

Electronic Supplementary Information (ESI)

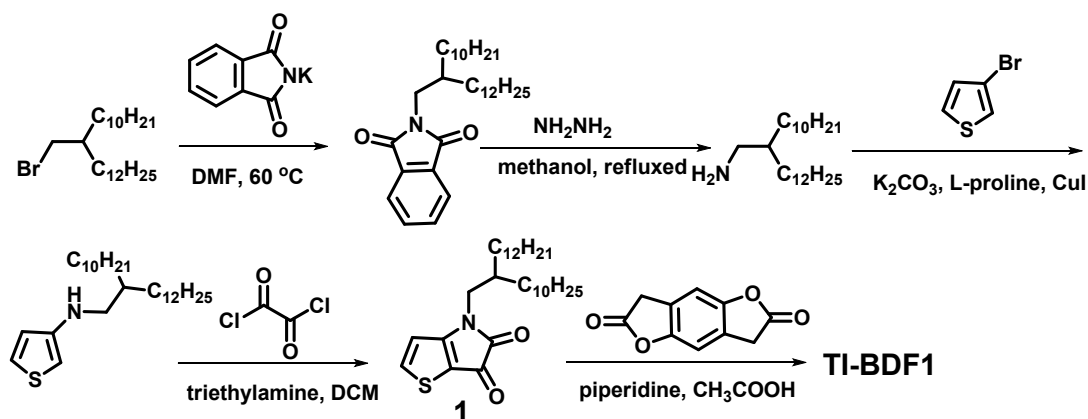
A Conductive Liquid Crystal via Facile Doping of an n-Type Benzodifurandione Derivative

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1. Materials

All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk technique. Unless otherwise specified, chemicals and solvents were purchased from Aldrich, or VWR International, and were used without further purification. All ¹H (500 MHz) and ¹³C (125 MHz) spectra were recorded on a Bruker AV500 spectrometer. Spectra were reported in parts per million from internal tetramethylsilane (δ 0.00 ppm) or residual protons of the deuterated solvent for ¹H NMR and from solvent carbon (e.g. δ 77.00 ppm for chloroform) for ¹³C NMR. Mass analyses were done in positive ion mode by electrospray ionization using linear ion trap mass spectrometer.

2. Synthetic routes



(1) Synthetic procedure for compound 1: 4-(2-Decyltetradecyl)-4H-thieno[3,2-*b*]pyrrole-5,6-dione

Step 1: A solution of 2-decyl-1-tetradecylbromide (14.62 g, 35 mmol) and potassium phthalimide (7.41 g, 40 mmol) in 40 mL DMF were heated and stirred at 60 °C overnight. The mixture was cooled to room temperature, then poured into 200 mL ice water and extracted by hexane. The organic layer was washed with brine and water, then dried by MgSO₄, and evaporated to dryness to give the crude 2-(2-decyltetradecyl)isoindoline-1,3-dione as a colorless liquid (14.4 g, 85 %). The crude product was used directly without further purification for the next step reaction.

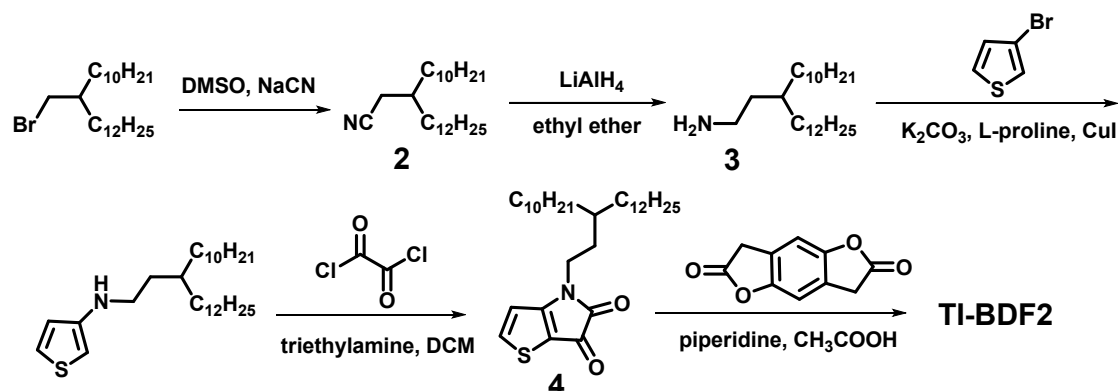
Step 2: A mixture of 2-(2-decyltetradecyl)isoindoline-1,3-dione (12.5 g, 30 mmol) and hydrazine (3.9 mL, 120 mmol) were refluxed in methanol (130 mL) for 24h under nitrogen. Then the solvent was vapored, and 40 mL 10 % KOH solution was added. The mixture was extracted by hexane, and the organic layer was washed with brine and water (3×20 mL), then dried by MgSO₄, filtered and concentrated to give the crude product of 2-decyltetradecylamine as a light yellow liquid (9.9 g, 93 %). The crude product was used directly without further purification for the next step.

