Design-dependence of the interface structure and crystalline order of organic semiconductor/dopant heterojunctions: Pentacene/C$_{60}$F$_{48}$

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**Abstract**

Planar and mixed heterojunctions are the common architectures respectively used for contact and bulk doping in organic electronics. Beyond the success of empirical methods, knowing how the incorporation of dopant molecules affects the structural properties of the organic semiconductor film is essential for the design optimization of devices with efficient electrical properties. With this aim, we exploit out-of-plane and grazing incidence x-ray diffraction (GIXD) to characterize engineered heterojunctions fabricated on native SiO$_2$ substrates with pentacene as organic semiconductor and C$_{60}$F$_{48}$ as dopant. A strong interaction between the two species is inferred, which dramatically influences the crystalline
order in the different architectures. While C60F48 crystalline domains orient randomly on the SiO2 surface, the ulterior deposition of pentacene is demonstrated to induce orientational order and reorganization of the underlying C60F48. In the inverse architecture, the highly [001]-oriented pentacene film on SiO2 has a template effect on C60F48 inducing the formation of a fcc [111]-oriented film and leading to an ordered planar heterostructure. Real-time GIXD reveals the presence of a strained C60F48 layer at the interface with a gradual relaxation and transition to 3D crystallites formation with increasing coverage. When mixed in the bulk by co-evaporation, the dopant adopts an amorphous state, embedded in a polycrystalline pentacene matrix. The interfacial effects reported here would have relevant repercussion on the efficiency of molecular doping, which makes it possible to foresee the establishment of guidelines for device performance improvement through interface engineering.

**Keywords:** organic semiconductors, molecular doping, interface, thermal stability, pentacene, C60F48, GIXD, AFM

**Introduction**

Molecular doping is one of the fundamental strategies aiming to increase the electrical conductivity of organic semiconductors (OSCs) and tune their electrical properties.\(^1\text{-}^3\) As such, it stands at the basis of organic electronics, being widely applied in organic emitting light diodes (OLEDs),\(^4\text{-}^7\) organic field effect transistors (OFETs)\(^8\text{-}^10\) and organic photovoltaics (OPV).\(^11\text{-}^12\) Despite its broad use in commercially available devices, a deep and univocal understanding of the principles behind molecular doping is still under discussion.\(^13\text{-}^15\) Depending on the role of the dopant in a specific technology, two strategies can be employed: bulk doping and contact doping (also referred as surface transfer doping). The former represents the conventional method to increase the film conductivity by co-deposition of OSC and
dopant molecules; the latter consists instead in the sequential deposition of OSC and dopant to form a planar heterojunction, with the primary role of improving the charge injection from an electrode. Numerous studies have been devoted to understanding the microscopic details of bulk doping in order to explain the fact that the free-charge carrier density is often far lower than the dopant concentration, with strong variations among OSC systems. Generally speaking, molecular doping occurs via charge transfer between the OSC material and the dopant molecules. An effective p-type molecular dopant must satisfy the requirement of having higher electron affinity than the OSC ionization energy to favor integer charge transfer (ICT). Although the ICT model seems to provide a reasonable description of doping for some systems (mostly conjugated polymers), extensive research has shown that this picture does not appropriately describe the behavior of small-molecule OSCs. In this case, an alternative doping mechanism has been proposed which rests on the formation of hybrid molecular orbitals and charge transfer complexes (CPXs). Intermolecular hybridization is intimately related to the interaction strength between OSC and dopant molecules and therefore depends on the structural characteristics of the heterojunction. Besides, for some of the most common p-type dopants, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) and 1,3,4,5,7,8-hexafluorotetracyanonaphthoquinodimethane (F6TCNNQ), x-ray diffraction studies have revealed that their planar shape results in co-crystallization when mixed with some donor molecules, resulting in the formation of a co-planar pi-stacking of alternating dopant and OSC molecules with pronounced intermolecular frontier-orbital hybridization. Electrical doping arises from the co-crystallites acting as dopants by generating holes in the OSC film and more efficient electrical doping is observed for those systems where co-crystallization does not occur. In other cases, as when pentacene (PEN) is used as OSC, the dopant molecules (F4TCNQ and F6TCNNQ) render the film amorphous under co-evaporation conditions. Ideally, the mobile carrier densities must be increased upon doping without
adversely affecting their mobility through a strong deterioration of the crystalline quality of the OSC film.  

Surface transfer doping finds its main application in improving the charge injection in devices like OFETs but it has also been employed to induce a two-dimensional layer of carriers at the surface of organic single-crystalline thin films or to dope the channel region in OFETs. The interfaces formed can be viewed as a particular case of a planar donor/acceptor (D/A) heterojunction, where charge transfer is expected to occur across the interface. The extent of charge transfer effects are intertwined with the local structural properties (distribution of the dopant, order, orientation, etc.), where a critical issue is the diffusion of the dopant through the OSC film at room temperature, a problem often encountered for F4TCNQ due to the small size of the molecule. This shortcoming can be avoided by using bulkier molecular dopants such as fluorinated fullerenes. Still the thermal stability of the heterojunction is an important issue given that intermixing can be promoted by thermal energy. In contrast to the large number of investigations devoted to the growth and structure of planar D/A heterojunctions in the context of organic photovoltaics, very few studies have addressed the OSC/dopant interface, when a strong acceptor material is used as a dopant layer.

