Shape Amphiphiles in 2D - Supporting Information
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I. Synthesis and Spectral Characterization

Abbreviations
DCM = Dichloromethane   EA = Ethyl Acetate
DMF = Dimethylformamide   THF = Tetrahydrofuran
HMPA = Hexamethylphosphoramide

General Procedures
NMR Spectra were collected using Bruker 300 MHz, 400 MHz and 600 MHz (proton)
spectrometers. Spectra were referenced to the monoprotio solvent residual peak (Gottlieb, H. E.;
Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512). Chemical shifts are reported in PPM
upfield of TMS (δ).

Dry Solvent
THF and DMF for reactions requiring anhydrous and deoxygenated solvents were from a solvent
column system. (Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J.
Organometallics **1996**, *15*, 1518)

Purification
All crude products were purified by flash chromatography on silica gel (60 Å, 230-400 mesh).
The eluting solvent was selected to generate an Rf of 0.1-0.3. Column fractions were analyzed by
thin layer chromatography, visualized using UV or phosphomolybdic acid (PMA) as stain.

Scheme I.
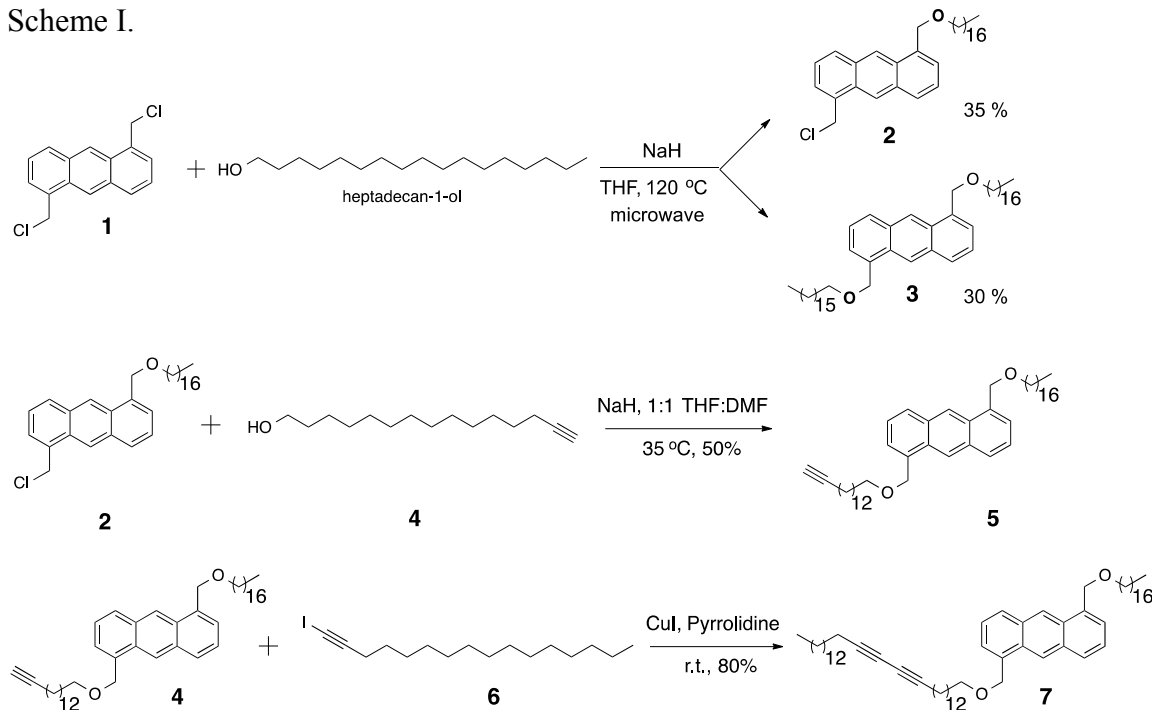
Preparation of 1-(chloromethyl)-5-(heptadecyloxymethyl)anthracene (2) and 1,5-bis-(heptadecyloxymethyl)anthracene (3).

Heptadecan-1-ol (0.12g, 0.45 mmol) was added to a 10 mL microwave vial with THF (2.5 mL) under argon, followed by addition of sodium hydride (60% dispersion in mineral oil, 20 mg, 0.51 mmol). Deprotonation was performed by heating in a microwave reactor for 1 hour at 120°C. Once the mixture cooled to room temperature, 1,5-bis-(chloromethyl)-anthracene (83 mg, 0.3 mmol) in anhydrous THF (2 mL) solution was added via syringe. The mixture was stirred at 120 °C for 6 hours in the microwave reactor. The reaction was quenched by slowly adding 0.5 M HCl (aq). The mixture was extracted with DCM (3×15mL). The organic layer was washed with 0.5M aq. HCl, d.i. water, brine and then dried with Na_2SO_4. The solvent was removed under reduced pressure affording a brownish yellow solid.

