SUPPORTING INFORMATION

Design, Synthesis, and Characterization of Ultralow Bandgap Molecular Semiconductors for Ambient-Stable and Solution-Processable Ambipolar Organic Field-Effect Transistors

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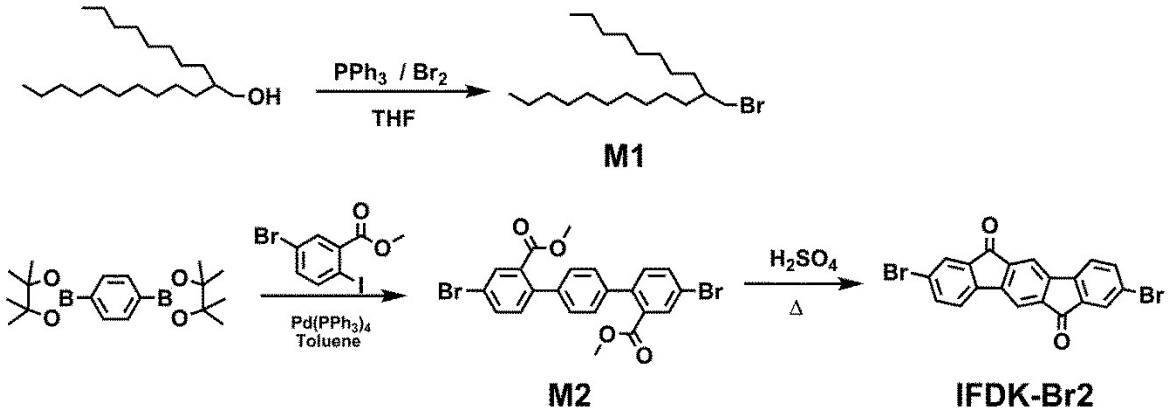

Scheme S1. Synthesis of 2-octyldodecyl bromide (**M1**) and 2,8-dibromoindeno[1,2-b]fluorene-6,12-dione (**IFDK-Br2**).

Synthesis of 2-octyldodecyl bromide (M1). A mixture of 2-octyl-1-dodecanol (4.0 g, 13.40 mmol) and triphenylphosphine (5.09 g, 53.60 mmol) was dissolved in 175 mL THF under ambient conditions. Bromine (2.58 mL, 53.60 mmol) was added slowly to this mixture, and the resulting reaction solution was stirred at room temperature for 3 h. Then, 5 mL of methanol was added and the solvent was removed on the rotary evaporator. The residue is suspended in hexane, and the insoluble part was removed by gravity filtration. Then, the resulting filtrate was concentrated on the rotary evaporator to give a crude oil, which was purified by column chromatography on silica gel using hexane as the eluent to give the pure product as colorless oil (4.54 g, 93.9%). ^{1}H NMR (400 MHz, CDCl3): δ 3.44 (2H, d, J = 4.8Hz), 1.58 (1H, m), 1.27 (32H, m), 0.88 (6H, t, J = 7.6 Hz).

Synthesis of dimethyl 4,4''-dibromo-[1,1':4',1''-terphenyl]-2,2''-dicarboxylate (M2). A mixture of 1,4-benzenediboronic acid bis(pinacol) ester (1.7 g, 5.15 mmol), methyl 5-bromo-2-iodobenzoate (3.846 g, 11.28 mmol), and Aliquat 336 (0.614 mL, 1.339 mmol) was suspended in 35 mL of dry toluene under nitrogen. Then, tetrakis(triphenylphosphine)palladium (0.357 g,

0.309 mmol) and 1M aqueous sodium carbonate solution (2.226 g in 21.0 mL of water), which was already deaerated for 2 h, were added under N_2. The mixture was heated at reflux for 2 days under nitrogen. The mixture was then cooled to room temperature and quenched with water. The reaction mixture was extracted with hexanes, and the organic phase was washed with water, dried over Na_2SO_4, filtered, and evaporated to dryness to give the crude product. The crude was then purified by column chromatography on silica gel using chloroform as the eluent to give the pure product as a white solid (1.212 g, 46.7% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ 3.71 (s, 6H), 7.32 (m, 6H), 7.67 (dd, 2H, J = 8.0 Hz and J = 2.0 Hz), 8.00 (d, 2H, 2.0 Hz).

