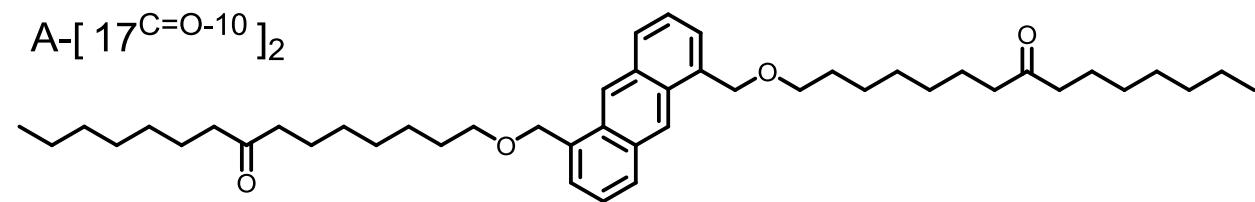
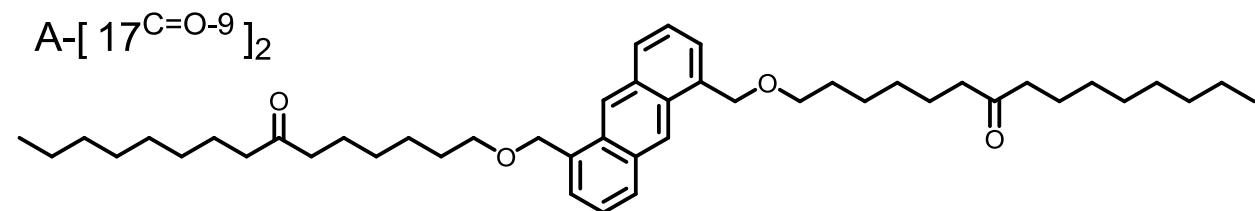


ESI - Monolayer Patterning Using Ketone Dipoles

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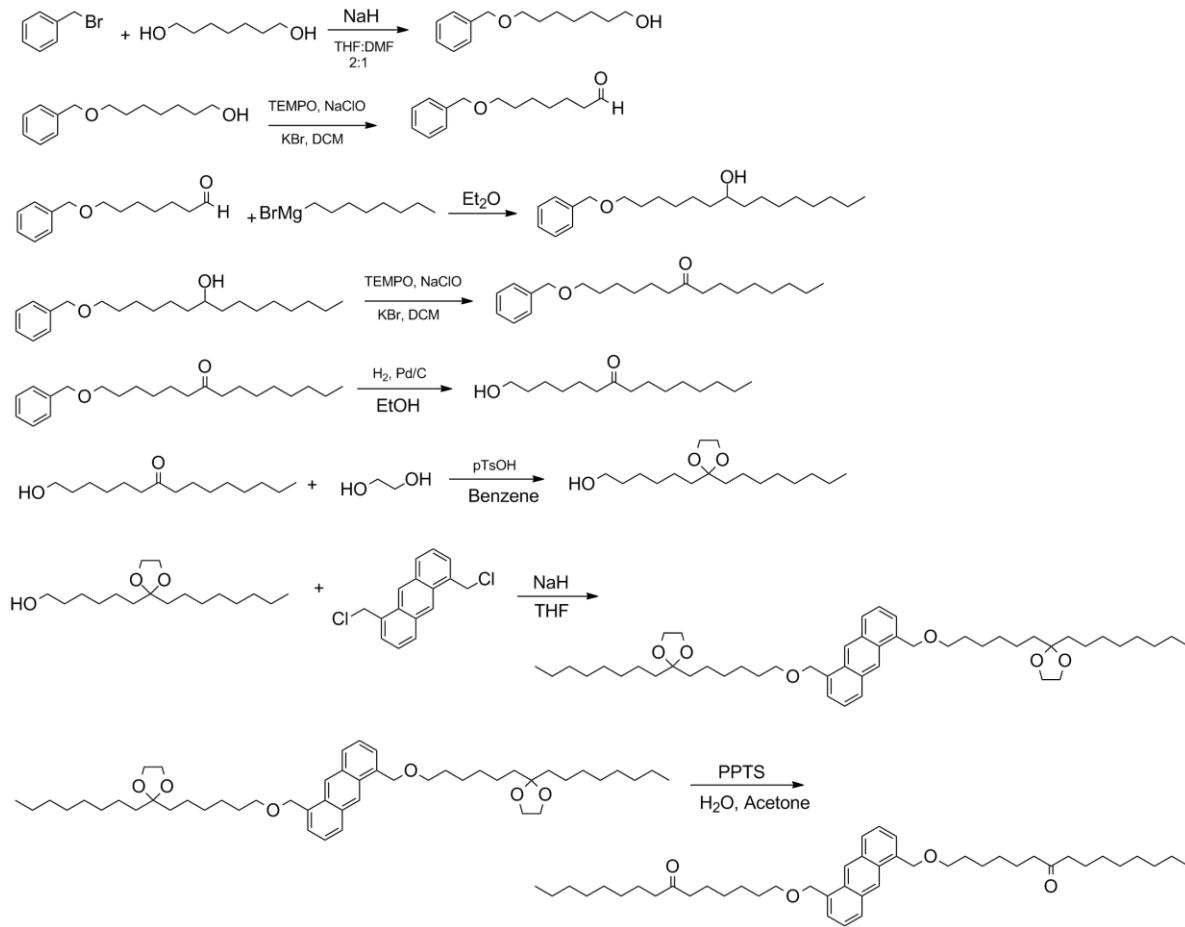
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A. Synthetic procedures and Spectral Characterization¹

