Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. 200460110

Synthesis of New Diode Molecules and Their Sequential Assembling to Control Electron Transport**

*Ping Jiang, Gustavo M. Morales, Wei You and Luping Yu**

General

Unless otherwise specified, all chemicals were purchased from commercial suppliers and used without further purification. All reactions were conducted under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled over sodium/benzophenone ketyl under a nitrogen atmosphere prior to use. 5'-trimethylsilyl-3, 4'-dimethyl-2, 2'-bithiophene and 5-triisopropylsilyl-3, 3'-dimethyl-2, 2'-bithiazole were prepared according to previous used procedure[1]. ^{1}H NMR spectra were recorded at 400 or 500 MHz (^{13}C spectra at 100 or 125 MHz) on Bruker DRX-400 or DRX-500 spectrometers, respectively.

Synthesis of 5-iodo-5'-trimethylsilyl -3, 4'-dimethyl-2, 2'-bithiophene 1: To a solution of 5'-trimethylsilyl-3, 4'-dimethyl-2, 2'-bithiophene (4.0g, 15.0 mmole) in dry THF (30 ml) in a flame-dried 100 ml Schlenk flask, under N_2 *n*-butylithium (11.25ml, 1.6 M solution in hexane) was added dropwise at –78 °C. The resulting mixture was allowed to stir at room temperature for 20 minutes, re-cooled to –78 °C, quenched with a solution of iodine (4.83g, 19.0mmole) in THF (15 ml). The reaction mixture was then warmed to room temperature for 4 hours and poured into dilute aq. sodium thiosulfate (100ml) and extracted with diethyl ether (100 ml). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered and purified on silica gel using hexane as eluent to afford 1 as red-yellow liquid (4.8g, 82%

yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 0.35 (s, 9H, $SiMe_3$), 2.32(s, 3H, CH_3), 2.33(s, 3H, CH_3), 6.94 (s, 1H, Ar-H), 6.99 (s. 1H, Ar-H).

Synthesis of 5-trimethylsilylethylthio-3, 4'-dimethyl-2, 2'-bithiophene 2: Under nitrogen sodium *tert*-butoxide (1.44g, 15.0mmole), CuI (190 mg, 1.0 mmole) and neoproine (217 mg, 1.0 mmole) were added into a 100 ml flame-dried Schlenk flask equipped with Teflon stirbar. Compound 1 (3.92g, 10.0mmole) and 2-trimethylsilyl-ethanethiol (1.47g, 11.0mmole) in anhydrous toluene (40 ml) were injected into the flask through a septum. The contents were then stirred at 110 °C for 24 hours. The reaction mixture was then cooled to room temperature and filtered to remove any insoluble residues. The filtrate was concentrated in vacuo and was purified by flash column chromatography on silica gel to obtain a yellow liquid as a crude product. This crude product was then dissolved in CH_2Cl_2 (30 ml), cooled to 0 °C and treated with a solution of trifluoroacetic acid (1.2ml, 24 mmole) in CH_2Cl_2 (10 ml). The mixture was stirred at r.t for 3 hours and poured into dilute sodium bicarbonate solution, extracted with CH_2Cl_2 (60 ml), dried (Na_2SO_4) and the solvent was removed in vacuo. The crude desilylated product was purified on silica gel using hexane to provide 2 as a yellow liquid (1.6g, 47 % overall in two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 0.02 (s, 9H, $SiMe_3$), 0.95(t, J=8.0 Hz 2H, CH_2), 2.25(s, 3H, Me), 2.31(s, 3H, Me), 2.87(t, J=8.0 Hz, 2H, CH_2), 6.84(s, 2H, Ar-H), 6.90 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): -1.8, 15.3, 15.7, 17.5, 34.9, 120.5, 127.6, 132.4, 133.7, 134.4, 135.8, 136.9, 137.9. MS (CI) $(M+1)^{+}$: 327.0

