ADVANCED MATERIALS

Supporting Information

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Synthesis, characterization, and FET performance of pentacene derivatives

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Supporting Information

Typical Synthesis Procedures:

Tetrabromination of *o*-xylenes,

To a solution of *N*-bromosuccimide (NBS) (2.03 mol amt.) in carbon tetrachloride (0.82 M based on *o*-xylenes) was added the catalyst benzoyl peroxide (BPO) (0.0325 mol amt.), which was dried over phosphorous pentoxide in vacuo overnight, and *o*-xylene (1.0 g, 7,62 mmol) under argon. The reaction suspension was stirred and heated under reflux for 4 hrs. The reaction mixture was cooled down to room temperature, additional NBS (2.03 mol amt.) and BPO (0.0325 mol amt) were added, and the reaction mixture heated to reflux again overnight. The final reaction mixture was cooled down. Firstly the succinimide formed was filtered off and washed thoroughly with dichloromethane. The filtrate obtained was washed with water three times, saturated sodium thiosulfate solution and brine, dried over magnesium sulfate, filtered, and concentrated under rotary evaporator. The resulting mixture was purified by either recrystallization from hexane or a silica gel column chromatography (mixture of hexane and dichloromethane as described below, respectively) to give pure compounds.

4,5-Dibromo-1,2-bis(dibromomethyl)benzene

^{1}H NMR (300 MHz, $CDCl_3$):δ 7.92 (s, 2H), 6.97 (s, 2H).

4-Bromo-1,2-bis(dibromomethyl)benzene

62% isolated yields. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.60-7.46 (m, 2H), 7.05 (s, 1H), 7.02 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.12, 136.65, 133.55, 132.23, 131.15, 124.18, 35.40, 34.96, MS (DEI) 500 (M^+), Anal. Calcd for $C_8H_5Br_5$: C, 19.19; H, 1.01; Br, 79.80. Found: C, 19.27; H, 1.00; Br, 79.70.

4-Cyano-1,2-bis(dibromomethyl)benzene

71% isolated yields. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.84 (d, 1H, *J* = 8.0 Hz), 7,65 (dd, 1H, *J* = 8.2 Hz, 1.6 Hz), 7.05 (d, 2H, *J* = 7.2 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.73, 138.76, 133.47, 130.66, 117.06, 114.35, 34.45, 34.05, MS (DEI) 448 (MH^+), Anal. Calcd for $C_9H_5Br_4N$: C, 24.20; H, 1.13; N, 3.14. Found: C, 24.29; H, 0.97; N, 3.11.

4-Trifluoromethyl-1,2-bis(dibromomethyl)benzene

72% isolated yields. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.85 (br-d, 2H), 7.63 (d, 1H, J = 8.0 Hz), 7.14-7.08 (br-d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.13, 138.26, 133.01, 132.58, 132.15, 131.71, 130.54, 128.43, 127.24, 126.30, 124.81, 121.20, 117.58, 34.91, MS (DEI) 489 (M^+), Anal. Calcd for $C_9H_5Br_4F_3$: C, 22.07; H, 1.03; Br, 65.26; F, 11.64. Found: C, 22.31; H, 0.99; Br, 64.97; F, 11.45.

Synthesis of pentance quinones

Symmetrical quinone

To a mixture of the 1,2-bis(dibromomethyl)benzene derivative (22.22 g, 44.4 mmol, 2,2 mol amt.) and 1,4-benzoquinone (2.18 g, 20.2 mmol, 1.0 mol amt.) was added sodium iodide (40.39 g, 269.5 mmol, 13.34 mol amt.) and anhydrous *N*,*N*-dimethylformamide (167 mL). The rusty red solution was stirred and heated to 60 °C for two days under argon conditions. The reaction mixture was cooled down before quenching with cold water and filtered off. The collected solid was washed with water and methanol, and dried under vacuum. The crude compound was then washed with hot methanol and hot chloroform to give the desired product. .

