Supplementary Information for

Acid-induced photochromic system switching of diarylethene derivatives between P- and T-types

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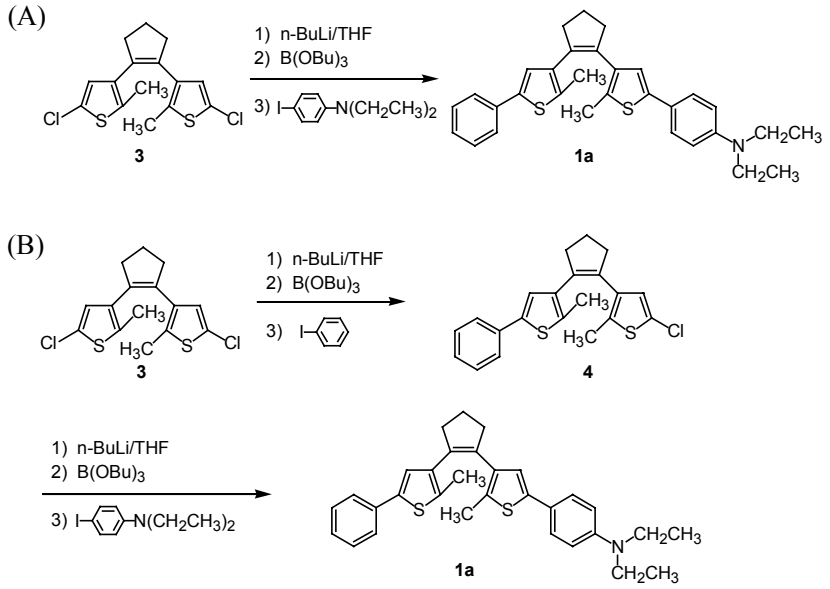
Synthesis

Diarylethene **1a** was synthesized according to two synthetic routes shown in Scheme S1. Route A was carried out by one pot synthesis from **3** accompanying elimination of diethylamino group during the reaction.



Scheme S1. Synthetic routes of diarylethene **1a**

Route A.

1-(2-Methyl-5-(4-*N*,*N*-diethylaminophenyl)thien-3-yl)-2-(2-methyl-5-phenyl-thien-3-yl)cyclopentene (1a). Under an argon atmosphere, a solution of 1.6 M *n*-butyllithium in hexane (3.0 mL, 4.8 mmol) was added dropwise to a stirred solution of 1,2-bis(5-chloro-2-methylthien-3-yl)cyclopentene (**3**)[S1] (0.50 g, 1.5 mmol) in dry THF (3.5 mL) at –78 °C. After 30 min, tri-*n*-butyl borate (1.3 mL, 4.8 mmol) was added to the reaction mixture at room temperature. After 1 h, the reaction was stopped by the addition of water. To this solution, *p*-iodo-*N*,*N*-diethylaniline[S2] (0.70 g, 2.5 mmol), THF (4 mL), $Pd(PPh_3)_4$ (0.10 g, 0.083 mmol), 2 M Na_2CO_3aq (12 mL), and 3 drops of ethylene glycol were added, and then the mixture was refluxed for 3 h. After cooling, the solution was extracted with ether. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (98:2) as the eluent. Compound **1a** was obtained as a colorless solid (0.148 g, 0.31 mmol, 20% based on **3**). 1,2-Bis(2-methyl-5-(4-*N*,*N*-diethylaminophenyl)thien-3-yl)cyclopentene (0.362 g, 0.65 mmol, 43% based on **3**) was also isolated.

1a: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) δ = 1.16 (t, *J* = 7.2 Hz, 6H), 1.95 (s, 3H), 1.98 (s,

3H), 2.05 (quintet, J = 7.6 Hz, 2H), 2.83 (t, J = 7.6 Hz, 4H), 3.35 (q, J = 7.2 Hz, 4H), 6.62 (d, J = 8.8 Hz, 2H), 6.85 (s, 1H), 7.05 (s, 1H), 7.2-7.6 (m, 7H). FAB-MS m/z = 483.2058 (M^+) (cal. 483.2054)

Route B.

