Self-assembled monolayers of perfluoroterphenyl-substituted alkanethiols: specific characteristics and odd–even effects†

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Self-assembled monolayers (SAMs) formed by perfluoroterphenyl-substituted alkanethiols (CnF5-C6F3-C6F3-(CH2)n-SH, FTPn) with variable length of the aliphatic linker (n = 2 and 3) were prepared on (111) Au and Ag and characterized by a combination of several complementary spectroscopic and microscopic techniques. A specific feature of these systems is the helical conformation of the FTP moieties, which, along with the high electronegativity of fluorine, distinguishes them from the analogous non-fluorinated systems and makes them attractive for different applications. The SAMs were found to be well-defined, highly ordered, and densely packed, which suggests a perfect correlation between the orientations and, in particular, twists of the FTP helices in the adjacent molecules. Significantly, the SAM exhibited pronounced odd–even effects, i.e. a dependence of the molecular orientation and packing density on the length of the aliphatic linker in the target molecules, with parity of n being the decisive parameter and the direction of the effects on Au opposite to that on Ag. The presence of the odd–even effects in the FTPn system brings new aspects into the discussion about the origin and mechanism of these phenomena. Specifically, the helical conformation of the FTP moieties in the dense phase excludes a variation of the intramolecular torsion and molecular twist as the mechanism behind the odd–even effects.

1. Introduction

The current progress in microelectronics is driven by the increasing density of the individual building blocks. This demand, along with the growing costs of standard top-down fabrication procedures upon further miniaturization, requires new strategies and materials. Promising systems in this regard are functional molecules, which can self-assemble into highly ordered aggregates (bottom-up behavior), revealing a variety of useful properties. In particular, self-assembled monolayers (SAMs),1,6 the properties of which can be ‘pre-programmed’ by the design of their molecular components, have been used for a number of applications in the area of microelectronics, such as insulators,9,14 charge-carrier injection layers,7,8 or for the control of organic semiconductor growth.12,15 In addition, SAM-like assemblies of the individual “device” molecules serve as prototypes of future molecular electronics.16,17

To achieve efficient charge transport through the monolayer, the use of aromatic molecules is essential.18–20 However, direct attachment of such moieties to metal substrates (electrodes) usually does not result in the formation of well-ordered monolayers,21–24 hampering application of aromatic SAMs in prototype and real devices. A reason for this behavior is presumably a strong interaction between the aromatic moieties in the film, which are frequently prone to form an arrangement that is not completely commensurate with the substrate.25 The arising stress results in the formation of small domains and appearance of dislocations and other defects.23,24,26 For the most popular thiolate-gold systems, one of the remedies is the substitution of the sulfur atoms by selenium ones, since these experience a lower corrugation of the headgroup–substrate binding potential that permits the adoption of less preferred adsorption sites, decoupling the optimal molecular arrangement and the structural template provided by the substrate.27,30 Another, presumably more general approach is the introduction of a short alkyl linker between the oligophenyl moiety and the headgroup.31–42 In the respective monolayers, such a linker decouples the structure adopted by the aromatic part from that of the substrate and transfers the predominant bonding geometry given by the substrate-specific bending potential to the aromatic moiety.31–43 This results in either smaller or larger inclination of the latter moiety depending on the bond angle at the binding atom (which itself is a function of the substrate metal) and the parity of the number of methylene groups in the linker.31,32,35,38,41,43
At a proper adjustment of the bonding angle and length of the linker, highly ordered aromatic molecular films can be prepared, what, among other applications, potentially permits their use as semiconducting films.

SAMs can be used not only as a structural mediator between metal electrodes and organic semiconductors but also to enhance the charge transport in the respective junctions which are e.g. realized in organic light emitting diodes and field effect transistors.44–45 By forming a dipole layer at the electrode/semiconductor interface, SAMs can lower the barrier for electron or hole injection into the organic semiconductor.44–50 In particular, partly fluorinated aliphatic SAMs were used for this purpose (enhancement of hole injection).44 Considering the much higher conductance of the SAMs can be expected as compared to their non-fluorinated analogs. An important parameter in this context is the SAMs structure is one of the crucial factors for such applications.

Following this argumentation and pursuing better understanding of structure-building interactions in SAMs, we decided to modify the terphenyl-substituted alkanethiols, which form SAMs of very high quality,35,37 by perfluorination of their aromatic part, i.e. prepare and characterize SAMs of perfluoroterphenyl-substituted alkanethiols (C₆F₅-C₆F₃-C₆F₄-(CH₂)ₙ-SH, n = 2, 3; see Fig. 1). The use of completely fluorinated oligophenyls is novel; so far only SAMs of partly fluorinated aromatic films would be a better alternative. The principle possibility to use such systems was indeed demonstrated by the examples of pentafluorothiophenol13,14 and partly fluorinated oligo(phenylene ethynylene),10 with, however, little or no information regarding the structural quality of the monolayers. Since defects in the dipole layer formed by SAMs will significantly influence the effective modification of the charge injection barrier, the analysis and possible optimization of the SAMs structure is one of the crucial factors for such applications.51

Following this argumentation and pursuing better understanding of structure-building interactions in SAMs, we decided to modify the terphenyl-substituted alkanethiols, which form SAMs of very high quality,35,37 by perfluorination of their aromatic part, i.e. prepare and characterize SAMs of perfluoroterphenyl-substituted alkanethiols (C₆F₅-C₆F₃-C₆F₄-(CH₂)ₙ-SH, n = 2, 3; see Fig. 1). The use of completely fluorinated oligophenyls is novel; so far only SAMs of partly (one or two rings) fluorinated terphenyl thiols on Au(111) have been studied.48,52,53 It was of particular interest to learn whether these systems form denser and less defective monolayers compared to the shorter fluorinated phenyl thiols, as would be needed for their applications in electronic devices, and what the exact structure of these monolayers would be.

Since the van-der-Waals radius of the fluorine atom is significantly larger than that of hydrogen, a different conformation and packing of the fluorinated molecules in the SAMs can be expected as compared to their non-fluorinated analogs. An important parameter in this context is the dihedral (torsion) angle between the phenyl rings, which is typically around 30° in the gas phase state of oligophenyls. However, in the respective crystals, the steric repulsion of the ortho hydrogen atoms, responsible for the torsion, can be overcompensated by the lattice energy, in particular by the T-shaped interaction,54,55 leading to the frequently observed herring-bone pattern with (almost) planar conformations of the individual molecules.56–58 Similar conformations can also be assumed for oligophenyl-based SAMs.59–61 In contrast, such a planarization is hardly possible for the perfluoro-derivatives, where a substantially higher rotational barrier has to be assumed, leading to different interactions and therefore different molecular arrangements.

In the following section we shortly address the experimental procedure. The results are presented and discussed preliminary in Section 3. A thorough discussion of the data is given in Section 4 followed by a summary in Section 5.

2. Experimental section

The synthesis of the perfluoro-p-terphenyl-4-yl-alkanethiols (FTPₙ, n = 2, 3) has been described elsewhere.62 The SAMs were prepared by immersion of the freshly prepared (111) gold and silver substrates into the solutions of the target compounds at room temperature (see ESI for details).

