Double Beneficial Role of Fluorinated Fullerene Dopants on Organic Thin Films Transistors: Structural Stability and Improved Performance

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ABSTRACT: The present work assesses improved carrier injection in organic field effect transistors (OFETs) by contact doping and provides fundamental insight on the multiple impacts that the dopant/semiconductor interface details have on the long-term and thermal stability of devices. We investigate donor [1]benzothieno[3,2-b]-[1]benzothiophene (BTBT) derivatives with one and two octyl side-chains attached to the core, therefore constituting asymmetric (BTBT-C8) and symmetric (C8-BTBT-C8) molecules, respectively. Our results reveal that films formed out of the asymmetric BTBT-C8 expose the same alkyl-terminated surface as the C8-BTBT-C8 films do. In both cases, the consequence of depositing fluorinated fullerene ($C_{60}F_{48}$) as molecular p-dopant is the formation of $C_{60}F_{48}$ crystalline islands decorating the step edges of the underlying semiconductor film surface. We demonstrate that local work function changes along with a peculiar nanomorphology lead to the double beneficial effect of lowering the contact resistance and providing long-term and enhanced thermal stability of the devices.

INTRODUCTION

Over the past three decades, significant research efforts have focused on improving the charge carrier mobility of thin-film organic field-effect transistors (OFETs). The investigation of structure–property relationships has underlined the strong implications of crystallinity, morphology and the importance of the two crucial interfaces: the electrode/semiconductor interface and the dielectric/semiconductor interface.^{1,2,3,4,5,6,7,8,9,10} A key strategy for enhancement of device properties is contact doping, where a dopant thin layer is incorporated at the source and drain metal/semiconductor interface.^{3,11,12} Selective electrical doping of the organic surface in contact with the electrode leads to improved charge injection by reduction of the contact resistance, where inefficient contacts represent often a serious bottleneck in OFETs.^{11,12,13,14,15} The structural integrity of doped films is a major concern because low molecular weight and planar dopant molecules may diffuse into the organic semiconductor (OSC) film and intercalate within the π -stacking,^{16,17,18,19} compromising the performance and lifetime of devices.^{20,21,22} The use of bulkier molecules as p-type dopants, as fluorinated fullerene derivatives can surmount such issues.^{23,24}

Along with the different strategies developed to improve device properties, there have been numerous advances in the synthesis of high mobility OSCs as it is the case of the benzothieno[3,2-b][1]benzothiophene (BTBT) derivatives,^{25,26,27,28} affording OFETs with field effect mobilities higher than $1.0 \text{ cm}^2/\text{Vs}$ and using diverse fabrication processes.^{29,30,31,32,33,34} Their low HOMO energy level (E_{HOMO}) has allowed air-stable electrical performance and alkyl side chain engineering has been widely applied to improve the materials' solubility for solution processability.²⁶ With the synthesis of OSCs with superior intrinsic charge transport properties and deep low-lying HOMO energy level ($E_{\text{HOMO}} \approx 5.4\text{-}5.8$),^{26,27,35} ensuring efficient charge

carrier injection by tailoring the electrode/semiconductor interface has become a stringent need.^{2,4} Besides, interfacial engineering may also reduce degradation with time due to film dewetting, a phenomenon strongly affecting the long-term stability of devices based on BTBT and related organic semiconductors.^{36,37,38,39}

Despite the importance of contact doping, very few studies have focused on specific properties of the dopant/OSC interface. Fundamental questions remain about how the physicochemical properties of the OSC surface influence the dopant/OSC interface characteristics and thereby the injection properties. Certainly, stability is a crucial aspect as well. To address these questions, we have investigated the nanoscale properties of the dopant/OSC interface and the electrical properties in the respective OFETs. As they constitute one of the most promising families of p-type OSCs used in OFETs,^{29,30,31,40} we have chosen two [1]benzothieno[3,2-b]-[1]benzothiophene (BTBT) molecules, the asymmetrically (BTBT-C8) and symmetrically (C8-BTBT-C8) alkylated derivatives, i.e., with one or two octyl side groups respectively. For efficient p-type doping, a molecule with larger electron affinity than the ionization energy of the OSC is required. Hence, as the p-type dopant, we employ here a bulky isotropic and thermally stable molecule, C₆₀F₄₈, the fluorofullerene with maximum fluorine content.⁴¹ The choice is made because the increase of fluorine entails an increase of the electron affinity up to ~5.5 eV, making this material a very strong electron acceptor.^{24,42}

We demonstrate a nanostructured morphology of the C₆₀F₄₈/OSC hetero-interface caused by the nucleation of C₆₀F₄₈ crystallites at the step edges of the underlying OSC thin film. We show that, in addition to the beneficial effect of the dopant in reducing the contact resistance of the BTBT-based OFETs, the specific morphology of the C₆₀F₄₈/OSC interface causes an outstanding

dewetting inhibition and, therefore, improvement of the stability of the films and the respective devices.

