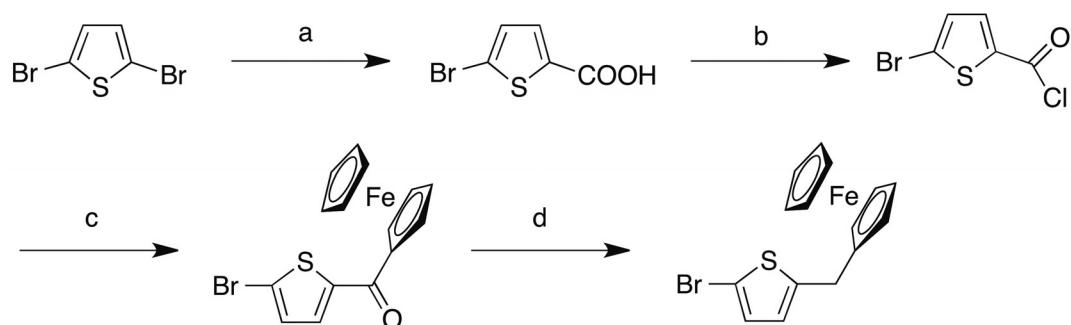


Experimental

Materials. Isopropylmagnesium chloride solution (2.0 M in THF), nBuLi (1.6M in hexanes), ferrocene, and bis(cyclooctadiene)nickel(0) were obtained from Acros Organics. Isopropylmagnesium chloride-LiCl (1.3M in THF), 2,5-dibromothiophene, thiourea, sodium hydroxide, 3-methylthiophene, iodobenzene diacetate, triethyl phosphite, bromotrimethyl silane, sodium borohydride (NaBH₄), aluminum chloride (AlCl₃), 1,8-dibromo-octane, thionyl chloride (SOCl₂), diisopropylamine, tetrahydrofuran (THF), toluene, dimethylformamide (DMF), dichloromethane, hexanes, isopropyl alcohol (IPA), methanol, and glass slides were obtained from VWR. Gold substrates were obtained from EMF corp., (Ithaca, NY). Silicon wafers were obtained from University Wafer (South Boston, MA). Indium tin oxide (ITO) substrates were obtained from Thin Film Devices (Anaheim, CA). Toluene and THF were distilled from sodium ketyl and degassed by sparging with argon before use. Dichloromethane was distilled from CaH₂. Unless indicated otherwise, materials were used as received.

Synthetic Methodology. All syntheses were carried out under an inert atmosphere of purified argon or nitrogen, using standard Schlenk techniques or a glovebox (Unilab BP with an MB10 purification system, MBraun, Inc.). NMR spectra were recorded using a Varian Mercury 300 NMR spectrometer working at 300 MHz. Chemical shifts are reported relative to an internal tetramethylsilane standard.



Scheme S1. a) isopropyl magnesium chloride, CO₂, HCl. b) thionyl chloride. c) ferrocene, AlCl₃. d) NaBH₄, AlCl₃, reflux

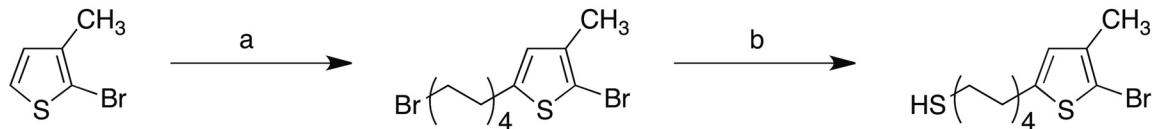
2-ferrocenyl-5-bromothiophene. To a nitrogen-purged 250 mL 3-neck flask was added 2,5-dibromothiophene (5g, 20.66 mmol) and 60 mL of THF. The solution was cooled to 0° C with rapid stirring, followed by addition of isopropyl magnesium chloride (14.45 mL, 20.66 mmol) dropwise. The reaction was stirred for an additional hour at 0° C. To a separate nitrogen-purged 250 mL 3-neck flask was added dry ice. The sublimed CO₂ was transferred via cannula and bubbled into the reaction for one hour, followed by additional stirring for one hour. A white precipitate was observed. The solvent was removed under vacuum and the resulting salt was dissolved in water and washed with hexanes. The product was precipitated by acidification with 6M HCl and filtered to yield 2.5 g 2-bromo-5-thiophenoic acid (58%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.639 (d, 1H, J=3.9 Hz), 7.115 (d, 1H, J=3.9 Hz). To a nitrogen-purged 100 mL 3-neck flask fitted with a distillation apparatus was added 2-bromo-5-thiophenoic acid (2.5 g, 12.07 mmol) and SOCl₂ (17.22 g, 144.7 mmol). The reaction was stirred overnight. The following morning, the temperature was increased to 80° C for one hour, and distilled under vacuum to yield pure 5-bromothiophene-2-acetyl chloride as a yellow solid (assumed quantitative yield). This was dissolved in 10 mL dry DCM and added dropwise to a separate nitrogen-purged 3-neck flask cooled to 0° C containing ferrocene (3.34 g, 17.95 mmol) and AlCl₃ (1.61 g, 12.07 mmol) in 100 mL dry DCM with rapid stirring. After 3 hours stirring, TLC indicated complete conversion. The reaction was neutralized slowly with nanowater, poured into ice water, and extracted with DCM. The extract was dried over MgSO₄, filtered, concentrated, and flashed through a column of silica gel using 2:8 hexane:EtOAc as the eluent to yield 1.84 g pure ferrocen-2-yl(5-bromothiophen-2-yl)methanone (41%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.660 (d, 1H, J=4 Hz), 7.115 (d, 1H, J=4 Hz), 4.982 (t, 2H, J=1.8 Hz), 4.606 (t, 2H, J=1.8 Hz), 4.225 (s, 5H). To a 250 mL nitrogen-purged 3-neck flask fitted with a reflux condenser containing 40 mL dry THF was added ferrocen-2-yl(5-bromothiophen-2-yl)methanone (1.50 g, 4.003 mmol), AlCl₃ (.907 g, 6.80 mmol), and NaBH₄ (.605 g, 16.01 mmol). The resulting solution was refluxed for 2 hours, upon which the solution color changed to orange. The reaction was allowed to cool to room temperature and slowly neutralized with nanowater, poured over ice water, extracted with DCM, dried over MgSO₄, filtered, and concentrated. The resulting concentrated solution was flashed through a column of silica gel using hexanes as the eluent to yield 1.3 g of 2-

ferrocenyl-5-bromothiophene as a crystalline orange solid (86%). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 6.758 (d, 1H, $J=3.7$ Hz), 6.451 (d, 1H, $J=3.7$ Hz), 4.063 (s, 5H), 4.041 (s, 2H), 3.734 (s, 2H). ^{13}C NMR (CDCl_3 , 300 MHz) δ (ppm): 146.544, 129.67, 125.002, 109.58, 86.89, 68.910 (5C), 68.534 (2C), 67.97 (2C), 30.821.



