Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supplementary Information for

Fluorescence Photoswitching of a Diarylethene-Perylenebisimide Dyad based on Intramolecular Electron Transfer

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1. Synthetic Procedure

2-Fluoro-1-(2'-methyl-6-nitro-benzo[*b*]thiophen-3-yl)perfluorocyclopentene (6)

Fuming nitric acid (1.2 ml) was slowly added to the solution of **5** (770 mg, 2.26 mmol) in acetic acid (24 ml) and acetic anhydride (3 ml) at 10 °C. After the mixture was stirred for 6 h at room temperature, water was added to the reaction mixture. The solution was neutralized by sodium hydroxide and extracted by ethyl acetate, dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/7) to give 480 mg (1.25 mmol) of **6** in 55 % yield as pale yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 3H), 7.59 (d, J = 8.8 Hz, 1H), 8.27 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 8.75 (d, J = 2.0 Hz, 1H); EI-MS m/z = 385 $[M]^+$; Anal. Calcd. for $C_{14}H_6F_7NO_2S$: C, 43.65; H, 1.57; N, 3.64. Found: C, 43.62; H, 1.55; N, 3.65.

2-Fluoro-1-(2'-methyl-6-amino-benzo[*b*]thiophen-3-yl)perfluorocyclopentene (7)

Sodium tetrahydroborate (155 mg, 4.09 mmol) was slowly added to the methanol solution (28 ml) of **6** (450 mg, 1.17 mmol) and nickel(II)chloride, 6-hydrate (555 mg, 2.34 mmol) at 0 °C and stirred at room temperature for 1 h. And then, the reaction catalysts were removed by suction filtration, and the filtrate was extracted by ether, dried over anhydrous magnesium sulfate, and concentrated. The product was used in next reaction without further purification.

^{1}H-NMR (400 MHz $CDCl_3$) δ *no data*; EI-MS m/z = 355 $[M]^+$.

2-Fluoro-1-{2'-methyl-6-(2,5-dimethyl-pyrrol-1-yl)-benzo[*b*]thiophen-3-yl}perfluoro cyclopentene (8)

The solution of **7** (200 mg, 0.56 mmol) and acetonylacetone (130 mg, 1.13 mmol) and small amount of acetic acid in toluene (5 ml) was refluxed for 14 h with a Dean-Stark condenser. The reaction mixture was extracted by ether, dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/7) to give 225 mg (0.52 mmol) of **8** in 92 % yield as pale yellow solid.

^{1}H-NMR (400 MHz $CDCl_3$) δ 2.05 (s, 6H), 2.56 (s, 3H), 5.93 (s, 2H), 7.25 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 2.0 Hz, 1H); EI-MS m/z = 433 $[M]^+$; Anal. Calcd. for $C_{20}H_{14}F_7NS$: C, 55.43; H, 3.26; N, 3.23. Found: C, 55.25; H, 3.31; N, 3.21.

1-(3-Methyl-5-phenylthiophen-2-yl)-2-{2-methyl-6-(2,5-dimethyl-pyrrol-1-yl)-benzo[*b*]thiophen-3-yl}perfluorocyclopentene (10)

Under nitrogen atmosphere, *n*-butyllithium hexane solution (0.3 ml, 0.46 mmol) was slowly added to the solution of **9** (105 mg, 0.42 mmol) in dry THF (3 ml) at -78 °C. After the mixture was stirred for 1 h, **8** (200 mg, 0.46 mmol) in dry THF (3 ml) was slowly added and the solution was stirred for 30 min. at -78 °C. When the reaction mixture cooled to room temperature, it was extracted by ether, dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1/7) to give 215 mg (0.37 mmol) of **10** in 88 % yield as yellow powder.

^{1}H-NMR (400 MHz $CDCl_3$) δ 1.95 (s, 3H), 2.02 (s, 6H), 2.40 (s, 3H), 5.91 (s, 2H), 6.98 (s, 1H), 7.16 – 7.19 (m, 1H), 7.29 – 7.36 (m, 3H), 7.42 – 7.45 (m, 2H), 7.57 – 7.60 (m, 2H); EI-MS *m/z* = 587 $[M]^+$; Anal. Calcd. for $C_{31}H_{23}F_6NS_2$: C, 63.36; H, 3.95; N, 2.38. Found: C, 63.39; H, 3.97; N, 2.38.

