High Performance, Acene-Based Organic Thin Film Transistors: 1,4,8,11-tetramethyl-6,13-substituted pentacene

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Supporting Information Available: Details of experimental procedures, UV-vis, X-ray OOP *d*-spacings, X-ray diffraction, graphs, transfer curves, and AFM images.

Experimental Details.

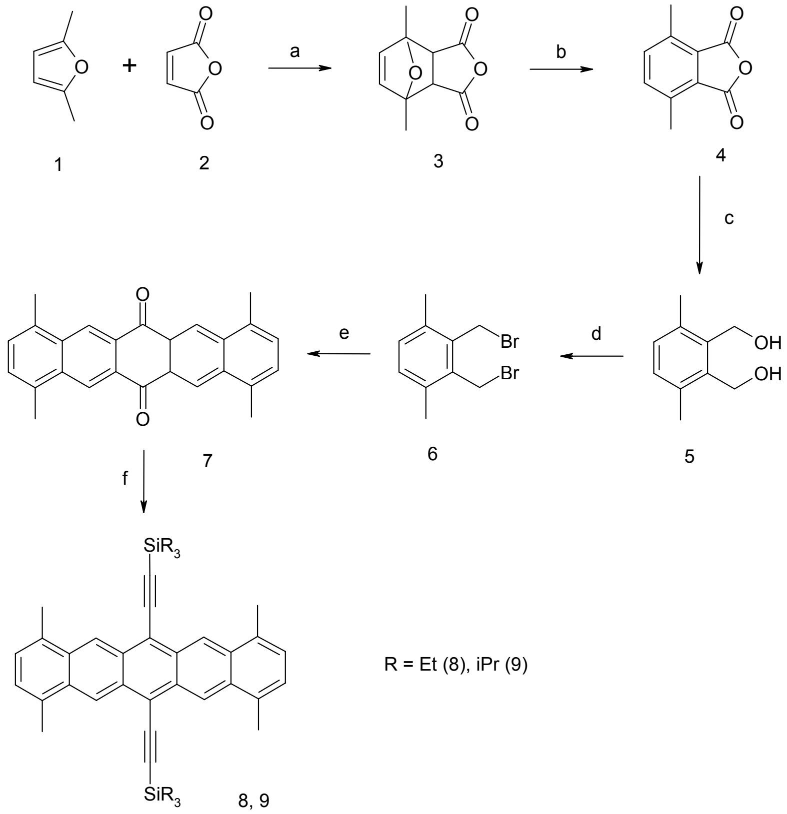
Instrumentation. Powder diffraction was performed using a Philips Xpert station with a Cu K_α source at 1.5405980nm. UV-vis was carried out on a Carry 5000 UV-Vis_NIR spectrophotometer form Varian using quartz cuvette. Atomic Force Microscopy (AFM) was performed using an AFM XE100 (PSIA Inc, Seoul, Korea) in contact mode at 1 Hz and a constant contact force of 21.4 nN. We used a soft commercial silicon nitride cantilever with a nominal spring constant of about 0.6 N/m, the back of the cantilever being coated with aluminum to increase signal feedback. Cyclic voltammetry (CV) was carried out in the solid state, using a Bas cell system (Working electrode: platinum foil coated with the compound thin film, Counter electrode: platinum wire, Reference electrode: silver nitrate, Electrolyte: 10mmol/l of PCBM in acetonitrile, Signal: acquired at 100mV/s). Samples were drop cast on to a platinum foil from a solution in DCM (1mg/ml) and left to dry slowly in a solvent saturated atmosphere. We extract the HOMO level from the onset of the first oxidation peak all data being referenced against ferrocene (HOMO is 4.8eV). In our system we recorded half wave potential of ferrocene at 0.106V.

