Para-halosubstituted thiophenols (X-TPs, where X is Br, Cl, or F) form ordered islands and monolayers on Cu(111) at temperatures as low as 81 K. At incomplete coverages, all X-TPs adsorb with the dehydrogenated thiol group attached to the substrate and the substituted ring inclined toward the surface, as verified experimentally and theoretically. The structure of ordered islands has a pronounced dependence on the nature of the halogen substituent: while unsubstituted TP and pentafluoro-TP molecules do not self-assemble into extended ordered patterns at 81 K, X-TP molecules form a range of different structures which depend both on the size and electronegativity of the substituent, as well as on the coverage.

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in its own UHV chambers. All measurements described here proceeded at 80–85 K, as measured by silicon diodes attached to the STMs (with exception of the data of Figure 4, which was obtained at 15 K). The base pressure of the STM chambers is consistently below 6 × 10⁻¹¹ Torr (measured with a nitrogen-calibrated hot-cathode ion gauge). The STM tips were made by electrochemical etching of a tungsten wire followed by hot (white) glue annealing in vacuum.

The Cu(111) samples (Monocrystals and MaTecK GmbH) are prepared using cycles of standard argon ion sputtering (up to 3 kV) and annealing (600 K). Sample cleanliness is ascertained by STM both at room temperature and after cooling to cryogenic temperatures. The samples were considered clean if no more than 1/10 000 of a monolayer of contamination was found on the surface (corresponding to one or two contaminants per image frame).

Deposition of the thiophenols onto the sample for STM purpose proceeded by backfilling of the turbo-pumped chamber to 1 × 10⁻⁹ Torr using a leak valve while the sample was protected behind the cryostat thermal shields. A mass spectrum was taken to confirm the purity of the reactant. Subsequently, all filaments of the chamber were turned off, the sample was extracted from the cryostat, and it was exposed to the backfilled chamber for up to 30 s at a time. The short exposure time ensures constant cryogenic temperature of the sample, as ascertained by virtually drift-free imaging immediately after sample exposure. Repeated exposure cycles were used to reach the coverages indicated here, as necessary.

Where mentioned, annealing of the adsorbate layer involved removal of the sample from the cryostat for a prolonged period (>1 h), which allows it to warm gradually to room temperature. During this period, all filaments in the chamber were switched off to avoid sample contamination.

**TPD Measurements.** Sample preparation for TPD experiments proceeded similarly except that the sample was held continuously on a temperature-controlled manipulator. The sample was prepared by several sputtering and annealing cycles between successive TPD experiments. The impact of various exposures to successive TPD runs will be described elsewhere.

Exposure of the sample used a line-of-sight dosing setup for enhanced purity of the adsorbates. The TPD experiments utilize a Stanford Research Systems mass spectrometer operated at a multiplier voltage of 1700 V. Mass scans ranging from 10 amu to slightly above the respective molecular mass were acquired at a ca. 10 s interval, while ramping the sample temperature at a constant 10 K/min.

**Computational Procedure.** Density functional theory calculations of the electronic and geometric structure and adsorption energy of TP on Cu(111) surface were carried out using the generalized gradient approximation for the exchange-correlation functional and the plane-wave pseudopotential method. Ultrafast pseudopotentials were used for all atoms in the system. The Cu(111) surface was modeled by a supercell consisting of a four-layer slab and 11 Å of vacuum. We used a 3 × 3 unit cell, which included nine Cu atoms per layer and one TP molecule. The entire supercell thus contains 49 atoms. To ensure independence of the result on the number of layers used, we also performed calculations with two and three layers, which lead to bond angles and lengths around the sulfur atom that vary by less than 2° and 0.05 Å from our four-layer result, respectively. The cutoff energy for the plane-wave expansion is taken to be 300 eV, and a 3 × 3 × 1 Monkhorst-Pack k-point mesh in the Brillouin zone sampling is used to obtain converged results for the total energy of the system. During lattice relaxation, atoms were allowed to move along all directions. The structure obtained was relaxed until the forces acting on each atom converged to better than 0.02 eV/Å.

