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Supporting Information

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Oligo(2,6-Anthrylene)s: Acene-Oligomer Approach for Organic Field-Effect Transistors

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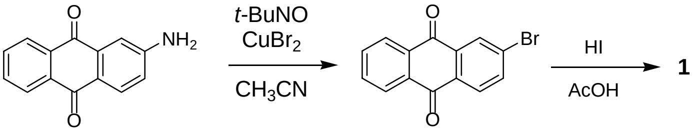
Supporting Information

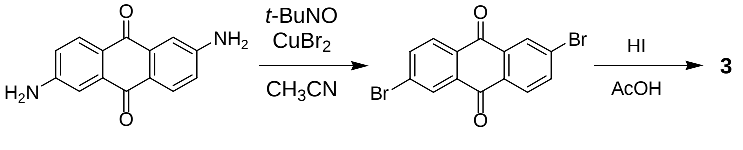
General. Melting points were obtained on a Büchi melting point apparatus B-540. ^{1}H NMR spectra were recorded on a JEOL JNM-LA 500 at 500 MHz. Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane. EI mass spectra were collected on a Shimadzu GCMS-QP5050A at 70 eV. MALDI-TOF mass spectra were obtained on a Perseptive Biosystems Voyager NESTR with dithranol matrix in positive ion mode. UV-vis spectra were recorded on a JASCO V-570 spectrophotometer. Emission spectra were collected on a JASCO FP-6600 spectrofluorophotometer. The calorimetric data were obtained on a TA Instruments DSC 2920 at a scanning rate 10 °C min^{-1} under a flow (50 mL min^{-1}) of argon. Cyclic and differential pulse voltammetries were recorded on a BAS-100B/W electrochemical analyzer. Analytical TLCs were performed on commercial Merck plates coated with silica gel 60 F254. Flash chromatographic separations were carried out on Fuji Silysia FL60D.

Materials. Hydriodic acid, 2-aminoanthraquinone, 2,6-diaminoanthraquinone, *t*-butyl nitrite, bis(pinacolato)diboron, $PdCl_2(dppf)(CH_2Cl_2)$, anhydrous DMSO, 9-BBN in THF, 1-hexene, and potassium phosphate were purchased from Sigma-Aldrich Co. and used without further purification. Anhydrous acetonitrile and THF were used as received from Kanto Chemicals. Copper(II) bromide, hypophosphorous acid, and tetrakis(triphenylphophine)palladium(0) were purchased from Nacalai Tesque and used without further purification.



2-Bromoanthraquinone. General Procedure for the Sandmeyer Reaction.[1] A 500-mL, three-necked, round-bottomed flask equipped with a reflux condenser and a gas outlet tube was charged with anhydrous copper(II) bromide (12.0 g, 53.8 mmol), *t*-butyl nitrite (6.90 g, 67.2 mmol), and anhydrous acetonitrile (160 mL). The mixture was heated to 65 °C, and 2-aminoanthraquinone (10.0 g, 44.8 mmol) was slowly added over a period of 5 min. After complete gas evolution, the reaction mixture was cooled to room temperature and poured into 6 M HCl (500 mL). The precipitate was filtered and washed with water and ethanol. Purification by sublimation (0.1 torr, 200 °C) gave 2-bromoanthraquinone (11.3 g, 88%) as a yellow solid. This material was used for the next reaction without further purification: ^1H NMR ($CDCl_3$) δ 7.82–7.84 (m, 2H), 7.93 (dd, J = 1.95 and 8.30 Hz, 1H), 8.18 (d, J = 8.05 Hz, 1H), 8.30–8.33 (m, 2H), 8.44 (d, J = 1.95 Hz, 1H); MS (EI) *m/z* 286, 287, 288, 289 (M^+, 100, 27.5, 88.4, 17.6), 258, 259, 260, 261 (M^+ – CO, 43.2, 9.3, 40.2, 5.8), 230, 231, 232 (M^+ – 2CO, 30.7, 6.9, 25.2), 207, 208 (M^+ – Br, 32.3, 7.9), 179, 180 (M^+ – Br – CO, 20.7, 5.7), 150, 151, 152 (M^+ – Br – 2CO, 73.9, 85.4, 15.2).