Synthesis of 2,8-dibromoindeno[1,2-b]fluorene-6,12-dione (IFDK-Br2). Compound **1** (0.550 g, 1.09 mmol) was added to 50.0 mL of 76-78% H_2SO_4 (prepared from 10.0 mL of H_2O and 40.0 mL of concentrated (95-97% H_2SO_4), and the reaction mixture was heated with stirring at 120 °C for 17 h. Then, the reaction mixture was poured into ice and stirred for 15 min to give a dark red solid, which was collected by filtration. The crude product was then washed with water, saturated sodium hydrogen carbonate ($NaHCO_3$) solution, and methanol, respectively. The crude product was then purified by thermal gradient sublimation under high vacuum (2×10^{-5} Torr) to afford the pure product as a cherry red crystalline solid (0.354 g, 73.7% yield). Note that during the sublimation single-crystals of this compound was also obtained. m.p.> 390 °C. Anal.calcd. for $C_{20}H_8O_2Br_2$: C, 54.58; H, 1.83 Found: C, 54.70; H, 1.96.

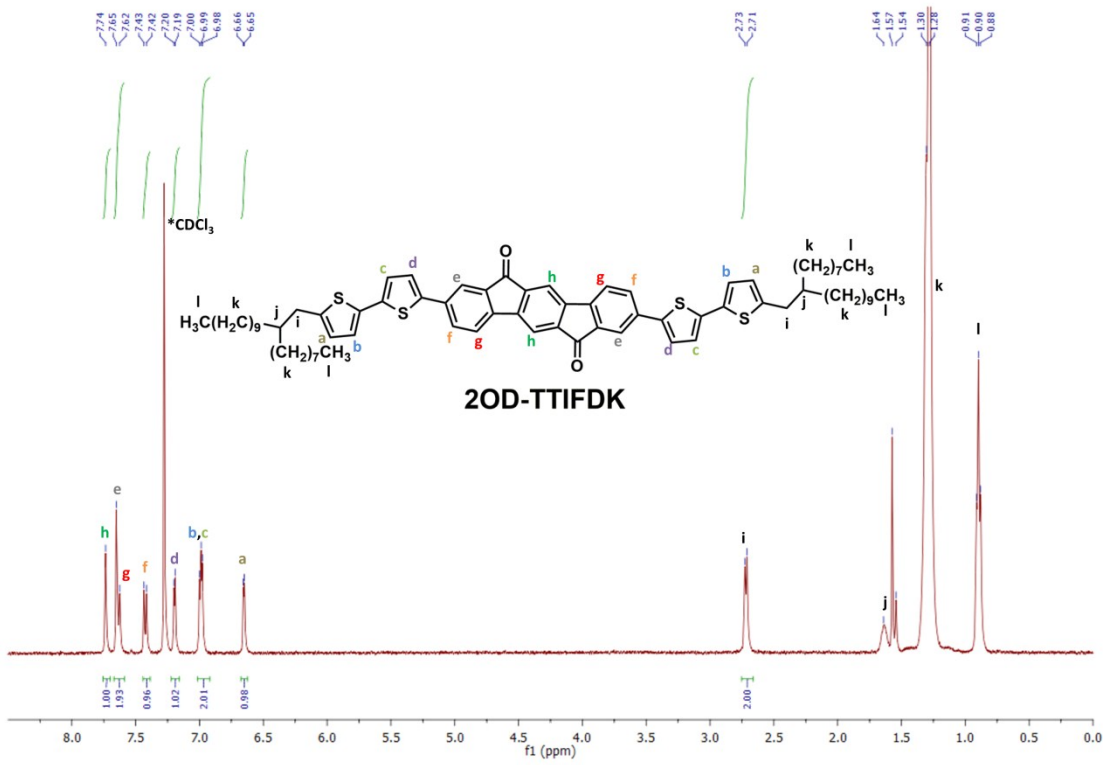

Figure S1. ^{1}H NMR spectra of **2OD-TTIFDK** measured in $CDCl_3$.

