**Supporting Information**

Impact of bulky phenylalkyl substituents on the air-stable n-channel transistors of birhodanine analogues

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Synthesis

All commercial chemicals and solvents were used without further purification. Benzylamine, 2-phenylethylamine, trimethylamine and dimethyl acetylene dicarboxylate were obtained from TCI.   Carbon disulfide was obtained from Wako. Chloroacetaldehyde (~50 wt. % in water) and triphosgene were obtained from Sigma-Aldrich.   Nuclear magnetic resonance spectra (NMR) and mass spectra (MS) were obtained with a JEOL JNM-AL300 spectrometer and a JEOL JMS-Q1050GC mass spectrometer, respectively.
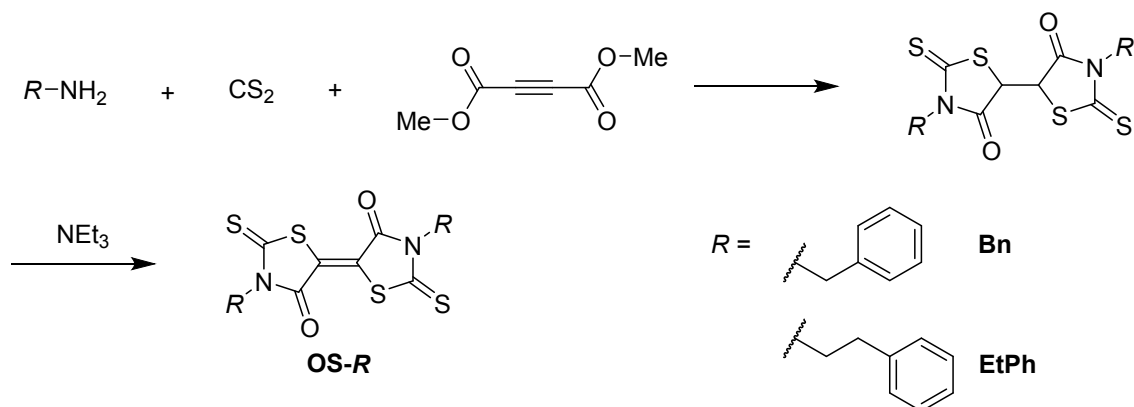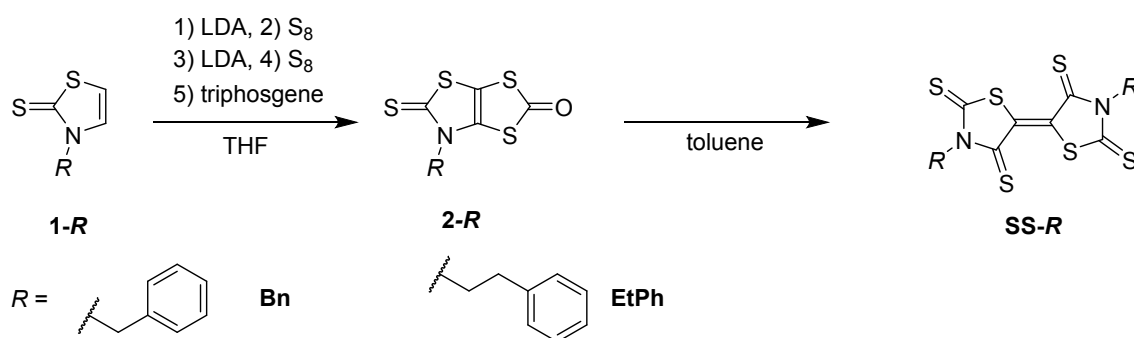

Scheme S1. Synthesis of **OS-R**.

