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Synthesis and photochromic reactivity of diarylethene trimers bridged by ethenyl and ethynyl unit

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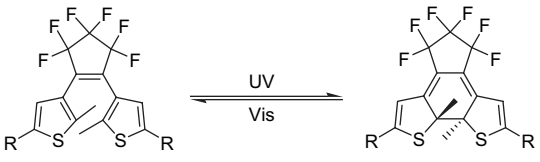
Abstract—Two diarylethene trimers bridged by ethenyl and ethynyl groups were synthesized and their photochromic behaviors were examined. Upon irradiation of the trimers **2** and **4** with UV light, one–three photoinduced cyclization reactions occur. Each isomer was isolated and analyzed by ^{1}H NMR spectrum. The quantum yield of **2** and **4** is 0.52 and 0.311, respectively.

1. Introduction

Photochromic compounds undergo reversible transformation between two distinct chemical isomers with different colors of light.[1] The photoreaction can be accompanied by changes in useful physical properties such as refractive index,[2] luminescence,[3] electronic conductance,[4] and optical rotation.[5] Photochromic diarylethene is very suitable for these purposes, due to their thermal stability and high fatigue resistance.[6] Some of these photoswitching effects are based on the changes in the extent of π-conjugation in diarylethene upon photochromic reaction (Scheme 1). Any π-electrons on the R groups can interact with each other through the π-conjugation in the ring-closed state.[7] The functionalization of the photochromic unit is a major issue because of some reasons, such as tuning the absorption wavelength or creating a system that can be used for information storage.[8] In substituted dithienylethenes some of the substituents cause a strong decrease or even a complete loss of the photochromic behavior.[9] It has been assumed that the photochromic state of one photochrome will influence the reactivity of another photochrome when they are covalently joined. Among the various types of diarylethene dimers connected with single bond,[10] phenylene,[11] ethynylene,[12] and diyne,[13] in most cases only one of the diarylethenes can convert to the closed-ring form upon UV irradiation. Even though some studies have been performed to clarify the effect of substituents,[14] a more general understanding of the way in which one photochromic unit interacts with another photochromic unit in a molecule is an important issue for practical applications. We envisioned that the strategic placement of diarylethene units within a macromolecular framework would help to understand the interaction between the diarylethene units. We now describe (i) the synthesis of macromolecules having three diarylethene units; (ii) their photochromic reactivities; (iii) the isolation of photocyclized products; (iv) the effect of bridging unit.



Scheme 1.

2. Results and discussion

2.1. Synthesis

Diarylethene trimers **2** and **4** were prepared according to the synthetic method shown in Schemes 2 and 3. Compound **2** was synthesized from 1,3,5-tris((*E*)-2-(tributylstannyl)-vinyl)benzene[15] in two steps. Stille cross coupling reaction of the stannyl with 3,5-dibromo-2-methylthiophene,[16] followed by the reaction of lithiated **1** with 4-(perfluorocyclopent-1-enyl)-2-phenylthiophene,[16] gave **2** in 50% yield. Compound **4** was synthesized in two steps from

