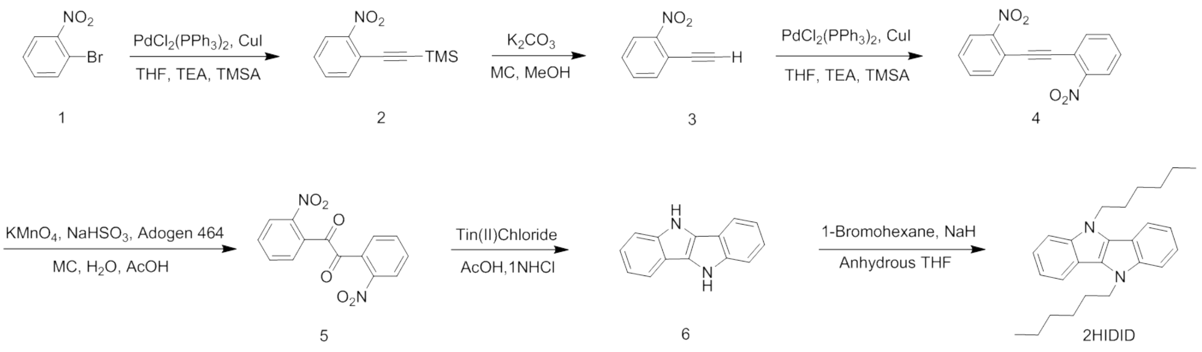
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Dicyanovinyl-Substituted Indolo[3,2-b]indole Derivatives: Low Band-Gap π-Conjugated Molecules for Single-Component Ambipolar Organic Field-Effect Transistor

Illhun Cho,[a] Sang Kyu Park,[a] Boseok Kang,[b] Jong Won Chung,[a] Jin Hong Kim,[a] Won Sik Yoon,[a] Kilwon Cho,[b] Soo Young Park[a]*

1. Synthesis



Scheme S1. Synthesis route for 5,10-dihexyl-5,10-dihydroindolo[3,2-b]indole (2HIDID)

Unless stated otherwise, all reagents were purchased at Sigma Aldrich, TCI, and Alfa Aesar

Synthesis of trimethyl((2-nitrophenyl)ethynyl)silane (**2**)

A mixed solution of 1-bromo-2-nitrobenzene (**1**, 4 g, 19.80 mmol), bis(triphenylphosphine)palladium(II)dichloride (0.695 g, 0.99 mmol), copper(I)iodide (0.377 g, 1.98 mmol), and tetrahydrofuran (THF, 40 mL) was purged with argon (Ar) gas. After then, trimethylsilylacetylene (1.945 g, 19.80 mmol) and trimethylamine (10mL) was added, and mixed solution was stirred at 50 °C. After 3 hours later, the reaction mixture was filtered through a silica plug and concentrated under reduced pressure. The concentrate filtrate purified by column chromatography (ethyl acetate/n-hexane 1:9, v/v) to afford **2** as brown oil (3.635 g, 83.7%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.01 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 0.29 (s, 9H).

Synthesis of 1-ethynyl-2-nitrobenzene (**3**)

A mixed solution of **2** (3.635 g, 16.57 mmol), K_2CO_3 (2.520g 18.23 mmol), methanol (20 mL), and methylene chloride (DCM, 80 mL) was stirred at room temperature. After 10 hours later, the reaction mixture was poured into water (300 mL), and extracted with DCM. The combined organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (ethyl acetate/n-hexane 1.5, v/v) to afford **3** as a brown powder (1.994 g, 81.8%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.06 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 3.51 (s, 1H).