2-Bromoanthracene (1). General Procedure for the Reduction of Anthraquinones.[2] A mixture of 2-bromoanthraquinone (7.90 g, 27.5 mmol), acetic acid (600 mL), 57% hydriodic acid (60 mL), and hypophosphorous acid (30 mL) was refluxed for 16 h. The mixture was cooled to room temperature and poured into ice-water. The precipitate was filtered and washed with water and ethanol. Recrystallization from ethanol gave **1** (3.00 g, 42%) as pale yellow crystals. This material contained a small amount of 2-iodoanthracene and was used for the next reaction without further purification: ^1H NMR ($CDCl_3$) δ 7.46–7.51 (m, 3H), 7.87 (d, J = 9.15 Hz, 1H), 7.98–8.01 (m, 2H), 8.17 (s, 1H), 8.39 (s, 1H), 8.42 (s, 1H); MS (EI) *m/z* 256, 258 (M^+, 45.7, 60.0), 177, 178 (M^+ – Br, 100, 26.1).



2,6-Dibromoanthraquinone.[3] The general procedure for the Sandmeyer reaction described above was followed using 2,6-diaminoanthraquinone (8.60 g, 36.1 mmol), anhydrous copper(II) bromide (19.4 g, 86.9 mmol), *t*-butyl nitrite (11.3 g, 109 mmol), and anhydrous acetonitrile (150 mL). Purification by sublimation (0.1 torr, 200 °C) gave 2,6-dibromoanthraquinone (10.9 g, 82%) as a yellow solid. This material was used for the next reaction without further purification: ^{1}H NMR ($CDCl_3$) δ 7.94 (dd, *J* = 2.15 and 8.25 Hz, 2H), 8.17 (d, *J* = 8.25 Hz, 2H), 8.44 (d, *J* = 2.15 Hz, 2H); MS (EI) *m/z* 364, 365, 366, 367, 368, 369 (M^+, 54.2, 14.1, 92.3, 17.5, 49.7, 7.4), 336, 338, 340 (M^+ – CO, 9.3, 19.1, 9.3), 308, 310, 312 (M^+ – 2CO, 6.5, 14.7, 7.2), 285, 286, 287, 288 (M^+ – Br, 30.0, 24.6, 31.7, 23.2), 257, 258, 259, 260 (M^+ – Br – CO, 11.3, 10.0, 11.5, 9.3), 229, 230, 231, 232 (M^+ – Br – 2CO, 22.3, 13.2, 21.9, 7.2), 150, 151 (M^+ – 2Br – 2CO, 100, 31.9).

2,6-Dibromoanthracene (3). The general procedure for the reduction of anthraquinones described above was followed using 2,6-dibromoanthraquinone (4.40 g, 12.0 mmol), acetic acid (250 mL), 57% hydriodic acid (25 mL), and hypophosphorous acid (12 mL). The reaction mixture was refluxed for 5 days. Recrystallization from toluene gave **3** (3.30 g, 82%) as pale yellow crystals. This material contained a small amount of 2-bromo-6-iodoanthracene and was used for the next reaction without further purification: ^{1}H NMR (DMSO-d_6) δ 7.70 (d, *J* = 8.85 Hz, 2H), 8.13 (d, *J* = 8.85 Hz, 2H), 8.46 (s, 2H), 8.67 (s, 2H); MS (EI) *m/z* 334, 336, 337, 338, 339 (M^+, 63.0, 100, 21.4, 64.4, 10.7), 255, 257 (M^+ – Br, 27.4, 25.9), 176, 177 (M^+ – 2Br, 77.5, 16.1).

