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Syntheses and photochromic properties of diaryl acenaphthylene derivatives

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ABSTRACT

A series of diaryl acenaphthylenes has been synthesized, and their photochromic properties are studied both in solution and in the crystalline state. 2,4-Dimethyl-5-phenylthiophene derivative **1a** showed no photochromic reaction, while 2-methyl-5-phenylthiophene derivative **2a** and 5-methyl-2-phenylthiazol derivative **3a** showed reversible photochromism in solution. Fluorescence spectrum of compound **3a** changed upon photoirradiation. In the single-crystal state, compound **3a** showed no photochromic reaction possibly because of $\pi-\pi$ and CH/S inter-molecular interactions. The photocyclization quantum yield of **3a** was determined to be as low as 0.7%. The closed-isomer **3b** showed relatively high thermal stability by the rigidity of acenaphtylene.

1. Introduction

Considerable recent attention in the field of organic materials chemistry has been focused on photochromic molecules, which exhibit reversible color change upon light irradiation [1–5]. Among wide variety of synthetic photochromic molecules, those having hexatriene–cyclohexadiene type structure such as diarylethenes and terarylenes have been extensively studied due to their thermal stability in both colored and bleached states and relatively high photochromic reactivity in solutions and even in solid states [6–10]. Various types of photochromic hexatriene molecules with different kinds of central and side ethene units have been recently reported [11–15]. For example, usual diarylethenes and terarylenes contain cyclopentene and various aromatic units, respectively, which are served as the central ethene unit of the hexatriene structure. In the sense of the number of π electrons in the central unit, diarylethenes and terarylenes have 2π- and $(4n+2)\pi$-electron systems, respectively. The photoisomerization from hexatriene to cyclohexadiene which proceeds under UV light irradiation induces considerable alteration in the π-electron systems. We here report on the photochromic properties of terarylene analogs having a 12π system, acenaphthylene unit as the central ring. Acenaphthylene is a simple and stable nonalternant aromatic hydrocarbon consisting of naphthalene with an ethylene bridge [16–22]. The bond length of double bond of its ethylene bridge is longer than those in cyclopentene and ethylene [23]. The double bond character in the ethylene bridge is, thus, considered to be lowered by its strained structure, which may also affect on the photochromic reactivity if it is used as the central ethene unit of the hexatriene motif. In the present work, we synthesized three diaryl acenaphthylene derivatives having 5-methyl-2-phenylthiazole, 2-methyl-5-phenylthiophene and 2,4-dimethyl-5-phenylthiophene moieties as the side aromatic units and their photochromic properties are studied.

2. Results and discussion

2.1. Photochromism

Scheme 1 shows molecular structures of diaryl acenaphthylene derivatives synthesized in the present study. Compound **1a** having 2,4-dimethyl-5-phenylthiophenes as the side units showed no photochromic color change even after UV light irradiation for 3 h and its absorption spectrum also showed no marked photoresponsive change. As shown in Fig. 1(a), **2a** having 2-methyl-5-phenylthiophenes as the side units exhibited a weak absorption band between 400 and 500 nm before irradiation [24], while a new absorption band appeared at 580 nm after irradiation with UV light ($\lambda = 313$ nm).

Similarly, the 5-methyl-2-phenylthiazol derivative **3a** also showed specific absorption band at 560 nm after irradiation with UV light as shown in Fig. 1(b). These colorations also occurred under irradiation between 400 and 500 nm. The colored solutions were bleached after visible light irradiation with longer than 500 nm and original absorption spectra of **2a** and **3a** were recovered. Since

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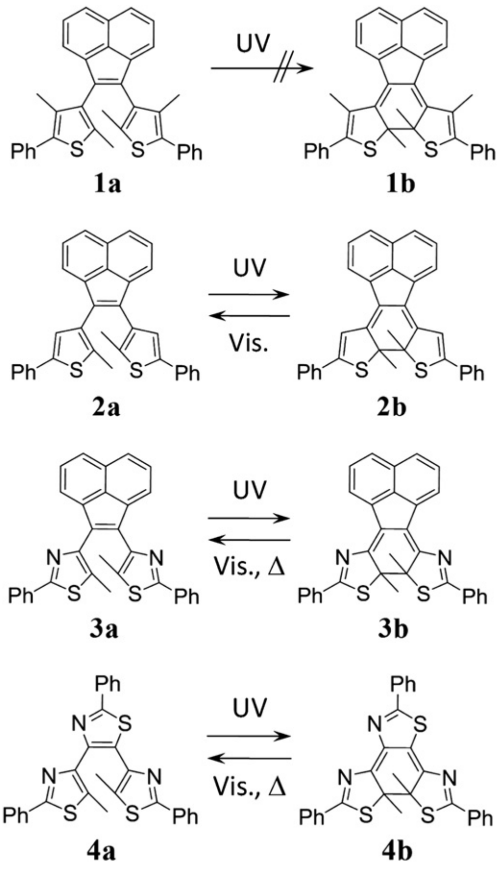


Scheme 1. Photochromic reactions of acenaphthylene derivatives **1**–**4**.

isosbestic points were clearly observed, these reversible spectral changes are attributed to the two-component photochromic reaction as observed for diarylethene and terarylene derivatives.