Dry Solvent

Reactions requiring dry and deoxygenated solvents employed THF, DCM and DMF from a Solvent Dispensing System (Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.)

Synthetic scheme for A-[17²-C=O^{9,9}]₂:



Preparation of 7-(benzyloxy)heptanal

Preparation of 7-(benzyloxy)heptan-1-ol: 1,7-heptane-diol (5.0g, 37.8mmol) was added to a flame-dried flask, followed by 20mL of dry THF under nitrogen with magnetic stirring. The solution was cooled down to 0°C, and sodium hydride (0.97g, 40.6mmol) was added. 10mL of dry DMF was then added. After one hour of equilibration, benzyl bromide (4.0mL, 33.8mmol) was added at 0°C. The solution was stirred at room temperature for 18 hours.

¹ Synthetic procedures taken from the Sc.B. thesis of Min Kyoung Kim (Brown University, 2013)

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Work-up: 2.5% HCl was added until the mixture turned acidic. The crude product was extracted using ethyl acetate (3 X 30 mL). The organic layer was washed with 2.5% HCl, water, brine and then dried over sodium sulfate. The solvent was removed under reduced pressure using a rotary evaporator. The crude product was used for the next step without purification.

Preparation of 7-(benzyloxy)heptanal: Crude 7-(benzyloxy)heptan-1-ol (4.89g) and TEMPO (45mg, 0.29mmol) were dissolved in methylene chloride. The solution was cooled down to 0°C, and potassium bromide (0.26g, 2.2mmol) was dissolved in 1mL water and then was added to the reaction flask. The reaction mixture was stirred at 0°C for 5 minutes, then 1M NaClO solution (22mL, pH~8; pH adjustment with NaHCO₃) was added dropwise. Then the solution was stirred at room temperature for 10 minutes.

Work-up and purification: The reaction was quenched with 0.5M HCl. The crude product was extracted using methylene chloride (3 X 30 mL). The organic layer was washed with 0.5M HCl, water, brine and then dried over sodium sulfate. The solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified by flash column chromatography (10% ethyl acetate/90% hexanes), affording 2.36g of 7-(benzyloxy)heptanal (colorless liquid, 10.7mol, yield over two steps: 32%). This compound was reported previously.²

Preparation of 6-(2-octyl-1,3-dioxolan-2-yl)hexan-1-ol

Preparation of Grignard reagent: Magnesium turnings (1.64g, 68mmol) and a magnetic stir bar were placed in a dry 20-mL microwave tube, which was sealed after the addition. The microwave tube was then dried over vacuum for one hour then charged with nitrogen. 1-bromoocetane (3.74mL, 21.7mmol) was added at 0°C, followed by 10mL of dry diethyl ether. The mixture was stirred at 0°C for about 5 minutes and then was stirred at room temperature until the solution turned dark. Then the tube was placed in a microwave reactor at 100°C for 1 hour.

Preparation of 1-(benzyloxy)pentadecan-7-ol: 7-(benzyloxy)heptanal (2.36g, 10.7mmol) was added to a flame-dried two-neck flask with a water condenser under nitrogen. The freshly prepared grignard reagent was added to the flask at 0°C followed by 20mL of dry diethyl ether. The solution was refluxed for 5 hours.

Work-up: The reaction was quenched by adding 2.5% HCl (15mL). The crude product was extracted using methylene chloride (3 X 30 mL). The organic layer was washed with 2.5% HCl, water, brine and then dried over sodium sulfate. The solvent was removed under reduced pressure using a rotary evaporator. The crude product was used for the next step without purification.