1-(3-Methyl-5-phenylthiophen-2-yl)-2-(2-methyl-6-amino-benzo[*b*]thiophen-3-yl)perfluorocyclopentene (11)

The solution of **10** (560 mg, 0.95 mmol), hydroxylammonium chloride (1.32 g, 19.1 mmol), and triethylamine (1.4 ml, 9.53 mmol) in ethanol (25 ml) and H_2O (5 ml) was vigorously refluxed for 36 h. The reaction mixture was extracted by ether, dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 4/6) to give 430 mg (0.84 mmol) of **11** in 89 % yield as orange oil.

^{1}H-NMR (400 MHz $CDCl_3$) δ 1.87 (s, 3H), 2.27 (s, 3H), 3.74 (s, 2H), 6.70 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 6.96 (s, 1H), 7.00 (d, J = 2.0 Hz, 1H), 7.28 – 7.36 (m, 4H), 7.45 – 7.48 (m, 2H); EI-MS m/z = 509 $[M]^+$; Anal. Calcd. for $C_{25}H_{17}F_6NS_2$: C, 58.93; H, 3.36; N, 2.75. Found: C, 58.92; H, 3.38; N, 2.74.

Compound 12

The solution of **11** (200 mg, 0.39 mmol) and perylene monoimide (**4**)[1] (150 mg, 0.26 mmol) and zinc acetate (30 mg, 0.16 mmol) in quinoline (14 ml) was heated at 155 °C for 20 h. After being cooled, the reaction mixture was poured into 2*N* HCl solution to give a precipitate. The precipitate was filtered and washed with water and extracted by chloroform, dried over anhydrous magnesium sulfate, and concentrated. The residue

was purified by silica gel column chromatography (CH_2Cl_2/hexane = 8/2) to give 253 mg (0.24 mmol) of **12** in 91 % yield as dark red solid.

^{1}H-NMR (400 MHz $CDCl_3$) δ 0.83 (t, J = 6.8 Hz, 6H), 1.20 – 1.36 (m, 16H), 1.84 – 1.92 (m, 2H), 1.97 (s, 3H), 2.21 – 2.30 (m, 2H), 2.41 (s, 3H), 5.15 – 5.23 (m, 1H), 7.02 (s, 1H), 7.28 – 7.39 (m, 4H), 7.49 – 7.52 (m, 2H), 7.73 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 7.78 (d, J = 2.0 Hz, 2H), 8.62 – 8.73 (m, 8H); FAB-MS m/z = 1065 $[M+1]^+$; Anal. Calcd. for $C_{62}H_{50}F_6N_2O_4S_2$: C, 69.91; H, 4.73; N, 2.63. Found: C, 69.90; H, 4.69; N, 2.65.

Dyad 1

The solution of **12** (150 mg, 0.14 mmol) and 65% *m*-chloroperoxybenzoic acid (450 mg, 1.68 mmol) in CH_2Cl_2 (6 ml) was stirred at room temperature. After the mixture was stirred for 5 days, $NaHCO_3$ solution was added to the reaction mixture and extracted by dichloromethane, dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by silica gel column chromatography (CH_2Cl_2) to give 50 mg (0.044 mmol) of **1** in 34 % yield as dark red solid.

^{1}H-NMR (400 MHz $CDCl_3$) δ 0.83 (t, J = 6.8 Hz, 6H), 1.22 – 1.37 (m, 16H), 1.84 – 1.92 (m, 2H), 2.13 (s, 3H), 2.20 – 2.28 (m, 2H), 2.31 (s, 3H), 5.13 – 5.21 (m, 1H), 6.76 (s, 1H), 7.39 – 7.45 (m, 4H), 7.63 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.68 – 7.71 (m, 2H), 7.83 (d, J = 2.0 Hz, 1H), 8.54 – 8.67 (m, 8H); MS (FAB^+) m/z = 1130 $[M+1]^+$; Anal. Calcd. for $C_{62}H_{50}F_6N_2S_2$: C, 65.95; H, 4.46; N, 2.48. Found: C, 66.04; H, 4.49; N, 2.62.

Compound 13

The solution of **11** (100 mg, 0.20 mmol) and phtalic anhydride (58 mg, 0.4 mmol) and zinc acetate (10 mg, 0.05 mmol) in quinoline (10 ml) was heated at 155 °C for 20 h. After being cooled, the reaction mixture was poured into 2*N* HCl solution to give a precipitate. The precipitate was filtered and washed with water and extracted by chloroform, dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by silica gel column chromatography (CH_2Cl_2/hexane = 1/1) to give 116 mg (0.18 mmol) of **13** in 92 % yield as pale yellow solid.

