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Synthesis and photochromic properties of novel pyridine-containing diarylethenes

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ABSTRACT

Three isomeric pyridine-containing diarylethenes were synthesized to study the effects of nitrogen atom position (ortho, para, meta) on their photochromic properties. Among these diarylethenes, the example with the nitrogen atom at the ortho-position of pyridine displayed the largest absorption maximum and molar absorption coefficients. The cyclization quantum yields increased in order of para < meta < ortho, whereas their cycloreversion quantum yields decreased in order of *para* > *meta* > *ortho*. Compared to the diarylethene with terminal phenyl ring, those with a terminal pyridine showed enhanced cyclization quantum yields and emission intensities. Moreover, these pyridine-containing diarylethenes exhibited multi-addressable switching behavior under the stimulation of both proton and light. Addition of trifluoroacetic acid to the solutions of the diarylethenes resulted in notable color change, and their Nprotonated forms also possessed excellent photochromism. These results indicated that the nitrogen atom position played a pivotal role in the process of photoisomerization of the diarylethenes.

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1. Introduction

Photochromic molecules which exhibit reversible color change upon light irradiation have attracted significant attention in recent years [1–5]. Currently, diarylethene derivatives are one of the most extensively investigated photochromic molecules [6]. The original studies on the photochromic properties of diarylethenes were reported by Irie and his coworkers [7-9]. Exploration of new diarylethene structures with improved properties has been a hot area of research in organic material science ever since [10–12].

It is well known that suitable functionalization of the aromatic rings with different substituents can effectively modify the photochromic behavior of diarylethenes [13-17]. The position of substituents is also important for fine tuning of their optoelectronic properties [18-22]. So far, related research has been mainly focused on the effects of substituted benzene ring in diarylethenes on their photochromic properties.

Among diarylethenes reported up to date, those based on benzothiophene [23–30] exhibited remarkable fatigue resistance and excellent thermal stability, which are essential to many applications, such as optical storage [29], fluorescence switching [31], dual image formation [32], and liquid crystals [33].

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The pyridine ring has good aromaticity with a similar structure to benzene [34]. But the nitrogen atom of pyridine can be protonated or alkylated to respond to external stimuli [35,36]. In the past few years, novel pyridine-based diarylethenes have been prepared [37–42]. The unusual characteristics of these new compounds have many potential applications in photoswitching, photomodulation of chemical reactivity, and control of biological systems. Piard et al. designed a ratiometric fluorescent photoswitch on the basis of a diarylethene with two pyridylthiazoles, which could reach a tradeoff between fluorescence and photochromism [37]. Using a symmetrical dithienylethene with two terminal pyridines, Branda et al. developed a photo-controlled molecular switch, which could be applied in living cells [39]. Yi et al. prepared an amphiphilic pyridine-containing diarylethene with high membrane permeability and low cytotoxicity. This molecule could be potentially utilized as an in vivo cellular marker and fluorescence switch with high-ratio signal change and excellent fatigue resistance [41]. Moreover, pyridine-containing diarylethenes are capable of recognizing ions due to the excellent coordination of pyridine with specific ions. Recently, we prepared a series of new asymmetric pyridine-containing diarylethenes, which selectively bound Cu(II) ions [43]. A multi-responsive fluorescence switch based on a terpyridine-containing diarylethene was synthesized by Yi and coworkers and applied as a detector for the biological process of metal ion transmembrane transport [44]. All the above research





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revealed that pyridine-containing diarylethenes have versatile applications due to their unique physicochemical properties.

To the best of our knowledge, the effects of both pyridine moiety and position of nitrogen atom on the properties of diarylethenes have rarely been reported. Therefore, we designed a series of three new asymmetric diarylethenes with a benzothiophene and a pyridylthiophene. In the present paper, we report the synthesis and photochromic properties of the three novel diarylethenes. The effects of pyridine ring and position of nitrogen atom on their photochromic properties are also discussed. The photoisomerization of the diarylethenes with nitrogen atom at *ortho*-, *para-*, *meta*-position of the pyridine moiety (1-3) along with a diarylethene with a phenylthiophene as a reference compound (4) is described in Fig. 1.

2. Experimental

2.1. General

Melting points were measured with a WRS-1B melting point apparatus. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer, with CDCl₃ as solvent and tetramethylsilane as internal standard. Infrared spectra (IR) were recorded on a Bruker Vertex-70 spectrometer. Elemental analysis was measured with an elemental analyzer labeled PE CHN 2400 analyzer. Fluorescent spectra were obtained with a Hitachi F-4500 fluorimeter. Absorption spectra were measured using an Agilent 8453 UV/VIS spectrophotometer. Photoirradiation was carried out with an SHG-200 UV lamp, a CX–21 ultraviolet fluorescence analysis cabinet, and a BMH-250 Visible lamp. The required wavelength was isolated by appropriate filters. The quantum yields of cyclization/cycloreversion were determined by comparing the reaction yields with that of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane [45].