Synthesis of 1,2-bis(2-nitrophenyl)ethyne (**4**)

4 was synthesized by the same synthetic procedure as that for **2** by using **3** (1.994 g, 13.55 mmol), **2** (2.738 g, 13.55 mmol), bis(triphenylphosphine)palladium(II)dichloride (0.467 g, 0.68 mmol), copper(I)iodide (0.258 g, 1.35 mmol), and tetrahydrofuran (THF, 60 mL). The crude products was purified by flash column chromatography (chloroform, CHCl3) and reprecipitation (methanol) to afford the **4** as a brown solid (0.861 g, 23.7%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.15 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.66 (t, *J* = 8.1 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 2H).

Synthesis of 1-2-bis(2-nitrophenyl)ethane-1,2-dione (**5**)

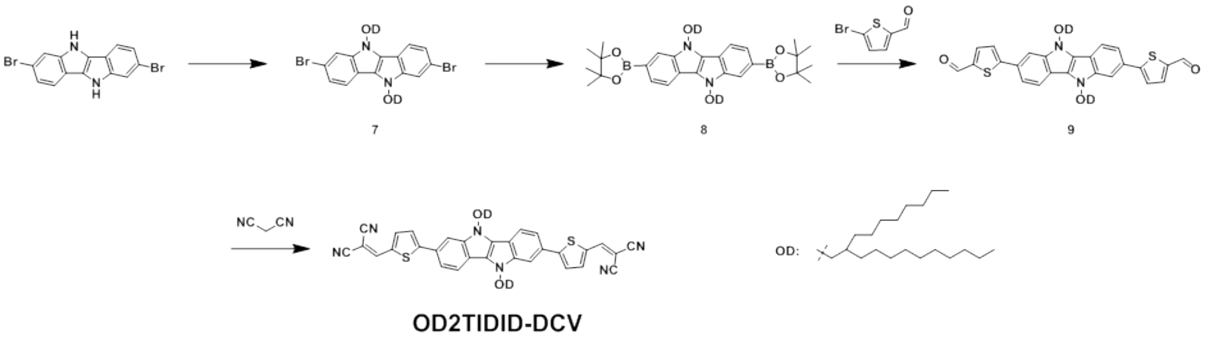
A mixed solution of potassium permanganate (1.522 g, 9.630 mmol), Adogen 464 (catalytic amount), distilled H_2O (30 mL), DCM (40 mL), and acetic acid (1.5 mL) was purged with Ar gas. After then, **4** (0.861 g, 3.210 mmol) was added and gently refluxed for 5 hours, cooled, and decolorizing (using $NaHSO_3$), sequentially. The combined organic phase was dried with $MgSO_4$ and filtered through a silica plug. The yellow filtrate was concentrated under reduced pressure, and the resulting solid was washed with methanol to afford **5** as a dim yellow crystalline solid (1.451 g, 85.2 %). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.30 (d, *J* = 7.5 Hz, 2H), 7.89 (t, *J* = 7.5 Hz, 2H), 7.76 (t, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 6Hz, 2H).

Synthesis of 5,10-dihydroindolo[3,2-b]indole (**6**)

The filtrate of stannous chloride (15.63 g, 82.413 mmol), acetic acid (35 mL), and 1 N HCl (15 mL) mixed solution was added to a mixed solution of **5** (1.237 g,, 4.121 mmol) and worm acetic acid (20 mL). The reaction mixture was gently refluxed for 5 hours at 80 °C. After cooled down to room temperature, the resulting precipitates were filtered, and filtered out was washed with acetic acid, 1 N HCl, H_2O, and ethanol. The crude product was purified by flash column chromatography (ethyl acetate) and washing ($CHCl_3$) to afford the **6** as a gray solid (0.557 g. 65.5%). ^{1}H-NMR (300 MHz, Acetone-*d6*, δ): 10.26 (s, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.19 (t, J = 6 Hz, 2H), 7.09 (t, J = 7.5 Hz, 2H).