FET Device Fabrication. Discrete bottom-gate, top-contact organic field effect transistor (OFET) devices were fabricated on OTS treated heavily n-doped silicon wafers comprising a 3000 Å thermally grown gate oxide layer. Substrates were cleaned by sonication in de-ionised water for 15 minutes, then acetone for 15 minutes and finally methanol for 15 minutes, prior to treatment or use. Hydrophobic surfaces were prepared by treating in a solution of 10mM OTS in toluene for 20 min maintained at 60 ºC. Substrates were then dried on a hot plate for 2 hours at 120 ºC under normal atmosphere. Super hydrophilic substrates were prepared by dipping in piranha solution for 1 min at room temperature and then thoroughly rinsed with deionised water to make the silica top surface super hydrophilic. Solutions of organic semiconductor in toluene (0.5 wt-%) were drop cast and dried as appropriate. Film quality for all measured devices was good with no sign evidence of pin holes or major de-wetting from the substrate. No post thermal annealing was employed. Gold source and drain channel electrodes, 60 µm width and 2 mm long were thermally evaporated, at 10^{-6} mBar at a rate of 0.1 nm/s for the first 10 nm and then 0.3 nm/s until a layer thickness of 50 nm was obtained, yielding 9 transistors per substrate. DC characteristics of the devices were obtained using an E5270B 8 Slot precision measurement frame from Agilent Technology coupled to a 3 Agilent E5287A atto level High Resolution Module. Contacts were made using Karl Sűss PH100 manual microprobes. Output characteristics were obtained at a constant gate voltage V_G = -80 V and transfer characteristics at a constant drain voltage V_{SD} = -80 V. From the slope of the square root of the drain intensity characteristic, we were able to calculate the saturated hole mobility (μ_{FET}) and the threshold voltage, according to the following equation:

$$I_D = \frac{\mu_{FET} W C_i}{2L} (V_G - V_T)^2 \qquad (1)$$

where W is the width of the channel (2 mm), L the length of the channel (60 µm), C_i is the equivalent capacitance of the dielectric intercepting the channel and V_T the threshold voltage. Measurements were performed in air, in the dark under normal atmospheric pressure.

Synthesis. Chemical reagents: All chemicals unless other wise stated were acquired from Sigma Aldrich and used without further purification. Toluene (step d) (Fisher Scientific) was distilled over sodium before use. THF (steps c and f) (Fisher Scientific) was distilled over sodium and benzophenone before use.



1,4-dimethyl-7-oxabicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride (3). 2,5-dimethylfuran (22g, 0.23mol) was added to a solution of maleic anhydride (22.55g, 0.23mol) in diethyl ether (40ml) at room temperature. The mixture was stirred overnight. The precipitated crystals were filtered off and washed with anhydrous diethyl ether. The mother solution was concentrated under vacuum and the second crop of crystals was combined with those obtained previously. Reaction yielded 27g (60%, Mpt 60-62^{o}C) of cream crystals. ^{1}H NMR (300MHz, $CDCl_3$): δ= 6.39(s, 2H), 3.20 (s, 2H), 1.81(s, 6H). IR

(υ_{max}/cm^{-1}): 3600, 3090, 2992, 1856, 1775, 1586, 1446, 1392, 1242, 1214, 1083, 900, 832.

3,6-dimethylphthalic anhydride (4). Compound **3**, 1,4-dimethyl-7-oxabicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride (20g, 0.1mol) was added in small portions to 200ml of concentrated H_2SO_4 cooled at -6°C. During the addition, the mixture was stirred vigorously and the temperature was not allowed to rise above 0°C. After complete addition the mixture become orange and the temperature was slowly raised to 10°C and was poured slowly into crushed ice (1000g). The resulting white crystals were collected and washed with ice water. The crystals were dissolved in 10% of NaOH solution (150ml). The solution was filtered and the filtrate acidified with HCl (36%) until a precipitated formed. The precipitated was collected and washed with water until the washing where neutral. The precipitate was added to toluene and azeotropically distilled. The hot solution was filtered and concentrated under reduced pressure. 8.65g (50%, Mpt 143-144°C) of **4** was obtained. ^{1}H NMR (300MHz, $CDCl_3$): δ= 7.44 (s, 2H), 2.61(s, 6H). Mass spectrum: (El) 176 (58%), 148 (43%), 132 (18%), 131 (18%), 103 (100%), 91 (32%), 76 (36%). IR (υ_{max}/cm^{-1}): 3030, 2929, 1844, 17775, 1569, 1497, 1386, 1349, 1241, 1186, 1022, 911, 890, 748.

3,6-dimethylphthalyl alcohol (5). $LiAlH_4$ (1.14g, 0.030mol) was added to dry THF (50ml) The addition was carried out with stirring under a static atmosphere of N_2. A solution of compound **4**, 3,6-dimethylphthalic anhydride (4g, 0.023mol) in dry THF (40ml) was added drop wise over a period of 45 minutes. After the addition was complete the resulting mixture was refluxed overnight. The mixture was then cooled to 0°C and treated sequentially with 2 ml of water, 2ml of 15% aqueous solution of sodium hydroxide and 4 ml of water. The granular solid was filtered and the filter cake was washed several times with ether. The combined filtrate was then concentrated and the resulting yellow oil which solidified upon standing was recrystallised from ethyl acetate/petroleum ether to give 2.69g of **5** (70% yield, Mpt. 69-70°C). ^{1}H NMR (300MHz, $CDCl_3$): δ= 7.09 (s, 2H), 4.80 (s, 4H), 2.84 (s, 2H), 2.41 (s, 6H). Mass spectrum: (El): 189 (100%), 356 (20%). Elemental analysis. Found: C, 72.43; H, 8.93;

Calculated for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. IR (υ_{max}/cm^{-1}): 3290, 2956, 2920, 1746, 1484, 1456, 1243, 992, 810.

