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Supporting Information

Design and Structure-Property Relationship of Benzothienoisoindigo in Organic Field Effect Transistors

Tsukasa Hasegawa,[a] Minoru Ashizawa,[a,*] Hidetoshi Matsumoto[a,*]

[a] *Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152-8552, Japan.*

Corresponding Authors

ashizawa.m.aa@m.titech.ac.jp

matsumoto.h.ac@m.titech.ac.jp

Contents of Supporting Information

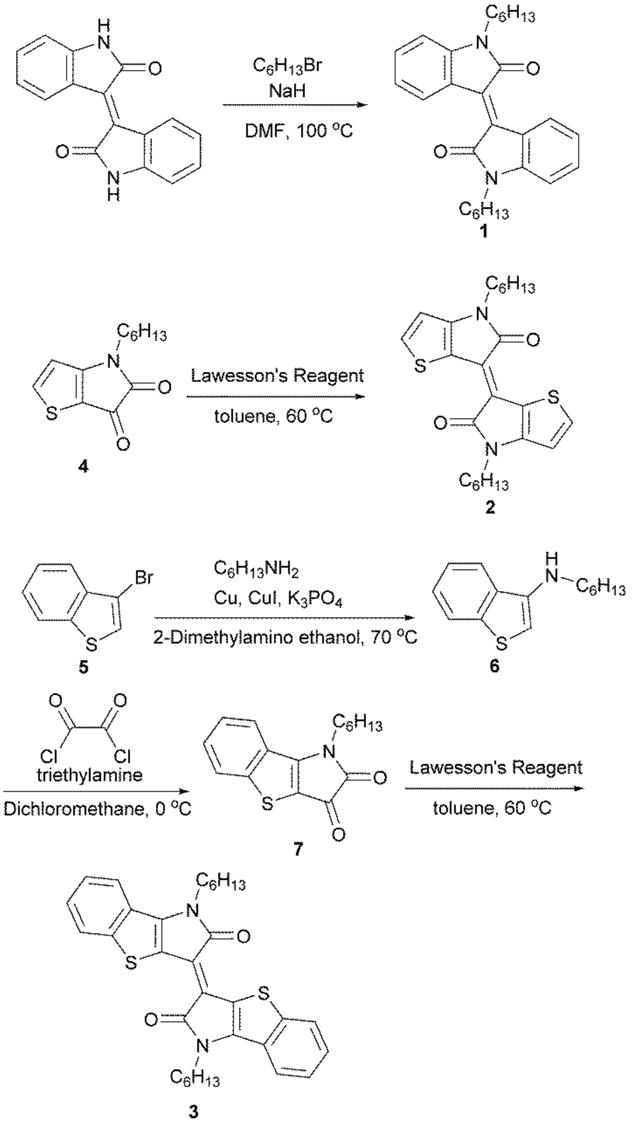
I. General

All the chemicals and solvents were of reagent grade purchased from Tokyo Kasei Chemical Industries, Wako Pure Chemical Industries, and Aldrich and used without further purification. All reactions were carried out under an argon atmosphere. The ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-AL300 spectrometer (300 MHz) in deuterated chloroform at 298 K and tetramethylsilane was used as the internal standard. Mass spectrograms were recorded by a Shimadzu QP-5000 (EI-MS) or Shimadzu MALDI-AXIMA time of flight mass spectrometer (MALDI-TOF) operated in the linear mode. The UV-Vis-NIR absorption spectra of the dilute solution and spin-coated thin film of the present compounds were collected using a Jasco Corporation V-630 UV-VIS-NIR spectrophotometer. The optical energy gaps $E_{\mathrm{g}}^{\mathrm{opt}}$ were estimated from the low-energy band edge of the absorption spectra of the thin films. Cyclic voltammetry (CV) was carried out using an ALS/CH Instruments Electrochemical Analyzer Model 700C. The measurement was performed in dehydrated dichloromethane solution containing 0.1 M n-Bu$_4$NPF$_6$ as the supporting electrolyte using a glassy carbon working electrode, a platinum counter electrode, and an Ag/AgNO$_3$ electrode as a reference electrode at the scan rate of 100 mV s^{-1}. The films of the present compounds were formed on a glassy carbon working electrode. From the onset oxidation and reduction potentials $E_{\mathrm{ox,\ onset}}$ and $E_{\mathrm{red,\ onset}}$, the HOMO and LUMO levels were estimated by assuming the ferrocene/ferrocenium energy level to be -4.8 eV under the vacuum level. Density Functional Theory (DFT) calculations were performed using the Gaussian 09 program based on the B3LYP/6-31G^{+}(d,p)[1]. Elemental analyses were performed at the Center for Advanced Materials Analysis, Tokyo Institute of

Technology.

