Thiolate-Bonded Self-Assembled Monolayers on Ni(111): Bonding Strength, Structure and Stability

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ADDITIONAL EXPERIMENTAL SPECTRA

- Thermal Programmed Desorption (TPD) on 4-FTP and 4-CTP

![Multilayer desorption graph](image1)

**Figure S1:** Desorption spectra of 4-FTP and 4-CTP multilayers measured with a quadrupole mass spectrometer (QMS) for TPD, while ramping the temperature with a constant heating rate of 2K/s. In both cases the condensed multilayers were deposited at 80 K. Peak values for multilayer desorption are indicated. The measured QMS signals correspond to the mass/charge ratio of the intact molecules upon double ionization.

- X-ray Photoelectron Spectroscopy (XPS) on 4-FTP

![XPS spectra](image2)

**Figure S2:** Comparison of core-level spectra for the 4-FTP multilayer prepared at 80 K (top) and the respective monolayer obtained after brief annealing of the Ni(111) substrate to 200 K (bottom). Left panel: S 2p core level (photon energy: 260 eV); right panel: F 1s core level (photon energy: 800 eV). The clear shift to lower binding energy in the S 2p spectrum of the monolayer signals the formation of a thiolate bonding.
to the Ni substrate. Conversely, the absence of any appreciable shift in the F 1s spectrum indicates that the F endgroup is directed away from the surface in the saturated monolayer and not involved in chemical bonding.

- **Near-Edge X-ray Absorption Fine Structure (NEXAFS) on 4-FTP multilayers**

![Figure S3](image)

**Figure S3:**
Polarization-dependent NEXAFS spectra of a condensed multilayer of 4-FTP taken at the carbon K-edge. The angle $\theta$ of the polarization (electric field vector) is measured relative to the surface normal and is varied between 90° and 7°. The absence of polarization dependence (zero dichroism) most likely indicates that in the multilayer a strong preferential orientation of the molecules is missing; namely, the condensed (physisorbed) 4-FTP film is orientationally disordered. The estimated thickness of the multilayer is in excess to 5-6 ML, as judged by XPS where no substrate signal was detected. Due to the different probing depth of the PEY detection, a contribution of the molecular layer at the organic/metal interface to the spectra cannot be entirely ruled out but is expected to be minor.

The inset in the carbon spectrum shows a zoom-in in the region of the resonances relevant for quantitative NEXAFS analysis in the case of the 90° spectrum, together with the corresponding peak labeling. According to the literature [1-2], all three spectral features highlighted are attributed to transitions from the C 1s core level to the lowest unoccupied molecular orbital (LUMO). The feature labeled '1' has $\pi^*$ C-C(H) character and is therefore associated to transition to the LUMO from the C 1s level of the four C atoms of the phenyl ring that are bonded to hydrogen; the distinct peak labeled '3' has $\pi^*$ C-C(F) character, and the S-bonded carbon atom of the phenyl ring contributes to the shoulder labeled '2', which has $\pi^*$ C-C(S) character [1]. The photon energies of the three resonance features are listed in Table S1.

**Table S1:**
Photon energies and the associated final state – initial state character of the three sharp resonances observed in the 4-FTP C K-edge NEXAFS, as shown in Figure S3.

<table>
<thead>
<tr>
<th>Pre-edge resonance</th>
<th>Photon energy position</th>
<th>Character [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>'1'</td>
<td>285.0 eV</td>
<td>$\pi^*$ C-C(H)</td>
</tr>
<tr>
<td>'2'</td>
<td>285.6 eV</td>
<td>$\pi^*$ C-C(S)</td>
</tr>
<tr>
<td>'3'</td>
<td>287.2 eV</td>
<td>$\pi^*$ C-C(F)</td>
</tr>
</tbody>
</table>
• **X-ray Photoelectron Spectroscopy (XPS) on 4-CTP**

**Figure S4:**
Comparison of XP core-level spectra for a 4-CTP multilayer prepared at 80 K (top, black), and the respective monolayer prepared by sequential deposition of 4-CTP molecules up to monolayer completion, followed by brief annealing of the Ni(111) substrate to 200 K (bottom, green). Left: S 2p core level (photon energy: 260 eV); middle: C 1s core level (photon energy: 380 eV); right: N 1s core level (photon energy: 500 eV). The pronounced shift to lower binding energy of all three core levels of the monolayer phase points towards a considerable interaction with the Ni surface not only for the headgroup but also for the phenyl ring (backbone) and the endgroup (nitrile) of the molecule.

**Figure S5:**
Comparison of XP core-level spectra for the saturated monolayers of 4-CTP (red) and 4-FTP (blue). Spectra for the two molecules have been acquired under the same conditions (photon energy and photon incidence angle, analyzer pass energy, detection geometry at normal emission) and during the same beamtime (beamline UE49/2 at Bessy II). The different photoemitted intensity is indicative of the lower molecular coverage of the 4-CTP SAM, which is consistent with the larger fingerprint obtained by projecting the adsorbed molecules onto the surface (4-CTP being more tilted relative to the surface normal, see main manuscript). Note that the intensity difference is larger for the C 1s core level (right).
compared to the S 2p core level (left), presumably due to the different degree of attenuation in the material of the photoelectron signal coming from the organic-vacuum interface (C 1s) or from the organic-metal interface (S 2p). This is especially true for the 4-FTP monolayer, where the molecular plane orientates almost perpendicular to the surface and the S 2p signal is more attenuated. The S 2p and C 1s spectra were acquired at photon energy of 260 eV and 380 eV, respectively.