Synthesis of compound 4: To a solution of 5-triisopropylsilyl-3, 3'-dimethyl-2, 2'-bithiazole (1.06g, 3.0mmol) in dry THF (10 ml) was added drop wise a Tetrabutylamonium fluoride (TBAF) solution (4.5ml, 1.0M in THF) at room temperature. After stirring at r.t 15

minutes, the solution was quenched with saturated NH_4Cl aqueous solution. The organic layer was extracted with ether, dried (Na_2SO_4) and the solvent was removed in vacuo. After column chromatography (silica gel, hexane /ethyl acetate, 4:1,v/v), pure compound 3, 4'-dimethyl-2, 2'-bithiazole was obtained (480 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.45 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 6.90 (s, 1H, Ar-H), 8.69 (s, 1H, Ar-H).

Fresh LDA (2.4ml, 1.2 ml of 2M solution, 1.2eq.) was added drop wise to the solution of 3, 4'-dimethyl-2, 2'-bithiazole (392 mg, 2.0mmol) in dry THF (15ml) at –78 °C. The reaction mixture was warmed to 0 °C for 30 min., then re-cooled to -78°C, and iodine (640mg, 2.5mmol) in 5ml dry THF was added to this solution. The resulting solution was allowed to stir at r.t for 2 hours and washed with sodium bisulfite aqueous solution, brine and dried with anhydrous Na_2SO_4. After the solvent was removed, the crude product was separated by column (silica gel, hexane/ethyl acetate, 4/1,v/v) and a yellow-reddish solid 4 (516 mg, 80%) was obtained. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.47 (s, 3H, CH_3), 2.69(s, 3H, CH_3), 6.93 (s, 1H, Ar-H).

Synthesis of compound 5: To a solution of 2 (489 mg, 1.5 mmole) in dry THF (15ml) cooled at –78 °C was added drop wise *n*-BuLi (1.2 ml, 1.6M in hexanes). The resulting solution was allowed to warm to room temperature for 30 minutes, recooled to –78 °C, and quenched with tributyltin chloride (814mg, 2.5mmol). The mixture was stirred at r.t for 4 hours, poured into aqueous sodium carbonate solution and extracted with diethyl ether. The combined organic extracts were washed with brine, dried (Na_2SO4) and the solvent was removed in vacuo. The crude organostannane intermediate 3 was obtained in almost quantitatively yield (monitored by proton NMR). A mixture of this crude product 3 and compound 4 (483 mg, 1.5 mmole) were dissolved in anhydrous DMF (20 ml) and a mixture of $Pd_2(dba)_3$

(30mg, 0.03mmol), PPh_3(60mg, 0.23mmol), Cu_2O (65mg, 0.45mmol) were added in one portion. The resulting mixture was heated at 130-135 °C for 12 hours, and then was cooled to r.t. DMF was removed under high vacuum and $CHCl_3$ was added to the residue, and resulting mixture was filtered through a pad of silica gel. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate, 10:1, v/v) to afford 5 (468mg, 60%) as a pink solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 0.01 (s, 9H, $SiMe_3$), 0.94(t, J=8.5 Hz 2H, CH_2), 2.37(s, 3H, Me), 2.47(s, 3H, Me), 2.49(s, 3H, Me), 2.68 (s, 3H, Me), 2.88 (t, J=8.5 Hz 2H, CH_2), 6.82(s, 1H, Ar-H), 6.88 (s, 1H, Ar-H), 6.91(s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): -1.8, 15.8, 16.5, 17.0, 17.5, 17.6, 34.8, 113.5, 126.7, 128.4, 129.4, 131.5, 132.2, 133.9, 135.0, 136.8, 138.0, 150.7, 153.2, 158.1, 158.9.

