

## Supporting Information

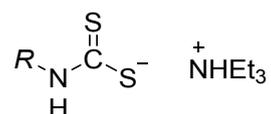
### Structures and transistor properties of extended and unsymmetrical birhodanines

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#### Synthesis

All commercial chemicals and solvents were used without further purification. The data of Nuclear Magnetic Resonance spectrum (NMR) and Mass spectrum (MS) were obtained with a JEOL JNM-AL300 spectrometer and JEOL JMS-Q1050GC mass spectrometer, respectively.

#### Alkylcarbamodithioate (**6-R**)<sup>S1</sup>



To a solution of alkylamine (30 mmol) in 15 mL tetrahydrofuran at 0°C were added carbon disulfide (30 mmol, 1.8 mL) and 5 mL triethylamine. The mixture was stirred at this temperature for 2 h. The solvent was evaporated *in vacuo* and dried to afford **6-R**.

**Methylcarbamodithioate (6-Me)**: White solid (89%), MS(EI):  $m/z = 73$  [M –S–NC<sub>3</sub>H<sub>6</sub>]<sup>+</sup>.

**Ethylcarbamodithioate (6-Et)**: White solid (85%), MS(EI):  $m/z = 87$  [M –S–NC<sub>3</sub>H<sub>6</sub>]<sup>+</sup>.

**Propylcarbamodithioate (6-Pr)**: White solid (86%), MS(EI):  $m/z = 101$  [M –S–

$\text{NC}_3\text{H}_6]^+$ .

**Butylcarbamodithioate (6-Bu):** Yellow liquid (87%), MS(EI):  $m/z = 115$  [ $\text{M} - \text{S} - \text{NC}_3\text{H}_6]^+$ .

**Phenylcarbamodithioate (6-Ph):** Yellow solid (92%), MS(EI):  $m/z = 135$  [ $\text{M} - \text{S} - \text{NC}_3\text{H}_6]^+$ .

### **3-Alkyl-2-thioxothiazolidin-4-one (3-R)<sup>S1</sup>**

To a solution of chloroacetic acid (9.3 mmol 0.87 g) in 30 mL acetone at 0°C was added sodium carbonate (4.6 mmol 0.49 g), and the mixture was stirred at this temperature for 20 min. To the solution was added **6-R** (9.3 mmol), and the mixture was stirred at room temperature for 3 h. The solution was evaporated *in vacuo* and dried. This mixture was added slowly into 40 mL boiling 6 N HCl, and refluxed for 3 h. After cooling, the product was extracted by  $\text{CH}_2\text{Cl}_2$  to afford **3-R**.

**3-Methyl-2-thioxothiazolidin-4-one (3-Me):** Yellow solid (79%), MS(EI):  $m/z = 147$  [ $\text{M}]^+$ ,  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.99 (s, 2H), 3.37 (m, 3H).

**3-Ethyl-2-thioxothiazolidin-4-one (3-Et):** Yellow solid (73%), MS(EI):  $m/z = 161$  [ $\text{M}]^+$ ,  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.05 (q,  $J = 7.2$  Hz, 2H), 3.95 (s, 2H), 1.21 (t,  $J = 7.2$  Hz, 3H).

**3-Propyl-2-thioxothiazolidin-4-one (3-Pr):** Yellow liquid (53%), MS(EI):  $m/z = 175$  [ $\text{M}]^+$ ,  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.96 (s, 2H), 3.93 (m, 2H), 1.66 (m, 2H), 0.93 (t,  $J = 7.4$  Hz, 3H).

**3-Butyl-2-thioxothiazolidin-4-one (3-Bu):** Yellow liquid (70%), MS(EI):  $m/z = 189$  [ $\text{M}]^+$ ,  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.97 (m, 2H), 3.95 (s, 2H), 1.61 (m, 2H), 1.35 (m, 2H), 0.94 (t,  $J = 7.3$  Hz, 3H).

**3-Phenyl-2-thioxothiazolidin-4-one (3-Ph):** Yellow solid (43%), MS(EI):  $m/z = 209$

[M]<sup>+</sup>, <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.52 (m, 3H), 7.19 (m, 2H), 4.18 (s, 2H).

### **3-Alkyl-2-thioxothiazolidine-4,5-dione (5-R)<sup>S2</sup>**

To a solution of **6-R** (28 mmol) in 30 mL CH<sub>2</sub>Cl<sub>2</sub> at 0°C was slowly added oxalyl chloride (28 mmol, 2.4 g), and the mixture was stirred at this temperature for 2 h. The solution was evaporated *in vacuo* and dried. The product was purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent to afford **5-R** as an orange liquid.

