Expression and Amplification of Chirality in Two-Dimensional Molecular Crystals Karl-Heinz Ernst*

Karl-Heinz Ernst^{*}
Dedicated to Professor Jack D. Dunitz on the occasion of his 85th birthday

Abstract: Chirality can be bestowed onto achiral surfaces by adsorption of chiral molecules. This offers ^a good hirality can be bestowed onto achiral surfaces by adsorption of chiral molecules. This offers a good
to study two-dimensional chiral crystallization phenomena. like lateral resolution of enantiomers or the t: Chirality can be bestowed onto achiral surfaces by adsorption of chiral molecules. This offers a good
inity to study two-dimensional chiral crystallization phenomena, like lateral resolution of enantiomers or the
of han Abstract: Ch homochirality can be bestowed onto achiral surfaces by adsorption of chiral molecules. This offers a good to study two-dimensional chiral crystallization phenomena, like lateral resolution of enantiomers or the andedness f opi is a new phenomenon of superioristic and the surface chiralization phenomena, like lateral resolution of enantiomers or the inster of handedness from single molecules into mesoscopic ensembles with high resolution by scann transfer of handedness from single molecules into mesoscopic ensembles with high resolution by scanning probe
microscopy. Induction of homochirality on surfaces via cooperatively amplified interactions in molecular monolay microscopy. Induction of homochirality on surfaces *via* cooperatively amplified interactions in molecular monolay-
ers is a new phenomenon of supramolecular surface chirality. Prochiral molecules will turn into either han ers is a new phenomenon of supramolecular surface chirality. Prochiral molecules will turn into either handedness ew phenomenon of suprancorption, but doping with infect is induced by a small eight
fect is induced by a small eight of single lattice chirality. upon adsor similar effect is induced by a small enantiomeric excess. The excess molecules provide the chiral bias that becomes
amplified into single lattice chirality.

Keywords: Chirality · Conglomerates · Crystallization · Enantiomorphism · Scanning tunneling microscopy

1. Introduction

Introduction
his famous experiment in 1848 Pasteur **luction**
mous experiment in 1848 Pasteur
left- and right-handed ammonihis famous experiment in 1848 Pasteur
arated left- and right-handed ammoni-
sodium tartrate crystals manually and In his far mous experiment in 1848 Pasteur
1 left- and right-handed ammoni-
1 m tartrate crystals manually and
0 opposite optical activity for their separated left- and right-handed ammoni-
um sodium tartrate crystals manually and
observed opposite optical activity for their
aqueous solutions.^[1] His insight that the orum sodium tartrate crystals manually and
observed opposite optical activity for their
aqueous solutions.^[1] His insight that the or-
igin of chirality is based on molecular strucobserved opposite optical activity for their
aqueous solutions.^[1] His insight that the or-
igin of chirality is based on molecular struc-
ture laid the foundation of modern structural aqueous solutions.^[1] His insight that the origin of chirality is based on molecular structure laid the foundation of modern structural organic chemistry. Two important details of igin of chirality is based on molecular strucn of chirality is based on molecular structural
e laid the foundation of modern structural
ganic chemistry. Two important details of
experiment actually allowed the manual ture laid the foundation of modern structural
organic chemistry. Two important details of
his experiment actually allowed the manual
separation: i) Handedness was transferred organic chemistry. Two important details of
his experiment actually allowed the manual
separation: i) Handedness was transferred
from the molecular structure to the macro-

Tel.: +41 44 823 43 63
Fax: +41 44 823 40 34

E-mail: Karl.Heinz.Ernst@empa.ch

 $\overline{\cdots}$

-
PD Dr. K.-H. Ernst

shape of the crystal (hemihedrism), pic shape of the crystal (hemihedrism),
ii) the racemate precipitated into a conappe of the crystal (hemihedrism), racemate precipitated into a con-
of homochiral crystals. The unscopic s hape of the crystal (hemihedrism),
he racemate precipitated into a con-
te of homochiral crystals. The un-
mechanisms of both processes are and ii) the racemate precipitated into a conii) the racemate precipitated into a con-
merate of homochiral crystals. The un-
ying mechanisms of both processes are
poorly understood. We are neither able glomerate of homochiral crystals. The un-
derlying mechanisms of both processes are
still poorly understood. We are neither able
to predict the shape of a crystal from moderlying mechanisms of both processes are
still poorly understood. We are neither able
to predict the shape of a crystal from mo-
lecular structure^[2] nor do we know why less still poorly understood. We are neither able
to predict the shape of a crystal from mo-
lecular structure^[2] nor do we know why less
than ten percent of all racemates crystallize to predict the shape of a crystal from mo-
lecular structure^[2] nor do we know why less
than ten percent of all racemates crystallize
into conglomerates.^[3,4] One reason for the lecular structure^[2] nor do we know why less
than ten percent of all racemates crystallize
into conglomerates.^[3,4] One reason for the
difficulty to understand and investigate than ten percent of all racemates crystallize ten percent of all racemates crystallize
conglomerates.^[3,4] One reason for the
ulty to understand and investigate
processes is their cooperative nature. into conglomerates.^[3,4] One reason for the difficulty to understand and investigate these processes is their cooperative nature.
Extremely small structural influences govdifficulty to understand and investigate
these processes is their cooperative nature.
Extremely small structural influences gov-
ern the macroscopic result when they bethese processes is their cooperative nature.
Extremely small structural influences govern the macroscopic result when they become amplified by many cooperating units. Extremely small structural influences govern the macroscopic result when they become amplified by many cooperating units.
Cooperativity among different homochiral ern the macroscopic result when they be-
come amplified by many cooperating units.
Cooperativity among different homochiral
biomolecules is also of fundamental imcome amplified by many cooperating units. in plified by many cooperating units.
tivity among different homochiral
cules is also of fundamental im-
in life.^[5] Furthermore, the transfer Cooperativity among different homochiral ooperativity among different homochiral
omolecules is also of fundamental im-
prtance in life.^[5] Furthermore, the transfer
chirality into mesoscopic structures – a biomolecules is also of fundamental imnolecules is also of fundamental im-
ance in life.^[5] Furthermore, the transfer
hirality into mesoscopic structures – a
important issue in liquid crystal sciporta % and in the (5) Furthermore, the transfer irrality into mesoscopic structures – a important issue in liquid crystal sci-
- is difficult to predict in three dimenof chirality into mesoscopic structures – a
very important issue in liquid crystal sci-
ence – is difficult to predict in three dimen-
sions. More tractable and easier understood very important issue in liquid crystal science – is difficult to predict in three dimensions. More tractable and easier understood are two-dimensional (2D) crystals formed ence – is difficult to predict in three dimensions. More tractable and easier understood are two-dimensional (2D) crystals formed at surfaces, in particular because of the sions. More tractable and easier understood
are two-dimensional (2D) crystals formed
at surfaces, in particular because of the
possibility to study these processes at the are two-dimensional (2D) crystals formed level improvements
in particular because of the
intervel by exploitation of scanning
level by exploitation of scanning at surfaces, in particular because of the
possibility to study these processes at the
molecular level by exploitation of scanning
tunneling microscopy (STM). Different aspossibility to study these processes at the bility to study these processes at the
cular level by exploitation of scanning
eling microscopy (STM). Different as-
of chirality in two-dimensional momolecu lat level by exploitation of scanning
ng microscopy (STM). Different as-
of chirality in two-dimensional mo-
lattices self-assembled on *C*₂ - and tunneling micropects of chiral oscopy (STM). Different as-
ity in two-dimensional mo-
self-assembled on C_{3v} - and
single-crystalline copper pects of chirality in two-dimensional mo-
attices self-assembled on C_{3v} - and
nmetric single-crystalline copper
are reviewed. The examples inlecula ar lattices self-assembled on C_{3v} - and
ymmetric single-crystalline copper
ces are reviewed. The examples in-
monolavers of enantiopure and ra- C_{2v} -symmetric single-crystalline copper
surfaces are reviewed. The examples in-
clude monolayers of enantiopure and ra-
cemic heptahelicene $(C_{20}H_{19})$, a helically surfaces are reviewed. The examples inare reviewed. The examples in-
monolayers of enantiopure and ra-
heptahelicene $(C_{30}H_{18})$, a helically
aromatic hydrocarbon on Cu(111). clude monolayers of enantiopure and ranonolayers of enantiopure and ra-
teptahelicene $(C_{30}H_{18})$, a helically
aromatic hydrocarbon on Cu(111),
tartaric acid on Cu(110) as well as cemic heptahelicene $(C_{30}H_{18})$, a helically
shaped aromatic hydrocarbon on Cu(111),
racemic tartaric acid on Cu(110) as well as
chirally doped *meso*-tartaric acid and sucshaped aromatic hydro
racemic tartaric acid of
chirally doped *meso*-t
cinic acid on Cu(110).

