Supporting Information for

Large Area Synthesis of a Nanoporous Two-Dimensional Polymer at the Air/Water Interface

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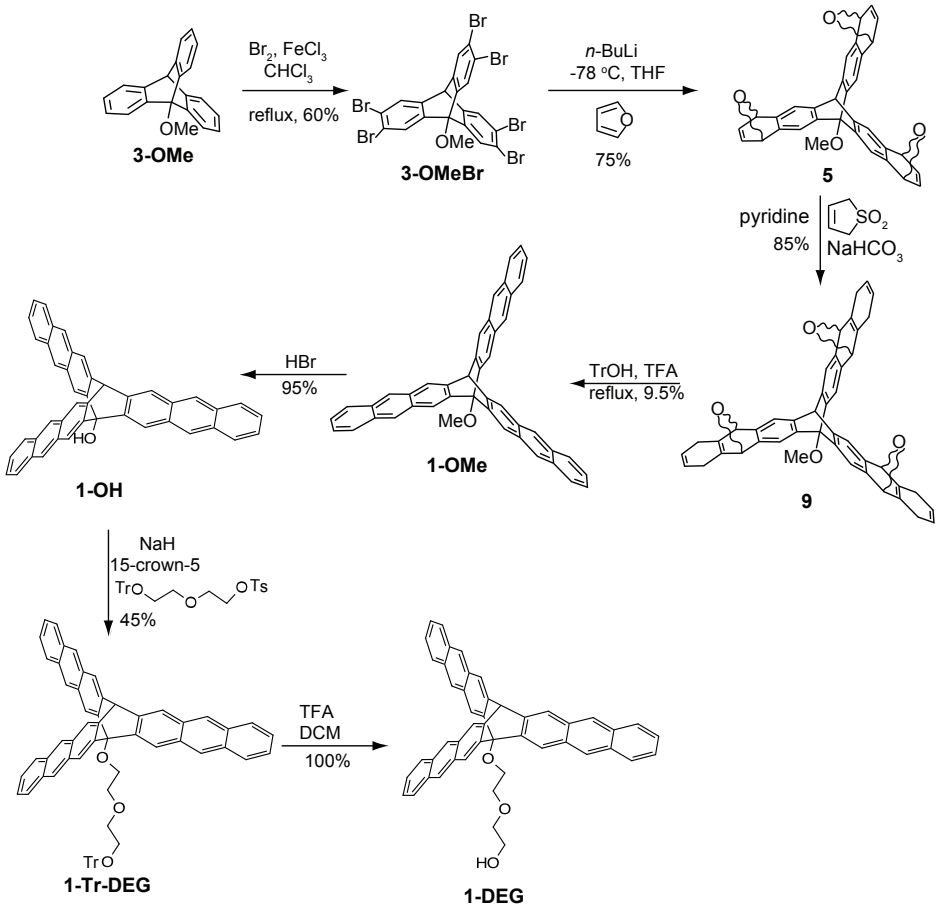
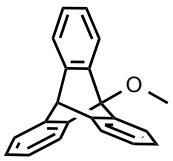
Table of Contents

Synthetic Procedures



Scheme S1. Synthesis of Antrip-DEG (**1-DEG**)



Synthesis of 9-methoxytriptycene (3-OMe):[1] 9-Methoxyanthracene[2] (8.52 g, 0.03 mmol) and isoamyl nitrite (6.0 mL, 0.04 mmol) were dissolved in 1,2-dimethoxyethane (DME) (60 mL) in a three-neck round bottom flask. A water cooled condenser was attached to the flask. The solution was heated to reflux at 96 °C. Anthranilic acid (15.6 g, 0.113 mmol) was dissolved in DME (70 mL) in a separate flask. The first half of the anthranilic acid solution was added dropwise,

over 3 hr, using a syringe pump to the refluxing reaction mixture. When the addition was complete, the reaction mixture was refluxed for additional 15 min, followed by cooling the reaction mixture. Then a second portion of isoamyl nitrite (6 mL) was added (DO NOT ADD TO BOILING SOLUTION) reaction mixture was again heated to reflux. Once at reflux the remaining anthranilic acid solution was added dropwise, over 3 hr, using a syringe pump to the reaction mixture. After complete addition of anthranilic acid solution, the reaction mixture was cooled to room temperature. Then 95% ethanol (60 mL) was added, followed by a solution of sodium hydroxide (9.0 g in 120 mL water). The precipitated solids were filtered and washed with cold methanol:water (4:1) solution (100 mL). The crude product was dried and weighed (6.2 g). The crude product was dissolved in xylene (60 mL) and maleic anhydride (3.0 g) was added. The mixture was refluxed for 30 min. After 30 min, the solution was cooled to 100 °C, followed by addition of 95% ethanol (29 mL) and sodium hydroxide solution (8.8 g in 118 mL water). Reaction mixture was stirred overnight. The organic layer was evaporated under reduced pressure and the product was recrystallized from dichloromethane methanol to give clean 9-methoxytriptycene (5.5 g, 19.3 mmol).

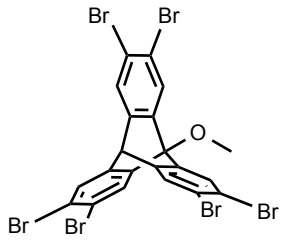
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (d, *J* = 7.4 Hz, 1H), 7.32 – 7.26 (d, *J* = 8.4 Hz, 1H), 7.01 – 6.89 (dtd, *J* = 25.2, 7.5, 1.3 Hz, 3H), 5.31 (s, 1H), 4.35 (s, 3H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 145.3, 144.6, 125.5, 125.1, 123.5, 121.6, 88.1, 57.7, 53.6.

IR (ATR) [cm^{-1}] 3066, 3001, 2900, 2834, 1448, 1290, 1237, 1071, 988, 744, 640.

UV-Vis λ_{max}/nm ($CHCl_3$) (log ε): 236 (3.65), 277 (3.46).

HRMS calcd for $C_{21}O_1H_{16}$ 284.1201, found 284.1216. m.p. 204 – 205 °C.



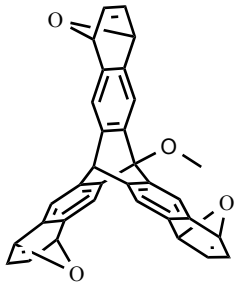
9-Methoxyhexabromotriptycene (3-OMeBr):[1] **(9-Methoxytriptycene)** (1.0 g, 3.9 mmol) is dissolved in chloroform, dried over mol sieves, (250 mL). Then iron powders, fine mesh, (0.03 g, 0.50 mmol) was added, followed by addition of 6 eqv of bromine (1.19 ml, 23.4 mmol) to a room temperature solution. The reaction mixture is refluxed overnight under N_2. The reaction mixture is cooled to room temperature and the solvent is evaporated. The remaining solid tends to be a mixture of **3-OMeBr** and **3-OHBr**, due to the ability of HBr to deprotect the methoxy group. The reaction solution is dissolved in a 30% toluene 70% hexanes mixture and ran through a pad of silica. The first band, **3-OMeBr**, is collected (r.f. of ~.7) and dried under reduced pressure evaporation. The target product is then recrystallized from a dichloromethane acetone solution and filtered to give (1.59 g, 2.09 mmol) of a white to yellowish solid **3-OMeBr** (60%). The remaining **3-OHBr** can be isolated and re-methylated using a well established literature method.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.58 (s, 1H), 5.11 (s, 1H), 4.26 (s, 3H). ^{13}C ^{13}C NMR (500 MHz, $CDCl_3$) δ 144.4, 143.3, 128.9, 127.4, 122.3, 122.2, 86.3, 57.7, 50.4.

IR (ATR) [cm^{-1}] 3061, 2956, 2915, 2839, 1431, 1355, 1230, 1077, 993, 886, 849, 803, 749.

UV-Vis λ_{max}/nm ($CHCl_3$) (log ε): 236 (4.42), 294 (3.81).

HRMS calcd for $C_{21}Br_6O_1H_{10}$ 751.5832, found 751.5862. m.p. 354 – 355 °C.



