Enhancing long-term device stability using thin film blends of small molecule semiconductors and insulating polymers to trap surface-induced polymorphs

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The lack of long-term stability in thin films of organic semiconductors can often be caused by the low structural stability of metastable phases that are frequently formed upon deposition on a substrate surface. Here, we fabricated thin films of 2,7-dioctyloxy[1]benzothieno[3,2-b]benzothiophene (C₈O-BTBT-OC₈) and blends of this material with polystyrene by solution shearing. Both types of films exhibited the metastable surface-induced herringbone phase (SIP) in all the tested coating conditions. The blended films revealed a higher device performance with a field-effect mobility close to 1 cm²/Vs, a threshold voltage close to 0 V and an on/off current ratio above 10⁷. In situ lattice phonon Raman microscopy was used to study the stability of the SIP polymorph. It was found that films based on only C₈O-BTBT-OC₈ slowly evolved

to the Bulk cofacial phase, significantly impacting device electrical performance. In contrast, the blended films stabilized the SIP phase, leading to devices that maintained a high performance over 1.5 years. This work demonstrates that blending small-molecule organic semiconductors with insulating binding polymers can trap metastable polymorphs which can lead to devices with both improved performance and long-term stability.

1. Introduction

Organic printed electronics is an emerging field for device technology. The active material in such printed devices is an organic semiconductor (OSC), which can be either a conjugated polymer or a small conjugated molecule. Despite the impressive charge carrier mobilities that have been reported for OSCs used in organic field-effect transistors (OFETs) in recent years, two major challenging issues remain unsolved in order to implement these devices in real applications: reproducibility and long-term stability.^[1]

In thin films of small molecule OSCs the charge transport properties are governed by two parameters: the reorganization energy and the intermolecular electronic couplings.^[2] The first parameter is related to the energy loss of a charge carrier transfer due to conformational changes and, hence, is mainly related to the molecular structure. On the other hand, the intermolecular electronic couplings between adjacent molecules evaluate the strength of the interactions between the electronic levels of the molecules involved in the charge transfer and is determined by the molecular packing in the solid state.^[3,4] Since molecules are bound together through weak van der Waals interactions, they are prone to polymorphism.^[5-9] Slight differences between polymorphs can lead to dramatic changes in their mobilities.^[10-12] Further, some technologically desirable polymorphs are metastable^[13,14] but can degrade with time to the most thermodynamically stable form, thus significantly impacting device performance. Thus,

controlling the polymorphism of OSCs is of paramount importance to realize high device reproducibility.^[15]

Among the wide spectrum of studied OSCs, one of the most promising families is based on benzothieno[3,2-b][1]benzothiophene (BTBT), which has led to OFETs with excellent device mobilities.^[16,17] The functionalisation of the BTBT core with solubilising groups has been shown to be a promising route to make this material compatible with printing techniques.^[18] We focus here on the OSC 2,7-bis(octyloxy)[1]benzothieno[3,2-b]-benzothiophene (C₈O-BTBT-OC₈, **Figure 1a**).^[19] It has been reported that the Bulk C₈O-BTBT-OC₈ phase crystallizes in a triclinic P-1 system with two molecules per unit cell presenting a displaced cofacial stacking (Figure 1b).^[20] A surface-induced phase (SIP) has also been found for this material.^[21] which crystallizes in a monoclinic P2₁/c structure with a herringbone packing (**Figure 1b**). However, it has been observed that spin coated thin films of C₈O-BTBT-OC₈ exhibiting the SIP phase, slowly convert to the Bulk form over a period of six months.^[20]

In this work, we fabricated OFETs based on C₈O-BTBT-OC₈ and blends of this OSC with polystyrene (PS) employing a scalable solution shearing technique. In all cases we could controllably obtain the metastable SIP phase by modifying the film deposition parameters. The Bulk phase on surface could be prepared as single crystals only by drop casting and slow evaporation. Our transport measurements further showed that the SIP phase is more suitable than the Bulk phase for charge transport. Importantly, by blending the OSC with PS, we were able to persistently trap the SIP polymorph. Our work thus demonstrates that using blends of OSCs can be a practical and effective means to achieve long-term device stability with promising metastable polymorphs.