2. Methods and Materials

thods and Materials
adsorbate systems have been inves**thods and Materials**
adsorbate systems have been inves-
under ultra-high vacuum (UHV) forbate systems have been inves-
(p ≈ 10⁻⁸ Pa). The organic All adso probate systems have been inves-
ler ultra-high vacuum (UHV)
($p \approx 10^{-8}$ Pa). The organic
were evaporated from Knudtiga ated under ultra-high vacuum (UHV)
ditions ($p \approx 10^{-8}$ Pa). The organic
mpounds were evaporated from Knud-
cells *in vacuo* onto the conner crystal conditions ($p \approx 10^{-8}$ Pa). The organic
compounds were evaporated from Knud-
sen cells *in vacuo* onto the copper crystal
surfaces at room temperature. The polcompounds were evaporated from Knudsen cells *in vacuo* onto the copper crystal surfaces at room temperature. The polished Cu crystal surfaces (MaTecK) were sen cells *in vacuo* onto the copper crystal *viacuo* onto the copper crystals at room temperature. The pol-
*v*iacuristal surfaces (MaTecK) were
via argon ion bombardment and surfaces at room temperature. The polsubsequent the pol-
i Cu crystal surfaces (MaTecK) were
ned *via* argon ion bombardment and
subsequently annealed at 950 K for ished Cu crystal surfaces (MaTecK) were
cleaned *via* argon ion bombardment and
were subsequently annealed at 950 K for
one minute. Cleanliness and quality of the cleaned *via* argon ion bombardment and
were subsequently annealed at 950 K for
one minute. Cleanliness and quality of the
surfaces and the surface coverage of the were subsequently annealed at 950 K for
one minute. Cleanliness and quality of the
surfaces and the surface coverage of the
adsorbate systems were determined *via* Xone minute. Cleanliness and quality of the
surfaces and the surface coverage of the
adsorbate systems were determined *via* X-
ray photoelectron spectroscopy (XPS), low surfaces and the surface coverage of the
adsorbate systems were determined *via* X-
ray photoelectron spectroscopy (XPS), low
energy electron diffraction (LEED), temadsorbate systems were determined via Xthe systems were determined *via* X-
oelectron spectroscopy (XPS), low
electron diffraction (LEED), tem-
programmed desorption (TPD) ray photoelectron spectroscopy (XPS), low photoelectron spectroscopy (XPS), low
rgy electron diffraction (LEED), tem-
ature programmed desorption (TPD)
STM. TPD curves were acquired with energy electron diffraction (LEED), temnergy electron diffraction (LEED), tem-
erature programmed desorption (TPD)
nd STM. TPD curves were acquired with
heating rate of $4 K s^{-1}$ using a quadrupole perat Fraure programmed desorption (TPD)
STM. TPD curves were acquired with
ting rate of 4 K s^{-1} using a quadrupole
spectrometer as detector. Synthesis and STM. TPD curves were acquired with
a heating rate of 4 K s^{-1} using a quadrupole
mass spectrometer as detector. Synthesis
and enantiomeric separation ($ee > 99.9\%$) a heating rate of 4 K s⁻¹ using a quadrupole
mass spectrometer as detector. Synthesis
and enantiomeric separation (ee > 99.9%)
of heptahelicene (171H) was performed mass spectrometer as detector. Synthesis
and enantiomeric separation ($ee > 99.9\%$)
of heptahelicene ([7]H) was performed
as described previously.^[6] The absolute and enantiomeric separation (ee > 99.9%)
of heptahelicene ([7]H) was performed
as described previously.^[6] The absolute
configuration was assigned to a high of heptahelicene ([7]H) was performed
as described previously.^[6] The absolute
configuration was assigned to a high
level of confidence by comparison of exas described previously.^[6] The absolute configuration was assigned to a high level of confidence by comparison of experimental and calculated VCD spectra.^[7] configuration was assigned to a high puration was assigned to a high
of confidence by comparison of ex-
ental and calculated VCD spectra.^[7]
photoelectron diffraction studies level of confidence by comparison of exof confidence by comparison of ex-
ental and calculated VCD spectra.^[7]
photoelectron diffraction studies
of (*M*)-[7]H on the stepped Cu(332) perimental and calculated VCD spectra.^[7]
X-ray photoelectron diffraction studies
(XPD) of (M) -[7]H on the stepped Cu(332)
surface also confirmed this assignment.^[8] X-ray photoelectron diffraction studies photoelectron diffraction studies
of (M) -[7]H on the stepped Cu(332)
also confirmed this assignment.^[8]
acid $(R.S$ -, $R.R$ -, $S.S$ - & racemate) (XPD) of (M) -[7]H on the stepped Cu(332) PD) of (M) -[7]H on the stepped Cu(332)
face also confirmed this assignment.^[8]
taric acid (*R*,*S*-, *R*,*R*-, *S*,*S*- & racemate)
succinic acid were purchased from Alsurface also confirmed this assignment.^[8]
Tartaric acid (*R*,*S*-, *R*,*R*-, *S*,*S*- & racemate)
and succinic acid were purchased from Al-
drich and Merck with purities better than Tartaric acid $(R,S₋, R,R₋, S,S₋ &$ racemate) ric acid $(R, S-, R, R-, S, S-$ & racemate)
uccinic acid were purchased from Al-
and Merck with purities better than
STM images were acquired in conand succinic acid were purchased from Alacid were purchased from Al-
erck with purities better than
mages were acquired in con-
mode with the sample slowly drich and Merck with purities better than
99%. STM images were acquired in constant-current mode with the sample slowly
cooled to 50 K. Molecular modeling cal-99%. STM images were acquired in constant-current mode with the sample slowly cooled to 50 K. Molecular modeling calculations (MMC) were performed using

<u>ndence:</u>
PD Dr. K
Surface Science **Formance:**
Formance: PD Dr. K.-H. Ernst
Surface Science
for Nanoscale Materials Science – Suppondence: PD Dr. K.-H. Ernst

Sular Surface Science

atory for Nanoscale Materials Science

– Swiss Federal Laboratories for Materials Molecular Surface Science pensence:

Ilar Surface Sc

tory for Nanos

- Swiss Federa

and Research Mondalandstrasse 125

Empa – Swiss Feder

Testing and Researc

Überlandstrasse 125 Empa - Swiss Federal Laboratories for Materials Swiss Feder
Swiss Feder
Ind Researc
Dübendorf Enting and Research
Testing and Research
Überlandstrasse 125
CH-8600 Dübendorf
and University of Zürich Überlandstrasse 125 dstrasse 125
0 Dübendorf
versity of Zürich
of Organic Chemistry CH-8600 Dübendorf َ
f
irich
190 and University of Zürich ersity o
pf Orga
urerstra
Zürich and University of Zanc
Institute of Organic Cr
Winterthurerstrasse 19
CH-8057 Zürich
Tel.: +41 44 823 43 63 Winterthurerstrasse 190 CH-8057 Zürich

 AMBER force field of the Hyperchem ne AMBE
package. **3.1.**

3. Results and Discussion

Transfer of Handedness from read Discussion
*2015 and Discussion
<i>2D Crystals*
Molecules into 2D Crystals **nnsfer of Handedness from
Molecules into 2D Crystals**
enantiomers at surfaces form in $3.1.$ **Transfer of Handedness from

re Molecules into 2D Crystals**

ure enantiomers at surfaces form in

cases 2D enantiomorphous struc-**Single Molecules into 2D Crystals**

ie Molecules into 2D Crystals
ture enantiomers at surfaces form in
cases 2D enantiomorphous struc-
in close-packed monolavers.^[9] That Pure enantiomers at surfaces form in
ost cases 2D enantiomorphous struc-
res in close-packed monolayers.^[9] That
chirality is transferred from the single most cases 2D enantiomorphous structures in close-packed monolayers.^[9] That
is, chirality is transferred from the single
molecule into a long-range chiral motif at tures in close-packed monolayers.^[9] That es in close-packed monolayers.^[9] That
chirality is transferred from the single
lecule into a long-range chiral motif at
surface. The created motifs are mirror is, chirality is transferred from the single
molecule into a long-range chiral motif at
the surface. The created motifs are mirror
images for the opposite enantiomers. One molecule into a long-range chiral motif at
the surface. The created motifs are mirror
images for the opposite enantiomers. One
example are the pure [7]H enantiomers on the surface. The created motifs are mirror α r The created motifs are mirror
the opposite enantiomers. One
e the pure [7]H enantiomers on
Close to monolaver saturation. images for the opposite enantiomers. One
e are the pure [7]H enantiomers on
).^[10] Close to monolayer saturation,
pinwheel structures are observed *via* example are the pure [7]H enantiomers on ple are the pure [7]H enantiomers on
11).^[10] Close to monolayer saturation,
ed pinwheel structures are observed *via*
(Fig 1a,b). The (*M*)-[7]H-pinwheels $Cu(1)$ 11).^[10] Close to monolayer saturation,
led pinwheel structures are observed *via*
I (Fig 1a,b). The (*M*)-[7]H-pinwheels
the opposite handedness to the (*P*)-[7] handed pinwh heel structures are observed *via*,

b, D. The (*M*)-[7]H-pinwheels

site handedness to the (*P*)-[7]

In addition, at full monolaver STM (Fig 1a,b). The (M) -[7]H-pinwheels
have the opposite handedness to the (P) -[7]
H-pinwheels. In addition, at full monolayer
coverage 'three-molecule-cloverleaf' units have the opposite handedness to the (*P*)-[7]
H-pinwheels. In addition, at full monolayer
coverage "three-molecule-cloverleaf" units
show opposite tilt angles with respect to the H-pinwheels. In addition, at full monolayer rels. In addition, at full monolayer

"three-molecule-cloverleaf" units

osite tilt angles with respect to the

lattice unit cell (Fig 1c,d). In all coverage 'three-molecule-cloverleaf' units
show opposite tilt angles with respect to the
adsorbate lattice unit cell (Fig 1c,d). In all
cases, the adsorbate lattice is aligned in an show opposite tilt angles with respect to the posite tilt angles with respect to the
te lattice unit cell (Fig 1c,d). In all
he adsorbate lattice is aligned in an
angle to the underlying substrate adsorbate lattice unit cell (Fig 1c,d). In all
cases, the adsorbate lattice is aligned in an
oblique angle to the underlying substrate
lattice. Especially this latter mode of excases, the adsorbate lattice is aligned in an
oblique angle to the underlying substrate
lattice. Especially this latter mode of ex-
pression of chirality in ordered adsorbate oblique angle to the underlying substrate angle to the underlying substrate
Especially this latter mode of ex-
a of chirality in ordered adsorbate
is a common phenomenon.^[9,11] lattice. Es pecially this latter mode of ex-
of chirality in ordered adsorbate
s a common phenomenon.^[9,11]
modeling calculations (MMC) pression of chirality in ordered adsorbate on of chirality in ordered adsorbate
ns is a common phenomenon.^[9,11]
ular modeling calculations (MMC)
that these structures are governed by systei ms is a common phenomenon.^[9,11]
cular modeling calculations (MMC)
I that these structures are governed by
constraints. The lowest-energy struc-Molecular modeling calculations (MMC)
reveal that these structures are governed by
steric constraints. The lowest-energy struc-
ture for the close-packed monolaver (Fig. reveal that these structures are governed by eal that these structures are governed by
ric constraints. The lowest-energy struc-
e for the close-packed monolayer (Fig.
d) delivers identical adsorption sites for steric constraints. The lowest-energy strucric constraints. The lowest-energy struc-
re for the close-packed monolayer (Fig.
, d) delivers identical adsorption sites for
molecules of the unit cell. Their respecture for the close-packed monolayer (Fig. 1c, d) delivers identical adsorption sites for all molecules of the unit cell. Their respective azimuthal orientations, however, are 1c, d) delivers identical adsorption sites for
all molecules of the unit cell. Their respec-
tive azimuthal orientations, however, are
different and depend strongly on the sign all molecules of the unit cell. Their respec-I molecules of the unit cell. Their respec-
ve azimuthal orientations, however, are
fferent and depend strongly on the sign
indicity of the molecules, so that oppotive azimuthal orientations, however, are Exercise example a critical orientations, however, are
ferent and depend strongly on the sign
nelicity of the molecules, so that oppo-
lattice enantiomorphism is observed for different and depend strongly on the sign
of helicity of the molecules, so that oppo-
site lattice enantiomorphism is observed for
the enantiomers. Assuming that the brightof helicity of the molecules, so that opposite lattice enantiomorphism is observed for
the enantiomers. Assuming that the bright-
est features of the STM images reflect the site lattice enantiomorphism is observed for
the enantiomers. Assuming that the bright-
est features of the STM images reflect the
off-centered topmost part of the molecular the enantiomers. Assuming that the bright-
est features of the STM images reflect the
off-centered topmost part of the molecular
helix, the MMC-structure in Fig. 1e agrees est features of the STM images reflect the eatures of the STM images reflect the entered topmost part of the molecular
is, the MMC-structure in Fig. 1e agrees
with the experimentally observed off-centered topmost part of the molecular entered topmost part of the molecular, the MMC-structure in Fig. 1e agrees with the experimentally observed structure in Fig. 1c.^[10] Similar to the helix, the MMC-structure in Fig. 1e agrees
the experimentally observed
cture in Fig. 1c.^[10] Similar to the
lattice structures observed for well with the experimentally observed
ture in Fig. 1c.^[10] Similar to the
lattice structures observed for
polymers of single helicity, *e.g.* STM structure in Fig. 1c.^[10] Similar to the frustrated lattice structures observed for crystalline polymers of single helicity, *e.g.* isotactic poly(propylene).^[12] not all helices frustrated lattice structures observed for strated lattice structures observed for stalline polymers of single helicity, e.g. actic poly(propylene), $[12]$ not all helices be aligned 'in phase'. This shows that, crystalline polymers of single helicity, $e.g.$ the polymers of single helicity, e.g.
poly(propylene), $[12]$ not all helices
ligned 'in phase'. This shows that,
the packing is mediated by the Cu isotactic poly(propylene),^[12] not all helices
igned 'in phase'. This shows that,
the packing is mediated by the Cu
grid, the 'one-pitch' [7]H helices can be aligned 'in phase'. This shows that,
although the packing is mediated by the Cu
substrate grid, the 'one-pitch' [7]H helices
follow the same sterically controlled packalthough the packing is mediated by the Cu rules are particles is mediated by the Custrate grid, the 'one-pitch' [7]H helices low the same sterically controlled pack-
rules as extended helical molecules in substrate grid, the 'one-pitch' [7]H helices
follow the same sterically controlled pack-
ing rules as extended helical molecules in
3D crystals. [7]H on Cu(111) is therefore follow the same sterically controlled pack-
ing rules as extended helical molecules in
3D crystals. [7]H on Cu(111) is therefore
an example for short-range sterically coning rules as extended helical molecules in
3D crystals. [7]H on Cu(111) is therefore
an example for short-range sterically con-
trolled supramolecular self-assembly medi-3D crystals. [7]H on Cu(
an example for short-rang
trolled supramolecular self
ated by the surface lattice. **3.2.** *Racemic Crystals versus*
3.2. *Racemic Crystals versus* trolled supramolecular self-assembly medi-