The crude product was purified by gradient flash column chromatography (20% DCM / Hexanes then 30% DCM/Hexanes then 50% DCM/Hexanes) affording compound **2** (mono substituted) as a yellow solid (48 mg, 0.097 mmol, yield 35%) and compound **3** (disubstituted) a light yellow solid (68 mg, 0.095 mmol, yield 30%)

Spectral data for 1-(chloromethyl)-5-((heptadecyloxy)methyl)anthracene (**2**):

^{1}H NMR (400MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.70 (s, 1H), 8.06 (s, 1H), 8.04 (s, 1H), 7.48 (m, 4H), 5.18 (s, 2H), 5.08 (s, 2H), 3.59 (t, $J = 6.4$ Hz, 2H), 1.66 (t, $J = 7.2$ Hz, 2H), 1.26 (m, 30H), 0.91 (t, 3H).

Spectral data for 1,5-bis((heptadecyloxy)methyl)anthracene ($3 = \{19_2\}$)

^{1}H NMR (400MHz, CDCl$_3$): δ 8.71 (s, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 6.4 Hz, 2H), 7.46 (m, 2H), 5.08 (s, 4H), 3.59 (t, *J* = 6.4 Hz, 4H), 1.26 (m, 60H), 0.90 (t, 6H).

^{13}C NMR (150MHz, CDCl$_3$): δ 134.29, 132.41, 130.14, 129.59, 126.03, 125.07, 123.87, 72.05, 70.87, 32.23, 30.20, 30.05, 29.84, 29.72, 26.66, 23.05, 14.47.

MS (FAB): m/z Calcd for M$^+$ (C$_{50}$H$_{82}$O$_2$) 714.63, found 714.80.

MS (MALDI): m/z Calcd for (M+H)$^+$ (C$_{50}$H$_{82}$O$_2$) 715.64, found 715.45.

Preparation of pentadec-14-yn-1-ol (4):
Tetrahydropyranyl-protected propargyl alcohol (0.56 mL, 4 mmol) was added to a flame-dried two-neck flask containing THF (6.5 mL) and HMPA (1.1 mL) under argon with stirring. The solution was cooled to -78 °C and n-butyl lithium (3.75 mL of 1.6 M solution in hexane, 6 mmol) was added dropwise via syringe. The mixture was stirred for 45 minutes before it was warmed to -20 °C. 1-bromododecane (1.15 mL, 4.8 mmol) was added at -20°C. The solution was stirred at room temperature for 12 hrs and quenched by adding saturated NH$_4$Cl(aq). The mixture was extracted with EA (3 × 20 mL). The organic layer was washed with d.i. water, brine and then dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure, giving the crude product as a viscous brown oil. The crude product was diluted with anhydrous methanol (5 mL) and added to a round bottom flask containing TsOH•H$_2$O (0.12g, 0.63 mmol) in anhydrous methanol (15 mL). The reaction was stirred at room temperature for 3 hours and then neutralized with NaHCO$_3$ (aq). The mixture was extracted with EA (3 × 15 mL). The organic layer was washed with d.i. water, brine and then dried over Na$_2$SO$_4$. The solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography (20 % EA/hexanes) affording pentadec-2-yn-1-ol as a clear oil (0.667 g, 3 mmol, yield 75%).

^{1}H NMR (400MHz, CDCl$_3$): δ 4.25 (s, 2H), 2.21 (t, *J* = 6.8 Hz, 2H), 1.78 (broad s, 1H), 1.49 (m, 2H), 1.26 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H).

Acetylene zipper reaction: 1,3-diaminopropane (8 mL) was added by syringe to a flame-dried two-neck flask under argon. Lithium (83 mg, 12 mmol) was added to the flask and the mixture was heated and stirred in an oil bath at 70°C, forming a dark blue suspension. After stirring for approx. 3 hours, the blue color disappeared, giving an off-white suspension. The mixture was allowed to cool to room temperature and potassium tert-butoxide (0.9 g, 8 mmol) was added in one portion, affording a pale yellow suspension. After stirring for 15 minutes, pentadec-2-yn-1-ol (0.45 g, 2 mmol) was added in one portion. The mixture was stirred for 2 hours at room temperature and then poured into ice-water (100mL). The aqueous mixture was extracted with EA (3 × 50mL). The organic layer was washed with 0.5M HCl (aq), water, brine and then dried with Na$_2$SO$_4$. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (20 % EA/hexanes) affording a clear oil, pentadec-14-yn-1-ol (0.37g, 1.65 mmol, yield: 83%).

¹H NMR (400MHz, CDCl₃): δ 3.54 (t, $J = 6.4$ Hz, 2H), 2.57 (broad s, 1H), 2.12 (td, $J = 5.2$ Hz, 3.0Hz, 2H), 1.91 (t, $J = 2.4$ Hz, 1H), 1.49 (m, 2H), 1.22 (m, 20H).

