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### **Dipolar Substitution Impacts Growth and Electronic Properties of** *para-*Sexiphenyl Thin Films

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#### Abstract

It is shown that fluorination of para-sexiphenyl (6P) at the meta- or ortho- positions of one terminal phenyl ring, as well as the addition of a terminal cyano-group has an eminent impact on both growth and electronic properties of thin films. X-ray diffraction techniques indicate that films of meta-substituted 6P (m-2F-6P) develop a smooth, layered structure showing crystalline order within the layers only. Contrary, both ortho-substituted (o-2F-6P) and cyanosubstituted 6P (CN-6P) form films of three-dimensional crystalline order. The correlation of structural information with data from ultraviolet photoelectron spectroscopy reveals that m-2F-6P and CN-6P do not show preferentially oriented dipoles in the film, while o-2F-6P grows with collective upward orientation of the dipole moments. The subtle difference in substitution position has a dramatic impact on the thin-film ionization energy, which increases from 5.40 eV (ortho) to 6.80 eV (meta) and reaches even 7.50 eV for CN-6P. The present study shows that nonsymmetric substitution, which induces molecular dipole moments via intramolecular polar bonds, strongly impacts structure, morphology, and electronic properties of thin films. Thusly modifying common conjugated organic materials represents therefore a valuable tool to establish smooth, crystalline layers with altered energetics at hetero-interfaces with organic or electrode materials in electronic devices.

Our ability to tailor the electronic properties of organic semiconductors (OSCs) by altering the chemical structure of the constituting molecules represents a key advantage of this material class over their inorganic counterparts.<sup>[1]</sup> For both OSCs based on conjugated organic molecules and conjugated polymers this is often done by modifying the peripheral substitution pattern of a given parent compound.<sup>[1, 2]</sup> This can significantly alter its electronic properties, particularly those of thin films through collective electrostatic effects.<sup>[3-5]</sup> The energies of the OSC frontier molecular orbital levels and their energy-level alignment at heterointerfaces both with other OSCs and conductive electrodes play a crucial role in device applications.<sup>[6, 7]</sup> This is mainly because interface properties define charge-injection barriers in light emitting diodes or promote exciton dissociation in solar cells. As shown in several studies, adding strong intramolecular polar bonds, such as C-F, to the parent compound allows changing the ionization energy (IE) of ordered molecular assemblies substantially,<sup>[8, 9]</sup> e.g., from 4.80 eV for pentacene (PEN) to 6.65 eV for perfluoropentacene<sup>[8]</sup> in thin films grown on native silicon oxide (SiO<sub>x</sub>). Notably, *via* partial fluorination of the compound this dramatic effect can be deliberately tuned.<sup>[7, 10]</sup> In general, partial non-symmetric fluorination allows introducing a net molecular dipole moment, the direction and strength of which depends on the position of respective fluorine substitutions. For rod-like molecules, the addition of dipolar terminal groups at only one end of the molecule therefore results in a dipole moment along the long molecular axis.<sup>[11, 12]</sup> In thin films, the orientation of these dipole moments with respect to both the substrate and the surface plane of the film has a strong impact on the thin film IE, which is altered by  $\Delta$ IE as compared to a film of the parent compound.

Here, we focus on the rod-like molecule *para*-sexiphenyl (6P) as parent molecule for non-symmetric substitution at one end. We obtain significantly different net dipole moments of opposite orientation *via* the substitution of intramolecular polar bonds at different positions. 6P is a prototypical material in the field of OSC research and organic surface science,<sup>[13, 14, 15, 16]</sup> which has been thoroughly characterized regarding its electronic,<sup>[17]</sup> structural<sup>[17, 18]</sup> and optical

