

Synthesis of Fluorescent Diarylethenes Having a 2,4,5-Triphenylimidazole Chromophore

Kyoko Yagi, Chai Fong Soong, and Masahiro Irie*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, and CREST, Japan Science and Technology Corporation (JST), Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan

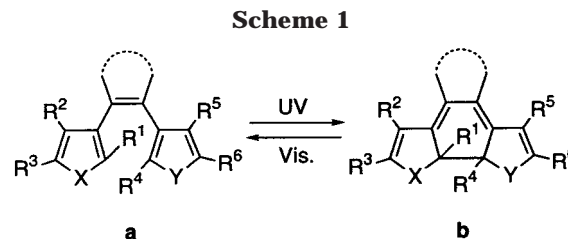
irie@cstf.kyushu-u.ac.jp

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Diarylethenes **1a–4a**, having a fluorescent 2,4,5-triphenylimidazole chromophore in the aryl group, were synthesized. Upon excitation of the triphenylimidazole chromophore with 366 nm, **1a–4a** underwent photocyclization reactions, and the solutions containing **1a–4a** changed color from colorless to red-purple or to blue. The colors disappeared by irradiation with visible ($\lambda > 480$ nm) light. The fluorescence intensity of the solutions also reversibly changed with the photochromic reactions. The fluorescence quantum yields of **1a**, **2a**, **3a**, and **4a** were determined to be 4.6, 7.7, 9.1, and 8.4%, respectively. The fluorescence quantum yields decreased with the increase in photocyclization quantum yields.

Photochromic compounds have attracted much attention because of their potential ability for photonic devices, such as optical memory media and photooptical switches.^{1–4} Among various types of photochromic compounds, diarylethene derivatives are the most promising compounds for these applications because of their thermally irreversible and fatigue resistant photochromic performance.⁵ Photochromic reactions of diarylethenes are based on the following reversible hexatriene–cyclohexadiene type photocyclization. Upon irradiation with UV light, the open-ring isomer **a** converts to the closed-ring isomer **b**, which has a well-separated absorption band in the visible wavelength region. The isomer **b** returns to the initial isomer **a** by irradiation with visible light (Scheme 1).

Although many diarylethene derivatives have been reported, compounds which exhibit strong fluorescent emission are rare.^{6–9} Fluorescent photochromic compounds, which reversibly change fluorescence intensity with photochromic reaction, are useful for optical memory media as well as fluorescent probes. In the present study, diarylethene derivatives **1a–4a** having a fluorescent 2,4,5-triphenylimidazole chromophore have been synthesized, and the relation between the fluorescent property and photochromic reactivity has been examined (Scheme 2).



Results and Discussion

Synthesis. Various types of diarylethene derivatives with different aryl groups were synthesized to know the effect of the aryl groups on the fluorescent property. Scheme 3 shows the synthetic route of diarylethene **1a**.

Diarylethene **1a** was synthesized from 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene (**5a**) by a two-step procedure. Diarylethenes having boronic acid substituents were extremely unstable.⁶ Therefore, in situ palladium-catalyzed Suzuki coupling with 4'-bromo-2,4,5-triphenylimidazole was performed.¹⁰ A colorless powder was obtained in 19% yield.

Scheme 4 shows the synthetic route to diarylethenes **2a–4a**.

3-Bromo-2,4-dimethyl-5-[4'-(2'',4'',5''-triphenylimidazolyl)]thiophene (**9**), the starting material for the synthesis of the diarylethenes **2a–4a**, was obtained from 2,4-dibromo-3,5-dimethylthiophene (**7**) by a two-step procedure as a yellow powder in 53% yield.¹¹ The monosubstituted perfluorocyclopentene **11** was synthesized from triphenylimidazole thiophene bromide **9**. For the lithiation of the thiophene bromide having a 2,4,5-triphenylimidazolyl group, 2 equiv of *n*-BuLi was used because of the presence of an N–H group in 2,4,5-triphenylimidazole. The N–H group in triphenylimidazole was not substituted in the

