Supporting Information for

Employing X-ray Photoelectron Spectroscopy for Determining Layer Homogeneity in Mixed Polar Self-Assembled Monolayers

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S1. Details on the experimental methods

The gold substrates (Georg Albert PVD-Beschichtungen) were prepared by thermal evaporation of 100-200 nm of gold (99.99% purity) onto polished single-crystal Si(100) wafers (Silicon Sense) primed with a 5 nm adhesion layer of titanium or chromium. These substrates were polycrystalline, with predominant (111) orientation and a grain size of 20-50 nm. The SAMs were formed by immersion for 24 h of freshly prepared substrates into mixed solutions of TP1-up and TP1-down in tetrahydrofuran with a joint concentration of ~0.1 mM at room temperature. The mixing ratio was varied. After immersion, the samples were carefully rinsed with pure solvent and blown dry with a stream of N₂.

Work function measurements were carried out using a UHV Kelvin Probe 2001 system (KP technology Ltd., UK). The pressure in the UHV chamber was ~10⁻¹⁰ mbar. Freshly sputtered gold and SAMs of hexadecanethiol and non-substituted terphenyl-methanethiol (TP1; see Figure 1 in the main paper) on Au were used as references.

XPS measurements were performed at the HE-SGM beamline (bending magnet) of the synchrotron radiation facility BESSY II at Helmholtz-Zentrum Berlin (HZB). The spectra were acquired in normal emission geometry using a Scienta R3000 spectrometer. The photon energy was set to 350 eV. The energy resolution was 0.2-0.3 eV. The BE scale was referenced to the Au 4f7/2 emission of the gold substrate at 84.0 eV.¹ The quality of the films was verified by additional XPS and X-ray absorption spectroscopy measurements.
S2. Details about the quantum-mechanical simulations

The simulations have been performed in the framework of density functional theory (DFT) using the VASP\textsuperscript{2–5} package (version 5.3.2) and employing the repeated slab approach decoupling periodic replicas of the slab by a vacuum gap of ≈20Å in z-direction. The vacuum gap contained a self-consistently determined dipole layer.\textsuperscript{6} For relaxing the geometries, we employed the advanced optimization tool GADGET\textsuperscript{7} which enables performing geometry optimization in internal coordinates instead of Cartesian ones. The initial guess for the Hesse matrix was made according to Fischer’s model.\textsuperscript{8,7} We used the PBE functional\textsuperscript{9} together with PAW\textsuperscript{10,11} potentials (see Table S1) and a cutoff energy of 300 eV for the plane wave basis set. For the geometry optimization we chose a convergence criterion of $10^{-2}$ eV Å\textsuperscript{-1} for the maximum residual force per atom. The total energy in the self-consistency cycle of each DFT step was converged to at least $10^{-6}$eV enforcing at the same time a convergence of the z-component of the dipole moment per unit to $10^{-4}$ eÅ . For the smallest considered surface unit cell (\(\sqrt{3} \times 3\)), a 8x5x1 Monkhorst-Pack\textsuperscript{12} k-point grid was chosen, which was suitably rescaled for larger cells. No explicit van der Waals correction was included, as preliminary tests using the vdW-surf\textsuperscript{13} approach for the pure films resulted in tilt angles clearly higher than the experimental ones. To what extent this is a consequence of an inappropriate description of the screening of the van der Waals interactions between the substrate and the adsorbate by the comparably thick adsorbate layer will require further investigations. The unit cells included five layers of gold substrate with the topmost two layers allowed to relax in the geometry optimizations. The used gold lattice constant was optimized by applying the same methodology to avoid spurious surface relaxations. A value of 4.175 Å was found. As a starting condition for the geometry optimization the molecules were placed on fcc hollow sites of the Au(111) surface; in the course of the geometry optimization, they
moved to an intermediate position between hollow and bridge sites. For all investigated systems, except the striped phase, a geometry optimization was performed. The unit cell of the striped phase was too large for a geometry optimization of the whole system. Instead, this unit cell was created from the individual (geometry optimized) unit cells of the pure TP1-up and TP1-down SAMs. Core-level energies were calculated employing the initial state approach,\(^{14}\) which for systems like the present one is preferable over final state approaches for avoid charge-transfer dipole related artefacts.\(^{15}\) Screening effects were included through an image charge model\(^{16,17}\) in a post-processing step assuming a dielectric constant of the SAM of \(\varepsilon = 3.0\). XP spectra were calculated as described in ref \(^{15}\). In short, they were obtained from the individual core level energies employing a Gaussian broadening (variance = 0.1 eV), setting the incident photon energy to \(h\nu = 350\) eV (in accordance to experiment) and including exponential damping\(^{18}\) using a dimensionless damping coefficient \(\beta = 0.65\),\(^{15}\) adjusted to reproduce the experimental spectra (for details see ref. \(^{18}\)). A variance of 0.1 eV was chosen for the Gaussian broadening, to fit the peak width of the calculated XP spectrum of the pure TP1-up SAM to the experimental spectrum. The same variance was then used to evaluate all other calculated spectra.

