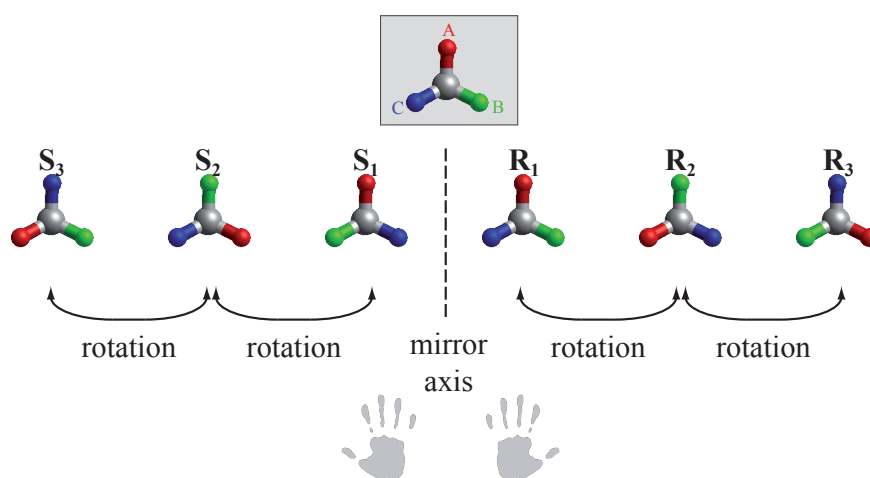


# 6 Chirality of Molecular Assemblies

## 6.1 Chirality

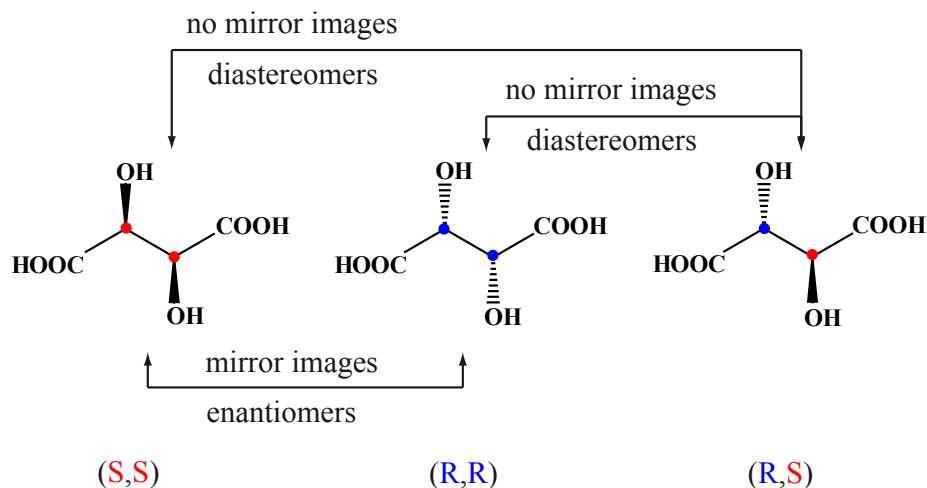
The number of possibilities to arrange substituents around a planar C=C-double-bond is rather limited - two, i.e. “cis” and “trans”. On the first glance the number of possibilities seems to increase drastically for the substituents around a single atom. For carbon, which is the atom of consideration in this work, dealing with organic molecular adsorbates, this can be four single bound substituents - named “A”, “B”, “C” and “D”. If “D” points into the back, i.e. into the paper plane, the possibilities shown in figure 6.1 remain.



**Figure 6.1:** In a carbon atom with four different ligands A, B, C and D, the ligands A, B and C (D pointing backwards) can be arranged in six different ways. Either three of them can be transformed into each other by simple rotation. Thus just two forms exist, that are not superimposable and behave like mirror images to each other. These are the two enantiomers.

Only two isomers exist that cannot be transformed into each other by rotation but only by a mirror plane reflection. These two isomers are related to each other like two hands - explaining the origin of their structural description as chiral: “chiros” is the greek word for “hand”. The definition of chirality is: *Every object that is not superimposable with its mirror image is chiral. An achiral object has a congruent mirror image.*[90] The two isomers of a chiral compound are mirror images to each other. They are referred to as the

two *enantiomers*, normally in the form of a one-to-one *racemic* mixture. If they are not mirror images, the two isomers are denoted as *diastereomers*. A typical example molecule that exhibits enantiomers and diastereomers is the tartaric acid shown in figure 6.2.



**Figure 6.2:** These are the three isomers of tartaric acid with their two chiral centers (red dots). While the two isomers on the left are mirror images of each other and therefore enantiomers, the isomer on the right is a mirror image of neither of them. Thus they are diastereomers with respect to each other. Lines represent bonds in the paper plane, the solid arrow represents a bond sticking out of the plane, the dashed arrow one, sticking into the plane, respectively.

Chiral molecules may have one or more chiral centers, where all possible ligands are different from each other. Most common is the carbon atom as chiral center, but also silicon, phosphorus, sulfur or nitrogen may act as such. For chiral centers, several descriptors exist, which are explained below (chapter 7.1.1). If the different ligands are ordered pairwise around an axis instead of a single atom, this is referred to as *axial chirality*. Depending on the order of the ligands around the main axis, the molecules are described as “aR” or “aS” for right clockwise or left counterclockwise order, respectively. Although helices are in principle also axial chiral molecules, they are described differently. If the helix is right-handed, they are described as a “P”-, if left-handed as an “M”-helix. DNA is probably the best known example for helical chirality<sup>1</sup>. Cyclic molecules incorporating a stiff double bond exhibit a chiral plane. They are described as “pR” for right and “pS” for left.

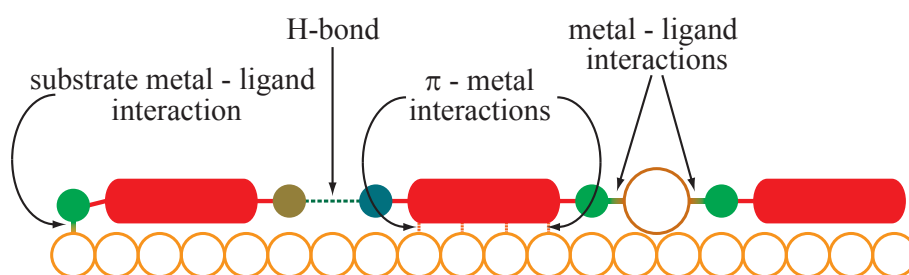
<sup>1</sup>Surprisingly, only (P)-DNA exists in nature.

## 6.2 Molecular Assemblies

### 6.2.1 Molecular Adsorption and Self Assembly on Surfaces

The order and assembly of molecules (and also atoms) adsorbed on a surface is a result of various processes acting on an atomistic scale. These processes can be divided in kinetics and thermodynamics, the result being the outcome of the competition between both. While kinetically limited autonomous ordering is commonly described as *self-organized growth*, *self-assembly* describes the spontaneous formation of a long range order from its molecular constituents. *Self-organization*, finally, is commonly used for macromolecular, dissipative structure formations that are usually far away from thermodynamic equilibrium[6].

The principal mechanism underlying every ordering is the transport of the adsorbing species on the surface. This surface diffusion, described by the mean square distance traveled per time i.e. diffusivity  $D$ , is thermally activated and therefore obeys an Arrhenius law. It has been shown that this not only holds true for atoms but also for molecular entities[166]. The ratio between diffusivity  $D$  and adsorption rate  $F$ ,  $D/F$ , describes the average traveling distance after which two adsorbates meet on the surface. If  $D/F$  is large, the ordering takes place under equilibrium conditions and the species have enough time to reach a minimum energy configuration. In the opposite case, if  $D/F$  is small, the system is kinetically controlled and predominately metastable structures are formed.



**Figure 6.3:** Possible interactions between molecules (red) and surfaces (yellow). The molecules may bond to the surfaces via a ligand (green), e.g. a carboxylic or a thiol group or via  $\pi$ -metal-interactions (red). Hydrogen bonds between different ligands (olive, blue) may stabilize supramolecular assemblies as well as ligand-metal-interactions.

The bonding functionality of the adsorbates also affects the ordering mechanism. While metal bonds are primarily of a covalent nature and have no directionality, metallic nanostructures obey kinetic control of the involved motions over the surface, e.g. hopping along terraces, over steps, along edges or across corners and kinks. The energy barrier for every displacement scales approximately with the local coordination of the diffusing atom. Thus, apart from external parameters as temperature and deposition flux, the appropriate

choice of the surface geometry can be used to influence the organisation of metal atoms on the surface[167].

In molecules, the bonding and interaction functionality is highly directed and weaker than in metals. Thus the surface mobility is higher and ordering takes place in thermodynamic equilibrium conditions. The surface mobility, the lateral interactions between the adsorbates and their coupling to the substrate lattice, and thus the proper choice of this “template”, can be utilized to control the molecular assembly[166, 168, 169]. Intermolecular interactions may only take place if the adsorbate-substrate interactions allow for a lateral interaction, i.e. a “meeting”, of the molecules on the surface. Thus too strong a bonding of the adsorbates to the substrate inhibits the formation of networks at the beginning. If the interaction is too weak, the mobility of the molecules is too high for network formation to occur.

