Supporting Information

Performance Enhancement of Air-Stable Thieno[2,3-*b*]Thiophene Organic Field-Effect Transistors via Alkyl Chain Engineering

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Keywords: organic field effect transistors; organic semiconductor; solution shearing; air stability; alkyl chain engineering; thieno[2,3-*b*]thiophene

2. Experimental details

2.1 Materials and methods

Thermogravimetric analysis (TGA) was performed using a platinum pan in a nitrogen atmosphere (TA Instrument, Q50-1555), heating the samples from 30 °C to 800 °C at 10 °C/min. Differential scanning calorimetry (DSC) was conducted between 20 °C and 250 °C with a scan rate of 10 °C/min (TA instrument, Q20-2487). UV-visible spectroscopy (JASCO V-750) was conducted on chloroform solutions and thin films over a wavelength range of 200 – 900 nm. For solution-state measurements, samples were dissolved in chloroform at a concentration of 5.0×10^{-2} mM. For thin-film measurements, glass substrates were sequentially cleaned by ultrasonication in acetone and isopropanol for 10 min each, followed by oxygen plasma treatment for 5 min (Harrick plasma, PDC-32G, 18W). Thin films were fabricated by drop-casting a 4 mg/mL chloroform solution onto the pretreated substrates. Cyclic voltammetry (CV) measurements were carried out in a dichloromethane solution containing tetrabutylammonium perchlorate as the supporting electrolyte, using a three-electrode cell setup with a platinum working electrode, a platinum spiral wire counter electrode, and an Ag/AgCl reference electrode (Autolab, PGSTAT204). All electrochemical potentials were referenced against the Fc+/Fc internal standard. Density functional theory (DFT) calculations were performed utilizing the B3LYP (Becke's 3 parameters employing the Lee-Yang-Parr) functional method along with the 6-31G(d) basis set. These calculations were executed using the Gaussian 09W software.

2.2 Synthesis

2.2.1. Synthesis of 2,5-diiodothieno[2,3-*b*]thiophene (1a)

A mixture of thieno[2,3-*b*]thiophene (204.1 mg, 1.46 mmol), n-iodosuccinimide (852 mg, 3.78 mmol), and acetic acid (5 mL) in $CHCl_3$ (10 mL) was stirred in an ice bath until the temperature reached 25 °C.[1, 2] The mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using hexane as the mobile phase to afford compound **1a** as a white solid (495.2 mg, 86 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 142.5, 134.6, 76.7, 17.4.

2.2.2. Synthesis of 2,5-diiodo-3,4-dimethylthieno[2,3-*b*]thiophene (1b)

A mixture of 3,4-dimethylthieno[2,3-*b*]thiophene (215.4 mg, 1.28 mmol), n-iodosuccinimide (748.7 mg, 3.33 mmol), and acetic acid (5 mL) in $CHCl_3$ (10 mL) was stirred in an ice bath until the temperature reached 25 °C.[1, 2] The mixture was extracted with CH_2Cl_2, and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel using hexane as the mobile phase to afford compound **1b** as a white solid (535 mg, 99 %). ^1H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 143.6, 128.4, 75.2. HRMS-APCI(m/z): [M^+] calcd. for $C_8H_6I_2S_2$, 419.8000; found, 419.8002.

2.2.3. Synthesis of 2,5-bis((trimethylsilyl)ethynyl)thieno[2,3-*b*]thiophene (1c)

A mixture of compound **1a** (200.5 mg, 0.51 mmol), trimethylsilylacetylene (0.29 mL, 2.05 mmol), CuI (9.7 mg, 10 mol%) and $Pd(PPh_3)_4$ (29.6 mg, 5 mol%) in anhydrous THF (5 mL) and isopropylamine (8 mL) was stirred at 55 °C for 20 h under N_2 atmosphere.[3] The mixture was extracted with Et_2O, and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel using hexane as the mobile phase to afford compound **1c** as a brown solid (150 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 2H), 0.26 (s, 18H).

