***Supplementary Information for***

# Photocyclization reaction of a diarylmaleimide derivative in polar solvents

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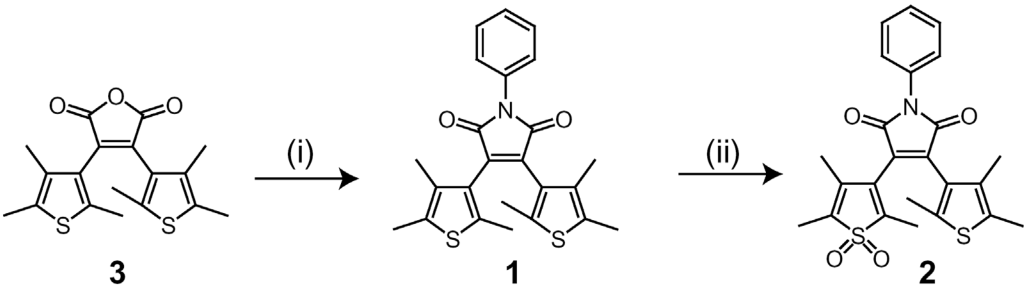
## General.

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 $CDCl_3$ with tetramethylsilane as an internal standard. Mass spectra were measured with a mass spectrometer (Shimadzu GCMS-QP5050A and JEOL GC mate II). Absorption and fluorescence spectra were measured with a Hitachi U-3500 absorption spectrophotometer and a Hitachi F-2500 fluorescence spectrophotometer, respectively. 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-10 N) or a band-pass filter ($\Delta\lambda_{1/2}$ = 15 nm).

## Materials.

Synthetic procedures are shown in Scheme S1.

*Scheme S1*



(i) aniline, $Et_3N$, toluene, 2h, reflux, 99 %; (ii) mCPBA, $CH_2Cl_2$, 16h, 67 %

### *N*-phenyl-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 (**3**) (520 mg, 1.50 mmol), aniline (156 mg, 1.68 mmol), and triethylamine (0.5 mL) in toluene (50 mL) was refluxed for 2 h with a Dean–Stark condenser. The reaction mixture was extracted with $CHCl_3$, and organic layer was washed with brine, dried over $MgSO_4$, and evaporated to drieness. The crude product was purified by silica gel column chromatography (Hexane/AcOEt = 80:20) to yield **2** (650 mg, 99%) as orange powder.

mp 128–129 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.79 (s, 3H), 1.95-1.96 (m, 6H), 2.11 (s,3H), 2.26-2.28 (m, 6H), 7.33-7.40 (m, 1H), 7.45-7.54 (m, 4H); MS (FAB$^+$) *m/z* = 422 $[M+H]^+$; analysis calculated for $C_{24}H_{23}NO_2S_2$: C, 68.38; H, 5.50; N, 3.32. Found: C, 68.32; H, 5.59; N, 3.32.

### *N*-phenyl-2-(1,1-dioxide-2,4,5-trimethyl-3-thienyl)-3-(2,4,5-trimethyl-3-thienyl)maleimide (2):

*N*-phenyl-2,3-bis(2,4,5-trimethyl-3-thienyl)maleimide (**1**) (135 mg, 0.32 mmol), mCPBA (65 %) (186 mg, 0.70 mmol) in $CH_2Cl_2$ (2.8 mL) was stirred for 16 h at room temperature. The solution was washed with $NaHCO_3$ aqueous solution. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Purification was carried out by silica gel column chromatography ($CH_3Cl$) to give **2** (97 mg, 0.214 mmol) with 67 % yield.

mp 118–119 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.54 (s, 3H), 1.82 (s, 3H), 2.23 (d, 3H, $J$ = 0.8 Hz), 2.32 (s, 3H), 2.41 (s, 3H), 2.48 (d, 3H, 0.8 Hz), 7.35–7.43 (m, 3H), 7.48–7.52 (m, 2H); MS (FAB$^+$): *m/z* = 454 $[M+H]^+$; Analysis calculated for $C_{24}H_{23}NO_4S_2$: C, 63.55; H, 5.11; N, 3.09. Found: C, 63.21; H, 5.32; N, 2.97.

