Structure Effects on Organic Thin-Film Transistor Properties of Dinaphthyl Substituted Pentacene Derivatives

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Pentacene moiety has been widely studied in Organic Thin-Film Transistor (OTFT) device as a channel layer because of high carrier mobility. In this study, we have fabricated vertical type Organic Static Induction Transistors (SITs) using pentacene, 6,13-Dinaphthalen-1-ly-Pentacene (1-DNP, **3**), and 6,13-Dinaphthalen-2-ly-Pentacene (2-DNP, **4**). 1-DNP and 2-DNP have same naphtyl group with pentacene, but different linked position and spatial arrangement. We have checked the static characteristics of materials in vertical type SITs device. We found that pentacene has as on/off ratio of 14.56, 1-DNP and 2-DNP shows as on/off ratio of 36.58 and 6.61 at V_{DS} = 2V in SIT, respectively.

Key Words : OTFT (organic thin-film transistor), Naphthyl, Pentacene, Vertical type, On/off ratio

Introduction

Organic thin-film transistors (OTFTs) have been extensively studied over the last decade, and remarkable progress in the performance of these devices have been made.[1-5] OTFTs can be used for circuit application of large area coverage, structural flexibility, low temperature processing and especially low process cost such as screenprinting and an ink jet process. Among many organic materials, pentacene-based OTFTs have been widely focused up to now and showed the highest mobility for hole transport (*p*-channel).[5-8] Field-effect transistors (FETs) using organic materials have generally low-speed, low-power, and relatively high operation voltage due to their low-mobility and high-resistivity of organic materials.[9] However, static induction transistor (SITs) are also known to high-speed and high-power operation against FETs.[9] In this study, we fabricated vertical type Organic SITs using pentacene, 6,13-Dinaphthalen-1-ly-Pentacene (1-DNP) and 6,13-Dinaphthalen-2-ly-Pentacene (2-DNP) and characterized SITs property upon spatial arrangement of 1-DNP and 2-DNP compare to pentacene.

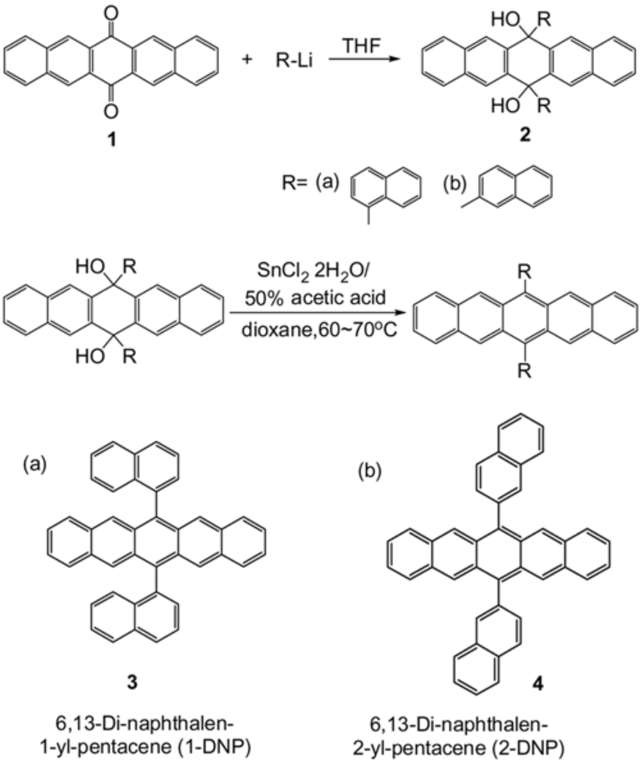
Experimental Section

Pentacene (99%) was bought from Polysis and 6,13-Pentacenequinone (99%) and *n*-buthyllithium (1.6 M solution in hexanes) were purchased from Acros, 1-bromonaphthalene (97%), 2-boronaphthalene (97%) were purchased from Aldrich and used without further purification unless otherwise noted. Solvents were purified by normal procedures and handled under moisture free atmosphere.

^{1}H-NMR spectra were recorded with Bruker, Avance DPX-500 NMR spectrometer in $CDCl_3$ and chemical shift were recorded in ppm units with the residual proton solvent resonance. FAB-Mass spectra were measured with JEOL, JMS-AX505WA.

We were carried out by Spartan program ’02 using the Hartree-Fock SCF calculation fot studying differential of characteristics by spatial arrangement.