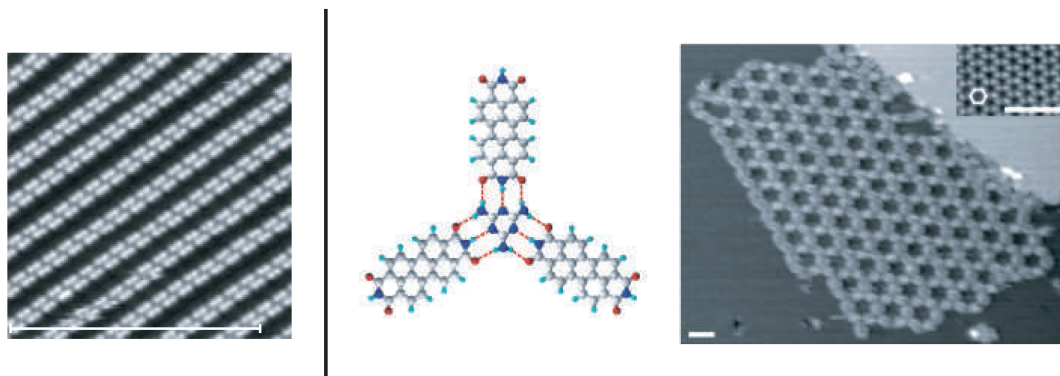
The atomic corrugation of the substrate surface leads to a modulation of the adsorption energy  $\Delta E_{ads}$  of the molecules (or atoms). At low temperature, molecules are in their ground state and have to overcome the activation barrier  $\Delta E_{diff}$  to be able to diffuse across the surface. With increasing coverage, the influence of the lateral forces between the molecules gains influence on the adsorbate-substrate interaction. Attractive forces between the molecules cause an increase of the adsorption energy, while repulsive forces lead to a reduction[170]. At the point when the repulsion between the adsorbates equals the adsorption energy, the saturation coverage of that specific adsorbate is reached. Then steric influence becomes significant and the shape and geometry of the molecule have a strong impact on the lateral ordering of the molecules, in the extreme case inhibiting the favored adsorption site for a sterically better suited one.

Planar molecules (especially with an extended conjugated  $\pi$ -system) predominantly adsorb in a mainly flat adsorption geometry, the ordering of which is influenced by the symmetry and geometry of the substrate lattice. The interplay between the molecules can be controlled by the introduction of a large variety of functional groups whose interactions, mainly hydrogen bonds and ligand-metal-interactions, are well known from chemistry[171, 172]. While the hydrogen bonds (H-bonds) are rather weak in nature, but originate from the molecules themselves, metal-ligand interactions are much stronger and, depending on the choice of the metal, add further functionality to the surface. The challenge is the proper deposition of the metal adatoms on the surface.

Such ligand-metal-interactions may not only appear between molecules and adatoms, but also between molecules and surface atoms. Since these interactions are stronger than the intermolecular interplay, they will determine the molecular adsorption on the surface[173, 174].

Upon adsorption, the substrate lattice with its electronic structure will more or less influ-

ence the electronic properties of the functional group and thereby influence the intermolecular interactions. In extreme cases, even chemical modification of the groups might occur. In return, the adsorbed molecule may perturb the surface-state free electron gas[175]. The geometry and symmetry of the substrate lattice may not be neglected as in most cases the adsorbate network tries to adapt to the underlying template in order to accomplish a commensurate overlayer.

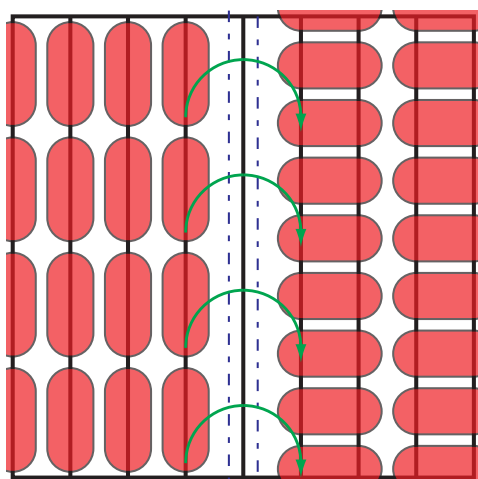


**Figure 6.4:** *Examples for supramolecular assemblies on surfaces. On the left, long bimolecular chains of PVBA forming on Ag(111), on the right hexagonal assemblies of PTCDI are shown. – Figure reproduced from [6].*

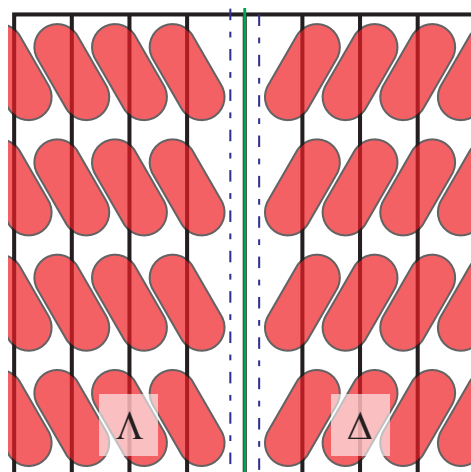
An impressive example is the variety of structures formed by 4-[trans-2-(pyrid-4-yl-vinyl)]benzoic acid (PVBA), which has been studied intensively by Barth and coworkers. The head group of this linear-shaped molecule is a benzoic acid, the tail a pyridyl group[176, 177], which are prone to hydrogen bond formation. On substrates such as Pd, where substrate-adsorbate interactions are strong, no regular surface pattern is formed. On noble metal surfaces this interaction decreases and one-dimensional supramolecular arrangements of two discrete chains of hydrogen-bonded PVBA molecules appear, which orient along the dislocation arrays of the substrate. The combination of perylene tetracarboxylic diimide (PTCDI) and melamine yields a 2D bimolecular honeycomb network adsorbed on Ag-passivated Si(111) which assumes a supportive surface corrugation[178]. Although the individual intermolecular hydrogen bonds may be weak, the multiple weak couplings result in a stable network. Only very recently Grill and coworkers have shown that by using the right molecular precursor, here brominated porphyrins, covalent bonds may be formed between the molecular adsorbates after activation through heating[179].

## 6.2.2 Prochirality in low Dimensions

Molecules, as they adsorb and self-assemble on a surface, may acquire a large number of possible adsorption geometries[6]. These adsorption geometries vary from simple rods[177],



**Figure 6.5:** Schematic adsorption of oblong molecules along the main crystal axes of a surface. Every phase can be transformed by a rotation into each other. The phases as well as the overall surface is chiral.



**Figure 6.6:** Schematic adsorption of oblong molecules on a surface breaking a symmetry axis of the surface. Therefore two mirror domains that are not superimposable are formed. These mirror domains are chiral with respect to each other. As both of them appear at the same amount the overall surface is achiral.

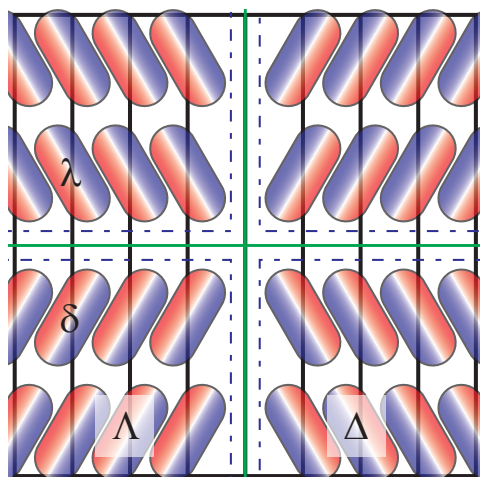
over 2D casket networks[180] to complex honeycomb structures[178] and more.

Although the symmetry observed may vary for every case, e.g. two-fold or three-fold, all these supramolecular assemblies form high symmetry domains. Only in very rare cases the long-range order is of such strength, that one single domain is formed over all surface distortions. Normally several domains are formed. In the simplest case, every domain can be transferred into each other by translation and rotation. For this to be true, the single domains themselves have to be of high symmetry, with their unit cells containing a center of inversion, and they have to be aligned along one of the high symmetry axes of the underlying crystal lattice.

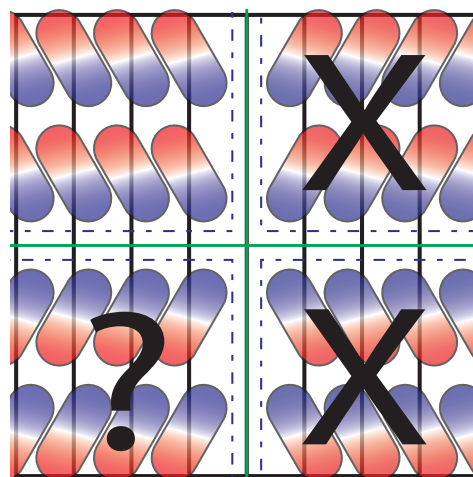
If the molecules align to the surface in an angle off the main surface lattice axes as in figure 6.6, the transformation from one domain into the other is no longer possible by simple means of rotation and translation. Although the molecules themselves in each domain are interchangeable and possess no handed orientation, the growth direction lies at an off-angle to the surface lattice axes and thus the symmetry planes of that surface are destroyed. Two types of domains with opposite orientation are formed, which can only be transformed into each other by a mirror operation, and are thus chiral with respect to each other. Depending on their orientation they are denoted as  $\Delta$  (“D” for dexter, right (greek)) and  $\Lambda$  (“L” for laevus, left (greek)). As the nature of the adsorbed molecules is achiral, both mirror image domains of *local organisational chirality* can and do occur with

the same probability, making the overall assembly achiral.

If upon adsorption the molecular reflection plane does not align with the surface axes, two possible alignments of the molecule with respect to the surface exist. A *local chiral motif* is created shown in figure 6.7. A molecule that is inherently achiral but creates such a local chiral motif upon adsorption is called prochiral. The off-angle between surface and molecular reflection plane can be either positive or negative, both angles are energetically equivalent. Thus domains of both orientations coexist on the surface, which can only be transformed into each other by a mirror operation, and are again denoted as  $\Delta$  or  $\Lambda$ . As only a flipping-over would transfer one adsorption-enantiomer into the other, i.e. a transformation in three dimensions, this chirality-induction is often referred to as “2D chirality” [169]. Due to the energy-equivalence of the  $\Delta$  and  $\Lambda$  domain, they indeed occur in an equivalent number which corresponds to a racemic mixture of  $\Delta$ - and  $\Lambda$ -domains, making the overall ensemble achiral. This form of chirality is not only restricted to oblong molecules adsorbed in a planar fashion onto the surface; also linear molecules that are adsorbed upright on the surface but with a tilt of the molecular axis with respect to the surface normal can create such chiral motifs.



