



# Fabrication Guide

Controlling the crystallisation of TIPS-pentacene with drop casting angle

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## Overview

Crystalline films of small molecules have produced some of the highest mobilities for organic transistors reported in the literature so far.

For solution processed OFETs, high performance small molecules transistors can be obtained providing that the conductive channel consists of well-ordered, almost defect-free crystallite domains (or, desirably, a single crystal) whose molecules are oriented with the backbone perpendicular to the channel length in order to allow for maximum molecular orbital overlap along the direction of highest mobility.

TIPS-pentacene, a soluble small molecule obtained by adding two identical side chains to the insoluble pentacene, can be grown as a highly ordered crystal by, for example, drop casting, blade coating or dip coating. The quality of the resulting crystal strongly depends on the purity of the material, solvent choice, chemical and physical properties of the substrate, processing temperature and, most importantly, crystallisation time.

In this report, we describe a drop casting protocol for fabricating top contact OFETs affording mobility as high as  $\sim 0.92 \text{ cm}^2/(\text{V}\cdot\text{s})$ . The TIPS-pentacene film is obtained through a slow crystallisation growth at raised temperature ( $50^\circ\text{C}$ ), in a solvent-saturated ambient, on top of silicon oxide substrates treated with phenyl-terminated silane molecules as well as methyl-terminated ones, with two different architectures.

Ossila Prefabricated OFET Test Chips (Low-Density) with gold source-drain contacts:

- Substrate size:  $20 \times 15 \text{ mm}$
- Gate conductivity:  $1\text{-}30 \Omega\cdot\text{cm}$  (Boron doped)
- Silicon oxide thickness:  $300 \text{ nm}$
- Device per substrates: five; common gate
- Channel length:  $30 \mu\text{m}$
- Channel width:  $1000 \mu\text{m}$

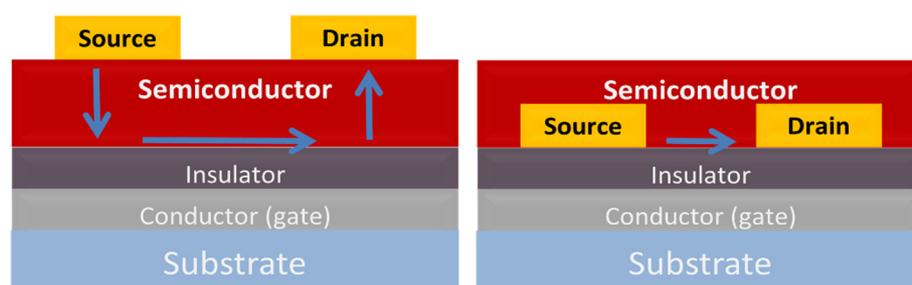


Figure 1. Left side: top contact/bottom gate OFET architecture; right side: bottom contact/bottom gate architecture. The arrows represent the carriers path from source to drain.

## Experimental

The direction of the crystal growth, and therefore the orientation of the crystal axes (with respect to the channel length), can be controlled by imposing a preferential drying direction to the drop casted solution. This is achieved by positioning the substrate inside a Petri dish at a 3.5° angle with respect to the horizontal line of a perfectly flat hot plate, see Fig 2 and 3.

Substrates are placed inside the Petri dish in a manner such that the length of the channel is perpendicular to the receding direction of the drying solution, see Fig 3. Drop casting is carried out using a pipette with the substrate at a temperature of 50 °C; the lid was put back immediately afterward to trap the solvent vapour and create vapour saturated condition inside the Petri dish.

Note. The Petri dish allows us to easily achieve vapour saturated conditions; however, it is not possible to evacuate the solvent condensing on the top of the lid. Caution must then be taken when removing the lid since the solvent can drop back onto the substrate and damage the crystal.

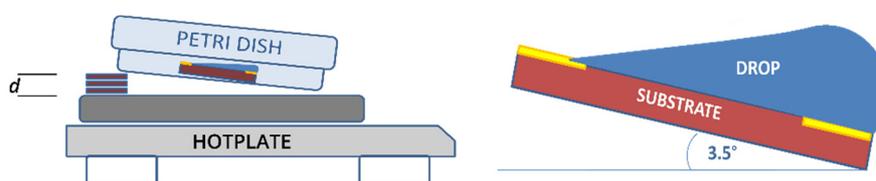


Figure 2. For a 5-mm Petri dish, a 3.5° slope is obtained when  $d$  is 3.5 mm. The temperature inside the dish was measured using a surface thermometer.

