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Synthesis and the effect of alkyl chain length on optoelectronic properties of diarylethene derivatives

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Abstract—Photochromic symmetrical diarylethene derivatives **1a**–**6a** bearing different long alkyl chains at 2-position of thiophene rings have been synthesized and their structures have been determined by single-crystal X-ray diffraction analysis. The effect of alkyl chain length on their optoelectronic properties, such as photochromism in solution as well as in the crystalline phase and electrochemical performance was investigated in detail. These diarylethenes have showed good photochromic behavior both in solution and in the single crystalline phase. Introduction of the long alkyl chains at 2-position of bis(5-formyl-3-thienyl)perfluorocyclopentene increased the absorption coefficients of both open- and closed-ring isomers and induced bathochromic shifts of the maximal wavelength absorption of the closed-ring isomers. The long alkyl chains can also decrease the cyclization/cycloreversion quantum yields and the oxidation potentials. The cyclic voltammetry indicated that the band gap of these diarylethene derivatives was significantly affected by the alkyl chain length.

1. Introduction

During the past several decades, various types of photochromic compounds, such as diarylethenes,[1] fulgides,[2] and phenoxynaphthacenequinines,[3] have been synthesized in an attempt to apply these compounds to optoelectronic devices, such as optical memories and optical switches.[4] Of these compounds, diarylethenes with thiophene or benzothiophene ring systems are the most promising candidates for these applications because of their excellent thermally irreversible properties of the two isomers,[1a,5] high sensitivity,[6] and rapid response[7] and remarkable fatigue resistance.[1f,8]

Upon photo-irradiation, the diarylethene derivatives can undergo the cyclization/cycloreversion photochromic reactions either in solution or in the solid state. In solution, the open-ring isomer of diarylethene has two interconverting conformations, namely anti-parallel conformation with the two aryl-rings in C_2 symmetry and parallel conformation with them in mirror symmetry[1a,9] in almost equal amounts. Only anti-parallel isomers can undergo effective photocyclization reaction by a conrotatory mechanism according to the Woodward–Hoffmann rule, while the parallel isomers are photochemically inactive.[10] The photo-generated closed-ring isomers of diarylethenes showed some colors with broad absorption bands in the visible region, and they could regenerate their open-ring isomers upon irradiation with appropriate wavelength visible light. The reversible cyclization/cycloreversion photochromic reactions upon photo-irradiation can also lead to global changes in the bulk material characteristics, such as UV–vis absorption spectra, fluorescence spectra, and oxidation/reduction potentials and refractive indices etc.[4a,11]

Up to date, diarylethenes with various substitute groups are synthesized.[12,13] Among different substitutents, the terminal phenyl groups and the formyl groups on the end are of special interest. The former have different substitute positions and can be substituted by electron-donating groups or electron-accepting groups, which inevitably influence the optoelectronic properties of corresponding diarylethenes.[11a,13a,13c] On the other hand, the latter can be converted further to many other groups by some simple reactions, such as hydroxymethyl,[14] *N*,*N*-dimethylaminophen,[14c] 2,2-dicyanovinyl,[14c,15] diporphyrin,[16] and phenylquinoline unit[17] etc. Moreover, compounds bearing formyl groups can be converted to Schiff bases by Schiff bases' reaction.[13a,18] So far, several publications concerning substituent effect on the photochromic performance of diarylethene have been reported. Morimitsu et al. reported that the introduction of

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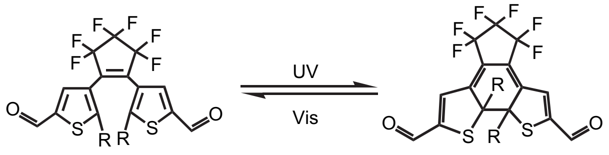
the ethynyl groups at 2- and 2′-positions of both the thiophene and benzothiophene rings would increase the cycloreversion quantum yields.[11a] Irie et al. revealed that electron-donating substituents could increase the ring-opening quantum yield.[12b] Morimitsu et al. and Takami and Irie also revealed that bulky alkoxy substituents at 2- and 2′-positions of the thiophene rings would extraordinarily decrease the cycloreversion quantum yield and the thermal stability of the colored closed-ring isomers at high temperature.[19] Tanifuji et al. synthesized the diarylethene derivatives bearing imino nitroxide and nitronyl nitroxide, which could reduce the cyclization/cycloreversion quantum yield.[20] Recently, Morimoto et al. demonstrated the photochemical control of intermolecular charge-transfer interaction between electron donor and acceptor molecules by the photochromic reaction.[21]

As described above, it can be easily concluded that these reports can be classified into two categories. On one hand, they elucidated that different substituents at the same position of the terminal phenyl rings affected the photochromic and photochemical properties of diarylethenes. On the other hand, they revealed that different substituents at the 2- or 3-position of the thiophene rings affected the photochromic performance of diarylethenes. Until now, there are few reports on the substituent effect at the 2-position of the thiophene rings on the photochromic properties of diarylethenes, especially concerning of the alkyl length effect on the photochromic behaviors of diarylethenes.

Recently, there is an example of the effect of alkyl length on the photochromic properties of diarylethenes reported by Yamaguchi et al.[12a] They presented a series of diarylethenes bearing benzothiophene rings and revealed that introduction of the long alkyl chains at 2-position of bis(1-benzothiophen-3-yl)perfluorocyclopentene increased the cyclization quantum yield and induced bathochromic shifts of the absorption spectra of the closed-ring isomers. The results are very interesting and important, and they also give us some good suggestions. We supposed that diarylethene had some new properties when benzothiophene rings were replaced by thiophene rings.

To validate our prediction described above, we have synthesized a series of bis(2-alkyl-5-formyl-3-thienyl)perfluorocyclopentene derivatives, i.e., 1,2-bis(2-methyl-5-formyl-3-thienyl)perfluorocyclopentene (**1a**), 1,2-bis(2-ethyl-5-formyl-3-thienyl)perfluorocyclopentene (**2a**), 1,2-bis(2-*n*-propyl-5-formyl-3-thienyl)perfluorocyclopentene (**3a**), 1,2-bis(2-*n*-butyl-5-formyl-3-thienyl)perfluorocyclopentene (**4a**), 1,2-bis(2-*n*-pentyl-5-formyl-3-thienyl)perfluorocyclopentene (**5a**), and 1,2-bis(2-*n*-hexyl-5-formyl-3-thienyl)perfluorocyclopentene (**6a**) (see Scheme 1). Their X-ray crystal structure, photochromism, optical, and electrochemical properties were also investigated in detail. Among the six compounds, diarylethenes **3a**–**6a** were new compounds. Although diarylethene **1a** was reported by Lehn and Lucas et al., respectively,[22] they had only used it as an intermediate and never reported its crystal structure and property. In our previous paper, we reported the syntheses and crystal structures of diarylethene **1a** by a new method.[23] In addition, we also reported the crystal structure of diarylethene **2a**.[24] The results indicated that compounds **1a** and **2a** differed from each other in their crystal structures as well as in their various photochromic properties, such as the absorption maximum, ease of cyclization and cycloreversion quantum yield. Therefore, we have now introduced different alkyl chains at 2-position of the thiophene rings of diarylethenes **1a**–**6a** in order to investigate systematically the effect of alkyl length on the properties of diarylethenes in the present work.



1a-6a

1a: R=CH_3, **2a**: R=C_2H_5,
3a: R=n-C_3H_7, **4a**: R=n-C_4H_9,
5a: R=n-C_5H_{11}, **6a**:R=n-C_6H_{13}

1b-6b

1b: R=CH_3, **2b**: R=C_2H_5,
3b: R=n-C_3H_7, **4b**: R=n-C_4H_9,
5b: R=n-C_5H_{11}, **6b**:R=n-C_6H_{13}

Scheme 1. Photochromism of diarylethenes **1**–**6**.

2. Experimental

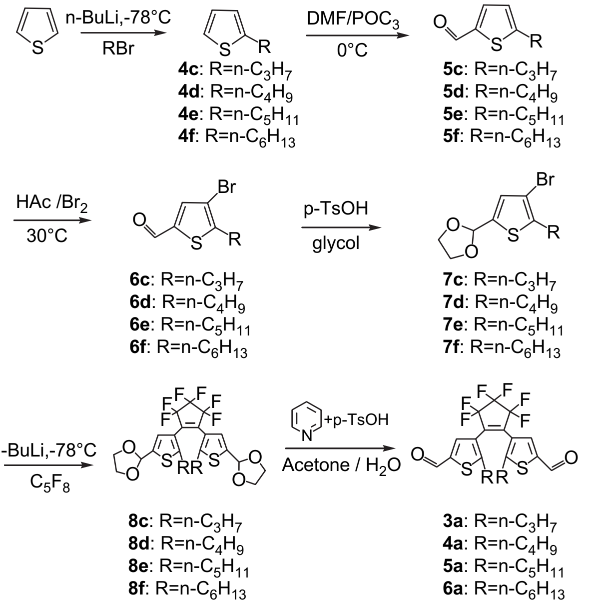
2.1. General methods

NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. IR spectra were recorded on Bruker Vertex-70 spectrometer and mass spectra were measured with Agilent MS Trap VL spectrometer. The elemental analysis was measured with PE CHN 2400. The absorption spectra were measured using Agilent 8453 UV/VIS spectrometer. Photo-irradiation was carried out using SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet and BMH-250 Visible lamp. Light of appropriate wavelengths was isolated by different light filters. The X-ray experiment of the single crystal was performed on Bruker SMART APEX2 CCD area-detector equipped with graphite monochromatized Mo Kα radiation at room temperature (290±2 K). Electrochemical examinations were performed in a one-compartment cell by using a Model 263 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. All solvents used were of spectrograde and were purified by distillation before use.

