

Supplementary Information

AFM Study of β -7T Oligothiophene Films on Mica: Mechanical Properties and Humidity Dependent Phases

Jinyu Chen[†], Imma Ratera[†], D.F. Ogletree, Miquel Salmeron^{†}, Amanda R. Murphy[‡], and Jean M. J. Fréchet[†]*

Lawrence Berkeley National Laboratory, Berkeley, California 94720 and Department of Chemistry, University of California, Berkeley, California 94720

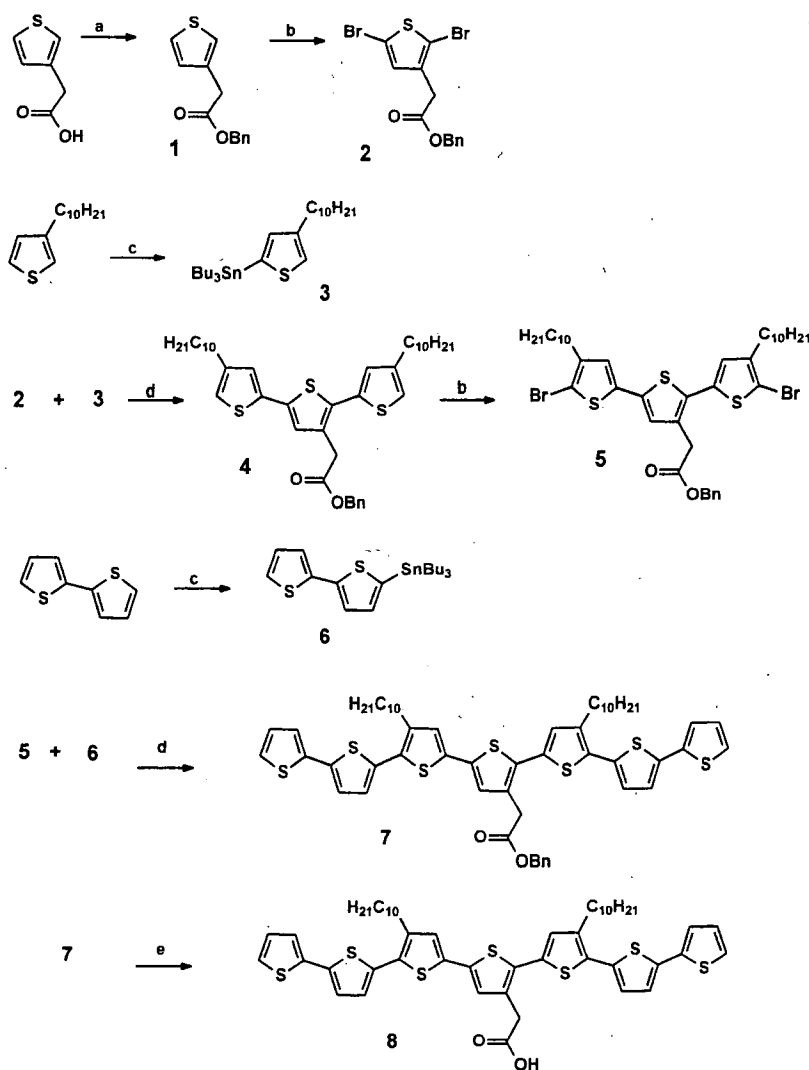
[†] Lawrence Berkeley National Laboratories.

[‡] *Department of Chemistry, University of California, Berkeley.*

Experimental

Materials. All chemicals were purchased from Aldrich and used without further purification unless otherwise noted. 2,2'-Bithiophene was purified by filtering through silica gel using hexane as the eluent. N-bromosuccinimide was recrystallized from 1:1 acetic acid /water prior to use. THF and toluene were distilled over Na/benzophenone, dichloromethane and pyridine from calcium hydride just prior to use. N,N'-dimethylformamide used was anhydrous packed under N₂. All reactions were performed under dry N₂ unless otherwise noted. All extracts were dried over MgSO₄ and solvents were removed by rotary evaporation with aspirator pressure. Flash chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica.

Characterization. Infrared spectra were measured on neat samples unless otherwise indicated with a Mattson Genesis II FT-IR with a diffuse reflectance accessory (Pike). UV-Vis data were measured with a Varian Cary 50 spectrophotometer. Emission spectra were measured with a ISA/SPEX Fluorolog 3.22 equipped with a double excitation and double emission monochromators and a digital photon-counting photomultiplier. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker AMX-300, AM-400 or DRX-500 instruments using CDCl_3 as the solvent. Matrix Assisted Laser Desorption Ionization -Time Of Flight (MALDI-TOF) mass spectrometry was performed on a Perseptive Biosystems Voyager-DE instrument in positive ion mode using α -cyano-4-hydroxycinnamic acid as the matrix. High Resolution Mass Spectrometry (HRMS) using Fast Atom Bombardment (FAB) was done with a Micromass ZAB2-EZ double focusing mass spectrometer (BE geometry). Elemental analyses were performed at the UC Berkeley Microanalysis Laboratory.