2.2. Synthesis

The synthetic route for diarylethenes 1-4 is shown in Fig. 2. Suzuki coupling of bromobenzene and three bromopyridines with thiophene boronic acid gave the phenylthiophene and pyridylthiophenes **5a–5d**. Mono-substituted (2-methyl-3-benzothiophene) perfluoro- cyclopentene **7** was synthesized by lithiation of 3bromo-2-methylbenzothiophene and reaction with perfluorocyclopentene. Lithiation of **5a–d** and coupling with **7** gave



Fig. 1. Photochromism of diarylethenes 1-4.

diarylethenes **1–4**. The structures of **1–4** were confirmed by elemental analysis, NMR, and IR spectroscopy. The PMMA films were prepared by dissolving 10 mg diarylethene sample and 100 mg polymethylmethacrylate (PMMA) in chloroform (1 mL) with the aid of ultrasound; then the homogeneous solution was spin-coated on a quartz substrate (10 mm \times 10 mm \times 1 mm).

2.2.1. 3-Bromo-2-methyl-5-(2-pyridyl)thiophene (5a)

Compound **5a** was prepared by reacting 3-bromo-2-methyl-5thienylboronic acid [46] (3.10 g, 14.00 mmol) with 2bromopyridine (2.20 g, 14.00 mmol) in the presence of Pd(PPh₃)₄ (0.27 g, 0.23 mmol) and Na₂CO₃ (6.36 g, 60.00 mmol) in THF (80 mL containing 10% water) for 15 h at 343 K. The reaction was allowed to cool to room temperature. After being extracted with ether, the organic layer was dried over MgSO₄, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford 3.00 g of **5a** as a pale yellow solid in 83% yield. M.P. 344–345 K; ¹H NMR (400 MHz, CDCl₃): δ 2.44 (s, 3H, –CH₃), 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 according to the method used for **5a**. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate ($\nu/\nu = 8/1$) as eluent to afford 2.60 g of **5b** as a pale yellow solid in 72% yield. M.P. 312–313 K; ¹H NMR (400 MHz, CDCl₃): δ 2.44 (s, 3H, –CH₃), 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 according to the method used for **5a**. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate ($\nu/\nu = 6/1$) as eluent to afford 2.82 g of **5c** as a pale yellow solid in 78% yield. M.P. 361–362 K; ¹H NMR (400 MHz, CDCl₃): δ 2.44 (s, 3H, –CH₃), 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-Bromo-2-methyl-5-phenyl-thiophene (5d)

Compound **5d** was prepared according to the method used for **5a**. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford 2.91 g of **5d** as a pale yellow solid in 82% yield. M.P. 339–340 K; ¹H NMR (400 MHz, CDCl₃): δ 2.34 (s, 3H, –CH₃), 7.02 (s, 1H, thienyl-H), 7.20 (d, 1H, J = 8.0 Hz, phenyl-H), 7.29 (t, 2H, J = 8.4 Hz, phenyl-H), 7.42 (d, 2H, J = 8.0 Hz, phenyl-H); IR (ν , KBr, cm⁻¹): 754, 792, 827, 904, 946, 1007, 1032, 1072, 1155, 1326, 1443.

2.2.5. 2-Methyl-3-benzothiophene-perfluorocyclopentene (7)

To a stirred THF solution (80 mL) of compound **6** (4.56 g, 20.10 mmol) was added dropwise a 2.5 M *n*-BuLi/hexane solution (8.80 mL, 22.00 mmol) at 195 K under argon 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 temperature. The reaction was quenched by addition of water. After being extracted with ether, the organic layer was washed with 1 M aqueous HCl and water. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated. The crude product was purified by column chromatography on



Fig. 2. Synthetic route for diarylethenes 1–4.



Fig. 3. Absorption spectra and color changes of diarylethenes 1–4 by photoirradiation in hexane (2.0×10^{-5} mol L⁻¹) at room temperature: (A) Spectral changes for 1; (B) Spectral changes for 2; (C) Spectral changes for 3; (D) Spectral changes for 4; (E) Color changes for 1–4.

silica gel using petroleum ether as eluent to afford 4.30 g compound **7** as a white crystalline solid in 63% yield. M.P. 322–323 K; ¹H NMR (400 MHz, CDCl₃): δ 2.52 (s, 3H, –CH₃), 7.40 (m, 2H, benzothiophene-H), 7.48 (d, 1H, *J* = 8.0 Hz, benzothiophene-H), 7.80 (t, 1H, *J* = 8.0 Hz, benzothiophene-H); IR (ν , KBr, cm⁻¹): 723, 754, 827, 858, 968, 1028, 1137, 1204, 1282, 1330, 1354, 1387, 1435, 1462, 1536, 1706, 2930, 3469.

