Electronic Supplementary Information

Turn-on mode fluorescent diarylethenes: Effect of electron-donating and electron-withdrawing substituents on photoswitching performance

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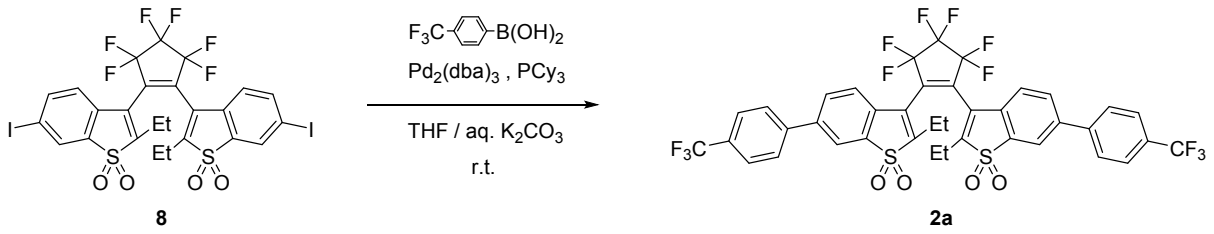
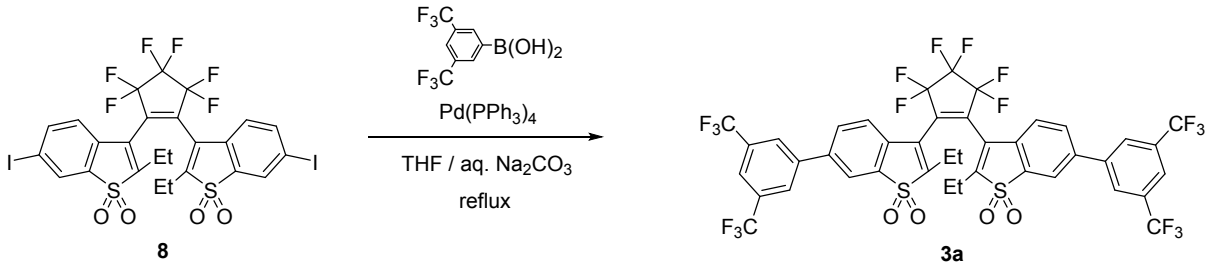
Experimental

^{1}H NMR spectra were measured with a 400 MHz NMR spectrometer (Bruker, Avance 400). Tetramethylsilane (TMS) was used as an internal standard. Mass spectrometry (MS) was carried out with a mass spectrometer (Shimadzu, GCMS-QP2010Plus) based on electron-impact (EI) ionization.

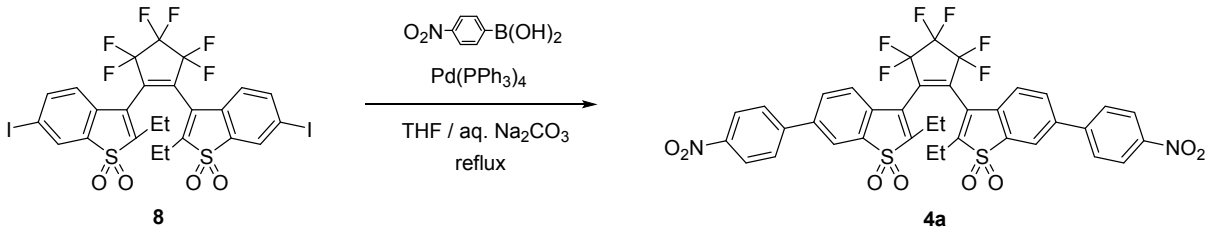


To a THF solution (7.0 mL) containing **8**[S1] (502 mg, 0.618 mmol) were added 4-(trifluoromethyl)phenylboronic acid (282 mg, 1.48 mmol), saturated aqueous K_2CO_3 (5.0 mL), tris(dibenzylideneacetone)dipalladium(0) (71 mg, 0.078 mmol), and ca. 20% tricyclohexylphosphine toluene solution (4 drops), and the mixture was stirred at room temperature for 2 h. The resulting mixture was extracted with chloroform. The organic layer was washed with aqueous $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered, and then evaporated in vacuo. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 4 : 1) to give **2a** (331 mg, 0.390 mmol, 63% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13 (t, *J* = 7.6 Hz, 6.0H), 1.44 (t, *J* = 7.6 Hz, 3.9H), 2.41-2.75 (m, 6.6H), 7.25 (d, *J* = 8.0 Hz, 1.3H), 7.30 (d, *J* = 8.0 Hz, 2.0H), 7.60-7.71 (m, 7.2H), 7.77 (d, *J* = 8.0 Hz, 4.0H), 7.83 (dd, *J* = 8.0 and 1.6 Hz, 2.0H), 7.91 (d, *J* = 1.6 Hz, 1.3H), 7.97 (d, *J* = 1.6 Hz, 2.0H); MS (EI) *m*/*z* 848 $[M]^+$.