Mixture of 2,9-Dibromo-6a,13a-dihydropentacene-6,13-dione and 2,10-Dibromo-6a,13a-dihydropentacene-6,13-dione

24% isolated yield, yellow solids, Both ^{1}H NMR and ^{13}C NMR could not be measured due to its poor solubility. MS (DEI) 466 (M^+).

Asymmetrical quinones

To a mixture of corresponding 1,2-bis(dibromomethyl)benzene and 1,4-anthraquinone (1.58 mol amt.) was added sodium iodide (6.67 mol amt.) and anhydrous *N*,*N*-dimethylformamide (0.28 M based on 1,2-bis(dibromomethyl)benzene). The rusty red solution was stirred and heated to 60 °C

for about one day under argon conditions. The reaction mixture was cooled down before quenching with cold water and filtered off, and the collected solid was washed with water and acetone, and then dried under vacuum. The crude compound was washed with hot methanol and then hot chloroform to give the asymmetrical pentacene quinones in 73-88 % yields, as described below.

2-Bromo-6a,13a-dihydropentacene-6,13-dione.

82 % isolated yield. ^{1}H NMR (500 MHz, d_6-DMSO, 90 ^{o}C): δ 8.95 (m, 3H), 8.72 (s, 1H), 8.63 (s, 1H), 8.33 -8.29 (m, 4H), 7.91 (d, 1H, J = 9.0 Hz), 7.82-7.79 (m 2H), ^{13}C NMR could not be measured due to its poor solubility, MS (DEI) 386 (M^+), Anal. Calcd for $C_{22}H_{11}BrO_2$: C, 68.24; H, 2.86. Found: C, 67.99; H, 2.59.

2-Trifluoromethyl-6a,13a-dihydropentacene-6,13-dione.

88 % isolated yield. MS (DEI) 376 (M^+), Anal. Calcd for $C_{23}H_{11}F_3O_2$: C, 73.41; H, 2.95. Found: C, 73.39; H, 2.68.

2-Cyano-6a,13a-dihydropentacene-6,13-dione.

73 % isolated yield. ^{1}H NMR (500 MHz, DMSO-d6, 90 ^{o}C): δ 9.09 (s, 1H), 9.04 (s, 1H), 8.97 (s, 1H), 8,96 (s, 1H), 8.52 (d, 1H, *J* = 8.5 Hz), 8.38-8.33 (m, 2H), 8.02 (d, 1H, *J* = 8.5 Hz), 7.85-7.82 (m, 2H). ^{13}C NMR could not be measured due to its poor solubility.

MS (DLI) 333 (M^+), from MS spectra, some other peaks contained on the range of 450 to 760..

Anal. Calcd for $C_{23}H_{11}NO_2$: C, 82.87; H, 3.33; N, 4.20. Found: C, 82.59; H, 3.60; N, 4.10.

Reduction of Pentacene Quinones

To a mixture of aluminum wire (6.0 mol amt.), mercury (II) chloride (4.2×10^{-3} mol amt.), and carbon tetrabromide (0.12 mol amt.) was added anhydrous cyclohexanol (0.16 M based on the quinone) and heated to 100°C. The mixture was stirred and heated to 100°C under argon until the solution became clear. The solution was cooled down to 80°C before the pentacene quinone was added, then heated to 160°C for three days, turning a black bluish color. It was then cooled to room temperature and poured into an equivolume solution of 6M hydrochloric acid / ethanol, filtered off, washed with ethanol, and vacuum dried to give the desired pentacene.

2-Bromopentacene (2-BrP)

50% isolated yield, Both ^{1}H NMR and ^{13}C NMR could not be measured due to its poor solubility. MS (DEI) 356 (M^+), Anal. Calcd for $C_{22}H_{13}Br$: C, 73.97; H, 3.67; Br, 22.37. Found: C, 74.19; H, 3.31; Br, 22.31.

2,3-Dibromopentacene (2,3-Br_2P)

87% yield, Both ^{1}H NMR and ^{13}C NMR could not be measured due to its poor solubility. MS (DLI) 436 (M^+), from MS spectra, some other peaks contained. Anal. Calcd for $C_{22}H_{12}Br_2$: C, 60.59; H, 2.77; Br, 36.64. Found: C, 60.64; H, 2.98; Br, 36.58.