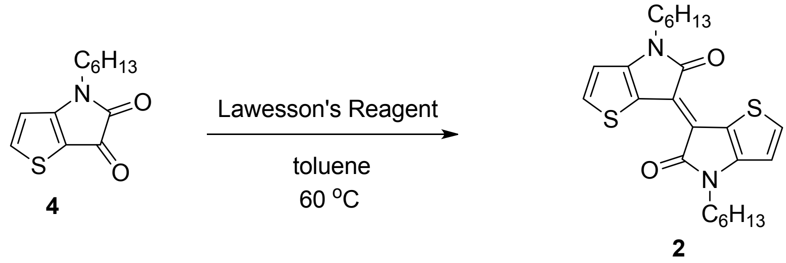
II.Material Synthesis

Compounds of **1**, **4** and **5** were prepared according to previous reports.[2-4]



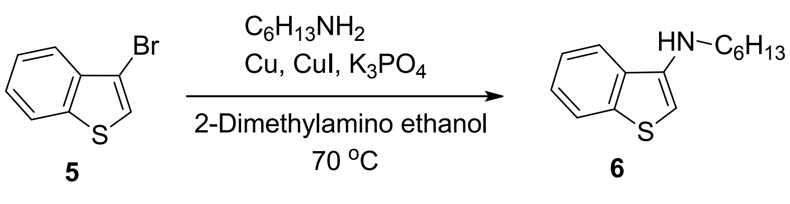
Scheme S1. Synthetic routes of **1-3**

(*E*)-4,4'-dihexyl-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (2)



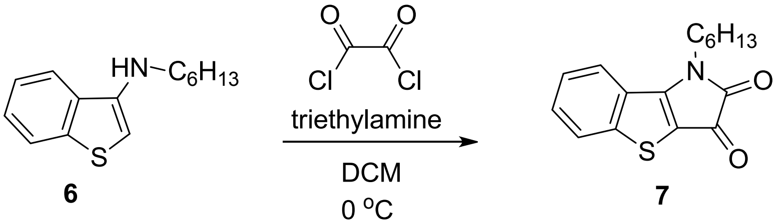
Compound **4** (3.92 g, 16.5 mmol) and Lawesson's Reagent (3.34 g, 8.26 mmol) were dissolved in anhydrous toluene (50 mL) under an argon atmosphere. The resulting mixture was heated to 60 ˚C and stirred for 2 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. The residue was purified by silica-gel chromatography eluting with CH_2Cl_2-hexane (2/1 = v/v) and recrystallization from toluene to provide 1.24 g (34%) of a dark purple solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C): δ 7.50 (d, J = 5.1 Hz, 2H), 6.78 (d, J = 5.1 Hz, 2H), 3.78 (t, J = 7.5 Hz, 4H), 1.73-1.68 (m, 4H), 1.38-1.27 (m, 12H), 0.86 (t, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C): δ 171.17, 151.40, 134.51, 121.20, 114.31, 111.30, 41.79, 31.47, 28.57, 26.58, 22.52, 14.00. MS (MALDI-TOF) *m/z*: 442.06 $[M]^+$. Anal. Calcd for $C_{24}H_{30}N_2O_2S_2$: C, 65.12; H, 6.83; N, 6.33; S, 14.49; found: C, 65.36; H, 6.80; N, 6.29; S, 14.31.