Preparation of 1-((heptadecyloxy)methyl)-5-((pentadec-14-yn-1-yloxy)methyl)anthracene (5):

Penta-14-yn-1-ol (54 mg, 0.24 mmol) was added to a flame-dried two-neck flask containing 1:1 THF/DMF (3 mL) under argon. The solution was cooled to 0°C and sodium hydride (60% dispersion in mineral oil, 12 mg, 0.3 mmol) was added. After stirring at room temperature for 40 min, 1-(chloromethyl)-5-(ethoxymethyl)anthracene (**2**) (30 mg, 0.06 mmol) was added. The mixture was then warmed to 35 °C in an oil bath and stirred for 15 hrs. The reaction was quenched by adding d.i. water and extracted with DCM (3×10mL). The organic layer was washed with 0.5M HCl (aq), water, brine and then dried with Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (50% DCM/Hexanes) affording compound **5** as a light yellow solid (20 mg, 0.03 mmol, yield: 50%)

Spectral data for 1-((heptadecyloxy)methyl)-5-((pentadec-14-yn-1-yloxy)methyl)anthracene (**5**):

¹H NMR (300MHz, CDCl₃): δ 8.71 (s, 2H), 8.01 (d, $J = 8.4$ Hz, 2H), 7.44 (m, 4H), 5.08 (s, 4H), 3.59 (t, $J = 6.4$ Hz, 4H), 2.11 (t, $J = 6.0$ Hz, 2H), 1.94 (s, 1H), 1.66 (m, 4H), 1.26 (m, 48H), 0.88 (t, 3H).

Preparation of 1-iodohexadec-1-yne (6):

1-hexadecyne (0.195 mL, 0.7 mmol) was added to a flame-dried two-neck flask under Ar. 5 mL of deoxygenated acetone was added to the reaction flask via syringe, followed by addition of *N*-iodosuccinimide (190 mg, 0.84 mmol). The mixture was stirred for a minute, forming a yellow solution. Silver (I) nitrite (12 mg, 0.07 mmol) was quickly added and the mixture was protected from light and stirred for one hour followed by extraction with EA (3×20mL). The organic phase was washed with d. i. water, saturated sodium thiosulfate (aq), brine and then dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (100% hexanes) affording compound **6** (220 mg, 0.006 mmol, yield 90 %).

¹H NMR (400MHz, CDCl₃): δ 2.25 (t, $J = 6.8$ Hz, 2H), 1.51 (t, $J = 7.2$ Hz, 2H), 1.27 (m, 22H), 0.90 (t, $J = 7.2$ Hz, 3H).

Preparation of 1-((hentriaconta-14,16-diyn-1-yloxy)methyl)-5-((heptadecyloxy)methyl)-anthracene (7 = {33,19}): Cadiot-Chodkiewicz cross-coupling reaction

To a two-neck flask under argon were added compound **5** (20 mg, 0.03 mmol), 1-iodohexadec-1-yne (**6**, 20 mg, 0.06 mmol) and pyrrolidine (1 mL). The light yellow solution was cooled to 0°C and copper (I) iodide (1.2 mg, 0.06 mmol) was added. The reaction mixture was stirred at room

temperature for 12 hrs. The reaction was quenched by adding saturated NH_4Cl aqueous solution. The mixture was extracted with DCM (3×10mL). The organic phase was washed with d.i. water, brine and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (40% DCM/hexanes) affording compound **7** as a light yellow solid. (22 mg, 0.024 mmol, yield 80 %).

[1]**H NMR** (400MHz, CDCl$_3$): δ 8.70 (s, 2H), 8.01 (d, J = 6.0Hz, 2H), 7.44 (m, 4H), 5.08 (s, 4H), 3.60 (t, J = 6.4 Hz, 4H), 2.24 (t, J = 6.8 Hz, 4H), 1.66 (t, J = 6.8 Hz, 4H), 1.51 (t, J = 6.8 Hz, 4H), 1.26 (m, 68H), 0.90 (t, 6H).

[13]**C NMR** (150MHz, CDCl$_3$): δ 134.02, 132.14, 129.87, 129.32, 125.75, 124.81, 123.59, 77.63, 65.34, 32.02, 29.93, 29.71, 29.57, 29.46, 29.19, 28.95, 28.45, 26.39, 22.78, 19.10, 14.21.

MS (FAB): m/z Calcd for M$^+$ ($C_{64}H_{102}O_2$) 902.79, found 903.20.

MS (MALDI): m/z Calcd for (M+H)$^+$ ($C_{64}H_{102}O_2$) 903.80, found 903.61.

II. STM Sample Preparation and Acquisition Protocols

Scanning tunneling microscopy data was acquired using a Digital Instruments NanoScope MS-10 STM interfaced with a Digital Instruments NanoScope IIIa controller. Data was collected at the solution-graphite interface (HOPG, ZYB grade, Momentive Performance, Strongsville, OH) with mechanically cut 80/20 Pt/Ir tips (0.25 mm, Goodfellow, Oakdale, PA). Solutions of each single compound were prepared by dissolving 2-3 mg of compound in ~800 µL of phenyl octane (99%) at 20 °C and then filtered (0.02 µm filters). These concentrated solutions (2~3 mM) were stored in the fridge. Solutions of lower concentrations (1mM to 0.05 mM) were prepared prior to STM experiments and stored at a cool room temperature. The two-component mixture solution was prepared by mixing solutions of {19$_2$} and {33,19} with R$_S$=1, 2, 4, and 8 at C$_T$ = 0.25 mM (or 0.38 mM for one of the 8:1 samples) assuming volumes are additive. To give an example, to prepare a R$_S$=1, C$_T$ = 0.25 mM solution, 1mM single component solutions of {19$_2$} and {33,19} were diluted from the aforementioned 2~3 mM concentrated solutions with phenyl octane. Equal volume (50 µL) of 1mM {19$_2$} and {33,19} single component solution were mixed to give a R$_S$=1, C$_T$ = 1 mM solution. To test the feasible concentration range for monolayer formation, R$_S$=1 solutions with C$_T$ = 0.5 mM, 0.25 mM, and 0.125 mM were prepared through serial dilution.