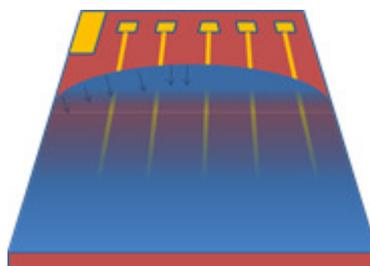


Figure 3. A meniscus perpendicular to the channel length is a necessary condition to obtain the optimal crystallisation direction for charge transport.

### TIPS-pentacene Solution Preparation

Preparation of the solution took place in a glove box ( $O_2 < 10$  PPM;  $H_2O < 0.1$  PPM).

- TIPS-pentacene dissolved in anhydrous Toluene, 10 mg/ml
- Vial is placed on a hotplate at 60°C for 1 hour at 1000 rpm with a magnetic stirrer
- Solution was then filtered with 0.45  $\mu$ m filter into a new vial
- Prior to decanting the stock solution was placed on a hotplate at 60°C for 1 hour
- Required amount was diluted with anhydrous Toluene 2mg/ml

The solution used for drop casting was prepared only when needed. TIPS-pentacene is relatively resilient to oxidation at room temperature; however, long permanence in normal ambient condition (>24 hrs) can result in molecular degradation and increased water content of the solution.

## Bottom-gate, top-contact (BGTC) architecture

### Substrate Cleaning

- Sonicate for 5 min in 1% v/v solution of Hellmanex III in deionised (DI) water in a sonic bath with hot water
- Rinse twice in hot water
- Sonicate 5 min in isopropyl alcohol (IPA) in a sonic bath with hot water
- Rinse twice in DI water (cold)
- Store substrates in DI water
- UV Ozone treatment for 5 min
- PTES treatment of trichloro(phenethyl)silane, 3 mMol in toluene, for 15 hrs in glove box at 90 °C
- Rinse substrates twice in glove box with toluene, then blow-dry and bring outside a glove box
- Sonicate in toluene for 10 minutes
- Blow dry, rinse with running IPA, blow dry
- Put in glove box on hotplate at 150 °C for 5 min

### TIPS-pentacene drop casting

- Pipette 50 µl of TIPS-pentacene solution (2 mg/ml) onto the substrate
- Cover with glass lid for 5 minutes on a hot plate at 50 °C
- Switch off the hot plate, swap the glass lid with filter paper and leave for one minute to cool down
- Remove the Petri dish from the hot plate and leave the substrate in Petri dish to cool down for extra three minutes
- Wipe clean the substrate with the exception of the area over which the drain and source are to be deposited, using cleanroom swabs dipped in a small volume of solvent
- Load the evaporation stack

### Deposition of top contact gold

- Load stack into thermal evaporator
- Leave the substrates for 15 hrs in vacuum ( $2.3 \times 10^{-6}$  mBar)
- Deposition of about 100 nm of gold on TIPS-pentacene
- Cool for 1 hour under vacuum

### Measurement

- Measure OFETs under air and light.

## Bottom-gate, bottom-contact (BGBC) architecture

### Cleaning routine

- See above

### Device fabrication

- Cr (2 nm) adhesion layer followed by Au (70 nm) thermally vacuum evaporated at  $P \approx 3 \cdot 10^{-6}$  mBar through Ossila Source-Drain Deposition Mask for Low Density OFETs inside Ossila Evaporation Stack for Low-Density OFETs.
- UV Ozone treatment for 5 min prior to surface treatments

### PFBT treatment

- Submerge substrates into 5 mMol PFBT solution in toluene (use IPA/ethanol instead) for 2 min (in fume hood)
- Clean twice with IPA
- Blow dry with nitrogen gun

### HMDS treatment

HMDS was used instead of PTES for the BGBC due to the presence of Aluminium contacts on an earlier design of the Ossila OFET test chips

- Place the substrate in spin coater within glove box
- Pipette 30  $\mu$ l of HMDS (high purity grade, Sigma Aldrich) directly on the surface of the test chip
- Waiting 30 seconds before spinning at 2000 rpm for 2 min
  - I. After 0.5 seconds, spin coat 1 ml of chlorobenzene on substrate to wash the excess HMDS off

### TIPS-pentacene drop casting

- The TIPS-pentacene crystallisation is carried out in the same manner as above

## Results

### Bottom-gate, top-contact OFETs

The best device afforded a mobility of 0.928  $\text{cm}^2/\text{Vs}$  (PTES surface treatment). On this particular device, the TIPS-pentacene crystallised with the main crystallisation axis perpendicular to the channel length, which is the direction of greatest intermolecular overlap and therefore charge transport. The second-best group of working devices were showing mobility in the range of 0.20-0.4  $\text{cm}^2/\text{Vs}$ , with the worst performing devices giving mobility in the range of 0.1 to 0.2  $\text{cm}^2/\text{Vs}$ .