Synthesis of 3,6-dimethyl-1,2-bis(bromomethyl)benzene (6). A solution of compound **5**, 3,6-dimethylphthalyl alcohol (3g, 18mmol) in dry toluene (50 ml) was added drop-wise to a stirred solution of phosphorus tribromide (9.72g, 36mmol) in dry toluene (12.5ml). After complete addition, the mixture was stirred at room temperature for 1 hour and then for an additional hour at 40^{o}C. The mixture was then poured onto ice (60g). The mixture was extracted with 1:1 diethyl ether/toluene (3x20ml). The combined organic layers were washed with a saturated solution of NaCl (2x25ml) and dried over magnesium sulphate. Filtration and removal of the solvent under vacuum gave 4.90g of **6** (95%, Mpt 101-103^{o}C). ^{1}H NMR (500MHz, $CDCl_3$): δ= 7.08 (s, 2H), 4.69 (s, 4H), 2.41 (s, 6H). Mass spectroscopy (accurate mass): 292 (2%), 211 (36%), 132 (100%), 115 (35%), 91 (26%), 51 (19%). Elemental analysis. Found: C, 41.58; H, 4.00; Br, 53.04. Calculated for $C_{10}H_{12}Br_2$: C, 41.13; H, 4.14; Br, 54.73. IR(υ_{max}/cm^{-1}): 2924, 1480, 1443, 1222, 1999, 1167.

1,4,8,11-tetramethyl-6,13-pentacenequinone (7) To an oven dried round bottomed flask, cooled under nitrogen, were added 50ml of dimetylacetamide. The solvent was degassed for 30 minutes with nitrogen. Compound **6**, 3,6-dimethyl-1,2-bis(bromomethyl)benzene (4.5g, 15mmol) was added to the flask with vigorous stirring, followed by p-benzoquinone (0.81g, 7.5mmol) and of sodium iodide (11.46g, 76mmol). The mixture was then stirred at 90^{o}C for 48H. The mixture was filtered and the yellow-brown solid was washed with acetone and water. The recovered solid was dried under vacuum (40^{o}C) to yield 0.35 g of **7** (15%, Mpt 271-272^{o}C). Mass spectra (EI/CI): 390 (17%), 364 (100%), 313 (12%), 170 (8%). Elemental Analysis. Found: C, 85.52; H, 5.91. Calculated for $C_{26}H_{20}O_2$. C, 85.69; H, 5.53. IR (υ_{max}/cm^{-1}): 2917, 1672, 1657, 1604, 1456, 1387, 1300, 1208.

1,4,8,11-tetramethyl-6,13-triethylsilylethinylpentacene (8) n-buthyllithium (1.2ml, 1.92mmol) was added drop-wise to a solution of triethylsilylacetylene (0.26g, 1.92mmol) in dry THF (5ml) at 0°C. The mixture was kept at 0°C for 40 minutes before it was transferred to a solution of compound **7,** 1,4,8,11-tetramethyl-6,13-pentacenequinone (0.35g, 0.96mmol) in THF (5ml) at 0°C. The mixture was allowed to warm up to room temperature and stirred overnight. The reaction was quenched with 10% HCl (1.5ml). The material was extracted with chloroform (10x3ml) and washed with water (2x10ml). The solvent was removed under vacuum yielding a blue-green solid. The crude solid was dissolved in acetone (5ml) and then a solution of tin (II) chloride dihydrated (0.43g, 1.92mmol) in 50% acetic acid aqueous solution (5ml) was added dropwise. The mixture was left to stir overnight. The resulting crude product was filtered. The solid was then dissolved in DCM, washed with water and sodium bicarbonate solution and dried over magnesium sulphate. The solvent was removed under vacuum. Purification was made with a silica plug using hexane as eluent. Hexane was removed to yield 0.30g of blue crystals (50%, Mpt 257-259°C). ^{1}H NMR (400MHz, $CDCl_3$): δ= 9.41 (s, 4H), 7.17 (s, 4H), 2.83 (s, 12H), 1.31 (t, *J*=7.82Hz, 18H), 0.94 (q, *J*=7.91,12H). Mass spectroscopy (APCI): 610.3 (100%). Elemental analysis. Found: C, 81.82; H, 8.47. Calculated for $C_{42}H_{50}Si_2$: C, 82.56; H, 8.25. IR(υ_{max}/cm^{-1}): 2952, 2127, 1455, 1369.