_N_-hexylbenzo[_b_]thiophen-3-amine (6)



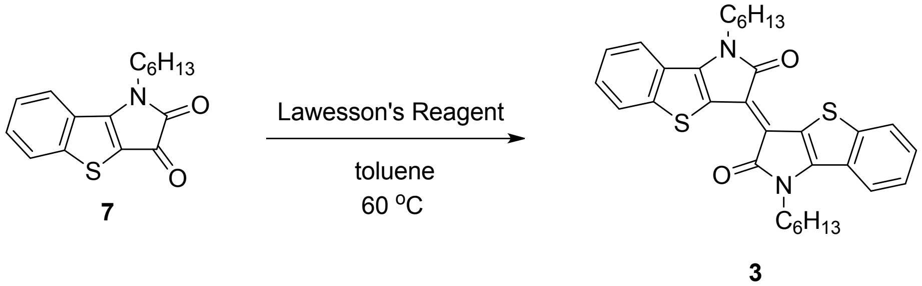
Compound **5** (7.06 g, 33.3 mmol), hexylamine (5.06 g, 50.0 mmol), copper (0.106 g, 1.67 mmol), and copper (I) iodide (0.318 g, 1.67 mmol) were suspended in *N, N*-dimethylamino ethanol (30 mL) under an argon atmosphere. The resulting mixture was heated at 70 ˚C for 48 h. After cooling to room temperature, the reaction mixture was filtered and evaporated under reduced pressure. The residue was purified by silica-gel chromatography eluting with CH_2Cl_2 to provide 6.49 g (84%) of a pale green solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C): δ 7.92-7.86 (m, 1H), 7.64-7.61 (m, 1H), 7.46-7.41 (m, 2H), 6.11 (s, 1H), 3.85 (bs, 1H), 3.25 (t, J = 7.2 Hz, 2H), 1.83-1.73 (m, 2H), 1.57-1.45 (m, 6H), 1.09 (t, J = 4.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C): δ 141.74, 139.31, 132.92, 124.64, 123.36, 123.20, 119.42, 94.37, 45.74, 31.65, 29.39, 26.93, 22.61, 14.04. MS(EI) m/z: 233 $[M]^+$ Anal. Calcd for $C_{14}H_{19}NS$: C, 72.05; H, 8.21; N, 6.00; S, 13.74; found: C, 71.76; H, 8.13; N, 5.93; S, 13.72.

1-hexyl-1*H*-benzo[4,5]thieno[3,2-*b*]pyrrole-2,3-dione (7)



To a solution of oxalyl chloride (3.10 g, 24.5 mmol) diluted in anhydrous dichloromethane (20 mL), which was cooled at 0 ˚C under an argon atmosphere, a solution of compound **6** (4.28 g, 18.3 mmol) dissolved in anhydrous dichloromethane (10 mL) was dropwise added over 20 min. After 30 min, triethylamine (8.23 g, 81.3 mmol) was dropwise added over 20 min. The resulting mixture was allowed to warm to room temperature. After stirring for 12 h at room temperature, the mixture was filtered and evaporated under the reduced pressure. The residue was purified by silica-gel chromatography, eluting with CH_2Cl_2 to provide 1.79 g (34%) of a red solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C): δ 7.88-7.83 (m, 2H), 7.58-7.45 (m, 2H), 3.94 (t, *J* = 7.5 Hz, 2H), 1.81-1.71 (m, 2H), 1.44-1.28 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ˚C): *δ* 174.56, 161.79, 160.49, 148.69, 130.57, 126.32, 125.82, 125.28, 124.05, 109.74, 41.98, 31.34, 29.67, 26.38, 22.47, 13.93. MS (MALDI-TOF) *m/z*: 288.00 $[M+H]^+$. Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87; S, 11.16; found: C, 66.82; H, 5.84; N, 4.86; S, 11.33.

(*E*)-1,1'-dihexyl-[3,3'-bibenzo[4,5]thieno[3,2-*b*]pyrrolylidene]-2,2'(1*H*,1'*H*)-dione (3)



Compound **3** was synthesized from **7** (1.00 g, 3.48 mmol) using the same procedure for **2**. Purification by silica-gel chromatography eluted with CH_2Cl_2-hexane (1:1 = v/v) solution and recrystallization from toluene gave 0.49 g (53%) of a dark green solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ˚C): *δ* 7.89-7.80 (m, 4H), 7.42-7.39 (m, 4H), 4.12 (t, *J* = 7.5 Hz, 4H), 1.89-1.80 (m, 4H), 1.51-1.29 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 6H). The ^{13}C NMR failed to obtain a spectra because of the limited solubility of the product in chloroform. MS (MALDI-TOF) *m/z*: 542.31 $[M]^+$. Anal. Calcd for $C_{32}H_{34}N_2O_2S_2$: C, 70.81; H, 6.31; N, 5.16; S, 11.82; found: C, 70.90; H, 6.20; N, 5.15; S, 11.91.