**Results**

Figure 2a shows TPD traces acquired after exposure of a Cu(111) sample at 110 K to low (grey) and high (black)

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**Figure 1.** 1. Ball and stick models of the molecules of this study (clockwise from the top left corner): Thiophenol (C₆H₅SH), p-fluorothiophenol (C₆F₅SH₅), p-chlorothiophenol (C₆ClSH₅), and p-bromothiophenol (C₆BrSH₅), and pentafluorothiophenol (C₆F₅SH). All STM images represent molecules, whose thiol (—SH) group is dehydrogenated, so that the S atom is not bound to a hydrogen atom but rather to the substrate.
characteristic patterns that are identical to known Cu(111) surface taken after desorption of thiophenol reveal 1013 Hz, the multilayer desorption temperatures of 180 K, 190 K, 220 K, and 240 K correspond to binding energies to the formula of Redhead and assuming a prefactor of 360 K; FTP, 370 K; CTP, 380 K; BTP, 440 K. According toward higher temperatures (for the monolayer peaks: F-TP, Cl-TP, and Br-TP, we find halogen abstraction and formation of biphenyl.

dosages of F-TP. The desulfurized species (bottom) desorbs from the surface at 370 K, and the peak size is independent of the initial coverage. Consequently, we regard this species as the monolayer, which desorbs by scission of the C=S bond similar to ethanethiol and other alkanethiols. The top curves show desorption of the intact molecule; their high-coverage peak at 190 K represents desorption from the multilayer. This peak varies strongly with initial exposure. We obtained a series of various initial exposures both in the monolayer and the multilayer regime for TP, F-TP, Cl-TP, and Br-TP, all of which follow a similar pattern of multilayer desorption at ca. 200 K and dissociative desorption of the monolayer at ca. 400 K. Figure 2b shows for each molecule two traces obtained simultaneously: the black trace indicates molecular desorption from the multilayer and the gray one indicates dissociative desorption of the main product of the monolayer (for TP, F-TP, and Cl-TP, the desulfurized species, for Br-TP, we find abstraction of the Br resulting in biphienyl formation along the Ullmann reaction scheme). STM images of the Cu(111) surface taken after desorption of thiophenol reveal characteristic patterns that are identical to known structures of S/Cu(111).

With increasing size of the halogen, the desorption shifts toward higher temperatures (for the monolayer peaks: TP, 360 K; FTP, 370 K; CTP, 380 K; BTP, 440 K). According to the formula of Redhead and assuming a prefactor of 10^{13} Hz, the multilayer desorption temperatures of 180 K, 190 K, 220 K, and 240 K correspond to binding energies of ~0.52, 0.55, 0.63, and 0.69 eV for TP, FTP, CTP, and BrTP, respectively.

...
of the STM image but no change of the shape of the adsorbate. Correspondingly, we assume that X-TP molecules attain the same surface orientation at LN2 temperatures as at 15 K. For the remainder of this manuscript, we will assume that each of the protrusions in the STM images will represent one X-TP molecule.

Figure 5a shows several isolated islands formed after exposure of the sample to 0.008 L of Br-TP. The islands cover only a small fraction of the otherwise clean Cu(111) terraces, and they nucleate both adjacent to step edges (inset) and on the terraces. The islands exhibit a variety of simple lattice structures, which we analyze by Fourier Transformation (FT) of the corresponding portion of the STM images (Table 1). This results in a pattern in that can be interpreted similarly to low-energy electron diffraction (LEED). The advantage of this approach over measurements in real space lies in the precise measurement of the lattice vectors. In contrast to LEED, the FT of STM images can be chosen to originate exclusively from one island of a specific orientation and symmetry, so that rotational domains, etc. do not affect the pattern. Further, the availability of a real space image in STM offers direct information about the number of molecules in each unit cell. Also, electron damage, as common with conventional (non channel-plate) LEED systems, is avoided. The most-common pattern of Br-TP islands are (3 x 4) and [3^-2] (Table 1), both of which correspond to a coverage of 0.083 monolayers (ML). On the basis of the determination of the molecular adpositions at low temperatures, these lattice vectors correspond to a film geometry as that shown in Table 1. The primitive vectors of the mesh are also indicated in the FT patterns in Table 1.

