Supporting Information

Modulating Charge Transport and Optoelectronic Properties through N-Substitution in Annulated Thiophene–Phenylene Oligomers

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Synthetic procedures

Compound 1 (4-bromo-1-iodo-2-nitrobenzene): A mixed solution of water (105 mL) and H_2SO_4 (97 mL) was added dropwise to a mixture of acetic acid (AcOH) (97 mL) and 4-bromo-2-nitroaniline (30 g, 138 mmol) at 0°C using a dropping funnel. Afterwards, a solution of $NaNO_2$ (10.5 g, 152 mmol in 42 mL H_2O) was added dropwise and the mixture was stirred for an hour. Then, a solution of KI (27.5 g, 166 mmol in 42 mL H_2O) was added dropwise and the reaction mixture was refluxed at 60 °C for 3 hours. Separation was carried out by extraction in a water-dichloromethane mixture and the organic phase was washed with saturated NaCl and Na_2SO_3

solutions. The organic phase was then combined and dried over Na_2SO_4. The solvent was evaporated under vacuum and the residue was dried at 1 Torr. The crude product was purified by recrystallisation from ethanol to produce compound **1** as an orange powder (35.3 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 7.39 (dd, 1H, J_1 = 2.2 Hz, J_2 = 8.4 Hz), 7.88 (d, 1H, J = 8.4 Hz), 7.98 (d, 1H, J = 2.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 84.38, 122.62, 128.46, 136.49, 142.89, 153.41. Anal. calcd. (%) for $C_6H_3BrINO_2$: C, 21.98; H, 0.92; N, 4.27. Found: C, 22.20; H, 0.83; N, 4.23. MALDI-TOF MS: found m/z 329.17; calculated for $[M]^+$ 328.84. m.p. 97-98 °C.

Compound 2 (((4-bromo-2-nitrophenyl)ethynyl)trimethylsilane): A mixture of compound **1** (17 g, 52 mmol), bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) (0.36 g, 0.5 mmol) and copper(I) iodide (CuI) (0.98 g, 5.2 mmol) was purged with argon. Dry THF (135 mL) was then added to the mixture. Then, trimethylsilylacetylene (TMSA) (5.1 g, 52 mmol) and triethylamine (TEA) (34 mL) were added and the mixture stirred for three hours at room temperature. The reaction mixture was then filtered and concentrated under reduced pressure. The concentrated filtrate was purified by column chromatography using a 1:9 ethyl acetate/petroleum ether mixture to afford compound **2** as a brown oil (13,14 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 0.26 (s, 9H), 7.50 (d, 1H, J = 8.3 Hz), 7.67 (dd, 1H, J_1 = 2.0 Hz, J_2 = 8.4 Hz), 8.15 (d, 1H, J = 2.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] -0.49, 98.36, 105.38, 117.29, 122.15, 127.57, 135.77, 136.02, 150.33. Anal. calcd. (%) for $C_{11}H_{12}BrNO_2Si$: C, 44.30; H, 4.06; N, 4.70. Found: C, 44.41; H, 4.11; N, 4.62. MALDI-TOF MS: found m/z 299.03; calculated for $[M]^+$ 298.98. m.p. 26-28 °C.

Compound 3 (4-bromo-1-ethynyl-2-nitrobenzene): A solution containing compound **2** (13.1 g, 43.9 mmol), K_2CO_3 (6.7 g, 48.3 mmol) and methanol (140 mL) in MC (280 mL) was stirred at room temperature. After 24 hours, the reaction mixture was poured into water and extracted with MC. The combined organic phase was dried using Na_2SO_4 and concentrated under reduced pressure. Column chromatography (ethyl acetate/petroleum ether 1:1) was used to purify the crude product, affording compound **3** as a brown powder (9.6 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 3.56 (s, 1H), 7.54 (d, 1H, J = 8.4 Hz), 7.70 (dd, 1H, J_1 = 2.0 Hz, J_2 = 8.4 Hz), 8.19 (d, 1H, J = 1.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] 77.68, 86.38, 116.31, 122.84, 127.70, 135.98, 136.41, 150.45. Anal. calcd. (%) for $C_8H_4BrNO_2$: C, 42.51; H, 1.78; N, 6.20. Found: C, 42.59; H, 1.83; N, 6.13. MALDI-TOF MS: found m/z 226,64; calculated for $[M]^+$ 226,94. m.p.105-107 °C.

Compound 4 (1,2-bis(4-bromo-2-nitrophenyl)ethyne): Compound **4** was synthesized using the same procedure as for compound 2. The reaction mixture contained compound 3 (9.4 g, 41.6 mmol), compound 1 (13.6 g, 41.2 mmol), bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) (0.29 g, 0.4 mmol), copper(I) iodide (CuI) (0.79 g, 4.2 mmol) and THF (190 mL),

and was carried out in the presence of triethylamine (TEA) (38 mL). Compound **4** was purified by column chromatography using toluene as the eluent to give a brown solid (8.7 g, 49%). ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 7.67 (d, 2H, J = 8.5 Hz), 7.78 (dd, 2H, J_1 = 1.8 Hz, J_2 = 8.2 Hz), 8.30 (d, 2H, J = 2.1 Hz). Anal. calcd. (%) for $C_{14}H_6Br_2N_2O_4$: C, 39.47; H, 1.42; N, 6.58. Found: C, 39.35; H, 1.38; N, 6.64. MALDI-TOF MS: found m/z 426,70; calculated for $[M]^+$ 425.87. m.p. 241-243 °C.

