Electronic Supporting Information

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

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1. Experimental Setup and Conditions

The synthesis of the FTPn compounds is described elsewhere.¹ The gold and silver substrates were prepared by thermal evaporation of 100 nm of gold or 100 nm of silver (99.99% purity) onto polished single-crystal silicon (100) wafers (Silicon Sense) primed with a 5 nm titanium adhesion layer. The resulting metal films were polycrystalline, with a grain size of 20-50 nm. In addition, for the scanning tunneling microscopy (STM) experiments (see below), Au substrates with a large terrace size (100-200 nm) were prepared by thermal evaporation of 150 nm of Au on freshly cleaved mica (rate 2 nm/s, temp. 340 °C).² The grains and terraces of the gold substrates on both silicon and mica exhibited predominantly the (111) orientation, which was corroborated by the spectroscopic^{3,4} and STM⁵ measurements, respectively. The SAMs were prepared by immersion of the freshly prepared substrates into a 1 mM solution of either FTP2 or FTP3 in THF or ethanol at room temperature for 24 h. The films prepared from both solvents were quite similar, as checked by several spectroscopic techniques. After immersion, the samples were carefully rinsed with pure solvent and blown dry with argon. They were either characterized immediately or stored under inert gas atmosphere in glass containers until the experiments at the synchrotron (see below).

The FTPn SAMs were characterized by high-resolution X-ray photoelectron spectroscopy (HRXPS), X-ray photoelectron spectroscopy (XPS), 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. The HRXPS and NEXAFS spectroscopy measurements were carried out under UHV conditions at a base pressure <1.5 x 10⁻⁹ mbar. The time for these measurements was selected as a compromise between spectra quality and damage induced by X-rays.⁶⁻⁹

The HRXPS experiments were performed at the D1011 beamline (bending magnet) at the MAX II storage ring of the MAX-lab synchrotron radiation facility in Lund, Sweden. The spectra were acquired in normal emission geometry at photon energies of 350 and 580 eV for the C 1s range, 350 eV for the S 2p region and 750 eV for the F 1s region, respectively. The energy resolution was better than 100 meV allowing a clear separation of individual spectral components. The energy width of the individual emissions was close to the intrinsic energy spread of the respective core-level photoemission process. The binding energy (BE) scale of every spectrum was individually calibrated using the Au $4f_{7/2}$ emission line of either the underlying Au substrate (the samples on Au) or n-alkanethiolate covered Au substrate (the samples on Ag) at 83.95 eV.⁴ The latter value is given by the latest ISO standard.¹⁰ It is very close to a value of 83.93 eV, which has been obtained by us for Au $4f_{7/2}$ using a separate calibration to the Fermi edge of a clean Pt-foil.^{4,8}

HRXPS spectra were fitted by symmetric Voigt functions and a Shirley-type background. To fit the S $2p_{3/2,1/2}$ doublet we used two peaks with the same full width at half-maximum (fwhm), the standard¹¹ spin-orbit splitting of ≈ 1.18 eV (verified by fit), and a branching ratio of 2 (S2p_{3/2}/S2p_{1/2}). The fits were performed self-consistently: the same fit parameters were used for identical spectral regions.

XPS measurements were performed using a Mg K α X-ray source and a LHS 11 analyzer. The spectra acquisition was carried out in normal emission geometry with an energy resolution of ≈ 0.9 eV. The X-ray source was operated at a power of 260 W and positioned ~ 1.5 cm away from the samples. The fitting of the XPS spectra was performed in a similar way as for the HRXPS ones. Since the spectra quality of the latter technique was superior, XPS data were only used to determine the effective thickness of the FTPn SAMs. The thickness was determined on the basis of either I_{Au4f} or I_{Ag3d} intensity, assuming a standard exponential

attenuation of the photoelectron signal and using the attenuation lengths reported in ref 72 (the procedure has been verified for several reference samples).

The ellipsometry measurements were carried out using the M-44 ellipsometer of J.A. Woollam Co. Inc. The data were analyzed with the respective software. The incident angle was set to 75° and calibrated with a silicon wafer as a reference. As reported earlier, the bulk refractive index of these materials is about 1.475, which also was assumed for all films in the calculation of their thickness.¹

The NEXAFS measurements were performed at the HE-SGM beamline (bending magnet) of the synchrotron storage ring BESSY II in Berlin, Germany and at the beamline D1011 at the MAX II storage ring of the MAX-lab synchrotron radiation facility in Lund, Sweden. The results obtained on both facilities are consistent even though the shape of the spectra is somewhat different, which is related to the individual parameters of the respective experimental setups. The spectral acquisition was carried out both at the carbon and fluorine K-edge in the partial electron yield mode with retarding voltages of -150 and -450 V, respectively. Linear polarized synchrotron light with polarization factors of \approx 82% (BESSY II) or \approx 95% (MAX-lab) was used. The energy resolution was either \approx 0.40 eV (BESSY II) or better than 100 meV (MAX-lab). The incidence angle of the light was varied from 90° (**E**vector in the surface plane) to 20° (**E**-vector nearly normal to the surface) in steps of 10°-20° to monitor the orientational order of the FTPn molecules within the films. This approach is based on the linear dichroism in X-ray absorption, i.e., the strong dependence of the crosssection of the resonant photoexcitation process on the orientation of the electric field vector of the linearly polarized light with respect to the molecular orbital of interest.¹²

The raw NEXAFS spectra were normalized to the incident photon flux by division through a spectrum of a clean, freshly sputtered gold sample. In the case of the Ag substrate, a spectrum of clean silver was subtracted from the raw spectrum of a SAM sample before normalization.^{13,14} Further, the spectra were reduced to the standard form by subtracting linear pre-edge background and normalizing to the unity edge jump (determined by a nearly horizontal plateau 40-50 eV above the respective absorption edges). The energy scale was referenced to the most intense π^* resonance of highly oriented pyrolytic graphite (HOPG) at 285.38 eV.¹⁵ For the absolute energy calibration of the F K-edge NEXAFS spectra, we utilized the apparent shift in the position of the Au 4f_{7/2} core level of a clean Au wafer on going from the beamline settings used for the C K-edge NEXAFS data collection to those for the F K-edges; a similar approach was used at the measurement of NEXAFS spectra of

proteinogenic α -amino acids and nucleobases.^{16,17} The resultant energy positions are expected to be accurate and reproducible to within ±0.05 eV.