Preparation of 1-(benzyloxy)pentadecan-7-one: Crude 1-(benzyloxy)pentadecan-7-ol (4.0g) and TEMPO (24mg, 0.16 mmol) were dissolved in methylene chloride. The solution was cooled down to 0°C, and potassium bromide (0.14g, 1.2mmol) was dissolved in 1mL water and then was added to the reaction flask. The reaction mixture was stirred at 0°C for 5 minutes, then 1M NaClO solution (18mL, pH~8; pH

² (a) Davis, A.F.; Zhang, J.; Li, Y.; Xu, H.; DeBrosse, C. *J. Org. Chem.* **2005**, 70, 5413-5419. (b) Mohapatra, D.K.; Bhattacharjee, D.; Gurjar, M.K.; Khan, M.L.; Shashidhara, K.S. *Eur. J. Org. Chem.* **2008**, 36, 6213–6224. (c) Yadav, J.S.; Reddy, C.S. *Org. Lett.*, **2009**, 11, 1705–1708.

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adjustment with NaHCO_3) was added dropwise. The reaction mixture was stirred at room temperature for 30 minutes.

Work-up: The reaction was quenched by adding 0.5M HCl. The crude product was extracted using methylene chloride (3 X 30 mL). The organic layer was washed with 0.5M HCl, 0.1M NaI solution, saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution, water and brine then dried over sodium sulfate. The solvent was removed under reduced pressure using a rotary evaporator. The crude product was used for the next step without purification.

Preparation of 1-hydroxypentadecan-7-one : 0.27g palladium/carbon powder and a stir bar were placed in a round-bottom flask. The flask was flushed with nitrogen for 10 minutes then 120mL of ethanol and crude 1-(benzyloxy)pentadecan-7-one (3.0g) was added. The reaction mixture was then charged with a hydrogen balloon and stirred at room temperature for 20 hours. The palladium/carbon was then filtered out using celite. The solvent was removed under reduced pressure using a rotary evaporator. The crude product was used for the next step without purification.

Preparation of 6-(2-octyl-1,3-dioxolan-2-yl)hexan-1-ol: Crude 1-hydroxypentadecan-7-one (4.0g), p-toluenesulfonic acid (0.23g, 1.2mmol), ethylene glycol (2.2mL, 0.40mol), benzene (140mL) were placed in a round-bottom flask. The reaction mixture was refluxed for 20 hours with a Dean-Stark trap.

Work-up and purification: The reaction mixture was extracted using ethyl acetate (3 X 30 mL). The organic layer was washed with saturated NaHCO_3 solution, water and brine then dried over sodium sulfate. The solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified by flash column chromatography (20/80 ethyl acetate/hexanes then 30/ 70 ethyl acetate in hexanes), affording 1.72g of 6-(2-octyl-1,3-dioxolan-2-yl)hexan-1-ol (white solid, 6.0mmol, yield over 4 steps: 56%)

^1H NMR (300MHz, CDCl_3): δ 3.89 (s, 4H), 3.59 (t, $J=7.5\text{Hz}$, 2H), 1.53 (m, 6H), 1.30 (m, 18H), 0.85 (t, $J=6\text{Hz}$, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 111.84, 64.82, 63.12, 62.77, 37.10, 36.98, 32.64, 32.48, 31.83, 29.90, 29.65, 29.53, 29.21, 25.67, 23.81, 23.73, 14.04.

**Preparation of 1,1'-(anthracene-1,5-diylbis(methylene))bis(oxy))bis(pentadecan-7-one)
(i.e. A-[17²-C=O^{9,9}]₂)**

Step 1: Sodium hydride (19mg, 0.80mmol) was added to a flame-dried microwave tube under argon atmosphere. 6-(2-octyl-1,3-dioxolan-2-yl)hexan-1-ol (0.20g, 0.69mmol) was dissolved in 6mL dry THF and was added into the microwave tube using a syringe. Then the tube was placed in a microwave reactor at 130°C for 1 hour. 1,5-bis(chloromethyl)anthracene (50mg, 0.18mmol) was dissolved in 2mL of dry THF and was added to the mixture. The reaction mixture was placed in the microwave reactor at 130°C for 5 hours.

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The reaction mixture was quenched with water and was extracted using methylene chloride (3 X 15mL). The organic layer was washed with 0.5M HCl, water, and brine. The solvent was removed under reduced pressure using a rotary evaporator.

Step 2: The resulting crude product (0.25g) was placed in a round-bottom flask with 4.3mg pyridinium *p*-toluenesulfonate, 9mL acetone and 1mL of water. The reaction mixture was refluxed for 3 hours.