Overall, the studies on molecular doping highlight that the microstructure and stability of doped films are of crucial relevance to understand the effectiveness of doping and to guide optimization strategies. Doping can strongly affect and be affected by the OSC crystal structure, degree of crystallinity, miscibility and distribution of the dopant with crystalline and amorphous phases of the OSC.

In this article, we investigate how the design of surface doped films by sequential deposition or bulk doped films by co-evaporation, affects the microstructure of the OSC film and the interface structure of dopant and OSC. Our dopant choice fell on fluorinated fullerenes, which have been employed as molecular dopants in pentacene OFETs as well as for other OSC materials. In particular, C60F48 is
the fluorofullerene with the maximum fluorine content, which entails an electron affinity of \( \sim 5.5 \) eV, making this material a very strong electron acceptor.\(^{36,39}\) While the growth of its precursor, \( \text{C}_{60} \), has been extensively studied on different OSC layers,\(^{40-44}\) \( \text{C}_{60}\text{F}_{48} \) still lacks an exhaustive structural investigation as dopant of organic thin films. In this context, we have previously reported the microscopic view of the nucleation of \( \text{C}_{60}\text{F}_{48} \) deposited on pentacene and BTBT derivatives,\(^{45,46}\) demonstrating that the crystallographic characteristics of the OSC film surface dramatically affect the growth dynamics of \( \text{C}_{60}\text{F}_{48} \).

Here, we combine grazing incidence x-ray diffraction (GIXD), out-of-plane x-ray diffraction (XRD) and atomic force microscopy (AFM) to characterize the structure and morphology of planar heterojunctions as architecture for contact doping, prepared by sequential evaporation of pentacene and \( \text{C}_{60}\text{F}_{48} \), as well as the mixture (bulk doping), realized by co-evaporation of the two molecules. The results show remarkable structural differences, for pentacene and \( \text{C}_{60}\text{F}_{48} \), depending on the deposition sequence in the case of planar heterojunctions and a lack of crystallinity of \( \text{C}_{60}\text{F}_{48} \) in bulk heterojunctions. Overall, the obtained results point to a significant interaction between pentacene and \( \text{C}_{60}\text{F}_{48} \) molecules that substantially impacts the structural characteristics of both materials and the interfacial properties.

**Experimental**

Pentacene was purchased from Sigma-Aldrich and purified by gradient-sublimation; the fluorinated fullerene \( \text{C}_{60}\text{F}_{48} \) was provided by the Nanoelectronic Center of Technion (Haifa, Israel) where it was synthesized using the method developed at the Josef Stefan Institute (Slovenia).\(^{47}\) The product was characterized by chemical analysis, electron-ionization mass spectrometry and IR-spectroscopy and its purity was estimated to be 95%. The thin films were prepared by organic molecular beam deposition (OMBD) depositing the two molecules via thermal sublimation under high vacuum conditions \( (10^{-7} \text{ mbar}) \) while keeping the substrate at room temperature (RT). The Knudsen cells were resistively heated up to 180-200°C for both pentacene and \( \text{C}_{60}\text{F}_{48} \), giving deposition rates of about 2 Å/min. Arsenic n-
doped silicon with native oxide was used as the substrate in all the presented experiments. Prior to transfer to the vacuum chamber, the substrates were cleaned by ultra-sonication for 10 minutes in acetone and then 10 minutes in ethanol. Both substrates and cells were degassed in vacuum for 15 minutes at temperatures around 250°C and 100°C, respectively. The growth rates were monitored with a quartz crystal microbalance. For pentacene, the coverage is determined from the AFM topographic images, one monolayer being a single full layer of nearly standing-up molecules, corresponding to a nominal layer thickness of \( \sim 15 \, \text{Å} \). In the case of \( C_{60} F_{48} \), the coverage is determined from out-of-plane XRD by evaluating the change in the oscillation period of the Kiessig fringes upon the deposition of \( C_{60} F_{48} \) on pentacene. We are aware that this method can underestimate the real coverage.

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 geometry was used to investigate the film structure in the direction perpendicular (out-of-plane) to the substrate. 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 (\( \sim 0.14° \) at this energy) and above the critical angle of pentacene assuming a material density of 1.3 g/ml. Therefore, the whole film thickness is probed by the incoming beam. The mean size of the crystalline domains has been obtained from the full width half maximum (FWHM) of the Bragg peaks (\( \Delta q \)) by using the approximated expression of the Scherrer equation \( 2\pi/\Delta q \). To avoid radiation damage, each measurement set (2D-GIXD map plus out-of-plane XRD) was performed in a different sample location (fresh spot). Accordingly, the procedure employed for the real-time structural evolution of \( C_{60} F_{48} \) growth was the following: (i) monitoring during the first 15 Å deposition; (ii) acquisition of the 2D map in a fresh spot (post-growth); (iii) monitoring in another area during the evaporation of additional 30 Å; (iv) acquisition of the 2D-GIXD map in a fresh spot (post-growth). Intensity changes detected when repositioning to a fresh spot after (i) or (iv) indicate certain beam effect during real-time monitoring. The
in-plane spectra were obtained from the 2D-GXID maps by integrating the diffraction intensity in a qz range of \( \sim 0.09 \) Å\(^{-1}\).

