Organic Thin Film Transistors Based on 2,3-Dimethylpentacene and 2,3-Dimethyltetracene

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2,3-Dimethylpentacene (DMP) and 2,3-dimethyltetracene (DMT) were synthesized, characterized and employed as the channel material in the fabrication of thin-film transistors. The two methyl groups increase the chemical stability of the compounds versus the pristine acene analogues. The crystals maintain herringbone-like molecular packing, whereas the weak dipole associated with the unsymmetrical molecule induces an anti-parallel alignment among the neighbors. This structural motif favors layered film growth on SiO₂/Si surface. Thin film transistors prepared on SiO₂/Si and *n*-nonyltrichlorosilane-modified SiO₂/Si at different substrate temperatures were compared. DMP-based transistors prepared on rubbed *n*-nonyltrichlorosilane-modified SiO₂/Si substrate gave the highest field-effect mobility of 0.46 cm²/Vs, whereas DMT-based transistor gave a mobility of 0.028 cm²/Vs.

Keywords: 2,3-Dimethylpentacene; 2,3-Dimethyltetracene; Organic thin film transistors; Monolayer.

INTRODUCTION

Organic semiconductors are of scientific and technological interest because of their electrical properties and potential use in low-cost, large-area electronic applications such as in organic light-emitting diodes, organic field-effect transistors (OFETs), and organic photovoltaics.¹ Different properties are desired in different applications though. The most important material properties for applications in OFETs are high charge mobility, large on/off ratio, low threshold voltage, besides stability, and processability. In recent years, much progress has been made in developing oligothiophenes and acene derivatives,²⁻⁵ among others, as promising p-type organic semiconductors in OFETs.

While impressive increase in charge mobility has been achieved, mainly through improved device fabrication techniques including optimization in film deposition parameters, dielectric surface modifications and etc. to influence the film morphology and crystallinity.^{6,7} A quest for more materials is always needed to push the intrinsic molecular property to a higher level.

One strategy in molecular design is to modify a promising material by introducing various substituents at different positions and seek for property enhancement as well as performance improvement. These modifications nevertheless will change the crystal packing and thus the electronic coupling between the molecules, which is believed to be crucial to the charge transport between the molecules.^{8,9} Pentacene is a well-known and benchmark example that attracts much attention for its high mobility and on/off ratio. A reproducible mobility of $> 1 \text{ cm}^2/\text{Vs}$ can be achieved in thin film configurations in various laboratories.^{10,11,12} A lot of efforts have been devoted to modifying the pentacene framework. For example, 2,9-dimethylpentacene and 2,3,9,10-tetramethylpentacene have been shown to give thin film transistors with high mobility. The introduction of small electron-donating methyl groups presumably increases the p-type behavior of these molecules. Yet substitution at these symmetric positions does not change the non-polar nature of these molecule, so that very similar packing as pentacene itself was obtained.^{13,14} The replacement of one end ring with a thiophene unit,^{15,16} which breaks the symmetry of the molecule and imparts a dipole to the molecule, may enhance the intermolecular packing without major change in the molecular arrangement in the crystal. Indeed similar herringbone packing was obtained and reasonably good field-effect mobility was achieved with this compound as the channel material. Another example is the substitution of the two hydrogen atoms on the central ring with two bulky triisopropylsilylethynyl groups,

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which discourage the herringbone packing. Instead, a shifted π - π stacking of the molecules resulting in a brick wall-like structure in crystal was observed. Enhanced electronic coupling and good mobility were obtained.¹⁷ These efforts have been reviewed recently.¹⁸