^{1}H-NMR (400 MHz $CDCl_3$) δ 1.95 (s, 3H), 2.40 (s, 3H), 7.00 (s, 1H), 7.27 – 7.37 (m, 3H), 7.41 – 7.50 (m, 3H), 7.62 - 7.68 (m, 1H), 7.78 – 7.84 (m, 2H), 7.85 – 7.87 (d, J = 1.6 Hz, 1H), 7.95 – 8.00 (m, 2H); MS (FAB^+) m/z = 640 $[M+1]^+$; Anal. Calcd. for $C_{33}H_{19}F_6NO_2S_2$: C, 61.97; H, 2.99; N, 2.19. Found: C, 61.88; H, 3.04; N, 2.16.

Model diarylethene 2

The solution of **13** (100 mg, 0.16 mmol) and 65% *m*-chloroperoxybenzoic acid (200 mg, 0.75 mmol) in CH_2Cl_2 (5 ml) was stirred at room temperature. After the mixture was stirred for 5 days, $NaHCO_3$ solution was added to the reaction mixture and extracted by dichloromethane, dried over anhydrous magnesium sulfate, and concentrated. The residue was purified by silica gel column chromatography (CH_2Cl_2) to give 41 mg (0.058 mmol) of **2** in 37 % yield as pale yellow solid.

^{1}H-NMR (400 MHz $CDCl_3$) δ 2.11 (s, 3H), 2.27 (s, 3H), 6.74 (s, 1H), 7.35 – 7.46 (m, 4H), 7.64 – 7.69 (m, 2H), 7.77 – 7.85 (m, 3H), 7.93 – 7.99 (m, 2H), 8.01 (d, J = 1.6 Hz, 1H); MS (FAB$^+$) m/z = 704 $[M+1]^+$; Anal. Calcd. for $C_{33}H_{19}F_6N_2O_6S_2$: C, 56.33; H, 2.72; N, 1.99. Found: C, 56.18; H, 2.76; N, 2.07.

2. Cyclic voltammetry

The open-ring isomer of **2** (**2a**)

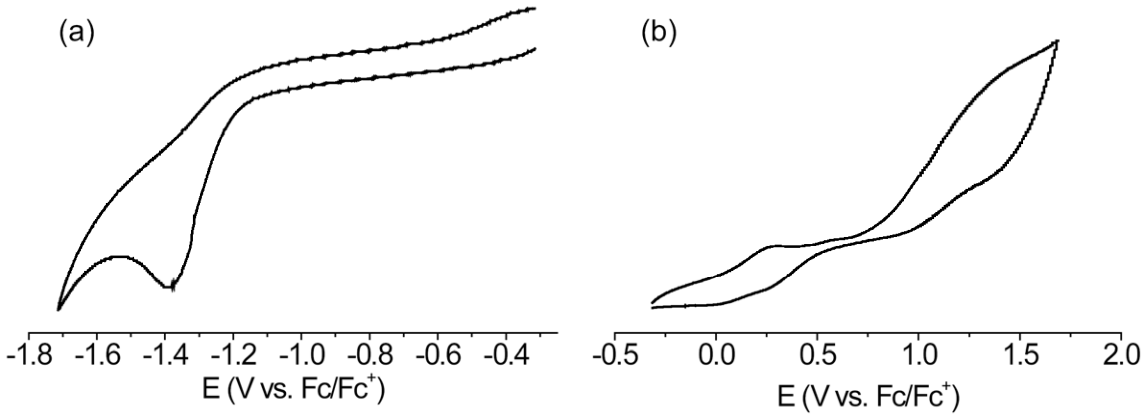

Figure S1. Cyclic voltammogram of **2a** in CH_2Cl_2, concentration = 5×10^{-4} M. (a) reduction side, (b) oxidation side. Scan rate 100 mV/sec; supporting electrolyte: 0.1 M TBAF.

The closed-ring isomer of **2** (**2b**)