2.2.4. Synthesis of ((3,4-dimethylthieno[2,3-*b*]thiophene-2,5-diyl)bis(ethyne-2,1-diyl))bis(trimethylsilane) (1d)

A mixture of compound **1b** (201.9 mg, 0.48 mmol), trimethylsilylacetylene (0.28 mL, 1.92 mmol), CuI (9.2 mg, 10 mol%) and $Pd(PPh_3)_4$ (27.8 mg, 5 mol%) in anhydrous THF (5 mL) and isopropylamine (8 mL) was stirred at 55 °C for 20 h under N_2 atmosphere.[3] The mixture was extracted with Et_2O, and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel using hexane as the mobile phase to afford compound **1d** as a brown solid (149 mg, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 6H), 0.27 (s, 18H).

2.2.5. Synthesis of 2,5-bis((5-octylthiophen-2-yl)ethynyl)thieno[2,3-*b*]thiophene (1)

A mixture of compound **1c** (104.3 mg, 0.31 mmol), K_2CO_3 (4.3 mg, 0.031 mmol) in MeOH (10 mL) was stirred at room temperature for 1.5 h. The mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. Without extra purification, the solvent was removed in vacuo. The resulting brown solid, 2-iodo-5-octylthiophene (0.25 mL, 0.94 mmol), $Pd(PPh_3)_4$ (18.1 mg, 5 mol%), CuI (5.97 mg, 10 mol%) in triethylamine (10 mL) were stirred at 55 °C for 20 h under N_2 atmosphere.[4, 5] The mixture was extracted with Et_2O and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using hexane as the mobile phase to afford compound **1** as a yellowish solid (78.1 mg, 43 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 2H), 7.12 (d, J = 3.7 Hz, 2H), 6.69 (d, J = 3.7 Hz, 2H), 2.82-2.78 (m, 4H), 1.71-1.64 (m, 4H), 1.41-1.25 (m, 20H), 0.88 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 144.7, 139.2, 132.7, 126.4, 124.5, 124.3, 119.7, 88.2, 85.6, 32.0, 31.6, 30.4, 29.4, 29.3, 29.2, 22.8, 14.2. HRMS-APCI(m/z): [M + H^+] calcd. for $C_{34}H_{41}S_4$, 577.2086; found, 577.2088.

2.2.6. Synthesis of 2,5-bis((5-(2-ethylhexyl)thiophen-2-yl)ethynyl)thieno[2,3-*b*]thiophene (2)

A mixture of compound **1c** (52.2 mg, 0.16 mmol), K_2CO_3 (2.2 mg, 0.016 mmol) in MeOH (10 mL) was stirred at room temperature for 1.5 h. The mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. Without extra purification, the solvent was removed in vacuo. The resulting brown solid, 2-(2-ethylhexyl)-5-iodothiophene (0.13 mL, 0.47 mmol), $Pd(PPh_3)_4$ (9 mg, 5 mol%), CuI (2.99 mg, 10 mol%) in triethylamine (10 mL) were stirred at 55 °C for 20 h under N_2 atmosphere.[4, 5] The mixture was extracted with Et_2O and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using hexane as the mobile phase to afford compound **2** as a yellowish solid (33.9 mg, 37 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 2H), 7.13 (d, J = 3.7 Hz, 2H), 6.67 (d, J = 3.7 Hz, 2H), 2.75 (d, J = 6.9 Hz, 4H), 1.65-1.55 (m, 2H), 1.39-1.25 (m, 16H), 0.93-0.86 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 144.7, 139.2, 132.7, 126.4, 125.5, 124.3, 119.9, 88.2, 85.7, 41.6, 34.3, 32.4, 28.9, 25.6, 23.1, 14.2, 10.9. HRMS-APCI(m/z): [M + H^+] calcd. for $C_{34}H_{41}S_4$, 577.2086; found, 577.2088.

