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Photochromic diarylethenes with a naphthalene moiety: synthesis, photochromism, and substitution effects



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ABSTRACT

Five unsymmetrical diarylethenes with a naphthalene moiety were synthesized, and the structures of four diarylethenes were determined by single crystal X-ray diffraction analysis. The naphthalene was connected directly to the central perfluorocyclopentene ring as an aryl moiety and available to participate in photoisomerization reaction. Their properties, such as photochromism, thermal stability, fatigue resistance, and fluorescence, were investigated systematically. All five diarylethenes, which are thermally stable, exhibit favorable photochromism, and function as notable fluorescence switches in both solution and solid media. The electron-donating substituents effectively suppressed the cycloreversion quantum yield of diarylethenes with a naphthalene moiety. The results indicated that the naphthalene moiety and the substituent effects played an important role during the process of photoisomerization reaction for these diarylethene derivatives.

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1. Introduction

Upon stimulation with light, photochromic compounds can interconvert their molecular structures between two isomers with different properties including color, refractive indices, dipole moments, as well as oxidation/reduction potentials, and electro-conductivities.¹ Photochromic compounds are the most promising candidates for photoelectronic applications, such as optical memory, chemical sensor, and molecular switching, because of their thermally-irreversible and fatigue-resistant photoisomerization performances.² To date, a large amount of organic photochromic molecular systems were reported, including spiropyrans,³ azobenzenes,⁴ fulgides,^{2b} diarylethenes.⁵ Among these photochromic molecules, diarylethenes have been extensively reported due to their rapid response rate and high photochromic reactivity.^{2b,5,6}

Generally, the photochromic properties of diarylethenes mainly depend on several factors, such as nature of heterocycle moieties, electron-withdrawing/donating substituents, conformation of open-ring isomer, and π -conjugation length of aryl groups.⁷ For instance, diarylethenes bearing thiophene/benzothiophene moieties exhibit excellent thermal stability and outstanding fatigue resistance,^{2b,5} whereas symmetrical diarylethene with two pyrrole rings is thermally unstable and returns to the open-ring isomer

even in the dark.⁸ Moreover, Tanifuji et al. reported the effect of radical substituents on photochromic reactivity of bis(3benzothiophene)perfluorocyclopentene,9 and Yamaguchi et al. investigated the substitution effects on photochromic properties of diarylethenes bearing two benzofuran groups.¹⁰ In our previous publications, we have explored several classes of diarylethenes and discussed the effects of substituents and their positions on photochromic properties.¹¹ The thermal stability of diarylethene plays an important role in application of optical memory media. According to different thermally stable of photo-generated isomers, diarylethenes are typically classified into two types, P-type (thermally stable photogenerated isomer) and T-type (thermally unstable photogenerated isomer).¹² During the past decade, a huge number of diarylethenes containing five-membered aryl rings, such as thiophene,¹³ benzothiophene,¹⁴ oxazole,¹⁵ pyrrole,¹⁶ thiazole,¹⁷ have been developed. The diarylethenes with six-membered aryl rings were rarely reported due to their poor thermal stability and fatigue resistance.^{11b,18} To date, few research on the diarylethenes containing six-membered aryl rings have been reported.¹⁹ In previous research, we reported diarylethenes with either benzene or pyridine moiety, and found that all of them exhibited favorable photochromism.^{11b,20} However, reports on unsymmetrical diarylethenes with a naphthalene moiety are still rare.²¹

In this work, five unsymmetrical diarylethenes with a naphthalene moiety were synthesized. In order to discuss the substitution effects on their physicochemical properties, different substituents were introduced into *meta*-position of the terminal benzene. The



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synthesized diarylethenes are 1-(2-methyl-1-naphthyl)-2-[2-methyl-5-(3-cyanophenyl)-3-thienyl]perfluorocyclopentene (**10**), 1-(2-methyl-1-naphthyl)-2-[2-methyl-5-(3-fluorophenyl)-3-thienyl]perfluorocyclopentene (**20**), 1-(2-methyl-1-naphthyl)-2-[2-methyl-5-(3-chlorophenyl)-3-thienyl]perfluorocyclopentene (**30**), 1-(2-methyl-1-naphthyl)-2-[2-methyl-5-(3-methyl)-3-thienyl]perfluorocyclopentene (**40**), and 1-(2-methyl-1-naphthyl)-2-(2-methyl-5-(3-methoxyphenyl)-3-thienyl]per-

fluorocyclopentene (**50**). The photochromic scheme of diarylethenes **10–50** is shown in Scheme 1.



Scheme 1. Photochromism of diarylethenes 1–5.

2. Experimental

2.1. General

All solvents used were spectroscopic grade and were purified by distillation before use. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with CDCl₃ as the solvent and tetramethylsilane as an internal standard. Infrared spectra (IR) were recorded on a Bruker Vertex-70 spectrometer. Melting point was taken on a WRS-1B melting point apparatus. Absorption spectra were measured using an Agilent 8453 UV/VIS spectrophotometer. Photoirradiation was carried out using an SHG-200 UV

lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. The required wavelength was isolated by the use of the appropriate filters. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. 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. Further details on the crystal structure investigation have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication CCDC 909429 for **10**, 909430 for **20**, 909431 or **30**, and 909432 for **50**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 0 1223 336033 or email:deposit@ccdc.cam.ac.uk).

2.2. Synthesis

The synthesis route for diarylethenes **10–50** is shown in Scheme 2. First, the phenylthiophene derivatives (**7a–e**) were prepared by Suzuki coupling of five bromobenzene derivatives with a thiophene boronic acid (**6**).²² Then, 1-bromo-2-methylnaphthalene (**8**) was lithated and coupled with octafluorocyclopentene to give (2-methyl-1-naphthyl)perfluorocyclopentene (**9**).^{21a} Finally, compounds **7a–e** was separately lithiated and then coupled with the compound **9** to give the unsymmetrical diarylethene derivatives **10–50**, respectively. The structures of **10–50** were confirmed by elemental analysis, NMR, and IR.