2.2. Synthesis of diarylethenes 1a–6a

Diarylethenes **1a** and **2a** were synthesized according to the procedure described in the previous literatures.[22–24] Diarylethenes **3a**–**6a** were derived originally from thiophene. The synthetic methods are described in Scheme 2 and experimental details were carried out as following.

2.2.1. Synthesis of 2-*n*-propylthiophene (4c). To a stirred solution of thiophene (15 g, 178.6 mmol) in THF (150 mL), 1.6 mol/L *n*-BuLi/hexane (111.6 mL, 178.6 mmol) was added slowly at −78 °C under nitrogen atmosphere. Stirring was continued for 50 min, bromoprotane (22 g, 178.6 mmol) was added to the solution. The reaction mixture was warmed to room temperature, kept stirring for 3 h, and slowly poured into water. The mixture was extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude product was purified by column chromatography on silica gel (petroleum ether) to give pure product 5.60 g in 25% yield. Colorless liquid; ^1H



Scheme 2. Synthetic route for diarylethenes **3a**–**6a**.

NMR ($CDCl_3$, 400 MHz, TMS): δ 0.97 (t, 3H, J=7.4 Hz, –CH_3), 1.69 (m, 2H, –CH_2), 2.79 (t, 2H, J=7.4 Hz, –CH_2), 6.77 (s, 1H, thiophene-H), 6.91 (s, 1H, thiophene-H), 7.09 (s, 1H, thiophene-H).

2.2.2. Synthesis of 2-*n*-butylthiophene (4d). Compound **4d** was prepared by a method similar to that used for **4c** (54% yield). Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.86 (t, 3H, J=7.2 Hz, –CH_3), 1.33 (m, 2H, –CH_2), 1.58 (m, 2H, –CH_2), 2.75 (t, 2H, J=7.6 Hz, –CH_2), 6.71 (s, 1H, thiophene-H), 6.84 (s, 1H, thiophene-H), 7.03 (d, 1H, J=4.8 Hz, thiophene-H).

2.2.3. Synthesis of 2-*n*-pentylthiophene (4e). Compound **4e** was prepared by a method similar to that used for **4c** (90% yield). Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): 0.83 (t, 3H, J=6.8 Hz, –CH_3), 1.28 (m, 4H, –CH_2), 1.61 (m, 2H, –CH_2), 2.74 (t, 2H, J=7.6 Hz, –CH_2), 6.71 (d, 1H, J=2.8 Hz, thiophene-H), 6.84 (d–d, 1H, J=3.6 Hz, thiophene-H), 7.03 (d, 1H, J=2.8 Hz, thiophene-H).

2.2.4. Synthesis of 2-hexylthiophene (4f). Compound **4f** was prepared by a method similar to that used for **4c** (81% yield). Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.82 (t, 3H, J=6.6 Hz, –CH_3), 1.27 (m, 6H, –CH_2), 1.61 (m, 2H, –CH_2), 2.75 (t, 2H, J=7.6 Hz, –CH_2), 6.70 (s, 1H, thiophene-H), 6.83 (d–d, 1H, J=4.8 Hz, thiophene-H), 7.03 (d–d, 1H, J=5.2 Hz, thiophene-H).

2.2.5. Synthesis of 5-*n*-propylthiophene-2-carbaldehyde (5c). To a stirred solution of compound **4c** (5.60 g, 44.4 mmol) in DMF (9.74 g, 133.2 mmol), $POCl_3$ (12.2 mL, 133.2 mmol) was added slowly at 0 °C. Stirring was continued for 20 min at this temperature. The reaction mixture was warmed to 75 °C and refluxed for 2 h, and then it was poured into ice water and neutralized by NaOH to neutrality. After extraction with $CHCl_3$, the organic phase was dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, v/v=1/6) to give pure product 4.81 g in 70% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.0 (t, 3H, J=7.2 Hz, –CH_3), 1.74 (m, 2H, –CH_2), 2.86 (t, 2H, J=7.6 Hz, –CH_2), 6.92 (d, 1H, J=3.6 Hz, thiophene-H), 7.63 (d, 1H, J=4.0 Hz, thiophene-H), 9.82 (s, 1H, –CHO).

2.2.6. Synthesis of 5-*n*-butylthiophene-2-carbaldehyde (5d). Compound **5d** was prepared by a method similar to that used for **5c** (68% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.87 (t, 3H, J=7.2 Hz, –CH_3), 1.33 (m, 2H, –CH_2), 1.61 (m, 2H, –CH_2), 2.80 (t, 2H, J=7.2 Hz, –CH_2), 6.83 (s, 1H, thiophene-H), 7.53 (s, 1H, thiophene-H), 9.74 (s, 1H, –CHO).

2.2.7. Synthesis of 5-*n*-pentylthiophene-2-carbaldehyde (5e). Compound **5e** was prepared by a method similar to that used for **5c** (91% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.90 (t, 3H, J=6.4 Hz, –CH_3), 1.36 (d, 4H, J=2.8 Hz, –CH_2), 1.72 (m, 2H, –CH_2), 2.87 (t, 2H, J=7.6 Hz, –CH_2), 6.90 (s, 1H, thiophene-H), 7.61 (d, 1H, J=3.2 Hz, thiophene-H), 9.82 (s, 1H, –CHO).

2.2.8. Synthesis of 5-*n*-hexylthiophene-2-carbaldehyde (5f). Compound **5f** was prepared by a method similar to that used for **5c** (62% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.82 (t, 3H, J=6.4 Hz, –CH_3), 1.26 (m, 6H, –CH_2), 1.64 (m, 2H, –CH_2), 2.80 (t, 2H, J=7.6 Hz, –CH_2), 6.83 (d, 1H, J=3.6 Hz, thiophene-H), 7.53 (d, 1H, J=3.6 Hz, thiophene-H), 9.74 (s, 1H, –CHO).

2.2.9. Synthesis of 4-bromo-5-*n*-propyl-2-formylthiophene (6c). To a stirred solution of compound **5c** (4.81 g, 31.2 mmol) in acetic acid, an acetic acid solution of Br_2 (1.6 mL, 31.2 mmol) was added at room temperature. Stirring was continued for 24 h at this temperature, the reaction was stopped by the addition of water. The reaction mixture was neutralized by Na_2CO_3 to neutrality. The product was extracted with ether, dried, and filtrated. The solvent was evaporated to obtain the goal product 3.04 g in 42% yield as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 1.03 (t, 3H, J=7.2 Hz, –CH_3), 1.73 (m, 2H, –CH_2), 2.82 (t, 2H, J=7.6 Hz, –CH_2), 7.61 (s, 1H, thiophene-H), 9.79 (s, 1H, –CHO).

2.2.10. Synthesis of 4-bromo-5-*n*-butyl-2-formylthiophene (6d). Compound **6d** was prepared by a method similar to that used for **6c** (68% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.89 (t, 3H, J=7.4 Hz, –CH_3), 1.36 (m, 2H, –CH_2), 1.61 (m, 2H, –CH_2), 2.77 (t, 2H, J=7.6 Hz, –CH_2), 7.53 (s, 1H, thiophene-H), 9.71 (s, 1H, –CHO).

2.2.11. Synthesis of 4-bromo-5-*n*-pentyl-2-formylthiophene (6e). Compound **6e** was prepared by a method similar to that used for **6c** (78% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.85 (t, 3H, J=6.4 Hz, –CH_3), 1.31 (m, 4H, –CH_2), 1.64 (m, 2H, –CH_2), 2.76 (t, 2H, J=7.6 Hz, –CH_2), 7.52 (s, 1H, thiophene-H), 9.71 (s, 1H, –CHO).

2.2.12. Synthesis of 4-bromo-5-*n*-hexyl-2-formylthiophene (6f). Compound **6f** was prepared by a method similar to that used for **6c** (51% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.83 (t, 3H, J=6.8 Hz, –CH_3), 1.25 (m, 4H, –CH_2), 1.33 (m, 2H, –CH_2), 1.62 (m, 2H, –CH_2), 2.76 (t, 2H, J=7.6 Hz, –CH_2), 7.53 (s, 1H, thiophene-H), 9.71 (s, 1H, –CHO).