**3-Ethyl-2-thioxothiazolidine-4,5-dione (5-Et)**: Orange liquid (84%), MS(EI): *m/z* = 175 [M]<sup>+</sup>.

**3-Propyl-2-thioxothiazolidine-4,5-dione (5-Pr)**: Orange liquid (70%), MS(EI): *m/z* = 189 [M]<sup>+</sup>.

**3-Butyl-2-thioxothiazolidine-4,5-dione (5-Bu)**: Orange liquid (62%), MS(EI): *m/z* = 203 [M]<sup>+</sup>.

### **5,5'-(1,4-Phenylenebis(methaneylylidene))bis(3-alkyl-2-thioxothiazolidin-4-one) (1-R)**

To a solution of **3-R** (1.8 mmol) in 30 mL chloroform was added terephthalaldehyde (0.90 mmol, 0.12 g) and 3 mL triethylamine. The mixture was refluxed for 3 h. The resulting precipitate was collected by filtration, washed with methanol and dried to give an orange powder. The product was purified by recrystallization from toluene.

**5,5'-(1,4-Phenylenebis(methaneylylidene))bis(3-propyl-2-thioxothiazolidin-4-one) (1-Pr)**: Orange solid (31%), EI-HRMS: Calcd. for [M]<sup>+</sup> 448.0408, Found 448.0396. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.70 (s, 1H), 7.60 (s, 2H), 4.11 (t, *J* = 7.7 Hz, 2H), 1.76 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H).

**5,5'-(1,4-Phenylenebis(methaneylylidene))bis(3-phenyl-2-thioxothiazolidin-4-one)**

(1-Ph): Orange solid (31%), EI-HRMS: Calcd. for  $[M]^+$  516.0095, Found 516.0098.

**5,5'-(Cyclohexane-1,4-diylidene)bis(3-alkyl-2-thioxothiazolidin-4-one) (4-R)<sup>13</sup>**

Rhodanine **3-R** (14 mmol) was warmed to 70°C with 0.78 g (7.0 mmol) cyclohexane-1,4-dione in 40 mL ethanol. This solution was treated with warmed 5.0 mL concentrated aqueous ammonia and successively a 5.0 mL warmed saturated solution of aqueous ammonium chloride. The mixture was stirred at this temperature for 3 h. The solution was evaporated *in vacuo* and dried. Water was added and the product was extracted by CH<sub>2</sub>Cl<sub>2</sub>, and the CH<sub>2</sub>Cl<sub>2</sub> solution was evaporated *in vacuo* and dried. The product was purified by recrystallization from toluene to afford **4-R** as an orange powder.

**5,5'-(Cyclohexane-1,4-diylidene)bis(3-methyl-2-thioxothiazolidin-4-one) (4-Me):**

Orange solid (24%) MS(EI):  $m/z = 370 [M]^+$ .

**5,5'-(Cyclohexane-1,4-diylidene)bis(3-ethyl-2-thioxothiazolidin-4-one) (4-Et):**

Orange solid (55%) MS(EI):  $m/z = 398 [M]^+$ .

**5,5'-(Cyclohexane-1,4-diylidene)bis(3-propyl-2-thioxothiazolidin-4-one) (4-Pr):**

Orange solid (16%) MS(EI):  $m/z = 426 [M]^+$ .

**5,5'-(Cyclohexane-1,4-diylidene)bis(3-butyl-2-thioxothiazolidin-4-one) (4-Bu):**

Orange solid (19%) MS(EI):  $m/z = 454 [M]^+$ .

**5,5'-(Cyclohexane-1,4-diylidene)bis(3-phenyl-2-thioxothiazolidin-4-one) (4-Ph):**

Orange solid (15%) MS(EI):  $m/z = 494 [M]^+$ .

**5,5'-(Cyclohexa-2,5-diene-1,4-diylidene)bis(3-alkyl-2-thioxothiazolidin-4-one) (2-*R*)**<sup>13</sup>

2.27 g (10 mmol) 2,3-dichloro-5,6-*p*-benzoquinone (DDQ) was added in Ar to a solution of **4-*R*** (0.94 mmol) in 40 mL chlorobenzene. The mixture was refluxed for 24 h. The solvent was evaporated *in vacuo* and dried. The product was purified by recrystallization from toluene to afford **2-*R*** as a violet powder.

**5,5'-(Cyclohexa-2,5-diene-1,4-diylidene)bis(3-methyl-2-thioxothiazolidin-4-one) (2-Me)**: Violet solid (81%), EI-HRMS: Calcd. for [M]<sup>+</sup> 365.9625, Found 365.9615.

**5,5'-(Cyclohexa-2,5-diene-1,4-diylidene)bis(3-ethyl-2-thioxothiazolidin-4-one) (2-Et)**: Violet solid (67%), EI-HRMS: Calcd. for [M]<sup>+</sup> 393.9938, Found 393.9932.