OMe-furan adduct (5): The title compound was prepared following a modified literature method.[3] (1.0 g, 1.3 mmol) **3-OMeBr** is fully dissolved in tetrahydrofuran and evaporated twice.* Freshly distilled tetrahydrofuran (120 mL) is then added to **3-OMeBr** and is transferred to a flame dried schlenk flask followed by 3 evacuation and N_2 purge cycles. Dry, freshly distilled furan (2 mL) is added via syringe under a N_2 atmosphere to the stirring mixture of **3-OMeBr**. The mixture is brought down to −78 °C in a dry ice acetone bath and 1.6M n-BuLi (3 mL) is added slowly (between 10 to 20 mins) via syringe to the vigorously stirring, atmospherically inert solution. The solution is stirred under nitrogen at −78 °C for 1 hr after n-BuLi addition. The reaction is quenched at −78 °C with methanol and is then evaporated under reduced

pressure. The remaining solid is dissolved in dichloromethane and filtered using a Whatman grade 1 filter paper to remove insoluble salts. The resulting solution is precipitated from dichloromethane and methanol followed by filtration yielding (0.477 g, 0.989 mmol) of an off white solid **OMe-furan adduct (5)**, 75% yield.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (m, 3H), 7.25 (m, 3H), 6.94 (m, 6H), 5.58 (m, 6H), 5.04 (s, 1H), 4.29 (s, 3H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 146.97,146.92, 146.85, 146.56, 143.42, 143.18, 116.46, 116.35, 114.57, 114.48, 114.33, 88.96, 82.46, 82.22, 57.73, 53.92, 30.59, 30.44, 30.28, 30.13, 29.98, 29.82, 29.67.

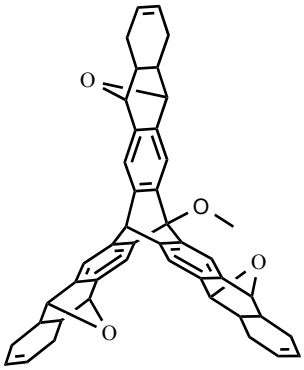
HRMS calcd for $C_{33}H_{28}O_4$ 482.1518, found 482.1527.

IR (ATR) [cm^{-1}] 3050, 3007, 2956, 2870, 2836, 1431, 1324, 1268, 1208, 1023, 984, 847, 731, 696

UV-Vis λ_{max}/nm (CH_2Cl_2) (log ε): 235 (0.519), 264 (0.102), 296 (0.217).

* The internal free volume of **3-OMeBr** allows for undesirable solvents such as chloroform to become trapped in its solid phase; solvents such as chloroform and dichloromethane will form reactive carbenes in the presence of n-BuLi which lead to undesired side products and yields for this reaction. Therefore, the **3-OMeBr** substrate is dissolved in THF and evaporated multiple times to allow for solvents such as chloroform to be removed from the substrate.

** **OMe-furan adduct (5)** is believed to degrade upon interaction with silica, therefore, the crude material is purified only by precipitation.



OMe-sulfolene product (9): The title compound was prepared following a modified literature method.[3] 250 mL pressure vessel is charged with sodium bicarbonate (200 mg, 2.38 mmol), 3-sulfolene (1 g, 8.46 mmol), **5** (500 mg, 1.03 mmol), and pyridine (40 mL). The vial is capped and heated to 120 ^{o}C for 4 days. The reaction mixture is cooled and evaporated to dryness under reduced pressure. The remaining solid is dissolved in dichloromethane and filtered using a Whatman grade 1 filter paper to remove insoluble salts. The resulting crude solution is purified by precipitation with the addition of methanol and subsequent evaporation of dichloromethane followed by filtration to give (0.567 g, 0.879 mmol) of an off white solid, 85% yield*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (m, 3H), 7.17 (m, 3H), 5,87 (m, 6H), 5.16 (s, 1H), 4.86 (m, 6H), 4.33 (s, 3H), 2.41 (m, 6H), 1.97 (m, 6H), 1.8 (m, 6H).

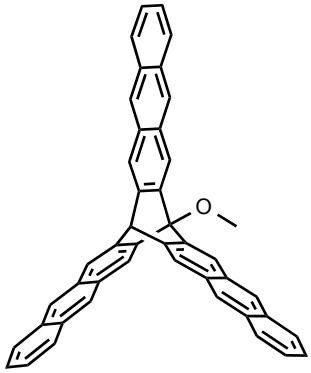
^{13}C NMR (500 MHz, $CDCl_3$) δ 144.29, 143.91, 143.82, 143.78, 143.62, 143.22, 143.15, 143.00, 142.93, 142.87, 142.79, 129.12, 129.07,129.01, 114.71, 114.60, 114.45, 112.81, 112.69, 112.48, 88.84, 85.11, 85.05, 84.98, 84.87, 84.81, 84.74, 57.63, 54.09, 42.43, 42.39, 42.37, 42.33, 42.24, 42.22, 42.18, 27.45, 27.40

HRMS calcd for $C_{45}H_{40}O_4$ 644.2926, found 644.2903.

IR (ATR) [cm^{-1}] 3080, 3003, 2952, 2909, 2836, 1770, 1435, 1324, 1276, 1255, 1216, 1023, 988, 842, 731, 696

UV-Vis λ_{max}/nm (CH_2Cl_2) (log ε): 234 (0.732), 296 (0.289).

* **OMe-sulfolene product (9)** is believed to degrade upon interaction with silica, therefore, the crude material is purified only by precipitation.



OMe-Antrip (1-OMe):[4] A flask was charged with the **OMe-sulfolene product (9)** (472 mg, 0.746 mmol) and 3.5 eqv triphenylmethanol (666 mg, 2.55 mmol) followed by the slow addition of trifluoroaceticacid (40 mL). The reaction was refluxed under N_2 and stirring for 18 hr. The resulting mixture was evaporated under reduced pressure. The excess triphenylmethanol and triphenylmethane byproduct were sublimed from the reaction mixture using a Kugelrohr at 200 ^oC and 300 millitorr overnight. The resulting dark brown solid was then dry loaded onto a column using 40% tetrahydrofuran in hexanes as the mobile phase. The first major band was carefully collected and evaporated followed by a precipitation with

dichloromethane and cyclohexane to yield (42 mg, 0.072 mmol) of yellow solid, 9.5% yield.

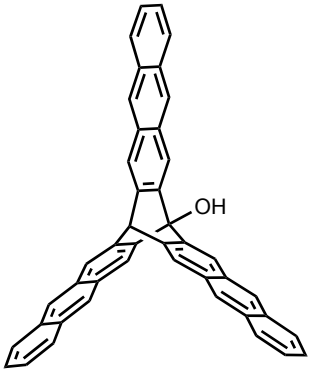
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 3H), 8.28 (s, 3H), 8.24 (s, 3H), 8.00 (s, 3H), 7.92 (m, 6H), 7.40 (m, 6H), 5.67 (s, 1H), 4.69 (s, 3H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 139.61, 138.72, 131.87, 131.75, 130.54, 130.42, 128.11, 128.01, 126.54,125.61, 125.55, 125.26, 125.16, 121.57, 120.31, 86.46, 57.57, 52.54.

IR (ATR) [cm^{-1}] 3630, 3043, 2951, 2921, 2850, 2157, 2025, 1943, 1778, 1717, 1625, 1536, 1420, 1295, 1258, 1218, 1163, 1136, 1056, 1004, 977, 949, 891, 855, 787, 735, 699, 638

HRMS calcd for $C_{45}H_{34}O$ 584.2140, found 584.2143.

UV-Vis λ_{max}/nm (CH_2Cl_2): 279, 329, 344, 362, 380.



OH-Antrip (1-OH): A flask was charged with **OMe-Antrip** (45 mg, 0.077 mmol) and acetic acid (1 mL) followed by the slow addition (5 to 10 mins) of 48% HBr (1 mL). The mixture was stirred at reflux overnight under N_2. The reaction mixture is cooled and quenched with ice and the precipitate is filtered. The precipitate is

dissolved in 30% dichloromethane 70% hexanes and loaded on a pad of silica to push off any unreacted starting material then the mobile phase is switched to dichloromethane to push off product. The target band is collected and evaporated under reduced pressure to yield (0.041 g, 0.073 mmol) of a yellow solid (95%).