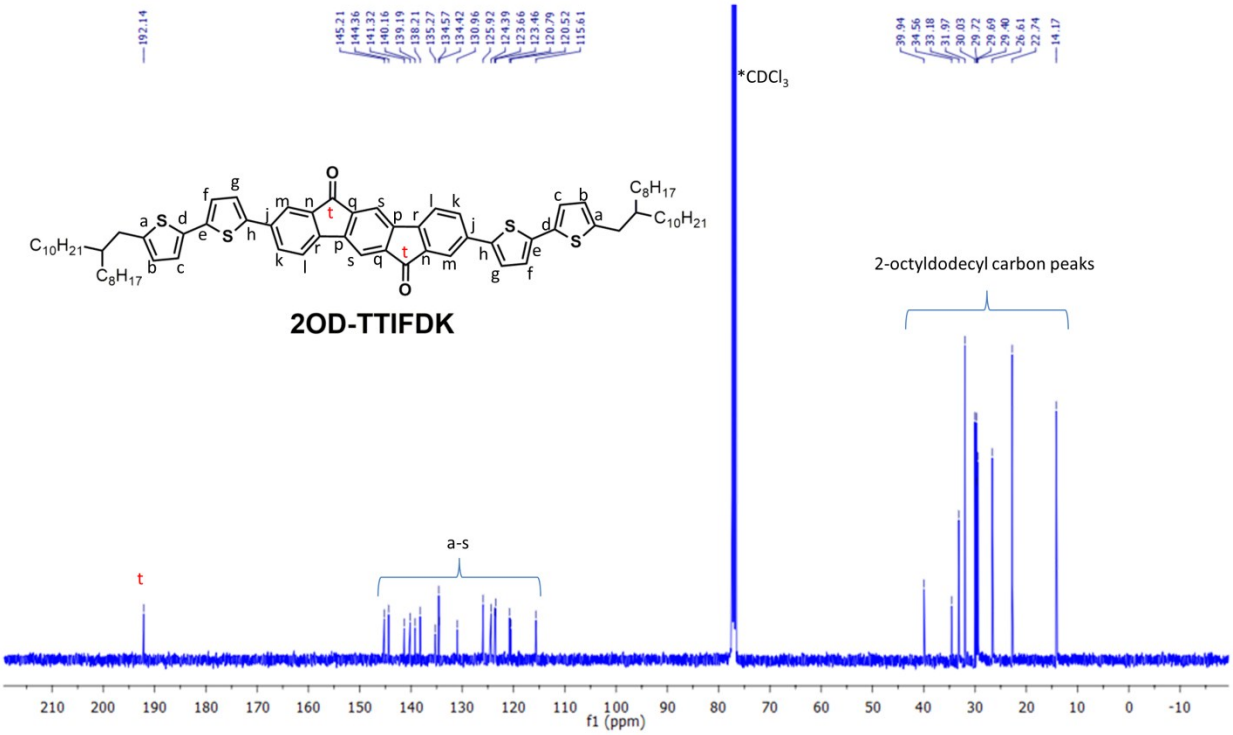

Figure S2. ^{13}C NMR spectra of **2OD-TTIFDK** measured in $CDCl_3$.

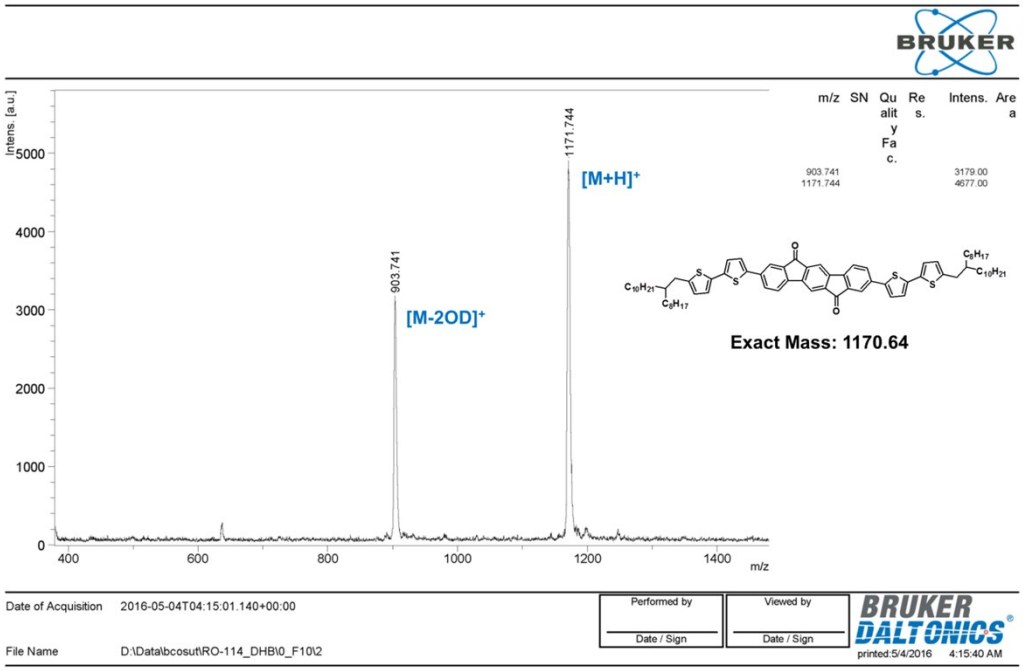

Figure S3. Positive ion and linear mode MALDI TOF-MS spectrum of **2OD-TTIFDK**.