In this work, we report the synthesis and characterization of 2,3-dimethylpentacene (DMP, 1) and 2,3-dimethyltetracene (DMT, 2) and the fabrication of transistor devices with these materials. We figured that by substituting hydrogen atoms at 2,3-positions for methyl groups is expected to introduce a small dipole moment (e.g. calculated to be 0.76 Debye for 2,3-dimethylpentacene), which may enhance the intermolecular packing through anti-parallel disposition without major change in the molecular arrangement in the crystal. The closer packing may improve the electronic coupling and thus charge transport. It is noted that single crystals of DMP had been used to fabricate FET devices to explore the effect dielectric surface modification.¹⁹ Here, thin film transistors were prepared on SiO₂/Si surfaces. It was shown that depending on the surface treatment of the dielectric layer, bare SiO₂, *n*-nonyltrichlorosilane (NTS) monolayer-covered SiO2, or NTS monolayer pre-rubbed before material deposition, the mobility varies significantly. A high mobility of 0.46 cm²/Vs was obtained for DMP and 0.028 cm^2/Vs was observed for DMT on SiO₂ covered with a rubbed monolayer of n-nonyltrichlorosilane.



EXPERIMENTAL SECTION

All starting materials were purchased from Aldrich, TCI and Across. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. ¹H-Nuclear magnetic resonance (NMR) spectra were recorded with Bruker AMX400 spectrometer, with proton chemical shifts (δ) reported in parts per million (ppm) relative to the methine singlet at 7.24 ppm for the residual CHCl₃ in the deuteriochloroform. Electron Impact (EI)-mass spectra were obtained on a JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan). Elemental analyses were carried out on FlashEA 1112 Series CHNS-O Analyzer.

The silicon wafers, with 300 nm thermally grown oxide layer, were cleaned by Piranha solution (70% H_2SO_4 : 30% H_2O_2) and rinsed thoroughly with ultra high purity water. The cleaned silicon wafers were soaked into 1% *n*-nonyltrichlorosilane (NTS) solution in dry toluene for 3 minutes to generate the NTS-modified silicon oxide surface (NTS-SiO₂/Si). The substrate surface turned from totally hydrophilic to highly hydrophobic (with a water contact angle ~102°-104°), as a result of the adsorption of a self-assembled monolayer (SAM). Rubbing of the NTS-SiO₂/Si substrates with a rubbing machine (machine type: LY-E, with the roller kept at 140 mm height scale and rotated at 600 rpm) for two minutes in the same direction served to generate a smoother surface.²⁰ These samples are designated as r-NTS-SiO₂/Si. Thin films of DMP and DMT were thermally evaporated under a vacuum of 1.33×10^{-3} Pa and deposited on the bare SiO_2/Si , NTS-SiO₂/Si, or r-NTS-SiO₂/Si surfaces at different substrate temperatures in the same batch. The film thickness was monitored with a quartz crystal microbalance and the deposition rate was controlled at 0.1~0.3 Å/sec.

The powder X-ray diffraction pattern of DMP was recorded at the BL01C2 beamline of National Synchrotron Radiation Research Center in Taiwan. The structure was determined from the powder diffraction data with the program DASH.²¹ Powder diffraction data were indexed with Dicvol and Treor. The structure factors of the powder diffraction patterns were extracted with Pawley's method, and simulated annealing was employed to determine the crystal structure. The final refinement with the Rietveld method was performed with the GSAS program.

Atomic force microscopic analyses were carried out by using a Digital Instruments Multi-mode 3 atomic force microscope. Images were captured by tapping mode with a silicon tip at 300 kHz frequency. The powder X-ray diffraction was carried out by using the Philips X'Pert diffractometer with X'Celerator detector. The Cu K α radiation at a power of 45 kV and 40 mA with a scanning step size of 0.008° was used.

FET devices were fabricated on silicon wafers with the 300 nm-thick SiO₂ surface as the gate dielectric and the underlying highly *n*-doped silicon as the gate electrode. The 50 nm-thick gold source and drain electrodes were deposited on the organic films (top contact) through a shadow mask. The channel length (*L*) and width (*W*) are 50 μ m and 500 μ m respectively. The electrical characteristics of the devices were measured in air using a computer-controlled Agilent 4156C Semiconductor Parameter Analyzer. The field-effect mobility of the OFET device was calculated from the saturation region according to equation 1: Organic Thin Film Transistors Based on Acene Derivatives

 $I_{ds,sat} = (WC_i/2L) \,\mu_{sat}(V_{gs} - V_{th})^2 \tag{1}$

where C_i is the capacitance per unit area of the SiO₂ insulator, V_{gs} is the gate voltage and V_{th} is the threshold voltage.

