Impact of the ink formulation and coating speed on the polymorphism and morphology of a solution-sheared thin film of a blended organic semiconductor

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Despite the recent encouraging advances in achieving high-performance organic field effect transistors employing meniscus-guided processing techniques compatible with roll-to-roll manufacturing, there is still a very limited knowledge about how all the coating parameters influence the thin film electrical characteristics. Here, the polymorphism and morphology of thin films of the organic semiconductor dibenzo-tetrathiafulvalene (DB-TTF) blended with polystyrene (PS) deposited by bar-assisted meniscus shearing (BAMS) were investigated in-depth by modifying the coating speed and ink formulation. It was found that all these parameters significantly affect the crystallisation process and the resulting thin film characteristics. Remarkably, pure polymorphs with optimized field-effect mobilities could be achieved only within a narrow range of conditions. The precise control of the film morphology and crystal structure is of paramount importance in order to move towards real applications achieving high device-to-device reproducibility.

1. Introduction

Small molecule organic semiconductors (OSCs) are intensely studied as active materials in organic electronics and, particularly, in organic field-effect transistors (OFETs). The solution processability of OSCs opens the possibility to employ low-cost techniques to fabricate devices which, in addition, do not require high temperatures and so can be applied on flexible plastic substrates.^[1–4] Among all solution-based deposition techniques, those that are compatible with high throughput roll-to-roll processes are of particular interest due to their potential for scaling up.^[5–8] However, preparing homogenous thin films of small molecule OSCs on large areas can be very challenging due to the dewetting issues that organic molecules often suffer. Therefore, an elegant approach that has been used in the last few years has been focused on the use of blends of OSCs with insulating binding polymers.^[9–15] Blending the OSCs typically results in an enhanced thin film processability due to the higher solution viscosity that gives rise to more uniform and reproducible films, as well as an improved thin film crystallinity caused by the vertical phase separation that takes place during the deposition of the solution.^[16–19]

Despite the recent encouraging advances in achieving high-performance OFETs employing meniscus-guided processing techniques compatible with roll-to-roll manufacturing,^[11,20–23] there is still very limited knowledge about how all the coating parameters influence the thin films morphology and polymorphism. It is well-known that it is crucial to have a high control of these two features to realise high performing OFETs with high device-to-device reproducibility.^[24–29] Intuitively, the parameter that one might think most affects the thermodynamics and kinetics of the OSC crystallisation is the deposition rate. In fact, the coating speed has been demonstrated to have a direct impact on the OSC film morphology and crystal packing since it determines the crystallisation regime.^[30–34] At low speeds, the convective regime dominates since the crystallisation takes place at the meniscus contact line as the solvent is evaporated.^[35] However, very high speeds might lead to a wet film behind

that dries after the deposition process,^[36] what is known as the Landau–Levich regime.^[37,38] Further, when using OSC blends additional formulation parameters, such as the polymer binder nature, its molecular weight or the OSC:polymer binder ratio, combined with the deposition speed might also impact the films characteristics, significantly increasing the complexity of the systems. In the field of organic semiconductors, all the crystalline phases accessed without reaching the thermodynamic equilibrium, due to the modification of parameters such as evaporation rate, solvent or surface that affect molecule–molecule, molecule–solvent and molecule–substrate interactions, are named after kinetic polymorphs.^[39,40]

The OSC dibenzo-tetrathiafulvalene (DB-TTF) has been successfully used as active material in OFETs.^[18,41–44] Blends of DB-TTF with polystyrene (PS) deposited by bar-assisted meniscus shearing (BAMS) at $10\text{ mm}\cdot\text{s}^{-1}$ has been shown to give OFETs with single crystal-like performance.^[44] However, DB-TTF displays complex polymorphism^[45,46] which has a crucial influence on the electrical performance. In a previous work, we showed that at low coating speeds ($1\text{ mm}\cdot\text{s}^{-1}$) ribbon-like films based on the thermodynamic α -phase were formed, whereas at higher speeds the kinetic plate-like γ -phase was observed.^[25]

Here, the polymorphism and morphology of DB-TTF thin films deposited by BAMS (Figure 1) were investigated in-depth at three coating speeds whilst systemically modifying the PS molecular weight and the DB-TTF:PS ratio. We demonstrate that all these parameters have an important effect on the film morphology and electrical characteristics and that films exhibiting polymorph purity might only be found under very specific and narrow conditions.