properties before.<sup>[19]</sup> It has been shown previously that 6P offers the possibility of nonsymmetric functionalization.<sup>[20]</sup> However, the impact of partial substitution on the growth behavior has so far only been investigated in the monolayer regime on metals for fluorination at the meta- (m-2F-6P) and ortho-positions (o-2F-6P), as well as for cyano-substitution at the para-position (CN-6P);<sup>[11, 21]</sup> for the chemical structures see Figure 1a. In monolayers on Ag(111) it has been found that the subtle difference in fluorine position at one terminal phenyl ring has an eminent impact on the supramolecular organization.<sup>[11]</sup> This is related to the highly different net dipole moments and their opposite orientation in m-2F-6P and o-2F-6P, the absolute values of which have been derived for the gas phase to amount to 2.2 D and 1.1 D, respectively.<sup>[11]</sup> On Ag(111) the molecules adopt a lying molecular orientation and the molecular dipole moment is therefore oriented parallel to the substrate plane. As a result, fluorination cannot be expected to have an impact on the thin-film IE in this case. Also for multilayer films, we have recently reported a similar lying orientation of o-2F-6P for highlyoriented pyrolytic graphite (HOPG) as substrate, however, with a crystal structure that was found to be fundamentally different from that of 6P (orthorhombic instead of monoclinic).<sup>[22]</sup> In contrast, on insulating substrates such as SiO<sub>x</sub> 6P adopts a standing orientation in thin films<sup>[18]</sup> and we expect the same to hold for our dipolar 6P-derivatives as well. In such films three scenarios are then principally possible for the orientation of the individual molecular dipole moments, which can be (i) random, (ii) anti-parallel, or (iii) parallel. Clearly, only the latter case will result in pronounced extended dipole layers that energetically represent a step in the electrostatic potential along the surface-normal direction. This then changes the IE by  $\Delta$ IE as compared to the same film of pristine 6P. The sign of  $\Delta$ IE is dictated by the collective direction of the molecular dipole moments, which is for films of standing molecules either upward (iiia) or downward (iiib). Note that also an anti-parallel (or even totally random) orientation of such dipolar 6P derivatives would lead to some (however smaller)  $\Delta IE$ , again due to the collective impact of the molecular dipole moments.<sup>[3]</sup> Intuitively, one might expect such an antiparallel orientation of neighboring dipole moments in the films to be the most likely growth scenario, as it minimizes the dipole-dipole interaction energy.<sup>[11]</sup> However, this driving force might in fact be overcome by various effects including the molecular interaction with the substrate, a complex electric potential landscape in the near field close to the molecule,<sup>[11]</sup> or kinetic processes during the nucleation and growth of the film.<sup>[23]</sup>

In the present work, we first explore the structure of m-2F-6P, o-2F-6P, and CN-6P thin films grown on SiO<sub>x</sub> by specular X-ray diffraction (XRD) and grazing-incidence X-ray diffraction (GIXRD), which allows us further to draw conclusions on the morphology of the films. We then correlate this information with the electronic properties of the films as determined by ultraviolet photoelectron spectroscopy (UPS). Overall, we observe a strong impact of the position of dipolar substitution not only on structure and morphology of the films, but also on their energetics. Based on these findings we will be working towards exploiting end-group substitution as a tool to tailor the structure and electronic properties of thin films in prospect of their use in organic electronic devices.

**Results and Discussion** 

For first assessing the molecular orientation, we performed specular XRD on thin films of *o*-2F-6P, *m*-2F-6P, CN-2F-6P and on a 6P reference, as shown in Figure 1a. In all three cases we find diffraction features characteristic of an essentially upright orientation of the long molecular axes with respect to the substrate plane. The morphology<sup>[24]</sup> and structure<sup>[18, 25, 26]</sup> of thin 6P films is well covered in literature and typically growth in two different polymorphs is found, which have been denoted as  $\gamma$ - and  $\beta$ -phase before. The  $\beta$ -phase is the crystal structure found in single crystals of 6Pwhere the long molecular axes are inclined by ca. 17° with respect to the substrate normal in thin films which grow in 001-texture with a lattice spacing of 25.975 Å.<sup>[25]</sup> In contrast, in the  $\gamma$ -phase 6P molecules are essentially perpendicular to the substrate plane in thin films with a 001-lattice spacing of 27.213 Å.<sup>[26]</sup> Both polymorphs are found in our reference with the expected lattice spacings.

