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CHIRALITY

Amplification of Chirality at Solid Surfaces

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Abstract Symmetry-breaking phenomena in two-dimensional crystallization at surfaces are reviewed and the potential impact to chiral amplification in three-dimensional systems in connection with the origin of homochirality in the biomolecular world is discussed. Adsorption of prochiral molecules leads to two-dimensional conglomerates, i.e., on a local scale spontaneously to homochiral crystal structures. Small enantiomeric excess or chiral impurities in this environment install homochirality on a global scale, that is, on the entire surface.

Keywords Chiral amplification · Conglomerates · Scanning tunneling microscopy · Surface crystallography ·

Introduction

Molecules associated with life are usually chiral and occur only in one of the two enantiomeric forms. The question of how this homochirality of biomolecules evolved from an achiral prebiotic environment has intrigued scientists for long time and led to numerous suggestions for symmetry-breaking scenarios at various stages of the emergence of life (Mason 1983; Bonner 1988; Siegel 1998; Podlech 2001; Janoschek 1991). Laboratory experiments, however, produce mainly racemic results (Dunitz 1996) although statistical fluctuations will inevitably create a small chiral bias. This led to the quest for finding the appropriate amplification mechanism that might have been involved at the early stages of life (Feringa and van Delden 1999; Blackmond 2004; Weissbuch et al. 2005). Amplification of chirality in chemical reactions has been observed in several systems. Kagan was the first to report nonlinear effects in catalytic asymmetric reactions (Puchot et al. 1986) and Soai demonstrated that a chiral alcohol can catalyze its own production (Soai et al. 1995). Cooperative response to a small chiral bias leads also to large magnification effects in macromolecules. Such amplification phenomena have been observed for helical polyisocyanate copolymers (Green et al. 1989, 1995). Small amounts of chiral groups or small *ee* in the side chains provide enough bias for single helicity in the entire polymer

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chain. Because helix reversals are energetically unfavorable, this small symmetry breaking influence suffices to induce single helicity (Green et al. 1999). These effects have been coined as “sergeants-and-soldiers” principle and “majority rule”. A similar effect has been observed for non-covalent assemblies of disk-shaped molecules (Palman and Meijer 2007). Finally, it is noteworthy that the formation of homochiral oligopeptides has been observed in a racemic two-dimensional crystalline self-assembled monolayer of amino acids on water (Zepik et al. 2002). Among the various symmetry-breaking scenarios, chemical reactions at crystal surfaces or asymmetric crystallization processes have also been considered (Kahr and Freudenthal 2008; Welch 2001; Viedma 2001).

Here we discuss symmetry-breaking processes in two-dimensional (2D) crystals of organic molecules at solid surfaces in context with further symmetry breaking of 3D systems and emergence of homochirality. Chirality is created spontaneously upon adsorption of prochiral molecules at achiral model surfaces, that is, metal single crystal substrates. Depending on the substrate quality, homochiral adsorbate domains have typically a diameter of 20 to 100 nanometer. Homochirality throughout the monomolecular thick crystals, i.e., on the entire substrate surface, can be induced, however, due to chiral impurities or enantiomeric excess. The 2D crystal systems have been studied with a surface diffraction technique, i.e., low energy electron diffraction (LEED), and with scanning tunneling microscopy (STM). These methods allow identification of enantiomorphism and characterization with submolecular resolution. Finally, we speculate on the potential influence of these chiral amplification effects on three-dimensional crystallization or amplification processes in liquid solutions in contact with the surface.

