

Self-Assembly of Patterned Monolayers with Nanometer Features

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Supporting Information

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A. Spectral Data for compounds 1 – 4.

1 1-Undecyloxymethyl-5-(12-methoxy-dodecyloxymethyl)-anthracene (C₄₀H₆₂O₃)

¹H NMR(300 MHz, CDCl₃)

δ8.73 (s, 2H), 8.03 (d, 2H), 7.51 (d, 2H), 7.44 (t, 2H), 5.10 (s, 4H), 3.62 (t, 4H), 3.38 (t, 2H), 3.35 (s, 3H), 1.66 (m, 4H), 1.58 (m, 2H), 1.40 (m, 4H), 1.26 (m, 28H), 0.90 (t, 3H)

¹³C NMR(100MHz, CDCl₃)

δ133.88, 132.01, 129.74, 129.20, 125.65, 124.69, 123.48, 72.94, 71.66, 70.48, 58.50, 31.88, 29.81, 29.58, 29.54, 29.44, 29.30, 26.27, 26.11, 22.66, 14.10

m/z calcd for **1** M⁺ 590.5, found 590.7

2 1-(2-Octadecyloxy-ethyl-5-[2-(10-ethoxy-decyloxy)-ethyl]-anthracene (C₄₈H₇₈O₃)

¹H NMR(300 MHz, CDCl₃)

δ8.66 (s, 2H), 7.95 (d, 2H), 7.40 (m, 4H), 3.88 (t, 4H), 3.52 (m, 10H), 3.42 (t, 2H), 1.62 (m, 6H), 1.28 ((broad s), 42H), 1.23 (t, 3H), 0.91 (t, 3H)

¹³C NMR(100MHz, CDCl₃)

δ134.69, 132.02, 130.28, 127.61, 125.79, 125.02, 123.21, 71.22, 70.97, 70.77, 66.01, 33.52, 31.89, 29.77, 29.67, 29.59, 29.50, 29.33, 26.18, 22.66, 15.22, 14.09

m/z calcd for **2** M⁺ 703.1, found 703.0; (M+Na)⁺ 726.1, found 726.0.

3 1,5-Bis-(12-methoxy-dodecyloxymethyl)-anthracene (C₄₂H₆₆O₄).

¹H NMR(300MHz, CDCl₃)

δ8.72 (s, 2H), 8.02 (d, 2H), 7.51 (d, 2H), 7.44 (t, 2H), 5.10 (s, 4H), 3.61 (t, 4H), 3.38 (t, 4H), 3.35 (s, 6H), 1.68 (m, 4H), 1.58 (m, 4H), 1.87, 1.37(m, 4H), 1.27 (m, 28H)

¹³C NMR(100MHz, CDCl₃)

δ128.94, 127.07, 124.80, 124.26, 120.71, 119.75, 118.54, 68.00, 66.72, 65.55, 53.57, 24.87, 24.68, 24.60, 24.53, 21.33, 21.17

m/z calcd for **3** M⁺ 635.0, found 635.2; (M+Na)⁺ 658.0, found 658.2

4 1-Undecyloxymethyl-5-tetradecyloxymethyl-anthracene (C₄₁H₆₄O₂).

¹H NMR(300 MHz, CDCl₃)

δ8.72 (s, 2H), 8.02 (d, 2H), 7.51 (d, 2H), 7.44 (t, 2H), 5.10 (s, 4H), 3.61 (t, 4H), 1.68 (m, 4H), 1.37 (m, 4H), 1.27 (m, 34H), 0.90 (t, 6H)

¹³C NMR(100MHz, CDCl₃)

δ133.95, 132.07, 129.81, 129.27, 125.71, 124.75, 123.54, 71.73, 70.54, 31.94, 29.86, 29.72, 29.69, 29.64, 29.50, 29.39, 29.35, 26.32, 22.71, 14.15