2.2.1. 3-Bromo-2-methyl-5-(3-cyanophenyl)thiophene (**7a**). Compound **7a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid (3.0 g, 11.3 mmol) with 3-bromobenzonitrile (2.47 g, 13.6 mmol) in the presence of Pd(PPh_3)₄ (0.15 g, 0.01 mmol) and Na₂CO₃ (2.0 mol L⁻¹, 50 mL) in tetrahydrofuran (THF) (80 mL containing 10% water). After refluxing for 16 h, the product was extracted with diethyl ether. The organic layer was dried over MgSO₄, filtrated, and evaporated. The crude product was purified by column chromatography on SiO₂ using petroleum ether as the eluent and 2.0 g of **7a** obtained as a yellowish solid in 53% yield. Mp 377–378 K; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.46 (s, 3H, –CH₃),



Scheme 2. Synthetic route to diarylethenes 1-5.

7.18 (s, 1H, thiophene–H), 7.50 (t, 1H, benzene–H, *J*=8.0 Hz), 7.57 (d, 1H, benzene–H, *J*=8.0 Hz), 7.73 (d, 1H, benzene–H, *J*=8.0 Hz), 7.79 (s, 1H, benzene–H).

2.2.2. 3-Bromo-2-methyl-5-(3-fluorophenyl)thiophene (**7b**). Compound **7b** was prepared by an analogous method similar to that used for **7a** and obtained as a light green solid in 67% yield. Mp 312–313 K; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.44 (s, 3H, –CH₃), 6.99 (s, 1H, thiophene–H), 7.22 (d, 1H, benzene–H, *J*=8.0 Hz), 7.30–7.37 (m, 3H, benzene–H).

2.2.3. 3-Bromo-2-methyl-5-(3-chlorophenyl)thiophene (**7c**). Compound **7c** was prepared by an analogous method similar to that used for **7a** and obtained as a pale yellow liquid in 66% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.44 (s, 3H, -CH₃), 7.12 (s, 1H, thiophene-H), 7.28 (t, 2H, benzene-H), 7.45 (d, 1H, benzene-H, *J*=8.0 Hz), 7.62 (d, 1H, benzene-H, *J*=8.0 Hz).

2.2.4. 3-Bromo-2-methyl-5-(3-methylphenyl)thiophene (**7d**). Compound **7d** was prepared by an analogous method similar to that used for **7a** and obtained as a light green liquid in 80% yield. ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.38 (s, 3H, -CH₃), 2.43 (s, 3H, -CH₃), 7.11 (s, 1H, thiophene-H), 7.14 (t, 1H, benzene-H, J=8.0 Hz), 7.28 (t, 1H, benzene-H, J=8.0 Hz), 7.32 (t, 1H, benzene-H, J=8.0 Hz), 7.34 (s, 1H, benzene-H).

2.2.5. 3-Bromo-2-methyl-5-(3-methoxyphenyl)thiophene (**7e**). Compound **7e** was prepared by an analogous method similar to that used for **7a** and obtained as a light green liquid in 53% yield. ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.34 (s, 3H, -CH₃), 3.86 (s, 3H, -CH₃), 6.84 (d, 1H, thiophene-H), 7.05 (s, 1H, benzene-H), 7.12 (s, 2H, benzene-H), 7.30 (t, 1H, benzene-H, *J*=8.0 Hz).

2.2.6. (2-Methyl-1-naphthyl)perfluorocyclopentene (**9**). To a stirred THF solution (60 mL) of compound **8** (3.0 g, 13.5 mmol) was added dropwise a 2.5 mol L⁻¹ *n*-BuLi/hexane solution (6.0 mL, 14.9 mmol) at -78 °C under argon atmosphere. After 30 min, octafluorocyclo pentene (C₅F₈) (2.0 mL, 14.9 mmol) was slowly added and the reaction mixture was stirred for 2.0 h at this low temperature. The reaction was quenched by water. The product was extracted with diethyl ether. The organic layer was washed with saturated sodium chloride aqueous and water, and then dried over anhydrous MgSO₄, filtrated and evaporated in vacuo. The crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to give 3.9 g compound **9** obtained as colorless crystalline in 87% yield. Mp 335–336 K; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.45 (s, 3H, –CH₃), 7.45 (s, 1H, naphthalene–H), 7.52–7.56 (m, 3H, naphthalene–H), 7.88–7.94 (m, 2H, naphthalene–H).

2.2.7. 1-(2-Methyl-1-naphthyl)-2-[2-methyl-5-(3-cyanophenyl)-3thienyl]perfluorocyclopentene (10). To a stirred anhydrous THF containing **7a** (1.37 g, 4.9 mmol) was added dropwise a 2.5 mol L^{-1} *n*-BuLi/hexane solution (2.2 mL, 5.4 mmol) at -78 °C under argon atmosphere. After the mixture has been stirred for 30 min, compound 9 (1.6 g, 4.9 mmol) in solvent of anhydrous THF was added. The reaction was further stirred at -78 °C for 2 h, and the reaction was allowed to slowly warm to the room temperature. The reaction was quenched with distilled water. The product was extracted with diethyl ether, dried with MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as the eluent to afford to 0.87 g compound 10 as a white powder solid in 43% yield. Calcd for C₂₈H₁₇F₆NS (%): calcd C, 65.49; H, 3.34; N, 2.73. Found C, 65.55; H, 3.38; N, 2.77; mp 422–423 K; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.25 (s, 3H, -CH₃), 2.37 (s, 3H, -CH₃), 6.89 (s, 1H, thiophene-H), 7.35-7.40 (m, 4H, benzene-H), 7.48-7.52 (m, 3H, naphthalene-H), 7.54 (d, 1H, naphthalene–H), 7.86 (t, 2H, naphthalene–H, *J*=8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ =14.90, 20.46, 113.27, 118.23, 123.25, 124.83, 124.96, 125.32, 125.80, 127.15, 128.44, 128.57, 128.67, 129.35, 129.71, 130.18, 130.73, 131.90, 134.57, 135.49, 138.44, 142.468; IR (*v*, KBr, cm⁻¹): 622, 677, 742, 788, 811, 871, 894, 981, 1049, 1107, 1133, 1193, 1273, 1339, 1438, 1494, 1581, 2230, 2918, 3692; HRMS (ESI): *m*/*z* calcd for C₂₈H₁₇F₆NS [M+H]⁺ 513.0986; found 513.0993.