For *o*-2F-6P six strong diffraction features are observed, which we assign—in analogy to non-substituted 6P—to the (00*ℓ*)-diffraction series. The corresponding (001) lattice spacing is here (27.353 ± 0.004) Å which is similar to that of pristine 6P in its  $\gamma$ -phase. As the molecular van der Waals length of 6P is ca. 28.48 Å<sup>[27]</sup> this points to molecules oriented almost perpendicular to the substrate plane in the *o*-2F-6P film. In the vicinity of the peaks we observe pronounced Laue-oscillations indicating high crystalline quality of the film and pronounced texture.<sup>[28, 29]</sup> From the spacing of the Laue fringes  $\Delta q_z = (0.020 \pm 0.001)$  Å<sup>-1</sup> we can derive the crystalline coherence length  $D_{coh}$  of the crystalline grains in the out-of-plane direction to be  $D_{coh} = 2\pi/\Delta q_z = (314 \pm 15)$  Å. This is about three times the nominal film thickness (i.e., the thickness the film would have if grown perfectly layer-by-layer), which clearly indicates island growth of *o*-2F-6P on SiO<sub>x</sub>.

The extreme opposite scenario is found for the *m*-2F-6P film, which shows strong oscillations at low  $q_z$  (Kiessig fringes)<sup>[28, 30]</sup> that are due to the thickness interference of the primary X-ray beam at a smooth and uniformly thick layer (independent of its crystallinity). From their spacing  $\Delta q_z = (0.054 \pm 0.001)$  Å<sup>-1</sup> we can derive the thickness of the film to  $D_{film} = 2\pi / \Delta q_z = (116.4 \pm 2.2)$  Å, which equals the nominal film thickness within the error margin. From the (004) reflection (which is not superimposed by Kiessig fringes) we determine the corresponding (001) lattice spacing to  $(28.005 \pm 0.004)$  Å, pointing again to essentially upright standing molecules in the film.

Finally, the CN-6P film does not show any interference features at all, but yet a series of strong Bragg peaks with a (001) lattice spacing of  $(26.84 \pm 0.05)$  Å, which is close to the value of pristine 6P in its  $\beta$ -phase. Given that CN-6P is longer than 6P by ca. 2 Å, this points to even more inclined molecules as compared to the pristine 6P structure.<sup>[25]</sup> Note that the peak shape of the (003) reflection around 0.7 Å<sup>-1</sup> (marked with an asterisk in Figure 1a) suggests the presence of two components of slightly different 001 lattice spacing, where fitting by two Voigt functions leads to values of (26.67 ± 0.05) Å and (28.12 ± 0.05) Å, respectively. As we do not

observe higher-order reflections (where the two components, if present, would then be more separated) we cannot unambiguously conclude on the presence of two different orientations or, alternatively, crystal polymorphs in the film from these data.

To gain deeper insight into the molecular arrangement of the dipolar 6P derivatives, we performed GIXRD on the same samples, as shown in Figure 1b-d. For o-2F-6P, where island growth was deduced from XRD, GIXRD demonstrates that this film is crystalline in both inplane and out-of-plane direction. This can be seen from the presence of well-defined Bragg peaks in the RSM, e.g., at  $(q_{xy}, q_z) = (1.36, 0.13) \text{ Å}^{-1}$  or from (at least) four peaks in  $q_z$  direction at  $q_{xy} = 1.95$  Å<sup>-1</sup> (Figure 1b); note that faint rings of equal q indicate the presence of a small (less-textured) film portion. However, the molecular arrangement in the o-2F-6P crystal structure appears to be significantly different from that of pristine 6P,<sup>[22]</sup> as illustrated by a comparison to the calculated reflections (radii of the white circles correspond to calculated intensities based on the structure in Ref. [25]). It is not possible to derive a full structure solution from this limited data set and, therefore, the orientation of the fluorine atoms (and that of the dipole moment) cannot be determined therefrom. However, the presence of a three-dimensional crystalline molecular arrangement in this film suggests that the fluorine atoms, and thus dipoles, are not randomly distributed. Given that both known pristine 6P herringbone structures comprise two molecules in the unit cell (Z = 2), this means that the dipole moments are either parallel pointing out/in of the film surface or are arranged antiparallelly throughout the crystalline film [cf. scenarios (ii) and (iiia/iiib) as introduced above].

