

Supplementary information for

Non-volatile hybrid memory devices with excellent reliability

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The syntheses of all monomers and the PDPPDBTE polymer are outlined in Scheme S1. All chemicals were purchased from Aldrich and Alfa : thiophene-2-carbonitrile, dimethyl succinate, 11-(bromomethyl)tricosane, DMF, THF, NBS, n-BuLi, and were used without further purification. 3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1), 2,5-bis(2-decyltetradecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (2), and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3) were synthesized via published literature procedures.

¹H-NMR spectra were recorded using a Bruker AM-200 spectrometer. The melting points were determined using an Electrothermal Mode 1307 digital analyzer. Thermal analysis was performed using a TA TGA 2100 thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 10°C/min. Differential scanning calorimeter (DSC) was conducted under nitrogen using a TA instrument 2100 DSC. The sample was heated at 10°C /min from 30°C to 250°C.

The molecular weights and polydispersities of the copolymers were determined by gel permeation chromatography (GPC) analysis calibrated using a polystyrene standard (high-pressure GPC assembly Model M515 pump, u-Styragel columns HR4, HR4E, and HR5E, with 500 and 100 Å resolution, refractive index detectors, CHCl₃ solvent). Cyclic voltammetry (CV) was performed using an EG and G Parc model 273 Å potentiostat/galvanostat system with a three-electrode cell in a solution containing Bu₄NClO₄ (0.1 M) in acetonitrile at a scan rate of 100 mV/s. The polymer films were coated on a square carbon electrode (0.50 cm²) by dipping the electrode into the corresponding solvents then drying in air. A Pt wire was used as the counter electrode, and an Ag/AgNO₃ (0.1 M) electrode was used as the reference electrode.

Synthesis and characterization

Poly[2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione-(*E*)-1,2-di(2,2'-bithiophen-5-yl)ethene] (4)

The polymer was prepared using a palladium-catalyzed Stille coupling reaction. Monomer (3) (0.5 g, 0.4 mmol) and monomer (6) (0.229 g, 0.4 mmol) were dissolved in dry chlorobenzene (7.5 mL). After degassing under nitrogen for 60 min, Pd₂(dba)₃ (8 mg) and P(*o*Tol)₃ (11 mg) were added to the mixture, which was then stirred for 48 h at 110 °C. 2-bromothiophen and tributyl(thiophen-2-yl)stannane were injected sequentially into the reaction mixture for end-capping, and the solution was stirred for 6h after each addition. The polymer was precipitated in methanol. The crude polymer was collected by filtration and purified by Soxhlet extraction with methanol, acetone, hexane, toluene, and chloroform, successively. The final product, poly[2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione-(*E*)-1,2-di(2,2'-bithiophen-5-yl)ethene] (PDPPDBTE) was obtained by precipitation in methanol. (M_n = 31,900, M_w = 54,230, PDI = 1.7). ¹H NMR (CDCl₃, 500MHz), δ(ppm) : δ8.91 (broad, 4H), 6.75 (broad, 4H), 3.99 (broad, 4H), 1.21 (m, 63H), 0.85 (m,15H).

