

Synthesis of conjugated D-A polymers bearing bi(dithienogermole) as a new donor component and their applications to polymer solar cells and transistors

Joji Ohshita,^{a,*} Masayuki Miyazaki,^a Makoto Nakashima,^a Daiki Tanaka,^a Takuya Suzuki,^b Yoshihito Kunugi,^b Yasushi Morihara^c

^a Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

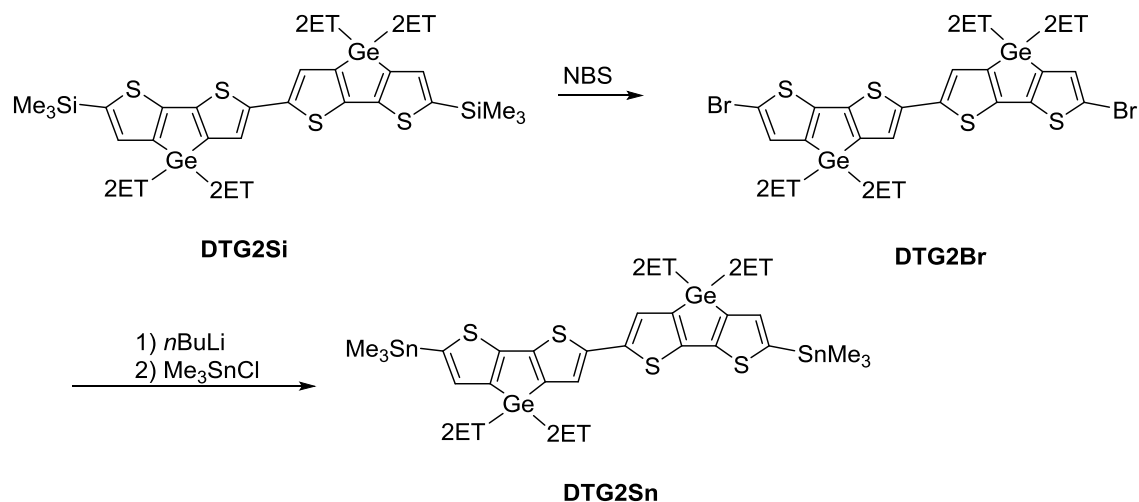
^b Department of Applied Chemistry, Faculty of Engineering, Tokai University, 4-1-1 Kitakaname, Hiratsuka 259-1292, Japan

^c Synthesis Research Laboratory, Kurashiki Research Center, Kuraray Co., Ltd., 2045-1 Sakazu, Kurashiki 710-0801, Japan

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Experimental Procedure for Monomer Preparation



Preparation of **DTG2Br**

To a solution of **DTG2Si** (1.889 g, 1.767 mmol) (see reference 8) in 40 mL of chloroform was added NBS (0.634 g, 3.56 mmol) in several portions at 0 °C and the mixture was stirred at room temperature overnight. The resulting mixture was poured into 200 mL of water. The organic layer was separated and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was subjected to silica gel column chromatography using hexane as the eluent to provide 1.444 g (75% yield) of **DTG2Br** as a diastereomeric mixture: viscous orange oil; ^1H NMR (δ in CDCl_3 , 500 MHz) 7.07 (s, 2H), 6.987 (s, 0.5H), 6.989 (s, 1H), 6.991 (s, 0.5H), 1.49 (sept, 4H, $J = 6.0$ Hz), 1.33-1.12 (m, 40H), 0.86-0.78 (m, 24H); ^{13}C NMR (δ in CDCl_3 , 125 MHz); 146.71, 146.68, 146.65, 144.51, 144.41, 144.30, 143.98, 143.96, 143.94, 143.91, 143.80, 143.69, 138.12, 132.44, 125.91, 110.78, 110.77, 110.76, 36.93, 35.44, 35.41, 28.91, 28.88, 28.74, 28.71, 23.00, 20.76, 20.73, 14.12, 10.87, 10.84; HR-MS (APCI) Calcd: $[\text{M}^+]$ 1082.13017, Found: 1082.12784.