2.2.8. 1-(2-Methyl-1-naphthyl)-2-[2-methyl-5-(3-fluorophenyl)-3thienyl]perfluorocyclopentene (20). Diarylethene 20 was prepared by a method similar to that used for **10**. The crude product was purified by column chromatography on SiO₂ using petroleum ether as eluent to give 20 (0.98 g, 53%) as a yellow solid. Calcd for C₂₇H₁₇F₇S (%): calcd C, 64.03; H, 3.38. Found C, 64.13; H, 3.43; mp 357–358 K; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.21 (s, 3H, –CH₃), 2.37 (s, 3H, -CH₃), 6.87 (s, 1H, thiophene-H), 6.90 (d, 2H, benzene-H, J=8.0 Hz), 6.99 (d, 1H, benzene-H, J=8.0 Hz), 7.23 (t, 1H, benzene–H, *J*=8.0 Hz), 7.35 (d, 1H, naphthalene–H, *J*=8.0 Hz), 7.50-7.56 (m, 2H, naphthalene-H), 7.71 (d, 1H, naphthalene-H, *J*=8.0 Hz), 7.84 (t, 2H, naphthalene–H, *J*=8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ =14.86, 20.43, 112.06, 112.29, 114.28, 114.49, 120.99, 123.27, 124.10, 124.85, 125.86, 127.02, 128.34, 128.53, 130.09, 130.33, 130.41, 131.85, 135.49, 137.42, 139.42, 139.78, 141.21, 141.56, 148.60; IR (v, KBr, cm⁻¹): 676, 734, 776, 811, 863, 897, 981, 1047, 1135, 1192, 1273, 1338, 1401, 1464, 1500, 1633, 3437; HRMS (ESI): *m*/*z* calcd for C₂₇H₁₇F₇S [M+H]⁺ 506.0939; found 506.0945.

2.2.9. 1-(2-Methyl-1-naphthyl)-2-[2-methyl-5-(3-chlorophenyl)-3thienvllperfluorocyclopentene (**30**). Diarylethene **30** was prepared by a method similar to that used for **10**. The crude product was purified by column chromatography on SiO₂ using petroleum ether as the eluent to give 0.34 g 30 as a colorless solid in 38% yield. Calcd for C₂₇H₁₇ClF₆S (%): calcd C, 62.01; H, 3.28. Found C, 62.31; H, 3.36; mp 349–350 K; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.18 (s, 3H, -CH₃), 2.34 (s, 3H, -CH₃), 6.85 (s, 1H, thiophene-H), 7.05-7.07 (m, 1H, benzene-H), 7.12-7.18 (m, 3H, benzene-H), 7.33 (d, 1H, naphthalene–H, J=8.0 Hz), 7.46–7.56 (m, 2H, naphthalene–H), 7.69 (d, 1H, naphthalene–H, J=8.0 Hz), 7.84 (t, 2H, naphthalene–H, J=8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): $\delta=15.30, 20.48, 123.29,$ 123.43, 124.21, 124.86, 125.00, 125.36, 125.70, 127.05, 127.54, 128.37, 128.56, 130.11, 131.86, 134.78, 134.96, 135.49, 139.51, 141.69; IR (v, KBr, cm⁻¹): 743, 773, 811, 832, 870, 893, 976, 987, 1048, 1083, 1105, 1133, 1192, 1274, 1341, 1425, 1497, 1572, 1596, 3061, 3632; HRMS (ESI): m/z calcd for C₂₇H₁₇ClF₆S [M+H]⁺ 522.0644; found 522.0652.

2.2.10. 1-(2-Methyl-1-naphthyl)-2-[2-methyl-5-(3-methylphenyl)-3thienyl]perfluorocyclopentene (40). Diarylethene 40 was prepared by a method similar to that used for **10**. The crude product was purified by column chromatography on SiO₂ using petroleum ether as eluent to give **40** (0.57 g, 42%) as a yellow-green solid. Calcd for C₂₈H₂₀F₆S (%): calcd C, 66.92; H, 4.01. Found C, 67.03; H, 4.12; mp 323–324 K; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.21 (s, 3H, –CH₃), 2.30 (s, 3H, -CH₃), 2.36 (s, 3H, -CH₃), 6.83 (s, 1H, thiophene-H), 7.06 (t, 1H, benzene-H), 7.10-7.16 (m, 2H, benzene-H), 7.32 (d, 1H, benzene-H, J=8.0 Hz), 7.47-7.55 (m, 3H, naphthalene-H), 7.70 (d, 1H, naphthalene–H), 7.81 (t, 2H, naphthalene–H, J=8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ=14.89, 20.47, 21.32, 122.46, 122.63, 123.33, 124.79, 124.99, 125.02, 125.62, 126.08, 126.23, 126.98, 128.30, 128.42, 128.58, 128.74, 130.01, 131.87, 131.93, 133.14, 135.55, 138.52, 140.77, 141.27; IR (v, KBr, cm⁻¹): 684, 743, 775, 811, 870, 894, 984, 1049, 1105, 1134, 1191, 1274, 1341, 1509, 1924, 3299, 3694; HRMS (ESI): m/z calcd for $C_{28}H_{20}F_6S$ [M+H]⁺ 502.1190; found 502.1195.