EXPERIMENTAL SECTION

BTBT-C8 and C8-BTBT-C8 were purchased from Sigma-Aldrich and used without further purification except in-situ degasification in vacuum at 120 °C for 15 min. Fluorinated fullerene C₆₀F₄₈ was synthesized as per the method developed at the Josef Stefan Institute (Slovenia).⁴³ The product was characterized by chemical analysis, electron-ionization mass spectrometry and IR-spectroscopy. The estimated purity was 95%. Thin films of few monolayers (ML) of one or the other BTBT molecules were grown on native oxide silicon surfaces via physical vapour deposition under an ultra-high-vacuum (UHV) of $\sim 10^{-8}$ mbar at room temperature (RT) at a rate of 5-9 Å/min as determined from a quartz crystal microbalance (QCM). The native oxide covered Si (100) substrates were sonicated, in acetone and ethanol for 10 min, and then annealed up to ~ 300 °C in UHV just prior to their use.

Atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) measurements were carried out under ambient conditions using a commercial head and control unit from Nanotec Electrónica S.L. KPFM was measured in the frequency modulation mode (FM-KPFM), in which the tip is excited by an ac voltage (~ 0.5 V) at a frequency ($f_{AC} \sim 0.7$ kHz) while a feedback loop adjusts the dc bias needed to nullify the frequency shift (Δf) at f_{AC} . In our setup, the voltage is applied to the tip so that the higher the surface potential the lower the local effective work function. The surface potential maps are obtained simultaneously with the topography in a single pass and confirmed in the lift mode (tens of nm), ensuring no crosstalk

between signals. CrPt-coated Si tips mounted in cantilevers with nominal $k = 3 \text{ Nm}^{-1}$ from Budget Sensors were used for dynamic measurements while Silicon Nitride tips mounted in soft cantilevers ($k \approx 0.01\text{--}0.5 \text{ Nm}^{-1}$, Veeco) for contact mode (normal and lateral force) AFM. Data were analyzed by using the WSxM freeware.⁴⁴ The contact resistance was measured by KPFM in operando devices from the potential drop at the channel/contact edges. The ohm's law gives the contact resistance at the electrode by dividing the voltage drop at the electrodes by the current flowing through the channel simultaneously collected using Keithley 2450.

Out-of-plane X-ray diffraction (XRD) and grazing incidence X-ray diffraction (GIXD) were carried out on the six-circle diffractometer at the SpLine beamline^{45,46} (BM25B at ESRF, Grenoble, France) with $\lambda = 1.2 \text{ \AA}$. XRD measurements were performed on in-situ grown films before and after evaporating $\text{C}_{60}\text{F}_{48}$ on their top. The experiments were performed in a multipurpose portable UHV-compatible chamber mounted in a vertical geometry on the six-circle multipurpose diffractometer.⁴⁷ The specular diffraction data presented in Figure 2a were measured in-situ for C8-BTBT-C8 while those in Figure 2b correspond to two different samples for BTBT-C8.

OFETs fabrication: Films of symmetric C8-BTBT-C8 ($\sim 25 \text{ nm}$) were grown as mentioned above on Si (100) substrates with 200 nm-thick silicon oxide. Top electrodes were fabricated by thermal evaporation of 30 nm gold through a mask (OSSILA) with 6 different channel lengths ($L = 30, 40, 50, 60, 80$ and $100 \text{ }\mu\text{m}$) and fixed channel width ($W = 4 \text{ }\mu\text{m}$). Devices with $\text{C}_{60}\text{F}_{48}$ under the gold contacts (contact doping) were fabricated by patterning with the same shadow mask. In addition, devices with $\text{C}_{60}\text{F}_{48}$ deposited over the entire OSC surface (including the channel) were also investigated. The electrical characterization of OFETs was performed in ambient conditions using an Agilent B1500A semiconductor device analyzer connected to the

samples with a Karl Suss probe station. The field effect mobility (μ), V_{on} , I_{on}/I_{off} ratios were calculated from the transfer curves in the saturation regime.