The colored compound formed after UV light irradiation was isolated from the reddish hexane solution by a normal-phase HPLC. The isolated compound was characterized as the ring-closed isomer **3b** by the ^{1}H NMR spectroscopy in a $CDCl_3$ solution. No considerable by-product was detected by the HPLC. **3b** showed same mass-number as that of **3a**, also supporting its chemical structure. Although isolation of **2b** from the colored solution was tried, its amount was too low to characterize the colored compound **2b** by NMR measurements. Judging from the similar photochromic behavior of **2** as those of **3**, however, the colored compound having the absorption band at 560 nm might be attributed to the ring-closed isomer **2b**. The colored compound isolated by HPLC also showed same mass-number of **2a**.

The values of λ_{max} and ε in **1**–**3** are summarized in Table 1. The conversion ratios from **2a** to **2b** and from **3a** to **3b** at their photostationary states achieved under irradiation with UV light ($\lambda = 313$ nm) of long period (for 5–10 h) were estimated to be 14 and 75%, respectively. These results suggested that **3a** has higher photochromic reactivity than that of **2a**.

2.2. DFT calculations

Since photochromic cyclization reactivity of similar hexatriene-type diarylethene and terarylene derivatives have been reported to markedly depend on the conformation of the ring-open-form isomer, we evaluated stable conformation of the compounds by using density functional theory (DFT) [25] calculations at the B3LYP/6-31G^{++} [26] level. Fig. 2 shows the optimized structures of **1a**–**3a**, which were determined to be the most stable geometries by the vibrational frequency calculations. The evaluated distance between the reacting carbon atoms are also given in Fig. 2. **1a** is expected to have twisted structure due to the steric hindrance between the methyl groups at 4- and 4′-positions of the thiophene rings and acenaphthylene unit, which should make the distance between the reacting carbon atoms longer and suppress the photochromic reactivity. Moreover, LUMO is rather localized on the acenaphthylene moiety as shown in Fig. 2 (a), which may also suppress the peri-cyclization reactivity of **1a** regarding its reaction machanism. **3a** has lowest steric hindrance between the side aryl groups and the central acenaphthylene unit among these derivatives.

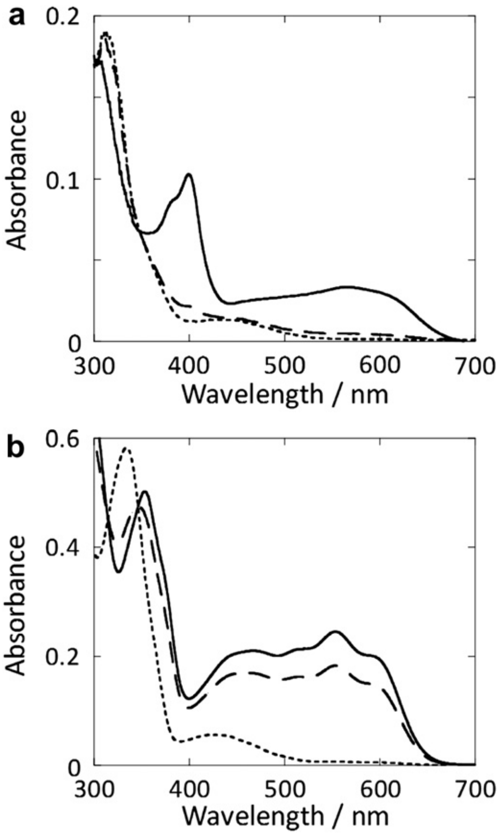


Fig. 1. Absorption spectral changes of **2**(a) and **3**(b) in hexane: open-form **a** (dotted lines), closed-form **b** (solid lines) and photo-stationary state under irradiation with 313 nm light (dashed lines). The concentrations of **2** and **3** were 7.6×10^{-6} and 1.8×10^{-5} M, respectively.

2.3. Photomodulation of emission spectra of **3** in solution

In the following discussions, we focus on the photochromic performance of the compounds **3a** and **3b**. Compound **3a** showed

Table 1
Absorption maxima and coefficients of acenaphtylene derivatives **1**–**3**, together with the conversion ratios at photostationary states in hexane.

Compounds	λ_{max}[nm] (ε[10^4 M^{-1} cm^{-1}])		Conversion[%]
	a	**b**	
1	323(1.5) 429(0.18)	–	–
2	313(2.5) 433(0.19)	399(0.82) 566(0.27)	14
3	338(2.8) 442(0.28)	353(2.8) 553(1.4)	75