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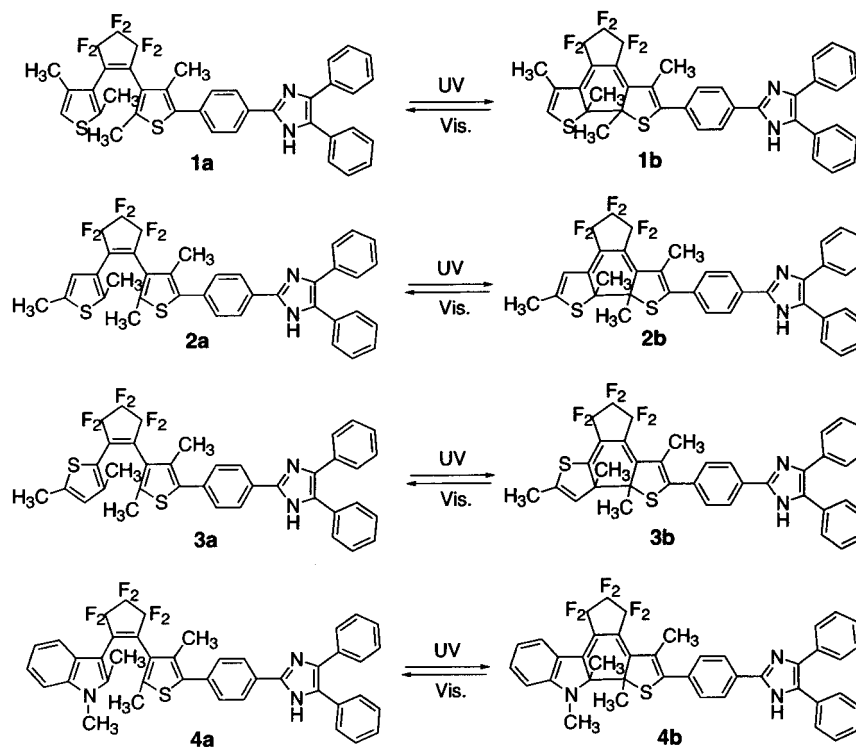
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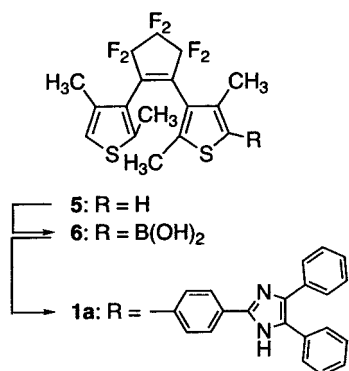
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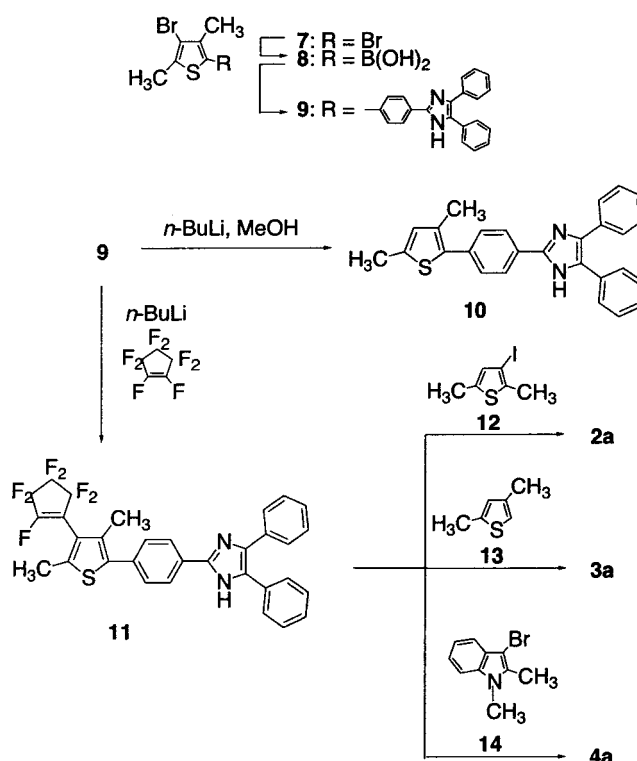
Scheme 2