AFM measurements were performed in contact and dynamic modes at RT using a commercial head and control unit from Nanotec Electronica. Si\(_3\)N\(_4\) V-shaped cantilevers (Veeco) with nominal force constant ranging between 0.03 and 0.5 N/m were employed for contact mode while Cr/Pt coated silicon tips on rectangular cantilevers (BudgetSensors) with nominal resonance frequency of 75 kHz and force constant of 3 N/m were used for dynamic mode. The WSxM freeware was used to analyze all the presented AFM images.\(^{48}\)

Note: all cartoons shown in the figures of the article are devoted to illustrate in a simplistic way the diverse results, with no attempt of providing an accurate representation of the molecular packing.

**Results and discussion**

We first address the deposition of C\(_{60}\)F\(_{48}\) (Figure 1a) on native silicon oxide (SiO\(_2\)) at RT. The AFM topographical image of 30 Å C\(_{60}\)F\(_{48}\) on SiO\(_2\) (Figure 1b) shows aggregates with a wide range of diameters (up to 100 nm) and heights (up to 10 nm), yielding a root mean square (rms) roughness of 1.6 nm. A close inspection between aggregates points to the presence of a molecular layer covering the surface, a fact supported by out-of-plane XRD data (Figure S1 in the Supporting Information). The 2D-GIXD pattern (Figure 1c) shows Debye-Scherrer rings, indicating that C\(_{60}\)F\(_{48}\) crystalline domains orient randomly on the SiO\(_2\) surface. From the q-position of the diffraction rings \( q_{xy} \approx 0.61 \) Å\(^{-1}\), \( q_{xy} \approx 1.03 \) Å\(^{-1}\), \( q_{xy} \approx 1.18 \) Å\(^{-1}\) we cannot safely differentiate if we are dealing with a body centered tetragonal (bct) structure reported in the bulk material\(^{49}\) or a face centered cubic (fcc), as it is the case of C\(_{60}\)F\(_{48}\) evaporated on pentacene (see discussion below). From the FWHM of the peak at \( q_{xy} \approx 1.03 \) Å\(^{-1}\), an in-plane coherence size of about 8 nm is estimated. No out-of-plane order is present in the C\(_{60}\)F\(_{48}\) aggregates as revealed by the absence of Bragg peaks in the out-of-plane XRD (Figure S1).
Figure 1. (a) Molecular structure of C$_{60}$F$_{48}$, (b) AFM topographical image, (c) 2D-GIXD map and (d) in-plane GIXD spectrum for C$_{60}$F$_{48}$(30 Å)/SiO$_2$. (e) Cartoon representing the non-oriented aggregates of C$_{60}$F$_{48}$ grown on SiO$_2$ at RT.

Figure 2. (a) 2D-GIXD map of pentacene(120 Å)/C$_{60}$F$_{48}$(30 Å)/SiO$_2$. (b) Out-of-plane spectra before (black) and after (yellow) the pentacene deposition (c) Cartoon representing the pentacene/C$_{60}$F$_{48}$/SiO$_2$ planar heterojunction, with no attempt to draw molecules to scale.
The 2D-GIXD pattern of the heterostructure formed when depositing pentacene (120 Å) on top of C₆₀F₄₈ (30 Å) displays characteristics from each of the two materials (Figure 2a). We first note that pentacene features consist of Debye-Scherrer rings arising from randomly oriented crystalline domains, indicating that the underlying C₆₀F₄₈ hinders the development of a [001]-oriented pentacene film. The in-plane positions of the rings (qₓᵧ ≈ 1.35 Å⁻¹, qₓᵧ ≈ 1.67 Å⁻¹ and qₓᵧ ≈ 1.98 Å⁻¹) agree with the thin film (TF) structure of pentacene⁵⁰,⁵¹ and are labelled accordingly. The lack of orientation of pentacene can have various causes. On the one hand, the roughness of the underlying C₆₀F₄₈ layer (Figure 1b) can be detrimental for the crystalline quality of pentacene films⁵²-⁵⁶. On the other hand, the intermolecular interaction with C₆₀F₄₈ may drive impinging pentacene molecules to adopt a partially disordered configuration and form crystallites with random orientation at the interface. Comparison between Figures 1c and 2a indicates that the mosaicity of the pristine C₆₀F₄₈ (i.e., the angular distribution of crystalline domains) is reduced to some extent upon deposition of pentacene. In addition, the out-of-plane XRD (yellow curve of Figure 2b) indicates, with respect to the pristine C₆₀F₄₈ (black curve of Figure 2b), the emergence of a reflection at qᵣ ≈ 0.63 Å⁻¹ attributed to the fcc-(111) C₆₀F₄₈ Bragg reflection (see below). These results give evidence of a reorganization of the underlying dopant crystallites (inducing texture) by effect of the interaction with pentacene. Elucidating the mechanism at the origin of such remarkable result would require further investigation but some plausible reasons might be the reorientation of the initial C₆₀F₄₈ small aggregates or even the formation of new ones at the interface with pentacene.

