Effect of the organic semiconductor side groups on the structural and electronic properties of their interface with dopants

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ABSTRACT

Two derivatives of [1]benzothieno[3,2-b][1]benzothiophene (BTBT), namely 2,7-dioctyl-BTBT (C8-BTBT) and 2,7-diphenyl-BTBT (DPh-BTBT), belonging to one of the best performing organic semiconductors (OSCs) family, have been employed to investigate the influence of the substitutional side groups in the properties of the interface created when they are in contact with dopant molecules. As molecular p-dopant, the fluorinated fullerene C₆₀F₄₈ is used because of its adequate electronic levels and its bulky molecular structure. Despite the dissimilarity introduced by the OSC film termination, dopant thin films grown on top adopt the same (111)-oriented FCC crystalline structure in the two cases. However, the early stages' distribution of the dopant on each OSC film surface is dramatically influenced by the group side, leading to distinct host-dopant interfacial morphologies that strongly affect the nanoscale local work function. In this context, Kelvin probe force microscopy and photoelectron emission spectroscopy provide a comprehensive picture of the interfacial electronic properties. The extent of charge transfer and energy level alignment between OSCs and dopant are debated in the light of the differences in the ionization potential of the OSC in the films, the interface nanomorphology, and the electronic coupling with the substrate.

INTRODUCTION

Extensive research in the design and synthesis of different π -conjugated materials has afforded organic semiconductors (OSCs) with enhanced mobility, environmental robustness and tuned optoelectronic properties.¹ However, their performance in device architecture is sometimes not as high as expected. This undesired outcome is often due to inconvenient interfacial mismatches,^{2,3} which can result from high injection barriers, interfacial traps, inefficient charge transport across adjacent organic layers,⁴ etc. Among other approaches, the so called contact doping, i.e., adding dopant molecules at the interface, has been developed as a strategy to improve charge injection at contacts and charge transport across OSC heterojunctions.^{4,5,6,7,8,9,10,11} Even though the doping mechanisms in these materials are not fully understood and may depend on the particular system, it is widely accepted that the chemical structure and relative orientation of host and dopant molecules play a key role.^{12,13,14} The effectiveness and extent of interfacial doping therefore relate to both structural and electronic characteristics of the interface. Understanding the influence of these factors during the interface formation would help obtaining, via interfacial engineering, more efficient devices.

[1]benzothieno[3,2-b][1]benzothiophene (BTBT) derivatives are among the most promising small-molecule OSCs for organic field-effect transistors (OFETs) applications due to their high intrinsic charge-carrier mobility.^{15,16,17,18,19,20,21,22} As expected from the relatively low-lying highest occupied molecular orbital (HOMO) a notable feature of BTBT-based OFETs is their

ability to operate in ambient conditions.²³ Unfortunately, these devices often suffer from large contact resistance, a drawback particularly critical for the devices with very short channel length ($L < 10\ \mu\text{m}$).²⁴ In this context, contact doping is employed to reduce the injection barrier and improving device performance. To address the influence of structural and electronic interfacial details, this work focuses on two symmetric derivatives of BTBT, containing either octyl or phenyl side groups, i.e., 2,7-dioctyl-BTBT (C8-BTBT) and 2,7-diphenyl-BTBT (DPh-BTBT), respectively. Despite their dramatically different side groups, the BTBT cores make these molecules quite similar in terms of reported calculated HOMO values of $-5.39\ \text{eV}$ for C8-BTBT²⁵ and -5.41 for DPh-BTBT (respect to the vacuum level).^{26,27} It should be emphasized that for thin films the ionization potential (IP) of highly anisotropic molecules may importantly depend on factors as the orientation of the molecules and degree of crystalline order.²⁸ This explains the large range of reported values for thin films of both molecules spanning from 4.9 up to 5.7 eV.^{29,30,31,32,33,34} From the structural point of view, the two BTBT derivatives studied form layered thin films^{26,29,35,36,37} where the molecules pile up vertically in a lamella stacking, forming a monoclinic (001)-oriented structure. Because of their different side groups (long linear chains versus short cyclic groups), each film presents specific structural and electronic differences of particular interest for the comparative investigation proposed here. On the one hand, within the C8-BTBT thin films, insulating double-chain aliphatic layers separate the BTBT core layers where π -orbitals overlap constitutes the main conducting channels. The exposed film surface is alkyl-terminated. On the other hand, face-to-face phenyl groups separate the core BTBT layers in the DPh-BTBT thin films that have a phenyl-terminated surface. As molecular p-dopant, we have selected the fluorinated fullerene with highest halogen content, $\text{C}_{60}\text{F}_{48}$, which, in addition to a strong acceptor character with adequate lowest unoccupied molecular orbital (LUMO) level (-5.0

to -5.5 eV), presents the advantages of low volatility, high thermal stability and bulkier shape than other already established dopants.^{38,39,40,41} As recently demonstrated by our group,^{42,43} this dopant molecule confers structural and thermal stability when deposited on planar OSCs.