2.2.6. 1-(2-Methyl-3-benzothiophene)-2-[2-methyl-5-(2-pyridyl)-3-thienyl]perfluorocyclopentene (1)

To a stirred anhydrous THF (80 mL) of compound **5a** (0.70 g, 2.50 mmol) was added dropwise a 2.5 M *n*-BuLi/hexane solution (1 mL, 2.50 mmol) at 195 K under argon atmosphere. After 30 min, THF (15 mL) containing compound **7** (0.85 g, 2.50 mmol) was added and the reaction mixture was stirred for 2 h at this temperature. The reaction was allowed to warm to room temperature and quenched

by addition of water. The product was extracted with diethyl 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 = 6/1) as eluent to afford 0.39 g compound **1** as a reddish brown liquid in 32% yield. Calcd for C₂₄H₁₅F₆NS₂: Calcd C, 58.17; H, 3.05; N, 2.83. Found C, 58.44; H, 2.87; N, 2.67; ¹H NMR(400 MHz, CDCl₃): δ 1.92 (s, 3H, -CH₃), 2.29(s, 3H, -CH₃), 7.13 (t, 1H, *J* = 8.0 Hz, pyridine-H), 7.36 (t, 2H, I = 8.0 Hz, benzothiophene-H), 7.45 (s, 1H, thiophene-H), 7.49(d, 1H, I = 8.0 Hz, benzothiophene-H), 7.58 (d, 1H, I = 8.0 Hz, pyridine-H), 7.64 (t, 1H, J = 8.0 Hz, pyridine-H), 7.73 (d, 1H, J = 8.0 Hz, benzothiophene-H), 8.51 (d, 1H, I = 8.0 Hz, pyridine-H); ¹³C NMR (100 MHz, CDCl₃): δ 14.9, 15.0, 118.4, 120.3, 122.1, 122.2, 123.8, 124.5, 124.9, 125.2, 126.4, 136.7, 138.2, 139.5, 142.4, 142.6, 144.6, 149.6, 151.5; IR (v, KBr, cm⁻¹): 773, 893, 965, 993, 1051, 1112, 1142, 1192, 1275, 1341, 1400, 1619, 1685, 3130, 3414.



Fig. 4. Absorption spectra and color changes of diarylethenes 1–4 by photoirradiation in PMMA films (10%, w/w) at room temperature: (A) Spectral changes for 1; (B) Spectral changes for 2; (C) Spectral changes for 3; (D) Spectral changes for 4; (E) Color changes for 1–4.

2.2.7. 1-(2-Methyl-3-benzothiophene)-2-[2-methyl-5-(3-pyridyl)-3-thienyl]perfluorocyclopentene (**2**)

Diarylethene **2** was prepared according to the method used for diarylethene **1** from 3-bromo-5-(3-pyridyl)-2-methylthiophene (**5b**). The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 2/1) as eluent to afford 0.49 g compound **2** as a reddish brown liquid in 40% yield. Calcd for C₂₄H₁₅F₆NS₂: Calcd C, 58.17; H, 3.05; N, 2.83. Found C, 57.97; H, 3.21; N, 2.94; ¹H NMR(400 MHz, CDCl₃): δ 1.98 (s, 3H, -CH₃), 2.31(s, 3H, -CH₃), 7.21 (s, 1H, thiophene-H), 7.34 (m, 3H, benzothiophene-H), 7.56 (d, 1H, J = 8.0 Hz, benzothiophene-H), 8.67 (d, ¹H, J = 8.0 Hz, pyridine-H); ¹³C NMR (100 MHz, CDCl₃): δ 14.8, 15.3, 120.2, 122.0, 122.1, 122.1, 123.6, 123.8, 124.6, 125.0, 125.5, 129.3, 132.6, 138.1, 138.2, 142.5, 142.8, 146.7, 148.8; IR (v, KBr, cm⁻¹): 706, 756, 801, 892, 966, 993, 1049, 1113, 1141, 1192, 1275, 1339, 1400, 1619, 1684, 3128, 3414.

2.2.8. 1-(2-Methyl-3-benzothiophene)-2-[2-methyl-5-(4-pyridyl)-3-thienyl]perfluorocyclopentene (**3**)

Diarylethene **3** was prepared according to the method used for diarylethene **10** from 3-bromo-5-(4-pyridyl)-2-methylthiophene (**5c**). The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v = 2/1) as eluent to give 0.44 g compound **3** as a reddish brown liquid in 36% yield. Calcd for C₂₄H₁₅F₆NS₂: Calcd C, 58.17; H, 3.05; N, 2.83. Found C, 58.37; H, 2.96; N, 2.96; ¹H NMR(400 MHz, CDCl₃): δ 1.97 (s, 3H, -CH₃), 2.31(s, 3H, -CH₃), 7.29 (t, 2H, *J* = 8.0 Hz, pyridine-H), 7.31 (s, 1H, thiophene-H), 7.32–7.37 (m, 2H, benzothiophene-H), 7.54 (t, 1H, *J* = 8.0 Hz, benzothiophene-H), 8.55 (d, 2H, *J* = 8.0 Hz, pyridine-H), 8.55 (d, 2H, *J* = 8.0 Hz, pyridine-H), 13C NMR (100 MHz, CDCl₃): δ 14.8, 15.3, 119.5, 122.0, 122.1, 124.6, 125.0, 125.7, 128.9, 130.9, 138.1, 138.3, 138.6, 140.3, 142.5, 144.0, 150.4; IR (v, KBr, cm⁻¹): 756, 814, 893, 965, 992, 1050, 1113, 1141, 1193, 1275, 1340, 1402, 1596, 1721, 3129, 3414.