2. Results and Discussion

Thin films from solutions of DB-TTF:PS in chlorobenzene 2.5 % wt. were deposited by BAMS at three coating speeds: $1\text{ mm}\cdot\text{s}^{-1}$ (low), $10\text{ mm}\cdot\text{s}^{-1}$ (medium) and $100\text{ mm}\cdot\text{s}^{-1}$ (high). For each coating speed the DB-TTF:PS ratio (ranging from 1:3 to 3:1.) and PS molecular

weight ($PS_{MW} = 3000, 10000$ and 100000 g/mol, namely PS3K, PS10K and PS100K, respectively) were modified to analyse their influence on the morphology and crystal packing of the films. A minimum of 20 parallel and 10 perpendicular devices were measured under each condition.

2.1. Thickness dependence

The thickness and the roughness of the deposited films, which will impact their electrical properties, can be controlled by modifying the coating speed but will be also affected by the DB-TTF:PS ratio and PS_{MW} . As it can be observed in Figure 2, the thickness dependence with the coating speed is not influenced by the solution formulation. For all DB-TTF:PS ratios and all PS_{MW} , the minimum thickness is observed where the films are deposited at intermediate speed (~ 30 nm), as previously reported by Le Berre et al.^[30] This is in agreement with the fact that at this rate there is a change in the deposition regime from the evaporation regime (low speed) to the Landau–Levich regime (high speed). Further, it is worth mentioning that in the films deposited at low speed a higher thickness was found when lower PS_{MW} was used. On the contrary, at high speeds the films deposited using the most viscous solutions showed a greater thickness.

2.2. Morphology and polymorphism at different coating conditions

2.2.1. Low coating speed

The polarized optical images of the films permit to inspect the morphology and orientation of the crystalline domains. As it can be seen in the polarized optical images from Figure 3 (see Figure S1 for the corresponding bright field optical images), the thin film morphology is clearly influenced by the polymer molecular weight and the DB-TTF:PS ratio. Most of the films show stripe-shaped crystals oriented along the casting direction and, generally, smaller crystal domains are obtained with high PS_{MW} and lower content of DB-TTF. However, the films formed with PS3K and PS10K with a low proportion of semiconductor (i.e., 1:3 DB-

TTF:PS) show plate-like crystals parallel to the substrate but with random orientation in the x-y plane.

At low coating speed, the thermodynamic α -phase should be energetically more favoured. Nevertheless, other aspects that can determine the polymorph formed are the ink viscosity, which determines the facility of the molecules to migrate, and the DB-TTF:PS ratio. All the prepared films were analysed by X-ray diffraction (XRD) in order to investigate the polymorphs present (Figure 4). Remarkably, the thermodynamic α -phase was only obtained in a pure form by depositing a solution of DB-TTF:PS in a 1:2 ratio blended with PS3K or PS10K or from a solution with a ratio 1:3 and PS100K. Most of the other cases exhibited the pure γ -phase, with some exceptions where the coexistence of the two polymorphs was observed (Figure 3). It should be highlighted that distinct morphologies have been achieved with films based on only the γ -phase depending on the ink formulation; although most of the γ -phase films prepared at this coating speed show long oriented stripe-shaped crystals, which are reminiscent of the α -phase shape,^[25,43] at some specific conditions the crystal morphology is modulated to the above-mentioned plate-like type.

2.2.2. Medium coating speed

When the coating speed was $10 \text{ mm}\cdot\text{s}^{-1}$, the intermediate regime was reached. This regime reflects the equilibrium between solvent evaporation and viscous drag out and gives rise to the thinnest films.^[25,30,31] Figure 5 shows the polarized optical microscopy images achieved at $10 \text{ mm}\cdot\text{s}^{-1}$ tuning the formulation of the OSC solution (see Figure S2 for their corresponding bright field optical images). Blends containing 50 % wt. of DB-TTF or less form again the previously mentioned plate-like crystallites. On the other hand, films with more than 50 % wt. of DB-TTF showed a morphology with larger crystals which were more oriented along the coating direction when PS3K and PS10K were used, that is, with the less viscous inks (Figure S3). The analysis of the domain size revealed that it decreases when the PS_{MW} increases, also

as a result of the higher viscosity of the solution, which diminishes the diffusion of the molecules limiting the crystal growth.^[47]

Regarding the crystal phase, at intermediate regime the γ -phase is always obtained at proportions below 50 % wt. of DB-TTF with respect to PS, showing its characteristic plate-like structure. The films deposited with low and medium PS_{MW} and higher DB-TTF content exhibited a mixture of the α - and γ -phases, regardless of the OSC:binding polymer ratio. However, in the films with high PS_{MW} and higher OSC content, only the γ -phase was detected as large striped crystals, probably caused by the lower diffusion of the molecules in this viscous solution that always results in the entrapment of the kinetically more favourable polymorph. Thus, also in this deposition regime two morphologies have been identified for the pure γ -phase.