2. Results and Discussion

In order to compare the hole transport tendencies in the Bulk and SIP polymorphs of C₈O-BTBT-OC₈, we first analyzed all independent pairwise HOMO-HOMO (Highest occupied

molecular orbital) intermolecular electronic couplings (J_{HOMO}) in the two crystal structures using density functional theory (DFT) based calculations (see **Figure 1b** and **Supp.Info.**). For the Bulk phase we find a highly anisotropic one dimensional (1D) electronic structure with only a single dominant J_{HOMO} value of 42 meV in a direction parallel to the a -axis of the crystal with all other J_{HOMO} values being ≤ 6 meV.^[20] In contrast, we find that the SIP polymorphic phase has two main independent intermolecular couplings with moderate J_{HOMO} values of 12-13 meV, which span over three different directions in the ab plane of the material, indicative of a more 2D electronic isotropy. Thus, although a larger electronic coupling is found in the Bulk phase, the electronic dimensionality in the SIP phase is enhanced, which is also a key aspect to achieve higher device performance.^[22]

Solutions of C₈O-BTBT-OC₈ and C₈O-BTBT-OC₈:PS (4:1) in chlorobenzene 2 % wt. were prepared. Two types of PS of different molecular weight were employed, namely, PS3K ($M_w = 3000$ g/mol) and PS100K ($M_w = 100000$ g/mol). These solutions were deposited by Bar-Assisted Meniscus Shearing (BAMS) on a Si/SiO₂ substrate with interdigitated gold electrodes at a coating speed of 10 mm/s and at a stage temperature of 105 °C (for details see experimental section). Such a technique has been proven to give rise to homogenous and crystalline large area thin films.^[23,24] Interestingly, BAMS is also appealing due to its compatibility with high throughput roll-to-roll processes, of great interest for large-area applications. In these conditions and with the three ink formulations (i.e., C₈O-BTBT-OC₈, C₈O-BTBT-OC₈:PS3K and C₈O-BTBT-OC₈:PS100K) uniform and crystalline films were obtained (**Figure 2a** and **Figure S1**), which were subsequently electrically characterized as active layers in OFETs. **Figures 2b-c** show representative transfer and output characteristics of the device based on C₈O-BTBT-OC₈:PS100K (see **Figure S2** for the electrical characteristics of the devices with the other two formulations) elucidating the efficient p-type behavior of the OSC layer. The devices based on only the bare OSC exhibited an average hole mobility (μ) of 0.09 cm²/Vs and a threshold voltage (V_{TH}) of 6.9 V, indicative of some unintentional doping. Remarkably, the

devices based on blends of PS3K and PS100K revealed a significantly improved performance with average μ values of 0.43 and 0.9 cm²/Vs, respectively, and a V_{TH} of -0.9 V in both cases. In the transfer and output characteristics (**Figures 2b-c**) some non-idealities commonly found in OFETs can be observed, which can be related to contact effects and charge carrier density mobility dependence.^[25–28] The devices based on blends also showed a sharper switch on (small sub-threshold swing), which can be related to a lower density of traps at the OSC/dielectric interface (**Table S1**).^[29,30] Further, the on/off ratio was very high, exceeding 10⁷ in the devices based on blends of PS100K. Thus, clearly the blending of the OSC with PS gives rise to higher performing devices with μ values of up to one order of magnitude higher with respect to the devices based on only the bare OSC.

In order to gain insights into the thin films structural properties, we analysed which polymorphs were present in the prepared solution-sheared films. The two known C₈O-BTBT-OC₈ polymorphs (i.e., SIP and Bulk) have a completely different crystal packing, nevertheless, when they crystallize on a Si/SiO₂ surface in thin film, they both exhibit a stand-up organization (i.e., the molecules are oriented with their long molecular axis perpendicular to the substrate). In such a case, the use of common out-of-plane X-ray diffraction (XRD) is not enough to distinguish between the two phases because they display an almost identical out-of-plane axis length.^[21] Accordingly, the XRD measurements of the films were similar and displayed only the reflections corresponding to the (00l) family, confirming that the *ab* plane is parallel to the substrate (**Figure S3**). A spectroscopic study by using mid-infrared and lattice phonon Raman microscopy has been previously reported to be a suitable approach for recognizing the Bulk and SIP phases of C₈O-BTBT-OC₈.^[19,31] Therefore, the phase of all the freshly fabricated thin films was characterized by Polarization-Modulated Infrared Reflection Absorption Spectroscopy (PM-IRRAS). Thereby, phase differentiation can be achieved as the absorption peak corresponding to the aromatic quadrant stretching is located differently for the SIP phase, 1605