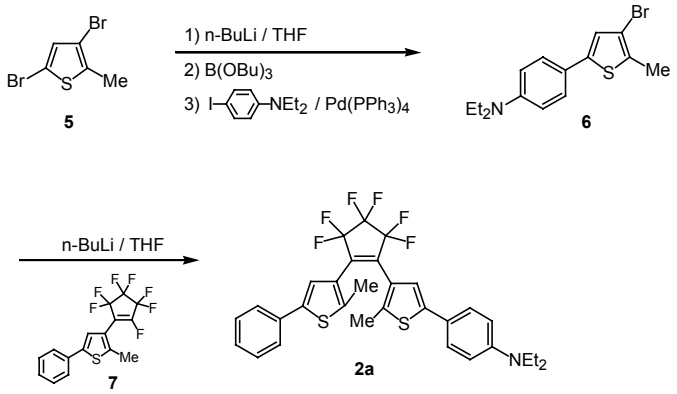
1-(5-Chloro-2-methylthien-3-yl)-2-(2-methyl-5-phenylthien-3-yl)cyclopentene (4). To a solution of compound **3**[S1] (1.0 g, 3.0 mmol) in dry THF (20 mL), 1.6 M *n*-butyllithium in hexane (1.9 mL, 3.0 mmol) was added dropwise under an argon atmosphere at –78 °C. The mixture was stirred for 30 min at room temperature and tri-*n*-butyl borate (1.3 mL, 4.8 mmol) was added dropwise. The solution was stirred for 1 h at room temperature. To this solution, iodobenzene (0.62 g, 3.0 mmol), THF (15 mL), $Pd(PPh_3)_4$ (0.10 g, 0.083 mmol), 2 M Na_2CO_3aq (12 mL), and 3 drops of ethylene glycol were added, and then the mixture was refluxed for 3 h. After cooling, the solution was extracted with ether. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (95:5) as the eluent. Compound **4** was obtained as a colorless solid (0.73 g, 65%).

4: ^{1}H-NMR (400MHz, $CDCl_3$, TMS) δ = 1.88 (s, 3H), 1.99 (s, 3H), 2.05 (quintet, J = 7.6 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 2.81 (t, J = 7.6 Hz, 2H), 6.62 (s, 1H), 6.99 (s, 1H), 7.2-7.6 (m, 5H).

1-(2-Methyl-5-(4-*N*,*N*-diethylaminophenyl)thien-3-yl)-2-(2-methyl-5-phenyl-thien-3-yl)cyclopentene (1a). To a solution of compound **4** (0.35 g, 0.94 mmol) in dry THF (6 mL) was added dropwise 1.46 M *t*-butyllithium in pentane (0.66 mL, 0.96 mmol) under an argon atmosphere at –78 °C. The mixture was stirred for 1 h at 0 °C and tri-*n*-butyl borate (0.38 mL, 1.4 mmol) was added dropwise. The solution was stirred for 1 h at room temperature. To this solution, *p*-iodo-*N*,*N*-diethylaniline[S2] (0.26 g, 0.94 mmol), THF (15 mL), $Pd(PPh_3)_4$ (0.032 g, 0.026 mmol), 2 M Na_2CO_3 aq (4 mL), and 3 drops of ethylene glycol were added, and then the mixture was refluxed for 2 h. After cooling, the solution was extracted with ether. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (95:5) as the eluent. Compound **1a** was obtained as a colorless solid (0.030 g, 6.6%).

1a: ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) δ = 1.16 (t, J = 7.2 Hz, 6H), 1.95 (s, 3H), 1.98 (s, 3H), 2.05 (quintet, J = 7.6Hz, 2H), 2.83 (t, J = 7.6 Hz, 4H), 3.35 (q, J = 7.2 Hz, 4H), 6.62 (d, J = 8.8 Hz, 2H), 6.85 (s, 1H), 7.05 (s, 1H), 7.2-7.6 (m, 7H)

Diarylethene **2a** was synthesized according to the synthetic route shown in Scheme S2.



Scheme S2. Synthetic routes of diarylethene **2a**

3-Bromo-2-methyl-5-(4-*N*,*N*-diethylaminophenyl)thiophene (6). Under an argon atmosphere, 1.6 M *n*-butyllithium in hexane (7.1 mL, 11 mmol) was added dropwise to a solution of 2,4-dibromo-5-methylthiophene (**5**) (2.8 g, 1.1 mmol) in dry THF (100 mL) at –78 °C. The solution was stirred for 1 h at the temperature. Tri-*n*-butyl borate (5.0 mL, 13 mmol) was added dropwise to the reaction mixture, and then the mixture was stirred for 1 h at –78 °C. The reaction was stopped by the addition of water. To this solution, *p*-iodo-*N*,*N*-diethylaniline (3.0 g, 11 mmol), THF (100 mL), $Pd(PPh_3)_4$ (0.35 g, 0.56 mmol), and 2 M Na_2CO_3aq (2.5 mL) were added, and then the mixture was refluxed for 3 h. After cooling, the solution was extracted with ether. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by recrystallization from hexane to give **6** (1.3 g, 37%).

^{1}H-NMR (400 MHz, $CDCl_3$, TMS) δ = 1.18 (t, *J* = 7.2 Hz, 6H), 2.38 (s, 3H), 3.37 (d, *J* = 7.2 Hz, 4H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.90 (s, 1H), 7.35 (d, *J* = 8.8Hz, 2H).