Step 3: 3-Bromothiophene (3.3 g, 20 mmol), 2-decyltetradecylamine (9.6 g, 27 mmol), potassium carbonate (8.3 g, 60 mmol), L-proline (0.92 g, 8 mmol) and 40 mL DMSO were mixed and bubbled by nitrogen for 30 min, then copper (I) iodide (0.765 g, 4 mmol) was added. The mixture was heated to 80 °C and stirred for 20 h. The mixture was cooled to room temperature, then 50 mL ice water was added. The mixture was extracted by hexane (3×50 mL). The organic layer was washed with brine and water (3×30 mL), then dried by MgSO₄, filtered and quickly separate by flash column chromatography (sand core funnel with 10 cm silica gel, first hexane, then hexane: CH₂Cl₂ (10:1)), the solution was concentrated to give the crude product N-(2-decyltetradecyl)-3-thiophenamine as a brown black liquid (4.4 g, 50%). The crude product was used directly without further purification in the next step reaction.

Step 4: N-(2-decyltetradecyl)-3-thiophenamine (3.49 g, 8 mmol) in 20 mL of DCM was added dropwise to oxalyl dichloride (1.0 mL, 12 mmol) in 150 mL of DCM at 0 °C. After 30 min, triethylamine (4.8 mL, 36 mmol) in 10 mL of DCM was added dropwise at 0 °C, and the mixture was stirred overnight at room temperature. Solvents were removed under vacuum and the crude product was purified by a silica gel column using hexane: CH₂Cl₂ (1:1) as the eluent to afford 4-(2-decyltetradecyl)-4H-thieno[3,2-*b*]pyrrole-5,6-dione was obtained as red oil (1.96 g, 50 %). ¹H NMR (CDCl₃, 500 MHz): δ/ppm 7.98 (d, J=4.93,1H), 6.74 (d, J=4.93, 1H), 3.51 (d, J=7.32, 2H), 1.77 (m, 1H), 1.24 (m, 40H), 0.87 (m, 6H); ¹³C NMR (CDCl₃, 125 MHz): δ/ppm 172.92, 165.46, 161.69, 143.68, 113.07, 111.00, 46.42, 36.95, 31.89, 31.36, 29.88, 29.64, 29.62, 29.58, 29.52, 29.32, 26.33, 29.30, 22.66, 14.08.

(2) Synthetic procedure for TI-BDF1: (3E, 7E)-3,7-Bis(4-(2-decyltetradecyl)-4H-thieno[3,2-*b*]pyrrole-5,6-dione)benzo[1,2-*b*:4,5-*b'*]difuran-2,6(3H,7H)-dione

Benzo[1,2-*b*:4,5-*b'*]difuran-2,6(3H,7H)-dione (0.190 g, 1 mmol), 4-(2-decyltetradecyl)-4H-thieno [3,2-*b*]pyrrole-5,6-dione (0.984 g, 2 mmol), and piperidine (0.0085 g, 0.1 mmol) were stirred in acetic acid (10 mL) at 120 °C under nitrogen overnight. The reaction mixture was then cooled to room temperature and filtered. The solid was washed with acetic acid and then methanol. The crude product of a dark green solid was purified through column chromatography on silica gel (dichloromethane: hexane 1:3, v:v) to yield 0.45 g as a green solid (yield: 40 %). ¹H NMR (CDCl₃, 500 MHz): δ/ppm 8.94 (s, 1H), 7.65 (d, J=5.16, 1H), 6.69 (d, J=5.17, 1H), 3.64 (d, J=7.43, 2H), 1.84 (m, 1H), 1.25 (m, 40H), 0.88 (m, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ/ppm 169.93, 169.34, 155.40, 151.17, 139.73, 131.81, 125.21, 116.70, 115.39, 111.31, 109.27, 46.27, 37.14, 31.92, 31.53, 29.95, 29.69, 29.67, 29.65, 29.58, 29.36, 29.35, 26.45, 22.69, 14.12. MS (ESI, m/z): [M+H]⁺ calcd for C₇₀H₁₀₄N₂O₆S₂, 1133.7; found 1133.8.