Scheme 1: Synthesis of -substituted-T7. a) K_2CO_3 , benzyl bromide, THF. b) NBS, DMF. c) *n*-BuLi, -78 °C; tributyltin chloride. d) $Pd(PPh_3)_2Cl_2$, DMF e) 5% aq. KOH, THF.

General Bromination Procedure. The compound was dissolved in *N,N'*-dimethylformamide (DMF) at 0.5 M concentration. The flask was protected from light and two equivalents of NBS were added. The mixture was allowed to stir overnight at room temperature. The mixture was diluted with ethyl acetate using four times the volume of DMF, and washed three times with equal volumes of brine followed by four water washings. The organic layer was dried and the solvent evaporated.

General Stille Coupling Procedure. The corresponding halide and 2.5 equivalents of the stannate were combined in anhydrous DMF at 0.5 M concentration. The mixture was degassed with four freeze-pump-thaw cycles, backfilling each time with argon. Four mole percent of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ was subsequently added, and the mixture was subjected to one more degassing cycle. The flask was heated to 80 °C, and the mixture was stirred overnight under argon. The reaction was diluted with ethyl acetate with four times the volume of DMF and washed twice with equal volumes of brine and four times with equal volumes of water. The organic layer was dried and the solvent evaporated.

Benzyl thiophene-3-acetate (1). To 5.00 g (35.0 mmol) of 3-thiophene acetic acid, 9.71 g (70.0 mmol) of K_2CO_3 , 6.00 g (35.0 mmol) of benzyl bromide and 0.56 g (2 mmol) of 18-crown-6, 100 mL of dry THF was added. The heterogeneous mixture was heated at reflux for 4 hours, then cooled to room temperature. The solvent was removed and the residual solid was taken up in 1:3 ethyl acetate/hexanes filtered through silica gel. The solvent was removed and the white solid was dried *in vacuo* to give a quantitative yield of 8.12 g. ^1H NMR (300 MHz): 3.71 (s, 2H), 5.15 (s, 2H), 7.06 (dd, $J = 1.2$ and 5.1 Hz, 1H), 7.16 (m, 1H), 7.30 (dd, $J = 2.7$ and 4.8 Hz, 1H), 7.32-7.40 (m, 5H).

Benzyl 2,5-dibromo-thiophene-3-acetate (2). This compound was prepared as described in the General Bromination Procedure. No further purification was necessary to obtain 98% yield of an orange liquid. ^1H NMR (300 MHz): 3.61 (s, 2H), 5.16 (s, 2H), 6.93 (s, 1H), 7.31-7.40 (m, 5H).

2-Tributylstannyl-4-decylthiophene (3). To 2.0 g (8.9 mmol) of 3-decylthiophene in 100 mL dry THF, 1.34 mL (8.9 mmol) of *N,N,N,N*-tetramethyl-1,2-ethylenediamine was added. The flask was cooled to 0 °C and 3.56 mL (8.9 mmol) 2.5 M *n*-BuLi in hexanes was added dropwise via syringe.

The mixture was warmed to room temperature then heated at reflux for 30 minutes. The flask was cooled to 0 °C, and 2.9 g (8.9 mmol) tributyltin chloride dissolved in 8 mL dry THF was added dropwise via syringe. The flask was allowed to warm to room temperature overnight. The solvent was evaporated and the resulting liquid was taken up in 100 mL ethyl acetate and washed twice with saturated NH₄Cl and three times with water. The organic layer was dried and evaporated. The resulting brown liquid was distilled under reduced pressure to give 3.36 g (74%) of an orange liquid that contained a mixture of isomers that could not be separated. The desired isomer was present in 67% and is notated as isomer A in the NMR data, while the regioisomer 3-decyl-2-tributylstannylthiophene is notated as isomer B. ¹H NMR (300 MHz): δ 0.85-0.97 (m, 18H, A and B), 1.04-1.13 (m, 9H, A and B), 1.19-1.38 (m, 32H, A and B), 1.52-1.67 (m, 14H, A and B), 2.62-2.67 (m, 3H, A and B), 6.93 (s, 0.16H, B), 6.96 (d, *J* = 0.9 Hz, 1H, A), 7.00 (s, 0.11H, B), 7.09 (d, *J* = 4.5 Hz, B), 7.17 (s, 0.16H, B), 7.19 (d, *J* = 0.9 Hz, 1H, A), 7.20 (s, 0.15H, B), 7.52 (d, *J* = 4.5 Hz, 0.13H, B).