2.2.7. Synthesis of 3,4-dimethyl-2,5-bis((5-octylthiophen-2-yl)ethynyl)thieno[2,3-*b*]thiophene (3)

A mixture of compound **1d** (41.5 mg, 0.12 mmol), K_2CO_3 (1.6 mg, 0.012 mmol) in MeOH (10 mL) was stirred at room temperature for 1.5 h. The mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. Without extra purification, the solvent was removed in vacuo. The resulting brown solid, 2-iodo-5-octylthiophene (0.09 mL, 0.35 mmol), $Pd(PPh_3)_4$ (6.6 mg, 5 mol%), CuI (2.2 mg, 10 mol%) in triethylamine (10 mL) were stirred at 55 °C for 20 h under N_2 atmosphere.[4, 5] The mixture was extracted with Et_2O and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using hexane as the mobile phase to afford compound **3** as a yellowish solid (25.5 mg, 36 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 3.7 Hz, 2H), 6.69 (d, J = 3.7 Hz, 2H), 2.80 (t, J = 7.5 Hz, 4H), 2.57 (s, 6H), 1.72-1.64 (m, 4H), 1.42-1.25 (m, 20H), 0.90 (t, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 144.6, 137.8, 135.8, 132.4, 124.4, 121.2, 120.1, 90.0, 85.3, 32.0, 31.7, 30.4, 29.4, 29.3, 29.2, 22.8, 14.5, 14.2. HRMS-APCI(m/z): [M + H^+] calcd. for $C_{36}H_{45}S_4$, 605.2399; found, 605.2399.

2.2.8. Synthesis of 2,5-bis((5-(2-ethylhexyl)thiophen-2-yl)ethynyl)-3,4-dimethylthieno[2,3-*b*]thiophene (4)

A mixture of compound **1d** (48.4 mg, 0.13 mmol), K_2CO_3 (1.85 mg, 0.013 mmol) in MeOH (10 mL) was stirred at room temperature for 1.5 h. The mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. Without extra purification, the solvent was removed in vacuo. The resulting brown solid, 2-(2-ethylhexyl)-5-iodothiophene (0.1 mL, 0.40 mmol),

$Pd(PPh_3)_4$ (7.75 mg, 5 mol%), CuI (2.55 mg, 10 mol%) in triethylamine (10 mL) were stirred at 55 °C for 20 h under N_2 atmosphere.[4, 5] The mixture was extracted with Et_2O and the combined organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using hexane as the mobile phase to afford compound **4** as a brownish solid (33 mg, 40 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 3.4 Hz, 2H), 6.68 (d, J = 3.7 Hz, 2H), 2.75 (d, J = 6.6 Hz, 4H), 2.57 (s, 6H), 1.64-1.55 (m, 4H), 1.4-1.31 (m, 14H), 0.93-0.88 (t, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 144.6, 137.8, 135.8, 132.3, 125.5, 121.3, 120.3, 90.0, 85.4, 41.6, 34.3, 32.5, 29.0, 25.6, 23.1, 14.5, 14.2, 10.9. HRMS-APCI(m/z): [M + H^+] calcd. for $C_{36}H_{45}S_4$, 605.2399; found, 605.2401.

Table S1.

Reported Thieno[2,3-*b*]thiophene Derivatives for Organic Field-Effect Transistors. (μ: charge carrier mobility, I_{on}/I_{off}: current on/off ratio).

No	**Compound**	**μ_{sat} (cm^2/V·s)**	**I_{on}/I_{off}**
1	1,4-bis(benzo[*b*]thieno[3,2-*d*]thiophen-2-yl)benzene[6]	0.46	1.0×10^7
2	2,5-distyryl-dithieno[2,3-*b*:3′,2′-*d*]thiophene[7]	2.0	1.0×10^5
3	2,5-bis(phenylethynyl)thieno[2,3-*b*]thiophene[8]	0.076	1.0×10^6
4	2,5-distyryl-dithieno[2,3-*b*:2′,3′-*d*]thiophene[9]	0.1	1.0×10^4
5	2,5-bis(5-octylthiophen-2-yl)thieno[2,3-*b*]thiophene[10]	0.03	1.0×10^6
6	dinaphtho[2,3-*b*:2′,3′-*e*]thieno[2,3-*b*]thiophene[11]	5.1×10^{-5}	-
7	poly(2,5-bis(3-dodecylthiophen-2-yl)thieno[2,3-*b*]thiophene)[12]	0.15	1.0×10^5
8	poly(2,5-bis(2-octyldodecyl)-3-(5-(thieno[2,3-*b*]thiophen-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione)[13]	0.16	1.0×10^4