2.2.11. 1-(2-Methyl-1-naphthyl)-2-(2-methyl-5-(3-methoxyphenyl)-3-thienyl)perfluorocyclopentene (50). Diarylethene 50 was prepared by a method similar to that used for **10**. The crude product was purified by column chromatography on SiO₂ using petroleum ether as eluent to give 50 (0.87 g, 58%) as a yellow solid. Calcd for C₂₈H₂₀F₆OS (%): calcd C, 64.86; H, 3.89. Found C, 64.99; H, 3.94; mp 362-363 K; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.22 (s, 3H, -CH₃), 2.34 (s, 3H, -CH₃), 3.71 (s, 3H, -CH₃), 6.61 (s, 1H, thiophene-H), 6.74 (d, 1H, benzene-H, J=8.0 Hz), 6.79 (d, 2H, benzene-H, *I*=8.0 Hz), 7.15 (t, 1H, benzene–H, *I*=8.0 Hz), 7.33 (d, 1H, naphthalene–H, J=8.0 Hz), 7.47 (t, 1H, naphthalene–H, J=8.0 Hz), 7.52 (d, 1H, naphthalene–H, *I*=8.0 Hz), 7.79 (d, 1H, naphthalene–H), 7.81 (t, 2H, naphthalene–H, *J*=8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ =14.91, 20.42, 55.18, 110.48, 113.54, 117.89, 123.66, 125.00, 125.63, 126.99, 128.30, 128.59, 129.87, 130.04, 130.00, 131.67, 133.26, 135.68, 140.96, 141.46; IR (v, KBr, cm⁻¹): 678, 742, 767, 810, 872, 894, 982, 1046, 1101, 1132, 1190, 1257, 1342, 1437, 1468, 1503, 1582, 1608, 1904, 3300, 3628; HRMS (ESI): *m*/*z* calcd for C₂₈H₂₀F₆OS [M+H]⁺ 518.1139; found 518.1147.

3. Results and discussion

3.1. Photoisomerization of diarylethenes

The photochromic behaviors of 1–5 induced by photoirradiation were measured at room temperature in both hexane $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ and ploy (methyl methacrylate) (PMMA) films (10%, w/w). The absorption spectral changes of 1 in both hexane and a PMMA film upon photoirradiation are shown in Fig. 1. In hexane, **10** exhibited a sharp absorption peak at 264 nm (ε , 2.45×10^4 L mol⁻¹ cm⁻¹) due to a $\pi \rightarrow \pi^*$ transition.²³ Upon irradiation with 297 nm light, the colorless solution of **10** turned red and a new visible absorption band was observed at 513 nm (ε , 1.89×10^4 L mol⁻¹ cm⁻¹), while the intensity of the original peak at 264 nm decreased due to the formation of the closed-ring isomer **1c.** Upon irradiation with visible light (λ >500 nm), the red colored solution was entirely bleached to colorless due to the reproduction of the original open-ring isomer **10**. In photostationary state, a clear isosbestic point of **1** was observed at 275 nm, which supported the reversible two-component photochromic reaction scheme.^{6b} 2–5 showed similar photochromism in hexane. The color changes of 1–5 by photoirradiation are shown in Fig. 2. Upon irradiation with 297 nm light, the colorless solutions of **20–50** turned red due to the formation of the closed-ring isomers **2c**–**5c**, which the absorption maxima appeared at 511, 510, 514, and 514 nm, respectively. All the red solutions of 2c-5c were decolorized upon irradiation with visible light (λ >500 nm). When arrived at photostationary state, the isosbestic points of 2-5 were observed at 285, 286, 291, and 290 nm, respectively. As shown in Fig. 3, the photoconversion ratios from open-ring to closed-ring isomers of 1-5 were analyzed by HPLC in photostationary state. The photoconversion ratios of 1-5

were 55% for **1**, 65% for **2**, 62% for **3**, 52% for **4**, and 78% for **5** in photostationary state. Compared to diarylethenes with a pyrrole moiety,²⁴ the photoconversion rations of **1–5** decreased remarkably in hexane. In PMMA films, **1–5** also showed similar photochromism to that in hexane, and the color changes are also shown in Fig. 2. Compared to those in solution, the absorption maxima of **1c–5c** were observed at a longer wavelength in PMMA films. The redshift values are 8 nm for **1c**, 8 nm for **2c**, 9 nm for **3c**, 12 nm for **4c**, and 14 nm for **5c**. The phenomena may be ascribed to more planar structure and stabilization of molecular arrangement in solid state.²⁵

The photochromic features of **1–5** in hexane and PMMA films are summarized in Table 1. In hexane, the absorption maxima only changed slightly, when different substituents were attached at the *meta*-position of the terminal benzene. But other photochromic features including molar absorption coefficients and cyclization/ cycloreversion quantum yields were dependent on the substituents. When strong electron-withdrawing groups (cyano, fluorine, and chlorine group, 1-3) were introduced to the metaposition of the terminal benzene, the cyclization quantum yields (from $\Phi_{3, 0-c}=0.23$ to $\Phi_{1, 0-c}=0.49$) and cycloreversion quantum yields (from $\Phi_{3, c-o}=0.12$ to $\Phi_{1, c-o}=0.25$) gradually increased accompanied with the increase of electron-withdrawing ability. Similarly, when electron-donating groups (methyl and methoxy, 4 and **5**) were introduced, the cyclization guantum yields (from Φ_4 $_{\rm o-c}$ =0.42 to $\Phi_{\rm 5, o-c}$ =0.55) and cycloreversion quantum yields (from $\Phi_{4, c-0}=0.09$ to $\Phi_{5, c-0}=0.13)$ increased with the increase of electron-donating ability. As a result, 5 has the largest cyclization quantum vield and **4** has the smallest cycloreversion quantum yield. Furthermore, all cyclization quantum yields were higher than their cycloreversion quantum yields for 1-5. The result is quite different from that of diarylethenes with a pyrazole moiety, whose cyclization quantum yields were much smaller than their cycloreversion quantum yields.²⁶ The cycloreversion quantum yields of 1–3 were much higher than those of 4 and 5, suggesting that the electron-donating substituents could effectively suppress the cycloreversion quantum yields, which was well consistent with the diarylethenes with pyridine and thiophene moieties.^{19b} But this result is different from that of diarylethenes with a benzene moiety, which their cycloreversion quantum yields significantly decreased accompanied with the increase of the electron-withdrawing ability.11b,27