cm^{-1} , and for the Bulk phase, 1610 cm^{-1} .^[31] The direct comparison of the PM-IRRAS spectra obtained for the our-prepared thin-films with those previously the reported for the SIP and Bulk phases confirmed that, in all the cases, the SIP phase was formed and no traces of the Bulk phase were identified (**Figure 2d**).

In previous work, we reported that by modifying the substrate temperature and the shearing speed during the thin film preparation, it was possible to tune OSC polymorph formation to produce either a kinetically stable or the thermodynamically stable phase.^[15,32] Therefore, in this work the $\text{C}_8\text{O-BTBT-OC}_8$ and $\text{C}_8\text{O-BTBT-OC}_8\text{:PS100K}$ ink solutions were deposited at three coating speeds (*i.e.*, 0.1, 1, 5, 10 $\text{mm}\cdot\text{s}^{-1}$) and in the temperature range 25-125 °C. It was observed that the domain size, homogeneity and directionality of the crystallites are strongly dependent on the employed deposition parameters (see section 5 in Supporting Info). The most homogeneous films were found at low/intermediate speed when the temperature was low and at high speed when the temperature was high. Thus, the best films were obtained when the deposition speed and temperature led to an instantaneous drying of the solvent. In addition, only some of the thin films prepared at the lowest speed (*i.e.*, 0.1 $\text{mm}\cdot\text{s}^{-1}$) showed some preferential alignment of the crystallites.

In **Figure S10**, the μ of all the thin films fabricated at different temperatures and speeds are displayed. Generally, we again found that the devices based on blends tend to give rise to better OFET performances. Remarkably, the PM-IRRAS measurements performed on all the thin-films displayed the same absorption peak corresponding to the SIP phase. Hence, contrary to previously reported works,^[15,32] even when a low deposition speed and low temperature were employed to deposit the films by BAMS, the Bulk thermodynamic phase was never formed.

A key issue is to understand the polymorphic stability of the promising metastable SIP phases, since transformation to the thermodynamically favoured Bulk phase would directly impact device performance. **Figure 3** (top) shows the polarized optical microscopy (POM) images of

the thin films based on the bare OSC and blends of the OSC with PS3K and PS100K (deposited at 10 mm/s and 105 °C) taken on the freshly deposited samples and after 3 months and 1.5 years of storage in atmospheric conditions. Thin films of C₈O-BTBT-OC₈ are less smooth than the blended films with smaller crystal domains, and after 3 months the films suffer an significant dewetting effect, as previously reported for similar derivatives (**Figure 3**).^[33–35] After 1.5 years a recrystallization process takes place and clearly defined crystals are observed on the surface which belong to the Bulk phase, as previously observed in spin-coated films of C₈O-BTBT-OC₈ (**Figure S11 and S12**).^[21] In the case of the thin films based on the lower molecular weight PS3K some morphological changes were observed after 3 months, although the films continued to be uniform and continuous (**Figure 3**). To investigate the nature of these morphology variations at the micrometric scale we analyzed the lattice phonon Raman modes. Lattice phonon Raman spectroscopy has been reported to be a very sensitive tool to study of polymorphism in OSCs^[9,36], even for very similar molecular packings.^[37] Raman in the low wavenumber region (10-150 cm⁻¹) probes the dynamics of the crystal lattice and each structure has its peculiar unambiguous fingerprint. Analyzing two regions of the C₈O-BTBT-OC₈:PS3K films which showed distinct morphologies (i.e., region with unaltered continuous film and areas with defects highlighted with a red circle in the POM image in **Figure 3**), a different signal in the low Raman shift region was detected, giving the hint that a structural change had occurred. The Raman spectrum of the continuous films coincides with the signal reported by Bedoya-Martinez et al.^[19] for the SIP phase, whereas the spectrum of the defects are in agreement with the signal of the Bulk phase (**Figure 3** (bottom)). It is worth noting that this transformation is very slow and even after 1.5 years no significant conversion in these films is observed. On the other hand, the films with the higher molecular weight PS100K did not show any change in morphology for over 1.5 years and only displayed the SIP phase signal in their Raman spectra. These results importantly indicate that processing an OSC together with a binding polymer

