Electronic Supplementary Information

Chemical Control of Photochromic Reactivity of Diarylethene Derivatives

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Experimental

Solvents used in photochemical measurements were spectroscopic grade and were purified by distillation before use. ^{1}H NMR spectra were recorded on a NMR spectrometer (Bruker-AVANCE-400, 400 MHz). Samples were dissolved in $CDCl_3$ and tetramethylsilane was used as an internal standard. Mass spectra were measured with a mass spectrometer (Shimadzu GCMS-QP5050A and JEOL JMS mate II). Absorption spectra were measured with a Hitachi U-3500 absorption spectrophotometer. Photoirradiation was carried out using an USHIO 1000 W high-pressure mercury lamp or an USHIO 500 W xenon lamp as the light sources. Monochromic light was obtained by passing the light through a monochromater (Ritsu MV-10N) or a band-pass filter ($\Delta\lambda_{1/2}$ = 15 nm).

Synthesis

Synthetic procedures are shown in Scheme S1 and S2.

N-(2-Hydroxyphenyl)-2,3-bis(2,4,5-trimethyl-3-thienyl)maleimide (1)

A solution of 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**5**) (520 mg, 1.50 mmol), *o*-aminophenol (183 mg, 1.68 mmol), and triethylamine (0.5 ml) in toluene (50 ml) was refluxed for 24 h with a Dean-Stark condenser. The reaction mixture was washed with brine, dried over $MgSO_4$, and concentrated. **1** (650 mg, ~ 100 %) was obtained as a yellow powder. mp 224-225 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.76 (s, 3H), 1.92 (s, 3H), 1.94 (s, 3H), 2.08 (s, 3H), 2.27 (s, 3H), 2.29 (s, 3H), 6.09 (s, 1H),7.05-7.38 (m, 4H); HRMS (FAB^+): m/z = 437.1111 $[M]^+$ (calcd. for $C_{24}H_{23}NO_3S_2$: 437.1119); Anal. Calcd. for $C_{24}H_{23}NO_3S_2$: C, 65.88; H, 5.30; N, 3.20. Found: C, 66.08; H, 5.31; N, 3.15.

***N*-(2-Acetoxyxyphenyl)-2,3-bis(2,4,5-trimethyl-3-thienyl)maleimide (2)**

A solution of **1** (100 mg, 0.23 mmol) and acetic anhydride (233 mg, 2.3 mmol) in THF (5 ml) was stirred for 24 h at room temperature. The reaction mixture was washed with brine, dried over $MgSO_4$, and concentrated. **2** (110 mg, ~ 100 %) was obtained as a yellow powder. mp 156-157 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.79 (s, 3H), 1.95 (s, 3H), 1.97 (s, 3H), 2.11 (s, 3H), 2.19 (s, 3H), 2.25 (s, 3H), 2.28 (s, 3H), 7.31-7.54 (m, 4H); HRMS (FAB^+): m/z = 479.1228 $[M]^+$ (calcd. for $C_{26}H_{25}NO_4S_2$: 479.1225); Anal. Calcd. for $C_{26}H_{25}NO_4S_2$: C, 65.11; H, 5.25; N, 2.92. Found: C, 65.07; H, 5.31; N, 2.96.

Hydrolysis of 2

A solution of **2** (10 mg, 0.021 mmol) and hydrochloric acid (1.0 ml) in acetonitrile (10 ml) was heated for 2 h at 75 ˚C. The reaction mixture was extracted with chloroform, dried over $MgSO_4$, and concentrated. **1** was isolated as a yellow powder by column chromatography on silica gel (9.1 mg, ~ 100 %).

1,2-Dicyano-1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)maleimide (7)

To 10 ml of 50 % NaOH aqueous solution containing tetra-n-butylammonium bromide (70 mg, 0.22 mmol) was added a mixture of 3-cyanomethyl-2,4-dimethyl-5-phenylthiophene **6** (2.0 g, 8.8 mmol) and CCl_4 (10 ml) at room temperature. The solution was stirred for 1.5 h at 50 ˚C. The reaction mixture was poured into water and the product was extracted with chloroform. After the solvent was removed, the cis form was isolated in 77 % yield by column chromatography on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 3H), 2.05 (s, 3H), 2.23 (s, 3H), 2.28 (s, 3H), 7.31-7.48 (m, 10H); HRMS (FAB$^+$): m/z = 450.1217 $[M]^+$ (calcd. for $C_{26}H_{22}N_2S_2$: 450.1224).

