

Electronic Supplementary Information for

A conjugated polymer with high planarity and extended π -electron delocalization via a quinoid structure prepared by short 3 synthetic steps

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Contents :

- 1. Materials and general experimental procedures**
- 2. Synthetic procedures**
- 3. Optimized geometry of QuBTV dimer**
- 4. TGA**
- 5. DSC**
- 6. AFM**
- 7. NMR and MALDI**
- 8. OFET characteristics depending on different annealing temperature**

1. Materials and general experimental procedures

All chemical reagents were purchased from commercial sources and were used as received. Density functional theory (DFT) calculations were performed using the Gaussian 09 package at the B3LYP/6-311G(d,p) level, and the pictures were obtained using Gauss View 5.0 software. ¹H-NMR data were recorded using a JEOL ECX-400P (400 MHz) in CDCl₃ at room temperature. Mass data were measured using gas chromatography-mass spectrometry (GC-MS) (Shimadzu, GCMS-QP2010), and a matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometer (AXIMA-CFR, Shimadzu). Gel permeation chromatography (GPC) measurements were carried out using an ACQUITY Advanced Polymer Chromatography (Waters) in chloroform, and calibrated using polystyrene as a standard. Thermogravimetric analysis (PerkinElmer, TGA 4000) and differential scanning calorimetry (TA instrument DSC-Q20) were performed at a heating rate of 10 °C/min under a nitrogen atmosphere. UV-vis spectrometry was performed using a Perkin Elmer Lambda 750. Cyclic voltammetry (CV) was performed using an Eco Chemie Autolab PGSTAT 30 in an acetonitrile solution with 0.1 M tetrabutylammonium perchlorate (Bu₄NClO₄) as the supporting electrolyte, indium tin oxide (ITO) as the working electrode, a Pt wire as the counter electrode, and a Ag/AgCl electrode as the reference electrode at a scan rate of 50 mV/s. 2D grazing incidence wide angle X-ray scattering (GIWAXS) data were obtained using the synchrotron source at the 5A beamline of the Pohang Accelerator Laboratory (PAL). Atomic force microscopy (AFM) images were obtained using an atomic force microscope (Nanoscope III, Veeco Instruments, Inc) in the tapping-mode at the Korea Basic Science Institute.

Top gate/bottom contact organic field-effect transistor (OFET) devices were fabricated using a Corning eagle XG glass substrate with patterned Ni/Au (3 nm/15 nm) S/D electrodes using lift-off photolithography. The patterned channel width/length was 1.0 mm/20 μm. The substrates were cleaned with ultrasonication in DI water, acetone, and isopropanol and were exposed to UV/O₃ for 20 min. The polymer films were spin coated onto the prepared substrate using a 1,2-DCB (15 mg/mL) solution in a N₂-purged glove box, and were subsequently annealed at 200 °C for 30 min under nitrogen. PMMA in n-butylacetate was deposited as the dielectric layer by spin coating with a 0.45 μm PTFE syringe filter on the top of the semiconductor films. The films were soft baked at 80 °C for 2 h. Finally, the fabrication of the devices was completed by thermal evaporation of an Al gate electrode (50 nm) using a metal shadow mask. The electrical characteristics were measured using a Keithley 4200-SCS instrument in a glove box under nitrogen atmosphere. The field-effect mobilities (μ) and threshold voltages (V_{th}) were calculated in the saturation regime according to the following equation $I_{DS} = (W/2L)\mu C_i (V_G - V_{th})^2$, where L and W are the channel length and width, C_i is the gate dielectric capacitance per unit area (~6 nF/cm²), and V_G is the gate voltage.