For *m*-2F-6P the RSM data is notably different (Figure 1c). While we again find the three characteristic features known from the 6P structure, which are indicative of a molecular herringbone arrangement (i.e., the  $-11\ell$ ,  $-20\ell$ ,  $-21\ell$  series),<sup>[18]</sup> we here do *not* observe peaks in out-of-plane direction. Instead, we record perfectly vertical diffraction rods in  $q_z$ -direction for the *m*-2F-6P film. Such Bragg rods are typically observed for textured, crystalline *monolayers* only.<sup>[31]</sup> However, in XRD we observed the 00 $\ell$  peak series (which is impossible for a

monolayer) and deduced that this smooth film exhibits a thickness corresponding to about *four* monolayers of standing molecules. Therefore, in this case the presence of Bragg rods is indicative of a layered structure, where the individual layers show crystalline molecular order *in-plane*. From the three characteristic  $q_{xy}$ -positions of the Bragg rods that are similar to those of 6P, we can conclude on a herringbone arrangement of the m-2F-6P molecules within the layers, which is similar to the structure of pristine 6P. However, the overall film is clearly not three-dimensional crystalline, as this would give rise to a series of *Bragg peaks* in  $q_z$ -direction (see the RSM of o-2F-6P in Figure 1b) instead of *Bragg rods*. In particular, a random up/down dipole orientation in the layers would be well in line with these GIXRD data. Note that in single crystals of symmetrically substituted m-4F-6P (with two fluorine atoms at each end) the two molecules in the unit cell are strongly shifted (by two phenyl units) along the long molecular axis, which has been interpreted as resulting from dipole-dipole interaction.<sup>[11]</sup> Therefore, our XRD-based finding of upright standing molecules strongly supports the notion of randomly distributed dipole moments in the *m*-2F-6P film, as this likewise minimizes the dipole-dipole interaction energy between neighboring molecules. We note that the marked differences in the structural properties of the ortho- and meta- substituted 6P derivatives further agree with what has recently been reported for monolayers of these compounds on Ag(111).<sup>[11]</sup> There, the differences have been explained by substrate-mediated interactions and ground-state charge transfer, which, however, can only play a minor role on SiO<sub>x</sub> both due to the upright molecular orientation and as charge transfer is not expected with the dielectric substrate.

Finally, GIXRD on the CN-6P film again shows the three characteristic in-plane features at positions similar to those of pristine 6P, however, with the scattering intensity now being more distributed along rings of equal q (Figure 1d). While this indicates pronounced mosaicity of the crystalline grains on the substrate, both the absence of these three diffraction features in XRD (see Figure 1a), and the absence of the strong (00 $\ell$ ) reflections in GIXRD at low  $q_{xy} < 1$  Å<sup>-1</sup> (see full RSM data in the Supporting information) demonstrate that this film is still grown well fiber-textured on the substrate, i.e., the crystallites forming the film share a common crystallographic plane parallel to the  $SiO_x$  surface. The large breadth of the diffraction features in GIXRD does not allow deciding over the presence of either two slightly different orientations or polymorphs, as suggested by XRD (see above).

We now turn to exploring the thin-film electronic structure of these systems by photoelectron spectroscopy. Figure 2 shows the UPS spectra of the three dipolar 6P derivatives deposited with incremental thickness on SiO<sub>x</sub>. For *o*-2F-6P (Figure 2a, left), at a nominal thickness of 25 Å we observe the characteristic double peak assigned to photoemission from the highest occupied molecular orbital (HOMO) level and from the HOMO-1, located around 2 eV binding energy (BE) and 1.2 eV BE (onset), respectively.<sup>[13, 15, 32]</sup> Up to this thickness the vacuum level, as given by the SECO position (Figure 2a, right), stays almost constant at 4.35 eV above the Fermi level (E<sub>F</sub>). For higher coverage, the valence electron features shift *towards* E<sub>F</sub> and the vacuum level shifts in the same direction (i.e., *away* from E<sub>F</sub>). Note that this shift is not fully rigid, and the IE slightly decreases with the film thickness.