Scheme S2. a) nBuLi, 1,8-dibromooctane. b) NBS, DMF. c) thiourea, NaOH, HCl

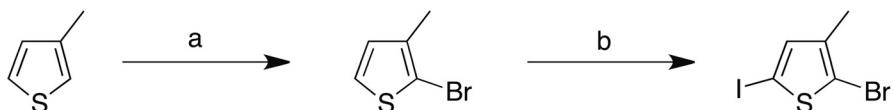
8-(5-bromothiophene-2-yl)octane-1-thiol. To a nitrogen-purged 3-neck pear flask was added thiophene (1.5 g, 17.82 mmol) and 30 mL of THF. The solution was cooled to -78 °C and nBuLi (11.13 mL, 17.82 mmol) was added dropwise. The reaction was allowed to stir at -78 °C for one hour. This was transferred dropwise via cannula to separate nitrogen-purged 3-neck flask containing dibromooctane (10g, 36 mmol) and 40 mL of THF at -78 °C. The reaction was allowed to warm to room temperature overnight. The reaction was poured into ice water, extracted with hexanes, dried over MgSO_4 , filtered, and concentrated. The excess dibromooctane was removed via distillation in the first fraction, and 1.84 g of 2-(8-bromoctyl)thiophene was obtained in the second fraction as a clear oil (38%). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 7.102 (d, 1H, $J=5.4$ Hz), 6.912 (t, 1H, $J=3.9$ Hz) 6.772 (d, 1H, $J=3.2$ Hz), 3.401 (t, 2H, $J=6.4$ Hz), 2.817 (t, 2H, $J=7.9$ Hz), 1.849 (p, 2H, $J=7.8$ Hz), 1.673 (p, 2H, $J=6.8$ Hz), 1.391 (m, 8H). To a 100 mL 3-neck flask was added 2-(8-bromoctyl)thiophene (1.84 g, 6.67 mmol) and 20 mL of DMF. In one portion was added NBS (1.3 g, 7.3 mmol) and the reaction was allowed to stir at room temperature overnight. The reaction was poured into ice water, extracted with hexane, dried over MgSO_4 , filtered, and concentrated. The concentrated was flashed through a column of silica gel using hexanes as the eluent to yield 2.18 g 5-bromo-2-(8-bromoctyl)thiophene (92%). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 6.835 (d, 1H, $J=3.5$ Hz), 6.524 (d, 1H, $J=3.6$ Hz), 3.40 (t, 2H, $J=6.9$ Hz), 2.732 (t, 2H, $J=7.6$ Hz), 1.847 (p, 2H, $J=7.1$ Hz), 1.623 (p, 2H, $J=7$ Hz), 1.397 (m, 8H). The well known thiourea route was used for the next step. To an argon purged 250 mL 3-neck flask fitted with a reflux condenser was added 5-bromo-2-(8-bromoctyl)thiophene (2.18 g, 6.15 mmol), thiourea (1.17 g, 15.37 mmol) and 100 mL of degassed ethanol. The reaction was refluxed overnight. The reaction was cooled to room temperature and 30 mL of 1M NaOH was added. The reaction was refluxed for an additional 4 hours, cooled to room temperature, and brought to neutral pH with dilute HCl. The solvent was removed, diluted with DCM, washed with brine 3x, dried over MgSO_4 , filtered, and concentrated. The concentrated was flashed through a column of silica gel using 1:10 EtOAc:Hex as the eluent to yield 1.5 g 8-(5-bromothiophene-2-yl)octane-1-thiol (79%). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 6.838 (d, 1H, $J=3.7$ Hz), 6.526 (d, 1H, $J=3.7$ Hz), 2.740 (t, 2H, $J=7.6$ Hz), 2.519 (q, 2H $J=7.2$ Hz), 1.625 (p, 4H, $J=7.3$ Hz), 1.2-1.5 (m, 9H). ^{13}C NMR (CDCl_3 , 300 MHz) δ (ppm): 129.615, 124.631, 34.046, 31.813, 31.482, 30.445, 28.572, 28.183, 24.771, 22.865.



Scheme S3. a) LDA, -78 °C, 1,8-dibromooctane. b) thiourea, NaOH, HCl

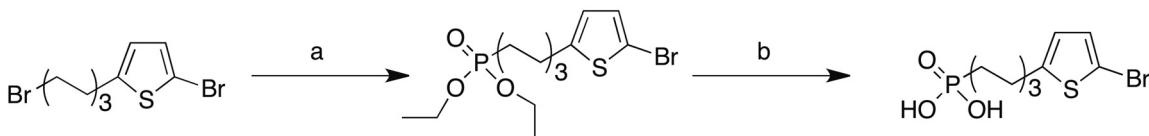
8-(5-bromo-3-methyl-thiophene-2-yl)octane-1-thiol. LDA was made in situ via addition of nBuLi (40 mmol, 25 mL) to diisopropylamine (44 mmol, 4.45 g) in 40 mL THF at -78 °C. To a solution of 2-bromo-3-methylthiophene (7.08g, 40 mmol) in 40 mL THF at -78 °C was added the LDA solution dropwise. After stirring for 1 hour, the resulting solution was transferred to a 250 mL 3-neck flask containing 1,8-dibromooctane (27.2 g, 100 mmol) in 80 mL THF at -78 °C. This was allowed to warm to room temperature overnight. The solvent and 1,8-dibromooctane was removed under vacuum. After column chromatography using hexanes as the eluent yielded 9.6 g 2-bromo-5-(8-bromoctyl)-3-methylthiophene (65 %) ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 6.457 (s, 1H), 3.403 (t, 2H, $J=6.8$ Hz), 2.682 (t, 2H, $J=7.3$ Hz), 2.116 (s, 3H), 1.851 (p, 2H, $J=7.5$ Hz), 1.606 (m, 2H, $J=7.3$ Hz), 1.424 (p, 2H, $J=7.3$ Hz), 1.317 (m, 6H). ^{13}C NMR (CDCl_3 , 300 MHz) δ (ppm): 145.43, 136.819, 126.543, 105.768, 34.183, 32.989, 31.503, 30.451, 29.320, 29.047, 28.832, 28.325, 15.378. The well-known thiourea route was used for the next step. To an argon purged 250 mL 3-neck flask fitted with a reflux condenser was added 2-bromo-5-(8-bromoctyl)-3-methylthiophene (3.68 g, 10 mmol), thiourea (1.9 g, 25 mmol mmol)

and 100 mL of degassed ethanol. The reaction was refluxed overnight. The reaction was cooled to room temperature and 40 mL of 1M NaOH was added. The reaction was refluxed for an additional 4 hours, cooled to room temperature, and brought to neutral pH with dilute HCl. The solvent was removed, diluted with DCM, washed with brine 3x, dried over MgSO_4 , filtered, and concentrated. The concentrated was flashed through a column of silica gel using 1:10 EtOAc:Hex as the eluent to yield .5 g 8-(5-bromo-3-methyl-thiophene-2-yl)octane-1-thiol (15 %). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 6.453 (s, 1H), 2.676 (t, 2H, J =8.1 Hz), 2.515 (q, 2H, J =7.3 Hz), 2.112 (s, 3H), 1.601 (p, 4H, J =7.6 Hz), 1.306 (m, 8H). ^{13}C NMR (CDCl_3 , 300 MHz) δ (ppm): 145.404, 136.900, 126.388, 105.806, 34.167, 31.432, 30.498, 29.392, 29.310, 28.529, 24.845, 22.695, 15.332.



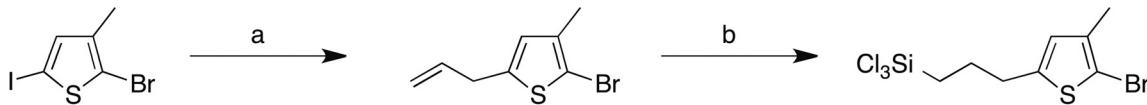
Scheme S4. a) NBS, THF, 0 °C. b) iodine, iodobenzene diacetate, CHCl_3

2-bromo-3-methyl-5-iodothiophene. To a 3-neck flask was added 3-methylthiophene (9.818g, 100 mmol) and 100 mL THF. This was cooled to 0° C and NBS (17.798 g, 100 mmol) was added in one portion. This reaction was allowed to warm to room temperature overnight. The solvent was removed, redissolved in ether, washed with water, dried over MgSO_4 , and concentrated. The concentrated product was purified through an alumina plug using hexanes as the eluent to yield 13.2 g pure 2-bromo-3-methylthiophene as a colorless oil (75%). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 7.160 (d, 1H, J =5.4 Hz), 6.773 (d, 1H, J =5.8 Hz), 2.194 (s, 3H). To a solution of 2-bromo-3-methylthiophene (6.6g, 37 mmol) in chloroform (60 mL) was added iodine (5.96g, 18.5 mmol), followed by iodobenzene diacetate (4.695 g, 18.5 mmol). This was stirred at room temperature overnight. The following day, the reaction was washed with a dilute solution of sodium sulfite and water, dried over MgSO_4 , and concentrated. The iodobenzene was distilled off under vacuum in the first fraction and 7.75 g pure 2-bromo-3-methyl-5-iodothiophene was obtained in the second fraction (70%). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 6.952 (s, 1H), 2.159 (s, 3H).