2.2.13. Synthesis of 4-bromo-5-*n*-propyl-2-(1,3-dioxolane)thiophene (7c). Compound **6c** (3.04 g, 13.03 mmol), glycol (3.6 mL, 65.1 mmol), and *p*-toluenesulfonic acid (0.05 g, 0.26 mmol) were dissolved in benzene (160 mL). Under the Dean–Stark condition, the reaction mixture was refluxed overnight, and then washed sequentially three times with NaOH (3.0 mol/L) and water. The combined benzene layers were dried, filtered, and evaporated in vacuum to give acetal **5** as yellow oil (2.6 g, 84% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.92 (t, 3H, J=7.2 Hz, –CH_3), 1.63 (m, 2H, –CH_2), 2.66 (t, 2H, J=7.6 Hz, –CH_2), 3.94 (t, 2H, J=6.6 Hz, –CH_2), 4.05 (t, 2H, J=6.8 Hz, –CH_2), 5.93 (s, 1H, –CH–), 6.91 (s, 1H, thiophene-H).

2.2.14. Synthesis of 4-bromo-5-*n*-butyl-2-(1,3-dioxolane)-thiophene (7d). Compound **7d** was prepared by a method similar to that used for **7c** (78% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.87 (t, 3H, J=7.2 Hz, –CH_3), 1.33 (m, 2H, –CH_2), 1.56 (m, 2H, –CH_2), 2.68 (t, 2H, J=7.6 Hz, –CH_2), 3.93 (t, 2H, J=6.4 Hz, –CH_2), 4.04 (t, 2H, J=6.4 Hz, –CH_2), 5.93 (s, 1H, –CH–), 6.89 (s, 1H, –CHO).

2.2.15. Synthesis of 4-bromo-5-*n*-pentyl-2-(1,3-dioxolane)-thiophene (7e). Compound **7e** was prepared by a method similar to that used for **7c** (67% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.83 (t, 3H, J=6.4 Hz, –CH_3), 1.29 (m, 4H), 1.58 (m, 2H, –CH_2), 2.67 (t, 2H, J=7.6 Hz, –CH_2), 3.93 (t, 2H, J=6.8 Hz, –CH_2), 4.04 (t, J=7.4 Hz, 2H, –CH_2), 5.93 (s, 1H, –CH–), 6.90 (s, 1H, thiophene-H).

2.2.16. Synthesis of 4-bromo-5-*n*-hexyl-2-(1,3-dioxolane)-thiophene (7f). Compound **7f** was prepared by a method similar to that used for **7c** (88% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.82 (t, 3H, J=6.6 Hz, –CH_3), 1.24 (m, 6H, –CH_2), 1.56 (t, 2H, J=7.6 Hz, –CH_2), 2.67 (t, 2H, J=7.6 Hz, –CH_2), 3.93 (t, 2H, J=6.8 Hz, –CH_2), 4.03 (t, 2H, J=3.8 Hz, –CH_2), 5.93 (s, 1H, –CH–), 6.89 (s, 1H, thiophene-H).

2.2.17. Synthesis of 1,2-bis{2-*n*-propyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (8c). To a stirred solution of compound **7c** (2.60 g, 9.38 mmol) in THF, 1.6 mol/L *n*-BuLi/hexane (5.86 mL, 9.38 mmol) was added at −78 °C under nitrogen atmosphere. Stirring was continued for 40 min, perfluorocyclopentene (0.64 mL, 4.69 mmol) was slowly added to the reaction mixture, and the mixture was stirred for 3.0 h at this low temperature. The reaction was stopped by the addition of water. After extracting with ether, the organic layer was washed sequentially by concentrated sodium chloride solution and water. The organic layer was dried over anhydrous $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on SiO_2 using chloroform and petroleum ether mixture (v/v=1/1) as the eluent to give 1.14 g of compound **8c** in 42% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.78 (t, 6H, J=7.2 Hz, –CH_3), 1.30 (m, 4H, –CH_2), 2.14 (t, 4H, J=7.6 Hz, –CH_2), 3.44 (t, 4H, J=7.0 Hz, –CH_2), 4.12 (t, 4H, J=6.8 Hz, –CH_2), 6.01 (s, 2H, –CH–), 7.09 (s, 2H, thiophene-H); ^{19}F NMR (376 MHz, TMS): δ −110.51 (4F), −131.99 (2F); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 13.70, 24.23, 31.07, 65.29, 99.92, 123.28, 125.83, 140.09, 149.13.

2.2.18. Synthesis of 1,2-bis{2-*n*-butyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (8d). Compound **8d** was prepared by a method similar to that used for **8c** (43% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.74 (t, 6H, J=7.2 Hz, –CH_3), 1.14 (m, 4H, –CH_2), 1.22 (m, 4H, –CH_2), 2.09 (t, 4H, J=7.8 Hz, –CH_2), 3.96 (t, 4H, J=6.8 Hz, –CH_2), 4.04 (t, 4H, J=6.8 Hz, –CH_2), 5.94 (s, 2H, –CH–), 6.90 (s, 2H, thiophene-H).

2.2.19. Synthesis of 1,2-bis{2-*n*-pentyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (8e). Compound **8e** was prepared by a method similar to that used for **8c** (26% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.77 (t, 6H, J=7.2 Hz, –CH_3), 1.27 (m, 8H, –CH_2), 2.09 (m, 4H, –CH_2), 2.80 (t, 4H, J=7.6 Hz, –CH_2), 3.95 (t, 4H, J=6.8 Hz, –CH_2), 4.03 (t, 4H, J=6.8 Hz, –CH_2), 5.93 (s, 2H, –CH–), 7.01 (s, 2H, thiophene-H).

2.2.20. Synthesis of 1,2-bis{2-*n*-hexyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (8f). Compound **8f** was prepared by a method similar to that used for **8c** (17% yield). There is no structural analysis data for compound **8f** because it is very difficult to purify completely and the unpurged compound **8f** can be easily and directly converted to diarylethene **6a** by a hydrolyzing reaction.

2.2.21. Synthesis of 1,2-bis(2-*n*-propyl-5-formyl-3-thienyl)perfluorocyclopentene (3a). Compound **8c** (1.14 g, 2.00 mmol) and *p*-toluenesulfonic acid (0.4 g) were dissolved in mixture of water (30 mL) and acetone (90 mL); 2 mL pyridine was added into the mixture and reaction mixture was refluxed for 24 h. After stopping the reaction, the mixture was washed sequentially by aqueous $NaHCO_3$ and water. The organic layer was dried over anhydrous Na_2SO_4, filtrated, and evaporated. The crude product was purified by column chromatography on SiO_2 using ethyl acetate and petroleum ether mixture (v/v=1/6) as the eluent to give 0.8 g of compound **3a** in 83% yield. The compound crystallized from diethyl ether at room temperature and produced the suitable crystals for X-ray analysis. Colorless crystal: mp 100.7–101.2 °C; MS *m/z* (M^+) 479.0 (–H), 503.0 (+Na); Anal. Calcd for $C_{21}H_{18}F_6O_2S_2$ (%): Calcd C, 52.49; H, 3.78. Found C, 52.41; H, 3.59; ^{1}H NMR ($CDCl_3$, 400 M Hz, TMS): δ 0.75 (t, 6H, J=7.4 Hz, –CH_3), 1.34 (m, 4H, –CH_2), 2.18 (t, 4H, J=7.8 Hz, –CH_2), 7.65 (s, 2H, thiophene-H), 9.80 (s, 2H, –CHO); ^{19}F NMR (376 MHz, TMS): δ −110.57 (4F), −131.85 (2F); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 13.53, 24.17, 31.66, 124.94, 135.38, 142.28, 157.86, 181.74; IR (KBr, ν, cm^{-1}): 941, 1120, 1217, 12,661, 1329, 1461, 1539, 1670, 2928, 2976.

2.2.22. Synthesis of 1,2-bis(2-*n*-butyl-5-formyl-3-thienyl)perfluorocyclopentene (4a). Compound **4a** was prepared by a method similar to that used for **3a** (80% yield). Colorless crystal: mp 81.9–82.3 °C; MS *m/z* (M^+) 507.0 (–H), 531.1 (+Na); Anal. Calcd for $C_{23}H_{22}F_6O_2S_2$ (%): Calcd C, 54.32; H, 4.36. Found C, 54.43; H, 4.24; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.82 (t, 6H, J=7.2 Hz,

–CH_3), 1.22 (m, 4H, –CH_2), 1.35 (m, 4H, –CH_2), 2.27 (t, 4H, J=7.6 Hz, –CH_2), 7.71 (s, 2H, thiophene-H), 9.86 (s, 2H, –CHO); ^{19}F NMR ($CDCl_3$, 400 MHz, TMS): δ −110.57 (4F), −131.90 (2F); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 13.438, 22.239, 29.464, 32.930, 124.884, 135.305, 142.242, 158.135, 181.646; IR (KBr, ν, cm^{-1}): 954, 1013, 1077, 1122, 1193, 1235, 1272, 1334, 1382, 1460, 1543, 1669, 2932, 2966.

