Multiaddressing Fluorescence Switch Based on a New Photochromic Diarylethene with a Triazole-Linked Rhodamine B Unit

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1. Details of experiments

Synthesis of 1-(2-methyl-3-benzothiophenyl)-2-[2-methyl-5-(4-hydroxymethylphenyl)-3-thienyl]perfluorocyclopentene (3)

To a stirred solution of compound **2** (2.61 g, 5.00 mmol) in THF (50 mL), $NaBH_4$ (0.27 g, 7.00 mmol) was added and continuously stirred. After refluxing for 2 hrs, the mixture was cooled to room temperature and quenched with water (40 mL). The mixture was extracted with ethyl acetate, dried over $MgSO_4$, filtered and the solvent was removed. The residue was purified by chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 2:1) to get **3** (2.43 g, 4.65 mmol) as while solid with 93% yield. M.p. 342–343 K; ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.93 (s, 3H), 2.30 (s, 3H), 4.69 (s, 2H), 7.17 (s, 1H), 7.29–7.35 (m, 4H), 7.48 (d, 2H, J = 8.0 Hz), 7.57 (d, 1H, J = 8.0 Hz), 7.74 (d, 1H, J = 8.0 Hz).

Synthesis of 1-(2-methyl-3-benzothiophenyl)-2-[2-methyl-5-(4-azidomethylphenyl)-3-thienyl]perfluorocyclopentene (4)

To a stirred anhydrous THF (40 mL) of compound **3** (1.13 g, 2.0 mmol) was added dropwise 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.44 g, 2.88 mmol) with vigorous stirring in the cold water bath under argon atmosphere. Stirring was continued for 15 min at 273 K, 10 mL THF containing diphenylphosphoryl azide (DPPA) (0.91 g, 3.29 mmol) was added and the reaction mixture was stirred for 30 min at this temperature. The reaction was warmed to room temperature and stirred for

12 hrs. The product was extracted with ethyl acetate. The organic layer was washed with saturated sodium bicarbonate and water, then dried over $MgSO_4$, filtrated and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 10:1 as the eluent to obtain compound **4** (1.07 g, 2.45 mmol) in 89% yield as while solid. M.p. 335–336 K; ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.93 (s, 3H), 2.30 (s, 3H), 4.33 (s, 2H), 7.20 (s, 1H), 7.29–7.37 (m, 4H), 7.44 (d, 2H, J = 8.0 Hz), 7.57 (d, 1H, J = 8.0 Hz), 7.75 (d, 1H, J = 8.0 Hz).

Synthesis of rhodamine B hydrazide (6)

To a solution of Rhodamine B (**5**) (2.00 g, 4.18 mmol) in methanol (80 mL) was added Hydrazine hydrate (1.00 mL, 16.72 mmol), and the resulting mixture was heated at 383 K for 4 hrs, The solution changed from dark purple to light orange and became clear. Then the mixture was cooled and solvent was removed under reduced pressure. 1.0 mol L^{-1} HCl (about 100 mL) was added to the solid in the flask to generate a clear red solution. After that, 1.0 mol L^{-1} NaOH (about 140 mL) was added slowly with stirring until the pH of the solution reached 9~10. The resulting precipitate was filtered and washed 3 times with 50 mL water, and then dried in air. The product was then chromatographed on silica gel using dichloromethane/methanol = 30:1 (v/v) as eluant to afford compound **6** (1.52 g, 3.33 mmol) as pink solid in 80% yield. M.p. 471–474 K; ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.17 (t, 12H, J = 7.0 Hz), 3.31–3.37 (m, 8H), 3.61 (s, 2H), 6.28–6.31 (m, 2H), 6.42 (d, 2H, J = 2.4 Hz), 6.46 (d, 2H, J = 8.8 Hz), 7.11 (t, 1H, J = 4.0 Hz), 7.44–7.46 (m, 2H), 7.93–7.95 (m, 1H).