2-Anthracen-2-yl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2). General Procedure for the Arylboronate Synthesis.[4] A 100-mL, three-necked, round-bottomed flask fitted with Ar inlet and rubber septum was charged with **1** (1.00 g, 3.89 mmol), bis(pinacolato)diboron (1.19 g, 4.67 mmol), $PdCl_2(dppf)(CH_2Cl_2)$ (95 mg, 0.12 mmol), and potassium acetate (1.15 g, 11.7 mmol). After anhydrous DMSO (30 mL) was introduced into the flask with a syringe, the mixture was stirred at 80 °C for 24 h. To the resulting solution was added water, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried with $MgSO_4$, and filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was chromatographed over silica gel with *n*-hexane/CH_2Cl_2 (1:1) to provide **2** (806 mg, 68%) as a pale yellow solid: Mp 143–144 °C; ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 12H), 7.46–7.48 (m, 2H), 7.78 (d, *J* = 8.55 Hz, 1H), 7.98 (d, *J* = 8.55 Hz, 1H), 8.01 (t, *J* = 8.85 Hz, 2H), 8.41 (s, 1H), 8.48 (s, 1H), 8.57 (s, 1H); MS (EI) *m/z* 303, 304, 305 (M^+, 46.9, 100, 37.9), 203, 204, 205 (M^+ – $C_6H_{12}O$, 39.6, 84.4, 34.7). Anal. Calcd for $C_{20}H_{21}BO_2$: C, 78.97; H, 6.96. Found:

C, 78.75; H, 7.01.

[2,2']Bianthracenyl (2A). General Procedure for the Suzuki Coupling Reaction. To the suspension of **1** (682 mg, 2.65 mmol) and **2** (806 mg, 2.65 mmol) in toluene (100 mL) was added 1 M Na_2CO_3 (20 mL). The mixture was degassed and purged with Ar for 5 min. Tetrakis(triphenylphophine)palladium(0) (153 mg, 0.133 mmol) was added, and the system was degassed again. The mixture was refluxed for 3 days and allowed to cool to room temperature. The precipitate was filtered and washed with water, ethanol, acetone, and hot toluene. The dark green solid was dissolved in hot 1,2-dichlorobenzene and filtered. The yellow filtrate was evaporated to dryness under reduced pressure. The residue was purified by train sublimation[5] (300 °C) to give **2A** (329 mg, 35%) as bright yellow crystals: Mp 374 °C (DSC); MS (EI) *m/z* 354, 355 (M^+, 100, 31.1), 177 (M^{2+}, 49.7). Anal. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 94.59; H, 5.34.

[2,2';6',2'']Teranthracene (3A). The general procedure for the Suzuki coupling reaction described above was followed using **3** (288 mg, 0.857 mmol), **2** (600 mg, 1.97 mmol), tetrakis(triphenylphophine)palladium(0) (114 mg, 0.0986 mmol), toluene (300 mL), and 1 M Na_2CO_3 (30 mL). The mixture was refluxed for 10 days. The precipitate was filtered and washed with water, ethanol, acetone, hot toluene, and hot 1,2-dichlorobenzene. The dark green solid was dissolved in hot 1,2,4-trichlorobenzene and filtered. The filtrate was evaporated to dryness under reduced pressure. The yellow solid was purified by train sublimation (420 °C) to give **3A** (60 mg, 13%) as bright yellow crystals: Mp 490 °C (DSC); MS (MALDI-TOF) *m/z* 530, 531, 532, 533 (M^+, 100, 75.2, 23.9, 4.3). Anal. Calcd for $C_{42}H_{26}$: C, 95.06; H, 4.94. Found: C, 95.02; H, 4.93.

2-Bromo-6-hexylanthracene (4) and 2,6-Dihexylanthracene (5).[6] To 0.5 M 9-BBN in THF (37.0 mL, 18.5 mmol) was added 1-hexene (1.56 g, 18.5 mmol) at 0 °C, and the mixture was stirred at room temperature for 6 h. A 1-L, three-necked, round-bottomed flask fitted with Ar inlet and rubber septum was charged with **3** (6.20 g, 18.5 mmol), $PdCl_2(dppf)(CH_2Cl_2)$ (376 mg, 0.460 mmol), and potassium phosphate (5.89 g, 27.8 mmol). After anhydrous THF (1 L) was introduced into the flask, the mixture was vigorously stirred under reflux. To this mixture was added the above solution of 9-hexyl-9-BBN with a syringe. The reaction mixture was refluxed for 16 h. The resulting mixture was evaporated under reduced pressure, and the residue was dissolved in CH_2Cl_2. To this solution was added water, and the mixture was extracted with CH_2Cl_2.