2,3-Bis(2,4-dimethyl-5-phenyl-3-thienyl)maleic Anhydride (8)

7 (2.9 g, 6.5 mmol) and ethylene glycol monoethyl ether were added to 10 ml of a 50 % potassium hydroxide aqueous solution, and the solution was refluxed for 24 h. The reaction mixture was poured into water and 2 N hydrochloric acid aqueous solution was added until the mixture became acidic. The yellow precipitate was extracted with chloroform. After the chloroform was removed, **8** was isolated in 12 % yield by column chromatography on silica gel. The product was further purified with GPC and HPLC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.95 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 2.23 (s, 3H), 7.41-7.55 (m, 10H); HRMS (FAB$^+$): m/z = 470.1032 $[M]^+$ (calcd. for $C_{28}H_{22}O_3S_2$: 470.1010).

***N*-(2-Hydroxyphenyl)-2,3-bis(2,4-dimethyl-5-phenyl-3-thienyl)maleimide (3)**

2,3-Bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**5**) (360 mg, 0.77 mmol), *o*-aminophenol (92 mg, 0.84 mmol), and triethylamine (0.25 ml) in toluene (30 ml) was refluxed for 24 h with a Dean-Stark condenser. The reaction mixture was washed with brine, dried over $MgSO_4$, and concentrated. **3** (420 mg, 97 %) was obtained as a yellow powder. mp 143-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 2.25 (s, 3H), 5.59 (s, 1H), 7.11-7.49 (m, 14H); HRMS (FAB$^+$): m/z = 561.1422 $[M]^+$ (calcd. for $C_{34}H_{27}NO_3S_2$: 561.1432); Anal. Calcd. for $C_{34}H_{27}NO_3S_2$: C, 72.70; H, 4.84; N, 2.49. Found: C, 72.12; H, 4.91; N, 2.52

***N*-(2-Acetoxyphenyl)-2,3-bis(2,4-dimethyl-5-phenyl-3-thienyl)- maleimide (4)**

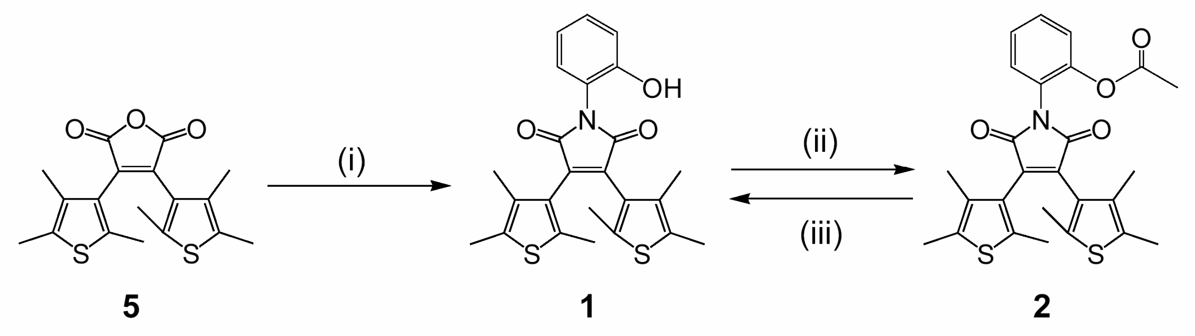
A solution of **3** (210 mg, 0.37 mmol), acetic anhydride (377 mg, 3.7 mmol) in THF (10 ml) was stirred for 24 h at room temperature. The reaction mixture was washed with brine, dried over $MgSO_4$, and concentrated. **4** (220 mg, ~ 100 %) was obtained as a yellow powder. mp 124-125 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 3H), 2.11 (s, 3H), 2.12 (s, 3H), 2.21 (s, 3H), 2.25 (s, 3H), 7.33-7.52 (m, 14H); HRMS (FAB$^+$): m/z = 603.1527 $[M]^+$ (calcd. for $C_{36}H_{29}NO_4S_2$: 603.1538); Anal. Calcd. for $C_{36}H_{29}NO_4S_2$: C, 71.62; H, 4.84; N, 2.32. Found: C, 71.57; H, 5.14; N, 2.21.