The FTPₙ SAMs were characterized by X-ray photoelectron spectroscopy (XPS), high-resolution X-ray photoelectron spectroscopy (HRXPS), ellipsometry, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, infrared reflection absorption spectroscopy (IRRAS), scanning tunneling microscopy (STM), and contact angle goniometry. All experiments were performed at room temperature; only in the case of STM, we have tried elevated temperatures of incubation in solution up to 65 °C but without any significant improvement or modification in the film structure. The NEXAFS experiments were carried out at both a moderate and high energy resolution at the synchrotron storage rings BESSY II (Berlin, Germany) and MAX II (Max-lab, Lund, Sweden), respectively. The XPS, HRXPS, and NEXAFS spectroscopy measurements were conducted under UHV conditions at a base pressure <1.5 × 10⁻⁹ mbar. The time for these measurements was selected as a compromise between spectra quality and damage induced by X-rays.63–66 The experimental setups and parameters are described in detail in ESI.

3. Results and discussions

3.1 Molecular geometry

As mentioned in the Introduction, the important geometrical parameters of the terphenyl backbone, which can have a pronounced effect on the structure of the derived SAMs, are the torsion angles of the outer rings with respect to the middle one, with the outer rings being not necessarily coplanar but rotated differently with respect to the central ring. In the molecular state (gas phase), the dihedral rotation is predominantly governed by two interactions, viz. the interaction between the π orbitals of the adjacent phenyl rings and the repulsion between either hydrogen (general case) or fluorine
(our case) atoms in the ortho-positions of these rings. The π orbital interaction tends to make the whole backbone planar, achieving thus the maximum conjugation between the rings. In contrast, the repulsion between the ortho-atoms (hydrogen or fluorine) forces a non-planar conformation. Balance of these interactions gives the resulting structure.

The substitution of hydrogen atoms by fluorine ones does not change significantly the length of the aromatic C–C bonds and, what is even more important in the present case, the C–C interring distance. Only a slight shortening of the respective bond lengths can be expected. Under these circumstances, due to the larger atomic radius of fluorine and the fact that the C–F bond length (∼1.34 Å) is noticeably longer than that of the C–H bond (∼1.09 Å), the planar conformation is not possible in the case of FTP moiety even in the molecular state—the fluorine atoms in the ortho-positions of the adjacent rings will just come across one another. Simple semi-empirical calculations of the FTP2 structure in the molecular state performed with the MOPAC2009 software package using the PM3 set gave torsion angles of −54.8° and +55.2° for the outer rings with respect to the middle one, with both outer rings rotated in the opposite directions as emphasized by the −/+ signs and all three rings forming a helix. Geometry optimization using ab initio calculations done with GAMESS.08 using STO3G basis set gave roughly the same, helical molecular conformation and very similar values of the torsion angles (with respect to the middle ring), viz. −59.1° and +59.2°.

Most significantly, the structure of the FTP moiety should persist largely in the condensed state as shown by published X-ray crystallographic structural data for closely related compounds, viz. 2H-nonafluorobiphenyl and perfluorobiphenyl, in which the torsion angle was reported to be ∼59.5°. This value is very close to our calculated angles for the molecular state of FTP2. However, since the molecules studied so far have only two rings, it became of importance that during this project we were able to obtain the first solid state structure of a perfluorinated terphenyl derivative. In this compound, (perfluoroterphenyl-4-yl)methanol, the torsion angles of the outer rings are −57° and +58° with respect to the central ring. This not only verifies the calculated angles for the molecular state and suggests their persistence in the densely packed phase but also shows that the phenyl rings in the latter case form a distinct helix, in contrast to the situation observed in most non-fluorinated terphenyl derivatives.

Another interesting feature of the crystallographic structure of bulk (perfluoroterphenyl-4-yl)methanol is a relatively small spacing of ∼4.5 Å between the parallel FTP moieties. Such a small spacing is presumably only achieved due to vertical shift (by ∼1.4 Å) of the adjacent chains with respect to one another and due to the correlated orientation of the FTP helices of the neighboring molecules. Whereas such a vertical shift is possible to a limited extent only in the densely packed phase but also shows that the phenyl rings in the latter case form a distinct helix, in contrast to the situation observed in most non-fluorinated terphenyl derivatives.

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3.2 HRXPS and XPS

HRXPS gives information about integrity, identity, chemical composition, and effective thickness of the target films. The S 2p, C 1s, and F 1s spectra of FTP2 and FTP3 adsorbed on Au and Ag are shown in Fig. 2 and 3, and Fig. S2 (ESI†), respectively. The S 2p spectra in Fig. 2 are dominated by a
characteristic doublet at a BE of 161.8–161.9 eV (S 2p_{3/2}), with slightly lower (by ~0.1 eV) BEs in the case of Ag. This doublet can be clearly assigned to thiolate species bonded to the surfaces of gold or silver. \(^{21-24}\) The FWHM of the S 2p_{3/2} and S 2p_{1/2} components of the thiolate-related doublet is quite small for FTP3/Au (~0.50 eV) and noticeably larger for the other films (0.60–0.64 eV). The FWHM value for FTP3/Au is close to the values expected for the case of equivalent adsorption sites for all SAM constituents, \(^{24,75}\) which suggests a single or at least one dominant adsorption site for all FTP3 molecules in this particular film. The higher FWHM values for the other films can be associated with the superposition of several S 2p signals with slightly different BEs, which implies the presence of several different adsorption sites. In addition to the thiolate-related doublet, there is a further, less intense doublet at a BE of ~161.0 eV (S 2p_{3/2}); the intensity of this feature constitutes, depending on the system, 12–23% of the total S 2p intensity. This feature can be ascribed either to atomic sulfur \(^{16}\) or a thiolate-type bound sulfur with a different binding chemistry and/or geometry as compared to the “standard” thiolate-type bond observed in thiol-derived SAMs on coinage metal substrates. \(^{33,77}\) Both assignments are discussed in detail in ref. 78 and 79, but we would like to note here that in most situations, including the present case, the “different thiolate” assignment can be favoured. The doublet at 161.0 eV, which is a general phenomenon in thiolate-related SAMs, is frequently present in the XPS spectra of these systems but is usually not recognised in the case of conventional laboratory experimental setup because of low quality of the S 2p spectra. In contrast, in many cases, this doublet can be clearly distinguished when performing synchrotron-based HRXPS. \(^{74,75,78,80}\) Apart from the 161.9 and 161.0 eV doublet, there are no other features related to decomposed, physisorbed or oxidized FTP3 molecules in the S 2p spectra. This suggests that all SAM constituents are bound to the surface in the thiolate-like fashion and have an upright orientation associated with dense molecular packing.

The C 1s HRXPS spectra of FTPn/Au and FTPn/Ag in Fig. 3 exhibit three emissions at ~284.4, ~285.8, and ~287.5 eV assigned to the carbon atoms in the aliphatic linker (284.4 eV) and FTP moiety (285.8 and 287.5 eV), respectively; the FWHM of these emissions are 0.67–0.83 eV. The ~285.8 eV emission can be associated with the carbon atoms in the para positions (except for the terminal carbon), whereas the ~287.5 eV emission can be related to the carbon atoms in the ortho and meta positions and the terminal carbon atom. This assignment is supported by comparison of the spectra of FTP3/Au acquired at photon energies of 350 and 580 eV (see Fig. S1 in ESI†), which show, apart from a lower energy resolution at 580 eV, comparable intensities of the ~285.8 and ~287.5 eV peaks and considerably lower intensity of the 284.4 eV emission at a PE of 350 eV. Indeed, the relative intensity of the peak associated with the alkyl linker is expected to increase with increasing photon energy due to a smaller attenuation by the FTP overlay, which is exactly what we observe. Based on the molecular composition, \(2:5:13\) (FTP2) or \(3:5:13\) (FTP3) intensity relations can be expected for the 284.4, 285.8 and 287.5 eV peaks, respectively. These relations are coarsely reproduced by the C 1s spectra but are, as expected, modulated by attenuation and self-attenuation of the respective photoemission signals in the films. \(^{81}\)

The F 1s HRXPS spectra of FTPn/Au and FTPn/Ag (see Fig. S2 in ESI†) exhibit a single emission at a BE of 687.4–687.6 eV. This 687.4–687.6 eV emission can be clearly assigned to the fluorine atoms of the FTP moiety. 

