Supporting Information

Nucleobase-Functionalized 1,6-Dithiapyrene-Type Electron-Donors: Supramolecular Assemblies by Complementary Hydrogen-Bonds and π-Stacks

Tsuyoshi Murata, Eigo Miyazaki, Kazuhiro Nakasuji, Yasushi Morita

Procedures for the synthesis of DTPY-nucleobases

2-(*N*$^{1'}$-*n*-Butyluracil-5′-yl)-1,6-dithiapyrene (1a). DTPY (300 mg, 1.25 mmol) was placed in a 100-mL Schlenk-tube under an argon atmosphere, and dissolved with THF (30 mL). After being cooled to –78 °C, *n*-BuLi (1.6 M hexane solution, 0.78 mL, 1.25 mmol) was added. The solution was stirred at –78 °C for 0.5 h. To this mixture Bu_3SnCl (0.34 mL, 1.25 mmol) was added and stirred at –78 °C for 0.5 h. The reaction mixture was poured to a phosphate buffer solution (pH 7.0, 0.1 M, 15 mL) and extracted with ethyl acetate (50 mL). The organic extract was washed with a saturated NaCl aqueous solution (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure, to give crude **4** (701 mg) as a dark red oil. The resulting oil was used for the following reaction without further purification.

In a 100-mL Schlenk-tube, **4** (701 mg), 5-iodo-*N*^{1}-*n*-butyluracil (**5a**) (367 mg, 1.25 mmol), $Pd(PPh_3)_4$ (144 mg, 0.125 mmol) and CuI (71 mg, 0.37 mmol) were placed, and dissolved with DMF (25 mL). The solution was degassed by the freeze-pump-thaw method, and stirred at 70 °C for 12 h. After being cooled to room temperature, the precipitate was removed by filtration. The filtrate was extracted with ethyl acetate (250 mL) and 10% ethylenediamine aqueous solution (50 mL). The organic extract was washed with a 10% ethylenediamine aqueous solution (50 mL), a saturated KF aqueous solution (50 mL) and a saturated NaCl aqueous solution (50 mL), then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude solid was recrystallized from CH_2Cl_2–hexane, and the resulting precipitate was collected by filtration, then washed with hexane, to give **1a**. The filterate was concentrated and purified by column chromatography (SiO_2 containing 6% water, charged with CH_2Cl_2, eluted with a 20:1–0:1 mixture of hexane and ethyl acetate containing 0.5% Et_3N). By these operations, **1a** (234 mg, 46%) was obtained as a red powder. Mp 105–106 °C; TLC R_f 0.73 (1:1 hexane/ethyl acetate); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.98 (t, 3, J = 7.2 Hz), 1.38 (m, 2), 1.69 (m, 2), 3.75 (t, 2, J = 7.4 Hz), 5.68 (d, 1, J = 10 Hz), 5.88 (d, 1, J = 10 Hz), 6.16 (d, 1, J = 7.6 Hz), 6.32 (d, 1, J = 7.8 Hz), 6.37 (d, 1, J = 7.8 Hz), 6.39 (d, 1, J = 7.6 Hz), 6.94 (s, 1), 7.24 (s, 1), 8.02 (brs, 1); EI-MS, *m/z* 406 (M^+, 100%); IR (KBr) 1715, 1696, 1684, 1660, 1684 cm^{-1}; UV (KBr) 476, 422, 250, 222 nm; Anal. Calcd for $C_{22}H_{18}N_2O_2S_2$: C, 65.00; H, 4.46; N, 6.89. Found: C, 64.69; H, 4.48, N, 6.72.

Single crystals of **1a**·CH_2Cl_2 were prepared by slow evaporation method using CH_2Cl_2 or

recrystallization from CH_2Cl_2–hexane. Mp 106–108 °C (dec); IR (KBr) 3169, 3053, 1684 cm^{-1}; Anal. Calcd for $(C_{22}H_{18}N_2O_2S_2)(CH_2Cl_2)_{0.6}$: C, 59.33; H, 4.23; N, 6.12%. Found: C, 59.69; H, 4.18, N, 6.06%.

