

Electronic supplementary information for:

Semiconducting alternating multi-block copolymers via a di-functionalized macromonomer approach

By A. Gasperini, M. Johnson, X. Jeanbourquin, L. Yao, A. Rahmanudin, N. Guijarro, and K. Sivula*

*Institut des Sciences et Ingénierie Chimiques
Ecole Polytechnique Fédérale de Lausanne
1015 Lausanne (Switzerland)
E-mail: kevin.sivula@epfl.ch
Homepage: limno.epfl.ch*

Contents :

| | |
|---|---|
| 1. <i>Synthetic methods and standard characterization</i> | 1 |
| 2. <i>Supporting Figures and Tables</i> | 3 |
| 3. <i>FET fabrication and electrical characterization</i> | 7 |

1. *Synthetic methods and standard characterization*

Basic chemical synthesis and characterization: All reagents were of commercial reagent grade (Sigma-Aldrich, Acros and Fluorochem) and were used without further purification. Tetrahydrofuran (Fisher Chemical, HPLC grade) and chlorobenzene (Alfa Aesar, HPLC grade) were purified and dried on a Pure Solv-MD Solvent Purification System (Innovative Technology, Amesbury, United States) apparatus. Standard silica gel chromatography was performed with an Acros Organic silicon dioxide (pore size 60 Å, 40–50 µm technical grades). The (¹H) NMR spectra were recorded at 80°C using *d*₄-*ortho*-dichlorobenzene as internal standards on a Advance III-400 spectrometer (Bruker). Chemical shifts are given in parts per million (ppm) referenced to residual *o*-dichlorobenzene (¹H: 6.94, lower shift doublet). Mass determination was recorded on an Axima-CFR™ MALDI-TOF mass spectrometer in reflection mode using *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile as matrix. The monomers 5,5'-dibromo-4,4'-ditetradecyl-2,2'-bithiophene (**1**), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (**2**), and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**3**) were prepared using standard literature techniques: (see *Macromolecules* **2013**, *46*, 9349-9358 and *Adv. Mater.* **2013**, *25*, 3182-3186, respectively).

Other characterization details: AFM characterization was performed with an Asylum Research Cypher in AC mode at room temperature in air. Cantilevers with a typical resonance frequency of $f_0 = 70$ kHz and $k = 2$ N/m were used (Asylum research AC240TS). Scan rates between 0.5 and 1 Hz were applied with images resolution varying according to features size from 10 µm x 10 µm to 500 nm x 500 nm. Out-of-plane, specular X-ray scattering was performed with a Cu Kα X-ray source ($\lambda = 0.15418$ nm) on a Bruker D8 Advanced goniometer using detector scan mode with an incidence angle of 0.2°, a scan speed of 0.05 deg min⁻¹, and a Lynx Eye linear detector. Preparative size exclusion chromatography was performed by firstly dissolving 100 mg of product dissolved in 10 ml of chlorobenzene (80°C) and injecting the solution in a size exclusion preparative column (PSS SDV preparative linear M, 40mm×250mm) at 80°C using chlorobenzene as mobile phase at a constant elution flow of 6 mL/min. Fraction collection was carried out every 20 seconds (0.33 mL). Single fractions (and crude polymerizations) were analyzed through an analytical size exclusion PSS SDV analytical linear M column (8mm×250mm, 80°C, CB mobile phase, 1mL/min). The CB was removed and the samples were stored in an Ar glovebox until further use. Cyclic voltammetry (CV) was performed using a SP-200 potentiostat (Bio-Logic) in a three-electrode configuration using a Ag/Ag⁺ electrode and a platinum wire as pseudo-reference and counter electrode, respectively. The working electrode was prepared by drop-casting a solution containing the corresponding organic molecule in a platinum wire. The characterization of the samples by CV was carried out using a 50 mM tetrabutylammonium perchlorate (TBAP, Sigma-Aldrich >99.0%) solution in dry acetonitrile (Sigma-Aldrich, 99.5%) as electrolyte and a scan rate of 50 mV s⁻¹. Conversion of potentials referred to Ag/Ag⁺

to energy scale was performed using ferrocene as internal reference and according to this reference: (Inorg. Chem. **1980**, *19*, 2854-2855).

