

Giant Phototransistor Response in Dithienyltetrathiafulvalene Derivatives

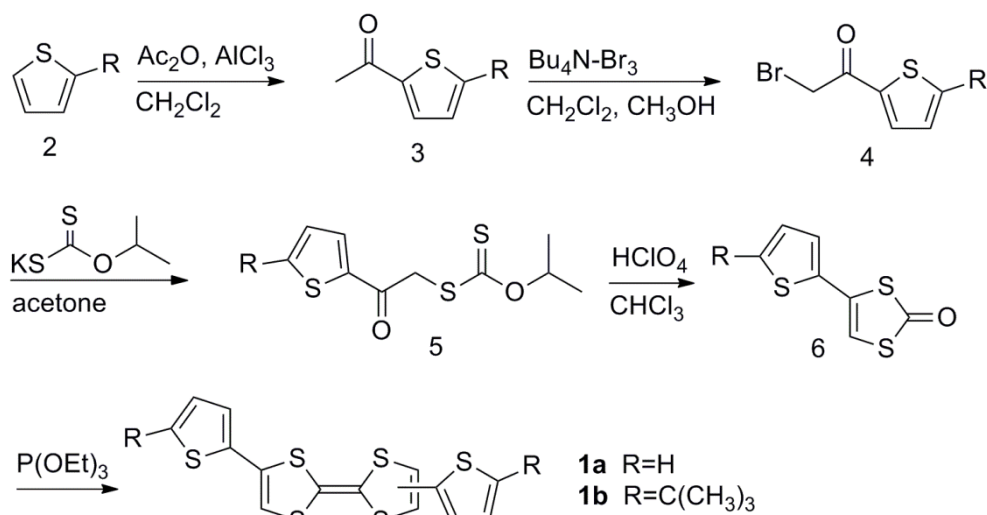
Supporting Information

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1. Synthesis



Scheme S1. Synthesis of **1a** and **1b**

General: All chemicals and solvents were of reagent grade unless otherwise indicated. Reactions were carried out under ambient atmosphere unless otherwise indicated. Nuclear magnetic resonance spectra were obtained in deuterated chloroform by a JEOL LA-300 spectrometer operating at 300 MHz for ¹H with TMS as internal reference; chemical shifts (δ) were reported in parts per million. EI-MS spectra were obtained on a Shimadzu QP-5000 spectrometer using an electron impact ionization procedure (70 eV).

2-Acetylthiophene (3a): To a mixture of 4.2 g thiophene (50 mmol) and 5.1 g acetic anhydride (50 mmol) was added 25.4 mg iodine (0.2 mmol) with agitation. The mixture changed to brown

within a few minutes. The mixture was heated to 100 °C under stirring for 1h. After cooling, the mixture was diluted with 5 mL of water and stirred for 15 minutes. The product was extracted by chloroform, and washed with aqueous sodium sulfite, aqueous sodium hydrocarbonate, and water. After dried over magnesium sulfate, the solvent was evaporated. The product was distilled under vacuum, to afford a light yellow oil **3a** (4.74 g, 37.6 mmol, yield 75%). ¹H-NMR δ 2.57 (s, 3H), 7.13-7.15 (m, 1H), 7.63-7.65 (m, 1H), 7.69-7.70 (m, 1H), Mass (EI) *m/z* = 126 (M⁺).

2-Bromoacetylthiophene (4a): To a solution of 2.13 g **3a** (16.7 mmol) in 200 mL dichloromethane and 80 mL methanol was added 9.0 g tetrabutylammonium tribromide (18.8 mmol). The solution was stirred for 24 h until the color of the orange solution disappears. The solvent was removed by distillation and the obtained residue was extracted with diethyl ether and water. The ether layer was dried with magnesium sulfate and evaporated. The product was obtained as a yellow oil **4a** (2.9 g, 14.2 mmol, yield 84%). ¹H-NMR δ 4.38 (s, 2H), 7.17-7.18 (m, 1H), 7.72-7.73 (m, 1H), 7.81-7.82 (m, 1H), Mass (EI) *m/z* = 204, 206 (M⁺).