Thermal evaporation chamber used ULVAD VTR-300M/IERH evaporator. (pressure < 10^{-6} Torr) Three SIT's materials were fabricated at the deposition rate of 0.5 Å/s at 25 °C. Source and Drain voltages were independently monitored by the Keithley 238 and 2400 to evaluate I_{DS} in the devices.



Scheme 1

Pentacene, 1-DNP and 2-DNP SITs were thermally evaporated (pressure < 10^{-6} Torr and rate = 0.5/s) through a shadow as well as aluminium electrode. Source, Drain voltage were applied with Keithley 2400 & 238 sourcemeter. We fabricated SITs device as follow (Figure 1): ITO (150 nm)/pentacene or 1-DNP or 2-DNP (100 nm)/Al (30 nm)/pentacene or 1-DNP or 2-DNP (100 nm)/Al (100 nm) device.

6,13-dinaphthalen-1-yl-pentacene (1-DNP, **3**) and 6,13-dinaphthalen-2-yl-pentacene (2-DNP, **4**) were synthesized as shown in scheme 1.

6,13-Di-naphthalen-1-yl-6,13-dihydro-pentacene-6,13-diol. (**2-(a)**) A solution of 1-bromonaphthalene (2.4 mL, 16.81 mmol) in THF (60 mL) was stirred under N_2 and cooled to −78 °C in a dry ice/acetone bath. Upon cooling, 12.0 mL (16.81 mmol) of *n*-butyllithium was added to make metal-halogen exchange and 6,13-pentacenequinone (**1**) (600 mg, 1.681 mmol) was added to the yellow solution, and the mixture was for 7 hrs up to room temperature. Orange color product of diol (**2-(a)**) was recrystallized under hexane-EA solvent after common work-up process (774 mg, 70% yield).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.88 (d, 2H), 8.10 (d, 2H), 8.02 (d, 2H), 7.88 (d, 2H), 7.83 (d, 2H), 7.70 (s, 4H), 7.54 (m, 4H), 7.27 (m, 4H), 7.21 (d, 2H), 7.04 (m, 2H), 4.15 (m, 4H); mass (positive ion FAB) 563 (M^+).

6,13-Dinaphthalen-1-ly-pentacene. (1-DNP, 3) To a stirred solution of 6,13-di-naphthalen-1-yl-5a,6,13,13a-tetrahydro-pentacene-6,13-diol (**2-(a)**) (774 mg, 1.0 mmol) in 1,4-dioxane (70 mL) was added a suspension of tin (II) chloride dihydrate (13.2 g) in 50% aqueous acetic acid (15 mL). The reaction mixture was wrapped in foil and heating to 70-80 °C for 3 hrs. The mixture was extracted with chloroform. The product concentrated on a Rotary evaporator and isolated by typical silica column method (445 mg, 63% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.22 (d, 2H), 8.10 (m, 4H), 7.87 (d, 2H), 7.83 (d, 2H), 7.77 (d, 1H), 7.54 (m, 4H), 7.23 (d, 2H), 7.19 (d, 4H), 7.15 (m, 5H); mass (positive ion FAB) 530 (M^+).

6,13-Di-naphthalen-2-yl-6,13-dihydro-pentacene-6,13-diol. (**2-(b)**) A solution of 2-bromonaphthalene (5.1 g, 24.38 mmol) in THF (60 mL) was stirred under N_2 and cooled to −78 °C in a dry ice/acetone bath. Upon cooling, 15.0 mL (24.38 mmol) of *n*-butyllithium was added to make metal-halogen exchange and 6,13-pentacenequinone (**1**) (600 mg, 1.92 mmol) was added to the yellow solution, and the mixture was for 7 hrs up to room temperature. Orange color product of diol (**2-(b)**) was recrystallized under hexane-EA solvent after common work-up process. (792 mg, 72% yield).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.31 (s, 4H), 7.91 (m, 4H), 7.54 (m, 4H), 7.35 (d, 4H), 7.19 (d, 4H), 7.15 (t, 4H), 7.11 (t, 4H); mass (positive ion FAB) 563 (M^+).

Synthesis of 6,13-di-naphthalen-2-yl-pentacene. (2-DNP, 4) was proceeded with same method as 1-DNP's.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.35 (d, 4H), 8.20 (s, 2H), 8.14 (d, 2H), 7.79 (d, 2H), 7.70 (m, 12H), 7.20 (m, 4H); mass (positive ion FAB) 530 (M^+).