Before discussing possible origins of these shifts, we recall the different impact of a two-dimensional dipole layer (i.e., a dense layer of molecular dipoles with the same orientation) representing a step in the electrostatic potential for electrons<sup>[3, 5]</sup> on the vacuum level and on the BE of valence electron features in UPS.<sup>[13, 33, 34-36]</sup> First, let us consider a closed molecular monolayer with all molecular dipoles either on the vacuum ("top") or the substrate ("bottom") side of the thin film. In both cases, these dipoles affect the vacuum level position, as the secondary electrons experience the electrostatic potential difference between the sample surface and the spectrometer.<sup>[34]</sup> However, as the energy reference for valence electrons is  $E_F$ , their BE values are *only* affected if the dipoles are located at the *bottom side* of the molecular layer from which the valence electrons originate.<sup>[36]</sup> For the opposite scenario, i.e., the dipoles all located at the top side of the layer, the BE of the valence electrons (with respect to  $E_F$ ) remains unaffected.

In the present case of o-2F-6P, beyond nominal monolayer coverage we observe both a shift of the valence photoemission features (particularly visible for HOMO and HOMO-1) towards E<sub>F</sub> (i.e., to lower BE) and a concomitant shift of the vacuum level in the same direction (away from E<sub>F</sub>, see Figure 2a). Given the specific direction of the dipole moment in an individual o-2F-6P molecule (pointing outward along the long molecular axis), only a location of the molecular dipoles at the bottommost position in the film can lead to such a shift direction.<sup>[36]</sup> This, at first glance counterintuitive, parallel dipole orientation of neighboring molecules can be understood by the relatively small dipole moment (1.1 D) of o-2F-6P and the pronounced deviation from a simple dipolar electric potential distribution pattern in the near field of the terminal substituted phenyl ring.<sup>[11]</sup> The dipoles of the first o-2F-6P layer formed on the substrate increase the vacuum level and, as a result, decrease the BE of valence electrons from further layers above. This explains the constant HOMO/HOMO-1 BE for the submonolayer ( $\leq 25$  Å) and the shift to lower BE for higher coverages (50 Å and beyond). This insight now augments the information from XRD and GIXRD results with the most probable position of the partially fluorinated phenyl ring in the thin film structure of o-2F-6P, which is schematically illustrated in Figure 3a. Note that UPS is highly surface sensitive, because the mean free path of electrons with a kinetic energy around 15 eV in organic materials is only a few Å,<sup>[37]</sup> which is a fraction of the length of one *o*-2F-6P molecule. Consequently, for the present films formed by molecules in standing molecular orientation, only the top molecules can contribute notably to the UPS spectra, as photoelectrons originating from molecules below are inelastically scattered and form the signal background in UPS. Recalling that XRD indicated island growth (Figure 1a), we can therefore expect individual layers to be only partially closed and, thus, both different layers and uncovered substrate patches to contribute to the UPS data (see schematic in Figure 3a). This is well in line with the observation of an essentially constant vacuum level for nominal sub-monolayer coverage and the not completely rigid shifts of vacuum level and valence levels.

For *m*-2F-6P we observe a simpler spectral evolution, with the HOMO-onset at 2.70 eV (Figure 2b) and no coverage-dependent energy shift. However, the spectral features are less distinct and broader, in particular, for sub-monolayer coverage and beyond 200 Å. The vacuum level stays essentially constant at 4.10 eV above  $E_F$  beyond 5 Å coverage. The absence of energy shifts clearly points to a random or anti-parallel orientation of the molecular dipole moments. This is, in fact, further in line with the observation of broad HOMO and HOMO-1 emission features, as a random dipole orientation leads to local variations of the electrostatic potential in the sample. In such a case, the BE of valence electrons is determined by the *local* potential below the molecule from which the photoelectrons have been emitted (see discussion above).<sup>[13, 35, 38]</sup> Our finding of a smooth layered film of only two-dimensional crystalline order readily supports the perception of statistically oriented molecular dipoles in the thin film of *m*-2F-6P.