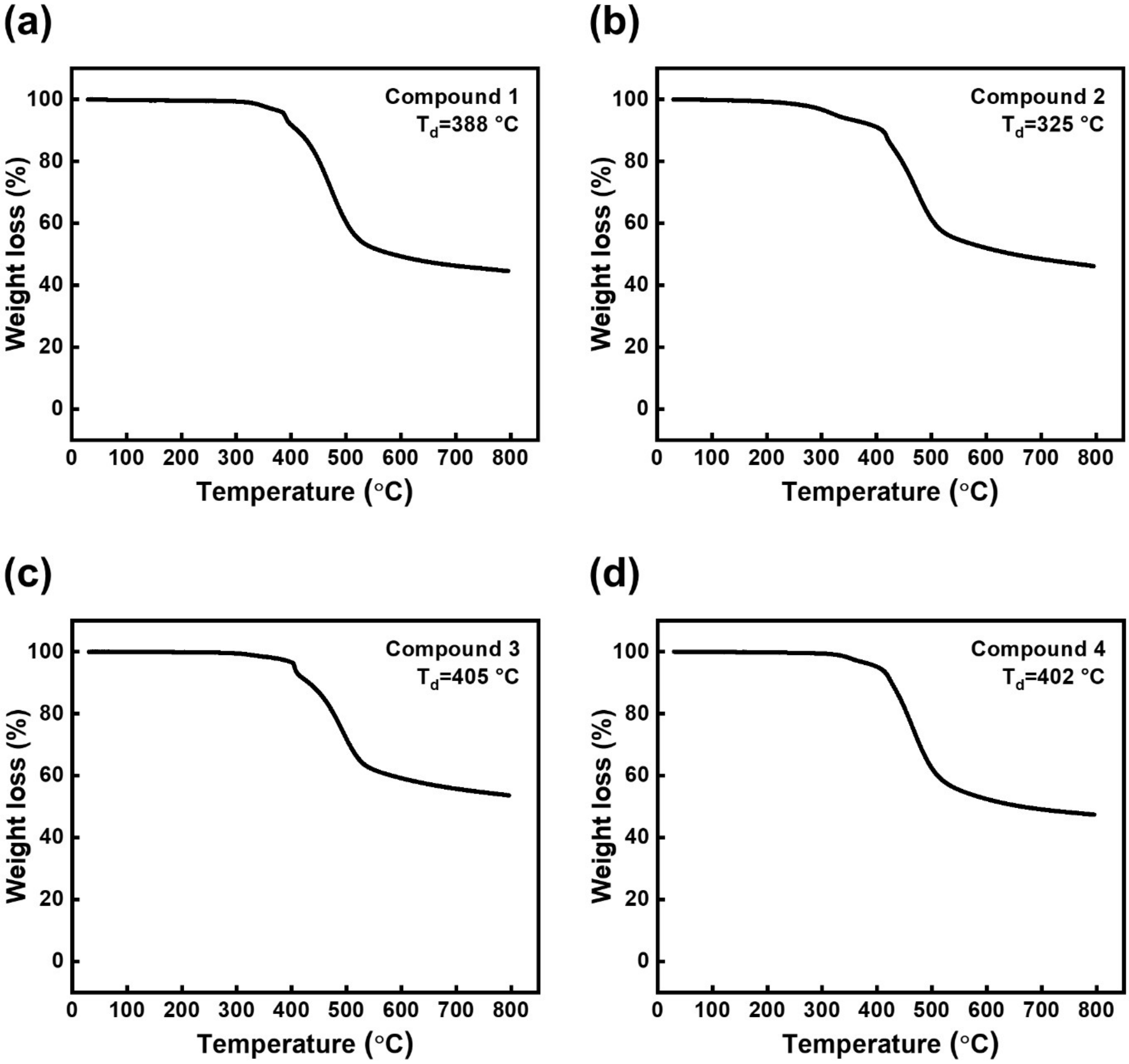

Fig. S1. Thermogravimetric analysis of TT-derivatives, (a) compound **1**, (b) compound **2**, (c) compound **3**, and (d) compound **4** (T_d: 5 % weight loss temperature).