2-(*O*-Isopropylthiocarbonato) thiophene (5a): 2.9 g **4a** (14.2 mmol) and 2.47 g potassium isopropylxanthate (14.2 mmol) in 50 mL acetone were refluxed for 1h. After cooling, the mixture was filtered and the solvent was evaporated. The residue was dissolved in diethyl ether and the solution was washed with water. After drying over magnesium sulfate, the solvent was evaporated. The product was obtained as a yellow oil **5a** (3.0 g, 11.5 mmol, yield 81%). ¹H-NMR δ 1.35-1.40 (s, 6H), 4.53 (s, 2H), 5.67-5.77 (m, 1H), 7.16-7.19 (m, 1H), 7.69-7.72 (m, 1H), 7.87-7.88 (m, 1H), Mass (EI) *m/z* = 260 (M⁺).

4-(2-Thiophenyl)-1,3-dithiole-2-one (6a): Perchloric acid (70%) (1.15 mL) was added with stirring to a solution of 1.39 g **5a** (5.35 mmol) in chloroform (50 mL) and the mixture was refluxed for 8 h. After cooling, the product was poured into water. The organic phase was washed with aqueous sodium hydrocarbonate and then with water and dried over magnesium sulfate. The solvent was evaporated and dark yellow crystals were formed. The product was subjected to silica-gel column chromatography (hexane : dichlorometahane = 1 : 1). The first yellow fraction was collected, and a yellow solid **6a** was obtained (0.91 g, 4.55 mmol, yield 85%). ¹H-NMR δ 6.75 (m, 1H), 7.02-7.03 (m, 1H), 7.05-7.07 (m, 1H), 7.30-7.32 (m, 1H), Mass (EI) *m/z* = 200 (M⁺).

4,4'(5')Bis(2-thiophenyl)-tetrathiafulvalene (1a): Under nitrogen, 0.91 g **6a** (4.55 mmol) in 3 mL triethylphosphite was heated to 135 °C with stirring for 14 h. After cooling, the triethylphosphite was distilled off in vacuum. The product was subjected to silica-gel column chromatography with carbon disulfide. The first orange fraction was collected, and an orange solid was obtained.

Three-time crystallization from toluene and ethanol mixed solvent (toluene : ethanol = 1 : 3) gave orange flakes of **1b** (0.40 g, 1.1 mmol, 48%). mp 174 °C, $^1\text{H-NMR}$ δ 6.38-6.44 (m, 2H), 6.94-6.95 (m, 2H), 6.94-7.01 (m, 2H), 7.22-7.26 (s, 2H), Mass (EI) m/z = 368 (M^+). Calcd for $\text{C}_{14}\text{H}_8\text{S}_6$: C, 45.62; H, 2.19; S, 52.19. Found: C, 45.42; H 2.09; S, 52.18.

2-*t*-Butylthiophene (2b): 13.3 g Aluminium chloride (100 mmol) in 40 mL dichloromethane was cooled to -78°C in an Ar atmosphere, and a mixture of 8 mL thiophene (100 mmol) and 11 mL *t*-butyl chloride (100 mmol) was dropwise added during the period of 10 min. After stirred for 1 h, the reaction mixture was allowed to warm up to room temperature, and stirred for 2 days. The product was poured into ice water, neutralized by aqueous sodium hydrocarbonate, and extracted. After dried over magnesium sulfate, the solvent was evaporated. Distillation afforded a colorless liquid **7** (8.9 g, 63.5 mmol, yield 64%). $^1\text{H-NMR}$ δ 1.39 (s, 9H), 6.82-6.83 (m, 1H), 6.89-6.92 (m, 1H), 7.10-7.12 (m, 1H), Mass (EI) m/z = 140 (M^+).

2-Acetyl-5-*t*-butylthiophene (3b): Under nitrogen atmosphere, 3.0 g aluminium chloride (22.5 mmol) in 20 mL chloroform was dropwise added to a mixture of 2.7 g **2b** (19.3 mmol), 1.97 g acetic anhydride (19.3 mmol), and 5 mL chloroform, and refluxed for 3 h. After cooling, the reaction mixture was dropwise added to ice-cooled dilute hydrochloric acid. The product was extracted by chloroform, washed with dilute hydrochloric acid, aqueous sodium hydrocarbonate, and water. After dried over magnesium sulfate, the solvent evaporated, and the product was obtained as a brown oil. The product was distilled in vacuum, to afford a colorless liquid **3b** (1.8 g, 9.8 mmol, yield 51%). $^1\text{H-NMR}$ δ 1.39 (s, 9H), 2.51 (s, 3H), 6.87-6.89 (m, 1H), 7.52-7.54 (m, 1H), Mass (EI) m/z = 182 (M^+).