m/z calcd for **4** M⁺ 588, found 588.4

B. Synthesis of 1 – 4.**(i) Preparation of 1 and 3.**

(a) 1-Bromo-12-methoxy-dodecane (Br-[14¹³]). 90mg NaH (3mmol, 80% in mineral oil) was added into a dry, 2-neck flask, followed by washing with 2×5ml dry DMF by syringe. To the NaH suspension was added 81μl methanol (2mmol) and 2ml DMF. After stirring 45min, to the reaction solution was added 2.6g 1,12-dibromo-dodecane (8mmol) dissolved in 10ml DMF by syringe. After stirring at room temperature and under N₂ overnight, 20ml ether and 30ml H₂O were added into the reaction mixture. The organic layer was separated and the aqueous phase was extracted with 2×10ml ether. The combined organic layers were washed with water, dried and filtered. The solvent was removed to give **Br-[14¹³]** with 68% yield (column: silica, 50% hexane in CH₂Cl₂). **Br-[14¹³]**: ¹H NMR (300MHz, CDCl₃) δ3.41 (t, 2H), 3.37 (t, 2H), 3.34 (s, 3H), 1.86 (m, 2H), 1.57 (m, 2H), 1.43 (m, 2H), 1.28 (br s, 14H)

(b) An-[16^{2,15}][2²] and 3 (An-[16^{2,15}]₂). 54mg NaH (1.8mmol, 80% in mineral oil) was added into a dry, 2-neck flask, followed by washing with 2×5ml dry DMF by syringe. To the NaH suspension was added 120mg 1,5-bis-(hydroxymethyl) anthracene (0.5mmol) dissolved in 4ml DMF. After stirring 1 hour, 126 mg **Br-[14¹³]** (0.45mmol) dissolved in 8ml DMF was added by syringe to the reaction solution. After stirring under N₂ overnight, 20ml ether and 30ml H₂O were added into the reaction mixture. The organic layer was separated and the aqueous phase was extracted with 2×10ml ether. The combined organic layers were washed with water, dried and filtered. The solvent was removed to give **An-[16^{2,15}][2²]** and **3 (An-[16^{2,15}]₂)**. **An-[16^{2,15}][2²]** and **3** were isolated using silica column chromatography (8 % EtOAc/Hexane followed by 30% EtOAc/hexane). **An-[16^{2,15}][2²]**: ¹H NMR(300 MHz, CDCl₃) δ8.75 (s, 1H), 8.71 (s, 1H), 8.03 (d, 2H), 7.48 (m, 4H), 5.31 (d, 2H), 5.10 (s, 2H), 3.61 (t, 2H), 3.37 (m, 5H), 1.93 (t, 1H), 1.67 (m, 2H), 1.56 (m, 2H), 1.25 (br s, 20H). Spectral data for **3** listed above.

(c) An-[16^{2,15}][13²] (**1**). 15.5 mg NaH (0.52mmol, 80% in mineral oil) was added into a dry, 2-neck flask, followed by washing with 2×5ml dry DMF by syringe. To the NaH suspension was added 45mg **An-[16^{2,15}][2²]** (0.103mmol) dissolved in 12ml DMF. After stirring 1 hour, 140 μl BrC₁₁H₂₃ (0.62mmol) was added by syringe to the reaction solution. After stirring at room temperature under N₂ overnight, 20ml ether and 30ml H₂O were added into the reaction mixture. The organic layer was separated and the aqueous phase was extracted with 2×10ml ether. The combined organic layers were washed with water, dried and filtered. The solvent was removed to give **1** in a 62 % yield (column: silica, methylene chloride). Spectral data for **1** provided above.

(ii) Preparation of 2.

(a) 1-Bromo-10-ethoxy-decane ((Br-[13¹¹])). **Br-[13¹¹]** was prepared by the same procedure used to prepare **Br-[14¹³]** except that methanol was replaced by ethanol. The yield after column chromatography (silica, 50% hexane in CH₂Cl₂) was 60%. **Br-[13¹¹]**: ¹H NMR (300MHz, CDCl₃) δ3.48 (t, 2H), 3.41 (td, 4H), 1.86 (m, 2H), 1.57 (m, 2H), 1.42 (m, 2H), 1.30 (br s, 10H), 1.20 (t, 3H).