2-($N^{1'}$-Phenyluracil-5′-yl)-1,6-dithiapyrene (1b). DTPY (100 mg, 0.42 mmol) was placed in a 20-mL Schlenk-tube under an argon atmosphere, and dissolved with THF (10 mL). After being cooled to –78 °C, *n*-BuLi (1.5 M hexane solution, 0.28 mL, 0.42 mmol) was added. The solution was stirred at –78 °C for 1 h. To this mixture Bu_3SnCl (0.11 mL, 0.42 mmol) was added and stirred at –78 °C for 0.5 h. The reaction mixture was poured to a phosphate buffer solution (pH 7.0, 0.1 M, 5 mL) and extracted with ethyl acetate (50 mL). The organic extract was washed with a saturated NaCl aqueous solution (20 mL), then dried over Na_2SO_4, filtered and concentrated under reduced pressure, to give crude **4** (229 mg) as a dark red oil. The resulting oil was used for the following reaction without further purification.

In a 20-mL Schlenk-tube, **4** (229 mg), 5-iodo-N^1-phenyluracil (**5b**) (145 mg, 0.42 mmol), $Pd(PPh_3)_4$ (48 mg, 0.042 mmol) and CuI (24 mg, 0.12 mmol) were placed, and dissolved with toluene (10 mL). The solution was degassed by freeze-pump-thaw method, and refluxed for 30 h. After being cooled to room temperature, the resulting precipitates were collected, then washed with toluene, to give **1b**. The filtrate was extracted with ethyl acetate (50 mL) and a 10% ethylenediamine aqueous solution (40 mL). The organic extract was washed with a saturated NaCl aqueous solution (20 mL × 3), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude red oil was purified by column chromatography (SiO_2 containing 6% water, charged with CH_2Cl_2, eluted with a 10:1–0:1 mixture of hexane and ethyl acetate). By these operations, **1b** (123 mg, 69%) was obtained as a reddish brown powder. Mp 228–230 °C (dec); TLC R_f 0.12 (2:1 hexane/ethyl acetate); ^{1}H NMR (270 MHz, DMSO-d_6) δ 5.96 (d, 1, J = 10 Hz), 5.99 (d, 1, J = 10 Hz), 6.29 (d, 1, J = 7.8 Hz), 6.34 (d, 1, J = 7.9 Hz), 6.45 (d, 1, J = 7.8 Hz), 6.47 (d, 1, J = 7.9 Hz), 6.65 (s, 1), 7.43–7.53 (m, 5), 7.67 (s, 1), 11.7 (brs, 1); EI-MS, *m/z* 426 (M^+, 100 %); IR (KBr) 3447, 3031, 1718 cm^{-1}; UV (KBr) 490, 426 nm; Anal. Calcd for $(C_{24}H_{14}N_2O_2S_2)(H_2O)_{0.4}$: C, 66.46; H, 3.44; N, 6.46. Found. C, 66.60; H, 3.23; N, 6.41.

2-{$O^{4'}$-(2′′-nitrophenyl)-$N^{1'}$-butyluracil-5′-yl}-1,6-dithiapyrene (8). DTPY (300 mg, 1.25 mmol) was placed in a 100-mL schlenk-tube under an argon atmosphere, and dissolved with THF (30 mL). After being cooled to –78 °C, *n*-BuLi (1.6 M hexane solution, 0.78 mL, 1.25 mmol) was added over 5 min at –78 °C. The solution was stirred at –78 °C for 1 h. To this mixture Bu_3SnCl (0.34 mL, 1.25 mmol) was added and stirred at –78 °C for 0.5 h. The reaction mixture was poured to a phosphate buffer solution (pH 7.0, 0.1 M, 15 mL) and extracted with ethyl acetate (70 mL). The organic extract was washed with a saturated NaCl aqueous solution (20 mL × 2), dried over Na_2SO_4, filtered and concentrated under reduced pressure, to give crude **4** (229 mg) as a dark red oil. The resulting oil was used for the following

reaction without further purification.