Synthesis of compound 6: To a solution of compound 5 (260 mg, 0.5mmol) in dry THF (10 ml) cooled at -78°C was added drop wise a solution of n-BuLi (0.4 ml, 1.6M in hexanes). The resulting solution was allowed to r.t for 20 min., re-cooled to -78°C, quenched with sulfur powder (22.4mg, 0.7mmol). The mixture was warmed to 0°C for 20 min., then re-cooled to -78°C and treated with a solution of 3-bromopropionitrile (113mg, 0.84mmol) in THF (2ml). The mixture was allowed to stir at r.t overnight, poured into water and extracted with diethyl ether. The combined organic extracts were washed with brine, dried (Na_2SO_4) and the solvent was removed in vacuo. The crude product was purified on silica gel (hexane-ethyl acetate, 4:1, v/v) and final product 6 (202 mg, 62%) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 0.02 (s, 9H, SiMe3), 0.97(t, J=8.5 Hz 2H, CH_2), 2.41(s, 3H, Me), 2.54(s, 3H, Me), 2.56(s, 3H, Me), 2.66 (t, J=7.0 Hz, 2H, CH_2), 2.71(s, 3H, Me), 2.91(t, J=8.5 Hz, 2H, CH_2), 3.02(t, J=7.0 Hz, 2H, CH_2), 6.87(s, 1H, Ar-H), 6.97(s, 1H, Ar-H). ^{13}C NMR (125

MHz, $CDCl_3$): δ (ppm): -1.8, 15.5, 15.9, 16.5, 17.4, 17.7, 18.0, 33.3, 34.7, 117.5, 119.9, 126.4, 129.3, 130.8, 133.1, 134.1, 135.2, 136.6, 137.7, 138.5, 151.9, 159.0, 159.6, 160.4. λ_{max} = 421nm. MS (CI) $(M+1)^+$, 605.8; Calculated Mass (M^+) for C26H31N3S6Si, 605.06.

Synthesis of compound 8: A solution of 2-trimethlsilyl-3-methylthiophene (850 mg, 5.0 mmols) in dry THF (15ml) cooled at –78 °C was added drop wise a solution of n- butyllithium (3.0ml, 2.5 M in hexanes). The resulting solution was allowed to warm to room temperature for 30 minutes, cooled to –78 °C, and then quenched with tributyltin chloride (2.6g, 8.0 mmoles). The mixture was stirred at r.t for 4 hours and poured into water and extracted with diethyl ether. The combined organic extracts were washed with brine, dried (Na_2SO_4) and the solvent was removed in vacuo. The crude organostannane intermediate 7 was obtained in almost quantitatively yield (monitored by proton NMR). A mixture of this crude product 7 and compound 4 (1.29g, 4.0 mmoles) was dissolved in anhydrous DMF (30 ml) and a mixture of $Pd_2(dba)_3$ (90mg, 0.1mmol), PPh_3 (180mg, 0.69mmol), Cu_2O (195mg, 1.36mmol) were added in one portion. The resulting mixture was heated at 130-135 °C for 12 hours, and then was cooled to r.t.. DMF was removed under high vacuum and $CHCl_3$ was added to the residue, and resulting mixture was filtered through a pad of silica gel. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate, 8:1, v/v) to afford 8 (0.96g, 66%) as a yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 0.36 (s, 9H, $SiMe_3$), 2.34(s, 3H, Me), 2.49(s, 3H, Me), 2.70(s, 3H, Me), 6.92(s, 1H, Ar-H), 7.38(s, 1H, Ar-H).

Synthesis of compound 9: Compound 8 (0.96g, 2.6 mmole) was dissolved in dry THF (30 ml) in a flame-dried 100 ml Schlenk flask. Under N_2 n-butylithium (1.3ml, 2.5M solution in hexane) was added

dropwise to the solution at –78 °C. The resulting mixture was allowed to warm to room temperature for 30 minutes, then cooled to –78 °C, and quenched with a solution of iodine (0.89g, 3.5mmole) in THF (10 ml). The reaction mixture was then stirred at room temperature for 3 hours and was poured into a dilute sodium thiosulfate solution (100ml) and extracted with diethylether (100 ml). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered and purified on silica gel using hexane as eluent to afford compound 9 (1.03g, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 0.36 (s, 9H, $SiMe_3$), 2.32(s, 3H, Me), 2.45(s, 3H, Me), 2.62(s, 3H, Me), 7.35 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): -0.3, 16.6, 17.4, 17.6, 68.1, 125.9, 131.6, 137.9, 139.4,145.3, 151.8,157.2, 160.3, 162.2.

