

8 Summary, Conclusion and Outlook

Three different topics have been covered in this thesis – the photoinduced isomerisation of adsorbed molecules, the handedness of adsorbed prochiral molecules, and the detection of inherent chirality in adsorbates. These have a common denominator, i.e. functionalisation of surfaces through molecules with specific properties.

In the first part of the thesis, the two isomers of stilbene have been investigated. Stilbene is a molecule that has already proven its potential as molecular switch in the gas phase and solution. The goal of my work was the determination whether, and under which conditions, this isomerisation can also be performed on a surface. In order to investigate the isomerisation behavior on the surface, a spectroscopic method allowing for clear identification of both isomers is needed. I could show that the π^* -resonance in NEXAFS is isomer specific. This resonance shows a distinct lineshape, that can clearly be attributed to one of the isomers. This characteristic property is not only present in the gas phase, but remains unperturbed upon adsorption on surfaces. Here Si(100) and Cu(110) have been investigated as exemplary semiconductor and metal substrates. I show that on the semiconductor surface a UV light induced isomerisation is impossible, while the metal surface allows for a partial cis-to-trans isomerisation. NEXAFS investigations, aided by the results from photoelectron spectroscopy, showed that the interaction of the π -system at the C=C bridge of stilbene with the substrate atoms has a direct influence on the isomerisation process. It is known that the isomerisation requires an excitation into the unoccupied bridge orbitals. On Si(100), the bonding of the molecules to the surface takes place via this C=C bridge thereby inhibiting the isomerisation. On Cu(110) this interaction is not directed as on the semiconductor surface. This weaker, diffuse interaction therefore does not inhibit the isomerisation. For different coverages cis-to-trans isomerisation with an overall conversion of about 25% is possible. This is to my knowledge the first time ever, that such a high conversion rate for an adsorbed photocromic switch has been shown. A disadvantage, on the other hand, is the limitation of this pathway. These 25% seem to be the maximum conversion possible (with the UV excitation source used). A trans-to-cis isomerisation, which would be necessary for a reversible and thus usable

switch cannot be induced so far. The molecules as used here seem to prevent this reaction. The comparison of the experimental data with theoretical calculations played an important role in this part of the work. Single molecule DFT calculations, using the Gaussian software package, are sufficient to explain the photoemission results obtained for adsorbed stilbene. The agreement between the binding energies calculated for the molecular orbitals of both isomers and the valence band spectra are remarkably good. On both substrates, the small but distinct differences in the spectra can clearly be assigned to the two isomers with the help of the Gaussian calculations. The StoBe software package was used for the prediction of the NEXAFS spectra. For the gas phase, it was possible to predict the line-shape of the π^* -resonance supporting the experimental findings. This result clearly shows that isomer identification is possible by means of NEXAFS. In the adsorbed phase the predicted results do not agree with the experimental findings. Here the limitations of the software were clearly observable. Nevertheless, the few existing agreements support again the interpretation of the measured data.

Although slight improvements of the isomerisation ability should be possible by the proper choice of the substrate, e.g. the use of passivated surfaces such as H-passivated Si, real advances will only be possible by tailoring the substrate-adsorbate interactions from the molecular side. In order to increase the overall conversion, the switching entity has to be decoupled from the bonding. This may be done by attaching an anchor group to the molecule, i.e. a functional group that bonds preferably to the substrate instead of the stilbene entity.

A large number of possible anchor groups exist. One well investigated is the COOH carboxylic acid group, which bonds in a defined way to copper surfaces. The simplest stilbene with carboxylic endgroups is the disubstituted 4,4'-stilbene-dicarboxylic acid (DCSB). Indeed this molecule adsorbs in a well defined fashion on the Cu(110) surface through the oxygen atoms of the COOH-groups, but only via both endgroups simultaneously. Therefore its ability for isomerisation is inhibited. Due to its Z-like stilbene backbone the molecules may adsorb either in a Z-or in a Δ -manner. These two adsorbates are mirror images to each other and therefore not superimposable. They are adsorption enantiomers, the DCSB molecule is prochiral. In addition to this adsorption handedness, two different adsorption sites could be identified, along and across the Cu rows. Thus in total four different surface isomers exist for DCSB. These isomers give rise to various supramolecular assemblies on the surface. Two of those have been realised with DCSB: a herringbone phase (*H*) and a parquet phase (*P*), both of which exist in a left- and right handed fashion.

