Supporting Information

for Formation of Conjugated Polymer Brushes by Surface-Initiated Catalyst-Transfer Polycondensation

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Ellipsometry. Ellipsometric measurements were performed on a Multiskop (Optrel GbR) with a 632.8 nm HeNe laser light source. Thickness data for films were obtained by fitting ellipsometric data using integrated specialized software. Measurements given are the average of three or more data points.

PM-IRRAS measurements. All PM-IRRAS measurements were made on a Nicolet Model 6700 spectrometer equipped with a photoelastic modulation (PEM) accessory (ThermoNicolet, Madison, WI) using OMNIC 8.0 software. All measurements were made with the grazing angle set at 80 degrees.

Cyclic voltammetry measurements. All electrochemical measurements were made using a CH Instruments CHI832B bipotentiostat. Unless otherwise indicated, electrochemical experiments were performed using .1M tetrabutylammonium hexafluorophosphate as the supporting electrolyte in DCM or THF and taken vs. a Ag/Ag^+ pseudoreference electrode with Fc/Fc^+ used as an internal standard (.414 V/SCE). Potentials reported in this solvent system are given vs. SCE. Electrochemistry of PPh brushes was performed in 95% H2SO4 and potentials are given directly vs. an Ag/Ag^+ pseudoreference electrode. The area of the working electrode immersed in the electrolyte solution was kept at approximately 1 cm x 1 cm for all samples.

Atomic Force Microscopy. The AFM topography images of the films were recorded in tapping mode using a Multimode NanoScope IIIa (Digital Instruments/Veeco Metrology Group) at a scan rate of 1 Hz and tip velocity of 2 um/sec. Silicon AFM probes with a resonant frequency of 300 kHz, spring constant of 40 N/m, and tip radius of <10 nm were used. In all AFM images, differences in height are indicated by color: white is the highest and dark is the lowest.

Materials. Solvents and reagents were obtained from TCI or Sigma-Aldrich unless otherwise indicated. Solvents used were purified by distillation from calcium hydride (toluene, methylene chloride) or sodium ketyl (THF), and sparged with argon gas to remove oxygen before use in the glove box.

Synthesis of initiator 6-(5-bromothiophen-2-yl)hexane-1-thiol. 23.8 ml of n-butyl lithium (2.5 M in hexane, 59.4 mmol) was added dropwise to a solution of thiophene (5 g, 59.4 mmol) in 50 ml of THF at -78 °C under N_2 via syringe. After 45 min., the mixture was transferred dropwise to another flask containing 1,6-dibromohexane (36.23 g, 148.5 mmol) in 100 ml of THF. After complete addition, the mixture was warmed to room temperature overnight. The solution was then poured into ice water, extracted with methylene chloride, and dried over $MgSO_4$. After distillation, the product was purified by flash chromatography using hexanes as the eluent to yield 10.44 g (71%) pure liquid 2-(6-bromo-hexyl)-thiophene. 1H NMR (300 MHz, CDCl3); δ 7.10 (dd, 1H, J = 5.1, 1.2 Hz), 6.91 (dd, 1H, J = 5.1, 3.5 Hz), 6.77 (dd, 1H, J = 3.5, 1.2 Hz), 3.40 (t, 2H, J = 6.8 Hz), 2.83 (t, 2H, J = 7.5, 15.1 Hz), 1.87 (m, 2H), 1.70 (m, 2H), 1.45 (m, 4H). NBS (8.3 g, 46.6 mmol) in DMF was added dropwise to a solution of 2-(6-bromo-hexyl)-thiophene (10.44 g, 42.4 mmol) in 15 ml of DMF under darkness. After stirring overnight, the mixture was poured into ice water and extracted with methylene chloride, dried with $MgSO_4$, and purified by flash chromatography using hexanes as the eluent, which afforded 8.62 g (62.3%) 2-bromo-5-(6-bromo-hexyl)-thiophene. 1H NMR (300 MHz, CDCl3); δ 6.84 (d, 1H, J = 3.5 Hz), 6.53 (d, 1H, J = 3.5 Hz), 3.40 (t, 2H, J = 7.0 Hz), 2.75 (t, 2H, J = 7.7 Hz), 1.86 (m, 2H), 1.65 (m, 2H), 1.42 (m, 4H). The following procedure was obtained from a similar procedure used by Hu and Fox.[1] To a solution of 2-bromo-5-(6-bromo-hexyl)-thiophene (.86 g, 2.60 mmol) in 5 ml THF at -10 °C was added hexamethyldisilathiane (.56 g, 3.1 mmol) and TBAF (2.9 ml, 1.0 M in THF). TLC indicated completion after overnight stirring, and the mixture was diluted with diethyl ether and washed with aqueous ammonium chloride (sat.). Purification of the thiol was obtained by flash chromatography using 1:9 DCM:hexane, which yielded .10 g (11.6%) 6-(5-bromothiophen-2-yl)hexane-1-thiol. 1H NMR (300 MHz, CDCl3); δ 6.83 (d, 1H, J = 3.5 Hz), 6.52 (dt, 1H, J = 3.5, .9 Hz), 2.74 (t, 2H, J = 7.5 Hz), 2.51 (q, 2H, J = 7.5 Hz), 1.62 (m, 4H) 1.39 (m, 5H). 13C NMR (300 MHz, CDCl3); δ 131.90, 129.45, 124.55, 108.66, 33.72, 31.26, 30.10, 28.23, 27.94, 24.47.