Preparation of DTG2Sn

To a solution of 0.616 g (0.569 mmol) of **DTG2Br** in 30 mL of diethyl ether was added slowly 0.70 mL (1.1 mmol) of a 1.64 M *n*-BuLi solution in hexane at -80 °C and the mixture was stirred for 30 min at this temperature. To this was added 0.458 g (2.298 mmol) of trimethyltin chloride and the resulting mixture was stirred overnight at room temperature. After quenching the reaction with ice-water, the organic layer was separated and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was subjected to preparative GPC eluting with toluene to give 0.248 g (35% yield) of **DTG2Sn**: ¹H NMR (δ in CDCl₃, 500 MHz) 7.08 (br s, 2H), 7.06 (s, 2H), 1.45-1.55 (m, 4H), 1.36-1.15 (m, 40H), 0.84-0.78 (m, 24H), 0.38 (s, 18H); ¹³C NMR (δ in CDCl₃, 125 MHz) 152.05, 152.03, 152.02, 145.27, 145.13, 144.99, 144.94, 144.89, 144.85, 144.59, 144.55, 144.50, 137.91, 137.78, 137.76, 137.75, 137.73, 137.71, 125.85, 36.98, 36.92, 35.44, 35.38, 28.94, 28.84, 28.76, 28.74, 23.04, 23.02, 20.69, 20.61, 20.59, 14.19, 10.89, 10.88, -8.166; HR-MS (APCI) Calcd: [M⁺] 1254.23874, Found: 1254.23505.