In order to dig into structural details of the interface related to specific OSC side groups, the structure and morphology of C8-BTBT and DPh-BTBT thin films are compared before and after depositing C₆₀F₄₈ on their top. We show how the dissimilar interfacial morphology, introduced by the distinct side groups of the BTBT derivatives, correlates with the nanoscale surface potential. To account for the contribution from charge exchange with the substrate, substrates with either native or thick oxide were employed. In summary, we report a full set of nanoscale morphological and surface potential data (AFM and KPFM) combined with crystallographic and electronic energy analysis (GIXRD and UPS/XPS) demonstrating the influence of the OSC thin film termination, and therefore the substitutional side groups of BTBT derivatives, on establishing electronic equilibrium in dopant/OSC heterojunctions of interest in organic electronic devices.

EXPERIMENTAL SECTION

C8-BTBT was purchased from Sigma Aldrich, DPh-BTBT has been synthesized according to a known procedure²⁶ and C₆₀F₄₈ molecules were synthesized as per the method developed at the Josef Stefan Institute (Slovenia).⁴⁴ The product was characterized by chemical analysis, electron-ionization mass spectrometry and infrared spectroscopy. The purity was estimated to be 95%. Si (100) substrates exhibiting their native SiO₂ (nSiO₂) were cleaned by sonication in acetone and

ethanol for 10 min and then annealed in vacuum at $\sim 300^\circ\text{C}$. After this procedure, thin films of one or the other BTBT derivative were grown by Molecular Beam Epitaxy under vacuum ($\sim 10^{-8}$ mbar) at room temperature (RT) on clean substrates (BTBT/nSiO₂). The C₆₀F₄₈ molecules were deposited in-situ from the vapour phase on top of the corresponding OSC film (C₆₀F₄₈/BTBT/nSiO₂). The amount of deposited molecules was monitored by a quartz monitor microbalance (QM). Commercial Si wafers (from Si-Mat) with a 200 nm thick thermal oxide (tSiO₂) were also used when indicated. Transmission electron microscopy grids were used as shadow masks.

A microscope head and control electronics from Nanotec Electronica were used for Atomic force microscopy (AFM) and Kelvin Probe Force Microscopy (KPFM). CrPt-coated Si tips mounted on cantilevers with nominal $k = 3 \text{ Nm}^{-1}$ from Budget Sensors were used for dynamic modes. A phase locked loop (PLL) is used to null the in phase signal, keep the system always at resonance and track the frequency shift. During KPFM measurements, the tip is excited by an ac voltage (~ 0.5 V) at a frequency ($f_{\text{AC}} \sim 0.7 \text{ kHz}$) while a feedback loop adjusts the dc bias needed to nullify the frequency shift (Δf) of the mechanical oscillation, which is proportional to the electrostatic force gradient. In our setup, the voltage is applied to the tip so that the higher the surface potential (SP), the lower the work function (ϕ). SP maps are obtained simultaneously with topography in a single pass mode and confirmed in the lift mode (tens of nm above) ensuring no crosstalk between signals. Freshly cleaved HOPG was used for calibration of the tips work function.

Care was taken to avoid uncertainties in measured contact potential difference between tip and surface, by regularly checking the surface potential of a reference sample. Data were analysed by using the WSxM freeware.⁴⁵

X-ray diffraction measurements were carried out at the ID03 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Out-of-plane and grazing incidence

geometries were used to investigate the film structure in the direction perpendicular (out-of-plane) and parallel (in-plane) to the substrate, respectively. A 2D Maxipix 2×2 detector was used for x-ray scattering measurements. The x-ray energy was 12.5 keV. For GIXD experiments an incident angle of 0.11° was set, which is below the critical angle of Si ($\sim 0.14^\circ$ at this energy). X-ray Photoelectron Spectroscopy (XPS) for core level measurements was performed using a Specs Phoibos 150 hemispherical energy analyser with a monochromatic X-ray source (Al K α , $h\nu = 1486.6$ eV). Ultraviolet photoelectron spectroscopy (UPS) was employed to measure the density of states at the Fermi-edge valence band (VB) and the secondary electron cut-off (SECO) using the same analyser and a monochromatic He I- α line ($h\nu = 21.21$ eV). To have access to the work function of the samples from the SECO signal, the corresponding spectra were taken with the samples biased at -10 V. An Au (111) single crystal was used as the reference for the determination of the Fermi energy. Both XPS and UPS were measured under ultra-high vacuum (UHV) for samples fabricated in-situ using the native SiO₂/Si as substrate.

RESULTS

Figure 1. Schematic structure of (a) DPh-BTBT and (b) C8-BTBT. Topography of DPh-BTBT(7nm)/nSiO₂ (c) and C8-BTBT(6nm)/nSiO₂ (d). Topographic profiles, both reaching the substrate, show the film thickness and growth mode schematics for each molecule (e and f). When regions with uncovered nSiO₂ remain (as in d), contrast is observed in the lateral force and frequency shift images (Figure S1).