(3) Synthetic procedure for compound 2: 3-Decylpentadecanenitrile

To a suspension of sodium cyanide (3.43 g, 42 mmol) in DMSO (15 mL) at 55 °C, 1-bromo-2-decyltetradecane (14.62 g, 35 mmol) was slowly added, then additional DMSO (2 mL) was added to keep the slurry stirring. The mixture was stirred for 48 h at 70 °C. The mixture was cooled to room temperature, then added cold water (60 mL). The mixture was extracted with hexane (3×50 mL). The organic extracts was washed with brine and water (3×50 mL), then dried by MgSO₄, filtered and concentrated to give the crude product. The crude product was purified by a silica gel column with hexane: CH₂Cl₂ (4:1, v:v) as eluent to give a light yellow liquid (5.97 g, yield: 46.9%).

^1H NMR (CDCl_3 , 300 MHz): δ /ppm 2.33 (d, $J=6.2$ Hz, 2H), 1.68 (m, 1H), 1.30 (m, 40H), 0.88 (t, $J=7.3$ Hz, 6H).
 ^{13}C NMR (CDCl_3 , 125 MHz): δ /ppm 118.94, 35.13, 33.53, 31.96, 31.94, 29.70, 29.64, 29.57, 29.40, 29.37, 26.62, 22.72, 21.71, 14.14.

(4) Synthetic procedure for compound 3: 1-Amine-3-decylpentadecane

A suspension of LiAlH_4 (2.0 g, 51 mmol) in ethyl ether (40 mL) was cooled to 0 °C and bubbled with nitrogen, then 3-decylpentadecanenitrile (5.82 g, 16mmol) in 20 mL ethyl ether was added dropwise. The mixture was warmed to room temperature and stirred overnight. The resulting suspension was cooled to 0 °C and quenched by slow addition of ice water (5 mL), followed by adding 1 M NaOH (10.0 mL). The organic layer was washed with brine and water (3×20 mL), then dried by MgSO_4 , filtered and concentrated to give the crude product. The crude product need not purify for using in next step (colorless liquid) (5.64 g, yield: 96%).

^1H NMR (CDCl_3 , 300 MHz): δ /ppm 2.67 (t, 2H), 1.37 (m, 2H), 1.25 (m, 40H), 1.10 (s, 1H), 0.88 (t, 6H). ^{13}C NMR (CDCl_3 , 125 MHz): δ /ppm 35.30, 31.93, 30.10, 29.70, 29.66, 29.36, 26.61, 22.69, 14.12.

(5) Synthetic procedure for compound 4: 4-(3-Decylpentadecyl)-4H-thieno[3,2-*b*]pyrrole-5,6-dione

Step 1: 3-Bromothiophene (2.12 g, 13 mmol), 1-amine-3-decylpentadecane (5.6 g, 14.4 mmol), potassium carbonate (5.39 g, 39 mmol), L-proline (0.598 g, 5.2 mmol) and 25 mL DMSO were mixed and bubbled by nitrogen for 30 min, then copper (I) iodide (0.497 g, 2.6 mmol) was added. The mixture was heated to 80 °C and stirred for 20 h. The mixture was cooled to room temperature, then 50 mL of ice water was added. The mixture was extracted by hexane (3×40 mL). The organic layer was washed with brine and water (3×20 mL), then dried by MgSO_4 , filtered and quickly separate by flash column chromatography (sand core funnel with 10 cm silica gel, first hexane, then hexane: CH_2Cl_2 (8:1)), the solution was concentrated to give the crude product N-(3-decylpentadecyl)-3-thiophenamine. The crude product can be used in the next step without purification (colorless liquid) (3 g, yield: 50%).