results not only in an improvement of the OFET performance, but it can enhance the phase stability, especially when higher molecular weight binding polymers are employed.

As measured by AFM, the pristine C₈O-BTBT-OC₈ films were laterally continuous and smooth at the micrometer scale, exhibiting 2-3 almost complete flat layers of one molecule thickness (≈ 3 nm) on the upper film surface. Further, a quasi-hexagonal molecular order was observed consistent with the herringbone structure of the *ab* plane of the SIP phase, *i.e.*, with the *c* axis perpendicular to the surface (see **Figure S15** in the Supporting Information). Conversely, in the case of the blended films with PS3K and PS100K, a distinct morphology is observed with some common characteristics, but subtle differences between the two (**Figure 4**). Firstly, in both cases, the lack of contrast in the frequency shift (insets in **Figure 4b, 4d**) and lateral force images (see **Figure S16** in the Supporting Information), signals extremely sensitive to chemical variations,^[34,38] reflects the unique composition of all layer levels exposed at the surface. Secondly, these levels are separated by ≈ 3 nm (or multiples) high steps that coincides with the molecular length, confirming the standing-up configuration within each layer. Therefore, this is in agreement with the formation of C₈O-BTBT-OC₈ stacked layers. In fact, high resolution images reveal the same pseudo-hexagonal order of the herringbone packing of the SIP structure at the top-most surface in the blended films as in the pristine C₈O-BTBT-OC₈ films (**Figure 4, Figure S15** and **Figure S17** in the Supporting Information). These C₈O-BTBT-OC₈ molecular layers can be removed in a controlled manner by a layer-by-layer experiment until reaching the PS bottom layer (see **Figure 4e-f** and below). Hence, these AFM data permit concluding that the upper layers of the two blended systems consist of crystalline C₈O-BTBT-OC₈ film that covers an underlying PS layer described below.

However, the most striking features differentiating both blends are a large density of dispersed small protrusions (bright spots) in the PS3K blend (**Figure 4a, 4b**) and the presence of several micrometers long stripes, which are more evident in the PS100K (yellow ellipse in **Figure 4c** and center of **Figure 4d**). Independently of the PS molecular weight, these stripes have a quite

regular width and height (~ 150 nm and ~ 2.5 nm, respectively) and can be as long as several micrometers. The stripes form local self-organized morphologies connected to a perforated but extended flat region (see lower right part of **Figure 4d** and **Figure S16e**). As demonstrated by the layer-by-layer peeling experiment illustrated in the 3D display of **Figure 4e** (see further details in the Supporting Information), these structures arise from a buried PS-rich layer in contact with the substrate. Note the 3 nm thickness of the intentionally uncovered layers (**Figure 4f**). Similarly, buried pellets (indicative of severe layer rupture) lead to faint protrusions that are rarely seen in the PS100K blend but spread over the whole surface in the case of the PS3K blended film. All these observations are a clear evidence of vertical phase separation between C₈O-BTBT-OC₈ and PS.

The impact of the PS molecular weight on the phase separation and resulting morphology of the PS layer confined at the SiO₂ interface (*i.e.*, pellets for the PS3K blend and perforated layer plus stripes for the PS100K case) are in accordance with reports showing that the decrease in PS molecular weight explicitly promote dewetting of PS films on SiO₂.^[39] The considerable discontinuity of the buried PS3K layer seems to be at the origin of the more favorable SIP to Bulk phase transformation of C₈O-BTBT-OC₈ and leads us to suggest that the observed differences on the lateral organization of the polymer at the SiO₂ surface influence the stability of the C₈O-BTBT-OC₈:PS films over time.