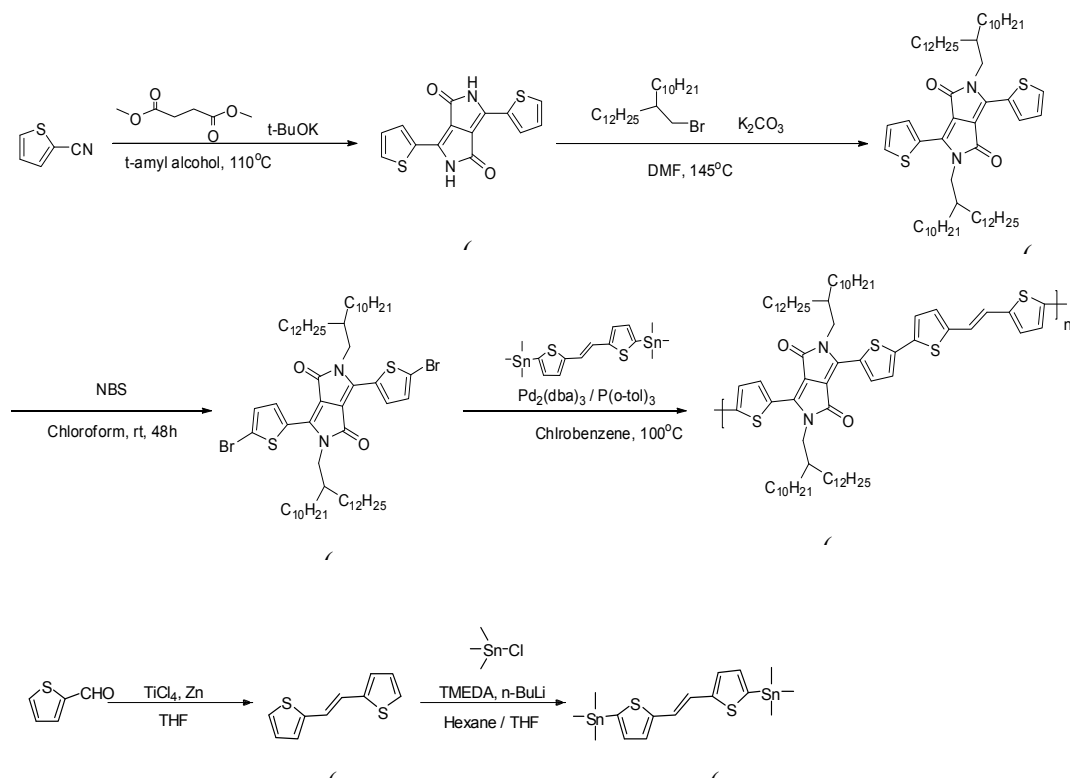
Synthesis of (*E*)-1,2-bis(2-thienyl)ethylene (5)

To a slurry solution containing 2-thiophenecarbaldehyde (5.6 g, 50 mmol) in THF (100 mL) was added, dropwise and with stirring, titanium (IV) chloride (6.5 mL) over a period of 30 min at -18°C. After stirring at this temperature for 30 min, zinc powder (7.8 g) was added in small portions over a period of 30 min. The mixture was stirred at -18 °C for 30 min, warmed to room temperature, and refluxed for 3.5 h. The reaction was quenched by the addition of ice

water (100 mL) and the resulting solid was collected by filtration then dried. The solid was dissolved in methylene chloride (80 mL), and the insoluble inorganic material was removed by filtration. The filtrate was evaporated and the residue was recrystallized from hexane to yield a yellow product. Yield : 4.70 g (98 %) of pure *E* isomer, ^1H NMR (CDCl_3 , 300MHz), $\delta(\text{ppm})$: 7.18 (d, 2H), 7.05 (s, 2H), 7.04 (d, 2H), 6.99 (m, 2H).

Synthesis of 1,2-(*E*)-Bis(5-(trimethylstannanyl-2(-*C*-thienyl)ethane (6).

To a solution of 1 (1.78 g, 9.26 mmol) in THF/hexane (2:1, 50 mL) was added TMEDA (3.10 mL, 20.7 mmol) at $-50\text{ }^\circ\text{C}$. A 2 M solution containing *n*-butyllithium in cyclohexane (11 mL, 22 mmol) was then added dropwise at $-78\text{ }^\circ\text{C}$. The mixture was refluxed for 1 h. The reaction solution was cooled to $-78\text{ }^\circ\text{C}$, and a 1.0 M solution of trimethyltin chloride in THF (22 mL, 22 mmol) was added. The solution was warmed to room temperature and stirred for 2 h. The reaction mixture was extracted with diethyl ether. After removal of the solvent, recrystallization from ethanol afforded the product as pale gray crystals. Yield: 3.88 g (80 %). ^1H NMR (CDCl_3 , 300 MHz), δ (ppm) : d 7.11 (d, 2H), 7.08 (s, 2H), 7.07 (d,2H), 0.36 (s, 18H).