The organic layer was washed with brine, dried with $MgSO_4$, and filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was purified by sublimation (0.1 torr, 200 °C) and recrystallization from hexane (1.8 L) to give a 37:63 mixture of **4** and **3** (515 mg). The filtrate was concentrated to 500 mL to afford a 90:10 mixture of **4** and **3** (525 mg). The filtrate was again concentrated to 100 mL to provide a 76:4:20 mixture of **4**, **3**, and **5** (1.35 g). The filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized from ethanol (10 mL) to give a 36:64 mixture of **4** and **5** (604 mg): **4** (1.91 g, 30 %) ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.00 Hz, 3H), 1.32–1.40 (m, 6H), 1.73 (m, 2H), 2.79 (t, *J* = 7.95 Hz, 2H), 7.35 (d, *J* = 8.80 Hz, 1H), 7.48 (d, *J* = 9.05 Hz, 1H), 7.73 (s, 1H), 7.85 (d, *J* = 9.30 Hz, 1H), 7.92 (d, *J* = 8.80 Hz, 1H), 8.14 (s, 1H), 8.27 (s, 1H), 8.30 (s, 1H); MS (EI) *m/z* 340, 341, 342, 343 (M^+, 100, 26.7, 92.2, 23.7), 269, 270, 271, 272 ($M^+ - C_5H_{11}$, 78.1, 34.2, 76.0, 32.7), 189, 190 ($M^+ - C_5H_{11}$ – Br, 69.9, 34.6). **5**: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.10 Hz, 3H), 1.31–1.40 (m, 6H), 1.73 (m, 2H), 2.78 (t, *J* = 7.80 Hz, 2H), 7.30 (d, *J* = 8.75 Hz, 2H), 7.71 (s, 2H), 7.90 (d, *J* = 8.75 Hz, 2H), 8.28 (s, 2H); MS (EI) *m/z* 346, 347 (M^+, 100, 29.1), 275, 276 ($M^+ - C_5H_{11}$, 48.3, 13.3), 204, 205 ($M^+ - 2C_5H_{11}$, 30.5, 10.5).

2-(6-Hexyl-anthracen-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (6). The general procedure for the arylboronate synthesis was followed using the above mixture (1.88 g) containing **4** in 80% (1.50 g, 4.40 mmol), bis(pinacolato)diboron (2.10 g, 8.27 mmol), $PdCl_2(dppf)(CH_2Cl_2)$ (180 mg, 0.220 mmol), potassium acetate (1.57 g, 16.0 mmol), and anhydrous DMSO (60 mL). Flash chromatography over silica gel with *n*-hexane/CH_2Cl_2 (1:1) provided **6** (1.15 g, 67%) as a pale yellow solid: Mp 134–135 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.10 Hz, 3H), 1.31–1.40 (m, 18H), 1.73 (m, 2H), 2.78 (t, *J* = 7.80 Hz, 2H), 7.32 (d, *J* = 8.75 Hz, 1H), 7.74 (s, 1H), 7.76 (d, *J* = 8.55 Hz, 1H), 7.94 (d, *J* = 8.55 Hz, 1H), 7.95 (d, *J* = 8.30 Hz, 1H), 8.30 (s, 1H), 8.42 (s, 1H), 8.54 (s, 1H); MS (EI) *m/z* 388, 389 (M^+, 100, 16.5), 317, 318 ($M^+ - C_5H_{11}$, 16.2, 6.0), 216, 217, 218 ($M^+ - C_5H_{11} - C_6H_{12}O$, 6.4, 18.6, 8.6). Anal. Calcd for $C_{26}H_{33}BO_2$: C, 80.41; H, 8.56. Found: C, 80.53; H, 8.65.