Materials and Methods

All adsorbate systems have been investigated under ultra-high vacuum (UHV) conditions ($p \approx 10^{-8}$ Pa). The organic compounds were evaporated from Knudsen cells *in vacuo* onto the copper crystal surfaces held at room temperature. The mechanically polished Cu(110) and Cu(111) crystal surfaces (MaTeck) have been prepared as described previously (Ernst et al. 1999, 2001). Cleanliness and quality of the surfaces and the surface coverage of the adsorbate systems have been determined via X-ray photoelectron spectroscopy (XPS), LEED, and STM. Synthesis and enantiomeric separation ($ee > 99.9\%$) of heptahelicene ([7]H) has been performed as described previously (Fasel et al. 2003). The absolute configuration of the enantiomers of [7]H was assigned with a high level of confidence by comparison of experimental and calculated VCD spectra (Bürge et al. 2004), in agreement with results obtained for (*M*)-[7]H on the stepped Cu(332) surface using X-ray photoelectron diffraction (XPD) (Fasel et al. 2001). Tartaric acid (*R,S*-, *R,R*-, *S,S*- & racemate) and succinic acid were purchased from Aldrich and Merck with purities better than 99%. Corannulene of high purity was prepared by literature methods (Seiders et al. 1999). STM images were acquired in constant-current mode with the sample slowly cooled to 50 K. Molecular modeling calculations (MMC) were performed using the AMBER force field of the Hyperchem 7 package.

Molecular Recognition at Surfaces

Supramolecular chemistry on crystalline surfaces is governed to a large extent by lateral interactions. Nevertheless, the substrate plays an important role in mediating these interactions. Intermolecular recognition on a surface, for example, can take place only if

the adsorbate–substrate interaction allows the molecules to meet each other. Therefore, the choice of the substrate plays a decisive role. Too strong interactions immobilize molecules and do not leave room for 2D supramolecular chemistry or may even induce decomposition; too weak adsorbate–substrate interactions cause high mobility and 2D crystallization phenomena will only occur at low temperature. The adsorption energy of a single molecule is modulated laterally due to the atomic corrugation of the crystalline surface. At low temperatures, the molecule will be in its ground state and is immobile. In order to migrate on the surface, the molecule must overcome the barrier for diffusion. At higher coverage (i.e., 2D density), lateral forces between molecules become more prominent and have an influence on the interaction with the substrate. Attractive forces between molecules cause an increase of the adsorption energy, while repulsion between adsorbates lowers the adsorption energy. The latter is often observed in close-packed monolayers. When finally the amount of repulsion energy within one layer becomes as strong as the adsorption energy of a single molecule, the saturation coverage at that particular temperature is reached. Under these conditions, theory predicts the strongest chiral discrimination forces (Schipper and Harrowell 1983). For the same reason, an energetically favored adsorption site for the single molecule at low coverage may switch to a different binding site at high packing density. This subtle balance between lateral intermolecular interaction and molecule substrate interaction determines the long-range 2D molecular crystal structure.

Adsorption-Induced Chirality

Adsorption of achiral molecules onto achiral surfaces leads quite often to chiral adsorbate structures (Ernst 2006). Either handedness is then formed, depending on which enantiotopic side faces the surface. Hence, 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 level, spontaneous symmetry breaking is a common phenomenon. As for intrinsically chiral molecules, the induced local chirality of adsorbed molecules is often transferred into the adsorbate lattice, which becomes aligned in an oblique angle with respect to the substrate lattice. The enantiomorphism in these structures is then easily identified via LEED.

Mirror domains might be just created, because the optimal packing arrangement breaks the symmetry of the underlying substrate lattice. The ‘buckybowl’ corannulene, for example, forms spontaneously mirror domains on Cu(110) (Parschau et al. 2007). The bowl-shaped fullerene fragment molecule has C_{5v} symmetry. Since fivefold-symmetry cannot be maintained in a tiling array, a lattice with p2 plane group symmetry is formed. Due to the presence of fivefold-symmetric molecules in the unit-cell, however, the structure actually belongs to the p1 plane group and the arrangement is indeed chiral. As manifestation of the enantiomorphism, the domains are tilted clockwise and counterclockwise in oblique angles with respect to the substrate lattice (Fig. 1). The LEED pattern therefore shows a superposition of both mirror domain lattices. In highly resolved STM images corannulene appears as doughnut, and comparison with results from semi-empirical extended Hückel calculations strongly favors an adsorption geometry in which the bowl opening points away from the surface. X-ray photoelectron diffraction (XPD) measurements additionally revealed a small tilt of the C_5 -rotational axis away from the surface normal (Parschau et al. 2007). Such adsorption geometry suggests, that the chemical bond between molecule and copper surface is formed via single a C–C bond (η^2) of the pentagonal ring and a copper surface atom. On the structurally different Cu(111) surface, however, one of the hexagonal rings is oriented parallel to the surface plane over hollow sites (Merz et al. 2009).