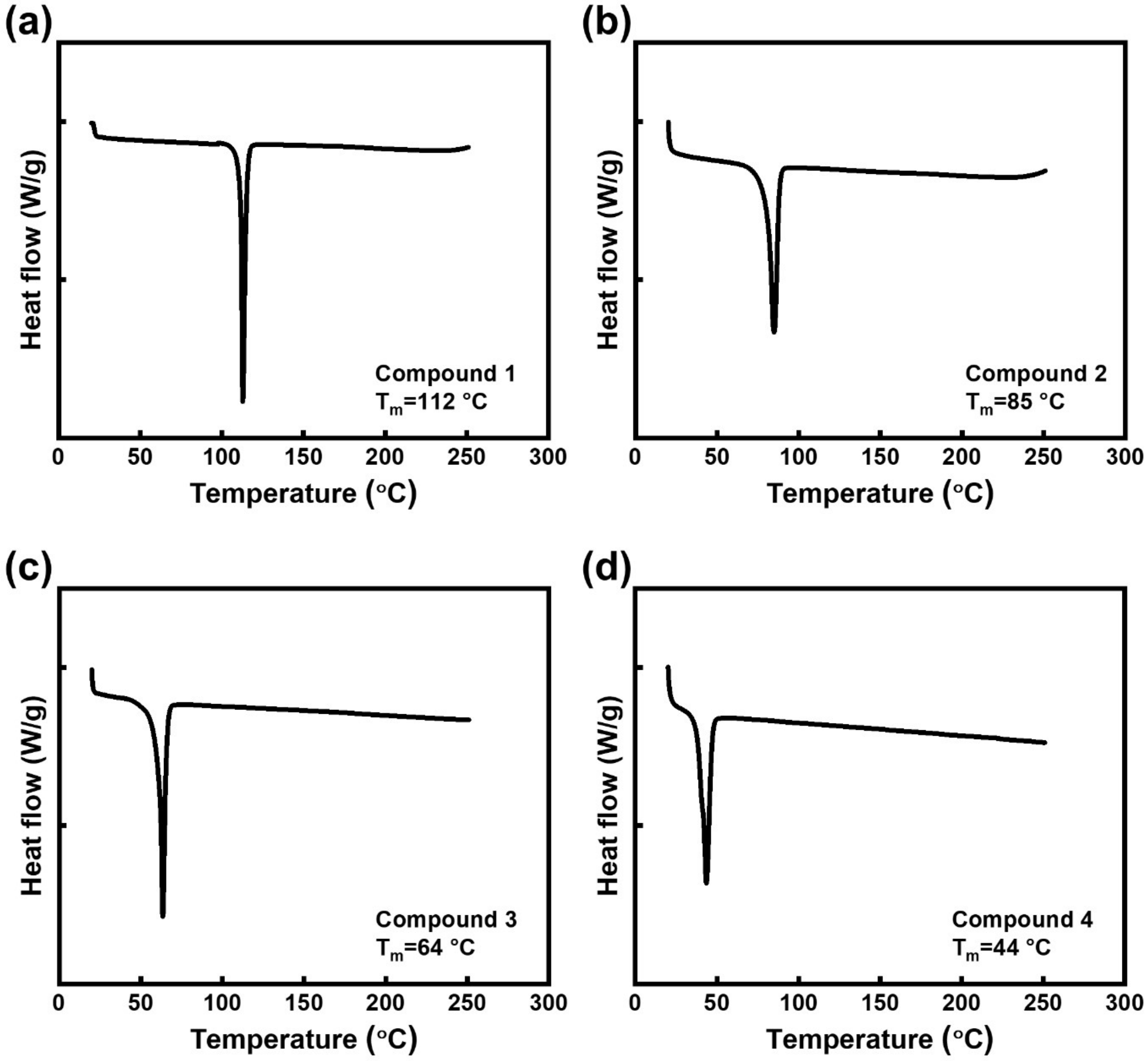

Fig. S2. Differential scanning calorimetry analysis of TT-derivatives, (a) compound **1**, (b) compound **2**, (c) compound **3**, and (d) compound **4** (T_m: melting temperature).