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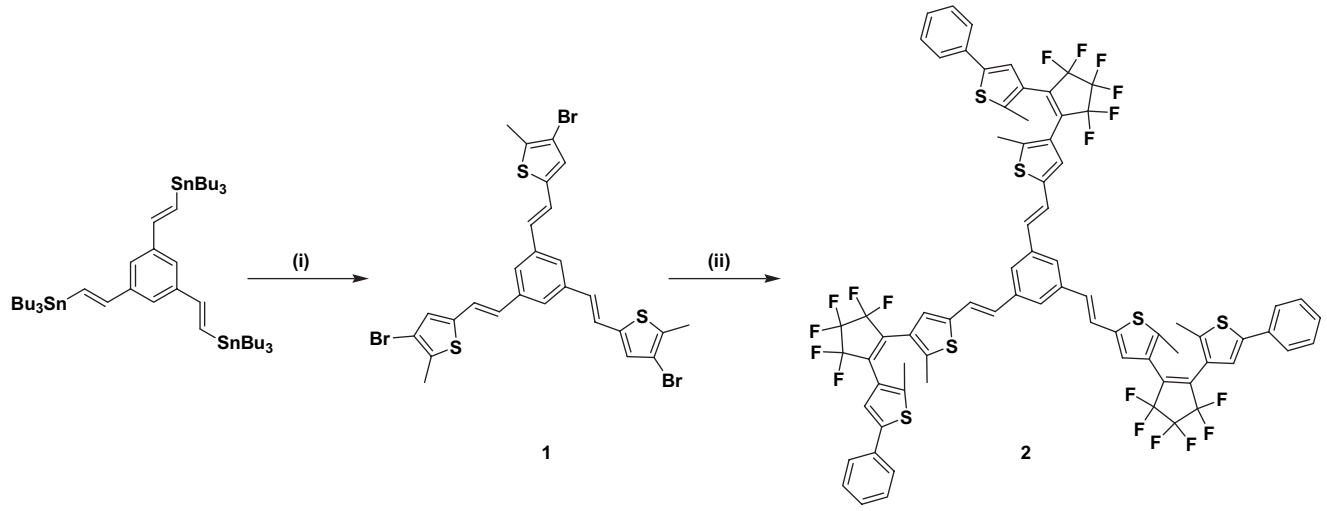
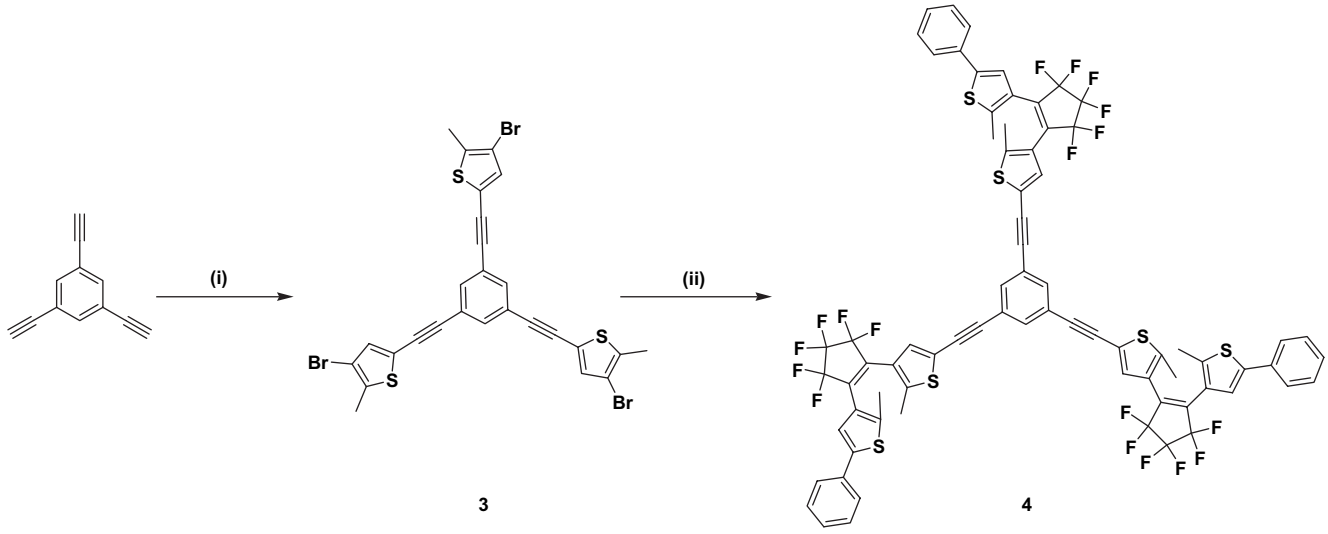


Scheme 2. (i) 3,5-Dibromo-2-methylthiophene, $Pd(PPh_3)_2Cl_2$, CsF in toluene; (ii) 4-(perfluorocyclopent-1-enyl)-2-phenylthiophene, *n*-BuLi in THF.



Scheme 3. (i) 3,5-Dibromo-2-methylthiophene, $Pd(PPh_3)_4$, CuI, NEt_3; (ii) 4-(perfluorocyclopent-1-enyl)-2-phenylthiophene, *n*-BuLi in THF.

1,3,5-triethynylbenzene.[17] Sonogashira coupling of 1,3,5-triethynylbenzene with 3,5-dibromo-2-methylthiophene followed by the reaction of lithiated **3** with 4-(perfluorocyclopent-1-enyl)-2-phenylthiophene yielded **4**. Spectroscopic data for **2** and **4** are completely consistent with their proposed structures. One resonance at 1.97 ppm for **2** and **4** in the ^1H NMR spectrum for the methyl group is observed. The mass spectra of **2** and **4** showed a molecular ion at *m*/*z* 1482 and 1476, respectively.