2.2.23. Synthesis of 1,2-bis(2-*n*-pentyl-5-formyl-3-thienyl)perfluorocyclopentene (5a). Compound **5a** was prepared by a method similar to that used for **3a** (77% yield). Colorless crystal: mp 90.0–90.8 °C; MS *m/z* (M^+) 535.0 (–H), 559.2 (+Na); Anal. Calcd for $C_{25}H_{26}F_6O_2S_2$ (%): Calcd C, 55.96; H, 4.88. Found C, 55.89; H, 4.97; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.82–0.85 (t, 6H, J=7.6 Hz, –CH_3), 1.13–1.22 (m, 8H, J=6.8 Hz, –CH_2), 1.36–1.40 (m, 4H, J=7.6 Hz, –CH_2), 2.24–2.28 (t, 4H, J=7.6 Hz, –CH_2), 7.72 (s, 2H, thiophene-H), 9.87 (s, 2H, –CHO); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 13.785, 22.215, 29.790, 30.626, 31.295, 124.941, 135.413, 135.517, 136.828, 142.303, 158.252, 181.793; IR (KBr, ν, cm^{-1}): 963, 1021, 1080, 1121, 1196, 1231, 1278, 1339, 1394, 1466, 1547, 1670, 2862, 2956, 3052.

2.2.24. Synthesis of 1,2-bis(2-*n*-hexyl-5-formyl-3-thienyl)perfluorocyclopentene (6a). Compound **6a** was prepared by a method similar to that used for **3a** (80% yield). Colorless crystal: mp 47.0–47.9 °C; MS *m/z* (M^+) 565.6 (–H), 587.3 (+Na); Anal. Calcd for $C_{27}H_{30}F_6O_2S_2$ (%): Calcd C, 57.43; H, 5.36. Found C, 57.55; H, 5.13; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.84–0.87 (t, 6H, J=7.0 Hz, –CH_3), 1.15 (s, 8H, –CH_2), 1.21–1.26 (m, 4H, J=6.8 Hz, –CH_2), 1.36 (s, 4H, –CH_2), 2.23–2.27 (t, 4H, J=7.8 Hz, –CH_2), 7.72 (s, 2H, thiophene-H), 9.87 (s, 2H, –CHO); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 13.966, 22.370, 28.803, 29.765, 30.878, 31.278, 115.723, 124.876, 135.391, 142.223, 158.223, 181.772; IR (KBr, ν, cm^{-1}): 936, 1014, 1082, 1127, 1193, 1227, 1271, 1334, 1392, 1465, 1550, 1674, 2859, 2961, 3063.

2.3. Determination of the crystal structures of diarylethenes 3a–6a

Crystal data of diarylethenes **3a**–**6a** were collected by a Bruker SMART APEX2 CCD area-detector equipped with graphite monochromatized Mo Kα radiation at room temperature (λ=0.71073 Å). The linear absorption coefficients, μ, of diarylethenes **3a**–**6a** for Mo Kα radiation were 3.08, 2.97, 2.64, and 2.46 cm^{-1}. Direct phase determination yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically with C–H bond distances of 0.93–0.97 Å according to criteria described in the SHELXTL manual. They were included in the refinement with $U_{iso}(H)=1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). Further details on the crystal structure investigation have been deposited to The Cambridge Crystallographic Data Centre as supplementary publication number CCDC 631249 for **3a** and CCDC 632713−632715 for **4a**–**6a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by emailing at data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

3. Results and discussion

3.1. Synthesis of the diarylethenes 3a–6a

The synthetic route for diarylethenes **3a**–**6a** is shown in Scheme 2. First, 2-*n*-alkylthiophene derivatives (**4c**–**4f**) were obtained by reacting thiophene with 1-bromo-*n*-alkane in the presence of *n*-BuLi/hexane solution at −78 °C. Then, acylation reaction of **4c**–**4f** with DMF/$POCl_3$ gave *n*-alkylthiophene-2-carbaldehyde derivatives (**5c**–**5f**). The **5c**–**5f** were brominated and protected as the dioxolane acetal prior to coupling with the fluorinated ring to give the bis-acetals **8c**–**8f**. Finally, compounds **3a**–**6a** were prepared by hydrolyzing the compounds **8c**–**8f** in the presence of pyridine and *p*-toluene sulfuric acid (Ts-OH) in acetone/water solvent. The structures of **3a**–**6a** were confirmed by NMR, IR, and mass spectra, elemental analysis, and X-ray crystallographic analysis (Section 2).

3.2. Photochromic reactions in solution

In hexane solution, the photochromic reactivity of diarylethenes **1**–**6** was examined. The absorption spectral changes induced by UV light at room temperature (2.0×10^{-5} mol/L) were showed in Figure 1. Diarylethenes **1**–**6** showed good photochromic properties and could be toggled between their colorless open-ring isomers (**1a**–**6a**) and colored closed-ring isomers (**1b**–**6b**) (see Scheme 1) by alternating irradiation with UV light and appropriate wavelength visible light, as monitored using UV–vis absorption and ^{1}H NMR spectroscopy. For example, the absorption maximum of the colorless compound **1a** was observed at 260 nm (ε, 2.6×10^4 L mol^{-1} cm^{-1}) (shown in Fig. 1). Upon irradiation with 254 nm light, the colorless solution of **1a** turned blue with a new visible absorption band centered at 609 nm (ε, 5.8×10^3 L mol^{-1} cm^{-1}). The blue color is due to the closed-ring isomer **1b**. Alternatively, the blue colored solution returned colorless by irradiation with visible light (λ>510 nm). This indicated that **1b** returned to the initial state **1a**, for which the absorption maximum was observed at 260 nm. The coloration–decoloration cycle could be repeated more than 100 times and a clear isosbestic point was observed at 315 nm.

Similarly, compounds **2a**–**6a** also showed photochromism in hexane solution (Fig. 1). The absorption characteristics of **2a**–**6a** and **2b**–**6b** were similar to **1a** and **1b**. Upon irradiation with 254 nm light, absorption bands in the visible region appeared and the solutions turned green as a result of the cyclization reactions to produce **2b**–**6b**; all the solutions of **2b**–**6b** can be decolorized by irradiating them with visible light of wavelengths greater than 510 nm to induce the cycloreversion reactions and reproduce **2a**–**6a**. After repeating 100 coloration–decoloration cycles, the isosbestic points of compounds **2**–**6** were observed at 316, 317, 318, 318, and 317 nm, respectively. The absorption spectral properties of these compounds are summarized in Table 1. The quantum yields were determined by comparing the reaction yields of