For dropcast samples, a solution drop (1-3 µL) was deposited on a newly cleaved HOPG surface. 5-10 minutes were given before the imaging process began. For annealed samples, 2-10 µL of solution was deposited on the dimple cut into the center of an aluminum chamber. The graphite piece was placed on top of the solution with freshly cleaved side facing down. The fitted aluminum lid was placed on top to minimize solvent evaporation during annealing. Annealing temperature was controlled by a programmable heating block. Typically, half an hour was required to heat a sample from room temperature (18 °C) to 45 °C. The sample was maintained at the target temperature for the reported annealing period before it was allowed to cool down to room temperature (30 minutes minimum).

During image acquisition, the STM tip was engaged through the solution phase and scanned in constant height or constant current mode. Tip scan velocities were in the range of 0.20-0.60 µm/s. During initial surveys of single component monolayers, multiple samples of single component monolayer of $\{19_2\}$ or $\{33,19\}$ were prepared and imaged to evaluate monolayer morphology and unit cells. Thermal drift distortions in the data were corrected using a program that solves for the X and Y thermal drift velocities in consecutively captured images (up and down scans) at the same region. The program minimizes differences in the two scans' unit cell parameters. STM scanner X- and Y-calibration was performed prior to monolayer imaging using thermal drift corrected HOPG images (5 nm × 5 nm scale). When scanning a mixed 2-component sample, STM images of independent monolayer regions were collected for statistical evaluation. In a local region of HOPG, 3~4 images were collected by moving the X-, and Y-offsets at least 1.5 times the scan dimension. Then the HOPG was moved manually so that the tip would scan in a completely different region. A minimum of three different regions were scanned and a total of 10~12 independent STM images were analyzed for each sample.

III. STM images in Figure 2, 4, and 6

Note: All STM images were captured at i_{SET} =100 pA, V=800 mV.