2.2. Photochromism of trimer 2 in chloroform

Figure 1 shows the absorption spectra of **2** in chloroform upon photoirradiation. Upon irradiation of **2** with 365 nm light, the colorless solution of the open-ring form turned blue, in which initial maximum was observed at 594 nm. It grew with shifting of the absorption maximum, and reached the photostationary state after 6 min. Upon visible light irradiation (λ>532 nm) for 2 h, the colored solution was

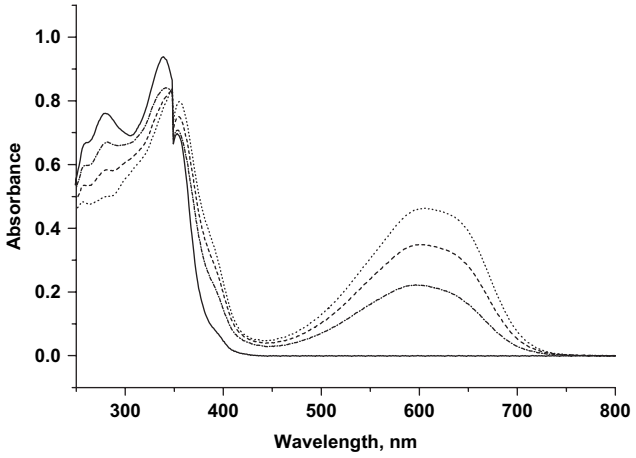
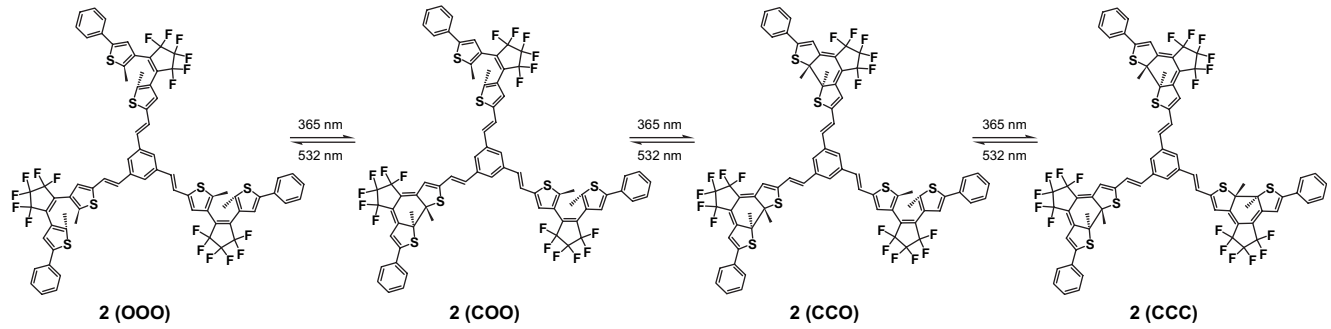


Figure 1. Absorption spectral change of the trimer **2** in chloroform upon irradiation with 365 nm light: (—) before irradiation, (-·-·-) after UV light irradiation for 2 min, (- - -) for 4 min, (···) for **8**.



Scheme 4. The photochromic reactivity of **2**.

completely bleached, indicating return to the initial open-ring isomer. In first 2 min of irradiation, an absorption band centered at 594 nm rapidly grows in as most of the **2** is converted from the colorless-open form **2** (OOO) to the blue-closed form **2** (COO) (Scheme 4). The presence of an isosbestic point at 342 nm indicates that **2** (OOO) is cleanly converted to a second photocyclized product. The closed-ring isomer **2** (COO) was isolated from the above blue colored solution by HPLC (silica gel, eluent hexane/ethyl acetate (10:1)) in 74% yield. Further irradiation (2 min) of **2** (COO) with 365 nm light afforded the anticipated red-shift of the absorption maximum at 602 nm that would have resulted from the two closed-ring isomers **2** (CCO). The photoirradiated product **2** (CCO) was analyzed with HPLC from the above solution. The fully closed-ring isomer **2** (CCC) can be achieved after an 8 min irradiation period of **2** (OOO) using 365 nm light in 52% yield. Absorption maximum of **2** (CCC) at 610 nm is shifted to longer wavelength by 8 nm in comparison with that of **2** (CCO) due to the extension of π-conjugation. The photogenerated ring-closed isomers **2** (COO), **2** (CCO), and **2** (CCC) were stable at room temperature. Figure 2 shows the ^{1}H NMR spectrum of methyl proton of **2** (OOO) in $CDCl_3$ before photoirradiation and in the ring-closed form **2** (COO), **2** (CCO), and **2** (CCC). In the ^{1}H NMR spectrum of **2** (OOO), one methyl resonance was observed at 1.97 ppm. In the blue isomer **2** (COO), one distinct new band appeared at 2.16 ppm, together with one singlet at 1.97 ppm. The integral ratio of the two signals was 1:2, indicating that the colored isomer is **2** (COO). Another key feature of **2** (COO) is the presence of four new thienyl signals at 7.28, 7.10, 6.70, and 6.42 ppm. The two new resonances at 6.70 and 6.42 ppm are significantly shifted up-field as would be expected for the ring-closed isomer. Such an up-field shift was observed in covalently linked double 1,2-dithienylethenes[10–13] and macromolecules[18] incorporating four dithienylethene units. The dissymmetric nature of the photogenerated product indicates that one of three thienyl units has cyclized to form **2** (COO). Figure 2c shows the ^{1}H NMR spectrum of methyl protons of **2** (CCO) separated from the photogenerated product by HPLC after the photoirradiation of **2** (OOO) for 4 min. Two distinct bands appeared at 2.16 and 1.97 ppm. The integral ratio of the two signals was 2:1, which indicates that the colored isomer is **2** (CCO). Figure 2d shows the ^{1}H NMR spectrum of methyl protons of **2** (CCC). One distinct band appeared at 2.16 ppm, demonstrating that **2** (OOO) was completely converted into the closed form **2** (CCC).