When thermally evaporated on clean native SiO₂ substrates, DPh-BTBT and C8-BTBT (Figure 1a and 1b) form layered films with single layer thickness close to the molecular length, ≈ 2 nm for DPh-BTBT and ≈ 3 nm for C8-BTBT,^{26,36} in agreement with a standing up configuration of the molecules within each layer. The analysis of topographical AFM images of diverse molecular films reveals the same terrace height for all individual layers of each molecule but important

differences in the early stages of the growth (Figure 1). Whereas DPh-BTBT forms a laterally continuous bottom film (Figure 1c) on top of which other layers start to form, 3D growth of C8-BTBT leaves uncovered substrate areas (regions appearing bright in frequency shift channel, Figure S1d). Both BTBT films have similar aromatic core planes, which are distinctly separated, structurally and electronically, in the direction perpendicular to the surface due to the distinct side groups (short cyclic groups versus long linear chains) (Figure 1e and 1f). The different growth behaviour of DPh-BTBT and C8-BTBT on SiO₂ is a direct consequence of their different side groups, which probably result in an important difference in interfacial and surface energy.^{46,47,48} Nevertheless, for the thicknesses typically employed in OFETs (>20 nm), C8-BTBT forms a closed film.⁴²

Out-of-plane XRD shows (00L) Bragg peaks up to multiple orders, proving that the films are oriented with the (001) crystal face parallel to the surface for both molecules (see Supporting Information Figure S2a for DPh-BTBT and reference 42 for C8-BTBT). The inter-planar spacing (d_{001}) obtained from the Bragg peaks is 2.01 nm for DPh-BTBT and 2.91 nm for C8-BTBT, in full agreement with the reported crystalline structure^{35,37} and the AFM topographical data (Figures 1e and 1f). Whereas for DPh-BTBT the value of d_{001} coincides with the molecular length of the molecule, indicating a completely upright configuration, d_{001} is slightly lower than the molecular length for C8-BTBT (3.08 nm) due to the tilt of the alkyl chains.

Figure 2. (a) 2D-GIXD map of C₆₀F₄₈(2nm)/DPh-BTBT(11nm)/nSiO₂. (b) In-plane GIXD data extracted from the 2D-GIXD maps of DPh-BTBT/nSiO₂ before (black) and after (blue) deposition of C₆₀F₄₈. (c) 2D-GIXD map C₆₀F₄₈(9nm)/C8-BTBT(9nm)/nSiO₂ and (b) The schematic structures of C₆₀F₄₈ and DPh-BTBT are also depicted.

Figures 2a and 2c display 2D-GIXD maps for the heterostructures C₆₀F₄₈/DPh-BTBT/nSiO₂ and C₆₀F₄₈/C8-BTBT/nSiO₂ and formed when C₆₀F₄₈ is deposited, respectively, on top of DPh-BTBT and C8-BTBT films grown on native silicon oxide (see the 2D-GIXD map of the pristine DPh-BTBT film in Figure S2b of the Supporting Information). Diffraction intensities observed for both films, where $q_{xy} \sim 13.1 \text{ nm}^{-1}$, $q_{xy} \sim 15.7 \text{ nm}^{-1}$ and $q_{xy} \sim 18.8 \text{ nm}^{-1}$ assigned to (11L), (02L) and (12L) rods, correspond to the characteristic herringbone packing in the ab plane.^{35,49,50} From the peaks position we obtain a rectangular in-plane unit cell with $a=6.03 \text{ Å}$ and $b=7.97 \text{ Å}$ for DPh-BTBT and $a=5.95 \text{ Å}$ and $b=8.03 \text{ Å}$ for C8-BTBT. In addition, we also note that, as reported for C8-BTBT,³⁵ a slight in-plane unit cell variation is found with the film's thickness for both molecules. The additional diffraction features at $q_{xy}=5.99 \text{ nm}^{-1}$, $q_{xy}=10.39 \text{ nm}^{-1}$ and $q_{xy}=11.90 \text{ nm}^{-1}$ correspond to crystalline C₆₀F₄₈. A series of Bragg peaks along the q_z -direction observed for both systems evidences a good degree of 3D crystallinity (intensity broadening along z is related to the finite size of the crystallites along this direction). These results agree with C₆₀F₄₈ in an FCC structure with the (111) plane parallel to the surface. From the in-plane peak at 10.39 nm^{-1} assigned to the (2-20), the calculated unit cell parameter of the FCC structure is 1.714 nm , which corresponds to a lattice spacing of $d_{111}=1.0 \text{ nm}$. The (111) reflection can be seen in the out-of-plane XRD data reported in our previous work.⁴² Indeed, the in-plane scans of bare DPh-BTBT/nSiO₂ (black spectrum in Figure 2b) are accompanied by new diffraction features at $q_{xy}=5.99 \text{ nm}^{-1}$, $q_{xy}=10.39 \text{ nm}^{-1}$ and $q_{xy}=11.90 \text{ nm}^{-1}$ in C₆₀F₄₈/DPh-BTBT/nSiO₂ (blue spectrum in

Figure 2b). These data clearly show that the position and width of the peaks of the BTBT films remain unaltered, i.e., $C_{60}F_{48}$ deposition does not disrupt the structure and packing of the underlying films.