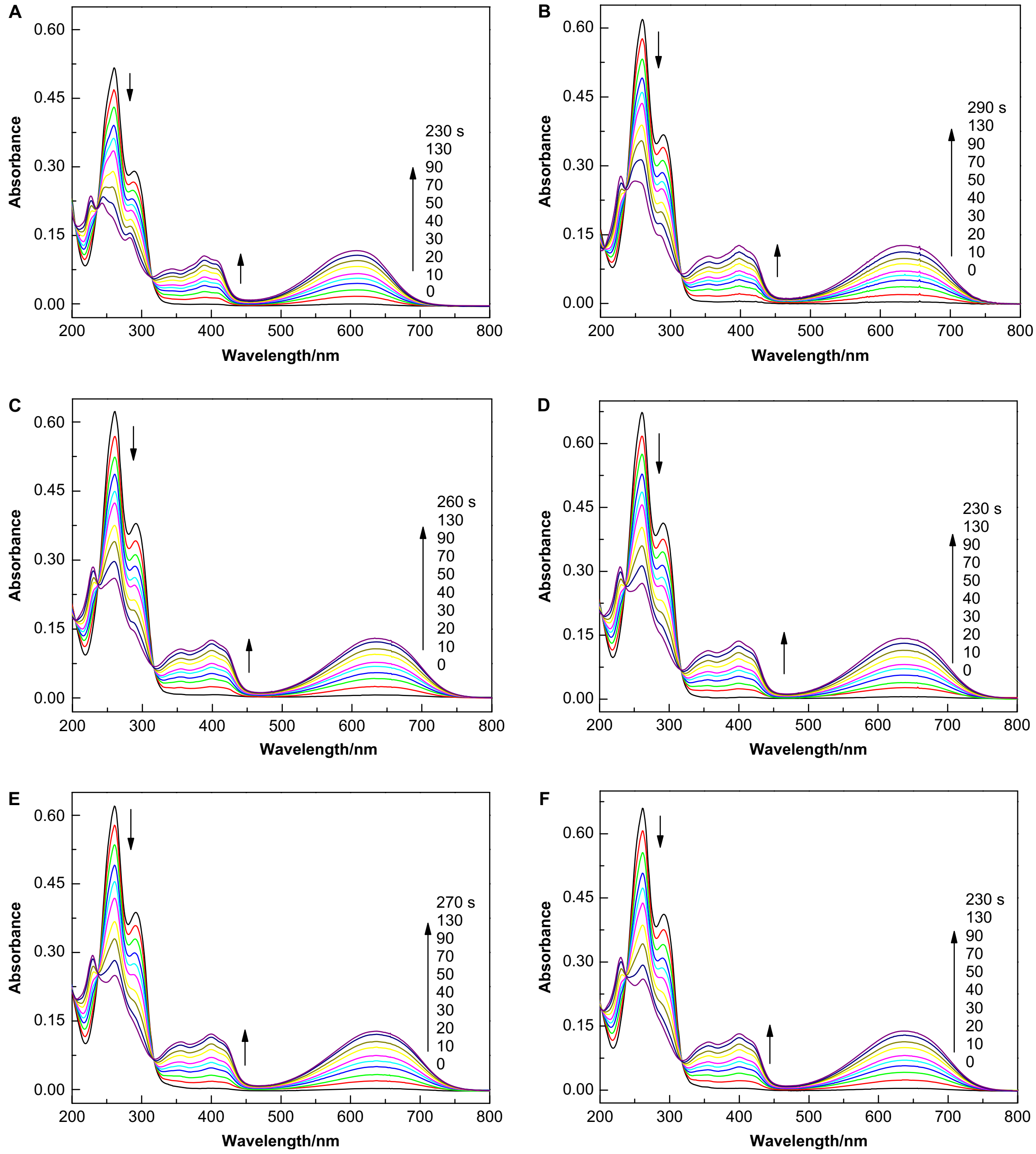


Figure 1. Absorption spectra of diarylethenes **1**–**6** in hexane solution (C=2.0×10^{-5} mol/L) at room temperature: (A) **1**, (B) **2**, (C) **3**, (D) **4**, (E) **5**, and (F) **6**.

Table 1. Absorption spectral properties of diarylethenes **1**–**6** in hexane at 2.0×10^{-5} mol/L

Compound	Absorption spectra		Quantum yield		Conversion	
	$\lambda_{a,max}$/nm (ε/L mol^{-1} cm^{-1})	$\lambda_{b,max}$/nm (ε/L mol^{-1} cm^{-1})	Cyclization (Φ_{a-b})	Cycloreversion (Φ_{b-a})	Calculated (%)	Observed (%)
1	260 (2.6×10^4)	609 (5.8×10^3)	0.44	0.095	95.4	>95
2	260 (3.1×10^4)	635 (6.3×10^3)	0.38	0.072	96.3	>95
3	261 (3.1×10^4)	632 (6.5×10^3)	0.38	0.078	95.9	>95
4	261 (3.4×10^4)	633 (7.1×10^3)	0.38	0.065	96.6	>95
5	261 (3.1×10^4)	637 (6.4×10^3)	0.39	0.070	96.4	>95
6	261 (3.3×10^4)	637 (6.9×10^3)	0.40	0.067	96.6	>95

The hexane used as solvent was of spectrograde and was purified by distillation before use.

diarylethenes **1–6** in hexane against 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane at room temperature,[5] and the results are also included in Table 1. These data indicated that the maximum absorption wavelengths of open-ring isomers of the six diarylethenes were not evidently different. However, their maximum absorption wavelengths of closed-ring isomers, molar absorption coefficients of both open- and closed-ring isomers and their cyclization/cycloreversion quantum yields are significantly different. As shown in Table 1, although the maximum absorption of **1b** was observed at 609 nm, the maximum shifted to 635 nm in **2b** upon replacing the methyl groups at the 2-position of the thiophene rings with ethyl ones. Even if the alkyl chain becomes longer (from ethyl to *n*-hexyl), further shift of the absorption maximum was not observed evidently (632–637 nm). This phenomenon is well coincided with that of bis(2-alkyl-1-benzothiophen-3-yl)-perfluorocyclopentene derivatives reported by Yamaguchi and Irie.[12a] For compounds **1–6**, trends of molar absorption coefficients changing of both open- and closed-ring isomers are similar to those of the maximum absorption wavelengths of their closed-ring isomers. That is, all of the values were remarkably increased compared to those of diarylethene **1**, and no further increase was observed if the alkyl chain became longer (from ethyl to *n*-hexyl). However, the trend of the cyclization/cycloreversion quantum yields change was contrary to that described above. When replacing the methyl groups at the 2-position of the thiophene rings with ethyl ones, the cyclization/cycloreversion quantum yields of compound **2** ($\Phi_{a\text{–}b}$=0.38, $\Phi_{b\text{–}a}$=0.072) were much less than those of compound **1** ($\Phi_{a\text{–}b}$=0.44, $\Phi_{b\text{–}a}$=0.095). The cyclization/cycloreversion quantum yields of **2–6** fluctuate in a small numerical value range with increasing alkyl chain length, indicating that the alkyl chain did not affect significantly the cyclization/cycloreversion reaction when the number of carbon atoms of alkyl chain was larger than two. The result differed from that reported in Ref. 12a. In that paper, the alkyl chain length could increase the cyclization quantum yields, but it did not affect the cycloreversion quantum. The possible reason was ascribed to the rigidity of benzothiophene plane greater than that of thiophene ring, leading to the greater effect of alkyl chain on the conformation of bis(2-alkyl-1-benzothiophen-3-yl)perfluorocyclopentene derivatives in solution.

Photochromism of diarylethenes **1–6** by irradiation with UV light changed the chemical shifts of their formyl and aryl protons. To investigate the conversion from the open-ring to closed-ring forms in cyclization reaction, ^{1}H NMR measurement was carried out. The ^{1}H NMR spectral changes of compound **1** in a $CDCl_3$ solution upon irradiation with 254 nm UV light are displayed in Figure 2. The ^{1}H NMR spectra exhibited an array of resonances corresponding to the formyl and the aromatic protons in the molecule. For instance, the formyl and thienyl proton compound **1a** appeared as a singlet at δ 9.86 and δ 7.75 (Fig. 2). Upon irradiation with 254 nm UV light, two new signals appeared at δ 9.88 and δ 6.96, which are assigned to the formyl and the thiophene protons of **1b** (Fig. 2). The integrated intensity increase was highly correlated with the irradiation time and reached photostationary after 3 h of irradiation in $CDCl_3$. As shown in Figure 2, the ratio of the peak intensity at δ 9.85 and δ 9.89 (or δ 7.75 and δ 6.96) was estimated to be 0:1, indicating that the conversion of photo-cyclization for **1a** in $CDCl_3$ was greater than 95%. Just as **1a**, the ^{1}H NMR spectra of **2–6** also showed the presence of two conformers (Table 2). The ratio of the peak intensity rate of the two formyl or thienyl proton signals also indicated that the conversion between the two isomers was greater than 95% in the photostationary state. The conversion at the photostationary state can also be calculated according to the following equation.[12a,22]

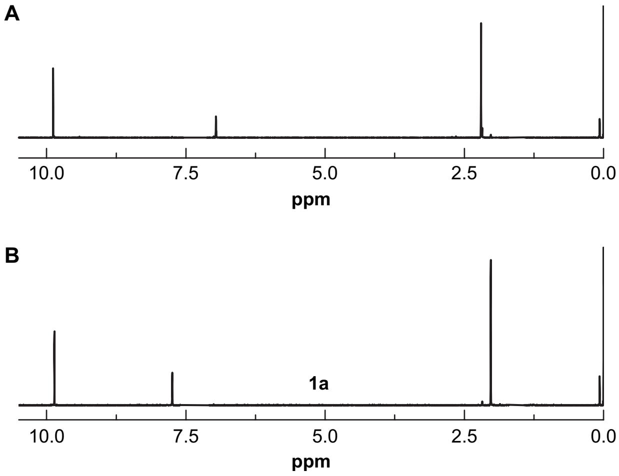


Figure 2. ^{1}H NMR spectral changes of diarylethene **1** upon irradiation with 254 nm UV light in $CDCl_3$: (A) **1a** and (B) **1b**.

$$\text{conversion}_{a\rightarrow b} = \frac{\Phi_{a\rightarrow b}\varepsilon_a}{\Phi_{a\rightarrow b}\varepsilon_a + \Phi_{b\rightarrow a}\varepsilon_b} \qquad (1)$$

where ε_a and ε_b are molar absorption coefficients at irradiated wavelength and $\Phi_{a\rightarrow b}$ and $\Phi_{b\rightarrow a}$ are cyclization and cycloreversion quantum yields. The calculated ratios and the experimental ones are also shown in Table 2. These two values showed relatively good agreement.