Synthesis of N-(rhodamine-B)lactam-2-(N-propinyl) imine (7)

Compound **6** (1.38 g, 3.00 mmol) was added to anhydrous CH_3CN (100 mL) with K_2CO_3 (0.50 g, 3.60 mmol). After 5 min, propargyl bromide (1.2 mL, 15.00 mmol) was slowly added to the stirred suspension, and the mixture was heated at 353 K for 10 hrs. Then, the reaction mixture was cooled and solvent was removed under reduced pressure, extracted with diethyl ether. The organic layer was washed with water and then dried over anhydrous Na_2SO_4. Then, the solvent was evaporated, and the obtained product was purified by column chromatography using petroleum ether/ethyl acetate = 3:1 as the eluent to obtain compound **7** (0.68 g, 1.38 mmol) in 46% yield. M.p. 459–460 K; ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.09 (t, 12H, J = 6.8 Hz), 2.04 (t, 1H, J = 2.4 Hz), 3.22–3.28 (m, 10H), 4.52 (t, 1H, J = 6.0 Hz), 6.18–6.21 (m, 2H), 6.33 (d, 2H, J = 2.0 Hz), 6.39 (d, 2H, J = 8.8 Hz), 7.03 (d, 1H, J = 8.0 Hz), 7.37–7.40 (m, 2H), 7.85 (d, 1H, J = 7.2 Hz).

Synthesis of 1-(2-methyl-3-benzothiophenyl)-2-{2-methyl-5-[4-(rhodamine B hydrazyl-methyl-(1,2,3-triazole))tolyl]methyl-3-thienyl}perfluorocyclopentene (1O)

To a solution of compound **4** (0.36 g, 0.80 mmol) and compound **7** (0.40 g, 0.80 mmol) in THF (40 mL) / H_2O (10 mL), were added $CuSO_4 \cdot 5H_2O$ (0.02 g, 0.08 mmol) and sodium ascorbate (0.032 g, 0.16 mmol). The resulting mixture was stirred at room temperature overnight. Then the mixture was washed with water and brine, and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered and then concentrated in vacuum. The resulting residue was purified by

column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to afford compound **1O** (0.50 g, 0.48 mmol) in 60% yield. M.p. 399–400 K; ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.14 (t, 12H, J = 7.0 Hz), 1.90 (s, 3H), 2.23 (s, 3H), 3.30–3.33 (m, 8H), 3.91 (d, 2H, J = 5.6 Hz), 4.30 (t, 1H, J = 5.6 Hz), 5.39 (d, 2H, J = 3.2 Hz), 6.22 (d, 2H, J = 8.8 Hz), 6.40 (s, 3H), 6.43 (s, 1H), 6.85 (s, 1H), 7.08 (d, 1H, J = 6.8 Hz), 7.16 (s, 1H), 7.21–7.28(m, 2H), 7.42–7.48 (m, 3H), 7.67 (d, 1H, J = 7.6 Hz), 7.90 (d, 1H, J = 14.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm): 12.13, 14.31, 43.82, 46.34, 52.95, 65.13, 97.25, 105.11, 107.34, 119.75, 121.58, 121.87, 122.32, 122.43, 123.52, 124.04, 124.47, 124.75, 125.53, 127.65, 128.08, 129.59, 132.26, 133.02, 133.98, 137.70, 140.37, 141.59, 141.99, 145.59, 148.28, 151.11, 153.25, 166.31; MS (m/z): 1066.3 $[M+Na]^+$; IR (KBr, υ, cm^{-1}): 993, 1049, 1091, 1118, 1141, 1192, 1220, 1272, 1306, 1342, 1429, 1476, 1515, 1548, 1614, 1631, 1695, 2928, 2970; Anal. calcd. for $C_{57}H_{51}F_6N_7O_2S_2$ (%): C, 65.49; H, 4.99; N, 9.43, found: C, 65.56; H, 4.92; N, 9.39.

2. Supplementary data

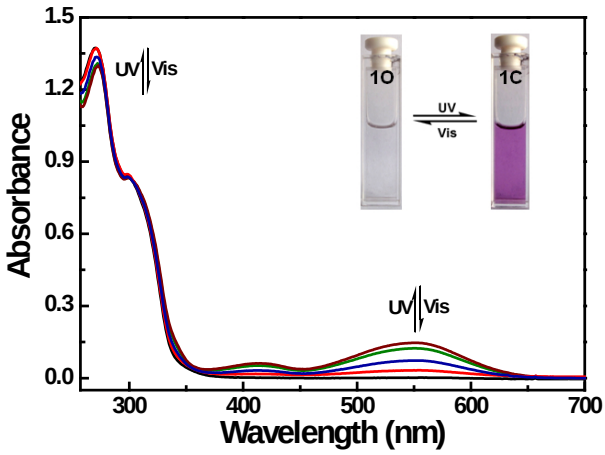

Figure S1. Absorption spectral and color changes of **1O** in acetonitrile (2.0×10^{-5} mol L^{-1}) at room temperature.

