



Preface to the *Surface Science* Topical Issue on *Chirality at Surfaces*



This Topical Issue of *Surface Science* focuses on the rapidly growing interest in the structure and enantioselective properties of chiral surfaces and chiral organic layers on surfaces. Chirality has intrigued scientists since the time of Pasteur and his 1848 [1] demonstration of the relationship between the optical rotation of light and the atomic structure of the compounds through which it propagates. The origin of optical rotation in the structure of organic molecules and the tetrahedral nature of the carbon atom was first appreciated and articulated by van't Hoff in 1874 [2]. In biochemistry, the importance of molecular chirality arises from the fact that most naturally occurring chiral biomolecules exist in homochiral form. For example, the fundamental building blocks of proteins are the amino acids which all appear in the L-enantiomeric form in nature. The implications of biomolecular homochirality were not truly appreciated until the late 1950s [3] when the stereochemistry of the artificially produced drug thalidomide was implicated in the physical defects observed in thousands of children born to mothers who had used the drug during pregnancy. This then sparked an explosion in asymmetric synthesis and enantioselective chemical processing in general, as regulations required that chiral pharmaceuticals be manufactured in enantiomerically pure form. The development of heterogeneous catalysts for industrial-scale production of enantiomerically pure molecules is still a huge challenge. Many of the studies in this Topical Issue are aimed at developing a molecular level understanding of the surface processes which direct enantioselective reactions at gas–solid and liquid–solid interfaces.

Surfaces of materials can also be chiral and, therefore, have enantiospecific interactions with chiral molecules. In fact, there are a number of hypotheses that implicate surfaces in the origin of the homochirality of naturally occurring biomolecules [4]. The greater importance of surfaces lies in their application in numerous forms of chemical processing (catalysis, adsorption, crystallization, etc.) and the potential for chiral surfaces to render these processes enantioselective. The use of state-of-the-art surface characterization techniques and powerful computational methods to study chiral surfaces and their enantiospecific interactions with chiral molecular adsorbates has gained interest relatively recently. The ultimate goal of this body of work is to develop an understanding of the properties of chiral surfaces and of their interactions with chiral adsorbates that can serve as the basis for the design of new chiral materials for new or improved enantioselective chemical processing. The contents of this Topical Issue provide the reader with a broad exposure to the cumulative progress that has been made in the field over the past decade.

In reading the contents of this Topical Issue, it is helpful to appreciate that any study of enantiospecific surface chemistry involves three components: a chiral surface, a chiral molecular adsorbate, and a measurement methodology that can reveal the enantiospecific interactions

between the two. Creating chiral surfaces is relatively straight forward. Adsorption of anything that breaks the existing mirror symmetry of the surface renders it chiral. Even the adsorption of atoms on an achiral, low Miller index crystal plane with mirror symmetry can result in the formation of domains with local chirality. Adsorption of an enantiomerically pure chiral molecule on an achiral surface must impart chirality; either locally or through the formation of an overlayer with long range periodicity that lacks mirror symmetry. Materials such as metals with high symmetry, *achiral* bulk structures can be rendered chiral simply by cleaving them along low symmetry directions. Examples of all of these forms of chiral surfaces can be found in the studies compiled in this issue.

The ultimate goal is the demonstration and understanding of enantiospecific interactions between chiral probe molecules and chiral surfaces. These are the root origins of enantioselectivity. Chiral molecules can be bought commercially in enantiomerically pure form. The challenge is to identify the combination of chiral surface, chiral adsorbate, and methodology that will reveal enantiospecificity. This is compounded by the fact that enantioselectivity is often based on enantiospecific differences in energetics that are only a few kJ mol^{-1} . In other words, enantioselectivity is arguably the most subtle form of chemical selectivity. The reports found herein, document the many creative approaches that have been developed over the past decade and around the world to advance the field from its infancy into the intellectually rich field that it is today. The articles published in this Topical Issue can be divided into five subtopics as follows:

Enantioselectivity

Dependence of the Adsorption of Chiral Compounds on their Enantiomeric Composition – PO and NEA adsorption on Pt(111) depend on the enantiomeric excess in the adsorbed phase.

Enantioselective adsorption on rock-forming minerals: A thought experiment – detection of enantioselective adsorption by a simple adsorption experiment.

Quantitation of Enantiospecific Adsorption on Chiral Nanoparticles from Optical Rotation.

Enantiospecific interactions

Chiral effects in amino acid adsorption on Au(111): A comparison of cysteine, homocysteine and methionine – formation of zwitterions results in significant difference in the heats of formation of homo and heterochiral clusters. Homochiral clusters are more stable than heterochiral ones.

A first-principles study of methyl lactate adsorption on the chiral Cu (643) surface – S/R is bound by 9.5 kJ/mol more than R/R, roughly twice what is observed experimentally.

Contributions of Dispersion Forces to R-3-Methylcyclohexanone Physisorption on Low and High Miller Index Cu Surfaces.

Organizational Chirality Expression as a Function of the Chirality Measure of Simple Amino Alcohols on Cu(100) – several adsorbates create chiral overlayers on Cu(100).

Structure determination of chemisorbed chirality transfer complexes: accelerated STM analysis and exchange-correlation functional sensitivity – chiral interaction of substrates and chiral modifiers.

Chiral structures

Theoretical Modeling of the Formation of Chiral Molecular Patterns in Self-Assembled Overlayers – Study of simple shapes that can pattern to form chiral 2D layers.

Chiral Surface Networks of 3-HPLN – A Molecular Analog of Rounded Triangle Assembly – 3-HPLN forms trimers that assemble into chiral overlayers.

Chiral reconstruction of Cu(110) after adsorption of fumaric acid – rows of Cu adatoms are formed along chiral directions.

On the role of molecular chirality in amino acid self-organization on Cu{311} – Alaninate can form achiral overlayers and chiral overlayers. The chiral overlayers exist at high coverage. Adsorption of the racemate results in the formation of conglomerate domains.

Atomic Layer Deposition of Enantioselective Thin Film of Alumina on Chiral Self-Assembled-Monolayer – prepared chiral alumina films on chiral SAMs.

The templated growth of a chiral transition metal chalcogenide – formed a chiral Cu telluride phase on a Cu(643)R surface.

Chemistry of chiral adsorbates

Chiral Assemblies of Nickel Lysinate via the Corrosive Adsorption of (S)-lysine on Ni/Au{111} – lysine reacts with Ni nanoclusters to form lysinate.

Chiral modification of Ni nanoparticles using Scanning Transmission X-ray Microspectroscopy – tartaric acid undergoes keto-enol tautomerization and does not oxidize the Ni.

Surface Chemistry of Alanine on Cu{111}: Adsorption Geometry and Temperature Dependence – forms alaninate and zwitterion depending upon conditions. Alaninate can be very stable.

Walking-like diffusion of two-footed asymmetric aromatic adsorbates on Pt(111) – TFAP diffuses much more rapidly than R-NEA.

Structure and Decomposition Pathways of D-(–)-Tartaric Acid on Pd(111) – can form either monotartrate or bitartrate species as in Cu.

References

- [1] L. Pasteur, (*Memoir on the relationship which can exist between crystalline form and chemical composition, and on the cause of rotary polarization*), C. R. Acad. Sci. (Paris) 26 (1848) 535.
- [2] J.H. van't Hoff, Arch. Neerl. Sci. Exactes Nat. 9 (1874) 445.
- [3] G.W. Mellin, M. Katzenstein, N. Engl. J. Med. 267 (1962) 1184.
- [4] R.M. Hazen, Cold Spring Harb. Perspect. Biol. 2 (2010) a002162.