Synthesis of 2HIDID

A round-bottom flask, equipped with a magnetic stirrer bar and reflux condenser was baked under reduced pressure and backfilled with Ar. After then, **6** (400 mg, 1.94 mmol), anhydrous THF (20 mL), NaH (0.23 g, 9.700 mmol) were added to the baked reaction vessel. After 10 minutes at room temperature, 1-bromohexane (1.6 g, 9.700 mmol) was added into the reaction mixture. After being stirring 10 minutes, the reaction mixture was gently refluxed during 48 hours. After reaction finished, the reaction mixture was poured into brine (300 mL), and extracted with DCM. The combined organic phase was dried with MgSO4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography (ethyl acetate/n-hexane 1:4, v/v) and recrystallization (ethanol) to afford 2HIDID as white solid (0.553 g, 76.1%). ^{1}H-NMR (300 MHz, Acetone-*d6*, δ): 7.92 (d, J = 7.92 Hz, 2H), 7.61 (d, J = 8.37 Hz, 2H), 7.27 (td, J = 7.11 Hz, 1.2 Hz, 2H), 7.13 (td, J = 7.02 Hz, 0.99 Hz, 2H), 4.60 (t, J = 7.08 Hz, 4H), 1.98 (q, J = 7.14 Hz, 4H), 1.47-1.19 (m, 12H), 0.83 (t, J = 7.2 Hz, 6H). 13C-NMR (500MHz, tetrahydrofuran-*d8*, δ): 141.85, 126.77, 122.30, 118.84, 118.51, 115.84, 110.59, 45.89, 32.75, 31.44, 27.80, 23.59, 14.49. HRMS (FAB, m/z) Calcd. for $C_{26}H_{34}N_2$: 374.27; found: 374.2716. Elem. Anal. Calcd. for $C_{26}H_{34}N_2$: C 83.37, H 9.15, N 7.48; found: C 83.2017, H 9.1471, N 7.6164.



Scheme S2. Synthesis route for OD2TIDID-DCV

Synthesis of 2,7-dibromo-5,10-bis(2-octyl)-5,10-dihydroindolo[3,2-b]indole (**7**)

A round-bottom flask, equipped with a reflux condenser was baked under reduced pressure and backfilled with Ar (3 times). 2,7-dibromo-5,10-dihydroindolo[3,2-b]indole (0.720 g, 1.978 mmol), anhydrous THF (30 mL), NaH (0.190 g, 7.911 mmol), were added into the baked reaction vessel. After 10 minutes later, 3.230 g (7.911 mmol) of 1-iodo-2-octyldodecane was added to the reaction mixture. After being stirring 10 minutes, the reaction mixture was gently refluxed during 48 hours. After reaction finished, the reaction mixture was quenched with brine (300 mL), and extracted with DCM. The combined organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (ethyl acetate/n-hexane 1:100, v/v) to afford **7** as colorless oil (1.260 g, 68%). ^{1}H-NMR (300 MHz, Acetone-*d6*, δ): 7.84 (d, J = 8.49 Hz, 2H), 7.77 (d, J = 1.5 Hz, 2H), 7.28 (dd, J = 8.49 Hz, 1.59 Hz, 2H), 4.46 (d, J = 7.65 Hz, 4H), 2.21 (m, 2H), 1.37-1.16 (m, 64H), 0.90-0.83 (m, 12H)

Synthesis of 5,10-bis(2-octyldodecyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,10-dihydroindolo[3,2-b]indole (**8**)

7 (0.624 g, 0.665 mmol) and anhydrous THF (25 mL) were added into a 100 mL RBF and evacuated and backfilled with Ar. After then, reaction vessel was cooled down to -78°C. An hour later, n-BuLi (3.324 mmol) was drop-wisely added at -78°C. After an hour, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.324 mmol) was added and warmed to room temperature. After reaction finished, reaction mixture was quenched with brine (300 mL), and extracted with DCM. The combined organic phase was concentrated under reduced pressure, and purified by column chromatography (ethyl acetate/n-hexane 1:100, v/v) to afford **8** as dim yellow solid (0.320 g, 46.5%). ^{1}H-NMR (300 MHz, Acetone-*d6*, δ): 7.97 (s, 2H), 7.95 (d, *J* = 7.98 Hz, 2H), 7.56 (d, *J* = 7.98 Hz, 2H), 4.53 (d, *J* = 7.56 Hz, 4H), 2.26 (m, 2H), 1.38-1.17 (m, 88H), 0.90-0.83 (m, 12H)