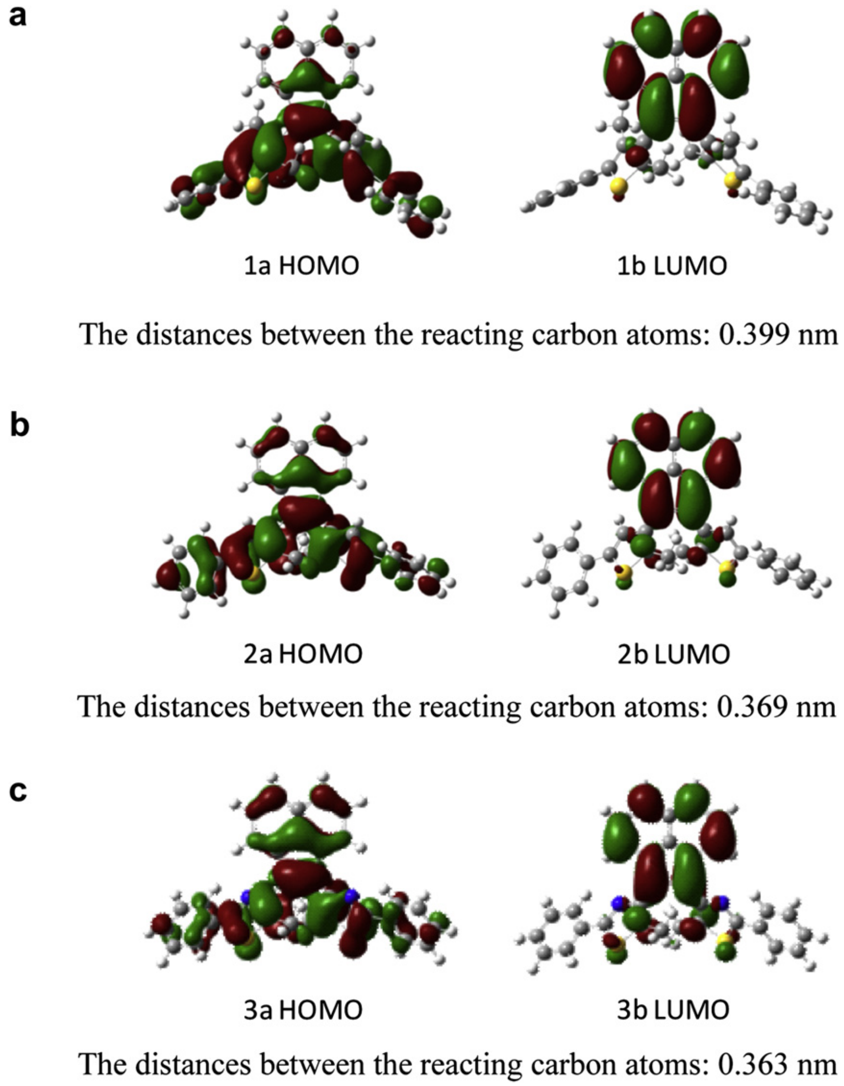


Fig. 2. Spatial plots of selected TDDFT frontier molecular orbitals of (a) **1a**, (b) **2a** and (c) **3a**.

characteristic fluorescence emission at 580 nm as shown in Fig. 3, which is attributed to the LUMO-HOMO transition with certain Stokes' shift. The fluorescence peak wavelength of **3** was found to reversibly change along with the photochromic reactions in the hexane solution. Fig. 3 shows emission spectrum of pure **3b** in the hexane solution, where a clear emission band was observed at 680 nm and no emission of **3a** at 580 nm. The excitation spectrum of the colored state at the detection wavelength of 650 nm revealed an excitation band at 550 nm which is specific for **3b**. Similar modulation of emission wavelength has also been reported in bisbenzothiophenylethene derivatives [27,28].

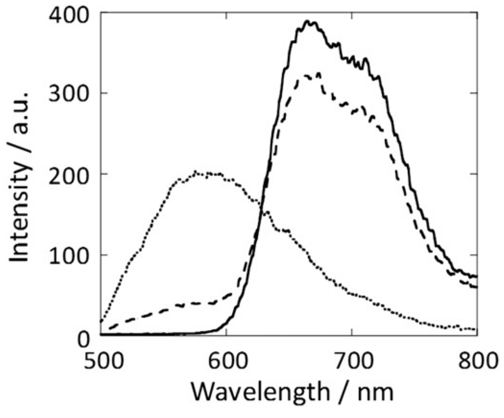


Fig. 3. Emission spectral change of **3** in hexane (1.8×10^{-5} M, $\lambda_{ex} = 420$ nm): open-form **3a** (dotted line), closed-form **3b** (solid line) and emission at photo-stationary state under irradiation with 313 nm light (dashed line).

2.4. *Crystal structures of **3a** and **3b***

Crystals of **3a** and **3b** were obtained by recrystallization from their hexane solutions and were characterized by X-ray analyses. The ORTEP drawings of **3a** and **3b** are presented in Fig. 4 [29,30]. The structure of **3a** in crystal phase was found to be similar to the optimized structures estimated by the DFT calculation (Fig. 2(c)). **3a** exhibits the conformation of quasi-C2 symmetry around the central hexatriene moiety, which is favorable for the photochromic cyclization reaction with a contra-rotational cyclization reaction [31]. The **3a** crystal is the racemic crystal having a couple of enantiomeric comformers in the unit cells. The distance between the reacting carbon atoms in **3a** was evaluated to be 0.358 nm, which roughly coincides with the evaluated value by the DFT calculation. It seems to be short enough for the photochromic ring-cyclization reaction.