Due to the very simple experimental set-up, this lack of uniformity is not surprising. The high mobility of TIPS-pentacene is a direct consequence of the quality of the crystals. However, as for any highly ordered structure, the mobility is also highly anisotropic. Therefore high mobility and consistency can be achieved only if

1. well-ordered single crystal or crystallite domains are consistently grown over the substrates;
2. the crystal are oriented in such a way that the mobility is maximum along the drain-source direction;
3. the single-crystal boundaries should be parallel to the channel length since any crystal boundary/defect or crack perpendicular to the channel length acts as a bottleneck for charge transport.

In addition, Dektak measurement showed a crystal thickness of approximately 700 nm, which means that the carriers are forced to travel twice across the thick crystal bulk before being collected at the drain (see Figure 1). A thick crystal can be detrimental to charge transport since it increases the likelihood of a carrier being trapped by bulk defects. Further optimisation is then required to improve the present protocols in term of crystal thickness and uniformity.

Figure 4, which depicts the best performance OFET, shows that the boundaries of the crystals forming the crystallite domain have boundary parallel to the channel length. Cracks perpendicular to the growth direction are also clearly visible. These cracks act as defects (bottleneck for charge transport) and must be minimised (or, if possible, avoided) in order to obtain high performing OFETs.

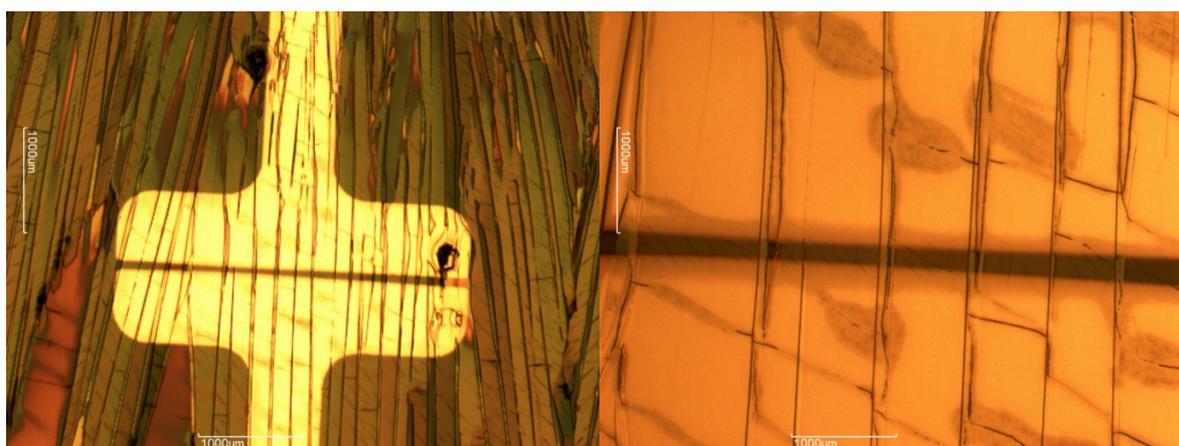


Figure 4. Left: Microscopic photograph of the best performing bottom gate/top contact architecture. Right: detail of the channel region for the same device.

The table below summarises the mobility and threshold voltage for the three PTES-treated substrates. The I-V output currents and the saturation mode transfer characteristics for the best performing OFETs are shown in Figure 5 below.