Conglomerates **Racemic Crystals versus
glomerates
has been predicted that two-dimen-**3.2. Racemic Crystals versus

**Racemic Crystals versus

Reflomerates**

has been predicted that two-dimen-

enantiomeric resolution on a surface **Sumerates**

has been predicted that two-dimen-

enantiomeric resolution on a surface

occur more easily than in 3D crys-It has been predicted that two-dimensional enantiomeric resolution on a surface
should occur more easily than in 3D crys-
tals. Due to confinement in the plane cersional enantiomeric resolution on a surface al enantiomeric resolution on a surface
uld occur more easily than in 3D crys-
Due to confinement in the plane cer-
symmetry elements, *e.g.* the center of should occur more easily than in 3D crys-
tals. Due to confinement in the plane cer-
tain symmetry elements, *e.g.* the center of
inversion or the glide plane parallel to the tals. Due to confinement in the plane certain symmetry elements, $e.g.$ the center of inversion or the glide plane parallel to the surface, are precluded and enhanced chiral

(a-d) High-resolution STM images (10 nm x 10 nm) of (M) - and (P) -[7]H structures. The tive adlattices (red unit cells) have opposite tilt angles with respect to the substrate lattice arrow). (M) -[7]H forms at 91% of th Fig. 1. (a-d) High-resolution STM images (10 nm x 10 nm) of (*M*)- and (*P*)-[7]H structures. The ective adlattices (red unit cells) have opposite tilt angles with respect to the substrate lattice w arrow). (*M*)-[7]H forms at respective adlattices (red unit cells) have opposite tilt angles with respect to the substrate lattice adlattices (red unit cells) have opposite tilt angles with respect to the substrate lattice ow). (*M*)-[7]H forms at 91% of the saturated monolayer clockwise rotated pinwheels (a), there clockwise rotated pinwheels are ob (yellow arrow). (M)-[7]H forms at 91% of the saturated monolayer clockwise rotated pinwheels (a), rrow). (M)-[7]H forms at 91% of the saturated monolayer clockwise rotated pinwheels (a),
unterclockwise rotated pinwheels are observed *via* STM for (P)-[7H] (b). For the saturated
pr lattices, opposite tilt angles of clov while monolayer lattices, opposite tilt angles of cloverleaf clusters with respect to the adlattice are observed, indicated by red triangles in the unit cells, (c,d). (e) Model for the M-[7]H cloverleaf structure obtained
from M

 $\overline{\mathbf{r}}$ enantiomorphism is achieved via alignment of heteroch hism is achieved *via* alignment of he
are expected. For lateral resobeen determined *via* high-resolution
been determined *via* high-resolution [7]H on Cu(111). Superposition of the molecular orientation and STM imag of the mirror domains $(\lambda \& \rho)$ of the highest coverage structure. The observis achieved *via* alignment of heterochiral pairs in opposite chiral co

 $\frac{1}{\pi}$ ctions are expected. For lateral reso-
of [7]H on Cu(111), this should lead teractions are expected. For lateral resotion of [7]H on $Cu(111)$, this should lead the same structures as observed for the interactions are expected. For lateral resolution of [7]H on $Cu(111)$, this should lead
to the same structures as observed for the
isolated enantiomers. However, racemic [7] lution of [7]H on Cu(111), this should lead
to the same structures as observed for the
isolated enantiomers. However, racemic [7]
H forms a heterochiral lattice structure (Fig. to the same structures as observed for the ılat Exercise as observed for the ed enantiomers. However, racemic [7] ms a heterochiral lattice structure (Fig. Nevertheless, mirror domains are obisolated enantiomers. However, racemic [7]
H forms a heterochiral lattice structure (Fig.
2).^[13] Nevertheless, mirror domains are ob-
served *via* LEED and STM.^[6b,13] Overall. H forms a heterochiral lattice structure (Fig. 2).^[13] Nevertheless, mirror domains are observed *via* LEED and STM.^[6b,13] Overall, three pairs of enantiomorphous structures. 2).^[13] Nevertheless, mirror domains are observed *via* LEED and STM.^[6b,13] Overall, three pairs of enantiomorphous structures, denoted as ε/δ . λ'/ρ ' and λ/ρ , successively served via LEED and STM.^[6b,13] Overall, ed *via* LEED and STM.^[6b,13] Overall,

pairs of enantiomorphous structures,

ted as ϵ/δ , λ'/ρ : and λ/ρ , successively

with increasing coverage.^[14] All these three pairs of enantiomorphous structures, is of enantiomorphous structures,
is ϵ/δ , λ'/ρ : and λ/ρ , successively
increasing coverage.^[14] All these
have a common feature in that denoted as ε/δ , λ'/ρ : and λ/ρ , successively
form with increasing coverage.^[14] All these
adlattices have a common feature in that
the molecules are aligned in zigzag double form with increasing coverage.^[14] All these
adlattices have a common feature in that
the molecules are aligned in zigzag double
rows. The lattice structure of the λ/ρ phase

 $\frac{1}{100}$ been determined *via* high-resolution
in combination with extended Hückel determined *via* high-resolution
nbination with extended Hückel
as well as MMC (Fig. 2). The has been determ ined *via* high-resolution
ion with extended Hückel
ell as MMC (Fig. 2). The
is based on two possible STM in alignment combination with extended Hückel
ions as well as MMC (Fig. 2). The
morphism is based on two possible
alignments of the two enantiosimulations as well as MMC (Fig. 2). The lations as well as MMC (Fig. 2). The
tiomorphism is based on two possible
ive alignments of the two enantio-
in a heterochiral pair on the surface. enantiomorphism is based on two possible
relative alignments of the two enantio-
mers in a heterochiral pair on the surface.
A glide plane along [IT0] interconverts relative alignments of the two enantio-
mers in a heterochiral pair on the surface.
A glide plane along [IT0] interconverts
the two enantiomers, but is not a symmemers in a heterochiral pair on the surface.
A glide plane along [IT0] interconverts
the two enantiomers, but is not a symme-
try element of a single domain lattice. It is A glide plane along [IT0] interconverts
the two enantiomers, but is not a symme-
try element of a single domain lattice. It is
noteworthy here that chiral expression at the two enantiomers, but is not a symmeenantiomers, but is not a symme-
ent of a single domain lattice. It is
thy here that chiral expression at
requires a minimum of mobility of try element of a single domain lattice. It is
noteworthy here that chiral expression at
surfaces requires a minimum of mobility of
the molecules. At nickel surfaces with their noteworthy here that chiral expression at surfaces requires a minimum of mobility of
the molecules. At nickel surfaces with their
higher affinity to [7]H, for example, no dif-

 for pure enantiomers and racemate hees for pure enanti-
been observed.^[15] the case of pure enantiomers and racemate
been observed.^[15]
the case of different local molecular ferences for pure enantiomers and racemate
have been observed.^[15]
In the case of different local molecular
adsorption geometries, lateral interactions have been observed.[15]