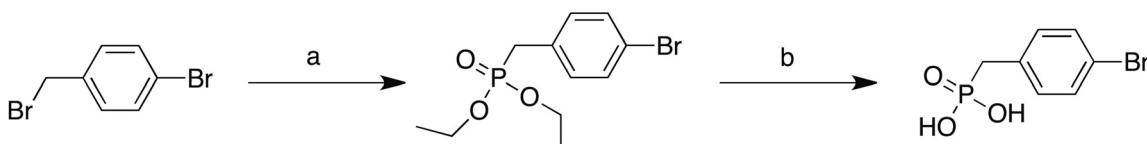
Scheme S5. a) triethyl phosphite, 170 °C. b) BrSiMe_3 , methanol

(6-(5-bromothiophen-2-yl)hexyl)phosphonic acid. 2-(8-bromohexyl)thiophene was synthesized as reported previously.¹ Triethylphosphite (10.19 g, 61 mmol) and 2-(8-bromohexyl)thiophene (2 g, 6.1 mmol) was added to a 3-neck flask fitted with a reflux condenser. This solution was refluxed vigorously for 24 hours. Upon cooling, excess triethylphosphite was removed under vacuum to yield pure diethyl (6-(5-bromothiophen-2-yl)hexyl)phosphonate (assumed quantitative yield). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 6.824 (d, 1H, J =4.1 Hz), 6.508 (d, 1H, J =4.1 Hz), 4.069 (m, 4H, J = 3.5 Hz), 2.720 (t, 2H, J =7.6 Hz), 1.616 (m, 6H), 1.369 (m, 2H), 1.307 (t, 6H, J =7.3 Hz). ^{13}C NMR (CDCl_3 , 300 MHz) δ (ppm): 147.67, 129.65, 124.66, 108.97, 61.659, 31.349 (2C), 30.422 (2C), 28.505, 26.783, 24.849, 22.371, 16.812. In a 3-neck 100 mL flask was added diethyl (6-(5-bromothiophen-2-yl)hexyl)phosphonate and bromotrimethylsilane (1.87 mL, 14.1 mmol). This was allowed to stir overnight. The following day, excess trimethylsilane was removed under vacuum. Under nitrogen, methanol (30 mL) was added and this was brought to reflux for 4 hours. The methanol was removed under vacuum to yield (6-(5-bromothiophen-2-yl)hexyl)phosphonic acid (quantitative yield). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 6.822 (d, 1H, J =4.2 Hz), 6.511 (d, 1H, J =4.2 Hz), 2.718 (t, 2H, J =7.4 Hz), 1.614 (m, 5H), 1.368 (m, 5H). ^{13}C NMR (DMSO-d_6 , 300 MHz) δ (ppm): 148.095, 130.773, 126.0, 108.425, 49.091, 31.188, 29.979, 28.504, 26.990, 23.118.



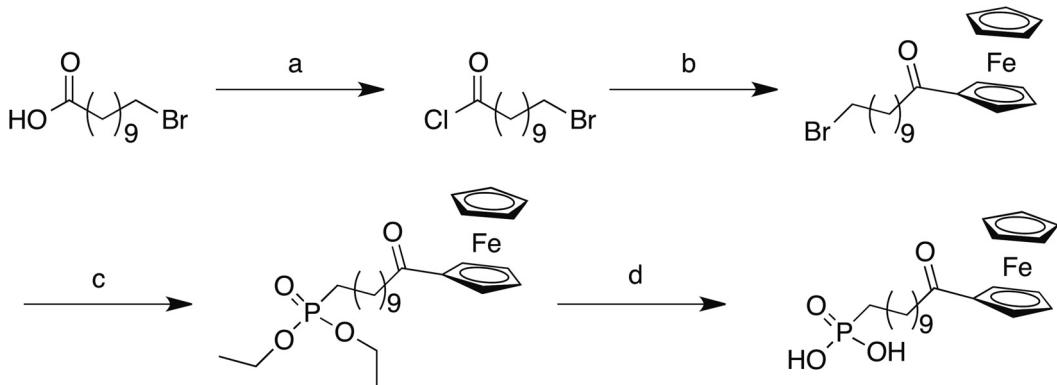
Scheme S6. a) isopropyl magnesium chloride, allyl bromide. B) HSiCl_3 , H_2PtCl_6

(3-(5-bromo-4-methylthiophen-2-yl)propyl)trichlorosilane. To a 3-neck flask containing 2-bromo-3-methyl-5-iodothiophene (1.455g, 4.80 mmol) in 20 mL THF was added isopropyl magnesium chloride (2.47 mL, 4.80 mmol) at 0 °C. This was stirred for 1 hour and quenched with allyl bromide (.7 g, 5.76 mmol). The THF was removed under vacuum and the product was redissolved in ether, washed with water and brine, dried over MgSO_4 , and concentrated. The crude product was flashed through a plug of alumina to yield 1g pure 2-bromo-3-methyl-5-allylthiophene (95.8%). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 6.499 (s, 1H), 5.918 (m, 1H), 5.121 (m, 2H), 3.439 (d, 2H, $J=6.9$ Hz), 2.121 (s, 3H). In a 3-neck flask was added 2-bromo-3-methyl-5-allylthiophene (1g, 4.6 mmol), trichlorosilane, and one crystal of chloroplatinic acid hexahydrate. This was stirred at room temperature overnight. The following day, trichlorosilane as removed under vacuum to yield pure (3-(5-bromo-4-methylthiophen-2-yl)propyl)trichlorosilane (quantitative yield). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 6.502 (s, 1H), 2.814 (t, 2H, $J=7.2$ Hz), 2.129 (s, 3H), 1.904 (p, 2H, $J=8.4$ Hz), 1.437 (t, 2H, $J=8.4$ Hz). ^{13}C NMR (CDCl_3 , 300 MHz) δ (ppm): 143.006, 137.049, 127.456, 106.531, 32.237, 24.303, 23.465, 15.728.



Scheme S7. a) triethyl phosphite, 170 °C. b) BrSiMe_3 , methanol

(4-bromobenzyl)phosphonic acid. In a 3-neck 100 mL flask was added triethylphosphite and 4-bromobenzyl bromide. This was heated to reflux for 24 hours. Upon cooling, excess triethylphosphite was removed under vacuum to yield pure diethyl 4-bromobenzylphosphonate (quantitative yield). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 7.435 (d, 2H, $J=8.6$ Hz), 7.174 (dd, 2H, $J=8.6$ Hz), 4.023 (p, 4H, $J=7.2$ Hz), 3.140 (d, 2H, $J=21.5$ Hz), 1.251 (t, 6H, $J=7.1$ Hz). To a 3-neck flask was added diethyl 4-bromobenzylphosphonate (1.22 g, 4 mmol) and bromotrimethylsilane (2 g, 13 mmol). This was stirred overnight. Excess trimethylsilane was removed under vacuum and methanol (30 mL) was added under nitrogen. This was refluxed for 4 hours. The methanol was removed under vacuum to yield pure (4-bromobenzyl)phosphonic acid (quantitative yield). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 7.447 (d, 2H, $J=8.5$ Hz), 7.181 (dd, 2H, $J=8.5$ Hz), 2.921 (d, 2H, $J=21.3$ Hz).