3. NMR

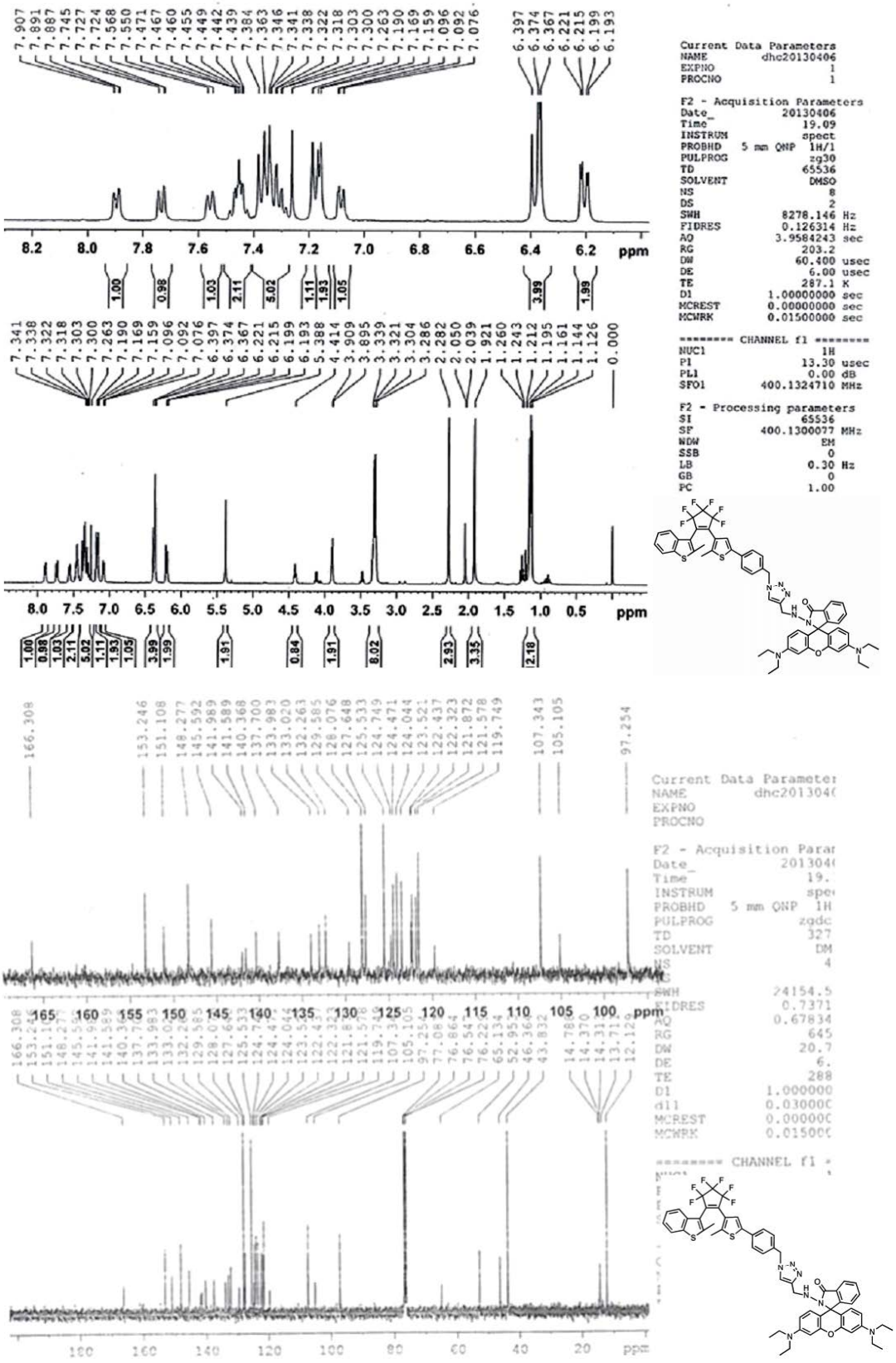

Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1O**.