3.3. Photochromic reactions in the crystalline phase

Colorless crystals of **1a–6a** suitable for X-ray analysis were obtained by the slow evaporation in diethyl ether. To know better the relation between the conformation and the

Table 2. Partial ^{1}H NMR data of **1–6** upon irradiation with 254 nm UV light in $CDCl_3$

Compound	Formyl protons	Aromatic protons
1a	9.86	7.75
1b	9.88	6.96
2a	9.88	7.73
2b	9.79	6.90
3a	9.87	7.73
3b	9.80	6.90
4a	9.87	7.73
4b	9.80	6.90
5a	9.87	7.73
5b	9.80	6.90
6a	9.87	7.73
6b	9.80	6.90

The solvent is $CDCl_3$ containing tetramethylsilane as an internal standard.

photochromic behaviors of diarylethenes **1a–6a** in the crystalline phase, final structural confirmations of **1a–6a** were provided by X-ray crystallographic analysis. The X-ray crystallographic analysis data are listed in Table 3 and the ORTEP drawings of the single crystals **1a–6a** are shown in Figure 3. As shown in Figure 3C, for compound **3a**, there were two independent molecules in the asymmetric unit and both of them occupied approximately in C_2 symmetry, and it was packed in a photoactive anti-parallel conformation in the crystalline phase, which can undergo photo-cyclization reaction.[25] In the hexafluorocyclopentene rings of the two molecules, the F atoms of the CF_2 groups were disordered and two distinct conformations were modeled. The site occupancies are 0.50:0.50 for the F atoms attached to C10, C12, C31 and C33, and 0.60:0.40 for the F atoms attached to C11 and C32. The orientations of the propyl groups at C5, C15, and C26 and C36 are defined by the torsion angles C5–C6–C7–C8 [−179.1(5)°], C15–C16–C17–C18 [178.4(5)°], and C26–C27–C28–C29 [175.7(4)°] and C36–C37–C38–C39 [177.4(4)°]. So, the *n*-propyl groups are located on opposite sides of the double bonds and thus trans with respect to the double bond. Such a conformation is crucial for the compound to exhibit photochromic and photo-induced properties.[10a] The two planar thiophene ring systems have similar geometries in each molecule, with dihedral angles between the cyclopentene ring and thiophene rings of 55.5(6)° (S1/C2–C5) and 59.4(6)° (S2/C15/C14/C19/C20) in one molecule and 54.2(6)° (S3/C23–C26) and 55.3(6)° (S4/C36/C35/C40/C41) in the other. The distances between the potentially photoactive carbon atoms (C5···C15 and C26···C36) in each molecule were 3.732(5) and 3.773(5) Å, respectively. These distances indicate that the crystal can be expected to undergo photochromism to generate its closed isomer (**3b**) (see Scheme 1), because photochromic reactivity usually appears when the distance between the reactive C atoms is less than 4.2 Å.[26] In the structure of the methyl analogue (**1a**) (Fig. 3A), the corresponding values for the dihedral angles between the central cyclopentene ring and the thiophene rings were both 46.1(3)°, resulting in a reactive C-atom separation of 3.600(7) Å.[23] While those corresponding dihedral angles of **2a** (Fig. 3B) were 55.2(2)° and 65.1(1)°, leading to a reactive C-atom separation of 3.893(7) Å.[24] The corresponding dihedral angles were 60.1(7)° and 56.9(7)° for **4a**, both 59.2(1)° for **5a** and 54.1(2)° and 58.7(2)° for **6a** (Table 4). The ORTEP drawings of **4a**, **5a** and **6a** are shown in Figure 3D–F. The drawings indicated that **4a**, **5a** and **6a** were also packed in an anti-parallel conformation in the crystalline phase. The distances between the reacting carbon atoms were 3.972(3), 3.763(9) and 3.818(3) Å for **4a–6a**, respectively. As described previously, one can easily see that the distance between the two reactive carbon atoms increased significantly (from 3.600(7) to 3.893(7) Å) replacing the methyl groups with ethyl ones. But further increase was not observed with the alkyl chain becoming longer; the values only fluctuate in a small numerical value (3.732–3.972 Å) range with increasing the alkyl chain length. As shown in Figure 3 and Table 4, all molecules of crystals **1a–6a** were fixed in an anti-parallel mode in the crystalline phase and the distances of the two reactive carbon atoms were less than 4.2 Å, which was close enough for the reaction to take place, indicating that they could be expected to undergo photochromism in the single crystalline phase.

It is well known that the absorption spectrum and color are dependent on the substituent effects and the π-conjugation length in molecule. The arrangement described above was very beneficial to form the extended π-conjugation. After irradiation with UV light, the π-conjugation extended throughout the whole molecule, and the UV–vis absorption spectra displayed drastic changes resulting in displaying remarkable different color.[27] In fact, crystal of **1a–6a** showed photochromic reaction coincident with the theoretical analysis. Their color changes upon photo-irradiation are shown in Figure 4. Upon irradiation with 254 nm light, the colorless crystal of **1a–6a** turned to blue quickly. When the blue crystal was dissolved in hexane, the solution turned to blue,

Table 3. Crystal data for diarylethenes **1a–6a**

	3a	**4a**	**5a**	**6a**	**1a**	**2a**
Formula	$C_{21}H_{18}F_6O_2S_2$	$C_{23}H_{22}F_6O_2S_2$	$C_{25}H_{26}F_6O_2S_2$	$C_{27}H_{30}F_6O_2S_2$	$C_{17}H_{10}F_6O_2S_2$	$C_{19}H_{14}F_6O_2S_2$
Formula weight	480.47	508.53	536.58	564.63	424.37	452.42
Temperature (K)	294(2)	113(2)	291(2)	291(2)	293(2)	295(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	*P*-1	*C*12/*c*1	*C*2/*c*	*P*-1	Pbcn	*P*2(1)/*n*
Unit cell dimensions						
a (Å)	10.6721(18)	32.126(3)	19.825(2)	8.7913(9)	12.182(2)	11.2889(11)
b (Å)	14.059(2)	16.2196(15)	9.3357(11)	10.5806(11)	8.7063(13)	13.4306(13)
C (Å)	16.532(3)	18.8455(16)	15.0784(18)	17.3953(19)	16.622(3)	13.4236(12)
α (°)	88.656(3)	90	90.00	74.1910(10)	90.00	90.00
β (°)	73.603(3)	109.617(4)	109.0670(10)	75.6910(10)	90.00	96.816(7)
γ (°)	67.958(3)	90	90.00	69.3600(10)	90.00	90.00
Volume (Å^3)	2196.1(7)	9249.8(14)	2637.6(5)	1436.3(3)	1763.0(5)	2020.9(3)
Z	4	16	4	2	4	4
Density (calcd) (g/cm^3)	1.453	1.461	1.351	1.306	1.599	1.487
Goodness-of-fit on F^2	1.028	1.118	1.054	1.039	1.013	1.040
Final *R* indices [$I/2\sigma(I)$]						
R_1	0.0558	0.0899	0.0470	0.0604	0.0683	0.0690
wR_2	0.1325	0.2362	0.1281	0.1649	0.1207	0.1243
R indices (all data)						
R_1	0.1066	0.1221	0.0552	0.0940	0.0879	0.1109
wR_2	0.1651	0.2729	0.1363	0.1939	0.1305	0.1413