Scheme S8. a) thionyl chloride. b) ferrocene, AlCl_3 , 0 °C. c) triethyl phosphite, reflux. d) bromotrimethylsilane, methanol

(11-oxo-11-ferrocenylundecyl)phosphonic acid. To a 3-neck flask containing 11-bromoundecanoic acid (5.3 g, 20 mmol) and DCM (10 mL) was added thionyl choride (2.9 mL, 40 mmol). This was stirred at room temperature overnight. The following day, DCM and excess thionyl chloride was removed under vacuum, and the product was distilled under vacuum and added dropwise to a 3-neck flask containing ferrocene (7.44 g, 40

mmol) and AlCl_3 (4 g, 30 mmol) in 60 mL DCM at 0 °C. This was stirred at room temperature overnight. The solution was neutralized with nanowater, poured over water, and extracted with DCM. The product was concentrated and purified on a silica gel column using 1:9 EtOAc:hexanes as the eluent to yield 5.68 g 11-bromoundecanoylferrocene (57 %). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 4.779 (t, 2H, J =1.7 Hz), 4.487 (t, 2H, J =1.7 Hz), 4.193 (s, 5H), 3.407 (t, 2H, J =6.5 Hz), 2.692 (t, 2H, J =7.6 Hz), 1.854 (p, 2H, J =6.9 Hz) 1.700 (p, 2H, J =7.2 Hz), 1.315 (m, 12H). To a 3-neck flask was added 11-bromoundecanoylferrocene (2.16 g, 5 mmol) and triethyl phosphite (8.3 g, 50 mmol). This was heated to reflux overnight. The following day, excess triethyl phosphite was distilled off to yield pure diethyl (11-oxo-11-ferrocenylundecyl)phosphonate (2.1 g). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 4.780 (t, 2H, J =1.9 Hz), 4.485 (t, 2H, 1.9 Hz), 4.194 (s, 5H), 4.085 (m, 4H), 2.690 (t, 2H, J =7.3 Hz), 1.667 (m, 8H), 1.320 (t, 6H, J =6.5 Hz), 1.343 (m, 10H). To a 3-neck flask was added diethyl (11-oxo-11-ferrocenylundecyl)phosphonate (2.1 g, 4.3 mmol) and bromotrimethylsilane (1.98 g, 12.9 mmol). This was stirred at room temperature overnight. The following day, bromotrimethylsilane was removed and methanol (30 mL) was added. This was heated to reflux for four hours. The methanol was removed under vacuum, and the product was dissolved in dilute base, precipitated by addition of 6 M HCl, filtered, and dried to yield .6 g (11-oxo-11-ferrocenylundecyl)phosphonic acid as a brown solid (33 %). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 4.766 (2H), 4.461 (2H), 4.165 (5H), 2.663 (2H), 1.621 (8H), 1.281 (10H).

Preparation of Si-KCTP initiator substrates. Silicon wafers (Silicon Quest) and glass slides (VWR) were cut into 2×3 cm rectangles and subjected to plasma cleaning using argon plasma (Harrick Plasma) for 5 min. The substrates were then treated for 15 min in a UV-ozone cleaner and transferred to a nitrogen-filled glove box. 40 μL of 3-(5-bromo-4-methylthiophene-2-yl)propyltrichlorosilane was dissolved in 10 mL of toluene, and the solution was poured over the substrates, which were capped and left overnight. The substrates were then removed from the solution, sonicated one minute in toluene, one minute in DCM, one minute in IPA, and finally rinsed with IPA. The substrates were dried in a stream of nitrogen gas and transferred back inside a glovebox. For gold substrates, the same cleaning procedure was used, but without the UV-ozone treatment. The cleaned substrates were then placed in a 5 mM toluene solution of 8-(5-bromothiophene-2-yl)octane-1-thiol overnight. Substrates were then removed from the solution, rinsed as described above, and transferred back inside a glove box. For ITO, the substrates were sonicated in 18 $\text{M}\Omega$ and isopropanol for 15 minutes followed by cleaning using a $\text{H}_2\text{O}_2:\text{NH}_4\text{OH}:\text{H}_2\text{O}$ bath (1:1:5) at 80 °C for 1 hour. Slides were extensively rinsed with water and ethanol, and placed in a 5mM ethanol solution of the phosphonic acid self-assembly molecule for 48 hours. Contact angle after cleaning was <10° and after self-assembly 75°.

Magnesiation of 2-ferrocenyl-5-bromothiophene. To a 40 mL THF solution of 2-ferrocenyl-5-bromothiophene (.288 g, .797 mmol) at 0 °C was added isopropyl magnesium chloride (.36 mL, .7173 mmol). This was allowed to stir for 30 minutes at 0 °C and then one hour at room temperature. This solution was then transferred to the glovebox. NMR confirmed complete conversion upon quenching with D_2O . For reactions that involved LiCl, an isopropyl magnesium chloride-lithium chloride complex was used (1.3M).

Magnesiation of 2-bromo-5-iodo-3-methylthiophene. To a 20 mL THF solution of 2-bromo-5-iodo-3-methylthiophene (.302 g, 1 mmol) was added isopropyl magnesium chloride (.45 mL, .9 mmol). This was allowed to stir for one hour at 0 °C and then a half hour at room temperature. This solution was then transferred to the glovebox.

Formation of Initiators. In a glovebox, 30 mg of $\text{Ni}(\text{COD})_2$ and 17 mg of 2,2'-bipyridine (bpy), 43 mg dppe, 45 mg dppp, or 46 mg of dppb was weighed out in a 20 mL scintillation vial, followed by the addition of 10 mL toluene. Silicon, gold or ITO substrates containing an aryl bromide monolayer was placed in the solution. For the ligand exchange step from bpy, the substrates were extensively rinsed with toluene and placed in a 10 mL .1M toluene solution of dppe, dppp, or dppb for one hour. Just prior to polymerization, substrates were removed from the ligand exchange solution and rinsed extensively with toluene and THF.

Ellipsometric measurements. Null ellipsometry measurements of monolayers were performed on a Multiskop (Optrel GbR) with a 632.8 nm HeNe laser light source at 70°. Film thickness was obtained by fitting ellipsometric data using manufacturer provided specialized software. At least three spots on each wafer were measured, and the thickness was averaged. To obtain thickness values of the samples, a simple box model was employed and a refractive index of $n = 1.5$, $k = 0$ was used.

Electrochemical measurements. Electrochemical measurements were obtained using a CH Instruments bipotentiostat equipped with a platinum counter electrode and a silver wire pseudo reference electrode. The gold substrates were used as the working electrode. Tetrabutylammonium hexafluorophosphate in DCM (.1M, degassed) was used as the supporting electrolyte. All scan rates are recorded at 100 mV/sec unless otherwise noted.

FTIR measurements. Infrared spectra of films were acquired using a Thermo-Nicolet Model 6700 spectrometer equipped with a variable angle grazing angle attenuated total reflection (GATR-ATR) accessory (vari-GATR, Harrick Scientific) and processed using OMNIC 8.0 software (ThermoNicolet, Madison, WI). All PM-IRRAS measurements were obtained using 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 and a modulation frequency of either 3000 cm^{-1} or 1500 cm^{-1} .

UV-VIS measurements. UV-vis spectra of polymer substrates were taken using a Cary 50 UV-vis spectrophotometer from Varian. Variable angle polarized light UV-Vis was performed using a custom-built variable angle sample holder fitted with a rotatable polarizing filter.