6,6'-Dihexyl-[2,2']bianthracenyl (DH-2A). The general procedure for the Suzuki coupling reaction described above was followed using a 36:64 mixture of **4** and **5** (355 mg), **6** (146 mg, 0.376 mmol), tetrakis(triphenylphophine)palladium(0) (22 mg, 0.019 mmol), toluene (15 mL), and 1 M Na_2CO_3 (3 mL). The mixture was refluxed for 24 h and cooled to room temperature. Ethanol (100 mL) was added to the mixture, and the precipitate was filtered and washed with water, ethanol, and acetone. The dark green solid was dissolved in hot toluene and filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was washed with CH_2Cl_2 and purified by train sublimation (310 °C) to give **DH-2A** (77 mg, 39%) as bright yellow crystals: Mp > 320 °C (dec); MS (EI) *m/z* 522, 523, 524 (M^+, 100, 42.7, 9.1), 451, 452 ($M^+ – C_5H_{11}$, 26.0, 10.3), 380, 381 ($M^+ – 2C_5H_{11}$, 26.2, 9.3). Anal. Calcd for $C_{40}H_{42}$: C, 91.90; H, 8.10. Found: C, 92.19; H, 8.02.

6,6''-Dihexyl-[2,2';6',2'']teranthracene (DH-3A). The general procedure for the Suzuki coupling reaction described above was followed using **3** (395 mg, 1.17 mmol), **6** (1.05 g, 2.71 mmol), and tetrakis(triphenylphophine)palladium(0) (157 mg, 0.136 mmol), toluene (300 mL), and 1 M Na_2CO_3 (60 mL). The mixture was refluxed for 3 days. The precipitate was filtered and washed with water, ethanol, acetone, hot toluene, and hot 1,2-dichlorobenzene. The yellow solid was dissolved in hot 1,2,4-trichlorobenzene and filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was purified by train sublimation (410 °C) to give **DH-3A** (113 mg, 14%) as bright yellow crystals: Mp > 420 °C (dec); MS (MALDI-TOF) *m/z* 698, 699, 700 (M^+, 100, 65.2, 19.3), 642, 643 ($M^+ – C_4H_9$, 17.7, 6.1), 627, 628, 629, 630 ($M^+ – C_5H_{11}$, 16.4, 53.1, 23.7, 10.9), 614, 615, 616 ($M^+ – C_6H_{13}$, 40.0, 18.6, 5.8), 556, 557, 558, 559 ($M^+ – 2C_5H_{11}$, 7.1, 13.7, 25.4, 7.3), 543, 544, 545 ($M^+ – C_5H_{11} – C_6H_{13}$, 10.6, 17.9, 5.2). Anal. Calcd for $C_{54}H_{50}$: C, 92.79; H, 7.21. Found: C, 92.97; H, 6.62.

Fabrications of OFETs. OFETs were constructed on heavily doped n-type silicon wafers (< 0.018 Ω cm) covered with 4000 Å-thick thermally grown silicon dioxide. The silicon dioxide acts as a gate dielectric layer, and the silicon wafer serves as a gate electrode. Anthracene oligomers were deposited on the silicon dioxide by vacuum evaporation at a rate of 0.3–0.5 Å s^{-1} under pressure of 10^{-4} Pa. The thickness of the semiconductor layer was 500 Å. During the evaporation, the temperature of the substrate was maintained by heating a copper block on which the substrate was mounted. Gold was used as source and drain electrodes and deposited on the organic semiconductor layer through a shadow mask with a channel width (W) of 1000 μm and a channel length (L) of 100 μm. Finally, the device was encapsulated using a glass cover and an epoxy resin under nitrogen. The electrical measurements were performed at room temperature with Hewlett-Packard 4140A and 4140B models.

X-ray Diffraction Studies. X-ray diffraction (XRD) measurements were carried out with a JEOL JDX-3530 X-ray diffractometer system. XRD patterns were obtained using Bragg-Brentano geometry (θ–2θ) with Cu Kα radiation as an X-ray source with an acceleration voltage of 40 kV and a beam current of 30 mA.

AFM Studies. AFM measurements were made in air using a Digital Instruments Nanoscope III in tapping mode.