We discuss next the heterostructures obtained by the reversed deposition sequence, i.e., C₆₀F₄₈ on top of a pentacene film grown on SiO₂. In a previous study on the C₆₀F₄₈/pentacene interface formation, carried out by combining different microscopic techniques, we demonstrated that the specific morphology of the dopant deposits is strongly affected by the structural quality of the underlying
pentacene film.45 Here we address the structure of the C_{60}F_{48}/pentacene planar heterojunction for two thicknesses of the pentacene film, namely 30 Å and 120 Å. Because similar results were obtained for both, we discuss here in detail the case of the thinner film, whereas those obtained for the thicker one are provided in Figure S3 of Supporting Information. Figure 3a displays the typical topography for a submonolayer coverage of C_{60}F_{48} on the 30 Å pentacene film. The dopant molecules self-assemble partially covering the surface as clearly seen by the contrast in the composition-sensitive frequency shift channel (Figure 3b). The ∼10 Å height of these patches (Figure 3c) is fully coherent with one C_{60}F_{48} molecular layer. As already reported45 the growth mode of C_{60}F_{48} dramatically differs when it is deposited on the pentacene film surface (see also Figure S2) or directly on the SiO₂ substrate (Figure 1b).
Figure 3. (a) AFM topography and (b) simultaneous excitation frequency channel for a submonolayer coverage of C$_{60}$F$_{48}$ on pentacene(30 Å)/SiO$_2$. Packed dopant assemblies are distinguished in the images as taller areas in (a) and darker patches in (b). (c) Line profile along the segment indicated in (a), crossing a C$_{60}$F$_{48}$ island on a pentacene terrace. (d) Out-of-plane diffraction spectra of the pentacene(30 Å)/SiO$_2$ film, before and after each of the C$_{60}$F$_{48}$ depositions (total 15 Å and 45 Å). Black and red peak labels correspond to pentacene and C$_{60}$F$_{48}$, respectively.
Figure 3d shows the out-of-plane XRD data for the pristine pentacene film and after each step of the sequential deposition to get 15 Å and 45 Å of C₆₀F₄₈, respectively. Though the structural features of the pristine film are strongly convoluted with the Kiessig oscillations arising from the interference pattern produced by the film thickness, the (002) reflection is clearly visible at $q_z = 0.80$ Å⁻¹, giving a (001) interplanar spacing of about 15.7 Å, in good agreement with the reported TF structure (molecules standing nearly upright on the surface). Upon evaporation of 15 Å of C₆₀F₄₈, a variation of the Kiessig oscillations arise from the increase in total film thickness and a peak appears visible at $q_z = 0.63$ Å⁻¹ after additional 30 Å of C₆₀F₄₈. As we will discuss, the observed peak is attributed to the fcc-(111) C₆₀F₄₈ Bragg reflection, also observed for C₆₀F₄₈ on 2,7-dioctyl[1]benzothieno-[3,2-b][1]benzothiophene (C₈-BTBT). The corresponding interplanar distance of $d = 10.1$ Å agrees with the single layer height measured by topographic AFM (Figures 3a and S2). From the width of the (111) peak, a 14 nm mean crystallize size is estimated, which is an indication of island formation.

The GIXD data shown in Figure 4 for the same samples confirm the above description. The 2D diffraction pattern of pentacene (30 Å) on SiO₂ consists of sharp diffraction rods revealing the 2D crystalline structure of [001]-oriented pentacene (Figure 4a). The deduced in-plane unit cell ($a = 5.96$ Å, $b = 7.56$ Å, $γ = 90°$) is in good agreement with what reported for the TF structure. After evaporating 15 Å of C₆₀F₄₈ on top, new well-defined diffraction rods appear at $q_{xy} = 0.60$ Å⁻¹, $q_{xy} = 1.05$ Å⁻¹ and $q_{xy} = 1.21$ Å⁻¹ (Figure 4b). The developed pattern is consistent with the formation of a fcc-structure with a lattice parameter of $a ≈ 17.0$ Å (see discussion in Figure S4) with the (111) plane parallel to the surface and is labelled accordingly in Figure 4b. The evolution from narrow rods to fusiform features with increasing C₆₀F₄₈ coverage (Figure 4b-c) is a proof of a transition from the 2D crystalline packing of the first layer towards the vertical development of crystals (3D growth). The enhanced crystalline order of C₆₀F₄₈ on pentacene contrasts by far with its polycrystalline characteristics on SiO₂ (Figure 1c), which
goes on the line of the reported template effect that organic layers have on C₆₀.⁶⁴–⁶⁷ At this point, it is worth mentioning that the in-plane pentacene packing remains unaltered throughout the whole dopant deposition process (Figure S5).