III. Thermal properties

Thermal gravimetric analyses (TGA) were performed using a RIGAKU Thermo plus EVO TG8120 thermal analyzer at the heating rate of 10 ˚C min^{-1} under a N_2 atmosphere. The melting point was measured by a Yanaco micro melting pointappartus.

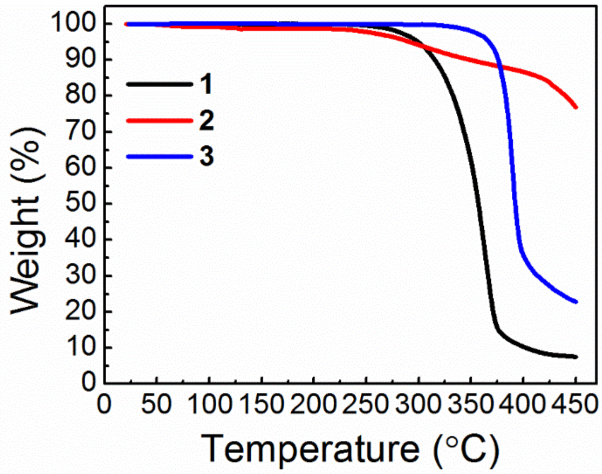


Figure S1. TGA curves of **1-3** at the heating rate of 10 ˚C / min under N_2 atmosphere.

IV. X-ray Single Crystal Structure Analysis

The crystal structures were determined from single-crystal X-ray diffraction data. The measurements were made by a RIGAKU R-AXIS RAPID II imaging plate with Cu-Kα radiation from a rotation anode source with a confocal multilayer X-ray mirror (RIGAKU VM-spider, λ = 1.54187 Å). The diffraction data were corrected under -100 °C. The structures were solved by the direct method (SHELX-97).[5] The structures were refined by the full-matrix least-squares procedure by applying anisotropic temperature factors. The positions of the hydrogen atoms were calculated.

V. Fabrication and Characterization of Organic Field-Effect Transistors

A 300-nm thermally grown SiO_2 on a highly-doped silicon wafer (capacitance (C_i) = 11.5 nF cm^{-2}) was cleaned in a piranha solution (70% H_2SO_4 + 30% H_2O_2) for 15 min, and then washed with distilled water.[6] As a gate insulator layer, the TTC was thermally evaporated to form a 20-nm-thick TTC layer on the Si substrate. The SiO_2 dielectric surface was modified with an octadecyltrimethoxysilane (OTMS) self-assembled monolayer by spin-coating from 3.0 mM OTMS solution at 3000 rpm in 1,2-dichloroethane and then exposed to an ammonia atmosphere for 20 h[7]. The OTMS modified SiO_2 substrates were washed with anhydrous toluene. The active layer was formed by thermal deposition under a vacuum of ca. 1.0×10^{-4} Pa, in which the resulting thickness was 45 nm. Finally, the source and drain electrodes were formed by the vapor deposition of Au (50 nm). The standard channel length (L) and width (W) were 50 μm and 1000 μm, respectively. The organic field-effect transistor (OFET) properties were measured by a Keithley 4200 semiconductor parameter analyzer under vacuum conditions. The field-effect mobility (μ) and threshold voltage (V_{th}) were calculated in the saturation region using the equation, $I_{DS} = \mu(WC_i/2L)(V_G - V_{th})^2$, where I_{DS} and V_G are the drain current and gate voltage, respectively. The capacitance including the TTC layer on the SiO_2 substrate was calculated to be 1.25×10^{-8} F cm^{-2}.[8, 9] Atomic force microscopic (AFM) images were obtained using an SII Nanonavi SPA400 scanning probe microscope with an SII SI-DF40 cantilever. The XRD patterns were carried out using a Phillip X-PERT MPD-OEC with CuKα radiation (λ = 1.541 Å).