Synthesis of 5,5'-(5,10-bis(2-octyldodecyl)-5,10-dihydroindolo[3,2-b]indole-2,7-diyl)bis(thiophene-2-carbaldehyde) (**9**)

9 was synthesized by the same synthetic procedure as that for 5,5'-(5,10-dihexyl-5,10-dihydroindolo[3,2-b]indole-2,7-diyl)bis(thiophene-2-carbaldehyde) by using the **8** (0.180 g, 0.177 mmol), 5-bromothiophene-2-carbaldehyde (74.2 mg, 0.388 mmol), tetrakis(triphenylhosphine)palladium(0) (30.6 mg, 0.027 mmol), 2N K_2CO_3 aqueous solution (10 mL), and THF (20 mL). The crude product was purified by column chromatography (chloroform/ethyl acetate/n-hexane 1:0.1:9, v/v) to afford **9** as red solid (160 mg, 91.7%) ^{1}H-NMR (300 MHz, tetrahydrofuran-*d8*, δ): 9.90 (s, 2H), 7.98 (d, *J* = 7.68 Hz, 2H), 7.95 (s, 2H), 7.87 (d, *J* = 3.9 Hz, 2H), 7.64 (d, *J* = 4.05 Hz, 2H), 7.61 (d, *J* = 8.58 Hz, 2H), 4.57 (d, *J* = 7.56 Hz, 4H), 2.23 (m, 2H), 1.46-1.23 (m, 64H), 0.92-0.85 (m, 12H)

Synthesis of OD2TIDID-DCV

OD2TIDID-DCV was synthesized by the same synthetic procedure as that for 2HIDID-DCV by using the **9** (180 mg, 0.186 mmol), malononitrile (36.9 mg, 0.0.559 mmol), Al_2O_3 (0.171 g, 1.676 mmol), and methylene chloride (70 mL). The crude product was purified by flash column chromatography (THF) and recrystallization (ethyl acetate) to afford OD2TIDID-DCV as dark purple solid (0.155 g, 76.9%) ^{1}H-NMR (500MHz, tetrahydrofuran-*d8*, δ): 8.22 (s, 2H), 7.94-7.90 (m, 4H), 7.85 (d, *J* = 4Hz, 2H), 7.69 (d, *J* = 4Hz, 2H), 7.60 (d, *J* = 8.5Hz, 2H), 4.49 (d, *J* = 7.5Hz, 4H), 2.24 (m, 2H), 1.39-1.18 (m, 56H), 0.88-0.82 (m, 12H). 13C-NMR (500MHz, tetrahydrofuran-*d8*, δ):158.82, 151.92, 143.05, 141.81, 135.08, 129.51, 127.69, 125.01, 120.03, 118.33, 116.11, 115.44, 114.77, 109.36, 76.22, 50.37, 40.03, 33.05, 33.00, 32.70, 31.10, 30.79, 30.76, 30.63, 30.58, 30.48, 30.44, 27.58, 23.74, 23.71, 14.62. HRMS (FAB, m/z) Calcd. for $C_{50}H_{42}N_6S_4$: 1082.70; found: 1082.6974. Elem. Anal. Calcd. for $C_{70}H_{94}N_6S_2$: C 77.58, H 8.74, N 7.76, S 5.92; found: C 77.5827, H 8.7514, N 7.7111, S 5.9135.