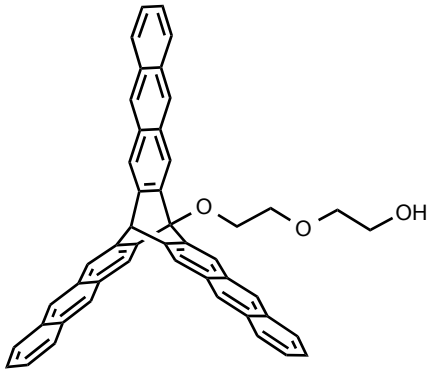
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.29 (s, 1H), 8.17 (s, 1H), 8.01 (s, 1H), 7.94-7.91 (m, 6H), 7.43-7.37 (m, 6H), 5.78 (s, 1H), 3.80 (s, 1H).

^{13}C NMR (500 MHz, $CDCl_3$) δ 140.9, 138.3, 132.1, 132.0, 131.0, 130.6, 128.3, 128.2, 126.6, 126.0, 125.5, 125.4, 122.0, 118.1, 79.6, 52.2.

IR (ATR) [cm^{-1}] 3375, 3043, 1424, 1293, 1203, 1027, 890, 736, 639.

HRMS calcd for $C_{44}O_1H_{26}$ 570.1984, found 570.1972. m.p. > 243 °C (decomposes).

UV-Vis λ_{max}/nm (CH_2Cl_2): 279, 327, 343, 360, 379.



DEG-Antrip (1-DEG): The DEGylation of **OH-Antrip** was prepared following a modified literature procedure.[5] A flame dried schlenk flask was loaded with **OH-Antrip** (48 mg, 0.084 mmol) followed by an evacuation and back fill with N_2. 15-

crown-5 (0.05 mL, 0.24 mmol) was syringed in followed by the addition of freshly distilled tetrahydrofuran (5 mL). The flask was placed in an ice bath followed by the addition of sodium hydride, 60%/wt. in mineral oil (0.024 mmol) dissolved in freshly distilled tetrahydrofuran (1 mL), and syringed into the stirring inert solution. The flask was let to react at room temperature for 6 hr. A second portion of 15-crown-5 (0.05 mL, 0.24 mmol) was added followed by another portion of sodium hydride, 60%/wt. in mineral oil (0.024 mmol) dissolved in tetrahydrofuran (1 mL). The reaction is left to react for another 6 hr after which it was quenched with 5% isopropanol in toluene. The reaction mixture was evaporated under reduced pressure and dissolved in 20% hexanes 80% dichloromethane and loaded onto a column of silica. The column was monitored by TLC and ^{1}H NMR. The target band, first major band (r.f. 0.7), was isolated to yield a yellowish white solid (42 mg, 0.047 mmol). A portion of the trityl protected product (5 mg, 0.006 mmol) was carried through on to the deprotection step by dissolving it in a 5% trifluoroaceticacid dichloromethane solution at room temperature and immediately passing it through a plug of silica using dichloromethane as the mobile phase.[6] The resulting crude material was purified by HPLC using a 90% toluene 10% ethyl acetate mobile phase to yield pure final product (3.8 mg, 0.006 mmol) as a yellowish solid with an overall yield of (44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (dd, *J* = 7.4, 1.3 Hz, 4H), 7.38 – 7.31 (dd, *J* = 7.1, 1.3 Hz, 4H), 7.07 – 6.93 (dtd, *J* = 19.1, 7.5, 1.4 Hz, 7H), 5.31 – 5.26 (s, 1H), 4.85 – 4.78 (t, *J* = 4.9 Hz, 2H), 4.23 – 4.15 (t, *J* = 4.9 Hz, 2H), 3.93 – 3.84 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 144.6, 125.5, 125.2, 123.6, 121.7, 86.7, 73.3, 72.0, 67.0, 62.3, 53.74.

IR (ATR) [cm^{-1}] 3575, 3309, 3065, 2923, 1452, 1291, 1230, 1187, 1132, 1076, 1053, 746, 640, 605.

UV-Vis λ_{max}/nm ($CHCl_3$): 281, 330, 346, 363, 382

HRMS calcd for $C_{24}\ O_3H_{22}$ 658.1569, found 658.1564. m.p. 131 – 132 °C.

Langmuir Film Preparation

Two different Langmuir troughs where used in this study. The first being a KSV 2000 System 2 and the other is a modified NIMA 312. Surface pressures were measured with a platinum or paper Wilhelmy plate. Both troughs are made from Teflon and the barriers are made from Delrin.

Antrip-DEG was dissolved in a 1:1 mixture of chloroform:cyclohexane to a concentration of 0.5 mg/mL. It was found that spreading from a pure chloroform solution resulted in the formation of a non-homogenous film. For spreading on the KSV 2000 System 2 60 uL was used and 10 uL was used for the NIMA 312. After spreading 45 minutes was allowed for solvent to evaporate if experiments were conducted at 1 °C and 30 min for isotherms at room temperature. Compression rates where 3 mm/min and 4 mm/min for the two troughs, respectively.

Brewster Angle microscopy

Brewster angle microscopy was performed with ether a KSV MicroBAM or a home built microscope constructed following the details provided by Knobler et al.[7] The KSV MicroBAM uses a 649 nm laser and the home built BAM uses a 532 nm laser.

Polymerization and Film Transfers

For polymerizations at 1 °C the trough was first cleaned at room temperature with chloroform and ethanol. The trough was then filled with milli-pure water and cooled to 1 °C. Antrip-DEG was then spread on the interface as described above. After spreading the film was compressed until the start of the phase transition (~0.5 mN/m) and held at that pressure. A 40 W 365 nm light emitting diode (Led-Engin, LZC-70U600) was used for the irradiation (see figure S1). The LED was placed ~5 in above the interface and the compressed film was irradiated for 30 min. This setup allows the entire trough to be irradiated. Before transfer of the film, the subphase was warmed to 30 °C. It was found that warming the subphase was necessary for successful film transfer.

Transfer to TEM grids (PLANO G2780C) was accomplished by placing the grids horizontally on top of the irradiated film, much like a Langmuir-Schaefer film deposition. The grids were removed from the interface by placing a small piece of paper over them such that they adsorb onto the paper. The paper can then be pulled off the interface taking the grids with it.

For vertical transfer to SiO_2 wafers or any hydrophilic surface, substrates were immersed in the subphase before antrip-DEG was spread at the interface. Spreading, compression, and polymerization was performed as stated above. After polymerization was complete the substrate was pulled from the interface at a rate of 1 mm/min.

Transfer of a single layer to HOPG (ZYB Quality) with DEG tails facing down was achieved by modification of the subphase. HOPG has a hydrophobic surface, which classically inhibits single layer transfer on the up stroke. In order to achieve transfer in this manner, minimization of the surface energy difference between the subphase and the substrate is required.[8] This was accomplished by using a 0.2 M solution of 2-propanol in water as the subphase. This solution has a much lower surface tension than pure water and a lower contact angle on HOPG. The film was found to have all the same behavior on this subphase as on pure water.

The horizontal lifting method was used for the transfer. Freshly cleaved HOPG was placed on a home made wire "basket" and placed under the subphase which was held at 1 °C. Antrip-DEG was then spread on the interface, compressed, and polymerized. After polymerization the subphase was warmed to ~30 °C and the HOPG was lifted out of the subphase at a rate of 0.5 mm/min.