Hydrolysis of 4

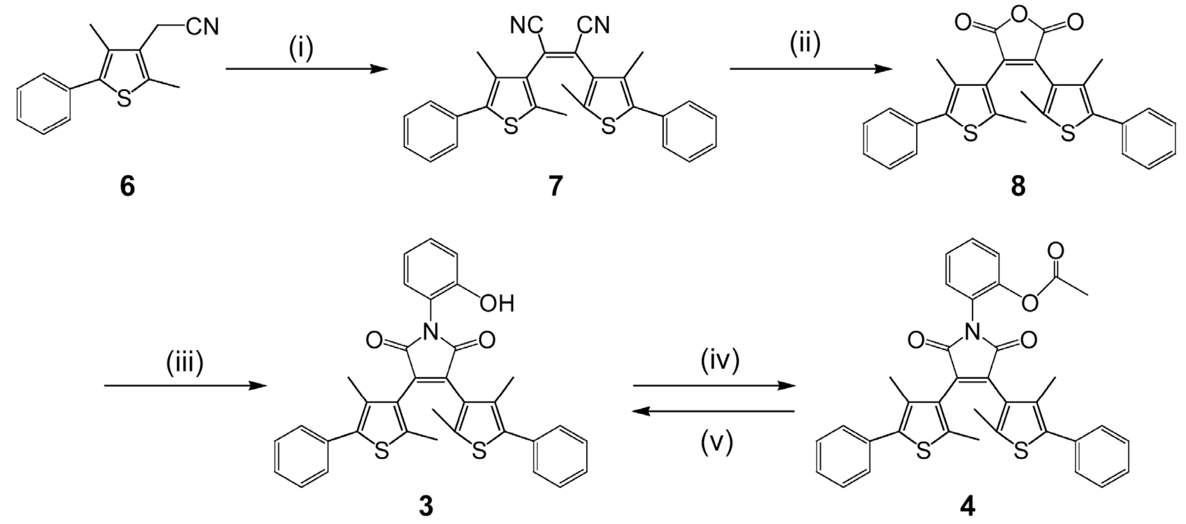
A solution of **4** (10 mg, 0.016 mmol) and hydrochloric acid (1.0 ml) in acetonitrile (10 ml) was heated for 2 h at 75 ˚C. The reaction mixture was extracted with chloroform, dried over $MgSO_4$, and concentrated. **3** was isolated as a yellow powder by column chromatography on silica gel (9.3 mg, ~ 100 %).

N-(3-Hydroxyphenyl)-2,3-bis(2,4,5-trimethyl-3-thienyl)maleimide (Reference molecule)

A solution of 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**5**) (100 mg, 0.43 mmol), *m*-aminophenol (50 mg, 0.46 mmol), and triethylamine (0.5 ml) in toluene (50 ml) was refluxed for 24 h with a Dean-Stark condenser. The reaction mixture was washed with brine, dried over $MgSO_4$, and concentrated. **1** (178 mg, ~ 95 %) was obtained as a yellow powder. mp 109-110 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.78 (s, 3H), 1.94 (s, 3H), 1.95 (s, 3H), 2.10 (s, 3H), 2.26 (s, 3H), 2.28 (s, 3H), 4.89 (s, 1H), 6.84 (dd, 1H, J = 8.4 Hz, 2.4 Hz), 7.01-7.02 (m, 1H), 7.09 (d, 1H, J = 8Hz), 7.35 (t, 1H, J = 8Hz); HRMS (FAB$^+$): m/z = 437.1113 $[M]^+$ (calcd. for $C_{24}H_{23}NO_3S_2$: 437.1119); Anal. Calcd. for $C_{24}H_{23}NO_3S_2$: C, 65.88; H, 5.30; N, 3.20. Found: C, 65.98; H, 5.32; N, 3.18.



Scheme S1. (i) *o*-aminophenol, triethylamine, toluene, reflux, 24 h; (ii) acetic anhydride, THF, r.t., 24 h; (iii) HCl, acetonitrile, 75 ˚C, 2 h.