Apart from the above analysis of the spectra, we used the HRXPS data to compare the packing density of the FTPn molecules in the respective films. A tentative fingerprint of the packing density is the ratio of the signals related to the film and substrate. In our case, we can rely on the C 1s and F 1s emissions from the films and on either the Au 4f or Ag 3d emission from the substrates. For Au, both C1s/Au4f and F1s/Au4f ratios for FTP3 were found to be larger by ~30% than for FTP2, suggesting a higher packing density for FTP3. For Ag, the opposite situation occurred: both C1s/Ag3d and F1s/Ag3d ratios for FTP2 were found to be larger by ~20–30% than for FTP3 suggesting a higher packing density for FTP2.

In addition to the above qualitative considerations, we estimated the effective thickness of the FTPn films on the basis of the XPS data. For this purpose, we utilized the intensities of either Au 4f (FTPn/Au) or Ag 3d (FTPn/Ag) signal, assumed a standard expression for the attenuation of the photoemission signal, \(^{81}\) and took attenuation lengths reported in ref. 82. To determine the spectrometer-specific coefficients, we took molecular films of known thickness (and packing density) as direct reference; the respective samples were adjusted to the sample holder along with FTPn SAMs and measured at the same conditions. As reference films we used dodecanethiolate (DDT) and octadecanethiolate (ODT) SAM on Au(111) and Ag(111). The films on Au had a molecular density of 4.63 \(\times\) 10\(^{14}\) cm\(^{-2}\), which corresponds to an area per molecule of 21.6 Å\(^2\).\(^4\) The films on Ag possessed a molecular density of 5.41 \(\times\) 10\(^{14}\) cm\(^{-2}\), which corresponds to an area per molecule of 18.5 Å\(^2\).\(^4\) The effective thicknesses of the FTP2 and FTP3 films were estimated at 16.8 and 20.4 Å, respectively, for Au and at 19.7 and 15.6 Å, respectively, for Ag. This behaviour correlates precisely with the above HRXPS results for the film/substrate intensity ratios. Considering that the thickness of the FTP2 and FTP3 films in the case of the upright orientation of the SAM constituents is expected to be ~19.2 and ~20.2 Å, respectively, the XPS results suggest practically vertical molecular orientation in FTP3/Au and FTP2/Ag and only slight molecular inclination (by ca. 30°) in FTP2/Au and FTP3/Ag.

On the basis of the effective thickness, the molecular packing density in the FTP2 and FTP3 films can be estimated, using e.g. the approach of ref. 83. An alternative possibility, at least for the films on Au, is the comparison of the S2p/Au4f intensity ratios of the FTPn films with those for the reference DDT and ODT systems. This ratio is a direct measure of the molecular packing density. As compared to the S 2p signal itself, this ratio does not suffer from all the problems related to the absolute intensity comparison and to the different attenuation of this signal in different films. Due to the quite close binding energies of the Au 4f and S 2p emissions, both signals are attenuated similarly as far as the primary excitation is performed at high photon energy. The S2p/Au4f intensity
ratios for C18/Au, FTP2/Au, and FTP3/Au are 0.0103, 0.00637, and 0.00864, respectively. Considering that the area per molecule in C12/Au and C18/Au is 21.6 Å² (see above), the areas per molecule in FTP2/Au and FTP3/Au are 34.9 and 25.8 Å², respectively. These values are further proof of the odd–even behaviour in the FTPn system. Note that the ratio between these values (1.35) is somewhat higher than the respective ratio for the effective thicknesses of FTP3/Au and FTP2/Au (1.21), which reflects a limited accuracy of the evaluation procedure.

As for the silver substrate, in view of the quite close effective thickness values, FTP2/Ag should have a similar molecular packing density as FTP3/Au while FTP3/Ag should have a similar molecular packing density as FTP2/Au.

3.3 Ellipsometry

The effective thicknesses of the FTP2 and FTP3 films on Au derived from the ellipsometry measurements are 14.9 and 20.0 Å, respectively. These values reproduce the thickness relation between FTP2/Au and FTP3/Au, obtained by XPS, and are quite close to the XPS-derived thicknesses, even though somewhat lower, especially for FTP2/Au (similar results were reported in a preliminary study using another ellipsometer). In the case of Ag, the effective thicknesses of the FTP2 and FTP3 films were estimated at 16.4 and 12.1 Å, respectively. Whereas the thickness relation between FTP2/Ag and FTP3/Ag, obtained by XPS, is reproduced quite well, similar to the Au case, the absolute values of the thicknesses are noticeably different. We believe that this difference is related to the sensitivity of the native Ag substrate, used as the reference, against air during the ellipsometry measurements. In this case, we rather trust the absolute values derived from the XPS data, also in view of the NEXAFS results (see next section).

3.4 NEXAFS spectroscopy

Sampling the electronic structure of unoccupied molecular orbitals, NEXAFS spectroscopy provides information about the chemical identity of the adsorbed film. Further, using the angular dependence of the transition matrix elements for resonant excitations, the average orientation of the constituents can be probed. A fingerprint of such an orientation is the linear dichroism, i.e. the dependence of the absorption resonance intensity on the orientation of the electric field vector of the synchrotron light with respect to the molecular orbital of interest. An efficient way to monitor the linear dichroism is to plot the difference of the NEXAFS spectra acquired at normal (90°) and grazing (20°) angles of X-ray incidence. In contrast, a spectrum acquired at the so-called magic angle of X-ray incidence (55°) is not affected by any effects related to molecular orientation and gives only an information on the chemical identity of investigated samples. The exact value of the magic angle depends, however, on the polarization factors of the primary X-ray light; in particular it decreases to ≈51° for \( P = 0.82 \).

Carbon K-edge NEXAFS spectra of FTPn/Au and FTPn/Ag acquired at an X-ray incident angle of 51° are shown in Fig. 4; these spectra were collected with an energy resolution of \( \sim 0.40 \) eV (BESSY II). The observed absorption structure was fully reproduced in the high-resolution (≈50 meV; Max-lab) NEXAFS spectra, with some of the low intensity resonances (e.g. 2', 3', and 3'*) being better visible (see Fig. S3 in ESI†). The most prominent absorption resonances in the spectra are marked by numbers; the respective photon energy positions are compiled in Table 1. The assignment of the absorption resonances, which is also given in Table 1, was performed in accordance with ref. 94 and 95. In these studies, NEXAFS spectra of fluorine-substituted benzenes have been analyzed in detail. The aromatic part of the FTP2 and FTP3 molecules can be considered as a superposition of 1,2,4,5-tetrafluorobenzene (the inner rings) and pentafluorobenzene (the terminal ring), NEXAFS spectra of which are considered in detail in ref. 85 and 86. The above consideration is strongly supported by visual comparison of the theoretical spectra of these moieties from ref. 85 and 86 and the spectra of the FTPn films in this work. The calculated and experimental positions of the individual absorption resonances in 1,2,4,5-tetrafluorobenzene and pentafluorobenzene are very close to each other, with only slightly higher values in the latter case, so that no splitting or significant broadening of these resonances can be expected for the FTPn films, which is indeed the case as seen in Fig. 4 and Fig. S3 (ESI†). Overall, both absorption structure and general spectral shape are very similar for all the films of this study. The spectra are dominated by two sharp resonances at \( \sim 285.7 \) eV (1) and \( \sim 287.6 \) eV (2) corresponding to the C1s → π* transitions from the FTP carbon atoms which are not bonded and directly bonded to fluorine atoms, respectively. Further, there are several less intense π*- and σ*-like resonances, with the positions and assignments given in Table 1. The assignments of the weak resonances 2', 3', and 3' are elusive. The characteristic R* resonance of the aliphatic linker at \( \sim 287.7 \) eV is presumably weak and overlaps with the C1s-C → π* feature, so that no information on this linker can be obtained from the NEXAFS data.
In addition to the C K-edge data, fluorine K-edge NEXAFS spectra of the FTPn films on Au and Ag were measured (see Fig. S4 in ESI†). The spectra of all four films are very similar; they exhibit characteristic absorption resonances of perfluorinated oligophenyl (see ESI† for tentative assignment).

