SUPPLEMENTARY INFOMATION

Directed Nanotube Assembly Using a Pyrene Functionalized Polymer

Eric Schopf,[a] Rebecca Broyer[b], Lei Tao[b], Yong Chen[a] and Heather D. Maynard*[b]

[a] *Department of Mechanical and Aerospace Engineering, University of California, Los Angeles, CA 90095, USA*
[b] *Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095. USA. E-mail: maynard@chem.ucla.edu*

Materials.

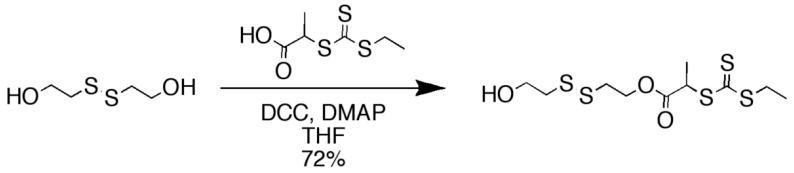
All reagents were purchased from Sigma Aldrich and used as received unless otherwise specified. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from acetone prior to use.

Analytical Techniques.

All operations were conducted under a dry Argon atmosphere. Gel Permeation Chromatography (GPC) was carried out using a Shimadzu LC-10ATvp pump equipped with a refractive index detector (RID-10A) and two PLgel mixed-D columns (Polymer Laboratories LTD, 300 mm, 5 μm) with a guard column. HPLC grade *N,N*-dimethylformamide (DMF) with 0.1 M LiBr was used as the eluent (flow rate: 0.8 mL/min, temperature: 40 °C). Instrument calibration was carried out using poly(methyl methacrylate) standards (Polymer Laboratories) and chromatograms were processed using EZStart 7.2 software. ^{1}H and ^{13}C NMR spectra were acquired on an Avance DRX 400 or 500 MHz spectrometer.

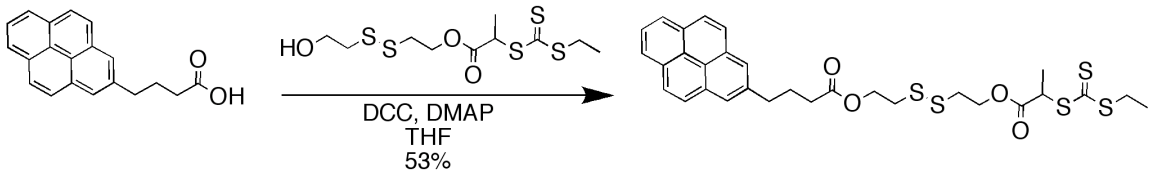
Synthetic Procedures.

Synthesis of SS-CTA-1:



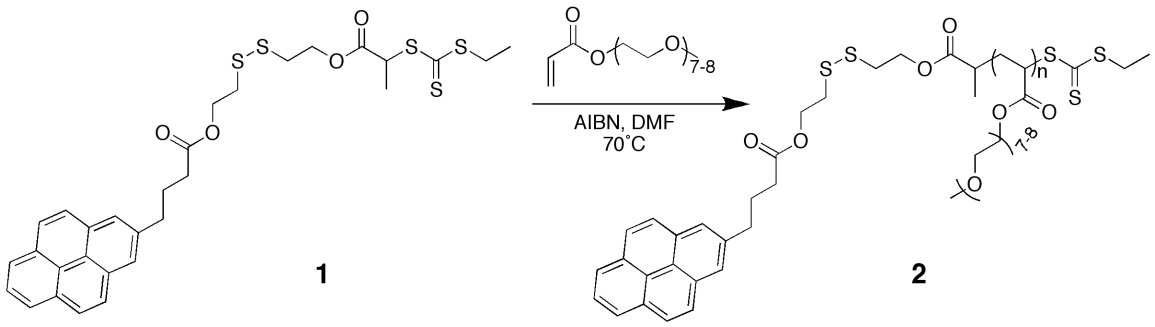
2,2'-Disulfanediyldiethanol (6.16 g, 40 mmol), 2-(ethyl trithiocarbonate)propionic acid (2.10 g, 10 mmol), and 4-dimethylaminopyridine (DMAP) (0.122 g, 1 mmol) were dissolved in dry THF (50 mL). Dicyclohexylcarbodiimide (DCC) (2.27 g, 11 mmol) was then added, and the contents were stirred at 23 °C for 16 h, and then filtered to remove the solids. The solvent was removed *in vacuo*, and the crude product was purified by silica gel chromatography (4:1 hexanes:EtOAc) yielding 2-((2-hydroxyethyl)disulfanyl)ethyl 2-(ethylthiocarbonothioylthio)propanoate as a yellow oil in 72% yield (2.50 g). δ ^{1}H NMR (400 MHz, $CDCl_3$): 4.81 (q, *J* = 7.4 Hz, 1H, $CH_3C\mathbf{H}$), 4.43-4.39 (m, 2H, O=COC$\mathbf{H}_2$), 3.88 (t, *J* = 5.8 Hz, 2H, HOC$\mathbf{H_2}CH_2S$), 3.38-3.34 (q, J = 7.51, 2H, $CH_3C\mathbf{H_2}S$), 2.93 (t, *J* = 6.6 Hz, 2H, SC$\mathbf{H_2}CH_2O$), 2.88 (t, *J* = 5.7 Hz, 2H, $HOCH_2C\mathbf{H_2}S$), 1.60 (d, *J* = 7.4 Hz, 3H, C$\mathbf{H_3}$CH), 1.35 (t, *J* = 7.4 Hz, 3H, C$\mathbf{H_3}CH_2S$). δ ^{13}C NMR (600 MHz, $CDCl_3$): 221.91, 171.22, 63.62, 60.38, 47.89, 41.74, 36.83, 31.72, 16.85, 13.09.