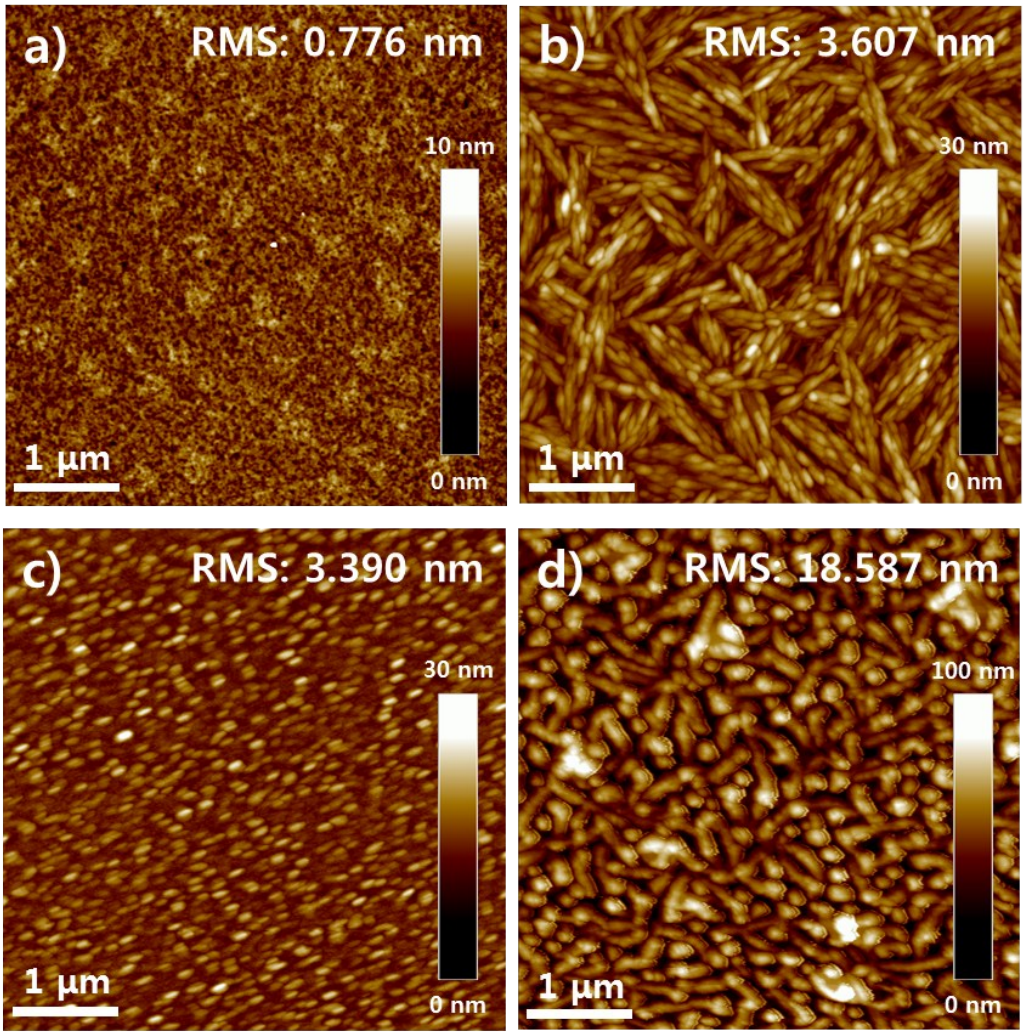


Fig. S1 AFM surface topologies (height images, 5 μm × 5 μm) of 2H2TIDID-DCV (a and b) and 2H4TIDID-DCV (c and d) VD thin films under different T_{sub} ((a and c) room temperature; (b and d) 70 °C).

