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) 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, S8 (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 $-10^\circ C$ 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 $-10^\circ C$ 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$_2$Cl$_2$.

**SS-Pen**: Yield: 45% (740 mg). $^1$H NMR (300MHz, CDCl$_3$) $\delta$ 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$_2$S$_6$ [M + H]$^+$: 434.776. Found: 434.8932; Anal. calcd for C$_{16}$H$_{22}$N$_2$S$_6$: 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$_3$) $\delta$ 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$_2$S$_6$ [M + H]$^+$: 462.828. Found: 462.9562; Anal. calcd for C$_{18}$H$_{26}$N$_2$S$_6$: 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$_4$N·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 CuKα 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. The hydrogen atoms were placed at geometrically calculated positions. Transfer integrals were estimated from the overlap of the molecular orbitals.

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 $\theta$-2$\theta$ technique with Cu-$K\alpha$ radiation for $2^\circ \leq \theta \leq 20^\circ$.

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 $\text{Si}_3\text{N}_4$ 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** (∥/∥), and (b) **SS-Hex** (∥/∥).

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