**5,5'-(Cyclohexa-2,5-diene-1,4-diylidene)bis(3-propyl-2-thioxothiazolidin-4-one) (2-Pr)**: Violet solid (61%), EI-HRMS: Calcd. for [M]<sup>+</sup> 422.0251, Found 422.0254.

**5,5'-(Cyclohexa-2,5-diene-1,4-diylidene)bis(3-butyl-2-thioxothiazolidin-4-one) (2-Bu)**: Violet solid (81%), EI-HRMS: Calcd. for [M]<sup>+</sup> 450.0564, Found 450.0563.

**5,5'-(cCyclohexa-2,5-diene-1,4-diylidene)bis(3-phenyl-2-thioxothiazolidin-4-one) (2-Ph)**: Violet solid (76%), EI-HRMS: Calcd. for [M]<sup>+</sup> 489.9938, Found 489.9928.

**3-Alkyl-2,2'-dithioxo-5,5'-bithiazolylidene-4,4'-dione (OS-*RH*)**

To a solution of **5-*R*** (16 mmol) in 40 mL toluene was added rhodanine (**3-*H***, 16 mmol, 2.1 g) and 5.0 mL trimethylamine. The mixture was refluxed for 3 h. The solution was evaporated *in vacuo* and dried. The product was purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent to afford **OS-*RH*** as an orange solid.

**3-Ethyl-2,2'-dithioxo-5,5'-bithiazolylidene-4,4'-dione (OS-EtH)**: Orange solid (16%),

EI-HRMS: Calcd. for  $[M]^+$  289.9312, Found 289.9313.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.19 (q,  $J = 7.2$  Hz, 2H), 1.29 (t,  $J = 7.1$  Hz, 3H).

**3-Butyl-2,2'-dithioxo-5,5'-bithiazolylidene-4,4'-dione (OS-BuH)**: Orange solid (18%),

EI-HRMS: Calcd. for  $[M]^+$  317.9625, Found 317.9632.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.99 (t,  $J = 7.2$  Hz, 2H), 1.59 (m, 2H), 1.31 (m, 2H), 0.88 (t,  $J = 7.5$  Hz, 3H).

**3,3'-Dialkyl-2,2'-dithioxo-5,5'-bithiazolylidene-4,4'-dione (OS-Ph and OS-RR')**

To a solution of **5-R'** (20 mmol) in 40 mL toluene was added **3-R** (20 mmol) and 5.0 mL trimethylamine. The mixture was refluxed for 3 h. The solution was evaporated *in vacuo* and dried. The product was purified by column chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$  as eluent to afford **OS-RR'** (**OS-Ph**) as an orange solid.

**3,3'-Diphenyl-2,2'-dithioxo-5,5'-bithiazolylidene-4,4'-dione (OS-Ph)**: Orange solid (30%), EI-HRMS: Calcd. for  $[M]^+$  413.9625, Found 413.9624.

**3-Ethyl-3'-methyl-2,2'-dithioxo-5,5'-bithiazolylidene-4,4'-dione (OS-EtMe)**: Orange solid (15%), EI-HRMS: Calcd. for  $[M]^+$  303.9469, Found 303.9467.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.11 (m, 2H), 3.53 (t,  $J = 7.0$  Hz, 3H), 0.98 (m, 3H).

**3-Propyl-3'-methyl-2,2'-dithioxo-5,5'-bithiazolylidene-4,4'-dione (OS-PrMe)**:

Orange solid (20%), EI-HRMS: Calcd. for  $[M]^+$  317.9625, Found 317.9624.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.10 (m, 2H), 3.49 (s, 3H), 1.74 (m, 2H), 0.96 (t,  $J = 7.5$  Hz, 3H).

**3-Butyl-3'-methyl-2,2'-dithioxo-5,5'-bithiazolylidene-4,4'-dione (OS-BuMe)**: Orange

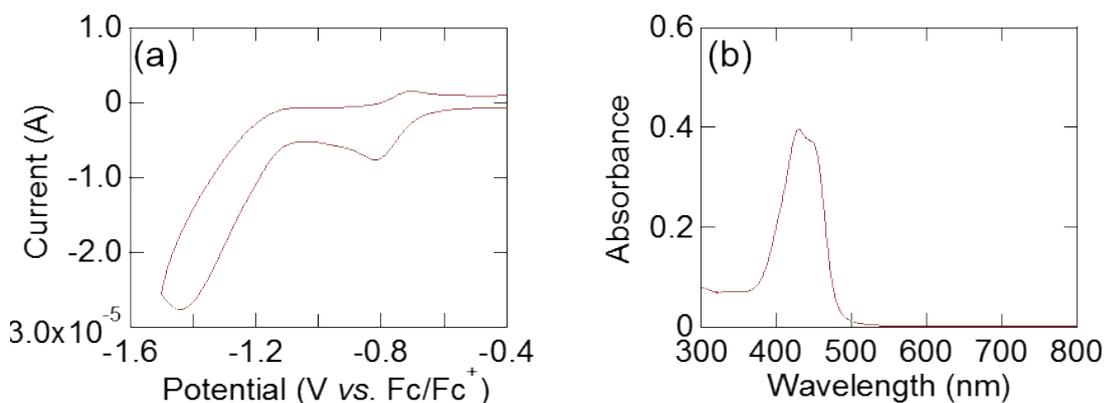
solid (25%), EI-HRMS: Calcd. for  $[M]^+$  331.9782, Found 331.9790.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.12 (t,  $J = 7.7$  Hz, 2H), 3.53 (s, 3H), 1.73 (m, 2H), 1.38 (m, 2H), 0.96 (t,  $J = 7.3$  Hz, 3H).