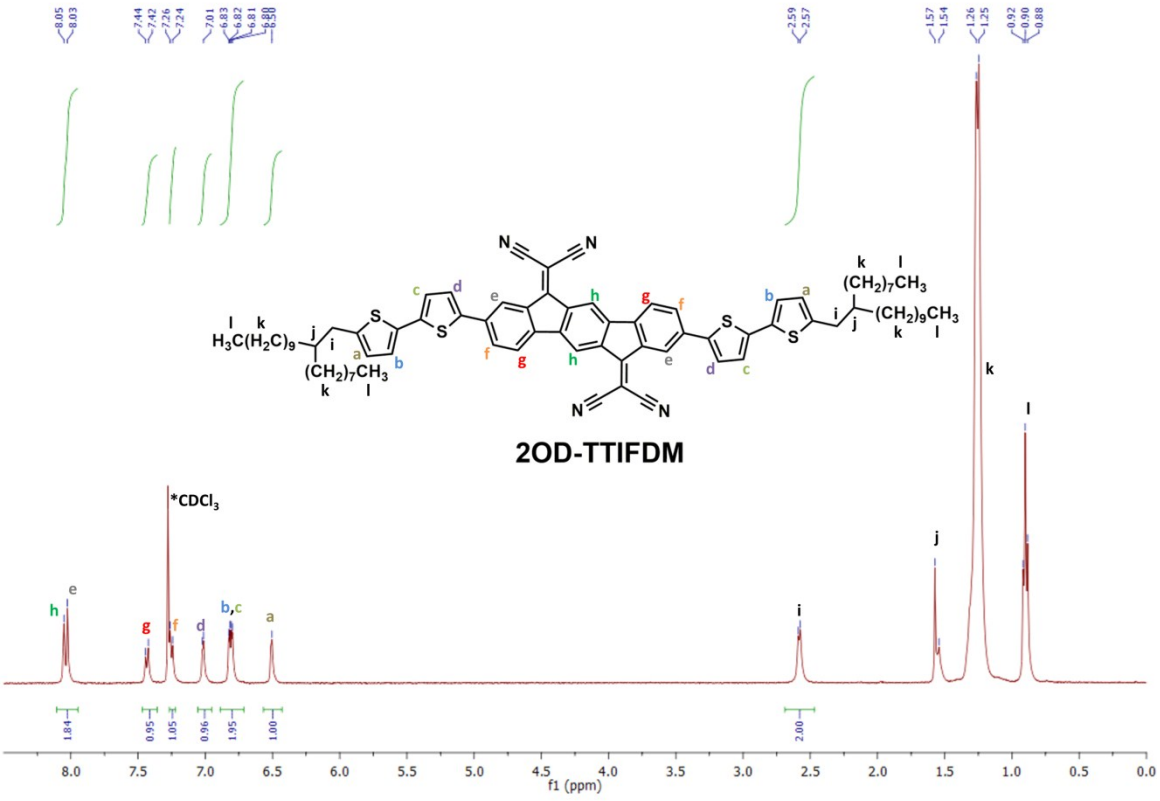

Figure S4. ^{1}H NMR spectra of **2OD-TTIFDM** measured in $CDCl_3$.

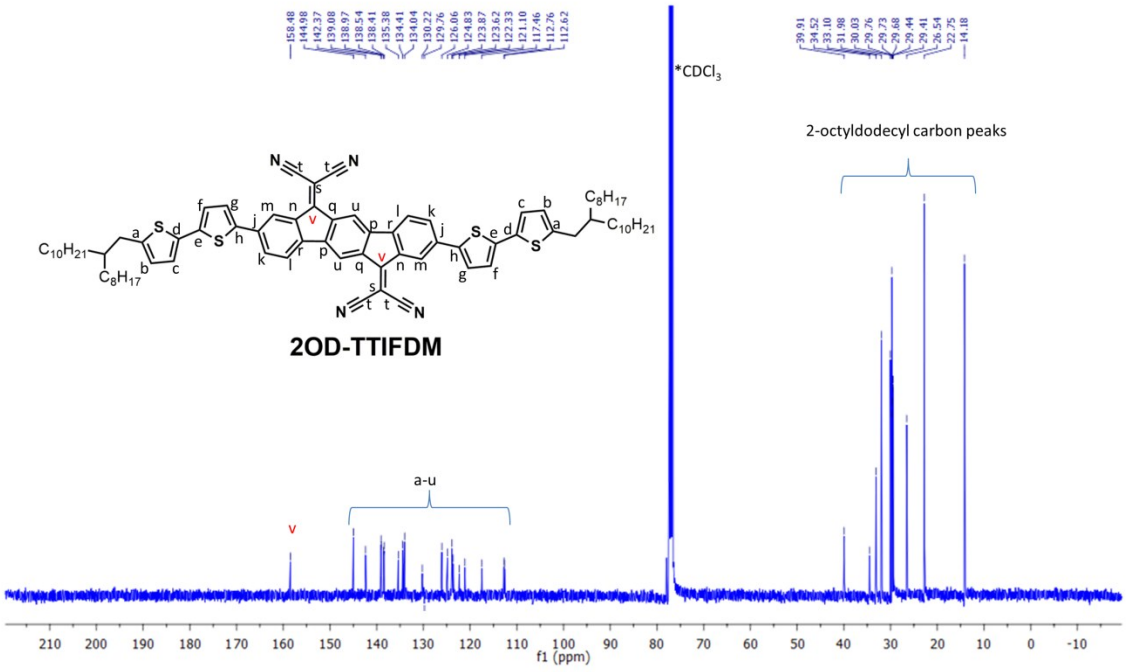

Figure S5. ^{13}C NMR spectra of **2OD-TTIFDM** measured in $CDCl_3$.