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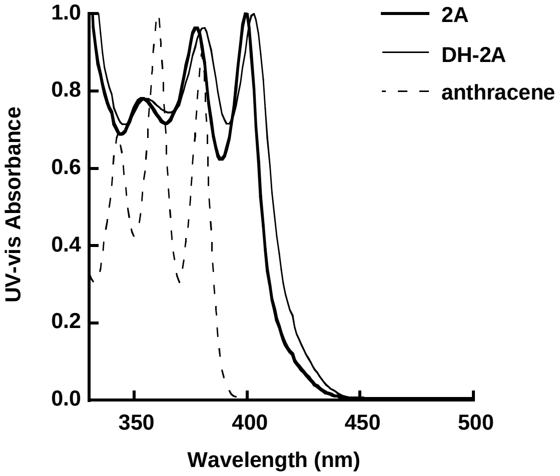

Figure 1. Absorption spectra of **2A**, **DH-2A**, and anthracene in 1,2-dichlorobenzene.

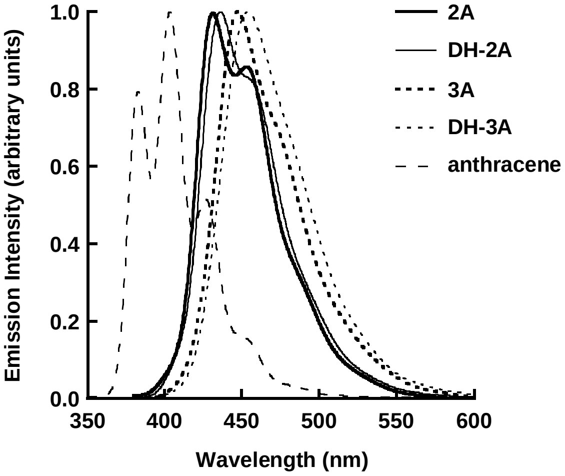

Figure 2. Emission spectra of **2A**, **DH-2A**, **3A**, **DH-3A**, and anthracene in $CHCl_3$.

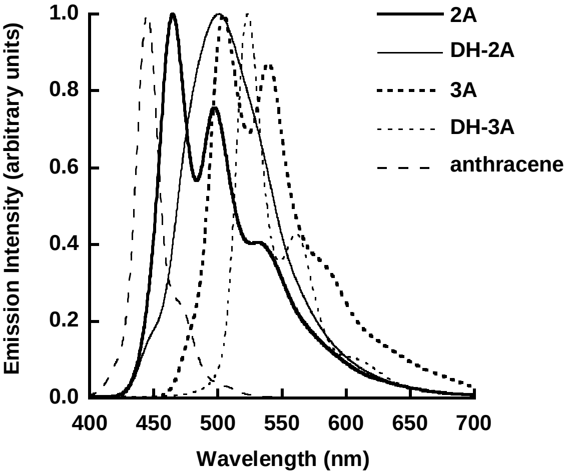

Figure 3. Emission spectra of **2A**, **DH-2A**, **3A**, **DH-3A**, and anthracene in the solid state.

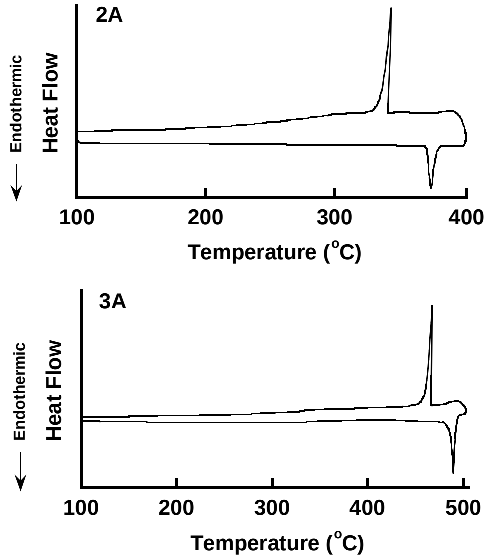

Figure 4. DSC traces of **2A** and **3A**. The heating rate is 10 °C min^{-1}, and the cooling rate is 40 °C min^{-1}.