Figure 4. (a, b, c) 2D-GIXD maps before and after depositing 15 Å and 45 Å of C₆₀F₄₈ on pentacene(30 Å)/SiO₂. White and yellow labels stand for pentacene and C₆₀F₄₈ reflections, respectively. (d) Real-time evolution of GIXD intensity during in-situ C₆₀F₄₈ deposition. (e) Peak position vs dopant coverage extracted from fitting the C₆₀F₄₈ (2-20) reflection. The crosses at 15 Å and 45 Å correspond to measurements on fresh areas used to consider any possible radiation effect (see experimental section). (f) Schematic cartoon of the C₆₀F₄₈/pentacene/SiO₂ planar heterojunction, representing the alignment of the (111) crystalline plane of C₆₀F₄₈ parallel to the surface (molecules are not drawn to scale).
In order to track the evolution of the interface structure during the early stages of C$_{60}$F$_{48}$ growth, we performed real-time GIXD. As described in the experimental section, the measurements were carried out in diverse steps: after monitoring during the deposition of the first 15 Å of C$_{60}$F$_{48}$, the growth was interrupted to acquire the 2D-GIXD map in a fresh spot in order to minimize radiation damage. The q$_{\text{xy}}$ range was selected to include in-plane peaks of C$_{60}$F$_{48}$ (q$_{\text{xy}}$ ≈ 1.05 Å$^{-1}$ and q$_{\text{xy}}$ ≈ 1.21 Å$^{-1}$) and pentacene (q$_{\text{xy}}$ ≈ 1.35 Å$^{-1}$). Because the position of the latter persists unaltered, only the C$_{60}$F$_{48}$ peaks are depicted in Figure 4d (wider GIXD scans are provided in Figure S5). With increasing coverage, both C$_{60}$F$_{48}$ peaks shift to lower q$_{\text{xy}}$, indicating an in-plane expansion of the structure. The magnitude of the shift is better appreciated in Figure 4e that represents the position of the (2-20) peak as a function of coverage. Remarkably, the peak remains at q$_{\text{xy}}$ ≈ 1.05 Å$^{-1}$ during the first 9 Å and only after it shifts towards lower values. The total displacement by ~0.01 Å$^{-1}$ corresponds to an increase of about 1% of the in-plane spacing. Interestingly, the shift observed from 15 to 45 Å is not accompanied by any detectable change of the in-plane crystalline size, confirming that C$_{60}$F$_{48}$ crystals grow vertically (3D growth).

We note that within the error in the calculated nominal thickness, a coverage of ~9 Å well corresponds to the formation of the first layer of C$_{60}$F$_{48}$ on pentacene. We propose that the 2D packing of C$_{60}$F$_{48}$ nucleating at the interface with pentacene is compressively strained as a means to reduce the total interfacial energy. With further coverage, the C$_{60}$F$_{48}$ in-plane structure undergoes a gradual relaxation that is accompanied by a transition towards a 3D growth. The importance of the pentacene-C$_{60}$F$_{48}$ interaction, manifested in a reorganization of C$_{60}$F$_{48}$ upon pentacene deposition in the pentacene/C$_{60}$F$_{48}$/SiO$_2$ heterojunction (Figure 2), is also invoked here to explain the 2D to 3D growth transition driven by strain effects at the interface. Although from our XRD data we cannot determine whether a weak van der Waals epitaxy relationship exists for C$_{60}$F$_{48}$/pentacene interface, we note that a
GIXD study has reported a crystallographic interrelation by coincidence of the reciprocal points for C$_{60}$ on pentacene single crystals.$^{68}$
As third type of heterojunction, we have investigated the mixture obtained by co-evaporation of pentacene:C$_{60}$F$_{48}$ film using the molar ratio of 10:1, a reasonable average value for doping. In the 2D-GIXD pattern of Figure 5a, it is observed that pentacene exhibits a polycrystalline structure with in-plane mean crystalline size comparable to that of pentacene films grown on C$_{60}$F$_{48}$. In contrast, C$_{60}$F$_{48}$ exhibits an amorphous diffraction pattern with a coherent in-plane crystalline size of only $\sim 3$ nm. These results suggest a scenario where short-range ordered C$_{60}$F$_{48}$ molecules are embedded within the pentacene polycrystalline matrix. Hence, we conclude that the interaction of C$_{60}$F$_{48}$ with pentacene, added to obvious differences in shape and size of the molecules, importantly inhibits the aggregation and ordering of C$_{60}$F$_{48}$ molecules in the co-evaporated film. We note that, while pentacene is polycrystalline in the pentacene:C$_{60}$F$_{48}$ film, co-deposition of pentacene with other molecular dopants, such as F4TCNQ and F6TCNNQ, resulted in the loss of crystalline order of pentacene.$^{22}$ Here we remarkably find that both, preservation of pentacene crystalline order and dispersed distribution of the dopant, make C$_{60}$F$_{48}$ a good molecular dopant for pentacene. We note that the present conclusions are obtained for a specific OSC:dopant ratio and only a systematic investigation by varying this ratio would permit the generalization of our results.