The electrical stability of the devices stored in ambient conditions was also investigated (**Figure 5**). The performance of the C₈O-BTBT-OC₈ films progressively decreased with time. Although this OSC is remarkably electrically stable in environmental conditions, after one year the field-effect mobility decreased more than one order of magnitude. Such decrease in performance is accompanied by a large negative shift in the V_{TH} of around 6 V. All this is attributed to the structural and morphological changes occurring in the film that results in the accumulation of the OSC material in some areas, leaving behind SiO₂ zones free of OSC. This dewetting process

severely disturbs the conduction percolation path. Consequently, the films did not exhibit field-effect behavior any more after 300 days. In order to measure a single crystal of the Bulk phase, we crystallized the material on top of the Si/SiO₂ substrate with a pre-patterned grid of gold contacts by drop casting followed by slow evaporation and confirmed its phase by PM-IRRAS (**Figure S13** and **S14**). Unfortunately, no current was measured, which could be due to non-efficient contacts. Further, the above described anisotropic intermolecular electronic coupling of this polymorph that favours charge transport only along one direction in the plane could also be hindering the transport.

For the blended films the scenario was completely different (**Figure 5**). Both formulations showed a small enhancement in μ during the first week after preparation, probably due to some doping or small molecular re-organization. After that, although the device mobility slightly decreased with time, even after 450 days the devices were still working well, with a μ in the range 0.3-0.6 cm²/Vs and with a very low positive V_{TH} shift (*i.e.*, around 1 V), highlighting the high long-term stability of the C₈O-BTBT-OC₈ blend for OFETs (**Figure S18**). Noticeably, the small detected slow conversion from the SIP to the Bulk phase observed in the C₈O-BTBT-OC₈:PS3K films did not seem to affect the electrical performance of the OFETs during this time period.

3. Conclusions

In summary, the OSC C₈O-BTBT-OC₈ was studied as a model system for understanding and controlling polymorphism in devices. This material is known to crystallize in the Bulk phase following a 1D π -stacking arrangement. However, a metastable SIP phase has also been reported, which shows herringbone structure exhibiting significant 2D intermolecular interactions. Thin films of C₈O-BTBT-OC₈ and of this material blended with polystyrene of two different molecular weights were prepared by a solution shearing technique and studied as active layers in OFETs. The SIP phase was always formed for the large range of processing

parameters explored in this work (i.e., varying ink formulation, temperature and coating speed). The devices based on blends exhibited a significantly enhanced performance. Further, the Bulk phase was only formed as large crystals when a solution of the OSC was drop casted on the Si/SiO₂ substrate and let to evaporate very slowly. The best device performances were found for the SIP phase, and blended films exhibited up to one order of magnitude higher field-effect mobility with respect to the devices based on only the bare OSC. More importantly, we demonstrated that while the films based on only the OSC undergo a phase transformation to the Bulk phase in a time scale of months, dramatically hampering the device performance, blending the OSC with PS strongly stabilizes the SIP phase in the films. When the lower molecular weight PS was used, some small local transformation could be detected with no impact in the active layer during the time period studied (i.e., one year and a half). On the other hand, in the films prepared with the higher molecular weight PS no conversion to the Bulk phase was found. The difference in the polymorphic transformation between the two blended films is attributed to a larger discontinuity found in the lower molecular weight PS-rich layer in contact with the SiO₂ substrate. Therefore, this work clearly demonstrates that using blended OSCs can not only lead to improved device performance, but can also stabilize metastable polymorphs, of crucial importance to ensure long-term device stability.

4. Experimental Section

Device preparation: Bottom gate/bottom contact (BGBC) OFETs were fabricated starting from heavily p-doped Si/SiO₂ wafers from Si-Mat (SiO₂ of thickness 200 nm, $C = 17.25 \text{ nF/cm}^2$). Interdigitated gold electrodes (5 nm Cr, 40 nm Au) of various channel lengths ($L = 50; 100; 150; 200 \text{ }\mu\text{m}$, W/L ratio kept at 100) were pre-patterned on the Si/SiO₂ substrates by means of photolithography (Micro-Writer ML3 from Durham Magneto Optics Ltd., resolution 5 μm) without requiring the use of a shadow mask. The gold electrodes were treated for 25 minutes by Ozone cleaner and then by immersion for 15 min in a pentafluorobenzothiol (PFBT,

purchased from Sigma-Aldrich) solution (2 $\mu\text{L/mL}$ in IPA) they were functionalized by creating a self-assembled monolayer (SAM) to reduce the contact resistance.