2.3. Photochromism of trimer 4 in chloroform

Figure 3 shows the absorption spectrum of trimer **4** in chloroform upon UV light irradiation. Irradiation of chloroform solution of **4** at 365 nm light resulted in an immediate increase in the absorption intensity at 607 nm. It grew with shifting of the absorption maximum to red-shifted region. Upon visible light irradiation (λ>532 nm) for 6 h, the blue colored solution was completely bleached. After the irradiation of **4** (OOO) for 2 min, the photogenerated products were analyzed with HPLC (silica gel, eluent hexane/ethyl acetate (9:1)). The elution peaks were detected at the isosbestic point of 342 nm. The open-ring form **4** (OOO) was eluted at 14 min. The photogenerated solution gave two peaks at

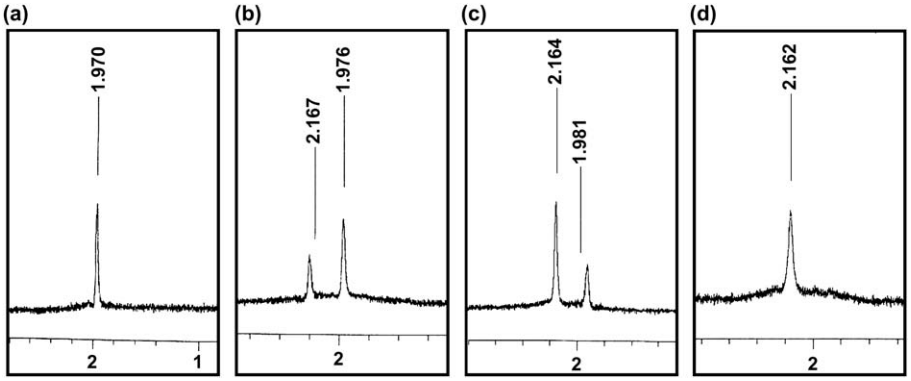


Figure 2. ^{1}H NMR methyl signals of the (a) **2** (OOO) trimer; (b) **2** (COO) trimer; (c) **2** (CCO) trimer; and (d) **2** (CCC) trimer.

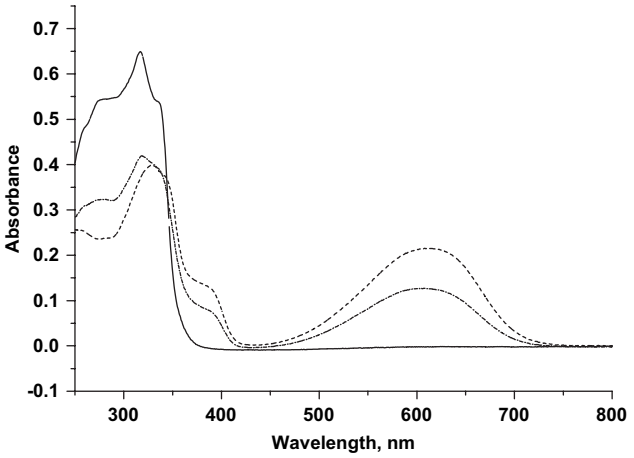


Figure 3. Absorption spectral change of the trimer **4** in chloroform upon irradiation with 365 nm light: (—) before irradiation, (-·-·-) after UV light irradiation for 2 min, (- - -) for 8 min.