Figure 5. 5. (a) STM image of islands on Cu(111) formed after exposure of the surface to 0.008L of Br-TP molecules (image size 134 Å x 112 Å, U = −0.8V, I = 26 pA). The insert shows a step edge at which Br-TP islands nucleate in an ordered fashion (image size = 34 Å x 30 Å, U = −0.8 V, I = 26 pA). (b) STM image of Cu(111) terraces after exposure to 0.05 L of Br-TP. The terraces are completely covered by a Br-TP film (image size = 93 Å x 90 Å, U = 1.1 V, I = 32 pA). The insert shows a magnification of the film structure (image size = 39 Å x 37 Å, U = −1.1 V, I = 57 pA).

Figure 4. 4. STM images of individual molecules adsorbed on Cu(111) at 15 K. (a) TP, (b) F-TP, (c) Cl-TP, and (d) Br-TP. Image size = 16 Å x 15 Å, U = −0.2 V, I = 32 pA. The black bar indicates the length of the TP footprint of ~8 Å for comparison. With larger size of the substituent, the apparent length of the molecule increases.

Figure 6. 6. (a) STM image of a Cl-TP island on Cu(111) formed after an exposure to 0.015L of Cl-TP (image size = 128 Å x 128 Å, U = −0.6 V, I = 30 pA). (b) Complete film of Cl-TP after 0.15 L of exposure (image size = 64 Å x 64 Å, U = −1.3 V, I = 27 pA).

Figure 7. 7. (a) Isolated islands of a honeycomb structure form after exposure of Cu(111) to 0.01 L of F-TP (image size = 144 Å x 105 Å, U = −1.4 V, I = 27 pA) and coexist on the same terrace with (b) islands of a (3 x 3) structure (image size = 116 Å x 89 Å, U = −1.4 V, I = 29 pA). (c) Magnified view (image size = 94 Å x 94 Å, U = −1.3 V, I = 37 pA) of the honeycomb structure of (d) (image size = 365 Å x 512 Å, U = −1.3 V, I = 37 pA) which was generated by annealing 0.11 ML of F-TP to 125 K. Further increase of the coverage leads to a complete coverage of the substrate (e) (image size = 116 Å x 116 Å, U = −1.3 V, I = 39 pA) Notice the protrusions at the domain boundaries (arrows).

Figure 5b shows Cu(111) terraces after exposures to 0.05 L of Br-TP. The entire surface is covered with adsorbates. For the remainder of the manuscript, we will refer to such coverages as complete, which shall imply that no unoccupied terrace area can be found anymore, while not ruling out that further compression of the film can create more dense structures. By FT of the STM image (Table 1), we identify this structure as [3^-2], which corresponds to an adsorbate density of 0.11 ML. For all film patterns described in this manuscript, we ascertained the assignment of the film structure by determining the surface coverage independently. To this end, we calibrate the piezo response (which depends on the precise piezo temperature) using the well-known Cu(111) step height. By counting several thousand molecules (manually), we then determined the actual coverage at high fidelity. All measured coverages fall well within the statistical (n^1/2) error of the densities associated with the patterns derived by FT; the match between density measurements and the theoretical value associated with the inferred surface pattern is typically better than 1% of the actual coverages or better than 1/1000 of a complete ML.

Figure 6a shows a Cu(111) surface after exposure to 0.015L of Cl-TP at 81 K. Similar to Br-TP, Cl-TP arranges itself in islands of distinctive periodicity. Its island structure is more complicated than that of Br-TP: the dominating motif involves rows of pairs of molecules. We identify it as a [1^-3] pattern, which is composed of two Cl-TP molecules adsorbed in two different (hcp vs fcc)
hollow sites. This arrangement corresponds to an adsorbate density of 0.10 ML.