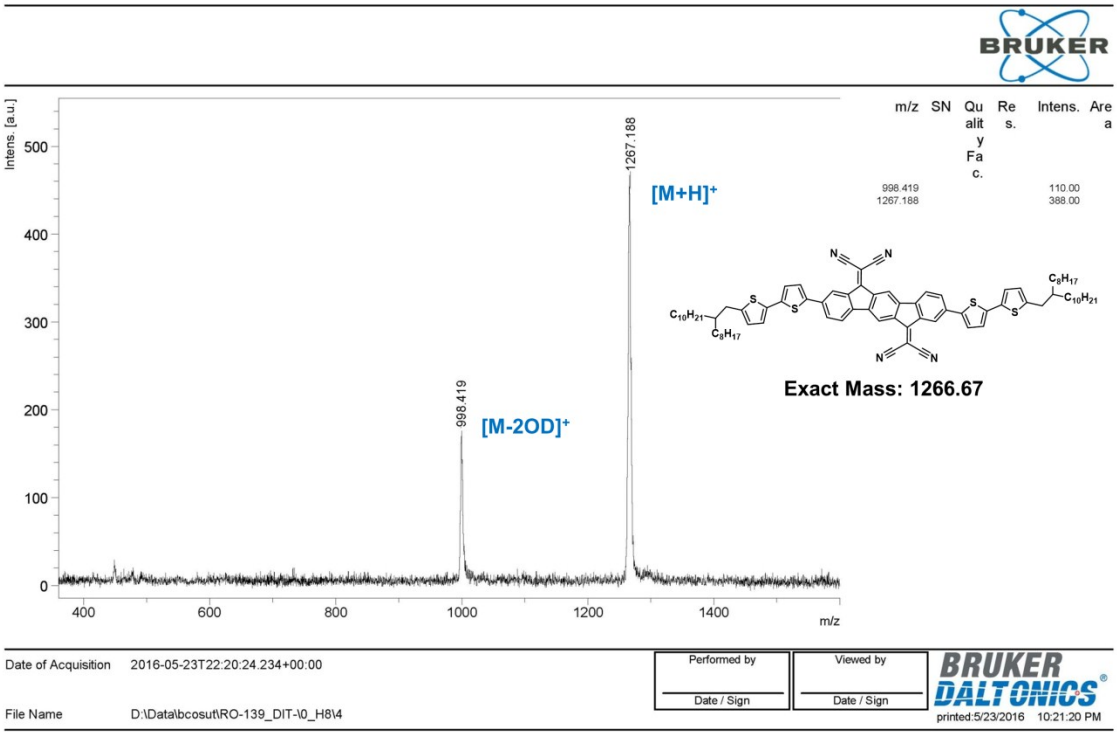

Figure S6. Positive ion and linear mode MALDI TOF-MS spectrum of **2OD-TTIFDM**.