**Figure 6.7:** Schematic adsorption of oblong molecules with a symmetry axis broken upon adsorption on a surface breaking a symmetry axis of the surface. Therefore two mirror domains that are not superimposable are formed for each of the surface enantiomers. These mirror domains are chiral with respect to each other. As all of them appear at the same amount the overall surface is achiral.



**Figure 6.8:** Schematic adsorption of oblong molecules with an intrinsically broken symmetry axis on a surface breaking a symmetry axis of the surface. Due to the intrinsic chirality of the molecule only one of the possible two mirror domains is formed. As only one domain appears the overall surface is chiral.

As such domains of local chiral motifs might also observe local organisational chirality, a larger number of possible domains is created. Still these are all energetically equivalent and therefore do exist at the same amount. The overall surface remains achiral.

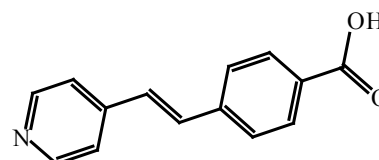
Such surface chirality may be due solely to the molecular assembly. There the interaction with the substrate mesh together with the packing of the molecules lead to the observed surface handedness. This may already appear upon adsorption of small alkylchains such as pentane on HOPG. There the linear molecules form rectangular patterns, but the molecules themselves are tilted by a few degrees with respect to these rectangles[181]. Another route to chiral surfaces is the symmetry breaking of molecules following a chemical reaction on the surface. Trans-2-butene for example adsorbs to Si(100) by cleavage of the central double bond. Then two possibilities for relative alignment of the methyl-endgroups with respect to the central bond and the Si dimers exist, i.e. two surface enantiomers can be observed[182].

A simple example for molecules possessing prochiral character with respect to surface adsorption are planar molecules with a reflection plane only in the surface plane. This is the case, amongst others, for a C=C-double bond as in stilbene. Its Z-like backbone can theoretically adsorb in two possible conformations if the planarity of the molecule is preserved: Z and  $\Delta$ . Pure stilbene adsorbs on metal and semiconductor surfaces via  $\pi$ -metal-interactions at the C=C-bridge. Thereby, as shown before, the planarity of the molecule is lost. Also no local or global ordering exists. In order to maintain the planarity and simultaneously to introduce the possibility of ordering, the stilbene molecule has to be equipped with functional groups that allow for intermolecular interactions and have a higher affinity for the underlying substrate.

Although there exist a variety of functional groups with such high bonding affinity, two stilbene derivatives up to now have been found to adsorb in such planar fashion via their functional groups.

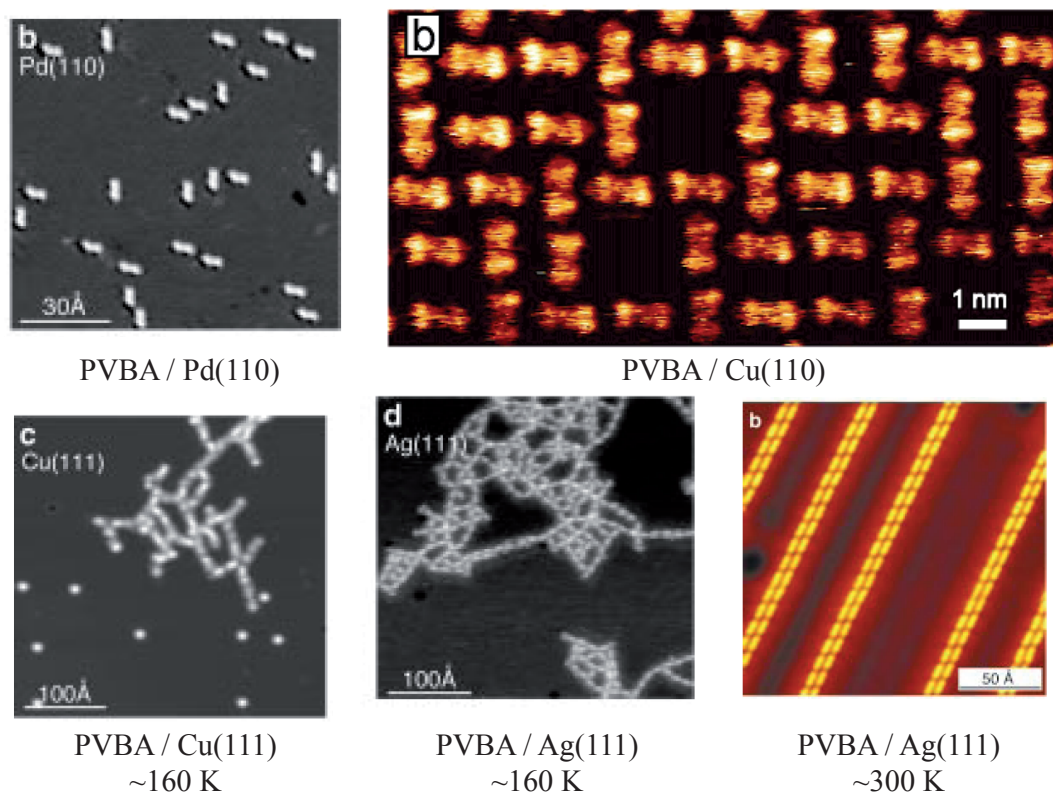
The 4-[trans-2-(pyrid-4-yl-vinyl)] benzoic acid (PVBA) is a stilbene derivative with additional functionalities on both benzene rings. The head of the molecule has

a carboxylic acid group at the 4 position, while the carbon in 4' position is substituted by a nitrogen to provide a pyridyl tail. Barth and coworkers showed that the ordering of PVBA on surfaces depends on the substrate metal and the adsorption temperature. While on Pd(110) the molecules adsorb quite randomly, on Cu(111) dendritic islands emerge together with isolated molecules in an upright bonding configuration, whereas on Ag(111) networks without long range order are being built[177]. These adsorption patterns all appear at temperatures around 160K. At higher temperatures (300K) long ordered chains are formed, which consist of a double row of PVBA molecules. Hydrogen bonds between the tail-nitrogen and the hydrogen in the carboxylic head-group are responsible for the chain formation. A second hydrogen bridge between carboxylic oxygen and a benzylic hydrogen connects the double row. Due to the intrinsic tilt of the molecule



**Figure 6.9:** 4-[trans-2-(pyrid-4-yl-vinyl)] benzoic acid (PVBA)





**Figure 6.10:** PVBA displays a huge variety of supramolecular assemblies on different surface. A few of them are depicted here, ranging from total disorder on Pd(110), disordered chains on Cu(111) and Ag(111) at low temperatures, over bimolecular chains at elevated temperatures on Ag(111), which show a handedness with respect to the main crystal axis, up to a handed parquet pattern on Cu(110). – Figures reproduced from [177, 183].

induced by the Z-shape from the C=C double bond depicted in figure 6.9, the double rows are formed with a tilt angle to the main crystal axes of the substrate along the  $\langle 1\ 1\ \bar{2} \rangle$  direction[177]. On Cu(110) PVBA forms a parquet pattern[183]. As the adsorption of the “Z” and the “ $\Delta$ ” are energetically equivalent, always the same amount of left- and right-oriented adsorption patterns may occur, each of them being an enantiomorphous phase.

A very interesting effect can be observed upon adsorption of PVBA onto Ag(110) and subsequent thermal activation. The molecular head groups form carboxylate-complexes with the silver atoms on  $\{1\ 1\ 0\}$  facets at the step edges after deprotonation of these groups[184]. Subsequently, the underlying surface is reshaped to form sawtooth arrangements mediated by the PVBA. Driving force here are probably metal-ligand interactions. Further molecules order around these PVBA-decorated facets. Interestingly, the two forms, Z and  $\Delta$ , align on separate sites of the sawtooth to form two enantiomorphous phases.

If chiral molecules are adsorbed to the surface (figure 6.8), they inevitably introduce

a global chirality to the surface, as their inherent chirality forbids the formation of an adsorbed mirror image. Thus even in a totally disordered adsorption geometry *local chiral motifs* exist in form of the molecular chirality. The overall surface is thus chiral. The major question is then whether this local chirality is transferred onto a global scale in form of a supramolecular enantiomorphous structure.

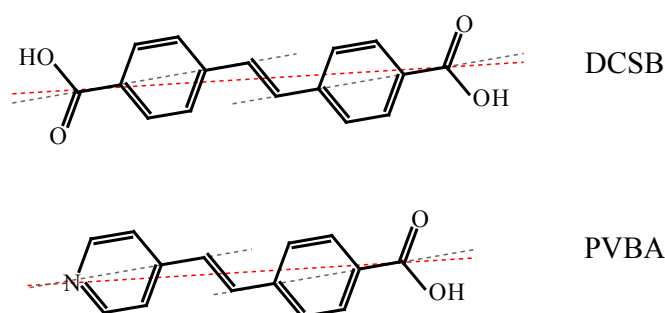
Chiral molecules also experience the same interplay between substrate-adsorbate interaction and lateral forces. Hence steric interactions and hydrogen bonds play an important role for the overall chirality of the surface. The interactions with the surface may also force the molecules to align in a strictly substrate-dictated fashion, which no longer has a chiral orientation. Alanine adsorbs on Cu(110) at room temperature in a chiral  $(2 \pm 2) \mp (5 \pm 3)$ -phase, bonding via the deprotonated carboxylic endgroup. Upon annealing, also the amino group bonds to the copper atoms and the adlattice is governed by this molecular motif. An achiral  $c(3 \times 2)$ -phase is formed[185–187]. Thus the surface exhibits no organisational chirality and the overall chirality is only provided by the inherently chiral motif of the pure enantiomer. Another example is tartaric acid, where on Cu(110) at coverages of 0.25 molecules per substrate atoms an achiral  $c(4 \times 2)$  monotartrate phase is formed, i.e. only one carboxylic endgroup is deprotonated and bonds to the surface[188]. Upon thermal activation, this phase is transformed into a bitartrate, which, upon further coverage, reacts back to a monotartrate phase (see chapter 7.2.1). In contrast to achiral molecules, only one of the possible domains may exist, as the other one is impossible due to the inherent molecular chirality. This would create a truly global chiral surface with local and global point-chirality. Nevertheless Raval and coworkers have predicted that theoretically chiral molecules organised in a chiral adsorption geometry may form a pseudo-mirror image domain if enough achiral molecules are present to mediate the domain formation[185]. Still this has not yet been shown experimentally.