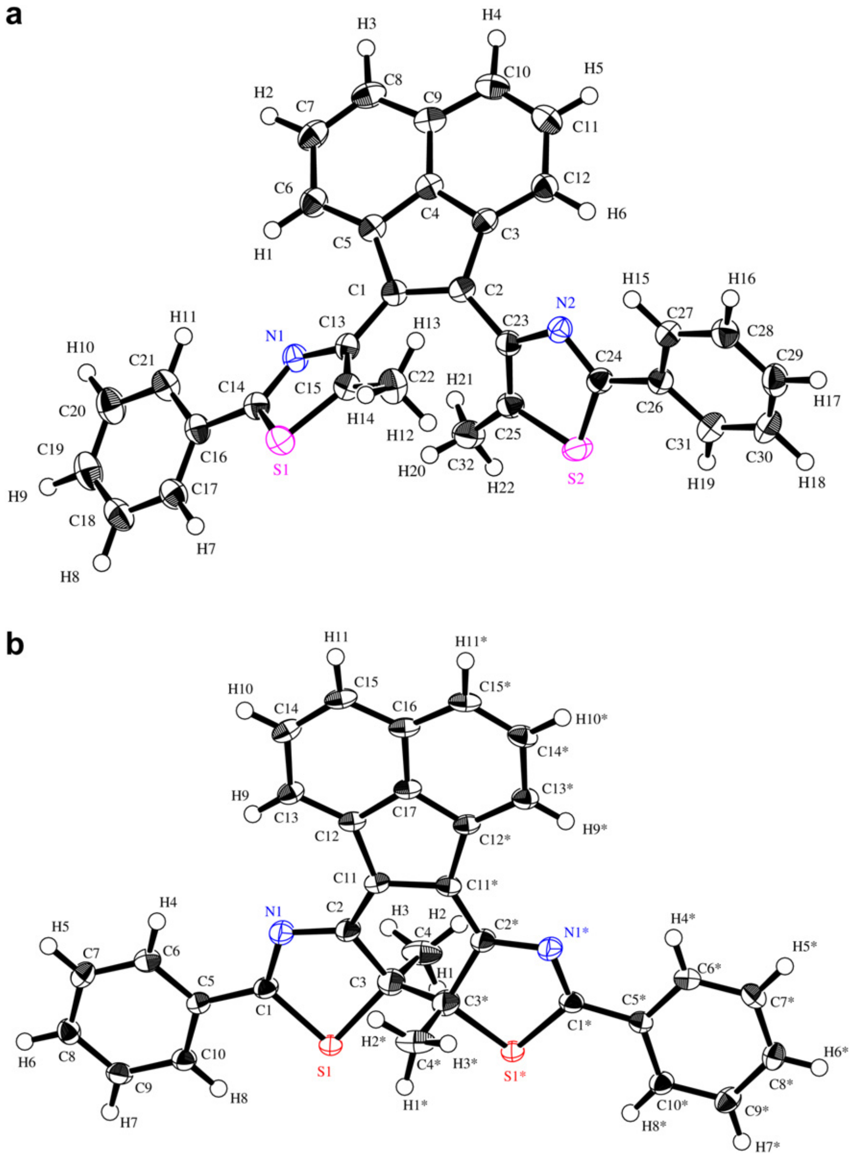


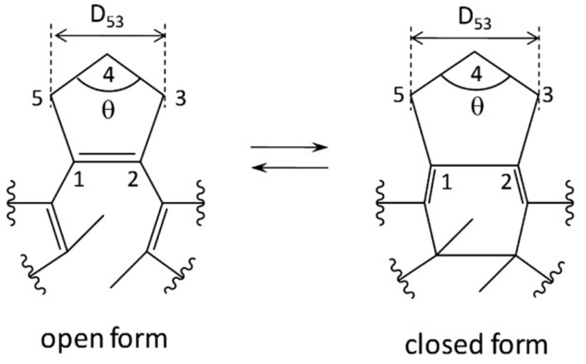
Fig. 4. ORTEP drawings of open-ring isomer in crystal **3a** (a) and closed-ring isomer in crystal **3b** (b), showing 50% probability displacement ellipsoids.

The distances between N1–C6 and N2–C12 were estimated to be 0.318 and 0.321 nm, respectively, which suggests the distance between CH and N of about 0.265–0.267 nm and less than sum of the van der Waals radii of (C–)H (0.155 nm) and N (0.12 nm) [32]. Weak intramolecular CH/N hydrogen bonding interactions between N1–H1 and N2–H6 seem to contribute to the stable conformation of **3a** in the crystalline phase as well as in solution phase. Similar intramolecular hydrogen bonding has been also observed in 4,5-bis(2,4-dimethyl-5-phenylthiophen-3-yl)-2-phenylthiazole and 4,5-bis(5-methyl-2-phenylthiazol-4-yl)-2-phenylthiazole (**4a**), which modulates their photocyclization reactivity in the crystal and solution phases [33]. Despite its conformation suitable for the photocyclization, compound **3a** showed no photochromic coloration in the crystalline phase.

Upon irradiation with 365 nm light, the crystal of **3a** exhibited fluorescence at 630 nm instead of photochromic coloration. The fluorescence peak of crystal showed considerable bathochromic-shift from that at 580 nm in the hexane solution. In the crystal structure of **3a**, specific $\pi-\pi$ stacking interaction was suggested from the distance of about 0.35 nm between the acenaphthylene units, which should be responsible for the orange emission. The distance between the proton in CH_3– and S atom of adjacent molecules were evaluated to be 0.28 nm, suggesting the intermolecular CH/S interaction. That is, **3a** molecules forms rather rigid 3D network with $\pi-\pi$ and CH/S interactions in the crystalline state, and photochromic cyclization which requires the collapse of the network structure is much suppressed in the crystalline lattice.