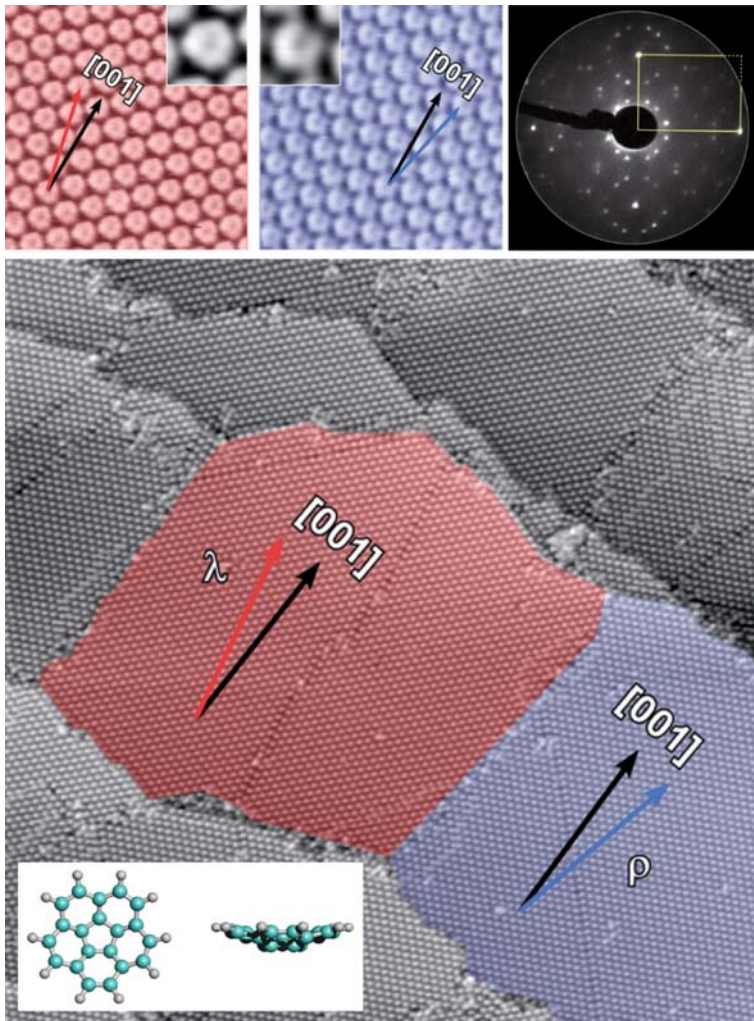


Fig. 1 Symmetry breaking due to symmetry and lattice mismatch. The fivefold-symmetric corannulene forms spontaneously left-handed and right-handed domains. The system is homochiral at the local scale, but overall racemic. The diffraction pattern (*upper right*) reveals the superposition of both mirror domains types. The reciprocal unit cell is indicated a *yellow rectangle*

Mirror-symmetry breaking can be also induced by a chiral distortion of the molecular frame due to interaction with the surface. For (*R,R*)- and (*S,S*)-bitartrate a zigzag distortion has been determined experimentally (Fasel et al. 2004). Density functional theory (DFT) calculations, however, also predict a zigzag conformation for achiral (*R,S*)-TA (*meso*-tartaric acid) and succinic acid (SU) on Cu(110) (Fig. 2) after deprotonation of both carboxyl groups (Barbosa and Sautet 2001). Experimental observations of long-range enantiomorphous patterns in connection with reasonable molecular structure considerations indeed suggest a chiral geometry for (*R,S*)-bitartrate and bisuccinate on Cu(110) (Parschau et al. 2006; Humblot et al. 2004). Because the probability of generating both enantiomer is identical, two-dimensional conglomerates are formed, i.e., all molecules in a single domain