Scheme 3



Scheme 4



coupling reaction. The diarylethenes **2a–4a** were obtained by the coupling of **11** with an excess of aryl halides **12**, **14**, or 2,4-dimethylthiophene. **2a–4a** were purified by column chromatography and recrystallization (hexane/chloroform). The structures of all compounds were confirmed by ¹H NMR, mass spectroscopy, and elemental analysis.

Photochromic Reactions. Figure 1 shows the absorption spectral change of **1** (1.7×10^{-5} M) in THF by UV irradiation. Upon irradiation with 366-nm light, an absorption band at 556 nm increased and reached the photostationary state. The color of the solution changed from colorless to red-purple, in which the absorption maximum was observed at 556 nm. When the red-purple solution was irradiated with visible light ($\lambda > 480$ nm), the spectrum returned back to the original one with retention of the isobestic points at 303 and 363 nm. The colored isomer was stable and could be isolated by high performance liquid chromatography (HPLC, hexane/ethyl acetate). **2**, **3**, and **4** also underwent similar photochromic reactions. Table 1 summarizes the main absorption bands of the open- and closed-ring form isomers **1a–4a** and **1b–4b**.

Figure 2 shows the absorption spectra of open-ring isomer **1a**, diarylethene unit **5a**, and 2,4,5-triphenylimidazole **15** in *n*-hexane.

The absorption edge of the diarylethene unit **5a** ($\lambda_{\text{max}} = 234$ nm) is around 330 nm and that of triphenylimidazole **15** ($\lambda_{\text{max}} = 308$ nm) is less than 360 nm. On the other hand, **1a** ($\lambda_{\text{max}} = 335$ nm) has the absorption band extending to 400 nm. The shift suggests that donor–acceptor interaction between the electron-donat-

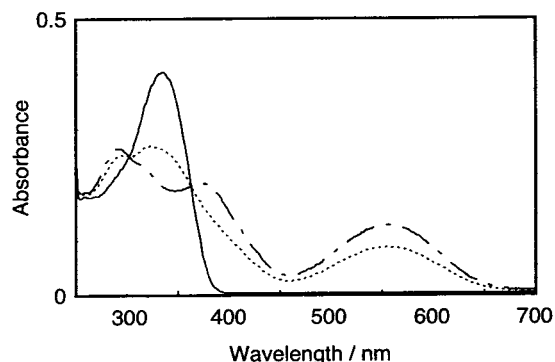


Figure 1. Absorption spectral change of **1** in THF (1.7×10^{-5} M) by photoirradiation: **1a** (—), **1** in the photostationary state under irradiation with 366-nm light (····), and **1b** (- · -).

Table 1. Absorption Maxima of the Open- and Closed-Ring Isomers of **1–4**

compounds	λ_{\max}/nm	$\epsilon_{\max}/\text{M}^{-1} \text{cm}^{-1}$
1a	339	21000
1b	565	6400
2a	336	20000
2b	546	6900
3a	332	23000
3b	505	6500
4a	313	26000
4b	589	6800

^a In THF.

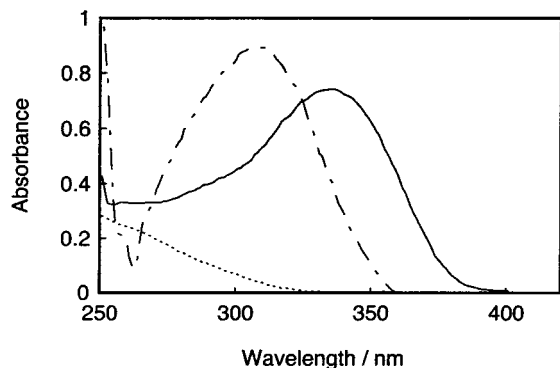
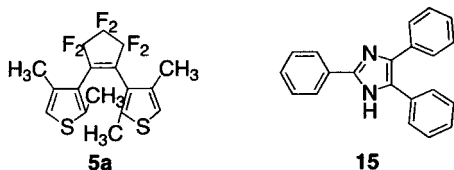


Figure 2. Absorption spectra of **1a** (—), **5a** (····), and 2,4,5-triphenylimidazole **15** (- · -) in hexane solution (3.5×10^{-5} M).