RESULTS AND DISCUSSION

We first present a study of the morphology and structure of pristine films of BTBT-C8 and C8-BTBT-C8 on native oxide/Si substrates. As derived from AFM and XRD the two molecules form high quality crystalline multilayers (Figure 1 and Figure 2). In the case of the symmetric C8-BTBT-C8 molecule, the heights measured by AFM for individual layers are multiples of 3 nm (Figure 1c and 1e) that coincides with the length of a single molecule and the reported standing up orientation on SiO₂ substrates.^{48,49} In full agreement with the AFM data, an interlayer spacing of 2.91 nm is obtained from the Bragg peaks observed in out-of-plane XRD data (Figure 2a). We note that (00n) Bragg peaks up to the seventh order of diffraction are visible, which is the manifestation of a (001)-oriented film with a well-ordered layered structure. The observed Kiessig fringes and Laue oscillations arise from the smoothness and coherent order of the film (Figure S1 in Supporting Information).

Figure 1. Scheme of the molecules, topographic AFM images and height profiles along with the segments in the images, for C8-BTBT-C8 (a, c, e) and BTBT-C8 (b, d, f). The nominal thickness is 27 nm and 16 nm, respectively.

On the other hand, the thin film topography of the asymmetric BTBT-C8 consists of terraces separated by steps of heights multiples of 4 nm in most cases (Figure 1d and 1f). As the length of BTBT-C8 is ~ 2 nm,^{48,49} the AFM data point to a bilayer (two molecules thick) stacking, in full agreement with the reported bulk crystal structure consisting of stacked lamellae, each formed by two head-to-head (or tail-to-tail) molecules. However, single molecule steps of 2 nm height were also found (Figure 1f). Out-of-plane XRD data in Figure 2b show the (001) Bragg peak (at $q_z = 1.47 \text{ nm}^{-1}$) and higher order diffraction peaks which correspond to a multilayer structure with an interlayer spacing of ~ 4.12 nm. However, based on the reported BTBT-C8 crystal structure by Gbabode et al.,⁴⁸ the relative intensity of the Bragg peaks is not the expected. Specifically, the intensity ratio measured for (001): (002) = 20:27 differs dramatically from the 20:1 expected

value. The anomalous high intensity of the (002) Bragg peak can be explained by the presence of a crystalline structure with single layer periodicity in coexistence with the reported bilayer structure, a scenario that agrees with the AFM observations. It is plausible to suggest that this single layer stacking is a metastable structure formed in films grown at RT.

The preferred orientation (001) along the surface normal results from the upright orientation of the molecules. Whereas it is indisputable that C8-BTBT-C8 thin films expose an alkyl-terminated surface, it is not evident for BTBT-C8 due to the asymmetric structure of the molecule. We elucidate this issue employing friction force microscopy (FFM), a valuable tool to identify materials with a different chemical nature at their surface.³⁶ Combined topographic AFM and FFM imaging (Figure S2 in Supporting Information) shows no significant friction differences between single-layer and bilayer areas, indicating similar alkyl-termination. For a bilayer BTBT-C8 stacking, an alkyl-terminated surface can only arise from a head-to-head assembly. This conjecture is supported by the identical growth behaviour of C₆₀F₄₈ on C8-BTBT-C8 and BTBT-C8 films described next.

Figure 2. Out-of-plane XRD for (a) C8-BTBT-C8 film (48nm) and (b) BTBT-C8 film (22nm) before (black line) and after (blue line) deposition of C₆₀F₄₈ on top (15nm). The spike at $q_z=7.8 \text{ nm}^{-1}$ is not a structural feature from the samples.