Figure 3. Topography and simultaneous SP maps measured by KPFM (colour scale corresponds to SP data). LEFT: DPh-BTBT (9 nm)/ $nSiO_2$ before (a, b) and after $C_{60}F_{48}$ deposition of 1 nm (c, d) and 3 nm (e, f); RIGHT: C8-BTBT (8 nm)/ $nSiO_2$ before (h, l) and after $C_{60}F_{48}$ deposition of 1

nm (j, k) and 3 nm (l, m); Larger scale images for the DPh-BTBT case are shown in Figure S3 of the Supporting Information. Cartoons with the growth models are shown for each case (g, n).

Though in both cases, $C_{60}F_{48}$ is found to pack in the same structure, the respective substitutional side groups of the two BTBTs investigated here have a strong impact on the dopant/OSC interface morphology. The topography and associated surface potential (SP) measured by KPFM are provided in Figure 3 for uncovered DPh-BTBT and C8-BTBT (3a-b and 3h-i, respectively) as well as for two amounts (1 nm and 3 nm) of dopant deposited on them (3c-f and 3j-m, respectively). Upon deposition of 1 nm of $C_{60}F_{48}$ on DPh-BTBT, an inhomogeneous SP map is observed (Figure 3d). At this scale, the correlation between dopant location and lower surface potential is evident despite a certain variability arising from differences in the density of such $C_{60}F_{48}$ assemblies, which are 1-2 nm high (see Figure S3 in the Supporting Information). As manifested by the low and nearly uniform surface potential of Figure 3f, upon 3 nm deposition of $C_{60}F_{48}$, the DPh-BTBT film surface (Figure 3e) is fully covered by the dopant as schematically modelled in Figure 3g. At this stage, the mean surface potential is 0.7 V lower than that of the pristine DPh-BTBT, which means an increase in work function ($\Delta\phi$) by the same magnitude (see experimental section). Remarkably, for the same amount of deposited $C_{60}F_{48}$, the growth on C8-BTBT is completely different. In the topographic images of the right panels in Figure 3, it can be nicely seen that $C_{60}F_{48}$ forms compact and flat assemblies decorating the step edges of the underlying C8-BTBT film while leaving uncovered the terraces, as schematically depicted in Figure 3n. The growth mode of $C_{60}F_{48}$ on C8-BTBT and the associated beneficial effect on the stability of the OSC film have been recently reported by our group.⁴² The $C_{60}F_{48}$ crystallites on C8-BTBT present a distribution of heights, varying in multiples of 1 nm, which equals the lattice spacing d_{111} of the oriented FCC structure.

For the deposited $C_{60}F_{48}$ coverages of 1 nm and 3 nm, the heights range 3-5 nm and up to 9-12 nm, respectively. The direct correlation between morphology (Figures 3j-3l) and SP (Figures 3k-3m) is evident, showing a considerable increase of ϕ (lower SP) at the areas covered by the $C_{60}F_{48}$ crystallites. In addition, as will be described next, the work function is found to increase as a function of the $C_{60}F_{48}$ island height.

Figure 4. Work function difference ($\Delta\phi$) between $C_{60}F_{48}$ on C8-BTBT (8 nm) and the uncovered C8-BTBT, as a function of $C_{60}F_{48}$ crystallites' height (h). The different symbols refer to growth on substrates with native SiO_2 (red circles) and 200 nm thermal SiO_2 (black squares), respectively. Error bars are the standard deviation from mean values obtained from diverse images. The cartoons illustrate charge transfer for each case, $C_{60}F_{48}/C8-BTBT/nSiO_2$ and $C_{60}F_{48}/C8-BTBT/tSiO_2$.

Figure 4 shows the comparison between KPFM results obtained as a function of the $C_{60}F_{48}$ islands height for heterostructures grown either on native oxide substrates ($C_{60}F_{48}/C8-BTBT/nSiO_2$) or on 200 nm thermal SiO_2 ($C_{60}F_{48}/C8-BTBT/tSiO_2$). The work function is found to