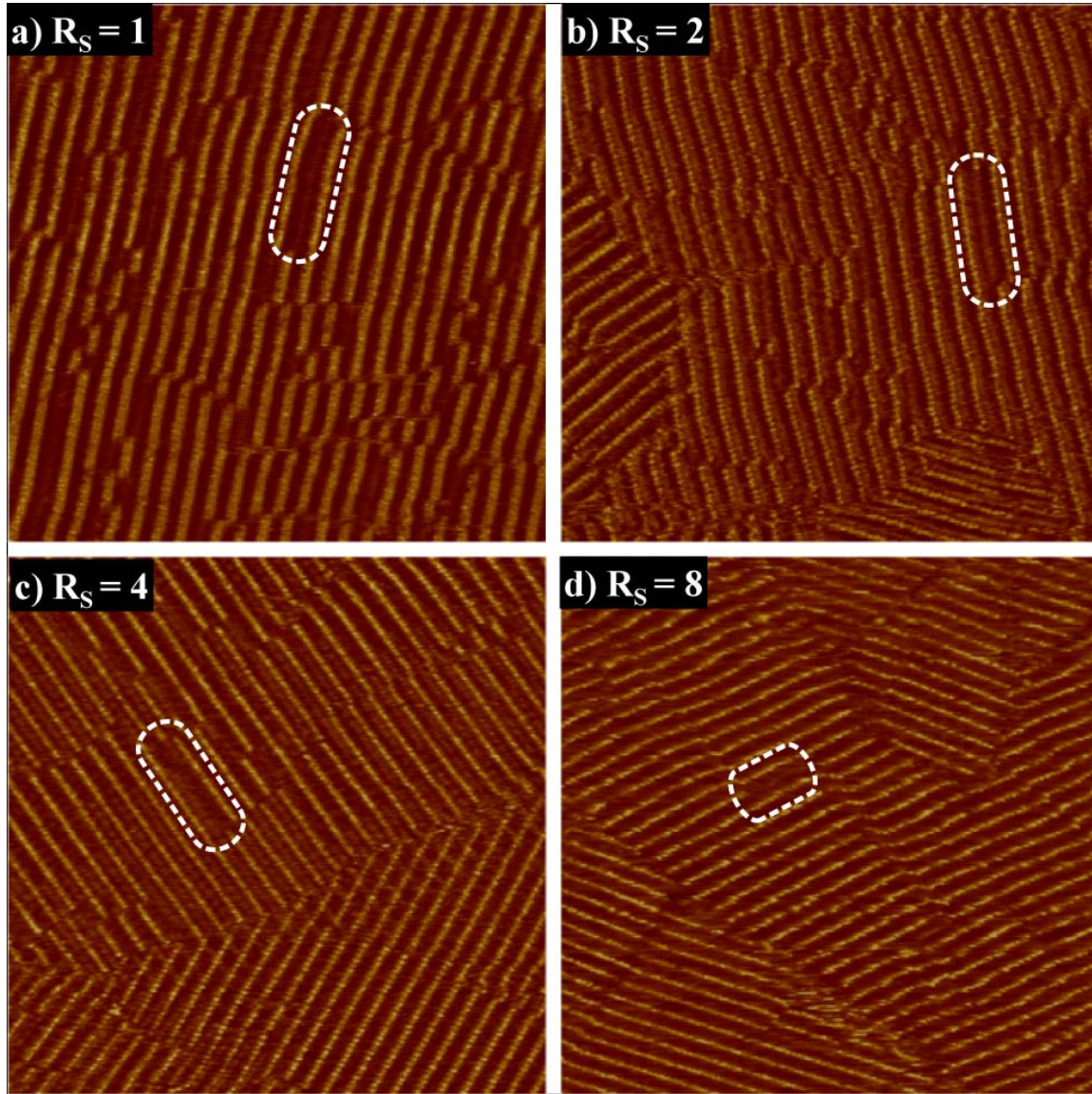Fig 2 (enlarged). Drop cast STM images (all 75 nm × 75 nm) of C_T = 0.25mM samples with dotted white rectangle indicating a {33} strip.
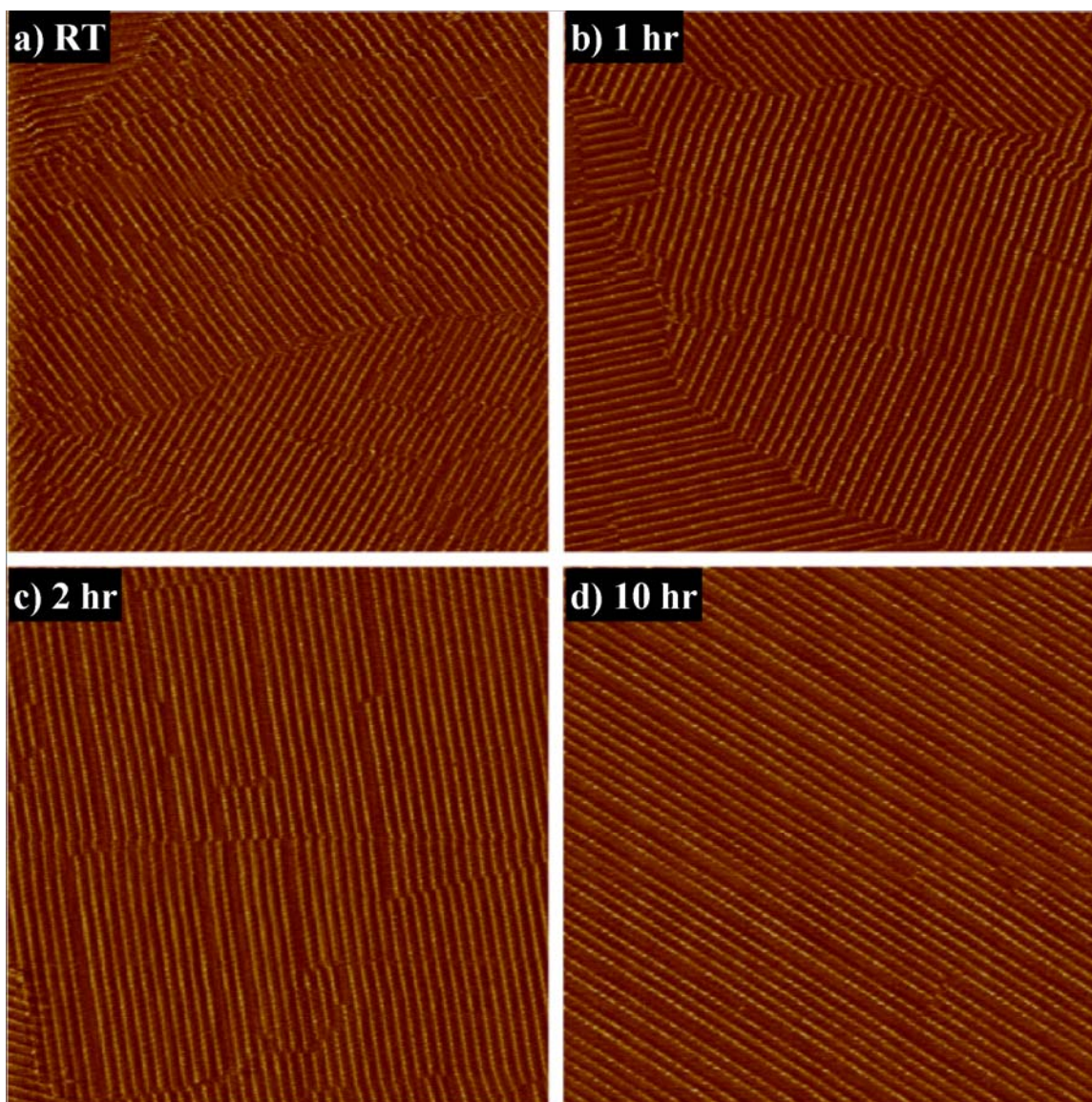