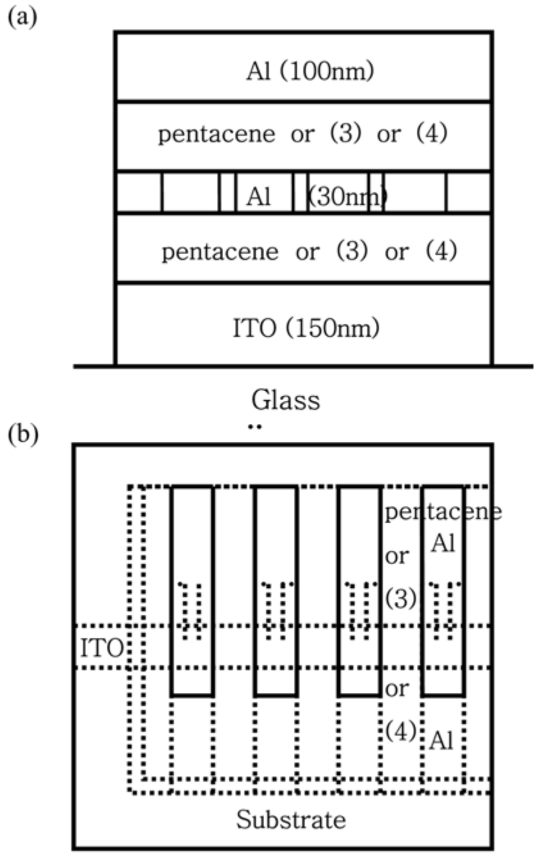


Figure 1. Schematic illustrations of vertical types organic transistor (a) The front side of device, (b) The lateral face of device Pentacene, 1-DNP (**3**) and 2-DNP (**4**).

Results and Discussion

We synthesized pentacene derivatives, 1-DNP (**3**) and 2-DNP (**4**) as shown in Scheme 1.[10-12] The resulting products are soluble in common organic solvents, such as chloroform, THF and toluene. The structure was identified by 500 MHz NMR, UV-Visible spectroscopy and FAB-Mass analysis.

In our previous paper, 1-DNP showed higher melting temperature value at about 272 °C than 2-DNP (160 °C). We suppose that 1-DNP shows the strongest interaction between molecules compared to 2-DNP. We also observed PL intensity variation as a function of solute concentration.[10]

1-DNP (**3**) and 2-DNP (**4**) exhibited similar two PL maximum wavelengths at around 620 nm and 660 nm. In PL spectrum, the intensity of 620 nm is typically larger than 660 nm's because PL of 620 nm originated from original chromophore itself and 660 nm came from the group states of the stacked chromophores. Therefore, as solute concentration of 1-DNP (**3**) increased, PL peak intensity at 660 nm rapidly increased as well as overall PL intensity increased.[10]

On the other hand, in 2-DNP (**4**) solution case, the overall peak intensity increased as the concentration of solute solution increased, but there was no clearly increased peak intensity of 660 nm at even high concentration. These results might be due to the capability of molecular interaction, 2-DNP has relatively lower packing ratio and molecular

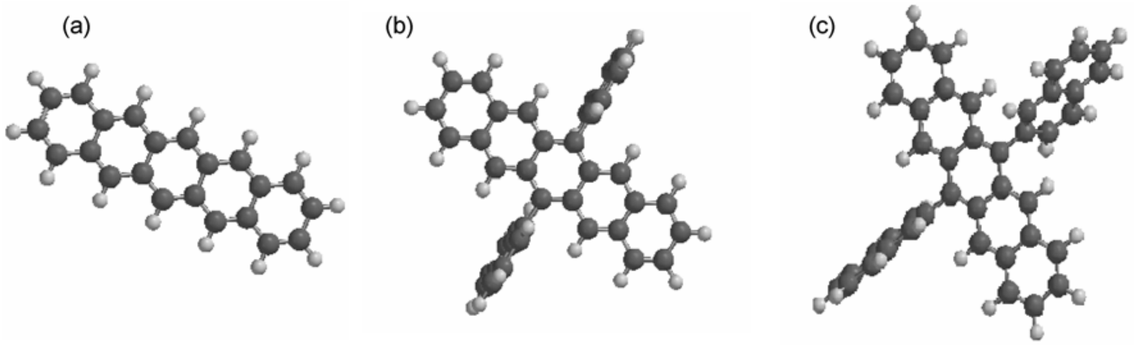


Figure 2. Molecular structure drawn by Spartan 02 of (a) Pentacene, (b) 1-DNP (**3**), (c) 2-DNP (**4**).