Mixture of 2,9-Dibromopentacene and 2,10-Dibromopentacene

80% yield, Both ^{1}H NMR and ^{13}C NMR could not be measured due to its poor solubility. MS (DEI) 436 (M^+), Anal. Calcd for $C_{22}H_{12}Br_2$: C, 60.59; H, 2.77; Br, 36.64. Found: C, 60.54; H, 2.77; Br, 36.51.

2,3,9,10-Tetrabromopentacene (2,3,9,10-Br_4P)

70% yield, Both ^{1}H NMR and ^{13}C NMR could not be measured due to its poor solubility.

2-Cyanopentacene (2-CNP)

71% yield, Both ^{1}H NMR and ^{13}C NMR could not be measured due to its poor solubility. MS (DLI) 303 (M^+), Anal. Calcd for $C_{23}H_{13}N$: C, 91.06; H, 4.32; N, 4.62. Found: C, 90.85; H, 4.32; N, 4.59

2-Trifluoromethylpentacene (2-CF_3P)

38% yield, Both ^{1}H NMR and ^{13}C NMR could not be measured due to its poor solubility. MS (DLI) 346 (M^+),

Anal. Calcd for $C_{23}H_{13}F_3$: C, 79.76; H, 3.78. Found: C, 79.91; H, 3.96.

Thermal Stability by TGA

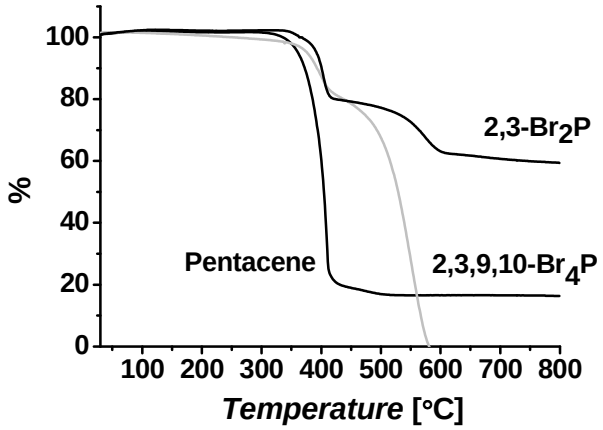

Figure 1S. Thermal Gravimetric Analysis of Bromo-containing Pentacenes and Pentacene.

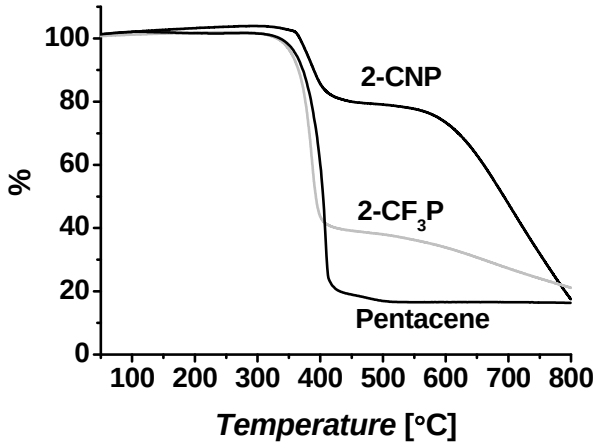

Figure 2S. Thermal Gravimetric Analysis of **2-CNP, 2-CF_3P** and Pentacene.

Table 1S. Onset of decomposition of all Pentacene Derivatives as measured by TGA.