3,3'-Dibenzyl-2,2'-dithioxo-[5,5']bithiazolidinylidene-4,4'-dione (OS-Bn)

To a stirred solution of carbon disulfide (1.45 mL, 24 mmol) and dimethyl acetylene dicarboxylate (1.23 mL, 10 mmol) was added dropwise benzylamine (2.18 mL, 20 mmol). When the vigorous and exothermic reaction ceased, trimethylamine (5 mL) was added. After stirring for 10 min, ethanol (50 mL) was added. The resulting precipitate was collected by filtration, washed with ethanol and dried to give a red powder (200 mg, 10%). The product was purified by recrystallization from DMF. For the fabrication of the thin-film transistors, the compound was further purified by sublimation under a vacuum of 10^{-4} Pa at 250°C for 24 h. m.p.: 299°C. EIMS m/z: 442 [M^+]. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.31 (m, 10H, Ar), 5.37 (s, 4H, CH$_2$); IR = 1684, 1347, 1292, 1189 cm^{-1}. Anal. Calcd for C$_{20}$H$_{14}$N$_2$O$_2$S$_4$: C, 54.28; H, 3.19; N, 6.33. Found: C, 53.99; H, 3.26; N, 6.36.

3,3'-Di(2-phenylethyl)-2,2'-dithioxo-[5,5']bithiazolidinylidene-4,4'-dione (OS-EtPh)

An orange powder (100 mg, 15%) was obtained following the procedure for the synthesis of **OS-Bn**. The product was purified by recrystallization from toluene. For the fabrication of the thin-film transistors, the compound was further purified by sublimation under a vacuum of 10^{-4} Pa at 220°C for 24 h. m.p.: 238°C. EIMS m/z: 470 [M^+]. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.34–7.23 (m, 10H, Ar), 4.34 (t, 4H, J = 8.1 Hz, CH$_2$-N), 2.99 (t, 4H, J = 8.1 Hz, CH$_2$-Ph); ^{13}C NMR (75 MHz, CDCl$_3$) δ 194.153 (C=S), 166.589 (C=O), 136.847 (C=C), 128.881 (Ar), 128.725 (Ar), 127.023 (Ar), 124.573 (Ar), 45.696 (CH$_2$-N), 33.019 (CH$_2$-Ar); IR = 1692, 1350, 1261, 1172 cm^{-1}; Anal. Calcd for C$_{22}$H$_{18}$N$_2$O$_2$S$_4$: C, 56.15; H, 3.86; N, 5.95. Found: C, 55.85; H, 3.63; N, 5.96.

Scheme S2. Synthesis of **SS-R**.

3,3'-Dibenzyl-5,5'-bithiazolidinylidene-2,4,2',4'-tetrathione (SS-Bn)

Under argon atmosphere, to a −10°C cooled solution of *N*-benzyl-1,3-thiazole-2-thione **1-Bn** (10 mmol, 1.1 g)[S1] in dry THF (100 ml) was added a solution of lithium diisopropylamide (LDA), freshly prepared from *n*-butyl lithium (*n*-BuLi) (15 mmol) and diisopropylamine (15 mmol, 2.1 mL) in 15 mL of dry THF.   After stirring for 30 min at −10 °C, S_8 (15 mmol, 480 mg) was added and the solution was stirred for additional 30 min.   To the medium a solution of LDA freshly prepared from n-BuLi (20 mmol) and diisopropylamine (20 mmol, 2.8 mL) in 20 mL of dry THF was added. The reaction mixture was stirred at −10 °C for 3 h, and sulfur S_8 (20 mmol, 720 mg) was added.   After 30 min, triphosgene (20 mmol, 5.9 g) was added and stirred for 30 min at −10°C and further stirred overnight at room temperature.   Then water (15 mL) was slowly added and he solvent was evaporated in *vacuuo*.   Dichloromethane (50 mL) was added and the solution was washed with water (3 x 20 mL) and dried over $MgSO_4$. The concentrated solution was purified by chromatography on silica gel using CH_2Cl_2-petroleum ether as the eluant to afford **2-Bn** (0.84 g. 53%) as a brown powder. m.p.: 165°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (m, 10H, Ar), 5.36 (s, 4H, CH_2); [13]C

NMR (75 MHz, CDCl$_3$) δ 53.8 (NCH$_2$) ; 103.5 (C=C) ; 126.4 (C=C) ; 128.5 (Ar) ; 129.3 (Ar) ; 129.4 (Ar) ; 132.8 (Ar) ; 187.5 (C=O); δ=188.1 (C=S); HRMS (ESI) calcd for C$_{11}$H$_8$NOS$_4$ [M+H]$^+$: 297.94888. Found 297.9484; Anal calcd for C$_{11}$H$_8$NOS$_4$: C, 44.42 ; H, 2.37 ; N, 4.71. Found : C, 44.40 ; H, 2.25 ; N, 4.59.