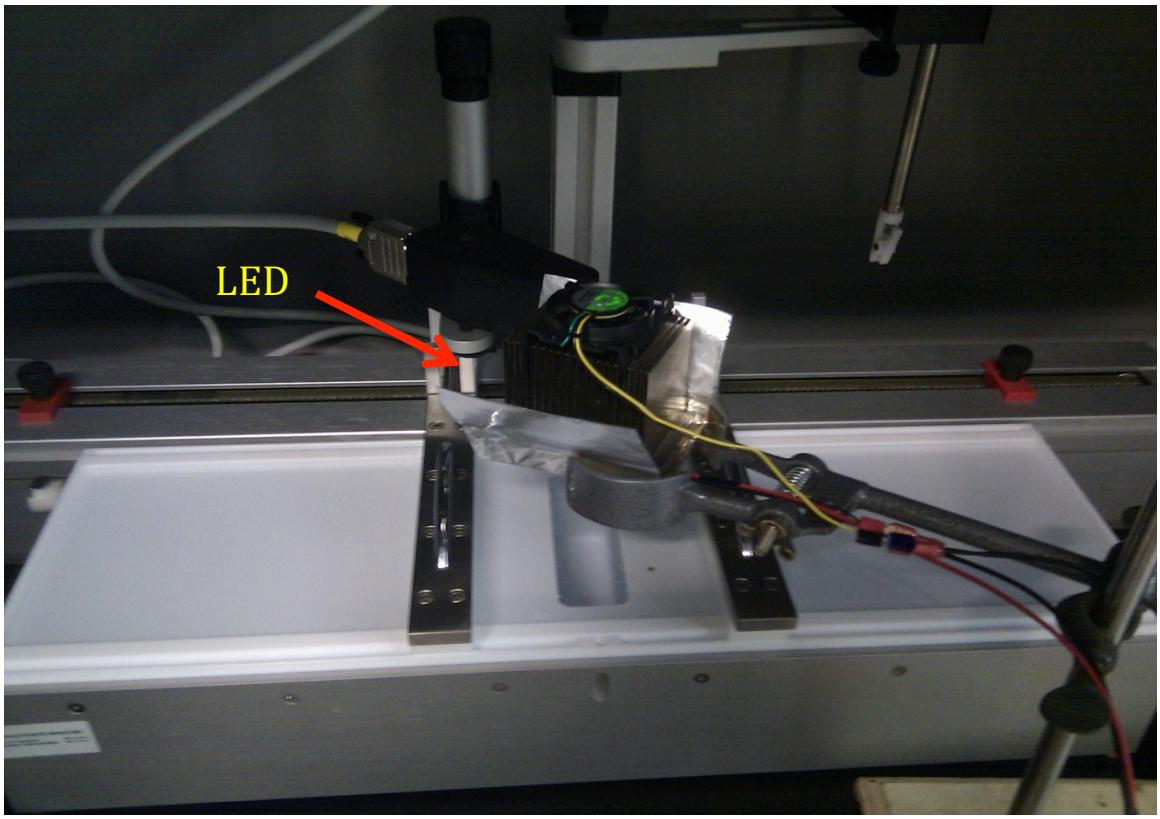


Figure S1. Setup for polymerization of antrip-DEG on the interface.

Atomic force Microscopy

AFM imaging was performed either a with a Nanosurf easyscan II AFM operated in contact mode in air or a pacific nanotechnology R2 operated in tapping mode. For the Nanosurf AFM, App Nano silicon SICONA cantilevers (Applied NanoStructures, Inc.) having a resonance frequency of 11-18 kHz and a spring constant of 0.1- 0.6 N/m were used. A set point of 15nN was used for both the monomer and polymer films. For the pacific nano AFM, Budget Sensors Tap300 probes with a resonance frequency of 300 kHz and a spring constant of 40 N/m were used.

Optical Microscopy

Optical microscopy was performed using a Leica DM2500P. Samples where prepared using the method described in the "polymerization and film transfer" section.

Contact Angle measurements

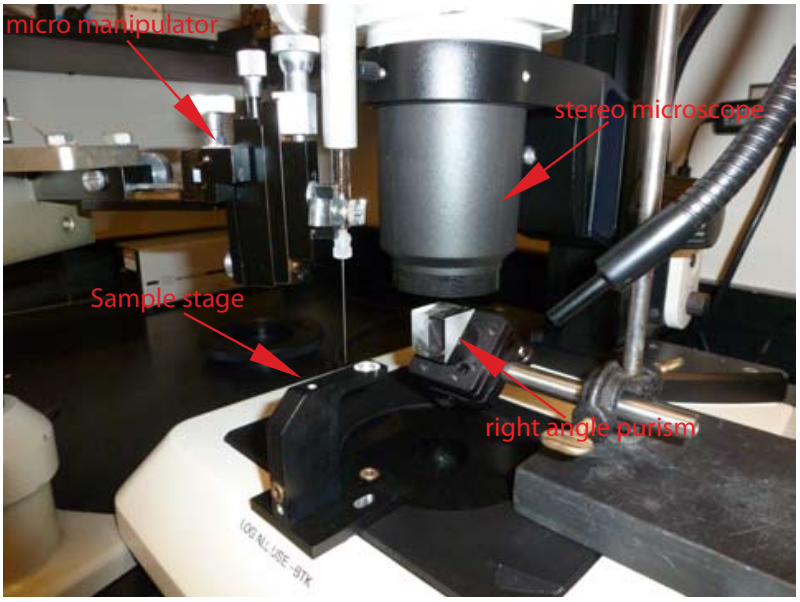


Figure S2. Homebuilt contact angle instrument employing a stereomicroscope**.**

Contact angle measurements were performed with a home built apparatus. A stereomicroscope was used for the optics and image capture. The microscope was focused on a right angle prism, which turned the optical path horizontal and permitted focusing on the sample. The sample was placed on a sample stage (see fig. S2) The syringe for drop application was controlled by a micromanipulator. Images where processed with Image J.

UV/Vis

UV/Vis spectra were obtained using a Perkin Elmer lambda 850 spectrophotometer. Samples were made by lifting a quartz substrate horizontally out of the interface. Spectra were recorded in transmission mode.

Scanning Tunneling Microscopy

STM images were acquired in constant current mode with a home-built microscope driven by a commercial ASC500 SPM controller (attocube Systems AG). The samples were imaged under ambient conditions in the dry state (i.e. without applying any solution) and under a drop of 1-phenyl octane using mechanically cut PtIr tips. The instrument was thoroughly calibrated with atomically resolved images of graphite. Other images were acquired with a Nanosurf easyscan II STM operated in constant height mode. The samples were imaged under trichlorobenzene using mechanically cut PtIr tips.

Supplemental Isotherms

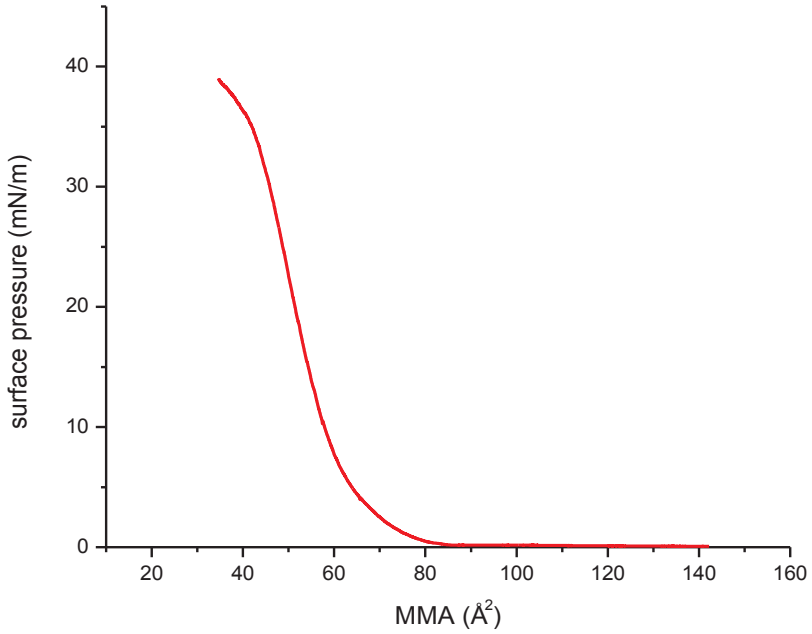


Figure S3. Isotherm of antrip-DEG at room temperature.