been observed.^[15]
in the case of different local molecular
rption geometries, lateral interactions
substantially for a single compound In the case of different local molecular n the case of different local molecular
rption geometries, lateral interactions
substantially for a single compound
possible consequences for 2D enantioadsorption geometries, lateral interactions
vary substantially for a single compound
with possible consequences for 2D enantio-
meric resolution. This has been shown for vary substantially for a single compound bstantially for a single compound
ssible consequences for 2D enantio-
ssolution. This has been shown for
tartaric acid (TA) on Cu(110).[16] with possible consequences for 2D enantio-
meric resolution. This has been shown for
racemic tartaric acid (TA) on Cu(110).^[16]
Depending on temperature and/or covermeric resolution. This has been shown for ic resolution. This has been shown for
mic tartaric acid (TA) on $Cu(110).$ ^[16]
ending on temperature and/or cover-
TA forms different lattice structures on racemic tartaric acid (TA) on Cu(110).^[16]
Depending on temperature and/or cover-
age, TA forms different lattice structures on
the surface.^[17] In particular, if one or both Depending on temperature and/or coveron temperature and/or cover-
ms different lattice structures on
 $[17]$ In particular, if one or both
groups react with the copper age, TA forms different lattice structures on
the surface.^[17] In particular, if one or both
carboxylate groups react with the copper
surface, bitartrate or monotartrate species the surface.^[17] In particular, if one or both surface.^[17] In particular, if one or both poxylate groups react with the copperace, bitartrate or monotartrate species be present, respectively. For (R, R) -TA, carboxylate groups react with the copper
surface, bitartrate or monotartrate species
will be present, respectively. For (R,R) -TA,
bitartrate species have been identified only surface, bitartrate or monotartrate species will be present, respectively. For (R,R) -TA, after thermal activation at lower coverage.^[17] be present, respectively. For (R,R) -TA,
trate species have been identified only
thermal activation at lower coverage.^[17]
increasing coverage, however, newbitartrate species have been identified only
after thermal activation at lower coverage.^[17]
With increasing coverage, however, new-
ly adsorbed TA molecules hydrogenate er thermal activation at lower coverage. [17]
th increasing coverage, however, new-
adsorbed TA molecules hydrogenate
doubly deprotonated bitartrate spe-With increasing coverage, however, newto increasing coverage, however, new-
adsorbed TA molecules hydrogenate
doubly deprotonated bitartrate spe-
to monotartrate again.^[17] Besides this ly ads orbed TA molecules hydrogenate
why deprotonated bitartrate spe-
monotartrate again.^[17] Besides this
in local adsorption geometry, an the doubly depi rotonated bitartrate spe-
ate again.^[17] Besides this
adsorption geometry, an
(9 0, 1 2) bitartrate latcies to monotartrate again.^[17] Besides this
change in local adsorption geometry, an
enantiomorphous (9 0, 1 2) bitartrate lat-
tice undergoes a phase transition into a change in local adsorption geometry, an ange in local adsorption geometry, an antiomorphous $(9\ 0, 1\ 2)$ bitartrate lat-
ce undergoes a phase transition into a
0, 2 1) lattice.^[18] Interestingly, this latenantiomorphous (9 0, 1 2) bitartrate latntiomorphous $(9 \t 0, 1 \t 2)$ bitartrate lat-
undergoes a phase transition into a
 $(0, 2 \t 1)$ lattice.^[18] Interestingly, this lat-
has only the substrate symmetry.*i.e.* no tice undergoes a phase transition into a
(4 0, 2 1) lattice.^[18] Interestingly, this lat-
tice has only the substrate symmetry, *i.e.* no
chirality is expressed at the supramolecular (4 0, 2 1) lattice.^[18] Interestingly, this lattice has only the substrate symmetry, *i.e.* no chirality is expressed at the supramolecular level. With further exposure to enantiopure tice has only the substrate symmetry, *i.e.* no
chirality is expressed at the supramolecular
level. With further exposure to enantiopure
TA, a slightly denser (4 1, 2 5) structure is chirality is expressed at the supramolecular $^{\prime\prime}$ ith expressed at the supramolecular
i further exposure to enantiopure
ntly denser (4 1, 2 5) structure is
This structure breaks again the level. With further exposure to enantiopure
slightly denser $(4\ 1, 2\ 5)$ structure is
 d ₁[17] This structure breaks again the
symmetry of the underlying copper TA, a slightly denser $(4\ 1, 2\ 5)$ structure is whitly denser $(4\ 1, 2\ 5)$ structure is
^{7]} This structure breaks again the
mmetry of the underlying copper
i.e. it is enantiomorphous. For formed. [17] This structure breaks again the symmetry of the underlying copper
e, *i.e.* it is enantiomorphous. For
TA, on the other hand, a 2D conmirror symmetry of the underlying copper
substrate, *i.e.* it is enantiomorphous. For
racemic TA, on the other hand, a 2D con-
glomerate is observed only for the bitartrate substrate, *i.e.* it is enantiomorphous. For e, *i.e.* it is enantiomorphous. For
TA, on the other hand, a 2D con-
te is observed only for the bitartrate
where homochiral $(9 \t0, 1 \t0)$ and racemic TA, on the other hand, a 2D concemic TA, on the other hand, a 2D con-
omerate is observed only for the bitartrate
ecies, where homochiral $(9\ 0, 1\ 2)$ and
 $(0,-1\ 2)$ domains coexist on the surface.^[16] glomerate is observed only for the bitartrate
species, where homochiral $(9\ 0, 1\ 2)$ and
 $(9\ 0, -1\ 2)$ domains coexist on the surface.^[16]
The corresponding LEED pattern shows a species, where homochiral $(9, 0, 1, 2)$ and e homochiral (9 0, 1 2) and
nains coexist on the surface.^[16]
nding LEED pattern shows a
of both structures (Fig. 3). (90) $r,-1$ 2) domains coexist on the surface.^[16]
corresponding LEED pattern shows a
erposition of both structures (Fig. 3).
racemate forms a $(40.2 1)$ monotartrate The corresponding LEED pattern shows a esponding LEED pattern shows a
ition of both structures (Fig. 3).
mate forms a (40, 21) monotartrate
as well, but in contrast to the pure superposition of both structures (Fig. 3).
The racemate forms a $(40, 21)$ monotartrate
structure as well, but in contrast to the pure
enantiomers, this is the monolaver satura-The racemate forms a $(40, 21)$ monotartrate
structure as well, but in contrast to the pure
enantiomers, this is the monolayer satura-
tion structure. This difference in achievable structure as well, but in contrast to the pure
enantiomers, this is the monolayer satura-
tion structure. This difference in achievable
packing density for pure enantiomer and enantiomers, this is the monolayer saturation structure. This difference in achievable packing density for pure enantiomer and racemate is a strong indication that the two tion structure. This difference in achievable
packing density for pure enantiomer and
racemate is a strong indication that the two
(4 0, 2 1) structures must be different. For a packing density for pure enantiomer and
racemate is a strong indication that the two
 $(4\ 0, 2\ 1)$ structures must be different. For a
conglomerate of coexisting $(4\ 0, 2\ 1)$ mirracemate is a strong indication that the two
(4 0, 2 1) structures must be different. For a
conglomerate of coexisting (4 0, 2 1) mir-
ror domains, further exposure to racemic $(40, 21)$ structures must be different. For a conglomerate of coexisting $(40, 21)$ mirror domains, further exposure to racemic TA should lead – equivalent to the enantioconglomerate of coexisting $(4, 0, 2, 1)$ mirglomerate of coexisting $(4 \ 0, 2 \ 1)$ mir-
domains, further exposure to racemic
hould lead – equivalent to the enantio-
case – to coexisting $(4 \ 1, \pm 2 \ 5)$ mirror ror domains, further exposure to racemic d lead – equivalent to the enantio-
 $t = -1$ to coexisting (4 1, ± 2 5) mirror

This difference is evidence for a TA should l ead – equivalent to the enantioto coexisting $(4 \, 1, \pm 2 \, 5)$ mirror
is difference is evidence for a
 $(4 \, 0, 2 \, 1)$ racemate lattice, not pure case – to coexisting $(41, \pm 25)$ mirror
domains. This difference is evidence for a
heterochiral $(40, 21)$ racemate lattice, not
allowing additional inclusion of TA moldomains. This difference is evidence for a
heterochiral (4 0, 2 1) racemate lattice, not
allowing additional inclusion of TA mol-
ecules. The lower thermal stability of the heterochiral $(40, 21)$ racemate lattice, not terochiral $(4\ 0, 2\ 1)$ racemate lattice, not
lowing additional inclusion of TA mol-
ules. The lower thermal stability of the
 $0.2\ 1)$ racemate structure with respect to allowing additional inclusion of TA molecules. The lower thermal stability of the (4 0, 2 1) racemate structure with respect to the same structure of enantiopure TA supecules. The lower thermal stability of the (4 0, 2 1) racemate structure with respect to the same structure of enantiopure TA supports this scenario.^[19] Monotartrate decom- $(40, 21)$ racemate structure with respect to 2 1) racemate structure with respect to
the structure of enantiopure TA sup-
this scenario.^[19] Monotartrate decom-
upon heating into carbon dioxide. the same structure of enantiopure TA supme structure of enantiopure TA sup-
his scenario.^[19] Monotartrate decom-
upon heating into carbon dioxide,
carbon and hydrogen on Cu(110). ports this scenario.^[19] Monotartrate decomposes upon heating into carbon dioxide, water, carbon and hydrogen on Cu(110).
The stability of monotartrate is substantialposes upon heating into carbon dioxide, beses upon heating into carbon dioxide,
ater, carbon and hydrogen on Cu(110).
he stability of monotartrate is substantial-
enhanced due to the close-packed monowater, carbon and hydrogen on Cu(110).
The stability of monotartrate is substantial-
ly enhanced due to the close-packed mono-
laver structure, not allowing interaction of The stability of monotartrate is substantial-
ly enhanced due to the close-packed mono-
layer structure, not allowing interaction of
upper parts of the molecule with the surface ly enhanced due to the close-packed mono-
layer structure, not allowing interaction of
upper parts of the molecule with the surface
in the first place. Consequently, the CO₂ TPD signal, reflecting the decomposition
reaction, shifts to higher temperatures with
increasing coverage (Fig. 3). Moreover, this
reaction is catalyzed by free surfaces sites. layer structure, not allowing interaction of structure, not allowing interaction of
tr parts of the molecule with the surface
e first place. Consequently, the CO_2
signal. reflecting the decomposition upper parts of the molecule with the surface rts of the molecule with the surface
rst place. Consequently, the $CO₂$
nal, reflecting the decomposition
shifts to higher temperatures with in the first place. Consequently, the $CO₂$ TPD signal, reflecting the decomposition reaction, shifts to higher temperatures with increasing coverage (Fig. 3). Moreover, this reaction, shifts to higher temperatures with
increasing coverage (Fig. 3). Moreover, this
reaction is catalyzed by free surfaces sites.
Since the decomposition. in turn. creates ac-

on
OD sites, the raceinate $(4, 0, 2, 1)$ monotarized structure.
Sites, the reaction is under autocatalytic \mathfrak{c} . \mathfrak{c} . \mathfrak{c} . \mathfrak{c} 8 K for the racemate (4 0, 2 1) monotartrate structure compared to the 3. LEED patterns and TPD curves for (R, R) -TA (bottom) and racemic
top). At 405 K, (R, R) -TA forms a (9 0, 1 2), a (4 0, 2 1) (not shown here)
a (4 1, 2 5) structure with increasing coverage. For the racemate a Fig. 3. LEED patterns and TPD curves for (R, R) -TA (bottom) and racemic
05 K, (R, R) -TA forms a (9 0, 1 2), a (4 0, 2 1) (not shown here)
1.5) structure with increasing coverage. For the racemate a
1.6 of the mirror-related (9 0, 1 2) **TA** a (top). At 405 K, (R, R) -TA forms a (9 0, 1 2), a (4 0, 2 1) (not shown here) d a (4 1, 2 5) structure with increasing coverage. For the racemate a perposition of the mirror-related (9 0, 1 2) and (9 0, -1 2) domains as and a (4 1, 2 5) structure with increasing coverage. For the racemate a d a $(4 \t1, 2 \t5)$ structure with increasing coverage. For the racemate a berposition of the mirror-related $(9 \t0, 1 \t2)$ and $(9 \t0, -1 \t2)$ domains as well a $(4 \t0, 2 \t1)$ structure are observed. The arrows point at th superposi for the mirror-related $(9 0, 1 2)$ and $(9 0, -1 2)$ domains as well
the and pure enantiomers is identical, it is lower by the bitartrate
for racemate and pure enantiomers is identical, it is lower by a s a (4 0, 2 1) structure are observed. The arrows point at the TPD traces for
ne respective lattice structures. While the thermal stability of the bitartrate
tructures for racemate and pure enantiomers is identical, it is *f*the respective lattice structures. While structures for racemate and pure enable K for the racemate (4 0, 2 1) monotartrate structure.