Figure 4 (enlarged). STM images (all 135 nm × 135 nm) of $C_T = 0.25$mM, R_s=4 samples annealed for various times.
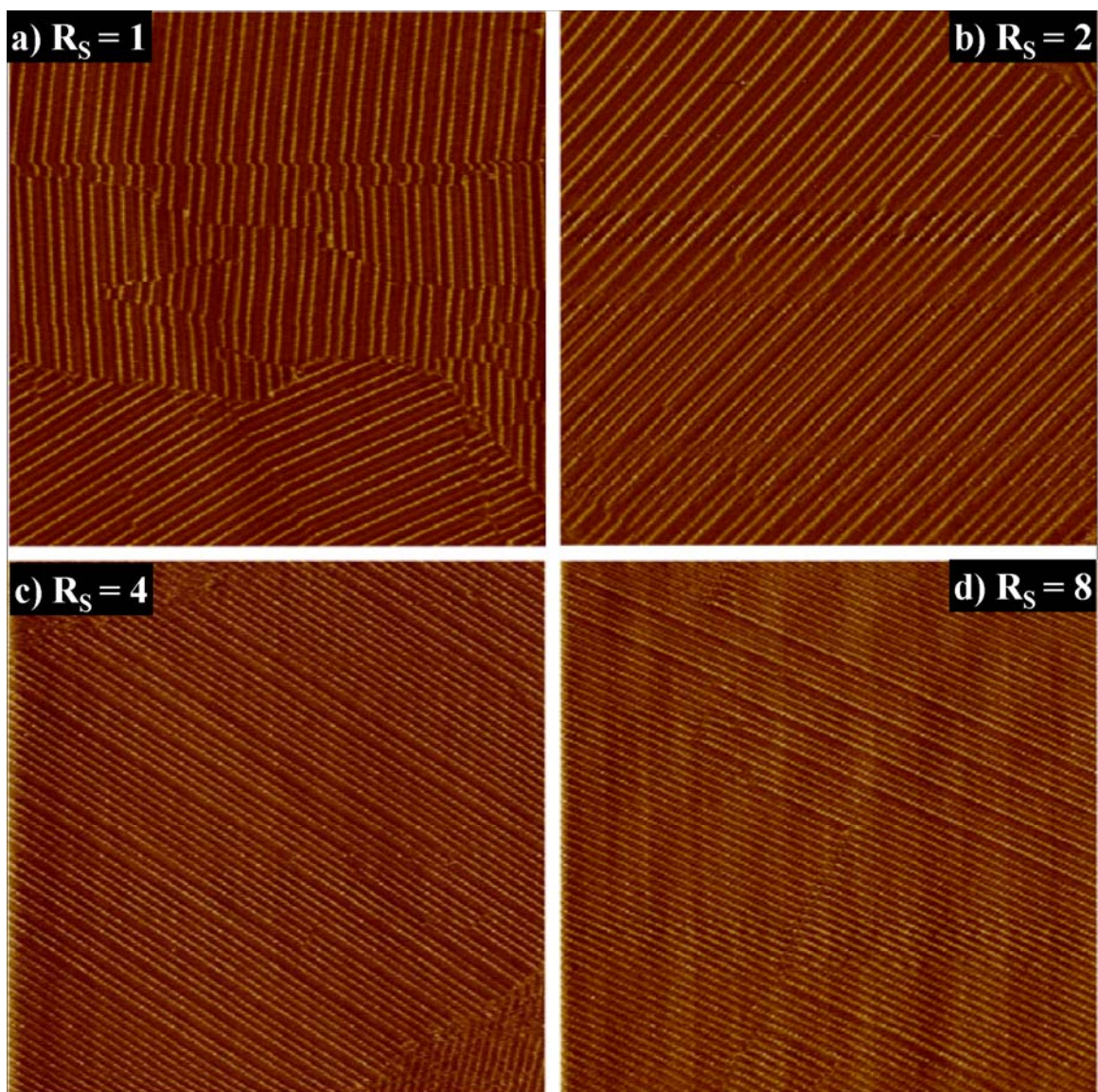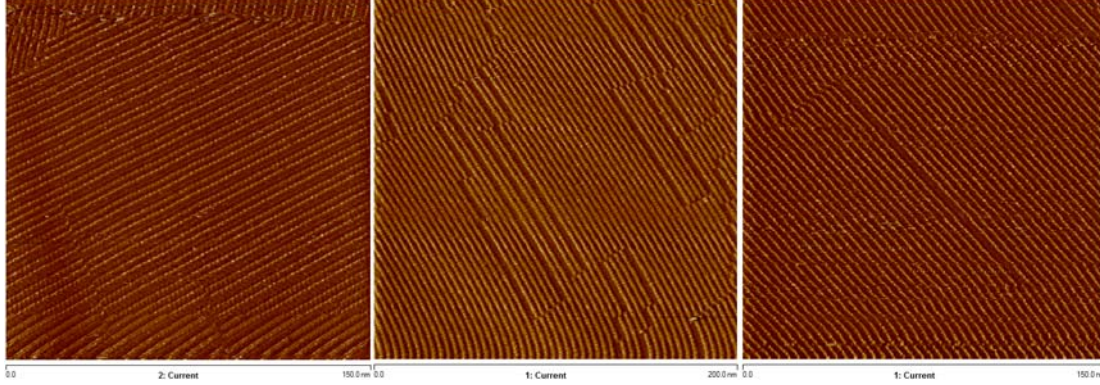
Figure 6 (enlarged). STM images of $C_T = 0.25$mM samples annealed at 45 ^{o}C for 10 hours.