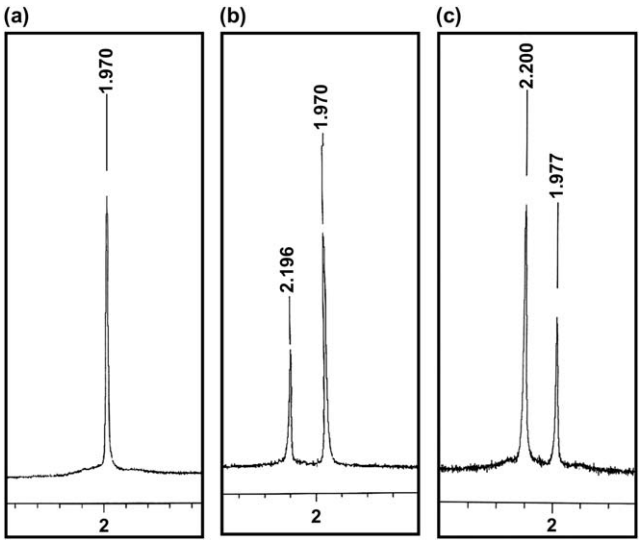
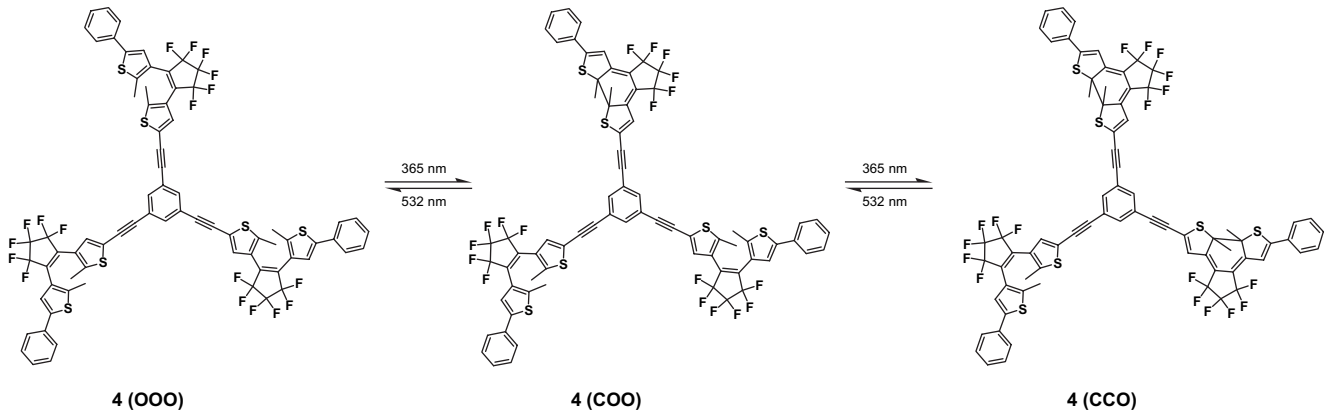


Figure 4. ^{1}H NMR methyl signals of the (a) **4** (OOO) trimer; (b) **4** (COO) trimer; and (c) **4** (CCO) trimer.

11 and 14 min. As the peak at 14 min can be assigned to be **4** (OOO), the peak at 11 min can be assigned as a photocyclized product. The ^{1}H NMR spectrum is demonstrated to be **4** (COO) (Scheme 5). Further irradiation (2 min) of **4** (COO) with 365 nm light gave the deep blue solution. The photogenerated products were analyzed with HPLC (silica gel, eluent hexane/ethyl acetate (9:1)). When monitored at the isosbestic point of 342 nm, two peaks were observed. The first peak of the isomer had an absorption maximum at 615 nm. The product was proven to be **4** (CCO) based on the ^{1}H NMR. Further irradiation of **4** (CCO) (4 min) with 365 nm light did not afforded the anticipated red-shift of the absorption maximum that would have resulted from the fully ring-closing isomer. Instead, the increase in the absorbance levels off. The ^{1}H NMR spectroscopy is a useful tool that determines the exact ratio between the open and closed forms. The most suitable signals, showing the largest shifts upon cyclization, are those of the methyl groups on the thiophene rings. Figure 4 shows the ^{1}H NMR spectrum of methyl protons **4** (OOO) in $CDCl_3$ before photoirradiation and in the ring-closed form **4** (COO) and **4** (CCO). In the ^{1}H NMR spectrum of **4** (OOO), only one methyl signal was observed at 1.97 ppm. In the ^{1}H NMR spectrum of blue isomer **4** (COO), a new methyl signal appeared at 2.20 ppm, together with one singlet at 1.97 ppm. The integral ratio of the two signals was 1:2, indicating that the colored isomer is **4** (COO). Figure 4c shows the ^{1}H NMR spectrum of methyl protons of **4** (CCO). The methyl protons show two resonances at 2.20 and 1.97 ppm with the integral ratio of 2:1. This indicates that two closed-ring forms **4** (CCO) are included in the trimer.

2.4. Quantum yield

The quantum yield of the macromolecules **2** and **4** are measured using 1,2-bis(2-methyl-3-thienyl)perfluorocyclopentene (TF_6) as a reference.[19] The cyclization quantum yield of **2** from the all open-ring form **2** (OOO) to the isomer **2** (COO), from **2** (COO) to the **2** (CCO), and **2** (CCO) to the all closed-ring form **2** (CCC) was determined to be 0.23, 0.18, and 0.11, respectively. The total cyclization quantum yield is 0.52, which is much higher than that of tridithienylethene array.[12] The quantum yield of **4** was determined to be 0.311. The cycloreversion quantum yield of **2** (CCC) and **4** (CCO) was measured to be 8.4×10^{-4} and 8.2×10^{-4}, respectively.