Step 2: N-(3-decylpentadecyl)-3-thiophenamine (2.48 g, 5.5 mmol) in 10 mL of DCM was added dropwise to oxalyl dichloride (0.7 mL, 7.7 mmol) in 100 mL of DCM at 0 °C. After 30 min, triethylamine (3.6 mL, 24.75 mmol) in 10 mL of DCM was added dropwise at 0 °C and stirred overnight at room temperature. Solvents were removed under vacuum and the crude product was purified by a silica gel column with hexane: CH_2Cl_2 (3:1, v:v) as

eluent. 4-(3-Decylpentadecyl)-4H-thieno[3,2-*b*]pyrrole-5,6-dione was obtained as a red oil (1.37g, yield 51 %). ¹H NMR (CDCl₃, 500 MHz): δ/ppm 8.00 (d, J=4.93, 1H), 6.77 (d, J=4.93, 1H), 3.66 (s, 2H), 1.61 (m, 2H), 1.35 (m, 1H), 1.25 (bm, 40H), 0.88 (m, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ/ppm 173.05, 165.01, 161.32, 143.72, 112.84, 111.11, 40.27, 35.28, 33.35, 31.92, 31.87, 29.98, 29.70, 29.66, 29.63, 29.35, 26.53, 22.69, 14.11.

(6) Synthetic procedure for Compound TI-BDF2: (3E, 7E)-3,7-Bis(4-(3-decylpentadecyl)-4H-thieno[3,2-*b*]pyrrole-5,6-dione)benzo[1,2-*b*:4,5-*b'*]difuran-2,6 (3H, 7H)-dione

Benzo[1,2-*b*:4,5-*b'*]difuran-2,6(3H,7H)-dione (0.110 g, 0.58 mmol), 4-(3-decyl-pentadecyl)-4H-thieno[3,2-*b*]pyrrole-5,6-dione (0.588 g, 1.67 mmol), and piperidine (0.0051 g, 0.06 mmol) were stirred in acetic acid (5 mL) at 120 °C under nitrogen overnight. The reaction mixture was then cooled to room temperature and filtered. The solid was washed with acetic acid and then methanol. The dark green solid was purified through a silica gel column chromatography with hexane: CH₂Cl₂ (3:1, v:v) as eluent to yield 0.31 g (46 %) as a green solid. ¹H NMR (CDCl₃, 500 MHz): δ/ppm 8.98 (s, 1H), 7.70 (d, J=5.21, 1H), 6.75 (d, J=5.22, 1H), 3.78 (t, J=7.54, 2H), 1.66 (m, 2H), 1.42 (m, 1H), 1.25 (m, 40H), 0.87 (t, 6H). ¹³C NMR (CDCl₃): δ/ppm 169.47, 169.27, 154.89, 151.15, 139.76, 131.88, 125.18, 116.66, 115.45, 110.99, 109.23, 40.00, 35.36, 33.43, 31.94, 30.03, 29.71, 29.67, 29.38, 26.58, 22.70, 14.13. MS (ESI, *m/z*): [M+H]⁺ calcd for C₇₂H₁₀₈N₂O₆S₂, 1160.8; found 1161.9.

3. Figures S1-S5

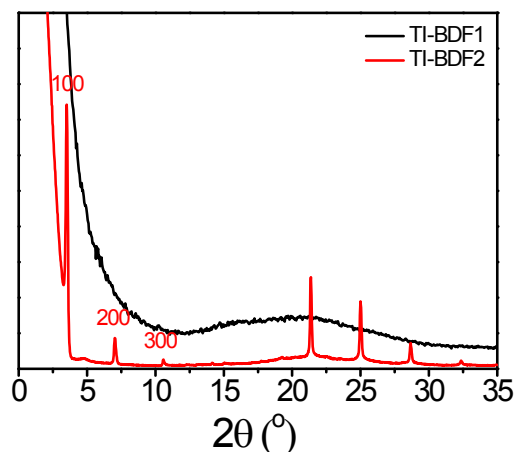


Figure S1. Wide angle X-ray diffraction of TI-BDF1 and TI-BDF2 prepared by slow cooling from melted materials.