The same procedure was followed to synthesise the triisopropylsilyl derivative (**9**). The yield achieved was ~55% (Mpt 260-262°C). ^{1}H NMR (400MHz, $CDCl_3$): δ= 9.45 (s, 4H), 7.16 (s, 4H), 2.82 (s,12H), 1.43-1.34 (m, 42H). Mass spectroscopy (APCI): 695.5 (100%), 696.8 (24%), 697.7 (11%). Elemental analysis. Found: C, 82.65; H, 9.56. Calculated for $C_{48}H_{62}Si_2$: C, 82.93; H, 8.99. IR(υ_{max}/cm^{-1}): 2942, 2850, 2121, 1420, 1366, 1080.

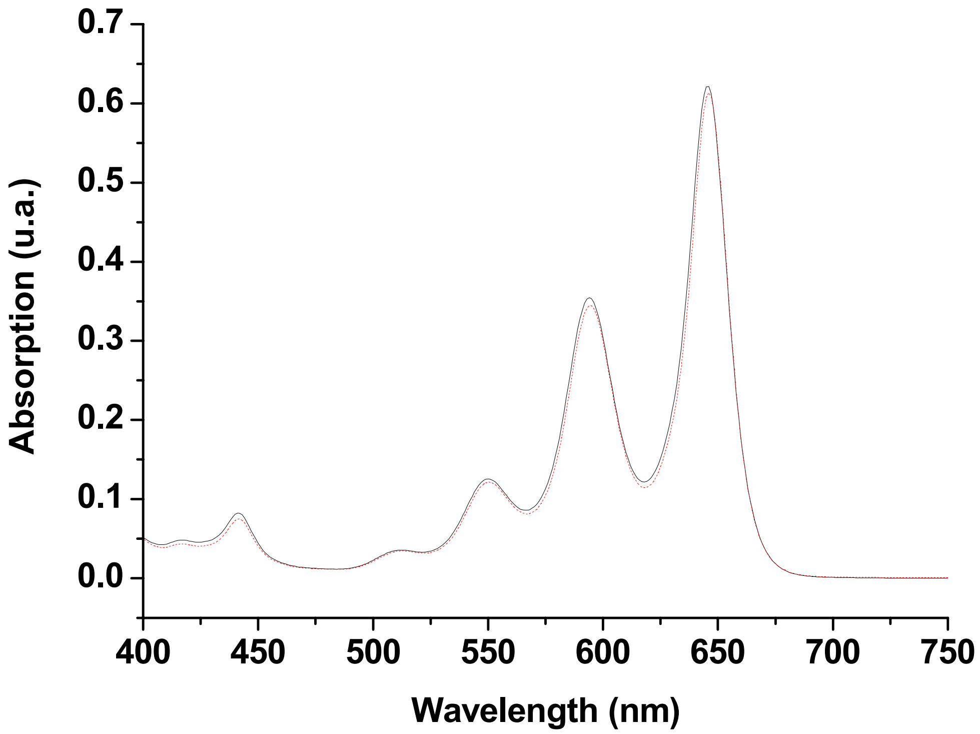
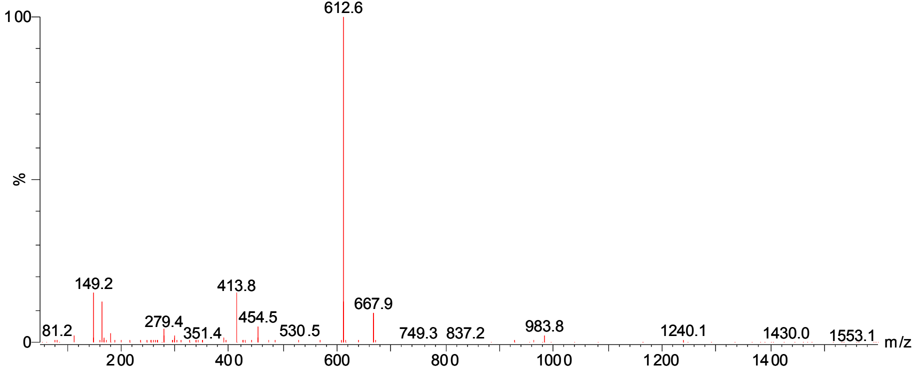


Figure 1. UV-Vis adsorption of 1,4,8,11-tetramethyl-6,13-triethylsilylethinylpentacene (**8**) (black solid line) and 1,4,8,11-tetramethyl-6,13-triisopropylsilylethinylpentacene (**9**) (dashed line) in a dilute solution 10^{-4}mol.l^{-1} in toluene. Baseline of measured solvent under the same conditions was subtracted to the signal.