(b) **An-[16^{3,14}][3³]** and **An-[16^{3,14}]₂**. 27 mg NaH (1.2mmol, 80% in mineral oil) was added to a dry, 2-neck flask, followed by washing with 2×5ml dry THF by syringe. To the NaH suspension was added 60mg 1,5-bis-(2-hydroxyethyl) anthracene (0.22 mmol) dissolved in 5ml THF and 1 ml DMF. After stirring 1 hour, 79 mg **Br-[13¹¹]** (0.29 mmol) dissolved in 5ml THF was added by syringe to the reaction solution. After stirring under N₂ overnight, 20ml ether and 30ml H₂O were added into the reaction mixture. The organic layer was separated and the aqueous phase was extracted with 2×10ml ether. The combined organic layers were washed with water, dried and filtered. The solvent was removed to give **An-[16^{3,14}][3³]** and **An-[16^{3,14}]₂**. **An-[16^{3,14}][3³]** and **An-[16^{3,14}]₂** were isolated using silica column chromatography (9 % EtOAc/Hexane followed by 30% EtOAc/hexane). **An-[16^{3,14}][3³]**: ¹H NMR(300 MHz, CDCl₃) δ8.68(s, 1H), 8.63 (s, 1H), 7.97 (dd, 2H), 7.42 (m, 4H), 4.12 (m, 2H), 3.87 (t, 2H), 3.51 (m, 8H), 3.42 (t, 2H), 1.60 (m, 4H), 1.29 (br s, 12H), 1.22 (t, 3H).