pBTTT-C₁₄, (*Br terminated*), (4): (from Chem. Sci. **2014**, *5*, 4922-4927.) pBTTT polymerization conditions were optimized in order to preferentially synthesize short chains that exclusively resulted to be end-functionalized with bromine. A ratio of 1.6-1.8 to 1 of 2,5-dibromo-3-tetradecylbithiophene (**1**) to 5,5'-trimethyltin thieno[3,2b]thiophene (**2**) was thus chosen. Typical polymerization yields were 90% based on thienothiophene monomer and number-average molecular weights (M_n) of 5.5-7 kDa (PDI 1.4) against polystyrene standards were calculated by analytical size exclusion chromatography (SEC) using chlorobenzene as eluent at 80°C. Successive fractionation by preparative SEC (in 80°C, chlorobenzene, 6 mL min⁻¹, 40.0 x 250 mm column, linear M packing, Polymer Standards Service GmbH) allowed the selection of a narrow distribution of chains at 10.2 kDa with $\bar{D} = 1.19$. The sample solution in chlorobenzene was passed through a polytetrafluoroethylene filter (5 μ m pore size) before injection. In addition to the characterization of (**4**) given in the main text, the MALDI-TOF results are described in Figure S1 (Table S1) and the ¹H NMR spectra of (**4**) is given in Figure S2 below.

pDBT-TT, (*trimethyltin-terminated*) (5): The pDBT-TT polymerization conditions were optimized in order to preferentially synthesize short chains that exclusively resulted to be end-functionalized with the organotin reactive group. A ratio of 2 to 1 of 5,5'-trimethyltin thieno[3,2b]thiophene (0.1 g, 0.21 mmol), (**2**) to 3,6-bis(5-bromo-2-thienyl)-2,5-bis(2-decyltetradecyl)-2,5-dihydro-Pyrrolo[3,4-*c*]pyrrole-1,4-dione, (**3**) (0.12 gr, 0.11 mmol) at 60°C in chlorobenzene (7 ml) under inert atmosphere using tris(dibenzylideneacetone)dipalladium (4 mg) and excess of tri(*o*-tolyl)-phosphine (15 mg) as catalyst was thus chosen. Precipitation in butanone afforded the polymer (45 mg, yield = 25%) with typical number-average molecular weight (M_n) of 5.5-7 kDa ($\bar{D} = 1.2$) against polystyrene standards, calculated by analytical size exclusion chromatography using chlorobenzene as eluent at 80°C. In addition to the characterization of (**5**) given in the main text, the MALDI-TOF results are described in Figure S1 (Table S1) and the ¹H NMR spectra of (**5**) is given in Figure S3 below.

MBC1. A molar ratio of 1:1 of pDBT-TT block (5 kDa, 5 mg) and pBTTT-Br block (10 kDa, 10 mg) was chosen. The reaction was run at 100°C in chlorobenzene (1 ml) under inert atmosphere using tris(dibenzylideneacetone)dipalladium (2 mg) and excess of tri(*o*-tolyl)-phosphine (6 mg) as catalyst for 1h. The crude polymer fraction was analyzed through an analytical size exclusion chromatography column (SEC) at 80°C using chlorobenzene as mobile phase at 1 mL min⁻¹. Successive fractionation by preparative SEC (in 80°C, chlorobenzene, 6 mL min⁻¹, 40.0 x 250 mm column, linear M packing, Polymer Standards Service GmbH) afforded to selective isolate the high molecular weight fraction with a M_n of 51 kDa and a dispersity, \bar{D} , of 1.2 (vs. PS standards). The yield for MBC1 was 5mg (yield = 30 %). In addition to the characterization of (**5**) given in the main text, the ¹H NMR spectra of **MBC1** is given in Figure S4 below.