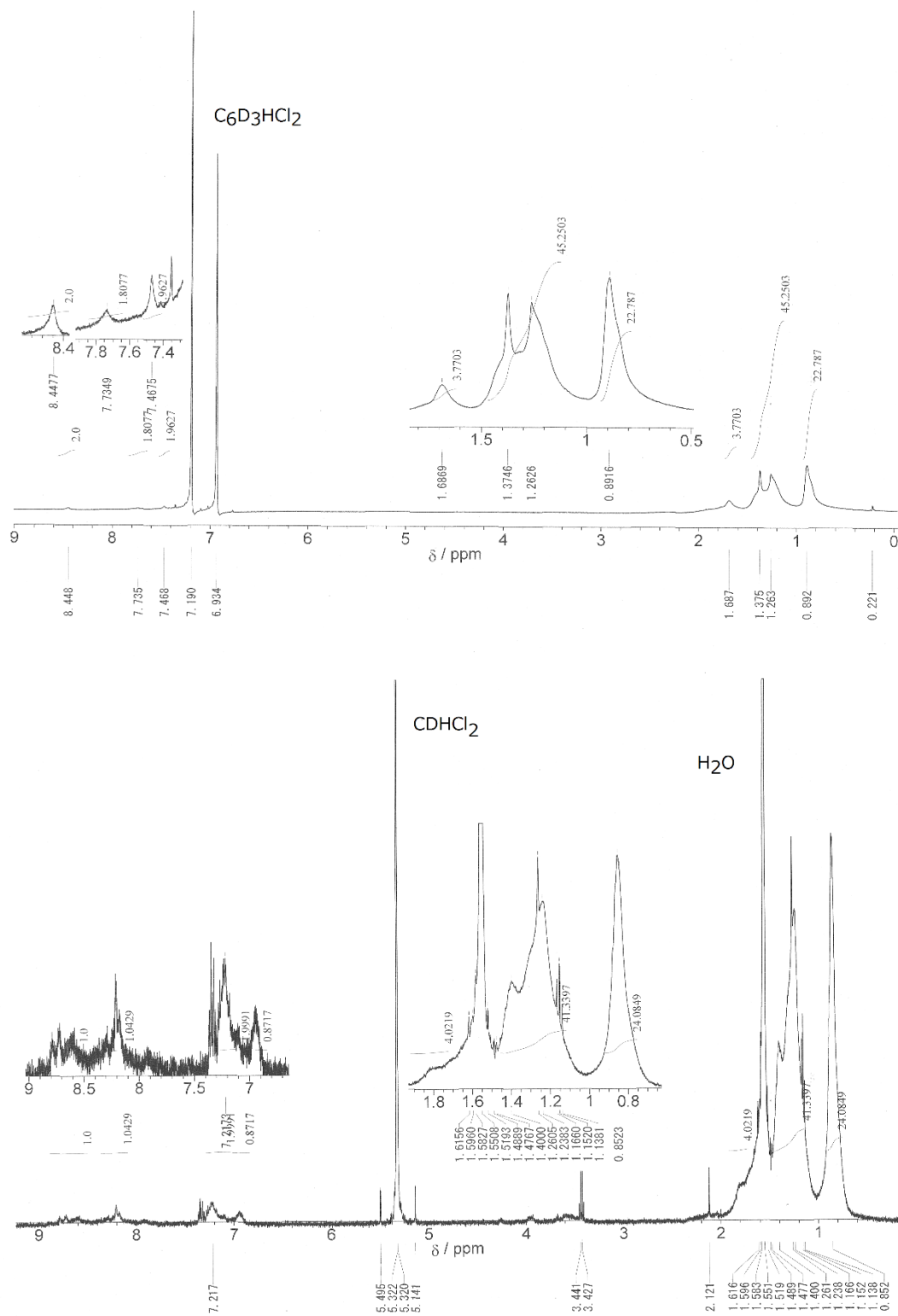


Fig. S-1 1H NMR spectra of **pDTG2-BT** (top) and **pDTG2-PT** (bottom).