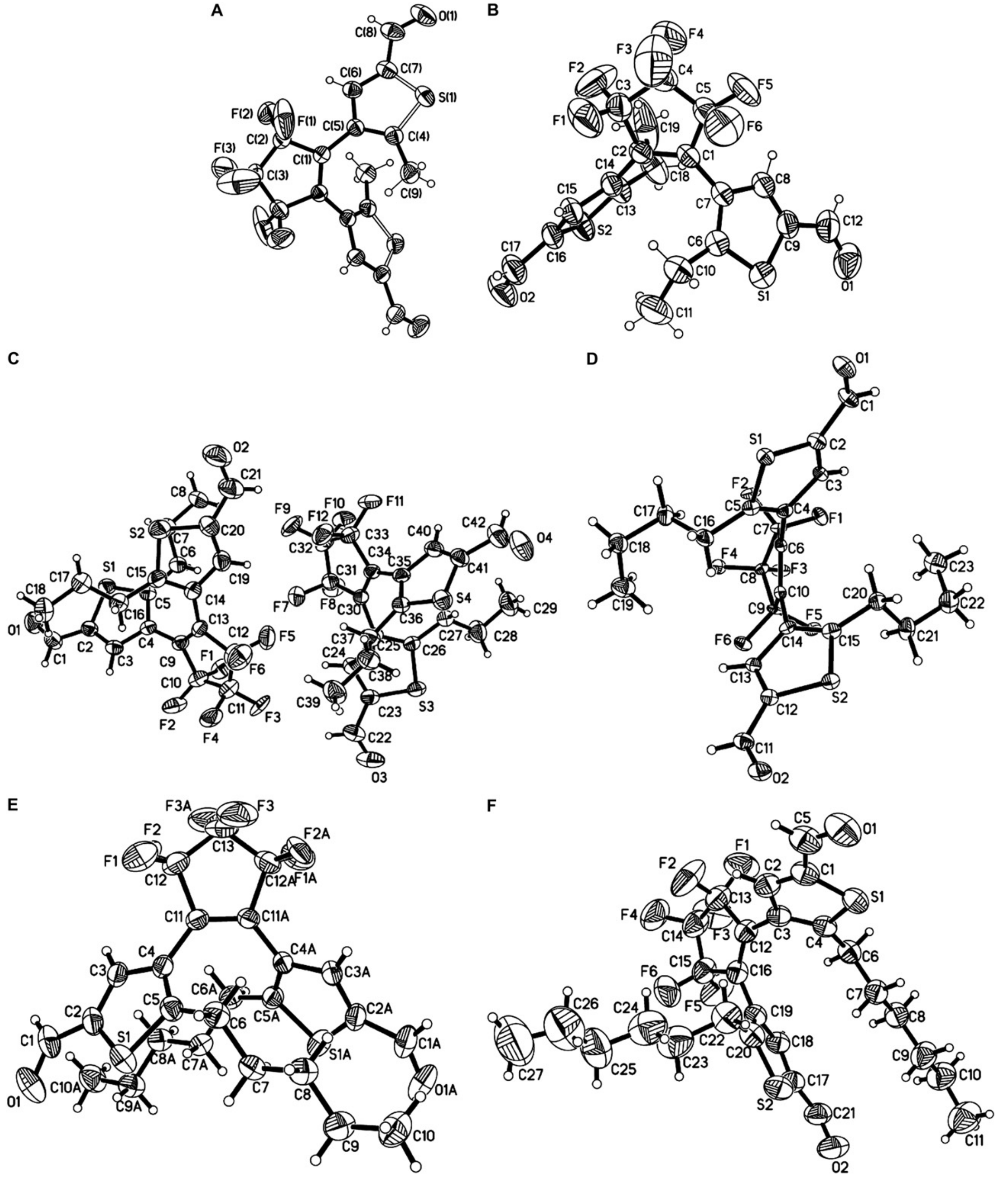


Figure 3. ORTEP drawings of crystals **1a**–**6a**, showing 35% probability displacement ellipsoids: (A) **1a**, (B) **2a**, (C) **3a**, (D) **4a**, (E) **5a**, and (F) **6a**.

Table 4. Distances between the reacting carbon atoms (*d*, Å) and dihedral angles (*θ*, °) of diarylethenes **1a**–**6a**

Compound	*d* (Å)		*θ* (°)			
1a	C4–C4A	3.600(3)	S1/C4–C7	46.1(5)	S2/C4A–C7A	46.1(5)
2a	C6–C15	3.893(7)	S1/C6–C9	55.2(2)	S2/C13–C16	65.1(1)
3a	C5–C15, C26–C36	3.732(5), 3.773(5)	S1/C2–C5, S3/C23–C26	55.5(6), 54.2(6)	S2/C15/C14/C19/C20, S4/C36/C35/C40/C41	59.4(6), 55.3(6)
4a	C5–C15	3.972(3)	S1/C2–C5	60.1(7)	S2/C12–C15	56.9(7)
5a	C5–C5A	3.763(9)	S1/C2–C5	59.2(1)	S2/C2A–C5A	59.2(1)
6a	C4–C20	3.818(3)	S1/C1–C4	54.1(2)	S2/C17–C20	58.7(2)

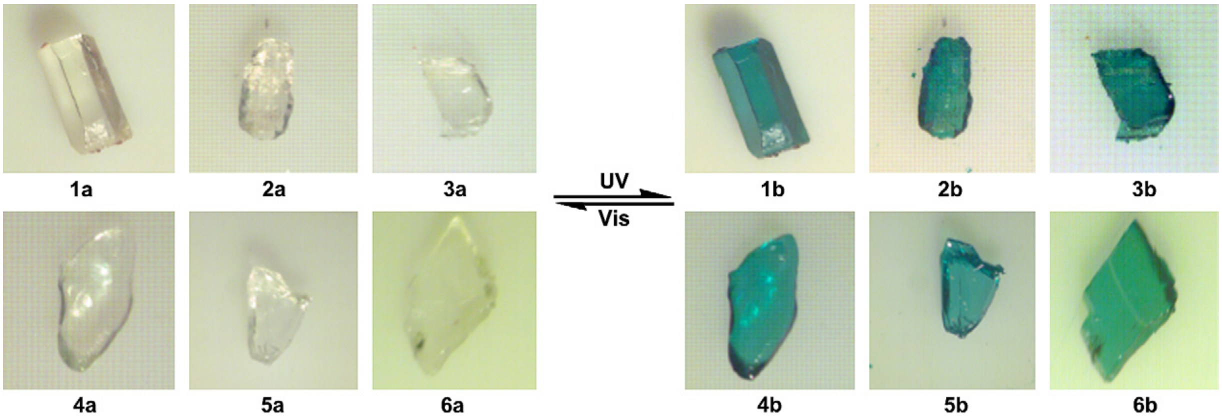


Figure 4. Photographs of photochromic processes of diarylethenes **1**–**6** in the crystalline phase.

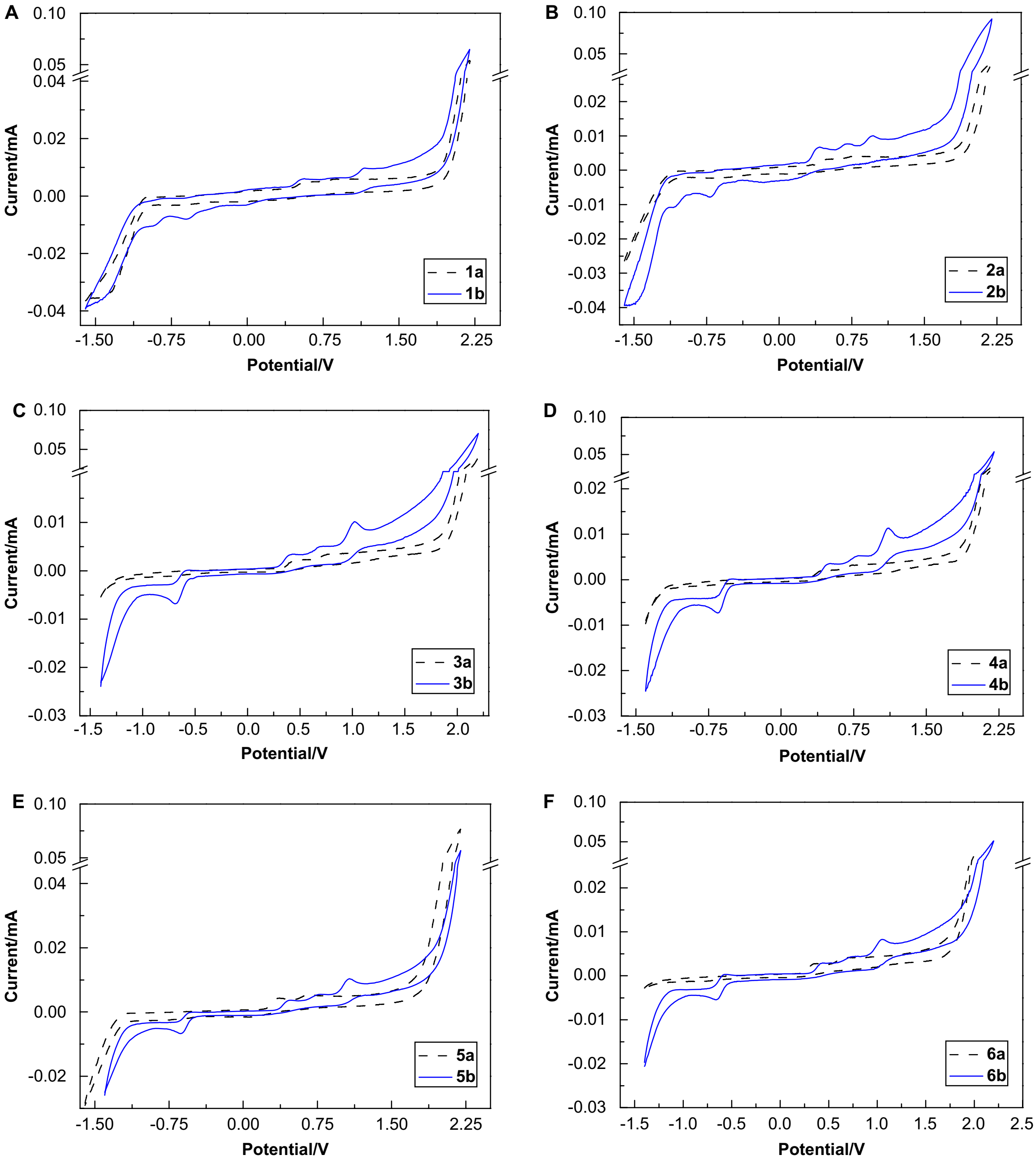


Figure 5. Cyclic voltammetry (second scan) of diarylethenes **1**–**6** in 0.1 mol/L ((TBA)BF_4) at a scan rate of 50 mV/s: (A) **1**, (B) **2**, (C) **3**, (D) **4**, (E) **5**, and (F) **6**.

