

# Upward and Downward Orientation of an Interface Dipole Monolayer on Pentacene Organic Field-Effect Transistors: A Comparison Study

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## 1. Introduction

Since the new millennium there has been a scientific boom for organic field-effect transistors (OFETs) because of their unique advantages [1]. It is well-known that the OFETs work quite different from traditional silicon based metal-oxide-semiconductor FETs (MOSFETs) [2], whose mechanism is well understood and thus design of the device has been already achieved. However, for an OFET since its carrier behavior is still not fully understood, the control of device's property is still under way. One of important solutions is the interface engineering, by virtue of Langmuir-Blodgett monolayer (LBM) or self-assembled monolayer (SAM), since it has been proved that the interfaces including electrode/organic layer interfaces and dielectric/organic layer interfaces are crucial for optimizing performance of OFET [3]. Although some primary studies have been done, less attention has been paid on electrical field effect of the interfacial dipole monolayer, which is quite strong across the thin film ( $\sim 1$  MV/cm).

Actually recently we have shown that the pentacene OFETs with an upward interfacial monolayer negatively shift threshold voltage ( $V_{th}$ ) [4], while those with a downward monolayer have more positive  $V_{th}$  [5]. Though the shift has been quantitatively interpreted based on the idea of importance of dielectric-semiconductor interface, the effect of dipole orientation, namely the direction of interfacial electric field has not been fully understood. Hence, in the present report, to further understand the effect of interface monolayer, by making a comparison study of dipole orientation of interfacial monolayer between organic active layer and dielectric layer, we concentrate the electrical field effect of interfacial monolayer on pentacene OFETs. Results showed orientation of the monolayer and corresponding local electric field are crucial for the prominent changes in effective mobility as well as threshold voltage, etc.

## 2. Experiment

For the OFET devices, top-contact structures with or without an aligned dipole monolayer between pentacene active layer and SiO<sub>2</sub> gate insulator were used. To study the electric field effect of interface monolayer, two kinds of dipole monolayers were introduced into the pentacene OFETs with opposite orientation by the LB technique, as sketched in Fig. 1(a) and (b) compared with reference sample without interfacial monolayer (not shown here). A highly doped n-type silicon wafer with 100 nm thick insu-

lating layer of thermally grown SiO<sub>2</sub> was directly used as the substrate after UV-ozone cleaning (Nippon Laser & Electronics Lab., NL-UV 253S) to get a quite hydrophilic surface. For the pentacene OFETs with an upward interface monolayer, we used dipalmitoyl-phosphatidylcholine (DPPC, purchased from Sigma-Aldrich company) Langmuir monolayer, while for the OFET with a downward interface monolayer, we chose a copolymer Langmuir monolayer of poly vinylidene fluoride and trifluoroethylene (P(VDF-TrFE) with VDF:TrFE molar ratio of 59:41, supplied by Daikin Kogyo Co. Ltd.), since they have opposite orientation of dipole moment on the water surface [6, 7]. The ways of preparing such a Langmuir monolayer were described in our previous studies [6, 7]. After a Langmuir film of condensed phase at target surface pressure of 20 mN/m was achieved on water surface at room temperature, the LB technique was applied to deposit a well-aligned monolayer onto the silicon substrate. Afterwards, pentacene (Tokyo Chemical Industry) thin film with a thickness of 100 nm was thermally evaporated onto the substrate in high vacuum less than  $2 \times 10^{-4}$  Pa. Finally, the source and drain Au electrodes with a thickness of 100 nm were thermally evaporated onto the pentacene layer at a pressure of about  $5 \times 10^{-4}$  Pa. The deposition speeds were kept constant at 0.7 Å/s for pentacene and around 4 nm/s for top gold electrodes with a quartz crystal microbalance (QCM). To estimate the contact resistance, we used certain masks to design the channel width ( $W$ ) to 3 mm and channel length ( $L$ ) varied from 30 to 100 μm. Meanwhile, a reference sample without the dipole monolayer was prepared at the same time. The current-voltage ( $I$ - $V$ ) characteristics of the OFET devices were measured using two source meters (Keithley Instruments, Inc., type 2400) in dark under ambient atmosphere.

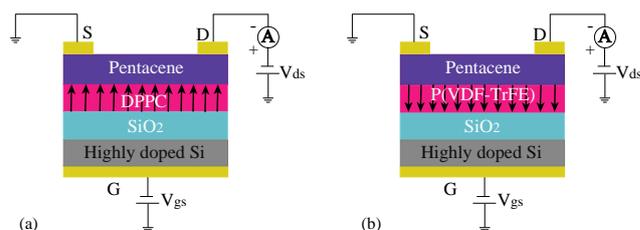


Fig. 1 Sketch of top-contact pentacene OFET structures (a) with an upward dipole monolayer, and (b) with an opposite downward dipole monolayer aligned at pentacene - SiO<sub>2</sub> interface for  $I$ - $V$  measurement.