A solution of **2-Bn** 300 mg (1.01 mmol) in 30 mL of toluene was refluxed for 16 h at 120°C.   80% of the solvent was removed *in vacuo* and the concentrated solution was filtrated and the precipitate was washed with ethanol and dried in *vacuo*.   A dark purple solid (100 mg, 10%) was obtained.   The product was purified by recrystallization from chlorobenzene.   For the fabrication of the thin-film transistors, the compound was further purified by sublimation under a vacuum of 10^{-4} Pa at 250°C for 24 h. m.p.: 286°C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.30 (m, 10H, Ar), 5.38 (s, 4H,CH$_2$); IR = 1651, 1357, 1186 cm^{-1}; HRMS (ESI) calcd for C$_{20}$H$_{14}$N$_2$S$_6$ [M]$^+$: 473.94758. Found 473.9479   Anal. calcd for C$_{20}$H$_{14}$N$_2$S$_6$: C, 50.60; H, 2.97; N, 5.90. Found: C, 50.67; H, 2.89; N, 5.85.

3,3'-Diphenylethyl-5,5'-bithiazolidinylidene-2,4,2',4'-tetrathione (SS-EtPh).

A dark purple solid (100 mg, 10%) was obtained from **1-EtPh** following the procedure for the synthesis of **SS-Bn**.   The product was purified by recrystallization from toluene. For the fabrication of the thin-film transistors, the compound was further purified by sublimation under a vacuum of 10^{-4} Pa at 250°C for 24 h.   m.p.: 252°C. EIMS *m/z*: 502 [M$^+$]. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.27–7.26 (m, 8H, Ar), 7.08–7.05 (m, 2H, Ar), 4.41 (broad, 4H, *J* = 6.8 Hz, CH$_2$-N), 3.07 (t, 4H, *J* = 6.8 Hz, CH$_2$-Ar); IR = 1651, 1350, 1261, 1165 cm^{-1}. Anal. Calcd for C$_{22}$H$_{18}$N$_2$S$_6$: C, 52.56; H, 3.61; N, 5.57. Found:

C, 52.48; H, 3.31; N, 5.56.

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

Reduction potentials were measured by cyclic voltammetry (Figs. 1(a) and (b)) on an ALS model 701E electrochemical analyzer using dry dichloromethane as a solvent and tetrabutylammonium hexafluorophosphate as an electrolyte.   The working electrode was glassy carbon, and the counter electrode was platinum.   Ag in a 0.1 M AgNO$_3$ solution was used as a reference electrode.   The LUMO levels were estimated from the reduction potentials by assuming the reference energy level of ferrocene/ferrocenium (Fc/Fc$^+$: $E^{1/2}$ = +0.195 V $vs.$ Ag/AgNO$_3$ measured under the identical conditions) to be 4.8 eV from the vacuum level.[11]

UV-Vis spectra (Figs. 1(c) and (d)) were collected on a Shimadzu UV1800 Spectrophotometer in CH$_2$Cl$_2$.   The HOMO levels were estimated from the LUMO levels and the optical gaps.

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$_2$ insulator (ε = 3.9 and the capacitance of 11.5 nF cm^{-2}) as a gate.[S2]   A passivation layer of TTC was evaporated (ε = 2.5 and 20 nm thickness with the capacitance of 106 nF cm^{-2}),[13] and the resulting overall capacitance of the gate dielectric was 10.4 nF cm^{-2}.   Then the birhodanine derivatives (50 nm) were vacuum evaporated at a rate of 0.1 Å s^{-1} under a pressure of 10^{-3} Pa.   Gold source and drain electrodes were evaporated through a shadow mask (L/W = 100/1000 μm) at a pressure of 10^{-3} 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 an average for at least eight devices.

Crystal Structures

Crystals for X-ray single crystal structure analyses were obtained by vapor diffusion of ethanol into a DMF solution of **OS-Bn,** toluene solutions of **OS-EtPh** and **SS-EtPh**, and chlorobenezene solutions of **SS-Bn**.   The diffraction data of **OS-Bn** and **OS-EtPh** were collected by a Rigaku four-circle diffractometer (AFC-7R) with graphite-monochromatized Mo-$K\alpha$ radiation (λ = 0.71069 Å).   The X-ray oscillation photographs of **SS-Bn** and **SS-EtPh** 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).   The structures were solved by the direct method (SIR2008) and refined by the full matrix least-squares procedure (SHELXL).[S3,S4]   Anisotropic thermal parameters were adopted for all non-hydrogen atoms.   The crystal structures are depicted in Figs. S1-S4.