**3-Propyl-3'-ethyl-2,2'-dithioxo-5,5'-bithiazolylidene-4,4'-dione (OS-PrEt)**: Orange

solid (23%), EI-HRMS: Calcd. for  $[M]^+$  331.9782, Found 331.9787.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  
 $\delta$  4.20 (m, 2H), 4.09 (m, 2H), 1.74 (m, 2H), 1.29 (t,  $J = 7.1$  Hz, 3H), 0.96 (t,  $J = 7.5$  Hz, 3H).

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

Reduction potentials were measured by cyclic voltammetry (CV) on an ALS model 701E electrochemical analyzer. The measurement was performed in dehydrated  $\text{CH}_2\text{Cl}_2$  solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate ( $n\text{-Bu}_4\text{N}\cdot\text{PF}_6$ ) as a supporting electrolyte using a glassy carbon working electrode, a platinum counter electrode, and Ag/AgNO<sub>3</sub> electrode as a reference electrode at a scan rate of 50 mV s<sup>-1</sup>. The half-wave potential of ferrocene appeared at 0.197 V from the Ag/AgNO<sub>3</sub> reference electrode. The LUMO levels of **1-R**, **2-R**, **OS-RH**, **OS-RR'**, and **OS-Ph** were estimated by assuming the ferrocene/ferrocenium energy level to be -4.8 eV under the vacuum level.<sup>17</sup> UV-Vis spectra were collected on a shimadzu UV1800 Spectrophotometer in DMF. From the calculation in Fig. S3, the optical gap corresponds to the HOMO-LUMO separation.



**Figure S1.** (a) Cyclic voltammogram, and (b) absorption spectrum of **OS-Ph**.

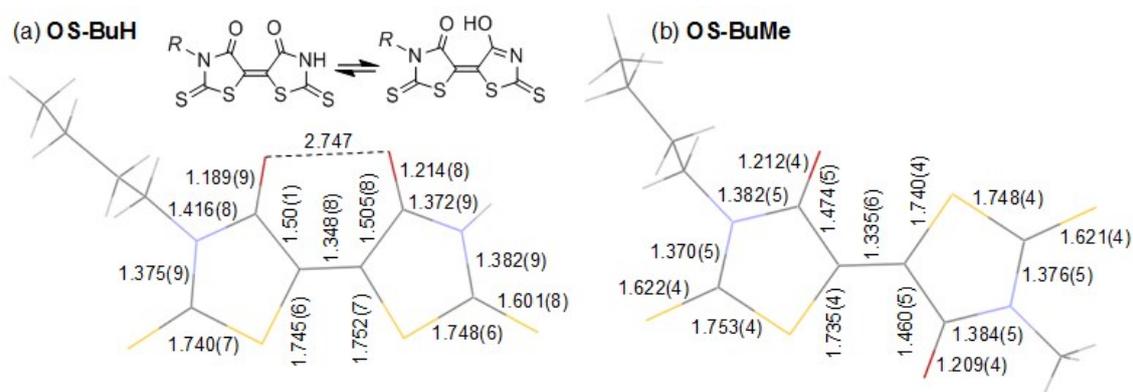
## Crystal Structures

Crystals for X-ray single-crystal structure analyses were obtained by vapor diffusion of ethanol into toluene solutions of **1-Pr**, **1-Ph**, **OS-Ph**, **OS-EtMe**, **OS-BuMe** and **OS-PrEt**, and chlorobenzene solutions of **OS-BuH**. The diffraction data of **1-Pr**, **OS-EtMe**, **OS-BuMe** and **OS-PrEt** were collected by a Rigaku four-circle diffractometer (AFC-7R) with graphite-monochromatized Mo- $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The X-ray oscillation photographs of **1-Ph**, **OS-Ph** and **OS-BuH** 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,  $\lambda = 1.54187 \text{ \AA}$ ). The structures were solved by the direct method (SIR2008) and refined by the full matrix least-squares procedure (SHELXL).<sup>S3,S4</sup> Anisotropic thermal parameters were adopted for all non-hydrogen atoms. Transfer integrals were estimated from the overlap of the molecular orbitals.<sup>S5</sup>

