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Synthesis and photochromic reactivity of macromolecules incorporating four dithienylethene units

Il Jung,[a] Hyunbong Choi,[a] Eunkyoung Kim,[b] Chai-Ho Lee,[c] Sang Ook Kang[a,*] and Jaejung Ko[a,*]

[a]*Department of Chemistry, Korea University, Jochiwon, Chungnam 339-700, South Korea*
[b]*Department of Chemical Engineering, Yonsei University 134 Sinchon-dong, Seodaemoon-gu, Seoul 120-749, South Korea*
[c]*Department of Chemistry, Wonkwang University, Iksan, Jeonbuk 570-749, South Korea*

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Abstract—Two macrocycles bearing four dithienylethene units were synthesized. Upon irradiation of the macrocycles **5** and **6** with ultraviolet light, only one or two photo-induced cyclization reaction occurs. Each isomers were isolated and analyzed by ^{1}H NMR spectrum. The quantum yield of **5** and **6** are 0.58 and 0.64, respectively. The high value is due to the presence of enforced antiparallel conformation in the macrocycles **5** and **6**.

1. Introduction

The conformationally rigid and shape-persistent supramolecules of nanometer size have attracted much interest because of their potential in host–guest systems,[1] fluorescence ion sensor,[2] self-aggregation,[3] organometallic coordination,[4] and liquid crystal.[5] The design of geometrically well-defined supramolecules will play an important role because the incorporation of orientationally-controlled functional units into molecules can be utilized as the encoding of information.[6] The combination of the self-assembly and photochromic unit promises to be useful in optical technological devices.[7] Photochromic 1,2-diarylethene is very suitable for this purpose, due to the remarkable thermal stability and high fatigue resistance.[8] The open-ring isomer of diarylethene has two conformations—antiparallel and parallel—in equal amounts. The conrotatory cyclization can proceed only from the antiparallel conformation. Therefore, the cyclization quantum yield cannot exceed 50% in solution. To achieve high quantum yield, it is required to increase the population of the antiparallel conformers. Thus, diarylethene—backbone photochromic polymer,[9] multi-dithienylethene arrays,[10] and diarylethene in the crystal lattice[11] showed a high cyclization quantum yield due to the geometrical restriction. In a recent development, new dithienylethene based mono- and multi-substituted phthalocyanine and tetraazaporphyrin hybrids have been introduced in the form of a macrocyclic photochromic system.[12] We envisioned that the strategic placement of diarylethene units within a macrocyclic framework would achieve high quantum yield because the macromolecule has the enforced antiparallel conformation of the diarylethene units. We now describe (i) the synthesis of macromolecules having diarylethene units; (ii) their photochromic reactivities; (iii) the isolation of photocyclized products.

2. Results and discussion

Our strategy for the synthesis of macrocycles is to incorporate the diarylethene units within a macrocyclic framework. New macromolecules **5** and **6** are conveniently synthesized in four steps from the 1,2-bis[2-methyl-5-bromo-3-thienyl]perfluorocyclopentene. The palladium-catalyzed cross-coupling of 1,3-diethynylbenzene with **1** afforded **2** in 53% yield. The Sonogashira coupling of **2** with 2.2 equiv of trimethylsilylacetylene followed by basic hydrolysis yielded **4**. Our synthesis of macrocycles **5** and **6** was prepared by the cross-coupling reaction of **2** with **4** and coupling reaction[13] of the dialkyne **4** with *trans*-$Pt(PEt_3)_2Cl_2$, respectively (Scheme 1). Spectroscopic data for **5** is completely consistent with its proposed structures. Four resonances at 2.07, 2.06, 1.96, and 1.95 ppm in the ^{1}H NMR spectrum and two peaks at 15.6 and 14.5 ppm in ^{13}C NMR spectrum of **5** for the methyl group are observed. The

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* Corresponding authors. Tel.: +82 41 860 1337; fax: +82 41 867 5396; e-mail: jko@korea.ac.kr