Compound 8:



Compound 9:

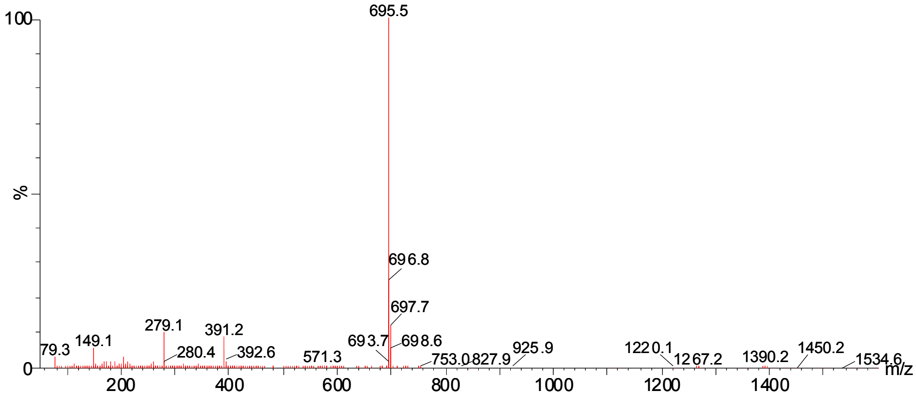
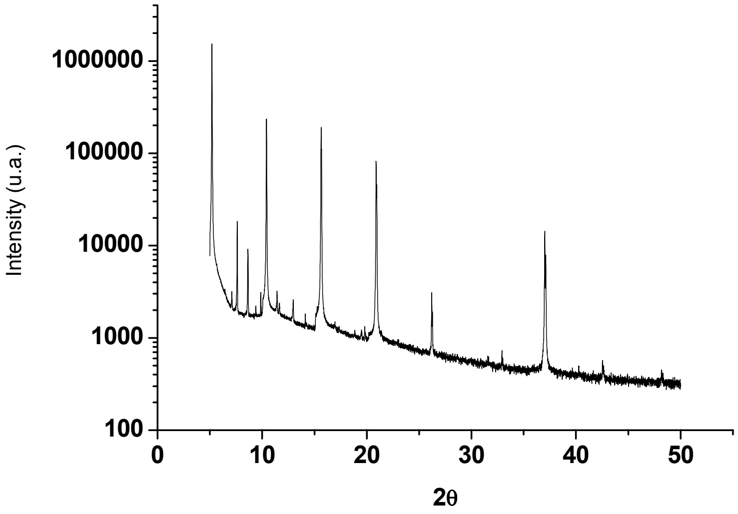


Figure 2. Electrospray Mass Spectroscopy of compound **8** and compound **9**. Note the absence of the doublet peak for a double mass indicative of pure material.

Compound 8:



Compound 9:

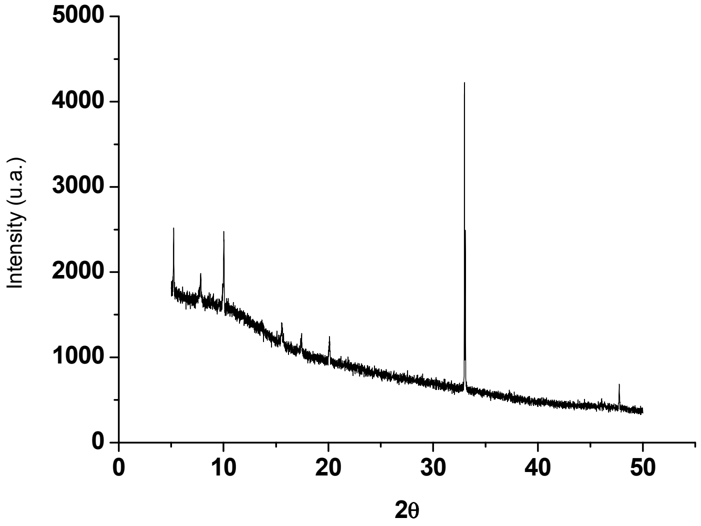


Figure 3. Out-of-plane (OOP) X-ray diffraction for compound **8** and compound **9** on OTS treated silica drop cast from a solution of 1 % w/w in tetralin at room temperature onto a thick silica substrate (about 300nm).and dried at room temperature.