Synthesis of compound 10: Into a 100 ml flame-dried Schlenk flask equipped with a Teflon stir bar was added sodium *tert*-butoxide (288mg, 3.0mmole), CuI (38 mg, 0.2 mmole) and neocuprorine (43 mg, 0.2 mmole). Under nitrogen compound 9 (0.98g, 2.0mmole) and 2-trimethylsilylethanethiol (268mg, 2.0mmole) in anhydrous toluene (20 ml) were injected into the flask through a septum. The contents were then stirred at 110 °C for 24 hours. The reaction mixture was then cooled to room temperature and filtered to remove any insoluble residues. The filtrate was concentrated in vacuo and was purified by flash column chromatography on silica gel to obtain a yellow liquid as a crude product. This crude product was then dissolved in CH_2Cl_2 (15 ml), cooled to 0 °C and treated with a solution of trifluoroacetic acid (0.3ml, 6 mmole). The mixture was stirred at r.t for 3 hours, poured into dilute sodium bicarbonate solution, extracted with CH_2Cl_2 (20 ml), dried (Na_2SO_4) and the solvent was removed in vacuo. The crude desilylated product was purified on silica gel using hexane to provide 10 (108 mg, 13 % overall in two steps) as a viscous yellow liquid. ^{1}H

NMR (500 MHz, $CDCl_3$): δ (ppm): 0.05 (s, 9H, $SiMe_3$), 0.92(t, J=8.5 Hz, 2H, CH_2), 2.32(s, 3H, Me), 2.54(s, 3H, Me), 2.72(s, 3H, Me), 2.83(t, J=8.5 Hz, 2H, CH2), 7.04(s, 1H, Ar-H), 7.38 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): -1.8, 15.5, 15.6, 17.1, 29.7, 34.7, 113.6, 124.0, 126.6, 129.3,136.5, 138.8, 151.7, 157.2, 158.8, 160.5.

Synthesis of compound 12: To a solution of 2-trimethlsilyl-3-methylthiophene (1.02 g, 6.0 mmols) in dry THF (20ml) cooled at –78 °C was added dropwise a solution of n- butyllithium (2.64ml, 2.5 M in hexanes). The resulting solution was allowed to warm to room temperature for 30 min., then cooled to –78 °C, and quenched with sulfur powder (224mg, 7.0mmol). The mixture was warmed to 0°C for 20 minutes, then cooled to -78°C and treated with a solution of 3-bromopropionitrile (1.07g, 8.0mmol) in THF (5ml). The mixture was allowed to stir at r.t overnight, then poured into water and extracted with diethyl ether. The combined organic extracts were washed with brine, dried (Na_2SO4) and the solvent was removed in vacuo. This crude product was then dissolved in CH_2Cl_2 (30 ml), cooled to 0 °C and treated with a solution of trifluoroacetic acid (1.4ml). The mixture was stirred at r.t for 3 hours, poured into dilute sodium bicarbonate solution, extracted with CH_2Cl_2 (40 ml), dried (Na_2SO_4) and the solvent was removed in vacuo. The crude desilylated product was purified on silica gel using hexane to provide 5-cyanoethylenethio-3-methylthiophene (730mg, 67 %): ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 2.22 (s, 9H, $SiMe_3$), 2.58(t, 2H, J=7.0 Hz, CH_2), 2.91(t, 2H, J=7.0 Hz, CH_2), 6.98(s, 1H, Ar-H), 7.00(s, 1H, Ar-H). ^{13}C NMR (125MHz, $CDCl_3$): δ (ppm): 15.8, 18.2, 33.8, 118.1, 126.3, 130.5, 137.8, 138.7.