Work-up and purification: Acetone was evaporated under reduced pressure using a rotary evaporator. 40mL of methylene chloride was used to extract the crude product. The organic layer was then washed with water, saturated NaHCO₃ solution, and brine. The solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified by flash column chromatography (100% methylene chloride then 95/5 methylene chloride/ethyl acetate), affording 15mg of 1,1'-(anthracene-1,5-diylbis(methylene))bis(oxy))bis(pentadecan-7-one) (yellow solid, 0.022mmol, yield over two steps: 11%)

¹H NMR (300MHz, CDCl₃): δ 8.73 (s, 2H), 8.02 (d, J=6Hz, 2H), 7.54 (d, J=6Hz, 2H), 7.45 (dd, J=6Hz and 5Hz, 2H), 5.10 (s, 4H), 3.62 (t, J=6Hz, 4H), 2.37 (m, 8H), 1.64 (m, 8H), 1.40 (m, 32H), 0.89 (t, J=6Hz, 6H).

¹³C NMR (75 MHz, CDCl₃): δ 210.55, 134.02, 132.05, 129.89, 128.95, 125.70, 124.53, 122.97, 71.70, 70.35, 43.01, 42.96, 32.24, 30.03, 29.80, 29.55, 29.24, 29.14, 26.11, 23.95, 23.69, 22.76, 15.01.

m/s (FAB) m/z Calcd for (M+Na)⁺ (C₄₆H₇₀O₄Na) 709.5, found 709.2.

A-[17²-C=O^{10,10}]₂ was synthesized using similar procedure, the spectral data are listed below:

1,1'-(anthracene-1,5-diylbis(methylene))bis(oxy))bis(pentadecan-8-one):

¹H NMR (300MHz, CDCl₃): δ 8.72 (s, 2H), 8.03 (d, J=9Hz, 2H), 7.52 (d, J=6Hz, 2H), 7.47 (dd, J=6Hz and 6Hz, 2H), 5.09 (s, 4H), 3.60 (t, J=6Hz, 4H), 2.35 (m, 8H), 1.64 (m, 8H), 1.35 (m, 32H), 0.89 (t, J=6Hz, 6H).

¹³C NMR (75 MHz, CDCl₃): δ 211.73, 133.89, 132.04, 129.77, 129.26, 125.73, 124.76, 123.52, 71.71, 70.41, 42.82, 42.75, 31.69, 29.76, 29.23, 29.19, 29.10, 26.13, 23.89, 23.79, 22.62, 14.09.

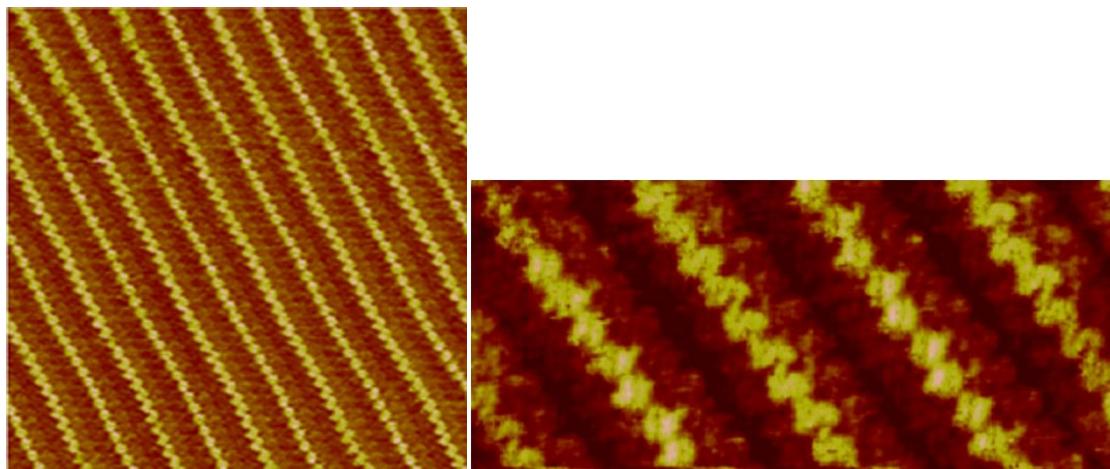
m/s (FAB) m/z Calcd for (M+Na)⁺ (C₄₆H₇₀O₄Na) 709.5, found 709.5.