2-Bromoacetyl-5-*t*-butylthiophene (4b): To a solution of 1.8 g **3b** (9.8 mmol) in 50 mL dichloromethane and 20 mL methanol was added 5.2 g tetrabutylammonium tribromide (10.8 mmol). The solution was refluxed for 8 h until the color of the orange solution disappears. The solvent was removed by distillation and the obtained residue was extracted with ether and water. The ether layer was dried with magnesium sulfate and evaporated. The product was obtained as a yellow oil **4b** (2.46 g, 9.4 mmol, yield 96%). $^1\text{H-NMR}$ δ 1.40 (s, 9H), 4.33 (s, 2H), 6.92-6.94 (m, 1H), 7.66-7.67 (m, 1H), Mass (EI) m/z = 260, 262 (M^+).

2-(*O*-Isopropylthiocarbonato)-5-*t*-butylthiophene (5b): 1.3 g **4b** (5.0 mmol) and 0.87 g potassium isopropylxanthate (5.0 mmol) were refluxed in 20 mL acetone for 1h. After cooling, the mixture was filtered and the solvent was evaporated. The residue was dissolved in diethyl ether and the solution was washed with water. After drying over magnesium sulfate, the solvent was

evaporated. The product was obtained as a yellow oil **5b** (0.87 g, 2.8 mmol, 55%). $^1\text{H-NMR}$ δ 1.35-1.41 (s, 6H), 1.41 (s, 9H), 4.49 (s, 2H), 5.66-5.78 (m, 1H), 6.91-6.93 (m, 1H), 7.70-7.71 (m, 1H), Mass (EI) $m/z = 316$ (M^+).

4-(5-(*t*-Butyl)thiophene-2-yl)-1,3-dithiole-2-one (6b): Perchloric acid (70%) (2.6 mL) was added with stirring to a solution of 3.0 g **5b** (9.4 mmol) in chloroform (50 mL) and the mixture was refluxed for 8 h. After cooling, the product was poured into water. The organic phase was washed with aqueous sodium hydrocarbonate and then with water and dried over magnesium sulfate. The solvent was evaporated and dark yellow crystals were formed. The product was subjected to silica-gel column chromatography (hexane : dichloromethane = 1 : 1). The first yellow fraction was collected, and a yellow solid **6a** was obtained. (1.93 g, 7.5 mmol, yield 80%). $^1\text{H-NMR}$ δ 1.38 (s, 9H), 6.64 (m, 1H), 6.73-6.75 (m, 1H), 6.85-6.86 (m, 1H), Mass (EI) $m/z = 256$ (M^+).

4,4'(5')Bis(5-(*t*-butyl)thiophene-2-yl)-tetrathiafulvalene (1b): Under nitrogen, 0.90 g **6b** (3.5 mmol) in triethylphosphite (3 mL) was heated to 135 °C with stirring for 14 h. After cooling, the triethylphosphite was distilled off in vacuum. The product was subjected to silica-gel column chromatography with carbon disulfide. The first orange fraction was collected, and an orange solid was obtained. Three-time crystallization from toluene and ethanol mixed solvent (toluene : ethanol = 1 : 3) gave orange flakes **1b** (0.17 g, 0.35 mmol, 20%). mp 194 °C, $^1\text{H-NMR}$ δ 1.38-1.42 (s, 18H), 6.63-6.65 (m, 2H), 6.73-6.75 (m, 2H), 6.85-6.87 (m, 2H). Mass (EI) $m/z = 480$ (M^+). Calcd for $\text{C}_{22}\text{H}_{24}\text{S}_6$: C, 54.96; H, 5.03; S, 40.01. Found: C, 54.83; H 5.00; S, 40.04.