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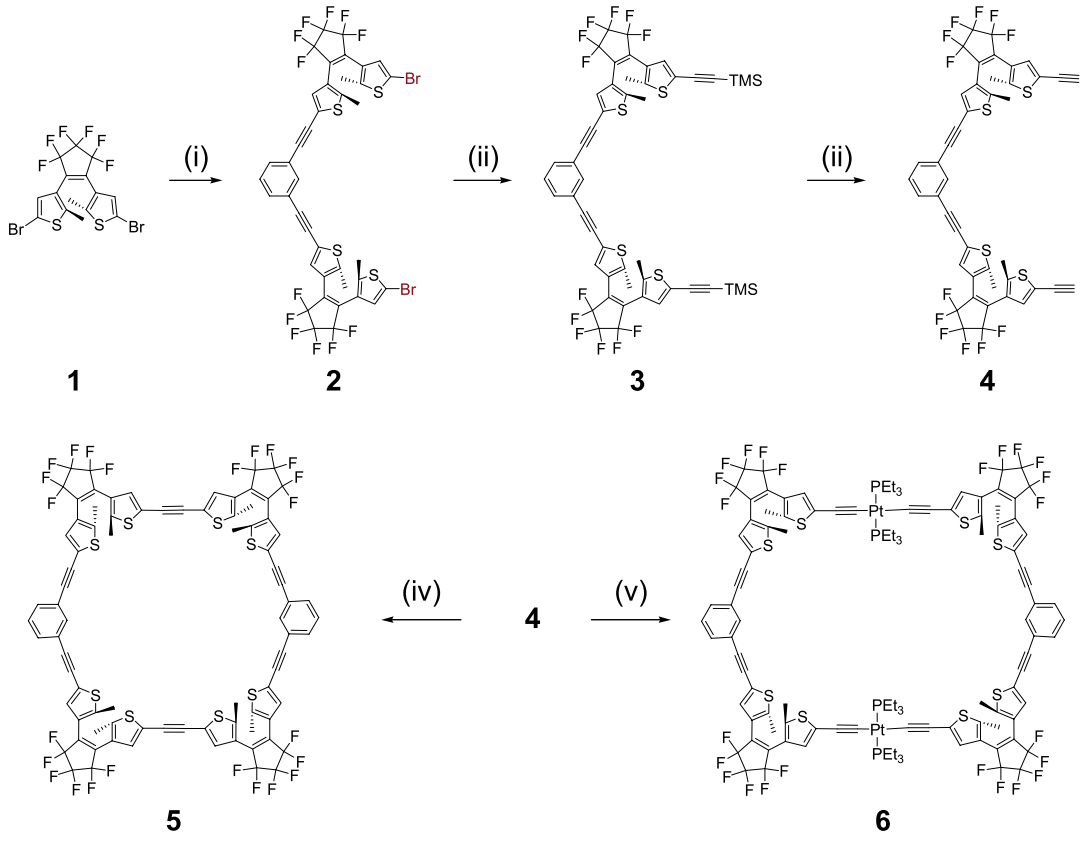


Scheme 1. Reagents and conditions: (i) 1,3-diethynylbenzene, $Pd(PPh_3)_4$, CuI in NEt_3; (ii) $Me_3SiC{\equiv}CH$, $Pd(PPh_3)_4$, CuI in NEt_3; (iii) KOH in MeOH and THF, then H_2O; (iv) **2**+**4**, $Pd(PPh_3)_2Cl_2$, P(*o*-tolyl)$_3$, CuI in NEt_3; (v) **4**, *trans*-$Pt(PEt_3)_2Cl_2$, CuCl in Et_2NH.

mass spectrum of **5** showed a molecular ion at *m/z* 1760. Compound **6** was characterized by ^1H, ^{13}C, and ^{31}P NMR, mass spectroscopy, and elemental analysis. The initial indication of the macromolecule **6** stemmed for the observation of an ion in the mass spectrum at *m/z* 2637. Three peaks in the ^1H NMR spectrum (1.96, 1.95, and 1.85 ppm) and four peaks at 16.5, 15.1, 9.7, and 8.7 ppm in the ^{13}C NMR spectrum of **6** proved that a macrocycle is formed in **6**. The ^{31}P NMR spectrum of **6** shows a singlet at 5.84 ppm with a small coupling constant of $^1J_{PtP}$ (2348 Hz), which is consistent with the trans configuration of **6**.[13]

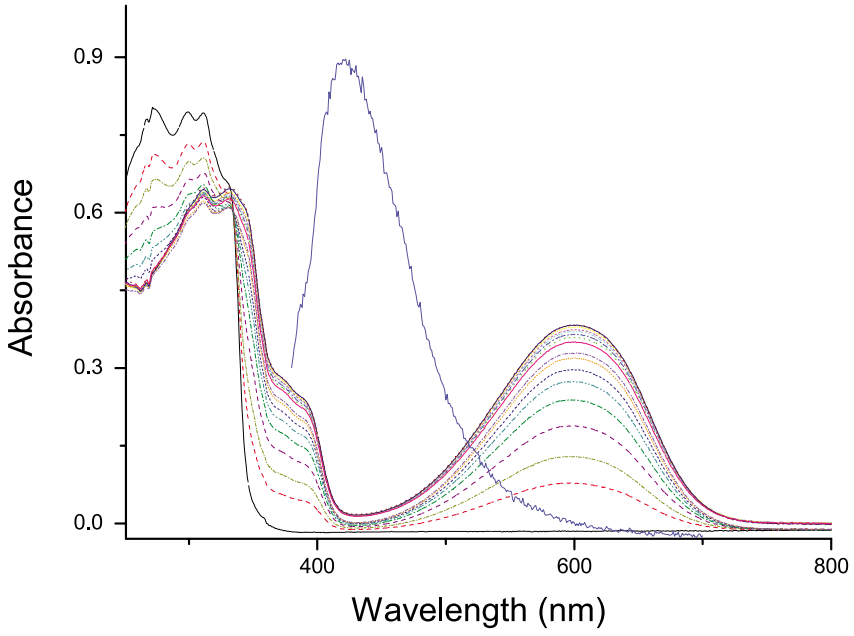


Figure 1. Absorption spectral change of **3** in chloroform upon irradiation with 325 nm light (- - -). Total irradiation periods are 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 150, 200, and 300 s. Steady-state fluorescence spectrum of the **3** (OO) (—) (excitation at 360 nm).