	Compound 8	
(n,0,0)	2θ/ ° calculated	2θ/ ° observed
100	5.15	5.20
200	10.32	10.41
300	15.51	15.62
400	20.73	20.89
500	25.99	26.2

Table 1. Out-of-plane X-ray diffraction 2θ vales and d-spacing’s for compound **8**.

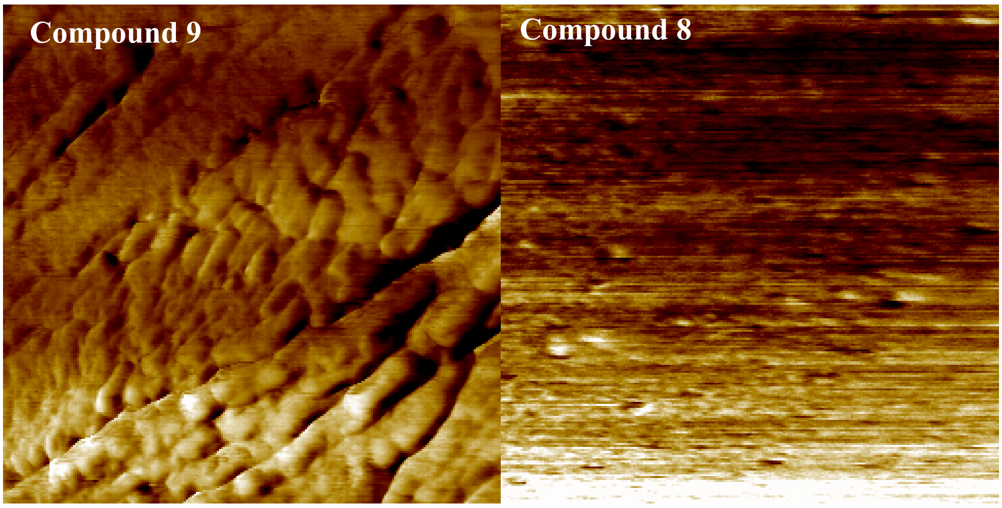


Figure 4. AFM images of compound 8 and compound 9, drop cast onto OTS treated silica from a solution of 0.5%w/w in toluene. Scan size was 2*2 microns.

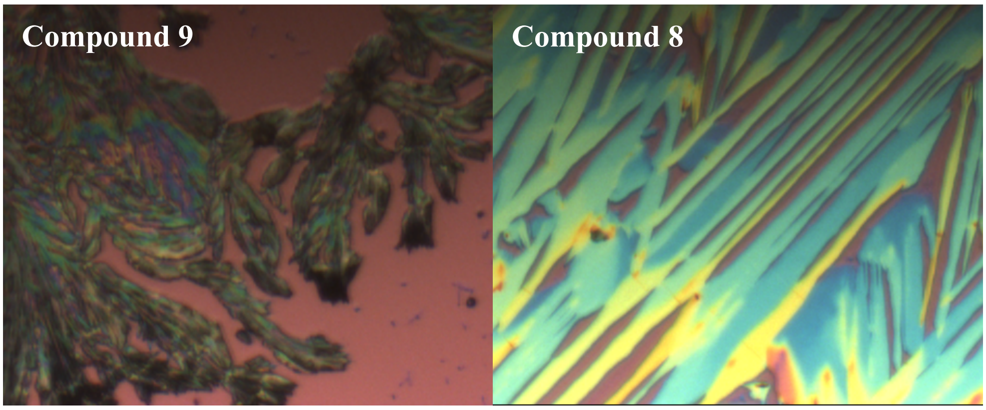


Figure 5. Optical micrographs (250 x 400 micron) of compound **8** and compound **9**, drop cast onto OTS treated silica from a solution of 0.5%w/w in toluene.