1,2-Bis(bromomethyl)-4,5-dimethylbenzene (3)

4,5-Dimethyl-1,2-phenylenedimethanol (7.5 g, 0.045 mol) was added to 200 mL concentrated hydrobromic acid (48%). The mixture was refluxed for 4 h., and then cooled to room temperature, diluted with water, extracted with dichloromethane. Drying and evaporation of solvent gave **2** as a white crystal (13.2 g, 98% yield). M.p. 118-120 °C. ¹H-NMR (400 MHz, CDCl₃) δ = 7.12 (s, 2H), 4.61 (s, 4H), 2.23 (s, 6H).

2,3-Dimethylpentacene-6,13-dione (4)

Dibromide **3** (2.92 g, 10.0 mmol), 1,4-anthraquinone (2.08 g, 10.0 mmol), and KI (16.6 g, 100 mmol) were dissolved in 50 mL of dry dimethylformamide (DMF) and stirred at 110 °C for two days. The reaction mixture was cooled to room temperature before 100 mL of water was added. The solid was filtered off, washed with water, ethanol, acetone, ethyl acetate (EA) and hexane, to gave 2.18 g (65% yield) of 2,3-dimethylpentacene-6,13-dione as a yellow solid. MS (EI, 70 eV) 336.1 (M⁺, 100%).¹H-NMR (400 MHz, CDCl₃) δ = 8.921 (s, 2H); 8.814 (s, 2H); 8.121-8.097 (dd, *J* = 3.12 Hz, *J* = 3.16 Hz, 2H); 7.852 (s, 2H); 7.697-7.673 (dd, *J* = 3.08 Hz, *J* = 3.12 Hz, 2H); 2.492 (s, 6H).

2,3-Dimethylpentacene (1)

LiAlH₄ (0.95 g, 25 mmol) was added to a suspension of 2.1 g (6 mmol) of 2,3-dimethylpentacene-6,13-dione in 100 mL of dry THF at 0 °C and the reaction mixture was stirred for 3 h. at room temperature. Hydrochloric acid (6 M, 50 mL) was added slowly under cooling with ice. The mixture was then refluxed for 30 min. The residue was filtered, washed with water, dried under vacuum and again treated with 0.95 g (25 mmol) LiAlH₄ and reacted with the same procedure. The solid was filtered and washed with water, ethanol, EA, dichloromethane, and hexane. The crude product was purified by vacuum sublimation at 310-320 °C (1.33×10^{-3} Pa), to give 1.44 g., 75% yield of 2,3-dimethylpentacene as a dark blue crystal. M.p. > 350 °C (dec.), MS (EI, 70 eV) 306.14 (M⁺, 100%). Anal. calc. C 94.08%, H 5.92%, Found: C 94.04%, H 5.72%.

8,9-Dimethyltetracene-5,12-dione (5)

Dibromide 4 (2.92 g, 10.0 mmol), 1,4-naphthaquinone (1.58 g, 10.0 mmol), and KI (16.6 g, 100 mmol), were dissolved in 50 mL of dry DMF and stirred at 110 °C for two days. The reaction mixture was cooled to room temperature before 100 mL of water was added. The solid was filtered off, washed with water, ethanol, EA and hexane, to gave 1.95 g (68% yield) of 8,9-dimethyltetracene-5,12dione as an orange-yellow solid. MS (EI, 70 eV) 286.1 (M⁺, 100%). ¹H NMR (400 MHz, CDCl₃) δ = 8.71 (s, 2H); 8.374-8.350 (dd, *J* = 3.36 Hz, *J* = 3.32 Hz, 2H); 7.82 (s, 2H); 7.799-7.776 (dd, *J* = 3.28 Hz, *J* = 3.32 Hz, 2H); 2.471 (s, 6H).