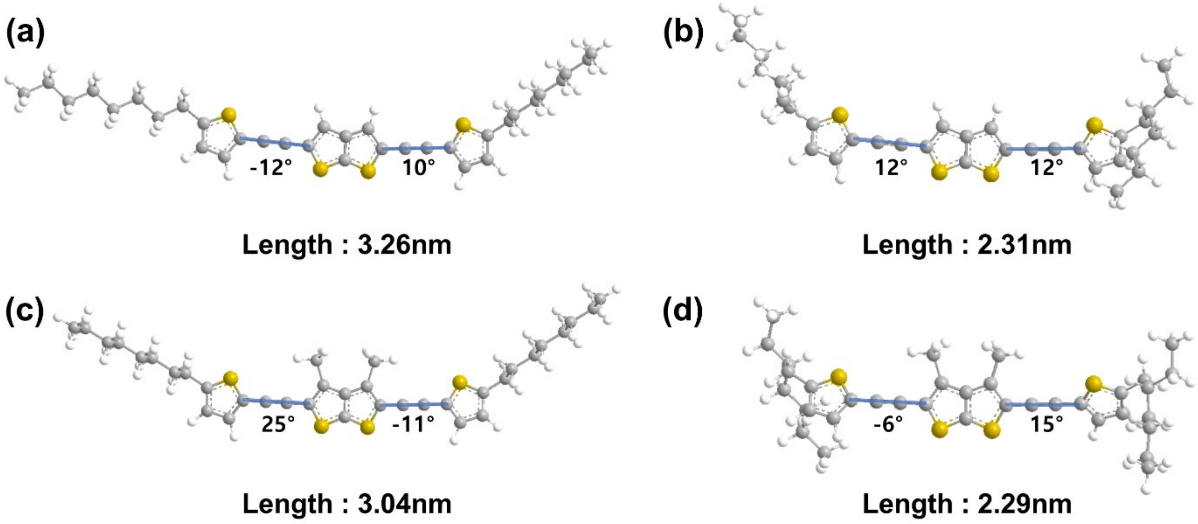

Fig. S3. Optimized structure of compounds (a) **1**, (b) **2**, (c) **3**, and (d) **4** with dihedral angles.

