Electronic Supplementary Material (ESI) for New Journal of Chemistry.

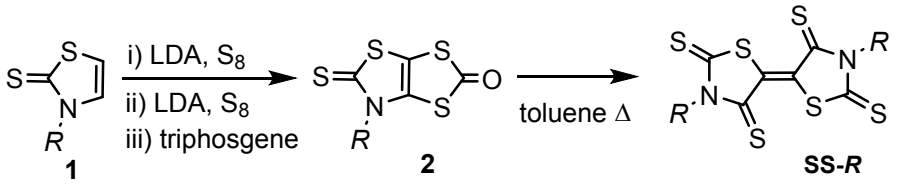
Supporting Information

Temperature-dependent characteristics of n-channel transistors based on 5,5'-bithiazolidinylidene- 2,4,2',4'-tetrathiones

Suho Ryo,[a] Dongho Yoo,[a] Kodai Iijima,[a] Ryonosuke Sato,[a] Yann Le Gal,[b] Dominique Lorcy,[b] and Takehiko Mori[a]*

Synthesis

All commercial chemicals and solvents were used without further purification. Amylamine (A0445), and hexylamine (H0134) were obtained from TCI. Carbon disulfide (038-01246) was obtained from Wako. The data of Nuclear Magnetic Resonance spectrum (NMR) and Mass spectrum (MS) were obtained with a JEOL JNM-AL300 spectrometer and a JEOL JMS-Q1050GC mass spectrometer, respectively.



3,3'-Dimethyl-5,5'-bithiazolidinylidene-2,4,2',4'-tetrathione (SS-*R*).

Under nitrogen atmosphere, to a −10 °C cooled solution of *N*-alkyl-1,3-thiazole-2-thione **1** (7.6 mmol)[8] in dry THF (50 ml) was added a solution of lithium diisopropylamide (LDA) freshly prepared from *n*-butyl lithium (*n*-BuLi) (11.5 mmol, 7.2 mL) and diisopropylamine (11.5 mmol, 1.6 mL) in 30 mL dry THF. After stirring for 30 min at −10 °C, S_8 (11.5 mmol, 366 mg) was added and the solution was stirred for additional 30 min. To the medium, a solution of LDA freshly prepared from n-BuLi (15.3 mmol, 9.6 mL) and diisopropylamine (15.3 mmol, 2.2 mL) in 30 mL dry

THF was added. The reaction mixture was stirred at −10 °C for 3 h and sulfur S_8 (12.6 mmol, 403 mg) was added. After 30 min, triphosgene (11.4 mmol, 3.38 g) was added and stirred for 30 min at −10 °C and further stirred at room temperature overnight. The solution was evaporated *in vacuo* and extracted with dichloromethane and washed with water. The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was purified by column chromatography using dichloromethane as eluent to afford **2** as a brown solid.

A solution of **2** in 50 mL toluene was refluxed overnight. 90% of the solution was evaporated in vacuo and the precipitate was filtered and washed with ethanol and dried in vacuo to afford **SS-*R*** as a black solid. Crystals of sufficient quality for X-ray diffraction were obtained by slow evaporation of CH_2Cl_2.

SS-Pen: Yield: 45% (740 mg). ^{1}H NMR (300MHz, $CDCl_3$) δ 0.98 (t, 3H, CH_3, J = 7.4 Hz), 1.74 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 3.78 (m, 2H, CH_2); HRMS (ASAP) calcd for $C_{16}H_{22}N_2S_6$ [M + H]+: 434.776. Found: 434.8932; Anal. calcd for $C_{16}H_{22}N_2S_6$: C, 44.20; H, 5.10; N, 6.44. Found: C, 43.96 ; H, 4.87; N, 6.18.

SS-Hex: Yield 48% (840 mg). ^{1}H NMR (300MHz, $CDCl_3$) δ 0.98 (t, 3H, CH_3, J = 7.4 Hz), 1.78 (m, 2H, CH_2), 1.35 (m, 2H, CH_2), 3.88 (m, 2H, CH_2); HRMS (ESI) calcd for $C_{12}H_{14}N_2S_6$ $[M + H]^+$: 462.828. Found: 462.9562; Anal. calcd for $C_{18}H_{26}N_2S_6$: C, 46.72; H, 5.66; N, 6.05. Found: C, 46.62; H, 5.46; N, 6.14.

Cyclic Voltammetry (CV) and ultraviolet-visible spectroscopy (UV-Vis)

Redox potentials were measured by cyclic voltammetry. Dry dichloromethane was used as a solvent, $Bu_4N \cdot PF_6$ as an electrolyte and ALS-701E as a measuring instrument. An $Ag/AgNO_3$ electrode was used for the reference electrode, and glassy carbon and platinum electrodes were used for the working electrode and the auxiliary electrode, respectively.