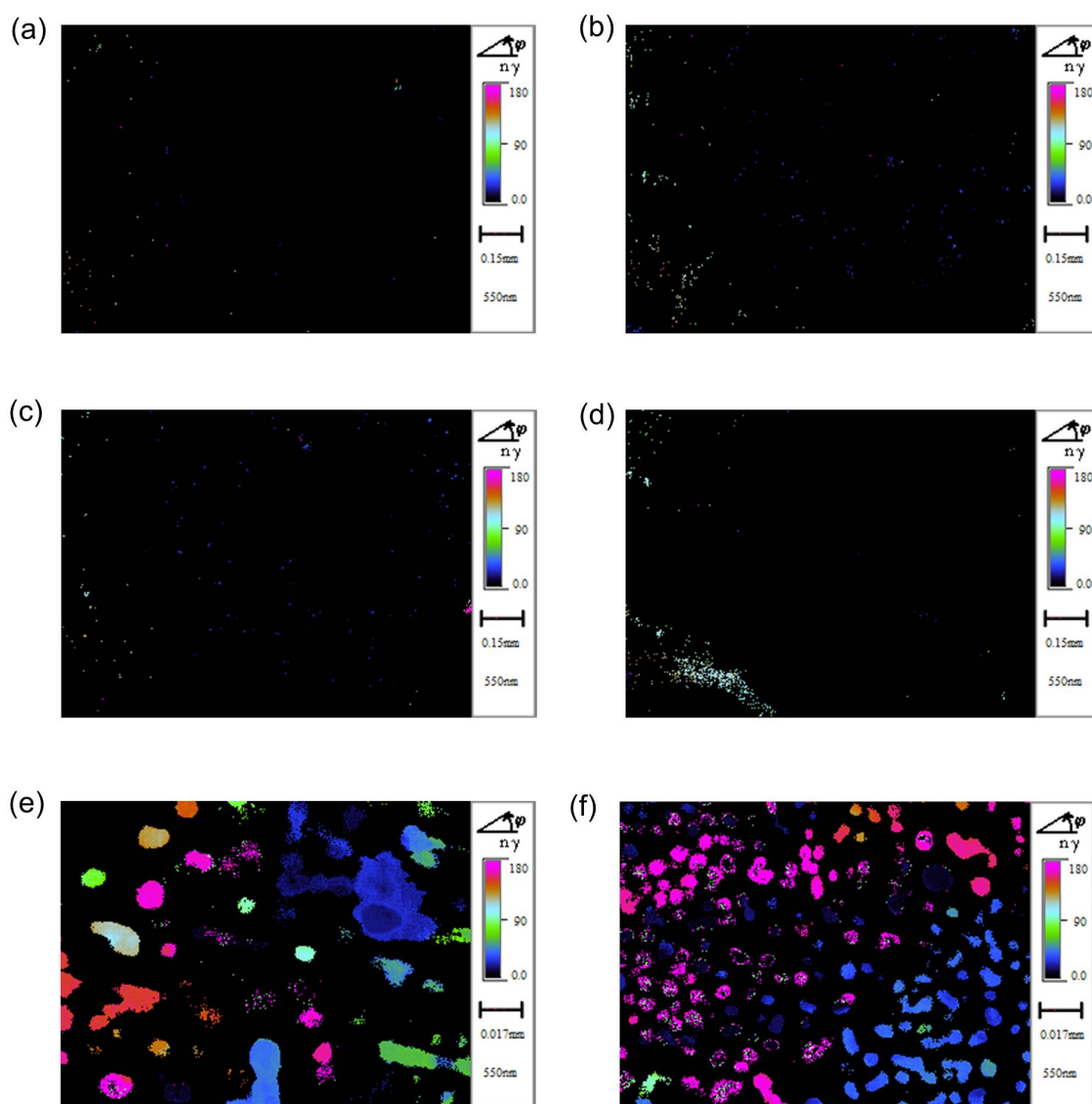


Figure S2. The optical orientation images of spin-coating film on microscope slide: TI-BDF1 annealed at (a) 80 °C, (b) 105 °C, (c) and 120 °C. TI-BDF2 annealed at (d) 120 °C, (e) 145 °C and (f) 180 °C for 30 min.