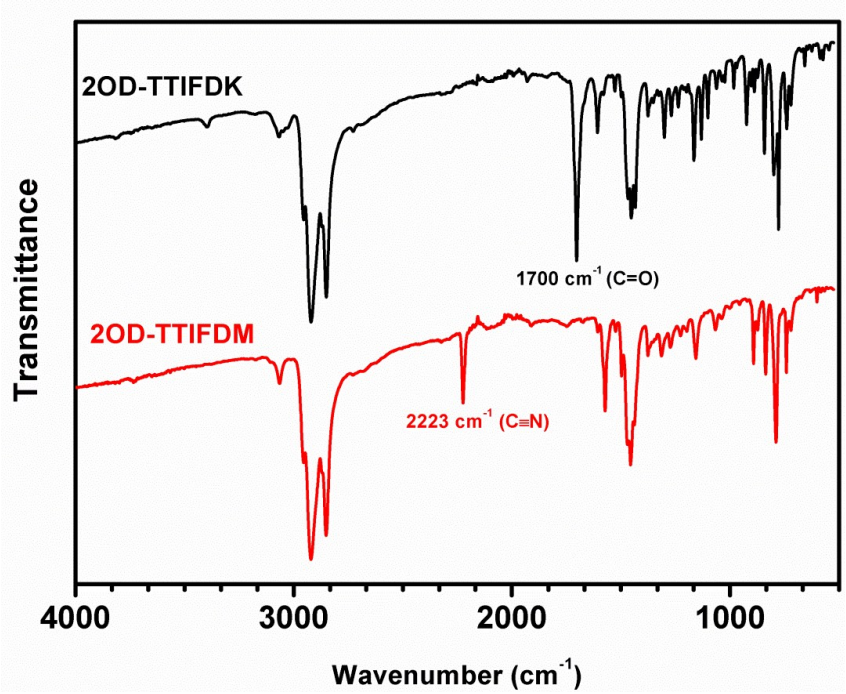

Figure S7. FT-IR Spectra of the semiconductors **2OD-TTIFDK** and **2OD-TTIFDM** showing C=O (1700 cm^{-1}) and C≡N (2223 cm^{-1}) stretching vibrational peaks.

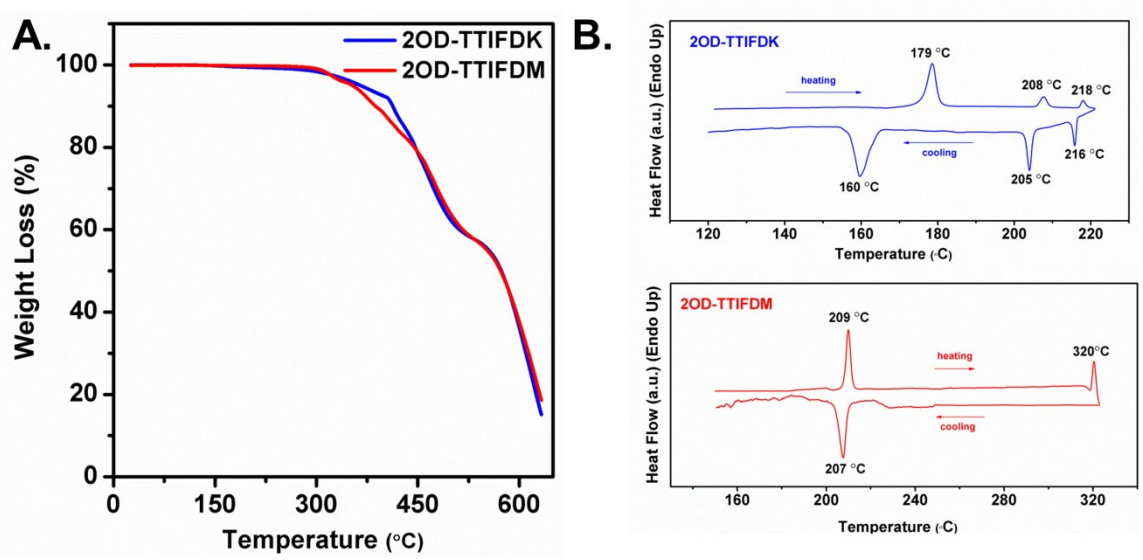

Figure S8. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the semiconductors **2OD-TTIFDK** and **2OD-TTIFDM** at temperature ramps of 10 °C/min under N_2.