5-cyanoethylenethiol-3-methylthiophene (730mg, 4.0mmole) and N-iodosuccinimide (900 mg, 4.0 mmole) in a mixture of $CHCl_3$-HOAC

(50 ml-5 ml) was stirred at r.t for 3 hours. The reaction mixture was washed with water, dilute sodium bicarbonate solution, sodium thiosulfate, dried (Na_2SO_4) and the solvent was removed in vacuo. The crude iodide compound was purified by column (silica gel, hexane) and pure 5-cyanoethylene thiol-2-iodo-3-methylthiophene 12 was obtained in more than 90% yield: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 2.18 (s, 9H, $SiMe_3$), 2.60(t, 2H, J=7.0 Hz, CH_2), 2.93(t, 2H, J=7.0 Hz, CH_2), 6.87(s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 18.2(2 c's overlap), 33.7, 79.2, 117.6, 134.8, 137.3, 143.8.

Synthesis of compound 13: To a solution of 10 (108 mg, 0.25 mmols) in dry THF (10ml) cooled at –78 °C was added drop wise a solution of n- butyllithium (0.2ml, 2.5 M in hexanes). The resulting solution was allowed to warm to room temperature for 30 minutes, then cooled to –78 °C, and quenched with tributyltin chloride (195mg, 0.6 mmoles). The mixture was stirred at r.t for 4 hours, poured into water and extracted with diethyl ether. The combined organic extracts were washed with brine, dried (Na_2SO_4) and the solvent was removed in vacuo. The crude organostannane intermediate 11 obtained and compound 12 (80 mg, 0.25 mmoles) was dissolved in anhydrous DMF (10 ml) and a mixture of $Pd_2(dba)_3$ (10mg), PPh_3(16mg), Cu_2O (20mg) were added in one portion. The resulting mixture was heated at 130-135 °C for 12 hours, and then was cooled to r.t.. DMF was removed under high vacuum and $CHCl_3$ was added to the residue, and resulting mixture was filtered through a pad of silica gel. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate, 5:1, v/v) to afford 13 (40mg, 26%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 0.02 (s, 9H, $SiMe_3$), 0.90(t, J=8.5 Hz, 2H, CH_2), 2.21(s, 3H, Me), 2.22(s, 3H, Me), 2.51(s, 3H, Me), 2.69(t, J=7.0 Hz, 2H, CH_2), 2.69(s, 3H, Me), 2.81(t, J=8.5Hz, 2H, CH_2), 3.01(t, J=7.0 Hz, 2H, CH_2), 7.06(s, 1H, Ar-H), 7.36(s, 1H, Ar-H). ^{13}C NMR (125 MHz,

$CDCl_3$): δ (ppm): -1.8, 15.0, 15.1, 15.6, 17.6, 17.7, 18.4, 33.6, 34.8, 117.8, 124.5, 127.0, 130.0,130.9, 131.7,134.0, 136.0,137.8, 137.9, 138.5, 151.8, 157.2, 158.6, 159.8. λ_{max} = 396nm. MS (CI): $(M+1)^+$ 605.9; calculated for Mass (M^+) of C26H31N3S6Si, 605.06.

Substrate Preparation: The gold electrodes used in the STM studies were grown by gold (99,999%) evaporation from a tungsten boat onto fresh cleaved highest quality V1 mica (Ted Pella, Inc.). The mica was heated at a temperature of ~ 450°C overnight under high vacuum.[2] The film was annealed in the same atmosphere at ~ 400°C for 10 h. and was stored under Argon. Since the gold surface became contaminated by absorption of carbonaceous materials from the air during a few minutes of exposition to the atmospheric air,[3] the Au surface was subjected to hydrogen flame annealing[4] until the film take a dim orange color (in a dark room) and then quenched in pure methanol saturated with Argon. The substrates used in the grazing incidence Fourier transform infrared spectroscopy (GI-FTIR) studies were prepared by evaporation of gold (99,999%) onto chromium coated silicon wafers (Si/Cr/Au) using a method similar to the previously detailed in the literature[5]. Prior to their use the gold substrates were cleaned in a mixture of H_2SO_4-H_2O_2 (7:1) (CAUTION, after use this solution must not be stored as explosive oxo-peroxides may form) at 90°C for 5 minutes. Then, the substrates were rinsed with ultra-pure water and dried in N_2.