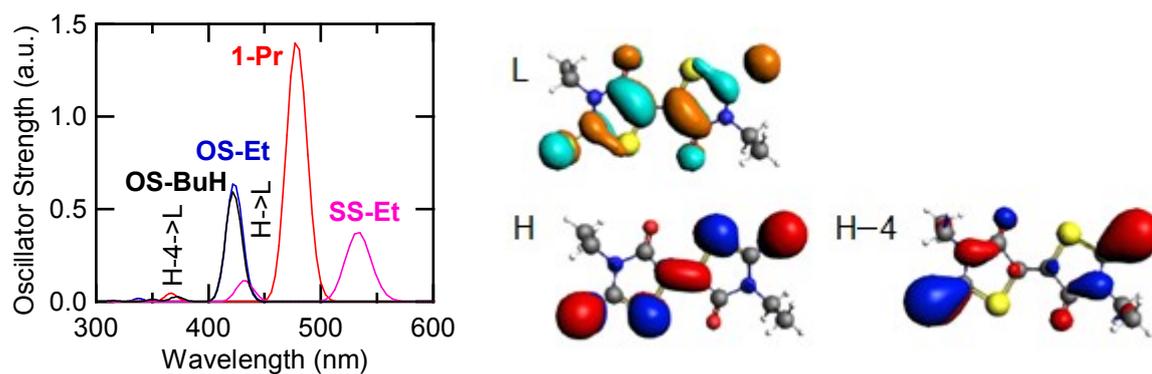
An attempt to refine the structure of **OS-BuH** in the enolic form (Fig. S2(a)) has not improved the analysis. Bond distances of **OS-BuH** in comparison with **OS-BuMe** do not exclusively indicate the enolic form (Fig. S2), but do not conflict with the enolic form. Geometry optimized calculation demonstrates the energy of the ketone form is only 0.071 eV lower than the enolic form.<sup>18</sup> We could not exclude significant contribution of the enolic form in **OS-BuH**.

In order to assign the absorption spectra, simplified time-dependent density functional theory (sTDDFT) calculations were performed (Fig. S3).<sup>18,S6</sup> The principal band around 400-500 nm comes from the HOMO-LUMO transition. The peak positions are in good agreement with the observations (Fig. 1).<sup>6,7</sup> The second band is a transition from C=S (H-4) to LUMO. The magnitude somewhat depends on the

molecular structures. There is no difference in the absorption spectra between **OS-Et** and the *Z*-form **OS-BuH**.



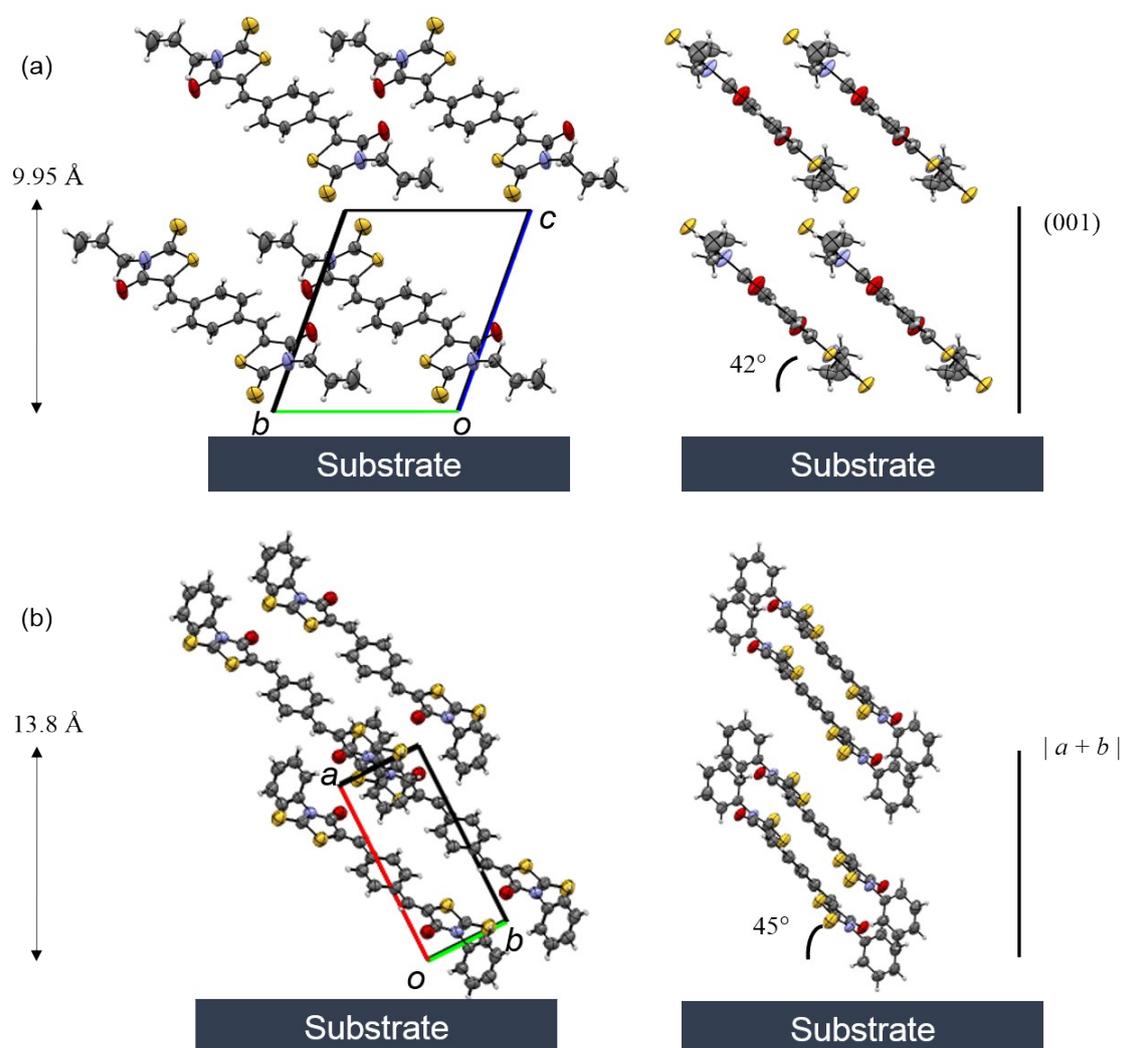
**Figure S2.** Bond lengths (Å) in (a) **OS-BuH**, and (b) **OS-BuMe**.