Benzyl 3,4''-didecyl-5,2';5',2''-terthiophene-4'-acetate (4). This compound was prepared as stated in the General Stille Coupling Procedure. The resulting brown liquid was purified by flash chromatography through silica using 1:20 ethyl acetate/hexanes as the eluent. The solvent was evaporated and the product was dried *in vacuo* to afford 0.36 g (60%) of a yellow oil. IR: 3103, 3061, 3032, 2952, 2925, 2852, 1740, 1462, 1377, 1322, 1260, 1212, 1148, 1004, 976, 858, 829, 733, 696, 645, 588 cm⁻¹. UV-vis (CHCl₃) λ_{max} = 344 nm. ¹H NMR (300 MHz): δ 0.88 (t, *J* = 6.9 Hz, 6H), 1.21-1.30 (m, 28H), 1.59-1.71 (m, 4H), 2.53-2.59 (m, 4H), 3.78 (s, 2H), 5.18 (s, 2H), 6.80 (d, *J* = 1.2 Hz, 1H), 6.89 (d, *J* = 1.2 Hz, 1H), 6.99 (dd, *J* = 3.0 and 1.5 Hz, 2H), 7.07 (s, 1H), 7.30-7.36 (m, 5H). ¹³C NMR (100 MHz) 170.66, 144.15, 144.07, 136.43, 136.08, 135.77, 134.47, 132.43, 130.15, 128.56, 128.28, 128.23, 128.05, 126.29, 125.22, 120.72, 119.33, 66.83, 35.00, 31.95, 30.52, 30.41, 29.66,

29.63, 29.49, 29.37, 29.33, 22.73, 14.16. HRMS (FAB) m/z calcd for $(C_{41}H_{56}O_2S_3)$: 676.3442, found 676.3440. Anal. Calcd for $C_{41}H_{56}O_2S_3$: C, 72.73; H, 8.34. Found C, 72.57; H, 8.27.

Benzyl 2,5''-dibromo-3,4''-didecyl-5,2';5',2''-terthiophene-4'-acetate (5). This compound was prepared as described in the General Bromination Procedure. The product was purified by silica gel flash chromatography using 1:3 dichloromethane/ hexanes as the eluent. The solvent was evaporated and the product was dried *in vacuo* to give 0.54 g (95%) yellow waxy solid, mp 49 °C. IR: 3103, 3061, 3032, 2949, 2924, 2851, 1741, 1464, 1449, 1376, 1309, 1262, 1147, 1003, 971, 824, 743, 696 cm^{-1} . 1H NMR (300 MHz): δ 0.88 (t, J = 6.3 Hz, 6H), 1.21-1.31 (m, 28H), 1.54-1.58 (m, 4H), 2.49-2.55 (m, 4H), 3.73 (s, 2H), 5.17 (s, 2H), 6.84 (s, 1H), 6.85 (s, 1H), 7.00 (s, 1H), 7.32-7.36 (m, 5H). ^{13}C NMR (125 MHz): 170.28, 143.00, 142.91, 135.91, 135.54, 135.51, 133.94, 131.70, 130.80, 128.57, 128.33, 128.24, 127.78, 126.45, 124.73, 109.57, 108.18, 66.92, 34.82, 31.87, 29.58, 29.54, 29.52, 29.37, 29.30, 29.20, 29.16, 22.65, 14.09. HRMS (FAB) m/z calcd for $(C_{41}H_{54}O_2S_3Br_2)$: 832.1653, found 832.1654. Anal. Calcd for $C_{41}H_{54}O_2S_3Br_2$: C, 58.99; H, 6.52; S, 11.52. Found C, 59.06; H, 6.39; S, 11.92.

5-(Tributylstannyl)-2,2'-bithiophene (6). To 2.0 g (12 mmol) of 2,2'-bithiophene in 100 mL dry THF, 1.8 mL (12 mmol) of *N,N,N,N*-tetramethyl-1,2-ethylenediamine was added. The flask was cooled to -78 °C and 4.8 mL (12 mmol) 2.5M *n*-BuLi in hexanes was added dropwise via syringe. The mixture was warmed to room temperature for 30 minutes then was cooled to -78 °C. A solution of 3.3 g (12 mmol) tributyltin chloride in 10 mL THF was added dropwise via syringe. The flask was allowed to warm to room temperature overnight. The solvent was evaporated and the resulting liquid was taken up in 100 mL ethyl acetate and washed twice with saturated NH_4Cl and three times with

water. The organic layer was dried and the solvent evaporated and the resulting liquid was further dried *in vacuo* to give 5.3 g (97%) brown liquid. $^1\text{H-NMR}$ (300 MHz): δ 0.88-0.97 (m, 9H), 1.11-1.12 (m, 6H), 1.2-1.32 (m, 6H), 1.36-1.60 (m, 6H), 6.98 (t, 1H), 7.05 (d, $J = 3.3$ Hz, 1H), 7.16 (m, 2H), 7.28 (d, $J = 3.3$ Hz, 1H). These data are in agreement with previously published physical data for this compound.¹

Benzyl 3'',4''''-didecyl-5,2';5',2'';5'',2''';5''',2'''';5''''',2''''';5''''',2''''''-heptathiophene-4'''-acetate (7).