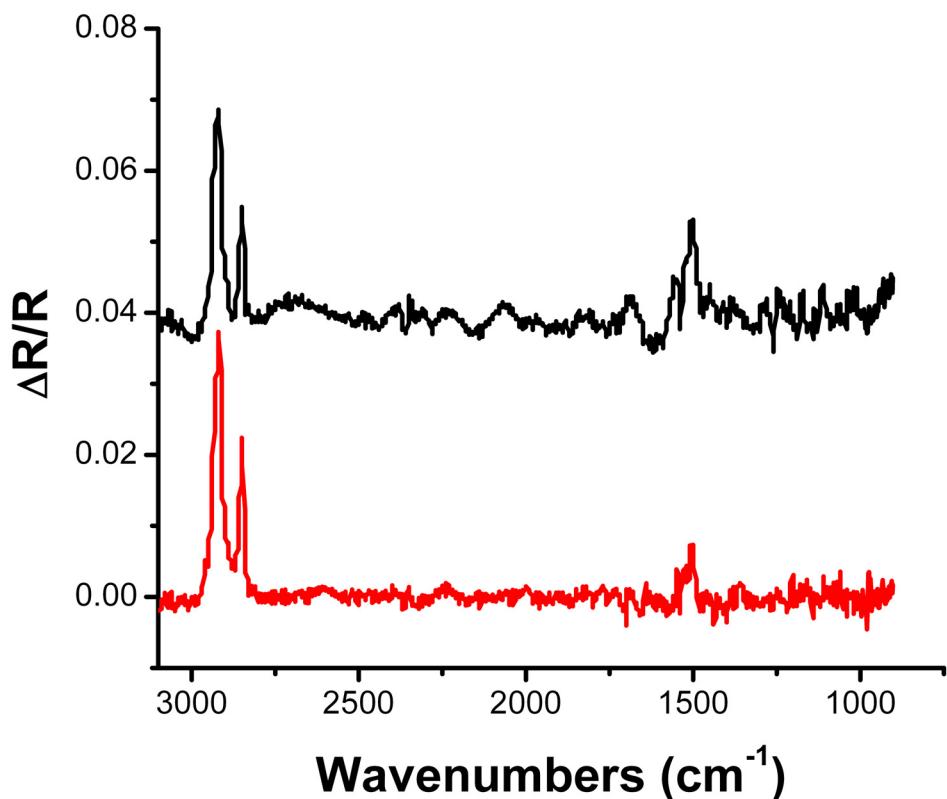


Figure S1. Baseline corrected PM-IRRAS image of **1** (red line) and **2** (black line) on gold.

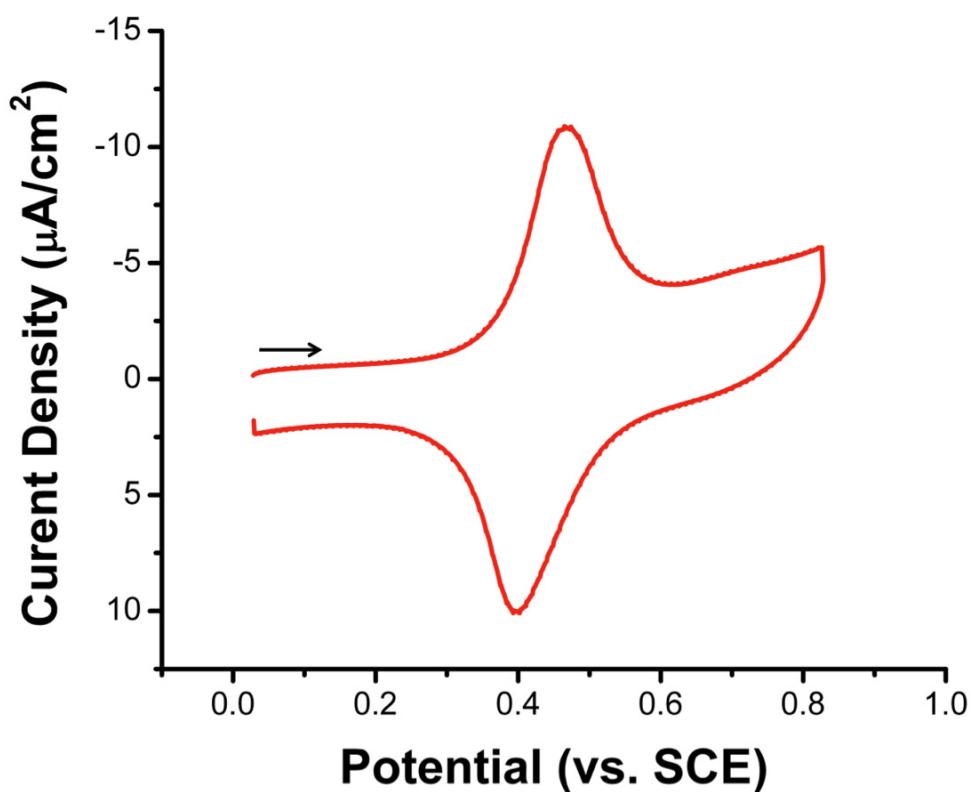


Figure S2. CV of 2PPh₃-based initiators after capping agent reaction using SAM of **1**. Arrow indicates start of the scan.

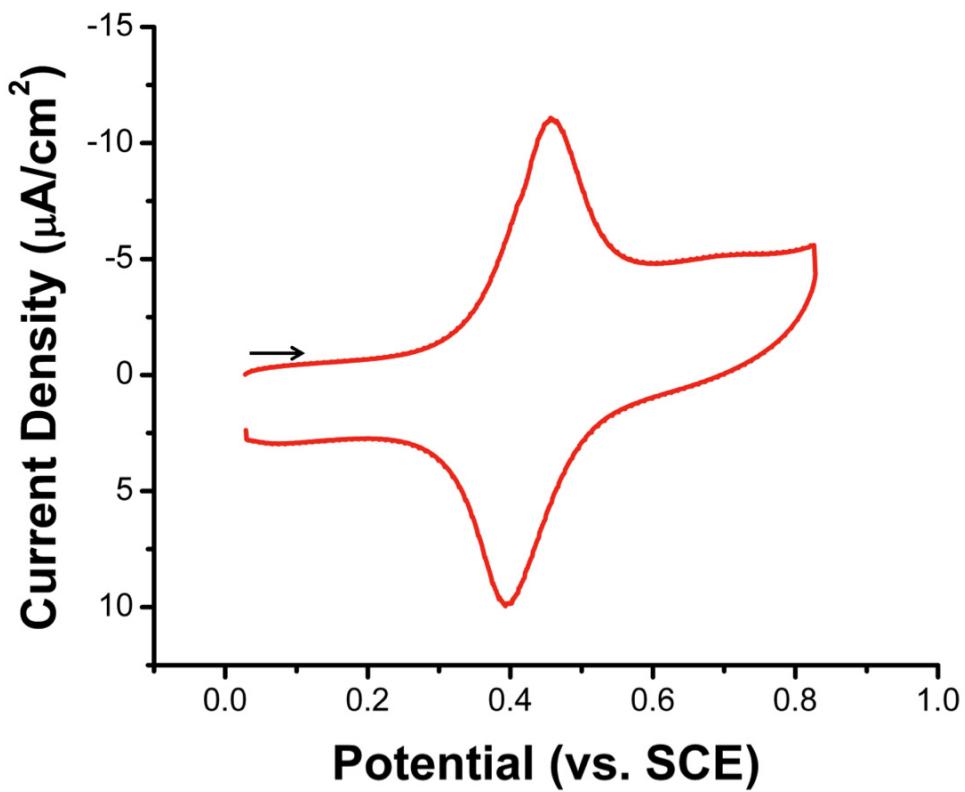


Figure S3. CV of dppe-based initiators after capping agent reaction using SAM of **1**. Arrow indicates start of the scan.