It requires ~0.15 L exposure to cover the substrate with a complete Cl-TP film. The most-common film motif of this film is shown in Figure 6b. It corresponds to a \( \left[\begin{array}{c}-3 \\ 3 \end{array}\right] \) structure with an adsorbate density of 0.125 ML. Similar to Br-TP, all pattern assignments used FT of corresponding sections of STM images (Table 1).

In contrast to Br-TP and Cl-TP, which form relatively simple structures at both low and high coverage, F-TP can form a low-coverage structure of significant complexity: Figure 7a,b shows two strikingly different types of F-TP islands that form on the same terrace in close vicinity after exposure of a Cu(111) substrate to 0.01 L of F-TP at 81 K. The simple structure of Figure 7b is a \( 3 \times 3 \) pattern (Table 1), which corresponds to an adsorbate surface density of 0.111 ML. Figure 7a shows a honeycomb-like structure involving seven molecules per unit cell, which can be identified as an \( (8 \times 8) \text{R}19^\circ \) (Table 1) pattern with a density of 0.109 ML. Upon gradual increase of the coverage, the islands develop a distinct propensity toward the honeycomb structure. Deposition of ~0.11 ML of F-TP on Cu(111) at 81 K and slight annealing to 120 K results in complete conversion of the \( 3 \times 3 \) structure to the honeycomb pattern (Figure 7d, enlargement in 7c). This suggests that the honeycomb structure is energetically more favorable than the simple \( 3 \times 3 \) pattern.

If the density of F-TP molecules on the surface is increased beyond the coverage associated with the honeycomb pattern (0.109 ML), a denser film structure is observed (Figure 7e). The dominant motif of this film is a \( \left[\begin{array}{c}1 \\ 2 \end{array}\right] \) pattern (Table 1) which corresponds to a coverage of 0.14 ML.

Table 1. Overview of Experimental Results

<table>
<thead>
<tr>
<th>Substance</th>
<th>X-S bond length (Å)</th>
<th>Halogen radius (Å)</th>
<th>Substituent Electron-</th>
<th>Reciprocal Lattice Vec.</th>
<th>Model</th>
<th>Structure</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Bromodiphenol</td>
<td>6.5</td>
<td>114</td>
<td>2.8</td>
<td></td>
<td>0.95Å</td>
<td>( \left[\begin{array}{c}3 \ -2 \ 0 \end{array}\right] )</td>
<td>1/12 = 0.083</td>
</tr>
<tr>
<td>p-Chlorodiphenol</td>
<td>6.4</td>
<td>90</td>
<td>3.0</td>
<td></td>
<td>0.38Å</td>
<td>( \left[\begin{array}{c}7 \ -1 \ -1 \end{array}\right] )</td>
<td>2/20 = 0.100</td>
</tr>
<tr>
<td>p-Fluorodiphenol</td>
<td>6.0</td>
<td>60</td>
<td>4.0</td>
<td></td>
<td>0.36Å</td>
<td>( (8 \times 8) \text{R}19^\circ )</td>
<td>7/64 = 0.109</td>
</tr>
</tbody>
</table>

Figure 8a shows (unsubstituted) TP molecules on Cu-(111) after adsorption at 81 K. The surface is scattered with small clusters of molecules, which coalesce if the coverage is high enough, but do not aggregate to a continuous ordered island. Annealing of the surface to various temperatures up to room temperature does not lead to the formation of an ordered film. This suggests that the lack of order is not due to insufficient mobility of the adsorbates, i.e., kinetically determined, but rather due to the lack of intermolecular interaction that sustains an ordering process. The absence of extended ordered regions persists at increasing coverage up to the point where the film appears as complete. Figure 8b shows an apparently complete layer of TP molecules with a density...
of 0.103 ML. The FT (Figure 8c) confirms the lack of lateral periodicity of the molecular arrangement on the surface. Figure 9 shows different coverages of 5F-TP on Cu(111) after exposure at 81 K. Similar to TP, 5F-TP forms ordered structures neither at incomplete nor at complete coverages. At low coverage, 5F-TP appears more mobile than the previously discussed molecules; diffusing molecules give rise to the streaky noise on the bottom of the STM image of Figure 9a. At high coverage, the molecules form a complete layer with a density of 0.079 ML. The FT (Figure 8c) confirms the lack of lateral periodicity of the molecular arrangement on the surface.