interaction than 1-DNP's because of steric hindrance of 2-naphthyl bulky group. These molecular interaction differences between 1-DNP and 2-DNP agree with melting point result.[10]

Figure 2 shows molecular structure drawn by Spartan 02 of synthesized molecule. As shown in Figure 2, 2-DNP showed relatively bulky structure compared to 1-DNP. We believe that intermolecular interaction of 1-DNP can be stronger than 2-DNP.

Figure 3 shows I-V curve as a function of gate voltage and I_{DS}-V_G curve of pentacene SIT device. As shown in Figure 3 (a), we found the typical I-V characteristics and I_{DS}-V_G relationship under V_{DS} of 5V was replotted in Figure 3(b). I_{DS} of pentacene at V_G = 0V is 0.436 mA and I_{DS} at V_G = 3V is 0.060 mA. So we could get on/off ratio of 7.21.

As shown in Figure 4, I_{DS} value of 1-DNP SIT was lower the pentacene and 2-DNP's, because 1-DNP has relatively more twisted structure and lower bulk conductivity. Although it is, 1-DNP device showed good gate swing property and high on/off ratio of 9.92 at V_{DS}=3V.

In Figure 5, we also checked I_{DS} current as a function of V_{DS} and V_G. We expected that 2-DNP shows lower I_{DS} value than 1-DNP's because of bulky structure of 2-DNP, but I_{DS} values are about 10 times bigger than 1-DNP's.

There is no clear explanation about this, but we suppose that two dimension of three dimension structure of synthesized pentacene derivatives might offer different spatial arrangement.

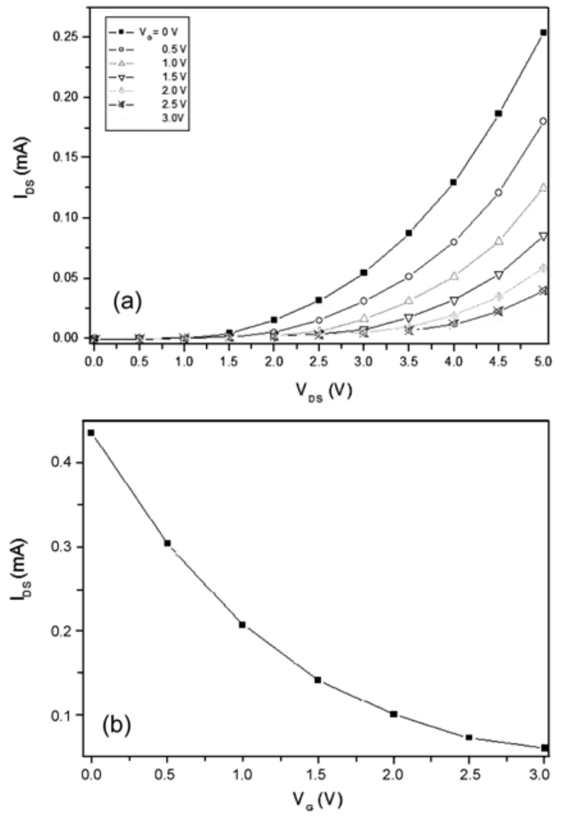


Figure 3. (a) I-V Characteristics of Pentacene SIT and (b) I_{DS}-V_G curve of Pentacene at V_{DS} = 5V.