$\text{C}_8\text{O-BTBT-OC}_8$, synthesized by the procedure previously described,^[20] and blends of this semiconductor with atactic polystyrene of molecular weights 3K and 100K g/mol (Sigma-Aldrich) in chlorobenzene (CB, Sigma-Aldrich) were deposited with the Bar-assisted meniscus shearing (BAMS) technique.^[23] The solution concentration and OSC:polymer ratio were fixed at 2% w/w and 4:1, respectively. The substrate temperature and the bar shearing speed were varied from 25 to 125 $^{\circ}\text{C}$ and from 0.1 to 10 mm/s, respectively. The final aspects of the fabricated films are displayed in Section 5 of the Supporting Information.

Single crystals of $\text{C}_8\text{O-BTBT-OC}_8$ belonging to the Bulk phase were prepared by drop casting a solution of $\text{C}_8\text{O-BTBT-OC}_8$ 2% w/w in CB on a Si/SiO₂ substrate containing pre-patterned gold square contacts (50x50 μm). The substrates were covered with a Petri dish and the solvent was left to evaporate overnight.

OFET electrical characterization: The electrical performance was assessed under ambient conditions using an Agilent B1500A semiconductor parameter analyzer coupled with a Karl SÜSS probe station. Transfer characteristics are measured both in the linear and saturation regimes, with V_D fixed at -5 V and -20 V respectively while V_G is swept between +10 V and -20 V forwards and backwards. Output characteristics are measured under constant $V_G = +5, -5, -15$ and -20 V while V_D is swept between +5 V and -20 V, also forward and backwards. The mobility and threshold voltage were extracted for the saturation regime as for the equation (1):

$$\mu_{SAT} = \frac{2L}{WC} \left(\frac{\partial \sqrt{|I_D|}}{\partial V_G} \right)^2 \quad (1)$$

Polarized optical microscopy (POM): Polarized optical microscopy (POM) images were taken with Olympus BX51 microscope equipped with polarizer and analyzer at 90° in reflection mode.

Raman: Raman spectra were recorded with a Horiba XploRA PLUS spectrometer equipped with a suitable edge filter and coupled to an Olympus BX51 confocal microscope with 100x and 10x objectives which allow for a lateral resolution lower than 1 μm with the higher magnification. This experimental configuration allows gathering information on the polymorphic composition in crystal domains of micrometric dimensions. The excitation wavelength used was the 532 nm line from a Diode-Pumped Solid State (DPSS) with a nominal power of 25 mW. The power was reduced by neutral density filters to avoid sample damage. The Horiba LabSpec 6 software was used to operate the spectrometer.

PM-IRRAS: Polarization Modulation-Infrared Reflection-Absorption Spectroscopy (PM-IRRAS) spectra were recorded by using a Bruker Vertex 70 spectrometer with PM50 module equipped with a liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) photodetector and a permanently aligned Rock Solid interferometer. To reduce absorption due to water and carbon dioxide, the spectrometer was purged by fluxing nitrogen gas. The Bruker spectroscopy software OPUS, version 4.2, was used to operate the spectrometer. Reflection measurements were performed with an aperture of 6 mm in diameter on the primary side and on aperture of the secondary side at a resolution of 2 cm^{-1} . The incidence angle was set to the Brewster angle of the SiO_2 at 57° to get the best signal-to-noise ratio.