s, ϵ , ϵ , is isomorphical that the state attack to com-
Upon heating, this leads to comdecomposition is under autocatalytic
col. Upon heating, this leads to com-
decomposition in a very narrow temtive sites, the reaction is under autocatalytic
control. Upon heating, this leads to com-
plete decomposition in a very narrow tem-
perature interval (2 K) once the reaction has control. Upon heating, this leads to com-Equivalent Upon heating, this leads to com-
ecomposition in a very narrow tem-
e interval $(2 K)$ once the reaction has
because the gaseous decomposition plete decomposition in a very narrow tem-
perature interval (2 K) once the reaction has
started, because the gaseous decomposition
products desorb instantaneously at decomperature interval $(2 K)$ once the reaction has i interval $(2 K)$ once the reaction has
because the gaseous decomposition
s desorb instantaneously at decom-
temperature and a sharp pressure started, because the gaseous decomposition ted, because the gaseous decomposition
ducts desorb instantaneously at decom-
ition temperature and a sharp pressure
is observed. This is shown in Fig. 3 for product $\mathbf i$ position Solution instantaneously at decom-

i temperature and a sharp pressure

bserved. This is shown in Fig. 3 for

product. Interestingly, the decomposition temperature and a sharp pressure
rise is observed. This is shown in Fig. 3 for
 $CO₂$ as product. Interestingly, the decom-
position temperature for the enantiopure rise is observed. This is shown in Fig. 3 for se is observed. This is shown in Fig. 3 for O_2 as product. Interestingly, the decom-
sition temperature for the enantiopure 0. 2 1) structure exceeds the one for the $CO₂$ as product. Interestingly, the decomposition temperature for the enantiopure (4 0, 2 1) structure exceeds the one for the same racemic structure by 8 K. This higher temperature for the enantiopure
(1) structure exceeds the one for the cemic structure by $8 K$. This higher
is explained by a supramolecular $(4\ 0, 2\ 1)$ structure exceeds the one for the same racemic structure by 8 K. This higher stability is explained by a supramolecular chiral ensemble effect. The initial decomsame racemic structure by 8 K. This higher
stability is explained by a supramolecular
chiral ensemble effect. The initial decom-
position step requires a rearrangement of stability is explained by a supramolecular
chiral ensemble effect. The initial decom-
position step requires a rearrangement of
the upper part of the molecule in order to chiral ensemble effect. The initial decom-
position step requires a rearrangement of
the upper part of the molecule in order to
reach for the surface in a densely packed position step requires a rearrangement of requires a rearrangement of
the molecule in order to
surface in a densely packed
The difference in handedthe upper part of the molecule in order to upper part of the molecule in order to
the for the surface in a densely packed
ronment. The difference in handed-
of adiacent molecules affects the exreach for the surface in a densely packed
environment. The difference in handed-
ness of adjacent molecules affects the ex-
tended H-bonding network of enantiopure environment. The difference in handedness of adjacent molecules affects the ex-
tended H-bonding network of enantiopure
and racemic lattices and has consequences ness of adjacent molecules affects the ex-
tended H-bonding network of enantiopure
and racemic lattices and has consequences
for this initial 'unhinging' process. Hence, tended H-bonding network of enantiopure
and racemic lattices and has consequences
for this initial 'unhinging' process. Hence,
the lower thermal stability is due to more and racemic lattices and has consequences
for this initial 'unhinging' process. Hence,
the lower thermal stability is due to more
heterogeneous bonding and leads again to for this initial 'unhinging' process. Hence,
the lower thermal stability is due to more
heterogeneous bonding and leads again to
the conclusion that the racemate forms a the lower thermal stability is due to more
heterogeneous bonding and leads again to
the conclusion that the racemate forms a
heterochiral (4 0, 2 1) monotartrate lattice. heterogeneous bonding and leads again to
the conclusion that the racemate forms a
heterochiral (4 0, 2 1) monotartrate lattice.
Consequently, the coexisting homochiral

ne compared to the
0, \pm 1 2) bitartrate domains show the same 2) bitartrate domains show the same
stability as the (R,R) -(9 0, 1 2) bi-2) bitartrate doma
1 stability as the (*i* structure (Fig. 3). **3.3.** $A \neq 1$ 2) bitartrate domains show the smal stability as the (R,R) - $(9\ 0, 1\ 2)$ ate structure (Fig. 3).
Adsorption-induced Chirality t artrate structure (Fig. 3). icture (Fig. 3).
rption-induced Chirality
molecules can become chiral

$3.3.$ Ads

Adsorption-induced Chirality
chiral molecules can become chiral
adsorption, either due to asymmetric **orption-induced Chirality**
al molecules can become chiral
orption, either due to asymmetric
of the molecular frame or just Achiral molecules can become chiral
upon adsorption, either due to asymmetric
distortion of the molecular frame or just
because of an adsorbate complex devoid upon adsorption, either due to asymmetric
distortion of the molecular frame or just
because of an adsorbate complex devoid
of mirror symmetry.^[9] However, all addistortion of the mole molecular frame or just
dsorbate complex devoid
netry.^[9] However, all adbecause of an adsorbate complex devoid
of mirror symmetry.^[9] However, all ad-
sorption-induced chirality processes have
in common that both enantiomers will be of mirror symmetry.^[9] However, all adfrom symmetry.^[9] However, all ad-
n-induced chirality processes have
mon that both enantiomers will be
as long as no further bias for single sorption-induced chirality processes have
in common that both enantiomers will be
created as long as no further bias for single
handedness is present. At a global level. in common that both enantiomers will be
created as long as no further bias for single
handedness is present. At a global level,
the surface remains achiral, but at a local created as long as no further bias for single
handedness is present. At a global level,
the surface remains achiral, but at a local
level, spontaneous symmetry breaking is a handedness is present. At a global level, the surface remains achiral, but at a local level, spontaneous symmetry breaking is a common phenomenon. As for intrinsically the surface remains achiral, but at a local reface remains achiral, but at a local
spontaneous symmetry breaking is a
non phenomenon. As for intrinsically
molecules, the induced local chirality level, spontaneous symmetry breaking is a wel, spontaneous symmetry breaking is a
mmon phenomenon. As for intrinsically
iral molecules, the induced local chirality
cadsorbed molecules is often transferred common phenomenon. As for intrinsically
chiral molecules, the induced local chirality
of adsorbed molecules is often transferred
into the adlattice, which is then aligned in chiral molecules, the induced local chirality
of adsorbed molecules is often transferred
into the adlattice, which is then aligned in
an oblique angle with respect to the subof adsorbed molecules is often transferred
into the adlattice, which is then aligned in
an oblique angle with respect to the sub-
strate lattice. Again, these enantiomorinto the adlattice, which is then aligned in
an oblique angle with respect to the sub-
strate lattice. Again, these enantiomor-
phous structures are then easily observed an oblique angle with respect to the sub-
strate lattice. Again, these enantiomor-
phous structures are then easily observed
via LEED. We note that mirror domains strate lattice. Again, these enantiomorphous structures are then easily observed *via* LEED. We note that mirror domains may be created with no chiral adsorbate phous structures are then easily observed
via LEED. We note that mirror domains
may be created with no chiral adsorbate
complex involved, because the optimal *via* LEED. We note that mirror domains may be created with no chiral adsorbate complex involved, because the optimal packing arrangement breaks the symmetry

the underlying substrate lattice.^[9,20] For and erlying substrate lattice.^[9,20] For
and (*S*,*S*)-bitartrate a zigzag distorthe underlying substrate lattice.^[9,20] I

(*S*,*S*)-bitartrate a zigzag dist

was determined experimentally. of the underlying substrate lattice.^[9,20] For mderlying substrate lattice.^[9,20] For
and (S,S) -bitartrate a zigzag distor-
as determined experimentally.^[21]
functional theory (DFT) calcula- (R,R) - and (S,S) -bitartrate a zigzag distor-- and (S, S) -bitartrate a zigzag distor-
was determined experimentally.^[21]
ity functional theory (DFT) calcula-
however, also predict a chiral zigtion was determined experimentally.^[21]
Density functional theory (DFT) calcula-
tions, however, also predict a chiral zig-
zag conformation after deprotonation of Density functional theory (DFT) calculasity functional theory (DFT) calcula-
s, however, also predict a chiral zig-
conformation after deprotonation of
carboxyl groups for achiral (*R*,*S*)-TA tions, howeve Fr, also predict a chiral zig-
ation after deprotonation of
l groups for achiral (R, S) -TA
acid) and succinic acid (SU) zag conformation after deprotonation of g conformation after deprotonation of
th carboxyl groups for achiral (R,S) -TA
eso-tartaric acid) and succinic acid (SU)
Cu(110).^[22] Experimental observations both carboxyl groups for achiral (R,S) -TA (*meso*-tartaric acid) and succinic acid (SU) on Cu(110).^[22] Experimental observations of long-range enantiomorphous patterns (*meso*-tartaric acid) and succinic acid (SU) *neso*-tartaric acid) and succinic acid (SU)
i Cu(110).^[22] Experimental observations
i long-range enantiomorphous patterns
connection with reasonable molecular on $Cu(110).$ ^[22] Experimental observations 10).^[22] Experimental observations
range enantiomorphous patterns
ection with reasonable molecular
considerations indeed suggest of long-range enantiomorphous patterns
in connection with reasonable molecular
structure considerations indeed suggest
a chiral geometry for (*R*,*S*)-bitartrate and in connection with reasonable molecular ion with reasonable molecular
considerations indeed suggest
ometry for (R, S) -bitartrate and
on Cu(110).^[23,24] Because the structure o considerations indeed suggest
cometry for (R, S) -bitartrate and
e on Cu(110).^[23,24] Because the
of generating both enantiomora chiral geometry for (R, S) -bitartrate and al geometry for (R, S) -bitartrate and
tinate on Cu(110).^[23,24] Because the
bility of generating both enantiomor-
lattices is identical, two-dimensional bisuccinate on c Cu(110).^[23,24] Because the generating both enantiomor-
is identical, two-dimensional are formed. *i.e.* all molecules probability of generating both enantiomor-
phous lattices is identical, two-dimensional
conglomerates are formed, *i.e.* all molecules
in a single domain of the adlattice have the phous lattices is identical, two-dimensional
conglomerates are formed, *i.e.* all molecules
in a single domain of the adlattice have the
same chirality. As in the case of racemic biconglomerates are formed, *i.e.* all molecules merates are formed, *i.e.* all molecules
gle domain of the adlattice have the
iirality. As in the case of racemic bi-
both mirror structures are observed in a single domain of the adlattice have the a single domain of the adlattice have the
me chirality. As in the case of racemic bi-
trate, both mirror structures are observed
the LEED pattern, provided that the size same chirality. As in the case of racemic bitartrate, both mirror structures are observed
in the LEED pattern, provided that the size
of the probing electron beam is larger than tartrate, both mirror structures are observed rate, both mirror struck
the LEED pattern, pro
the probing electron b
average domain size. In the LEED pattern, provided that
of the probing electron beam is laithe average domain size.
3.4. *Amplification of Chirality* the average domain size. erage domain size.
mplification of Chirality
shown above, adsorption-induced