increase with island height, saturating for $C_{60}F_{48}/C8-BTBT/nSiO_2$ at $\Delta\phi \sim 1$ eV with respect to C8-BTBT (red data) for crystallites taller than 8 nm. As it can be seen in Figure 3m, $C_{60}F_{48}$ in direct contact with the oxide surface, i.e., at the regions between OSC islands, also leads to an increase of work function, indicating charge transfer between Si and fullerenes through the thin native oxide. Charge transfer with the silicon substrate can be ruled out for heterostructures grown on the thick oxide (see schemes in Figure 4), thus permitting to assess the electronic changes arising at the dopant/OSC interface itself. Importantly, for $C_{60}F_{48}/C8-BTBT/tSiO_2$, $\Delta\phi$ saturates at ~ 0.5 eV, half of the value for $C_{60}F_{48}/C8-BTBT/nSiO_2$. This result confirms inhibition of charge transfer through $tSiO_2$ and indicates that, for establishing electronic equilibrium in the whole system,^{51,52,53} the absolute $\Delta\phi$ measured at the $C_{60}F_{48}/C8-BTBT/nSiO_2$ contains two contributions: charge transfer between OSC and dopant ($C_{60}F_{48}/C8-BTBT$ interface doping) and from the silicon substrate to $C_{60}F_{48}$ through the double barrier ($C8-BTBT/nSiO_2$). Interface doping with charge transfer to $C_{60}F_{48}$ in both substrates, $nSiO_2$ and $tSiO_2$, introduces a band bending which is manifested in the asymptotic dependence of $\Delta\phi$ with dopant thickness.

The comparison between dopant/OSC heterostructures grown on thick oxide substrates using the two BTBT derivatives, namely $C_{60}F_{48}/DPh-BTBT/tSiO_2$ and $C_{60}F_{48}/C8-BTBT/tSiO_2$, is shown in Figure 5. A shadow mask was used during the deposition of both OSC and dopant, to locally fabricate the organic/organic heterojunction while keeping uncovered regions of the silicon oxide. The electrostatic landscape described as low-SP rims decorating steps for $C_{60}F_{48}/C8-BTBT$ in Figure 3j and 3l can be easily recognized in the rounded region of Figure 5a. Because the dopant distribution over DPh-BTBT cannot be discerned at large scale, the shadow mask was laterally shifted (under vacuum), after deposition of the OSC and prior to dopant overgrowth, to obtain: uncovered areas of the $tSiO_2$, well-defined regions of $DPh-BTBT/tSiO_2$, $C_{60}F_{48}/tSiO_2$ and an

intersection zone with $C_{60}F_{48}$ /DPh-BTBT/tSiO₂ (Figure 5b). The most striking observation is that the work function for $C_{60}F_{48}$ /DPh-BTBT/tSiO₂ changes, on average, only by $\Delta\phi \sim 0.2$ eV with respect to the bare OSC as compared to $\Delta\phi \sim 0.45$ eV in the case of $C_{60}F_{48}$ /C8-BTBT/tSiO₂ (Figure 5c and 5d) for similar $C_{60}F_{48}$ thickness. As we will discuss, the smaller work function change observed for $C_{60}F_{48}$ /DPh-BTBT/tSiO₂, indicative of a smaller interface dipole due to charge transfer between OSC and dopant, is consistent with the differences in the ionization potential between C8-BTBT and DPh-BTBT films obtained from the valence band measurements shown in the following.

Figure 5: Surface potential maps for patterned $C_{60}F_{48}$ (1.5nm)/DPh-BTBT(5nm)/tSiO₂ (a) and $C_{60}F_{48}$ (1.5nm)/C8-BTBT(6nm)/tSiO₂ (b). Colour code: Blue/yellow means lower/higher SP. In order to have regions of diverse composition including the uncovered substrate, a shadow mask was used for the subsequent deposition of OSC and dopant (see text). (c) and (d) SP histograms, i.e., number of events with a given SP value, from areas containing bare and covered BTBTs in

the corresponding maps. The vertical black dashed lines in the histograms indicate SP for the uncovered tSiO₂.

The electronic differences appearing during dopant deposition, in particular any change in work function and molecular HOMO levels, have been also explored by measuring the Fermi-edge VB and SECO regions for each BTBT derivative before and after two depositions of C₆₀F₄₈. The films of both BTBT derivatives were considerably thicker (~15 nm) than the films shown so far pursuing the purpose of reducing charge exchange with the substrate. We first note that the growth of C8-BTBT(15 nm)/nSiO₂ does not significantly alter the vacuum level (VL) of the system whereas a considerable shift is observed for DPh-BTBT(15 nm)/nSiO₂ (blue spectra in the SECO panels of Figure 6). It is worth mentioning that, considering the work function of the bare nSiO₂ (3.3 eV) and the LUMO of the BTBT derivatives (~1.55 eV),^{23,25,26} integer charge transfer between OSC and substrate is not expected.⁵⁴ The contribution of diverse interfacial phenomena and/or electrical dipole building during film growth must be invoked to explain our results.^{32,55,56,57} Since the complexity of the interplay between concurrent mechanisms may easily lead to incorrect interpretations, we focus our discussion on the experimental evidences. The ionization potential, estimated from the corresponding onset of the observed HOMO (Figure 6a and 6d), is IP_{DPh-BTBT} = 5.3 eV and IP_{C8-BTBT} = 5.0 eV. Therefore, considering the reported position of the LUMO for C₆₀F₄₈ (-5.5 eV),^{39,58} favourable charge transfer from the HOMO of the OSC films is expected for both BTBT derivatives, with larger energy offset for the C₆₀F₄₈/C8-BTBT interface. Note that no occupied molecular orbitals of C₆₀F₄₈ exist within the energy range analysed.