Substrate No.	Measurement	Device 1	Device 2	Device 3	Device 4	Device 5
Substrate 1	$\mu$ (cm <sup>2</sup> /Vs)	-	0.928	-	-	0.145
	$V_T$ (V)	-	-3.53	-	-	+2.25
Substrate 2	$\mu$ (cm <sup>2</sup> /Vs)	0.174	0.148	0.307	0.105	0.28
	$V_T$ (V)	+0.27	-4.67	-3.21	-6.78	-0.76
Substrate 2	$\mu$ (cm <sup>2</sup> /Vs)	0.377	0.322	0.269	0.252	-
	$V_T$ (V)	-12.99	-9.45	-10.42	-7.57	-

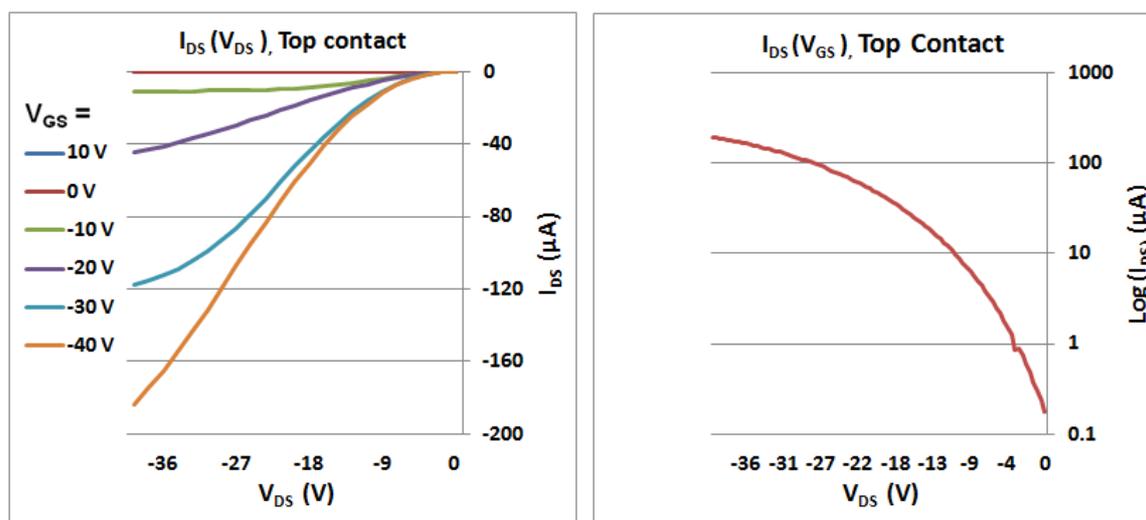


Figure 5. Left: Output currents of the best performing TOP Contact OFET for six different gate voltages. Right: Transfer characteristic in saturation mode ( $V_{DS} = -40$  V).

## Bottom gate/Bottom contact OFETs

The maximum mobility achieved with this architecture was  $0.38 \text{ cm}^2/(\text{Vs})$ . However, the threshold voltages were relatively high, ranging from -20 to -30 V.

An example of Bottom gate/Top Contact substrates is presented in Figure 6 below. A higher mobility is achieved when large area of monocrystals between source and drain electrodes are present (see reddish colour).

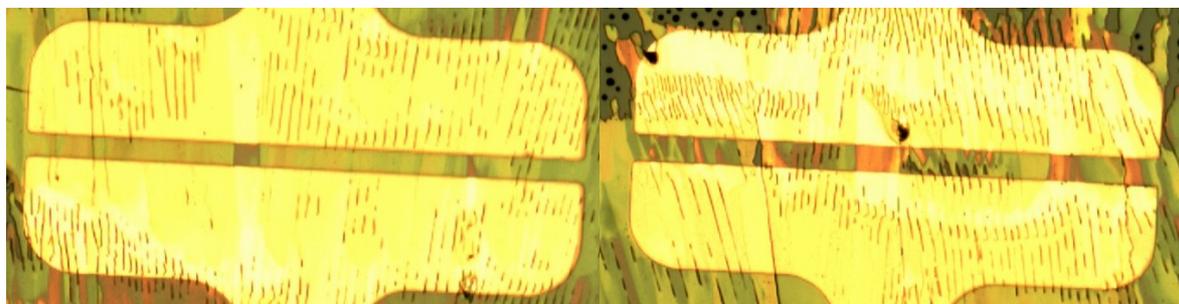


Figure 6. Two separate OFET devices on a single bottom-gate, bottom-contact OFET substrate showing different crystal growth of TIPS-pentacene. Left: Device with fewer monocrystals across the channel where  $\mu = 0.05 \text{ cm}^2/(\text{Vs})$ . Right: Device with more monocrystals across the channel and  $\mu = 0.30 \text{ cm}^2/(\text{Vs})$ .

## References

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