Finally, Figure 2c shows the UPS spectra of CN-6P on SiO<sub>x</sub>. Here, the typical doublepeak structure of HOMO and HOMO-1 can only be resolved for a nominal coverage beyond 100 Å. This observation can be readily understood by the significantly higher mosaicity of the films, as deduced from GIXRD (*cf.* Figure 1c). Thus, also the molecular dipole moments show a much broader orientational distribution as compared to the *o*-2F-6P and *m*-2F-6P cases. With increasing coverage, the HOMO-onset shifts to higher BE. Notably, for nominal thicknesses of 50 Å and beyond, a *double secondary electron cutoff* (SECO) is observed, which is indicative of laterally extended (mesoscale) sample patches of different electrostatic potentials;<sup>[39]</sup> following the procedure described in Ref. [40] we determine local vacuum levels of 3.65 eV and 3.95 eV, respectively. This might point to the presence of two different orientations/polymorphs in that film, as already suggested by XRD for a nominal film thickness of 100 Å (*cf.* Figure 1a); one dominates at low coverage, while the other one prevails at higher coverage. While we are well aware that we cannot unambiguously conclude on a more detailed growth scenario from the present data, we note that this resembles what we recently observed

for pentacene thin films, where a metastable thin film phase grows directly on  $SiO_x$  in the form of large islands;<sup>[41]</sup> its crystal facets mediate the nucleation of different, more stable polymorphs upon subsequent growth, comprising significantly tilted molecules.

Our results are summarized in energy-level diagrams and film-structure schematics in Figure 3. The overall impact of both molecular dipole *location* and *orientation* in the films is best seen from their respective IE, which is the energy separation between HOMO onset and SECO in Figure 2. For *o*-2F-6P, despite the addition of electron-withdrawing fluorine atoms, the IE at high coverage is 5.4 eV and, thus, lower than that of non-substituted 6P (5.8 eV).<sup>[14]</sup> This  $\Delta IE$  value of -0.4 eV (sign with respect to the IE of pristine 6P) is therefore attributed to the effect of preferential dipole orientation in downward direction, which implies the dipoles' location at the very bottom of the layer. Based on the observation that this film is threedimensionally crystalline-from its characteristic GIXRD pattern most likely in a herringbone structure with two molecules per unit cell-a collective downward orientation of all dipole moments emerges as growth scenario for the o-2F-6P film. A rough estimate of  $\Delta$ IE using the Helmholtz equation and the pristine 6P crystal structure as approximation for o-2F-6P (two dipoles per 8.091×5.568 Å<sup>2</sup>, dielectric constant  $\varepsilon_r$  = 3, dipole moment  $\mu$  = 1.1 D) yields a value of -0.6 eV, which is in good agreement with the experiment given the unknown precise crystal structure and  $\varepsilon_r$  value of the film. For *m*-2F-6P, where the molecular dipoles have opposite directions on average, the experimental  $\Delta IE$  is +1 eV and XRD/GIXRD point to a random orientation of the molecular dipoles in the film (vide supra). A positive  $\Delta IE$  is indeed expected and an estimate again using the Helmholtz equation for  $\mu = 2.2$  D yields a reasonable value of +0.6 eV. Finally, for CN-6P we find an even larger value of  $\Delta IE$  in the experiments, ranging from +1.4 eV to +1.7 eV. Assuming an antiparallel dipole orientation and  $\mu = 4.5$  D (the dipole moment of benzonitrile)<sup>[42]</sup> also yields a reasonable value for  $\Delta IE$  of +1.3 eV based on the Helmholtz equation.