Despite the fact that the physical mirror symmetry of a surface is removed by the adsorption of a chiral molecule, the substrate electronic structure is not automatically chirally perturbed. Kadodwala and coworkers investigated the band structure of metal surfaces with chiral adsorbates. They deduced that only a molecule in an adsorption geometry with at least three noncollinear inequivalent groups in close surface proximity may induce chiral behavior to the underlying electronic structure[189].

## 6.3 Chiral Adsorption of Stilbenedicarboxylic Acid

### 6.3.1 Adsorption Behavior of Stilbene Dicarboxylic Acid on Cu(110)

Stilbene molecules adsorb to semiconductor and metal surfaces via substrate- $\pi$  interactions through the C=C bridge. Since photoexcitation at the bridge is the initial step in photoisomerisation, the nature of the molecule-substrate interaction has a direct impact on the ability for isomerisation. This influence should be minimized, if different bonding mechanisms, e.g. via an anchor group, can be introduced. A suitable candidate is the 4,4'-stilbene-dicarboxylic acid.



**Figure 6.11:** 4,4'-stilbene-dicarboxylic acid (DCSB) and 4-[trans-2-(pyrid-4-yl-vinyl)]benzoic acid (PVBA) are both stilbene derivatives with different substituents. DCSB holds two carboxylic acid end groups, PVBA one of those. In the other phenyl group the C atom opposite the bridge is replaced by an N atom.

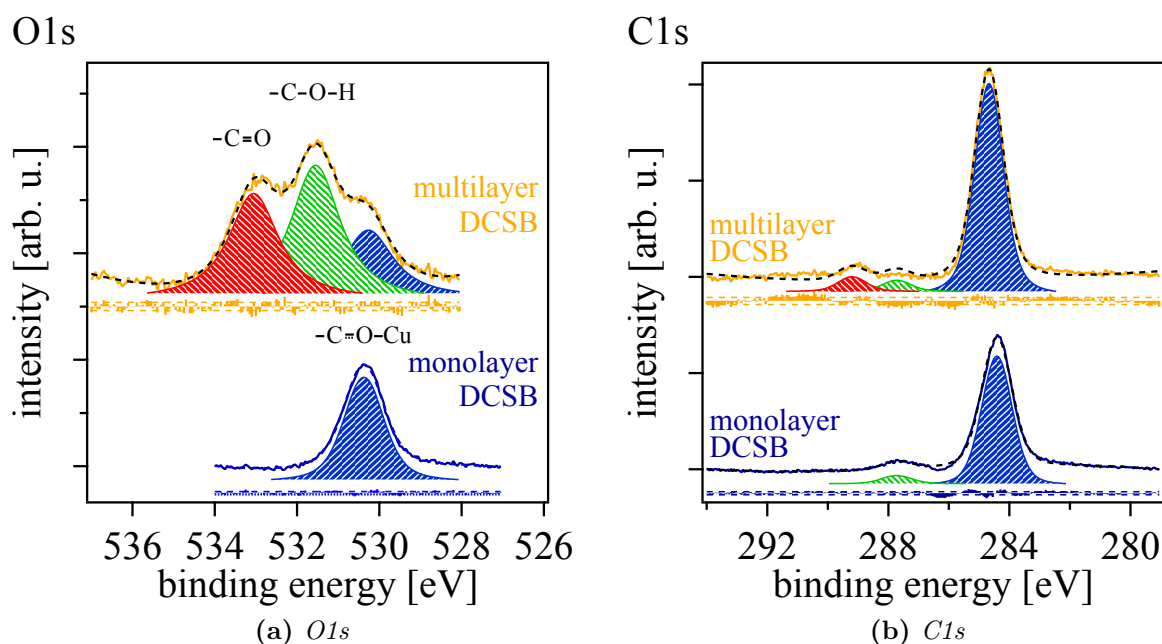
Although PVBA can also be seen as a stilbene-related molecule, the original stilbene-unit is perturbed by the nitrogen introduced into the molecular tail. Closer to the original stilbene is the 4,4'-stilbene-dicarboxylic acid (or dicarboxystilbene, DCSB) with a carboxylic endgroup at the head and the tail phenyl-group.

As the stilbene entity is completely preserved one can assume, that also the stilbene-functionality, its isomerisability, may be preserved. In an ideal case, the molecule would bond to the surface in an upright fashion via one carboxylic group. Tartaric acid is an example of a biacidic molecule that can under certain conditions, in this case lower substrate temperatures, adsorb only via one functional group.

First work on this molecule by Kern and coworkers gives no indication of an upright adsorption of dicarboxy-stilbene[190]. The adsorption onto Cu(110) at room temperature arised in two mirror image domains with the molecules adsorbed in a parquet pattern. The unit cell is tilted by  $\pm 54^\circ$  off the  $[0\ 0\ 1]$  direction of the copper surface. Hydrogen bonds

between the carboxylate end groups and the bridge located hydrogens were accounted for the formation of the parquet network. The tilt is resulting from the molecular C=C double bond, due to which the two phenyl-entities are displaced with respect to each other, as indicated by the grey dotted lines in figure 6.11. The overall molecule orientation (red dotted lines) is thereby tilted with respect to the single entities.

The adsorption of carboxylic acids on Cu(110) is well understood, from very simple acids like formic acid and acetic acid[191] or amino acids[163] to biacidic molecules like tartaric acid[185]. Especially tartaric acid, which has two acidic endgroups as the dicarboxy-stilbene, shows a large variety of adsorption phases on Cu(110)[185]. Bitartrate phases, where both carboxylic groups bond to the copper, are known as well as monotartrate phases with only one bound carboxy-group. Thus a similar variety seems to be possible for the adsorption of dicarboxy-stilbene on Cu(110)

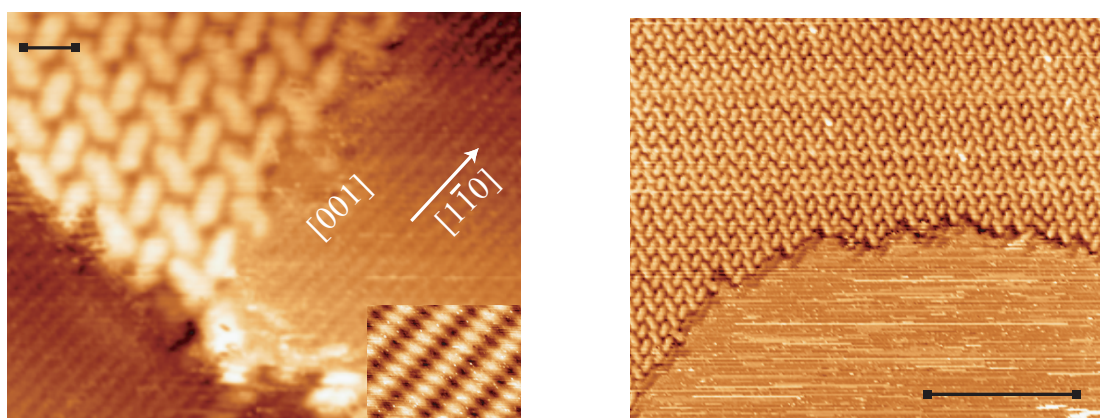


**Figure 6.12:** *C1s* and *O1s* core level emission of 4,4'-stilbene-dicarboxylic acid adsorbed on Cu(110) in mono- and multilayer coverage. The *O1s* spectrum clearly indicates that in the monolayer all molecules are bound via both carboxylic endgroups to the surface, additional layers adsorb in a planar fashion on top. This is supported by the *C1s* spectra displaying only a copper bound carboxylic component for the monolayer and an additional free carboxylic component for the multilayer.

To investigate the adsorption behavior of dicarboxy-stilbene a sub-monolayer coverage has been adsorbed on Cu(110). Core level spectra from the oxygen 1s core level in figure 6.12 show only one single signal at 530.3 eV binding energy up to monolayer coverage. This peak indicates, that after adsorption all four oxygens of the two carboxylic endgroups are chemically equivalent. In the pure molecule, each endgroup bears two inequivalent oxygens, one double bond =O, and one single bond hydroxy -OH. During adsorption, the

hydroxy-group is being deprotonated, as it is well known from other carboxylic acids like tartaric acid[185], and delocalisation of the electrons over the whole O-C-O group leads to chemical equivalence of both oxygens which both bond to the substrate copper atoms. This process has to appear on both endgroups to guarantee for chemical equivalence of all four oxygen atoms, as is observed in the O1s spectrum.

An adsorption via both carboxylic endgroups directly means an adsorption in a flat geometry with the stilbene entity parallel to the surface. No bonds due to the other moieties in the free molecule exist in the monolayer, and all four oxygen atoms are bound to neighboring Cu surface atoms[192]. The O1s spectrum of multilayer adsorption shows two additional peaks of same intensity at binding energies of 531.5 eV and 532.9 eV. These can directly be assigned to the two chemically inequivalent oxygens in the two carboxylic groups, the former being the emission from the double bond =O, the latter the hydroxy -OH. Thus higher adsorption layers have to adsorb in a parallel fashion onto the first layer via  $\pi$ - $\pi$ -interactions between the stilbene moieties.