and the absorption maximum was observed at 632–637 nm, which was the same as that of the closed-ring isomer **1b–6b**. The blue color disappeared upon irradiation with appropriate wavelength visible light and the absorption spectrum of the solution containing the colorless crystal was the same as that of the open-ring isomer **1a–6a**. Comparing these photographs shown in Figure 4, it clearly showed that the photochromic process had taken place in their respective crystalline phase upon irradiation with UV and visible light. Furthermore, these diarylethene crystals exhibited many times of coloration/decoloration cycles by alternate irradiation with UV and visible light. So, these crystals will be good candidates for optoelectronic applications.[28] The result also differs from that reported in Ref. 12a. In that paper, the crystals of diarylethenes bearing benzothiophene systems showed no photochromism when replacing the methyl groups with pentyl or hexyl groups. The reason is that the long pentyl/hexyl chain length leads to the long distance (larger than 4.2 Å) between the reactive carbons of the rigid benzothiophene plane in the crystalline phase.[12a]

3.4. Electrochemical properties of diarylethenes 1–6

The electrochemical properties of diarylethene are being used for molecular switching and also can be potentially applied to molecular-scale electronic switches.[1a,11d] The oxidative cyclization and cycloreversion and the reductive electrochemical cyclization of some diarylethene derivatives had been reported.[11d,13a,29] Herein, we investigated the electrochemical properties of **1**–**6** by cyclic voltammetry (CV). The typical electrolyte was acetonitrile (5 mL) containing 0.10 mol/L tetrabutylammonium tetrafluoroborate ($(\mathrm{TBA})\mathrm{BF_4}$) and 1.0×10^{-3} mol/L diarylethenes **1**–**6**. Platinum wire (0.5 mm) and steel electrodes were used as working and counter electrodes, respectively. Platinum wire (0.5 mm) in the supporting electrolyte solutions was used as a quasi-reference electrode, which was calibrated through the CV of ferrocene in similar electrolyte. Figure 5 showed the CV curves of diarylethenes **1**–**6** with the scanning rate of 50 mV/s. According to Eqs. 2 and 3,[30] the energy parameters EA and IP were calculated.

$$\text{HOMO}: \ \text{IP} = -\{[E_{\text{on}}]^{\text{ox}}+4.8\} \tag{2}$$

$$\text{LUMO}: \ \text{EA} = -\left\{[E_{\text{on}}]^{\text{red}}+4.8\right\} \tag{3}$$

where the units of onset potentials are volts, and those of IP and EA are electronvolts; 4.8 eV is the constant of the energy level of the ferrocene/ferrocenium (Fc) below the vacuum level.

With regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level), the HOMO and LUMO energy levels can also be estimated. As shown in Figure 5A, the onset potentials (E_{onset}) of oxidation and reduction for **1a** were observed at +1.93 and −1.04 V, respectively. Therefore, the values of IP and EA were calculated to be −6.73 and −3.76 eV according to Eqs. 2 and 3. Based on the HOMO and LUMO energy levels, the band gap (E_g, E_g=LUMO−HOMO) of **1a** can be determined as 2.97 eV. Similarly, the E_g of **1b** can be easily calculated as 3.04 eV. Corresponding values for diarylethenes **2**–**6** are summarized in Table 5.

Table 5. Electrochemical properties of diarylethenes **1**–**6**

Compound	Oxidation		Reduction		Band gap
	E_{onset} (V)	IP (eV)	E_{onset} (V)	EA (eV)	E_g
1a	+1.93	−6.73	−1.04	−3.76	2.97
1b	+1.93	−6.73	−1.11	−3.69	3.04
2a	+1.88	−6.68	−1.13	−3.67	3.01
2b	+1.80	−6.60	−1.22	−3.58	3.02
3a	+1.85	−6.65	−1.29	−3.51	3.14
3b	+1.84	−6.64	−1.08	−3.72	2.92
4a	+1.88	−6.68	−1.22	−3.68	3.10
4b	+1.97	−6.77	−1.06	−3.74	3.03
5a	+1.78	−6.58	−1.27	−3.53	3.05
5b	+1.88	−6.68	−1.12	−3.68	3.00
6a	+1.72	−6.52	−1.27	−3.53	2.99
6b	+1.89	−6.69	−1.11	−3.69	3.00

The acetonitrile used as solvent was of spectrograde and was purified by distillation before use.

To express more evidently the relationship between these data in Table 5, we convert Table 5 into Figure 6. From Figure 6, it can be clearly seen that both the HOMO and LUMO of the open-ring isomers **1a**–**6a** increased gradually with the exception of **4a** when the carbon numbers of alkyl chains increased. On the contrary, both HOMO and LUMO of the closed-ring isomers **1b**–**6b** showed a remarkable initial

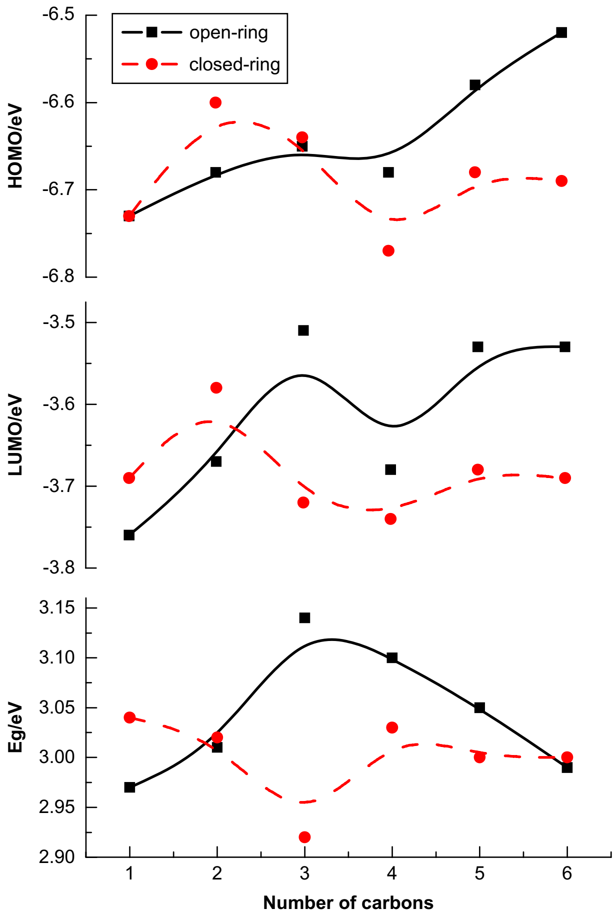


Figure 6. The effect of alkyl length on band gap of diarylethenes **1**–**6**.

increasing tendency (replacing the methyl groups with ethyl ones) with subsequent significant decrease with increasing the carbon numbers of alkyl chains (replacing the ethyl groups with propyl ones). But, even if the alkyl chains became longer (replacing the propyl groups with butyl, pentyl or hexyl ones), further decrease of the HOMO and LUMO values was not observed evidently. For the band gap of diarylethenes **1–6**, the carbon numbers of alkyl chains have almost no effect on their closed-ring isomers. However, E_g increased from methyl, ethyl to propyl, then decreased with the further increases of carbon chain length for the open-ring isomers of these compounds. All these data described above indicated that different chain lengths of alkyl substituents have significant effect on the band gap of the diarylethenes. It should be noted here that calculation of absolute HOMO and LUMO levels from electrochemical data in combination with the energy gap is still in debate.[30b]

4. Conclusion

In summary, six symmetrical diarylethenes, bis(2-*n*-alky-5-formylthien-3-yl)perfluorocyclopentene derivatives having different long alkyl chains at 2-positions of the thiophene rings were synthesized. They all exhibited reversible photochromism both in solution and in the single crystalline phase, and their conversions from open-ring to closed-ring isomers in the photostationary state were all close to 100% in solution. Introduction of the long alkyl chains at 2-position of the thiophene rings decreased the cyclization and cycloreversion quantum yields. The alkyl chain induced bathochromic shifts of the maxima absorption of the closed-ring isomers, but didn't affect those of the open-ring isomers. The distance between reactive carbon atoms was slightly influenced by the alkyl chain in crystals. In addition, cyclic voltammetry tests indicate that different chain lengths of alkyl substituent have a significant effect on the band gap of these diarylethenes. The results of this study are useful for the efficient design and synthesis of photoactive diarylethene derivatives with excellent characteristics.

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