2.2.9. 1-(2-Methyl-3-benzothiophene)-2-[2-methyl-5-phenyl-3-thienyl]perfluorocyclopentene (**4**)

Diarylethene **4** was prepared according to the method used for diarylethene **1** from 3-bromo-5-phenyl-2-methylthiophene (**5d**). The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate ($\nu/\nu = 10/1$) as eluent to afford 0.53 g compound **1** as a reddish brown liquid in 38% yield. Calcd for C₂₄H₁₆F₆S₂: Calcd C, 60.72; H, 3.26; S, 12.97. Found C, 60.49; H, 3.41; S, 13.13; ¹H NMR(400 MHz, CDCl₃): δ 1.93 (s, 3H, –CH₃), 2.30(s, 3H, –CH₃), 7.19 (s, 1H, thiophene-H), 7.27–7.37 (m, 5H, phenyl-H), 7.44 (t, 2H, *J* = 8.0 Hz, benzothiophene-H), 7.58 (d, 1H, *J* = 8.0 Hz, benzothiophene-H); ¹³C NMR (100 MHz, CDCl₃): δ 14.9, 15.3, 107.2, 109.3, 120.3, 122.0, 122.2, 122.4, 124.5, 124.9, 125.1, 125.5, 127.8, 128.9, 133.2, 136.4, 138.2, 141.7, 141.8, 142.5; IR (ν , KBr, cm⁻¹): 730, 754, 837, 892, 967, 993, 1020, 1051, 1135, 1192, 1276, 1340, 1400, 1436, 1630, 3130, 3452.

3. Results and discussion

3.1. Photochromism of diarylethenes 1-4

The photochromic behavior of diarylethenes **1–4** induced by photoirradiation was measured in both hexane $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ and PMMA films (10%, w/w) at room temperature. Their absorption spectra and color changes induced by alternating irradiation with UV and visible light were determined (Fig. 3.). The absorption maximum of diarylethene **10** in hexane was observed at 263 nm due to a $\pi - \pi^*$ transition [47]. Upon irradiation with UV light ($\lambda = 297$ nm), a new absorption band centered at 546 nm emerged. The formation of the ring-closed isomer **1c** resulted in a change in the color of solution from colorless to purple red. For the reverse reaction, the purple red solution of **1c** faded to colorless upon irradiation with visible light ($\lambda > 450$ nm).

I/MIN Fig. 5. The photoconversion ratios of diarylethenes 1–4 analysized by HPLC method in the photostationary state in hexane.



|--|

Compound	$\lambda_{o,max}/nm^a (e/L mol^{-1} cm^{-1})$		$\lambda_{c,max}/nm^{b} (e/L mol^{-1} cm^{-1})$		Φ ^c		Conversion at PSS in hexane
	Hexane	PMMA film	Hexane	PMMA film	$\Phi_{\mathrm{o-c}}$	Φ_{c-o}	
1	$263~(3.32 imes 10^4)$	263	$546~(1.94 imes 10^4)$	558	0.53	0.012	79%
2	$261~(2.18 imes 10^4)$	262	$534~(1.40 imes 10^4)$	547	0.40	0.020	78%
3	$261~(3.26 imes 10^4)$	262	541 (1.51×10^4)	552	0.34	0.023	75%
4	$262~(3.63 imes 10^4)$	264	$536(1.50\times10^4)$	548	0.16	0.020	94%

Table 1 Absorption parameters and photochromic reactivity of diarylethenes **1–4** in hexane (2.0×10^{-5} mol L⁻¹) and in PMMA films (10%, w/w).

^a Absorption maxima of open-ring isomers.

^b Absorption maxima of closed-ring isomers

^c Quantum yields of cyclization reaction (Φ_{o-c}) and cycloreversion reaction (Φ_{c-o}), respectively.

Diarylethenes **2–4** exhibited similar photochromic properties with absorption maxima at 534, 541, and 536 nm, respectively. As shown in Fig. 4, the absorption maxima of diarylethenes **1c–4c** in PMMA films were redshifted compared to those in hexane, which could be possibly ascribed to polar effect of polymer matrix as well as to stabilization of molecular arrangement in solid state [19–22,48]. In addition, the photoconversion ratios of **1–4** from ring-opened to ring-closed isomers in photostationary state in hexane were analyzed by HPLC (Fig. 5.). Compared to that of diarylethene **4** (94%), the photoconversion ratios of pyridine-containing diarylethenes **1–3** (75 ~ 79%) in hexane were significantly lower, suggesting that the presence of nitrogen atom in the pyridine moiety may increase the portion of molecules with a parallel conformation.

From the data of the photochromic properties of diarylethenes **1–4** summarized in Table 1, it was noticed that compound **1**, in which the nitrogen atom is located at an *ortho*-position of the pyridine moiety, has the largest molar absorption coefficients both for ring-opened and ring-closed isomers. The molar absorption coefficients of **1–3** for both ring-opened and ring-closed isomers decreased in order of **1** > **3** > **2** (*ortho* > *para* > *meta*). For the ring-closed isomers **1c–3c**, the absorption maxima decreased in order of **1** > **3** > **2** (*ortho* > *para* > *meta*) in both hexane and PMMA films. However, no significant changes in the absorption maxima of the ring-opened isomers **10–30** were observed.