3.4. Amplification of Chirality

polification of Chirality
shown above, adsorption-induced
creates a bistable system. Addi-**Amplification of Chirality**
s shown above, adsorption-induced
ity creates a bistable system. Addi-
chiral bias, however, may suppress As shown above, adsorption-induced
ality creates a bistable system. Addi-
al chiral bias, however, may suppress
state if the barrier of interconversion chirality creates a bistable system. Additional chiral bias, however, may suppress
one state if the barrier of interconversion
is not too high. The coadsorption of chitional chiral bias, however, may suppress nal chiral bias, however, may suppresse state if the barrier of interconversion
not too high. The coadsorption of chi-
molecules into such racemic lavers is one state if the barrier of interconversion e state if the barrier of interconversion
not too high. The coadsorption of chi-
l molecules into such racemic layers is
efficient way to induce further asymis not too i high. The coadsorption of chi-
les into such racemic layers is
t way to induce further asym-
towards single handedness. A ral molecules into such racemic layers is becules into such racemic layers is
ficient way to induce further asym-
zation towards single handedness. A
amount of a chiral impurity can be an efficient way to induce further asymmetrization towards single handedness. A small amount of a chiral impurity can be sufficient for induction of homochirality metrization towards single handedness. A
small amount of a chiral impurity can be
sufficient for induction of homochirality
on the entire surface! SU on Cu(110), for small amount of a chiral impurity can be sufficient for induction of homochirality on the entire surface! SU on $Cu(110)$, for example, switches from one handedness to sufficient for induction of homochirality ficient for induction of homochirality
the entire surface! SU on $Cu(110)$, for
umple, switches from one handedness to
other in its bisuccinate phase when the on the entire surface! SU on $Cu(110)$, for is expressed above 500 cm Cu(110), for vitches from one handedness to its bisuccinate phase when the is raised above 500 K. Coolexa mple, switches from one handedness to
other in its bisuccinate phase when the
pperature is raised above 500 K. Cool-
down such laver after doping with one the other in its bisuccinate phase when the
temperature is raised above 500 K. Cool-
ing down such layer after doping with one
TA enantiomer completely suppresses the temperature is raised above 500 K. Cooling down such layer after doping with one
TA enantiomer completely suppresses the
formation of one mirror domain and installs ing down such layer after doping with one
TA enantiomer completely suppresses the
formation of one mirror domain and installs
global homochirality.^[25] This process is il-TA enantiomer complet tiomer completely suppresses the
n of one mirror domain and installs
omochirality.^[25] This process is il-
in Fig. 4. Consequently, the oppoformation of one mirror domain and installs mation of one mirror domain and installs
bal homochirality.^[25] This process is il-
rated in Fig. 4. Consequently, the oppo-
TA-enantiomer suppresses the opposite global homochirality.[25] T his process is il-
uently, the oppo-
sses the opposite
easily detectable lustrated in Fig. 4. Consequently, the opposite TA-enantiomer suppresses the opposite
SU enantiomorph, which is easily detectable
in LEED (Fig. 4). Only 2% of chiral dopant site TA-enantiomer suppresses the opposite te TA-enantiomer suppresses the opposite
U enantiomorph, which is easily detectable
LEED (Fig. 4). Only 2% of chiral dopant
necessary to install global homochirality. SU enantiomorph, which is easily detectable
in LEED (Fig. 4). Only 2% of chiral dopant
is necessary to install global homochirality.
Smaller amounts of dopant lead to a lower in LEED (Fig. 4). Only 2% of chiral dopant
is necessary to install global homochirality.
Smaller amounts of dopant lead to a lower
intensity of the diffraction spots of the less is necessary to install global homochirality.
Smaller amounts of dopant lead to a lower
intensity of the diffraction spots of the less
favored enantiomorphous lattice. A similar Smaller amounts of dopant lead to a lower
intensity of the diffraction spots of the less
favored enantiomorphous lattice. A similar
effect – coined as the sergeant-and-soldiers intensity of the diffraction spots of the less of the diffraction spots of the less

enantiomorphous lattice. A similar

coined as the sergeant-and-soldiers

– has been observed for helical favored enantiomorphous lattice. A similar
effect – coined as the sergeant-and-soldiers
principle – has been observed for helical
polymers where a small concentration of $effect$ – coined as the sergeant-and-soldiers ined as the sergeant-and-soldi
- has been observed for heli
where a small concentration
chains induced single helicity. principle – has been observed for helical chiral side chains induced single helicity.[26] iple – has been observed for helical
ners where a small concentration of
side chains induced single helicity.^[26]
hydrogen bonds between the bisucpolymers where a small concentration of
chiral side chains induced single helicity.^[26]
Since hydrogen bonds between the bisuc-
cinate molecules as a means of transferring de chains induced single helicity.^[26]
cdrogen bonds between the bisuc-
olecules as a means of transferring
can safely be excluded, one must Since hydrogen bonds between the bisucrefrequent bonds between the bisuc-
olecules as a means of transferring
can safely be excluded, one must
a substrate-mediated mechanism. cinate molecules as a means of transferring
chirality can safely be excluded, one must
consider a substrate-mediated mechanism.
That is, a chiral footprint in the surface chirality can safely be excluded, one must
consider a substrate-mediated mechanism.
That is, a chiral footprint in the surface
acts as a chiral bias and suppresses oppoconsider a substrate-mediated mechanism. sider a substrate-mediated mechanism.
ht is, a chiral footprint in the surface
is as a chiral bias and suppresses oppo-
handedness in the adiacent adsorbate That is, a chiral footprint in the surface a chiral footprint in the surface
chiral bias and suppresses oppo-
ledness in the adjacent adsorbate
This explains the amplification of acts as a chiral bias and suppresses opposite handedness in the adjacent adsorbate
complex. This explains the amplification of
the preferred handedness due to chiral dopsite handedness in the adjacent adsorbate handedness in the adjacent adsorbate
plex. This explains the amplification of
preferred handedness due to chiral dop-
The TA sergeant has only one kind of complex. This explains the amplification of
the preferred handedness due to chiral dop-
ing: The TA sergeant has only one kind of
a chiral footprint, forcing adjacent SU molthe preferred handedness due to chiral dop-
ing: The TA sergeant has only one kind of
a chiral footprint, forcing adjacent SU mol-
ecules into similar configuration. These.

homochirality in the entire 2D crystal. Electron beam energies and the Cu(110) lattice orientation are indicated ^ρ domain-pair-alignment. This chiral bias Sergeant-and-soldiers principle at surfaces revealed by LEED: Prochiral SU and (R,S)-TA riglomerates at the surface and both mirror domains are observed as superposition in the diffraction experiment (first column). Doping Fig. 4. Serge electron diffraction experiment (first column). Doping with chiral TA provides the chiral bias inducing form conglomerates at the surface and both mirror domains are observed as superposition in the

 turn, force their SU neighbors into the rn, force their SU neighbors into the
configuration for energetic reasons. m, force their SU neighbors into the configuration for energetic reasons.
achiral (R,S) -TA becomes chiral on in turn, force their SU neighbors into the
same configuration for energetic reasons.
Since achiral (R, S) -TA becomes chiral on
Cu(110) as well, this type of homochiralsame configuration for energetic reasons.
Since achiral (R, S) -TA becomes chiral on
Cu(110) as well, this type of homochiral-
ity induction can be likewise observed after Since achiral (R, S) -TA becomes chiral on achiral (R, S) -TA becomes chiannolation (*R*,*R*)-TA doping (Fig. 4).^[27] (110) as well, this type of homochiral-
induction can be likewise observed after
 S)- or (R,R) -TA doping (Fig. 4).^[27]
In contrast to the chiral doping mechaity induction can be likewise observed after (S, S) - or (R, R) -TA doping (Fig. 4).^[27]
In contrast to the chiral doping mechanism. a small enantiomeric excess *(ee*) (S, S) - or (R, R) -TA doping (Fig. 4).^[27]

b- or (R,R) -TA doping (Fig. 4).^[27] n contrast to the chiral doping mech n, a small enantiomeric excess (also induce lattice homochirality. ha-In contrast to the chiral doping mechanism, a small enantioneric excess (ee)
y also induce lattice homochirality.^[28]
mentioned above, the heterochiral nism, a small enantiomeric excess (ee) , a small enantiomeric excess (ee) also induce lattice homochirality.^[28] mentioned above, the heterochiral of [7]H on Cu(111) may exist in two may also induce lattice homochirality.^[28] As mentioned above, the heterochiral pairs of [7]H on Cu(111) may exist in two enantiomorphous states due to two pos-As mentioned above, the heterochiral pairs of [7]H on Cu(111) may exist in two enantiomorphous states due to two possible alignment on the Cu(111) surface. pairs of $[7]$ H on Cu(111) may exist in two
enantiomorphous states due to two pos-
sible alignment on the Cu(111) surface.
The chiral bias from a small *ee* is sufficient enantiomorphous states due to two posnantiomorphous states due to two pos-
ble alignment on the $Cu(111)$ surface.
he chiral bias from a small *ee* is sufficient
order to suppress formation of one unsible alig mirror on the Cu(111) surface.
I bias from a small ee is sufficient
to suppress formation of one un-
mirror domain and induces ho-The chiral bias from a small ee is sufficient lation at to suppress to
to suppress the mirror dom
lattice order. for mall *ee* is sufficient
mation of one un-
and induces ho-
Because of strong in order to suppress formation of one un-
favorable mirror domain and induces ho-
mochiral lattice order.^[13] Because of strong
steric constraints, any *ee* is expelled from favorable mirror domain and induces ho-
mochiral lattice order.^[13] Because of strong
steric constraints, any *ee* is expelled from
the racemic enantiomorphous domains mochiral lattice order.^[13] Because of strong
steric constraints, any *ee* is expelled from
the racemic enantiomorphous domains
during crystallization. From the domain steric constraints, any *ee* is expelled from
the racemic enantiomorphous domains
during crystallization. From the domain
edges, however, the excess molecules have the racemic enantiomorphous domains
during crystallization. From the domain
edges, however, the excess molecules have
an influence on the relative alignment of during crystallization. From the domain edges, however, the excess molecules have an influence on the relative alignment of the heterochiral pairs at the domain edge. edges, however, the excess molecules have wever, the excess molecules have
nce on the relative alignment of
ochiral pairs at the domain edge.
excess favors formation of λ doan influence on the relative alignment of fluence on the relative alignment of
eterochiral pairs at the domain edge.
[7]H excess favors formation of λ do-
pairs and *(P*)-[7]H excess favors the