Compound 5 (1,2-bis(4-bromo-2-nitrophenyl)ethane-1,2-dione): A mixed solution containing potassium permanganate ($KMnO_4$) (9.8 g, 62.4 mmol), Adogen 464 (a catalytic amount), water (207 mL), dichloromethane (DCM, 275 mL) and acetic acid (AcOH) (10.4 mL) was purged with argon gas. Compound **4** (8.73 g, 20.4 mmol) was then added and the mixture was refluxed for 5 hours. The reaction mixture was then cooled and decolourised using $NaHSO_3$. The combined organic phase was then dried using Na_2SO_4 and concentrated under reduced pressure. The resulting solid was washed with methanol to produce compound **5** as a yellow crystalline solid (9.08 g, 97% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ [ppm] 7.51 (d, 2H, J = 8.2 Hz), 8.00 (dd, 2H, J_1 = 1.8 Hz, J_2 = 7.9 Hz), 8.40 (d, 2H, J = 1.8 Hz). Anal. calcd. (%) for $C_{14}H_6Br_2N_2O_6$: C, 36.71; H, 1.32; N, 6.12. Found: C, 36.80; H, 1.43; N, 6.18. MALDI-TOF MS: found m/z 457.67; calculated for $[M]^+$ 457.86. m.p. 256-258 °C.

Compound 6 (2,7-dibromo-5,10-dihydroindolo[3,2-b]indole): A filtered mixture of stannous chloride ($SnCl_2$) (88.6 g, 393 mmol), acetic acid (AcOH) (222 mL) and 1 N HCl (90 mL) was added to a mixture of compound **5** (9.0 g, 19.6 mmol) and warm AcOH (160 mL). The reaction mixture was refluxed for five hours at 80 °C. The resulting precipitates were filtered and washed with acetic acid, 1 N HCl, water and ethanol. The crude product was then purified using column chromatography with an ethyl acetate eluent to produce compound **6** as a grey solid (6.5 g, 91%). ^{1}H NMR (250 MHz, Acetone-d_6): δ [ppm] 7.21 (dd, 2H, J_1 = 1.5 Hz, J_2 = 8.2 Hz), 7.67-7.76 (overlapping peaks, 4H), 10.54 (s, 2H). Anal. calcd. (%) for $C_{14}H_8Br_2N_2$: C, 46.19; H, 2.22; N, 7.70. Found: C, 46.27; H, 2.28; N, 7.62. MALDI-TOF MS: found m/z 363.97; calculated for $[M]^+$ 363.90. m.p. 264-265 °C.

Br-IDID (2,7-dibromo-5,10-dimethyl-5,10-dihydroindolo[3,2-b]indole): a round bottom flask equipped with a magnetic stirrer and a reflux condenser was baked, cooled and filled with Ar. After then, compound 5 (3.0 g, 8.2 mmol), NaH (1.32 g, 33.0 mmol) and anhydrous THF (80 mL) were added to the reaction vessel. Then 4.6 g (33.0 mmol) of iodomethane was added to the reaction mixture at room temperature. The reaction mixture was then heated for 3 hours at 40 ºC. Then aqueous hydrochloric acid solution and diethyl ether were added to the reaction mixture for neutralization. The obtained mixture was passed through a glass filter. The residue was purified by washing with water, diethyl ether and methanol. The **Br-IDID** is obtained as a gray powder (2.7

g, 84% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 4.05 (s, 6H), 7.28 (dd, 2H, J_1 = 1.2 Hz, J_2 = 8.4 Hz), 7.56 (d, 2H, J = 1.2 Hz), 7.71 (d, 2H, J = 8.5 Hz). Anal. calcd. (%) for $C_{16}H_{12}Br_2N_2$: C, 49.01; H, 3.08; N, 7.14. Found: C, 48,95; H, 3.13; N, 7.12. MALDI-TOF MS: found m/z 391.93; calculated for $[M]^+$ 391.93. m.p. 342-344 °C.

DPIDID (2,7-bis(4-decylphenyl)-5,10-dimethyl-5,10-dihydroindolo[3,2-b]indole): to Br-IDID (0.5 g, 1.3 mmol), compound 7 (1.1 g, 3.2 mmol), and $Pd(PPh_3)_4$ (92 mg, 0.1 mmol) in inert atmosphere were added degassed THF (35 mL), and 2M Ka_2CO_3 aqueous solution (4.7 mL). The reaction mixture was stirred under reflux for 20 h. After cooling, the reaction mixture was poured into water and diethyl ether. The organic phase was separated, and solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: toluene) and recrystallization in toluene. Final product was further dissolved in THF and precipitated with petroleum ether to give 0.44 g (52% yield) of **DPIDID** as a gray green solid. ^{1}H NMR (300 MHz, Acetone-d6): δ [ppm] 0.87 (t, 6H, J = 6.8 Hz), 1.25-1.36 (overlapping peaks, 28H), 1.52-1.60 (m, 4H), 2.13 (t, 4H, J = 7.5 Hz), 4.24 (s, 6H), 7.31 (d, 4H, J = 8.1 Hz), 7.46 (dd, 2H, J_1 = 1.5 Hz, J_2 = 8.3 Hz), 7.71 (d, 4H, J = 8.3 Hz), 7.80 (d, 2H, J = 1.5 Hz), 8.04 (d, 2H, J = 8.1 Hz). Anal. calcd (%) for $C_{48}H_{62}N_2$: C, 86.43; H, 9.37; N, 4.20. Found: C, 86.39; H, 9.35; N, 4.26. MALDI-TOF MS: found m/z 666.54; calculated for $[M]^+$ 666.49. m.p. 359-362 °C.