2. Synthetic procedures

6-bromo-N-(2-decyltetradecyl)-isatin (2): To a solution of anhydrous potassium carbonate (4.9 g, 35.4 mmol) in anhydrous DMF (150 mL), 6-bromoisatin (4 g, 17.7 mmol) was added and heated at 100 °C under nitrogen atmosphere. After stirring for 30 min, 2-decyltetradecylbromide was added and refluxed further overnight. The reaction mixture was cooled to room temperature. The organic layer was extracted using methylene chloride (MC) and dried over MgSO₄. The compound was purified by column chromatography with MC/hexane (v/v = 9/1), giving **2** as an orange liquid (6.57 g, yield 66%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): δ 7.43 (d, J= 7.79 Hz, 1H), 7.24 (d, J1= 8.24 Hz, 1H), 7.01 (s, 1H), 3.55 (d, J= 7.79 Hz, 2H), 1.82 (m, 1H), 1.15-1.40 (m, 40H), 0.85 (t, J= 6.87, 6H); MS (EI, m/z): calcd. for C₃₂H₅₂BrNO₂ 562.68; found 561.30 [M-H]⁺.

Dibromo-QuBT (3) : Concentrated sulfuric acid (0.1 mL) was added slowly to a rapidly stirring solution of 6-bromo-N-(2-decyltetradecyl)-isatin (1.148 g, 2.04 mmol) and thiophene (0.34 g, 4.08 mmol) in benzene (20 mL). After stirring at room temperature for 3 h, DI water (50mL) was added and the product was extracted using chloroform. The organic layer was dried over MgSO₄. The compound was purified by column chromatography with chloroform/hexane (v/v = 1:1), giving **3** as a blue sticky liquid (474 mg, yield 36 %). Subsequently, preparative TLC was performed for further increase purity with chloroform/hexane (v/v = 1:1). MS (MALDI-TOF, m/z): calcd. for C₇₂H₁₀₈Br₂N₂O₂S₂, 1257.6; found, 1257.0 [M]⁺.

PQuBTV : Dibromo-QuBT (162.7 mg, 129 μmol) and trans-1,2-bis(tri-n-butylstannyl)ethylene (78.19 mg, 129 μmol) were dissolved in 8 mL of degassed toluene. Pd₂(dba)₃ (2 mg, 2 mol%) and P(o-tol)₃ (2.6 mg, 8 mol%) were added to a two-neck flask under nitrogen, and the mixture was stirred at 110 °C for 60 h. After polymerization, the reaction mixture was added to a 200 mL methanol/HCl solution (1:1 v/v) and stirred overnight. The polymer was purified via Soxhlet extraction with methanol, acetone, and hexane. The hexane solution was concentrated by evaporation, precipitated into methanol, and filtered off to give a dark blue solid PQuBTV (103 mg, yield 71%).

3. Optimized geometry of QuBTv dimer

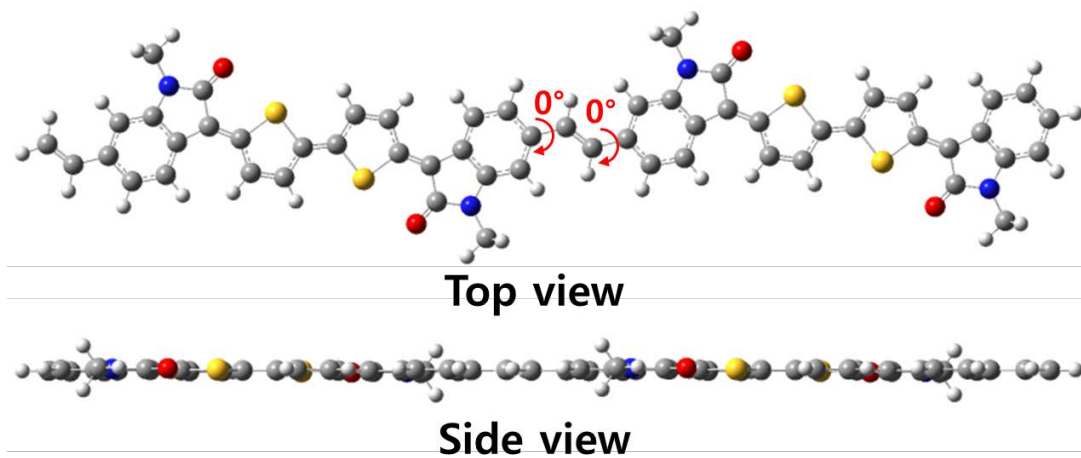


Figure S1. Optimized geometry of QuBTv dimer calculated by density functional theory (DFT).