In a 20-mL Schlenk-tube, **4** (707 mg), 1-*n*-butyl-5-iodo-4-(*o*-nitrophenoxyl)pyrimidin-2-one (**6**) (519 mg, 1.25 mmol), $Pd(PPh_3)_4$ (144 mg, 0.13 mmol) and CuI (71 mg, 0.38 mmol) were placed, and dissolved with toluene (40 mL). The solution was degassed by the freeze-pump-thaw method, and refluxed for 27 h. After being cooled to room temperature, the reaction mixture was poured into a saturated NaCl aqueous solution, and then extracted with CH_2Cl_2 (100 mL). The organic extract was washed with a 10% ethylenediamine aqueous solution (30 mL × 2), a saturated KF aqueous solution (10 mL × 3), and a saturated NaCl aqueous solution (30 mL), then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude red oil was purified by column chromatography (SiO_2 containing 6% water, charged with CH_2Cl_2, eluted with a 10:1–0:1 mixture of CH_2Cl_2 and ethyl acetate), to give **8** (353 mg, 53%) as a dark red powder. Mp 94–95 °C (dec); TLC R_f 0.65 (ethyl acetate); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.97 (t, 3, J = 7.3 Hz), 1.30–1.42 (m, 2), 1.69–1.78 (m, 2), 3.84 (t, 2, J = 6.3 Hz), 5.63 (d, 1, J = 10 Hz), 5.83 (d, 1, J = 10 Hz), 6.13 (d, 1, J = 7.6 Hz), 6.20 (d, 1, J = 7.6 Hz), 6.21 (s, 1), 6.30 (d, 1, J = 7.6 Hz), 6.34 (d, 1, J = 7.6 Hz), 7.32 (dd, 1, J = 8.1 and 1.2 Hz), 7.70 (s, 1), 7.39–7.45 (m, 1), 7.64–7.68 (m, 1), 8.16 (dd, 1, J = 8.3 and 1.6 Hz); EI-MS, *m/z* 527 (M^+, 100 %); IR (KBr) 2956, 2924, 2860 1675 1521 cm^{-1}; Anal. Calcd for $C_{28}H_{21}N_3O_4S_2$: C, 63.74; H, 4.01; N, 7.96. Found. C, 63.56; H, 4.27; N, 7.74.

2-(4′-Amino-$N^{1'}$-*n*-butyl-2′-pyrimidinone-5′-yl)-1,6-dithiapyrene (2a). In a 200-mL round-bottomed flask, **8** (360 mg, 0.68 mmol) was placed and dissolved with THF (50 mL). To this solution, a 28% ammonia aqueous solution (40 mL) was added and stirred at room temperature for 6 days. The reaction mixture was extracted with ethyl acetate (100 mL) and a saturated NaCl aqueous solution (20 mL). The organic extract was washed with a saturated $NaHCO_3$ aqueous solution (20 mL × 3) and a saturated NaCl aqueous solution (20 mL), then dried over Na_2SO_4, and concentrated under reduced pressure. The crude red solid was purified by column chromatography (SiO_2 containing 6% water, charged with CH_2Cl_2, eluted with a 1:0–1:1 mixture of CH_2Cl_2 and ethyl acetate, then a 5:1 mixture of ethyl acetate and MeOH containing 0.5% of NEt_3) and recrystallized from CH_2Cl_2 and MeCN, to give **2a** (159 mg, 57%) as red microcrystals. Mp 215–217 °C (dec); TLC R_f 0.18 (ethyl acetate); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, 3, J = 7.3 Hz), 1.27–1.47 (m, 2), 1.74–1.56 (m, 2), 3.51 (t, 2, J = 7.3 Hz), 5.65 (d, 1, J = 10 Hz), 5.75 (s, 1), 5.83 (d, 1, J = 10 Hz), 6.13 (d, 2, J = 7.6 Hz), 6.30 (d, 1, J = 7.6 Hz), 6.31 (d, 1, J = 7.6 Hz), 7.20 (s, 1); EI-MS, *m/z* 406 (M^+, 38 %); IR (KBr) 3442, 1658, 1636, 1595, 1559, 1498 cm^{-1}; UV (KBr) 472, 416 nm; Anal. Calcd for $C_{22}H_{19}N_3OS_2(H_2O)_{0.7}$: C, 63.19; H, 4.92; N, 10.05. Found. C, 62.83; H, 4.61; N, 10.10.