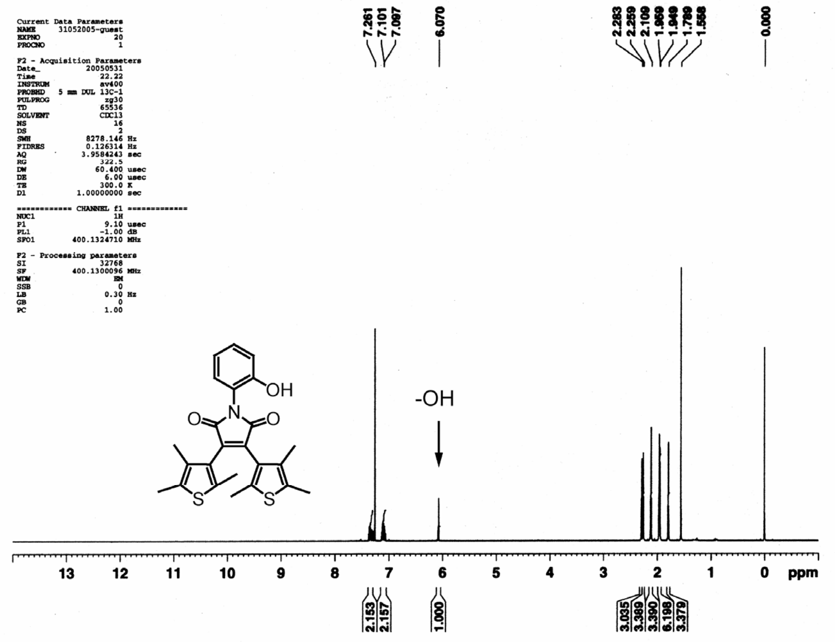


Scheme S2. (i) tetra-n-buthylammonium bromide, CCl$_4$, 50 % NaOH$_{aq}$, 50 ˚C, 1.5 h; (ii) ethylene glycol monoethyl ether, 50% KOH$_{aq}$, reflux, 24 h; (iii) *o*-aminophenol, triethylamine, toluene, reflux, 24 h; (iv) acetic anhydride, THF, r.t., 24 h; (v) HCl, acetonitrile, 75 ˚C, 2 h.

NMR experiments

^{1}H NMR spectra of *o*-hydroxyphenyl and *m*-hydroxyphenyl derivatives were measured with various solvents in order to confirm the contribution of intramolecular hydrogen bonding. The results are shown below.

($CDCl_3$)



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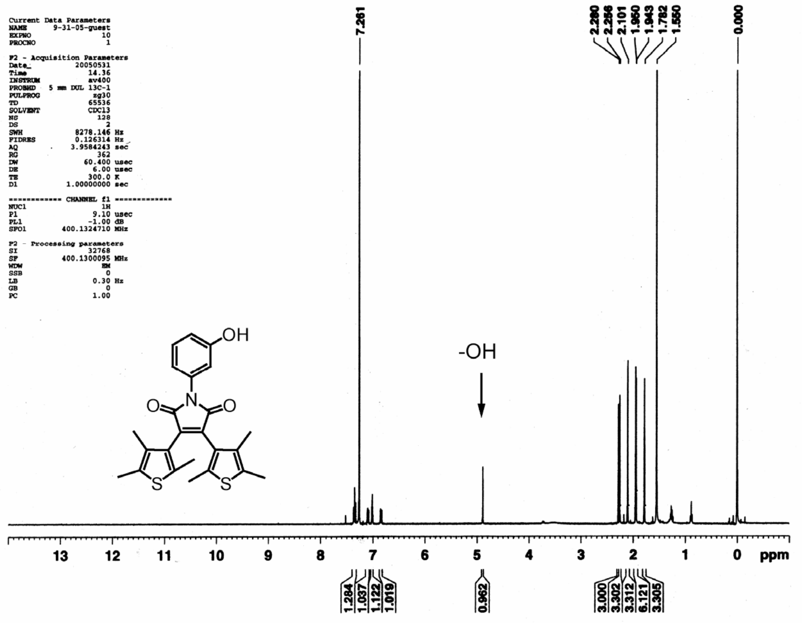