2.5. *Quantum yield and temperature dependent ^1H NMR*

The cyclization quantum yield of **3a** in hexane was determined to be as low as $\Phi = 0.007$ by using 4,5-bis(5-methyl-2-phenylthiazol-4-yl)-2-phenylthiazole (**4a**) as a reference compound [33]. This value is surprisingly lower than those of usual hexatriene-type molecules such as terarylene and diarylethene derivatives and seems to be the lowest one among them so far reported. In the hexane solution, **3a** seems to be stabilized into the photoreactive conformation by the intramolecular hydrogen bondings, as observed in the single crystals. In order to evaluate conformation of **3a** in the solution phase, the temperature dependence of the chemical shifts of C6–H, C12–H (3,8-protons, i.e. α-position, of acenaphthylene) and methyl protons was studied by temperature dependent ^{1}H NMR. ^{1}H NMR signal of equivalent C6–H and C12–H protons was observed at 8.17 ppm at 293 K as a doublet signal, which was the most low-field signal in **3a** because of the ring-current effects of the two aromatic groups. This peak showed systematic high-field shift to 8.08 ppm upon heating to 353 K in D_8-toluene. No other peak of the acenaphtylene unit exhibited such the significant temperature dependent chemical shift. These results suggest the decrease of the CH···N interaction and change in the conformation with rising temperature. At the higher temperature, that is, the distance of CH–N and the twisting angle between acenaphthylene and thiazole rings should become larger. NMR signal of the methyl protons also showed characteristic low-field shift at higher temperature as shown in Fig. 5. This characteristic shift suggests decrease in deshielding effect on the methyl groups from the adjacent thiazole groups. These observations suggest that the reactive conformation of quasi-C2 symmetry with relatively short C–C distance indicated by the DFT calculation and by the X-ray study would be dominant in the solution phase at 293 K and its population would decrease at higher temperature. Some diarylethene and terarylene derivatives with relatively high ring-cyclization quantum yield have been reported to have stable reactive conformation of quasi-C2 symmetry [34]. Although **3a** seems to also have conformation of quasi-C2 symmetry, it exhibits markedly small photochromic quantum yield of $\Phi = 0.007$. Since the fluorescence emission quantum yield of **3a** is about 2% in the solution phase, the emission process should not be the dominant origin of the suppressed photochromic reactivity. It has been reported that acenaphthylene has the lifetime of singlet excited state as short as 300 ps [16] because of efficient vibrational relaxations, which would be one of possible origins of the low photochromic quantum yield of **3a** to **3b**. The decreased double bond character in the ethene moiety in the acenaphthylene unit may also contribute to the suppressed reactivity.



Scheme 2. Schematic illustration of specific structural parameters around the reaction center and a part of central unit.

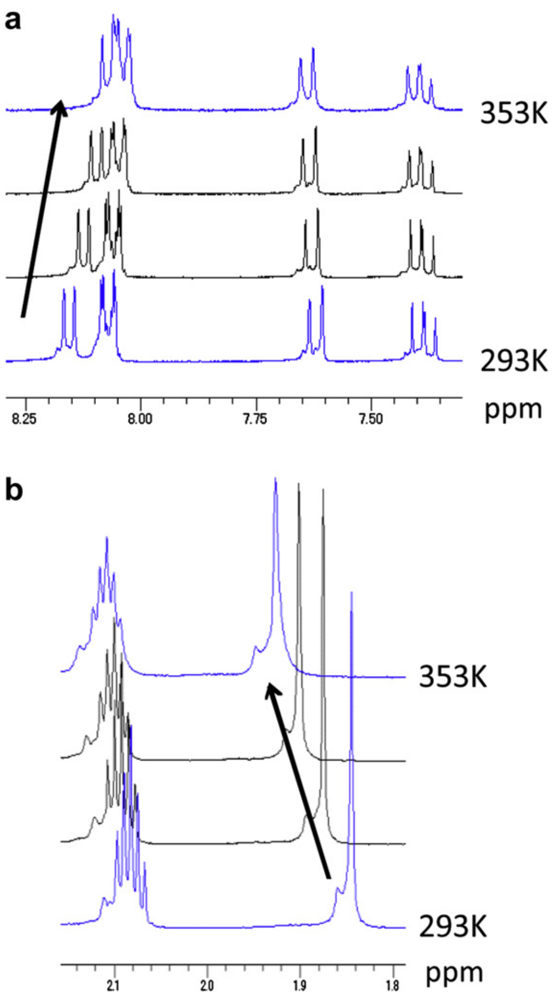


Fig. 5. Temperature dependence of ^{1}H NMR spectra of **3a** in toluene-d_8 in (a) low-field and (b) hight-field ranges.

2.6. Comparison of *3* and *4* in crystal structures

Effects of steric rigidity of acenaphthylene unit of **3a** and structural distortion in the ring-closed form isomer are then discussed by comparing structural change in **3a** to **3b** with that of a usual triangle tertarylene **4a**, whose quantum yield of photocyclization is 38% in the hexane solution. The changes in the crystal structure and the most stable structure evaluated by DFT calculations of **3a** and **3b** were compared with those of terthiazole **4a** and **4b**, respectively. Upon cyclization of 1,2-diaryl-fivemembered cycloethene structure, the C=C double bond in the central unit becomes single bond and thus both distances between 1,2-atoms and between 3,5-atoms should become longer as schematically illustrated in Scheme 2. In the following discussion, differences in distances between S and N atoms, D_{SN}, and S–C–N angles, θ_{SCN}, in the central thiazole of compounds **4a** and **4b** are compared with those of distances between C9 and C11, D_{CC} and C9–C12–C11 angles, θ_{CCC} of acenaphthylene units in the **3a** and **3b**, respectively. Table 2 summarizes the measured and calculated values of these structural parameters. The characteristic angles θ_{SCN} of **4b** and θ_{CCC} of **3b** were considerably lager than those of **4a** and **3a**, respectively, and D_{SN} and D_{CC} also expand in the ring-closed forms from those of the ring-open forms. Degree of change in D_{CC}, ($\Delta D_{CC} = D_{CC}$(**3b**) − D_{CC}(**3a**),) and that of D_{SN}, ($\Delta D_{SN} = D_{SN}$(**4b**) − D_{SN}(**4a**)) were 0.003 nm and 0.011 nm, receptivity.