2. Supporting Figures and Tables

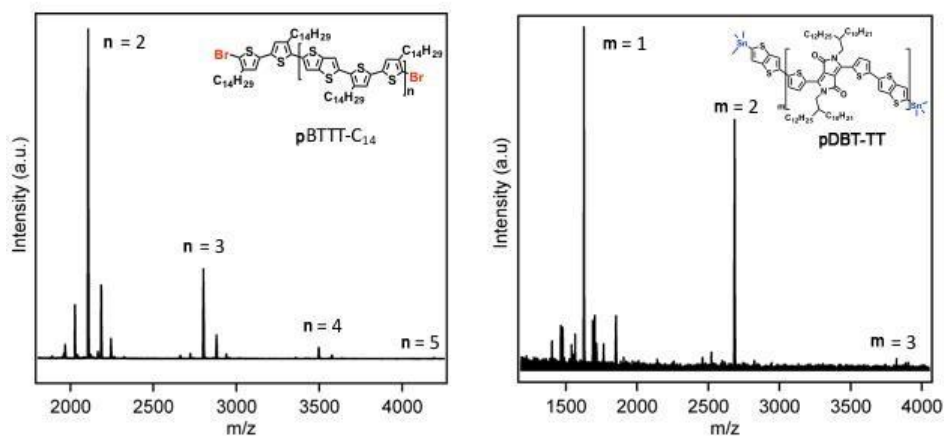


Figure S1: MALDI-TOF MS spectra of difunctionalized macromonomers pBTTT-C₁₄ (4) and pDBT-TT (5) in reflection mode using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile as matrix.

Table S1 : Calculated and experimentally found (MALDI-TOF MS) molecular weights of the di-brominated pBTTT (4) and the di stannylated pDBT-TT blocks. We note that as longer chains are less probable to be detected in the MALDI-TOF experiment, only the first peaks are found.

| Repeat units | pBTTT-C ₁₄ | | pDBT-TT | |
|--------------|-----------------------|---------|------------|---------|
| | Calculated | Found | Calculated | Found |
| 1 | 1412.21 | 1411.80 | 1575.66 | 1575.03 |
| 2 | 2107.42 | 2107.22 | 2685.52 | 2685.05 |
| 3 | 2802.63 | 2802.66 | 3795.38 | 3795.02 |
| 4 | 3497.84 | 3497.90 | - | - |
| 5 | 4193.05 | 4193.10 | - | - |