2.2.3. High coating speed

Finally, when the coating speed was 100 mm·s⁻¹, the deposition regime driving the crystallisation is the Landau-Levich regime, in which the bar is drawn fast enough to leave a wet film. As it can be seen in Figure 6 (see also for the bright field optical images Figure S4), here again we find that the crystal domain size was slightly smaller when PS_{MW} was increased. Concurrently, when the DB-TTF content was increased the morphology changed from the plate-shaped crystals to spherulitic crystals due to a higher and random nucleation. Such morphology changes are more evident when the PS_{MW} is low.

In contrast to what was observed with the films deposited at low and medium coating speeds, in this regime the kinetic γ -phase is favoured when the OSC solutions are less viscous. In fact, the γ -phase always formed for PS3K showing unusual morphologies (i.e., spherulite). Additionally, the γ -polymorph was also exclusively found when inks with lower content of DB-TTF were used (< 50 % wt. with respect to PS). However, mixtures of phases were observed with the other formulations.

2.3. DB-TTF composition diagram

In order to easily visualise this complicated scenario regarding the influence of the ink formulation and coating speed on the DB-TTF polymorphism (XRD is shown in Figure 4), the polymorph composition diagram shown in Figure 7 was constructed. The γ -phase was the phase most commonly obtained by the BAMS technique. This proves that this solution shearing technique that confines the solution and promotes a fast crystallisation of the OSC tends to trap the kinetically more favourable polymorph. On the other hand, the pure thermodynamic α -phase can only be obtained in the evaporation regime (i.e., at low coating speed) under three specific conditions: with low and medium PS_{MW} and DB-TTF:PS 1:2 ratio and with high PS_{MW} and 1:3 ratio. In other words, to promote this polymorph, we have to reach thermodynamic conditions, which are not only dependent on the coating speed, but also on the ink formulation. Finally, phase mixtures were concentrated in the regions where the DB-TTF content is high (> 50 wt% DB-TTF).

2.4. The γ -phase crystal structure

The knowledge of the crystalline structure is key to be able to determine and understand the electrical characteristics of the materials.^[48–53] The crystalline structures of the α , and the less common β and δ polymorphs, of DB-TTF have been reported, but the structure of the γ -phase had not been resolved yet.^[45,46]

The γ -phase crystal structure was characterised here employing specular X-ray diffraction and grazing incidence X-ray diffraction (GIXRD). The characterisation measurements were carried out employing a film prepared using the following formulation: DB-TTF:OSC 1:2, PS3K, $10 \text{ mm}\cdot\text{s}^{-1}$. The molecules showed a crystalline film with approximately upright standing molecules on the substrate ($d = 13.47 \text{ \AA}$ from the first observed peak, Figure S5). As

seen in the electron density profile from X-ray reflectivity data, the film is well organised in the direction normal to the substrate exhibiting a periodic and ordered structure consisting of defined molecular layers. GIXRD measurements are also in accordance with a crystalline film with a strong preferred orientation with the 001 plane parallel to the SiO₂ substrate (Figure 8). A very precise unit cell determination was difficult due to experimental artefacts and errors. However, a good agreement with the data can be found to give a probable unit cell (Table 1). Noticeably, the γ -phase unit cell contains 2 molecules of DB-TTF ($Z = 2$) and the increased volume per molecule in this phase compared to the α polymorph (i.e., less densely packed) is an indication that this is a less stable polymorph. Whilst it is not possible to solve the crystal structure of the γ -phase based on these data alone, it is likely that the γ -phase has the molecules organised in a herringbone structure; this can be determined based on the dimensions of the unit cell and the knowledge that it contains two unique molecules. This differs from the α -phase which was reported to display a parallel stacked structure.^[46]

2.5. Phase mixing influence on the OFET electrical properties

Typically, phase mixture and the grain boundaries between domains of different phases have a negative impact on the device performance.^[25,54] After characterising the OFET properties of all the prepared films, we aimed at unraveling the device performance of the different polymorphs as well as the influence of the percentage of phase mixture on the device characteristics. Figure 9 illustrates the mobility values achieved for representative formulations where films of pure polymorphs or of mixture of the two polymorphs in different proportions (qualitatively evaluated by the ratio of the first XRD diffraction peaks), were formed (Figure S6 and S7). In the case of the γ -phase, devices with three different morphologies, i.e., plates, large stripes and spherulites, were selected.