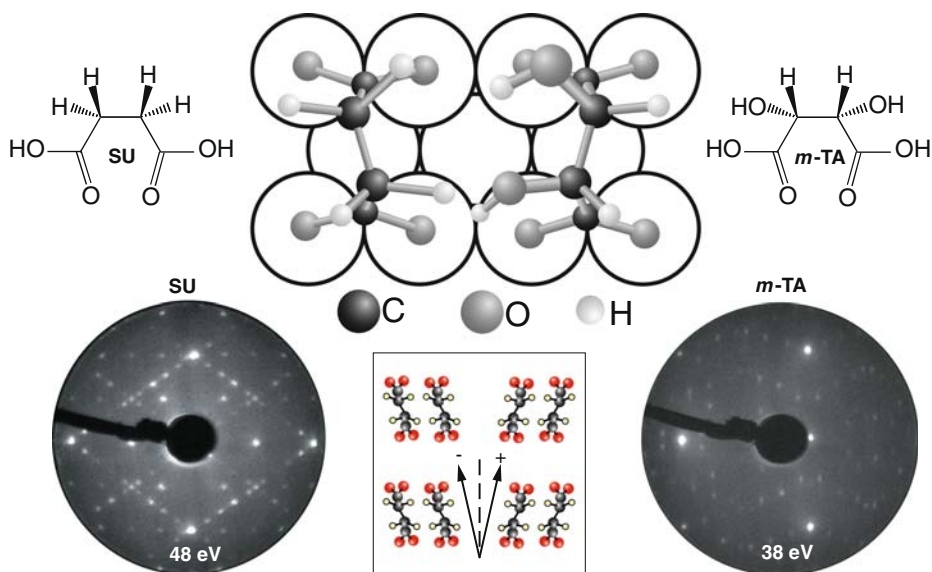


Fig. 2 Chirally distorted SU (*left*) and (*R,S*)-TA (*right*) molecules form a 2D-conglomerate of enantiomorphous domains. The diffraction patterns result from a superposition of coexisting enantiomorphs

of the adlattice have the same chirality. Since the bicarboxylic acid is deprotonated, substantial interactions with the substrate are expected. This may induce a “chiral footprint” into the surface shifting the copper atoms slightly and has consequences for the induced chirality of the adjacent molecules, strongly favoring identical handedness (Barbosa and Sautet 2001). As in the case of corannulene or for racemic bitartrate, which also forms a 2D-conglomerate (Romer et al. 2005), extended mirror domains are observed in the LEED pattern (Fig. 2), provided that the size of the probing electron beam is still larger than the average domain size. This recognition via the substrate is proposed, since intramolecular hydrogen bonding has been excluded via density functional theory (Barbosa and Sautet 2001).

Global Symmetry-Breaking by Chiral Impurities

As shown above, adsorption-induced chirality leads to two distinct enantiomeric states, but overall the surface remains achiral. Additional chiral bias, however, can suppress one state if the barrier of interconversion between the two distinct enantiomeric states is not too high. The coadsorption of chiral impurities into such racemic layers is an efficient way to induce further asymmetrization 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 example, is rather flexible and mobile above 500 K, and presumably switches from one handedness to the other in its bisuccinate phase. Cooling down such layer after doping with intrinsically chiral TA completely leads to formation of one mirror domain and installs global homochirality (Parschau et al. 2004). Consequently, the opposite TA-enantiomer induces crystallization of the opposite SU enantiomorph, which is easily detectable in LEED (Fig. 3, left). Only 2% of chiral dopant is sufficient here. Smaller amounts lead to a