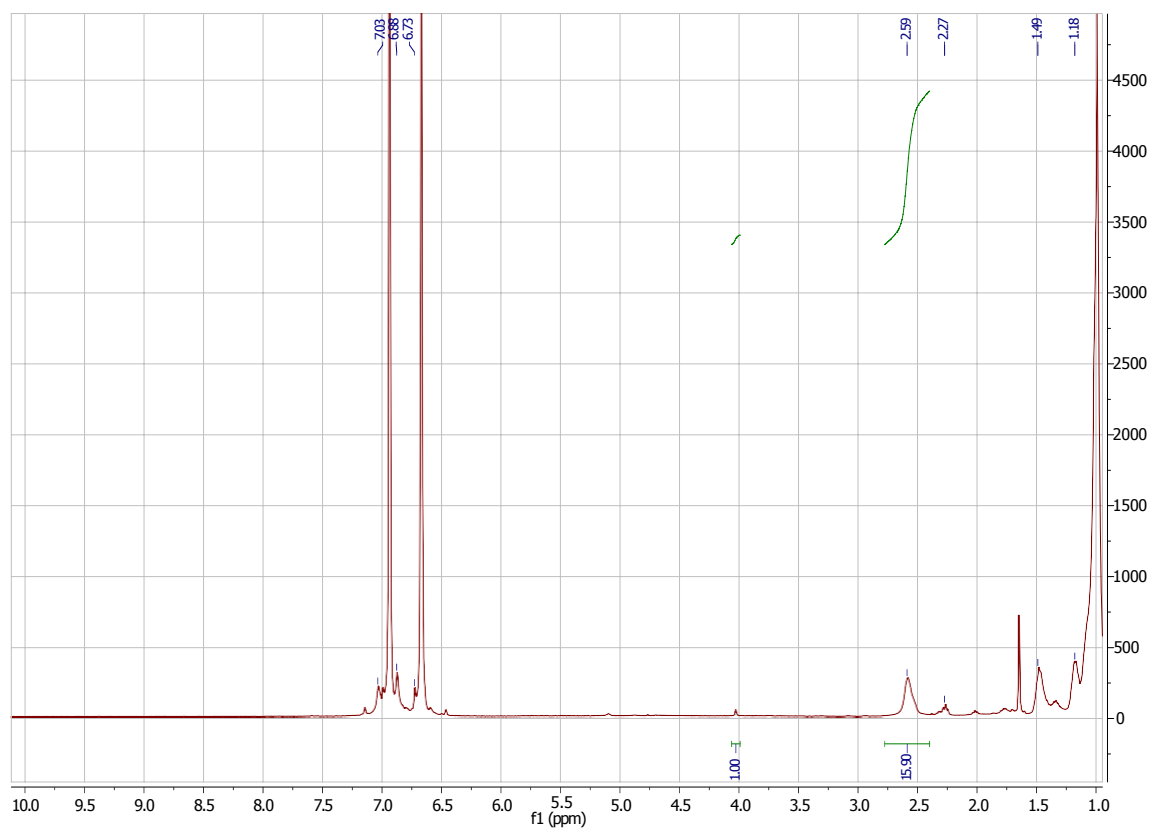


Figure S2: ¹H NMR spectra in o-DCB of the PBTTT-C₁₄ block (**4**) at 80°C.

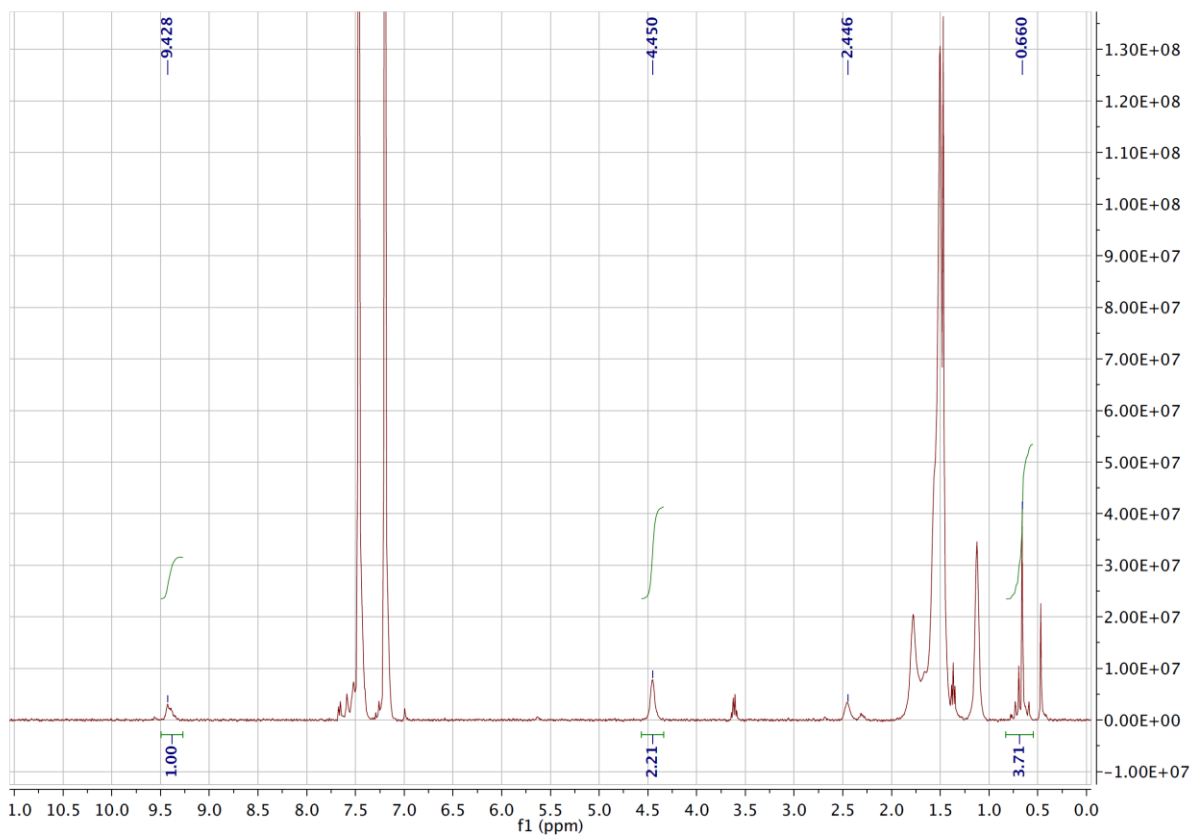


Figure S3: ¹H NMR spectra in *o*-DCB of the pDBT-TT block (5) at 80°C.