Supplemental BAM Images

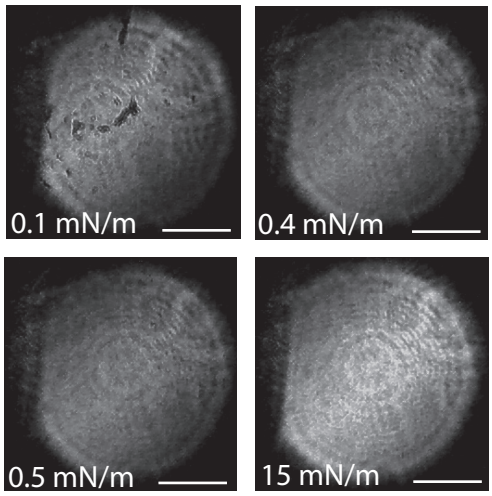


Figure S4. BAM images of the compression of antrip-DEG at 1 °C, All scale bars are 1 mm.

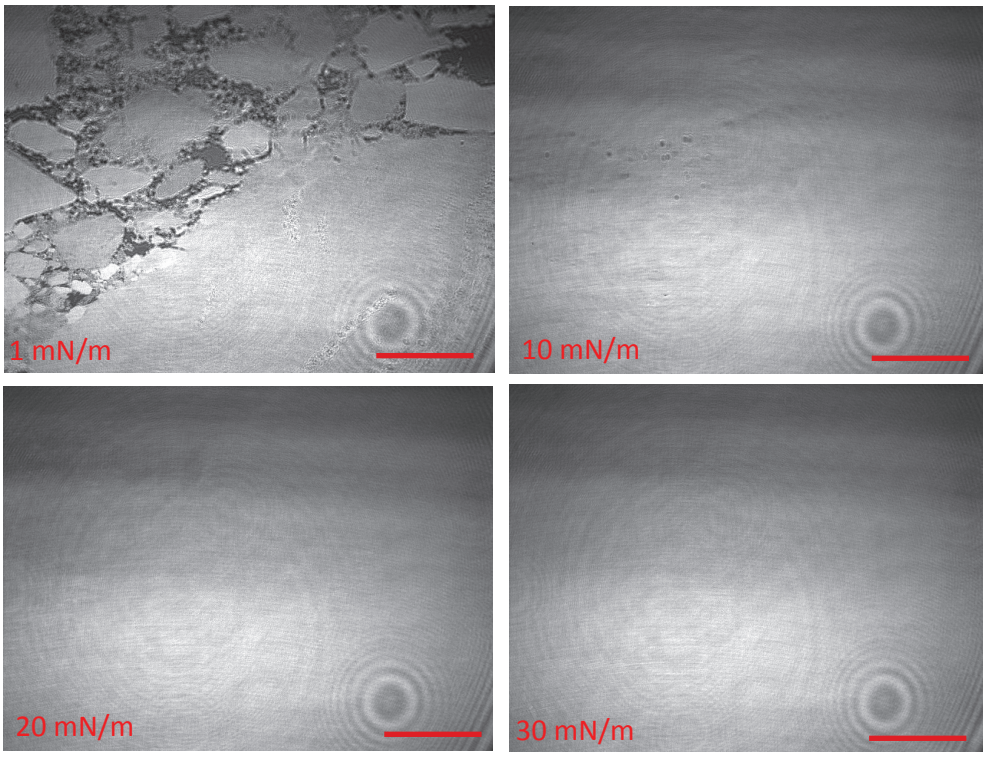


Figure S5. BAM images of the compression of antrip-DEG at room temperature. All scale bars are 700 µm.

Supplemental UV/Vis Spectra

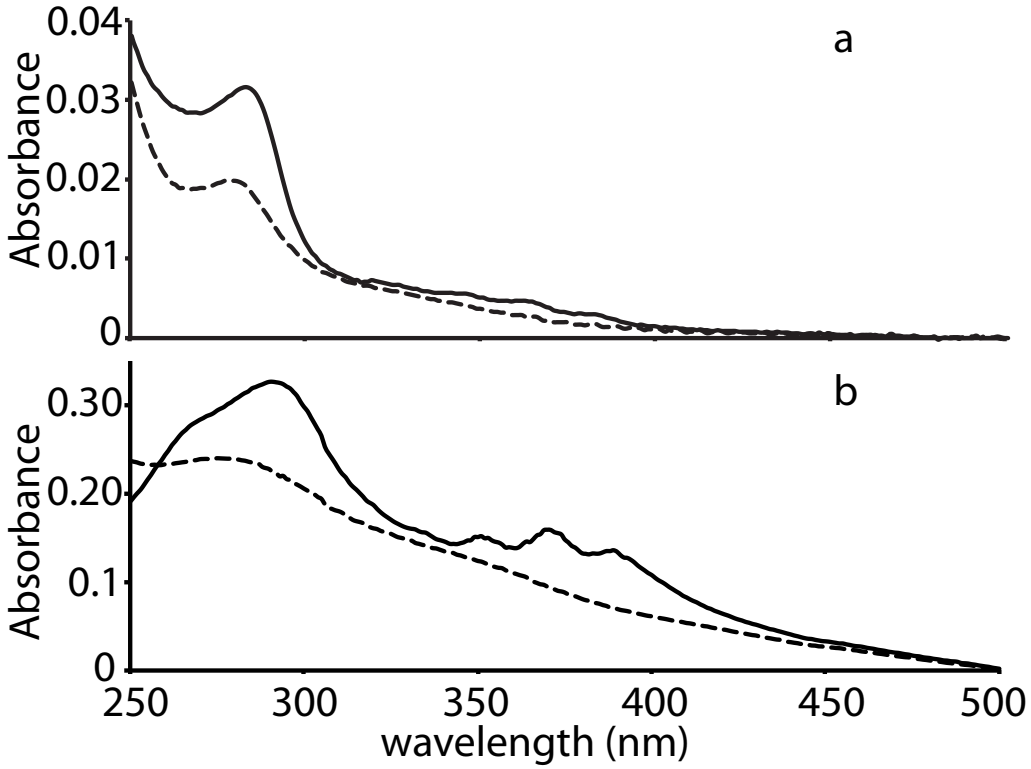


Figure S6. a. UV-Vis spectra of single layer antrip-DEG (-----), and poly(antrip-DEG) (-----) on a quartz slide. b) Solid state UV-VIS spectra of antrip (-----) and polyantrip (-----).

Supplemental AFM images

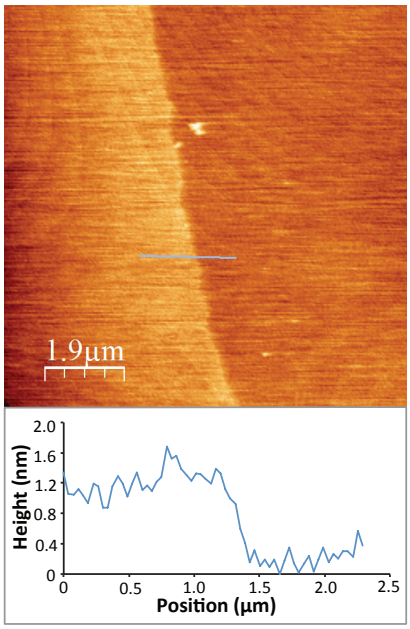


Figure S7. AFM height image of non-polymerized antrip-DEG film made at 1 °C on SiO_2. The observed height of the monomer film is ~1.2 nm.

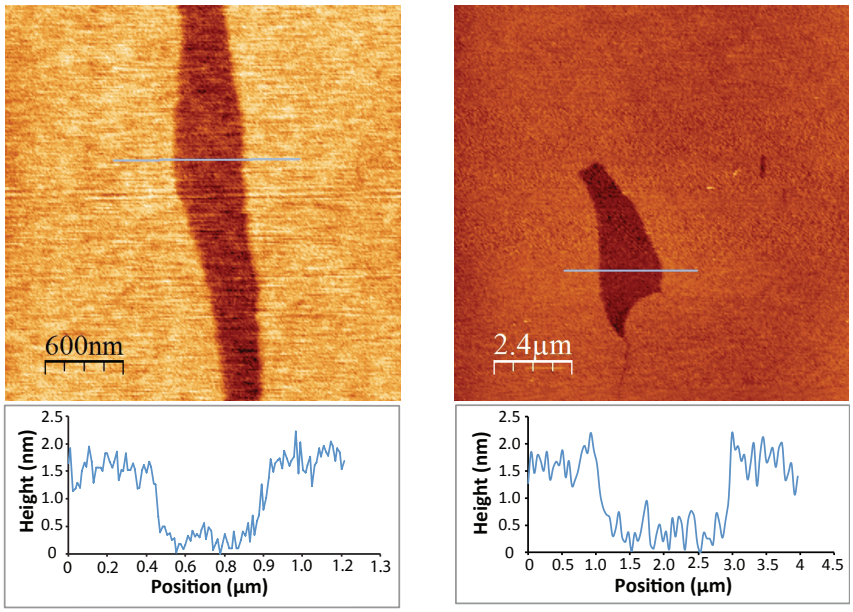


Figure S8. AFM height images of poly(antrip-DEG) made at 1 °C on SiO_2. Height analysis shows the observed height to be ~1.2 nm.