The thermal stability of the open-ring and closed-ring isomers of **1–5** was tested in hexane at room temperature and in ethanol at 351 K. The hexane solutions were stored at room temperature in the dark, and exposed to air for more than one month. No changes were detected in UV/Vis spectra for **1–5**. At 351 K, **1–5** also showed excellent thermal stability for more than 8 h in ethanol. As a key factor for practical applications in optical devices,^{5,28} fatigue



Fig. 1. Absorption spectral changes of diarylethene 1 by photoirradiation at room temperature: (A) in hexane (2.0×10⁻⁵ mol L⁻¹), (B) in a PMMA film (10%, w/w).



Fig. 2. Color changes of 1-5 by photoirradiation at room temperature: (A) in hexane, (B) in PMMA films.



Fig. 3. The photoconversion ratios of 1–5 in photostationary state by HPLC analysis.

hexane is much stronger than that in PMMA films. Compared to diarylethenes with a benzene moiety,^{11b,20} the fatigue resistance of the diarylethenes with a naphthalene moiety is superior in both hexane and PMMA films. In addition, the fatigue resistance of diarylethene bearing an electron-donating methoxy group was the best among these compounds in PMMA films. The results were well in agreement with that of diarylethenes with thiophene and pyridine moieties,^{19b} but are completely contrary to that of the reported analogs with a benzene moiety.^{11b}

3.2. Non-photochromism in crystalline phase

In general, diarylethene has two conformations with two heterocyclic rings in C_2 symmetry (anti-parallel conformation) and in mirror symmetry (parallel conformation). It is well known that only anti-parallel conformation can undergo effective photocyclization reaction by a conrotatory mechanism, whereas the parallel conformation is photochemically inactive.⁵ Therefore, in order to know



Fig. 4. Color changes of 1–5 by photoirradiation at room temperature: (A) in hexane, (B) in PMMA films.

resistance of **1–5** was examined in both hexane and PMMA films by photoirradiation at room temperature (Fig. 4). In hexane, the coloration/decoloration cycles of **1–5** could be repeated for more than 100 times with only 10% degradation of **1c**, 12% degradation of **2c**, 14% degradation of **3c**, 18% degradation of **4c**, and 12% degradation of **5c**. The degradation may be ascribed to the formation of an epoxide.^{18d} Similarly, the fatigue resistance of diarylethenes **1–5** was tested in PMMA films by alternatively irradiating with 297 nm and visible light, which could be repeated for more than 200 times with the degradation ca. 27% of **1c**, 54% of **2c**, 25% of **3c**, 26% of **4c**, and 21% of **5c**. As mentioned above, the fatigue resistance of **1–5** in

the relation between conformation and photochromic behaviors of diarylethenes in crystalline phase, it is necessary to acquire diarylethene crystals. In this work, the single crystals of **10**, **20**, **30**, and **50** were obtained by slow evaporation of hexane solutions. Their structures were provided by X-ray crystallographic analysis. Their ORTEP drawings are shown in Fig. 5, and X-ray crystallographic analysis data are listed in Table 2. The four derivatives crystallized with photoactive anti-parallel conformation in crystalline phase. For **10**, the double bond (C13–C17) of hexafluorocyclopentene ring is 1.321 Å being significantly shorter than other carbon–carbon single bonds (1.499 Å to 1.550 Å) of the ring. The naphthalene and

Compound	$\lambda_{o,max}/nm^a (\epsilon/L mol^{-1} cm^{-1})$		$\lambda_{c,max}/nm^b$ ($\epsilon/L mol^{-1}$	$\lambda_{c,max}/nm^b \ (\epsilon/L \ mol^{-1} \ cm^{-1})$			Conversion at
	Hexane	PMMA film	Hexane	PMMA film	$\Phi_{\mathrm{o-c}}$	$\Phi_{\rm c-o}$	PSS in hexane
1	264 (2.45×10 ⁴)	265	513 (1.89×10 ⁴)	521	0.49	0.25	55
2	262 (2.32×10 ⁴)	288	511 (2.18×10 ⁴)	519	0.47	0.24	65
3	263 (3.00×10 ⁴)	265	510 (2.00×10 ⁴)	519	0.23	0.12	62
4	264 (3.06×10 ⁴)	266	514 (2.79×10 ⁴)	526	0.42	0.09	52
5	264 (3.22×10 ⁴)	265	514 (2.10×10 ⁴)	528	0.55	0.13	78

Table 1 Absorption spectral properties of 1-5 in hexane (2.0×10^{-5} mol L⁻¹) and in PMMA films (10%, w/w) at room temperature

^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}).

thiophene moieties are linked by the C13=C17 double bond. The dihedral angles between the hexafluorocyclopentene ring and the two heteroaryl rings are 76.3° for C18–C27 and 64.0° for S1/C8–C11, and that between the thiophene ring and the linked benzene ring is 3.7°. The corresponding data of compounds **20**, **30**, and **50** are summarized in Table 3. The distance between the two reactive carbon atoms is 4.185 Å for 10 (C11...C19), 4.484 Å for 20 (C10...C26), 4.104 Å for **30** (C2...C28), and 4.017 Å for **50** (C11...C27). Based on the empirical rule that the molecule undergoes the photocyclization reaction if the molecule is fixed in an anti-parallel mode and the distance between reacting carbon atoms on the aryl rings is less than 4.2 Å,²⁹ crystals **20** should not exhibit photochromism but **10**, **30** and **50** could potentially display favorable photochromism by photoirradiation in the single crystalline phase. In fact, the crystals 20 showed no photochromism in accordance with the expected analysis upon irradiation with UV light. However, the crystals 10, 30 and 50 also showed no photochromism in the crystalline phase, in which was contrary to the theoretical analysis. That is to say, the four crystals showed no photochromism in crystalline phase. This is verified by the fact that irradiating crystals of 10, 20, 30, and 50 with UV light for 2 h resulted in no observable color change. When these crystals were dissolved in hexane, the solutions showed colorless and their