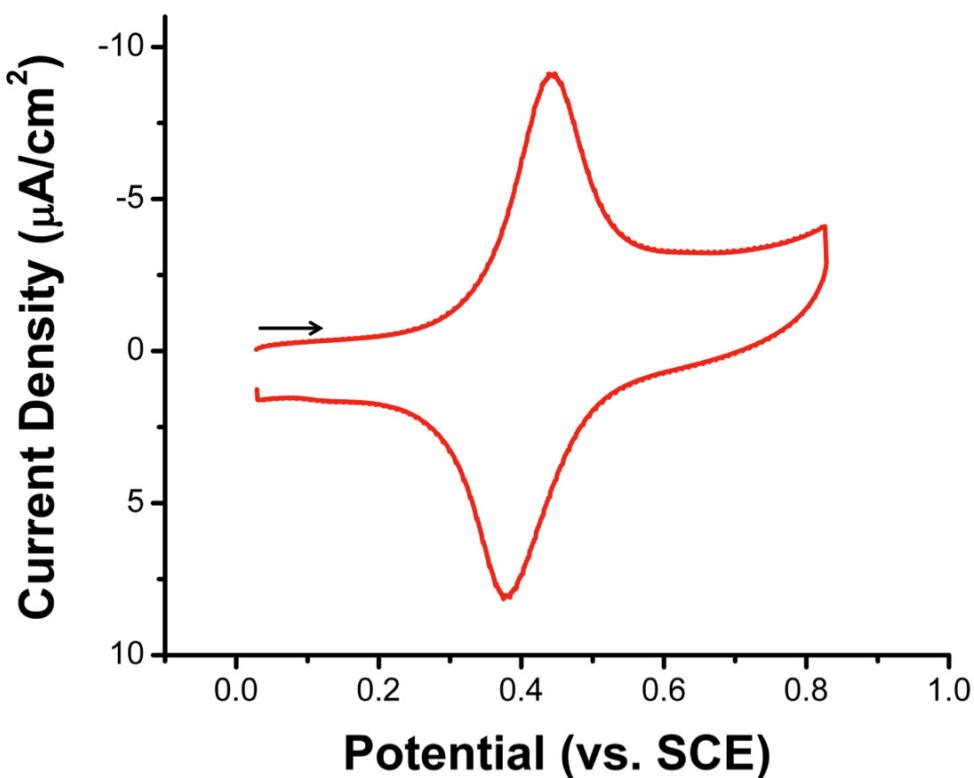


Figure S4. CV of dppp-based initiators after capping agent reaction using SAMs of **1**. Arrow indicates start of the scan.

Ligand	Coverage ($\times 10^{13}$ molecules/cm 2)
Bpy	5.2
Dppe	2.79
Dppe	2.83
Dppp	2.16
Dppp	2.22
Dppb	4.44
Dppb	4.92

Table S1. Data used to calculate average values for Table II in text.

Ligand	Coverage ($\times 10^{13}$ molecules/cm 2)	Yield (%) ^a	Overall Yield (%) ^b
Bpy	3.00 ^c	N/A	5
Dppe	2.17	72	3.6
Dppe	1.81	60	3
Dppp	.713	24	1.1
Dppp	.913	30	1.5
Dppb	2.02	67	3.3
Dppb	2.04	68	3.4

^aYield (%) of ligand exchange was calculated by dividing initiator coverage by bpy-based initiator coverage (3.0×10^{13} initiators/cm 2).

^bOverall Yield (%) was calculated by dividing initiator coverage by monolayer coverage for **1** (6×10^{14} molecules/cm 2).

^cNi(COD)bpy reaction time was one hour in this case.

Table S2. Initiator coverages using low concentration of exchange ligand (2.5 mM) using SAMs of **1**. Catalyst deposition time was one hour.

Ligand	Coverage ($\times 10^{13}$ molecules/cm 2)
Bpy	1.67
Dppe	1.52
Dppe	1.32
Dppp	1.07
Dppp	1.09

Table S3. Data used to calculate average values for Table III in main text.

Ligand	Coverage ($\times 10^{13}$ molecules/cm 2)
Bpy	1.50 ^c
Bpy	2.28 ^c
dppe	2.25
dppe	1.20
dppp	1.11
Dppp	2.38
Dppb	2.67
dppb	1.21

^aNi(COD)bpy reaction time was one hour in this case.

Table S4. Initiator coverages using SAMs of **3**.

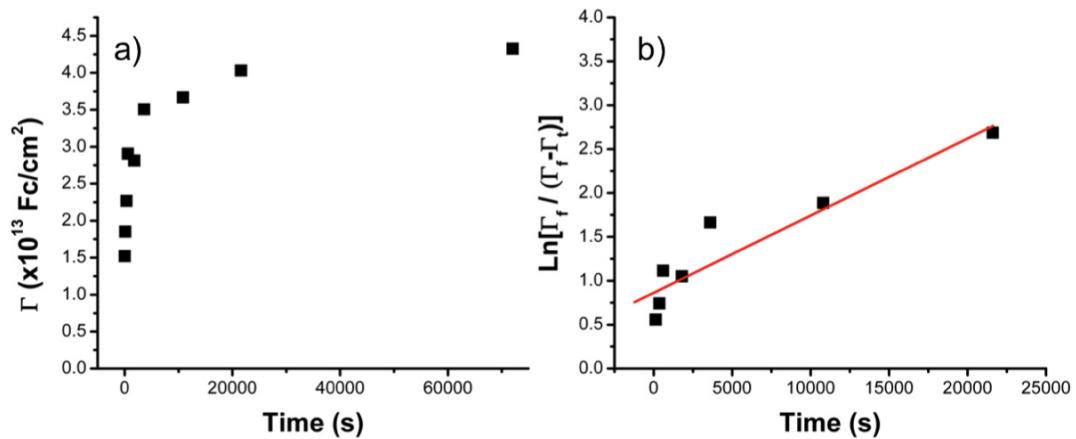


Figure S5. Dppe-based capping agent kinetics using SAMs of **1**.

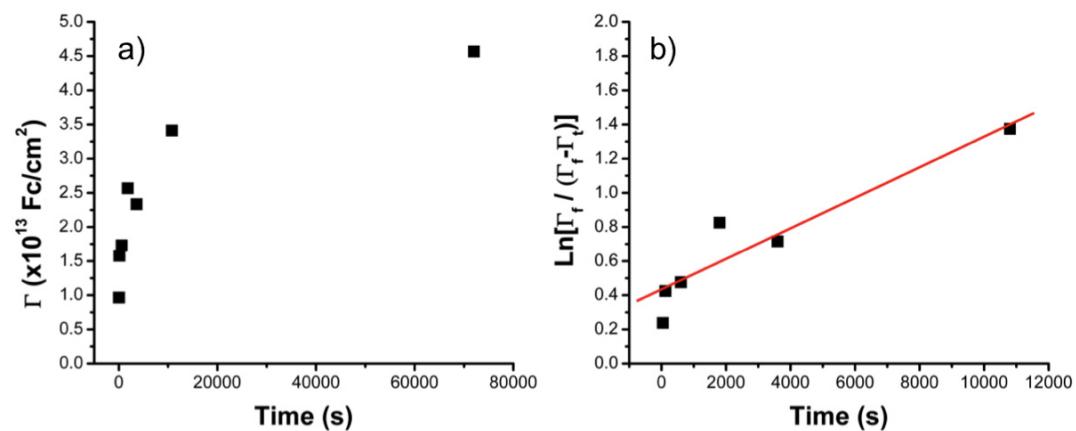


Figure S6. Dppp-based initiator capping agent kinetics using SAMs of **1**.