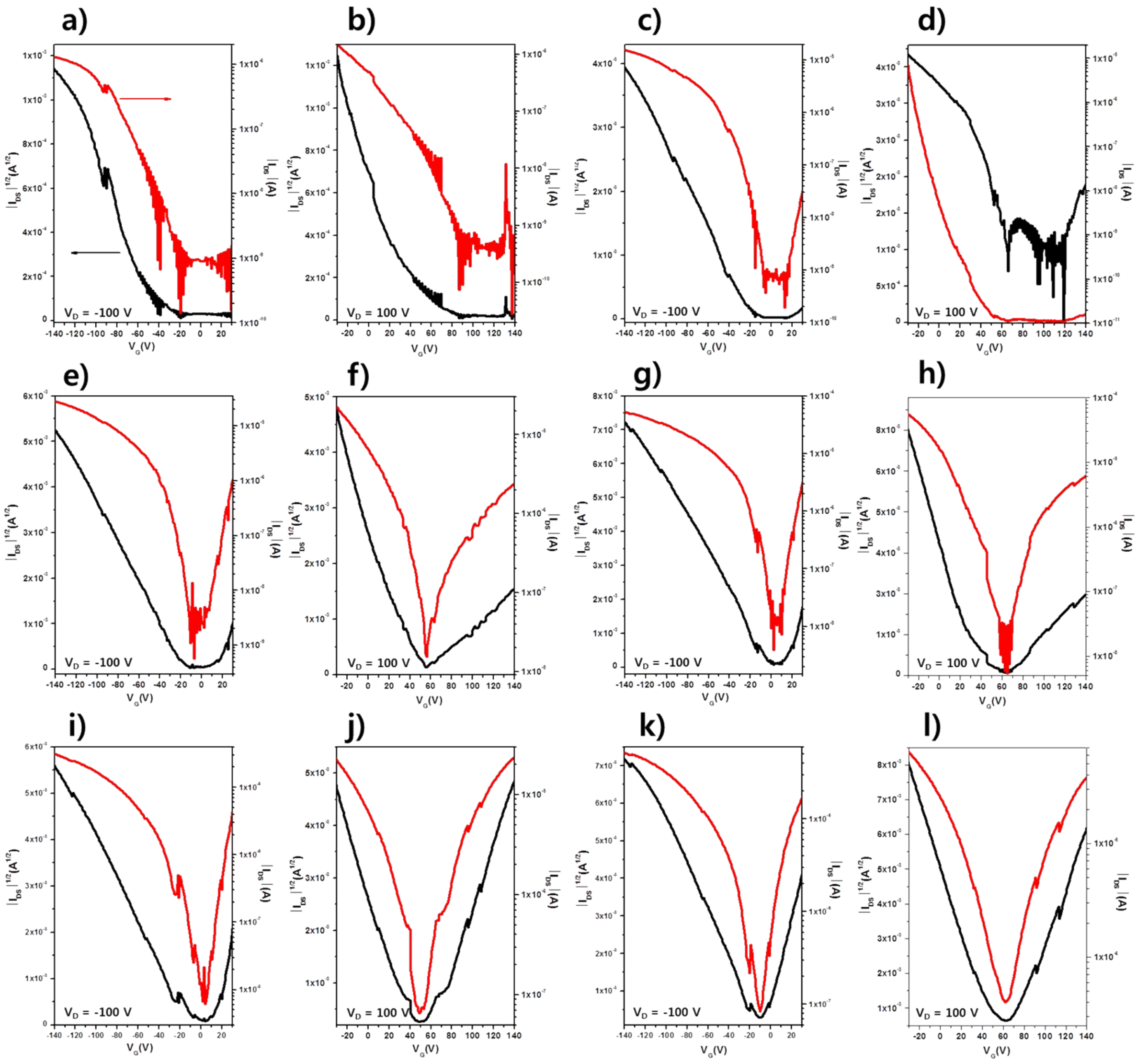


Fig. S2 The transfer curves of 2H2TIDID-DCV OFET devices for p- and n-channel operation with different T_{sub}, respectively ((a and b) T_{sub} RT, (c and d) T_{sub} 50°C, (e and f) T_{sub} 70°C, (g and h) T_{sub} 100°C, (i and j) T_{sub} 120°C, (k and l) T_{sub} 140°C).