The transfer integrals, t_i, listed in Figs. 3 and 4 captions, were estimated from the molecular orbital calculations.[S5]
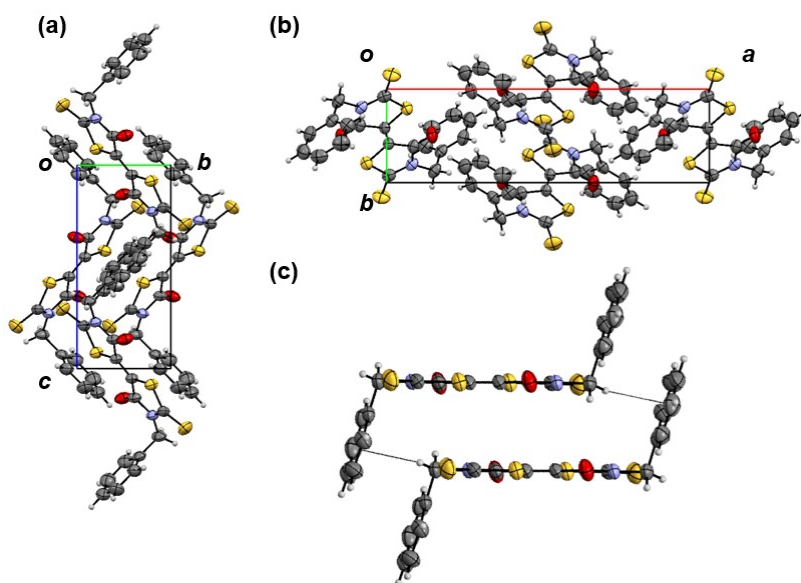
Figure S1. Crystal structure of **OS-Bn** viewed (a) along the *a* axis, (b) along the *c* axis, and (c) along the molecular short axis. A short contact shown in (c) is NCH–π: 2.829 Å.
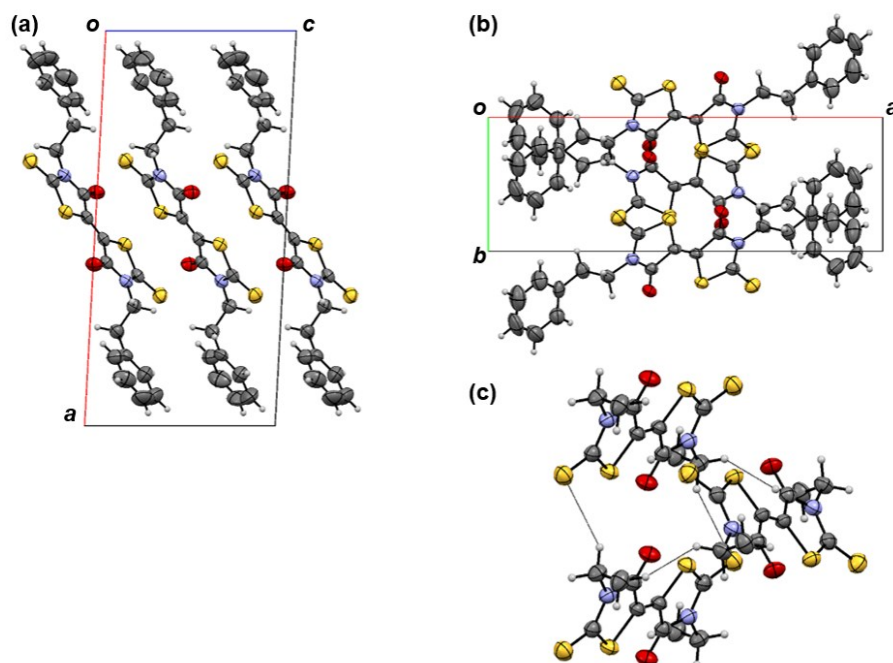