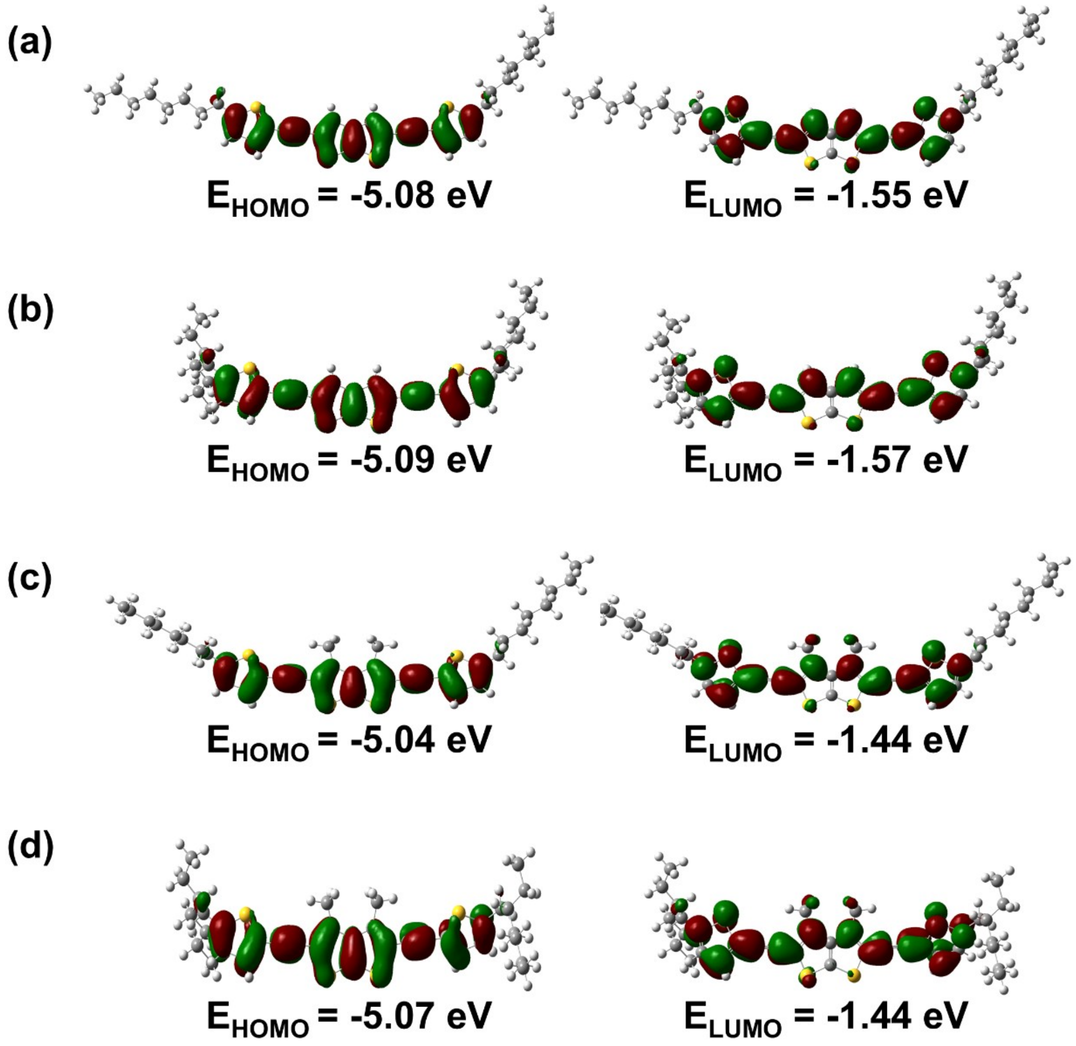

Fig. S4. Molecular orbital surfaces of compounds (a) **1**, (b) **2**, (c) **3**, and (d) **4** by density functional theory calculations.

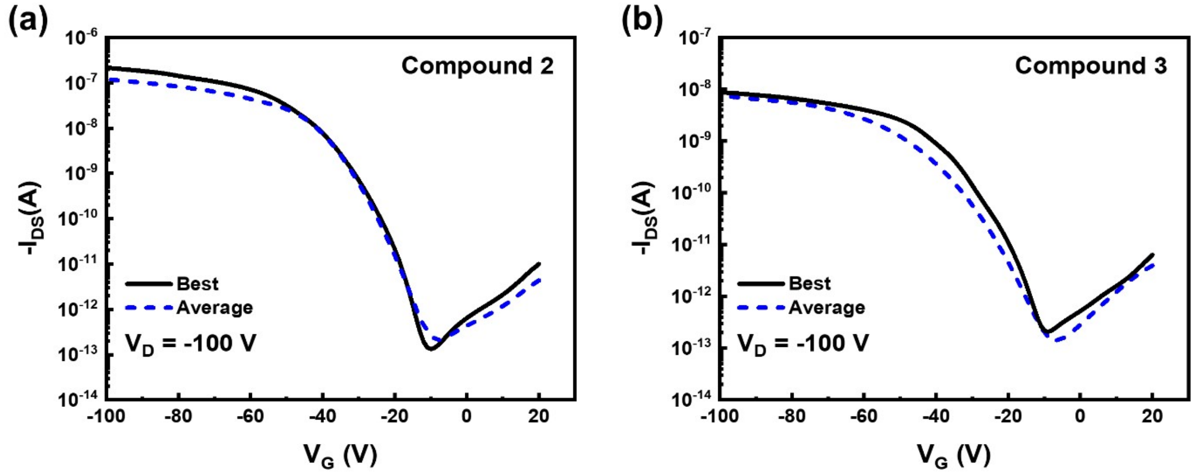

Fig. S5. Transfer characteristics of OFETs based on (a) compound **2** and (b) compound **3**.

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