4. Thermogravimetric analysis (TGA)

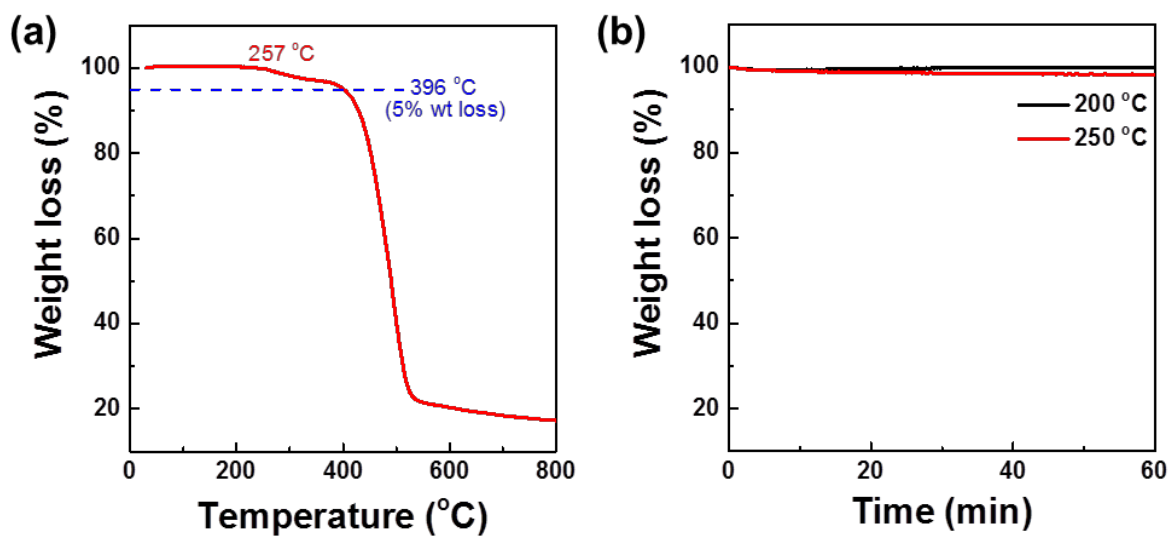


Figure S2. Thermogravimetric analysis (TGA) of PQuBTv (a) heating up to 800 °C (b) isothermal measurement for 60 min.

5. Differential scanning calorimetry (DSC)

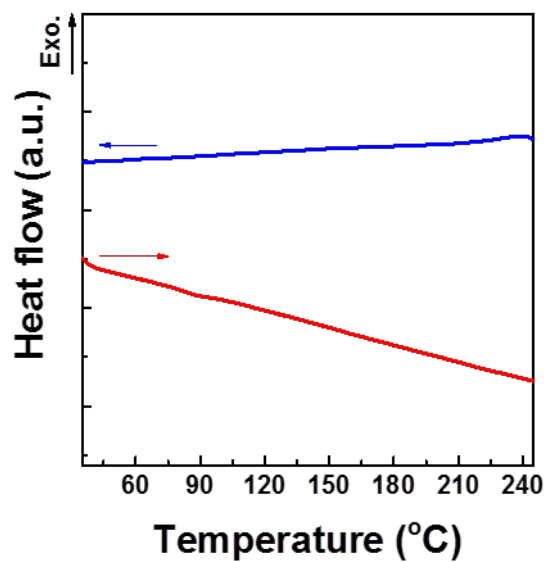


Figure S3. Differential scanning calorimetry (DSC) analysis of **PQuBTV**.