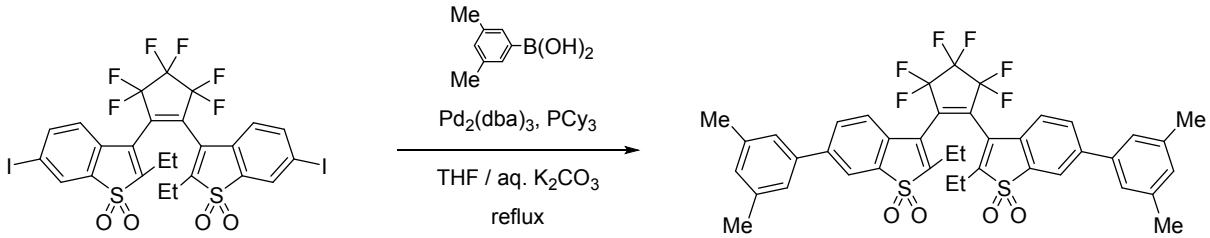
To a THF solution (9.5 mL) containing **8** (501 mg, 0.617 mmol) were added 3,5-bis(trifluoromethyl)phenylboronic acid (398 mg, 1.54 mmol), saturated aqueous Na_2CO_3 (6.0 mL), tetrakis(triphenylphosphine)palladium(0) (97 mg, 0.084 mmol), and the mixture was refluxed for 2.5 h. The resulting mixture was extracted with chloroform. The organic layer was washed with aqueous $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered, and then evaporated in vacuo. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 4 : 1) to give **3a** (238 mg, 0.242 mmol, 39% yield) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.15 (t, *J* = 7.6 Hz, 6.0H), 1.45 (t, *J* = 7.6 Hz, 3.6H), 2.43-2.76 (m, 6.4H), 7.29 (d, *J* = 8.0 Hz, 1.2H), 7.34 (d, *J* = 8.0 Hz, 2.0H), 7.69 (dd, *J* = 8.0 and 2.0 Hz, 1.2H), 7.87 (dd, *J* = 8.0 and 2.0 Hz, 2.0H), 7.93-7.94 (m, 4.8H), 7.97 (s(br), 2.0H), 8.00 (d, *J* = 1.6 Hz, 2.0H), 8.03 (s(br), 4.0H); MS (EI) *m*/*z* 984 $[M]^+$.

S1 K. Uno, H. Niikura, M. Morimoto, Y. Ishibashi, H. Miyasaka, M. Irie, *J. Am. Chem. Soc.* **2011**, *133*, 13558-13564



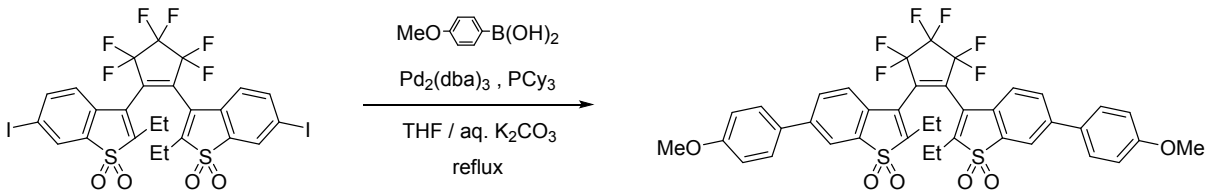
8 **4a**

To a THF solution (6.0 mL) containing **8** (295 mg, 0.363 mmol) were added 4-nitrophenylboronic acid (178 mg, 1.07 mmol), saturated aqueous Na_2CO_3 (3.0 mL), tetrakis(triphenylphosphine)palladium(0) (62 mg, 0.054 mmol), and the mixture was refluxed for 2.5 h. The resulting mixture was extracted with chloroform. The organic layer was washed with aqueous $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered, and then evaporated in vacuo. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 4 : 1) to give **4a** (88 mg, 0.110 mmol, 30% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.15 (t, *J* = 7.6 Hz, 6.0H), 1.45 (t, *J* = 7.6 Hz, 3.0H), 2.43-2.75 (m, 6.0H), 7.30-7.33 (m, 3.0H), 7.66-7.70 (m, 3.0H), 7.76 (d, *J* = 8.0 Hz, 4.0H), 7.86 (d, *J* = 8.0 Hz, 2.0H), 7.95 (s, 1.0H), 8.00 (s, 2.0H), 8.31 (d, *J* = 8.8 Hz, 2.0H), 8.36 (d, *J* = 8.8 Hz, 4.0H); MS (EI) *m*/*z* 802 $[M]^+$.