Finally, the thermal stability of the C$_{60}$F$_{48}$/pentacene/SiO$_2$ planar heterojunctions and the mixed film has been examined. Upon annealing at 90°C, all C60F48 diffraction traits have disappeared. The 2D-GXID pattern (Figure S6a) just shows the characteristic diffraction rods of pentacene/SiO$_2$. As seen in the in-plane GIXD spectra of Figure 6a, the in-plane peaks width of pentacene remains unchanged. We note that the scenario of inter-diffusion of the dopant within the pentacene film induced by annealing (which
would result in a mixing ratio of PEN:C60F48 ≈ 3:1) would lead to visible signs of increased disorder, such as peak broadening and/or a change in the line shape. Because of the utter absence of C60F48-related features and of any significant change of the pentacene peaks, the observations are attributed to the desorption of the dopant molecules. Yet the reduction of the pentacene diffraction intensity likely reflects partial desorption of molecules from the upper layers, with a lower cohesion energy than those within the film. Similar experiments performed on thicker pentacene films produced no appreciable changes on the pentacene after annealing (Figure S6b, c). For the co-evaporated heterojunction, a reduction of the intensity of all diffraction features is detected upon annealing at 90°C (Figure 6b). The reduction trend is identical for the two molecules suggesting that they are desorbed in the same proportion (Figure S7). As expected, in contrast to the case of the planar heterojunction, C₆₀F₄₈ is not completely desorbed and remains embedded in the pentacene polycrystalline film. Furthermore, no substantial change in the peaks’ width is observed for any of them, pentacene or C₆₀F₄₈, indicating that the bulk heterojunction retains its mixed nanomorphology.
Figure 6. In-plane GIXD spectra of (a) the C$_{60}$F$_{48}$(30Å)/pentacene(30Å) and (b) the pentacene:C$_{60}$F$_{48}$ (10:1) samples before (black) and after (green) annealing at 90°C. (c) Cartoon schematically illustrating the effects of thermal annealing in the two cases (molecules are not drawn to scale).

**Conclusions**

We presented a comprehensive structural investigation that demonstrates remarkable interfacial effects between C$_{60}$F$_{48}$ and pentacene for both planar and bulk heterojunctions. Whereas C$_{60}$F$_{48}$ forms crystallites randomly oriented on SiO$_2$, [001]-oriented pentacene films have a template effect on the C$_{60}$F$_{48}$ growth, leading to an ordered planar heterostructure with fcc [111]-oriented C$_{60}$F$_{48}$. During C$_{60}$F$_{48}$
growth on pentacene, the structure evolves from a compressed 2D packing in the first layer (1%) towards the vertical development of 3D crystals. The inverse deposition sequence, i.e., pentacene on top of C_{60}F_{48}, results in a heterostructure where both, dopant and OSC, exhibit a polycrystalline structure with large azimuthal disorder. Remarkably, in this case the deposition of pentacene induces reorganization of the underlying C_{60}F_{48} and the development of C_{60}F_{48} 3D crystallites with [111]-texturing. Finally, when co-evaporating the two components, C_{60}F_{48} appears to be embedded in a pentacene polycrystalline matrix, which is expected to be beneficial for electrical doping. In the absence of hints indicating intermixing in the case of planar heterojunctions or phase separation in the case of co-evaporated films, we infer that the investigated heterojunctions are structurally robust upon thermal annealing.

The presented results give evidence of significant interaction between C_{60}F_{48} and pentacene molecules with impact on the heterojunctions microstructure. Since the structure-function relationship has a crucial importance in understanding the doping mechanism and ameliorating doping efficiency, we expect that the present study will motivate future electrical investigation and guide strategies for improvement of the doping efficiency by interfacial engineering.

**Supporting Information**

The Supporting Information includes: (i) complementary x-ray diffraction data with further analysis and comments; (ii) additional AFM images; (iii) x-ray diffraction data and discussion for a thicker pentacene sample; (iv) the calculated fcc and bct diffraction patterns to confirm the C_{60}F_{48} crystalline structure; (v) estimation of the expected reduction of the pentacene diffraction intensity due to C_{60}F_{48} coverage; (vi) evaluation of the effects of annealing on the total diffraction intensity in the coevaporated sample.
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Supporting Information

Design-Dependence of the Interface Structure and Crystalline Order of Organic Semiconductor/Dopant Heterojunctions:

Pentacene/C_{60}F_{48}

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C_{60}F_{48} deposited on silicon oxide