Supplemental STM images

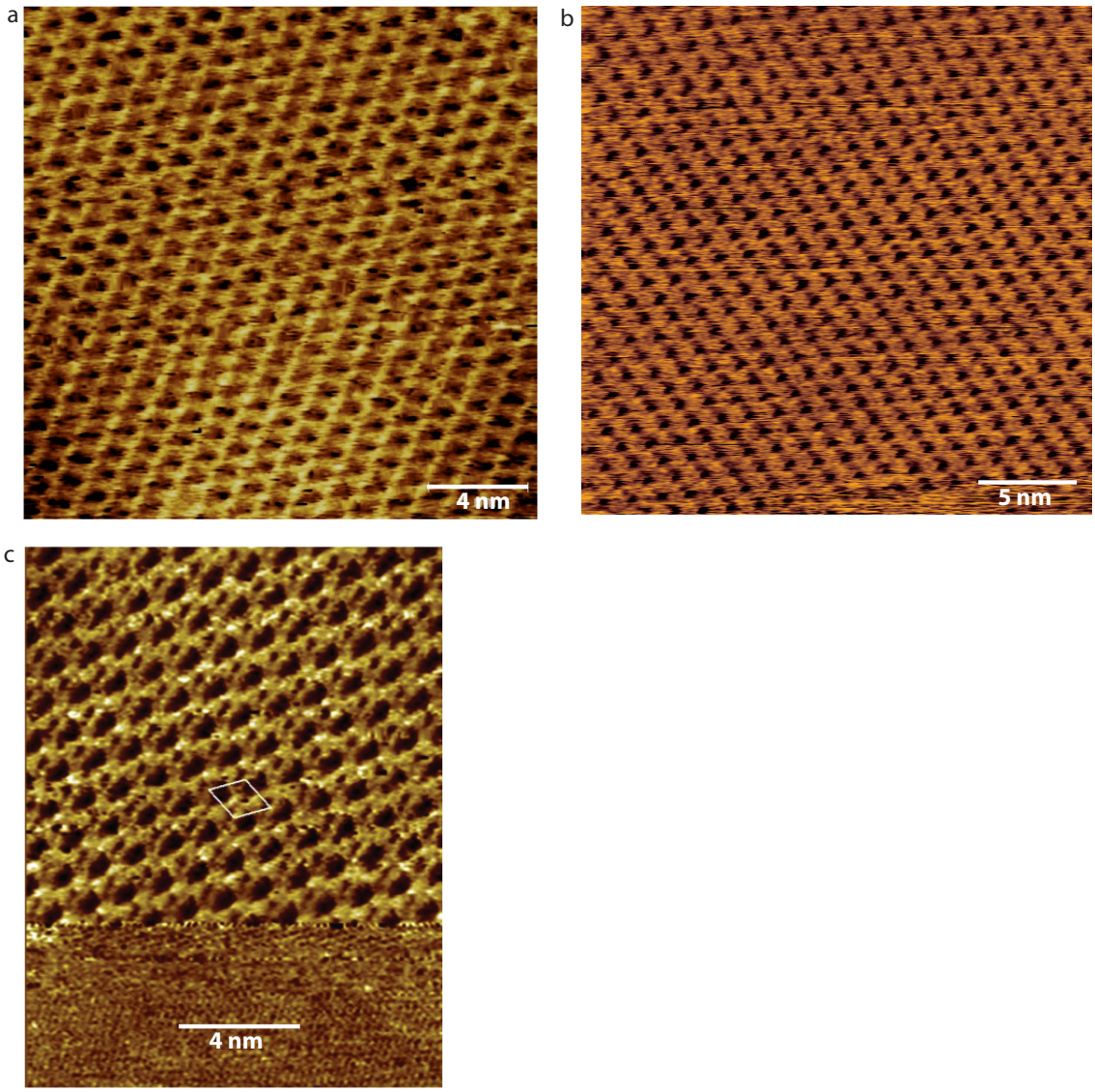


Figure S9. Supplemental STM images a) Poly(antrip-DEG) deposited on HOPG imaged in air b) Poly(antrip-DEG) deposited on HOPG imaged under 1-phenyloctane. c) Split image of poly(antrip-DEG) on HOPG. The upper portion of the image shows the 2DP, whereas in the lower half the underlying graphite was imaged by abruptly changing the tunneling parameters.

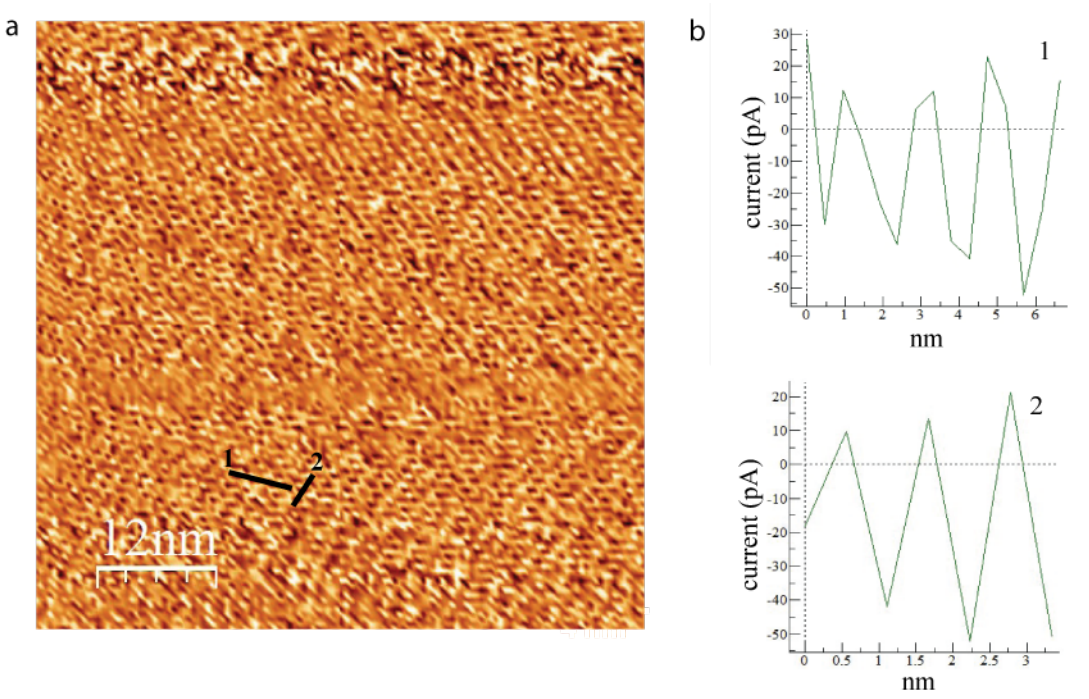


Figure S10. a) Constant height STM image of poly(antrip-DEG) on HOPG. b) Line traces along the black lines in **a.** analysis of the traces gives unit vectors of $a \approx 1.2$, $b \approx 1.6$. This image contains significant drift, which may skew the measured unit vectors.

Mean Molecular Area Discussion

Figure S11 shows a simulated packing of antrip-DEG which was proposed because of previous work with non-amphiphilic antrip in the crystalline state. In this packing all anthracene blades are co-facially stacked and could give rise to the observed polymer lattice. This lattice is consistent with the observed area for the first phase transition in the low temperature isotherms. Figure S12 shows another possible lattice that correlates with the observed MMA of the first phase transition. This lattice, however, must undergo rearrangement in order to obtain a conformation in which polymerization can occur.