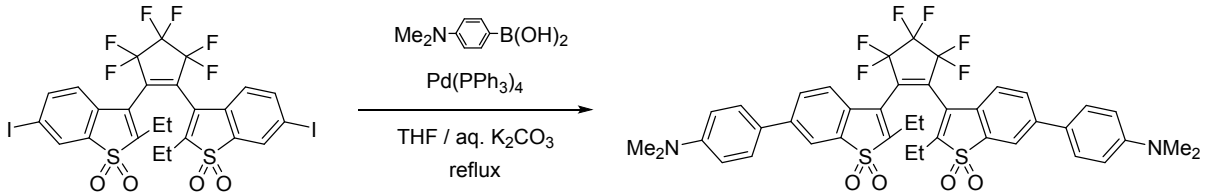
8 **5a**

To a THF solution (10 mL) containing **8** (308 mg, 0.379 mmol) were added 3,5-dimethylphenylboronic acid (182 mg, 1.21 mmol), saturated aqueous K_2CO_3 (5.0 mL), tris(dibenzylideneacetone)dipalladium(0) (38 mg, 0.041 mmol), and ca. 20% tricyclohexylphosphine toluene solution (10 drops), and the mixture was refluxed for 2.5 h. The resulting mixture was extracted with chloroform. The organic layer was washed with aqueous $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered, and then evaporated in vacuo. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 4 : 1) to give **5a** (153 mg, 0.199 mmol, 53% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.08 (t, *J* = 7.6 Hz, 6.0H), 1.43 (t, *J* = 7.6 Hz, 3.9H), 2.35 (s, 7.8H), 2.40 (s, 12.0H), 2.42-2.72 (m, 6.6H), 7.04 (s(br), 1.3H), 7.08 (s(br), 2.0H), 7.11 (s(br), 2.6H), 7.18-7.20 (m, 5.3H), 7.24 (d, *J* = 8.0 Hz, 2.0H), 7.59 (dd, *J* = 8.0 and 1.6 Hz, 1.3H), 7.79 (dd, *J* = 8.0 and 1.6 Hz, 2.0H), 7.88 (d, *J* = 1.6 Hz, 1.3H), 7.96 (d, *J* = 1.6 Hz, 2.0H); MS (EI) *m*/*z* 768 $[M]^+$.



8 **6a**

To a THF solution (8.0 mL) containing **8** (310 mg, 0.382 mmol) were added 4-methoxyphenylboronic acid (168 mg, 1.11 mmol), saturated aqueous K_2CO_3 (5.0 mL), tris(dibenzylideneacetone)dipalladium(0) (42 mg, 0.046 mmol), and ca. 20% tricyclohexylphosphine toluene solution (5 drops), and the mixture was refluxed for 1.5 h. The resulting mixture was extracted with chloroform. The organic layer was washed with aqueous $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered, and then evaporated in vacuo. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 4 : 1) to give **6a** (229 mg, 0.296 mmol, 77% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 (t, *J* = 7.6 Hz, 6.0H), 1.42 (t, *J* = 7.6 Hz, 3.9H), 2.38-2.70 (m, 6.6H), 3.84 (s, 3.9H), 3.87 (s, 6.0H), 6.96 (d, *J* = 8.0 Hz, 2.6H), 7.01 (d, *J* = 8.0 Hz, 4.0H), 7.18 (d, *J* = 8.0 Hz, 1.3H), 7.23 (d, *J* = 8.0 Hz, 2.0H), 7.45 (d, *J* = 8.0 Hz, 2.6H), 7.54 (d, *J* = 8.0 Hz, 4.0H), 7.57 (d, *J* = 8.0 Hz, 1.3H), 7.76 (d, *J* = 8.0 Hz, 2.0H), 7.85 (s, 1.3H), 7.92 (s, 2.0H); MS (EI) *m*/*z* 772 $[M]^+$.



8 **7a**

To a THF solution (10 mL) containing **8** (205 mg, 0.252 mmol) were added 4-(*N*,*N*-dimethylamino)phenylboronic acid (127 mg, 0.770 mmol), saturated aqueous K_2CO_3 (5.0 mL), tetrakis(triphenylphosphine)palladium(0) (29 mg, 0.025 mmol), and the mixture was refluxed for 7 h. The resulting mixture was extracted with chloroform. The organic layer was washed with aqueous $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered, and then evaporated in vacuo. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 1 : 1) to give **7a** (168 mg, 0.210 mmol, 83% yield) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.06 (t, *J* = 7.6 Hz, 6.0H), 1.42 (t, *J* = 7.6 Hz, 3.9H), 2.36-2.69 (m, 6.6H), 3.00 (s, 7.8H), 3.03 (s, 12.0H), 6.73 (d, *J* = 8.8 Hz, 2.6H), 6.79 (d, *J* = 8.8 Hz, 4.0H), 7.14 (d, *J* = 8.0 Hz, 1.3H), 7.20 (d, *J* = 8.0 Hz, 2.0H), 7.42 (d, *J* = 8.8 Hz, 2.6H), 7.51 (d, *J* = 8.8 Hz, 4.0H), 7.56 (dd, *J* = 8.0 and 1.6 Hz, 1.3H), 7.74 (dd, *J* = 8.0 and 1.6 Hz, 2.0H) , 7.85 (d, *J* = 1.6 Hz, 1.3H), 7.93 (d, *J* = 1.6 Hz, 2H); MS (EI) *m*/*z* 798 $[M]^+$.