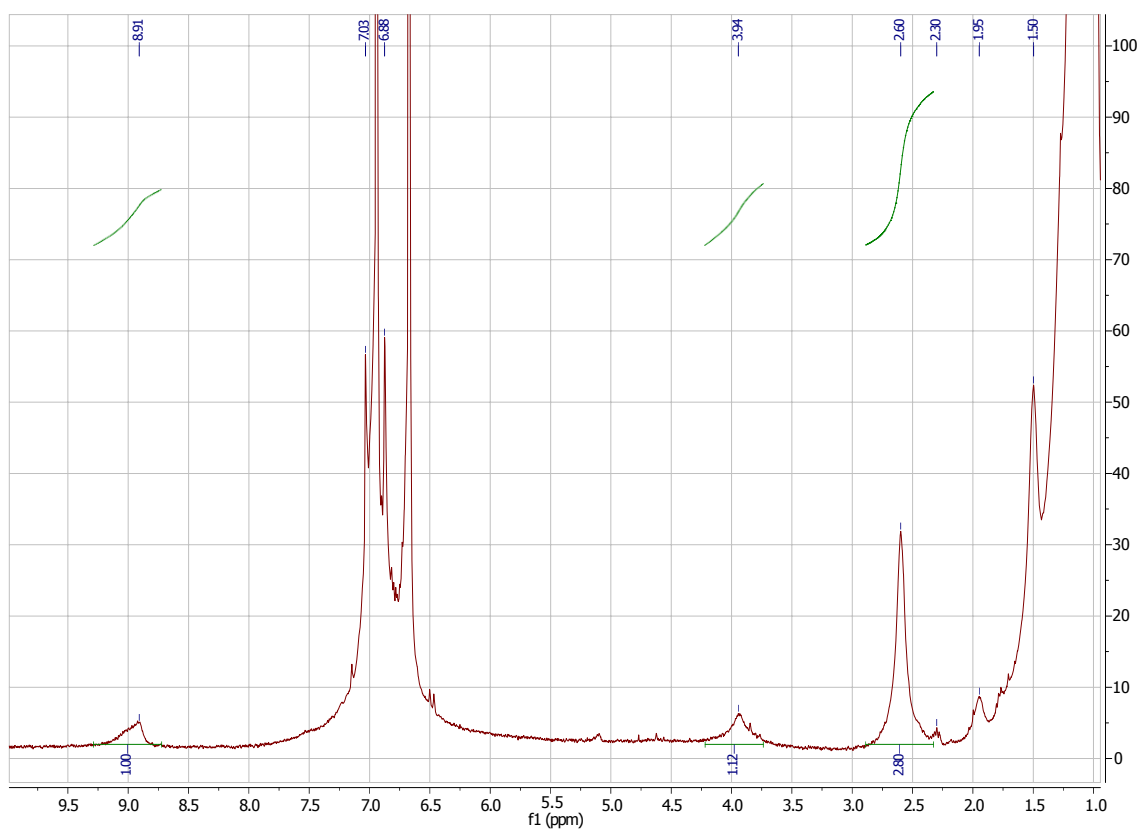


Figure S4: ^1H NMR spectra in *o*-DCB of the **MBC1** at 80°C .

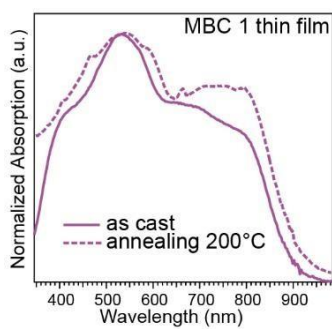


Figure S5: Solid state thin film UV-Vis of **MBC1** in the as-cast state and after annealing.