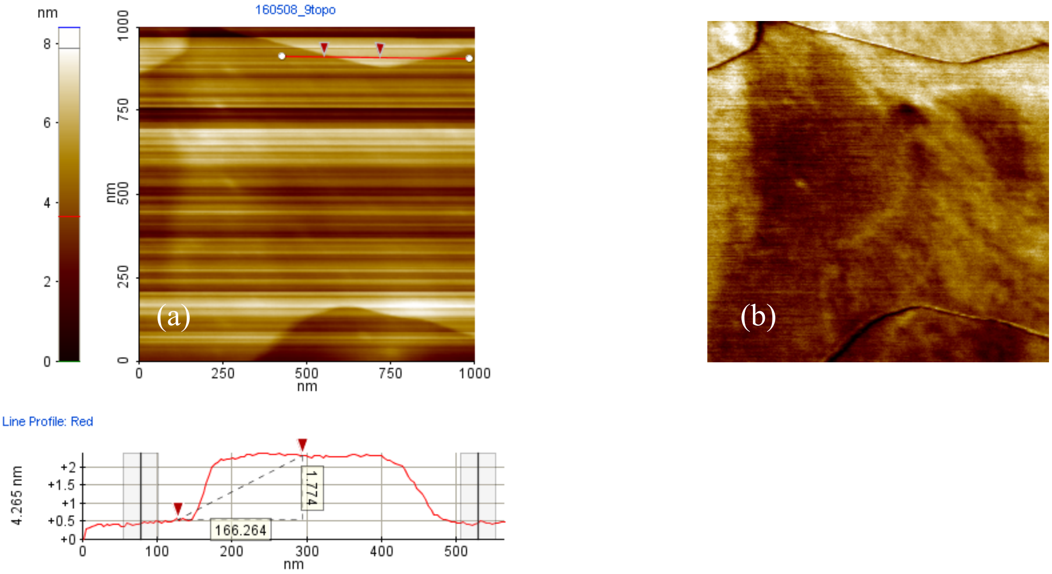


Figure 6. Observation by atomic force microscopy in dynamic mode of a terraced film deposited by drop casting of diluted solution of compound **8** (10^{-4} mol/l) in toluene HPLC grade onto a super hydrophilic silica wafer. Measurement of the step height from the topographic scan (a) indicates that the molecules are essential vertical with respect to the substrate being packed in the single crystal structure. The dynamic mode amplitude image (b) gives an enhanced viewing of the atomic step.

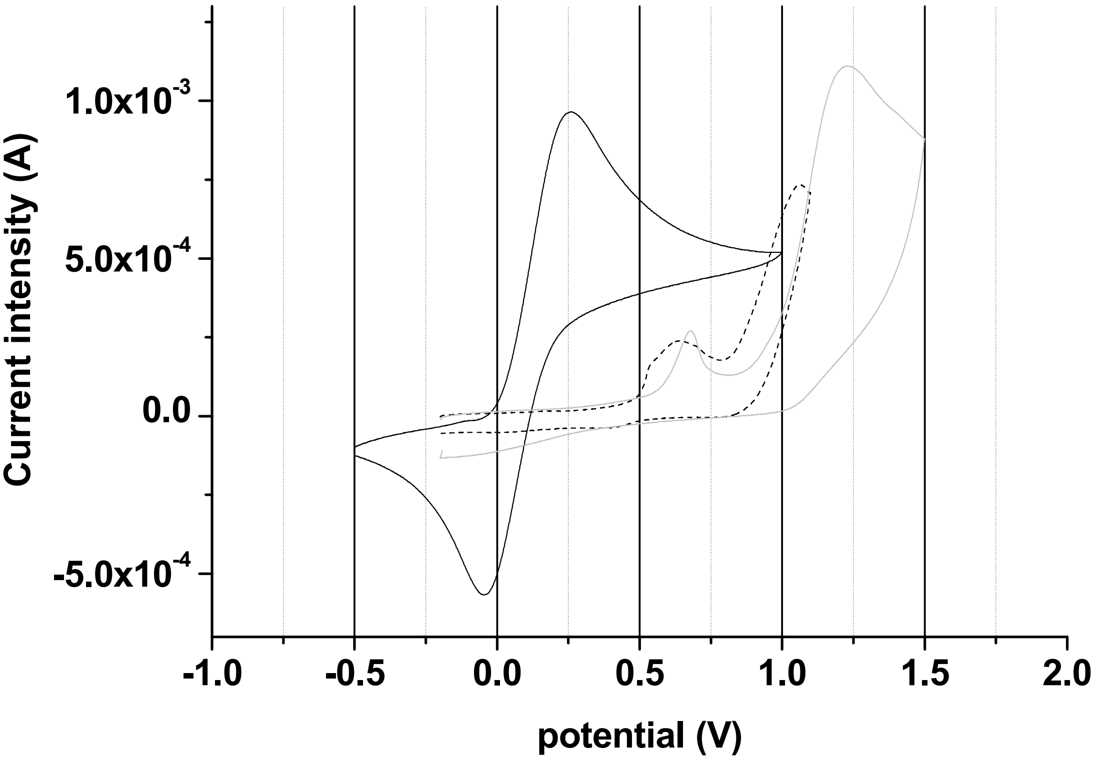


Figure 7: Cyclic voltametry (CV) of compound **8** (black dash line) and compound **9** (grey solid line) referenced against ferrocene (black solid line).