• Near-Edge X-ray Absorption Fine Structure (NEXAFS) on 4-CTP multilayers

Figure S6:
Nitrogen K-edge NEXAFS spectrum of a 4-CTP multilayer recorded at 7° grazing incidence with the electric field of the radiation lying in the surface plane. The spectrum exhibits three characteristic π* resonances and agrees very well with previous spectra of 4-CTP SAMs reported in Ref. [3] (see also Table S2 below), where the splitting between the π1* and π3* resonance is attributed to the effect of the conjugation between the π* orbital of the nitrile group and the adjacent phenyl ring. This leads to two states with different energy, polarized either perpendicular (π1*) or parallel (π3*) to the ring plane. The measured spectrum is therefore a characteristic fingerprint of the intact molecule and confirms that the integrity of the molecules employed in this work is preserved upon sublimation in UHV. It thus follows that the molecular decomposition observed in the monolayer has to stem from the interaction with the nickel surface and not, for example, from deterioration of the 4-CTP powders.

Table S2:
Photon energies of the three sharp resonances highlighted in Figure S6 compared with literature values.

<table>
<thead>
<tr>
<th>Resonance</th>
<th>Photon energy position§</th>
<th>Literature values [3]</th>
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<tbody>
<tr>
<td>π1*</td>
<td>398.8 eV</td>
<td>~398.8 eV</td>
</tr>
<tr>
<td>π3*</td>
<td>399.65 eV</td>
<td>~399.75 eV</td>
</tr>
<tr>
<td>π4*</td>
<td>401.5 eV</td>
<td>~401.5 eV</td>
</tr>
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</table>

§ Since calibration of the photon energy scale at the N K-edge was not possible in the experiments, to enable direct comparison with reference data the spectrum of Figure S6 was rigidly shifted to center the first resonance (π1*) at the energy of Ref. [3].
Effect of the preparation procedure on the SAMs' growth

The 4-FTP SAM was prepared under conditions similar to those used for the 4-CTP SAM. Specifically, 4-FTP was deposited by incremental exposures up to completion of the first layer only. These individual exposures, with the substrate held at 80 K, were separated by 1 minute intervals, and the total exposure time was kept in the range of that used for the 4-CTP counterpart, so as to reproduce the low-rate deposition conditions for UHV-sublimated 4-CTP. A final annealing step (200 K) was performed to ensure comparable preparation conditions with the single step deposition described in section 2.1 and section 3.1 of the main article.

XPS excited with Al Kα radiation was used to probe the films' chemical state and did not show any appreciable difference with the 4-FTP SAMs prepared through the standard procedure that involves annealing of the multilayer (see Figure S7, SI). Hence, the occurrence of C-F bond breaking, possibly triggered by flat adsorption at low coverage, can be ruled out. Interestingly, as discussed in the main text, no C-S bond scission is detected in the SAM grown stepwise, in contrast to the DFT predictions at low coverage. This might suggest that the SAM's growth proceeds via formation of densely packed islands or that there is an activation barrier for S-C bond scission that cannot be overcome at 80 K.

Polarization-dependent UPS measurements were performed to assess the similar molecular orientation in the two saturated monolayers. In Figure S8 valence spectra representative of 4-FTP SAMs prepared with the standard procedure are presented, acquired with the photon polarization either parallel (s-polarized radiation) or perpendicular (p-polarized radiation) to the surface plane, while keeping fixed the incidence angle of the photons (7° grazing
incidence) and the detection geometry (normal emission of photoelectrons). The resulting dichroism (i.e., the difference spectrum between s- and p-polarized radiation), shown in the inset of Figure S8 for the saturated monolayers prepared by both the single and incremental exposures, is a fingerprint of the molecular orientation, in much the same way as provided by NEXAFS. Therefore, the absence of substantial differences in the dichroism for either preparation excludes that the more lying-down configuration, characteristic of the 4-CTP SAM, is caused by the different deposition procedure. It follows that the difference between 4-CTP and 4-FTP SAMs (section 3.4, main manuscript) is intrinsically related to the pronounced interaction of the CN endgroup with the Ni substrate.

Figure S8:
Valence spectra (UPS) representative of the 4-FTP SAM prepared with the standard procedure, i.e. by brief annealing to 200 K of a condensed multilayer. He I radiation (photon energy: 21.2 eV) was used, and the spectra were taken in normal emission at different polarization of the UV light, specifically with the electric field oriented in-plane (black line) or out-of-plane (red dashed line, 7° off-normal) relative to the substrate surface. The spectra have been normalized to the step at the Fermi edge for comparison. The inset shows the difference signal (dichroism, violet line), averaged over three similarly prepared samples, compared to the analogous signal (blue dotted line) from a 4-FTP monolayer prepared by stepwise deposition. The absence of major differences in the dichroic signal confirms the very similar orientation of the molecules in both SAMs.

References