The observed MMA of the solid phase is much more dense and did not correlate with any lattices know to us. Due to this we began exploring more dense packing's. Figure S13 Shows a packing with the p2gg plane group which has an MMA of 100 Å^2 per molecule. This lattice has been shown to be the maximally dense packing for objects of this shape.[9] This lattice is, however, still larger than the observed MMA of the solid state. Because of this the exact structure of the solid phase remains unclear to use for now.

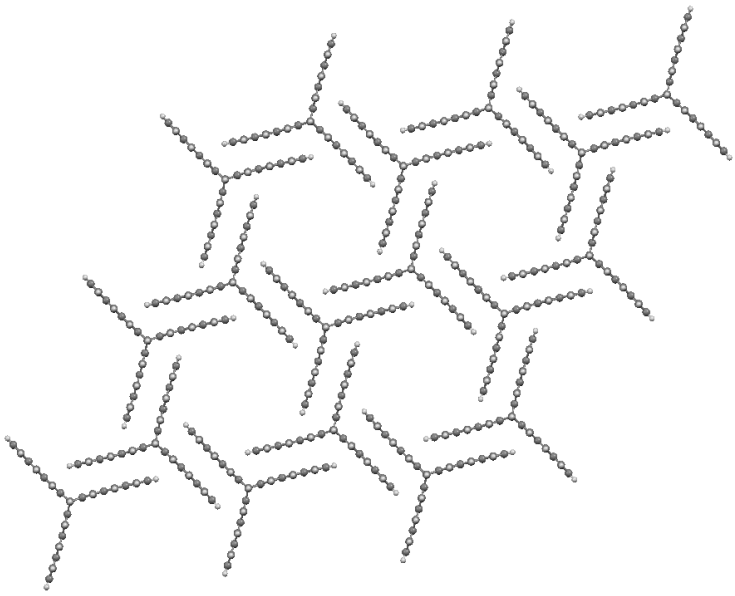


Figure S11. Simulated potential packing of antrip-DEG on the interface. This packing has a p6 plane group and gives a calculated mean molecular area of 155 Å^2 per molecule.

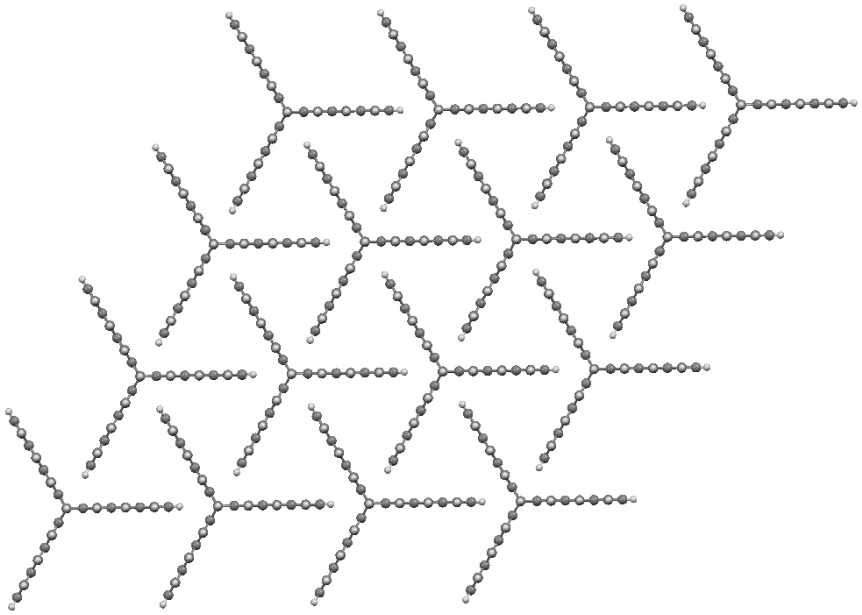


Figure S12. Simulated potential packing on the interface. This packing has a p31m plane group and gives a calculated mean molecular area of 140 Å^2 per molecule.

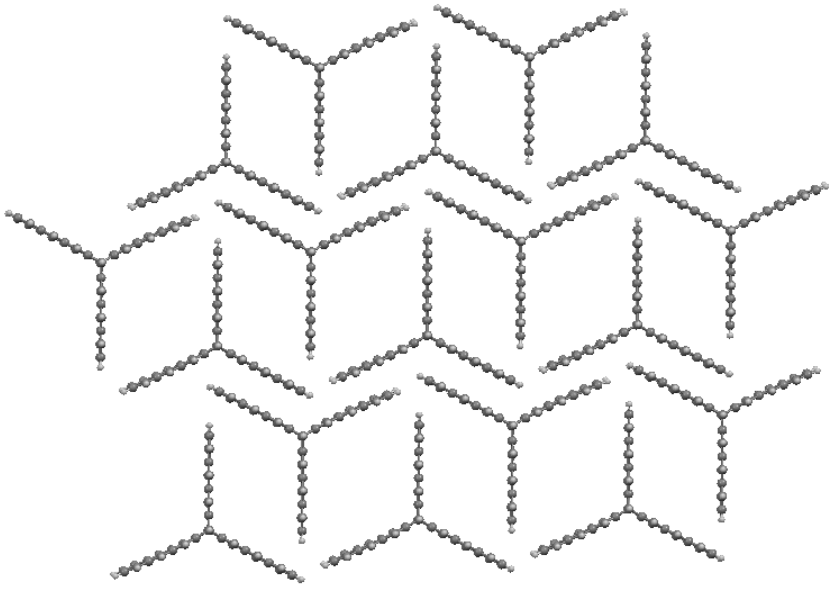


Figure S13. Simulated maximally dense packing of antrip-DEG. This packing has a p2gg plane group and gives a calculated MMA of 100 Å^2 per molecule.

Supplemental polymer simulations

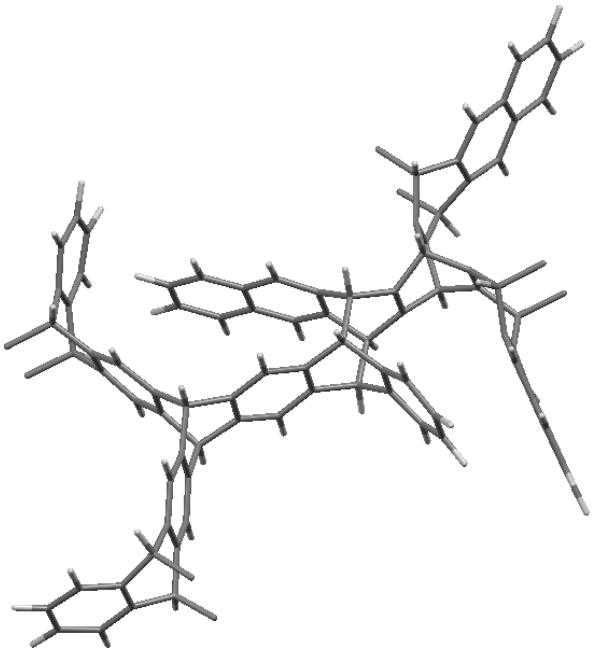


Figure S14. 1,4-9,10 connectivity of two repeat units.