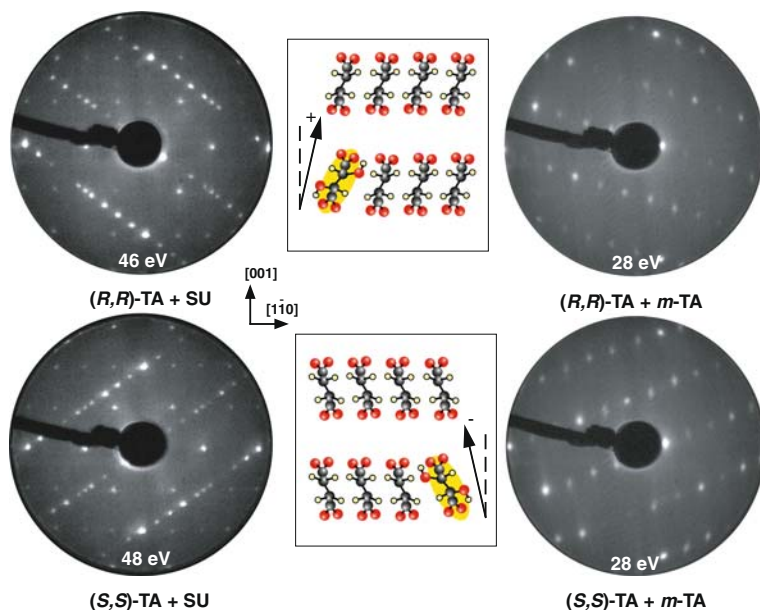


Fig. 3 Molecular sergent-and-soldiers at surfaces. Chiral TA as impurity in enantiomorphous SU (*left*) and meso-TA (*right*) lattices allows only one 2D enantiomorph to exist. The opposite TA enantiomer induces the opposite enantiomorph. Superposition of both diffraction patterns would lead to the pattern observed for the undoped layer

lower intensity of the diffraction spots of the less favored enantiomorphous lattice. We assume that the chiral dopant influences the chiral distortion of adjacent molecules. These in turn transfer the chiral information to the next neighbors via the substrate (footprint) as discussed above as. Consequently, all molecules on the entire surface have the same handedness. Although only single enantiomorphism is observed via electron diffraction here, we conclude that homochirality is installed on the entire surface. This is the 2D equivalent to the sergent-and-soldiers principle as observed for helical polymers (Green et al. 1989). Again, since hydrogen bonds between the bisuccinate 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 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 doping: The TA sergent has only one sense of chiral footprint, forcing adjacent SU molecules into similar configuration. These, in turn, force their SU neighbors into the same configuration for energetic reasons.

The molecular frame of achiral (*R,S*)-TA on Cu(110) is also forced into a zigzag distortion and becomes chiral. The sergent-and-soldiers principle works therefore as well and homochirality induction is likewise observed after (*S,S*)- or (*R,R*)-TA doping (Fig. 3, right column) (Parschau et al. 2005).

Similar to the chiral doping scenario, small enantiomeric excess (*ee*) may also induce lattice homochirality (Fasel et al. 2006). Racemic heptahelicene ([7]H) forms a lattice containing heterochiral pairs on Cu(111) (Parschau et al. 2008). Due to two mirror-symmetric relative alignments of the two enantiomers in the heterochiral pair, two enantiomorphs are formed at the surface (Fig. 4.). The chiral bias originating from a small *ee* is sufficient in order to suppress formation of one unfavorable mirror domain and