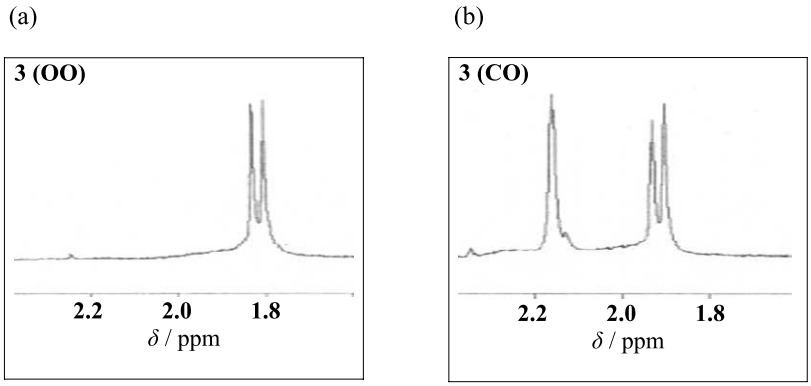
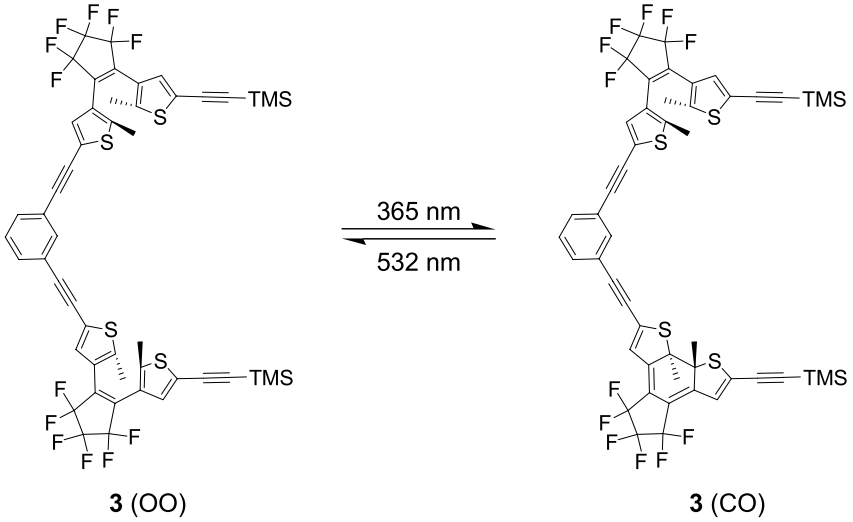


Figure 2. ^{1}H NMR methyl signals of (a) the **3** (OO) dimer; and (b) the **3** (CO) dimer.

Figure 1 shows a typical absorption spectral change of **3** in chloroform upon ultraviolet light irradiation. Irradiation of chloroform solution of **3** at 325 nm light resulted in an immediate increase in the absorption intensity at 600 nm. After visible light irradiation ($\lambda > 532$ nm) for 6 h, the colored solution was completely bleached. In the first 120 s of irradiation, an absorption band centered at 600 nm grows in as **3** is converted from the colourless-open form **3** (OO) to the blue-closed form **3** (CO). The presence of an isosbestic point at 334 nm indicates that **3** (OO) is cleanly converted to a second unique photocyclized product. The closed-ring isomer **3** (CO) was isolated from the blue colored solution by HPLC. The photogenerated ring-closed form **3** (CO) was stable at room temperature. Figure 2 shows the ^{1}H NMR spectrum of methyl protons of **3** in $CDCl_3$ before photoirradiation and in the ring-closed form, respectively. In the ^{1}H NMR spectrum of **3** (OO), two methyl resonances were observed at 1.83 and 1.80 ppm. In the blue isomer **3** (CO), one distinct new band was appeared at 2.16 ppm, together with two singlets at 1.93 and 1.88 ppm, which are slightly down-field shifted to those of **3** (OO). The integral ratio of the two signals was 1:1, which indicates that the colored isomer is a C– dimer. Another key feature in the ^{1}H NMR spectrum of **3** (CO) is the presence of four thienyl signals at 7.24, 7.22, 6.47, and 6.41 ppm. The two new resonances at 6.47 and 6.41 ppm are significantly up-field shifted as would be expected for the ring-closed isomer. Such an up-field shift was observed in covalently linked double 1,2-dithienylethenes.[10a] The dissymmetric nature of the photogenerated product indicates that only one of the thienyl units has cyclized to form **3** (CO) (Scheme 2). The fluorescence band of **3** (OO) ($\lambda = 420$ nm) shows a substantial spectral overlap with the absorption band of **3** (CO), and the Förster excitation energy transfer can take place from the photogenerated **3** (OO) to the colored form **3** (CO). Accordingly, the cyclization reaction of another open-ring form cannot take place. A similar result has been observed in the thienylethene dimer.[10]

Figure 3 shows the absorption spectral change of the macromolecule **5** in chloroform by photoirradiation. Upon irradiation with 325 nm light, the colourless solution of the open-ring isomer **5** (OOOO) with the absorption maximum at 313 nm turned blue, in which characteristic absorption maximum was observed at 602 nm. Upon visible ($\lambda > 532$ nm) light irradiation, the blue color was completely bleached.