This compound was prepared as described in the General Stille Coupling Procedure. The resulting orange solid was purified by flash chromatography using 1:3 dichloromethane/hexanes as the eluent. The solid was dried *in vacuo* at 70 °C to afford 0.12 g (27%) orange powder, mp 81 °C. IR: 3100, 3065, 3034, 1738, 1462, 1427, 1375, 1323, 1260, 1202, 1152, 1078, 1044, 1014, 834, 794, 742, 692 cm^{-1} . UV-vis (CHCl_3) $\lambda_{\text{max}} = 419$ nm. $^1\text{H NMR}$ (300 MHz): 0.90 (t, $J = 8.1$ Hz, 6H), 1.28-1.39 (m, 28H), 1.62-1.71 (m, 4H), 2.78 (q, $J = 4.8$ Hz, 4H), 3.84 (s, 2H), 5.20 (s, 2H), 7.00-7.05 (m, 6H), 7.10 (s, 1H), 7.14 (dd, $J = 1.8$ Hz, 2H), 7.20 (d, 2.1 Hz, 2H), 7.25 (dd, $J = 1.0$ and 5.1 Hz, 2H), 7.32-7.38 (m, 5H). $^{13}\text{C NMR}$ (125 MHz): 170.41, 140.48, 140.35, 137.29, 137.15, 137.02, 135.64, 135.47, 137.75, 134.47, 134.38, 132.66, 130.50, 129.47, 128.57, 128.28, 128.24, 127.85, 126.80, 126.67, 126.50, 126.34, 124.51, 124.00, 123.98, 123.69, 123.67, 66.89, 35.07, 31.88, 30.46, 30.42, 29.60, 29.58, 29.56, 29.51, 29.42, 29.40, 29.37, 29.31, 22.66, 14.09. HRMS (FAB) m/z calc for ($\text{C}_{57}\text{H}_{64}\text{O}_2\text{S}_7$) 1004.2951; found 1004.2955. Anal. Calcd for $\text{C}_{57}\text{H}_{64}\text{O}_2\text{S}_7$: C, 68.08; H, 6.24. Found C, 67.80; H, 6.24.

3'',4''''-didecyl-5,2';5',2'';5'',2''';5''',2'''';5''''',2'''''-heptathiophene-4''''-acetic acid (8). To 0.02 g (0.02 mmol) **7**, 1 mL THF and 1 mL 5% aq. KOH was added. The mixture was heated to 70 °C and was stirred overnight. The reaction was terminated by adding 1 mL 1 M HCl until pH 2 was achieved. The solvent was evaporated, and the solid suspended in water was isolated by filtration. The solid was washed with water until pH neutral then washed with methanol several times. The solid was dried *in vacuo* at 70 °C to give 0.018 (98%) of an orange solid, mp 142-143 °C. IR (KBr): 3080, 3066, 3037, 2949, 2919, 2849, 2708, 2608, 2518, 1696, 1496, 1463, 1422, 1307, 1218, 1046, 929, 820, 789, 720, 684, 616, 589, 538 cm⁻¹. UV-vis (CHCl₃) λ_{max} = 422 nm. ¹H NMR (300 MHz): 0.87 (t, *J* = 5.2 Hz, 6H), 1.25-1.38 (m, 28H), 1.59-1.68 (m, 4H), 2.72-2.76 (m, 4H), 3.84 (s, 2H), 7.00-7.03 (m, 6H), 7.10 (s, 2H), 7.12 (s, 2H), 7.19 (s, 1H), 7.20 (s, 1H), 7.23 (d, *J* = 1.2 Hz, 1H), 7.24 (d, *J* = 1.2 Hz, 1H). ¹³C NMR (125 MHz): 14.07, 22.64, 29.30, 29.39, 29.57, 31.87 (Only peaks resolvable due to poor solubility). HRMS (FAB) *m/z* calc for (C₅₀H₅₈O₂S₇) 914.2482; found 914.2473. Anal. Calcd for C₅₀H₅₈O₂S₇: C, 65.60; H, 6.39. Found C, 65.83; H, 6.60.