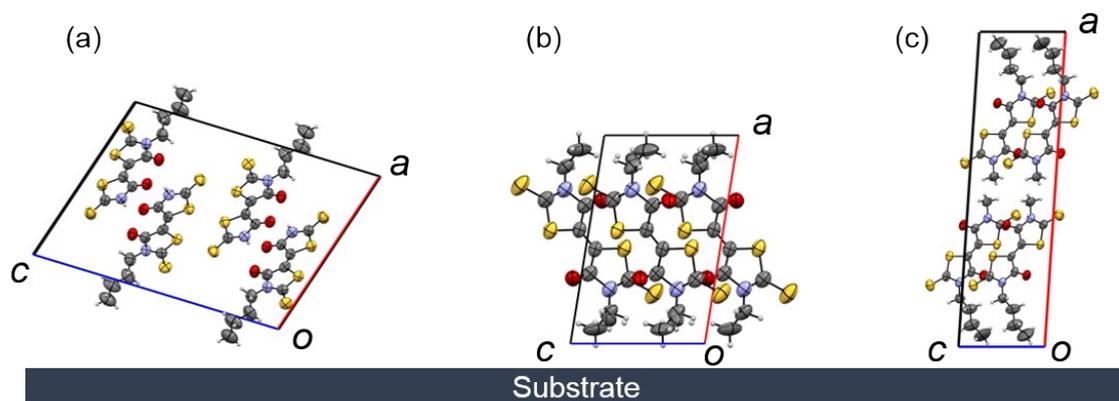
**Figure S3.** Calculated oscillator strength and the related orbitals.

### Thin film properties

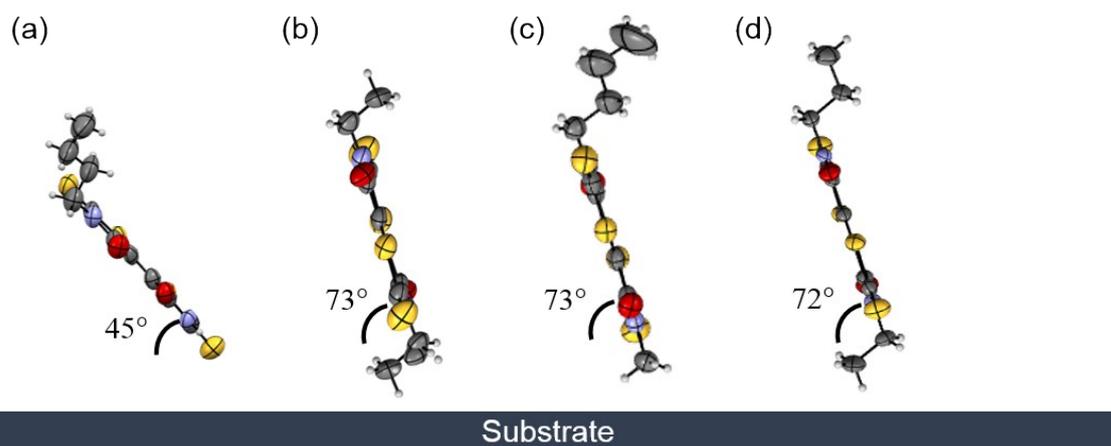
X-ray diffraction analyses of thin films (50 nm) on tetratetracontane (TTC, 20 nm) were performed by X'pert-Pro-MRD using the  $\theta$ - $2\theta$  technique with Cu- $K\alpha$  radiation for  $2^\circ \leq 2\theta \leq 20^\circ$ . The tilt angles were estimated from the crystal structures and  $d$ -spacing as shown in Fig. S4-S6. 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 (Fig. S7).