2-(4′-*n*-Butylamino-*N*$^{1'}$-*n*-butyl-2′-pyrimidinone-5′-yl)-1,6-dithiapyrene (2b). In a 100-mL round-bottomed flask, **8** (350 mg, 0.66 mmol) was placed and dissolved with THF (30 mL). To this solution, *n*-butylamine (0.25 mL, 2.53 mmol) was added and stirred at room temperature for 22 h. The reaction mixture was extracted with ethyl acetate (60 mL) and a saturated NaCl aqueous solution (30 mL). The organic extract was washed with a saturated $NaHCO_3$ aqueous solution (20 mL × 3) and a saturated NaCl aqueous solution (20 mL), then dried over Na_2SO_4, and concentrated under reduced pressure. The crude red solid was purified by column chromatography (SiO_2 containing 6% water, charged with CH_2Cl_2, eluted with a 1:0–0:1 mixture of CH_2Cl_2 and ethyl acetate containing 0.5% of NEt_3), to give **2b** (159 mg, 57%) as reddish brown powder. Mp 75–77 °C; TLC R_f 0.38 (ethyl acetate); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, 3, J = 7.3 Hz), 0.95 (t, 3, J = 7.3 Hz), 1.27–1.47 (m, 4), 1.74–1.96 (m, 4), 3.51 (t, 2, J = 7.3 Hz), 3.74 (t, 2, J = 7.3 Hz), 5.41 (bt, 1), 5.65 (d, 1, J = 10 Hz), 5.75 (s, 1), 5.83 (d, 1, J = 10 Hz), 6.13 (d, 2, J = 7.6 Hz), 6.30 (d, 1, J = 7.6 Hz), 6.31 (d, 1, J = 7.6 Hz), 7.20 (s, 1); EI-MS, *m/z* 461 (M^+, 30 %); IR (KBr) 2869, 1653, 1605, 1560, 1546, 1498 cm^{-1}; UV (KBr) 464, 418, 222 nm; Anal. Calcd for $C_{26}H_{27}N_3OS_2(H_2O)_{0.4}$: C, 66.61; H, 5.98; N, 8.96. Found. C, 66.45; H, 5.79; N, 9.23.

6-Amino-9-*n*-butyl-8-iodopurine (7a). THF (50 mL) and *i*-Pr_2NH (11 mL, 78 mmol) were placed in a 50-mL Schlenk-tube under an argon atmosphere, and cooled to –78 °C. *n*-BuLi (1.2 M in hexane, 64 mL, 77 mmol) was added at –78°C, and warmed up to 0 °C for 1 h. After being cooled to – 78 °C, a THF solution (80 mL) of 6-Amino-9-*n*-butylpurine (3.00 g, 15.7 mmol) was added into the THF solution of lithium diisopropylamide. This mixture was gradually warmed up to 0 °C, and stirred at this temperature for 1.5 h. After being cooled to –78 °C, a THF solution (30 mL) of I_2 (20 g, 78 mmol) was added by cannulation. After being stirred at –78 °C for 0.5 h, a phosphate buffer solution (pH 7.0, 0.1 M, 50 mL) and ethyl acetate (200 mL) were added to the reaction mixture. The organic extract was washed with a saturated $Na_2S_2O_3$ aqueous solution (50 mL × 3) and a saturated NaCl aqueous solution (50 mL), then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude solid was washed CH_2Cl_2–hexane, to give **7a** (4.93 g, 98%) as a white powder. Mp 171–173 °C (dec); TLC R_f 0.63 (4:1 ethyl acetate/MeOH); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.96 (t, 3, J = 6.7 Hz), 1.31–1.45 (m, 2), 1.74–1.85 (m, 2), 4.14 (t, 2, J = 7.4 Hz), 5.74 (brs, 2), 8.26 (s, 1); EI-MS, *m/z* 317 (M^+, 10%), 261 (M^+ – Bu, 28%), 190 (M^+ – I, 100%); IR (KBr) 3470, 3314, 3118, 2956, 2930, 1663, 1646, 1598 cm^{-1}; Anal. Calcd for $(C_9H_{12}N_5I)(C_6H_{14})_{0.13}$: C, 35.78; H, 4.24; N, 21.33. Found. C, 35.73; H, 4.34; N, 21.40.

2-(6′-Amino-9′-*n*-butylpurin-8′-yl)-1,6-dithiapyrene (3a). DTPY (600 mg, 2.50 mmol) was placed in a 200-mL Schlenk-tube under an argon atmosphere, and dissolved with THF (60 mL). After being

cooled to –78 °C, *n*-BuLi (1.6 M hexane solution, 1.6 mL, 2.56 mmol) was added over 2 min at –78 °C. The solution was stirred at –78 °C for 1 h, then Bu_3SnCl (0.70 mL, 2.58 mmol) was added and stirred at –78 °C for 0.5 h. The reaction mixture was poured to a phosphate buffer solution (pH 7.0, 0.1 M, 30 mL), and extracted with ethyl acetate (100 mL). The organic extract was washed with a saturated NaCl aqueous solution (50 mL), then dried over Na_2SO_4, filtered and concentrated under reduced pressure, to give crude **4** (1.34 g) as a dark red oil. The resulting oil was used for the following reaction without further purification.