DPBTBT (2,7-bis(4-decylphenyl)[1]benzothieno[3,2-b][1]benzothiophene): to **Br-BTBT** (0.45 g, 1.1 mmol), compound 7 (0.93 g, 2.7 mmol), and $Pd(PPh_3)_4$ (65 mg, 0.1 mmol) in inert atmosphere were added degassed toluene (38 mL), ethanol (6 mL), and 2M K_2CO_3 aqueous solution (4.1 mL). The reaction mixture was stirred under reflux for 22 h. After cooling, the reaction mixture was poured into water and toluene. The organic phase was separated, and solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: toluene) and recrystallization in toluene to give pure **DPBTBT** (0.63 g, 83 % yield) as a light green solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 0.89 (t, 6H, J = 7.0 Hz), 1.24-1.41 (overlapping peaks, 28H), 1.63-1.74 (m, 4H), 2.68 (t, 4H, J = 7.9 Hz), 7.28 (d, 4H, J = 8.4 Hz), 7.60 (d, 4H, J = 8.2 Hz), 7.69 (dd, 2H, J_1 = 1.6 Hz, J_2 = 8.2 Hz), 7.91 (dd, 2H, J_1 = 0.4 Hz, J_2 = 8.2 Hz), 8.11 (d, 2H, J = 1.6 Hz). Anal. calcd (%) for $C_{46}H_{56}S_2$: C, 82.09; H, 8.39; S, 9.53. Found: C, 82.01; H, 8.36; S, 9.56. MALDI-TOF MS: found m/z 672.62; calculated for $[M]^+$ 672.38. m.p. > 350 °C with decomposition.