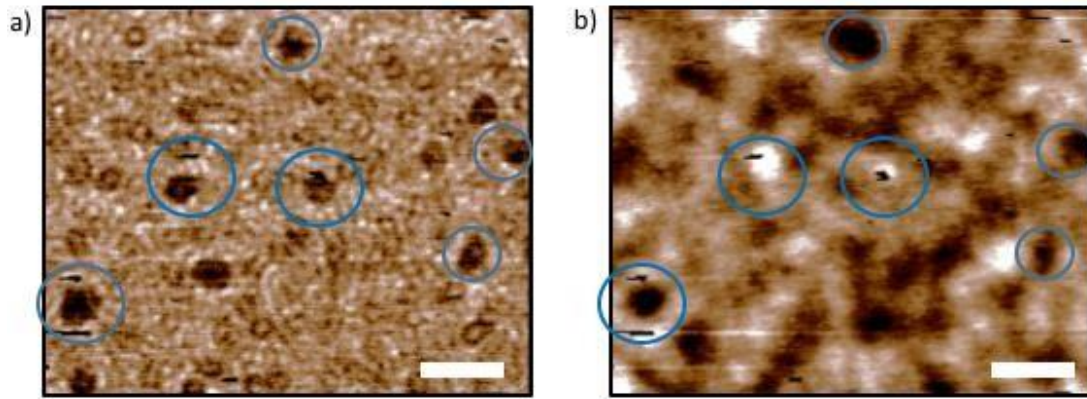


Figure S6: Phase image (a) and height image (b) of **MBC1** TFT annealed at 200°C. Black spots in the phase image are identified as 5-10 nm deep holes in the film. Scale bar 400 nm.

3. FET fabrication and electrical characterization

Bottom contact field-effect transistors (FETs) were fabricated on pre-patterned test substrates (purchased from Fraunhofer Institute for Photonic Microsystems IPMS) whose source and drain contacts were composed of a 30 nm thick gold layer on top of a 10 nm thick titanium layer. A 230 nm thick silicon oxide was used as gate dielectric and n-doped silicon crystal as gate electrode. The channel length (L) was 10 or 20 μm and channel width (W) was 10 mm. The transistor substrates were cleaned by sonication in acetone and isopropanol at RT for 15 min in each solvent. After drying under nitrogen, the substrates were subsequently exposed to a nitrogen plasma for 30 min. Films of ~ 80 nm thickness were spin-coated from 10 mg mL⁻¹ solutions in orto-dichlorobenzene at 1500 rpm (for 1 min). The solutions were prepared by dissolution at 80 °C for 2h under continuous stirring. All solutions and films were prepared in an argon atmosphere. Unannealed films were left overnight under vacuum before testing. Characterization of the OFETs was carried out in a nitrogen atmosphere using a custom-built probe station and a Keithley 2612A dual-channel source measure unit. Field effect mobilities (μ_{sat}) were determined from the current–voltage transfer characteristics in the saturation regime using the following equation:

$$\mu_{\text{sat}} = \frac{2L}{WC} \left(\frac{\partial \sqrt{I_d}}{\partial V_g} \right)^2 \quad \text{Eq. 1}$$

Here I_d is the source-drain current, V_g is the gate voltage, C_i is the capacitance per unit area of the gate dielectric (18 nF cm⁻²). At minimum six transistors were tested for each condition (two substrates and three transistors on each substrate), and the average values are reported with errors corresponding to ± 1 standard deviation. Device fabrication and testing were done under inert atmosphere in a nitrogen filled glovebox. A typical set of output curves for a transistor is shown in Figure S6 below.

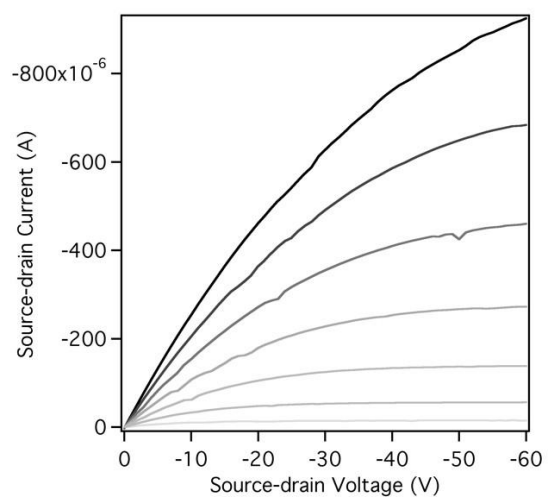


Figure S7. Output curve of **MBC1** TFTs at gate voltages $0 \text{ V} < V_g < -60 \text{ V}$ and annealed at 200°C for 15 min.