Compound	Temp. (^{o}C)
2-BrP	362
2,3-Br_2P	392
Br_2P	380
2,3,9,10-Br_4P	377
2-CNP	367
2-CF_3P	346
Pentacene	361

Optical Properties of Pentacene Derivatives

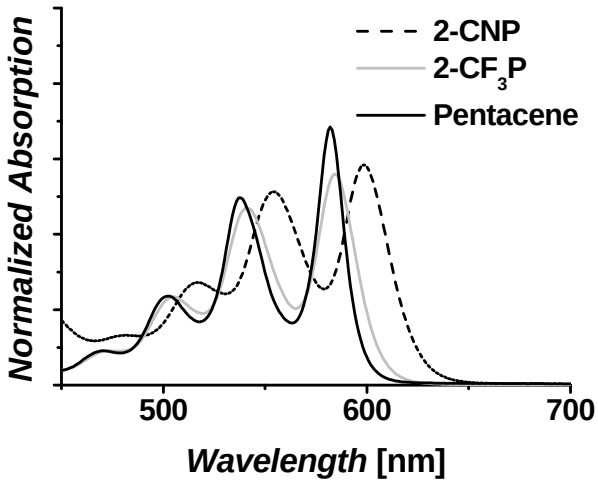

Figure 3S. UV-vis spectra for **2-CNP** and **2-CF_3P** and Pentacene in *o*-dichlorobenzene at 100°C.

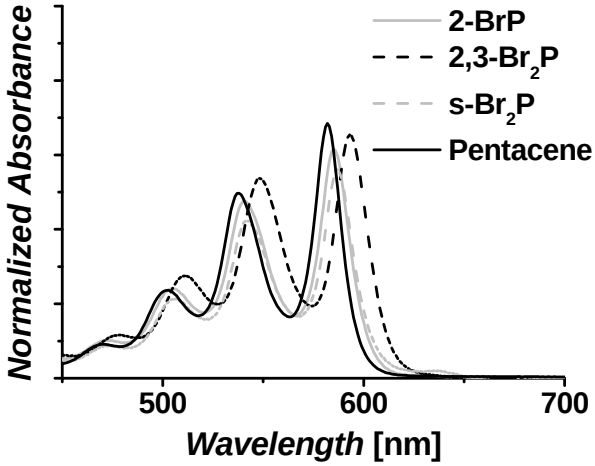

Figure 4S. UV-vis spectra for **2,3-Br_2P**, **2-BrP**, **s-Br_2P** and Pentacene in *o*-dichlorobenzene at 100°C.

Electrochemical Properties

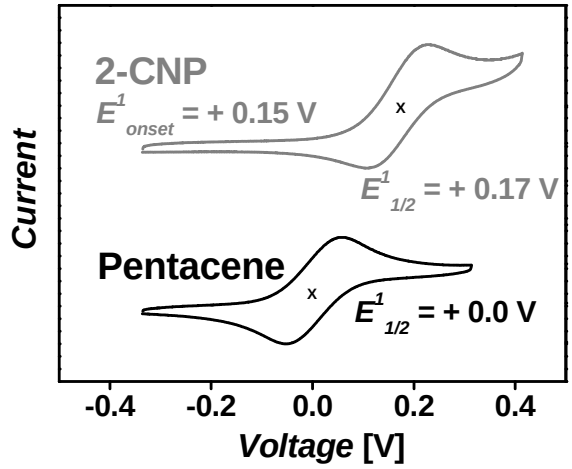

Figure 5S. Cyclic Voltammogram for **2-CNP** (top), Pentacene (bottom) in *o*-dichlorobenzene at 100 ^{o}C.

Device Performance

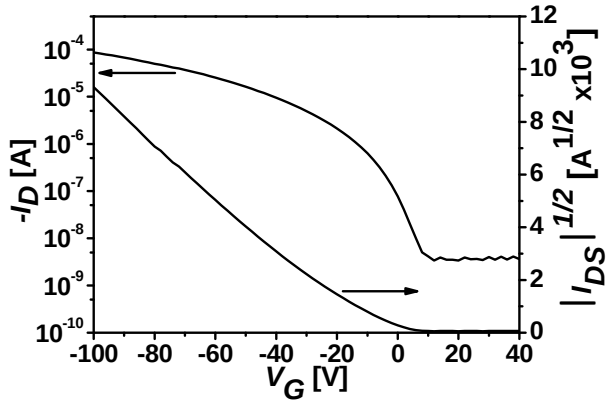

Figure 6S. V_G vs $-I_D$ for **2-BrP** at 80^{o}C.