6. Atomic force microscopy (AFM)

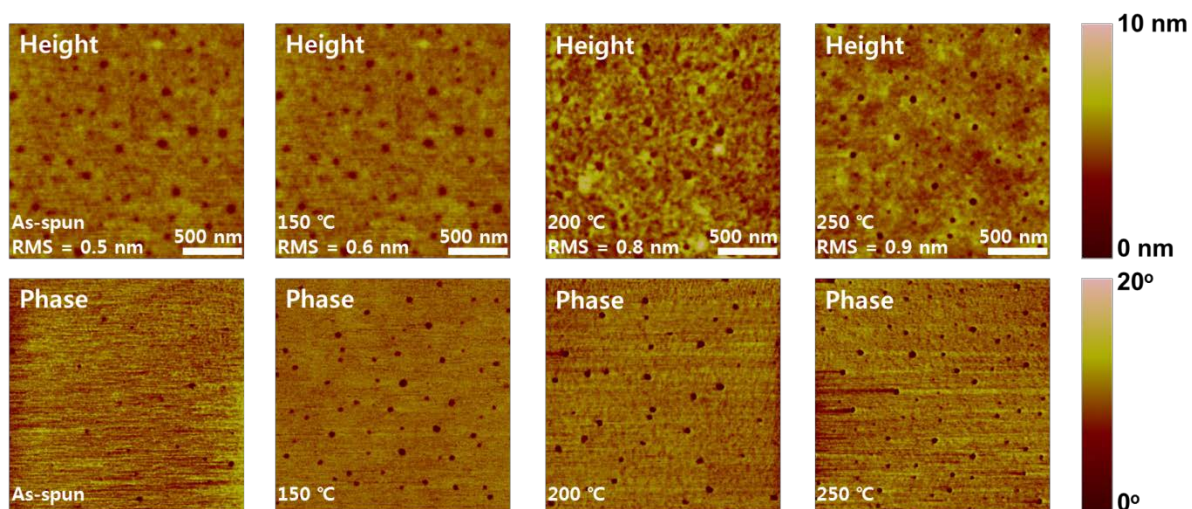


Figure S4. AFM height and phase images of **PQuBTV** thin films depending on annealing temperature ($2 \times 2 \mu\text{m}$).