Sub-monolayer coverages of C₆₀F₄₈ deposited in-situ onto both OSCs films lead to a considerable increase of the measured ϕ , though notable differences stand out for each case. The

changes in work function are taken with respect to the values of the pristine films. Successive depositions of dopant, spreading out over the entire DPh-BTBT film, provoke a progressive shift of the SECO by $\Delta\phi \sim 0.35$ eV and $\Delta\phi \sim 0.55$ eV for 2 Å and 4 Å of C₆₀F₄₈, respectively (Figure 6a). Concomitant changes in the HOMO onset and core levels shifts (CLS) of DPh-BTBT (sulphur and carbon) support p-doping. Though non-fully coincident (same trend but different magnitude), the observed $\Delta(\text{HOMO}) \sim 0.4$ eV (Figure 6a), CLS(S 2p) ~ 0.25 eV (Figure 6b) and CLS(C 1s) ~ 0.35 eV (Figure 6c) can be described as unconventional upward band bending of the energy levels of the DPh-BTBT at the interface.³² Similarly, C₆₀F₄₈ on the C8-BTBT film causes a work function increase, which is $\Delta\phi \sim 0.8$ eV for 4 Å of C₆₀F₄₈ (Figure 6d). This large $\Delta\phi$ is accompanied by a $\Delta(\text{HOMO}) \sim 0.3$ eV of C8-BTBT (Figure 6d). Only subtle changes are detected in the otherwise wide S 2p (Figure 6e) and a shift of only ~ 0.13 eV of the C 1s (Figure 6f) of the alkyl-terminated molecules. The faint or undetectable shift in the XPS peaks is likely due to several adding up effects, the main being that only the portion of the C8-BTBT molecules under the C₆₀F₄₈ islands are affected by doping (see discussion below). A striking clue for OSC/dopant charge transfer is provided by the binding energy (BE) of the small C 1s line introduced by dopant deposition on the depicted region shown in the insets of Figure 6c and 6f. This feature, at ~ 289.8 eV and 289.5 eV, respectively, is a signature of carbon atoms bonded to fluorine (C-F).^{58,59} The lower BE of (C-F) in C₆₀F₄₈/C8-BTBT/nSiO₂ correlates to the higher surface dipole expected at this interface.

The energy level diagram for both heterostructures C₆₀F₄₈/DPh-BTBT/nSiO₂ and C₆₀F₄₈/C8-BTBT/nSiO₂ is schematized in Figures 6g and 6h. We note that the different change of the VL with respect to that of the bare substrate in the two cases is not well explained in the context of the integer charge transfer model, which predicts equal electronic equilibrium via alignment of the Fermi level and the LUMO of C₆₀F₄₈ (negative polaron).⁵⁴ Differently from organic

heterojunctions with unpinned intermediate layers,¹² here the HOMO of the OSC films are pinned to the LUMO of the dopant (via interface charge transfer) and, therefore, the OSC film is involved in the process of thermodynamic electronic equilibrium with the substrate. The larger $\Delta\phi$ observed for $C_{60}F_{48}/C8-BTBT$ in comparison to $C_{60}F_{48}/DPh-BTBT$, with a difference of ~ 0.25 eV, is indicative of a larger surface dipole as expected from larger charge transfer at the OSC/dopant interface due to the lower ionization energy of C8-BTBT films ($IP_{C8-BTBT} = 5$ eV versus $IP_{DPh-BTBT} = 5.3$ eV).

Figure 6. SECO and VB regions measured by UPS for (a) DPh-BTBT (15 nm)/nSiO₂ and (d) C8-BTBT (16 nm)/nSiO₂, prior (blue) and after two $C_{60}F_{48}$ depositions (green and red). The respective S 2p and C 1s core levels measured by XPS are depicted in (b, c) and (e, f) for each case. Spectra of the initial nSiO₂ substrate are also depicted (grey lines). The asterisk in the red spectra of (e) highlights differences in intensity and width with respect to its counterpart in (b). For C8-BTBT,

the C 1s consists of two components, sp^3 (C-C) and sp^2 (C=C), arising from C atoms in aliphatic chains and aromatic cores, respectively, while only the second type contributes for DPh-BTBT. See fitting details in Figure S6 of the Supporting Information. (g) and (h) Energy level diagrams for DPh-BTBT/ $nSiO_2$ and C8-BTBT/ $nSiO_2$, respectively, extracted from the UPS data.