Scheme 5



ing 2,4,5-triphenylimidazole unit and the electron-withdrawing perfluorocyclopentene unit stabilizes the excited energy level in **1a**. **2a** has a similar absorption band as **1a**. The hypsochromic shift of **3a** and **4a** is ascribed to the electron-donating property of 2-thienyl and 3-indolyl groups, which weakens the electron-withdrawing character of the perfluorocyclopentene unit. The absorption maxima of **1b** and **2b** were similar each other. On the other hand, the absorption maximum of **3b** showed a hypsochromic shift. This is ascribed to shorter π -conjugation length of **3b** in comparison with **1b** and **2b**, because the thiophene ring is connected to

Table 2. Quantum Yields of Photochromic Reactions and Fluorescence Emission

compounds	Φ^a		Φ_f^c	conversion
	$\Phi_{\text{cyclization}}$	$\Phi_{\text{cycloreversion}}^b$		
1	0.59	0.13	0.046	0.67
2	0.49	0.049	0.077	0.82
3	0.34	0.058	0.091	0.82
4	0.40	0.073	0.084	0.93

^a Reference; fryl flugide ($\Phi_{\text{cyclization}} = 0.21$ in *n*-hexane, $\Phi_{\text{cycloreversion}} = 0.048$ in toluene).^{17,18} ^b Irradiation at λ_{\max} light ($\lambda > 480$ nm). ^c Reference; anthracene in cyclohexane ($\Phi_f = 0.31$, Ex; 366 nm).¹⁹

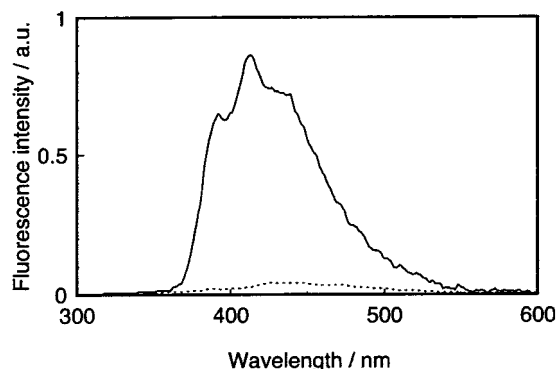


Figure 3. Fluorescence spectral change of **1a** in *n*-hexane upon irradiation with 366 nm: (—) before photoirradiation and (····) in the photostationary state.

perfluorocyclopentene at the 2-position.¹² The longest absorption band was observed for **4b**, in which π -conjugation length extends to the indole substituent.

Photocyclization reactions of **1a–4a** took place by irradiation with 366-nm light, while the reaction of **5a** was not observed.¹³ **5a** has no absorption at 366 nm. Photoexcitation of the triphenylimidazole chromophore is responsible for the photocyclization reactions. Table 2 summarizes the photocyclization and cycloreversion quantum yields. Relatively high cyclization quantum yields were observed for **1a–4a**. The cycloreversion quantum yields were moderate.

Fluorescent Properties. Figure 3 shows the fluorescence spectral change of **1a** in hexane by UV irradiation. The fluorescence maximum was observed at 420 nm. Upon irradiation with 366-nm light, the fluorescence intensity decreased and the emission was scarcely observed in the photostationary state. The isolated **1b** did not exhibit any fluorescence around 420 nm. Similar fluorescence intensity changes upon irradiation with 366-nm light were observed for **2–4**. The fluorescence quantum yields of **1a–4a** by irradiation with 366-nm light were measured and summarized in Table 2. The highest quantum yield of 9.1% was observed for **3a**.