7. NMR and MALDI spectra

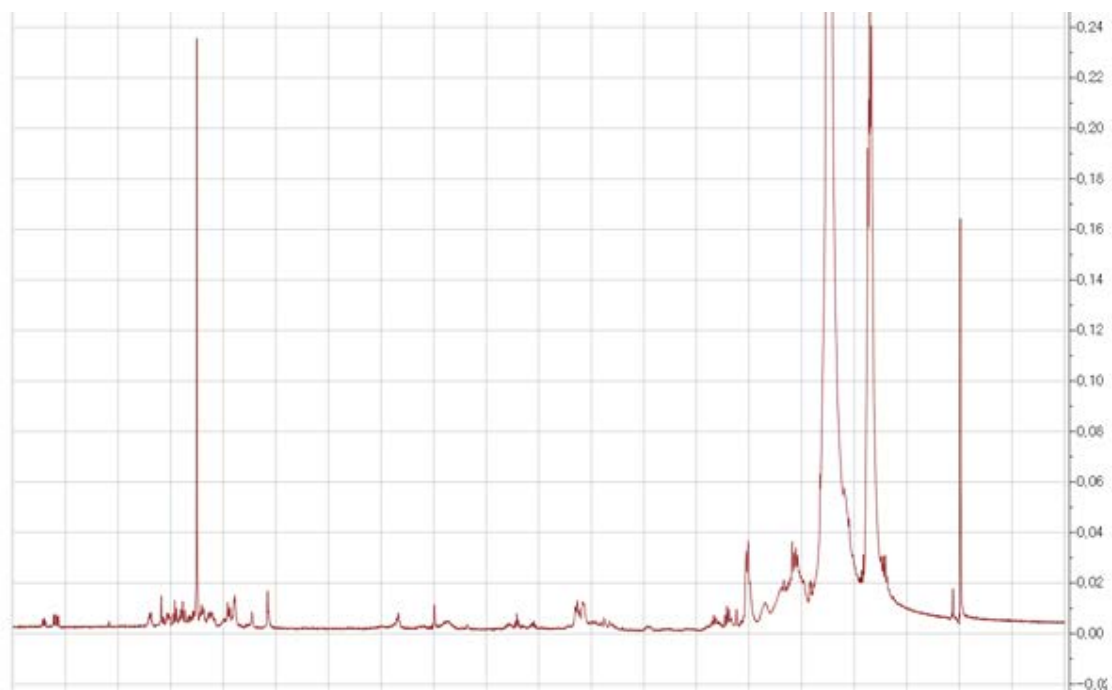


Figure S5. ¹H NMR spectra of *Dibromo-QuBT* (3).

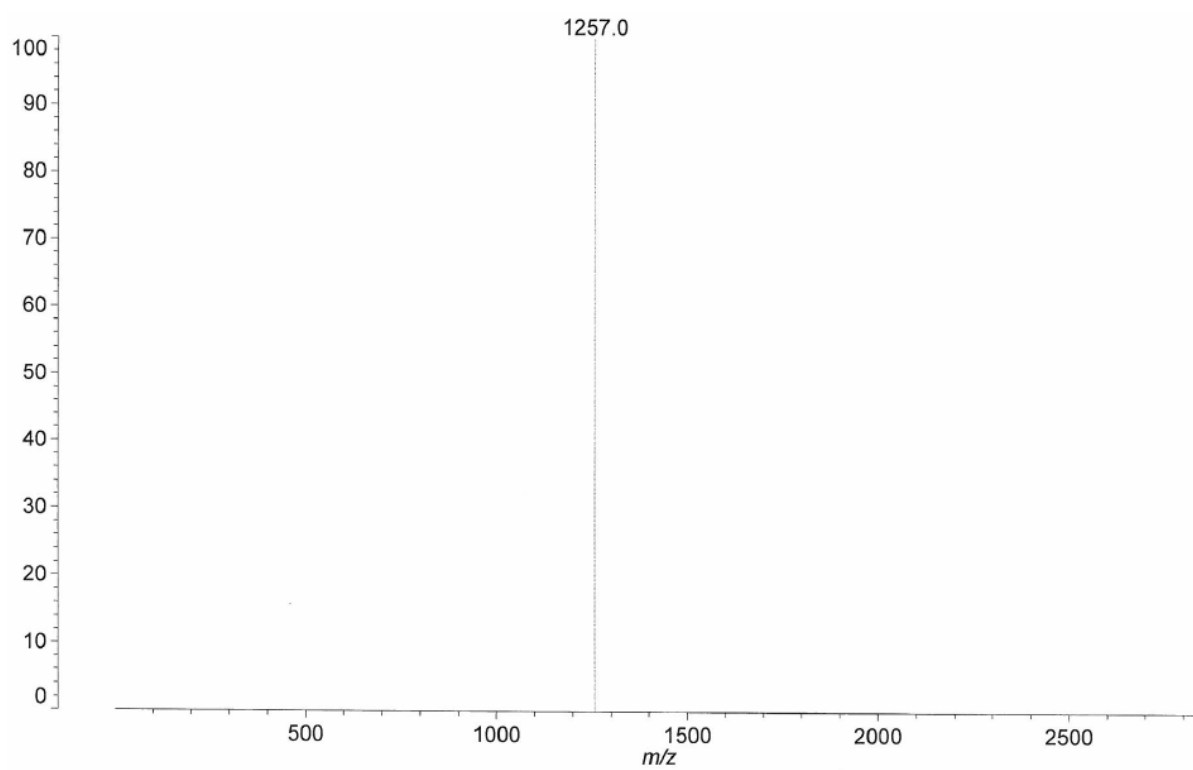


Figure S6. MALDI-TOF spectra of *Dibromo-QuBT* (3).