Optical data

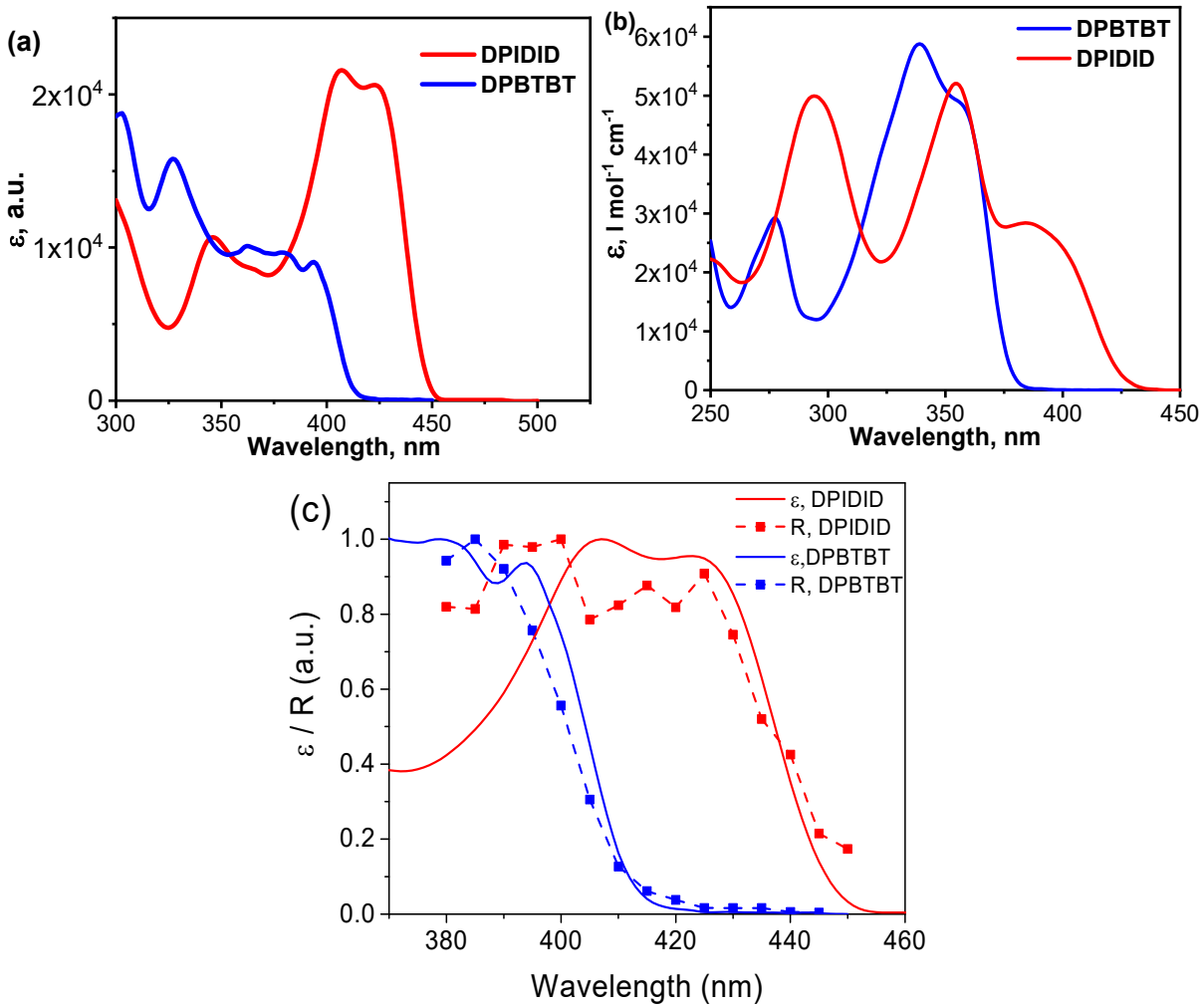


Figure S1. Spectra of absorption coefficient for DPBTBT and DPIDID in thin films (vacuum deposited) (a) and THF solutions (b). Spectra of normalized absorption coefficient in vacuum deposited thin films and normalized responsivity *R* for OFETs based on DPBTBT and DPIDID (c).

AFM data

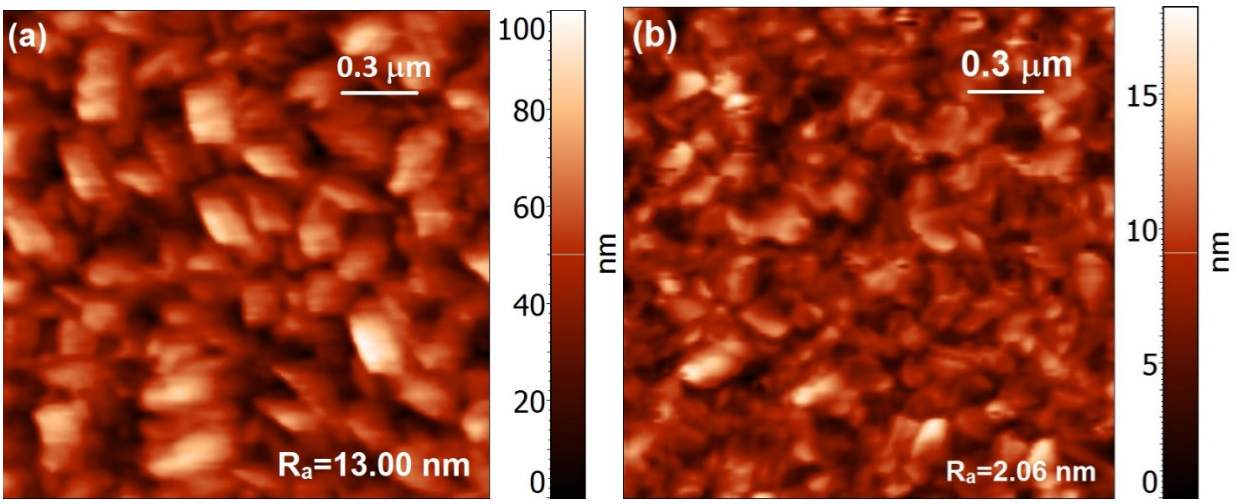


Figure S2. AFM maps of DPBTBT (a) and DPIDID(b) layer surfaces in 2x2 μm scale.