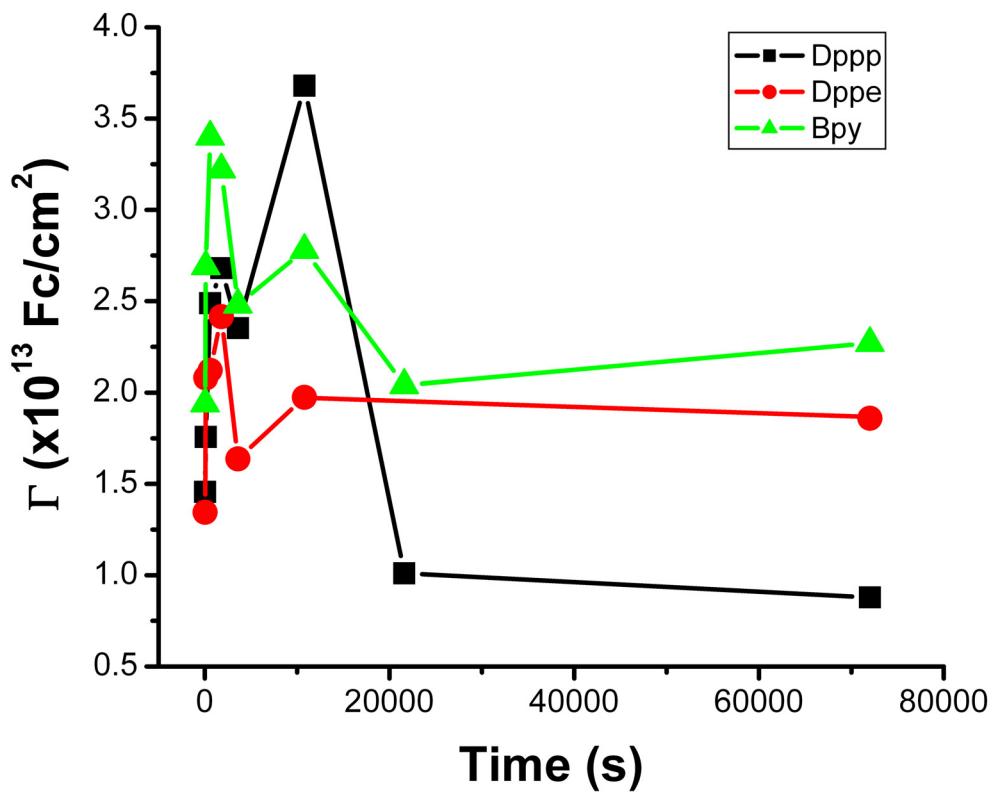


Figure S7. Ferrocene coverage vs. time with LiCl additive via Dppp-, dppe-, and bpy-based initiators using SAMs of **1**.

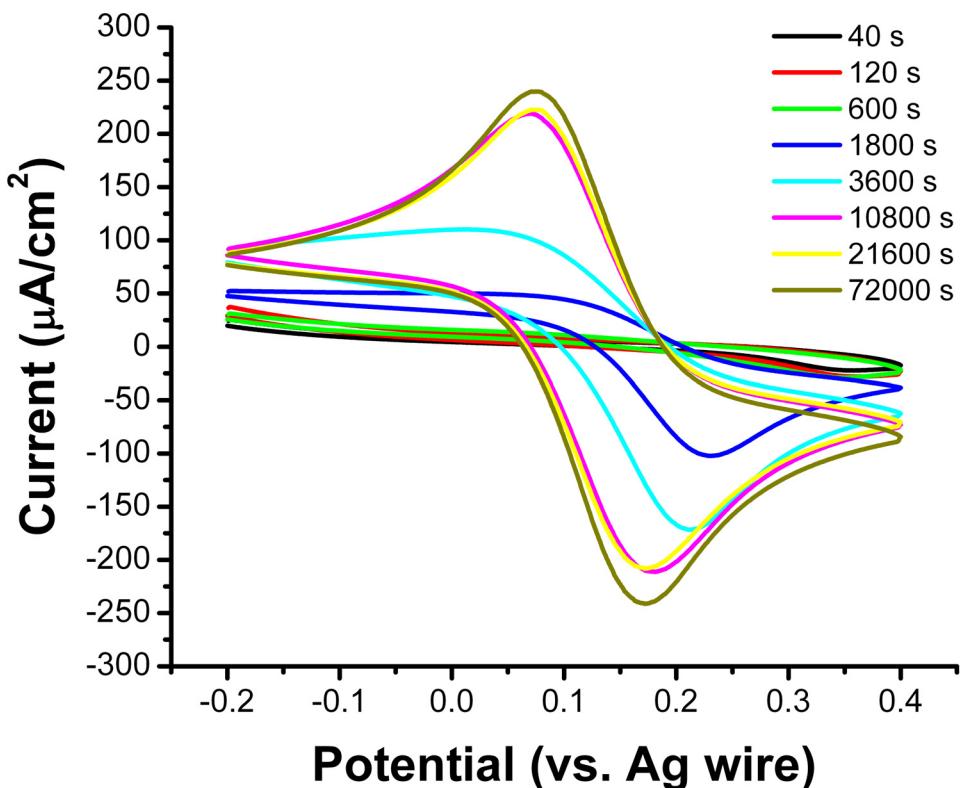


Figure S8. CV of bpy-based initiator substrate after LiCl complexed capping agent reaction in presence of aqueous electrode composed of 1 mM $\text{Fe}(\text{CN})_6$ in .1M KCl. Over time, pinholes form in the monolayer due to destructive nature of the LiCl Grignard species, as demonstrated by the appearance of $\text{Fe}(\text{CN})_6$ redox peaks.

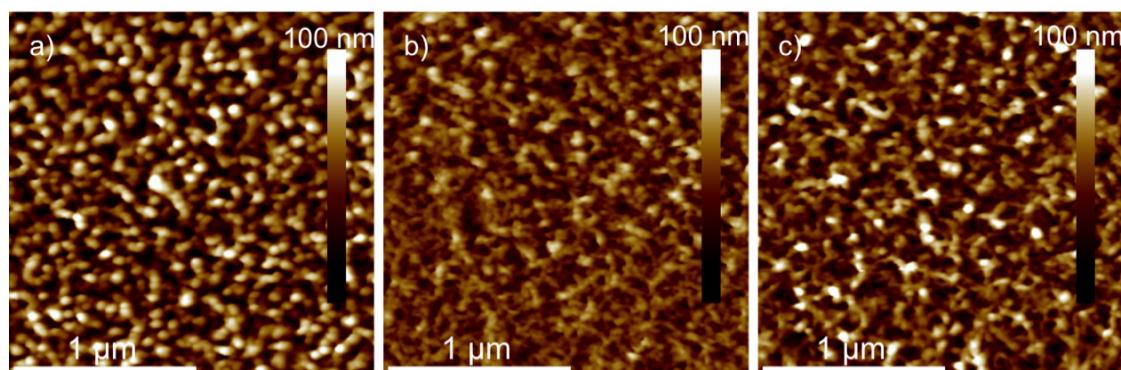


Figure S9. AFM topography images of P3MT films on Si/SiO₂ via **6**. a) 2 μm AFM topography image of P3MT film via dppe-based initiators. b) 2 μm AFM topography image of P3MT film via dppp-based initiators. c) 2 μm AFM topography image of P3MT film via dppb-based initiators.