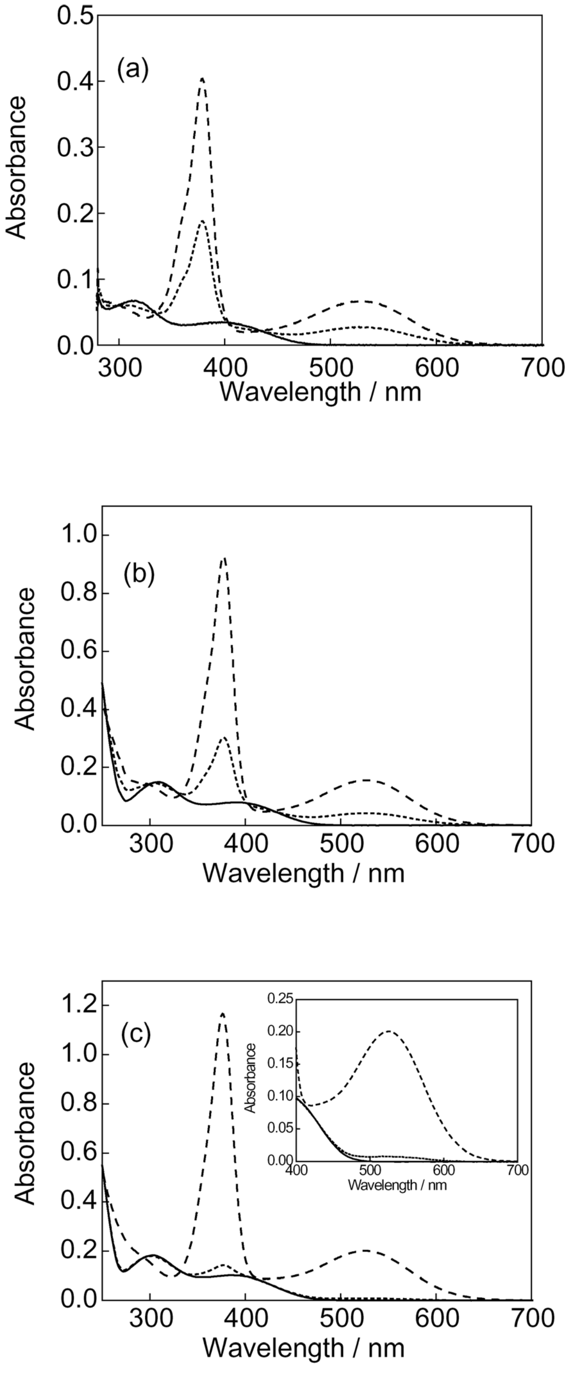


Figure S1 Absorption spectra of **1** (a) in toluene, (b) in THF, (c) in acetonitrile; the open-ring isomer (solid line), the photostationary state under irradiation with 405 nm light (dashed line), and the closed-ring isomer (broken line). The inset in Figure S1(c) is the extended absorption spectra between 400 nm and 700 nm.

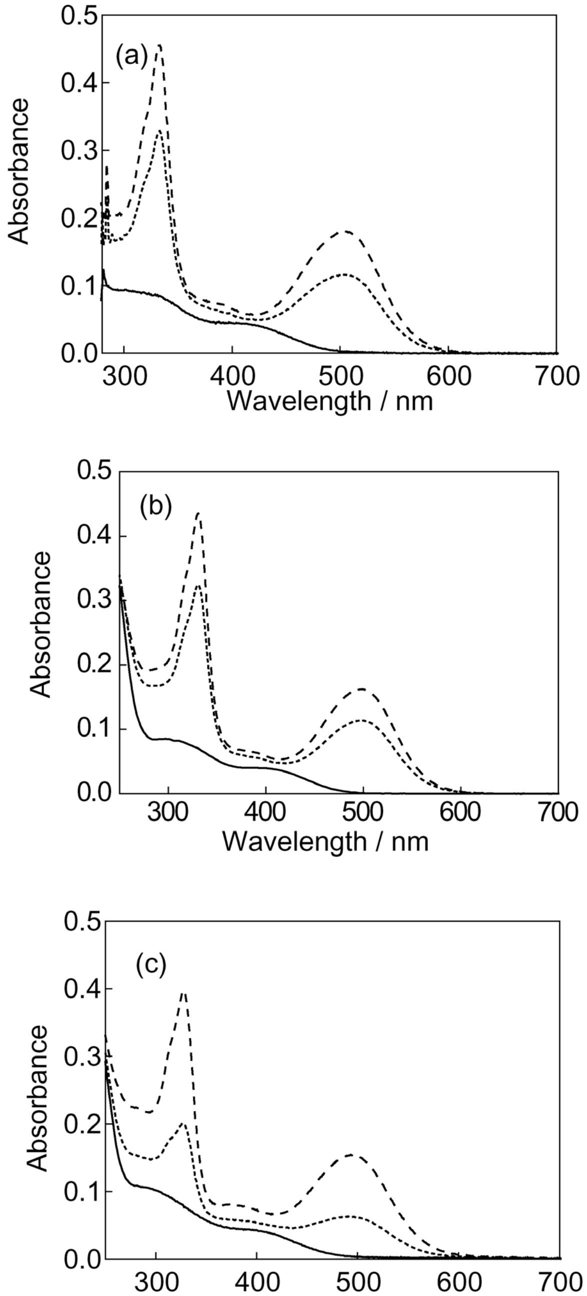


Figure S2 Absorption spectra of **2** (a) in toluene, (b) in THF, (c) in acetonitrile; the open-ring isomer (solid line), the photostationary state under irradiation with 405 nm light (dashed line), and the closed-ring isomer (broken line).