2,4,5-Triphenylimidazole **15** exhibits strong emission,^{14,15} but despite having the triphenylimidazole as a fluorophore, diarylethenes **1a–4a** exhibit weaker emission. The fluorescent properties of triphenylimidazole derivatives **10** and **11** were examined to compare their properties with those of **1a–4a**, as shown in Figure 4 and Table 3. Table 3 summarizes the fluorescence quantum

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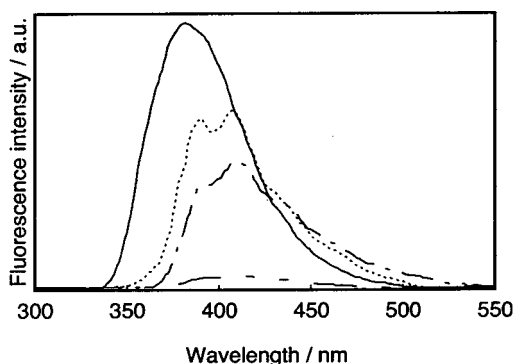


Figure 4. Fluorescence spectra of various triphenylimidazole derivatives: **15** (—), **10** (⋯⋯), **11** (— · —), and **1a** (— · — · —).

Table 3. Fluorescence Properties of Various Triphenylimidazole Derivatives

compounds	$\lambda_{f,max}/nm^a$	$\Phi_f^{a,c}$	τ_f/ns^d
1a	410	0.045, 0.046 ^b	0.42
2a	390, 410	0.077	0.54
3a	393, 410	0.091	0.42
4a	392, 413	0.084	0.48
10	395, 419	0.41	—
11	392, 420	0.31	—
15	382	0.48	1.3

^a Excited at 313 nm in *n*-hexane. ^b Excited at 366 nm in *n*-hexane. ^c Reference; anthracene in cyclohexane ($\Phi_f = 0.31$, Ex; 366 nm). ^d In *n*-hexane and these compounds are exhibited single exponential.

yields (Φ_f) of the triphenylimidazole derivatives and fluorescence lifetimes along with the values of **1a–4a**. Φ_f of 2,4,5-triphenylimidazole is 0.48, while Φ_f of triphenylimidazole derivatives **10** and **11** decreases to 0.41 and 0.31, respectively. Substitution of thiophene or perfluorocyclopentene-substituted thiophene to **15** decreased the fluorescence intensity and the lifetime. Substitution of thiophene or indole to **11** further decreased the fluorescent quantum yields. The rotation of the substituted thiophene or indole along the single bond connecting to the perfluorocyclopentene unit is considered to increase radiationless transition to the ground state.

Comparison of Cyclization and Fluorescence Quantum Yields. The fluorescence quantum yield decreased with the increase in the cyclization quantum yield, as shown in Table 2. In previous papers,^{16–18} it has been reported that the cyclization reactions of diethylenes take place on a picosecond time scale. On the other hand, the fluorescence lifetimes of diarylethenes **1a–4a** are several hundred picoseconds. The correlation between the quantum yield and fluorescence intensity and the large difference in the time scale of the cyclization reaction and fluorescence emission can be explained by two different mechanisms.

Diarylethene derivatives are known to be in two conformations, photoactive antiparallel and photoinactive parallel conformers.¹⁹ It is possible to assign the fluorescence species to the inactive parallel conformers, which are expected to have long lifetimes. The increase in the ratio of the photoactive antiparallel conformations in the

ground-state results in the increase in the cyclization quantum yield and decrease in the fluorescence intensity because of the decrease of the ratio of fluorescent parallel conformers. Another explanation is the competition in the excited state. A part of excited molecules, which cannot enter the cyclization reaction channel, deactivate to the relaxed fluorescence state and emit the fluorescence. When the cyclization quantum yield is high, the number of unreacted excited molecules becomes small and the fluorescence intensity decreases. Both mechanisms can explain the observed results. To judge the mechanism, it is required to measure the ratio of the two conformers in the ground state using a method other than NMR, because both conformers are in equilibrium in the NMR time scale.