**Discussion**

The ability of self-organization present for para-substituted TP molecules but absent for species that carry identical atoms at all but the thiol site of the ring (TP and 5F-TP) indicates that the identity and the site of substitution have a strong impact on the adsorbate–adsorbate interaction. In the case of Br-, Cl-, and F-TP, the molecules self-organize into distinctively different patterns depending on the nature of the halogen substituent. To be able to understand this difference, it is important to establish what properties of the molecules are changed when different halogens are introduced.

Table 1 indicates the intramolecular sulfur–halogen distance based on textbook bond lengths (which neither reflect intramolecular interactions specific to thiophenols nor any effects of the substrate). Going from F via Cl to Br, the X–S length of the molecule increases by almost 10%. Figure 10 shows the corresponding increase of area occupied by each of the molecules at different coverages. The densities scale with the molecular size at much smaller increments than suggested by the surface lattice constant of Cu(111) of 2.55 Å. This requires surface unit meshes of different symmetry/aspect ratio for different thiophenols. Consequently, the size of the molecule partially determines the film pattern. However, we find that even for closely related values of the coverage, there is more than one surface pattern available (e.g., Br-TP forms two different structures at a density of 1/12 ML).

The molecular densities of the disordered films of TP and 5F-TP also scale with the molecular size, yet the lack of order permits only smaller absolute densities than found for para-substituted molecules. This is consistent with the behavior of hard-sphere packing, where random arrangement in a container will lead to a lower density than ordered hcp or fcc packing. The higher molecular density of the complete films at no significant change to the molecular shape as observed in STM suggests that in order to accommodate a maximum number of molecules on the terrace in an orientation almost parallel to the substrate, the film is exposed to compressive strain. The difference in coverage between the low- and the high-coverage patterns for each of the substituted molecules directly indicates a compression by ~25% for all films investigated.

At domain boundaries of complete coverages, we find individual protrusions embedded in the film (see Figure 7e). We regard these protrusions as molecules that are forced in an upright position by compressive strain in the film. Further increase of the coverage leads to surfaces which can only be imaged reliably after annealing to room temperature. Figure 11 shows a complete Cl-TP film (green) with the periodicity described above. In the vicinity of step edges and in well-defined islands, we find areas that appear elevated (inset). Here the film corrugation is reduced and the molecules appear to be closer to each other; however, no reproducible film structure could be discerned. We interpret these areas as being covered by molecules whose phenyl moiety is tilted substantially toward the surface normal.

In addition to the molecular size, intermolecular interactions may determine the film pattern: here we wish to focus on the electrostatic interactions between neighboring molecules, which may be understood in terms of the polarization of the aryl–halogen bond. In first approximation, the polar nature of the Aryl–X bond is determined by the electronegativity (EN) difference between the halogen and the supporting carbon atom. Due to the large EN of the halogens (Br, 2.8; Cl, 3; F, 4), the negative side of the bond dipole is at the halogen atom.

Calculations by Ferral et al. indicate that, in thiol linkages to copper, the sulfur atom becomes partially negatively charged by donation from the substrate. For para-halosubstituted thiophenols, this results in ac-
at maximal the importance of the molecular quadrupole moment for indicators. In the following paragraph, we wish to validate unit cell as an indicator of the film’s complexity (open If we regard the number of molecules per superstructure this the molecular quadrupole moment. In Figure 12, we plot the para substituent may be regarded as an indicator of property that correlates with the pattern formation.