The photogenerated products were analyzed with HPLC chromatograph (silica gel column, eluent: hexane/ethyl acetate 4:1). When monitored at the isosbestic point of 338 nm, three peaks were observed. The first peak isomer had the absorption maximum at 610 nm, while the absorption maximum of the second peak isomer was shifted



Scheme 2. The photochromic reactivity of **3**.

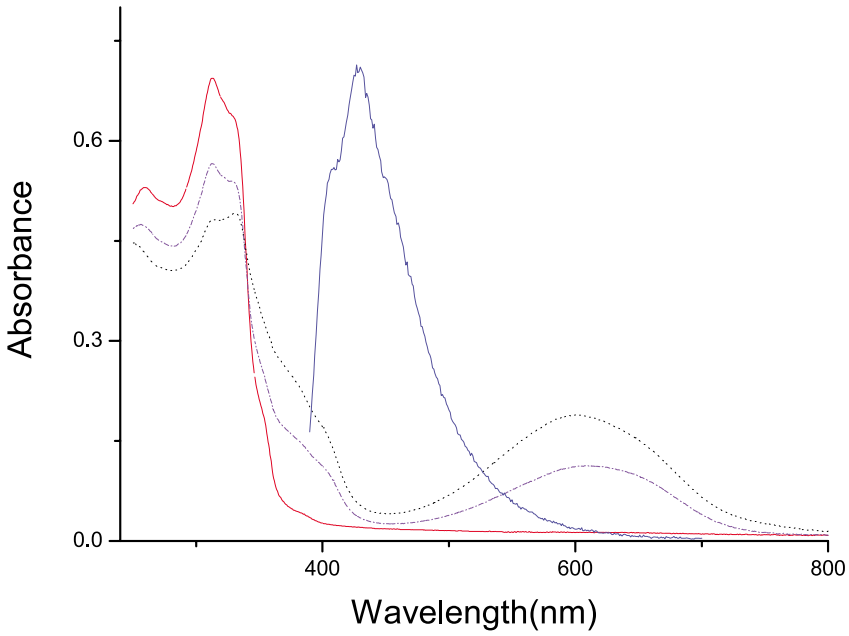


Figure 3. Absorption spectra of **5** (OOOO) (—), **5**(COOO) (– · – · –), and **5**(COCO) (- - -) in the photostaionary state under irradiation with 325 nm light, and fluorescence spectrum of **5** (OOOO) (—) in chloroform.

to 602 nm. The three isomers were isolated and analyzed by ^{1}H NMR. Figure 4 shows the ^{1}H NMR spectra of methyl protons of **5** in $CDCl_3$ before photoirradiation and in the ring-closed forms. The methyl protons of the first peak isomer show seven resonances at 2.18, 2.16, 2.07, 2.05, 1.96, 1.94, and 1.92 ppm. The first two signals at 2.18 and 2.16 ppm are assigned to the methyl protons of the closed-ring form. Other five signals are ascribed to the open-ring form. A characteristic feature in the ^{1}H NMR spectrum includes four singlets at 7.17, 7.13, 7.09, and 6.48 ppm in the region of thienyl protons. The new signal at 6.48 ppm is assigned to the proton of closed-ring thienyl unit. This indicates that the first peak isomer is due to the isomer having one closed-ring form **5** (COOO) (Scheme 3). The methyl protons of the second peak isomer show five resonances at 2.17, 2.07, 2.05, 1.97, and 1.95 ppm. The signal at 2.17 ppm is assigned to the protons of the closed-ring form. The integral ratio of a signal at 2.17 ppm with