2,3-Dimethyltetracene (2)

LiAlH₄ (0.95 g, 25 mmol) was added to a suspension of 1.72 g (6 mmol) of 8,9-dimethyltetracene-5,12-dione in 100 mL of dry THF at 0 °C and the reaction mixture was stirred for 3 h. at room temperature. Hydrochloric acid (6 M, 50 mL) was added slowly under cooling with ice. The mixture was refluxed for 30 min. The residue was filtered, washed with water, dried under vacuum and again treated with 0.95 g (25 mmol) $LiAlH_4$ and reacted with the same procedure. The solid was filtered and washed with water, ethanol, EA, and hexane. The crude product was purified by vacuum sublimation at 230-250 °C (1.33×10^{-3} Pa), to give 1.54 g., 85% yield of 2,3-dimethyltetracene as an orange crystal. M.p. > 350 °C (dec.), MS (EI, 70 eV) 256.13 $(M^+, 100\%)$, ¹H-NMR (400 MHz, CDCl₃) $\delta = 8.592$ (s, 2H); 8.502 (s, 2H); 7.964-7.331 (dd, *J* = 3.44 Hz, *J* = 3.20 Hz, 2H); 7.727 (s, 2H); 7.356-7.331 (dd, *J* = 3.12 Hz, *J* = 3.16 Hz, 2H); 2.454 (s, 6H). Anal. calc. C 93.71%, H 6.29%, Found: C 93.58%, H 6.38%.

RESULTS AND DISCUSSION

Scheme I shows the synthetic route of DMP and DMT. 1,2-Bis(bromomethyl)-4,5-dimethyl-benzene (3) was obtained by the reaction of (4,5-dimethyl-1,2-phenylene)dimethanol²² with concentrated hydrobromic acid in 98% yield. A cyclization reaction of the dibromide **3** with commercially available anthracene-1,4-dione or naphthalene-1,4-dione yielded the quinones **4** or **5** in 65-70% yield. Reduction of diketones **4** and **5** with LiAlH₄ resulted^{16,22} in DMP and DMT in 75-85% yield, respectively. The compounds were purified through chain sublimation. In contrast to previous method²³ of preparing substituted pentacene derivatives which requires ten steps, the method here involves three steps from the starting bis(phenylene)dimethanol to final products. Pure product was obtained without resorting to column chromatography.

DMP is a dark blue solid, slightly soluble in hot chloroform, dichloromethane, chlorobenzene and 1,2-dichlorobenzene. While it is stable in the solid state and can be vac-

Scheme I Synthesis of DMP and DMT



Reagents and conditions: (a) HBr, reflux, 4 h., 98%; (b) Anthracene-1,4-dione, KI, DMF, 48 h., 65%; (c) Naphthalene-1,4-dione, KI, DMF, 48 h., 68%; (d) LiAlH₄, THF, r.t., 3 h, HCl (20%), reflux., 30 min., 75% (1), 85% (2).

uum-sublimed, its solutions are unstable and bleached with time in the ambient. Yet it is more stable than similar solution of pentacene (see below). DMT is an orange solid, soluble in most organic solvents, including dichloromethane, chloroform, THF and etc. and its solutions are stable for more than 1 day.

Thermal analysis of compounds 1 and 2 were performed under nitrogen. The weight loss of DMP began at 335 °C, whereas DMT started at 267 °C (Figure 1). These temperatures are lower than that of corresponding acene derivatives. Thus the introduction of two methyl group does not improve the thermal stability.

The chemical stability of DMP and DMT was also compared with that of pentacene and tetracene by monitoring the time-dependence of UV-absorption spectra in solution. Figure 2a shows the UV absorption of pentacene in dilute dichloromethane. The absorption at 303 nm decayed nearly completely in 40 min. In the mean time, a new absorption peak at 252 nm grew. It is known that pentacene in solution tends to degrade upon exposure to air in the presence of light to give the peroxide.²⁴ With DMP of similar initial optical densities, one observed a 30% decay of the intensity of the long-wavelength absorption at 305 nm over



Fig. 1. Thermograms of DMP and DMT.

the same period of time. A new peak at 257 nm grew at the expense of the long-wavelength absorption (Figure 2b). Thus the introduction of two methyl groups improves the chemical stability of the pentacene framework. Similar measurements were made for DMT and tetracene (Figure 3). For tetracene, the intensity of the long-wavelength absorption at 276 nm decayed by 8% with a new peak grew at 236 nm after 2 h, but virtually no change in the intensity over 3 h duration for DMT.