Scheme 5. The photochromic reactivity of **4**.

2.5. MO calculation

Our interests are focused on examining the electronic communication between three intimately connected 1,2-dithienylethene photochromes in **2** and **4**. It is assumed that the photochromic state of one photochrome will influence the reactivity of another when they are covalently joined. In compounds **2** and **4**, we wondered why three dithienylethene units in **2** (OOO) are converted into the all closed-ring form **2** (CCC), and on the other hand, only two dithienylethene units in **4** (OOO) are partially converted into **4** (CCO). To clarify the effect of bridged unit in **2** and **4**, we have carried out ab initio calculations. Molecular orbital calculation for the compounds **2** and **4** were performed using Gaussian 03 program at the B3LYP/3-21G* level. Geometry was optimized at this level. The HOMO in **2** (CCC) is delocalized over the π-conjugated systems via the two thienylethene unit (Fig. 5, **2a**). The LUMO in **2** (CCC) is delocalized through three dithienylethene units. On the other hand, the HOMO in **4** (CCC) is localized on a dithienyl unit (Fig. 5, **4a**) and the LUMO in **4** (CCC) is delocalized through two dithienyl units. Examination of the HOMO and the LUMO of **2** (CCC) and **4** (CCC) indicates that the photochromic state of one photochrome in **2** bridged by ethenyl unit influences well the reactivity of another, compared with **4** bridged by ethynyl unit resulting in the all closed-ring form.

In summary, we have prepared two macromolecules incorporating three dithienylethene units. Upon irradiation of **2** (OOO) with UV light, one, two, and three photoinduced cyclization reaction occurs. Each isomer was isolated and analyzed by ^{1}H NMR spectrum. The quantum yield of **2** and **4** are 0.52 and 0.311, respectively. The formation of all closed-ring form **2** (CCC) is due to the delocalization of the π-conjugated systems through the three dithienylethene units.

3. Experimental

3.1. General

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. Perfluorocyclopentene was purchased from Fluorochem. 1,3,5-Tris((*E*)-2-(tributylstannyl)vinyl)benzene,[15] 3,5-dibromo-2-methylthiophene,[16] and 4-(perfluorocyclopent-1-enyl)-2-phenylthiophene[16] were synthesized using previous references. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer. The absorption was recorded on a Perkin–Elmer Lambda 2S UV–vis spectrometer.

3.2. Determination of quantum yields

The quantum yield of the photochromic ring-cyclization of **2** and **4** was determined from the absorption changes at λ_{max} in UV spectra upon excitation with a UV light for ring closure and visible light for ring opening reaction. Conversion and the number of absorbed photons were determined at a given radiation power and absorbance of the sample. Then,