Infrared absorption spectra of the target SAMs were measured in reflection mode using Vertex 70 Fourier transform spectrometer (Bruker) equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride detector. The spectra were taken using *p*-polarized light incident at a fixed angle of 80° with respect to the surface normal. The spectra were acquired at 2 cm⁻¹ resolution with the accumulation of 1024 scans over 4000-660 cm⁻¹ spectral range. The spectra are reported in absorbance units $A = -\log R/R_0$, where R is the reflectivity of the substrate with the monolayer and R_0 is the reflectivity of the reference. Substrates covered with a perdeuterated hexadecanethiolate SAM were used as a reference. The reference spectra of the bulk compounds were measured in ATR mode using a diamond cell on a Nicolet 6700 spectrometer.

The STM measurements were performed only in the gold case. In our experience, the quality of the STM images for SAMs on silver substrate is inferior to those for gold,^{18,19} so that we refrained from any STM experiments in the latter case. For the STM experiments, only the films on mica were used. The Au substrates were flame-annealed in a butane-oxygen flame prior to SAM preparation. The experiments were carried out in air at room temperature using a DI Nanoscope IIIa microscope. In all cases tips were prepared mechanically by cutting a 0.25 mm Pt/Ir alloy (8:2, Goodfellow) wire. The data were collected in constant current mode using a tunnelling current of 20-40 pA and a sample bias between 500 mV and 1.6 V (sample positive).

Advancing contact angles of millipore water were measured on freshly prepared samples with a Krüss goniometer Model G1. The measurements were performed under ambient conditions with the needle tip in contact with the drop. At least three measurements at different locations on each sample were made. The averaged values are reported. Deviations from the average were less than $\pm 1^{\circ}$.

2. Additional spectroscopic data



Figure S1. Normalized C 1s HRXPS spectra of FTPn/Au and FTPn/Ag (hollow circles) acquired at photon energies of 350 eV (a) and 580 eV, along with the corresponding fits by several individual peaks (solid lines) and a background (dashed line).

The spectra show, apart from a lower energy resolution at 580 eV, comparable intensities of the \approx 285.8 and \approx 287.5 eV peaks and considerably lower intensity of the 284.4 eV emission at a PE of 350 eV. Indeed, the relative intensities of the two former peaks are expected to be almost independent on the photon energy since the respective carbon atoms are located in a similar manner along the FTP backbone. In contrast, 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 overlayer, 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.²⁰



Figure S2. Normalized F 1s HRXPS spectra of FTPn/Au and FTPn/Ag (hollow circles) acquired at a photon energy of 750 eV, along with the corresponding fits by either a single peak or two peaks (solid lines) and a background (dashed line).



Figure S3. High-resolution (\approx 50 meV) carbon K-edge NEXAFS spectrum of FTP3/Au acquired at an X-ray incident angle of 55°; the spectrum was acquired at Max-lab and is characteristic of the entire FTPn series. The most prominent absorption resonances are marked by numbers. The absorption structure observed in the lower resolution spectra (BESSY) was fully reproduced. At the same time, some of the low intensity resonances (e.g. 2′, 3′, and 3′′) are better visible. See Table 1 in the manuscript for the assignments and manuscript text for details.



Figure S4. Fluorine K-edge NEXAFS spectra of FTPn/Au and FTPn/Ag acquired at an X-ray incident angle of 55°. The most prominent absorption resonances are marked by numbers. See text for details.

The spectra of all four films are very similar; they exhibit several characteristic resonances at 689.0-689.1 (1), \approx 693.1 (2), 697.2-697.3 (3), and 699.8 eV (4) and the absorption edge corresponding to the F1s→continuum transitions. Similar to the C K-edge case, the assignment of the absorption resonances at the F K-edge was performed using available theoretical and experimental data for 1,2,4,5-tetrafluorobenzene and pentafluorobenzene.²¹ According to these data and the observed angular dependence of the resonance intensity (see below), the resonances 1, 2, and 3 can be assigned to the F_{1s} \rightarrow 1 π *, F_{1s} \rightarrow 2 π *, and F_{1s} \rightarrow σ *(C–C) transitions, respectively. An alternative assignment of the \approx 693.1 eV resonance (2) to the F_{1s} \rightarrow σ *(C–F) transition²¹ seems to be wrong since this resonance exhibits the characteristic π * behaviour, similar to the 1 π * case (see below). An assignment of the weak resonance 4 is elusive, but it obviously has σ * character.



Figure S5. Difference between the fluorine K-edge NEXAFS spectra of FTPn/Au and FTPn/Ag acquired at X-ray incident angles of 90° and 20°. The most prominent difference peaks are marked by numbers; see text for details. Dashed lines correspond to zero. Significantly, the difference peak 2 has the same positive sign as the peak 1, which clearly implies π^* -like character for the resonance 2 at the F K-edge as mentioned above (see Figure S4).

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