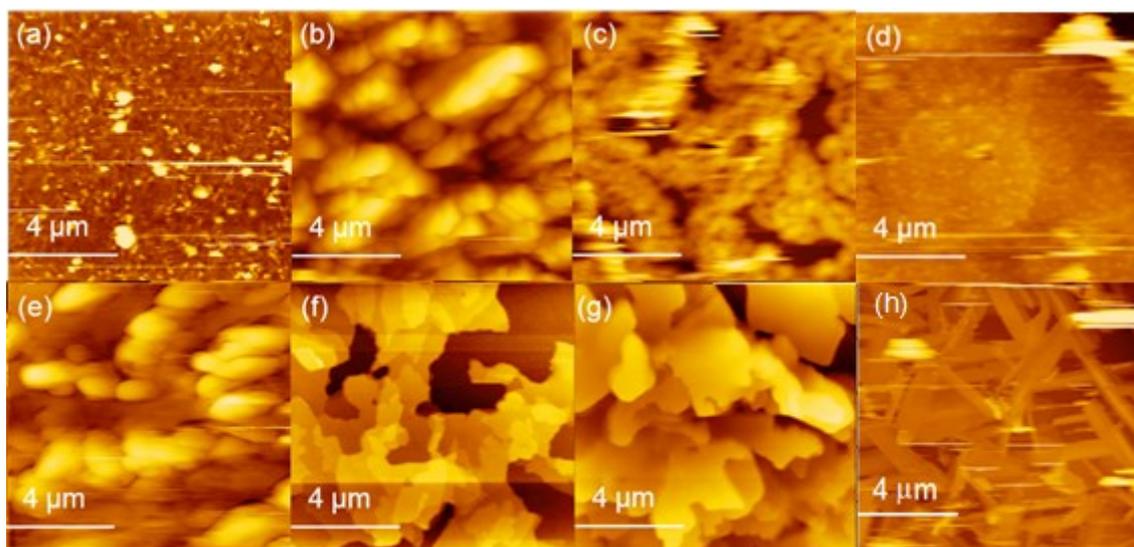
**Figure S4.** Tilt angles of (a) 1-Pr, and (b) 1-Ph.



**Figure S5.** Thin-film packing patterns of (a) **OS-BuH**, (b) **OS-EtMe**, and (c) **OS-BuMe**.



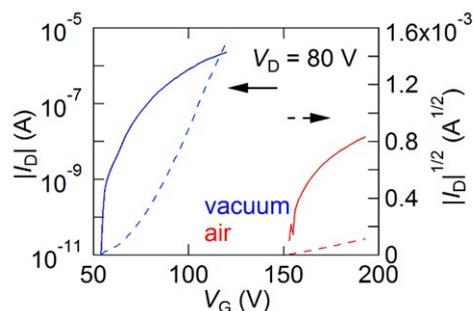
**Figure S6.** Tilt angles of (a) **OS-BuH**, (b) **OS-EtMe**, (c) **OS-BuMe**, and (d) **OS-PrEt**.



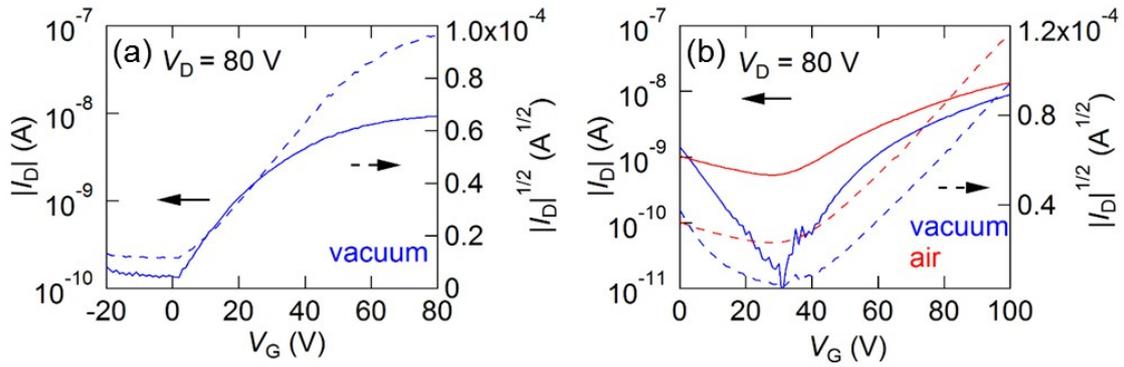
**Figure S7.** Atomic force microscopic (AFM) images of (a) **1-Ph**, (b) **2-Me**, (c) **2-Pr**, (d) **2-Bu**, (e) **2-Ph**, (f) **OS-EtH**, (g) **OS-PrMe**, and (h) **OS-Ph**.