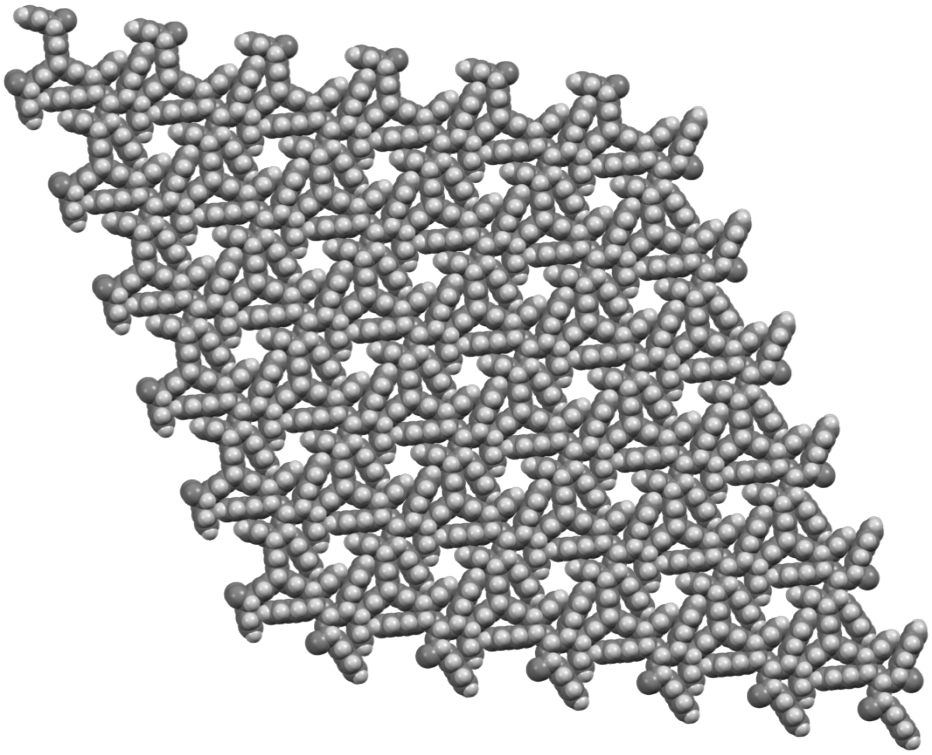


Figure S15. Simulated polymer lattice with 1,4-9,10 connectivity.

Contact Angle Images

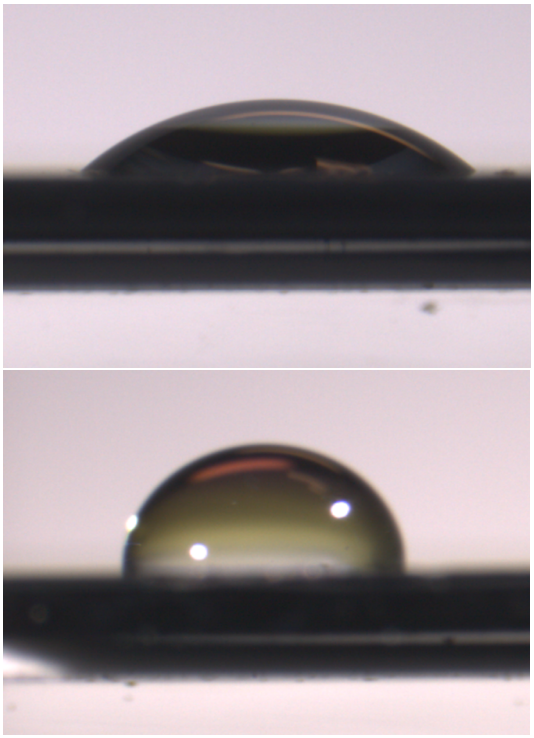


Figure S16. Contact angle images of bare SiO_2 giving a contact angle of 55° (top) and monolayer polyantrip-DEG on SiO_2 giving a contact angle of 90° (bottom).

Wilhelmy Plate Deflection

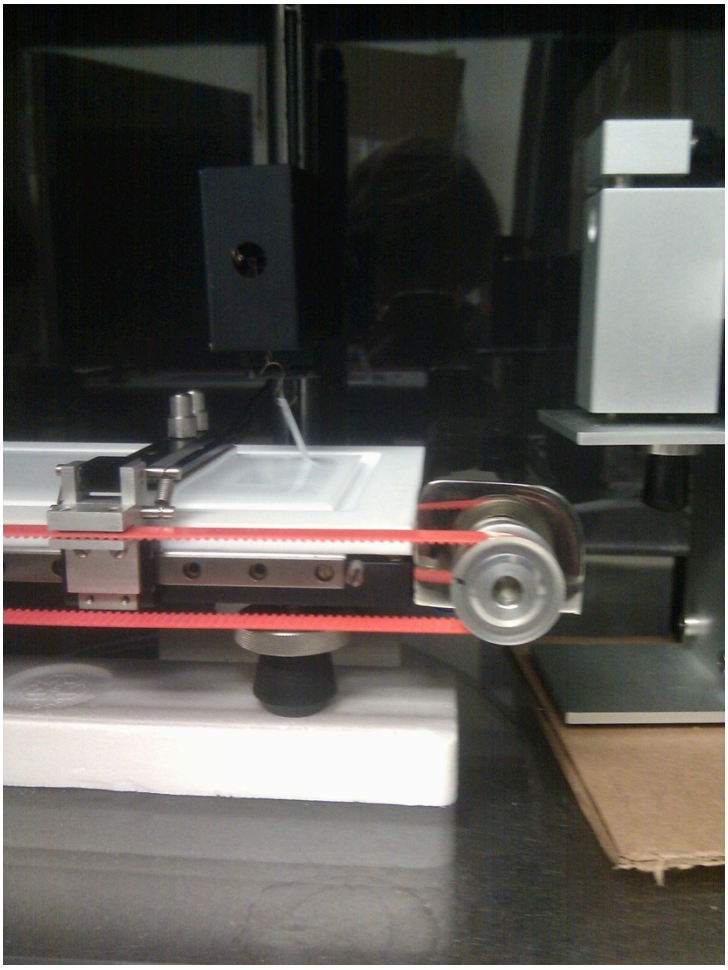


Figure S17. Image showing the existent to which the wilhelmy plate can be deflected during the course of a Langmuir experiment if a single barrier trough is used. If the surface is aspirated after compression the plate will fall back to normal position.

Supplemental optical images

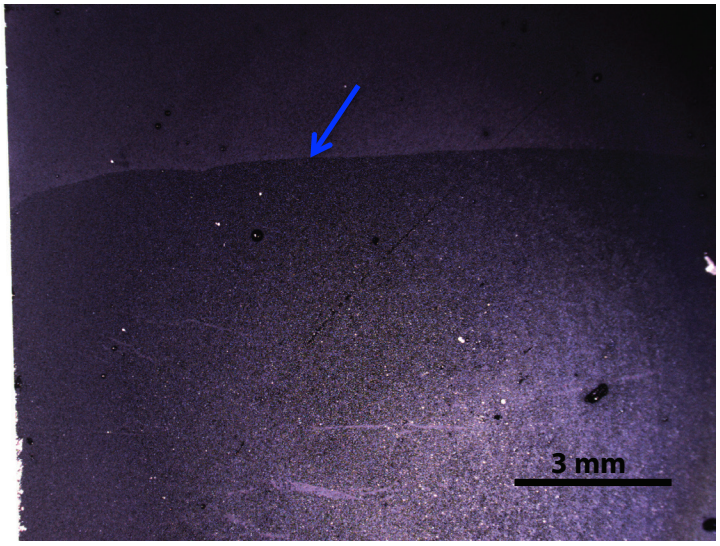


Figure S18. A ~0.9 cm² sheet of poly(antrip-DEG) imaged by selective condensation of water. The film starts at the blue arrow and extends down to the bottom of the image. The film is largely intact but some defects can be seen.

Refrences

1. Dehaen, W.; Corens, D.; L'abbe, G. *Synthesis* **1996**, *2*, 201.
2. Willner I; Halpern M; *Synthesis*, **1979**, *3*, 177.
3. Filatov, M; Baluschev, S; Ilieva, I; Enkelmann V; Miteva T; Landfester K; Aleshchenkov S; Cheprakov A; *J. Org. Chem.*, **2012**, *77*, 11119.
4. Fu, P; Harvey, R; *Tetrahedron Lett.* **1974**. *36*, 3217.
5. Baldini L; Bracchini C; Cacciapaglia R; Casnati A; Mandolini L; Ungaro R;. *Chem. Eur. J*. **2000**, *6*, 1322.
6. Pathak A; Pathak V; Seitz L; Tiwari K; Akhtar M; Reynolds R. *Tetrahedron Lett.* **2001**, *44*, 7755.
7. Marshall, G.; Dennin, M.; Knobler, C. M. *Rev. Sci. Instrum.* **1998**, *69*, 3699.
8. Egusa, S.; Gemma, N.; Azuma, M. *J. Phys. Chem.* **1990**, *94*, 2512.
9. Atkinson, S.; Jiao, Y.; Torquato, S. *Phys. Rev. E* **2012**, *86*.