IV. Apparent phase segregation at 55 $^{\circ}$C for $R_S = 4$, $C_T = 0.25$ mM sample

Three STM scans were captured from different regions on the same graphite substrate. The three STM scans revealed regions of (left) mostly pure {33,19}, (middle) {33} strips mixed with{19_2}, (right) predominantly {19_2}.

V. Strip length, area ratio, and linear density analysis methods
For each sample preparation condition (*i.e.,* R_S , C_T and annealing time variable), 10~12 independent STM images were analyzed. The same images were used to analyze strip length, area ratio, and linear density analyses.

Strip Length Analysis STM images were imported into Bruker's NanoScope Analysis software. Each {33} strip was measured by the software "ruler" tool. Strip length data was recorded in a spreadsheet and the reported normalized histograms were generated using IGOR Pro. Analogous to polydispersity analysis in polymer science, number averaged strip *length* and length averaged strip *length* were derived from measure strip length data as described below:

Number average strip length

$$L_N = \frac{\sum(l_i \cdot n_i)}{\sum n_i}$$

-l_i is the strip length
- n_i is the number of strips that fall into the corresponding l_i

Since in actual STM data, <u>every</u> strip length is measured and counted. To simplify the above equation, n_i is 1 and $\sum n_i$ is the total count of strips measured in any given sample preparation condition.

Length average strip length

$$L_L = \frac{\sum[l_i(l_i \cdot n_i)]}{\sum(l_i n_i)}$$

The ratio of weight average strip length to number average strip length gives the dispersity index.

$$DI = \frac{L_L}{L_N}$$

<u>Area Ratio Analysis</u> The mole ratio of each monolayer, R_{ML}, was determined by analyzing the area of {33,19} molecules in 1×10^4 - 4×10^4 nm^2 STM images. Each {33} strip is an assembly of two columns of {33, 19} molecules packed with interdigitated {33} side chains. Thus, the area of {33,19} molecules comprising a {33} strip is the area of *two* anthracene columns plus the area
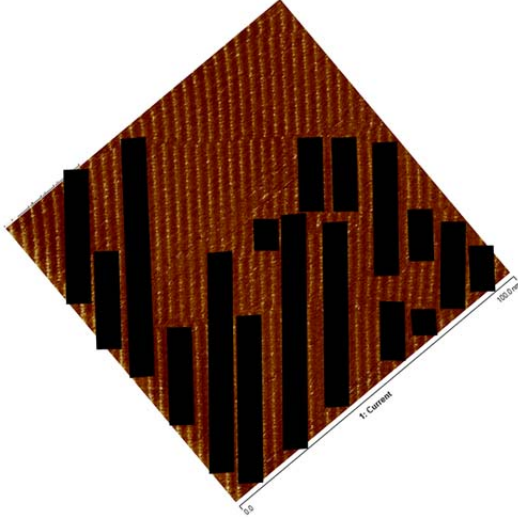
of the intervening {33} strip plus the area of one neighboring {19} column. As shown in the image (left), areas of {33,19} molecules are marked by the black rectangles. The sum of all black rectangles gives the total area of {33,19} molecules, $A_{\{33,19\}}$ in pix^2, and was determined using the particle analysis algorithm in IGOR Pro. Since the image area, A_i, is known, the difference between the image area and $A_{\{33,19\}}$ gives the area of {19$_2$} in pix^2. $A_{\{33,19\}} / A_i$ gives the area percentage of {33,19} molecules and the actual area in nm^2 is obtained by multiplying the image area (in nm^2) and the percentage, $A_{\{33,19\}} / A_i$. The same algorithm is applied to the area of {19$_2$} molecules. To convert area ratio to surface mole ratio, the unit cell areas of {33,19} and {19$_2$} were determined from experimental STM images of the single component monolayers {33,19} and {19$_2$}, giving 3.64 nm^2 and 2.88 nm^2 per molecule, respectively.

The mole ratio, R_{ML}, was calculated using the {19$_2$} and {33,19} areas from all images collected for a particular sample preparation condition as $R_{ML} = \dfrac{\sum A_{\{19_2\}} / unit\ cell\ of\ A_{\{19_2\}}}{\sum A_{\{33,19\}} / unit\ cell\ of\ A_{\{33,19\}}}$.