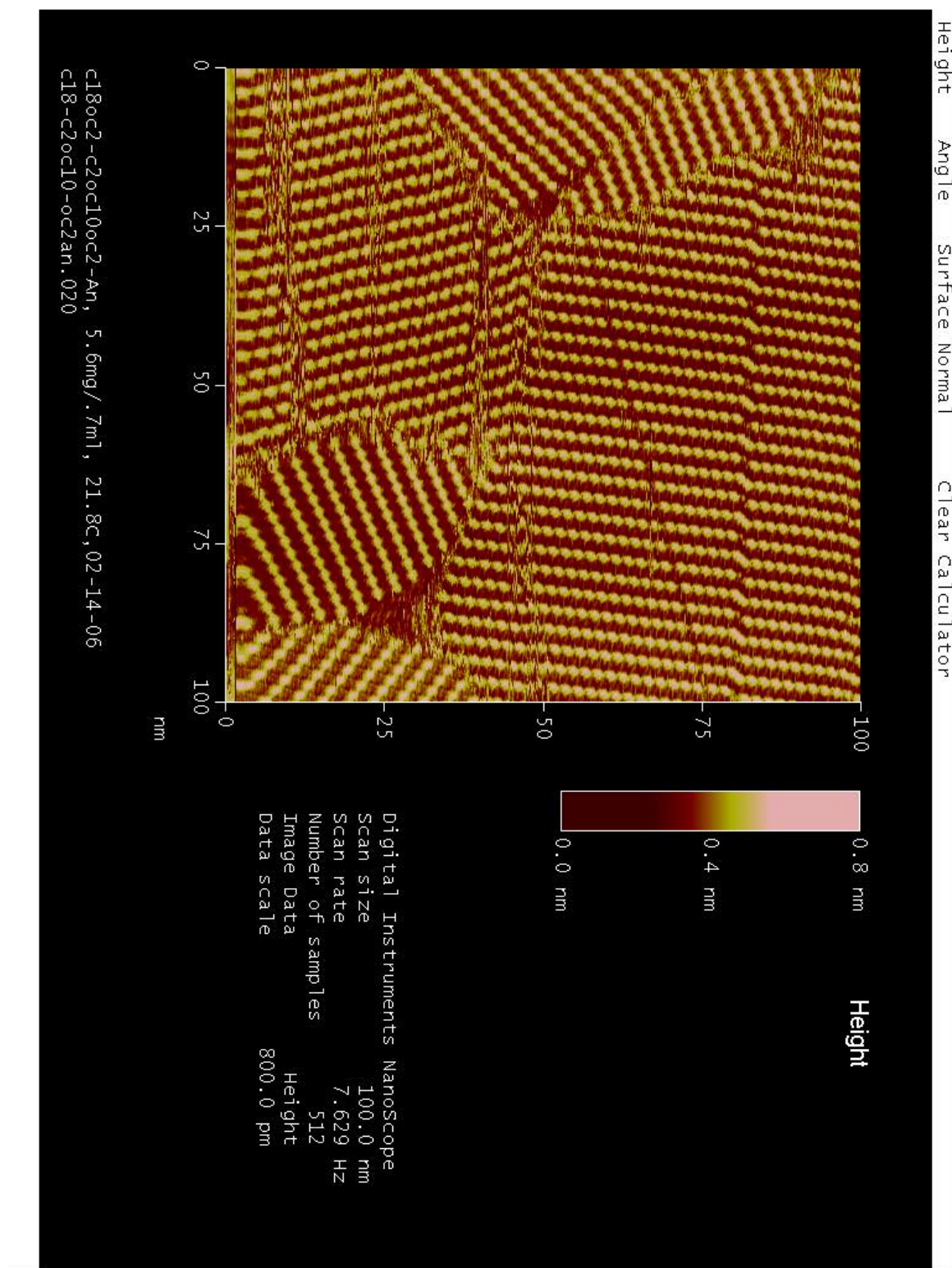
(c) **An-[21³][16^{3,14}](2)**. 6.6 mg NaH (0.22mmol, 80% in mineral oil) was added into a dry, 2-neck flask, followed by washing with 2×5ml dry DMF by syringe. To the NaH suspension was added 25mg **An-[16^{3,14}][3³]** (0.056 mmol) dissolved in 6ml DMF. After stirring 1 hour, 115 μl BrC₁₈H₃₇ (0.34 mmol) was added by syringe to the reaction solution. After stirring at room temperature under N₂ overnight, 20ml ether and 30ml H₂O were added into the reaction mixture. The organic layer was separated and the aqueous phase was extracted with 2×10ml ether. The combined organic layers were washed with water, dried and filtered. The solvent was removed to give **2** in an 82 % yield. The product was purified using silica column chromatography (1:1 CH₂Cl₂ / hexane). Spectral data for **2** provided above.