(a) *Substrate and Adsorbate.*

(b) *Long range order.*

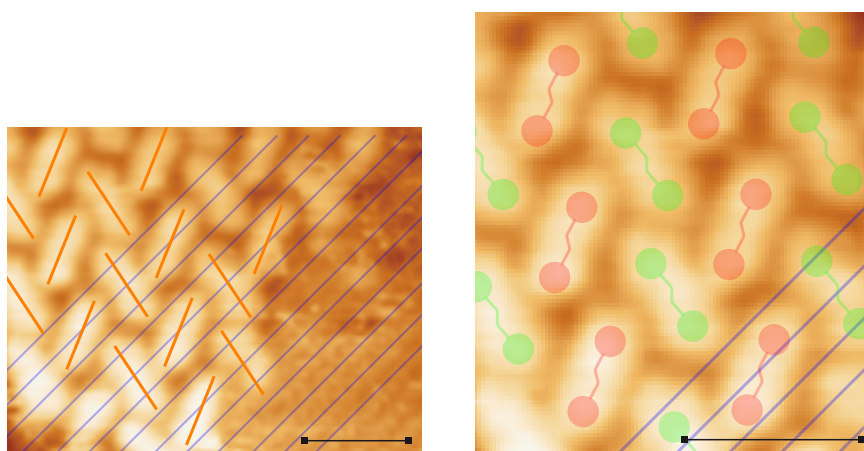
**Figure 6.13:** STM images of 4,4'-stilbene-dicarboxylic acid on Cu(110) ((a): -1.79 V, -0.69 nA, 1 nm scale; (c): -1.00 V, 2.00 nA, 10 nm scale). (a) shows the herringbone pattern together with the Cu(110) lattice, crystal axes are indicated. (b) shows the long range order of the herringbone pattern.

These findings are supported by the C1s core level emission spectra, that show a strong signal at 284.35 eV binding energy for mono- and multilayer. This corresponds nicely to the C1s-signal already observed for pure stilbene. The monolayer-spectrum exhibits an additional peak at higher binding energies (287.4 eV), while the multilayer spectrum has two additional small intensity components (287.4 eV and 289 eV). Both can be attributed to the carboxylic C. The shift observed for the C-atom is controlled by the electronegativity of the chemical environment, i.e. the carboxylic oxygens. In the monolayer situation,

these oxygens are bonding to the electron donating metal surface. Therefore their overall electronegativity is reduced in comparison to an unbound situation, and this decreased electronegativity is directly observed in a decreased binding energy for the carboxylic C1s emission in the monolayer (and the monolayer contribution in the multilayer spectrum).

The multilayer spectra are identical independent whether the multilayer was produced successively or at once. This indicates that dicarboxy-stilbene always adsorbs in the flat geometry and even for high coverages a upright monocarboxylate-configuration cannot be obtained.

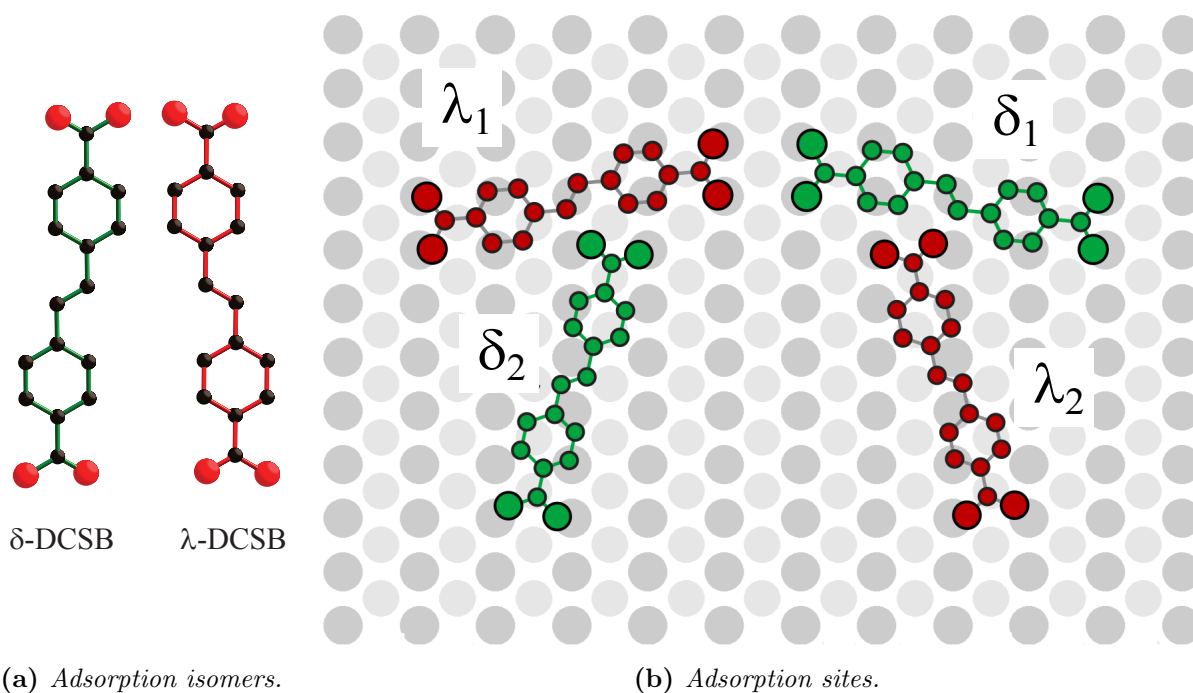
These findings from the XPS data are directly visible in the STM images. The dicarboxy-stilbene molecules adsorb in a flat manner on the Cu(110) surface, forming a network pattern. Figure 6.13a shows the adsorption pattern at elevated temperatures – a “heringbone pattern” (subsequently denoted as H). In the image the molecular network and the underlying surface lattice can be seen. No single molecules are observed. This indicates that the molecular mobility is very high. The smallest observed molecular entity was a tetramer, this also being highly mobile and rapidly increasing in size by the attachment of further molecules.



**Figure 6.14:** Details of the STM-image in figure 6.13a. On the left the Cu rows are indicated in blue. Two adsorption sites, along and across the rows can be seen, as indicated in orange. The oblong shapes of the molecules are not perfectly round and oblong but exhibit a kink. This kink indicates for the appearance of two adsorption isomers. Bars indicate 1 nm scale.

Looking more closely at the STM-image in figure in figure 6.13a, as done in figure 6.14, one can see that the molecules occupy two different adsorption sites. On the left of figure 6.14 the Cu rows are highlighted by blue lines. This pattern is also underlying the adsorbed molecules. The long axis of the oblong molecular shapes is indicated by an orange line. It is clearly observable that half of the molecules are oriented along the Cu rows, while the other half is oriented across the rows. Thus two different adsorption sites have to exist.

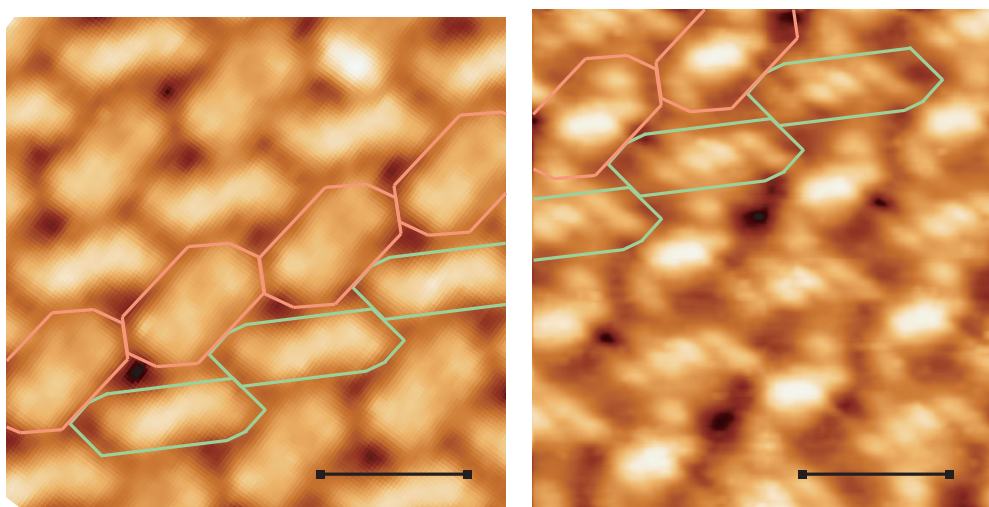
While the one species adsorbs with an angle of  $20^\circ$  to the  $[\bar{1}\bar{1}0]$  direction, the other has an angle of  $20^\circ$  to the  $[001]$ -direction of the substrate lattice. The oblong shapes depicted are not perfectly round, but exhibit a little kink. These kinks are visible upon further enlargement of the STM-image from figure 6.13a. Due to the double bond in the center, the dicarboxy-stilbene molecules are themselves kinked, as has already been indicated in figure 6.11. Upon adsorption, this Z-shaped molecular backbone can either adsorb in a right handed fashion ( $\lambda$ ) or in a left handed fashion ( $\delta$ ) (see figure 6.15a). The kinked shapes in figure 6.13a can be attributed to these two ways of adsorption. Figure 6.14 shows on the right an enlargement of the STM image in figure 6.13a. In red and green the two ways of adsorption are indicated. The correspondence to the kinks in the molecular shapes are clearly visible.



**Figure 6.15:** Two mirror image adsorption geometries are observed for the 4,4'-stilbene-dicarboxylic acid shown in (a). (b) In the  $\lambda_1$  geometry the molecules adsorb perpendicular to the copper rows, the carboxylic oxygen bonding to two adjacent row-atoms. In the  $\delta_2$  geometry the molecules adsorb along the copper rows, the carboxylic oxygen bonding to atoms in adjacent rows.