Monolayer Preparation: The self-assembled process was carried out at room temperature in a dry box. Immediately after the annealing process, the gold substrates were transferred from the ethanol to a ~1 mM solution of DDT in methanol. After 14-18 h. the electrode was removed from the solution, rinsed five times with pure ethanol and twice with fresh distilled THF. The fresh dodecanethiolated SAM/Au electrode was derivatized using a ~ 10^{-5} M solution prepared from

diode molecules molecule **6** and **13** by sequential deprotection in a three-step insertion process adapted from ref.[6]. The electrode was immersed for 3-4 h in a solution of compounds molecule **6** and **13** in THF with an excess of a sodium ethoxide in ethanol; previously prepared with metallic sodium in pure ethanol. Then, the electrode was washed consecutively five times with methanol and THF. This procedure removes the protection group cyanoethylene in the molecules leaving the group trimethylsilylethylene intact. The exposed S^- or SH groups can be covalently bonded to the gold surface. This procedure guarantees the correct orientation of the molecules on the metallic surface. The trimethylsilylethylene protecting group can be cleaved by dipping the electrode with the modified SAM into a 5 mM solution of TBAF in THF for 6-7 h. The resulting sample was rinsed several times with pure THF, methanol and toluene. Finally the electrode is immersed in a fresh prepared solution of gold nanoparticles in toluene (absorbance 0.12 at 520 nm) for 1-2 h. and subsequently rinsed with tetraoctylammonium bromide in toluene (several times), then pure toluene, THF and methanol. The samples were dried with a continuous and gentle flow of argon and immediately used for STM and STS measurements. Similar methodology was used for the preparation of the pure monolayer for **6** and **13** on Si/Cr/Au for the infrared studies.

Grazing Incidence FT-IR: The GI-FTIR data were recorded under a nitrogen atmosphere in a Nicolet Magna Spectrometer equipped with a FT-85 fixed 85° grazing angle accessory (Thermo Spectra-Tech). Prior to the measurement of the SAMs on gold-coated silicon wafers, a reference spectrum was recorded on a freshly cleaned gold substrate. Before each acquisition, the sample chamber was purged with dry N_2 until a constant spectrum was obtained during 100 consecutive scans (1-2 h.). Five thousands consecutive scans were averaged for the

sample and reference spectra, the spectra resolution was set at 4 cm^{-1}. Figure 1 show the spectra in the C-H stretching region of the reference compounds used for the assignment of the CH_2 absorption of the TMSE group.