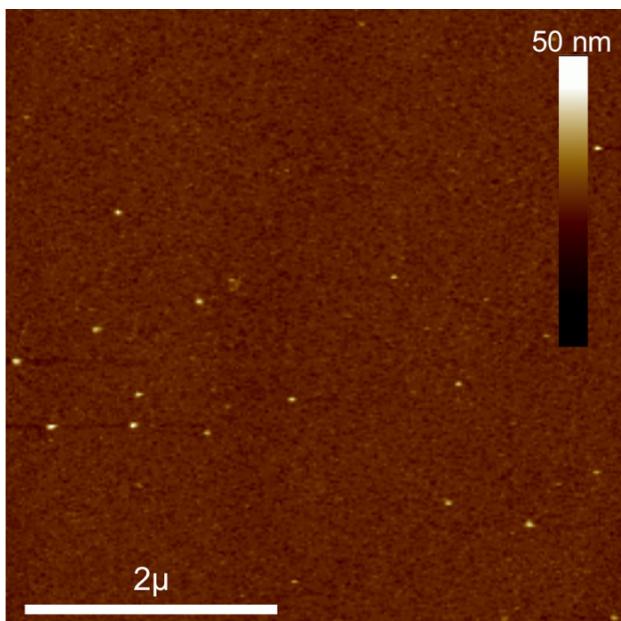


Figure S10. AFM topography image of a monolayer on SiO_2 using **6**.

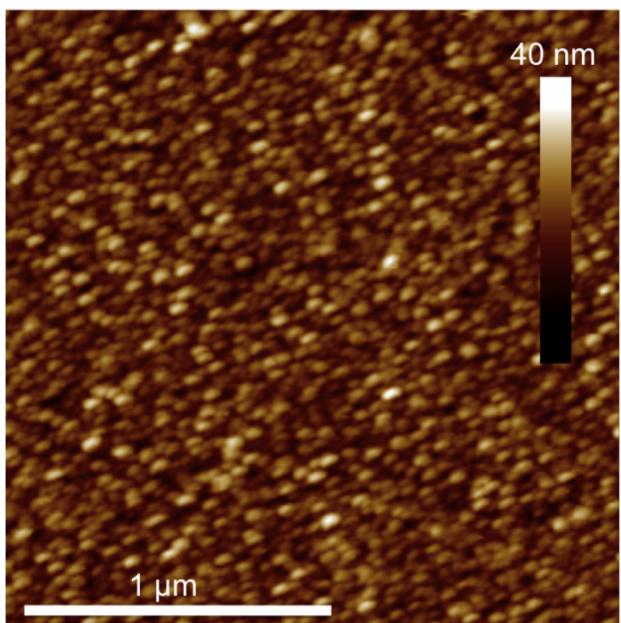


Figure S11. AFM topography image of P3MT on ITO using SAMs of **3**.

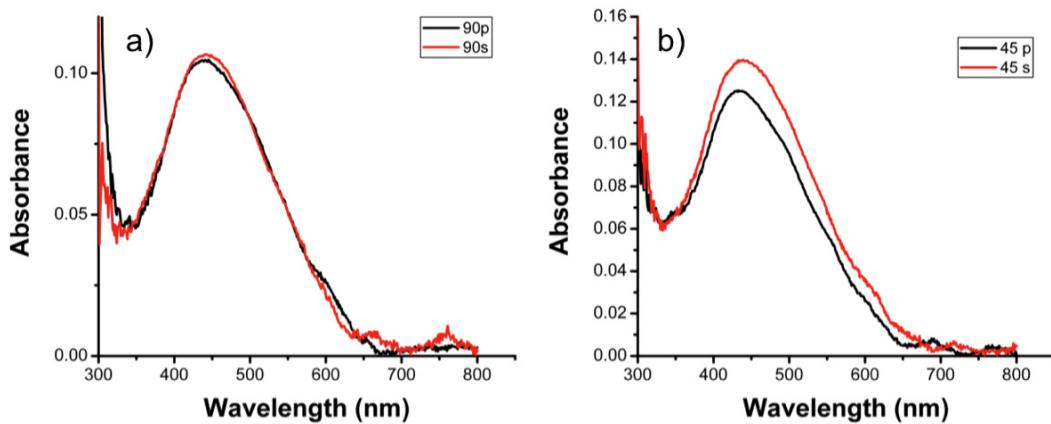


FIGURE S12. Polarized UV-Vis of a 10 nm P3MT film on glass via dppe-based initiator using SAM of **5**.

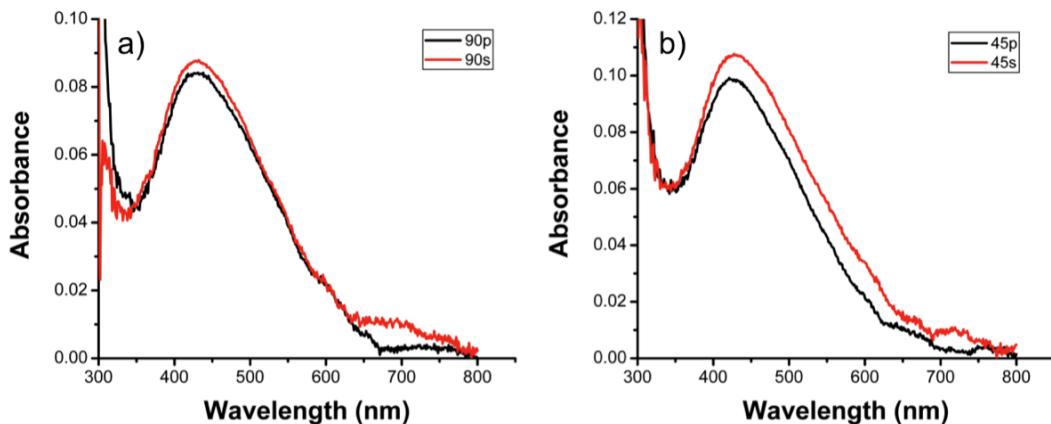


Figure S13. Polarized UV-Vis of a 10 nm P3MT film on glass via dppp-based initiator using SAM of **5**.

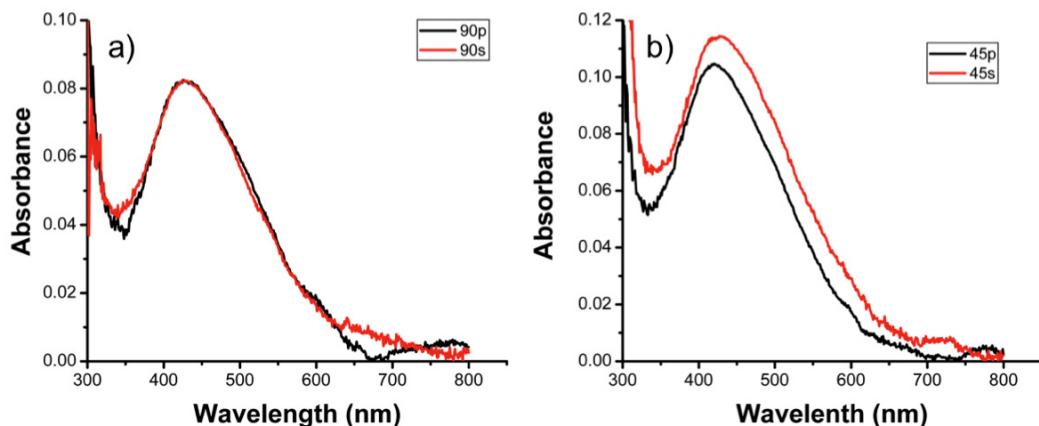


Figure S14. Polarized UV-Vis of a 10 nm P3MT film on glass via dppb-based initiator using SAM of **5**.

1. S. K. Sontag, N. Marshall and J. Locklin, *Chem. Commun. (Cambridge, U. K.)*, 2009, 3354-3356.