In conclusion, we have investigated the impact of non-symmetric fluorine and cyano substitution for the prototypical organic semiconductor 6P on its growth and on the energy levels in the solid state. We found that subtle changes in substitution that induce different orientation and strength of the molecular dipole moment lead to fundamentally different structure and morphology of thin films formed thereof. The one-side ortho-fluorinated 6P derivative o-2F-6P forms crystalline, three-dimensional islands with the molecular dipoles being aligned in parallel. In marked contrast, its meta-substituted variant m-2F-6P forms smooth, layered films with only lateral crystallinity in the individual layers, which exhibit a herringbone arrangement in-plane. However, adjacent layers are not in lateral registry with each other-a situation similar to that found in smectic structures. Complemented by UPS data on the thinfilm electronic properties, we conclude on statistically upward/downward oriented molecular dipoles throughout the m-2F-6P film. This is in line with its dipole moment being twice as strong as that of o-2F-6P, and its electric potential distribution being simply dipolar in the near field, as reported previously (Ref. [11]). This promotes statistic dipole-moment orientation via dipole-dipole interaction, instead of the parallel alignment found for o-2F-6P films. For the thin-film ionization energies, the difference in substitution and molecular orientation has a dramatic impact, as IE increases from 5.40 eV (ortho) to 6.80 eV (meta) reaching even 7.50 eV for para-cyano-substituted 6P. In principle, smooth films of lateral crystalline order as we find here for m-2F-6P are of high interest for applications in organic field-effect transistors, which require lateral charge transport in a channel close to the organic-dielectric interface, while charge-injection barriers (that depend on IE) are crucial at the interface between the organic and source/drain electrodes. For future research, our study suggests exploring in-depth under which circumstances the non-symmetric introduction of intramolecular polar bonds in common organic semiconductors can serve as a tool for equally tuning microstructure and energy levels of thin films in order to tailor interface properties in organic electronic devices.

#### **Experimental Section**

Thin films for our structural investigations were prepared via vacuum deposition (base pressure < 5×10<sup>-9</sup> mbar) from resistively heated crucibles on (100)-cut silicon wafers (Siegert Wafer GmbH., native oxide, n-doped, cut to  $1 \times 1$  cm<sup>2</sup>, prime grade); the nominal film thickness was  $(10 \pm 2)$  nm. Structure and morphology of the films were characterized at beamline W1 at the synchrotron radiation facility DORIS (HASYLAB, Hamburg). GIXRD experiments were performed together with specular XRD (on the same sample) using a goniometer in pseudo 2+2 geometry and a one-dimensional detector (MYTHEN, Dectris), the wavelength of the primary radiation was 1.1801 Å. GIXRD experiments were performed using incident angles of the primary beam relative to the SiO<sub>x</sub> substrate plane of  $\alpha_i = 0.15^\circ$ . Reciprocal space maps (RSM) were recorded by keeping the sample fixed with respect to the primary beam and by performing a series of detector scans along the in-plane scattering angle  $\theta_f$  at different out-of-plane scattering angles  $\alpha_{f}$ ; the vertical mounting of the 1D linear detector allows the simultaneous measurement of  $\Delta \alpha_f = 3.5^{\circ}$ . The diffraction pattern was transformed to reciprocal space using the custom-made software PyGID.<sup>[43]</sup> The resulting RSMs give the measured intensities on a logarithmic scale by a color code; the q<sub>z</sub> values of the peak positions were corrected for refraction effects.<sup>[44]</sup> UPS experiments were carried out in an ultrahigh vacuum (UHV) system consisting of three interconnected chambers: evaporation chamber (base pressure:  $3 \times 10^{-10}$  mbar), preparation chamber ( $3 \times 10^{-10}$  mbar), and analysis chamber (base pressure:  $2 \times 10^{-10}$  mbar). All materials were deposited onto SiO<sub>x</sub> substrates (held at room temperature) by vacuum sublimation with deposition rates of about 2 Å/min. The nominal film mass-thickness was monitored with a quartz-crystal microbalance positioned near the samples in the deposition chamber. UPS experiments were performed using monochromatized He I radiation (21.2 eV) and a Specs PHOIBOS 150 analyzer. The energy resolution was set to 80 meV. The angle between the incident beam and the sample surface was fixed to 40°. The spectra were collected at photoelectron take-off angles of  $0^{\circ}$  (normal emission) with an acceptance angle of  $\pm 12^{\circ}$ .