Table 2
Structural parameters of **3a**,**b** and **4a**,**b** in crystal structure and their differences.

(a)	θ_{C-C-C}/degree	D_{C-C}/nm
3a	110.75 (110.32*)	0.232 (0.232*)
3b	113.10 (112.39*)	0.235 (0.231*)
Difference	2.35 (2.07*)	0.003 (0.001*)
(b)	θ_{N-C-S}/degree	D_{S-N}/nm
4a	114.27 (113.50*)	0.257 (0.257*)
4b	118.87 (115.86*)	0.268 (0.264*)
Difference	4.60 (2.36*)	0.011 (0.007*)

*Based on optimized structures with DFT calculation.

Also, $\Delta\theta_{SCN}$ of **4** and $\Delta\theta_{CCC}$ of **3** were 4.6 deg and 2.35 deg, respectively. These changes in the structural parameters are considerably larger for thiazole derivative **4a**, **4b** than those for **3a**, **3b**. The rigid acenaphtylene unit seems to suppress structural change upon isomerization of **3a** to **3b**, contributing to the significantly low photocyclization quantum yield.

2.7. *Thermal stability of **3b***

The thermal stability of the closed-ring isomer **3b** was then examined. **3b** did not show the thermal cycloreversion reaction in the dark place at room temperature as well as **4b**. Fig. 6(a) shows the decay profile of the peak optical absorbance of ring-closed isomer **3b** at several temperatures. The decay profiles were well characterized with the simple exponential function indicating unimolecular first order bleaching kinetics. The bleaching rate constant exhibited Arrhenius-type temperature dependence as also shown in Fig. 6(b). The activation energy was evaluated from the slope of the Arrhenius plot to be 7.4 × 10 kJmol^{-1} (Table 3). This activation energy is obviously smaller than that of terthiazole **4b** (134 kJmol^{-1}). The activation energy of the thermal cyclereversible reactions of diarylethenes and terarylenes have been reported to decrease with increasing aromatic stabilization energy of the ring-open form isomers. Since acenaphtylene has 4nπ electron system and the aromatic naphthalene unit is preserved in the ring-closed form isomer **3b**, one may expect larger activation energy from **3b** to **3a** than that from **4b** to **4a**. Although the origin of this remarkable contradiction is not clear at the moment, present results may suggest specific nature of the 4nπ electron system as the central unit in the hexatriene systems. It is also worth to note that the frequency factor of the thermal kinetics is considerably small in the present molecule, which make the lifetime of **3b** as long as 11 years at the room temperature. The molecular rigidity of acenaphtylene as previously discussed might be responsible for both the small activation energy and frequency factor.

Table 3
Arrhenius parameters of thermal cycloreversion reactions of the closed-ring isomers and their half-lifetime in toluene solution.

	Ea [kJ mol^{-1}]	*A* [s^{-1}]	$t_{1/2}$ (20 °C)
3b	74	3.1×10^4	11 years
4b	112	7.1×10^{11}	3.3 years

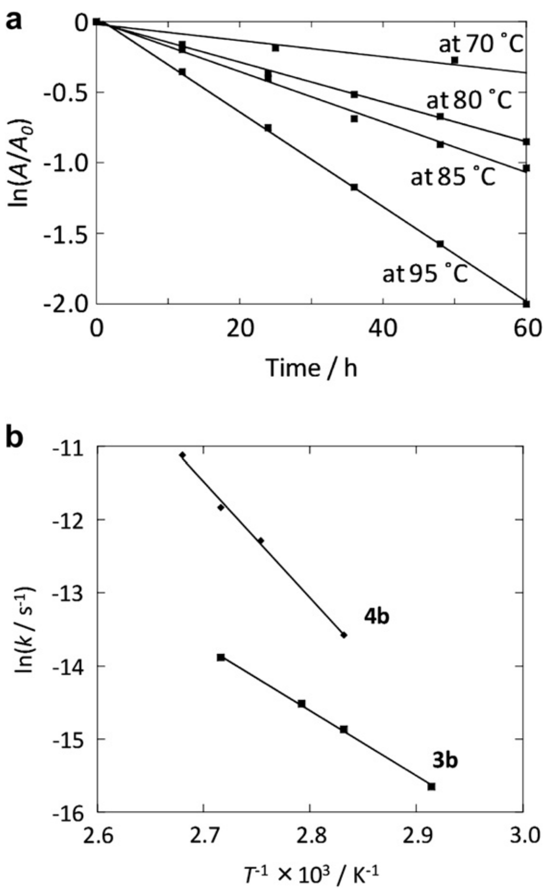


Fig. 6. Decay lines of peak absorbance by thermal cycloreversion reactions of **3b** at various temperatures (a), and temperature dependence of the thermal fading rates of **3b** and **4b** (b) in toluene.