Crystal structure

Attempts to grow thick enough single crystals of DMP and DMT for x-ray structure determination were unsuccessful. The crystal of DMP was nevertheless approached by power x-ray diffraction with synchrotron radiation. It was indexed as triclinic crystal system, with the space group P-1. The crystal data are shown in Table 1, together with that of pentacene's. Figure 4 shows the crystal packing along the long molecular axis and projection from top. The crystal packing looked down from the top of molecule (Fig. 4b) clearly shows zigzag arrangement, thus in a herringbone fashion similar to that of pentacene. Thus the two methyl groups at the end do not alter the packing motif much. Within the same layer (Fig. 4d), the unsymmetrical molecules are anti-parallel to the nearest neighbors, presumably to minimize the electrostatic repulsion of the weak dipoles associated with the molecules.



Fig. 2. Time-dependent UV-vis spectra for (a) pentacene, and (b) DMP in a solution of dichloromethane.



Fig. 3. Time-dependent UV-vis spectra for (a) DMT and (b) tetracene in a solution of dichloromethane.

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	DMP	Pentacene [4]
Space group	P -1	P -1
Ζ	4	2
Cell dimension a (Å)	5.9611(4)	6.2660(10)
b (Å)	7.7911(8)	7.7750(10)
c (Å)	33.4682(28)	14.5300(10)
α	92.480(21)	76.475(4)
β	94.078(25)	87.682(4)
γ	90.762(7)	84.684(4)

Table 1. Crystal data of DMP

Similar packing was observed for tetracenothiophene molecules.¹⁶ Such a packing will favor layered film formation, as shown in atomic force microscope (AFM) images below. One of the short axes is shorter than corresponding axis for pentacene (5.961 Å vs 6.266 Å). The molecules also tilt less than pentacene in the unit cell. Thus DMP appears to pack more closer with the introduction of methyl substituents.

Thin film deposition and structure characterization

The charge transport in an organic film is critically dependent on the morphology of the film, which is determined by the deposition conditions, including the vacuum, substrate temperature, substrate surface treatment and etc. "Hydrophobation" of silica surface by a SAM has been shown to be advantageous to the hole mobility of semiconducting films prepared on silica surface.²⁵ Recently we further showed that a rubbing treatment of a SAM of alkylsilane on silica resulted in much improved grain morphology and crystallinity of pentacene film deposited on it.²⁰ The rubbing process is suggested to smoothen the multi-



Fig. 4. Crystal packing of DMP (a, b) and Pentacene (c, d) viewed along the cell a axis and along the long molecular axis. domained SAM surface, reducing the number of nucleation sites and favoring larger grains. The orderliness of the SAM was also suggested to be important and crucial to larger grain formation in a work using SAM prepared by Langmuir-Blodgett technique.²⁶ We prepared and compared films deposited on substrates of bare SiO₂/Si, the *n*-nonyltrichlorosilane-modified surface (NTS-SiO₂/Si) and the NTS-SiO₂/Si that has been rubbed (r-NTS-SiO₂/Si) before semiconductor film deposition. Figure 5 shows the AFM images of 50 nm DMP deposited on these surfaces at different temperatures. In general, for films prepared on the same substrate, the grain size increases with increasing substrate temperature. However, the grains deposited on SiO₂/Si surface at 80 °C appeared less connected than that deposited on NTS-SiO₂/Si substrates. At the same substrate temperature, the grains on r-NTS-SiO₂/Si are significantly larger than that on unrubbed NTS-SiO₂/Si surface, and the grains on SiO₂/Si are the smallest. The larger grains show clear terrace structure and the section analysis shows that the layered morphology has similar step heights around 1.67 nm. Similar observations were made for films of DMT deposited on these surfaces, as shown in Figure 6. Section analysis of the terraced structure shows a step height of 1.45 nm. However, at a substrate temperature of 80 °C, no film was obtained, presumably due to the volatility of the molecules (or a low sticking ability) at this substrate temperature under the vacuum used.