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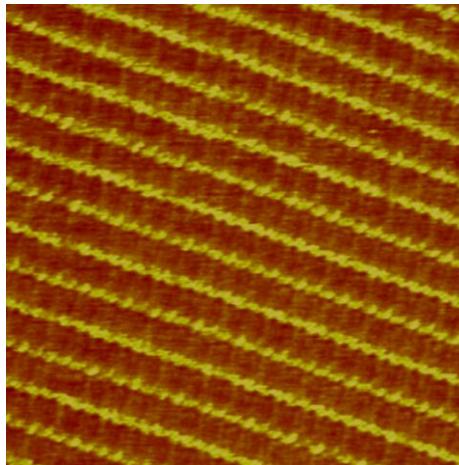
B. Additional STM images

S1. (left) 30nm x 30 nm constant height STM scan of 1mM A-[17^{C=O-10}]₂ in phenyloctane (0.9 V, 0.1 nA, 5.55 Hz, uncorrected). The 15 anthracene columns exhibit two distinct patterns, with nearest anthracene columns exhibiting distinct patterns and every other anthracene column exhibiting similar patterns.

(right) 15nm x 6.6nm monolayer section assembled from 1mM A-[17^{C=O-10}]₂ in phenyloctane (constant current, 1.2V, 0.1nA, 12.2Hz). To enhance the STM image resolution, a drop (~1μL) of phenyloctane solution containing 5μM C₆₀ fullerene was applied to a previously assembled monolayer.

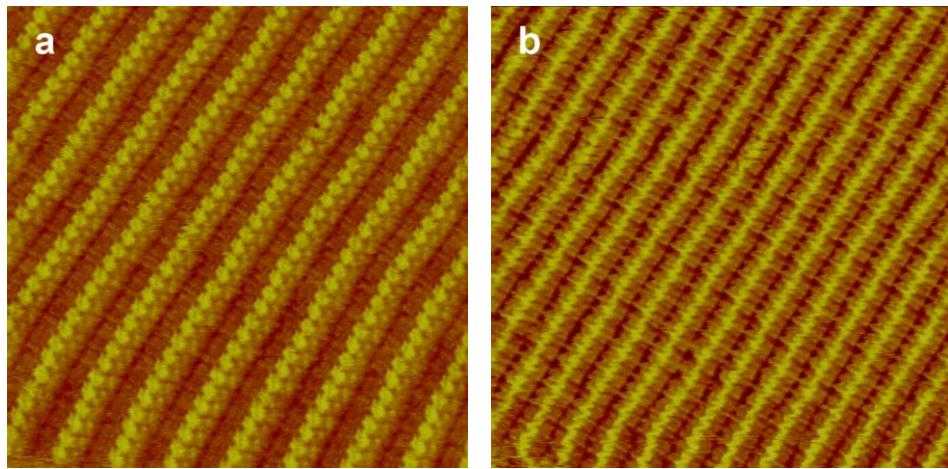


S2. 30nm x 30 nm constant height STM scan of A-[17^{C=O-9}]₂ in phenyloctane (0.8 V, 0.1 nA, 7.6Hz, uncorrected). Although the shapes of individual anthracene cores in this image are difficult to resolve, the 16 anthracene columns exhibit two distinct patterns, with nearest anthracene columns exhibiting distinguishable patterns and every other anthracene column exhibiting similar patterns.

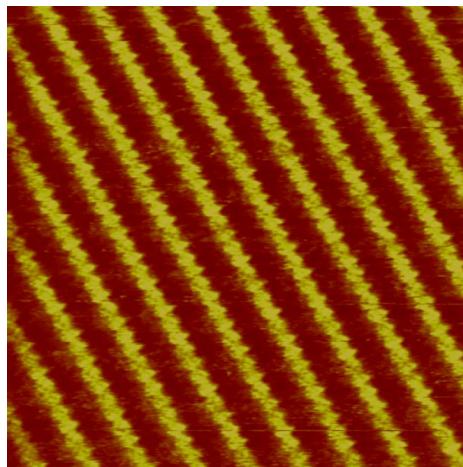


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S3. Larger area STM scans of the A-[17^{C=0-9}]₂ / A-[17^{C=0-10}]₂ patterned monolayer formed at the solution - HOPG interface. a) A 25 x 25 nm² scan (uncorrected) reveals parallel anthracene alignment in all columns. b) The similar tunneling patterns in all anthracene columns of a 35 x 35 nm² scan is consistent with the parallel anthracene alignments observed in Figure S3a and is inconsistent with alternating anthracene adsorption alignments observed for the individual components (Figures S1 and S2).