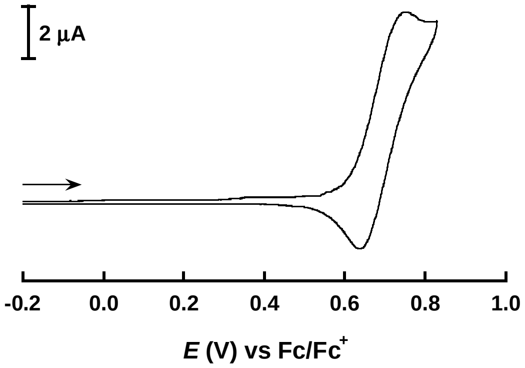

Figure 5. Cyclic voltammogram of **DH-2A**. Conditions: scan rate, 100 mV s^{-1}; 0.1 M (n-Bu)$_4$PF$_6$ in 1,2-dichlorobenzene; working electrode, Pt disk (1-mm diameter); counter electrode, Pt wire; reference electrode, Ag/0.01 M AgNO$_3$ and 0.1 M (n-Bu)$_4$NClO$_4$ in CH$_3$CN.

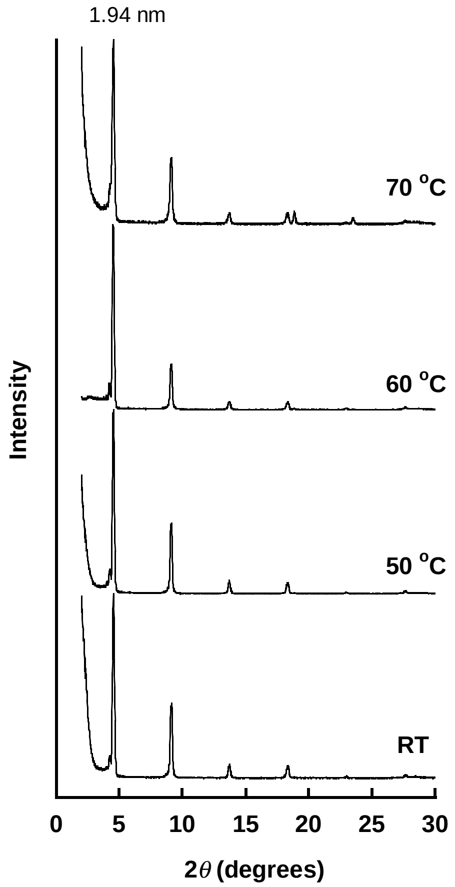

Figure 6. X-ray diffractograms of **2A** films on SiO_2/Si fabricated at T_{sub} = room temperature, 50, 60, and 70 °C.

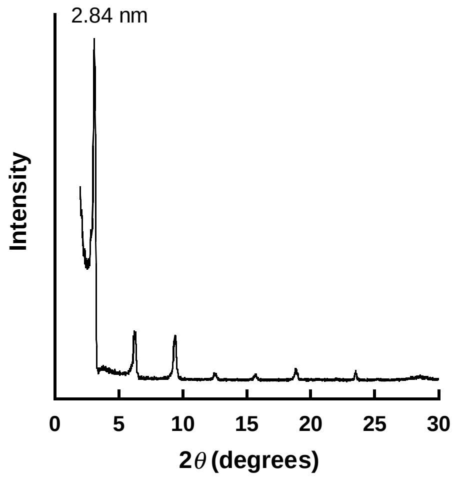

Figure 7. X-ray diffractogram of a **3A** film on SiO_2/Si fabricated at T_{sub} = 150 °C.

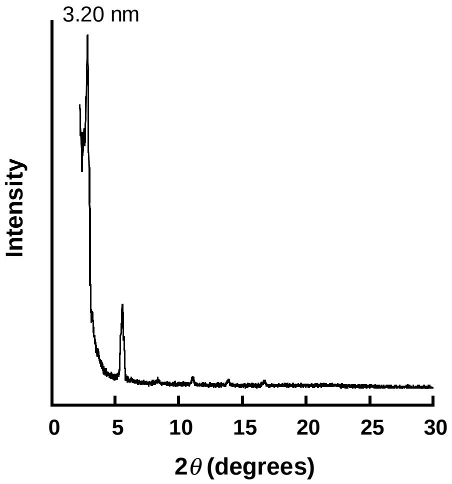

Figure 8. X-ray diffractogram of a **DH-2A** film on SiO_2/Si fabricated at T_{sub} = 70 °C.