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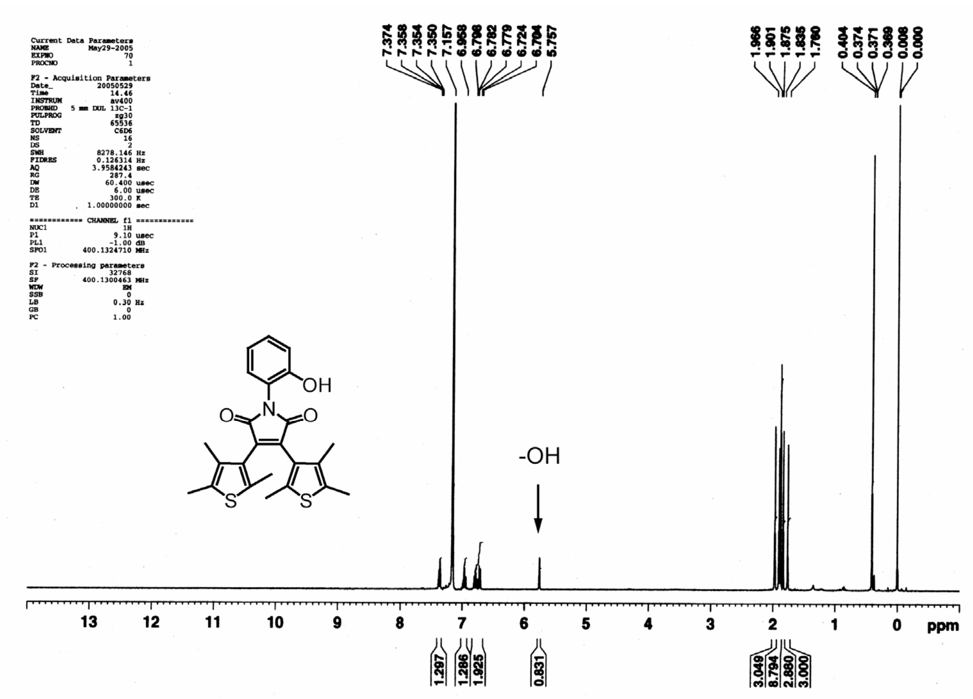
(C_6D_6)



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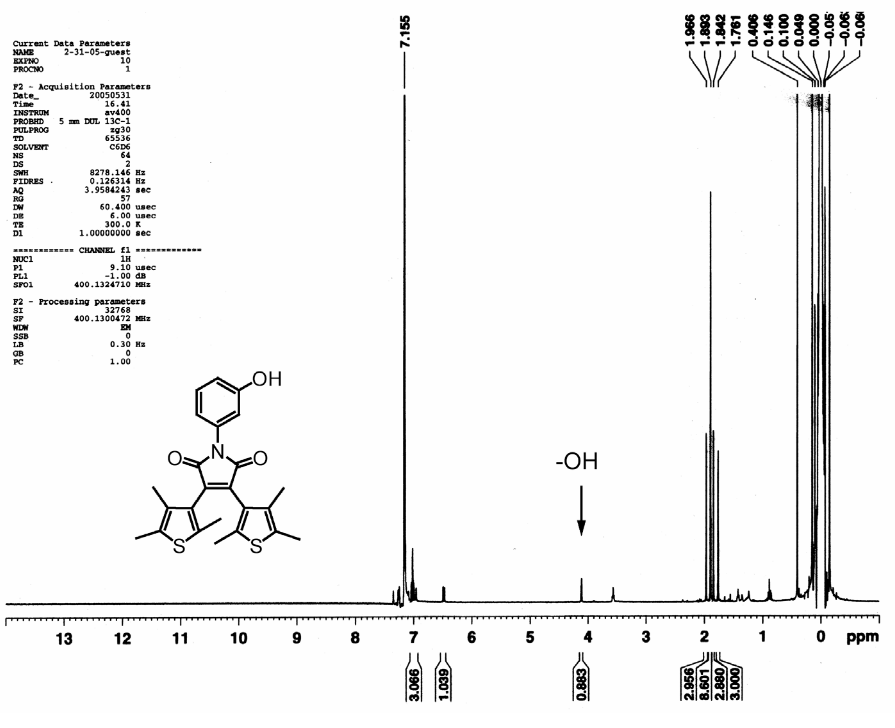

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Calculation

The geometry optimization was demonstrated by using an AM 1 semiempirical calculation method in WinMOPAC. The distance between the hydrogen atom in phenolic hydroxy group and the oxygen atom in an imide carbonyl group was estimated to be 2.079 Å, which is enough to form the intramolecular hydrogen bonding.