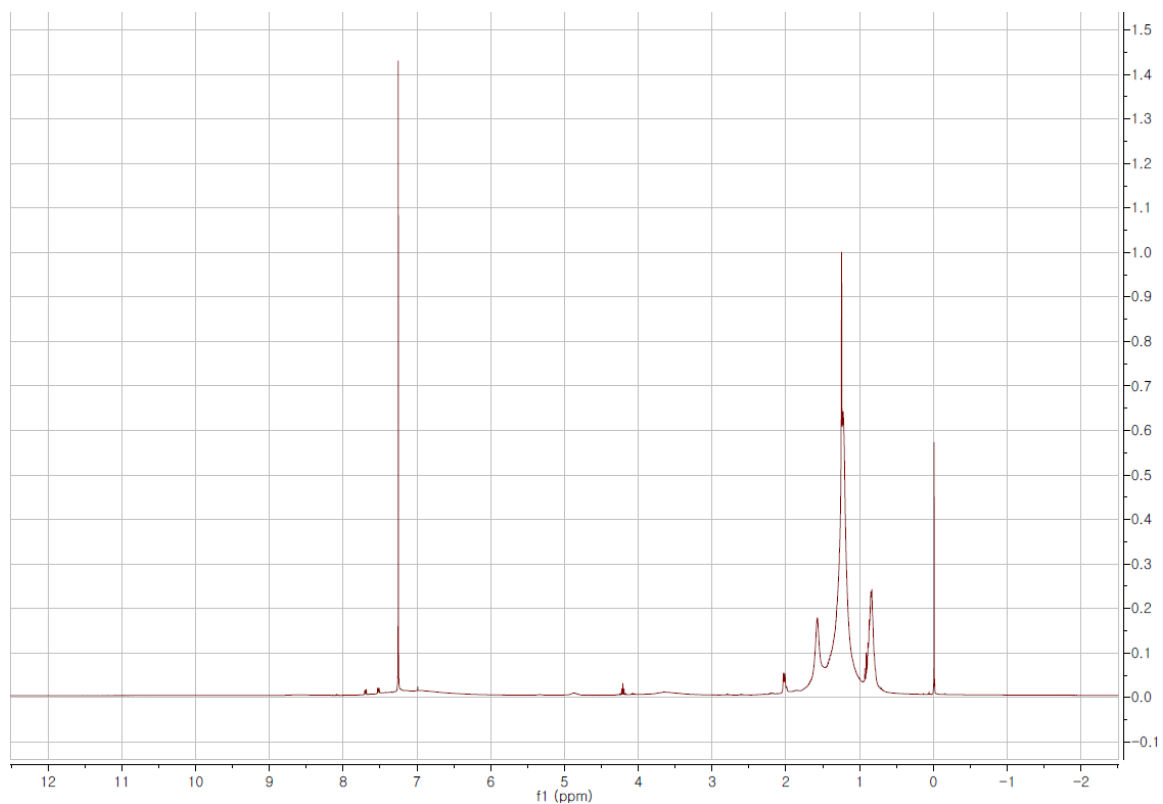


Figure S7. ¹H NMR spectra of PQuBTv.