Along with the above analysis of the NEXAFS spectra, the linear dichroism effects in the target films were monitored. As mentioned at the beginning of this section, a convenient way to follow the linear dichroism effects is to plot the difference between the NEXAFS spectra acquired at the normal and grazing incidence of the primary X-ray beam. Such difference curves (90°–20°) are presented in Fig. 5 for the C K-edge and in Fig. S5, ESI† for the F K-edge. According to these curves, the NEXAFS spectra of all the FTPn films exhibit a pronounced linear dichroism, i.e., a dependence of the absorption resonance intensity on the incidence angle of the X-ray beam. This is a clear signature of orientational order. In addition, the signs of the observed difference peaks, viz. the positive sign for the π*-like resonances and the negative sign for the σ*-like ones, suggest an upright molecular orientation in all the FTPn films.

In addition to the above qualitative considerations, a quantitative analysis of the entire set of the C K-edge NEXAFS spectra acquired at different X-ray incidence angles was performed. For this analysis we used the most prominent π*-like resonances 1 and 2 (see Fig. 4) which are related to the same molecular orbital (see Table 1). The intensity $I$ of these resonances was monitored as a function of X-ray incidence angle $\Theta$ and evaluated according to the theoretical expression for a vector-type orbital $^{84}$

$$ I(x,\Theta) = A(P \times \frac{4}{3} + 3\cos^2\Theta - 1)(3\cos^2\Theta - 1) $$

The absorption resonances related to the individual rings within the FTP backbone are practically not distinguishable, so that not the orientation of each individual ring but only their average orientation can be determined on the basis of the NEXAFS data. This refers not only to the twist angles of the rings but to the tilt angles of the π* orbitals as well. Indeed, since the angle $\beta$ is common for all rings, different values of $\gamma$ will mean different values of $\alpha$ for the individual rings. So, we are left with the option to estimate the average $\alpha$ values

<table>
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<tr>
<th>Peak no.</th>
<th>Assignment according to ref. 94</th>
<th>System</th>
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<tr>
<td>1</td>
<td>C_{1s}C–C → 1π*</td>
<td>FTP2/Au</td>
</tr>
<tr>
<td>2</td>
<td>C_{1s}C–F → 1π*</td>
<td>FTP3/Au</td>
</tr>
<tr>
<td>2'</td>
<td>C_{1s}C–F → 1π*</td>
<td>FTP2/Ag</td>
</tr>
<tr>
<td>3</td>
<td>C_{1s}C–F → σ*(C–F)</td>
<td>FTP3/Ag</td>
</tr>
<tr>
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<td>C_{1s}C–F → 2π*</td>
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<tr>
<td>7</td>
<td>C_{1s}C–F → σ*</td>
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**Fig. 5** Difference between the carbon K-edge NEXAFS spectra acquired at X-ray incident angles of 90° and 20° of FTPn/Au and FTPn/Ag, respectively. The most prominent difference peaks are marked by numbers; see Table 1 for the assignments and text for details. Dashed lines correspond to zero.
To avoid normalization problems, not the absolute intensities but the intensity ratios $I(Y)/I(2\theta)$ were evaluated, where $I(Y)$ and $I(2\theta)$ are the intensities of either $1\pi^*(C_{1s} C–C)$ or $1\pi^*(C_{1s} C–F)$ resonance at synchrotron light incidence angles of $Y$ and $2\theta$. The resulting angle dependences of the relative intensities are displayed in Fig. 7, along with the respective fits according to eqn (1). The obtained values of the average tilt angles of the $1\pi^*$ orbitals are compiled in Table 2; the accuracy of all angle values is within $3–5^\circ$, which is just an average accuracy of the NEXAFS experiment. The $1\pi^*(C_{1s} C–C)$ and $1\pi^*(C_{1s} C–F)$ derived results agree very well, which underlines the reliability of the experiment and data evaluation procedure. Most important, according to Fig. 7 and Table 2, molecular inclination in FTP$n$ SAMs exhibit distinct odd–even behavior in regard to the length of the aliphatic linker, which is opposite on Ag to that on Au.

To determine the average tilt angle of the FTP backbone in the target films, the values presented in Table 2 should be corrected for the twists of the individual rings. These values are not known but, on the basis of the theoretical calculations for the FTP$n$ molecules in the gas phase and the X-ray crystallographic data for the related compounds (62,67,68) (see Section 3.1 for details), a helical conformation of the FTP backbone with the relative torsions of the outer rings by $\phi = 0$ is the most realistic model. Since these values are close to $60^\circ$, the orientation of the $\pi^*$ orbitals of the individual rings with respect to the molecular axis is characterized by close-to-C3 symmetry. Under these circumstances, the average value of $\cos(\gamma)$ is only weakly dependent on the actual $\gamma$ values for the individual rings. In particular, at $\gamma = 0$ for the middle ring, the weighted sum of $\cos(\gamma)$ is equal to 0.67, whereas at $\gamma_{\text{middle}} = 90^\circ$ this value is equal to 0.58. The average between these limiting cases (0.625) is most representative for the entire variety of possible torsion angles. Taking this value and the average tilt angles of the $1\pi^*$ orbitals compiled in Table 2, we calculated an average tilt angle of the FTP backbone of $\sim 26^\circ$ for FTP3/Au and FTP2/Ag and $\sim 38^\circ$ for FTP2/Au and FTP3/Au.

Table 2  Average tilt angle of the $1\pi^*$ orbitals of the individual rings within the FTP backbone in FTP$n$ SAMs on Au and Ag. The angles were determined on the basis of the angular dependence of the $1\pi^*(C_{1s} C–C)$ and $1\pi^*(C_{1s} C–F)$ resonance intensity (see Fig. 7).

<table>
<thead>
<tr>
<th>Resonance</th>
<th>FTP2/Au</th>
<th>FTP3/Au</th>
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<tr>
<td>C_{1s} C–C</td>
<td>67.5°</td>
<td>75°</td>
<td>74°</td>
<td>68°</td>
</tr>
<tr>
<td>C_{1s} C–F</td>
<td>67.5°</td>
<td>73.5°</td>
<td>74°</td>
<td>66.5°</td>
</tr>
</tbody>
</table>

Fig. 6 A schematic drawing of the FTP3 molecule: (a) view along the FTP backbone; (b) side view. The orientation of the FTP backbone is given by the tilt angle $b$, twist angle $\gamma$, and torsion angle $\delta$. At $\gamma = 0$, normal to the ring plane (which is collinear with the $\pi^*$ orbitals) lies in the plane spanned by the $z$- and the 4,4'-axes. The torsion results in different values of $\gamma$ for the inner ring and outer rings.