Scheme S1. Synthesis of the monomers and of PDPPDBTE.

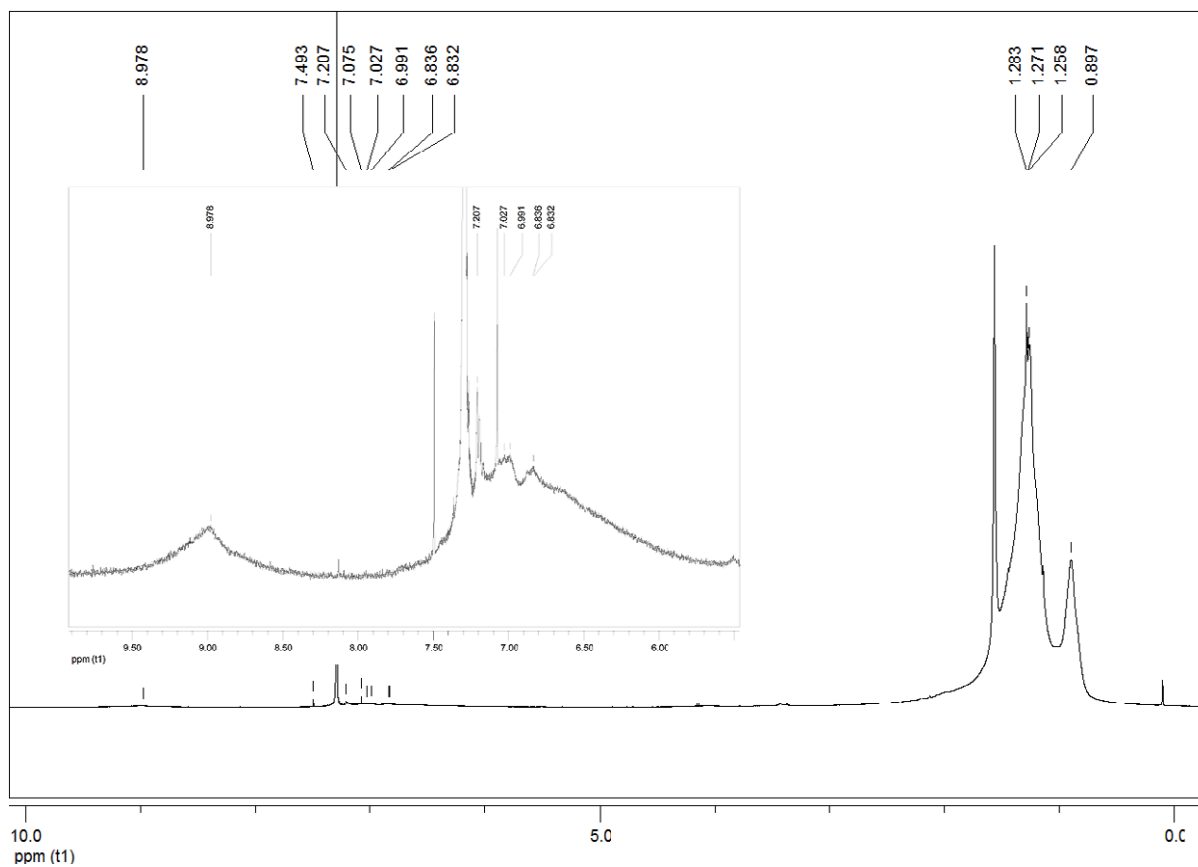


Figure S1. ¹H NMR spectrum of PDPPDBTE in CDCl₃ (δ 7.27 ppm).