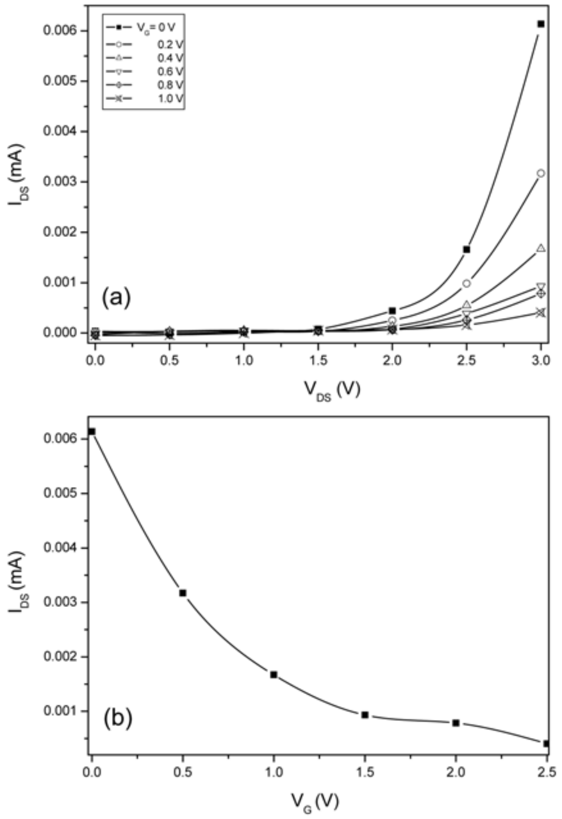


Figure 4. (a) I-V Characteristics of 1-DNP (**3**) SIT and I_{DS}-V_G curve of 1-DNP (**3**) at V_{DS} = 3V.

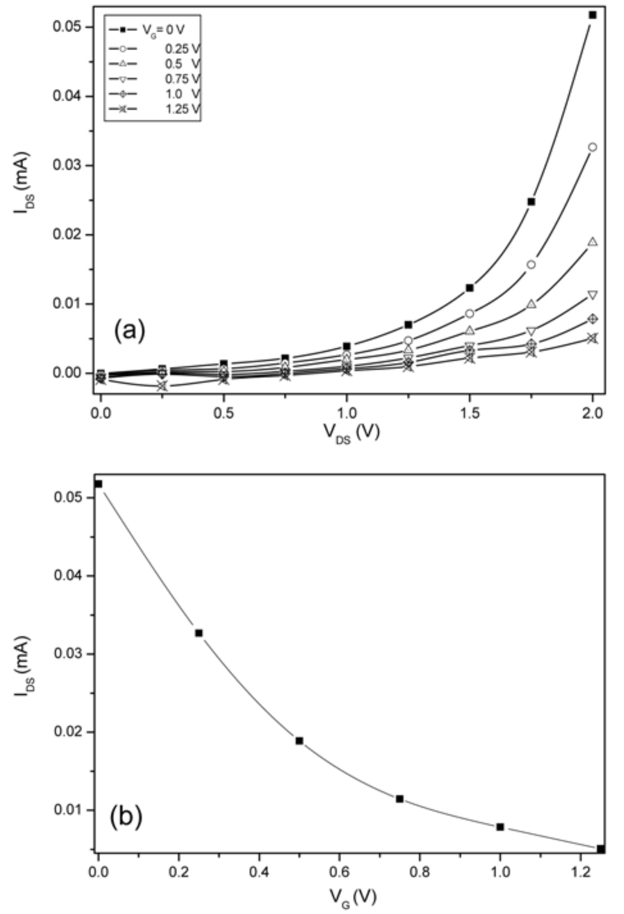


Figure 5. (a) I-V Characteristics of 2-DNP (**4**) SIT and I_{DS}-V_G curve of 2-DNP (**4**) at V_{DS} = 2V.

Table 1. Pentacene, 1-DNP (**3**) and 2-DNP (**4**)'s average on/off ratio at V_{DS} = 2V

Organic channel material	on/off ratio (average)
Pentacene	14.56
1-DNP (**3**)	36.58
2-DNP (**4**)	6.61

Further studies of molecular arrangement, aggregation and AFM surface analysis are underway.

The calculated on/off ratio values are summarized in Table 1. 1-DNP exhibited the highest value of 36.58 in this series.

We will introduce more substituent group into dinaphthyl pentacene in order to increase on/off ratio.

Conclusion

We synthesized new pentacene derivatives, 1-DNP and 2-DNP, which has twisted pentacene structure. According to link position of 1-DNP and 2-DNP, they showed different melting temperature, PL tendency, and different SIT device property.

In SIT device result, we could get pentacene on/off ratio of 7.21 at V_{DS} = 5V, 1-DNP on/off ratio of 9.92 at V_{DS} = 3V and 2-DNP on/off ratio of 6.61.

The calculated on/off ratio values are summarized at V_{DS} = 2V. 1-DNP exhibited the highest value of 36.58 in this series. Because 1-DNP has relatively more twisted structure and lower bulk conductivity, but 1-DNP device showed good gate swing property and high on/off ratio.

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