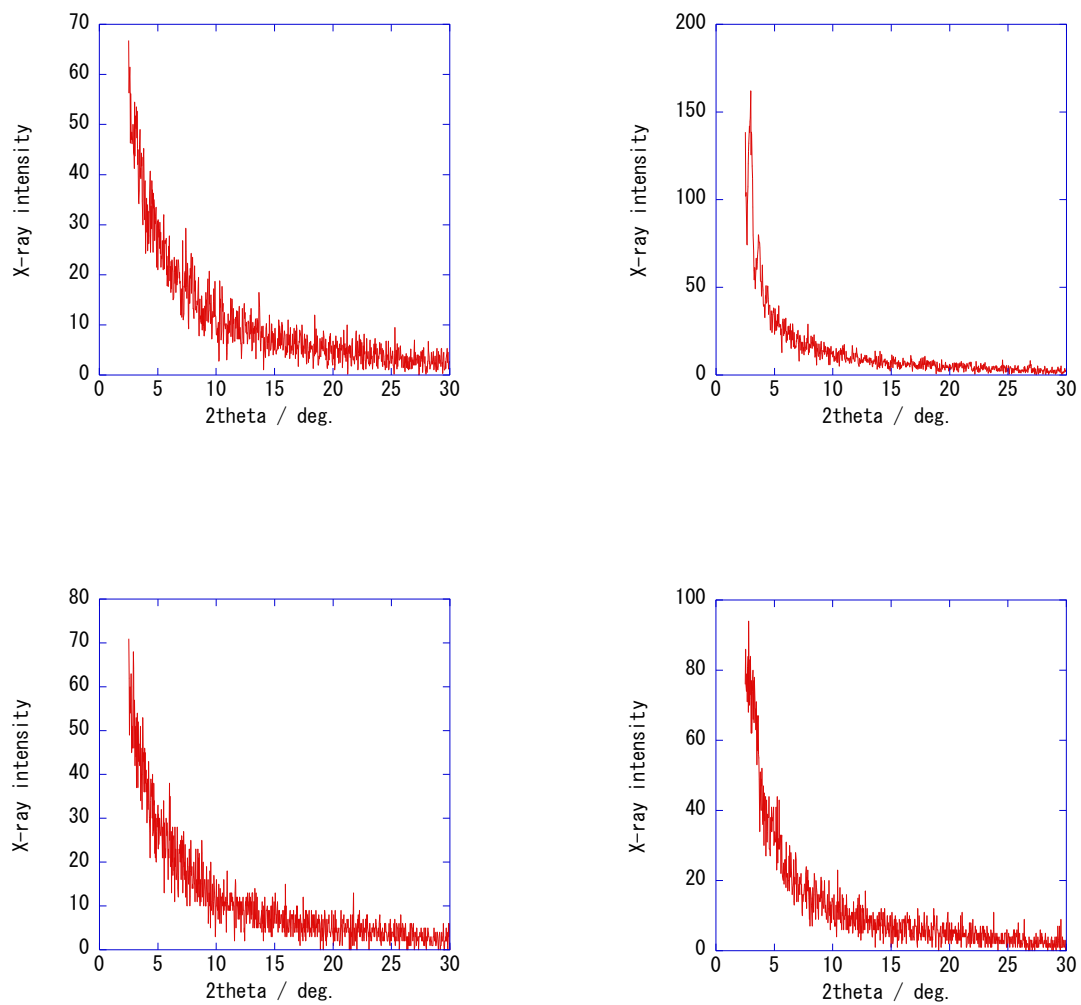


Fig. S-2 XRD patterns of **pDTG2-BT** (*top*) and **pDTG2-PT** (*bottom*) films, before (*left*) and after annealing (*right*) at 100 °C.