Table 2

Crystal data fo	r diarylethenes	10, 20,	30	and	50
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	Compounds				
	10	20	30	50	
Formula	C28H17F6NS	C ₂₇ H ₁₇ F ₇ S	C27H17ClF6S	C28H20F6OS	
Formula weight	513.49	506.47	522.92	518.50	
Temperature	296(2)	296(2)	293(2)	296(2)	
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	
Space group	P2(1)/c	P2(1)/c	Pbcn	Pbcn	
Unit cell	20.291(9)	18.472(7)	14.309(2)	13.9192(13)	
dimensions a (Å)					
b (Å)	14.114(6)	14.477(5)	8.3799(13)	8.4148(8)	
<i>c</i> (Å)	8.500(4)	8.936(3)	40.006(6)	41.020(4)	
α (0)	90.00	90.00	90.00	90.00	
β (o)	100.796(6)	102.821(5)	90.00	90.00	
γ (0)	90.00	90.00	90.00	90.00	
Volume (Å ³)	2391.1(18)	2330.2(15)	4797.0(12)	4804.5(8)	
Z	4	4	8	8	
Density (calcd) (g/cm ³)	1.426	1.444	1.448	1.434	
Goodness-of-fit on F ²	1.062	0.974	0.942	0.952	
Final $R_1[I > 2s(I)]$	0.1319	0.0730	0.2475	0.0708	
$wR_2[I>2s(I)]$	0.2956	0.1544	0.3611	0.1675	
R_1 (all data)	0.2173	0.1087	0.0961	0.1089	
wR_2 (all data)	0.3755	0.1762	0.2344	0.1958	



Fig. 5. ORTEP drawings of crystals of 10, 20, 30 and 50, showing about 30% probability displacement ellipsoids: (A) 10, (B) 20, (C) 30, and (D) 50.

Table 3 Distances between the reacting carbon atoms d(Å) and dihedral angles $\theta(\circ)$ of diarylethenes **10**, **20**, **30** and **50**

Compounds	d (Å)		θ (°) ^a	θ (°) ^a			
			θ_1	θ_2	θ_3		
10	C11…C19	4.185	76.3	64.0	3.7		
20	C10…C26	4.484	96.7	79.0	1.1		
30	C2…C18	4.104	75.3	58.5	4.8		
50	C11…C27	4.017	70.8	53.3	7.0		

^a θ_1 , Dihedral angle between the cyclopentene ring and the naphthalene ring; θ_2 , dihedral angle between the cyclopentene ring and the thiophene ring; θ_3 , dihedral angle between the thiophene ring and the adjacent benzene ring.

absorption spectra were the same as those of their open-ring isomers. The results indicated that the diarylethene systems with a naphthalene moiety showed no photochromism in crystalline phase although in accordance with the reported empirical rule.

3.3. Fluorescence of diarylethenes

The fluorescence modulation is becoming an intriguing approach, which can be widely applied to molecular-scale optoelectronics, ion-sensors, and digital photoswitches.^{12a,13a} As most reported diarylethenes,³⁰ **1–5** also exhibited notable fluorescence in both solution $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ and PMMA films (10%, w/w). Their fluorescence spectra were measured at room temperature using a Hitachi F-4500 spectrophotometer, and the result is shown in Fig. 6. In hexane, the emission peaks of **10–50** were observed at 422, 419, 402, 418, and 415 nm, when excited at 298 nm. The emission peaks of **10–50** were observed at 424, 431, 429, 438, and 425 nm, when excited at 310 nm in PMMA films. In comparison

with those in hexane solutions, the emission peaks of **10–50** showed a remarkable bathochromic shift in PMMA films, with the values of 2 nm for 1. 12 nm for 2. 27 nm for 3. 20 nm for 4. and 20 nm for 5. The emission intensity of diarylethenes with electronwithdrawing groups (cvano and fluorine, **1** and **2**) was much stronger than that of diarylethenes with electron-donating groups (methyl and methoxy, **4** and **5**) in hexane. Consequently, the emission intensity of **10** is the strongest in both hexane and a PMMA film. By using anthracene as the reference in acetonitrile, the fluorescence quantum yields of 10-50 were determined to be 0.042 for 10, 0.027 for 20, 0.143 for 30, 0.013 for 40, and 0.012 for 50. The results indicated that the electron-withdrawing substituents could effectively enhance the fluorescence quantum yield of diarylethene with a naphthalene unit. This observation is well agreement with that of diarylethenes with a pyridine moiety,^{19b} while contrary to that of reported diarylethenes with a benzene moiety, whose fluorescence quantum yields increased with the increase of the electron-donating ability.^{11b,27}

As has been observed for most reported diarylethenes,³¹ **1–5** exhibited a notable fluorescence switch from the open-ring isomers to the closed-ring isomers by photoirradiation in both hexane and PMMA films. Upon irradiation with UV light, the fluorescence of **1–5** effectively decreased along with photocyclization due to the production of the non-fluorescence closed-ring isomers **1c–5c**. The back irradiation with visible light of appropriate wavelength regenerated the open-ring isomers **1o–5o** and recovered original emission intensity. The emission intensity changes of **1** by photo-irradiation in both hexane $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ and a PMMA film (10%, w/w) at room temperature are shown in Fig. 7. When arrived at photostationary state, the emission intensity of **1** was quenched to ca. 26% in hexane and 38% in a PMMA film. Its fluorescence modulation efficiency in photostationary state was 74% in hexane and 62%



Fig. 6. Fluorescence emission spectra of 1–5 at room temperature: (A) in hexane (2.0×10⁻⁵ mol L⁻¹), excited at 298 nm; (B) in PMMA films (10%, w/w), excited at 310 nm.