Fig. 7 The angular dependence of the $1\pi^*(C_{1s} C–C)$ and $1\pi^*(C_{1s} C–F)$ intensity ratio $I(Y)/I(2\theta)$ for FTP2/Au (full circles), FTP3/Au (hollow circles), FTP2/Ag (full squares), and FTP3/Ag (hollow squares) along with the best fits according to eqn (1) (black and gray solid lines for FTP2 and FTP3 films, respectively).
FTP3/Au. We estimate the accuracy of these values to be ±5°, in view of the standard accuracy of the NEXAFS experiment and the difference between two limiting values for the weighted sum of |cos(γ)|). The difference in the packing density between FTP3/Au and FTP2/Au on one side and FTP2/Au and FTP3/Au on the other side can then be coarsely estimated as cos(26°)/cos(38°) ratio, which gives 15% for the extent of the odd–even packing density variations in the FTPn films.

3.5 IR spectroscopy

The main adsorption bands in the IR spectra of FTPn SAMs are expected to be located in two regions, viz. the C–H stretching region ranging from 3000 to 2800 cm⁻¹ and the bending and stretching vibration region ranging from 1600 to 800 cm⁻¹. According to the available experimental data for a variety of benzene- and biphenyl-based fluorinated compounds,92–96 the last region is particularly important since it contains information about different vibrations in the aromatic part of the molecules, including C–F stretching and bending modes, analysis of which can give us knowledge about the molecular orientation in the target films.

The IRRAS spectra of FTPn SAMs on Au and Ag in the range from 1750 to 700 cm⁻¹ are presented in Fig. 8. The analogous IR spectra of bulk FTP2 and FTP3, taken as references, are depicted in Fig. 9. Tentative assignments and positions of the most prominent absorption modes observed in the above spectra are compiled in Table 3. These assignments were made on the basis of literature data for a variety of benzene- and biphenyl-based fluorinated compounds.92–96

The IRRAS spectra of the FTPn SAMs on Au and Ag in Fig. 8 exhibit the characteristic absorption resonances of fluorinated aromatic moieties.92–96 All absorption modes observed in these spectra can be found in the spectra of the bulk compounds in Fig. 9, even though there are tremendous differences between the bulk spectra and the spectra of the monolayers assembled on Au and Ag regarding the relative intensity of the individual absorption bands. The most prominent bands of the bulk spectra at 1486, 1474, 977, and 714 cm⁻¹ are either noticeably weakened or almost completely disappeared in the spectra of the monolayers. At the same time, the absorption modes at 1658 and 1543 cm⁻¹ which were hardly visible in the bulk spectra, become quite prominent in the spectra of the monolayers, along with few other modes which are quite intense in both cases (1517, 1485, 1259, 1150, 1090, 720 cm⁻¹). The above differences can be rationalized in view of high orientational order and upright orientation of the constituents in the monolayers as shown in the previous section. The comparison of the bulk spectra and the spectra of the monolayers suggests that the TDMs of the absorption modes at 1658 and 1543 cm⁻¹ are directed along the 4,4' axis, whereas the TDMs of the absorption modes at 1474 and 985–935 cm⁻¹ are directed perpendicular to this axis. The TDMs of the further absorption modes mentioned above do not exhibit strongly preferential orientation along or perpendicular to the 4,4' axis, even though a definite extent of the preference cannot be excluded.

Further, comparing the IRRAS spectra of the FTP2 and FTP3 SAMs on either Au or Ag substrate, one can monitor the odd–even effects mentioned in the previous sections. Indeed, one sees noticeably higher intensity of the bands at 1658 and 1543 cm⁻¹ for FTP3/Au than for FTP2/Au and the inverse intensity relation occurring for the Ag substrate. Vice versa, the bands at 1474 and 985–935 cm⁻¹ are only prominent in the spectrum of FTP3/Ag and traceable in the spectrum of FTP2/Au. Taking into account the assumed TDM directions for all these bands, this behavior suggests a more upright orientation of the FTP3 moieties in the respective SAMs on
Au as compared to the FTP2 case. An inverse situation takes place for the Ag substrate: FTP2 moieties exhibit more upright orientation in the respective SAMs as compared to the FTP3 species.

### 3.6 STM

Representative STM results obtained for the FTP3/Au and FTP2/Au systems are presented in Fig. 10 and 11, respectively. Before discussing these results in detail, it is important to comment on the imaging conditions used in our experiments. In contrast to the previous STM studies of the analogous non-fluorinated systems, 4,4′-terphenyl-substituted alkanethiols (TPn), C₆H₄(CH₂)ₙSH on Au(111), we were unable to obtain stable imaging conditions with the respective parameters, i.e. the current set point in the range of 150–250 pA and bias voltage in the range of 400–800 mV. As documented by Fig. 10a and b, which show two consecutive STM images of the same sample area, the application of the previously used parameters resulted in visible modification of the surface morphology (compare the area of monoatomic substrate vacancies in Fig. 10a and b). A non-destructive imaging of the FTPn samples, as shown for comparison in Fig. 10c, which has the same resolution as Fig. 10a and b, was only possible at extremely low set point current in the range of 20–40 pA and rather high bias voltage in the range of 500–1500 mV (there was no significant dependence on the sign of the bias). These adjustments can be tentatively explained by taking into account the well-known fact that perfluorination of aliphatic SAM introduces a molecular dipole moment which significantly increases the work function of the surface. Recent experiments performed for the films of perfluorinated phenyl thiol confirm such behaviour also for perfluorinated aromatic SAMs. Therefore, we can assume that the observed reduction of the current set point, necessary for non-destructive imaging of perfluorinated systems, may result from the increased height of the tunnelling barrier, which is generally defined by the work functions of the substrate and the STM tip. For the given values of the set point current and bias voltage, a higher tunnelling barrier will most probably be compensated by a decrease of the spacing (gap) between the scanning tip and the sample what may eventually lead to the film modification during scanning by penetration of the tip into the monolayer.

To achieve non-destructive imaging, the set point current has to be reduced to restore a “safe” gap between the monolayer and the tip during scanning at a given bias voltage.

Now we turn to the analysis of the data obtained for the FTP3 system using the non-destructive imaging conditions specified above. An STM image obtained at higher resolution is presented in Fig. 10d; it shows that the adsorption of FTP3 molecules on the Au(111) surface at room temperature results in the formation of a rather dense network of depressions and islands visible as dark patches and bright spots, respectively. As documented by the cross-section A marked in this image, both the depth of the depressions and the height of the islands correspond (within the experimental error) to the height of the monoatomic substrate step on Au(111) surface, i.e. 2.4 Å, and thus indicates modification of the topmost Au(111) substrate atoms layer upon adsorption of the molecules. Such a modification of the Au(111) substrate upon thiol adsorption has been previously reported for different SAMs, including also the non-fluorinated analog of the FTPn system—TPn/Au. However, the density of the substrate defects for FTP3/Au is significantly higher as compared to its direct analog, TP3/Au (for comparison, see Supplementary Information data in ref. 36). The faceting of the Au(111) substrate edges (the result of the flame annealing process) enables identification of the closest neighbour directions on the Au(111) substrate—these are the (110) directions. A higher resolution image, presented in Fig. 10e, shows domains with molecular rows separated by ~8–9 Å and running along two directions marked by white arrows which intersect each other at an angle of ≈ 60°. In general, only three different directions of such stripe motive were observed, intersecting the (110) substrate directions at 30° or 90° and, thus, were oriented along the (112) directions of the Au(111) substrate. In contrast to the previously investigated non-fluorinated terphenyl- and biphenyl-based thiol SAMs, the acquisition of high-resolution data, and especially molecular resolution ones, turned out to be extremely difficult for the FTPn films, which was presumably related to a limited stability of the tunnelling conditions for these systems. As a result, high resolution images, revealing molecular resolution within a particular domain, were obtained only in limited sections of STM scans as indicated by the dashed lines.