The structure of C8-BTBT-C8 and BTBT-C8 films upon deposition of C₆₀F₄₈ ($\approx 15 \text{ nm}$) has been characterized by out-of-plane XRD (Figure 2). Importantly, the respective (00n) reflections characteristic of C8-BTBT-C8 and BTBT-C8 remain unchanged, demonstrating that the dopant does not alter the structure of the underlying OSC films. The two new Bragg peaks emerging at $q_z=6.27 \text{ nm}^{-1}$ and $q_z=12.52 \text{ nm}^{-1}$ are ascribed to C₆₀F₄₈ in agreement with a closed packed fcc structure with the (111) crystal plane parallel to the substrate. The peak position at $q_z=6.27 \text{ nm}^{-1}$ corresponds to an inter-plane spacing of $d_{111} = 1.00 \text{ nm}$. We note that the narrow C₆₀F₄₈ Bragg

peaks indicate the formation of islands with a mean crystalline size of ~ 27 nm, estimated from the full width half maximum (FWHM) of the (222) peak.

Figure 3. Topography and lateral force maps of C₆₀F₄₈ (~ 2 nm) deposited on top of (a, b) C₈-BTBT-C₈ (9 nm) and (c, d) BTBT-C₈ (16 nm) respectively. Note some areas of uncovered SiO₂ substrate in a. (e) Magnified topographic image illustrating the hexagonal shape of C₆₀F₄₈ crystallites on C₈-BTBT-C₈. (f) Height profile along the blue segment in (e).

To study the interface morphology for dopant thicknesses (few nanometers) relevant for contact doping,^{12,50} we investigate by AFM the first stages of the C₆₀F₄₈ growth on BTBT-C₈ and C₈-BTBT-C₈. Figure 3 shows representative topographic and lateral force FFM images

obtained for a nominal C₆₀F₄₈ coverage of ~2 nm. The growth mode is similar in both films: C₆₀F₄₈ nucleates forming islands, most of them decorating the BTBT step edges. These assemblies are clearly distinguished from the surrounding OSC surface by their lighter colour (i.e., higher friction) in the lateral force images. For the deposited C₆₀F₄₈ coverage, the island heights range between 5 and 12 nm (Figure 3c), i.e., corresponding to 5-12 individual C₆₀F₄₈ layers (~1 nm). The formation of extremely flat and hexagonal assemblies supports the crystalline fcc structure derived from XRD data. The origin of such equivalent results should be found in the same type of termination exhibited for both C8-BTBT-C8 and BTBT-C8 films. The low interaction of C₆₀F₄₈ with the alkyl-terminated surface gives rise to island growth (Volmer–Weber mode). From statistical AFM images analysis, we can confirm that the C₆₀F₄₈ islands decorating the steps sit on the lower terraces probably due to the interaction of C₆₀F₄₈ molecules with the aromatic core of BTBT molecules at the edges (Figure S3 in Supporting Information).

On the (001)-oriented BTBT films, C₆₀F₄₈ is separated from the conjugated BTBT core by the alkyl chains exposed at the surface. However, though this implies no π -orbital overlap between the dopant and the π -conjugated core, charge transfer between the HOMO of OSC molecules and the LUMO of C₆₀F₄₈ may occur across the alkyl chains by electron tunnelling. The electronic surface properties following the incorporation of the p-type dopant are revealed by KPFM, which provides a quantitative determination of the work function with nanoscale spatial resolution. The KPFM maps indicate a lower (higher) surface potential (work function) on the regions covered by C₆₀F₄₈ for both C8-BTBT-C8 and BTBT-C8 films (Figure S4 in Supporting Information). Figure 4 displays typical topographic and KPFM images of a C8-BTBT-C8 film upon deposition of 2 nm of C₆₀F₄₈. To avoid possible charge transfer between the Si substrate and the acceptor

molecules through the native SiO₂, this particular heterostructure was grown on a 200 nm thick SiO₂/Si substrate, the same used for the OFETs fabrication. The surface potential map entirely replicates the surface nanomorphology and reveals an important decrease of 0.5 ± 0.1 V on the areas covered by the C₆₀F₄₈ crystallites as can be seen in the surface potential (SP) and height profiles shown in Figure 4c-4d.

Figure 4. (a) Topography and (b) simultaneously measured KPFM surface potential (SP) map for C₆₀F₄₈ (2 nm)/C8-BTBT-C8(9 nm) on a 200 nm thick SiO₂. (c) and (d) Line profiles along the segments in the surface potential map and topography, respectively, show the correlation between the increase (decrease) in work function (SP) and the C₆₀F₄₈ crystallites. Blue and yellow regions in Figure 4d correspond to C₆₀F₄₈ and C8-BTBT-C8, respectively. Note: lower surface potential corresponds to higher work function (see experimental section).