Fig. 7. Emission intensity changes of diarylethene 1 upon irradiation with UV light at room temperature: (A) in hexane (2.0×10⁻⁵ mol L⁻¹), excited at 298 nm, (B) in a PMMA film (10%, w/w), excited at 310 nm.

in a PMMA film. Similarly, the fluorescence modulation efficiencies of the other four diarylethenes were 75% for **2**, 43% for **3**, 74% for **4**, and 76% for **5** in hexane, and were 63% for **2**, 60% for **3**, 69% for **4**, and 70% for **5** in PMMA films in photostationary state. Therefore, the fluorescence modulation efficiencies of **1**–**5** in hexane were higher than those in PMMA films except for **3**. The result is consistent with that of diarylethenes with a pyrrole or thiazole moiety.^{17b,24} Compared with diarylethenes bearing two thiophene moieties,³² the fluorescence modulation efficiencies of **1**–**5** were significantly enhanced in both solution and solid media. Among **1**–**5**, **5** showed the largest fluorescence modulation efficiency in both solution and a PMMA film, suggesting that it is the most promising candidate for application in photoswitchable devices, such as optical memory and fluorescent modulation switches.^{12,30c,31b}

4. Conclusions

Five unsymmetrical diarylethenes with a naphthalene moiety were synthesized, and their photochromic and fluorescent properties were investigated systematically. All of these diarylethene derivatives exhibited favorable photochromism and acted as notable fluorescent switches in both solution and PMMA films. Different substituents at the *meta*-position of the terminal benzene showed significant effects on the properties of these diarylethenes. The naphthalene moiety induced some new features, which were distinguishable from those of the reported diarylethenes bearing benzene, thiophene, pyrazole, or pyrrole rings. The results will be helpful in designing new diarylethene systems with tunable photochromic behaviors for further potential applications.

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References and notes

- 1. (a) *Photochromism Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, The Netherlands, 1990; (b) *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, Germany, 2001.
- (a) Natali, M.; Giordani, S. Chem. Soc. Rev. 2012, 41, 4010–4029; (b) Tian, H.; Yang, S. J. Chem. Soc. Rev. 2004, 33, 85–97; (c) Pu, S. Z.; Jiang, D. H.; Liu, W. J.; Liu, G.; Cui, S. Q. J. Mater. Chem. 2012, 22, 3517–3526; (d) Zhang, J. J.; Zou, Q.; Tian, H. Adv. Mater. 2013, 18, 378–399.
- 3. Fukushima, K.; Vandenbos, A. J.; Fujiwara, T. Chem. Mater. 2007, 19, 644-646.
- 4. Zhao, X. Y.; Wang, M. Z. Eur. Polym. J. 2006, 42, 247-253.
- 5. Irie, M. Chem. Rev. 2000, 100, 1685-1716.
- (a) Kawai, S.; Nakashima, T.; Atsumi, K.; Sakai, T.; Harigai, M.; Imamoto, Y.; Kamikubo, H.; Kataoka, M.; Kawai, T. Chem. Mater. 2007, 19, 3479–3483; (b)

Nakagawa, T.; Atsumi, K.; Nakashima, T.; Hasegawa, Y.; Kawai, T. *Chem. Lett.* **2007**, 36, 372–373; (c) Li, X.; Tian, H. *Tetrahedron Lett.* **2005**, 46, 5409–5412.