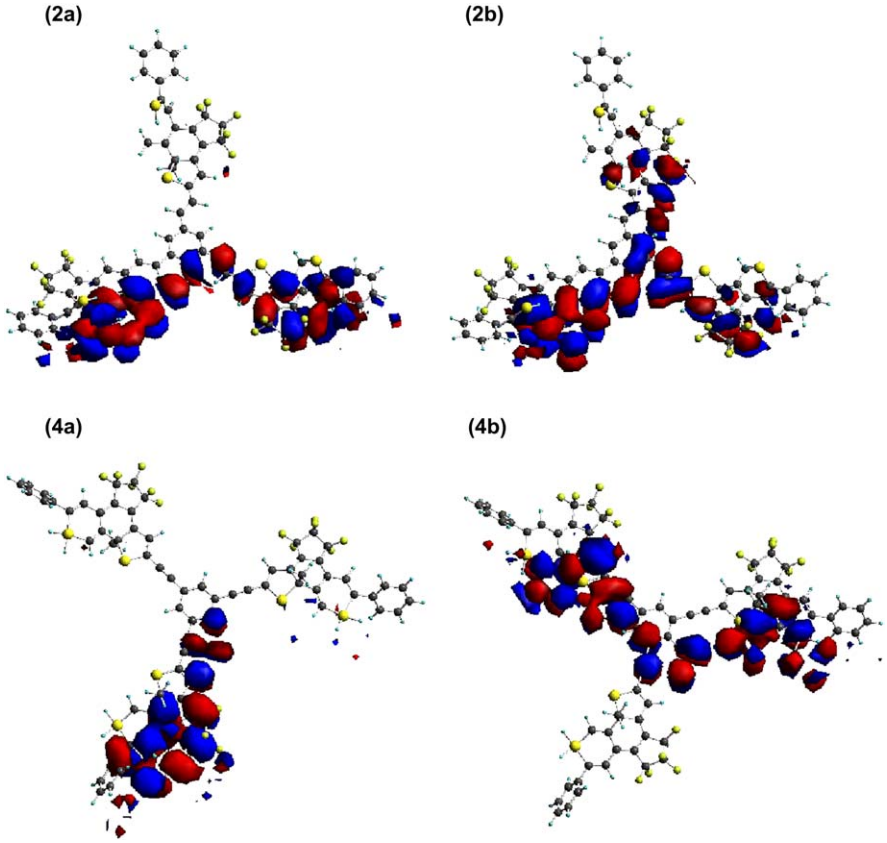


Figure 5. Representation of (a) HOMO and (b) LUMO of **2** (CCC); (a) HOMO and (b) LUMO of **4** (CCC) based on Gaussian 03 program at the B3LYP/3-21G* level.

quantum yield was determined according to the method described in Ref. 19.

3.2.1. Compound 1. To a mixture of 1,3,5-tris((*E*)-2-(tributylstannyl)vinyl)benzene (0.1 g, 0.1 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 10 mol %), and CsF (0.027 g, 0.66 mmol) in toluene (30 mL) was added 3,5-dibromo-2-methylthiophene (84.4 mg, 0.33 mmol). The solution was refluxed for 20 h. After cooling the solution, H_2O (10 mL) and brine were added to the solution. The organic layer was separated and dried in $MgSO_4$. The solvent was removed in vacuo. The pure product **1** was obtained by chromatographic work-up (1:3 ethyl acetate/hexane, R_f=0.5) as a yellow solid in 70% yield. Mp: 176 °C. ^{1}H NMR ($CDCl_3$): δ 7.37 (s, 3H), 7.11 (d, J=16.2 Hz, 3H), 6.89 (s, 3H), 6.79 (d, J=16.2 Hz, 3H), 2.40 (s, 9H).^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.5, 134.8, 133.6, 130.7, 129.2, 127.6, 126.8, 109.7, 14.5. MS: *m*/*z* 683 [M^+]. Anal. Calcd for $C_{27}H_{21}Br_3S_3$: C, 47.59; H, 3.11. Found: C, 47.46; H, 3.06.

3.2.2. Compound 2. To a stirred THF solution (50 mL) of **1** (0.31 g, 0.45 mmol) was added *n*-BuLi (1.43 mL, 2.29 mmol, 1.6 M in hexane) at −78 °C under argon atmosphere, and stirred for 1.5 h at the temperature. 4-(Perfluorocyclopent-1-enyl)-2-phenylthiophene (0.84 g, 2.29 mmol) in THF (5 mL) was slowly added to the solution at −78 °C and stirred for 3 h at the temperature. The reaction mixture was quenched by the addition of H_2O (1 mL). The product was extracted with ether. The organic layer was dried over $MgSO_4$. The pure product **2** was obtained by chromatographic work-up (1:5 ethyl acetate/hexane, R_f=0.3) as a blue solid in 70% yield. Mp: 143 °C. ^{1}H NMR ($CDCl_3$): δ 7.55 (d, J=8.1 Hz, 6H), 7.42 (s, 3H), 7.39 (t, J=6.2 Hz, 6H), 7.31 (t, J=7.1 Hz, 3H), 7.28 (s, 3H), 7.20 (d, J=16.2 Hz, 3H), 7.10 (s, 3H), 6.81 (d, J=16.2 Hz, 3H), 1.97 (s, 18H).^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.3, 141.4, 140.7, 137.6, 136.4, 133.4, 129.4, 128.8, 128.4, 127.7, 126.8, 125.9, 125.7, 124.1, 122.9, 122.1, 119.7, 116.3, 112.9, 111.1, 14.8. MS: *m*/*z* 1482 [M^+]. Anal. Calcd for $C_{75}H_{48}F_{18}S_6$: C, 60.72; H, 3.26. Found: C, 60.45; H, 3.13.

3.2.3. Compound 3. To a degassed mixture of 1,3,5-triethynylbenzene (0.576 g, 3.9 mmol), $Pd(PPh_3)_4$ (0.67 g, 0.58 mmol), and CuI (0.044 g, 0.24 mmol) in Et_3N (50 mL) was added 3,5-dibromo-2-methylthiophene (5 g, 19.5 mmol). The mixture was stirred at 45 °C for 7 h. The solvent was evaporated under reduced pressure. The pure product **3** was obtained by chromatographic work-up (1:10 ethyl acetate/hexane, R_f=0.5) as a pale yellow solid in 65% yield. Mp: 165 °C. ^{1}H NMR ($CDCl_3$): δ 7.55 (s, 3H), 7.08 (s, 3H), 2.41 (s, 9H).^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.2, 134.7, 133.7, 123.7, 120.2, 109.3, 91.9, 83.3, 15.1. MS: *m*/*z* 675 [M^+]. Anal. Calcd for $C_{27}H_{15}Br_3S_3$: C, 48.02; H, 2.24. Found: C, 47.75; H, 2.14.