Conclusions

Diarylethenes having a fluorescent 2,4,5-triphenylimidazole chromophore **1a–4a** were synthesized. **1a–4a** underwent reversible photocyclization reactions by alternate irradiation with UV ($\lambda = 366$ nm) and visible ($\lambda > 480$ nm) light. Relatively high cyclization quantum yields were observed for **1a–4a**. The fluorescence intensity also reversibly changed with the photochromic reactions. The fluorescence quantum yields of the open-ring isomers varied from 4.6 to 9.1%. The fluorescence quantum yields decreased with the increase in the photocyclization quantum yields.

Experimental Section

General. ¹H NMR spectra were recorded on a Varian Gemini 200 NMR spectrometer. Tetramethylsilane was used as an internal standard. Mass spectra were taken with a Shimadzu GCMS-QO5050A gas chromatography–mass spectrometer. Melting points were not corrected. Absorption and fluorescence spectra were measured with a Hitachi U-3410 absorption spectrophotometer and a Hitachi U-3010 fluorescence spectrophotometer, respectively. Photoirradiation was carried out using an USHIO 500W high-pressure mercury lamp or an USHIO-500W xenon lamp as the light source. Monochromatic light was obtained by passing the light through a monochromator (Ritsu MV-10N) or a band-pass filter ($\Delta\lambda_{1/2} = 15$ nm). Fluorescence lifetime was measured with a time-resolved spectrofluorometer (Hamamatsu Photonics. C4334 and C4792) excited with a 337-nm N₂ laser (ILEE. NN-100).

Materials. Solvents of spectroscopic grade were purified by distillation before use. All reactions were performed under dry argon atmosphere unless otherwise specified. The reactions were monitored by thin-layer chromatography. Column chromatography was performed on silica gel.

1-(2,4-Dimethyl-3-thienyl)-2-[2,4-dimethyl-5-(2''4'',5''-triphenylimidazol-4'-yl)-3-thienyl]perfluorocyclopentene (1a). To the solution of 1,2-bis(2,4-dimethyl-3-thienyl)-perfluorocyclopentene (**5a**; 200 mg, 0.51 mmol) and *N, N, N, N*-tetramethylethylenediamine (TMEDA; 0.17 mL, 1.15 mmol) in anhydrous ether (3 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 0.72 mL, 1.15 mmol) at -78 °C under argon atmosphere. The reaction mixture was stirred for 20 min at room temperature, and then tri-*n*-butyl borate (0.38 mL, 1.38 mmol) was added in one portion. The red-brown solution was stirred for 1 h and then diluted with anhydrous THF (3 mL). To the solution was added ethylene glycol (0.3 mL), Pd(PPh₃)₄ (20 mg), aqueous Na₂CO₃ (20% w/w; 3 mL), and anhydrous THF (50 mL). The solution was refluxed for 12 h at 70 °C. 2 N HCl was poured into the reaction mixture, and then the product was extracted with chloroform, dried with magnesium sulfate, and concentrated. Purification was performed by column chromatography (SiO₂; chloroform) followed by GPC. **1a** was obtained as a colorless powder (66 mg, 19%): ¹H NMR

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(200 MHz, CDCl₃) δ 2.08 (s, 3H), 2.10 (s, 3H), 2.36 (s, 6H), 6.73 (s, 1H), 7.26–7.96 (m, 14H); MS *m/z* 690 (M⁺). Anal. Calcd for C₃₈H₂₈F₆N₂S₂: C, 66.07; H, 4.09; N, 4.06. Found: C, 65.99; H, 3.87; N, 3.98.