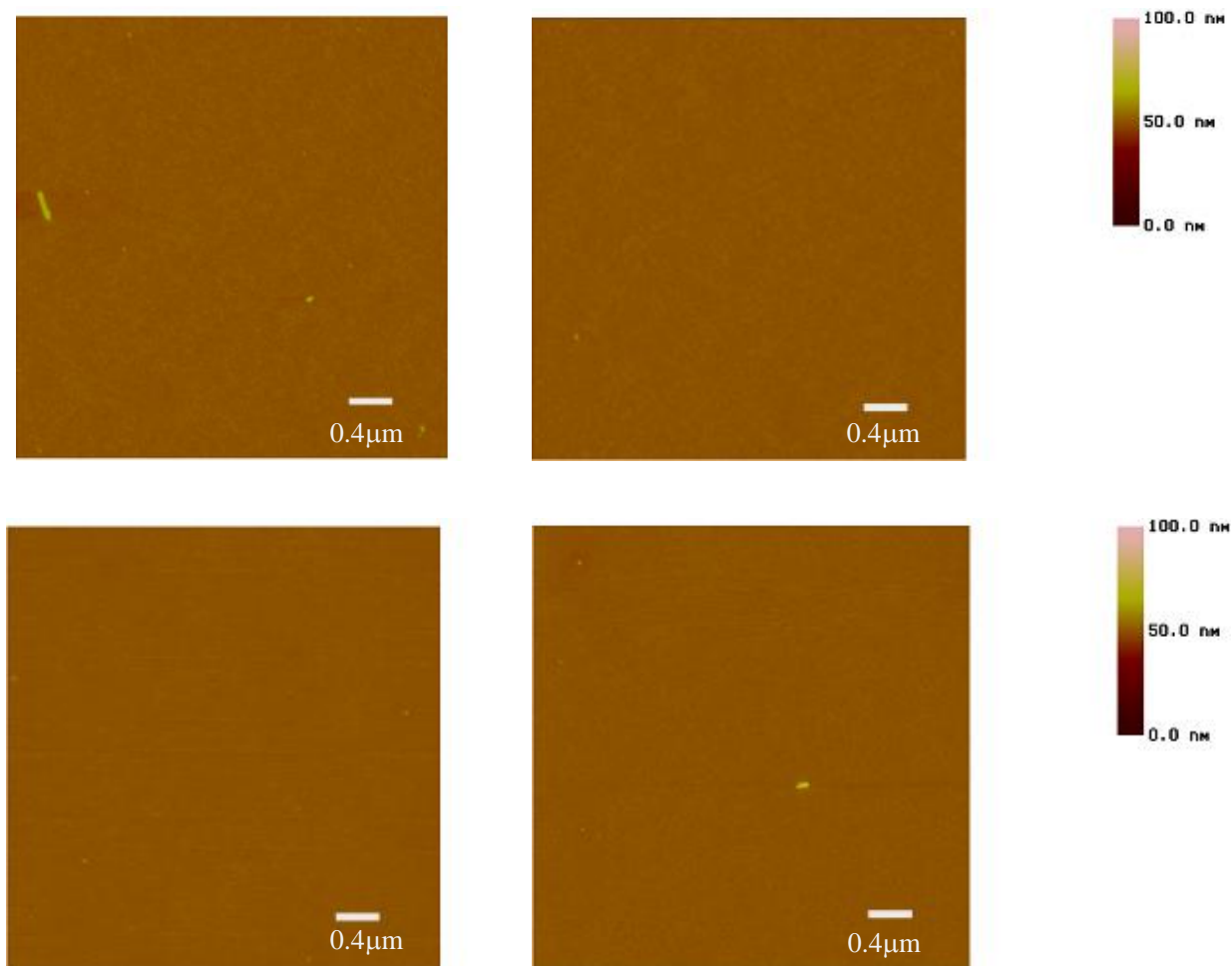


Fig. S-3 AFM images of **pDTG2-BT** (*top*) and **pDTG2-PT** (*bottom*) films, before (*left*) and after annealing (*right*) at 100 °C.

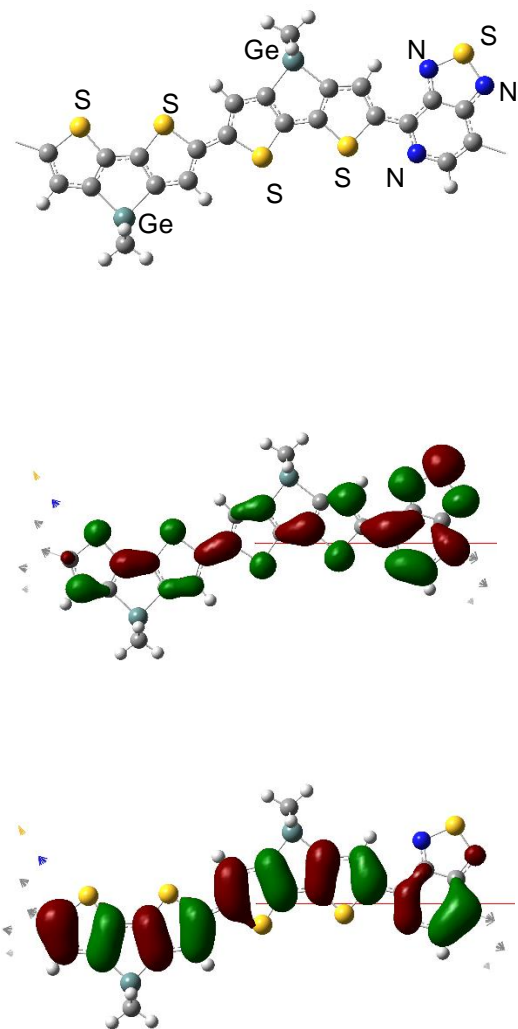


Fig. S-4 Optimized geometry (*top*), and LUMO (*middle*) and HOMO (*bottom*) profiles of unit cell of model polymer **pDTG2-PT0** with methyl groups on Ge atoms, derived from DFT calculations at B3LYP/6-31G(d).