Synthesis of 2,5-diiodothiophene. 49.9 mL of nBuLi (2.5 M, 124.7 mmol) was added to a solution of thiophene (5 g, 59.4 mmol) and TMEDA (18.6 mL, 124.7 mmol) in THF (60 mL). After one hour of stirring, iodine (31.6 g, 124.7 mmol) dissolved in 30 mL of THF was added dropwise. The solution was allowed to stir overnight. A small amount of 2-iodothiophene was distilled off under reduced pressure, and the dark brown residue was purified by flash chromatography using hexanes as the eluent, which yielded 4 g (20 %) of 2,5-diiodothiophene as a yellow-orange oil. 1H NMR (300 MHz, CDCl3); δ 6.93 (s, 2H).

Formation of gold substrates. Glass slides (VWR VistaVision microscope slides) were cleaned by sonicating in isopropanol for 15 min. Slides were dried under an argon stream and placed immediately in a thermal evaporator (Thermionics Northwest model SMR-4R). 10 nm of chromium was evaporated at a deposition rate of .1 A/sec, followed by 100 nm of gold at a deposition rate of .5 A/sec.

Formation of monolayers. Gold substrates (100 nm Au/10 nm Cr) were cut in rectangular pieces of approximate dimensions 2.5 x 1 cm, placed directly into a 2 mmol solution of thiol initiator (6-(5-bromothiophen-2-yl)hexane-1-thiol) in toluene, and incubated for 12-24 hours.

Formation of aryl A-B monomers. 2,5-dibromothiophene, (TCI) 1,4-diiodobenzene, (Eastman) or 2,5-diiodothiophene (1 mmol) was dissolved in anhydrous THF (10 mL) in a

Schlenk flask under nitrogen. The temperature was lowered to 0 degrees in an ice bath, and isopropylmagnesium chloride 2.0 M (.45 mL, 0.9 mmol) was added dropwise and stirred for 1 hour. The solution was allowed to come to room temperature, sealed, and transferred to the glove box.

Formation of brushes. Gold substrates functionalized with thienyl bromide monolayer were placed for three hours in a .05 wt % $Ni(COD)_2$ + $4PPh_3$ solution, prepared by adding 10 mL toluene to 5 mg $Ni(COD)_2$ and 19 mg PPh_3 immediately before the solution was to be used. Substrates were then removed from this solution, rinsed thoroughly with toluene and THF, and placed in monomer solution overnight. All polymerizations were carried out at room temperature in a glovebox. The polymer-grafted substrates were then removed from the glovebox and rinsed with 1M HCl, water, chloroform, and sonicated briefly in THF. In the case of PPh, the same procedure was carried out with a gold substrate functionalized with a monolayer of 11-undecanethiol as a control experiment. Some polymer formed on the control slide, (Table 1) presumably due to physisorption of polymer from solution; however, the control film was distinguishable from the polymer brush in that it was far thinner, rougher, and delaminated extensively under a Scotch tape peel while the PPh brush remained unchanged.

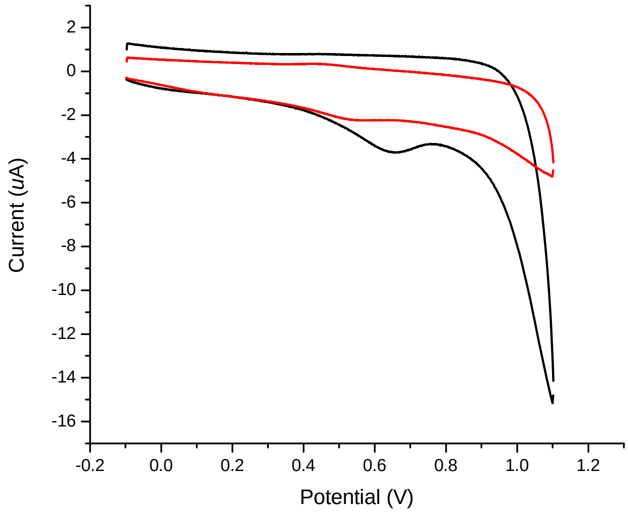

Figure S1. After gold substrate containing initiating monolayer was immersed in .05 wt % $Ni(COD)_2$ + $4PPh_3$ solution for 3 hours, substrate was removed and rinsed extensively with toluene and THF. Substrate was immediately immersed in an electrolyte solution as the working electrode. The CV shows an irreversible oxidation at 0.67V consistent with the presence of a Ni(II) species (black line). After immersing substrate in a .05 wt % $Ni(PPh_3)_4$ solution for 3 hours, the oxidation potential is shifted at .54 V/SCE and reversible (red).