In general, a critical aspect affecting the long-term stability of devices is the tendency of OSC films to dewet from SiO₂.^{37, 38} In a previous work, we showed that C8-BTBT-C8 thin films suffer from a strong dewetting with time provoking notable degradation of the fabricated OFETs.³⁶ Figures 5a and 5d show the topographic images of an as-grown BTBT-C8 film and the same

sample measured after two years, respectively. A strong dewetting of BTBT-C8 films is observed. The initial laterally continuous films evolved to high islands that leave uncovered large substrate regions. Outstandingly, film dewetting is frustrated by the passivating influence of C₆₀F₄₈ revealed by the similar morphology observed many months after preparation of the C₆₀F₄₈-covered samples. The comparison between the topographic images of the C₆₀F₄₈/C8-BTBT-C8 and C₆₀F₄₈/BTBT-C8 films freshly prepared (Figures 5b and 5c) and those measured more than one year later (Figure 5e and 5f) illustrates the morphological stability of the dopant/OSC interface. In general, dewetting is more pronounced for thinner films but also occurs in thicker ones (see Figure S5 in Supporting Information). Since thin film dewetting is expected to start by a mass retraction from steps edges, where the molecules have less binding energy, the above results point to step pinning due to C₆₀F₄₈ nucleation and are a clear proof of dewetting inhibition leading to increased stability of the OSC films over time. This revealing fact implies that the deposition of C₆₀F₄₈ can be used as a strategy to stabilize the morphology of thin layers, having the effect of a capping protecting layer.

Figure 5. Top: AFM topography of fresh samples of (a) pristine BTBT-C8 (16 nm), (b) C₆₀F₄₈ (2 nm)/ BTBT-C8 (24 nm) and (c) C₆₀F₄₈ (4 nm)/C8-BTBT-C8 (13 nm). Bottom: AFM topography of the same samples acquired two years later for (d) BTBT-C8, (e) C₆₀F₄₈/BTBT-C8 and one year later for (f) C₆₀F₄₈/C8-BTBT-C8. The insets of 5a and 5d show the height profiles along the marked lines in the respective images.

The same mechanism is responsible for the enhanced thermal stability of the films, shown next for BTBT-C8 (see results for C8-BTBT-C8 in Figure S6 of the Supporting Information). As can be seen in the XRD data of Figure 6, annealing a pristine BTBT-C8 film at 80 °C leads to film desorption (Figure 6a). In contrast, when a film has the dopant overlayer, the ordered lamellae structure stands even up to an annealing temperature of 100 °C (Figure 6b). The Bragg peaks

position remains unaffected, ruling out intermixing of $C_{60}F_{48}$ and BTBT molecules. Note, however, the strong intensity reduction of the (002) reflection upon annealing. As commented above, this peak has the contribution of a single layer-structure. Therefore, the decrease of the (002) intensity can be explained by the disappearance at ≤ 100 °C of the single-layer phase formed at RT, indicating it is a structure which is less stable than the lamellae.

Figure 6. Out-of-plane XRD of (a) BTBT-C8 (22 nm) and (b) $C_{60}F_{48}$ (15 nm)/ BTBT-C8 (22 nm). The black curves: as-deposited films. Blue curves: after annealing the films at 80 °C in (a) and 100 °C in (b).

The above XRD results support the beneficial effect of $C_{60}F_{48}$ in preserving the structure of OSC films by supplying them with a certain degree of thermal robustness. As we have already

demonstrated for the stability of the films with time, the preservation effect is attributed to the particular morphology of the C₆₀F₄₈/OSC heterointerface, with closed-packed crystallites anchored at the step edges. It is therefore plausible to think that these crystallites act as pinning centres, hampering sublimation and migration of the less bound edge OSC molecules when the temperature rises and, therefore, causing higher thermal stability of the films.