Figure 6.15a depicts the two ways, the molecular backbone of dicarboxy-stilbene can orient upon adsorption. They appear to be mirror images, which cannot be transferred into each other. A rotation around the axis along the molecule is forbidden, as the position of the substrate surface would be changed with respect of the molecule. Thus dicarboxy-stilbene exhibits an adsorption chirality. Depending on their orientation the two isomers are denoted as  $\delta$ -dicarboxy-stilbene and  $\lambda$ -dicarboxy-stilbene (DCSB), as shown in figure 6.15a. Closer investigation of figure 6.14 reveals that only  $\delta$ -molecules occur at the

adsorption sites along the Cu rows, and only  $\lambda$ -molecules at the sites across the Cu rows. Due to the achiral nature of the molecule, each adsorption isomer may occupy every bonding site, i.e.  $\delta$ -molecules may also assume the across sites and  $\lambda$ -molecules also the along sites. These four possibilities are shown schematically in figure 6.15b. For the across site (suffix 1) the DCSB molecule crosses five Cu atoms rows, with the oxygen atoms on either end displaced by one Cu-Cu distance, for the along one (suffix 2), the molecules are oriented roughly along the Cu rows, again with the oxygen atoms at either end displaced, here by one interchain distance.

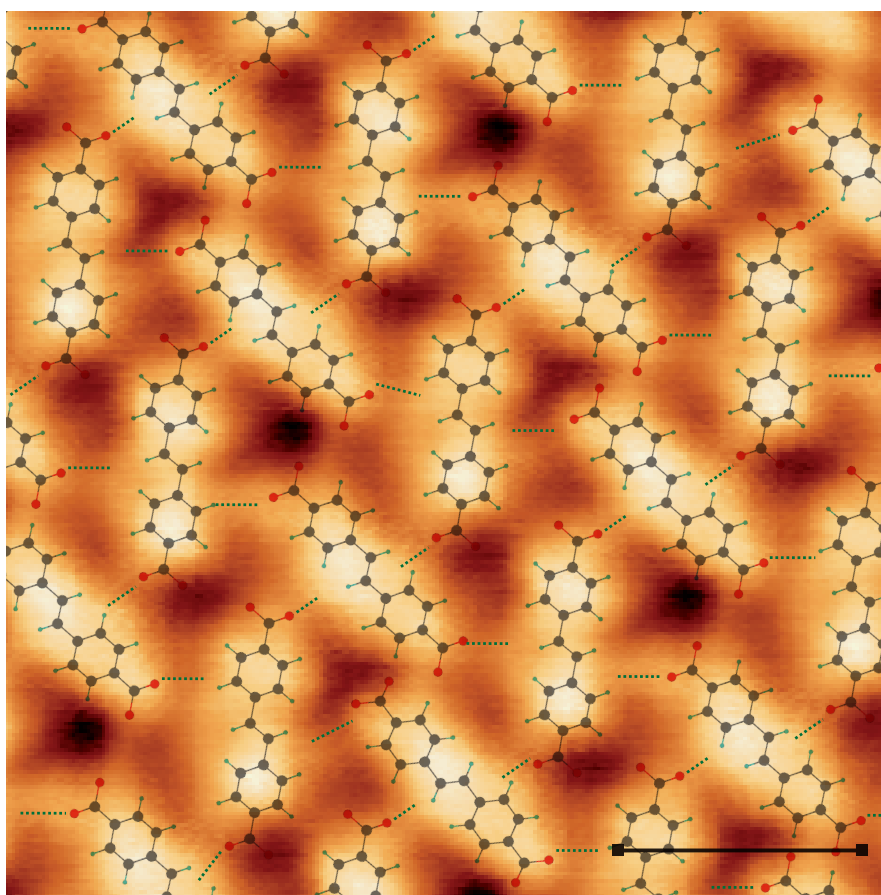


**Figure 6.16:** *4,4'-stilbene-dicarboxylic acid* in the herringbone phase imaged at positive and negative bias voltage. The occupied and unoccupied molecular orbitals are nicely visible. The different distortion of the electronic structure of the two isomers incorporated in the herringbone pattern due to hydrogen bonding is indicated by the red and green mesh. (left: 1.25 V, 0.83 nA; right: -1.683 V, -0.5 nA) Bar indicates 1 nm scale.

Depending on the bias voltage used for tunneling, the appearance of the molecules changes quite drastically and it is possible to image separately occupied and unoccupied molecular orbitals. Figure 6.16 exemplarily shows an unoccupied (left) and an occupied molecular orbital (right). The molecules at the two adsorption sites phase assume different adsorption on the Cu lattice as their appearance in the STM is unlike. The shape of the overlying mesh in figure 6.16 demonstrate this quite drastically.

The unlike appearance of the two adsorption isomers can be explained by a closer look on the supramolecular assembly on the surface. As mentioned before, hydrogen bonds are the main network driving forces, as due to the lack of metal adatoms ligand-metal interactions can be neglected. Figure 6.17 shows a close-up of the herringbone network. The oblong shapes of the molecules exhibit a small kink in the center which can be assigned to the C=C bridge bond. The  $\lambda$ - and  $\delta$ -type can thus be identified and are depicted on top of

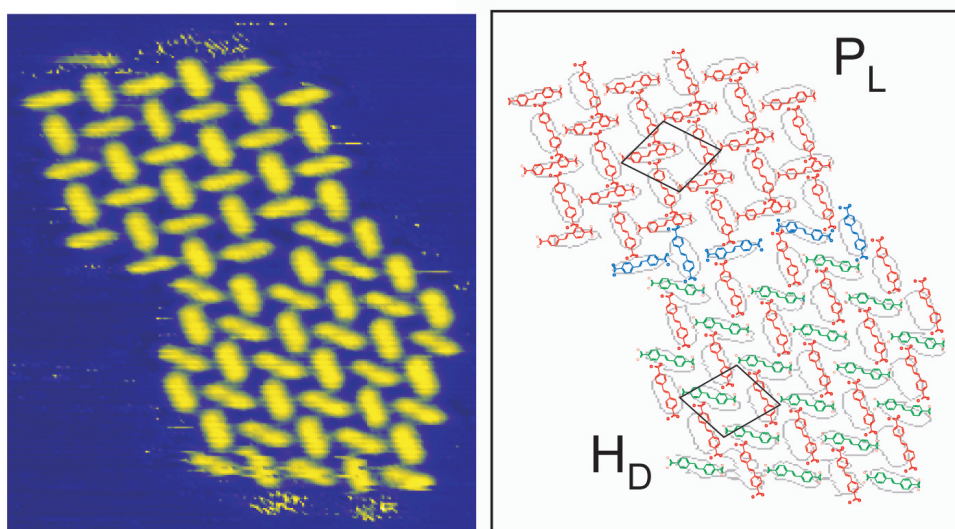




**Figure 6.17:** Detail from the herringbone phase depicted in figure 6.13 (-1.1 V). Ball-and-stick-models of the molecules illustrate their ordering within this assembly. Hydrogen bonds between the carboxylic oxygens and hydrogens of adjacent molecules are indicated by the dashed green lines. Bar indicates 1 nm scale.

the STM-image. The larger round shapes are assigned to the two phenyl groups of the stilbene entity. The molecular orbitals through which imaging proceeds at the chosen bias voltage are distorted into the direction of one of the adjacent molecules. I assume that these distortions point toward two hydrogen atoms as indicated by dotted lines in Figure 6.17. One of the hydrogen atoms is always located at the C=C-bridge, the other one is the ortho-hydrogen of the not directly adjacent phenyl-group. Both hydrogen atoms point directly toward the carboxy-group of the adjacent molecule. Thus this distortion can be seen as due to an electrostatic interaction between the oxygen and the hydrogen, which is exactly the explanation for hydrogen bonds that are expected to appear in such supramolecular assemblies. Since hydrogen bonds are mere electrostatic interactions lacking electron transfer, they cannot be imaged directly, but reveal themselves here through the distortion of the adjacent molecule. In addition to this stabilization of the molecular assembly, the distortion reduces the repulsive interaction between the carboxylic end-groups of neighboring molecules leading to an energetically more favorable configuration.

Figure 6.15b showed the four possible adsorption isomers of dicarboxy-stilbene on Cu(110). These were derived from the STM image shown in figure 6.13a, where molecule and substrate lattice were imaged in one set. Two of the four isomers,  $\delta_1$  and  $\lambda_2$ , could directly be identified. Obviously also other combinations of these molecular building blocks may be predicted. Besides the combination  $\delta_1$  and  $\lambda_2$  a mirror image phase  $\delta_2$  and  $\lambda_1$  has to be assumed. While the phase imaged in figure 6.13a is oriented “left” with respect to the Cu-rows and is thereby denoted as  $H_L$ , the mirror image would be  $H_R$ . Such a phase is shown in the lower part of the STM image in figure 6.18.



**Figure 6.18:** Both phases, rectangular and parquet phase, can coexist on the surface ( $-1\text{ V}$ ,  $-0.93\text{ nA}$ ). The scheme on the right shows the assembly of both phases from either pure left-handed molecules (red) in the parquet-phase and left- and right handed (green) molecules in the herringbone phase. Molecules that form the transition area between both phases are marked in blue. Bar indicates  $1\text{ nm}$  scale.

However also combinations of two  $\delta$ -type (or two  $\lambda$ -type) adsorbates are possible. Such combination is visible in the upper part of the STM image in figure 6.18. Such parquet type patterns have already been observed for PVBA adsorbed on Cu(100) for example [183] or for dicarboxy-stilbene on Cu(100)[190], as described at the beginning of this chapter. Figure 6.18 shows on the right a modeling of the two imaged phases using the building blocks depicted in figure 6.15b. From its orientation the parquet pattern shown can be identified as left oriented  $P_L$ . Obviously a  $P_R$  phase has to exist as well. The region at the island boundary in the top right is of particular interest: here the  $\lambda$ -species retain their orientation with respect to the copper atom rows in both structures, but are displaced by one more Cu atom row, while the  $\delta$ -species rotate by about  $40^\circ$  when the H converts to the P phase; this displacement permits the introduction of another  $\lambda$ -type species between the rows.