X-ray: The thin film orientation was performed by X-ray specular diffractograms in the 2θ range $5\text{--}40^\circ$ (step size, 0.02° ; time/step, 1 s; 35mA x 45kV) were collected on a Siemens D-5000 diffractometer using as source a Tub ceramic DRX and Cu anode (λ : $\text{CuK}\alpha_1 = 1.540560 \text{ \AA}$, $\text{CuK}\alpha_2 = 1.544390 \text{ \AA}$), equipped with scintillation detector in Bragg-Brentano geometry. The program Mercury2 was used for simulation of X-ray powder patterns on the basis of single crystal data. Thin film orientation and crystal plane were identified by comparison with theoretical morphologies calculated by classic BFDH model (Bravais, Friedel, Donnay and Harker)^[40–42]

AFM: A commercially Atomic Force Microscope from Nanotec Electronica was used to do Atomic force microscopy (AFM). Data were analysed by using the WSxM freeware.^[43] We used CrPt-coated Si tips mounted in cantilevers with nominal $k = 3 \text{ N}\cdot\text{m}^{-1}$ (Budget Sensors) for dynamic measurements (topography and frequency shift) and silicon nitride tips mounted on soft cantilevers with $k \approx 0.01\text{--}0.5 \text{ N}\cdot\text{m}^{-1}$ (Veeco) for contact-mode imaging (topography and lateral force) AFM. To provide non-invasive and accurate topographic data, contact mode AFM shown here was collected (unless indicated for induced layer peeling and described in the Supporting Information) at the lowest possible load, i.e., in the attractive regime and as close as possible to the pull off force.

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Figure 1. a) Molecular structure of C₈O-BTBT-OC₈. b) Crystal structures of the Bulk and SIP polymorphs (the grey solid lines indicate the unit cell boundaries). Coloured arrows indicate directions corresponding to the largest J_{HOMO} values in each case. The rest of the J values directions are shown in the Supp. Info. Right: list of all calculated independent J_{HOMO} values listed in decreasing magnitude for each polymorph.

Figure 2. a) Polarised optical microscopy image of a C₈O-BTBT-OC₈:PS100K thin film prepared at 105 °C with a shearing speed of 10 mm/s. Corresponding transfer (dot-lines backward sweep) b) and output c) electrical characteristics of the C₈O-BTBT-OC₈:PS100K thin film prepared (L = 150 μm, W/L= 100). This device exhibited a saturation mobility of 0.92 cm²/Vs, with a reliability factor calculated according to ref. 26 of 63%. d) Representative PM-IRRAS performed on one of the solution sheared C₈O-BTBT-OC₈-based film (C₈O-BTBT-OC₈:PS100K) plotted together with the reference spectra of the SIP and Bulk phase.

Figure 3. Top. POM images of the OSC thin films based on C₈O-BTBT-OC₈, C₈O-BTBT-OC₈:PS3K and C₈O-BTBT-OC₈:PS100K (deposited at 10 mm/s and 105 °C): freshly prepared, after 3 months and after 1.5 years. Bottom. Raman spectra taken at two different regions of the C₈O-BTBT-OC₈:PS3K films three months aged. The red spectrum corresponds to the areas with defects (marked as a red circle in the POM image) and the black one to the areas which have not been affected.

Figure 4. Topographic images for C_8O -BTBT- OC_8 :PS3K (a, b) and C_8O -BTBT- OC_8 :PS100K (c, d). The bottom images correspond to the areas marked by black squares in the large-scale images. Insets: respective frequency shift images. (e) 3D representation of a topographic image of C_8O -BTBT- OC_8 :PS100K after the layer-by-layer peeling experiment detailed in the Supporting Information. (f) Topographic profile taken at the line marked in (e). Panels 1 and 2 at the bottom are representative high-resolution lateral force maps for top layers and bottom layers, as indicated in (e). The measured periodicity ($\approx 5.0 \pm 0.5$ Å and $\approx 6.5 \pm 0.5$ Å) agrees within the error with the distances between molecules in the lattice as indicated in Figure S15c ($d=4.9$ Å and $a=6$ Å).

Figure 5. a) Mobility and b) threshold voltage evolution with time of devices based on pristine C_8O -BTBT- OC_8 (blue line), C_8O -BTBT- OC_8 :PS3K (black line) and C_8O -BTBT- OC_8 :PS100K (red line) deposited at 10 mm/s and 105 °C. Notice that in the case of the pristine C_8O -BTBT- OC_8 OFETs, the devices stopped working after 300 days due to film dewetting.