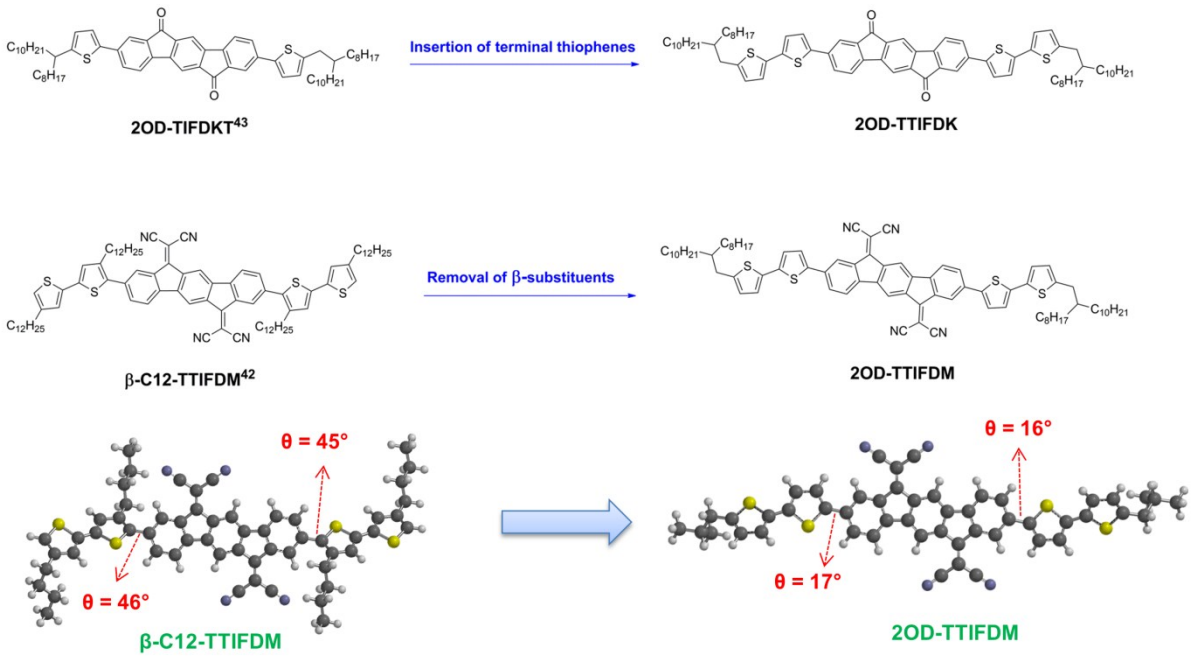

Figure S9. The chemical structures of **β-C12-TTIFDM**[42] and **2OD-TIFDKT**[43].

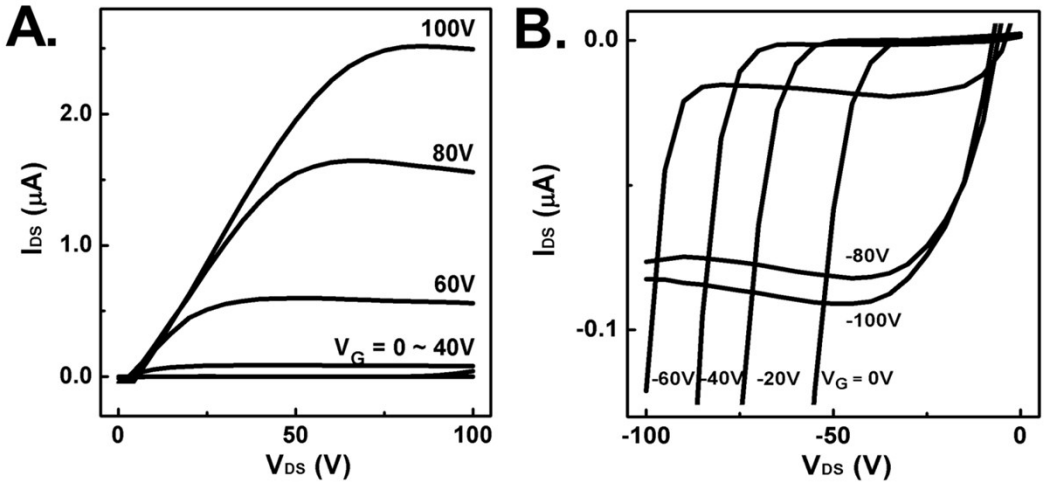

Figure S10. N-type (A) and P-type (B) output curves of the OFET devices fabricated with solution-sheared **2OD-TTIFDK**.

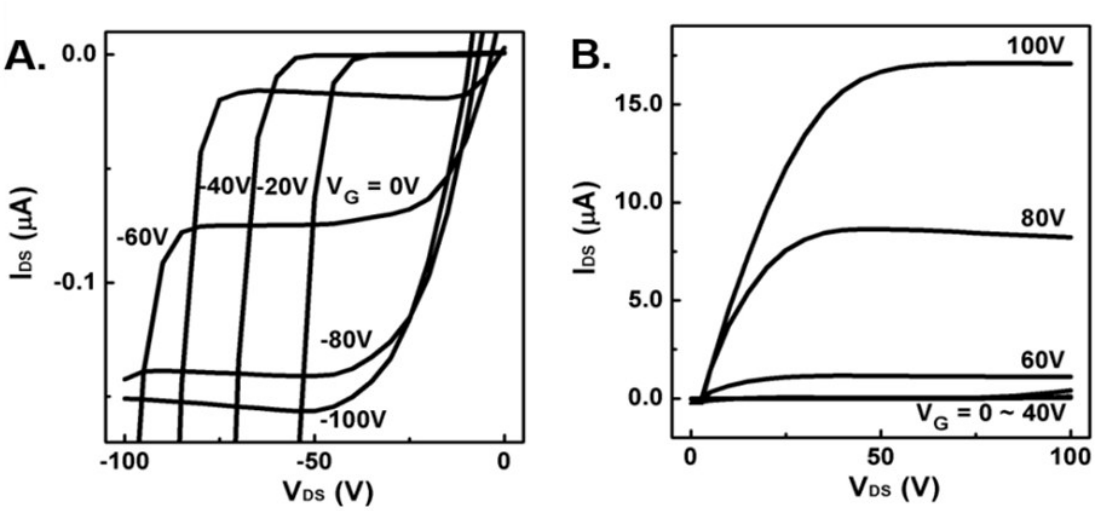

Figure S11. P-type (A) and N-type (B) output curves of the OFET devices fabricated with solution-sheared **2OD-TTIFDM**.