In a 200-mL Schlenk-tube, **4** (1.34 g), **7a** (0.80 g, 2.50 mmol), $Pd(PPh_3)_4$ (300 mg, 0.25 mmol) and CuI (48 mg, 0.25 mmol) were placed, and dissolved with toluene (50 mL). The solution was degassed by the freeze-pump-thaw method, and refluxed for 17 h. After being cooled to room temperature, the reaction mixture was poured into a 10% ethylenediamine aqueous solution, and then extracted with CH_2Cl_2 (500 mL). The organic extract was washed with a saturated NaCl aqueous solution (50 mL), then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude solid was purified by column chromatography (SiO_2 containing 6% water, charged with CH_2Cl_2, eluted with a 1:1–0:1 mixture of CH_2Cl_2 and ethyl acetate containing 1% of Et_3N) and reprecipitation using CH_2Cl_2–hexane, to give **3a** (220 mg, 20%) as a dark red powder. Mp 275–277 °C (dec); TLC R_f 0.68 (4:1 ethyl acetate/MeOH); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.00 (t, 3, J = 7.3 Hz), 1.29–1.48 (m, 2), 1.84–1.96 (m, 2), 4.31 (t, 2, J = 7.6 Hz), 5.52 (brs, 2), 5.64 (d, 1, J = 10 Hz), 5.85 (d, 1, J = 10 Hz), 6.16 (d, 1, J = 7.7 Hz), 6.20 (d, 1, J = 7.2 Hz), 6.21 (s, 1), 6.32 (d, 1, J = 7.7 Hz), 6.38 (d, 1, J = 7.2 Hz), 8.35 (s, 1); EI-MS, *m/z* 429 (M^+, 100%); IR (KBr) 3318, 3160, 1660 cm^{-1}; UV (KBr) 680, 518, 404, 332 nm; Anal. Calcd for $(C_{23}H_{19}N_5S_2)(H_2O)_{1.7}$: C, 60.03; H, 4.91; N, 15.22. Found: C, 60.08; H, 4.82; N, 15.00.

2-{6′-Amino-9′-(2′′,3′′,5′′-tri-*O*-*tert*-butyldimethysilyl-*β*-ribofuranosyl)purin-8′-yl}-1,6-dithiapyrene (3b). DTPY (300 mg, 1.25 mmol) was placed in a 100-mL Schlenk-tube under an argon atmosphere, and dissolved with THF (30 mL). After being cooled to –78 °C, *n*-BuLi (1.6 M hexane solution, 0.80 mL, 2.56 mmol) was added over 5 min at –78 °C. The solution was stirred at –78 °C for 1 h, then Bu_3SnCl (0.35 mL, 1.29 mmol) was added and stirred at –78 °C for 0.5 h. The reaction mixture was poured to a phosphate buffer solution (pH 7.0, 0.1 M, 15 mL), and extracted with ethyl acetate (80 mL). The organic extract was washed with a saturated NaCl aqueous solution (30 mL × 2), dried over Na_2SO_4, filtered and concentrated under reduced pressure, to give crude **4** (718 mg) as a dark red oil. The resulting oil was used for the following reaction without further purification.

In a 100-mL Schlenk-tube, **4** (1.34 g), *tert*-butyldimethylsilyl-protected 8-iodoadenosine **7b** (0.93 g, 1.26 mmol), $Pd(PPh_3)_4$ (145 mg, 0.13 mmol) and CuI (72 mg, 0.38 mmol) were placed, and dissolved with toluene (50 mL). The solution was degassed by the freeze-pump-thaw method, and refluxed for 19