In spite of the mere ordering, these two phases beared a number of interesting properties making this system quite unique. I could show, that both phases are energetically equivalent, are based on the same coverage and have the same unit cell. However, the

herringbone phase is constituted from left- and right handed adsorption enantiomers of DCSB, and it is a racemic mixture. The parquet pattern is an enantiomerically pure phase, i.e. consists only of left- or only of right handed molecules. This is the first time that the occurrence of a racemic and an enantiopure adsorption phase has been observed simultaneously.

The coexistence of the *H* and *P* phase is not surprising. Surprisingly instead is the fact, that upon thermal activation the parquet phase vanishes and only the herringbone phase remains. A possible explanation can be found in the different entropy of the phases during formation. Such finding is generally not new, this behavior is well known for liquid and gaseous mixtures. For the crystallization of chiral molecules an entropy driven preference of racemic crystals has been reported. Still no absolute proof for this model could be given here.

The example of DCSB shows how the substrate-adsorbate-interactions can be tailored introducing anchor groups to the adsorbates, and how the interplay between anchor groups and molecular backbone leads to supramolecular assemblies. In this case these adsorbate ensembles showed a behavior not yet demonstrated. With this in mind, it is easy to envision the next steps toward a better optoelectrical switch. A stilbene with only one carboxylic endgroup will most likely stand upright on a copper surface. Using Cu(110) again as substrate, the Cu rows will provide a template for long range ordering. Depending on the C atom of the phenyl group the COOH is attached to, the influence of the anchor onto the π -orbital in the C=C bridge should be tailored. In the para-position, opposite to the bridge, the coupling should be stronger than in the meta-position, i.e. at the C adjacent to the para-position. Also other anchor groups, specific for other substrates, and the introduction of spacers between stilbene and anchor, allow for a large variety of possibilities to improve the isomerisation of adsorbed stilbene. In this work I demonstrate, that the isomerisation is generally possible, and how the choice of substrate-adsorbate interplay has a huge impact on molecular ordering and isomerisation behavior.

An inherently achiral molecule like DCSB can become chiral upon adsorption and form chiral assemblies. Such chiral assemblies can also be realised by the adsorption of chiral molecules. Actually there exist chiral molecules, like tartaric acid, that can adsorb in chiral and achiral adsorption phases, which can also be transformed into each other by means of thermal activation.

Such adsorption phases may act as a heterogeneous catalyst in the synthesis of chiral molecules with high enantiomeric excess. But how can one determine the handedness of adsorbed molecules? Until today there exists no method that allows for the identification of chiral centers without any prior knowledge. Classical methods such as optical rotation can only be interpreted if the relation between geometrical ordering and optical rotation is known. I show that circular dichroism in the core level emission is exactly such a

tool. C1s core level emission provides valuable information about the different atoms in an adsorbate, i.e. the chemical shift in the emission allows not only for distinguishing between the different atoms, but also insight into the interaction of the atoms with the substrate can be gained. The angular dependent circular dichroism, appearing in the emission from the chiral center, provides information about the handedness of this chiral center. Besides this qualitative result, “left handed” or “right handed”, my results indicate that even a quantitative determination of the chirality index might be possible. With the present technique a typical C1s-CD spectrum needs about ten to twelve hours to acquire, and for some molecules, the detected effect is only slightly larger than the spectral noise. But as soon as technology develops and such measurements are easier to accomplish, this method is an extremely versatile tool to investigate chiral surfaces. The chirality of new and unknown molecules could be determined, the transition states and products of asymmetric synthesis could be investigated.

Another interesting experiment, where this method would be of use is the doping of achiral supramolecular assemblies with chiral molecules. For assemblies of achiral meso-tartaric acid and also for assemblies of succinic acid it has been observed, that both form two mirror domains. Upon coadsorption of few mol-% of chiral tartaric acid, a chiral supramolecular assembly can be observed. Whether this is only a reordering and reorientation of the molecules on the surface or indeed induction of chirality, is yet unclear. Our method, as soon as a quantitative analysis will be possible, would be the ideal tool to reveal this question, as the chirality of the molecules could be detected directly.

In this thesis some very fundamental questions were addressed: the substrate-adsorbate interactions and their coupling to the switching entity is determining, whether or not the photoinduced isomerisation can be performed. The “right” substrate minimizes these influences and partial cis-to-trans isomerisation is possible. The introduction of anchor groups tailors the adsorption and also provides fascinating supramolecular assemblies. For the investigations of chiral entities, I demonstrate, that the circular dichroism of C1s core level emission can be used to clearly identify the handedness.