- 7. Kobatake, S.; Irie, M. Annu. Rep. Prog. Chem. C 2003, 99, 277-313.
- 8. Yamaguchi, T.; Irie, M. J. Org. Chem. 2005, 70, 10323-10328.
- 9. Tanifuji, N.; Matsuda, K.; Irie, M. Org. Lett. 2005, 7, 3777-3780.
- Yamaguchi, T.; Takami, S.; Irie, M. J. Photochem. Photobiol., A 2008, 193, 146–152.
 (a) Pu, S. Z.; Liu, W. J.; Liu, G. Dyes Pigm. 2010, 87, 1–9; (b) Pu, S. Z.; Fan, C. B.; Miao, W. J.; Liu, G. Tetrahedron 2008, 64, 9464–9470.
- (a) Tian, H.; Feng, L. Y. J. Mater. Chem. 2008, 18, 1617–1622; (b) Zhang, J. J.; Tan,
 W. J.; Meng, X. L.; Tian, H. J. Mater. Chem. 2009, 19, 5726–5729.
- (a) Li, B.; Wang, J. Y.; Wen, H. M.; Shi, L. X.; Chen, Z. N. J. Am. Chem. Soc. 2012, 134, 16059–16067; (b) Yagai, S.; Iwai, K.; Karatsu, T.; Kitamura, A. Angew. Chem., Int. Ed. 2012, 51, 1–6.
- (a) Pang, S. C.; Hyun, H.; Lee, S.; Jang, D.; Lee, M. J.; Kang, S. H.; Ahn, K. H. *Chem. Commun.* **2012**, 3745–3747; (b) Iwasawa, N.; Takahagi, H.; Ono, K.; Fujiib, K.; Uekusab, H. *Chem. Commun.* **2012**, 7477–7479; (c) Bogacheva, A. M.; Yarovenko, V. N.; Levchenko, K. S.; Kobeleva, O. I.; Valova, T. M.; Barachevskyd, V. A.; Struchkovab, M. I.; Shmelinc, P. S.; Krayushkinb, M. M.; Charushin, V. N. *Tetrahedron Lett.* **2012**, 53, 5948–5951; (d) Kutsunugia, Y.; Coudretb, C.; Micheaub, J. C.; Kawaia, T. *Dyes Pigm.* **2012**, *92*, 838–846; (e) Yokoyama, Y.; Hasegawa, T.; Ubukata, T. *Dyes Pigm.* **2011**, *89*, 223–229.
- 15. Kuroki, L.; Takami, S.; Shibata, K.; Irie, M. Chem. Commun. 2005, 6005-6007.
- (a) Pu, S. Z.; Liu, G.; Shen, L.; Xu, J. K. Org. Lett. 2007, 9, 2139–2142; (b) Favaro, G.; Mazzucato, U.; Ortica, F.; Smimmo, P. Inorg. Chim. Acta 2007, 360, 995–999.
- (a) Yasukuni, R.; Boubekri, R.; Grand, J.; Félidj, N.; Maurel, F.; Perrier, A.; Métivier, R.; Nakatani, K.; Pei, Y.; Aubard, J. J. Phys. Chem. C 2012, 116, 16063–16069; (b) Liu, G.; Pu, S. Z.; Wang, X. M. Tetrahedron 2010, 66, 8862–8871; (c) Ouhenia-Ouadahi, K.; Métivier, R.; Maisonneuve, S.; Jacquart, A.; Xie, J.; Léaustic, A.; Yu, P.; Nakatani, K. Photochem. Photobiol. Sci. 2012, 11, 1705–1714.
- (a) Nakamuraa, S.; Yokojima, S.; Uchida, K.; Tsujioka, T.; Goldberg, A.; Murakamia, A.; Shinoda, K.; Mikami, M.; Kobayashi, T.; Kobatake, S.; Matsuda, K.; Irie, M. J. Photochem. Photobiol., A **2008**, 200, 10–18; (b) Yang, Y. H.; Xie, Y. S.; Zhang, Q.; Nakatani, K.; Tian, H.; Zhu, W. H. Chem.–Eur. J. **2012**, *18*, 11685–11694; (c) Liu, G.; Pu, S. Z.; Wang, R. J. Org. Lett. **2013**, *15*, 980–983; (d) Higashiguchi, K.; Matsuda, K.; Yamada, T.; Kawai, T.; Irie, M. Chem. Lett. **2000**, 1358–1359.
- (a) Uchida, K.; Nakamura, S.; Irie, M. Res. Chem. Intermed. 1995, 21, 861–866; (b)
 Pu, S. Z.; Yan, P. J.; Liu, G.; Miao, W. J.; Liu, W. J. Tetrahedron Lett. 2011, 52, 143–147.
- 20. Pu, S. Z.; Li, H.; Liu, G.; Liu, W. J. Tetrahedron Lett. 2010, 51, 3575-3579.
- (a) Wang, R. J.; Pu, S. Z.; Liu, G.; Liu, W. J.; Xia, H. Y. Tetrahedron Lett. 2011, 52, 3306–3310; (b) Wang, R. J.; Pu, S. Z.; Liu, G.; Cui, S. Q.; Liu, W. J. J. Photochem. Photobiol., A 2012, 243, 47–55.
- Pu, S. Z.; Liu, G.; Li, G. Z.; Wang, R. J.; Yang, T. S. J. Mol. Struct. 2007, 833, 23–29.
 Li, Z. X.; Liao, L. Y.; Sun, W.; Xu, C. H.; Zhang, C.; Fang, C. J.; Yan, C. H. J. Phys. Chem. C 2008, 112, 5190–5196.
- 24. Liu, G.; Pu, S. Z.; Wang, X. M. J. Photochem. Photobiol., A 2010, 214, 230-240.
- (a) Kasatani, K.; Kambe, S.; Irie, M. J. Photochem. Photobiol., A **1999**, 122, 11–15;
 (b) Hoshino, M.; Ebisawa, F.; Yoshida, T.; Sukegawa, K. J. Photochem. Photobiol., A **1997**, 105, 75–81.
- 26. Pu, S. Z.; Yang, T. S.; Xu, J. K.; Chen, B. Tetrahedron Lett. 2006, 47, 6473-6477.
- 27. Pu, S. Z.; Miao, W. J.; Cui, S. Q.; Liu, G.; Liu, W. J. Dyes Pigm. 2010, 87, 257-267.
- 28. Tian, H.; Wang, S. Chem. Commun. 2007, 781–792.
- (a) Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. Chem. Commun. 2002, 2804–2805; (b) Morimoto, M.; Irie, M. Chem. – Eur. J. 2006, 12, 4275–4282; (c) Ramamurthy, V.; Venkatesan, K. Chem. Rev. 1987, 8, 433–481.
- (a) Fukaminato, T.; Kawai, T.; Kobatake, S.; Irie, M. J. Phys. Chem. B 2003, 107, 8372–8377; (b) Xiao, S. Z.; Yi, T.; Zhou, Y. F.; Zhao, Q.; Li, F. Y.; Huang, C. H. Tetrahedron 2006, 62, 10072–10078; (c) Frigoli, M.; Mehl, G. H. Chem.—Eur. J. 2004, 10, 5243–5250; (d) Tian, H.; Qin, B.; Yao, R. X.; Zhao, X. L.; Yang, S. J. Adv. Mater. 2003, 15, 2104–2107.
- (a) Tian, H.; Chen, B. Z.; Tu, H. Y.; Müllen, K. Adv. Mater. 2002, 14, 918–923; (b) Feng, Y. L.; Yan, Y. L.; Wang, S.; Zhu, W. H.; Qian, S. X.; Tian, H. J. Mater. Chem. 2006, 16, 3685–3692; (c) Xiao, S. Z.; Zou, Y.; Wu, J. C.; Zhou, Y. F.; Yi, T.; Li, F. Y.; Huang, C. H. J. Mater. Chem. 2007, 17, 2483–2489.
- 32. Tsujioka, T.; Kume, M.; Irie, M. J. Photochem. Photobiol., A 1997, 104, 203-206.