domain-pair-alignment. This chiral bias
then amplified by the cooperative internain-pair-alignment. This chiral bias
a amplified by the cooperative inter-
among heterochiral pairs, strongly p domain-pair-alignment. This chiral bias
is then amplified by the cooperative inter-
action among heterochiral pairs, strongly
favoring their equal alignment. Like heis then amplified by the cooperative inter-
action among heterochiral pairs, strongly
favoring their equal alignment. Like he-
lix reversals in a polymer chain, oppoaction among heterochiral pairs, strongly From a mong heterochiral pairs, strongly
poring their equal alignment. Like he-
reversals in a polymer chain, oppo-
alignment would create energetically favoring their equal alignment. Like heeir equal alignment. Like he-
s in a polymer chain, oppo-
ent would create energetically
mirror domain boundaries. lix reversals in a polymer chain, opposite alignment would create energetically unfavorable mirror domain boundaries.
Even for the pure racemate, these boundaries. site alignment would create energetically
unfavorable mirror domain boundaries.
Even for the pure racemate, these boundaries are rarely observed on single Cu(111) unfavorable mirror domain boundaries.
Even for the pure racemate, these boundaries are rarely observed on single Cu(111)
terraces. Hence, spontaneous symmetry Even for the pure racemate, these boundaries are rarely observed on single Cu(111) terraces. Hence, spontaneous symmetry breaking is observed without chiral bias ies are rarely observed on single $Cu(111)$ For a single Cu(111)

Faces. Hence, spontaneous symmetry

eaking is observed without chiral bias

a smaller scale, but the probability for terraces. Hence, spontaneous symmetry
breaking is observed without chiral bias
on a smaller scale, but the probability for
 λ and ρ domain decorated terraces is equal. breaking is observed without chiral bias
on a smaller scale, but the probability for
 λ and ρ domain decorated terraces is equal.
At $ee = \pm 0.08$ the entire surface – although on a smaller scale, but the probability for λ and ρ domain decorated terraces is equal.
At $ee = \pm 0.08$ the entire surface – although still close to racemic content – is already λ and ρ domain decorated terraces is equal.
At $ee = \pm 0.08$ the entire surface – although still close to racemic content – is already driven into a homochiral arrangement dur-At $ee = \pm 0.08$ the entire surface – although $ee = \pm 0.08$ the entire surface – although
1 close to racemic content – is already
ven into a homochiral arrangement dur-
2D crystallization and only one of either still clc is to racemic content – is already
into a homochiral arrangement dur-
crystallization and only one of either
is observed (Fig. 5). In contrast to driven into a homochiral arrangement durven into a homochiral arrangement dur-
 *(*2D crystallization and only one of either main is observed (Fig. 5). In contrast to SU/TA-doped and (*R*,*S*)-TA/TA doped ing 2D crystallization and only one of either
domain is observed (Fig. 5). In contrast to
the SU/TA-doped and (R,S)-TA/TA doped
systems, where the molecular frame of the domain is observed (Fig. 5). In contrast to
the SU/TA-doped and (R,S) -TA/TA doped
systems, where the molecular frame of the
molecule is switched to its mirror configuthe SU/TA-doped and (R, S) -TA/TA doped
systems, where the molecular frame of the
molecule is switched to its mirror configu-
ration. interconversion between both strucsystems, where the molecular frame of the
molecule is switched to its mirror configuration, interconversion between both struc-
tures requires only a change in relative pomolecule is switched to its mirror configucule is switched to its mirror configu-
i, interconversion between both struc-
requires only a change in relative po-
of both enantiomers of a heterochiral ration, interconversion between both structures requires only a change in relative position of both enantiomers of a heterochiral pair. The TA-doped systems are truly ho-

Fig. 5. STM images (200 nm x 200 nm) of [7]H on Cu(111) with increasing enantiomeric exc
ee = 0.08 only a single mirror domain type (λ) can exist on the surface. The excess (grey area) is e
from the heterochiral domain, a *ee* = 0.08 only a single mirror domain type (λ) can exist on the surface. The excess (grey area) is expelled ee = 0.08 only a single mirror domain type (λ) can exist on the surface. The excess (grey area) is expelled

 $\overline{}$

eterochiral domain, and with increasin
i.e. all molecules have the same e. all molecules have the same
The *ee*-bias-amplified [7]H/ I, *i.e.* all molecules have the same
ess. The *ee*-bias-amplified [7] $H/$
system, however, is still of heteromoch iral, *i.e.* all molecules have the same
dness. The *ee*-bias-amplified [7] $H/$
11) system, however, is still of hetero-
composition, but possesses a lattice handedness. 7 The *ee*-bias-amplified [7] H , nowever, is still of hetero-
ition, but possesses a lattice
In order to observe this ee- $Cu(111)$ system, however, is still of hetero-
chiral composition, but possesses a lattice
homochirality. In order to observe this ee-
effect. lateral resolution of the enantiomers chiral composi
homochirality.
effect, lateral r
is not allowed.

4. Summary the

Immary
two-dimensional molecular systems **Summary**
In two-dimensional molecular systems
consequences of cooperativity are well*v* dimensional molecular systems
 via STM or surface diffraction In tw o-dimensional molecular systems
quences of cooperativity are well-
via STM or surface diffraction
Long-range chiral motifs are the con sequences of cooperativity are well-
ed *via* STM or surface diffraction
ls. Long-range chiral motifs are
after adsorption of chiral molecules observed via STM or surface diffraction betweed *via* STM or surface diffraction
ethods. Long-range chiral motifs are
rmed after adsorption of chiral molecules
due to spontaneous symmetry breaking \overline{m} ethods. Long-range chiral motifs are
transled after adsorption of chiral molecules
due to spontaneous symmetry breaking
prochiral molecules. Additional chiral formed after adsorption of chiral molecules ned after adsorption of chiral molecules
we to spontaneous symmetry breaking
prochiral molecules. Additional chiral
due to chiral impurities (dopant) or or due to spontaneous symmetry breaking
of prochiral molecules. Additional chiral
bias due to chiral impurities (dopant) or
small enantiomeric excess leads via coopof prochiral molecules. Additional chiral
bias due to chiral impurities (dopant) or
small enantiomeric excess leads via coop-
erative amplification to homochirality in bias due to chiral impus
mall enantiomeric exce
erative amplification to
the 2D molecular lattice. the 2D molecular lattice. lecular lattice.
dgement
- by the Schweizerischer National-

Acknowledgement

is grated in the Schweizerisch and Schwei e Schweizerischer National-
acknowledged.
Received: February 15, 2008

- L. Pasteur, *Ann. Chim. Phys.* **¹⁸⁴⁸**, *²⁴*, 442. J. D. Dunitz, *Chem. Commun.* **²⁰⁰³**, 545. L. Pasteur, Ann
- L. Pasteur, *Ann. Chim. Phys.* **1848**, 24, 442.
J. D. Dunitz, *Chem. Commun.* **2003**, 545.
J. Jacques, A. Collet, S. H. Wilen. J.D.I
- n. Chim. Phys. **1848**, 24, 442.
Chem. Commun. **2003**, 545.
A. Collet, S. H. Wilen,
Racemates and Resolu-'Enantiomers, Racemates and Resolu-J. Jacqu res, A. Colle
mers, Racema
Krieger Publ
Florida. **1994**. Enantiomers, Racemates and Resolutions', Krieger Publishing Company,
Malabar, Florida, 1994.
C. P. Brock. W. B. Schweitzer. J. D. tions', Krieger Publishing Company,
Malabar, Florida, **1994**.
C. P. Brock, W. B. Schweitzer, J. D.
Dunitz, *J. Am. Chem. Soc.* **1991**. 113. Malabar, Florida, 1994.
- [4] C. P. Brock, W. B. Schweitzer, J. D. C. P. Brock, W. B. Schweitzer,
Dunitz, *J. Am. Chem. Soc.* **1991**
9811.
J. S. Siegel. *Nature* **2001**, 409, 777. Dunitz, *J. Am. Chem. Soc.* **1991**, *113*,
9811.
J. S. Siegel, *Nature* **2001**, *409*, 777.
a) A. Sudharkar. T. J. Katz. *Tetrahedron Lett.*
- J. S. Siegel, Nature 2001, 409, 777.
- 9811.
J. S. Siegel, *Nature* **2001**, 409, 777.
a) A. Sudharkar, T. J. Katz, *Tetrahedron*
Lett. **1986**, 27. 2231: b) K.-H. Ernst, Y. egel, *Nature* 2001, 409, 777.
Sudharkar, T. J. Katz, *Tetrahedron*
986, 27, 2231; b) K.-H. Ernst, Y.
R. Fasel. M. Müller. U. Ellerbeck. dharkar, T. J. 1
26, 27, 2231; t.
2001, 13, 675. *Lett.* **1986**, 27, 2231; b) K.-H. Ernst, Y.
Kuster, R. Fasel, M. Müller, U. Ellerbeck,
Chirality **2001**, 13, 675.
T. Bürgi, A. Urakawa, B. Behzadi, K.-H. Kuster, R. Fasel, M. Müller, U. Ellerbeck, *R. Fasel, M. Müller, U. Ellerbeck,*
lity **2001**, *13*, 675.
rgi, A. Urakawa, B. Behzadi, K.-H.
A. Baiker. *New J. Chem.* **2004**. 28. Chirality 2001, 13, 675.
- $[7]$ T. Bürgi, A. Urakawa, B. Behzadi, K.-H.
Ernst, A. Baiker, *New J. Chem.* **2004**, 28, 332.
R. Fasel. A. Cossy. K.-H. Ernst. F. Ernst, A. Ba iker, *New J. Chem.* **2004**, 28,
A. Cossy, K.-H. Ernst, F.
T. Greber. J. Osterwalder. *J. Chem.*
- *Phys.* **A.** Cossy, K.-H.
Phys. **2001**, *115*, 1020. [9]R. Fasel, A. Cossy, K.-H. Ernst, F.
Baumberger, T. Greber, J. Osterwalder, *J. Chem. Phys.* **2001**, *115*, 1020.
K.-H. Ernst. *Top. Curr. Chem.* **2006**. 265. Baumberger, T. Greber, J. Osterwalder, J.
- Chem. Phys. **2001**, 115, 1020.
K.-H. Ernst, *Top. Curr. Chem.* **2006**, 265,
209.
R. Fasel. M. Parschau, K.-H. Ernst. *A.* -H. Ernst, *Top. Curr. Chem. 2006, 265,*
209.
*R. Fasel, M. Parschau, K.-H. Ernst,
<i>Angew. Chem.. Int. Ed. 2003, 42, 5178; Angew.*
- *Chem.* **²⁰⁰³**, *¹¹⁵*, 5336. [10] R. Fasel, M. Parschau, K.-H. Ernst, R. Fasel, M. Parschau, K.-H. Ernst,
Angew. Chem., Int. Ed. **2003**, 42, 5178;
Angew. Chem. **2003**, 115, 5336.
S. M. Barlow , R. Raval. *Surf. Sci. Rep. Angew. Chem.*
Angew. Chem.
S. M. Barlow
2003, 50, 201.
- *Angew. Chem.* **2003**, 115, 5336.