**Table S1. Overview of the PAW potentials used for VASP calculations in this work**

|     | PAW_PBE potentials          |
|-----|-----------------------------|
| Au  | PAW_PBE Au 06Sep2000        |
| S   | PAW_PBE S 17Jan2003         |
| C   | PAW_PBE C_s 06Sep2000       |
| H   | PAW_PBE H 15Jun2001         |
| N   | PAW_PBE N_s 07Sep2000       |
Figure S1. SAM-induced work-function change for a mixed TP1-up : TP1-down SAM compared to a TP1 reference SAM as a function of the mixing ratio. Red and blue triangles denote two independent experiments and black circles the simulations. For obtaining the averaged values shown in the main manuscript also at 10:90 and 90:10 mixing ratios, a polynomial interpolation has been applied for the second dataset (red triangles) for which these ratios had not been directly measured.
S4. Carbon 1s energies of the striped (inhomogeneous) and homogeneous 50:50 mixtures

Figure S2. Calculated carbon 1s core level energies of the striped (inhomogeneous) 50:50 mixture of TP1-down and TP1-up. The plot shows the individual 1s core level energies of all carbons of all 12 molecules in the unit cell as a function of atomic z-position relative to the average z-position of the top gold layer (z=0 Å). TP1-down type molecules are depicted by full dots, while TP1-up type molecules are shown as open diamonds. Molecules at the domain border are colored violet, while the central two molecules of each domain are colored orange (cf., Figure 1 in the main manuscript). The red arrow indicates the electrostatic energy shift between TP1-up and TP1-down molecules in the top phenyl ring.

Figure S2 shows, on the one hand, the electrostatically induced shifts originating from ordered assembly of the dipoles and, on the other hand, the influence of local potential variations at the domain boundaries impacting the molecules closest to the edges. These edge effects result in a rather broad distribution of core-level energies. The two molecules in
the center of each domain (depicted by orange symbols; see also Figure 1 of the main manuscript) show the largest electrostatic shift for the vacuum side phenyl ring (0.73 eV with respect to each other). The chemical shift of core level energies in the pyrimidine ring (z between 8 and 12 Å) is largely independent of the molecular position inside the unit cell.

The core level energies of the substrate-side rings ring (in Figure S2) are not exactly the same for molecules of type TP1-up and TP1-down. This at the first glance appears somewhat counterintuitive, as the dipolar pyrimidine unit is located above this first ring and, therefore, should only energetically shift atoms above it. However, one can consider the whole SAM as a combination of two substructures, the TP1-up and TP1-down stripes. Therefore, the TP1-up domains can be thought of as being embedded in the electrostatic potential of the surrounding TP1-down domains and vice versa. This influences the core level energies as described in detail for valence states in ref. 19.

![Figure S3](image.png)

**Figure S3.** Calculated carbon 1s core level energies of the homogeneous 50:50 mixture of TP1-down and TP1-up. The plot shows the individual 1s core level energies of all carbons of all 4 molecules in the unit cell as a function of atomic z-position relative to the average z-
This shift of the substrate side ring is not observed in the homogeneous 50:50 mixture (see Figure S3). In fact, in contrast to the striped SAM, the homogeneous 50:50 mixture (see Figure S3) shows no electrostatic shift of the upper phenylene ring between TP1-up and TP1-down molecules. C1s core level energies in the top ring are the same for both types of molecules.

S5. Details on the spectral shape of pure and mixed SAMs

As was already discussed briefly in ref. 20, the XP spectra of pure TP1-up and TP1-down SAMs contain several contributions. The main feature stems from the vacuum side phenyl ring due to the weakest associated attenuation of the photoemission signal. The deeper lying pyrimidine unit and the substrate side phenyl ring, which have different binding energies, give rise to the additional weak features in the vicinity of the main peak (also in part overlapping with the main peak). As the electrostatic shift of the top phenyl ring is of opposite sign for the TP1-down and TP1-up films, the additional features are situated at higher binding energies (more negative core level energies) than the main peak for TP1-down and at lower binding energies (less negative core level energies) for TP1-up. This can also be clearly discerned in the calculated spectra for the pure films shown in Figure 3a of the main paper. The effect is still present for the mixed SAMs shown in Figure 3a, although less pronounced.