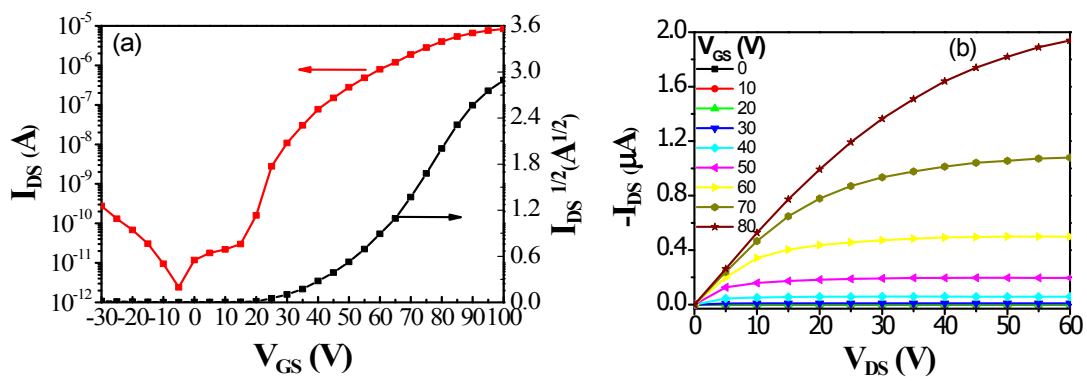


Figure S3. (a) Transfer and (b) output curves of TI-BDF2 film without annealing.

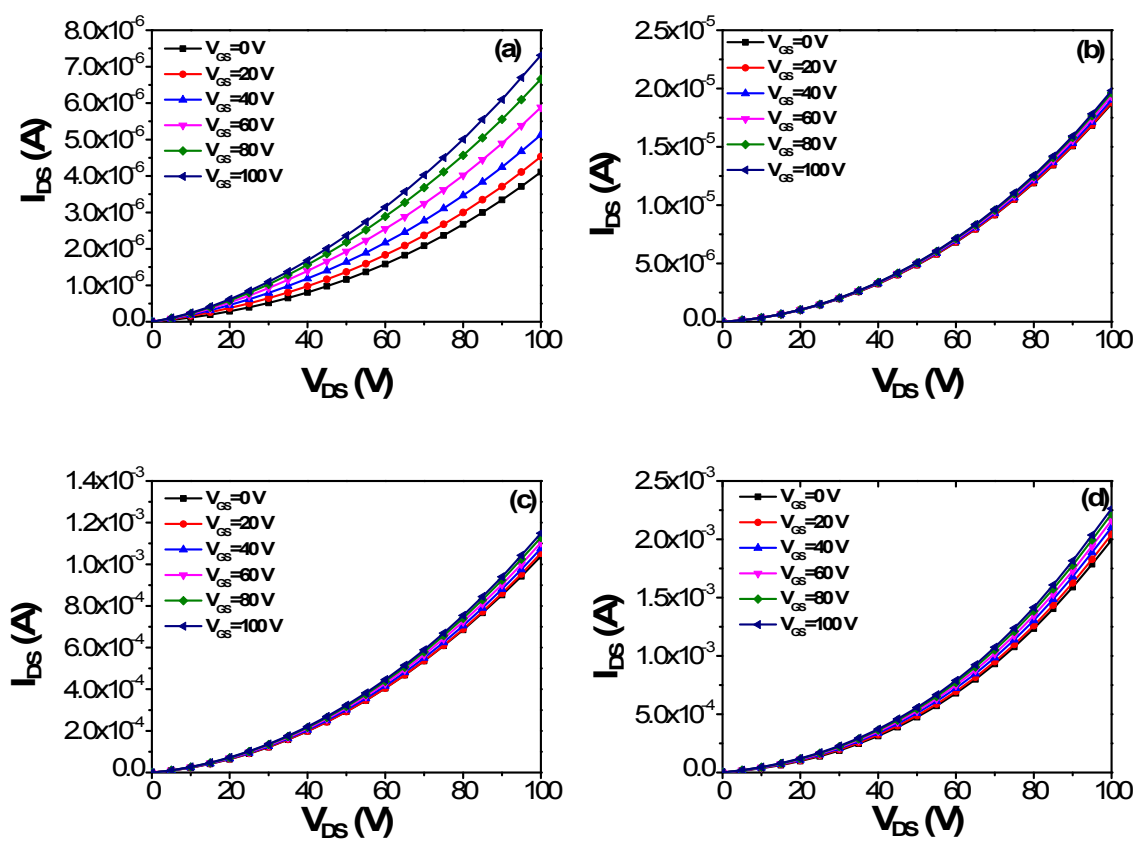


Figure S4. Output curves of TI-BDF2 blends with varied TBPB concentration: (a) 5%, (b) 10%, (c) 20%, (d) 30% mol.