3. Conclusions

In summary, 4nπ electron system was firstly introduced as the central unit of the hexatriene–cyclohexadiene type photochromic molecules. **3a** exhibited well defined reversible photochromic cyclization reaction with significantly low quantum yield. **3** shows reversible fluorescence switching behavior in the solution phase. Specific intra- and/or inter-molecular CH/N and CH/S interactions are suggested in the crystal structure of **3a** and also in the solution phase.

4. Experimental section

4.1. *General*

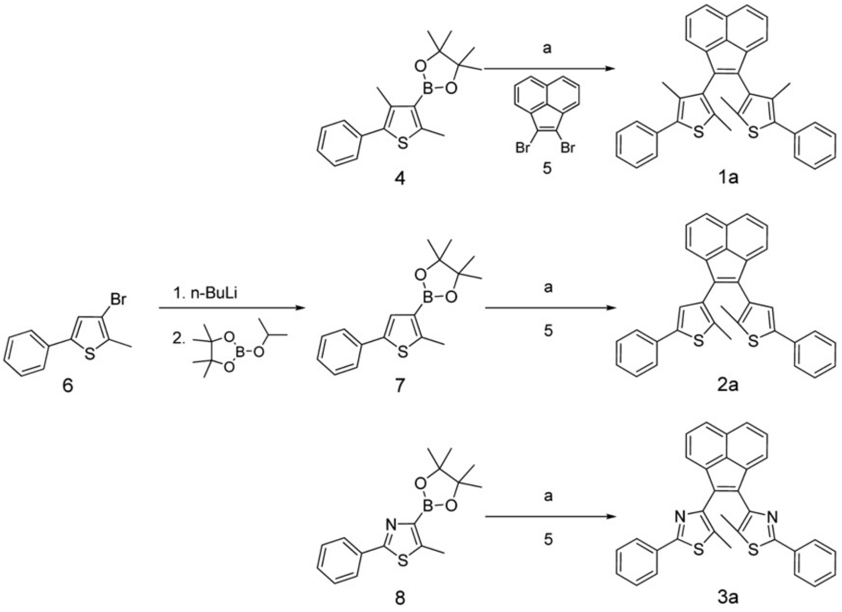
^{1}H NMR spectra were recorded on a JEOL AL-300 spectrometer (300 MHz). Separative HPLC was performed on a HITACHI LaChrom ELITE HPLC system and a JASCO LC-2000 Plus Series. Mass spectra were measured with a mass spectrometer JEOL JMS-T100LC AccuTOF. Absorption spectra in solution were studied with JASCO V-550 and V-670 spectrophotometers with a temperature control unit. Photoirradiation was carried out using an USHIO 500 W ultra-high-pressure mercury lamp or a Panasonic Aicure UV curing system (LED, $\lambda = 365$ nm) as the exciting light source. Monochromic light was obtained by passing the light through a monochromator (Shimazu SPG-120S, 120 mm, $f = 3.5$). X-ray crystallographic analyses were carried out with a Rigaku R-AXIS RAPID/s Imaging Plate diffractometer with Mo Kα radiation at 296 K.

4.2. *Syntheses*

Diaryl acenaphthylene derivatives **1a**–**3a** were synthesized according to Scheme 3.

5. 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl) acenaphthylene(1a)

A 100 ml four-necked flask was charged with 1,2-dibromoacenaphthylene [35] (**5,** 0.15 g, 0.5 mmol), **4**(0.31 g, 1.0 mmol), triphenylphosphane (0.08 g, 0.29 mmol), $Pd(PPh_3)_4$ (0.07 g, 0.06 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (10 mL/10 mL) solution. The mixture was then stirred at 110 °C under N_2. After having been stirred for a day the reaction mixture was extracted with ethyl acetate and the organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (hexane/ethyl acetate 10:1) and normal-phase HPLC (hexane/ethyl acetate 19:1) afforded **1a** (0.14 g, 0.26 mmol, 56%) as a yellow solid.



Scheme 3. Synthetic route for compounds **1a**–**3a**.

^{1}H NMR(300 MHz, CD_2Cl_2): δ 7.90–7.87(dd, 2 H), 7.64–7.58(m, 4 H), 7.50–7.40(m, 8 H), 7.34–7.32(m, 2 H), 2.28(s, 3 H), 2.18(s, 3 H), 2.13(s, 3 H), 2.04(s, 3 H).

^{13}C NMR(75 MHz, $CDCl_3$/TMS): δ 140.19, 136.52, 136.42, 135.58, 135.52, 135.23, 134.90, 134.54, 134.36, 132.91, 132.72, 128.98, 128.45, 128.30, 128.23, 127.71, 127.11, 126.82, 124.13, 15.65, 15.40, 14.93, 14.65.

EI HRMS (*m*/*z*) $[M]^+$ calcd. for $C_{34}H_{24}S_2^{+}$: 524.1627; Found: 524.1633.

Anal. Calcd. For $C_{36}H_{28}S_2$: C, 82.40; H, 5.38; N, 0. Found: C, 81.92; H, 5.28; N, 0.17.