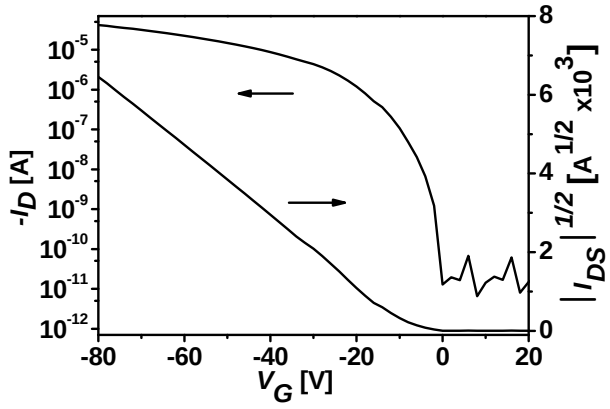

Figure 7S. V_G vs $-I_D$ for **s-Br$_2$P** at 80^{o}C.

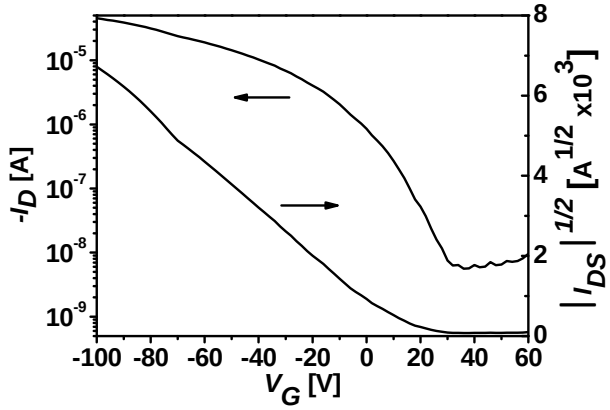

Figure 8S. V_G vs $-I_D$ for **2-CNP** at 80^{o}C.

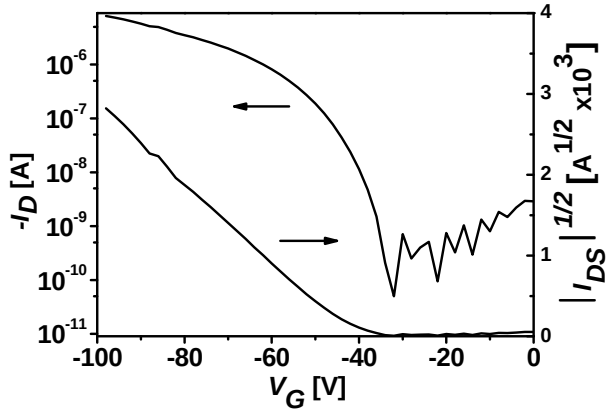

Figure 9S. V_G vs $-I_D$ for **2-CF$_3$P** at 80.^{o}C.

XRD data

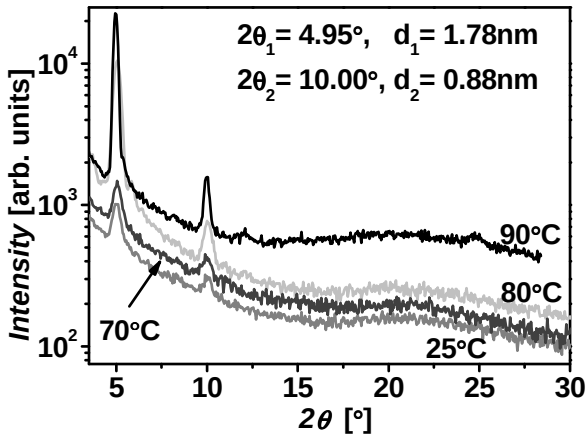

Figure 10S. XRD of **2,3-Br$_2$P** at a substrate temperature of 25^{o}C, 70^{o}C, 80^{o}C and 90^{o}C.