As anticipated, we interpret the UPS and XPS results for $C_{60}F_{48}$ /C8-BTBT/ $nSiO_2$ as due to the particular morphology of the formed interface. We have shown that conversely to what happens on the phenyl-terminated film, the dopant does not distribute uniformly over the whole alkyl-terminated film surface but forms islands. The resulting nanomorphology leads to surface potential inhomogeneity at small lateral dimensions (Figure 3, Figure S5 in the Supporting Information) not accessible to the UPS measurements.⁶⁰ In spite of the heterogeneity of the surface, we observe a single SECO threshold by UPS that matches the largest work function values measured on top of tall $C_{60}F_{48}$ crystallites by KPFM (Figure 4). Thus, although both techniques, KPFM and UPS, show similar trend with $C_{60}F_{48}$ coverage and for each of the two systems, KPFM provides the accurate local information.

On the other hand, topographical analysis of this sample (Figure S4 and S5) in the Supporting Information) indicates that only ~12% of the C8-BTBT film is covered by $C_{60}F_{48}$ islands and, therefore, the S 2p and C 1s core levels of the C8-BTBT species in the red spectra of Figure 6 basically arise from the dopant-free surface. This argument is well supported by considering that a given percentage of the intensity of the S 2p spectrum corresponds to the shifted contribution of those molecules underneath the dopant. The same reasoning applies to explain the small shift of the C 1s core level. See full details of the C 1s and S 2p core level interpretation for the two BTBT pristine films and $C_{60}F_{48}$ /C8-BTBT/ $nSiO_2$ in Figure S6 of the Supporting Information.

Additionally, the existence of the C 1s peak with highest BE, unambiguously related to (C-F) and only present at the dopant location, constitutes the ideal footprint used to determine the electrostatic environment of C₆₀F₄₈ in each dopant/OSC heterostructure.

Given that the doped interface is crucial for contact resistance reduction in contact-doped OFETs, we expect that this study, demonstrating the impact of the side groups in dopant-OSC interface formation, will trigger a future work focused on the optimization of devices.

Conclusions

The initial stages of the C₆₀F₄₈ growth on thin films of phenyl- and alkyl- BTBT derivatives indicate that the substitutional side groups have a strong effect on the morphology of the dopant/OSC interface. In both cases, an abrupt interface is formed with no visible alteration in the structure of the underlying film. However, while on the DPh-BTBT films C₆₀F₄₈ spreads out over the entire OSC surface, on the C8-BTBT surface it assembles in close-packed islands that mostly nucleate at step edges creating a discontinuous C₆₀F₄₈/OSC interface. This contrast suggests a significant influence of the phenyl-terminated films on the intermolecular binding of the fluoro-fullerenes that prevent self-assembly. Despite this difference, XRD data reveal the same FCC structure, as C₆₀F₄₈ growth develops, with crystalline (111)-oriented domains in both cases, forming a well-defined interface without detected inter-diffusion.

We show that interfacial charge transfer between OSC and dopant but also charge transfer with the substrate through the native oxide should be considered to understand electronic equilibrium in these systems, indicating that both, OSC film and substrate, are pinned to the LUMO of the dopant. To isolate contributions, KPFM data are presented for similar heterojunctions fabricated

on thick silicon oxide substrates, demonstrating interfacial charge transfer between the dopant and the OSC film, with the formation of a larger interface dipole in C₆₀F₄₈/C8-BTBT than in C₆₀F₄₈/DPh-BTBT. This result quantitatively correlates with the ionization potential difference extracted from UPS for each BTBT derivative.

Combining valence band and core level spectroscopic analysis with the differentiating details of the formed interfaces by KPFM, we provide a basic understanding of the energy alignment mechanism and prove the relevance of unique aspects arising from fine structural and morphological details of the dopant/OSC interface.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Additional X-ray diffraction data, AFM topographic and surface potential images as well as XPS analysis of diverse bare films and heterostructures are provided.

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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Table of Contents (TOC)/Abstract Graphic

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Supporting Information

Effect of the organic semiconductor side groups on the structural and electronic properties of their interface with dopants

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Figure S1. (a,b): Topography and corresponding lateral force image, for 7nm of DPh-BTBT/nSiO₂. (c, d) Topography and corresponding frequency shift image, for 6nm of C8-BTBT/nSiO₂. Since the DPh-BTBT film covers the surface, an uniform lateral force signal is observed in (b). The bright rim at the left side of the islands arises from the torsion of the tip at the ascending step edge in the forward direction of the scan. Frequency shift map of C8-BTBT (d) reflects the bimodal signal corresponding to the nSiO₂ substrate (lighter) and the C8-BTBT islands (darker), providing evidence of uncovered substrate.

Figure S2. Out of plane XRD pattern for (a) 11nm DPh-BTBT (black) and after 2 nm C₆₀F₄₈ deposition (blue). (b) Corresponding 2D GIXD map of the pristine DPh-BTBT (11 nm)/nSiO₂. As in the manuscript, nSiO₂ stands for native SiO₂ oxide on n-type Si.