(iii) Preparation of **4**.

(a) 24mg NaH (0.8 mmol, 80% in mineral oil) was added into a 2N dry flask, followed by washing with 2×5ml dry THF by syringe. 96 mg 1,5-bis-(hydroxymethyl) anthracene (0.4mmol) dissolved in 25ml THF and 2ml DMF was added to the NaH suspension. After 1.5 hour refluxing, 120 μl BrC₁₄H₂₉ (0.4mmol) was added to the reaction solution by syringe. After stirring under N₂ for two days, the reaction mixture was cooled and quenched with H₂O, followed by the standard work-up procedure to give **An-[16²]₂** and **An-[16²][2²]**. The two compounds were separated by silica column chromatography (1:1 CH₂Cl₂ / hexane). **An-[16²][2²]**: ¹H NMR(300 MHz, CDCl₃) δ8.75(s, 1H), 8.71 (s, 1H), 8.03 (d, 2H), 7.50 (m, 4H), 5.30 (s, 2H), 5.09 (s, 2H), 3.61 (t, 2H), 1.82 (t, 1H), 1.68 (m, 2H), 1.37 (m, 2H), 1.27 (br s, 20H), 0.90 (t, 3H).

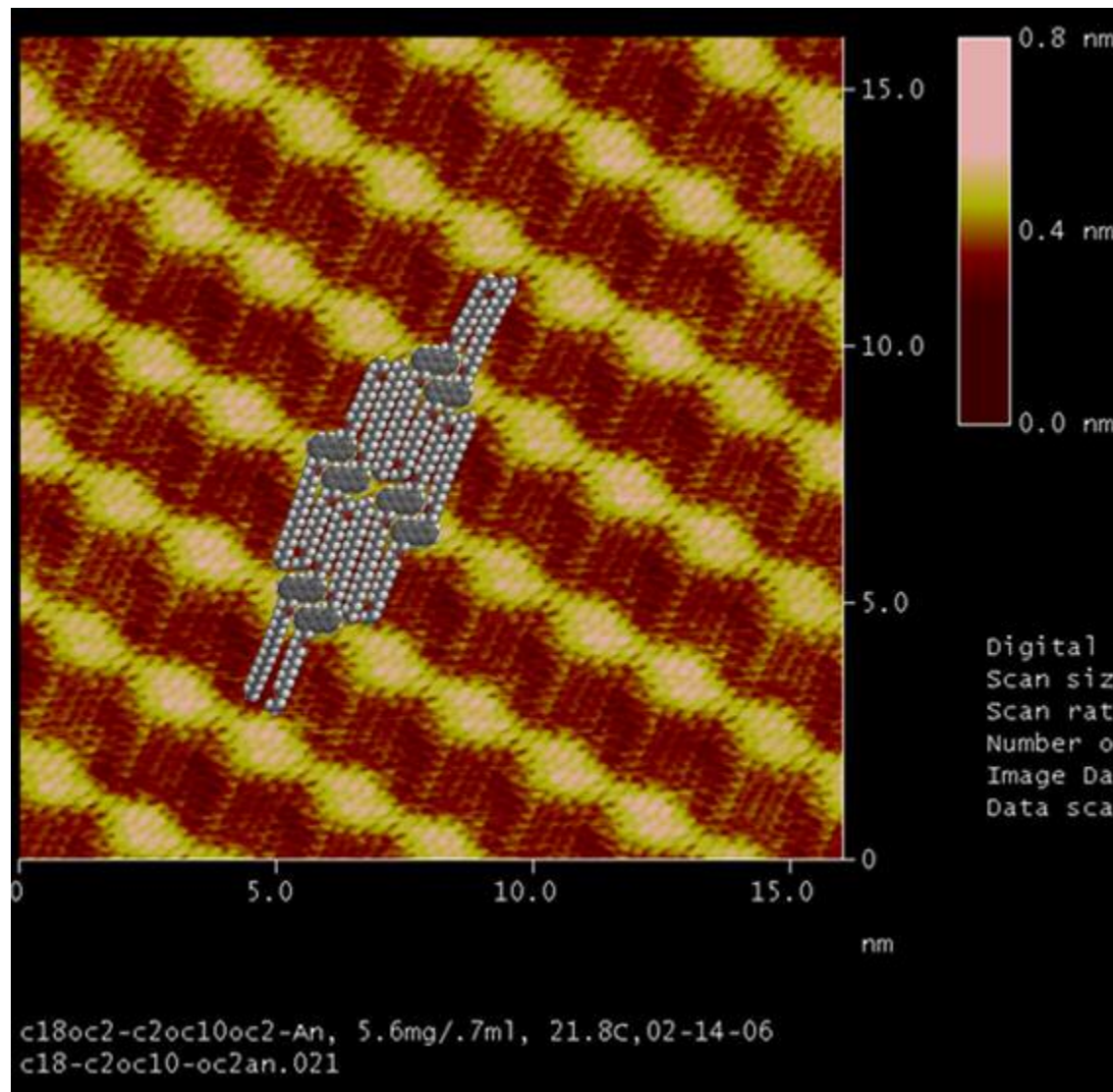
(b) **An-[16²][13²](4)**. 6 mg NaH (0.2 mmol, 80% in mineral oil) was added to a dry flask, followed by washing with 2×5ml dry THF by syringe. 22mg **An-[16²][2²]** (0.05mmol) dissolved in 4ml THF was added to the NaH suspension. After 1.5 hour refluxing, 45 μl BrC₁₁H₂₃ (0.2mmol) was added by syringe to the reaction solution. After refluxing under N₂ for two days, the reaction mixture was cooled, quenched with H₂O, and worked up using standard procedures to give **4** in a 30% yield. The product was purified using silica column chromatography (1:1 CH₂Cl₂ / hexane). Spectral data for **4** provided above.

C. STM Scan (100 nm x 100 nm; 60 pA, 0.9 V) of an unannealed, multidomain region formed by the deposition of a phenyloctane solution of **2 on HOPG.**