The cyclization quantum yields increased in order of $\mathbf{3} < \mathbf{2} < \mathbf{1}$ (*para* ($\phi_{o-c,3} = 0.34$) < *meta* ($\phi_{o-c,2} = 0.40$) < *ortho* ($\phi_{o-c,1} = 0.53$)), whereas the cycloreversion quantum yields decreased in order of $\mathbf{3} > \mathbf{2} > \mathbf{1}$ (*para* ($\phi_{c-o,3} = 0.023$) > *meta* ($\phi_{c-o,2} = 0.020$) > *ortho* ($\phi_{c-o,1} = 0.012$)). While the effect of position of nitrogen atom in pyridine is consistent with that of chlorine atom in chlorobenzene-containing diarylethenes [22], it is contrary to that of cyano group in cyanobenzene-containing diarylethenes [19]. Furthermore, the cyclization quantum yields of $\mathbf{1}$ - $\mathbf{3}$ were significantly larger than that of $\mathbf{4}$, indicating that the presence of nitrogen atom in the terminal aromatic ring enhanced the cyclization quantum yields of the corresponding diarylethenes.

The thermal stability of the ring-opened and ring-closed isomers of diarylethenes **1**–**4** was tested. At ambient temperature, exposure of the solution of **1**–**4** in hexane to air for 100 h in the dark caused no changes in color and absorption spectra. Compound **1**–**4** were stable in the dark for at least one year. When the solution of **1**–**4** in hexane was heated under reflux (342 K) for 24 h in darkness, no decomposition was detected by NMR spectroscopy.

The fatigue resistance of photochromic compounds is a crucial factor for their practical applications in optical devices [6,49]. Upon alternating irradiation with UV and visible light, the fatigue resistance of **1–4** was examined in both hexane and PMMA films. As depicted in Fig. 6, the coloration and decoloration cycle of **1–4** could repeat 50 times in hexane with only *ca*. 5% ~ 15% degradation, and repeat 200 times in PMMA films with only *ca*. 19% ~ 24% degradation.

3.2. Acidichromism of diarylethenes 1-3

The multiple switching behavior of diarylethenes **1–3** were studied with stimulation of acid/base and light. The structural and color changes among **1–3** and their N-protonated forms **1'–3'** in acetonitrile (2.0×10^{-5} mol L⁻¹) are illustrated in Fig. 7. Addition of trifluoroacetic acid in acetonitrile (5.0μ L, $6.8 \times 10^{-3} \text{ mol L}^{-1}$) to the solution of **10–30** produced the N-protonated diarylethenes **10'–30'**. The absorption maxima bathochromically shifted from 306 nm to 342 nm for **10'** ($\varepsilon = 8.03 \times 10^4$ L mol⁻¹ cm⁻¹), from 290 nm to 299 nm for **20'** ($\varepsilon = 6.60 \times 10^4$ L mol⁻¹ cm⁻¹), and from 299 nm to 345 nm for **30'** ($\varepsilon = 3.58 \times 10^4$ L mol⁻¹ cm⁻¹). **10'–30'** could be converted back into **10–30** by neutralization with



Fig. 6. Fatigue resistances of diarylethenes **1–4** in air atmosphere at room temperature: (A) In hexane; (B) In PMMA films. Initial absorptance of the sample was fixed to 1.0.



Fig. 7. The structural and color changes between diarylethenes 1-3 and diarylethenes 1'-3' in acetonitrile (2.0×10^{-5} mol L⁻¹).

triethylamine (10.0 μ L, 3.6 \times 10⁻³ mol L⁻¹). Upon irradiation with UV light, the colorless solution of 10'-30' turned into different colors, indicating the formation of N-protonated ring-closed isomers 1c'-3c'. Their absorption maxima were at 573 nm for 1c' $(\varepsilon = 1.13 \times 10^4 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1})$, 549 nm for **2c**' $(\varepsilon = 1.32 \times 10^4 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1})$, and 584 nm for **3c**' $(\varepsilon = 1.14 \times 10^4 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1})$. Alternatively, an interconversion between diarylethenes 1c-3c and 1c'-3c' could be conducted by stimulation with acid/base. Similar to reported pyridine-containing diarylethenes [36,43], the N-protonation process was accompanied with a notable change in the color of solution (Fig. 7) from purple red (1c) to blue (1c'), red (2c) to purple red (2c'), and purple red (3c)to blue (3c'). The bathochromic shift of absorption spectra of 1c'-3c' (Fig. 8) was possibly due to the lowering of excited state energy levels of protonated species [50]. Among another series of isomeric asymmetric diarylethenes with a pyridylisoxazole and pyridylthiophene, only the one with nitrogen atom at para-position of the pyridine moiety showed obvious acidichromism [51], suggesting that structure of the other aryl moiety of diarylethene and position of the nitrogen atom in pyridine moiety have a synergic effect on the acidichromism of pyridine-containing diarylethenes.



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

3.3. Fluorescence of diarylethenes 1-4

The fluorescence properties of diarylethenes **1–4** in both hexane $(5.0 \times 10^{-5} \text{ mol L}^{-1})$ and PMMA films (10%, w/w) were evaluated at room temperature. Their emission spectra are shown in Fig. 9. Compared to those in hexane, the emission peaks of **1–4** in PMMA films exhibited an evident hypsochromic shift (3 nm for **1**, 4 nm for



Fig. 9. Emission spectra of diarylethenes **1–4** at room temperature: (A) In hexane $(5.0 \times 10^{-5} \text{ mol } L^{-1})$, excited at 300 nm: (B) In PMMA films (10%, w/w), excited at 310 nm.