1-(2-methyl-5-(4-*N*,*N*-diethylaminophenyl)thien-3-yl)-2-(2-methyl-5-phenyl-thien-3-yl)perfluorocyclopentene (2a). Under an argon atmosphere, 1.6 M *n*-butyllithium in hexane (1.1 mL, 1.8 mmol) was added dropwise to a solution of **6** (0.50 g, 1.5 mmol) in dry THF (10 mL) at –78 °C. The solution was stirred for 1 h at the temperature. To the solution was added dropwise the mixture of 1-(2-methyl-5-phenylthien-3-yl)heptafluorocyclopentene (**7**)[S3] (0.56 g, 1.5 mmol) and dry THF (5 mL) at –78 °C, and then the mixture was stirred for 3 h at the temperature. The reaction was stopped by the addition of water. The solution was extracted with

ether. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography with hexane as the eluent. Compound **2a** was obtained as a pale yellow solid (0.43 g, 49%). ^{1}H-NMR (400MHz, $CDCl_3$, TMS) δ = 1.18 (t, *J* = 7.2 Hz, 6H), 1.92 (s, 3H), 1.95 (s, 3H), 3.37 (q, *J* = 7.2 Hz, 4H), 6.65 (d, *J* = 8.8 Hz, 2H), 7.08 (s, 1H), 7.29-7.40 (m, 6H), 7.54 (d, *J* = 7.2 Hz, 2H). FAB-MS *m*/*z* = 591.1483 (M^+) (cal. 591.1489)

Absorption spectra of 2a, 2b, 2a-H$^+$, and 2b-H$^+$

Figure S1 shows the absorption spectral changes of **2a** in acetonitrile. Upon irradiation with ultraviolet light (UV), the acetonitrile solution of **2a** changed from colorless to green. The absorption maximum of **2b** appeared at 630 nm. The colored solution was thermally stable and returned to the colorless one by irradiation with visible light. The photocyclization conversion was determined by comparing the absorption spectra of the isolated **2b** with the photostationary solution. The conversion in acetonitrile was 66% upon irradiation with 313-nm light. When trifluoromethane-sulfonic acid (TFMSA) was added to **2b**, the absorption spectrum immediately showed hypochromic and hypsochromic changes to give **2b-H**$^+$, as shown in Figure S1. The absorption maximum and absorption coefficient of **2b-H**$^+$ is almost similar to that of the unsubstituted compound, 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene.[S4]

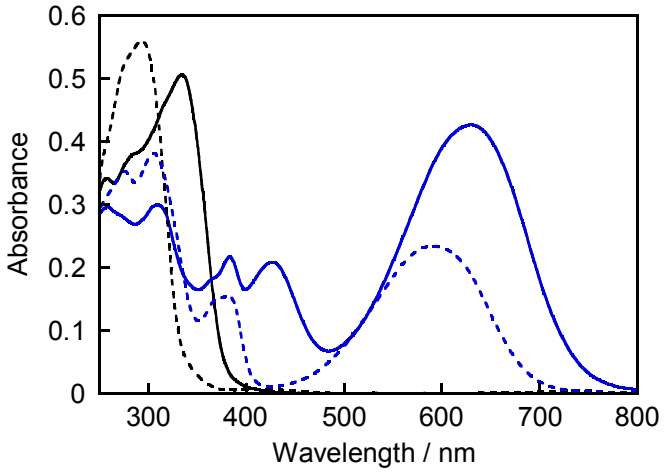


Figure S1. Absorption spectra of **2a** (——), **2b** (——), **2a-H**$^+$ (- - - -), and **2b-H**$^+$ (- - - -) in acetonitrile.

Effect of acid on thermal cycloreversion reactions

The protonation of **1b** was examined using other organic acids, benzoic acid, acetic acid, phenol, and methanol. Figure S2 shows color changes of **1a** in the presence of 10

eq of the acid in acetonitrile by irradiation with UV light and heating for 2 h at 80 °C. After heating, the solution including TFMSA turned to colorless. The thermal cycloreversion reaction rates depended on the protonation efficiency of the closed-ring isomer. When an acid with the smaller pK_a than 5 (in water) was used for the protonation, the thermal cycloreversion reaction was observed. TFMSA was the most efficient for the protonation under the present conditions.