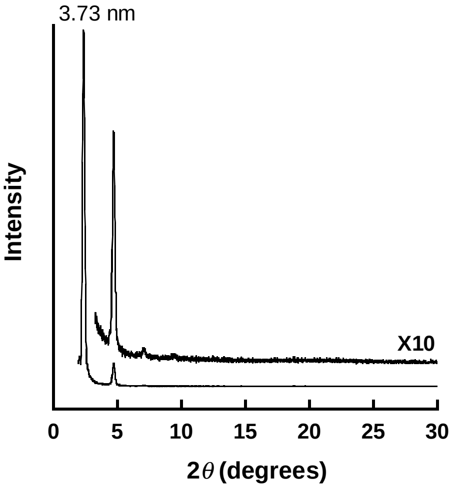

Figure 9. X-ray diffractogram of a **DH-3A** film on SiO_2/Si fabricated at T_{sub} = 175 °C.

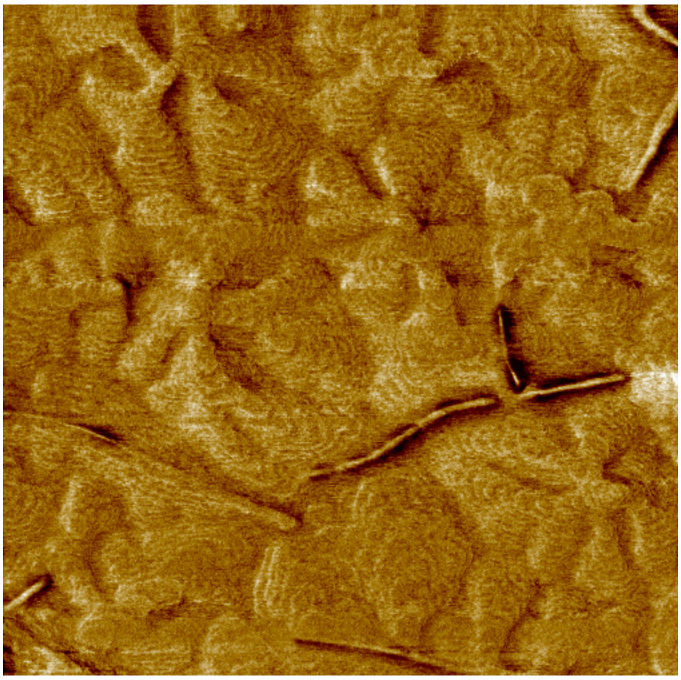

Figure 10. A 2 × 2 μm^2 AFM image of a **2A** film on SiO_2/Si fabricated at T_{sub} = room temperature.

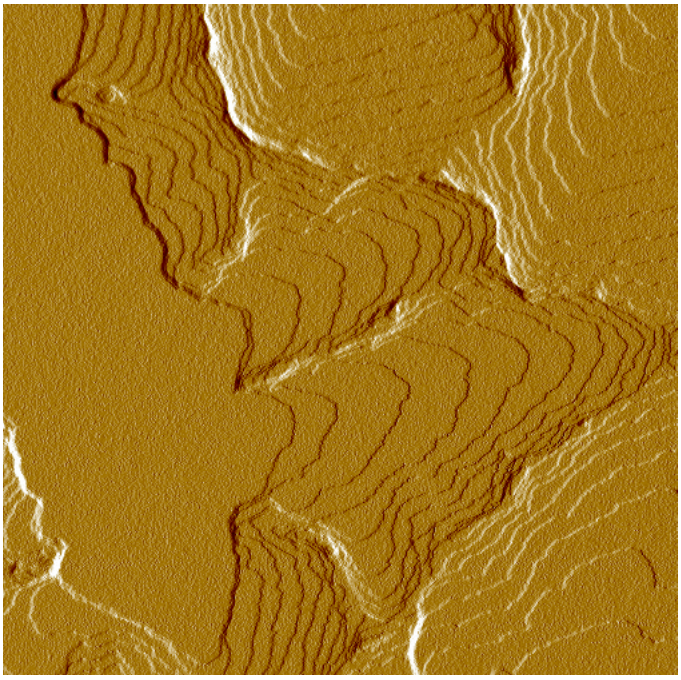

Figure 11. A 2 × 2 μm^2 AFM image of a **2A** film on SiO_2/Si fabricated at T_{sub} = 60 °C.