Ultraviolet-visible absorption spectra were measured at room temperature using a quartz cuvette having a 1 cm path using a UV-1800 ultraviolet-visible spectrophotometer (Shimadzu). Dichloromethane was used as a solvent. With increasing the alkyl chain length, the splitting of the 500-600 nm peak became less important probably because it is related to the intermolecular interaction. The optical band gap (HOMO-LUMO gap) was calculated from the edge of the visible absorption band.

Crystal Structures

The X-ray oscillation photographs for **SS-Pen** were taken using a RIGAKU R-AXIS RAPID II imaging plate with Cu$K\alpha$ radiation from a rotation anode source with a confocal multilayer X-ray mirror (RIGAKU VM-Spider, λ = 1.54187 Å). Diffraction data for **SS-Hex** were collected on a Rigaku AFC-7R four-circle diffractometer using MoKα radiation from a rotation anode source (λ = 0.71069 Å). The structures were solved by the direct method (SHELXT) and refined by the full-matrix least-squares method by applying anisotropic temperature factors for all non-hydrogen atoms using the SHELXL programs.[S1,S2] The hydrogen atoms were placed at geometrically calculated positions. Transfer integrals were estimated from the overlap of the molecular orbitals.[26]

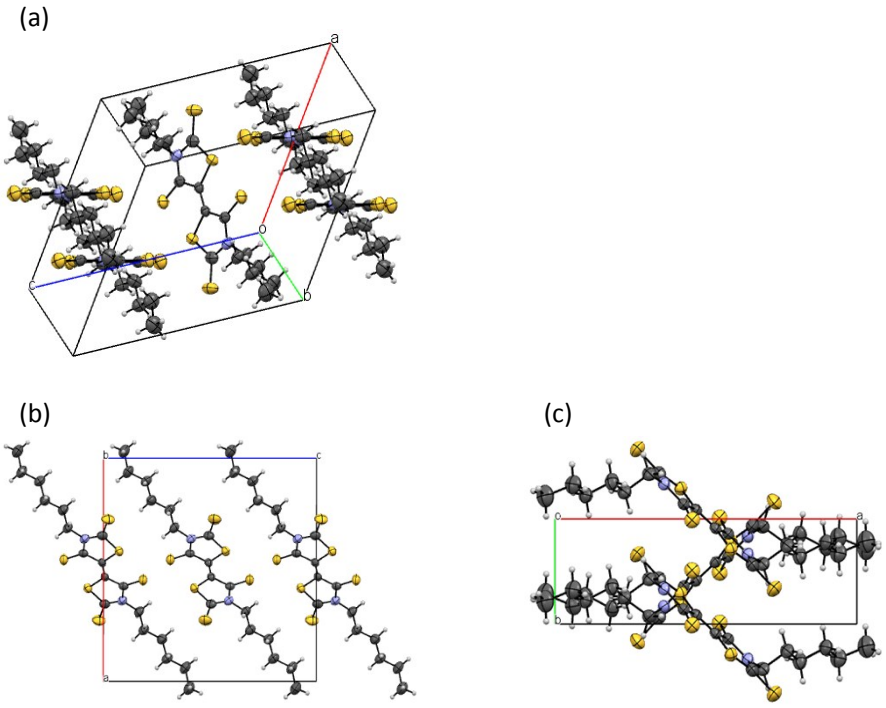


Figure S1. (a) Crystal structure of **SS-Hex** viewed along the molecular long axis. (b) Crystal structure of **SS-Hex** viewed along the *b* axis, and (b) along the *c* axis.

Thin film properties

X-ray diffraction analyses of thin films (50 nm) on TTC (20 nm) were performed by X'pert-Pro-MRD using the θ-2θ technique with Cu-$K\alpha$ radiation for $2° \leq 2\theta \leq 20°$. AFM images of thin films (50 nm) on TTC (20 nm) were taken by a SII scanning probe microscope system SPI3800N and SPA-300 by using a Si_3N_4 cantilever.

Transistor characteristics

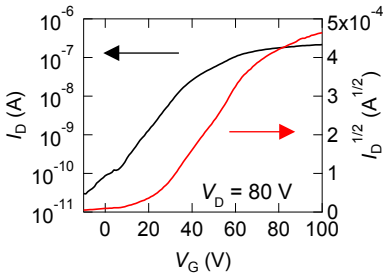


Figure S2. Transfer characteristics of an **SS-Hex** single-crystal transistor.

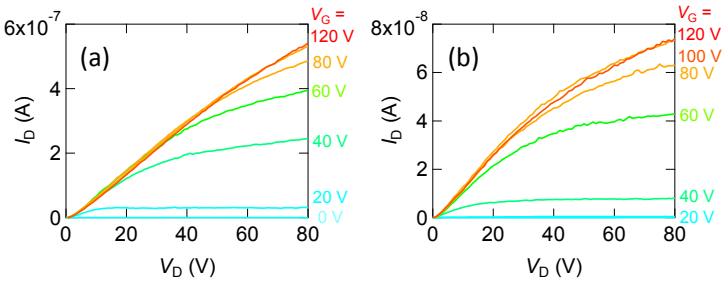


Figure S3. Output characteristics of single-crystal transistors measured at room temperature for (a) **SS-Pen** (*//b*), and (b) **SS-Hex** (*//b*).