The films were also examined for their powder X-ray diffraction. For DMP deposited on NTS-SiO $_2$ /Si and SiO $_2$ /



Fig. 5. AFM micrographs of DMP films deposited on
(a) NTS-SiO₂/Si at r.t.; (b) NTS-SiO₂/Si at 55
°C; (c) NTS-SiO₂/Si at 80 °C; (d) r-NTS-SiO₂/Si at r.t.; (e) r-NTS-SiO₂/Si at 55 °C; (f) r-NTS-SiO₂/Si at 80 °C; (g) SiO₂/Si at r.t. (h) SiO₂/Si at 55 °C; (i) SiO₂/Si at 80 °C.

Si surfaces at different temperatures. Diffraction peaks at 20 of 5.28°, 10.54° and 15.84° were obtained at all substrate temperatures and are assigned as the diffraction peaks from the (002), (004), (006) planes respectively (Figure 7). This indicates that the same crystal phase was obtained at different deposition conditions. The d-spacing calculated from (002) peak is 1.67 nm, which is half of the c-axis of the crystal cell, suggesting molecules were standing near upright on all surfaces. This is in agreement with the step heights obtained from the AFM microscopy. This orientation will facilitate charge transporting in a horizontal device configuration since this is the direction of π - π stacking of the herringbone arrangement along the conduction pathway. The intensity of the diffraction peaks shows a clear trend: higher with increasing substrate temperature on NTS-SiO₂/Si and r-NTS-SiO₂/Si surfaces, and higher on r-NTS-SiO₂/Si than on NTS-SO₂/Si surfaces if comparing at the same deposition temperature. The higher intensity correlates with improved crystallinity and grain size as shown by AFM results. Similar observation was noted for pentacene deposited on rubbed monolayer surface.²⁰ It is nevertheless noted that the diffraction peak intensities for



Fig. 6. AFM micrographs of films of DMT deposited on (a) NTS-SiO₂/Si at r. t.; (b) NTS-SiO₂/Si at 55 °C; (c) r-NTS-SiO₂/Si at r.t.; (d) r-NTS-SiO₂/Si at 55 °C; (e) SiO₂/Si at r.t. and (f) SiO₂/Si at 55 °C.



Fig. 7. X-ray diffraction of 50 nm thick film of DMP deposited on (a) NTS-SiO₂/Si and r-NTS-SiO₂/ Si, (b) SiO₂/Si, surfaces at different temperatures.

films deposited on bare SiO₂/Si surface are in general much lower than that on NTS-covered substrates. This could be attributed to the lower crystallinity and/or lower thickness. Films grown on bare SiO₂/Si surface at 80 °C also gave an intensity lower than that grown at 55 °C, a phenomena contrary to expectation. An examination of the AFM micrographs suggests that the semiconducting molecules are less adhering on SiO₂/Si surface than on NTS-SiO₂/Si surface. Material loss is more significant at higher substrate temperature. The AFM micrographs above also show that the grains are less connected than that deposited on silane-covered surfaces.

Figure 8 shows the x-ray diffraction results for DMT deposited on various substrates. Again a single crystalline phase was obtained giving diffraction peaks at 2θ of 6.09° . 12.28°, 18.45°, respectively. The d-spacing calculated from the first peak is 14.5 Å, close to the thickness with a perpendicularly oriented DMT on the surfaces and in agreement with the section analysis in AFM analysis. Thus similar packing as in DMP is suggested. Again, the diffraction peak intensity is much reduced for films deposited on SiO₂/ Si surfaces than on NTS-SiO₂/Si surfaces. Also at a substrate temperature of 55 °C, the peak intensity already became lower than that deposited at room temperature. In view of the absence of film formation on surface when the substrate was kept at 80 °C, the decreased intensity may be ascribed to partial material loss due to volatility of the molecules at this temperature.