2. Redox properties

Cyclic voltammograms were measured on a Yanaco VMA-010 voltammogram in 0.1 M tetrabutylammonium hexafluoro-phosphate ($n\text{-Bu}_4\text{N}\cdot\text{PF}_6$) solutions of benzonitrile at scan rates of 20, 50, and 100 mV/s. The reference electrode was Ag/AgNO₃ with a glassy carbon working electrode and a Pt supporting electrode. All the measured potentials were normalized with the ferrocene/ferrocenium redox potential of $E_{1/2} = 0.44$ V vs SCE.

3. UV-vis spectra

UV-vis absorption spectra in dichloromethane were measured on a Hitachi U-2800 UV-vis double beam spectrophotometer at room temperature using a quartz cuvette with a path of 1 cm. Optical bandgap (HOMO-LUMO gap) were calculated from the edge of the visible-absorption bands.

4. Single crystal structures and intermolecular overlap integral calculations

Crystal structures were determined by single crystal X-ray diffraction. Intensity data of **1a** and **1b**

were measured by a Rigaku four-circle diffractometer AFC-7R with graphite monochromatized MoK α ($\lambda = 0.71069 \text{ \AA}$) radiation ($2\theta < 60^\circ$). The crystal structures were solved by the direct method, SIR-92. The structures were refined by the full-matrix least-squares refinement by applying anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were determined from the calculation for **1a**, and from the experimental data for **1b**. The intermolecular transfer integrals t_i between the highest occupied molecular orbitals (HOMOs) were calculated on the basis of the extended Hückel molecular orbital calculation by using the same atomic parameters.

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5. Device fabrication

The organic field-effect transistor (OFET) devices were fabricated on a heavily doped n^+ -Si wafer with a 300 nm thermally grown SiO₂ (13.8 nF cm^{-2}) as the gate dielectric. The substrates were washed in an ultrasonic bath successively with acetone and ultrapure water respectively for 10 min. After washing, the substrates were dried in an oven at 150 °C for 10 min, and then exposed to O₃ by using a UV-O₃ Cleaning System Model 203 (Technovision Inc.). The washed substrates were dipped in a 50 mM *n*-octyltrichlorosilane (OTS) toluene solution at 70 °C for 12 h under Ar atmosphere. The substrates were washed three times with toluene and acetone respectively for 20 min to remove excess OTS on the substrate.

OFETs with top-contact (TC) Au source and drain (S/D) electrodes were fabricated. The electrodes were fabricated by vacuum deposition using a mask. The electrodes were deposited under the vacuum of 1.0×10^{-3} Pa on the top of the organic thin film through a metal mask. The S/D channel length (L) was from 50 μm to 200 μm with an interval of 50 μm , and the width (W) was 1 mm. The deposition temperature for **1a** was 125 °C and **1b** was 140 °C under the vacuum of 1.0×10^{-4} Pa. A substrate temperature of 50 °C was also attempted, but the thin films were not improved. Characteristics of the OFET devices were measured by a Keithley 4200 semiconductor parameter analyzer at room temperature in air. The field-effect mobility (μ) was calculated in the saturation region using an equation, $I_D = \mu(WC_i/2L)(V_G - V_{TH})^2$, where I_D was the drain current, C_i was the capacitance of the SiO₂ dielectric layer, and V_G and V_{TH} were the gate and threshold voltages, respectively. Current on/off ratio (I_{on}/I_{off}) was determined from the minimum and the maximum of I_D . For photoresponse measurements, OptoSupply OSHR5111A-TU for red light (625 nm, 12 cd), OSYL5111A-TU for yellow light (590 nm, 18 cd) and OSPG5111A-VW for green light (525 nm, 12 cd) were used. The LED was located by 3 cm apart from the substrate.

AFM images were obtained with Seiko Instruments SPA-300 and SPI3800 probe system by using a Si₃N₄ cantilever. XRD measurements of the thin films were carried out by Phillips X'Pert-MPD-OEC PW3050 with a monochromated Cu-K α radiation ($\lambda = 1.542512 \text{ \AA}$).

References

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- [2] T. Mori, H. Mori, S. Tanaka, *Bull. Chem. Soc. Jpn.*, **1999**, *72*, 179.