Fig. 10. Emission intensity changes of diarylethenes 1–4 by photoirradiation in hexane (2.0 × 10⁻⁵ mol L⁻¹) at room temperature, excited at 300 nm: (A) 1, (B) 2, (C) 3, (D) 4.

2, 5 nm for **3**, and 10 nm for **4**), which was in agreement with the results in our previous reports [19-21]. The emission intensities of **1–4** decreased in order of **1** > **2** > **3** > **4** in both hexane and PMMA

films. The fluorescence quantum yields of **1–4** were determined as 0.034, 0.059, 0.049, and 0.048, respectively (referenced to anthracene). The result showed that the fluorescence quantum yield could



Fig. 11. Emission intensity changes of diarylethenes 1–4 by photoirradiation in PMMA films at room temperature, excited at 310 nm: (A) 1, (B) 2, (C) 3, (D) 4.

be significantly enhanced, when the nitrogen atom was at the *meta*-position in pyridine.

Similar to most reported diarylethenes [52-56], 1-4 exhibited an evident fluorescent switch upon photoisomerization from ringopened isomers to ring-closed isomers in both hexane and PMMA films. As shown in Figs. 10 and 11, irradiation of 10-40 with UV light caused the formation of the non-fluorescent ring-closed isomers 1c-4c. Reversely, irradiation 1c-4c with visible light regenerated the ring-opened isomers 10-40 and recovered the original fluorescence emission. The emission intensities of 10-40 were quenched to ca. 55% for 1, 35% for 2, 25% for 3, and 34% for 4, when photostationary state was reached. Compound 3, which has the nitrogen atom at para-position of pyridine, displayed the highest fluorescent modulation efficiency of 75%. Similarly, fluorescent modulation efficiencies of 1-4 in PMMA films were determined as 73% for 1, 76% for 2, 76% for 3, and 67% for 4. The residual fluorescence for 1-4 in photostationary state may be attributed to the incomplete cyclization reaction as well as to the existence of parallel conformation [21,57]. In comparison with the diarylethenes reported in our previous research [19,21], 1-4 had significantly enhanced fluorescent modulation efficiencies in both liquid and solid media, which is ideal for applications, such as optical recording media and fluorescent photoswitches [23,58-61].

4. Conclusions

In this paper, three new asymmetric diarylethenes containing a benzothiophene and a pyridylthiophene were synthesized. These compounds showed notable photochromic characteristics and functioned as fluorescence switches in hexane and PMMA films. These compounds also underwent reversible isomerizations under acid/base stimuli, and the absorption maxima of the ring-closed isomers exhibited remarkable bathochromic shifts accompanied with significant color change in acetonitrile. These results revealed that both the pyridine ring and the position of nitrogen atom in pyridine had significant effects on the photochromic behavior of the corresponding diarylethenes.

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References

- Waldeck DH. Photoisomerization dynamics of stilbenes. Chem Rev 1991;91: 415–36.
- [2] Kumar GS, Neckers DC. Photochemistry of azobenzene-containing polymers. Chem Rev 1989;89:1915–25.
- [3] Heller HG, Oliver S. Photochromic heterocyclic fulgides. Part 1. Rearrangement reactions of (Ε)-α-3-furylethylidene(isopropylidene)succinic anhydride. J Chem Soc Perkin Trans 1981;1:197–201.
- [4] Yokoyama Y. Fulgides for memories and switches. Chem Rev 2000;100: 1717–40.
- [5] Alfimov MV, Fedorova OA, Gromov SP. Photoswitchable molecular receptors. J Photochem Photobiol A 2003;158:183–98.
- [6] Irie M. Diarylethenes for memories and switches. Chem Rev 2000;100: 1685–716.
- [7] Irie M, Mohri M. Thermally irreversible photochromic systems. Reversible photocyclization of diarylethene derivatives. J Org Chem 1988;53:803–8.
- [8] Nakayama Y, Hayashi K, Irie M. Thermally irreversible photochromic systems. Reversible photocyclization of 1,2-diselenenylethene and 1,2-diindolylethene derivatives. J Org Chem 1990;55:2592–6.
- [9] Irie M, Sayo K. Solvent effects on the photochromic reactions of diarylethene derivatives. J Phys Chem 1992;96:7671–4.