Figure S1 reports the out-of-plane XRD spectrum of 30 Å of C_{60}F_{48} deposited on silicon oxide in comparison with that of the bare SiO_2 substrate. The presence of a molecular layer is derived from the change of the reflectivity signal while the absence of Bragg peaks indicates there is no out-of-plane crystalline order.
C\textsubscript{60}F\textsubscript{48} deposited on Pentacene

In Figure S2a-c we show the 2D-GIXD maps, before (pristine) and after the stepwise deposition of two C\textsubscript{60}F\textsubscript{48} coverages on top of a 120 Å pentacene film. The labelling and position of the diffraction features remain identical to the 30 Å pentacene case as discussed in the main text of the manuscript. The out-of-plane XRD data (d) show the (001), (002) and (003) Bragg peaks characteristic of the pentacene thin film structure (black). After the deposition of 45 Å C\textsubscript{60}F\textsubscript{48}, we observe the emergence of the (111) and (222) peaks corresponding to the fcc crystal structure of C\textsubscript{60}F\textsubscript{48}. The corresponding in-plane GIXD spectra are also shown (e).
Figure S2. 2D-GIXD maps of (a) pentacene(120 Å)/SiO₂, (b) C₆₀F₄₈(15 Å)/pentacene(120 Å) and (c) C₆₀F₄₈(45 Å)/pentacene(120 Å). (d) Out-of-plane XRD and (e) in-plane GIXD spectra for the three cases (pentacene and C₆₀F₄₈ peak labels in black and red, respectively).

Figure S3 shows a representative topographical AFM image and the simultaneously acquired excitation frequency signal, for 14 Å of C₆₀F₄₈ deposited on a 20 Å pentacene film. The pentacene film consists of a complete 1st layer plus 2nd layer dendritic islands with an epitaxial core.¹ The excitation frequency contrast permits distinguishing those areas covered with C₆₀F₄₈. In particular, we observe a slightly rough monolayer of C₆₀F₄₈ covering completely the pentacene 1st layer and the formation of 2 nm-height C₆₀F₄₈ islands (meaning 2 molecular layers thick, as shown in the height histogram in S3c) on top of the dendritic arms of the 2nd layer pentacene islands.

¹ Reference [1] or any additional citation that is relevant to the description of the pentacene film structure.
Figure S3. (a) Topography and (b) excitation frequency AFM images of a C$_{60}$F$_{48}$(14 Å)/pentacene(20 Å) sample with (c) the height histogram of the area indicated in (a) including part of the uncovered core and the C$_{60}$F$_{48}$ covered arm of a 2$^{nd}$ layer pentacene island.

To determine if the observed diffraction pattern of C$_{60}$F$_{48}$ should be assigned to a face centered cubic (fcc) or to a body centered tetragonal (bct) structure oriented with the (111) direction perpendicular to the surface, we simulated the diffraction pattern for both cases, starting from the diffraction map of C$_{60}$F$_{48}$(45Å)/pentacene(30Å) (Figure 4c). In one case, we attributed the peak at $(q_{xy}, q_z) \approx (1.04, 0)$ Å$^{-1}$ to the in-plane (2-20) peak of a fcc; for the other case the initial assumption consisted in attributing the peaks at $(q_{xy}, q_z) \approx (0.60, 0.23)$ Å$^{-1}$ and $(q_{xy}, q_z) \approx (0.60, 0.87)$ Å$^{-1}$ to the (011) and (112) reflections of a bct, respectively. The calculated lattice parameters for this film are: $a \approx 17.1$ Å for the fcc, and $a = 12.23$ Å and $c = 16.28$ Å for the bct. From there, we were able to derive all relevant expected reflections in the investigated q space. The calculated Bragg peaks positions expected for the two structures are superimposed to the experimental 2D-GIXD map measured for C$_{60}$F$_{48}$(45Å)/pentacene(30Å) in Figure S4. From the comparison between the two maps, it is evident that the fcc structure matches better than the bct structure with the experimental features, reproducing in a reasonable way all the observed Bragg peaks.
Figure S4. Calculated diffraction patterns for (a) a fcc and (b) a bct structure superimposed to the experimental 2D-GIXD map of C\textsubscript{60}F\textsubscript{48}(45 Å)/pentacene(30 Å). The vertical axis of the experimental maps starts at \(q_z = 0.03\) Å\(^{-1}\).

In Figure S5 we report the in-plane GIXD spectra for the bare 30 Å pentacene film, before and after the two evaporations of C\textsubscript{60}F\textsubscript{48}. As commented in the main text, the packing of pentacene does not undergo any change after the dopant deposition. There is just a reduction in intensity of the pentacene peaks caused by absorption in the C\textsubscript{60}F\textsubscript{48} adlayer due to its higher electron density compared to that of pentacene, very clearly observed in Figure S5a and in the real-time experiment in Figure S5b.