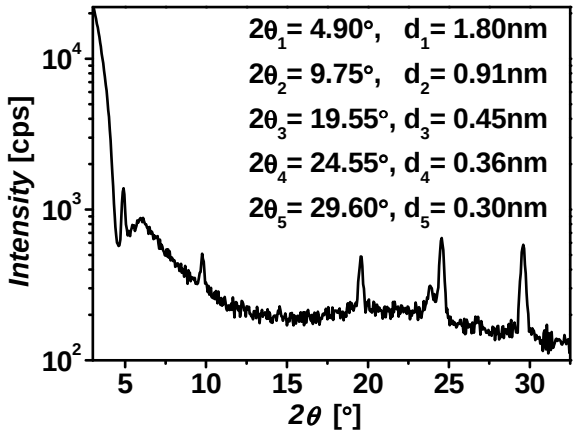

Figure 11S. XRD of **s-Br$_2$P** at a substrate temperature of 80^{o}C.

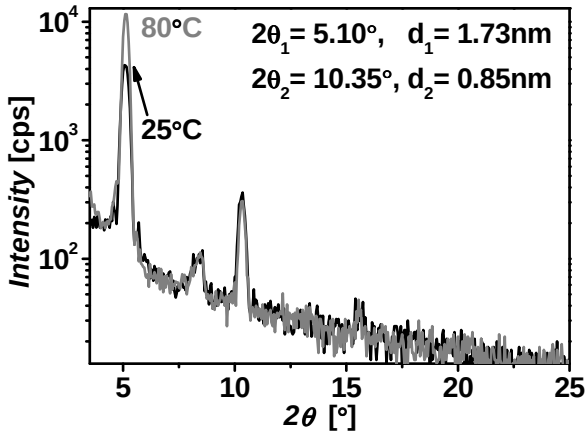

Figure 12S. XRD of **2-CNP** at a substrate temperature of 25°C and 80°C.

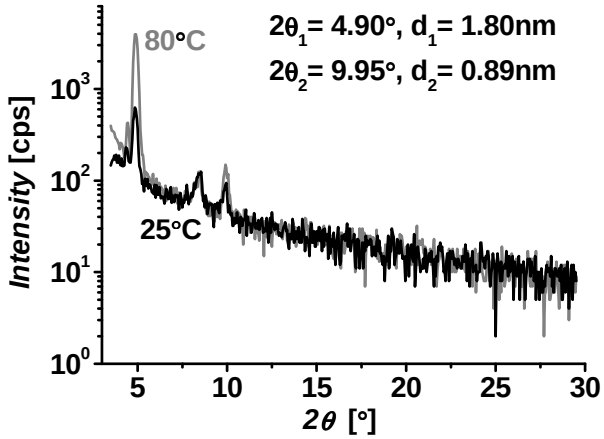

Figure 13S. XRD of **2-CF$_3$P** at a substrate temperature of 25 °C and 80 °C.

Atomic force microscopy (AFM)

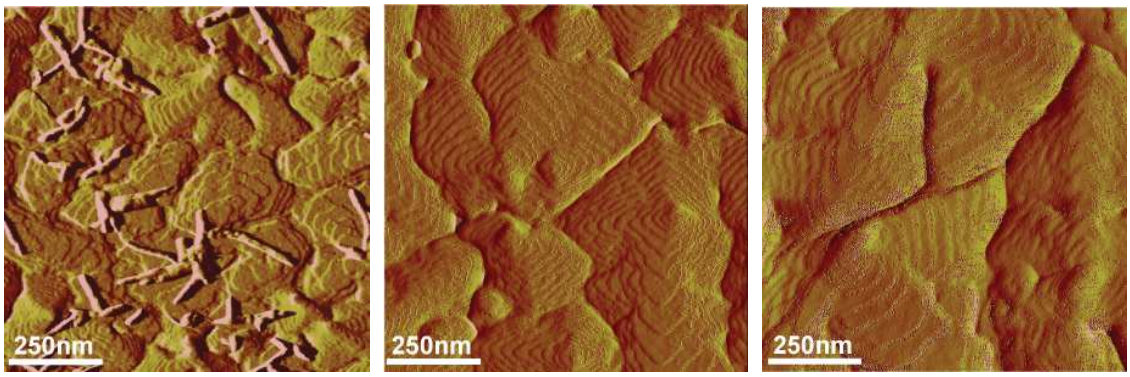

Figure 14S. 1μm AFM height images of **2,3-Br$_2$P** at 25 ^{o}C (right), 70 ^{o}C (middle) and 90 ^{o}C (left).