OFET data

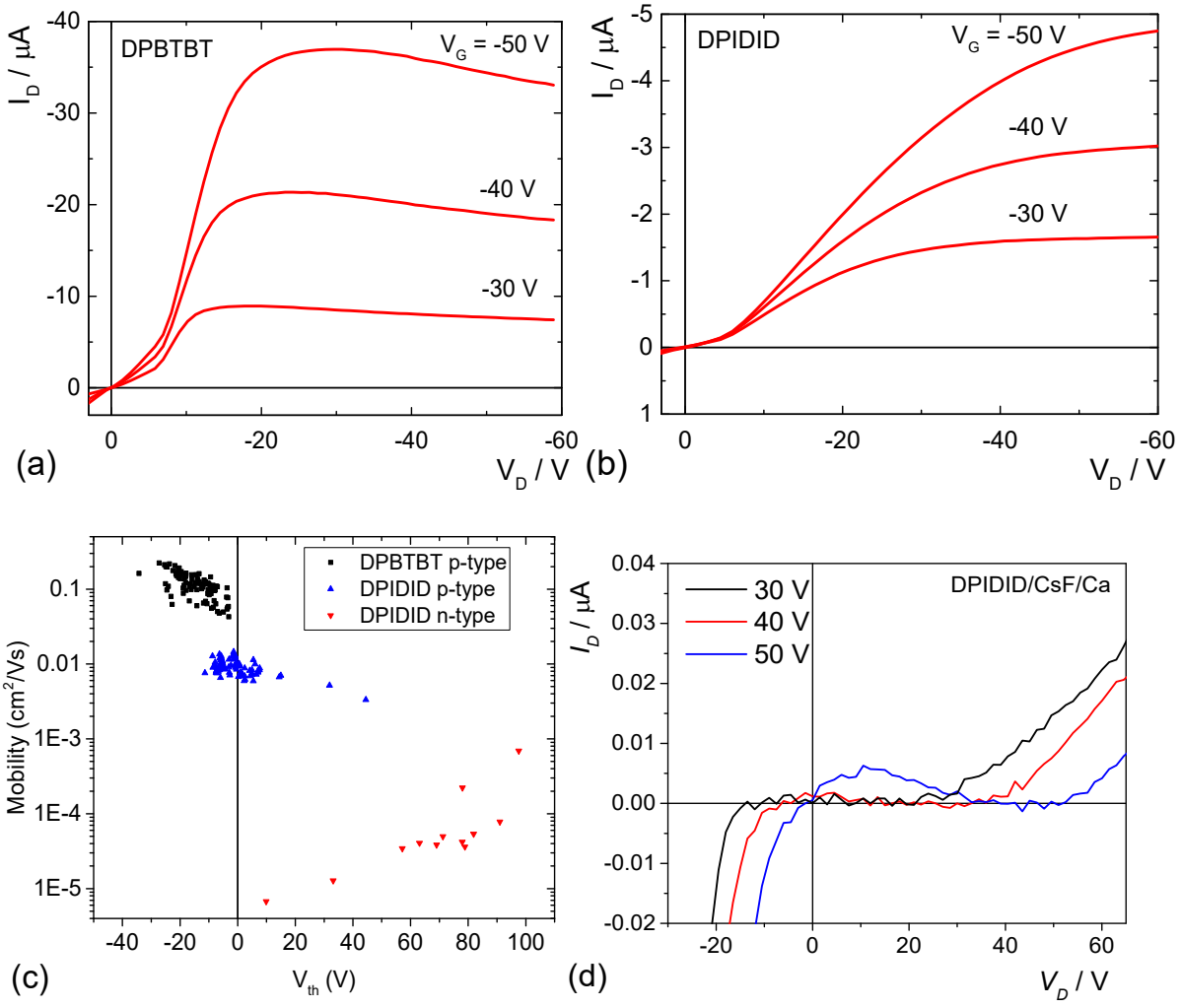


Figure S3. Typical output characteristics of OFETs based on DPBTBT (a) and DPIDID (b) and mobility vs threshold voltage diagram for all measured samples based on DPBTBT and DPIDID

with CsF/Ca/MoO_3/Ag top electrodes (c). Transfer characteristics of n-channel OFET with CsF/Ca top electrodes based on DPIDID (d).