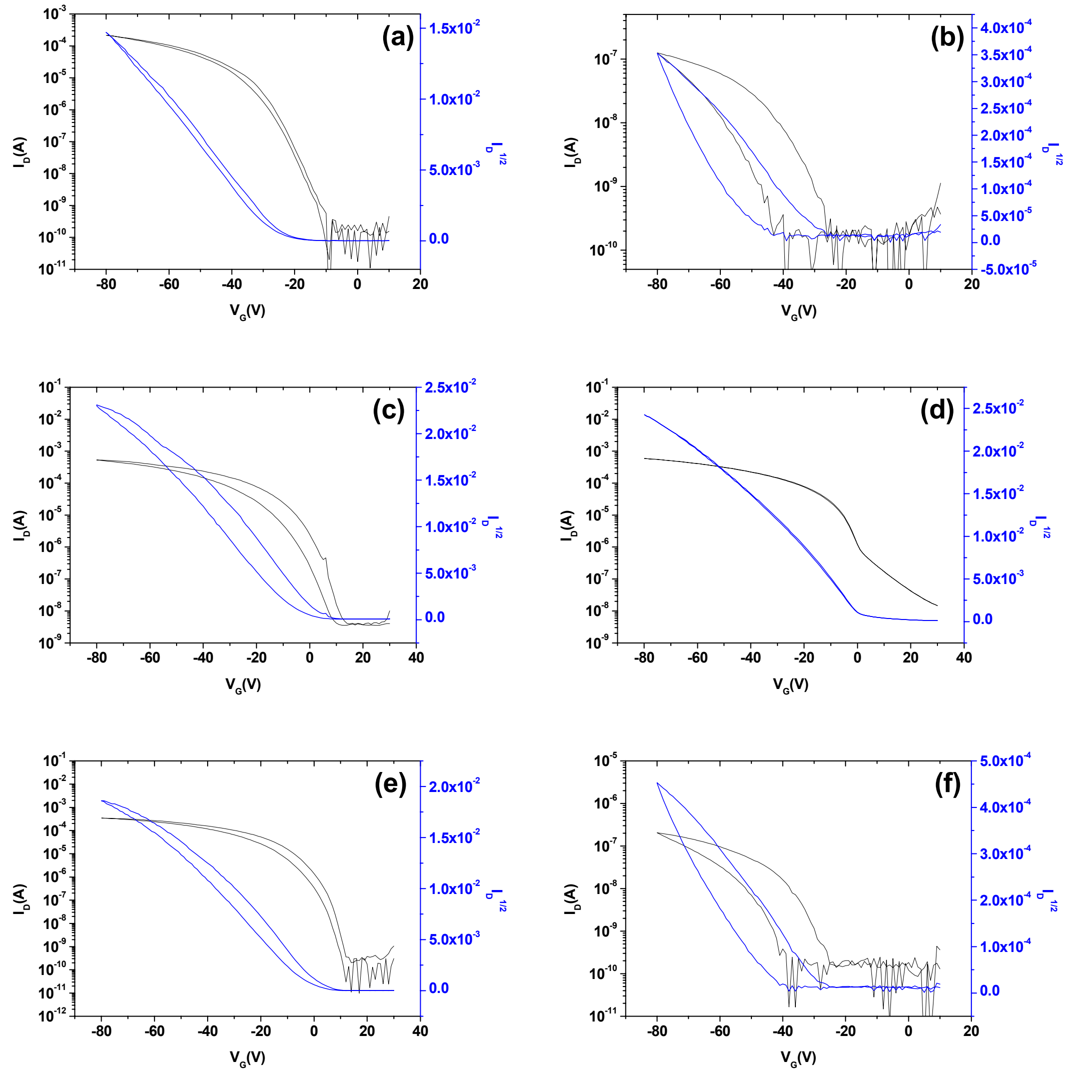


Figure 8. transfer characteristics of bottom gate top contact, with V_D fixed at -80V for (a) compound **8**, (b) compound **9** drop cast on OTS treated silica dried a 70°C, (c) compound **8**, (d) compound **9** drop cast on super hydrophilic silica and dried at room temperature, (e) compound **8** and (f) compound **9** drop cast on OTS treated silica and dried at room temperature.