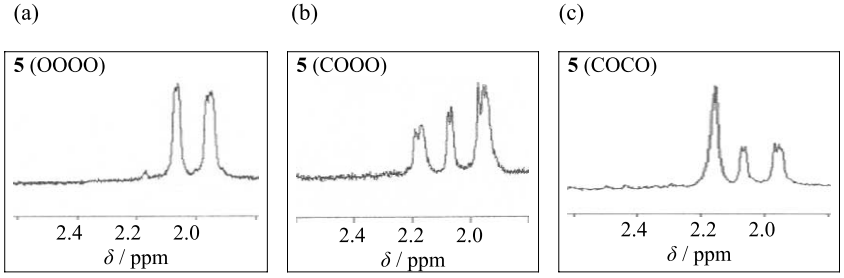
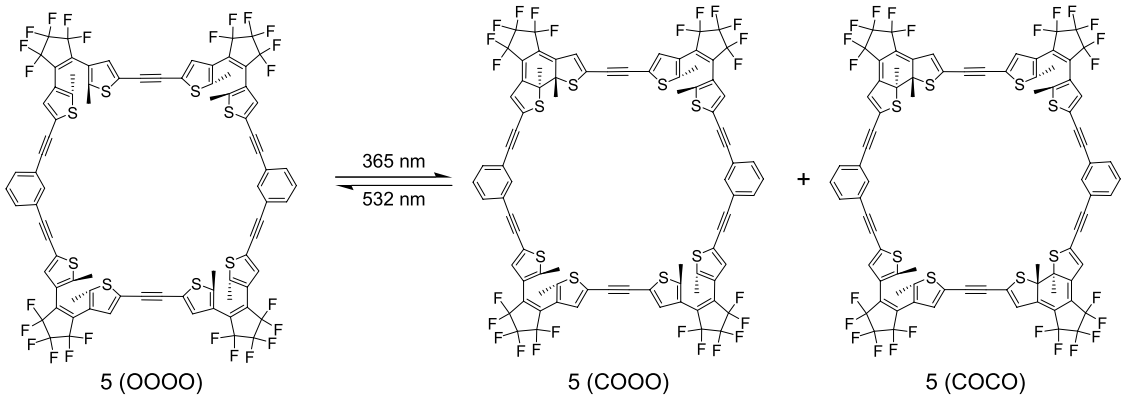
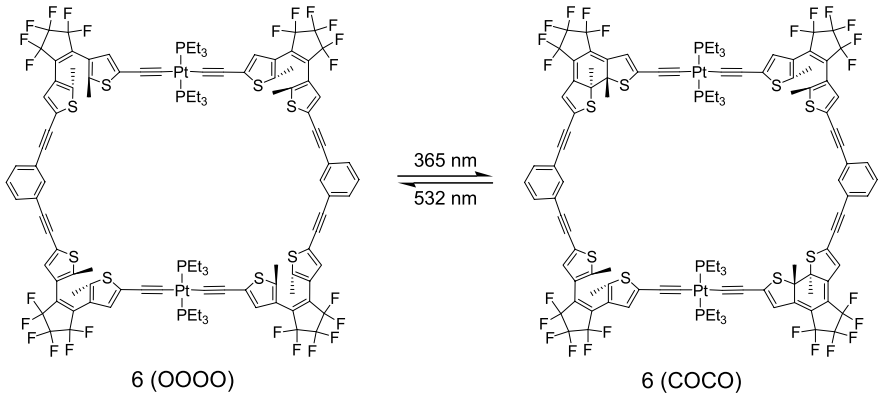


Figure 4. ^{1}H NMR methyl signals of the (a) **5** (OOOO); (b) **5** (COOO); and (c) **5** (COCO).



Scheme 3. The photochromic reactivity of **5**.



Scheme 4. The photochromic reactivity of **6**.

other signals is approximately 1:1. In addition, there are four distinct bands at 7.13, 7.09, 6.72, and 6.52 ppm in the thienyl region, in which the signals at 6.72 and 6.52 ppm is assigned to the closed-ring thienyl units. This indicates that two closed-ring form units are included in the macromolecule **5** (COCO). The methyl protons of the third peak isomer are identical to those of the open-ring form isomer **5** (OOOO). Excitation of **5** (OOOO) at 315 nm results in light emission with a maximum at 430 nm. Due to the spectral overlap of the fluorescence peak of **5** (OOOO) and absorption peak of **5** (COCO), followed by the Förster excitation energy transfer, the second peak isomer has the **5** (COCO) form. Such excited energy transfer is considered to prohibit the formation of further closed-ring form (Scheme 4).

Figure 5 shows the absorption spectra of **6** in chloroform before photoirradiation and in the photostationary state under irradiation with 325 nm light. Irradiation of chloroform solution of **6** at 325 nm light resulted in an immediate increase in the absorption intensity at 628 nm. The absorption maximum shifts to longer wavelength by 26 nm in comparison with **5**. Upon exposure of the dark blue solution to the visible light ($\lambda > 532$ nm) for 3 min, the colored solution was completely bleached. In the photostationary state, 88% of **6** is converted into the closed form. The closed-ring isomer **6** (COCO) is stable and isolated from the blue colored solution by HPLC. Figure 6 shows the ^{1}H NMR spectra of methyl protons of **6** in $CDCl_3$ before photoirradiation and in the ring-closed form. Before photoirradiation, three resonances are observed at 1.96, 1.95, and 1.85 ppm. In the ring-closed form, one new resonance appears at 2.14 ppm along with a decrease of the intensity of the three resonances. The strong one resonance at 2.14 ppm is assigned to the methyl protons of the closed form. No side reaction was detected from the ^{1}H NMR spectra.

The quantum yield of this macromolecules **5** and **6** are measured using 1,2-bis(2-methyl-3-thienyl)perfluorocyclopentene (TF_6) as a reference.[14] The cyclization quantum yield of **5** from the all open-ring form **5** (OOOO) to the **5** (COOO) isomer and form **5** (COOO) to the **5** (COCO) isomer was determined to be 0.33 and 0.25, respectively.