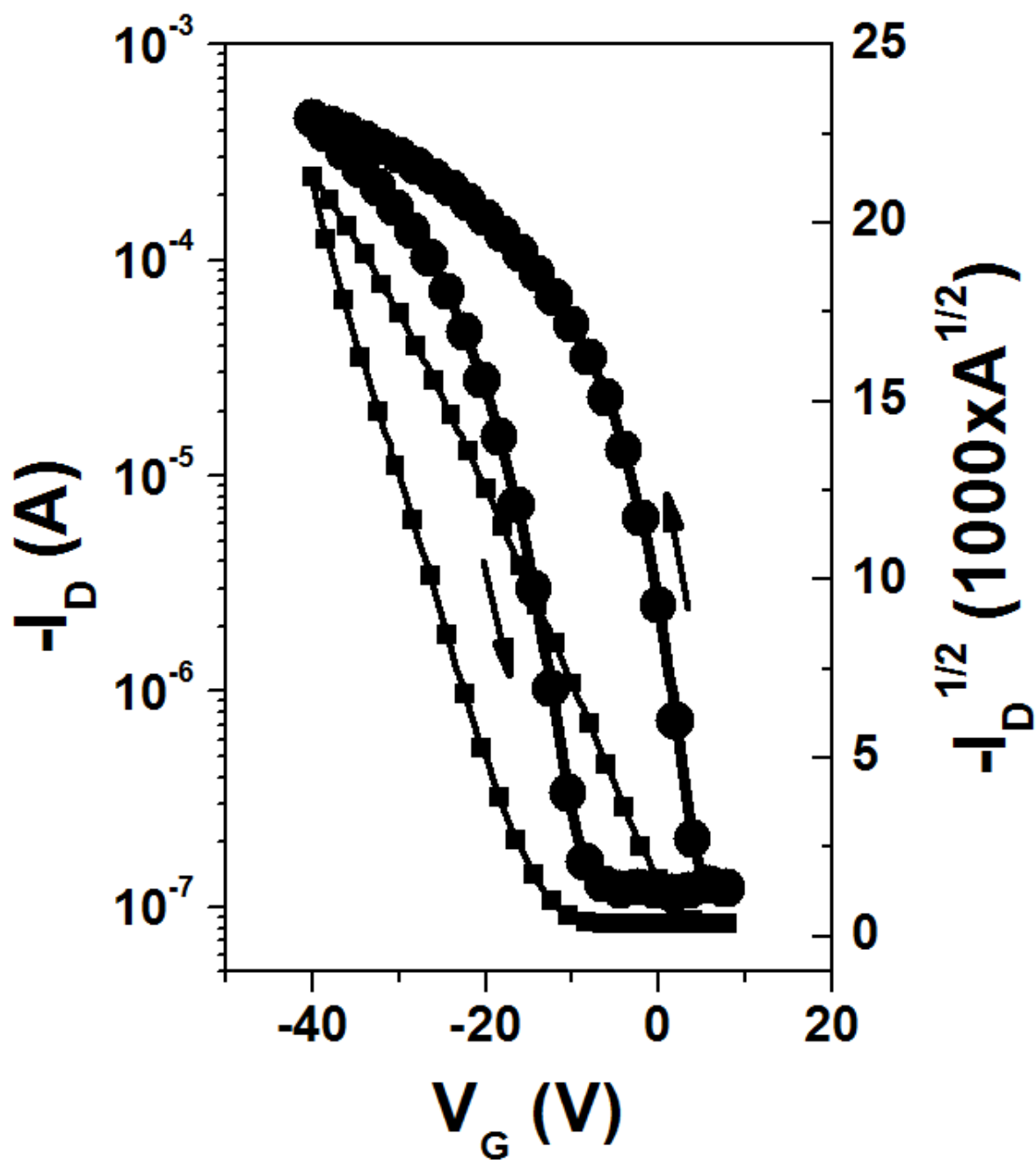


Figure S2. Transfer characteristics of PDPPDBTE based PFETs using conventional SiO_2 treated with OTS-SAM as dielectric layer