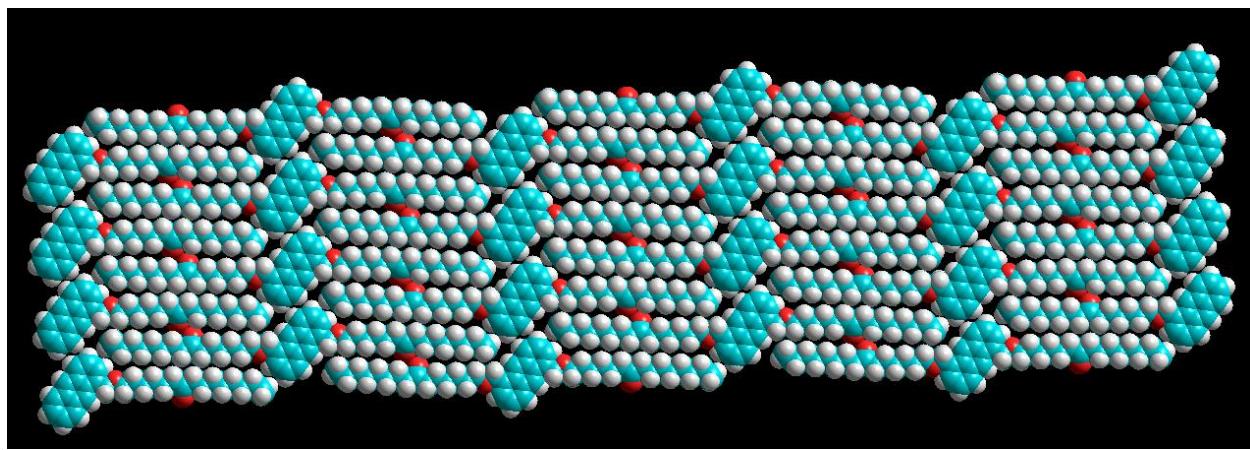


S4. 30nm x 30nm constant current image (1.2 V, 0.1 nA, 7.6 Hz, uncorrected) of a monolayer assembled from 1mM A-[17^{F-9,9}]₂ and A-[17^{C=0-10}]₂. The similar anthracene shapes and alignments within all 13 anthracene columns are consistent with the AB adsorption morphology seen in Figure 3a of the text.

