane solution (1.0 μ L, 6.8 \times 10⁻³ mol L⁻¹) to the solutions of **10–30** produced the protonated diarylethenes 10'-30'. The compounds 10'-30' could return to the initial state 10-30 by neutralization with triethylamine base (5.0 μ L, 3.6 \times 10⁻³ mol L⁻¹). Diarylethenes 10'-30' also exhibited notable photochromism by photoirradiation. Upon irradiation with UV light, the colorless solution of 10'-30' turned into different colors, indicating the formation of N-protonated closed-ring isomers **1c**'-**3c**'. Their absorption maxima in the visible region were observed at 567 nm for **1c**' ($\varepsilon = 5.33 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$), 458 nm for **2c**' ($\varepsilon = 4.02 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$), and 602 nm for **3c**' ($\varepsilon = 5.43 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$). Alternatively, a reversible transformation between the colored diarylethenes 1c-3c and 1c'-3c'



Fig. 7. The structural changes between diarylethenes 1 and 1' (A) and the color changes of diarylethenes 1-3 (B) by light and acid/base stimuli.

could be conducted by stimulating with acid/base. The absorption spectrum and color changes of 1c-3c by the addition of trifluoroacetic acid in the photostationary state are shown in Fig. 8. When trifluoroacetic acid was added to the solution of 1c, the absorption maximum shifted from 496 to 567 nm due to producing the protonated 1c', and this process was accompanied by a notable color change of solution from orange red to blue. The redshift phenomenon was in agreement with that of the reported pyridine-containing diarylethenes [15,33,45]. Similarly, the absorption maximum of **3c** shifted from 491 to 602 nm accompanied with a notable color change from orange red to blue. However, for **2c**, the absorption maximum shifted from 493 to 458 nm when trifluoroacetic acid was added. This process was accompanied by a notable color change from orange red to yellow. The result revealed that the nitrogen atom position in the pyridine ring had a significant effect on the acidichromism of these isomeric diarylethene.

3.3. Fluorescence of diarylethenes

The fluorescence properties of diarylethenes **10–40** in both solution (5.0 \times 10⁻⁵ mol \hat{L}^{-1}) and PMMA films (10%, w/w) at room temperature are shown in Fig. 9. In hexane, the emission peaks of 10-40 were observed at 407 nm for 10, 408 nm for 20, 407 nm for 30, and 401 nm for 40 when excited at 291 nm, and those in PMMA films were observed at 430 nm for 10, 426 nm for 20, 434 nm for 30, and 412 nm for 40 when excited at 288 nm. The result indicated that the nitrogen atom position in pyridine ring had no significant effect on the emission peaks of the three isomeric derivatives. Compared to those in hexane, the emission peaks of 10-40 in PMMA films showed an evident bathochromic shift with values of 23 nm for 10, 18 nm for 20, 27 nm for 30, and 11 nm for 40. This phenomenon is consistent with most of the reported diarylethenes [27,29,30]. The emission intensity of **10–30** increased in order of **20** < **30** < **10** in both hexane and PMMA films, indicating that the emission intensity of 20 was the lowest and that of 10 was the highest in both hexane and PMMA films. Compared to 40, the emission peaks of 10-30 were at a longer wavelength and the emission intensity was lower. This result indicated that the pyridine moiety could effectively enhance the emission peak wavelength and decrease the emission intensity, as compared with the benzene moietv.

As has been observed for most of the reported diarylethenes [46–48], **10–40** exhibited an excellent fluorescent switch on changing from the open-ring isomers to closed-ring isomers by photoirradiation in both hexane and PMMA films. When irradiated by UV light, the emission intensity of **10–40** quenched evidently due to the formation of the non-fluorescent closed-ring isomers

1c–4c. They could go back to their open-ring isomers by irradiation of appropriate wavelength visible light and recovered their original emission intensity. The emission intensity changes of **10–40** upon irradiation with UV and visible light at room temperature in hexane and in PMMA films are shown in Figs. 10 and 11, respectively. When arrived at the photostationary state, the emission intensity of **10** was guenched to ca. 39% in hexane and 14% in a PMMA film. Similarly, the emission intensity of diarylethenes 2-4 in hexane were quenched to ca. 46% for 20, 46% for 30, and 36% for 40, and that in PMMA films was quenched to ca. 18% for 20, 11% for 30, and 25% for **40** in the photostationary state. The result showed that the fluorescent modulation efficiency of 1-4 in PMMA films was much higher than that in the respective solutions. In addition, the fluorescence of **1–4** could not be guenched completely in the photostationary state, which may be ascribed to the incomplete cyclization reaction and the existence of parallel conformations [32,49]. For practical applications in optoelectronic devices, it is very important that diarylethenes can function as an effective fluorescent switch in a solid state, such as PMMA film. Therefore, these diarylethene derivatives could be potentially applied to optical memories with fluorescence readout method or fluorescent photoswitches [50-52].



Fig. 8. The absorption changes of diarylethenes **1–3** with addition of acid in the photostationary state: (A) **1**; (B) **2**; (C) **3**.



Fig. 9. Emission spectra of diarylethenes **1–4** in hexane $(5.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ when excited at 291 nm (A) and in PMMA films (10%, w/w) when excited at 288 nm (B) at room temperature.



Fig. 10. Emission intensity changes of diarylethenes 1–4 upon irradiation with UV and visible light at room temperature in hexane (5.0 × 10⁻⁵ mol L⁻¹) excited at 291 nm: (A) 1; (B) 2; (C) 3; (D) 4.



Fig. 11. Emission intensity changes of diarylethenes 1–4 upon irradiation with UV and visible light at room temperature in PMMA films (10%, w/w) excited at 288 nm: (A) 1; (B) 2; (C) 3; (D) 4.

4. Conclusion

Three new isomeric diarylethenes with a six-member pyridine moiety were synthesized and their properties were systematically investigated. Each of these diarylethenes showed favorable photochromism and functioned as notable fluorescence switches in both solution and PMMA films. Compared to the diarylethene with a benzene moiety, diarylethenes with a pyridine moiety had larger cycloreversion quantum yields and photoconversion ratios, but smaller molar absorption coefficients and emission intensity. Moreover, diarylethenes with a pyridine moiety also performed a reversible isomerization by acid/base stimuli, and their closed-ring isomers exhibited a notable absorption spectral and color changes. The behavior of the three isomeric diarylethenes were notably different from each other, which might be attributed to the effects of nitrogen atom position in methylpyridyl moiety. The results will be helpful in understanding the nitrogen atom position effect on the tunable behavior of isomeric diarylethenes with both benzofuran and pyridine moieties.

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