Figure S2. Crystal structure of **OS-EtPh** viewed (a) along the *b* axis and (b) along the *c* axis. Short contacts shown in (c) are NCH–HCPh: 2.322 Å, and NCH–S: 2.960 Å.
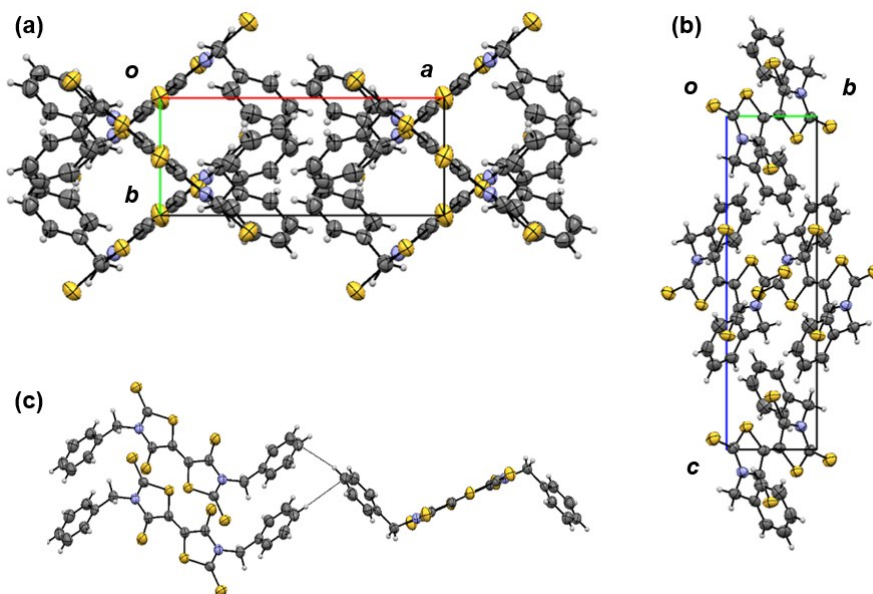
Figure S3. Crystal structure of **SS-Bn** viewed (a) along the *c* axis, and (b) along the *a* axis. A short contact shown in (c) is CH–π: 2.888 Å.
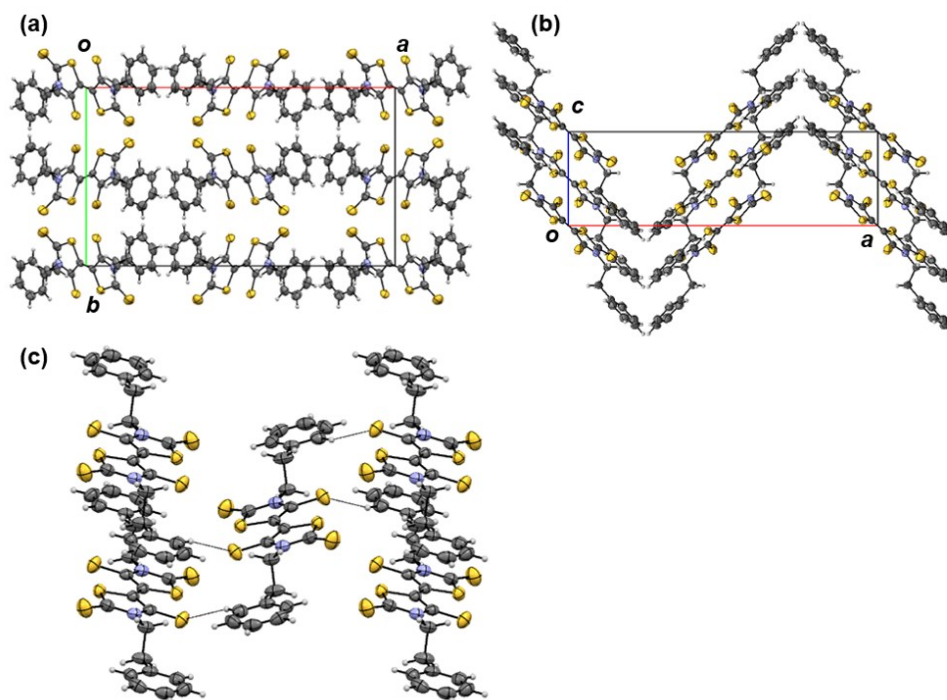

Figure S4. Crystal structure of **OS-Bn** viewed (a) along the *c* axis, and (b) along the *b* axis. A short contact shown in (c) is CH–S: 2.964 Å.