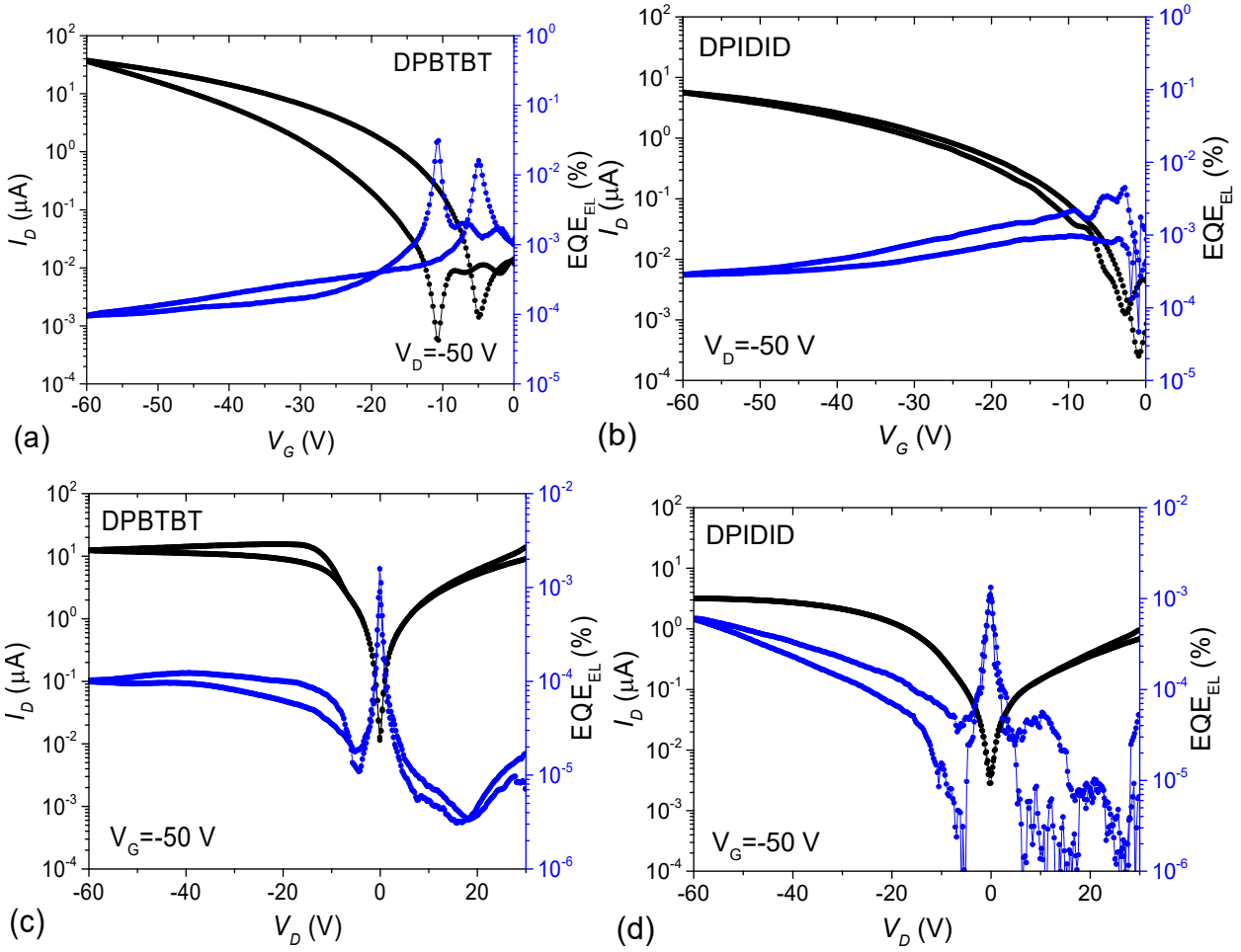


Figure S4. EL EQE dependences on V_G and V_D for DPIDID and DPBTBT-based OFETs. The peaks of EQE near zero voltages, where drain current is near its noise values, should be omitted.

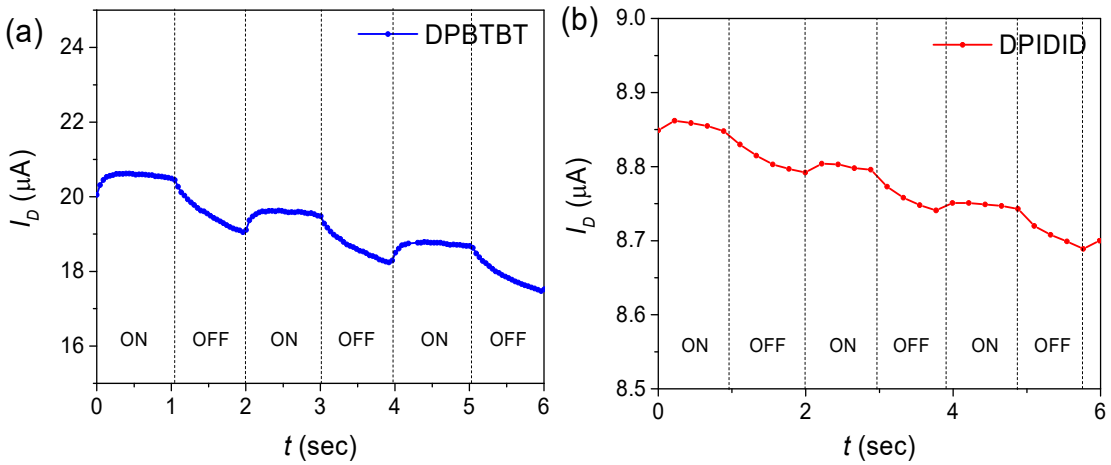
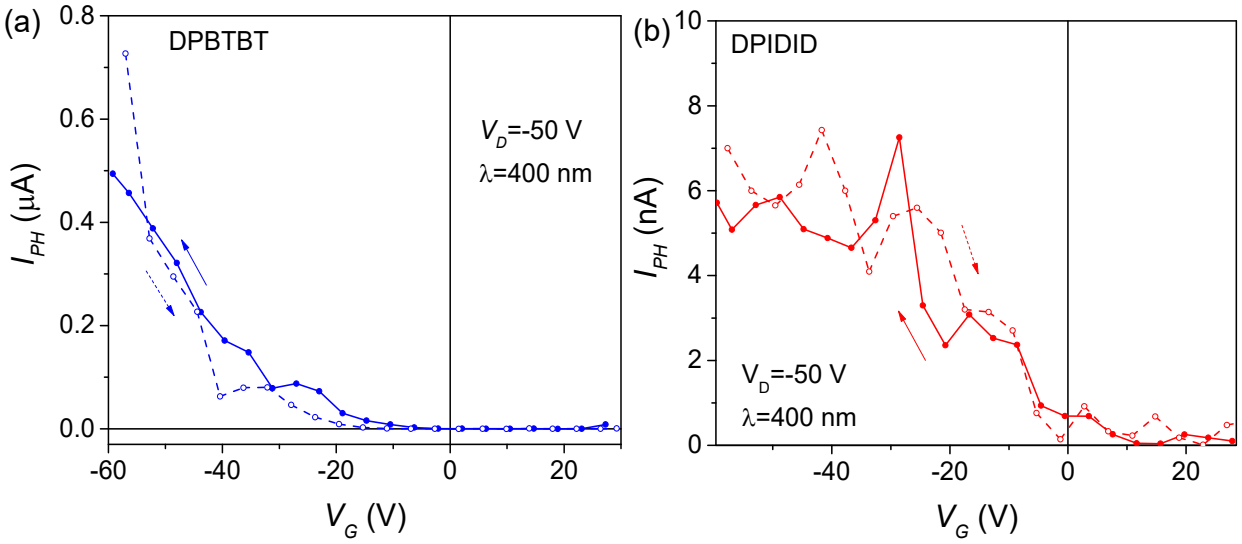


Figure S5. Time dependences of the drain current at $V_G = V_D = -50$ V for DPIDID and DPBTBT-based OFETs during periodic turning on/off of incident monochromatic light (λ = 400 nm, intensity 2.7 W/m^2).