### 3. Results and discussion

Figure 2 shows a typical transfer characteristics of the OFET with and without the dipole monolayer. Obviously we observe an impressive decrease of current in the presence of dipole monolayer, no matter what the orientation of the dipoles. This indicates in our case in the presence of dipole monolayer the pentacene OFETs have lower carrier mobility. In addition, there is a large threshold voltage shift. Actually the large shift ( $\Delta V_{th}$ ) can be well explained by our previously proposed model [4]

$$\Delta V_{th} \approx -\frac{P_s}{\epsilon_0 \epsilon_d} (t_s + t_g), \quad (1)$$

where  $P_s$  and  $\epsilon_d$  are spontaneous polarization and relative permittivity of the dipole monolayer,  $\epsilon_0$  is the vacuum permittivity,  $t_s$  and  $t_g$  are thickness of organic semiconductor (pentacene) and gate insulator, respectively. The slope of  $P_s/\epsilon_0 \epsilon_d$  represents the local electric field at the interface generated by the dipole monolayer, which is quite strong (around 1 MV/cm [4]). With the equation and parameters from Table 1, the expected threshold voltage shift due to the presence of DPPC dipole monolayer is around -22 V, and the extracted value is about -26 V (from 0.4 V for reference sample to -25.8 V for DPPC case, see Fig. 2). Likewise, the positive threshold voltage shift of 9.6 V could also be quantitatively interpreted in the case of P(VDF-TrFE) dipole monolayer ( $V_{th} = 10V$ ). Furthermore, it is necessary to point out that the positive and negative shift of threshold voltage represent different directions of local electric field at pentacene - SiO<sub>2</sub> interface, which are generated by the downward and upward dipole monolayer, respectively. Detailed analysis of subthreshold slope in subthreshold region and contact resistance as well as channel conductance in linear region as show in Table 1 revealed they have totally different carrier injection and transport mechanism. For pentacene OFET with upward orientation of dipole monolayer, there is an injection limited current condition, while for the inverse case there is a space charge limited current condition, which is also valid for the reference sample. These findings are found to have close relation to the orientation of dipole monolayer and give hints to design desired devices.

### 4. Conclusions

In the present study, we intensively investigated the current-voltage characteristics of pentacene OFETs with a well-aligned interfacial monolayer having preferred dipole orientation by LB technique. The comparison results

showed the orientation of interfacial dipole monolayer profoundly and directly influences properties of the pentacene OFETs. The observations reveal the strong interfacial electric field is crucial in organic devices.

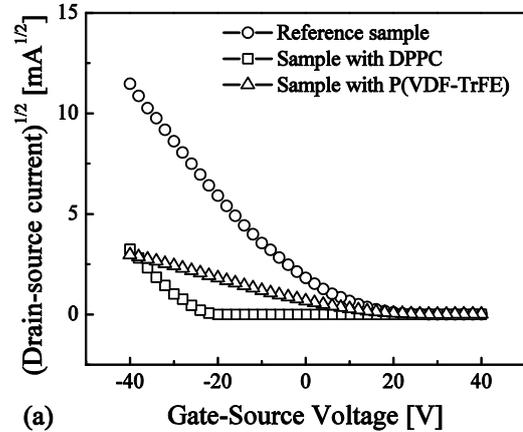


Fig. 2 Transfer characteristics of pentacene OFETs with an upward (DPPC) and downward (P(VDF-TrFE)) interface dipole monolayer between pentacene and gate insulator of silicon oxide, compared with reference sample without the monolayer.

### Acknowledgements

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Table 1. Parameters for the dipole monolayers and properties of corresponding pentacene OFET devices estimated from transfer characteristics.

Interface monolayer	$P$ [ $\mu\text{C}/\text{cm}^2$ ]	$\epsilon_r$	$\mu_{eff}$ [ $\times 10^{-2} \text{cm}^2/\text{V}\cdot\text{s}$ ]	$V_{th}$ [V]	S.S. <sup>a</sup> [V/decade]	On/off ratio <sup>a</sup>	$R_c$ <sup>a,b</sup> [M $\Omega$ ]	$g_d$ <sup>a,b</sup> [ $\mu\text{S}$ ]
No	0	NA	$9.85 \pm 0.51$	$-2.1 \pm 3.6$	2.0	$10^6$	0.3	5.1
DPPC	0.2 <sup>[4]</sup>	2 <sup>[8]</sup>	$5.76 \pm 0.41$	$-26.2 \pm 1.5$	0.7	$>10^6$	1.0	2.2
P(VDF-TrFE)	0.5 <sup>[7]</sup>	10 <sup>[9]</sup>	$0.42 \pm 0.12$	$6.6 \pm 4.2$	3.8	$10^5$	0.1	1.2

<sup>a</sup> Parameters for the samples with channel length of 60  $\mu\text{m}$

<sup>b</sup> Values at  $V_{gs} = -40$  V