As reported in previous studies,^{2,4,12,19,36,50,51} the contact resistance of OFETs can be reduced by contact doping. The significant increase of the local work function measured by KPFM on the areas covered by C₆₀F₄₈ (Figure 4) indicates the formation of an interface dipole. However, the observed discontinuity of the C₆₀F₄₈ layer is certainly not the optimal nanoscale morphology to improve charge injection. Within this context, we have evaluated the effect of contact doping for C8-BTBT-C8 OFETs employing an inverted staggered (bottom-gate, top-contact) device architecture with varying channel length between 30 μm and 100 μm and two dopant coverages, namely 0.5 nm and 1 nm. Using a shadow mask, first the C₆₀F₄₈ dopant and then the metallic Au drain and source contacts were deposited on top of 25 nm-thick films of C8-BTBT-C8. As shown in Figure 7a, the channel topography consists of flat C8-BTBT-C8 terraces, similar to that of Figure 1a. The corresponding transfer curve for 1 nm of C₆₀F₄₈ is plotted in Figure 7b for a channel length of 40 μm along with that of the undoped reference device (orange line). Although the devices still present a non-ideal behaviour, the beneficial effect of contact doping is manifested through an increase of the current by one order of magnitude and a positive shift of the turn-on voltage (V_{on}). The V_{on} , as well as the I_{on} and saturation mobility, are found to increase with the amount of dopant (see Figure S7 in the Supporting Information). We suggest that these observations are due to reduced contact resistance by contact doping. To extract the contact resistances, the potential drop across the electrode/channel was measured by KPFM

during the linear operation of the devices (Figure S8a in Supporting Information). The contact resistance decreases with contact doping at both electrodes, from 17.68 k Ω ·cm to 12.24 k Ω ·cm and from 8.88 k Ω ·cm to 4.24 k Ω ·cm at source and drain, respectively. For this particular device, the field effect mobility extracted from the current-voltage characteristics in the saturation regime increased from 1.03 cm²/Vs (in control device) to 3.34 cm²/Vs, being 5.00 cm²/Vs, the best value measured for contact-doped devices (Figure S7a in Supporting Information). The reduced contact resistance may reflect combined effects that improve charge injection at the contact/semiconductor interface and transport from the contacts to the channel.⁵² Among the invoked mechanisms for reducing contact resistance are decreasing the depletion-layer thickness, filling traps states at the organic semiconductor near the electrode interface or tuning the work function, all related to electron charge transfer at the dopant/OSC interface.^{2,11,53,54}

To benefit from the stabilizing effect that C₆₀F₄₈ has on the organic film, we have also evaluated the case of its deposition in the absence of a mask, so that there are dopant molecules at the OSC in the channel region as well. Figure 7d shows the data for 1 nm of C₆₀F₄₈. The topographic image obtained within the channel displays the discontinuous dopant layer with the characteristic step decoration of C8-BTBT-C8 described above (Figures 3, 4 and 5). The electrical characteristics of the devices exhibit the same behaviour as for only contact-doping: a positive shift of V_{on}, accompanied by an increase of I_{on} and field effect mobility. Figure 7e shows the transfer curve for the L = 40 μ m OFETs. As in the case of contact doping, the increase in field effect mobility is attributed to a decrease of source and drain contact resistances, as supported by KPFM (Table S1 in Supporting Information). An important result is that adding C₆₀F₄₈ over the entire BTBT film does not cause any significant change in the I_{on}/I_{off} current ratio ($\approx 10^6$), demonstrating that the channel conductivity is not affected. In other words, charge

transfer at the top dopant/OSC interface does not cause channel doping conversely to other systems.^{12,54} In Figures S8b and S8c we present a summary of the changes in V_{on} and μ obtained for the two types of devices, i.e., with dopant deposited: a) only under the contacts (using a mask) and b) under the contacts and over the channel (without mask), respectively.

Figure 7. Schematics, AFM topography and transfer curves for devices consisting of C8-BTBT-C8 (25 nm) thin films with $C_{60}F_{48}$ (1 nm) deposited (a, b) under the contacts and (d, e) under the contacts and at the channel region. ($V_{SD} = -5V$, $L = 40 \mu m$). (c, f) Transfer curves measured in freshly prepared doped devices (black curve) and after one year (blue line) ($V_{SD} = -5V$, $L = 80 \mu m$). The fabricated OFETs were measured in air.