- [10] Yokoyama Y, Hasegawa T, Ubukata T. Highly diastereoselective photochromic ring closure of bisbenzothienylethenes possessing dual fluorinated stereocontrollers. Dyes Pigm 2011;89:223–9.
- [11] Sanz-Menez N, Monnier V, Colombier I, Baldeck PL, Irie M, Ibanez A. Photochromic fluorescent diarylethene nanocrystals grown in solegel thin films. Dyes Pigm 2011;89:241–5.
- [12] Liu G, Pu SZ, Wang XM, Liu WJ, Fan CB. The effect of the cyano group position upon unsymmetrical isomeric diarylethenes bearing a pyrrole unit. Dyes Pigm 2011;90:89–99.
- [13] Tian H, Qin B, Yao RG, Zhao XL, Yang SJ. A single photochromic molecular switch with four optical outputs probing four inputs. Adv Mater 2003;15: 2104-7.
- [14] Pu SZ, Liu G, Shen L, Xu JK. Efficient synthesis and properties of isomeric photochromic diarylethenes having a pyrrole unit. Org Lett 2007;9:2139–42.
- [15] Perters A, Vitols C, McDonald R, Branda NR. Novel photochromic compounds based on the 1-thienyl-2-vinylcyclopentene backbone. Org Lett 2003;5: 1183-6.
- [16] Pu SZ, Zheng CH, Le ZG, Liu G, Fan CB. Substituent effects on the properties of photochromic diarylethenes. Tetrahedron 2008;64:2576–85.
- [17] Yamaguchi T, Takami S, Irie M. Photochromic properties of 1,2-bis(6substitute-2-methyl-1-benzofuran-3-yl)ethene derivatives. J Photochem Photobiol A 2008;193:146–52.
- [18] Liu WJ, Pu SZ, Liu G. Synthesis and optoelectronic properties of unsymmetrical isomeric diarylethene derivatives having a fluorine atom. J Mol Struct 2009; 936:29–36.
- [19] Pu SZ, Liu WJ, Miao WJ. Photochromism of new unsymmetrical isomeric diarylethenes bearing a methoxyl group. J Phys Org Chem 2009;22:954–63.
- [20] Pu SZ, Fan CB, Miao WJ, Liu G. The effect of substituent position upon unsymmetrical isomeric diarylethenes bearing a methoxy group. Dyes Pigm 2010;84:25–35.
- [21] Fan CB, Pu SZ, Liu G, Yang TS. Substituent position effect on the properties of new unsymmetrical isomeric diarylethenes having a chlorine atom. J Photochem Photobiol A 2008;197:415–25.
- [22] Pu SZ, Yan LS, Wen ZD, Liu G, Shen L. Synthesis and chlorine atom position effect on the properties of unsymmetrical photochromic diarylethenes. J Photochem Photobiol A 2008;196:84–93.
- [23] Yun CJ, You J, Kim J, Huh J, Kim E. Photochromic fluorescence switching from diarylethenes and its applications. J Photochem Photobiol C 2009;10:111–29.
- [24] Hu ZK, Zhang Q, Xue MZ, Sheng QR, Liu YG. Fluorescent photoswitchable nanohybrids based on photochromism. J Phys Chem Solids 2008;69:206–10.
- [25] Corredor BCC, Huang Z–L, Belfield KD. Two-photon 3D optical data storage via fluorescence modulation of an efficient fluorene dye by a photochromic diarylethene. Adv Mater 2006;18:2190–4.
- [26] Okuyama T, Tani Y, Miyake K, Yokoyama Y. Chiral helicenoid diarylethene with large change in specific optical rotation by photochromism1,2. J Org Chem 2007;72:1634–8.
- [27] Matsuda K, Irie M. Photoswitching of intramolecular magnetic interaction using a diarylethene dimmer. J Am Chem Soc 2001;123:9896–7.
- [28] Takeshita M, Choi CN, Irie M. Enhancement of the photocyclization quantum yield of 2,2'-dimethyl-3,3'-(perfluorocyclopentene-1,2-diyl)bis(benzo[b]-thiophene-6sulfonate) by inclusion in a cyclodextrin cavity. Chem Commun; 1997:2265–6.
- [29] Kawata S, Kawata Y. Three-dimensional optical data storage using photochromic materials. Chem Rev 2000;100:1777–88.
- [30] Matsuda K, Irie M. A diarylethene with two nitronyl nitroxides: photoswitching of intramolecular magnetic interaction. J Am Chem Soc 2000;122: 7195–201.
- [31] Kawai T, Kim M-S, Sasaki T, Irie M. Fluorescence switching of photochromic diarylethenes. Opt Mater 2002;21:275–8.
- [32] Utsumi H, Nagahama D, Nakano H, Shirota Y. Synthesis of a novel family of photochromic amorphous molecular materials based on dithienylethene, their photochromic properties and application for dual image formation. J Mater Chem 2002;12:2612–9.
- [33] Yamaguchi T, Inagawa T, Nakazumi H, Irie S, Irie M. Photoinduced pitch changes in chiral nematic liquid crystals formed by doping with chiral diarylethene. J Mater Chem 2001;11:2453–8.
- [34] Bachrach SM. Aromaticity of annulated benzene, pyridine and phosphabenzene. J Organomet Chem 2002;643–644:39–46.
- [35] Popova A, Christov M, Raicheva S, Sokolova E. Adsorption and inhibitive properties of benzimidazole derivatives in acid mild steel corrosion. Corros Sci 2004;46:1333–50.
- [36] Yumoto K, Irie M, Matsuda K. Control of the photoreactivity of diarylethene derivatives by quaternarization of the pyridylethynyl group. Org Lett 2008;10: 2051–4.
- [37] Piard J, Métivier R, Giraud M, Léaustic A, Yub P, Nakatani K. Photoswitching in diarylethene nanoparticles, a trade-off between bulk solid and solution: towards balanced photochromic and fluorescent properties. New J Chem 2009;33:1420–6.
- [38] Samachetty HD, Lemieux V, Branda NR. Modulating chemical reactivity using a photoresponsive molecular switch. Tetrahedron 2008;64:8292–300.
- [39] Al-Atar U, Fernandes R, Johnsen B, Baillie D, Branda NR. A photo-controlled molecular switch regulates paralysis in a living organism. J Am Chem Soc 2009;131:15966-7.
- [40] Masuda T, Irie M, Uosaki K. Photoswitching of electron transfer property of diarylethene-viologen linked molecular layer constructed on a hydrogenterminated Si(111) Surface. Thin Solid Films 2009;518:591–5.