Upon closer inspection it is noticeable that the “shoulder” extends over a somewhat larger energy range for TP1-down than for TP1-up. This is caused by the orientation of the
pyrimidine dipole. In TP1-down the vacuum side phenyl ring is shifted to less negative C1s energies than the substrate side ring. The carbons in the pyrimidine unit however are chemically shifted to more negative core level energies compared to the substrate side ring (see previous chapter). In the case of TP1-up the chemical shift in the pyrimidine ring as well as the electrostatic shift of the top phenyl ring move the C1s energies to more negative values compared to the substrate side ring. As a consequence, in the TP1-up case the signals of the pyrimidine unit and the vacuum side phenyl ring partially overlap as they are closer in energy.

This observation also explains the slightly different peak heights found in the simulated spectrum of large domains (gray curve in Figure 3b of the main paper) produced as weighted superpositions of the pure TP1-up and TP1-down spectra.

**S6. FWHM of the XP spectra of all investigated systems**

The FWHM of the main peak of the XP spectra has be obtained in two ways: First by directly measuring the full width at half maximum of the highest peak in the spectrum; secondly, by fitting the original spectrum using 3 separate Gaussian peaks and then determining the FWHM of the dominant feature representing core-level excitations from the topmost ring. Table S2 lists the FWHM values obtained with both methods for the calculated and measured XP spectra of all investigated systems (the striped (inhomogeneous) mixture was investigated only in simulations).
Table S2. Overview of the full width at half maximum values (FWHM) of the calculated and measured XP spectra of all investigated systems. Values measured directly in the original spectrum and results obtained by fitting the spectra by Gaussian peaks are given. All FWHM values are given in units of eV. A possible explanation for the slightly smaller FWHM of the peaks of mixed compared to pure SAMs observed in the experiments can be a better structural homogeneity of the mixed films due to the favorable interaction between the oppositely oriented molecular dipoles.

| system | FWHM\text{direct}^\text{calculation} | FWHM\text{direct}^\text{experiment} | FWHM\text{fit}^\text{calculation} | FWHM\text{fit}^\text{experiment} |
|--------|--------------------------------------|--------------------------------------|-----------------------------------|-----------------------------------|
| (up : down ratio) | | | | |
| TP1 | 0.83 | 0.75 | 0.83 | 0.75 |
| 100:0 | 0.91 | 0.93 | 0.85 | 0.83 |
| 75:25 | 0.89 | 0.84 | 0.86 | 0.82 |
| 50:50 | 0.83 | 0.81 | 0.81 | 0.79 |
| 25:75 | 0.87 | 0.82 | 0.82 | 0.77 |
| 0:100 | 0.86 | 0.98 | 0.83 | 0.91 |
| 50:50 inhom | 1.17 | - | - | - |
| 50:50 inhom, central | 1.46 | - | - | - |

S7. Electrostatic point dipole model for dipolar domains

To investigate whether infinitely extended stripes (as used in the DFT calculations in the main paper) are a good approximation of domains we performed test calculations based on a point dipole model. The classical electrostatic potential of a finite size 2D array of point dipoles was compared for configurations with square domains (creating a checkerboard structure) and striped domains of upward and downward pointing dipoles for various
domain sizes. To that aim, the electrostatic potential 4Å above the central dipole of the cluster was calculated. Dipoles were arranged in a square lattice with a nearest neighbor distance of 5 Å. All dipoles had an absolute value of 2.3 Debye\textsuperscript{20} (which is the dipole moment of the pyrimidine ring in TP1-up and TP1-down) and were oriented perpendicular to the plane of dipoles pointing either in +z or –z direction depending on the domain. Square domains of N\times N dipoles were considered and compared to striped domains with a stripe-width of N dipoles. These domain structures were compared to a homogeneous mixture of upward and downward pointing dipoles (square domains with a domain size of 1 dipole) and to a situation with all dipoles oriented parallel. The total cluster size in each case was chosen so that the electrostatic potential was converged to 0.0001 V. Figure S3 shows the calculated electrostatic potential for the various tested configurations relative to the situation with all dipoles aligned in the same direction.

![Graph](image)

**Figure S4.** Calculated classical electrostatic potential of a finite 2D array of point dipoles with a domains structure consisting either of square or striped domains of upward and downward pointing dipoles. The electrostatic potential is given relative to the potential obtained when
considering only parallel dipoles. Square shaped domains (red diamonds) of \( N \times N \) dipoles are compared to striped domains (black circles) with a stripewidth of \( N \) molecules. The potential of a “pure” SAM with all dipoles pointing in the same direction (solid blue line) and a homogeneous mixture of upwards and downwards pointing dipoles (dashed green line) are given for comparison.

Figure S4 shows that square and striped domain structures create similar electrostatic potentials above the 2D array. The difference in potential between the two configurations decreases with increasing domain size. These results show that using infinite stripes as domains is a reasonable approximation for what one can expect to encounter also for other domain shapes; i.e. striped domains do not give rise to any artifacts that qualitatively change the behavior of the monolayer.

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