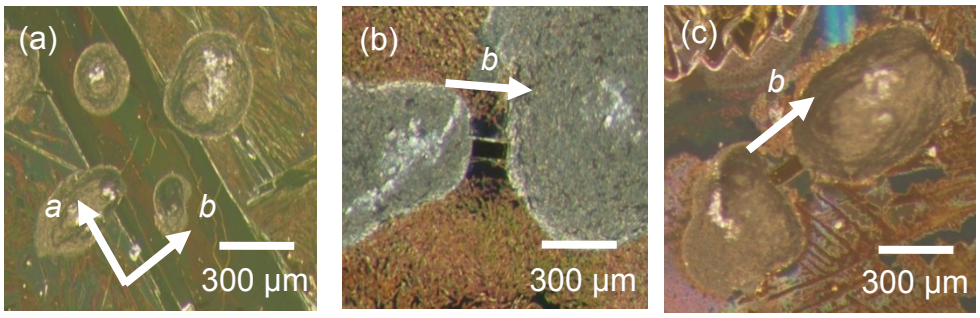


Figure S4. Single-crystal transistors of (a) **SS-Pr**, (b) **SS-Pen**, and (c) **SS-Hex**.

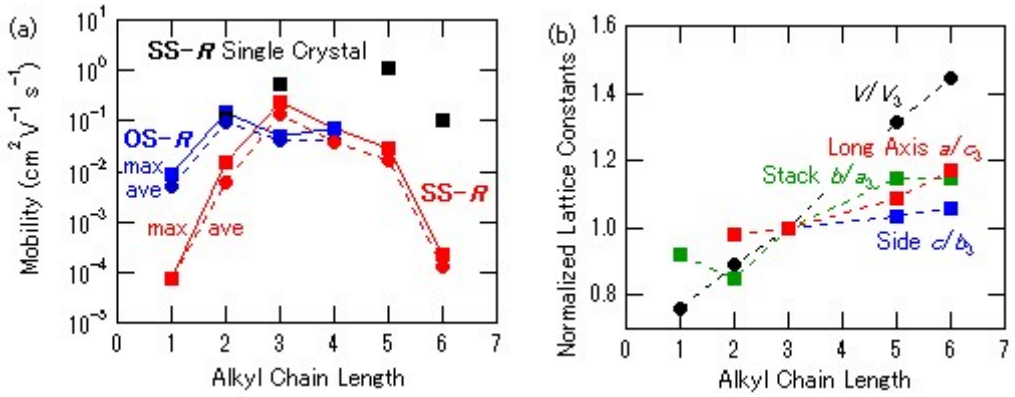


Figure S5. (a) Summary of mobility. (b) Lattice constants normalized by a_3~c_3 and V_3 of **SS-Pr**.

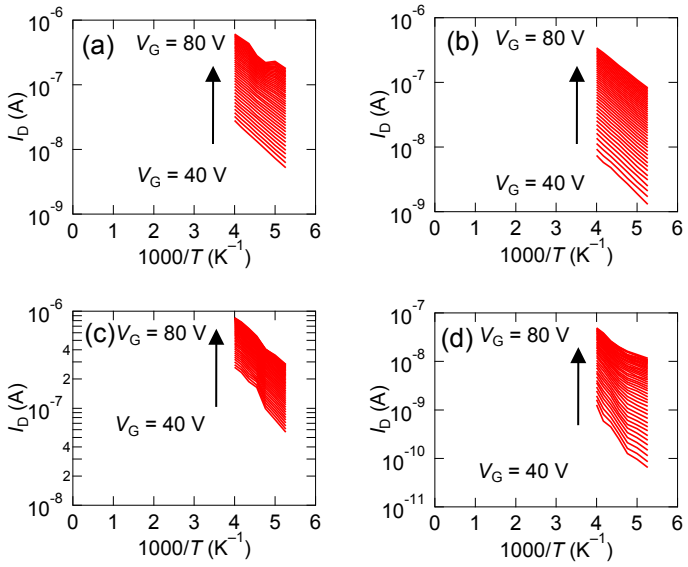


Figure S6. Arrhenius plots of I_D for transistors of (a) **SS-Pr** (//*a*), (b) **SS-Pr** (//*b*), (c) **SS-Pen** (//*b*), and (c) **SS-Hex** (//*b*).

References

S1 Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal Structure Determination. *Acta Crystallogr. A*. 2015, **71**, 3.

S2 Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. C*. 2015, **71**, 3.