- [41] Zou Y, Yi T, Xiao SZ, Li FY, Li CY, Gao X, et al. Amphiphilic diarylethene as a photoswitchable probe for imaging living cells. J Am Chem Soc 2008;130: 15750-1.
- [42] Matsuda K, Shinkai Y, Yamaguchi T, Nomiyama K, Isayama M, Irie M. Optical properties and dynamics of a photochromic bisthienylethene in solution and in a polymer film. Chem Phys Lett 1998;293:555–63.
- [43] Cui SQ, Pu SZ, Liu WJ, Liu G. Synthesis and photochromic properties of a multiple responsive diarylethene and its selective binding affinity for copper(II) ion. Dyes Pigm 2011;91:435–41.
- [44] Piao XJ, Zou Y, Wu JC, Li CY, Yi T. Multiresponsive switchable diarylethene and its application in bioimaging. Org Lett 2009;11:3818-21.
- [45] Irie M, Lifka T, Kobatake S, Kato N. Photochromism of 1,2-bis(2-methyl-5phenyl-3-thienyl)perfluorocyclopentene in a single-crystalline phase. J Am Chem Soc 2000;122:4871–6.
- [46] Pu SZ, Liu G, Li GZ, Wang RJ, Yang TS. Synthesis, crystal structure and its optical and electrochemical properties of a new unsymmetrical diarylethene. J Mol Struct 2007;833:23–9.
- [47] Li ZX, Liao LY, Sun W, Xu CH, Zhang C, Fang CJ, et al. Reconfigurable cascade circuit in a photo- and chemical-switchable fluorescent diarylethene derivative. J Phys Chem C 2008;112:5190–6.
- [48] Kasatani K, Kambe S, Irie M. Photochromic reaction and fuorescence of dithienylethenes in the solid state. J Photochem Photobiol A 1999;122: 11–5.
- [49] Tian H, Wang S. Photochromic bisthienylethene as multi-function switches. Chem Commun; 2007:781–92.
- [50] Sarkar A, Chakravorti S. Photophysics of phenyl pyridines and bipyridines in different media. J Lumin 1995;65:163–8.

- [51] Liu G, Liu M, Pu SZ, Fan CB, Cui SQ. Photochromism of new unsymmetrical isomeric diarylethenes bearing a pyridine group. Tetrahedron 2012;68:2267–75.
- [52] Pu SZ, Yang TS, Xu JK, Chen B. Syntheses and properties of new photochromic diarylethene derivatives having a pyrazole unit. Tetrahedron Lett 2006;47: 6473–7.
- [53] Suzuki Y, Yokoyama K. Design and synthesis of intramolecular charge transfer-based fluorescent reagents for the highly-sensitive detection of proteins. J Am Chem Soc 2005;127:17799–802.
- [54] Irie M, Fukaminato T, Sasaki T, Tamai N, Kawai T. Organic chemistry: a digital fluorescent molecular photoswitch. Nature 2002;420:759–60.
- [55] Giordano L, Jovin TM, Irie M, Jares-Erijman EA. Diheteroarylethenes as thermally stable photoswitchable acceptors in photochromic fluorescence resonance energy transfer (pcFRET). J Am Chem Soc 2002;124:7481–9.
 [56] Jeong Y-C, Yang SI, Kim E, Ahn K- H. Development of highly fluorescent photo-
- [56] Jeong Y-C, Yang SI, Kim E, Ahn K- H. Development of highly fluorescent photochromic material with high fatigue resistance. Tetrahedron 2006;62:5855–61.
- [57] Pu SZ, Fan CB, Miao WJ, Liu G. New photochromic diarylethenes with a sixmembered aryl unit. Tetrahedron 2008;64:9464–70.
- [58] Norsten TB, Branda NR. Photoregulation of fluorescence in a porphyrinic dithienylethene photochrome. J Am Chem Soc 2001;123:1784–5.
- [59] Chen BZ, Wang MZ, Wu YQ, Tian H. Reversible near-infrared fluorescence switch by novel photochromic unsymmetrical-phthalocyanine hybrids based on bisthienylethene. Chem Commun; 2002:1060–1.
- [60] Moriyama Y, Matsuda K, Tanifuji N, Irie S, Irie M. Electrochemical cyclization/ cycloreversion reactions of diarylethenes. Org Lett 2005;7:3315–8.
- [61] Polyakova S, Belov V, Blaaderen A, Bossi ML, Hell SW. Synthesis and characterization of photoswitchable fluorescent silica nanoparticles. Small 2008;4: 134–42.