Using these building blocks also other supramolecular assemblies would be possible. One would be the formation of rod-like structures utilizing only one building block, as seen for PVBA on Au(111)[193]. Such rodlike structure require the existence of a hydrogen atom at either head or tail of the molecule that is oriented in direction of the molecule and rod. Such hydrogen bonds, though existent in the carboxy-groups of the free molecule, are removed during protonation upon adsorption. Thus the essential driving force for rod formation is not given here. They have also never been observed. They may exist on other substrates. Another possible assembly would be the formation of a square pattern. This has e.g. been observed for 4,4'-biphenyldicarboxylic acid on Cu(100)[190]. While for the exactly linear dicarboxy-biphenyl such arrangement is favorable, for the dicarboxy-stilbene this is prevented by the kink introduced from the C=C-bridge. Again, this phase has never been observed here.

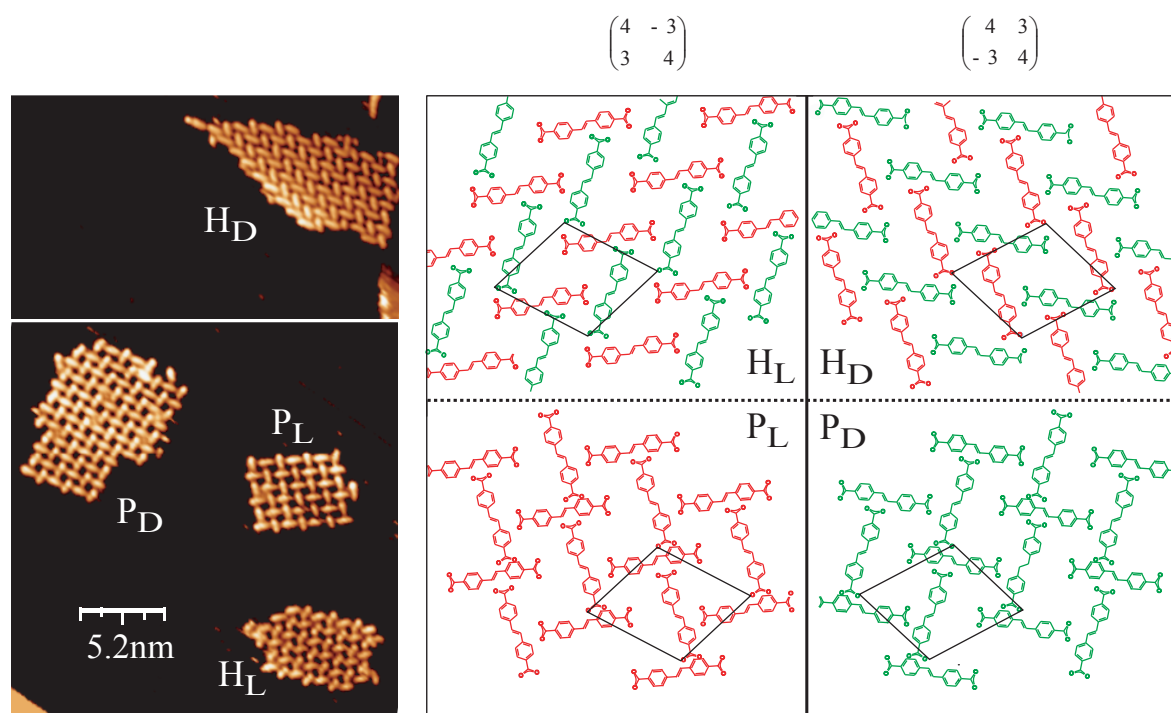
### 6.3.2 Chiral and Racemic Adsorption Domains

Starting from the four building blocks  $\lambda_1$ ,  $\lambda_2$ ,  $\delta_1$  and  $\delta_2$ , two supramolecular assemblies – parquet  $P$  and herringbone  $H$  – each of whom either left- or right-oriented (according to Fischer nomenclature denoted  $L$  and  $D$ ), have been predicted and identified on the surface. Figure 6.19 summarizes the models of all four. Depicted on the left is a single STM image in which all four phases are imaged. The white bar indicates a large area of uncovered surface that was cut out for imaging reasons.

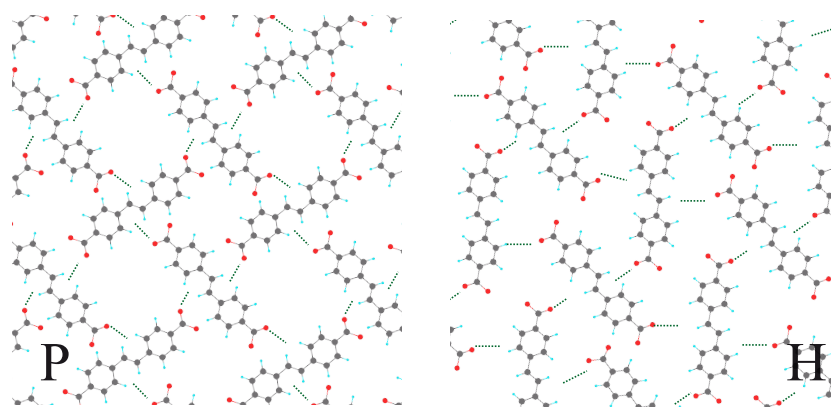
Each two of these phases (herringbone and parquet) are mirror images of each other. The parquet phases consist of only  $\lambda$ - or only  $\delta$ -type molecules. The herringbone phase, on the other hand, is always constituted of the same amount of  $\lambda$ - and  $\delta$ -molecules.

A closer inspection of those islands and their alignment with respect to the Cu(110) surface reveals that both left-handed phases ( $H_L$ ,  $P_L$ ) are described by one transformation matrix  $(4 \ -3|3 \ 4)$ . The transformation matrix for the right-handed phases ( $H_D$ ,  $P_D$ ) is  $(4 \ 3|-3 \ 4)$ . The existence of only two lattices describing either herringbone and parallelogram phases is a direct consequence of the low number of different adsorption complex structures possible as shown before. This case is, to the best of my knowledge, the very first example where all possible handed long-range structures, both racemic and enantiomerically pure, are realized.

The adsorption of the  $\lambda$ - and  $\delta$ -dicarboxy-stilbene has to be energetically equivalent. Due to the achiral nature of the molecule in the gas phase none of the isomers is preferred upon adsorption. Thus only the  $_1$  and  $_2$  adsorption sites can be distinguished from an energetically point of view. As both, the  $P$  and the  $H$  phase consist of an equal amount of  $_1$  and  $_2$  molecules, no energy difference in adsorption energy exists between both phases. Therefore a possible energy difference may only be caused by the supramolecular network.



**Figure 6.19:** Two different supramolecular structures can be formed from the surface enantiomers of 4,4'-stilbene-dicarboxylic acid. Depending on the enantiomers composing these structures, the structures themselves can be either left- or right handed. The superlattice is identical for herringbone and parquet phase. It was possible to image all phases simultaneously on one sample (-1.9 V, -0.38 nA, 1 nm scale), the white bar indicates a large area of bare surface cut out from the image for clarity.

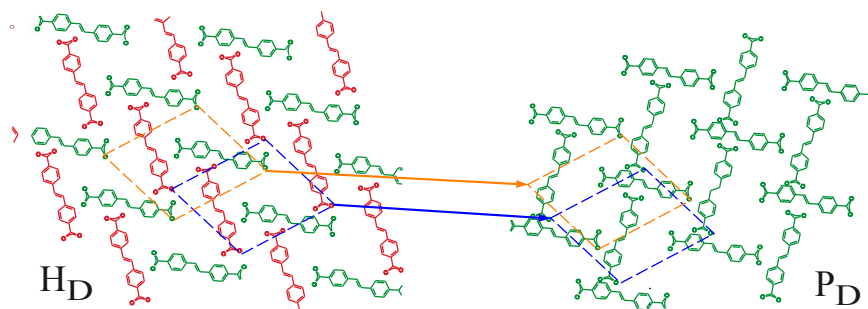


**Figure 6.20:** Hydrogen bond scheme for the herringbone and parquet phase.

As has been shown in figure 6.17, the supramolecular structure of the phases is governed by hydrogen bonding. Figure 6.20 shows a detail of a parquet and herringbone phase from figure 6.19. It is directly visible that hydrogen bonds are responsible for the formation of parquet and herringbone structure. Figure 6.20 shows a comparison of the molecular order

and the hydrogen bonding for the herringbone and parquet phase. For the herringbone phase, the model from figure 6.17 has been reproduced. In comparison with the parquet phase, it is clearly visible, that the same hydrogen bonds occur, connecting one of the carboxylic oxygens with the hydrogens at one of the bridge atoms and at the ortho-carbon of the nonadjacent phenyl group.

All these arguments indicate, that both supramolecular assemblies are energetically equivalent, as they are stabilised by the same number of hydrogen bonds that occur between the same atoms and are oriented in a similar fashion in  $H$  and  $P$  phase. This argument is also supported by the identical transformation matrices of both phases. Still a prove of this assumption would require a quantitative measure of the hydrogen bonds, which is up to now not possible.



**Figure 6.21:** Decomposition of  $H$  and  $P$  phase into an “along”-sublattice (blue) and an “across”-sublattice (orange). Both sublattices have the same transformation matrix and are not changed from  $H$  to  $P$ . Only the relative position to each other is changed.

A different line of argumentation would be the decomposition of the two phases  $H$  and  $P$  into two sublattices each. One sublattice for the  $_1$  adsorbates, one for the  $_2$  adsorbates. These are shown in figure 6.21 for the  $H$  and  $P$  matrix in orange and blue for  $_1$  and  $_2$ , respectively. In the  $H$ -phase both sublattices have the same transformation matrix as determined for the complete system with a certain displacement to each other. Changing virtually from the  $H$  to the  $P$  phase the  $_1$  atoms (orange matrix) are kept fixed, thus their lattice is preserved. The  $_2$  adsorbates are virtually mirrored. The resulting sublattice (blue) has the same transformation matrix as in the  $H$  phase, only its displacement with respect to the orange lattice is changed. This may be seen as an indication for an energy difference between the herringbone and the parquet phase.