### Device fabrication and thin-film properties

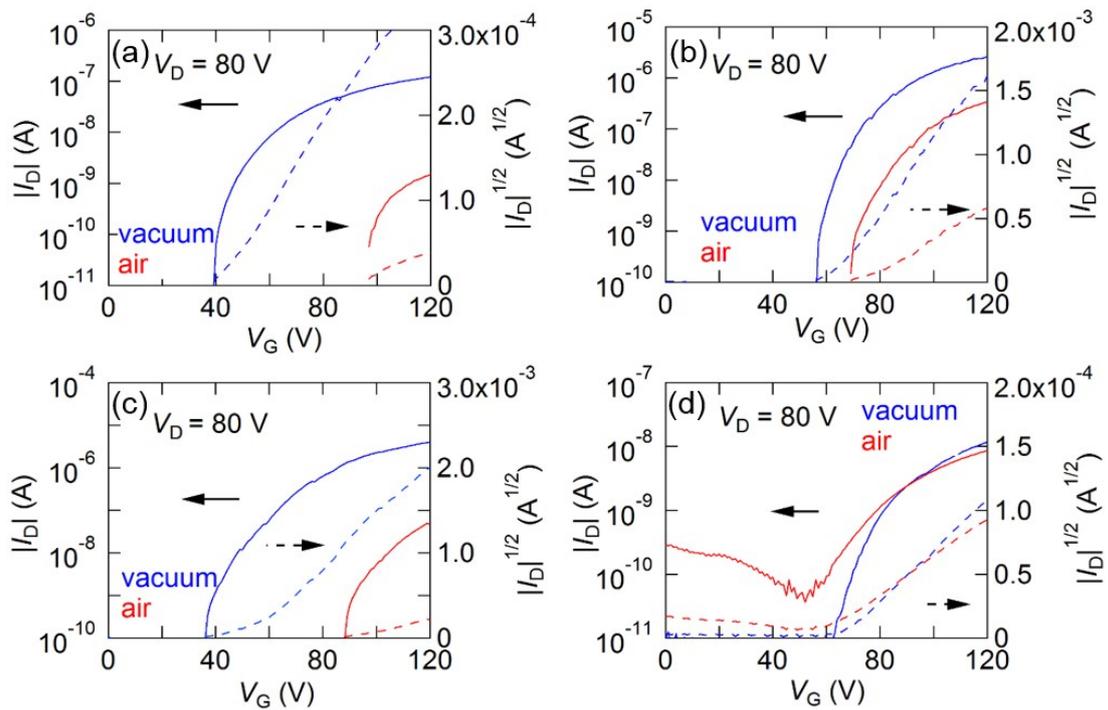
The transistors were prepared by using a commercially available heavily doped  $n$ -type Si wafer with 300 nm SiO<sub>2</sub> insulator ( $\epsilon = 3.9$  and the capacitance of 11.5 nF cm<sup>-2</sup>) as a gate. A passivation layer of 20 nm TTC was evaporated ( $\epsilon = 2.5$  with the capacitance of 10.6 nF cm<sup>-2</sup>), and the resulting overall capacitance of the gate dielectric was 10.4 nF cm<sup>-2</sup>. Then **1-R**, **2-R** and **OS-RR'** (50 nm) were vacuum evaporated at a pressure of 10<sup>-3</sup> Pa. Gold source and drain electrodes were evaporated through a shadow mask ( $L/W = 100/1000$   $\mu\text{m}$ ) at a pressure of 10<sup>-3</sup> Pa to accomplish the bottom-gate top-contact transistors. Transistor characteristics were measured with a Keithley 4200 semiconductor parameter analyzer under vacuum and in air. The mobility values were evaluated from the transconductance in the saturated region. The average values were average for at least six devices. The transfer characteristics are shown in Figs. S8-S10. The mobility values were estimated in the saturated region.



**Figure S8.** Transfer characteristics of thin-film transistors based on **1-Ph**.



**Figure S9.** (a) Transfer characteristics of thin-film transistors based on **2-Me**. (b) Transfer characteristics of thin-film transistors based on **2-Bu**.



**Figure S10.** Transfer characteristics of (a) **OS-EtH**, (b) **OS-PrMe**, (c) **OS-BuMe**, and (d) **OS-Ph** transistors.

## References

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