We shortly discuss here the reduction of the pentacene peaks' intensity after C\textsubscript{60}F\textsubscript{48} deposition and explain it in terms of attenuation effects. In the case of 30 Å pentacene, we observe an intensity reduction by about 20% and 40% after evaporating, respectively, 15 and 45 Å of C\textsubscript{60}F\textsubscript{48}. We theoretically estimated the expected attenuation of pentacene scattered intensity by the C\textsubscript{60}F\textsubscript{48} overlayer due to its higher electron density, following the model developed for total-external-reflection (TER) x-ray diffraction.\(^2\) The relevant equations necessary to calculate the so-called scattering depth \(\Lambda\), defined as the depth for which the scattered intensity is reduced by 1/e, are:
\[ I = I_0 e^{-\frac{d}{\Lambda}}; \quad \Lambda = \frac{\lambda}{2\pi (l_i + l_f)} \]

\[ l_{i,f} = \frac{1}{\sqrt{2}} \left\{ (2\delta - \sin^2\alpha_{i,f}) + [(\sin^2\alpha_{i,f} - 2\delta)^2 + 4\beta^2]^{1/2} \right\}^{1/2} \]

where \( I \) and \( I_0 \) are the scattered and incident intensities, respectively, \( d \) is the overlayer thickness, \( \lambda \) is the beam wavelength, \( \alpha_i \) and \( \alpha_f \) are the incident and exit angles, \( \delta \) and \( \beta \) are the real and imaginary parts of the refractive index. The electron density of C\textsubscript{60}F\textsubscript{48} is roughly estimated to be 0.6 electrons/Å\textsuperscript{3} (50% higher than for pentacene) from which a value for \( \delta \) of 2.6·10\textsuperscript{-6} is derived. On the other hand, \( \beta \) is very small for organic materials and it doesn’t contribute significantly to this calculation. Being \( \lambda=0.9912 \) Å and \( \alpha_i = \alpha_f = 0.00192 \) in our case, we obtain \( \Lambda \approx 60 \) Å. This leads to an attenuation of the intensity of about 20\% and 50\% for each of the two C\textsubscript{60}F\textsubscript{48} coverages (15 Å and 45 Å), which agrees quite well with our observations.

As explained in the main text, while the pentacene peak positions remained unaffected, C\textsubscript{60}F\textsubscript{48} peaks shift to lower \( q \) as the coverage increases (Figure S5a). This shift is observed also in the case of C\textsubscript{60}F\textsubscript{48} on the thick pentacene film (Figure S5c).
Figure S5. (a) In-plane GIXD spectra before and after deposition of C$_{60}$F$_{48}$ on the 30 Å pentacene film. (b) Wide $q_{xy}$ range of the real-time monitoring of C$_{60}$F$_{48}$ growth on 30 Å pentacene film shown in Figure 4. (c) Selection of the in-plane GIXD diffraction spectrum of the 120 Å pentacene film evidencing the shift of C$_{60}$F$_{48}$ peaks. In (a) and (c) black curves are for bare pentacene and blue and red for the two coverages of C$_{60}$F$_{48}$, 15 Å and 45 Å, respectively. Pentacene and C$_{60}$F$_{48}$ diffraction peaks are labelled in black and red, respectively.
Thermal annealing

Figure S6 presents the reciprocal space maps for $C_{60}F_{48}$ (45 Å)/pentacene(30 Å) and $C_{60}F_{48}$ (45 Å)/pentacene(120 Å) after annealing at 90°C in (a) and (b), respectively, plus the corresponding in-plane spectrum of the latter (c). By comparing these maps with those of the as-grown samples, i.e., at room temperature (Figure 4c and S2c), it becomes clear that the contribution from $C_{60}F_{48}$ disappears with annealing. As explained in the main text, the dopant is likely desorbed during the annealing process, leaving the underlying pentacene film unmodified.

![Figure S6. 2D-GIXD maps for (a) $C_{60}F_{48}$ (30 Å)/pentacene(30 Å) and (b) $C_{60}F_{48}$ (30 Å)/pentacene(120 Å) after annealing at 90°C. (c) In-plane spectra before (black) and after (green) annealing at 90°C for the case of the thicker pentacene film.](image)

Figure S6. 2D-GIXD maps for (a) $C_{60}F_{48}$ (30 Å)/pentacene(30 Å) and (b) $C_{60}F_{48}$ (30 Å)/pentacene(120 Å) after annealing at 90°C. (c) In-plane spectra before (black) and after (green) annealing at 90°C for the case of the thicker pentacene film.
Finally, in Figure S7 we show the effect of a two-steps annealing process on the total diffraction intensity (sum of the areas of the main features in the spectrum) for both components in the case of the co-evaporated sample PEN:C$_{60}$F$_{48}$ (see main text). We normalize the total intensity to the value obtained for the sample at room temperature (RT). It is clear that the trend is identical for both pentacene and C$_{60}$F$_{48}$, suggesting that the two molecules are desorbed at the same extent. No significant change is detected after the first step at 60°C while a strong reduction of more than 50% of the total diffraction signal occurs after annealing the films at 90°C.

Figure S7. Effects of the annealing process on the total diffraction intensity for the co-evaporated PEN:C$_{60}$F$_{48}$ (10:1) film.
References