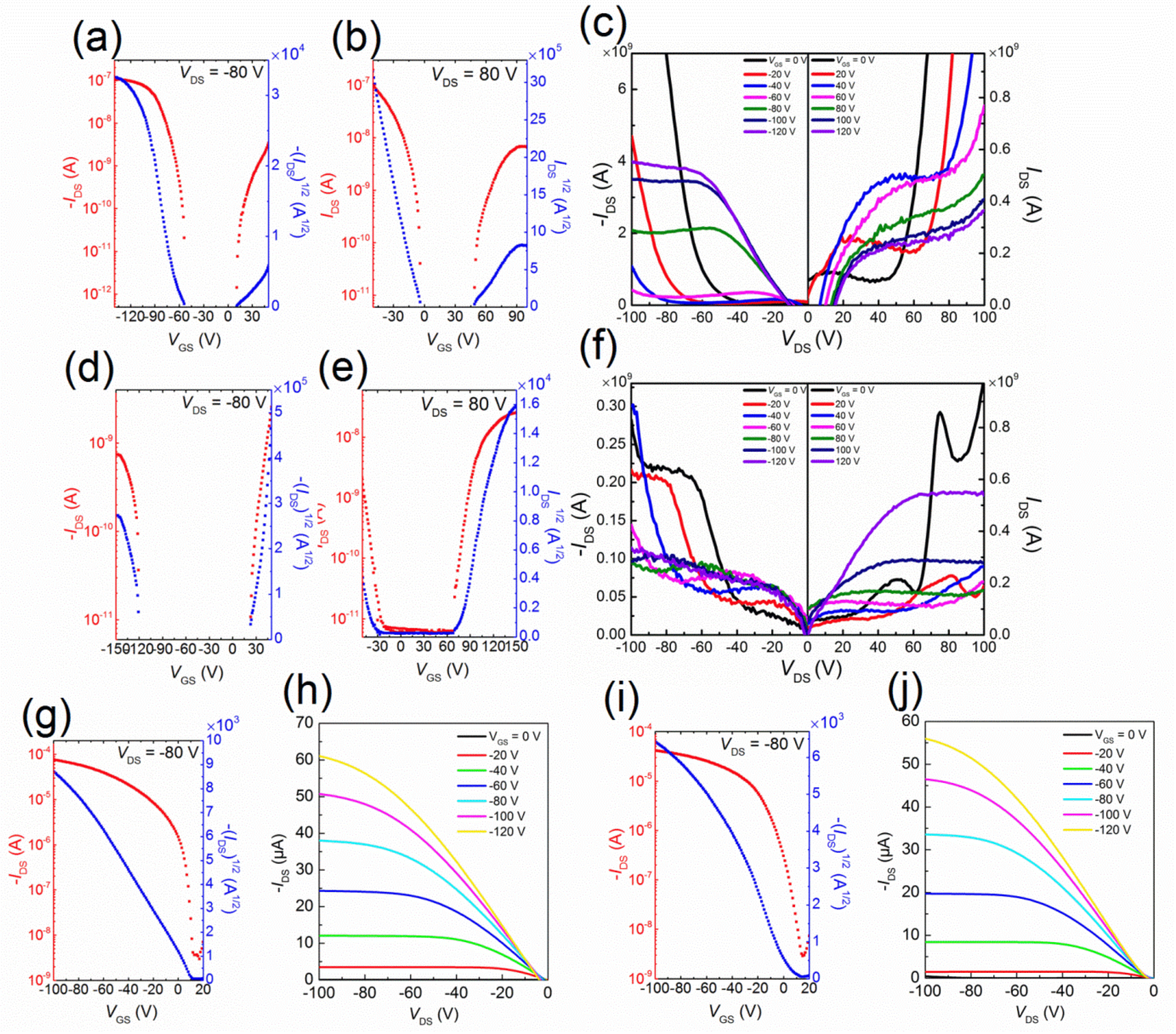


Figure S2. Transfer and output curves of (a), (b), (c) for **1**, (d), (e), (f) for **2**, (g), (h) for **3** on OTMS (r.t) and (i), (j) for **3** on OTMS (100 ˚C)

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