6. 4,4,5,5-Tetramethyl-2-(2-methyl-5-phenylthiophen-3-yl)-1,3,2-dioxaborolane(7)

nBuLi (1.6 M in hexane, 5.7 mL, 9.1 mmol) was added slowly under Ar at −78 °C to a solution of 3-bromo-2-methyl-5-phenylthiophene (**6**, 2.23 g, 8.8 mmol) in dry THF (60 mL), and the mixture was stirred for 1 h at that temperature. 2-Isopropoxy-4,4,5,5,-tetramethyl-1,3,2,dioxaboro lane (2.0 mL, 9.9 mmol) was then added in a dropwise fashion and the system was stirred for another 1 h. The reaction mixture was allowed to warm to room temperature. Methanol was added to the reaction mixture, which was extracted with ethyl acetate. The combined organic fraction was washed with water, dried with anhydrous magnesium sulfate, and concentrated to give 2.0 g (6.7 mmol, 76%) of **7** as colorless solid.

^{1}H NMR(300 MHz ACETN-D_6): δ 7.61–7.58(d, 2 H), 7.40–7.35(t, 3 H), 7.28–7.16(t, 1 H), 2.66(s, 3 H), 1.33(s, 12 H).

7. 1,2-bis(2-methyl-5-phenylthiophen-3-yl)acenaphthylene(2a)

This compound was prepared by same procedure as had been used for **1a**, except that **4** was replaced by **7**. From **7** (0.16 g, 0.5 mmol), **5** (0.08 g, 0.25 mmol), triphenylphosphane (0.03 g, 0.12 mmol), $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (8 mL/8 mL) solution, **2a** (0.07 g, 0.14 mmol, 58%) was obtained as a yellow solid.

^{1}H NMR(300 MHz, ACETN-D_6): δ 7.99–7.96(d, 2 H), 7.82–7.80(d, 2 H), 7.70–7.66(m, 6 H), 7.54(s, 2 H), 7.44–7.39(t, 4 H), 7.32–7.30(t, 2 H), 2.14(s, 6 H).

^{13}C NMR(75 MHz, $CDCl_3$/TMS): δ 140.48, 140.30, 136.59, 134.40, 134.26, 133.47, 128.90, 128.27, 128.15, 127.91, 127.25, 127.19, 125.43, 125.12, 123.70, 14.65.

EI HRMS (*m*/*z*) $[M]^+$ calcd. for $C_{34}H_{24}S_2^{+}$: 496.1314; Found: 496.1320.

Anal. Calcd. For $C_{34}H_{24}S_2+1/2H_2O$: C, 80.75; H, 4.98; N, 0. Found: C, 80.85; H, 4.63; N, 0.18.

8. 1,2-bis(5-methyl-2-phenylthiazol-4-yl)acenaphthylene(3a)

3a was prepared by same procedure as had been used as for **1a**, except that **4** was replaced by **8**. From **8** (0.63 g, 2.0 mmol), **5** (0.31 g, 1.0 mmol), triphenylphosphane (0.13 g, 0.50 mmol), $Pd(PPh_3)_4$ (0.07 g, 0.06 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (20 mL/20 mL) solution, **3a** (0.40 g, 0.80 mmol, 81%) was obtained as a yellow solid.

^{1}H NMR(300 MHz, $CDCl_3$): δ 8.06–8.01(m, 6H), 7.90–7.87(d, 2H), 7.64–7.62(t, 2H), 7.48–7.46(m, 6H), 2.03(s, 6H).

^{13}C NMR(75 MHz, $CDCl_3$): δ 164.56, 148.10, 139.88, 133.85, 133.13, 131.68, 129.74, 128.92, 128.54, 128.25, 127.88, 127.60, 126.33, 125.48, 12.56.

FAB HRMS (*m*/*z*) $[M + H]^+$ calcd. for $C_{32}H_{23}N_2S_2^{+}$: 499.1297; Found: 499.1297.

Anal. Calcd. For $C_{32}H_{22}N_2S_2$: C, 77.07; H, 4.45; N, 5.62. Found: C, 76.88; H, 4.15; N, 5.67.

3b: ^{1}H NMR(300 MHz, $CDCl_3$): δ 8.19–8.17(d, 2H), 8.19–8.07 (dd, 4H), 7.76–7.73(d, 2H), 7.66–7.60(t, 2H), 7.54–7.52(m, 6H), 2.03 (s, 6H).

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[29] Crystallographic data for **3a**: $C_{32}H_{22}N_2S_2$, $a = 11.0430(5)$, $b = 10.7191(5)$, $c = 20.7937(10)$Å, $\beta = 97.6518(13)^\circ$, monoclinic, space group $P2_1/c$, $Z = 4$, $V = 2439.45(19)$ Å^3, $\rho_{calc} = 1.358$ g cm^{-3}. Of 19437 reflections up to $2\theta = 50.7^\circ$, 4424 were independent ($R_{int} = 0.038$) and 4424 were with $I > 2\ \sigma(I)$. The structure was solved by direct methods and refined with a full matrix against all F^2 data. Hydrogen atoms were calculated in riding positions. $R = 0.0363$, $wR = 0.1042$.

[30] Crystallographic data for **3b**: $C_{32}H_{22}N_2S_2$, $a = 8.4421(4)$, $b = 21.9504(9)$, $c = 13.8442(6)$Å, $\beta = 109.9164(11)^\circ$, monoclinic, space group $C2/c$, $Z = 4$, $V = 2412.00(17)$ Å^3, ρ_{calc}=1.373 g cm−3. Of 9728 reflections up to $2\theta = 50.7^\circ$, 2218 were independent ($R_{int} = 0.025$) and 2218 were with $I > 2\sigma(I)$. The structure was solved by direct methods and refined with a full matrix against all F^2 data. Hydrogen atoms were calculated in riding positions. $R = 0.0512$, $wR = 0.1407$.

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