The C8-BTBT-C8 OFETs were characterized after one year of storage in air. We observed still a good performance of the devices having a comparable μ than the freshly prepared devices. The transfer characteristics for fresh and aged devices are shown in Figure 7c and 7f (output characteristics in Figure S9 in Supporting Information). Given that the device of Figure 7a-b was damaged during manipulation, results for OFETs with a different channel length ($L = 80 \mu\text{m}$) are shown. Despite the good performance of the aged devices, some changes are noticed. The most significant is the large shift to -30 V observed in V_{on} for contact-doped devices. This shift is contrary to what would be expected if the channel became hole-doped by $\text{C}_{60}\text{F}_{48}$ but is otherwise indicative of immobile trap holes at the organic/dielectric interface. In contrast, we do not observe any significant shift in V_{on} when there is dopant not only under the contacts but also at the channel region. Although the underlying reasons are unclear, we tentatively ascribe stability of V_{on} over time to diverse effects. First, the long-lasting morphology of the continuous and compact OSC film that protects the OSC/dielectric interface. On the other hand, the hydrophobic character of fluorinated fullerenes (due to the high fluorine content)^{55,56} and the nucleation of close packed $\text{C}_{60}\text{F}_{48}$ islands at the step edges of the OSC film can act as kinetic barrier preventing interlayer and/or intergrain (through grain boundaries or structural defects) water penetration.⁵⁷ It is remarkable that the off current in the transistors is not affected by the passage of time, indicating that the conductive channel remains undoped, a proof of the demonstrated long-term stability.

Provided deposition without shadow mask simplifies processing and, in addition, has the double beneficial role of improving charge injection and stability of the BTBT devices, we believe the procedure will reduce efforts in device doping manufacture. This work is considered as a proof of concept study and superior device performance is expected after optimization via

pretreatment of the dielectric surface and a systematic refinement of the dopant nominal thickness.

Conclusions

The interfaces between two BTBT derivatives, with one or two octyl side chains, and a fluorinated fullerene p-type dopant have been studied. Our results reveal that the asymmetric BTBT-C8 molecule adopts a packing sequence that defines an alkyl-terminated film surface as that of C8-BTBT-C8 films. In both cases, we find identical growth behaviour of C₆₀F₄₈ on their top, leading to the following key findings. The deposition of C₆₀F₄₈ molecules on the organic semiconductors surface at RT results in the formation of close-packed and oriented crystallites decorating the step edges of the film surface, leading to a nanostructured interface. The growth of C₆₀F₄₈ is likely determined by low interaction with the alkyl-terminated film surface and the cohesion energy between fullerene molecules. There is no incorporation by diffusion of C₆₀F₄₈ molecules into the underlying films that otherwise preserve their crystallinity, even after annealing. The particular nanostructuration of the interface has a beneficial effect on the long-term and thermal stability of the films. Steps pinning due to the nucleation of C₆₀F₄₈ inhibits upward mass transport and herewith undesired film dewetting and, in addition, it also hinders sublimation/detachment of less bounded molecules providing the films with increased thermal robustness, an endurance effect similar to film encapsulation.

The electrostatic landscape replicates the surface nanomorphology, with an important local increase of work function on the areas covered by C₆₀F₄₈ crystallites due to the formation of interfacial dipoles. Despite the discontinuity of the C₆₀F₄₈ overlayer, charge injection in OFETs

is improved by reduction of the contact resistance, which is reflected in an increase of the effective field effect mobility and a lower V_{on} (respect to control devices without $C_{60}F_{48}$). Thus, in inverted staggered devices, $C_{60}F_{48}$ can be deposited over the whole OSC film surface having the double role of improving the injection (contact doping) and the long-term time stability of the devices (channel endurance). The electrical stability of the OFETs in air was confirmed after one year.

For a given dopant/OSC system, the detailed morphology of their interface depends on the structural quality of the OSC layer as well as on its chemical termination and the interaction with the dopant molecules. By providing quantitative data correlating nanoscale properties and device characteristics, this work highlights the effect of the dopant/semiconductor interface on the assembly efficiency and stability and permits foreseeing that further improvement of device performances is conceivable by means of a deeper understanding of the interfacial properties.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

X-ray diffraction patterns, AFM topographic images and profiles, lateral force images, surface potential images of $C_{60}F_{48}$ doped C8-BTBT-C8 and BTBT-C8 thin films; Transfer and output characteristics of the devices; OFET parameters obtained for the studied devices; KPFM map during OFETs operation as used for contact resistance measurements.