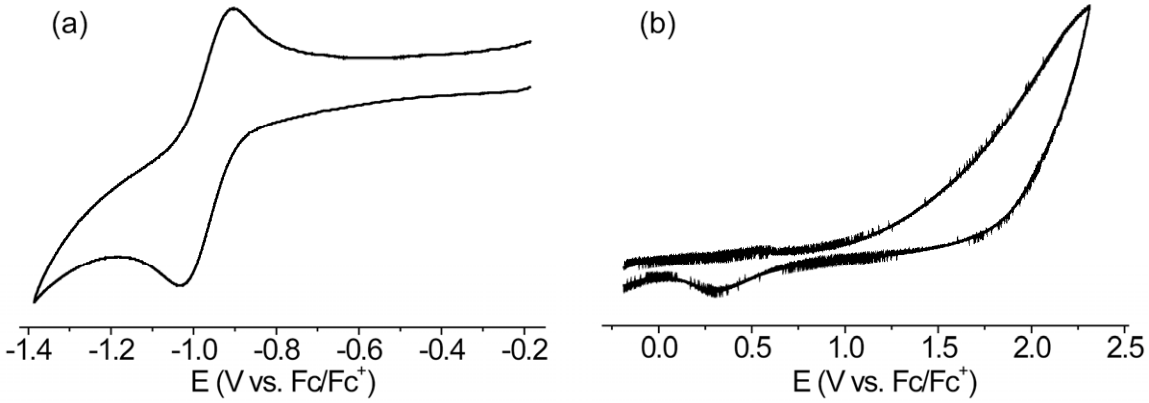

Figure S2. Cyclic voltammogram of **2b** in CH_2Cl_2, concentration = 5×10^{-4} M. (a) reduction side, (b) oxidation side. Scan rate 100 mV/sec; supporting electrolyte: 0.1 M TBAF.

N,N'-bis(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylbisimide (PBI) (**3**)

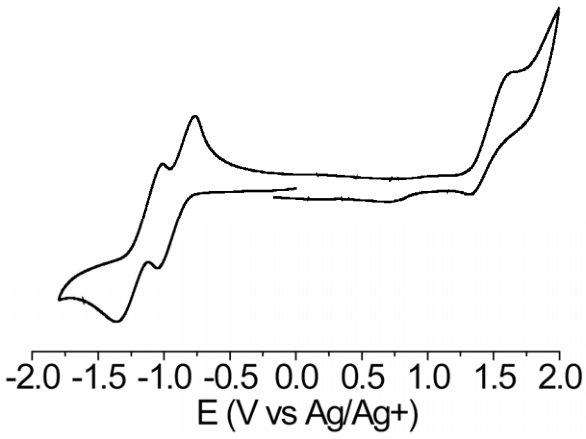

Figure S3. Cyclic voltammogram of **3** in CH_2Cl_2, concentration = 1×10^{-4} M. Scan rate 100 mV/sec; supporting electrolyte: 0.1 M TBAF.

3. Analysis of the transient absorption spectrum

In the time dependence on the sequential reaction processes as A → B → C as shown in Scheme 3, the time function for each species can be written by the following equations.

$$[A(t)] = [A(0)] \cdot \exp(-k_1 t) \quad \text{(S1)}$$

$$[B(t)] = \frac{k_q}{k_2 - k_1} \cdot [A(0)] \cdot \{\exp(-k_1 t) - \exp(-k_2 t)\} \quad \text{(S2)}$$

$$[C(t)] = [C] - \{[A(t)] + [B(t)]\} \quad \text{(S3)}$$

Here, k_1 and k_2 are decay rate constants for *A* and *B*, respectively. In the present case, the species *A* corresponds to the S_1 state of the PBI moiety and the species *B* to the transient species produced by the quenching process. The species *C* is the ground state of **1b** and [*C*] is the concentration of **1b** in the ground state before the excitation. The rate constant, k_1, is the summation of k_q and k_f, where the k_q and k_f are respectively the quenching constant and the reciprocal value of the fluorescent lifetime of the PBI moiety. By using these equations, the time profile of the transient absorbance at the wavelength, λ, is represented by the following equation.

$$\Delta A^{\lambda}(t) = \varepsilon_A^{\lambda} \times [A(t)] + \varepsilon_B^{\lambda} \times [B(t)] - \varepsilon_C^{\lambda} \times ([A(t)] + [B(t)]) \quad \text{(S4)}$$

Here, ε_A^{λ}, ε_B^{λ}, and ε_C^{λ} are respectively the molar extinction coefficients of species *A*, *B*,

and *C*. Because the transient absorbance is obtained as a difference absorbance signal, the constant signal of $\varepsilon_C^{\lambda}[C]$ is deleted in eq. (S4). At the wavelength region where the ground state of **1b** has no absorption, eq. (S4) is written by eq. (S5).

$$\Delta A(t) = [A(0)]\left\{\left(\varepsilon_A^{\lambda} + \varepsilon_B^{\lambda}\frac{k_q}{k_2 - k_1}\right)\exp[-k_1 t] - \left(\varepsilon_B^{\lambda}\frac{k_q}{k_2 - k_1}\right)\exp[-k_2 t]\right\} \qquad \text{(S5)}$$

In this calculation, the relative values of ε_A^{λ} and ε_B^{λ} by the least-square analysis for the time profile of the transient absorbance under the condition that k_1, k_2, and k_q are fixed, can be obtained.

4. Reference

1) M. W. Holman, R. Liu, D. M. Adams, *J. Am. Chem. Soc.*, 2003, **125**, 12649.