Synthesis of Pyrene-SS-CTA-2:



1-Pyrene butyric acid (432 mg, 1.5 mmol), 2-((2-hydroxyethyl)disulfanyl)ethyl 2-(ethylthiocarbono-thioylthio)propanoate (570 mg, 1.65 mmol) and DMAP (12.2 mg, 0.1 mmol) were dissolved in dry THF (50 mL). DCC (371 mg, 1.8 mmol) was then added and the solution was stirred at 23 °C for 20 h. The undissolved material was removed by filtration, and the crude product was purified by silica gel chromatography (4:1 hexane:ethyl acetate) yielding **1** as a yellow oil in 53% yield (502 mg). δ ^{1}H NMR (400 MHz, $CDCl_3$): 8.31-7.86 (m, 9H, protons on the pyrene ring), 4.80 (q, *J* = 7.4 Hz, 1H, $CH_3C\mathbf{H}S$), 4.39-4.30 (m, 4H, $CH_2C{=}OOC\mathbf{H_2}$, $CHC{=}OOC\mathbf{H_2}$), 3.40 (t, 2H, *J* = 7.6 Hz, pyrene-CH_2), 3.33 (q, 2H, *J* = 7.4 Hz, $SC\mathbf{H_2}CH_3$), 2.92-2.89 (m, 4H, $C\mathbf{H_2}SSC\mathbf{H_2}$), 2.49 (t, *J* = 7.2 Hz, 2H, $C\mathbf{H_2}COO$), 2.21 (m, 2H, $CH_2C\mathbf{H_2}CH_2$), 1.58 (d, *J* = 7.4, 3H, $C\mathbf{H_3}CHS$), 1.33 (t, *J* = 7.4 Hz, 3H, $C\mathbf{H_3}CH_2S$). δ ^{13}C NMR (100 MHz, $CDCl_3$): 222, 173.40, 171.15, 135.80, 131.58, 131.05, 130.14, 128.87, 127.61, 127.54, 127.51, 126.92, 126.02, 125.21, 125.10, 125.06, 124.95, 124.93,123.46, 63.52, 62.30, 47.89, 37.45, 36.99, 33.85, 32.85, 31.68, 26.86, 16.84, 13.05.

Polymerization of PEGA with CTA-2.