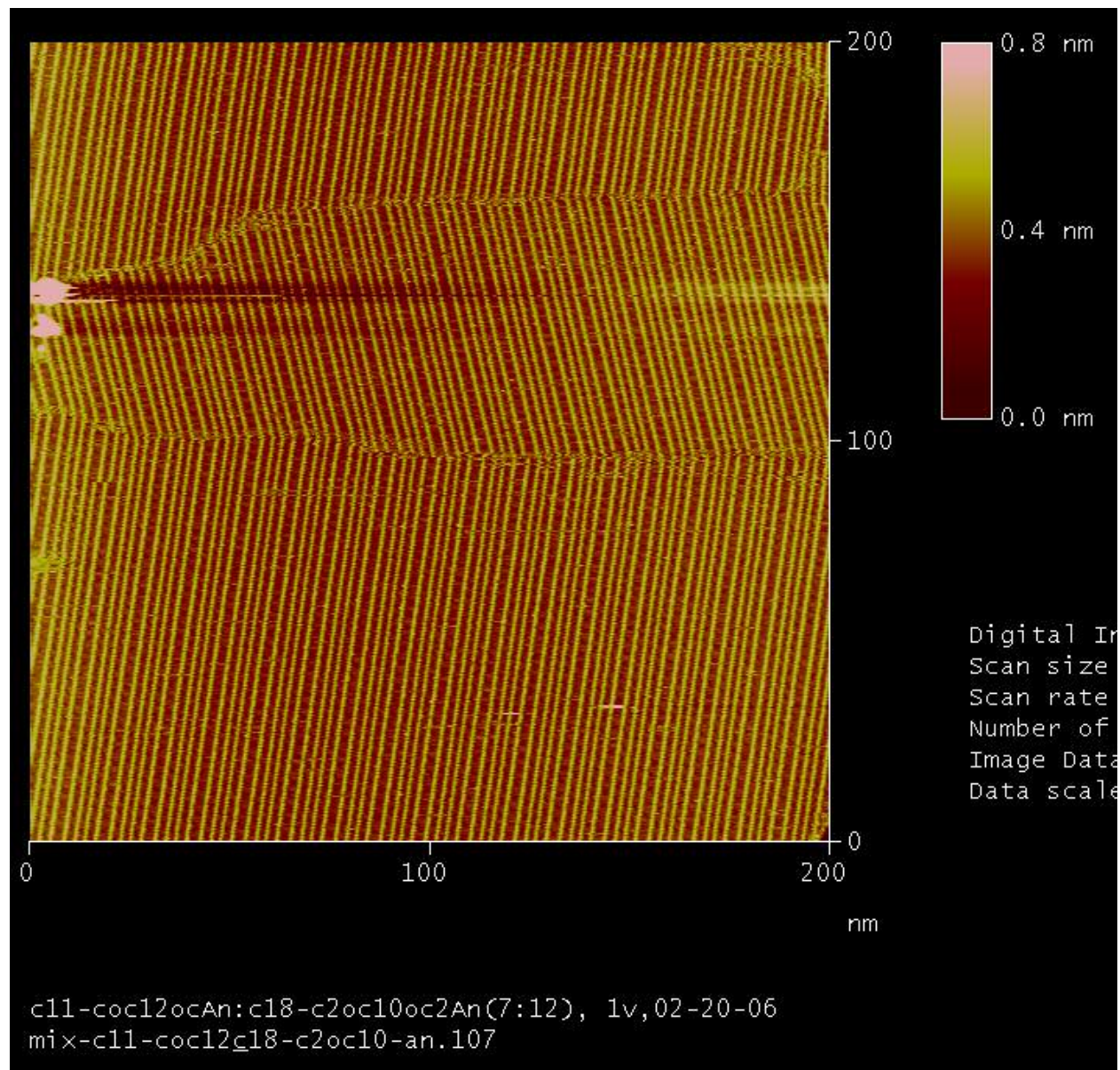
D. High resolution STM Scan (16 nm x 16 nm; 60 pA, 0.9 V) of the monolayer formed by **2 superimposed by a proposed CPK model of the monolayer.**

A proposed structure of the pure **2** monolayer is superimposed as CPK models on the STM image. This proposed morphology replaces dipolar repulsions from $\omega \leftrightarrow 2$ packing of the $[16^{3,14}]$ side chains with dipolar stabilization arising from $\omega \leftrightarrow 1$ packing of the $[16^{3,14}]$ side chains. In addition, each $[21^3]$ chain experiences favorable van der Waal interactions from $\omega \leftrightarrow 2$ packing with a second $[21^3]$ chain, from packing with a $[16^{3,14}]$ chain and with an anthracene ring.



E. 200 nm x 200 nm STM scan of the cocrystal monolayer formed by mixtures of 1 and 2.

This constant current scan exhibits the persistence of the cocrystal in the direction perpendicular to the anthracene columns and the presence of domain boundaries along the anthracene columns.



F. STM scan exhibiting both the underlying HOPG and the monolayer from 4.

Scan conditions of monolayer regions (top 1/3 and bottom 1/3: 70 pA, 1 V). Scan conditions of HOPG region (70 pA, 40 mV). The side chains' directions are roughly parallel to one of the three, equivalent repeat directions of the graphite.