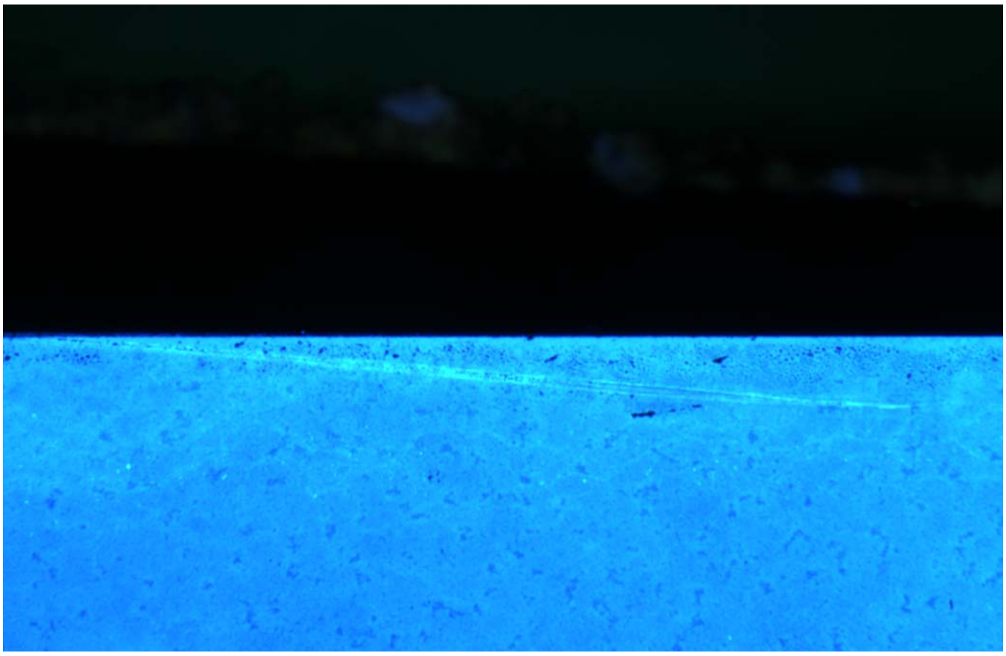

Figure S2. Fluorescence microscopy image of bare Au (top) and 42 nm PPh brush on Au, (bottom) displaying the characteristic blue fluorescence of PPh.

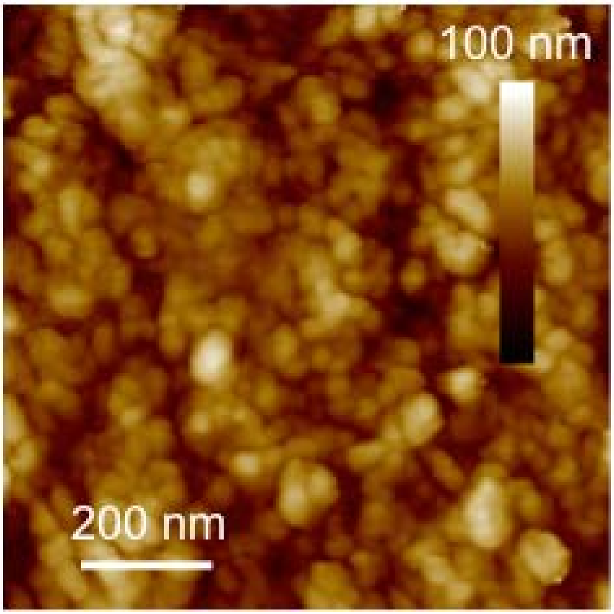

Figure S3. AFM image of a 42 nm PPh film prepared via SI-KCTP.

Table S1: Ellipsometric thicknesses of polymer brushes

Brush	**Thickness (nm)**
Poly(thiophene) from Br-T-MgCl	10 nm
Poly(thiophene) from I-T-MgCl	14 nm ± 2 nm
Poly(thiophene) from I-T-MgCl	36 nm
Poly(phenylene) from I-Ph-MgCl	42 ± 3 nm
Poly(phenylene) control slide	19 ± 7 nm

1. Hu, J. and M.A. Fox, *A Convenient Trimethylsilylthioxy-Dehalogenation Reaction for the Preparation of Functionalized Thiols.* The Journal of Organic Chemistry, 1999. **64**(13): p. 4959-4961.