FET device fabrication and characterization

Characteristics of FET devices prepared from DMP and DMT are collected in Table 2 and 3 with the representative curves for DMP provided in Figure 9. For DMP, the best device performance was obtained for film deposited on r-NTS-SiO₂/Si at a substrate temperature of 80 °C. A small anisotropy in the mobility was observed: 0.46 cm²/Vs along the rubbing direction and 0.39 cm²/Vs in direction



Fig. 8. X-ray diffraction of 50 nm thick film of DMT deposited on (a)NTS-SiO₂/Si and r-NTS-SiO₂/Si and (b) SiO₂/Si surfaces at different temperatures.

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Table 2.	Field-effect mobility, on/off ratio and threshold voltage for DMP-based transistors fabricated at
	different substrate temperature and surfaces

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	R.T.	55 °C	80 °C
NTS-SiO ₂	0.042~0.048/10 ³ /-10	$0.047 \sim 0.051/10^4/-17$	0.044~0.0537/10 ³ /-11
r-NTS-SiO ₂ (para)	0.063~0.081/10 ³ /-3	0.068~0.087/10 ³ /-13	$0.37 \sim 0.46 / 10^3 / -2$
r-NTS-SiO ₂ (perp)	0.017~0.032/104/-2	0.054~0.07/10 ⁴ /-2	$0.32 \sim 0.39 / 10^3 / +2$
SiO ₂	$(1.7 \sim 1.9) * 10^{-3} / 10^{2} / + 39$	$(1.1 \sim 1.31) * 10^{-2} / 10^{2} / +36$	$(4.7 \sim 4.84) * 10^{-3} / 10^{2} / + 20$

Table 3. Field-effect mobility, on/off ratio and threshold voltage for DMT transistors fabricated at different substrate temperature and surfaces

	R.T.	55 °C
NTS-SiO ₂	(8.5~9.4)*10 ⁻³ /10 ⁵ /-10	(6.2~7.1)*10 ⁻⁴ /10 ⁵ /-25
NTS-SiO ₂ (para)	$(2.4 \sim 2.8) * 10^{-2} / 10^{6} / -17$	(1.29~1.42)*10 ⁻² /10 ⁶ /-25
NTS-SiO ₂ (perp)	$(1.46 \sim 1.7) * 10^{-2} / 10^{5} / -5$	$(2\sim 2.3)*10^{-2}/10^{5}/-22$
SiO ₂	$(5.2 \sim 5.7) * 10^{-4} / 10^{3} / + 8$	*/*/*

perpendicular to the rubbing direction, with a similar on/off ratio of 10^3 . The mobility decreased with lower substrate temperature. This trend also parallels that revealed from AFM analyses. That is, the larger the grain size, the higher the mobility. For films deposited on bare SiO₂/Si surface, the highest mobility of 0.013 cm²/Vs was obtained at a substrate temperature of 55 °C. Further increasing substrate temperature to 80 °C resulted in reduced intensity of diffraction peaks and lower device performance. It is noted that the threshold voltages shifted to negative values for the SAM-covered surfaces and are positive on the bare SiO₂/Si surfaces. The on/off ratios for devices prepared on bare SiO₂/Si surfaces are also lower. It is suggested that some hole carriers are present at zero bias and the device is already on at zero bias. It takes a large positive gate to turn





off the device. For DMT, the best performance was also obtained on r-NTS-SiO₂/Si surface with the substrate temperature at room temperature. A mobility of 0.028 cm²/Vs and an on/off ratio up to 10^6 were achieved. Higher deposition temperatures greatly reduced the mobility.