h. After being cooled to room temperature, the reaction mixture was poured into a 10% ethylenediamine aqueous solution (30 mL), and then extracted with ethyl acetate (100 mL). The organic extract was washed with a saturated NaCl aqueous solution (30 mL × 2), then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residual oil was purified by column chromatography (SiO_2 containing 6% water, charged with benzene, eluted with a 10:1–1:1 mixture of hexane and ethyl acetate containing 0.5% of Et_3N) and a recycle preparative gel permeation chromatography (GPC) using tandemly connected two polystyrene gel columns (JAIGEL 1H, Japan Analytical Industry) with $CHCl_3$ as eluant, to give **3b** (320 mg, 30%) as a dark red powder. Mp 118–119 °C; TLC R_f 0.22 (2:1 hexane/ethyl acetate); 1H NMR (270 MHz, $CDCl_3$) δ –0.32 (s, 3), –0.11 (s, 3), 0.04 (s, 3), 0.05 (s, 3), 0.14 (s, 3), 0.15 (s, 3), 0.76 (s, 9), 0.88 (s, 9), 0.93 (s, 9), 3.71 (dd, 1, J = 9.0 and 3.0 Hz), 4.02–4.13 (m, 2), 4.49 (dd, 1, J = 4.1 and 1.5 Hz), 5.54 (brs, 2), 5.60–5.64 (m, 1), 5.61 (d, 1, J = 10 Hz), 5.83 (d, 1, J = 10 Hz), 6.05 (d, 1, J = 6.7 Hz), 6.13 (d, 1, J = 7.8 Hz), 6.18 (d, 1, J = 7.7 Hz), 6.28 (d, 1, J = 7.8 Hz), 6.34 (d, 1, J = 7.7 Hz), 6.36 (s, 1), 8.25 (s, 1); FAB-MS, *m/z* 847 (M^+); IR (KBr) 3402, 3184, 2953, 2928, 2856, 1636 cm^{-1}; UV (KBr) 570, 460, 412 nm; Anal. Calcd for $C_{42}H_6N_5O_4Si_3S_2$: C, 59.46; H, 7.25; N, 8.26. Found: C, 59.09; H, 7.18; N, 8.16.

Procedures for the preparation of CT complexes

1a–TCNQ. In a 30-mL round-bottomed flask, solutions of **1a** (20 mg, 0.050 mmol) in CH_2Cl_2 (10 mL) and TCNQ (10 mg, 0.050 mmol) in CH_2Cl_2 (5 mL) were combined, and the mixture was stirred at room temperature for 0.5 h. After being concentrated under reduced pressure, and residual black powder was dissolved in MeCN (15 mL) at 70 °C. Dark red solution was left stand at room temperature, and the resulting precipitate was collected by filtration, to give the CT complex (7.4 mg) as a black powder. Mp 225–226 °C (dec); IR (KBr) 3221, 2208, 2197, 1716, 1686 cm^{-1}; UV (KBr) 1782, 534, 396, 302, 260 nm; Anal. Calcd for $(C_{22}H_{18}N_2O_2S_2)(C_{12}H_4N_4)(H_2O)_{0.7}$: C, 65.51; H, 3.78; N, 13.48. Found. C, 65.79; H, 3.58; N, 13.10.

2a–TCNQ. In a 100-mL round-bottomed flask, solutions of **2a** (25 mg, 0.062 mmol) in CH_2Cl_2 (40 mL) and TCNQ (13 mg, 0.050 mmol) in CH_2Cl_2 (20 mL) were combined, and the mixture was stirred at room temperature for 0.5 h. After being concentrated to ca. 10 mL under reduced pressure, and residual solution was diluted with MeCN (40 mL) at 40 °C. Dark red solution was left stand at –30 °C, and the resulting precipitate was collected by filtration, to give the CT complex (24 mg) as a black powder. Mp 95–97 °C (dec); IR (KBr) 2280, 2209, 2201, 2179, 1669, 1647, 1590, 1559, 1526, 1499 cm^{-1}; UV (KBr) 1762, 860, 400 nm; Anal. Calcd for $(C_{22}H_{19}N_3OS_2)_3(C_{12}H_4N_4)_2(H_2O)_3$: C, 64.38; H, 4.26; N, 14.18. Found. C, 64.50; H, 3.91; N, 14.27.

2b–TCNQ. In a 100-mL round-bottomed flask, solutions of **2b** (40 mg, 0.087 mmol) in CH_2Cl_2 (40 mL) and TCNQ (18 mg, 0.087 mmol) in CH_2Cl_2 (20 mL) were combined, and the mixture was stirred at room temperature for 0.5 h. After being concentrated under reduced pressure, and residual solid was dissolved with MeCN (10 mL) at 50 °C. Dark red solution was left stand at –30 °C for 14 h, and the resulting precipitate was collected by filtration, to give the CT complex (38 mg) as a black powder. Mp 174–175 °C (dec); IR (KBr) 2925, 2854, 2207, 2198, 1654, 1636, 1586, 1558, 1522, 1498 cm^{-1}; UV (KBr) 1682, 386 nm; Anal. Calcd for $(C_{26}H_{27}N_3OS_2)_4(C_{12}H_4N_4)_3$: C, 68.38; H, 4.92; N, 13.67. Found. C, 68.11; H, 4.57; N, 13.65.