It can be noticed that the pure γ -phase revealed the best electrical properties, especially when the films are formed with the plate-like morphology, giving rise to an average field-mobility of $0.18 \pm 0.04 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ (Figure 9 (condition a)). This value is between 2 and 3 times larger than the values typically obtained for evaporated γ -phase thin films.^[55] Interestingly, when α -phase traces start to be present in the γ -phase films, the mobility decreases rapidly (Figure 9 conditions (c, d, e)). Instead, when the pure α -phase is formed, an increase in the field-effect mobility is observed compared to the films with phase mixtures (Figure 9 (condition f)). The pure α -phase thin films present average mobility of $0.05 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which is around one order of magnitude lower than the maximum mobility achieved in single crystals of this polymorph.^[43,56] Although a direct comparison between the two polymorphs cannot be directly realized since the thin film morphology and grain connectivity are distinct between the two films, better mobilities have been found with the γ -phase. In fact, very often it is encountered that the herringbone packing is more suitable for charge transport than the parallel stacked one.^[57,58] Further, all these results clearly elucidate the impact that the presence of more than one polymorph in OSC films has on the device performance.

2.6. Device Anisotropy

The different film morphologies can affect the anisotropy of the field effect mobility. Therefore, in γ -phase films exhibiting different morphologies we have analysed the mobility values found in the parallel and perpendicular to the coating directions. In particular, we selected the more typical film morphologies: 1) striped domains, 2) plate-like crystalline domains and 3) spherulite formations. (Figure 10 or Table S1).

The films where striped domains formed Figure 9(a) and (b) exhibited marked mobility anisotropy; the devices with the channel length parallel (black box) to the coating direction revealed a mobility between one and two orders of magnitude higher than the orthogonal (red

box) ones. This is probably caused by the presence of more crystal grain boundaries in the perpendicular direction.

In contrast, plate-like (Figure 10(c) and (d)) and spherulitic films (Figure 10(e) and (f)) showed mobility isotropy values in the two studied axes, perpendicular (red box) or parallel (black box) to the coating direction, in agreement with the fact that in both cases the crystal domains are distributed randomly on the surface without any preferential orientation. Also, the films with lower homogeneity in the crystal domain sizes (Figure 10 (d) and (f)) give higher dispersion in the mobility values.

Finally, the α -phase was only formed pure at low coating speeds and showing one type of morphology: long stripe-shaped crystals arranged along the deposit direction. In this case, the mobility values were one order of magnitude higher in the parallel direction with respect to the perpendicular one (Table S1).

3. Conclusion

Thin films of blends of the organic semiconductor dibenzo-tetrathiafulvalene with polystyrene deposited by BAMS have been systematically investigated by varying the coating speed and the ink formulation (i.e., polymer molecular weight and OSC:PS ratio). It was found that the coating speed affects the crystallisation regime from the evaporation regime at low speed to the Landau–Levich regime at high speed. At the intermediate regime the thinner, more homogenous and higher performing films have been typically observed.

The BAMS technique generally favors the trapping of the kinetic γ -polymorph since it is a fast deposition technique. However, often a mixture of the kinetic and thermodynamic (α -phase) polymorphs is encountered, significantly hindering the device electrical characteristics. In three very specific conditions at low coating speed the pure α -phase was formed.

Interestingly, films of the same γ -polymorph have been found exhibiting three different morphologies depending on the coating conditions, which range from large stripes, plate-like

and spherulites. The best performance was found with the plate-like films which gave an isotropic mobility of around $0.2 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. The devices prepared at low speed tend to reveal higher anisotropy, giving mobility values in the direction parallel to the coating one of up to one or two orders of magnitude higher than the perpendicular ones.

In conclusion, this work elucidates the importance of understanding the phase diagram of each particular organic semiconductor in order to gain a control on the thin films morphology and crystal structure and achieve optimised and reproducible devices.