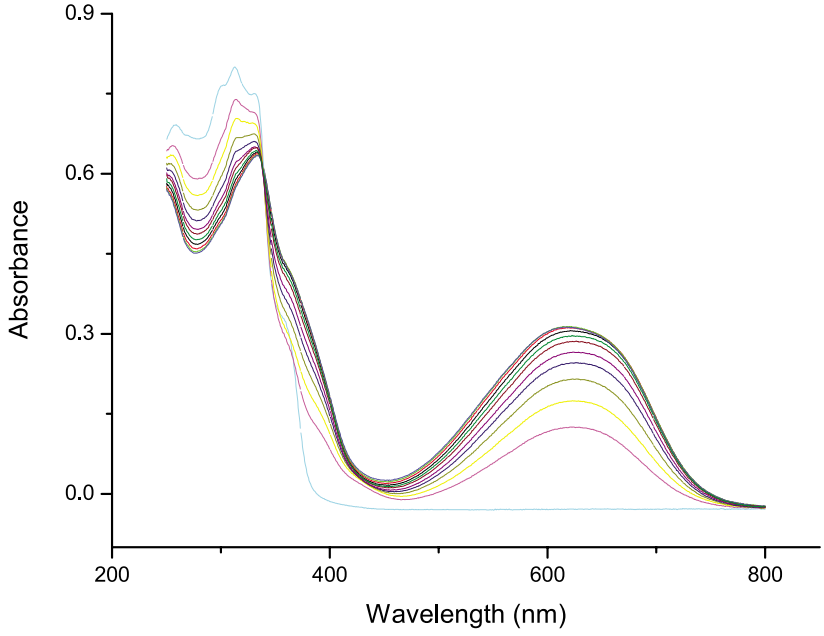


Figure 5. Absorption spectral change of **6** in chloroform upon irradiation with 325 nm light. Total irradiation periods are 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 and 150 s.

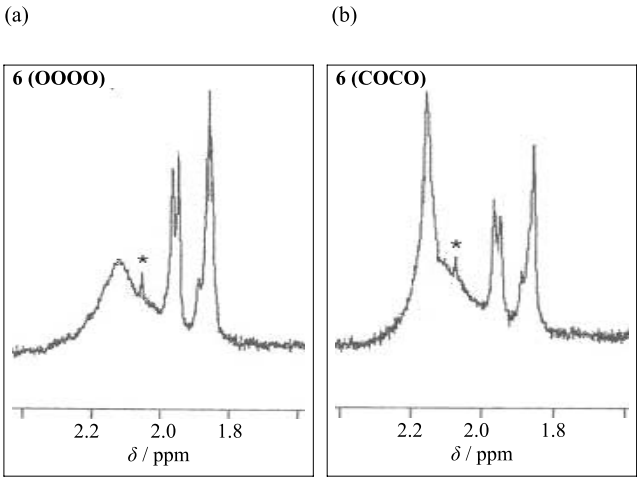


Figure 6. ^{1}H NMR methyl signals of the (a) **6** (OOOO); and (b) **6** (COCO). The asterisk denotes unidentified impurity.

The total cyclization quantum yield is 0.58, which is much higher than that of tetra-dithienylethene array.[10d] The coloration quantum yield of **6** was determined to be 0.64. The high value is due to the presence of enforced antiparallel conformation in the macromolecule **5**. The cycloreversion quantum yield of the **5** (COCO) and **6** (COCO) was measured to be 4.8×10^{-3} and 9.4×10^{-3}, respectively.

In order to obtain the geometrical configuration and characteristic features of the electronic structure, molecular orbital calculation of **5** was performed with the semi-empirical AM1. The optimized calculations show that two of four diarylethene units have different configurations. The HOMO is delocalized over the π-conjugated system via the 1,3-diethynylbenzene through two dithienylethene array. Examination of the HOMO and LUMO of **5** indicates that photoexcitation results in a net charge transfer from the π-conjugated system to the dithienylethene array (Fig. 7).

In summary, we have prepared two macromolecules incorporating four dithienylethene units. Upon irradiation of **5** and **6** with ultraviolet light, only one or two photo-induced cyclization reaction occurs. Each isomers were isolated and analyzed by ^{1}H NMR spectrum. The quantum yield of **5** and **6** are 0.58 and 0.64, respectively. The high value is due to the presence of enforced antiparallel conformation in the macrocycles **5** and **6**.

3. Experimental

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. Perfluorocyclopenthene was purchased from Fluorochem. 1,3-Diethynylbenzene[15] and 1,2-bis[2-methyl-5-bromo-3-thienyl]perfluorocyclopentene[16] were synthesized using a modified procedure of previous references. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer. The absorption and photoluminescence spectra were recorded on a Perkin–Elmer Lambda 2S UV–vis spectrometer and a Perkin LS fluorescence spectrometer, respectively. The fluorescence quantum yields using 9,10-diphenylanthracene as the standard were determined by the dilution method.[17]

3.1. Determination of quantum yields

The quantum yields of photochromic ring-cyclizaiton of **5** and **6** were determined form the absorption change at λ_{max} in UV spectra upon excitation with UV-light for the ring-closure reaction and visible light for the ring-opening reaction. The molar extinction coefficients of **5** and **6** are $3.11\times10^{4}\,M^{-1}\,cm^{-1}$ [**5** (OOOO)], $2.60\times10^{4}\,M^{-1}\,cm^{-1}$ [**5** (COOO)], $2.33\times10^{4}\,M^{-1}\,cm^{-1}$ [**5** (COCO)], $3.00\times10^{4}\,M^{-1}\,cm^{-1}$ [**6** (OOOO)], $2.46\times10^{4}\,M^{-1}\,cm^{-1}$ [**6** (COCO)]. Then, the quantum yield was determined according to the method described in Ref. 14.