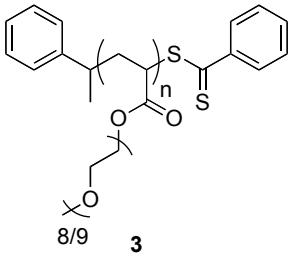


Typical RAFT polymerization of polyethylene glycol ethyl methyl ether acrylate (PEGA). Polymerization of PEGA was conducted using molar ratios of 1:100:0.1 of **1**:PEGA:AIBN in DMF using standard Schlenk techniques. PEGA (2.27 g, 5 mmol), CTA **1** (31 mg, 0.05 mmol) and AIBN (0.82 mg, 0.005 mmol) were dissolved in 5 mL of DMF in a Schlenk tube. After three freeze-pump-thaw cycles, the Schlenk tube was immersed in a 70 °C oil bath to begin the polymerization. The polymerization was allowed to proceed for 5 hours (conversion > 90%). The unreacted monomer and DMF were removed by dialysis (MWCO: 6-8,000) against methanol to give the final polymer. δ ^{1}H NMR (500 MHz, $CDCl_3$): 8.32-7.87 (protons on the pyrene chain end), 4.15 (COOC**H$_2$** polymer), 3.63 (CH_2**CH_2**O_n polymer), 3.37 (CH_2CH_2O**CH_3** polymer), 2.92 (C**H$_2$**S-SC**H$_2$** chain end), 2.30-1.69 (C**H$_2$**C**H** polymer backbone). GPC: M_n = 17,100 Da; PDI = 1.28.

Polymer patterning. Methanol was added to the pyrene-functionalized polymer to make a final concentration of 0.1 wt%. Silicon wafers were diced and cleaned in piranha solution (3:1 H_2SO_4/H_2O_2, **caution!**) for at least five minutes, and then rinsed with ultrapure water. 15 μL of the pyrene polymer solution was added to chips and spin-coated

at 4000 rpm for 40 sec. Samples were then loaded into a JEOL 5910 scanning electron microscope. Patterns were prepared using a JC Nabity electron beam lithographic system (Nanometer Pattern Generation System, version 9.0). An accelerating voltage of 30 kV and a beam current of approximately 7 pA was used to pattern all samples. Following electron beam patterning, samples were rinsed for approximately 10 seconds in methanol, subsequently in ultrapure water, and then dried under high-pressure air. No further sample preparation was performed.

A control surface was prepared using non-functionalized polyPEGA (**3**, M_n by GPC = 11,800 Da, PDI = 1.12) in a similar manner. 15 μL of a 1 wt% solution was made and spin coated on cleaned silicon wafer pieces at 4000 rpm for 20 sec. Patterning was accomplished as described above, with a line dose of 1 nC/cm and a beam current of 5 pA.



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Carbon nanotube solution preparation and use. Pyrene functionalized polymer was suspended in DMF to make a final concentration of 10 mg/mL. A small amount of multi-walled carbon nanotubes (Sigma-Aldrich, 677248) CNTs were weighed and added to the pyrene solution to prepare a final concentration of 2 mg/mL. This mixture was sonicated for approximately one hour, after which 100 μL was transferred into 900 μL of DMF.

The resultant 10-fold diluted nanotube solution was further sonicated for at least 90 minutes and used immediately. 40 μL of the nanotube solution was added onto the patterns and incubated for 1 h with no agitation. The nanotube solution was then rinsed off of the samples with 2 to 3 mL of DMF, after which samples were dried under high pressure air.

At this point, samples were imaged using an atomic force microscope (AFM) or scanning electron microscope (SEM). AFM images were collected on dry samples using a Dimension 3100 (Digital Instruments) in tapping mode (silicon cantilever, spring constant = ~ 40 N/m, tip radius = < 10 nm, scan rate = 1.5 Hz) and processed and analyzed using NanoScope IIIa Ver. 5.30r1 (Digital Instruments). SEM samples were mounted on a sample holder using carbon tape. Images were obtained on a JEOL JSM-6700F field-emission scanning electron microscope, with a working distance of 8 mm, an accelerating voltage of 10 kV, and a probe current of 10 pA.

Reduction of pyrene polymer. For post-patterning reduction experiments, dilutions of dithiothreitol (DTT) in either DMF or ultrapure water were prepared in concentrations ranging up to 100 mM. After e-beam patterning of the pyrene polymer, 50 μL of the DTT solution was added to the samples. After 1 h, samples were rinsed in either DMF or ultrapure water and subsequently dried under high pressure air. CNTs were then added to the samples as described and following rinsing, AFM images were taken to confirm the presence or absence of CNTs.

To investigate how reduction in solution affects CNT solubility, 50 mM DTT in DMF was added to a 10 mg/mL pyrene polymer solution and allowed to react for one hour. CNTs (2 mg/ml) were added to the solution and this solution was diluted 1:9 in 50 mM DTT in DMF, in a similar manner to the preparation of CNTs prior to incubation with the surfaces. A control was prepared at the same concentration but with no DTT. The two samples were sonicated at 23˚C for 1 hr, and then centrifuged at 4,000 rpm for 30 min.