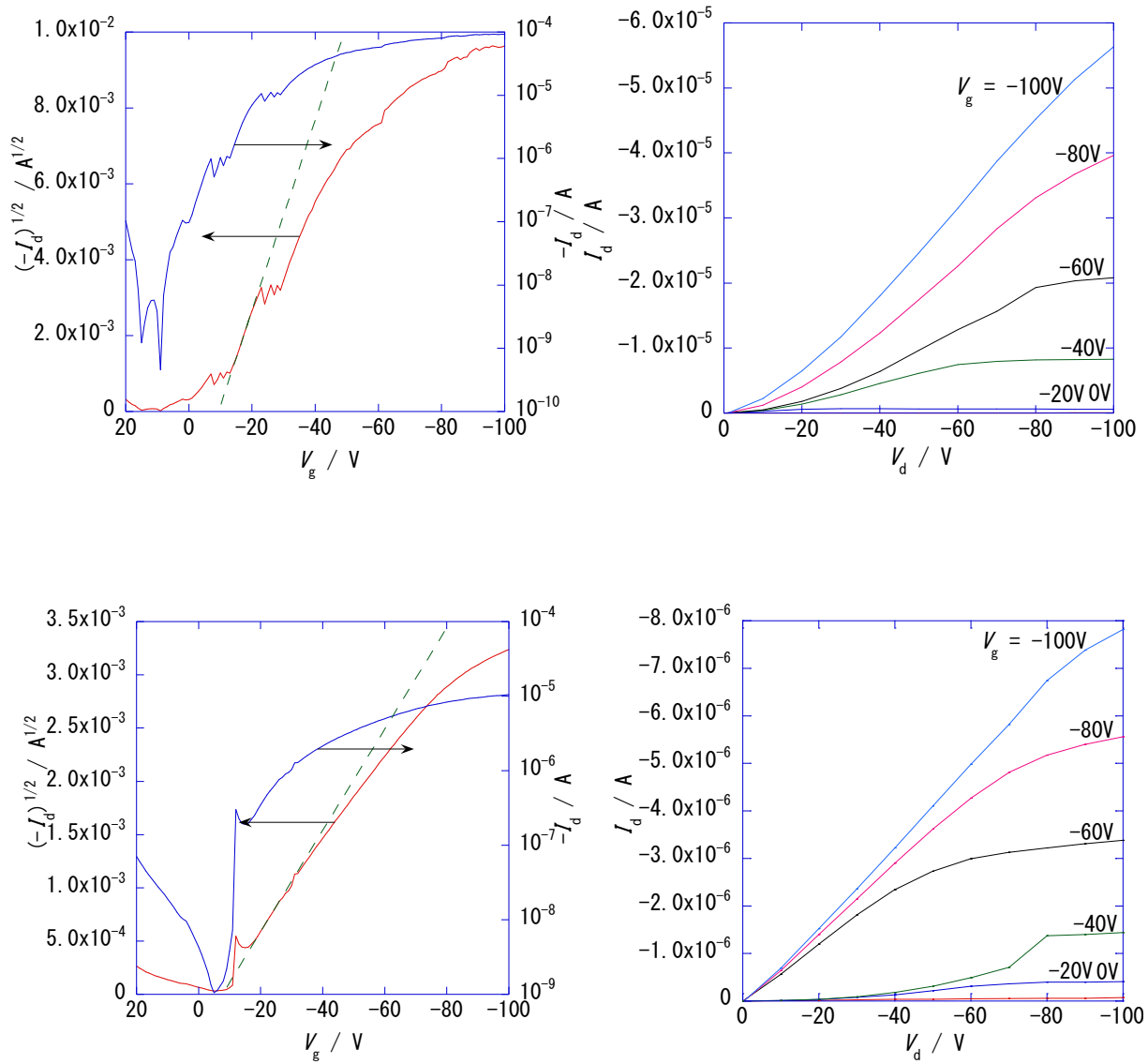


Fig. S-5 Response curves of TFTs with **pDTG2-BT** (*top*) and **pDTG2-PT** (*bottom*).