3.1.1. Compound 2. A mixture of 1,2-bis[2-methyl-5-bromo-3-thienyl]perfluoro-cyclopentene (9.28 g, 17.6 mmol), 1,3-diethynylbenzene (0.7 g, 5.5 mmol), $Pd(PPh_3)_4$ (1.0 g, 1 mmol), and CuI (0.1 g, 0.5 mmol) was vacuum-dried and added NEt_3 (40 ml). The solution was refluxed for 12 h and then evacuated to dryness. The product **2** was purified by chromatography on a silica gel column (1:10 methylene chloride/hexane, $R_f=0.3$) to afford **2** (2.99 g) in 53% yield. Mp: 205 °C. ^{1}H NMR ($CDCl_3$): δ

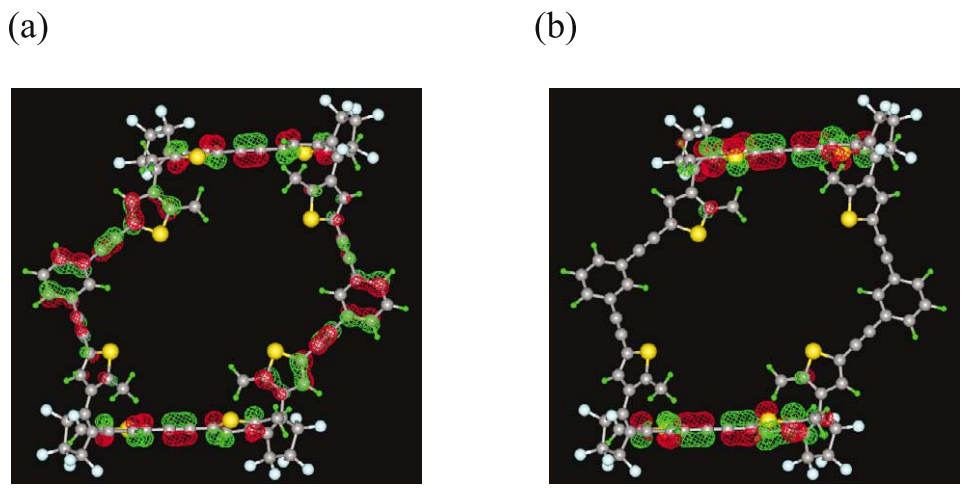


Figure 7. Representation of (a) HOMO; and (b) LUMO of **5** based on semi-empirical AM1.

7.64 (s, 1H), 7.45 (d, 2H, $J=8.40$ Hz), 7.33 (t, 1H, $J=8.40$ Hz), 7.23 (s, 2H), 7.02 (s, 2H), 1.98 (s, 6H), 1.88 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.4, 143.7, 143.5, 134.1, 131.8, 131.3, 129.9, 128.6, 125.3, 124.9, 123.0, 121.6, 155.9, 110.2, 93.0, 82.3, 14.9, 14.6. MS: *m/z* 1013 [M^+]. Anal. Calcd for $C_{40}H_{20}Br_2F_{12}S_4$: C, 47.26; H, 1.98. Found: C, 47.02; H, 1.90.

3.1.2. Compound 3. A mixture of **2** (1.0 g, 1 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol), and CuI (0.01 g, 0.5 mmol) was vacuum-dried and added NEt_3 (40 ml) and trimethylsilylacetylene (0.31 ml, 2.2 mmol). The solution was refluxed for 12 h and then evacuated to dryness. The pure product **3** was obtained by chromatography on a silica gel column (1:10 methylene chloride/hexane, $R_f=0.4$) to afford **3** in 81% yield. Mp: 164 °C. ^1H NMR ($CDCl_3$): δ 7.58 (s, 1H), 7.35 (d, 2H, $J=8.1$ Hz), 7.24 (t, 1H, $J=8.1$ Hz), 7.14 (s, 2H), 7.12 (s, 2H), 1.83 (s, 6H), 1.80 (s, 6H). 0.14 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.8, 143.5, 136.2, 132.7, 132.2, 131.6, 131.2, 125.0, 124.6, 123.1, 121.9, 121.5, 116.0, 111.0, 100.2, 96.3, 93.0, 82.0, 17.6, 17.2, −0.7. MS: *m/z* 1050 [M^+]. Anal. Calcd for $C_{50}H_{38}F_{12}S_4Si_2$: C, 57.13; H, 3.64. Found: C, 56.82; H, 3.52.

3.1.3. Compound 4. Compound **3** (1.0 g, 0.95 mmol) and KOH (0.01 g) were dissolved in THF (20 ml) and MeOH (20 ml) and then added H_2O (10 ml). The solution was stirred for 12 h and evacuated to dryness. The pure product **4** was obtained by chromatography on a silica gel column (1:10 methylene chloride/hexane, $R_f=0.2$) to afford **4** (0.73 g) in 81% yield. Mp: 151 °C. ^1H NMR ($CDCl_3$): δ 7.65 (s, 1H), 7.46 (d, 2H, $J=8.4$ Hz), 7.34 (t, 1H, $J=8.1$ Hz), 7.26 (s, 2H), 7.24 (s, 2H), 3.36 (s, 2H), 1.92 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.7, 143.8, 136.2, 133.2, 132.3, 132.0, 130.8, 124.9, 123.0, 121.6, 120.8, 119.1, 116.0, 111.2, 100.4, 95.4, 93.1, 82.3, 16.2. MS: *m/z* 906 [M^+]. Anal. Calcd for $C_{44}H_{22}F_{12}S_4$: C, 58.27; H, 2.45. Found: C, 58.01; H, 2.32.