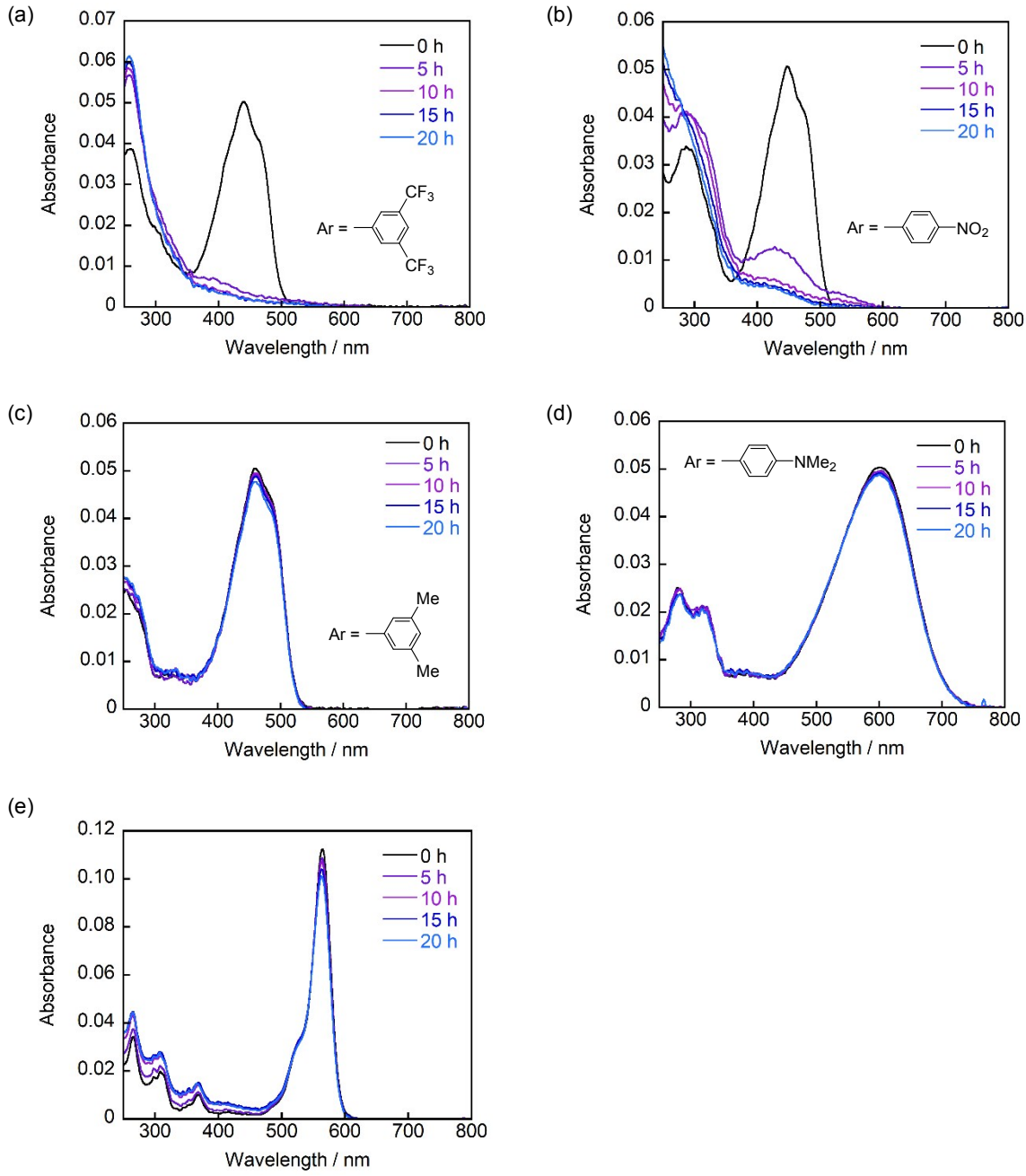


Fig. S1 Absorption spectral changes of **3b** (a), **4b** (b), **5b** (c), **7b** (d), and rhodamine 101 (e) in ethanol under continuous irradiation with 365 nm light (100 mW/cm^2, Keyence UV-400/UV-50H) in the presence of air.