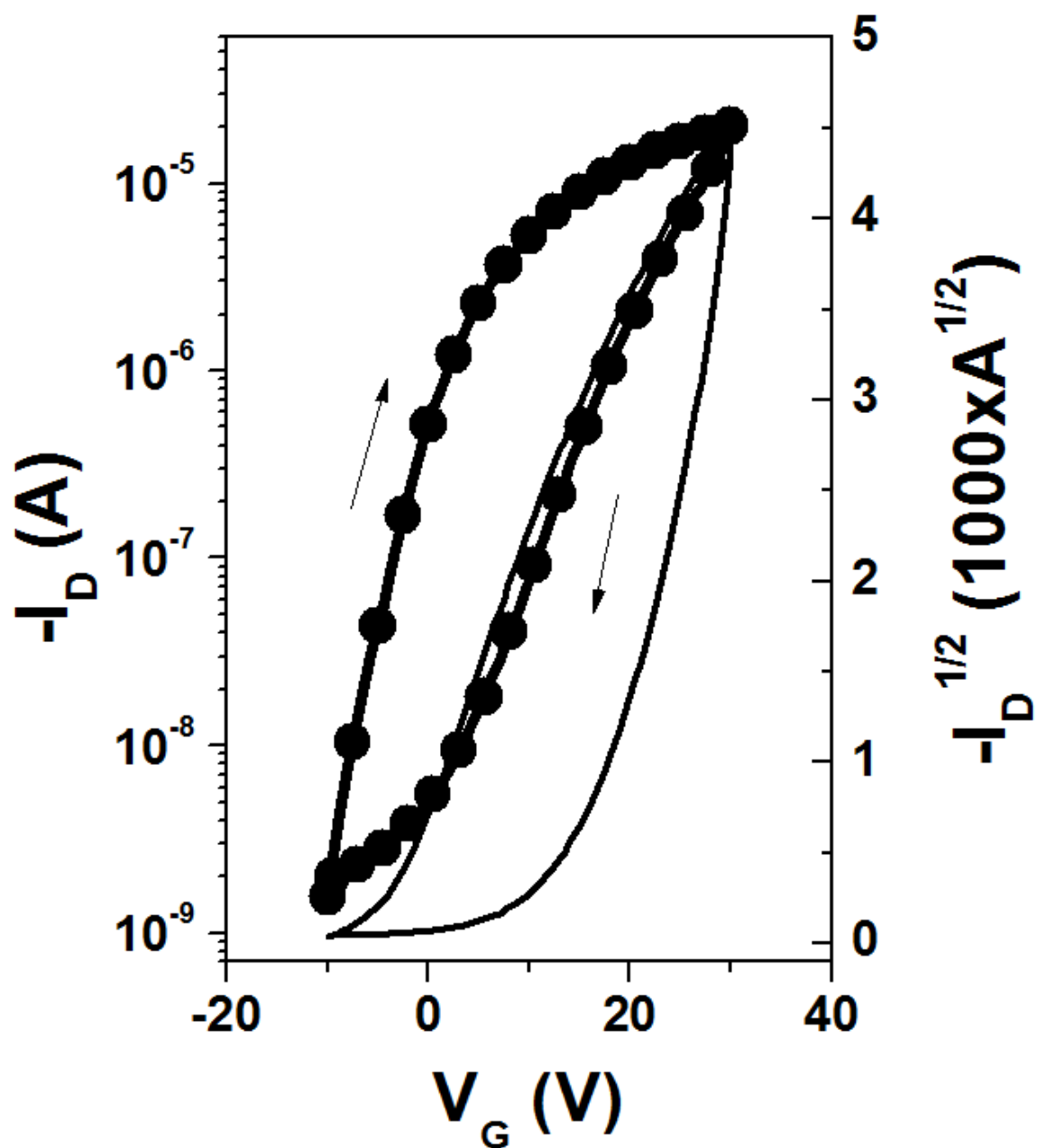


Figure S3. Transfer characteristics of PDPPDBTE based PFETs using conventional SiO_2 treated with OTS-SAM as dielectric layer and Al as source-drain electrode.