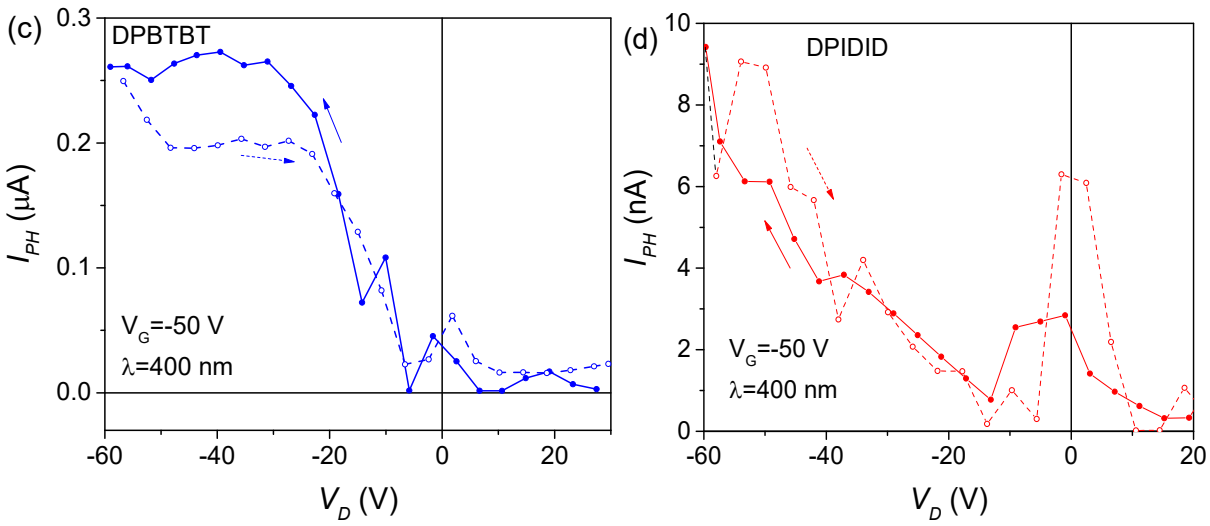


Figure S6. Gate (a,b) and drain (c,d) voltage dependences of the photocurrent I_{PH} in OFETs based on DPBTBT (a,c) and DPIDID(b,d) under incident monochromatic light with 400 nm wavelength and 2.7 W/m^2 intensity.

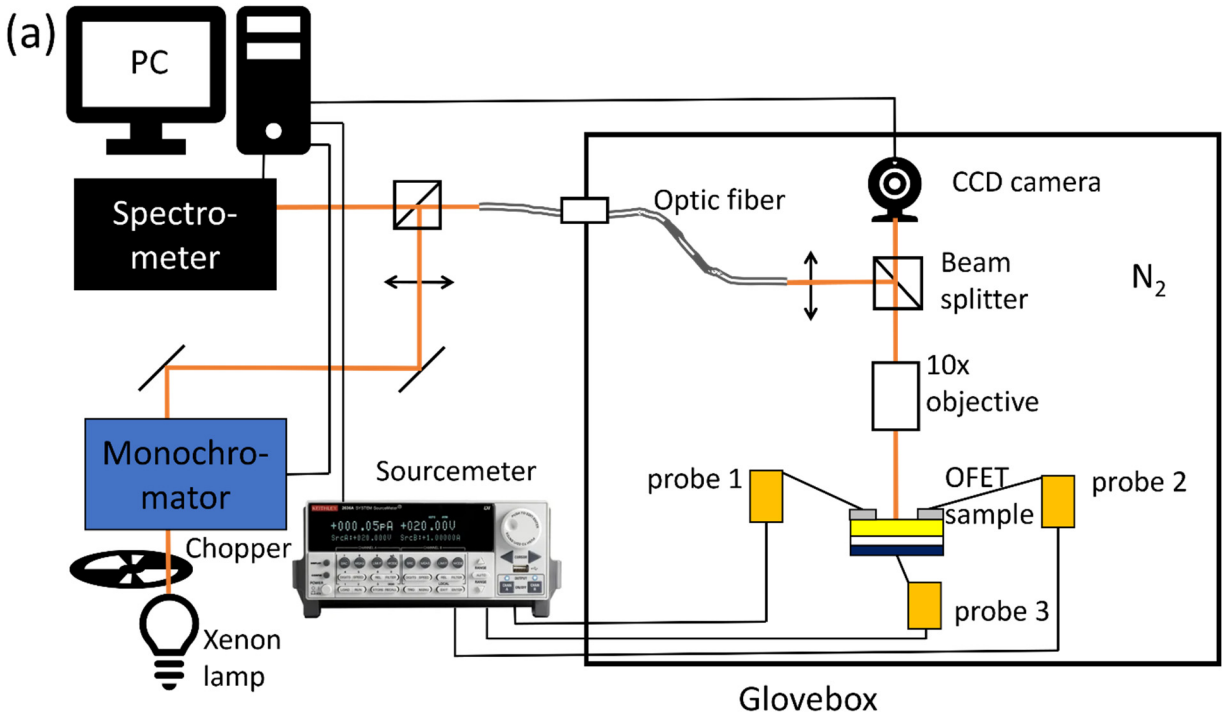


Figure S7. Experimental setup scheme for studying the EL and photoelectric effect in OFET samples.