Figure S3. Large-scale topography and simultaneous surface potential (SP) maps for the sample shown in Figure 3. Data measured by KPFM for DPh-BTBT (9 nm)/nSiO₂ before (a, b) and after $C_{60}F_{48}$ deposition of 1 nm (c, d) and 3 nm (e, f). (g) Magnified topography of the area indicated in (c), and (h) profile along the segment indicated in (g) showing the height of $C_{60}F_{48}$. Note the non-homogeneous surface of the covered regions and the correspondence with the lower SP in (c), independently of the DPh-BTBT film level.

Figure S4. Topographic images and the corresponding profiles obtained by AFM after the XPS/UPS measurements shown in Figure 6 of the manuscript. Samples description: 4 Å of $C_{60}F_{48}$ on (a, b) DPh-BTBT(15 nm)/nSiO₂ and (c, d) C8-BTBT(16 nm)/nSiO₂, respectively. The average height of the non-compact aggregates in the case of DPh-BTBT agrees with the $C_{60}F_{48}$ molecular size (1nm) while the heights of crystallites on C8-BTBT are multiples of it (3nm, 6nm). (e) Flooding analysis of the topography in (c) to show only areas covered with $C_{60}F_{48}$ crystallites. The flooded area is $\approx 12\%$ of the total surface area, which is the percentage of C8-BTBT at the OSC/dopant interface. “Flooding” is an imaging processing method that allows displaying regions from an image above or below a threshold value of the Z-scale (flooded region).

Figure S5. Topographic AFM images and the corresponding surface potential maps obtained by KPFM after the XPS/UPS measurements shown in Figure 6 of the manuscript. Samples description: 4 Å of $C_{60}F_{48}$ on (a, b) DPh-BTBT(15 nm)/nSiO₂ and (c, d) C8-BTBT(16 nm)/nSiO₂, respectively. The area covered by $C_{60}F_{48}$ crystallites on C8-BTBT is 12% of the total surface area. (e) Flooding analysis of the topography in (c) to show only areas covered with $C_{60}F_{48}$ crystallites. The flooded area is $\approx 12\%$ of the total surface area that corresponds to the percentage of C8-BTBT covered by the dopant (OSC/dopant interface).

Figure S6. XPS core level spectra and fitting curves. In order to explain the different behaviour observed for the C 1s and S 2p core level peaks, upon dopant deposition, in the case of C8-BTBT (data shown in Figure 6 of the manuscript), the XPS spectra have been fitted first for the pristine surfaces of (a) DPh-BTBT(15nm)/nSiO₂ and (b) C8-BTBT(15nm)/nSiO₂ (b). The C 1s spectrum for the pristine DPh-BTBT film (a) is fitted by a unique component (BE = 284.81 eV, $w = 0.95$ eV) because all C atoms in this molecule have a similar sp^2 surrounding. However, the C 1s corresponding to the pristine C8-BTBT film (b) is much wider. In fact, it consists of two components: sp^3 (C-C) and sp^2 (C=C) arising from the C atoms in aliphatic chains (BE= 285.42 eV) and the aromatic cores (BE=284.82 eV), respectively. As expected, the relative area between these two components equals the stoichiometric ratio between sp^2 and sp^3 C atoms in the molecule (16/14). The C 1s spectrum for C₆₀F₄₈(4Å)/C8-BTBT(15nm)/nSiO₂ is depicted in (c). As described in the manuscript and supported by the topographic analysis in Figure S4e and S3e, only a given percentage of the C8-BTBT film surface is covered by the dopant. First, we note that the C-C and C=C components of the C8-BTBT species are shifted by ~ 0.12 - 0.14 eV. This shift is small as compared to ~ 0.35 eV observed for similar conditions on the DPh-BTBT film (Figure 6c in the manuscript) and can be explained by the small percentage of C8-BTBT molecules under C₆₀F₄₈, i.e., affected by charge transfer. In addition, at higher BE two new peaks appear. They correspond to C atoms bonded to fluorine (C-F) or only to C (C-C-F), signature of the dopant molecules. The S 2p core level spectra of (d) correspond to C8-BTBT(15nm)/nSiO₂ (black) and C₆₀F₄₈(4Å)/C8-BTBT(15nm)/nSiO₂ (blue). The well resolved doublet for the pristine spectrum arises from the spin-orbit splitting of sulphur atoms (S2p_{3/2} and S2p_{1/2}, $\Delta = 1.2$ eV). After dopant deposition (blue), the intensity decreases at the peaks' maxima while it increases between peaks (*) and at the low BE side of the spectrum. This fact can be understood by taking into account that only part of the C8-BTBT film is covered by C₆₀F₄₈. This is illustrated by the linear combination (red) of two doublets: 76% of the pristine (black) plus 24% of a second one shifted by 0.3 eV to lower BE (pink). We note that the percentages can be different if estimated by XPS, a large-scale averaging method, or locally by AFM (see Figures S3c and S4c). The present analysis strongly supports the interpretation in terms of the particular growth mode of C₆₀F₄₈ depending on the side groups of the BTBT derivatives.