3-Bromo-2,4-dimethyl-5-(2'',4'',5''-triphenylimidazolyl)-thiophene (9). To the solution of 4'-bromo-triphenylimidazole (2.0 g, 5.2 mmol), Pd(PPh₃)₄ (200 mg), and aqueous Na₂CO₃ (6.5 mL; 20% w/w) in THF (200 mL) was added 4-bromo-3,5-dimethyl-2-thiopheneboronic acid⁸ (**8**; 2.75 g; 12 mmol) under argon atmosphere. The solution was refluxed for 48 h at 70 °C. 2 N HCl was poured into the reaction mixture, and then the product was extracted with chloroform, dried with magnesium sulfate, and concentrated. Purification was performed by column chromatography (SiO₂; chloroform). **9** was obtained as a yellow powder (1.38 g, 54%); mp. 202–204 °C; ¹H NMR (200 MHz, CDCl₃) δ 2.31 (s, 3H), 2.46 (s, 3H), 7.20–7.97 (m, 14H); MS *m/z* 484 (M⁺), 486 (M + 2)⁺. Anal. Calcd for C₂₇H₂₁-BrN₂S: C, 66.80; H, 4.36; N, 5.77. Found: C, 66.47; H, 4.46; N, 5.43.

2,4-Dimethyl-5-[4'-(2'',4'',5''-triphenylimidazolyl)]thiophene (10). To the solution of bromothiophene (**9**; 200 mg, 0.41 mmol) in anhydrous THF (8 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 0.5 mL, 0.82 mmol) at –78 °C under argon atmosphere. The reaction mixture was stirred for 1 h at –78 °C, and then methanol was added. The product was extracted with chloroform, dried with magnesium sulfate, and concentrated. Purification was performed by column chromatography (SiO₂, chloroform) followed by GPC. **10** was obtained as a yellow powder (38 mg, 23%); mp 207–208 °C; ¹H NMR (200 MHz, CDCl₃) δ 2.28 (s, 3H), 2.48 (s, 3H), 6.61 (s, 1H), 7.30–7.98 (m, 14H); MS *m/z* 406 (M⁺). Anal. Calcd for C₂₇H₂₂N₂S: C, 79.77; H, 5.45; N, 6.89. Found: 80.01; H, 5.60; N, 7.02.

1-[2,4-Dimethyl-5-(2'',4'',5''-triphenylimidazol-4'-yl)-3-thienyl]perfluorocyclopentene (11). To the solution of bromothiophene (**9**; 300 mg, 0.62 mmol) in anhydrous THF (20 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 1.12 mL, 1.86 mmol) at –78 °C under argon atmosphere. The reaction mixture was stirred for 1.5 h at –78 °C, and then perfluorocyclopentene (0.25 mL, 1.86 mmol) was added in one portion. The reaction mixture was stirred for 1 h at –78 °C, and then methanol was added. The product was extracted with chloroform, dried with magnesium sulfate, and concentrated. Purification was performed by column chromatography (SiO₂, chloroform) followed by GPC. **11** was obtained as a yellow powder (77 mg, 20%); ¹H NMR (200 MHz, CDCl₃) δ 2.15 (s, 3H), 2.40 (s, 3H), 7.27–7.99 (m, 14H); MS *m/z* 598 (M⁺). Anal. Calcd for C₃₂H₂₇F₇N₂S: C, 63.57; H, 4.50; N, 4.63. Found: C, 63.25; H, 4.11; N, 4.25.

1-(2,5-Dimethyl-3-thienyl)-2-[2,4-dimethyl-5-(2'',4'',5''-triphenylimidazol-4'-yl)-3-thienyl]perfluorocyclopentene (2a). To the solution of 3-iodo-2,5-dimethylthiophene (**12**; 90 mg, 0.38 mmol) in anhydrous THF (8 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 0.25 mL, 0.42 mmol) at –78 °C under argon atmosphere. The reaction mixture was stirred for 30 min at –78 °C, and then perfluorocyclopentene derivative (**11**; 77 mg, 0.13 mmol) in anhydrous THF (5 mL) was added. The reaction mixture was stirred for 1 h at –78 °C, and then methanol was added. The product was extracted with chloroform, dried with magnesium sulfate, and concentrated. The product was extracted with chloroform, dried with magnesium sulfate, and concentrated. Purification was performed by column chromatography (SiO₂, chloroform) followed by GPC. **2a** was obtained as a colorless powder (52 mg, 58%); ¹H NMR (200 MHz, CDCl₃) δ 2.04 (s, 6H), 2.27 (s, 3H), 2.39 (s, 3H), 6.63 (s, 1H), 7.26–7.96 (m, 14H); MS *m/z* 690 (M⁺).