Electrochemical data

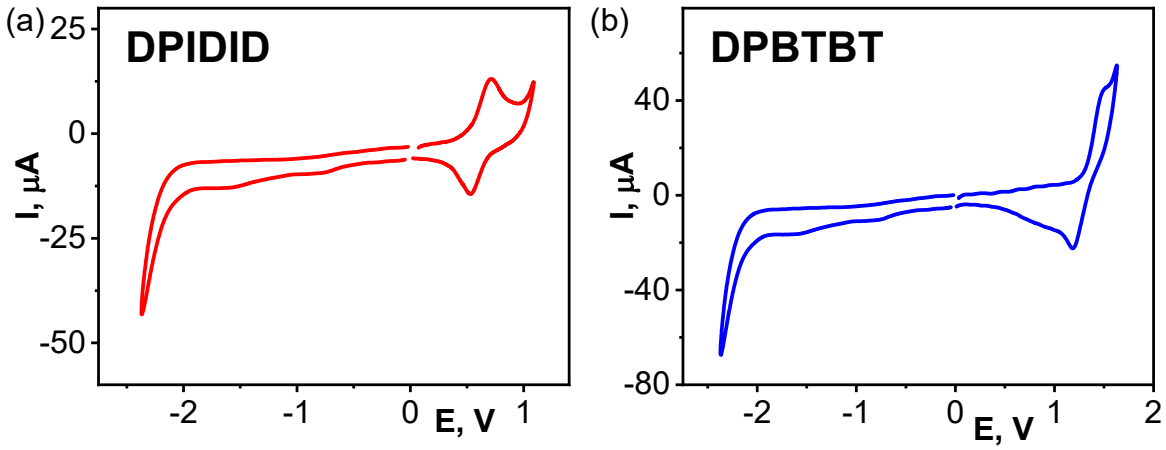


Figure S7. Cyclic voltammogram of a DPIDID (a) and DPBTBT(b) at solution. No reduction peaks were observed up to the background discharge potentials, i.e. LUMO energies are beyond the available electrochemical window.

X-ray data

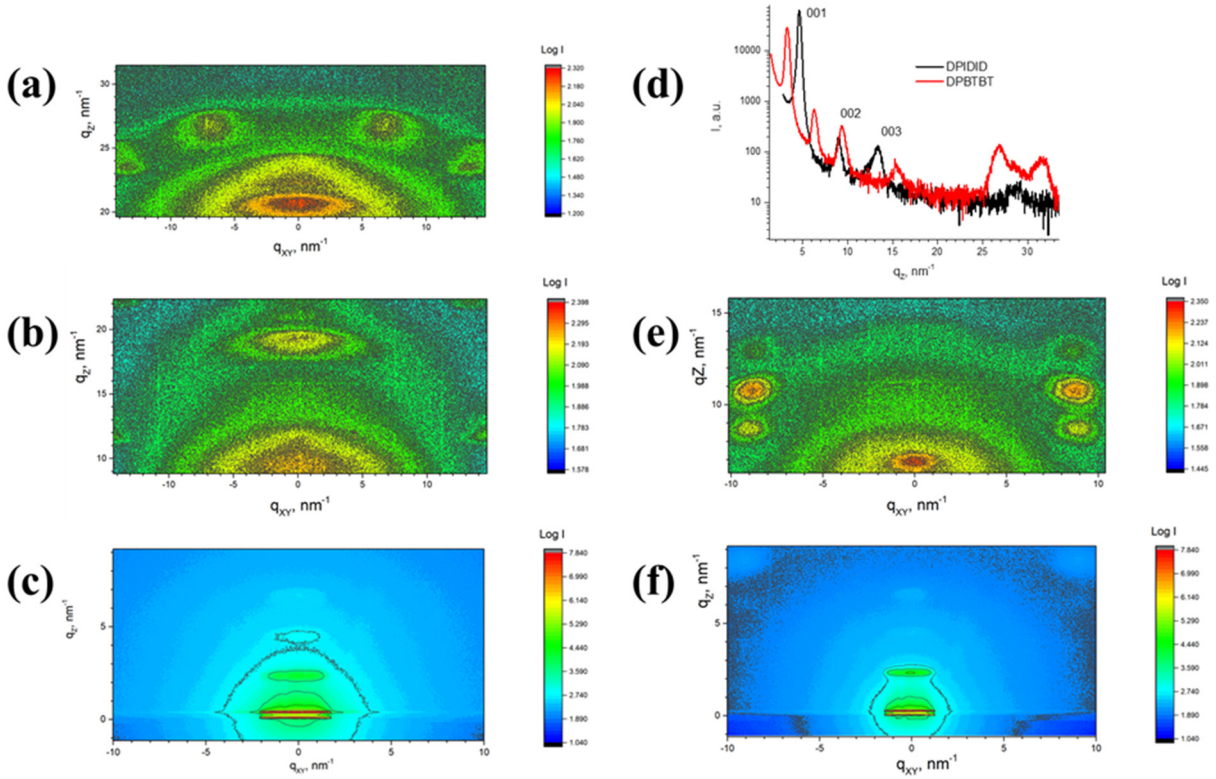


Figure S8. GIXD measurements for DPBTBT (a-c) and DPIDID (e-f) thin films at grazing angle of 0.1768° and 0.1705° correspondingly. The intensity is converted to logarithmic scale. (d) – the qz scans for both films with 00l reflections marked.