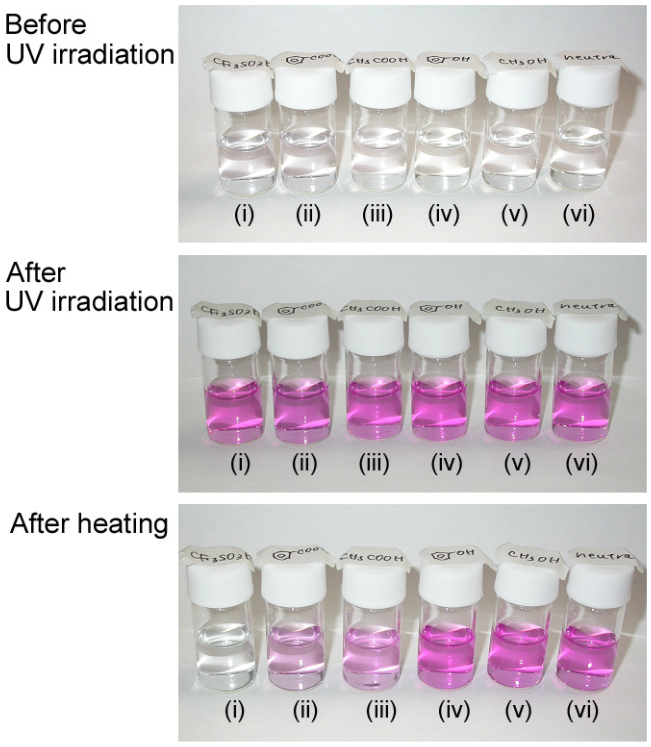


Figure S2. Color changes of diarylethene **1a** in the presence of 10 eq of acids in acetonitrile by irradiation with UV light and heating for 2 h at 80 °C: (i) trifluoromethanesulfonic acid (pK_a = –14), (ii) benzoic acid (pK_a = 4.25), (iii) acetic acid (pK_a = 4.75), (iv) phenol (pK_a = 10.0), (v) methanol (pK_a = 15.5), (vi) in the absence of acid. pK_a values in water are referred from ref. S5.

Determination of pK_a of protonated open- and closed-ring isomers.

Figure S3 shows the content of the protonation by the addition of the acid. For **1a** and **1b**, the relationship were almost the same. This means that pK of **1a** and **1b** were almost similar to each other. On the other hand, the difference of pK was observed between **2a** and **2b**. To evaluate the difference of pK of **2a** and **2b**, a curve fitting to the experimental data in Figure S3 was simulated according to the following parameters: K_a(TFMSA) = 2.5 × 10^{-3} mol/L in acetonitrile,[S6] [**1a**] = 2.0 × 10^{-5} mol/L, [**1b**] = 2.3 × 10^{-5}

mol/L, [**2a**] = 1.7×10^{-5} mol/L, [**2b**] = 2.5×10^{-5} mol/L. The presence of a small amount of water (2×10^{-5} mol% in acetonitrile) was assumed for calculation.

$$CF_3SO_3H \overset{K_a}{\rightleftharpoons} CF_3SO_3^- + H^+$$

$$DE + H^+ \overset{K}{\rightleftharpoons} DE\text{-}H^+$$

Figure S3 also shows the simulated lines that correspond to pK = –6.4 (**1a**, **1b**), –6.7 (**2a**), and –5.0 (**2b**). Therefore, pK_a values of the protonated compounds were determined to be 6.4 (**1a**, **1b**), 6.7 (**2a**), and 5.0 (**2b**).

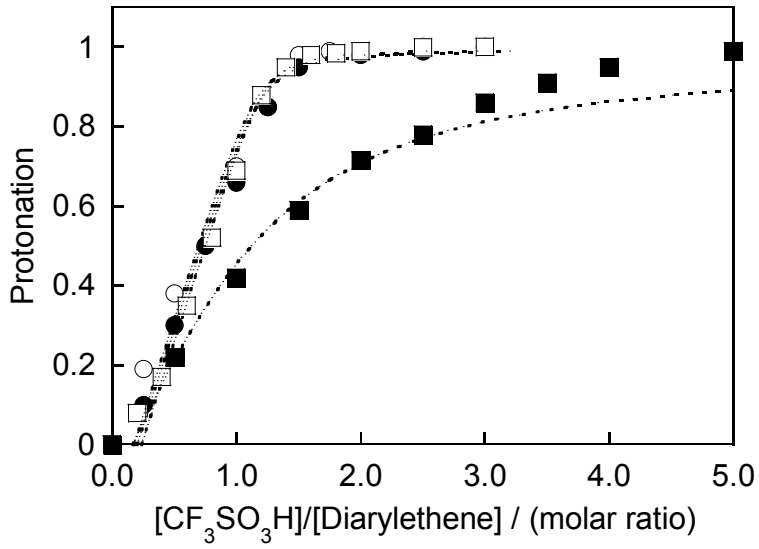


Figure 3. Protonation of **1a** (○), **1b** (●), **2a** (□), and **2b** (■) by trifluoromethanesulfonic acid in acetonitrile. The dotted lines were determined from the calculated values.

References

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