Anal. Calcd for C₃₈H₂₈F₆N₂S₂: C, 66.07; H, 4.09; N, 4.06. Found: C, 65.62; H, 4.22; N, 3.97.

1-(3,5-Dimethyl-2-thienyl)-2-[2,4-dimethyl-5-(2'',4'',5''-triphenylimidazol-4'-yl)-3-thienyl]perfluorocyclopentene (3a). To the solution of 2,4-dimethylthiophene (**13**; 71 mg, 0.3 mmol) and TMEDA (0.2 mL) in anhydrous ether (7 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 0.2 mL, 0.33 mmol) at 0 °C under argon atmosphere. The reaction mixture was stirred for 30 min at –78 °C, and then perfluorocyclopentene derivative (**11**; 60 mg, 0.1 mmol) in anhydrous THF (4 mL) was added. The reaction mixture was stirred for 1 h at –78 °C, and then methanol was added. The product was extracted with chloroform, dried with magnesium sulfate, and concentrated. Purification was performed by column chromatography (SiO₂, chloroform) followed by GPC. **3a** was obtained as a yellow powder (38 mg, 42%); ¹H NMR (200 MHz, CDCl₃) δ 2.06 (s, 3H), 2.01 (s, 3H), 2.28 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H), 6.52 (s, 1H), 7.30–7.98 (m, 14H); MS *m/z* 690 (M⁺). C₃₈H₂₈F₆N₂S₂: C, 66.07; H, 4.09; N, 4.06. Found: C, 66.32; H, 4.33; N, 4.02.

1-(2,5-Dimethyl-3-thienyl)-2-[2,4-dimethyl-5-(2'',4'',5''-triphenylimidazol-4'-yl)-3-thienyl]perfluorocyclopentene (4a). To the solution of 3-bromo-1,2-dimethylindole (**14**; 227 mg, 1.0 mmol) in anhydrous THF (8 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 0.68 mL, 1.1 mmol) at 0 °C under argon atmosphere. The reaction mixture was stirred for 1 h at 0 °C. The solution was cooled at –78 °C, and then perfluorocyclopentene derivative (**11**; 77 mg, 0.12 mmol) in anhydrous THF (5 mL) was added. The reaction mixture was stirred for 1 h at –78 °C and then methanol was added. The product was extracted with chloroform, dried with magnesium sulfate, and concentrated. Purification was performed by column chromatography (SiO₂, chloroform) followed by GPC. **4a** was obtained as a yellow powder (33 mg, 38%); ¹H NMR (200 MHz, CDCl₃) δ 1.71 (s, 1H), 1.77 (s, 2H), 1.83 (s, 2H), 1.90 (s, 1H), 2.57 (s, 3H), 2.46 (s, 3H), 6.70–7.87 (m, 18H); MS *m/z* 723 (M⁺). Anal. Calcd for C₄₂H₃₁F₆N₃S: C, 69.70; H, 4.32; N, 5.81. Found: C, 70.09; H, 4.66; N, 5.97.

Photochromic Quantum Yields. The cyclization quantum yields were determined by comparing the photocyclization rate of furyl flugide in *n*-hexane by using a normal procedure.²⁰ The cycloreversion quantum yields were also measured using furyl flugide in toluene as a reference.²¹

Fluorescence Quantum Yields. The fluorescence quantum yields were determined using anthracene in cyclohexane ($\Phi_f = 0.31$; excitation wavelength 366 nm) as a reference.²²

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Supporting Information Available: UV/visible absorption spectra of photochromic reaction in THF upon irradiation with 366-nm light: **2a**, **3a**, and **4a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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