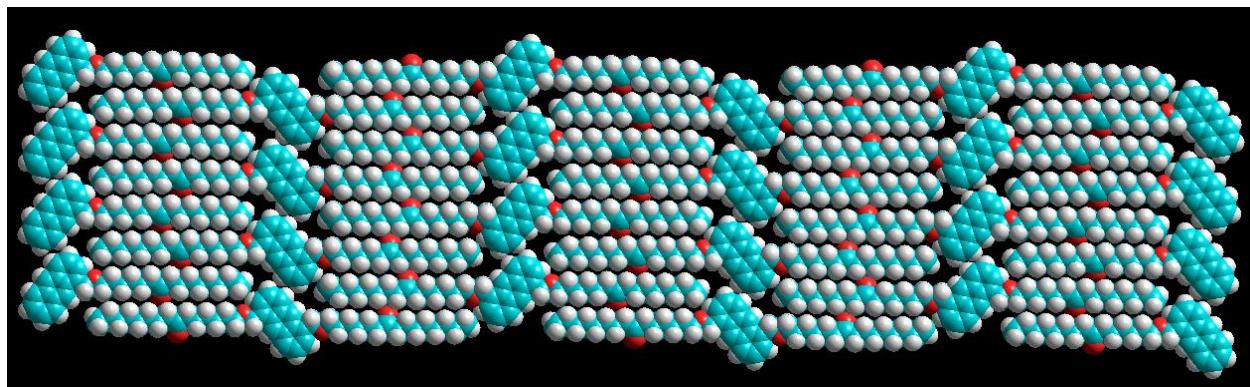


C. Monolayer Sections used to determine Self-Assembly Energetics (SAE) using Molecular Mechanics

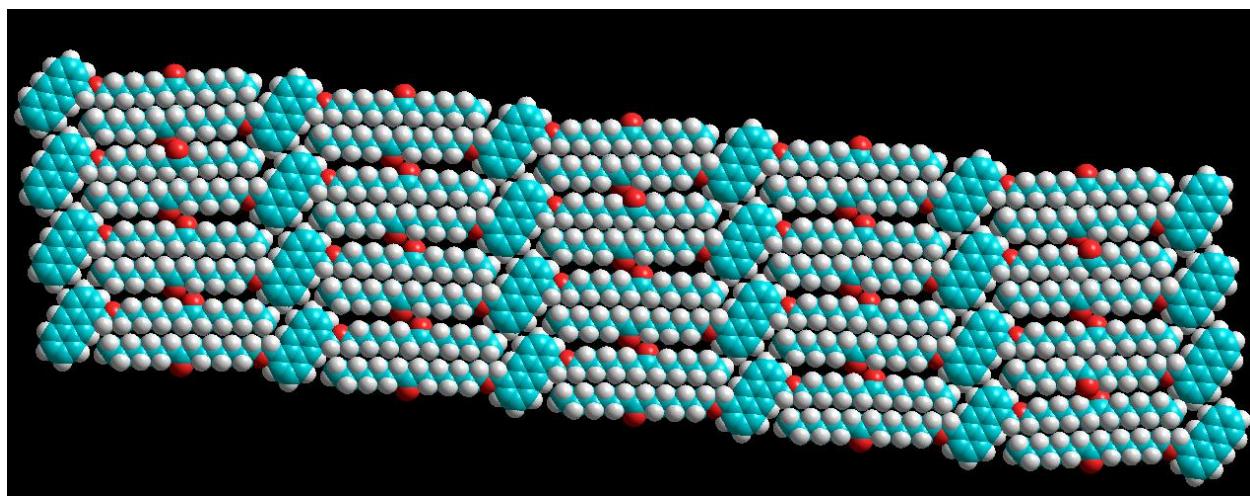
AA ($\omega \leftrightarrow 2$) packed monolayer section of A-[17^{C=O-9}]₂