CONCLUSION

In conclusion, two acene derivatives, DMP and DMT, were synthesized and characterized for applications in field-effect transistor fabrication. The introduction of two methyl groups at 2,3-positions results in improved chemical stability of the compounds in the solution. The methyl substitution also imparts a weak dipole moment to the molecule which dictates the molecules to pack in anti-parallel disposition of neighboring molecules without changing the herringbone-like packing motif. Layered films were obtained upon thermal deposition. Mobility for FET devices based on these compounds depends critically on the substrate on which they were deposited. Rubbing of the SAMcovered silica substrate much improved the mobility of DMP-based devices to a high value of 0.46 cm²/Vs, compared to 0.057 cm²/Vs obtained for the unrubbed counterpart. For DMT-based devices, a mobility of 0.028 cm²/Vs was observed on rubbed NTS-SiO₂ substrate.

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REFERENCES

- Murphy, A. R. M.; Fréchet, J. M. J. Chem. Rev. 2007, 107, 1066.
- Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. J. Am. Chem. Soc. 1993, 115, 8716.
- Akimichi, H.; Waragai, K.; Hotta, S.; Kano, H.; Sakati, H. Appl. Phys. Lett. 1991, 58, 1500.
- Gundlach, D. J.; Lin, Y. Y.; Jackson, T. N. *IEEE Electron*. Dev. Lett. **1997**, 18, 87.

- 5. Anthony, J. E. Chem. Rev. 2006, 106, 5028.
- Lin, Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. IEEE Trans. Electron Dev. 1997, 44, 1325.
- Koch, N.; Ghijsen, J.; Johnson, R. L.; Schwartz, J.; Pireaux, J.-J.; Kahn, A. J. Phys. Chem. B 2002, 106, 4192.
- Coropceanu, V.; Cornil, J.; Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J. L. *Chem. Rev.* 2007, *107*, 926.
- 9. Troisi, A. Adv. Mater. 2007, 19, 2000.
- Dimitrakopoulos, C. D.; Mascaro, D. J. *IBM J. Res. Div.* 2001, 45, 11.
- 11. Kraft, A. ChemPhysChem 2001, 2, 163.
- 12. Klauk, H.; Gunlach, D. J.; Nichols, J. A.; Jackson, T. N. *IEEE Trans Electron. Dev.* **1999**, *46*, 1258.
- Kelley, T. W.; Boardman, L. D.; Dinbar, T. D.; Muyres, D. V.; Pellerite, M. J.; Smith, T. Y. P. *J. Phy. Chem. B* 2003, *107*, 5877.
- (a) Meng, H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegist, T.; Kloc, C.; Chen, C. H. Adv. Mater. 2003, 15, 1090.
- 15. Tang, M. L.; Okamoto, T.; Bao, Z. J. Am. Chem. Soc. 2006, 128, 16002.
- 16. Valiyev, F.; Hu, W. S.; Chen, H. Y.; Kuo, M. Y.; Chao, I.; Tao,

Y. I. Chem. Mater. 2007, 19, 3018.

- Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C. C.; Jackson, T. N. J. Am. Chem. Soc. 2005, 127, 4986.
- Meng, Q.; Dong, H.; Hu, W.; Zhu, D. J. Mater. Chem. 2011, 21, 11708.
- Islam, M. M.; Pola, S.; Tao, Y. T. ACS Appl. Mater. Interfaces 2011, 3, 2136.
- Weng, S. Z.; Hu, W. S.; Kuo, C. H.; Tao, Y. T.; Fan, L. J.; Yang, Y. W. Appl. Phys. Lett. 2006, 89, 172103.
- David, W. I. F.; Shankland, K.; van de Streek, J.; Pidcock, E.; Motherwell, W. D. S.; Cole, J. C. J. Appl. Crystallogr. 2006, 39, 910.
- 22. Farooq, O. Synthesis 1994, 10, 1035.
- Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K. J. Org. Chem. 2006, 71, 7967.
- 24. Clar, E. *Polycyclic Aromatic Hydrocarbons*; Academic Press: London, 1964; Vol. 1.
- Shtein, M.; Mapel, J.; Benziger, J. B.; Forrest, S. R. Appl. Phys. Lett. 2002, 81, 268.
- Ito, Y.; Virkar, A.; Mannsfeld, S.; Oh, J. H.; Toney, M.; Locklin, J.; Bao, Z. J. Am. Chem. Soc. 2009, 131, 9396.

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