3.1.4. Compound 5. A mixture of **2** (0.28 g, 0.28 mmol), **4** (0.25 g, 0.28 mmol), $Pd(PPh_3)_4$ (0.003 g), and CuI (0.0005 g) was vacuum-dried and added NEt_3 (60 ml). The solution was refluxed for 12 h and then evacuated to dryness. The product **5** was separated by chromatography on a silica gel column (1:2 methylene chloride/hexane) to afford **5** in 9% yield. ^1H NMR ($CDCl_3$): δ 7.65 (s, 2H), 7.45 (d, 4H, $J=7.3$ Hz), 7.34 (t, 2H, $J=7.3$ Hz), 7.19 (s, 2H), 7.17 (s, 2H), 7.12 (s, 2H), 7.09 (s, 2H), 2.07 (s, 6H), 2.06 (s, 6H), 1.96 (s, 6H), 1.95 (s, 6H). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 148.0, 146.9, 144.3, 143.8, 136.4, 134.2, 133.3, 131.6, 129.2, 125.0, 123.0, 121.7, 121.1, 116.5, 111.5, 93.1, 86.0, 82.3, 15.6, 14.5. MS: *m/z* 1760 [M^+]. Anal. Calcd for $C_{84}H_{40}F_{24}S_8$: C, 57.27; H, 2.29. Found: C, 57.01; H, 2.20.

3.1.5. Compound 6. A mixture of **4** (0.45 g, 0.50 mmol), *trans*-$Pt(PEt_3)_2Cl_2$ in Et_2NH (50 ml) was added CuCl (0.001 g). The solution was stirred for 12 h and then evacuated to dryness. The product **6** was purified with chromatography on a silica gel column (1:3 methylene chloride/hexane) to give **6** in 27% yield. ^1H NMR ($CDCl_3$): δ 7.65 (s, 2H), 7.46 (d, 4H, $J=7.2$ Hz), 7.34 (t, 2H, $J=7.2$ Hz), 7.16 (s, 2H), 7.14 (s, 2H), 7.05 (s, 2H), 6.76 (s. 2H), 2.22–2.05 (m, 24H), 1.96 (s, 6H), 1.95 (s, 6H), 1.85 (s, 12H), 1.19 (t, 36H, $J=8.4$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.9, 143.9, 139.3, 131.5, 129.4, 127.8, 125.4, 124.1, 123.1, 121.1, 116.1, 115.0, 111.4, 108.2, 100.7, 92.8, 92.1, 82.5, 24.6, 16.5, 15.1, 9.7, 8.7, 4.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 5.84 (s, $J=2348$ Hz). MS: *m/z* 2673 [M^+]. Anal. Calcd for $C_{112}H_{100}F_{24}P_4S_8Pt_2$: C, 50.33; H, 3.77. Found: C, 50.18; H, 3.69.

3.1.6. Closed-ring isomer of 3 (CO). ^1H NMR ($CDCl_3$): δ 7.64 (s, 1H), 7.46 (d, 2H, $J=9.0$ Hz), 7.36 (t, 1H, $J=9.0$ Hz), 7.24 (s, 1H), 7.22 (s, 1H), 6.47 (s, 1H), 6.41 (s, 1H), 2.16 (s, 6H), 1.93 (s, 3H), 1.88 (s, 3H). 0.24 (s, 18H).

3.1.7. Closed-ring isomer of 5 (COOO). ^1H NMR ($CDCl_3$): δ 7.65 (s, 2H), 7.45 (d, 4H, $J=7.2$ Hz), 7.34 (t, 2H, $J=7.2$ Hz), 7.17 (s, 2H), 7.13 (s, 2H), 7.09 (s, 2H), 6.48 (s, 2H), 2.18 (s, 3H), 2.16 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.96 (s, 3H), 1.94 (s, 6H), 1.92 (s, 3H).

3.1.8. Closed-ring isomer of 5 (COCO). ^1H NMR ($CDCl_3$): δ 7.65 (s, 2H), 7.45 (d, 4H, $J=7.2$ Hz), 7.36 (t, 2H, $J=7.2$ Hz), 7.13 (s, 2H), 7.09 (s, 2H), 6.72 (s, 2H), 6.52 (s, 2H), 2.17 (s, 12H), 2.07 (s, 3H), 2.05 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H).

3.1.9. Closed-ring isomer of 6 (COCO). ^1H NMR ($CDCl_3$): δ 7.65 (s, 2H), 7.46 (d, 4H, $J=7.2$ Hz), 7.32 (t, 2H, $J=7.2$ Hz), 7.17 (s, 2H), 7.08 (s, 2H), 6.76 (s, 2H), 6.54 (s, 2H), 2.14 (s, 12H), 1.96 (s, 3H), 1.95 (s, 3H), 1.85 (s, 6H).

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