<u>Linear Density Analysis</u> To obtain the <u>mean</u> {33} strip spacing, $<D_{SS}>$, each STM image was segmented into triangular or trapezoidal regions with the bases perpendicular to the anthracene columns (see below). Each {33} strip within a region spans that region's entire height; wherever a {33} strip ends, a new region begins. The {33} strip density data from each region was

weighted by the region's area in calculating the mean strip spacing:
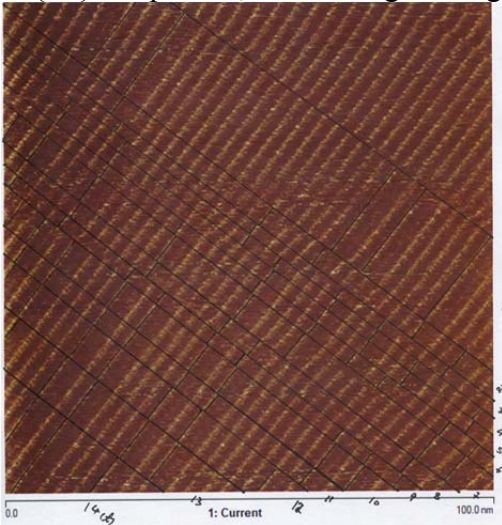
The area, A_i, width, W_i, and strip density, ρ_i, of each trapezoidal region, i, was calculated from the region's top base (a_i), bottom base (b_i), height (h_i) and number of {33} strips (n_i) :

$$A_i = (a_i + b_i) * h_i/2 \quad W_i = (a_i + b_i)/2 \quad \rho_i = n_i / W_i$$

The mean {33} strip spacing was calculated using ρ_i and A_i from all regions in all corresponding images:

$$<D_{ss}> = \sum_{i=1}^{n} \frac{A_i}{\sum A_i} \cdot \rho_i^{-1}$$

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Annealing rate data (R_{ML}) and equations used to analyze temperature dependence of monolayer composition

Annealing rate data (R_{ML})
$R_S = 4$

$19^{o}C$ dropcast	$R_{ML} = 7.49 \pm 1.43$
$45^{o}C$ anneal 1 hr	$R_{ML} = 5.17 \pm 0.97$
$45^{o}C$ anneal 2 hr	$R_{ML} = 3.65 \pm 0.26$
$45^{o}C$ anneal 10 hr	$R_{ML} = 2.50 \pm 0.46$

Fit to $R_{ML} = Offset_{45} + Amp_{45}*exp(-k_{45}T)$
$Offset_{45} = 2.5 \pm 0.3$
$Amp_{45} = 5.0 \pm 0.3$
$k_{45} = 0.69 \pm 0.13\ hr^{-1}$
(uncertainty ranges set by fit error increasing 5% from the best fit)

$R_S = 4$

$19^{o}C$ dropcast	$R_{ML} = 7.49 \pm 1.43$
$55^{o}C$ anneal 1 hr	$R_{ML} = 2.54 \pm 0.32$
$55^{o}C$ anneal 2 hr	$R_{ML} = 1.71 \pm 0.36$
$55^{o}C$ anneal 10 hr	$R_{ML} = 0.90 \pm 0.46$

Fit to $R_{ML} = Offset_{55} + Amp_{55}*exp(-k_{55}T)$
$Offset_{55} = 1.0 \pm 0.3$
$Amp_{55} = 6.5 \pm 0.4$
$k_{45} = 1.4 \pm 0.3\ hr^{-1}$
(uncertainty ranges set by fit error increasing 5% from the best fit)

Equations used to analyze temperature dependence of monolayer composition
$\underline{\Delta\Delta G^{o}{}_{ads}}$

$\{19_2\}_{SOLN} + (vacancy)_{ML} \leftrightarrows \{19_2\}_{ML}$	$\Delta G^{o}{}_{ads}\{19_2\}$
$\{33,19\}_{SOLN} + (vacancy)_{ML} \leftrightarrows \{33,19\}_{ML}$	$\Delta G^{o}{}_{ads}\{33,19\}$

$\{33,19\}_{ML} + \{19_2\}_{SOLN} \leftrightarrows \{19_2\}_{ML} + \{33,19\}_{SOLN}$ $\Delta\Delta G^{o}{}_{ads} = \Delta G^{o}{}_{ads}\{19_2\} - \Delta G^{o}{}_{ads}\{33,19\}$

$K_{EQ} = [\{33,19\}_{SOLN}][\{19_2\}_{ML}] / ([\{19_2\}_{SOLN}][\{33,19\}_{ML}]) \approx R_{ML} / R_S$

$\Delta\Delta G^{o}{}_{ads} = -RT\ ln(R_{ML} / R_S)$

The above model does not account for different surface areas and, thus, maximum monolayer concentrations of $\{33,19\}$ and $\{19_2\}$.

<u>van't Hoff analysis </u>(presuming temperature independent $\Delta\Delta H^{o}{}_{ads}$ and $\Delta\Delta S^{o}{}_{ads}$)

$\Delta\Delta H^{o}{}_{ads} = [ln(K_{EQ}(318K)) - ln(K_{EQ}(328K))] / [(328K \times R)^{-1} - (318K \times R)^{-1}]$

$\Delta\Delta S^{o}{}_{ads} = [\Delta\Delta H^{o}{}_{ads} - \Delta\Delta G^{o}{}_{ads} (328\ K)] / (328\ K)$