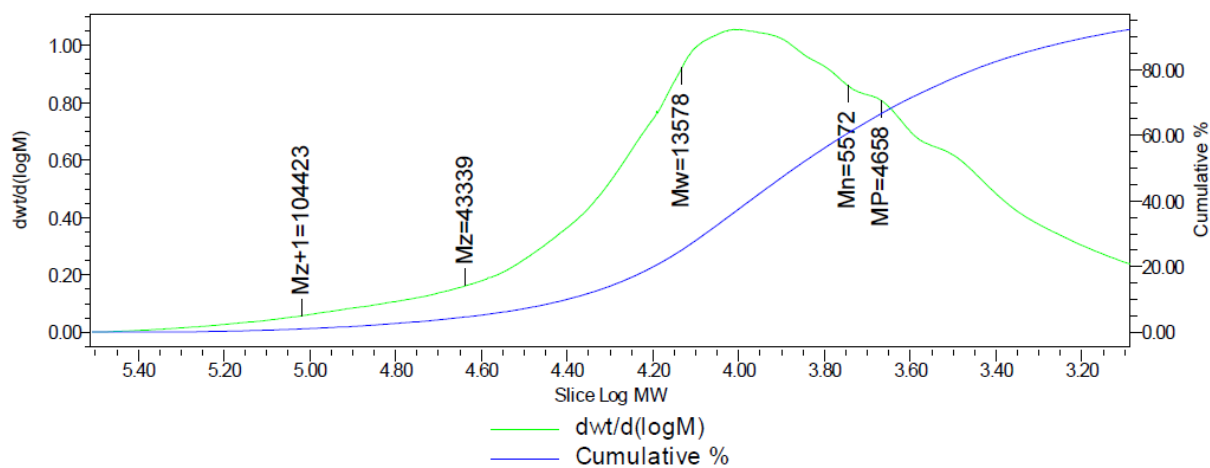


Figure S8. GPC trace of PQuBTv measured by using chloroform as an eluent with polystyrene as standards.

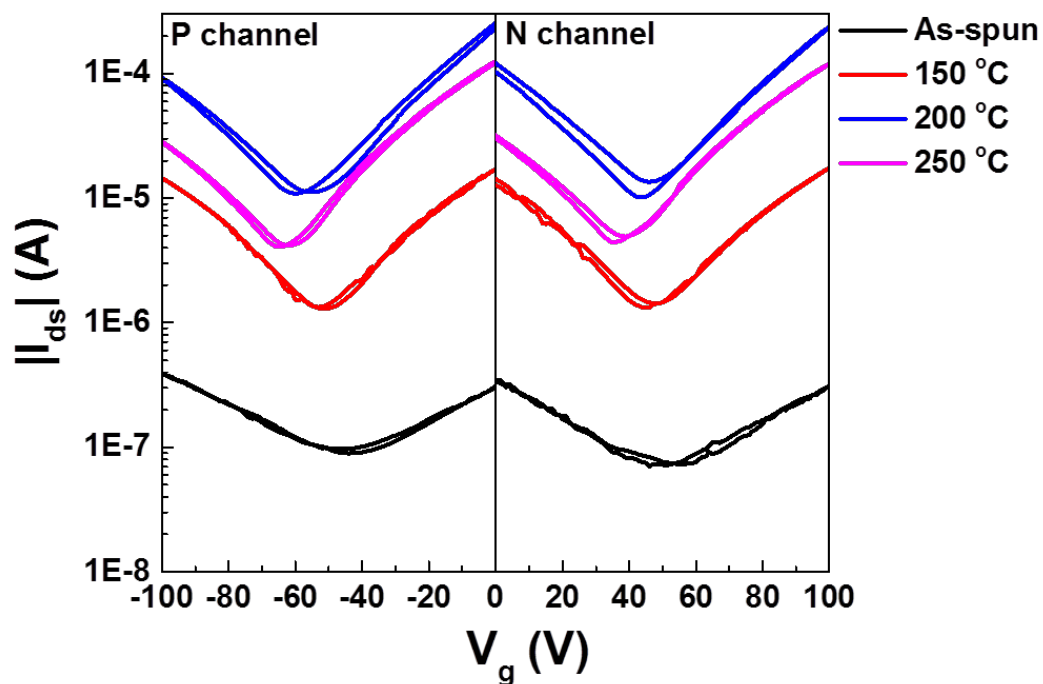


Figure S9. Transfer curve based on PQUBTV thin film depending on different annealing temperature.

Table S1. Average mobilities depending on different annealing temperature

	P channel		N channel	
	average μ_h	std. dev.	average μ_e	std. dev.
As-spun	3.26E-04	4.58E-05	3.16E-04	3.70E-05
150 °C	1.93E-02	6.73E-03	1.78E-02	6.26E-03
200 °C	2.55E-01	1.18E-01	3.24E-01	9.55E-02
250 °C	5.56E-02	6.60E-03	1.92E-01	4.33E-02