3a–TCNQ. In a 100-mL round-bottomed flask, solutions of **3a** (10 mg, 0.023 mmol) in CH_2Cl_2 (10 mL) and TCNQ (4.7 mg, 0.023 mmol) in CH_2Cl_2 (10 mL) were combined, and the mixture was stirred at room temperature for 0.5 h. After being concentrated to ca. 3 mL under reduced pressure, and residual solution was diluted with hexane (10 mL). The resulting precipitate was collected by filtration, to give the CT complex (8.8 mg) as a black powder. Mp 210–212 °C (dec); IR (KBr) 2202, 1653 cm^{-1}; UV (KBr) 1608, 864, 482, 400 nm; Anal. Calcd for $(C_{23}H_{19}N_5S_2)_2(C_{12}H_4N_4)(H_2O)_{0.6}$: C, 64.86; H, 4.05; N, 18.26. Found. C, 64.90; H, 3.65; N, 18.22.

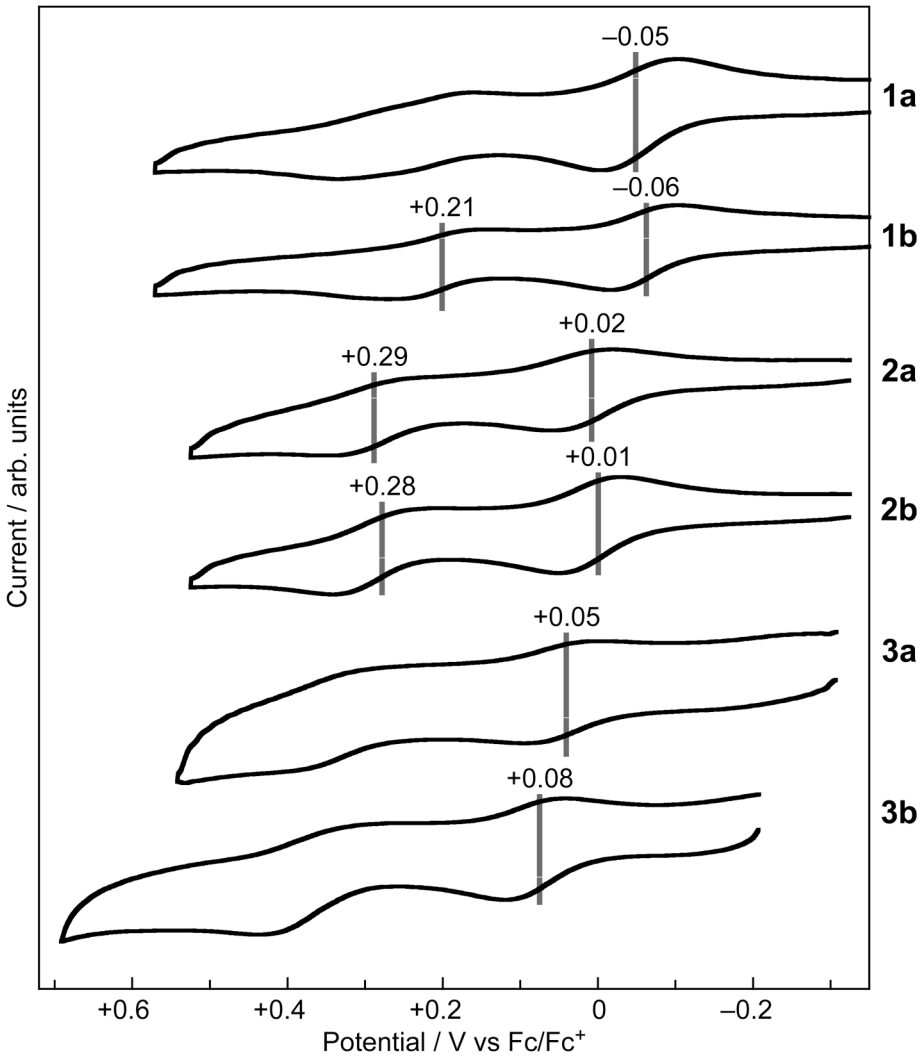

Figure S1. Cyclic voltammogram of DTPY-nucleobases **1–3** (V vs Fc/Fc^{+}).