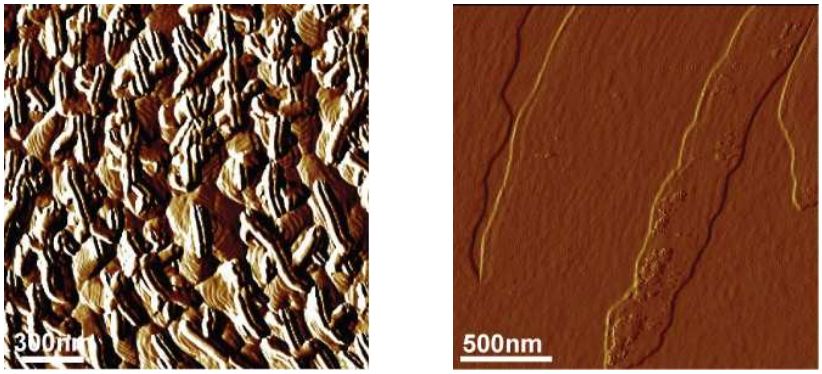

Figure 15S. AFM height images of **2-BrP** at 25^{o}C (right) and 80^{o}C (left).

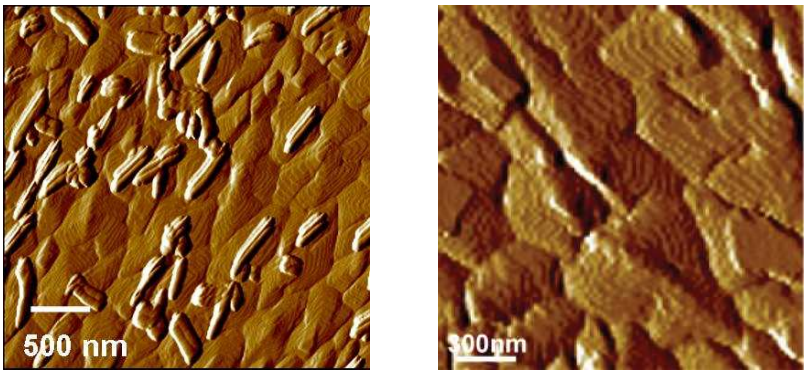

Figure 16S. 3μm AFM height images of **s-Br$_2$P** at 25^{o}C (right) and 80^{o}C (left).

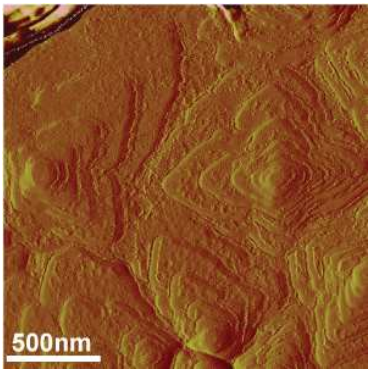

Figure 17S. 2μm AFM image of **2-CF_3P** at 80°C.

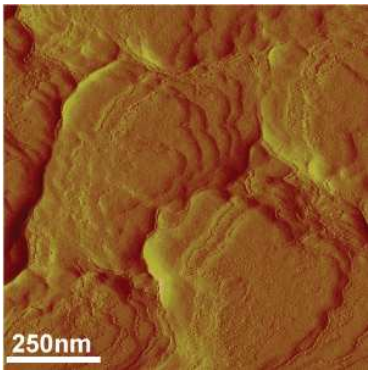

Figure 18S. 1μm AFM height image of **2-CNP** at 80°C.