Figure S1. Experimental result of cleaving the pyrene polymer in solution. On the left, the control sample prepared with no DTT showed no change in solubility after centrifugation. On the right, the DTT-reacted sample shows a drastic change in solubility of the CNTs as a result of polymer cleavage.

To investigate why DTT did not cleave the pyrene from the patterned polymer, a sample on which 200 x 200 µm pyrene patterns were prepared was analyzed via a PHI Quantum 2000 X-ray Photoelectric Spectroscopy (XPS) machine (Evans Analytical Group, Sunnyvale, CA). Results are shown in figure Fig. S2. Sulfur was not detected. The peak shown in Fig. S2C (right) corresponds to the Si2s satellite signal; this originates from the silicon substrate that the patterns were made on. Normalized out of all elements detected, 59.7% was carbon, 32.1% was oxygen, and 8.2% was silicon.

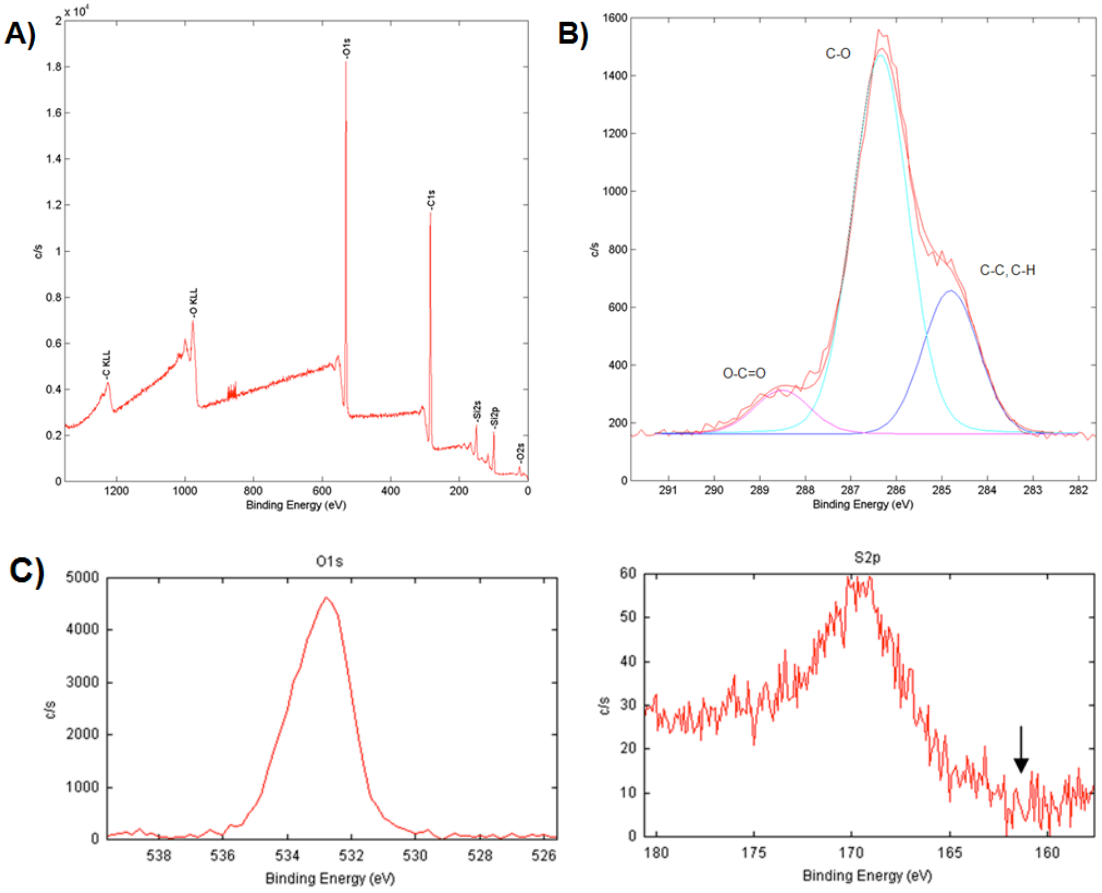

Figure S2. XPS data of patterned pyrene polymer. A) Binding energies from 0 to 1400 eV. B) A fit of the data with various carbon peaks shown. C) Two detailed enlargements. On the left is the O1s region. On the right, the Si2s satellite signal is shown. The arrow points to where the disulfide bond sulphur would be present, confirming its absence.