4. Experimental Section

Materials: Dibenzotetrathiafulvalene (DB-TTF, purity 97 %), polystyrene (PS, analytical standard) with different molecular weights $3 \cdot 10^3$, 10^4 and 10^5 g/mol, and chlorobenzene (CB, anhydrous 99.8%) were purchased from Sigma Aldrich and used as received. The substrates employed consisted of n-doped silicon wafer with 200 nm thick layer of SiO_2 from Si-Mat ($17.26 \text{ nF} \cdot \text{cm}^{-2}$).

Device Fabrication: Patterned electrodes were defined as interdigitated fingers by photolithography and a Cr (5 nm) and Au (40 nm) layer were deposited by thermal evaporation. The geometrical parameters were channel lengths of 25, 50, 75 and 100 μm and channel width was always set to 10 mm.

Before the deposition of the blend solutions, the substrates were cleaned in an ultrasonic bath with HPLC solvents (acetone and isopropanol) and then dried under nitrogen flow. We fabricated devices with bottom contact bottom gate (BCBG) architecture based on DB-TTF:PS blend solutions deposited by Bar-Assisted Meniscus Shearing.^[25,44] Blend solutions of DB-TTF and PS at 2.5 % (wt.) in chlorobenzene were prepared with different DB-TTF:PS ratio. The substrate temperature was kept at 105 °C during the coating process. The bar was positioned $\approx 300 \mu\text{m}$ above the substrates containing the pre-fabricated electrodes and, subsequently, it was moved to spread the solution over it at three different coating speeds 1,

10 and 100 mm s⁻¹. Note that all solutions preparation and device processing steps were carried out under ambient conditions and no post-thermal treatments were required. At least 40 devices were prepared for each combination of coating speed, molecular weight of PS and DB-TTF:PS ratio. It should also be noticed that the film morphology was identical on the electrode area than outside it, demonstrating that the gold electrodes were not influencing on the crystallization.

Device Characterization: Electrical characterizations were performed using an Agilent B1500A semiconductor device analyser at ambient conditions. For all transfer measurements the V_{DS} was -40 V. The devices were characterized extracting the field-effect mobility (μ) in the saturation regime. μ was extracted from the fitting of the I_{SD}^{1/2} vs. V_{GS}. A home-made software was employed to extract and analyse the parameters of all devices.

Thin-Film Characterization: Optical microscope images were taken using the Olympus BX51 equipped with polarizer. Powder X-ray diffraction measurements were carried out with a PANalytical X'Pert Pro MRD (Materials Research Diffractometer) diffractometer and Siemens D-5000. The used Cu K-alpha radiation was 1.54187 Å. The thickness of the films was examined by a profilometer KLA Tencor-Alphastep D500.

γ -Phase Characterization: Specular X-ray diffraction (XRD) and X-ray reflectivity (XRR) measurements were made on a PANalytical EMPYREAN reflectometer using Cu K α radiation ($\lambda = 1.54$ Å). On the primary side, a multilayer X-ray mirror was used to generate a parallel beam. On the secondary side, an anti-scatter slit and 0.02 rad Soller slit were used with a PANalytical PIXcel3D detector. Specular X-ray diffraction and XRR data are plotted as a function of q_z, the out-of-plane component of the scattering vector, with $q_z = 4\pi/\lambda \sin\Theta$, where λ is the X-ray wavelength and Θ is half of the scattering angle, 2Θ . XRR data were fitted and the electron density profile of films determined using the Stochfit software package.^[59] Grazing incidence X-ray diffraction (GIXRD) data were collected at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron, Trieste (Italy).^[60] A wavelength of

1.00 Å was used and diffracted intensities were recorded using a Pilatus 2M hybrid-pixel area detector. Generation of reciprocal space maps was performed using the home-made software package GIDVis. Unit cell indexation was performed using analytical expressions derived for the indexation of thin films with a preferred orientation and the ab-plane parallel to the substrate surface. ^[61]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. Schematic illustration of the BAMS coating technique with the molecules selected as active layer.

Figure 2. Thickness of DB - TTF:PS thin films deposited by BAMS at 105 °C and at different coating speeds, DB-TTF:PS ratios and PS_{MW} (a) PS3K, (b) PS10K and (c) PS100K.

Figure 3. Polarized optical microscopy images with crossed polarizer/analyzer setup of DB-TTF:PS films deposited by BAMS at $1 \text{ mm}\cdot\text{s}^{-1}$. All images display the films in the same orientation with respect to the coating direction. The film polymorphs are included in the bottom boxes.