AA* ($\omega \leftrightarrow 3$) packed monolayer section of A-[17^{C=O-9}]₂

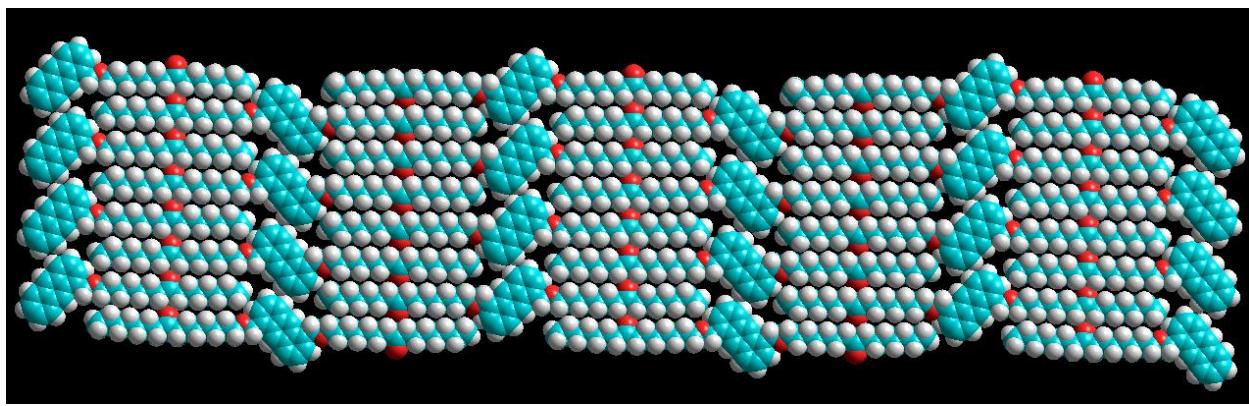


AA ($\omega \leftrightarrow 2$) packed monolayer section of A-[17^{C=O-10}]₂

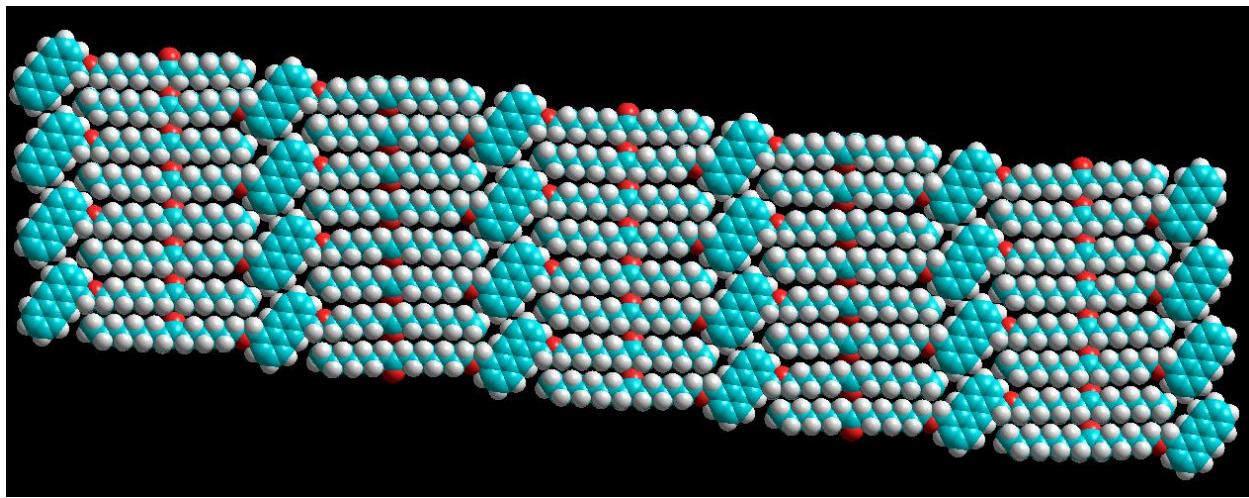


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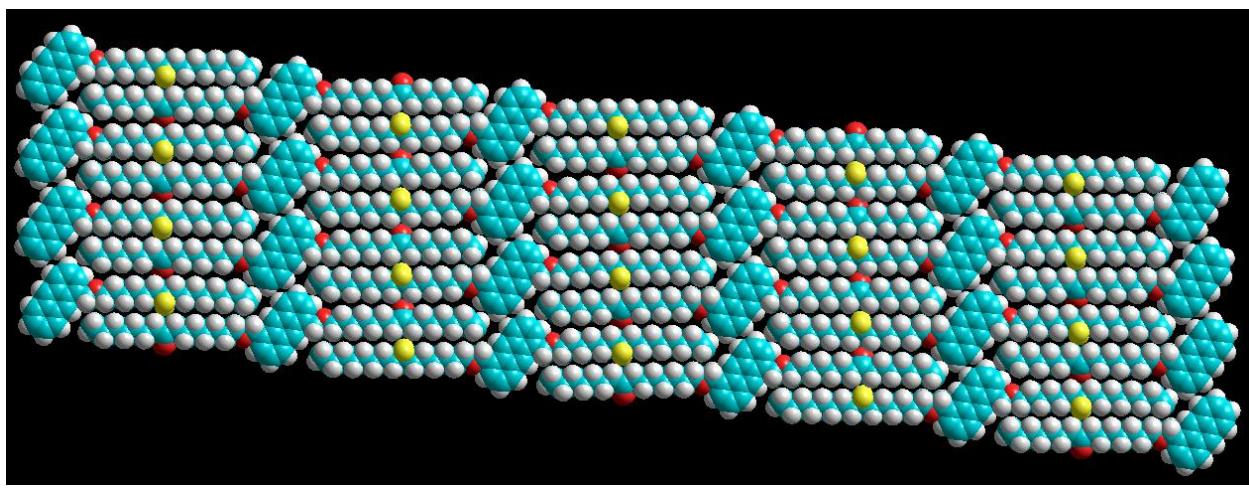
AA* ($\omega \leftrightarrow 3$) packed monolayer section of A-[17^{C=O-10}]₂



AB ($\omega \leftrightarrow 2$) packed, patterned monolayer of A-[17^{C=O-9}]₂ and A-[17^{C=O-10}]₂



AB ($\omega \leftrightarrow 2$) packed, patterned monolayer of A-[17^{F-9,9}]₂ and A-[17^{C=O-10}]₂



D. Unit Cells of Ketone Monolayers from STM scans and from Molecular Mechanics Simulations

Monolayer	Unit Cell Parameters					
	STM Measurements			Molecular Mechanics Simulations		
	a (nm)	b(nm)	α (°)	a (nm)	b(nm)	α (°)
A-[17 ^{C=O-9}] ₂	0.99 ± 0.04	6.01 ± 0.13	73.6 ± 2.7	0.94 ± 0.01	6.12 ± 0.02	79.6 ± 1.4
A-[17 ^{C=O-10}] ₂	1.00 ± 0.04	5.86 ± 0.11	77.0 ± 5.5	0.93 ± 0.01	6.04 ± 0.03	81.0 ± 1.4
A-[17 ^{C=O-9}] ₂ + A-[17 ^{C=O-10}] ₂	0.92 ± 0.03	5.70 ± 0.10	84.8 ± 3.5	0.96 ± 0.01	5.85 ± 0.02	81.4 ± 0.4
A-[17 ^{F-9,9}] ₂ + A-[17 ^{C=O-10}] ₂	0.92 ± 0.04	5.76 ± 0.14	86.2 ± 3.3	0.96 ± 0.01	5.84 ± 0.01	84.0 ± 0.9