3.2.4. Compound 4. To a stirred THF solution (50 mL) of **3** (0.2 g, 0.29 mmol) was added *n*-BuLi (0.93 mL, 1.48 mmol, 1.6 M in hexane) at −78 °C under argon atmosphere, and the solution was stirred for 1.5 h at the temperature. 4-(Perfluorocyclopent-1-enyl)-2-phenylthiophene (0.54 g, 1.48 mmol) in THF (5 mL) was slowly added to the solution at −78 °C, and stirred for 3 h at the temperature. The reaction mixture was quenched by the addition of H_2O (1 mL). The product was extracted with ether. The organic layer was dried over $MgSO_4$. The pure product **4** was obtained by chromatographic work-up (1:5 ethyl acetate/hexane, R_f=0.5) as a blue solid in 50% yield. Mp: 136 °C. ^{1}H NMR ($CDCl_3$): δ 7.60 (s, 3H), 7.55 (d, J=7.1 Hz, 6H), 7.39 (t, J=7.2 Hz, 6H), 7.33 (s, 3H), 7.32 (d, J=7.2 Hz, 3H), 7.29 (s, 3H), 1.97 (s, 18H).^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.1, 142.6, 141.4, 133.8, 133.3, 132.3, 129.1, 128.5, 128.1, 125.7, 125.6, 125.3, 123.7, 122.3, 121.1, 119.5, 116.2, 113.8, 92.1, 83.2 14.6. MS: *m*/*z* 1476 [M^+]. Anal. Calcd for $C_{75}H_{42}F_{18}S_6$: C, 60.97; H, 2.87. Found: C, 60.62; H, 2.72.

3.2.5. Closed-ring isomer of 2 (COO). ^{1}H NMR ($CDCl_3$): δ 7.55 (d, J=8.1 Hz, 6H), 7.42 (s, 3H), 7.39 (t, J=6.2 Hz, 6H), 7.31 (t, J=7.1 Hz, 3H), 7.28 (s, 2H), 7.20 (d, J=16.2 Hz, 3H), 7.10 (s, 2H), 6.81 (d, J=16.2 Hz, 3H), 6.70 (s, 1H), 6.42 (s, 1H), 2.16 (s, 6H), 1.97 (s, 12H).

3.2.6. Closed-ring isomer of 2 (CCO). ^{1}H NMR ($CDCl_3$): δ 7.55 (d, J=8.1 Hz, 6H), 7.42 (s, 3H), 7.39 (t, J=6.2 Hz, 6H), 7.31 (t, J=7.1 Hz, 3H), 7.28 (s, 1H), 7.20 (d, J=16.2 Hz, 3H), 7.10 (s, 1H), 6.81 (d, J=16.2 Hz, 3H), 6.70 (s, 2H), 6.42 (s, 2H), 2.16 (s, 12H), 1.97 (s, 6H).

3.2.7. Closed-ring isomer of 2 (CCC). ^{1}H NMR ($CDCl_3$): δ 7.55 (d, J=8.1 Hz, 6H), 7.39 (t, J=6.2 Hz, 6H), 7.31 (t, J=7.1 Hz, 3H), 7.20 (d, J=16.2 Hz, 3H), 6.81 (d, J=16.2 Hz, 3H), 6.70 (s, 3H), 6.42 (s, 3H), 2.16 (s, 18H).

3.2.8. Closed-ring isomer of 4 (COO). ^{1}H NMR ($CDCl_3$): δ 7.60 (s, 3H), 7.55 (d, J=7.1 Hz, 4H), 7.42 (d, J=7.1 Hz, 2H), 7.39 (t, J=7.2 Hz, 6H), 7.33 (s, 2H), 7.32 (d, J=7.2 Hz, 3H), 7.29 (s, 2H), 6.68 (s, 1H), 6.50 (s, 1H), 2.19 (s, 6H), 1.97 (s, 12H).

3.2.9. Closed-ring isomer of 4 (CCO). ^{1}H NMR ($CDCl_3$): δ 7.60 (s, 3H), 7.55 (d, J=7.1 Hz, 2H), 7.42 (d, J=7.1 Hz, 4H), 7.39 (t, J=7.2 Hz, 6H), 7.33 (s, 1H), 7.32 (d, J=7.2 Hz, 3H), 7.29 (s, 1H), 6.68 (s, 2H), 6.51 (s, 2H), 2.19 (s, 12H), 1.97 (s, 6H).

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