10. Increasing the Cl-TP coverage on Cu(111) beyond the \([3-3]\) pattern at 0.125 ML (green) leads to the formation of islands (red) on the terraces and at the step edges, which we interpret as molecules whose aromatic moiety is tilted away from the horizontal (image size = 150 Å × 150 Å, \(U = −1.5 \text{ V, } I = 32 \text{ pA}\)). The insert shows a linescan along the white line starting at a lower terrace (blue) and crossing an island of protruding molecules.

11. Increasing the Cl-TP coverage on Cu(111) the \([3-3]\) pattern at 0.125 ML (green) leads to the formation of islands (red) on the terraces and at the step edges, which we interpret as molecules whose aromatic moiety is tilted away from the horizontal (image size = 150 Å × 150 Å, \(U = −1.5 \text{ V, } I = 32 \text{ pA}\)). The insert shows a linescan along the white line starting at a lower terrace (blue) and crossing an island of protruding molecules.

12. Comparison between the number of molecules in the low-coverage adsorbate unit cell (as an indicator of the film complexity) and the difference in electronegativity between the atoms at the meta and para positions (as an indicator of the intramolecular quadrupole moment). The good correlation suggests that quadrupolar interactions affect the film pattern.

cumulation of negative charge both on the side of the halogen and the on the side of sulfur atom. Correspondingly, we expect the dipole moment of the para-substituted species to lie between that of thiophenol, where no halogen pulls charge to the para site of the aryl moiety, and pentafluoro-thiophenol, where five fluorine atoms pull charge toward the ring and away from the thiol group. In an earlier publication, Wong et al.\(^{55}\) confirmed these expectations by density functional calculations using methods developed by Kong et al.\(^{56}\) Given that neither thiophenol nor pentafluoro-thiophenol form ordered films, we look beyond the dipolar term in search of a molecular property that correlates with the pattern formation.

The difference between the EN of the ortho/meta and the para substituent may be regarded as an indicator of the molecular quadrupole moment. In Figure 12, we plot this AEN as a function of the substituent (solid columns). If we regard the number of molecules per superstructure unit cell as an indicator of the film’s complexity (open columns), we find a remarkable correlation between these indicators. In the following paragraph, we wish to validate the importance of the molecular quadrupole moment for the film geometry by closely analyzing the pattern found at maximal AEN.

The F-TP(8 \times 8)R19° structure consists of six-membered rings of molecules, which enclose a seventh molecule. The S–X axes of the six circumferential molecules are angled with respect to a radial line. In this orientation, the F apex of the S–X axis of each of the molecules approaches the neighboring molecule mesial, i.e., toward the center of the benzene ring. This is consistent with the assumption of a strong molecular quadrupole moment, which predicts partial positive charge toward the meta and ortho positions of the ring (inset in Figure 12). The seventh, center molecule is geometrically prevented from partaking in this quadrupolar interaction. Correspondingly, we find that the center position frequently remains unoccupied, especially at island boundaries, as shown in Figure 13.

The patterns of Cl-TP and Br-TP are not quite as indicative of quadrupolar interaction: these patterns consist of rows of molecules in which the row direction forms an angle with the S–X axes of the molecules. We note that, with decreasing substituent size and closer spacing of the rows, the sequence of molecules in neighboring rows becomes offset, so that the S or X group of a molecule of one row falls closer to the benzene ring of a molecule in the neighboring row, i.e., at higher AEN; the negatively charged groups of molecules of one row are better in phase with the positively charged benzene ring of the neighboring row.

Summary

We have shown that (halo-substituted) thiophenols adsorb inclined on Cu(111). They possess sufficient mobility at 81 K to form ordered adislands/layers, whose patterns intricately depend on the substituent-dependent molecular size and quadrupole moment. Increase of the coverage leads to compressed films of horizontally adsorbed molecules; upon further increase of the coverage, islands of vertically adsorbed molecules are generated.

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