Close investigation of the two adsorption phases – herringbone and parquet – provides arguments for and against an energy equivalence of both phases. Yet no absolute proof for one or the other assumption can clearly be made.

### 6.3.3 Chiral Behavior of Supramolecular Assemblies

Although the four possible adsorption phases of dicarboxy-stilbene are observable simultaneously their formation obeys a temperature dependence.

The adsorption and phase-formation of dicarboxy-stilbene on Cu(110) has been investigated at various temperatures. At all temperatures the high surface mobility of the molecules as well as the tetramer as minimum unit was observed. Adsorption at room temperature,  $298K$ , leads to the formation only of the herringbone phase. The parquet phase, on the other hand, is only detected at lower temperatures ( $200K$ ), however, at these temperatures the herringbone phase is also always detected. Upon temperature increase, molecules desorbed from the parquet phase reorder predominately in the herringbone pattern such that the parquet phase is dissolved and at some point only the herringbone phase remains.

The herringbone phase is thus the stable phase. The parquet phase represents a metastable state, whose formation is kinetically driven by the intermolecular hydrogen-bonds, but is thermodynamically not favored, in spite of their proposed energetic equivalence.

Table 6.1 summarizes the formation parameters of both,  $H$  and  $P$ , phases.

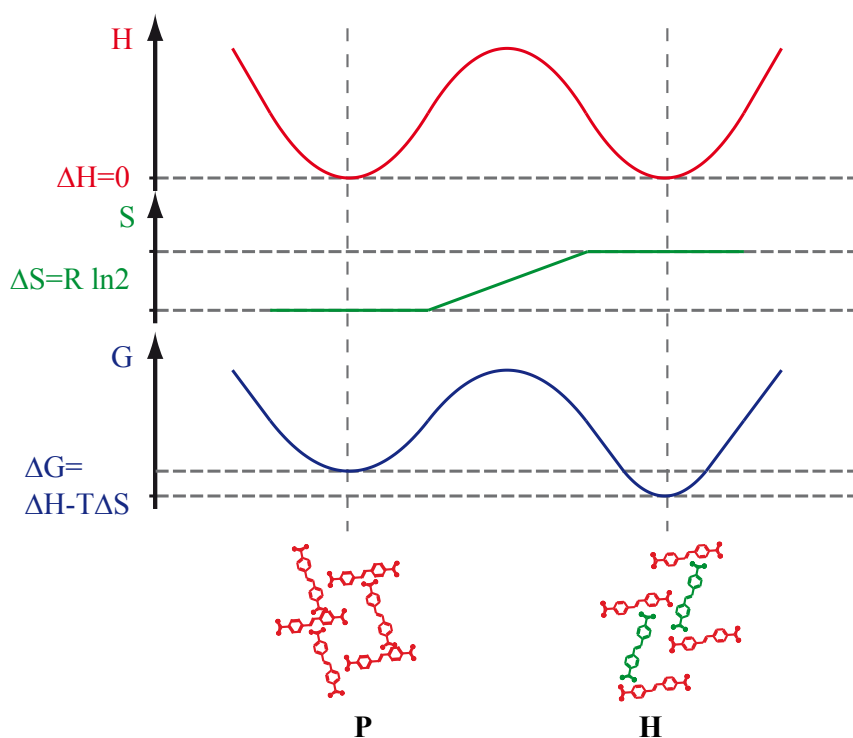
Phase	Substrate Temperature	Evaporation Temperature
herringbone	$298K$	$170^{\circ}C$
parquet	$395K$	$170^{\circ}C$

**Table 6.1:** *Different Phases prepared with 4,4'-Stilbene-dicarboxylic acid.*

The preference of the  $H$  phase after thermal activation can be used as an argument in favor of an energy difference between both phases. But also under the assumption of energy equivalence, an explanation for this behavior can be found, which is provided by the composition of the two phases. The parquet phase, constituted from only one of the adsorption isomers, is an enantiopure phase. The herringbone phase including both isomers is a so called racemic mixture. The adsorption energy of each adsorbed molecule, which is, more precisely, its enthalpy  $H$ , is equal for  $\lambda$  and  $\delta$  molecules. But the overall energy of the system, the Gibb's free energy  $G$  depends on enthalpy  $H$  and entropy  $S$ . The difference in Gibb's free energy for both phases is

$$\Delta G = \Delta H - T\Delta S . \quad (6.1)$$

The change in entropy, or disorder, can be derived from



**Figure 6.22:** The transformation and interchange of molecules between both phases is controlled by the change in Gibbs's free energy  $\Delta G = \Delta H - T\Delta S$ . Both phases are energetically equivalent ( $\Delta H = 0$ ), thus the difference in entropy  $\Delta S = R\ln 2$  is responsible for the preferred formation of the herringbone phase.

$$S = R\ln\Omega, \quad (6.2)$$

where  $R$  is the gas constant and  $\Omega$  is the number of microstate  $i$  (i.e. the isomers) that occur in a macrostate (the phase). In the enantiopure phase only one isomer exists and thus the entropy is 0, for the racemic mixture with its two isomers, the entropy per molecule is

$$S_H = R\ln 2 = 8.63 \cdot 10^{-5} \frac{\text{eV}}{\text{K} \cdot \text{molecule}} \cdot \ln 2 = 5.79 \cdot 10^{-5} \frac{\text{eV}}{\text{K} \cdot \text{molecule}}. \quad (6.3)$$

This gives for the difference in Gibbs's free energy  $\Delta G$  for the two phases at room temperature

$$\Delta S = -298\text{K} \cdot 5.79 \cdot 10^{-5} \frac{\text{eV}}{\text{K} \cdot \text{molecule}} = -0.0173 \frac{\text{eV}}{\text{molecule}}. \quad (6.4)$$

Thus each molecule orders for about two hundredth of an eV preferentially in the racemic mixture at room temperature.

Such racemic mixing is a well known phenomenon. In gaseous and liquid solutions of

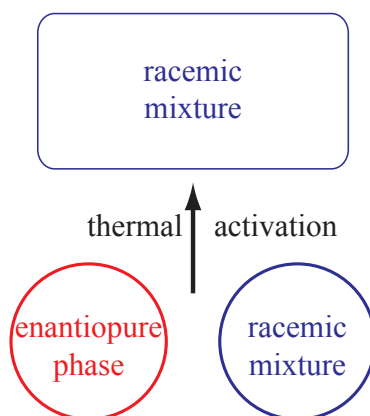
enantiomers, racemic mixtures arise directly and automatically for the above mentioned reason – the higher entropy. For organic crystals, the same phenomenon as described here has been observed. In general the racemic crystallization form is more stable than the enantiomerically pure one. This is known as Wallach's rule[194]. Wallach stated that a racemic crystal is always denser than the enantiopure conglomerate. The explanation for this phenomenon has also been sought in the entropy difference. Dunitz and coworkers investigated a large number of crystals and confirmed Wallach's rule, but they pointed out that the entropy explanation is not valid in that case[195], as it contradicts the third law of thermodynamics, which states that all ordered crystals have zero entropy at 0 K. They propose that the preference of the racemic form are due to additional possibilities for favorable packing arrangements available in racemic space groups. Furthermore Dunitz and coworkers claim that two biases mislead to Wallach's rule. Data may only be available for systems whose racemates are stable enough to exist (thermodynamic bias) and racemates may crystallize easier than conglomerates from racemic media (kinetic bias).

Yu and coworkers investigated the crystallization of several simple amino acids[196] and showed that the racemic crystal was in all cases energetically favorable to the conglomerate crystals. They determined Gibbs's free energy  $G$  of the conglomerate was in all cases higher than for the racemic crystal. This finding strongly supports the entropy argument given here. Vlot and coworkers studied the crystallization of racemic mixtures by means of theory[197] attributing the preferred formation of racemic crystals to their advantageous entropy. I have shown before, that the packing arrangement in both phases,  $P$  and  $H$ , is identical. Thus the argument by Dunitz fails here. Furthermore a submonolayer coverage cannot be compared with a molecular crystal. All these arguments strongly indicate an energetic equivalence of enantiopure and racemic phase. They favor the explanation given here, that the advantage in entropy leads to a preferential formation of the racemic herringbone phase upon thermal activation.

With 4,4'-stilbene-dicarboxylic acid, a stilbene derivative with two anchor groups has been investigated. For the adsorption on Cu(110) two adsorption sites, one along and one almost perpendicular the copper rows have been identified. Both of them were realized by the two adsorption isomers  $\lambda$  and  $\delta$ . Thus a total four different surface isomers exist. Not detected could an adsorption geometry in which the molecules attach in an upright fashion via only one carboxy-group, as it is known from tartaric acid on Cu(110).

With these four isomers two different supramolecular assemblies were identified. A parquet pattern that is constructed from only left- or only right-handed surface isomers, and a herringbone phase constituted from equal amounts of left- and right handed isomers. These two phases do not only behave in an enantiomorphous manner, as each of them exists in two mirror image geometries, but they also represent the two ideal states of isomeric assemblies – enantiomerically pure and racemic mixture.





**Figure 6.23:** *The prochiral molecule forms a left- and a right handed surface enantiomer upon adsorption on Cu(110). These two enantiomers may form either an enantiopure or a racemic supramolecular assembly. Upon thermal activation the molecules show the ideal behavior of chiral entities and undergo racemic mixing.*

As the herringbone pattern is thermodynamically stable and accessible under every experimental condition applied, and the parquet pattern is metastable at lower temperatures all four phases could be imaged simultaneously. Several indications could be found pointing to the fact that herringbone and parquet phase observe the same energy. Adsorption of both isomers,  $\lambda$  and  $\delta$ , is identical and the same hydrogen bonds seem to appear in both supramolecular assemblies. Yet I cannot present an absolute proof for this assumption.

This is the first case, where for a surface supramolecular assembly these two ideal states are detected. Theoretical prediction requires that enantiopure phases undergo racemic mixing, if the isomers are sufficiently mobilized. And indeed this ideal behavior could be detected after thermal activation.