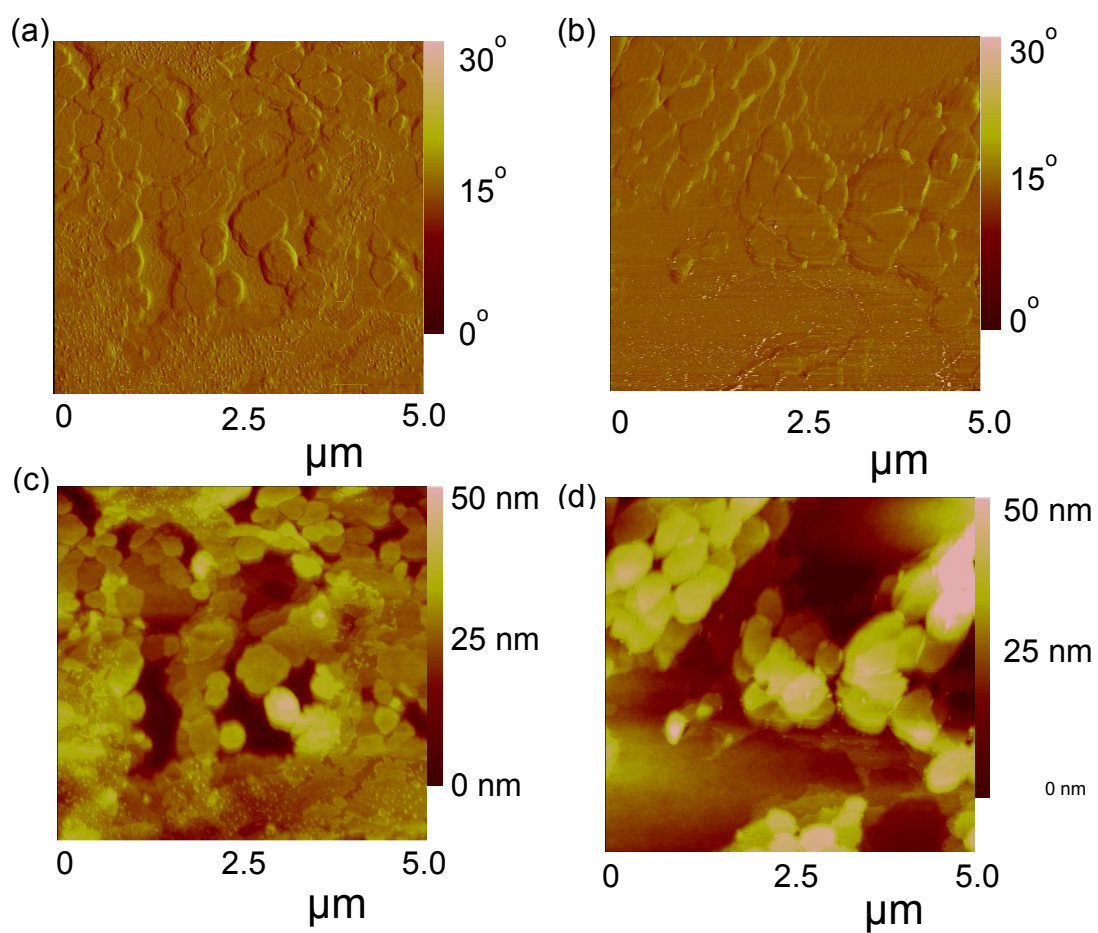


Figure S5. AFM phase image of (a) 5 mol % TBPB-doped TI-BDF2 film. (b) 30 mol % TBPB-doped TI-BDF2 film. AFM height image of (c) 5 mol % TBPB-doped TI-BDF2 film. (d) 30 mol % TBPB-doped TI-BDF2 film. (Spin-coating on BCB/Si substrate and annealed at 110 °C for 30 min)