Figure 4. X-ray diffraction measurements for all thin films prepared by solution shearing technique at different coating parameters and ink formulation. The gamma-phase peak appears to $\sim 6^\circ$ while that alpha phase peak appears to $\sim 8^\circ$. (a) $1 \text{ mm} \cdot \text{s}^{-1}$ PS3k, (b) $1 \text{ mm} \cdot \text{s}^{-1}$ PS10k, (c) $1 \text{ mm} \cdot \text{s}^{-1}$ PS100k, (d) $10 \text{ mm} \cdot \text{s}^{-1}$ PS3k, (e) $10 \text{ mm} \cdot \text{s}^{-1}$ PS10k, (f) $10 \text{ mm} \cdot \text{s}^{-1}$ PS100k, (g) $100 \text{ mm} \cdot \text{s}^{-1}$ PS3k, (h) $100 \text{ mm} \cdot \text{s}^{-1}$ PS10k and (i) $1 \text{ mm} \cdot \text{s}^{-1}$ PS100k.

Figure 5. Polarized optical microscopy images with crossed polarizer/analyzer setup of DB-TTF:PS films deposited by BAMS at 10 mm·s⁻¹. All images display the films in the same orientation with respect to the coating direction. The film polymorphs are included in the bottom boxes.

Figure 6. Polarized optical microscopy images with crossed polarizer/analyzer setup of DB-TTF:PS films deposited by BAMS at 100 mm·s⁻¹. All images display the films in the same orientation with respect to the coating direction. The film polymorphs are included in the bottom boxes.

Figure 7. Polymorph composition diagram showing the DB:TTF polymorph obtained when carrying the DB-TTF:PS ratio, the PS, and the coating speed. The scale is a qualitative value that represents the ratio between the intensity of the α -phase peak and total intensity peaks.

Figure 8. Reciprocal space map produced from a grazing Incidence XRD image of a DB-TTF:PS thin film showing the peaks indexed with the determined unit cell. Miller indices are provided for the most intense Bragg peaks.

Figure 9. Field-effect mobility of selected devices where different ratios of the α and γ - phase polymorphs were formed. All the explored thin films were prepared by BAMS using of solutions of DB - TTF:PS blends 2.5 wt.% at a substrate temperature of 105 ° C. (a) 10 mm·s⁻¹, DB-TTF 1:2 PS3K (plate-like crystals) (b) 10 mm·s⁻¹, DB-TTF 3:1 PS100K (long stripes) (c) 100 mm·s⁻¹, DB-TTF 3:1 PS3K (spherulites) (d) 10 mm·s⁻¹, DB-TTF 3:1 PS3K, (e) 1 mm·s⁻¹, DB-TTF 3:1 PS10K, (f) 1 mm·s⁻¹, DB-TTF 1:3 PS 100K and (g) 1 mm·s⁻¹, DB-TTF 1:2 PS3K.

Figure 10. Box data with mean values (black solid square), the median (line inside) and standard deviation (top and bottom lines) of the mobility where the active DB - TTF:PS layer with different pure γ -phase morphology. The black box represents the value of the devices printed parallel to the channel length and red box are the value of the devices printed perpendicular to the channel length. The deposition conditions of the film were (a) $1 \text{ mm} \cdot \text{s}^{-1}$, DB-TTF 2:1 PS10K, (b) $10 \text{ mm} \cdot \text{s}^{-1}$, DB-TTF 3:1 PS100K, (c) $10 \text{ mm} \cdot \text{s}^{-1}$, DB-TTF 1:2 PS3K, (d) $10 \text{ mm} \cdot \text{s}^{-1}$, DB-TTF 1:3 PS100K (e) $100 \text{ mm} \cdot \text{s}^{-1}$, DB-TTF 1:2 PS100K and (f) $100 \text{ mm} \cdot \text{s}^{-1}$, DB-TTF 2:1 PS3K.

Table 1. Experimental crystal structure data for the α and δ polymorphs of DB-TTF. The values in parentheses are the absolute errors. The experimental values of α -phase cell were extracted from reference 39.

	α -phase	γ -phase
$a(\text{\AA})$	12.082(2)	6.11
$b(\text{\AA})$	3.955(1)	8.13
$c(\text{\AA})$	14.553(2)	13.88
$\alpha(^{\circ})$	90	98.86
$\beta(^{\circ})$	114.36(1)	99.84
$\gamma(^{\circ})$	90	94.97
$V(\text{\AA}^3)$	633.494	666.71