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The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally. (match statement to author names with a symbol)

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Table of Contents (TOC)

Supporting Information

Double Beneficial Role of Fluorinated Fullerene Dopants on Organic Thin Films Transistors: Structural Stability and Improved Performance

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Figure S1. Out of plane XRD data for (a) 50 nm C8-BTBT-C8 film and (b) 23nm BTBT-C8 film grew on native Si. In (a) Kiessig fringes are observed, an interference pattern that arises from the reflection of the top and bottom interfaces of the film, indicating a smooth surface.

Figure S2. Height profile (a), topographic image (b) and corresponding lateral force map (c) of a bare thin film of BTBT-C8. The nominal thickness is 16 nm. Both types of terraces, one- and two-layers steps (see height profile), present the same frictional contrast.

Figure S3. (a) Height profile along the line marked in the topographic image. (b) Topography of a thin film of C8-BTBT-C8 covered by a sub-monolayer of $C_{60}F_{48}$. The substrate is 200 nm thick SiO_2 on Si. The contrast in the excitation frequency map (c) evidences the two different materials ($C_{60}F_{48}$ and C8-BTBT-C8) and permits identifying the location of the dopant crystallites.

Figure S4. Topography (a, c) and surface potential maps (b, d) measured by KPFM for $C_{60}F_{48}$ deposited on C8-BTBT-C8 (left) and BTBT-C8 (right) on Si.

Figure S5. Dewetting of a bare 30 nm-thick C8-BTBT-C8 film followed over 15 weeks. Though in general dewetting is more pronounced for thinner films, this set of images shows an incipient dewetting occurring in some local spots.

Figure S6. $C_{60}F_{48}$ /C8-BTBT-C8 film annealed at different temperatures (from 20 °C to 120 °C). Inset: The $C_{60}F_{48}$ peak at $q_z=12.52 \text{ nm}^{-1}$ decreases with temperature while the characteristic Bragg peak of C8-BTBT-C8 at $q_z=12.95 \text{ nm}^{-1}$ remains unaltered.

Figure S7. Saturation field effect mobility (a), Ion (b) and Von (c) for C8-BTBT-C8 (25 nm) OFETs with two different coverages of $C_{60}F_{48}$ contact doping. Values measured for different channel lengths, from $L = 30 \text{ }\mu\text{m}$ to $100 \text{ }\mu\text{m}$, are shown. Orange squares, light green circles and dark green triangles correspond to bare C8-BTBT-C8, with 0.5 nm $C_{60}F_{48}$ and 1nm $C_{60}F_{48}$, respectively.

Figure S8. (a) Line profile from the surface potential map measured by KPFM for a 40μm channel OFET of C8-BTBT-C8 with C₆₀F₄₈ contact doping (device in Figure 7 in the manuscript), operated at $V_{ds} = -5V$ and $V_{gs} = -40V$. The voltage drop at the source (ΔV_s) and drain (ΔV_d) contacts are measured from the surface potential profile. The source-drain current (I_{ds}) is simultaneously measured. The ratio between the V_{drop} at each electrode and I_{ds} gives the respective contact resistance ($R_c(s,d) = \Delta V_{sd} / I_{ds}$). (b) The average shift in V_{on} and (c) percentage increase in mobility with C₆₀F₄₈ (1 nm) under the contacts (dark green) and deposited over the entire surface (light green). (d) Scheme of evaporation of C₆₀F₄₈, with and without mask for dopant, under the contacts and deposited over the entire surface respectively.

	$R_c(s)$ ($k\Omega \cdot cm$)	$R_c(d)$ ($k\Omega \cdot cm$)	μ (cm^2/Vs)
Reference device without dopant	33.8	14.4	1.14
$C_{60}F_{48}$ over the entire surface	8.96	3.44	2.17

Table S1. Contact resistances measured from KPFM for 40 μm OFETs with and without $C_{60}F_{48}$ (1 nm) doping deposited over the whole surface (Figure 7d-e).

Figure S9. Scheme and output curves for devices consisting of C8-BTBT-C8 (25 nm) thin films with $C_{60}F_{48}$ (1 nm) deposited under the contacts (a, c, e, g) and also over the channel (b, d, f, h). (c and d) Comparison of doped (orange line) vs. undoped devices (green line), $L = 40 \mu m$. Comparison between doped devices, freshly prepared (e, f) and after one year (g, h), $L = 80 \mu m$.