<table>
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<tr>
<th>FTP3 (bulk)</th>
<th>FTP2/Au</th>
<th>FTP3/Au</th>
<th>FTP2/Ag</th>
<th>FTP3/Ag</th>
<th>Assignment</th>
<th>TDM direction</th>
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<tr>
<td>1657</td>
<td>1658</td>
<td>1658</td>
<td>1657</td>
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<tr>
<td>1516</td>
<td>1517</td>
<td>1517</td>
<td>1518</td>
<td>1516</td>
<td>ν(C–C)</td>
<td>/</td>
</tr>
<tr>
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<td>1483</td>
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<td>ν(C–F)</td>
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<tr>
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<td>1263</td>
<td>1262</td>
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</tr>
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<td>1148</td>
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<td>/</td>
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<tr>
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<tr>
<td>714</td>
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<td>719</td>
<td>718</td>
<td>γ(C–F)</td>
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* The TDM orientation is given with respect to the 4,4’-axis of the FTP moiety: /-TDM is perpendicular to this axis, ||-TDM is parallel to this axis, -/TDM is neither parallel nor perpendicular to the axis.
Fig. 10 Summary of the STM data for FTP3 SAMs on Au(111). (a)–(g) STM images collected in constant current mode with \( I = 200 \) pA, \( U = 700 \) mV for (a)–(b) and \( I = 20 \) pA, \( U = 700 \) mV for (c)–(g). The panels (a) and (b) show two consecutive STM images of the same sample area to illustrate a modification of the sample by the STM tip at the high tunnelling current; such a modification does not occur at the low current. The yellow lines in (d) and (g) mark cross-sections A, B and C displayed in panels (h), (i) and (j), respectively. The angle \( \alpha = 60^\circ \) in (c) marks relative orientation (given by the white arrows) of the stripe pattern lines (see text for details). The dashed lines in (f) mark scan lines where modification of the STM contrast took place (see text for details). A schematic illustration of the adsorption structure of FTP3 on Au(111) is depicted in (k). Open circles correspond to gold atoms on the Au(111) surface, light and dark grey filled circles correspond to S atoms with adsorption sites taken arbitrary. The presumable herringbone arrangement of the analogous phenyl rings in the neighbour molecules is marked only schematically by showing a single ring in the FTP3 molecule; no tilt is included.

in Fig. 10f which mark scan lines separating a change in the tunnelling conditions. Despite the above difficulties, the acquired STM data were sufficient for detailed analysis of the molecular structure, which is exemplified in Fig. 10g showing an enlarged fragment of the FFT filtered image from Fig. 10f. As evident from this figure, FTP3 molecules are assembled in a close-to-hexagonal structure. The cross-section B along the \( \langle 110 \rangle \) direction, displayed in Fig. 10i, provides a next neighbour distance of about 9 Å which corresponds to the period of the stripe motive visible in Fig. 10e. These findings could be associated with the same \((2\sqrt{3} \times \sqrt{3})R30^\circ\) packing motive as reported previously for TP3/Au.\(^3\) However, the cross-section C, presented in Fig. 10j, shows that the intermolecular spacing along the \( \langle 112 \rangle \) direction (6 Å) is noticeably larger than the value characteristic of the \((2\sqrt{3} \times \sqrt{3})R30^\circ\) structure (5 Å). Thus, the structure of FTP3 on Au(111) corresponds to the \((2\sqrt{3} \times \sqrt{3})R30^\circ\) lattice uniaxially expanded along one of the \( \langle 112 \rangle \) directions, as schematically shown in Fig. 10k (we assumed a standard\(^2\)\(^2\)\(^2\)\(^4\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\) herringbone arrangement of the individual rings). The respective area per molecule is about 26 Å\(^2\), which corresponds to a packing density of \(3.9 \times 10^{14}\) cm\(^{-2}\).

The STM results obtained for the FTP2/Au(111) system are summarized in Fig. 11; the images have been obtained using the same non-destructive imaging conditions as specified above for the FTP3/Au(111) case. The comparison of the low-resolution STM images for FTP2/Au (Fig. 11a and b) and FTP3/Au (Fig. 10c and d) shows that adsorption of the FTP2 molecules results in a much more defected surface. Similarly to
FTP2 is different from the (112) directions observed for the FTP3/Au(111) system, and is collinear with the (110) substrate directions. Moreover, as documented by the cross-section B in Fig. 11c taken along the (110) directions, the closest neighbour distance amounts to about 5.8 Å, whereas the next neighbour distance measured by cross-section C along the perpendicular (112) direction amounts to about 10.5 Å (see Fig. 11e and f). Considering these data, we can propose an arrangement of the FTP2 molecules on Au(111) substrate in the commensurate rectangular \((2\sqrt{3} \times 2)\) lattice as schematically presented in Fig. 11g. Such an arrangement is associated with an area per molecule of 28.7 Å\(^2\), which corresponds to a packing density of \(3.44 \times 10^{14}\) cm\(^{-2}\). Also in this case, we assume herringbone arrangement of phenyl rings.

It is interesting to compare the lateral arrangements of the FTP\(n\) molecules in the respective SAMs with their non-fluorinated analogs, TP\(n\) films on Au(111). For \(n = \text{odd}\), these films exhibit a periodic structure with a \((2\sqrt{3} \times 3)\)R30° arrangement and two molecules per cell, corresponding to an area of 21.6 Å\(^2\) per molecule.\(^{37}\) For \(n = \text{even}\), these films are characterized by a \((5\sqrt{3} \times 3)\)R30° structure with eight molecules per unit cell, corresponding to an area of 27 Å\(^2\) per molecule (for \(n = 2\) this structure is observed only at an elevated deposition temperature).\(^{37}\) According to the STM data presented in this section, FTP2 and FTP3 films on Au(111) have areas per molecule of about 29 and 26 Å\(^2\), and have distinctly different unit cells of the 2D lattice as compared to the TP\(n\)/Au case. These different cells can be related to different adsorption sites or their combination. Nevertheless, the courses of the odd–even effects in both systems are quite similar, even though the packing density at going from even to odd \(n\) is somewhat lower in the FTP\(n\) case, i.e. about 12% vs. 20–25% for TP\(n\)/Au. Note, however, that the 20–25% difference in the TP2/Au-TP3/Au case was only obtained at the elevated preparation temperature 333 K for TP2/Au.\(^{37}\)