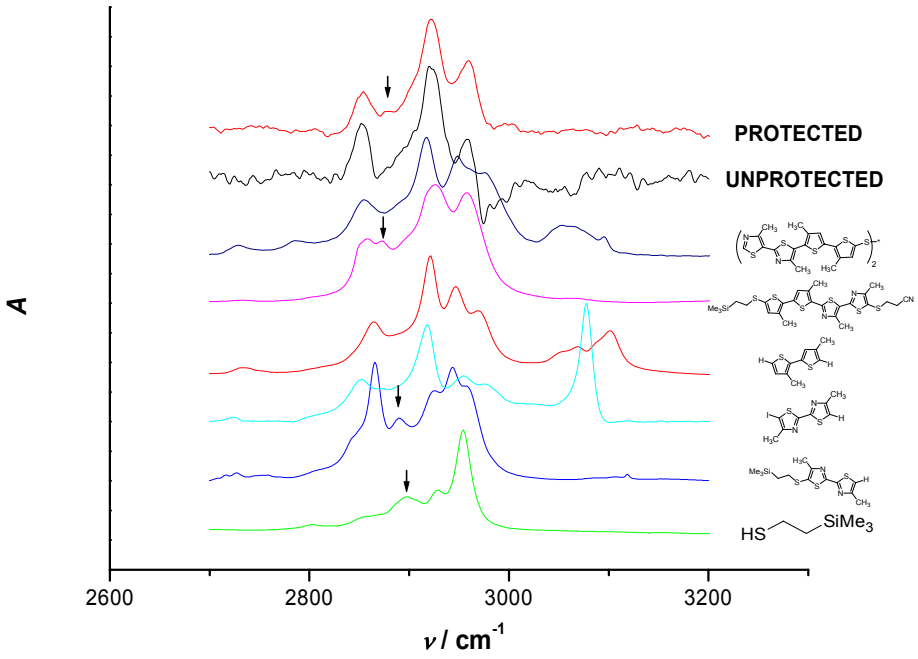

Figure 1. Transmission FTIR spectra for the reference compounds and compound **6** on a KBr plate, and the GI-FTIR spectra of a monolayer of **6** on Au before (PROTECTED) and after (UNPROTECTED) the deprotection of the TMSE groups. The arrows show the absorption from CH_2 (νCH_2^s symmetric stretching vibration) of the TMSE group.

Scanning Tunneling Microscopy (STM): STM measurements were carried out by utilizing a NanoScope III STM (Digital Instrument) equipped with a low current STM head and Picoamp Boos Box (Digital Instrument), which allows STM measurements with tunneling currents in the pA range. The tips used in the measurements were fabricated by electrochemical etching of a Pt/Ir wire (Molecular Imaging, Phoenix, AZ, USA) in 8 M NaOH. After the etching, the tips were rinsed with

deionized water and immediately mounted in the STM converter head. The experiments presented here were performed in air atmosphere at room temperature and the images were recorded in constant current operating mode.

Scanning tunneling spectroscopy (STS): STS data were acquired using a NanoScope software version 5.12 (Digital Instrument) working in the I(V) mode. This operation mode allows monitoring the variation of the tunneling current (I), due to variations of the bias voltage (V). After the tip was positioned at a specific point on the surface, the feedback is shut off and a spectroscopic plot is acquired (the tunnel current is measured as the sample voltage is ramped at 10 Vs^{-1}). In all the experiments, the bias potential was applied to the sample with respect to the grounded tip. In this configuration, a positive bias corresponds to an electron flow from the tip to the sample and in the opposite way for negative bias voltage.

In order to test the quality of tip and samples and avoid artifacts, the tips used for the STS characterizations were previously examined according to the following procedure: In the alkanethiol region, the tip must be able to produce atomically resolved images with the characteristic $(\sqrt{3} \times \sqrt{3})$ R 30° layer structure of alkanethiolate on Au (111). In the same area, the I(V) curve of these SAM should be almost symmetric according to the previously reported behavior in these systems[7]

[1] M.-K. Ng, D.-C. Lee, L. Yu, *J. Am. Chem. Soc*. **2002**, 124, 11862-11863.

[2] DeRose, J. A.; Thundat, T.; Nagahara, L. A.; Linsay, S. M. *Surf. Sci*. **1991**, *256*, 102.

[3] Smith, T. *J. Colloid Interface Sci*. **1980**, *75*, 51.

[4] Kolb, D. M.; Dakkouri, A. S.; Batina, N.; in: Gerwirth, A. A. and Siegenthaler, H. (Eds.), Nanoscale Probes of the Solid/Liquid Interface, NATO ASI Series E288, Kluwer, Dordrecht, 1995.

[5] Zehner, R. W.; Sita, L. R. *Langmuir;* **1997**, *13*(11); 2973

[6] Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N.F.; Burguin, T. P.; Jones II, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc*. **1998**, *120*, 2721.

[7] Cui, X. D.; Primax, A.; Zarate, X. Tomfohr, J.; Sankey, O. F.; Moore, A. L.; Moore, T. A.; Gust, D.; Harris, G.; Lindsay, S. M. *Science*, **2001**, *294*, 571.