A sketch of the measurement geometry can be found in Ref. [45]. In the plots of the secondary

electron region, the energy scale is corrected by the applied bias voltage (-3 V) and the analyzer

work function. Thus, the position of the secondary electron cut-off (SECO) corresponds to the

vacuum level with respect to the Fermi level, i.e., the sample work function.

### **Supporting Information**

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

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Figure 1. Chemical structures of the investigated molecules ortho-difluorosexiphenyl (o-2F-6P), meta-difluorosexiphenyl (m-2F-6P) and cyano-sexiphenyl (CN-6P). a) Specular X-ray diffraction of o-2F-6P, m-2F-6P, CN-6P and pristine 6P as reference (100 Å nominal thickness, SiOx substrates); Laue oscillations around the Bragg peaks of the ( $00\ell$ ) series of the o-2F-6P adsorbate are labelled as L (zoomed view as inset), film thickness oscillations (Kiessig fringes) in from the m-2F-6P film are labelled as K; the asterisks marks a peak likely composed of two; the 6P reference shows both phases known to grow in thin films, the peaks are denoted as β and  $\gamma$ , for details see text b) GIXRD reciprocal space map (RSM) for the o-2F-6P film showing distinct out-of-plane diffraction peaks along  $q_z$ , which is characteristic for a three-dimensionally crystalline film. The centres of white circles mark calculated peak positions for unsubstituted 6P, their radii are proportional to the calculated intensities;  $[42] q_{xy}$ ,  $q_z$  are the in-plane and outof-plane components of the scattering vector q. c) RSM for the m-2F-6P film showing vertical rods along  $q_z$  (Bragg rods) instead of peaks, which is characteristic for a two-dimensionally crystalline film; parasitic reflections from the silicon substrate are marked with "Si". d) RSM for CN-6P showing a weakly textured three-dimensionally crystalline film with the three characteristic reflections of the 6P herringbone arrangement.



**Figure 2.** UPS spectra of a) o-2F-6P on  $SiO_x$ , b) m-2F-6P on  $SiO_x$  and c) CN-6P on  $SiO_x$ . In all cases, the left plot shows the valence electron region and the nominal film thickness is indicated. The right plots show the secondary electron region and the onset of photoemission intensity corresponds to the vacuum-level w.r.t. the Fermi level.



**Figure 3.** Energy-level alignment diagrams and growth schematics of a) o-2F-6P on SiO<sub>x</sub>, b) m-2F-6P on SiO<sub>x</sub> and c) CN-6P on SiO<sub>x</sub>. In the energy-level diagrams (based on our UPS results) the vacuum level ( $E_{vac}$ ) w.r.t the Fermi-level ( $E_F$ ) is shown for nominal thicknesses of the organic thin films of 25 Å and 200 Å. The onset of the HOMO-derived peak and the ionization energy is given for each coverage. In the growth schematics, the morphology and the almost standing orientation of the 6P derivatives are based on XRD and GIXRD measurements. The downward orientation of the dipoles for o-2F-6P is based on our UPS results.

### **Table of Contents entry**

Nonsymmetric dipolar substitution of *para*-sexiphenyl (6P) at the *meta*- or *ortho*- and *para*-positions of one terminal phenyl ring severely impacts growth and electronic properties of thin films. By changing the substitution position, the thin-film ionization energies are altered by >1eV. Thin-film structures and morphologies range from crystalline and three-dimensional to liquid-crystalline and two-dimensional which are interesting for electronic applications.

### Keyword

Organic thin films

### Authors

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### Title

Dipolar Substitution Impacts Growth and Electronic Properties of para-Sexiphenyl Thin Films

## **ToC figure**