### 3.7 Contact angle goniometry

Advancing (\(\theta_{\text{adv}}\)) and receding (\(\theta_{\text{rec}}\)) water contact angles for FTP\(n\) SAMs on Au and Ag given in Table 4, along with the respective contact angle hysteresis, i.e. the difference between the advancing and receding contact angles (\(\theta_{\text{adv}} - \theta_{\text{rec}}\)). The water contact angle values are very similar for all the films of this study, without any systematic odd–even variation. Presumably the odd–even variation in the packing density and molecular inclination does not affect the wetting properties of the FTP\(n\) SAMs to a noticeable extent. Note that a similar situation occurs in TP\(n\) SAMs on polycrystalline (111) gold and silver substrates with the only difference that both \(\theta_{\text{adv}}\) and \(\theta_{\text{rec}}\) values are smaller by \(\sim 18°\).\(^{35}\) This is understandable in view of the substitution of hydrogen for fluorine but evidences, nevertheless, a high quality of the FTP\(n\) SAMs. Note that even a partial substitution of hydrogen for fluorine in oligophenyl SAMs results in increase of \(\theta_{\text{adv}}\) and \(\theta_{\text{rec}}\). In particular, \(\theta_{\text{adv}}\) in SAMs of CF\(_3\), and F-substituted biphenylthiols is 85° and 84°, respectively, which is by \(\sim 12°\) higher than the analogous value for SAMs of non-substituted biphenylthiols (73°).\(^{22}\) A more extensive substitution affecting the entire terminal phenyl ring gives values which are close to
those for the FTPn SAMs. In particular, the static water contact angles for SAMs of partly fluorinated alkanethiols, where the typical values of $\theta_{\text{adv}}$ are 114–118°,102-106 The difference is, however, not as large as for non-fluorinated systems: a typical $\theta_{\text{adv}}$ in SAMs of non-substituted alkanethiols is $\sim$110–112°,2,103 whereas that in most densely packed SAMs of non-substituted oligophenylthiols is only 90–93° (for the highly ordered TP$n$ SAMs).35 An interesting aspect is that the contact angle difference between the FTP$n$ and TP$n$ SAMs (16–19°) is larger than that between the SAMs of partly fluorinated and non-substituted alkanethiols (6–8°).

The contact angle hysteresis in the FTP$n$ films is typical for high quality SAMs on evaporated gold, if gold films on silicon with a chromium or titanium adhesion layer are used as substrates. In this case, the value of contact angle hysteresis reflects mostly the quality of the substrate and can be significantly reduced by its annealing or the exchange of silicon for mica.22

### Table 4

<table>
<thead>
<tr>
<th></th>
<th>$\Gamma_{\text{adv}}$</th>
<th>$\theta_{\text{rec}}$</th>
<th>$\theta_{\text{adv}} - \theta_{\text{rec}}$</th>
</tr>
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<tbody>
<tr>
<td>FTP2</td>
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<td>99.8 ± 2.0°</td>
<td>10.2°</td>
</tr>
<tr>
<td>FTP3</td>
<td>109.0 ± 1.4°</td>
<td>98.1 ± 1.8°</td>
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</tr>
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<td></td>
<td>$\Gamma_{\text{adv}}$</td>
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<td>109.0 ± 1.3°</td>
<td>99.4 ± 2.5°</td>
<td>9.6°</td>
</tr>
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</table>

### 4. Discussion

The results of the HRXPS, XPS, ellipsometry, NEXAFS spectroscopy, IRRAS, STM, and contact angle goniometry measurements are quite consistent and suggest high quality of the FTP$n$ SAMs on both Au(111) and Ag(111) in terms of dense molecular packing within the individual domains, chemical, structural and conformational homogeneity, and lack of contamination. The spectroscopic data exhibit characteristic emissions (HRXPS), absorption resonances (NEXAFS), and absorption bands (IRRAS) of the FTP$n$ molecules, implying their adsorption and assembly on the target substrates. According to the HRXPS data, all FTP$n$ molecules in the films are bound to the substrate via the thiolate anchor, with no molecules being oxidized or physisorbed. In accordance with this adsorption mode and as follows from the NEXAFS spectroscopy data, the SAM constituents have an upright orientation, with either slight or moderate molecular inclination as given by the respective tilt angles, which are close to 26–38°. This orientation can be associated with dense molecular packing, which is additionally evidenced by the XPS, ellipsometry, and contact angle goniometry data and directly demonstrated by STM. The packing density of the FTP$n$ SAMs on Au as determined by STM was estimated at $3.5 \times 10^{14}$ cm$^{-2}$ (FTP2) to $3.9 \times 10^{14}$ cm$^{-2}$ (FTP3). These values are somewhat lower than the ones reported for the non-fluorinated TP2 ($3.7 \times 10^{14}$ cm$^{-2}$) and TP3 ($4.6 \times 10^{14}$ cm$^{-2}$), what can be intuitively explained by the larger size of the fluorine atoms compared to hydrogen ones.

The small molecular inclination and high packing density are especially significant in view of the distinct non-planar conformation of the FTP$n$ moieties in the FTP$n$ SAMs (see Section 3.1). As mentioned above, it is usually assumed that the non-planar conformation of non-fluorinated oligophenyl moieties in the molecular state is lifted or at least given up to a significant extent upon packing these moieties into a 2D film such as a SAM. The introduction of sterical constrains for such a conformational change can result in the deterioration of the film quality and a decrease of the orientational order.64 However, according to the NEXAFS data, the orientational order in the FTP$n$ SAMs is comparable to that in the TP$n$ films.35 The high quality of the FTP$n$ SAMs is additionally emphasized by the comparably small values of the C1s FWHM (0.67–0.83 eV) which are similar to those of highly ordered alkanethiolate SAMs (0.73–0.81 eV).74,107

Apart from the high quality of the FTP$n$ SAMs, we observe pronounced and systematic odd–even effects with respect to the number $n$ of the methylene units in the aliphatic linker of the FTP$n$ molecules. As follows from the NEXAFS and IRRAS data, the FTP$n$ molecules on Au have a smaller molecular inclination at $n = 3$ (odd) and a larger molecular inclination at $n = 2$ (even). On Ag, the opposite situation, i.e. a smaller molecular inclination at $n = 2$ (even) and larger at $n = 3$ (odd), takes place. The change of the average molecular tilt angle is similar on Au and Ag and could be estimated at $\sim$12°. Due to the specific and basically invariable conformation of the FTP backbone (see Section 3.1 and Fig. 6), the respective average tilt angles and, following, their difference for the FTP2 and FTP3 films are only weakly affected by the molecular twist, so that the observed odd–even variation of the molecular inclination basically only depends (i) on the parity of the number of methylene groups in the alkyl chain and (ii) on the binding mode of the sulfur atom at the surface (Au vs. Ag, see below). This is in contrast to a recent theoretical model suggesting that the odd–even effects in oligophenyl-based SAMs can be mostly explained by the changes of the torsion and twist angles.108