S. M. Barlow , R. Raval, *Surf. Sci. Rep.*
 2003, 50, 201.

W. Stocker. M. Schumacher. S. Graff. [11] S. M. Barlow, R. Raval, Surf. Sci. Rep. M. Barlow, R. Raval, Surf. Sci. Rep.
03, 50, 201.
Stocker, M. Schumacher, S. Graff, Thierry. J. C. Wittmann, B. Lotz. **2003**, 50, 201.
- **1998**, *31*, 807.
- R. Fasel, M. Parschau, K.-H. Ernst, *Nature 439*, 449. R. Fasel, M. Parschau, K.-H. Ernst, *Nature*
2006, 439, 449.
M. Parschau. R. Fasel. K.-H. Ernst. *Cryst.* **R**. Fase *A D. M. Parschau, K.-H. E*
39, 449.
chau, R. Fasel, K.-H. I.
& Des. **2008**. in print.
- **2006**, 439 , 449 .
M. Parschau, R. Fasel, K.-H. Ernst, *Cryst.*
Growth & Des. **2008**, in print.
a) K.-H. Ernst. Y. Kuster. R. Fasel. C. F. M. Parscha u, R. Fasel, K.-H. Ernst, *Cryst.*
Des. **2008**, in print.
rnst, Y. Kuster, R. Fasel, C. F.
U. Ellerbeck. *Surf. Sci.* **2003**. *Growth & Des.* 2008, in print.
- *Nth & Des.* **2008**, in print.
[.-H. Ernst, Y. Kuster, R. Fasel, C. F.
²dden, U. Ellerbeck, *Surf. Sci.* **2003**, *195*: b) K.-H. Ernst. M. Neuber, M. a) $K.H$ Ernst, Y. Kuster, R. Fasel, C. F.
Ien, U. Ellerbeck, *Surf. Sci.* **2003**,
5; b) K.-H. Ernst, M. Neuber, M.
U. Ellerbeck. *J. Am. Chem. Soc.* McFadden, U.
530, 195; b) K
Grunze, U. Elle
2001, 123, 493. 530, 195; b) K.-H. Ernst, M. Neuber, M.
Grunze, U. Ellerbeck, *J. Am. Chem. Soc.*
2001, 123, 493.
S. Romer. B. Behzadi. R. Fasel. K.-H. Grunz *Chem. Eur. Eur. Eur. <i>Eur. Eur. Eur. Eur. L.* **2005**. *I1*, 4149. *Chem. Eur. J.* **2005**. *I1*, 4149.
- **2001**, 123, 493.
S. Romer, B. Behzadi, R. Fasel, K.-H.
Ernst, *Chem. Eur. J.* **2005**, 11, 4149.
M. Ortega Lorenzo. S. Haq. T. Bertrams. P.Romer, B. Behzadi, R. Fasel, K.-H.
rnst, *Chem. Eur. J.* **2005**, *11*, 4149.
I. Ortega Lorenzo, S. Haq, T. Bertrams,
Murray, R. Raval. C. J. Baddeley. *J. Phys.*
- *Chem. ^B* **1999,** *103,* 10661. [17] M. Ortega Lorenzo, S. Haq, T. Bertrams, M. Ortega Lorenzo, S. Haq, T. Bertrams,
P. Murray, R. Raval, C. J. Baddeley, J.
Phys. Chem. B **1999,** 103, 10661.
The expression in parentheses stands for P. Murray, R. Raval, C. J. Baddeley, *J.*
ys. *Chem. B* **1999,** 103, 10661.
e expression in parentheses stands for
2x2 transformation matrix connecting Phys. Chem. B 1999, 103, 10661.
- the $2x\overline{2}$ transformation matrix connecting The ex the 2x2 transformation matrix connecting
adsorbate lattice with substrate surface
lattice.
B. Behzadi, S. Romer, R. Fasel, K.-H. adsor *J. Am. Chem. R. Chem. Soc.* **2004**, *126*, *Am. Chem. Soc.* **2004**, *126*, lattice.
- [19] B. Behzadi, S. Romer, R. Fasel, K.-H.
Ernst, *J. Am. Chem. Soc.* **2004**, 126,
9176.
M. Parschau, R. Fasel, K.-H. Ernst. O. Ernst, *J. Am. Chem. Soc.* **2004**, *126*, 9176.
9176.
M. Parschau, R. Fasel, K.-H. Ernst, O.
Gröning.L. Brandenberger. R. Schillinger. 9176.
- 176.
I. Parschau, R. Fasel, K.-H. Ernst, O.
röning, L. Brandenberger, R. Schillinger,
Greber. A. Seitsonen, Y.-T. Wu, J. S. M. Pa *Anger. Exerme., E. Fasel, K.-H. Ernst, O.*
Anger. A. Seitsonen, Y.-T. Wu, J. S. Angew. Chem.. Int. Ed. 2007. 46, Gröning, L. Brandenberger, R. Schillinger, *Angew. A. Seitsonen, Y.-T. Wu, J. <i>Angew. Chem., Int. Ed.* **2007**, *Angew. Chem., 2007*, *119*, 8406*.* T. Greber, A. Seitsonen, Y.-T. Wu, J. S.
Siegel, *Angew. Chem., Int. Ed.* **2007**, 46,
8258; *Angew. Chem.* **2007**, 119, 8406.
R. Fasel. J. Wider. C. Ouitmann, K.-H. Siege 1, *Angew. Chem., Int. Ed.* **2007**, 46, *Angew. Chem.* **2007**, 119, 8406.
sel, J. Wider, C. Quitmann, K.-H.
T. Greber. *Angew. Chem., Int. Ed.* 8258; Angew. Chem. 2007, 119, 8406.
- *Angew. C*
Angew. C
43, 2853. [21] R. Fasel, J. Wider, C. Quitmann, K.-H.
Ernst, T. Greber, *Angew. Chem., Int. Ed.*
2004, 43, 2853.
[22] L. A. M. M. Barbosa. P. Sautet. *J. Am.* Ernst, T. Greber, *Angew. Chem., Int. Ed.* 2004, 43, 2853. *T. Greber, Angew. Ch*
43, 2853.
M. M. Barbosa, P. S
Soc. **2001**, 123, 6639.
- **2004**, 43, 2853.

L. A. M. M. Barbosa, P. Sautet, *J. Am.*
 Chem. Soc. **2001**, 123, 6639.

V. Humblot. M. Ortega Lorenzo, C. J. L. A. M. M. Barbosa, P. Sautet, *J. Am. c.* **2001**, *123*, 6639.
lot, M. Ortega Lorenzo, C. J. S. Hao. R. Raval. *J. Am. Chem.* Chem. Soc. 2001, 123, 6639.
- *m. Soc.* **2001**, *123*, *Humblot, M. Ort* deley, S. Haq, R. **2004**, *126*, 6460. $[23]$ V. Humblot, M. Ortega Lorenzo, C. J.
Baddeley, S. Haq, R. Raval, *J. Am. Chem.*
Soc. **2004**, 126, 6460.
M. Parschau. B. Behzadi. S. Romer. K.-H. Baddeley, S. Haq, R. Raval, *J. Am. Chem.
Soc.* **2004**, 126, 6460.
M. Parschau, B. Behzadi, S. Romer, K.-H.
Ernst. *Surf. Interface Anal.* **2006.** 38. Soc. 2004, 126, 6460.
- [24] M. Parschau, B. Behzadi, S. Romer, K.-H.
Ernst, *Surf. Interface Anal.* **2006**, 38,
1607
M. Parschau, S. Romer, K.-H. Ernst. J. *Am. Curf. Interface Anal.* **201**
1607
*M. Parschau, S. Romer, K.-H. E
<i>Am. Chem. Soc.* **2004**, 126, 15398.
- 1607
M. Parschau, S. Romer, K.-H. Ernst, *J.*
Am. Chem. Soc. **2004**, *126*, 15398.
M. M. Green, M. P. Reidv. R. J. Johnson. $\overline{\mathsf{M}}$ Parschau, S. Romer, K.-H. Ernst, *J.*
n. *Chem. Soc.* **2004**, 126, 15398.
M. Green, M. P. Reidy, R. J. Johnson, Darling. D. J. O'Leary. G. Wilson. *J.* Am. Chem. Soc. 2004, 126, 15398.
- *Chem. Soc.* **2004**, *126*, 15398
M. Green, M. P. Reidy, R. J.
Darling, D. J. O'Leary, G. W.
Chem. Soc. **1989**. *111*, 6454. [26] M. M. Green, M. P. Reidy, R. J. Johnson, M. M. Green, M. P. Reidy, R. J. Johnson, G. Darling, D. J. O'Leary, G. Wilson, J.
Am. Chem. Soc. 1989, 111, 6454.
M. Parschau. T. Kampen. K.-H. Ernst. G. Da *Phing, D. J. O'Leary, G. W.*
hem. Soc. **1989**, *111*, 6454.
Phys. Lett. **2005**. 407, 433.
- Am. Chem. Soc. **1989**, 111, 6454.
M. Parschau, T. Kampen, K.-H. Ernst,
Chem. Phys. Lett. **2005**, 407, 433.
K.-H. Ernst. *Curr. Opin. Coll. Interf. Sci.* M. Parschau
Chem. Phys.
K.-H. Ernst,
2008, 13, 54.
-