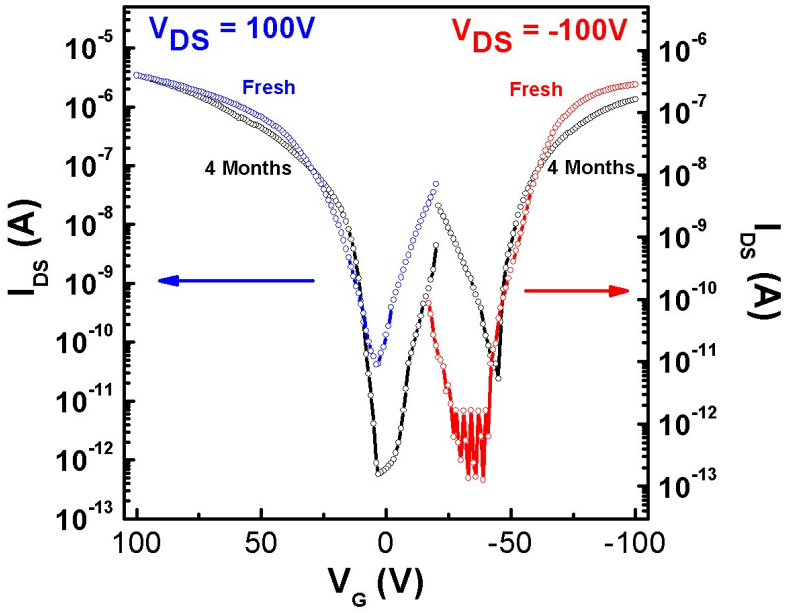

Figure S12. Transfer curves for fresh **2OD-TTIFDM**-based OFET devices (red and blue line) and after 4 months storage in ambient (black line).

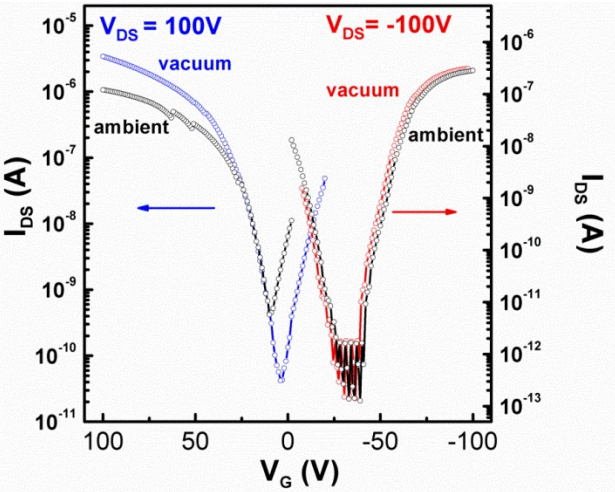

Figure S13. P-type and N-type transfer curves measured under vacuum (red and blue lines) and in ambient conditions (black lines) for the OFET devices fabricated with solution-sheared **2OD-TTIFDK**.

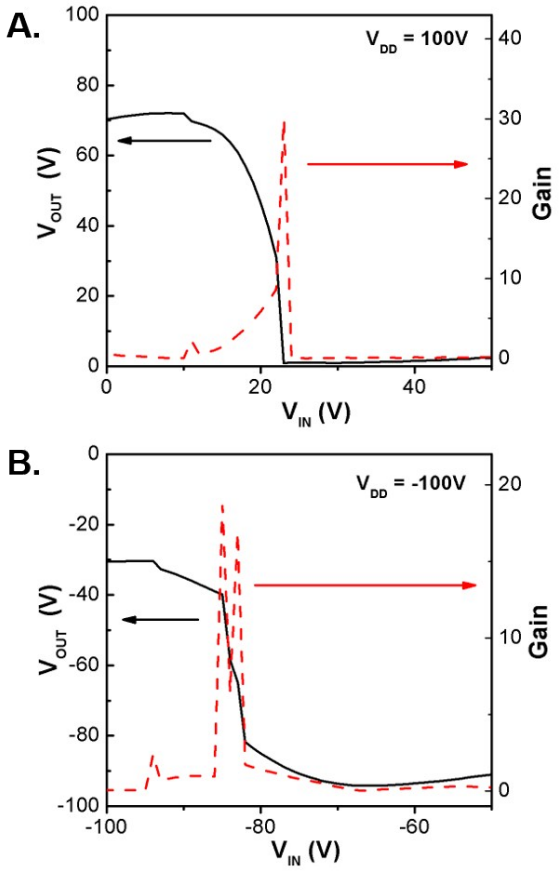

Figure S14. Voltage transfer curves of **2OD-TTIFDM** in first (A) and third (B) quadrants measured in ambient.