The odd–even changes in the orientation of the FTP$n$ moieties in the FTP$n$ SAMs are accompanied by the respective changes in the packing density of the SAM constituents: a higher packing density is observed by XPS and ellipsometry on Au at $n = 3$ (odd) and a lower packing density at $n = 2$ (even). Once again, the opposite situation occurs on Ag, with higher packing density at $n = 2$ (even) and lower at $n = 3$ (odd). In the case of Au, the odd–even variation of the packing density could be observed directly by STM. Whereas both FTP2/Au(111) and FTP3/Au(111) are characterized by the centred
rectangular lattice, the size and orientation of the respective unit cells are distinctly different. The unit cell of FTP2/Au(111) can be tentatively described as a commensurate \((2\sqrt{3} \times 2)\) one, with the short basis vector directed along the \((110)\) substrate directions and an area per molecule of 29 Å\(^2\). The unit cell of FTP3/Au(111) can be described as an expanded (along the \((112)\) substrate direction) \((2\sqrt{3} \times \sqrt{3})R30^\circ\) one, with the short basis vector directed along this direction and an area per molecule of 26 Å\(^2\). The latter value agrees precisely with the respective XPS-derived estimation (25.8 Å\(^2\); see Section 3.2), whereas the STM value for FTP2/Au(111) is noticeably less than the XPS value (34.9 Å\(^2\); see Section 3.2). This difference can be tentatively explained by the fact that the STM analysis involves only regions exhibiting ordered lattice, whereas spectroscopic analyses represent an average estimation over a macroscopically large sampling spot. Since the STM data indicate significantly higher portion of poorly ordered regions for FTP2/Au(111), where highly ordered structures are observed only inside little domains of 4–7 nm in diameter (in comparison to the FTP3/Au(111), where such domains are about 20–30 nm in diameter), it is reasonable to expect that the contribution of the poorly ordered regions, which have presumably a lower packing density, influence the spectroscopic data. This hypothesis correlates with the comparably large FWHM of the S 2p\(_{3/2,1/2}\) components of the thiolate-related photoemission doublet for FTP2/Au as compared to FTP3/Au (see Section 3.2), since this relation suggests quite a large heterogeneity of the adsorption sites for FTP2/Au. Note that a small portion of the ordered domains for FTP2/Au manifests presumably a difficulty to form molecular lattices in this particular case. This difficulty can be associated with the competitive balance of the structure-building interactions, in contrast to the cooperative balance in the case of FTP3/Au (see below).

The direction of the odd–even effects in the FTP\(_n\) SAMs on Au and Ag (i.e., the relation between the system behaviour and the parity of \(n\)) correlates precisely with the odd–even behaviour observed previously in the analogous films of non-fluorinated compounds, including biphenyl-, thiophene-, and terphenyl-substituted alkanethiols and biphenyl-substituted alkaneselenolates (selenium has the same valence electron configuration as sulfur and is its neighbour in the 16th column of the periodic table). In all these systems, a higher packing density and a smaller molecular inclination of the substituent moieties is observed for an odd number of methylene units in the aliphatic linker for Au, and an even number of these units for Ag. *Vice versa*, a lower packing density and a larger inclination of the substituent moieties was found for an even number of the methylene units in the aliphatic linker for Au and an odd number of these units for Ag. The occurrence of the odd–even effect in all the above systems, and, presumably, in the FTP\(_n\) SAMs as well, can only be explained assuming that there is a significant bending potential related to the anchoring of the SAM constituents to the substrate. This potential is associated with the additional energy required for the distortion of the optimal geometry of the substrate–S–C bond. This quite “rigid” bending potential, favoring a definite substrate–headgroup–C bonding angle, which is different for Au(111) and Ag(111) substrates, enters into the balance of the structure-building interactions and defines to a high extent the entire structure of the films. Depending on the substrate and the parity of \(n\), the bending potential enters either cooperatively or competitively into the balance of the structure-building interactions, resulting in correspondingly more or less dense molecular packing. The structure of the films in the latter case represents a compromise between the competitive interactions and can be associated with the presence of significant stress, which is released to some extent through a partial deviation from the optimal value of the substrate–headgroup–C angle and partial disordering of the aliphatic part of the FTP\(_n\) moieties. However, in spite of this disordering, the aliphatic linkers are rigid enough to “transfer” the predominant orientation given by the bending potential to the biphenyl moiety.

Apart from the above general issues, the exact molecular arrangement in the FTP\(_n\) films deserves a special attention. The nearest spacing between the FTP2 and FTP3 molecules in the respective lattices (see Fig. 10k and 11g) are 5.3 Å and 5.8 Å, respectively, with the distance between the FTP backbones being even smaller in view of the molecular tilt; these distances can be estimated at 4.75 and 4.60 Å, respectively. Within the accuracy of the experiment, these values correlate well with the FTP–FTP spacing in bulk (perfluoroterphenyl-4-yl)methanol (~4.5 Å; see Section 3.1 and ref. 62). This suggests a similar arrangement of the FTP moieties in the FTP\(_n\) films, i.e. correlated torsion of the analogous (with respect to the substrate) rings in the adjacent molecules. Thus, presumably, there are separate, internally correlated, long-range herring-bone arrangements for the bottom, middle, and topmost rings in the FTP\(_n\) films. An additional avoidance of the sterical constraints within the FTP\(_n\) lattice is achieved by the relative lateral shift (by 0.25–0.4 Å) mediated by the molecular tilt. This shift is smaller than that for bulk (perfluoroterphenyl-4-yl)methanol (~1.4 Å), what probably explains the slightly larger values of the FTP–FTP spacing in the FTP\(_n\) films as compared to the reference bulk system.

5. Conclusions

The integrity, chemical identity, packing density, and molecular structure of SAMs formed by perfluoroterphenyl-substituted alkanethiols with variable length of the aliphatic linker on Au(111) and Ag(111) were studied by a combination of several complementary spectroscopic and microscopic techniques. The FTP\(_n\) molecules were found to form well-defined and highly ordered SAMs on these substrates. A characteristic feature of these SAMs is the helical conformation of the FTP moieties in contrast to the planar and close-to-planar conformations of oligophenyl moieties in the analogous non-fluorinated systems. In spite of the helical conformation and larger atomic volume of fluorine as compared to hydrogen, FTP\(_n\) SAMs exhibit very high packing densities, which are ~3.9 × 10\(^{14}\) cm\(^{-2}\) in FTP3/Au and FTP2/Ag, in particular. Such densities are close to the values for the analogous non-fluorinated systems (~4.6 × 10\(^{14}\) cm\(^{-2}\)) and can only be possible at a correlated twist of the FTP helices of the neighboring molecules.
The FTPn SAMs exhibit pronounced odd–even effects, i.e. dependence of the molecular orientation and packing density on the length of the aliphatic linker in the target molecules, with the parity of n being the decisive parameter. The relation between the properties of the FTPn films and the parity of n is on Au opposite to that on Ag. FTP3 SAMs on Au and FTP2 SAMs on Ag exhibit a smaller molecular inclination and a higher packing density than those in FTP2/Au and FTP3/Ag by ~12% if one compares the ordered domains only and by ~15-30% if one compares overall packing densities. Note that FTP2/Au is characterized by a small portion of the ordered domains, which is associated with competitive balance of structure-building interactions in this particular system.

The odd–even behavior of the FTPn SAMs correlates precisely with the analogous performance of non-fluorinated oligophenylalkanethiolates and -selenolates and, similar to the latter systems, can be explained by the presence of a strong substrate–headgroup–C bending potential, which is different on Au and Ag. This quite “rigid” bending potential favors a certain substrate–headgroup–C bonding angle, which is transferred to the substituent moiety (FTP in the present case) by the sufficiently rigid aliphatic linker. An essential difference of the FTPn system as compared to the non-fluorinated case is the helical conformation of the FTP moiety, characteristic of the molecular state and persistent in the dense phase, what excludes a variation of the intramolecular torsion and molecular twist as the mechanism behind the odd–even effects.

The high quality of the FTPn SAMs makes them promising candidates for use as semiconductor SAMs189 or for controlling energy barriers between organic semiconductors and metal electrodes. As mentioned in Section 1, the Schottky energy barrier for charge injection can be decreased significantly if fluorine-substituted or semifluorinated SAMs are used to modify the metal–organic interface. In addition, aromatic SAMs, such as FTPn films, generally should provide an even more efficient charge transport through the molecular backbone than the aliphatic SAMs, which are frequently used for this purpose.

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