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 $2° \leq 2\theta \leq 20°$. The tilt angles were estimated from the crystal structures and d-spacing as shown in Fig. S5. 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 (Fig. 5).
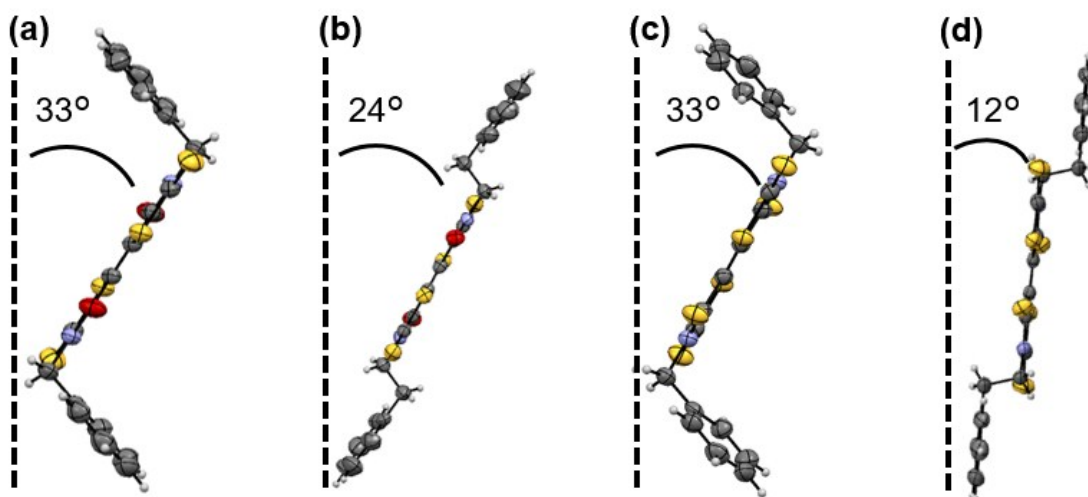

Figure S5.   Tilt angles of (a) **OS-Bn**, (b) **OS-EtPh**, (c) **SS-Bn**, and (d) **SS-EtPh**.

Molecular orbital calculations

Molecular orbitals and transfer integrals were calculated at PW91/TZP level by ADF program (Table S1).[S6] The reorganization energies of **SS-*R*** are smaller than those of **OS-*R***, reflecting the strong electron acceptor ability. The theoretically calculated mobility of **OS-EtPh** is in agreement with the experimental mobility. For **SS-EtPh**, the theoretically calculated mobility is much smaller than the experimental mobility, indicating the thin film structure is different from the crystal structure.

Table S1. LUMO levels, reorganization energies, transfer integrals, and theoretically calculated mobilities of the acceptors.

	OS-Bn	OS-EtPh	SS-Bn	SS-EtPh
E_{LUMO} (eV)	−4.327	−4.378	−4.632	−4.739
λ_1 (meV)	175	168	112	118
λ_2 (meV)	182	179	135	122
λ (meV)	357	346	247	240
t_1 (meV)	105.0	−32.1	37.0	2.3
t_2 (meV)	-	20.0	−14.2	−0.3
t_3 (meV)	-	-	2.6	-
r_1 (Å)	4.977	5.581	4.793	7.173
r_2 (Å)	-	6.409	9.454	7.710
r_3 (Å)	-	-	11.984	-
μ_1 (cm^{2}V^{-1}s^{-1})	0.927	0.122	0.212	3.5×10^{-3}
μ_2 (cm^{2}V^{-1}s^{-1})	-	0.063	0.375	6.9×10^{-5}
μ_3 (cm^{2}V^{-1}s^{-1})	-	-	0.011	-
μ_{calc} (cm^{2}V^{-1}s^{-1})	0.155	0.019	0.059	5.6×10^{-4}
μ_{exp} (cm^{2}V^{-1}s^{-1})	8.1×10^{-3}	0.02	-	0.27

References

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