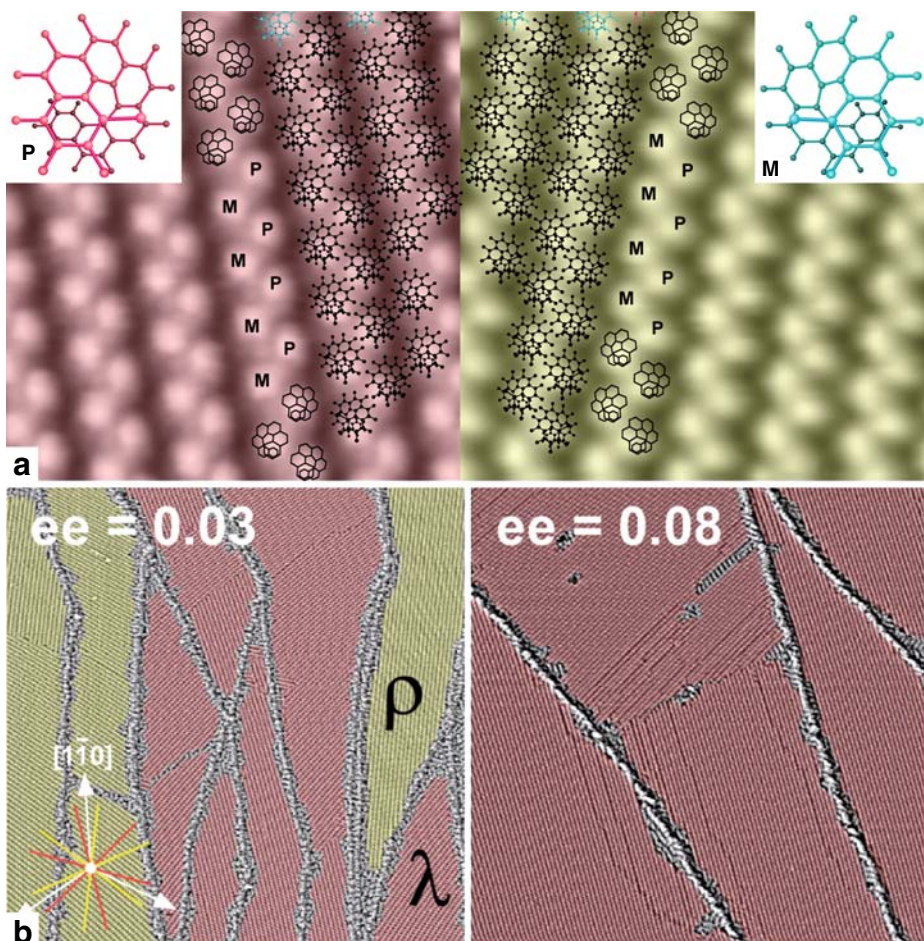


Fig. 4 Enantiomorphous structures formed by [7]H on Cu(111). (*P*)- and (*M*)-[7]H form heterochiral pairs that are, however, chiral due to mirror-like alignment possibilities. This leads to enantiomorphous domains on the surface. Small excess of either enantiomer leads to single enantiomorphism, although the lattice still contains both enantiomers at a 1:1 ratio

induces homochiral lattice order. Instead switching the molecular handedness, one relative alignment is suppressed. Compared to the tartaric or succinic acid systems, the molecules are relatively weakly adsorbed via dispersive interactions of up to three C6 rings with the Cu(111) surface. Therefore, they can easily slip into the favored enantiomorphous configuration induced by the chiral bias. Because of strong steric constraint, any *ee* is expelled from the racemic enantiomorphous domains 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. (*M*)-[7]H excess favors formation of λ domain pairs and (*P*)-[7]H excess favors the ρ domain-pair-alignment. This chiral bias is then amplified by the cooperative interaction among heterochiral pairs, strongly favoring their equal alignment. Like helix reversals in a polymer chain, opposite alignment would create energetically unfavorable mirror domain boundaries. Even for the pure racemate, these boundaries are rarely observed on single Cu(111) terraces (Ernst 2008). Hence, without any

chiral bias, spontaneous symmetry breaking is observed on this length scale, but the probability for formation of 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 during 2D crystallization and only one of either λ or ρ domains is observed (Fig. 4). 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 configuration, interconversion between both structures requires only a change in relative position of both enantiomers of a heterochiral pair. The TA-doped systems are truly homochiral, i.e., all molecules have the same handedness. The ee -bias-amplified $[7]H/Cu(111)$ system is still of heterochiral composition, but possesses lattice homochirality. In order to observe this ee -effect, lateral resolution of the enantiomers is not allowed. On the other hand, the heterochiral pairs in their mirror-breaking alignment is a noncovalently bound single chiral entity. In that respect, the entire 2D molecular film must be considered being homochiral and should possess symmetry-breaking properties towards 3D processes like bulk crystallization or solution chemistry as discussed below.

Discussion

The chiral impurity and enantiomeric excess systems presented here are chiral substrates that should have an influence onto further symmetry-breaking phenomena in the medium above these surfaces. For a chiral molecule, when either adsorbed on one or the other enantiomorphous domain, results a difference in adsorption energy. This effect of stereoselectivity during adsorption of chiral molecules on certain crystal faces has been shown before (Addadi et al. 1986). With only one 2D enantiomorph allowed due to a chiral impurity at the surface, the second and higher layer adsorption, i.e., further crystallization, will be strongly influenced.

Further amplification of crystallization may also occur in a feed-back scenario involving a racemisation equilibrium in the solution and a resolution—precipitation equilibrium between a solid conglomerate state. If chiral surfaces enantioselectively catalyze one of the two racemisation reactions, the concentration of one enantiomer will decrease. This would cause one of the conglomerate phases to go preferentially into solution in order to reestablish the racemization equilibrium. This leads inevitably to symmetry-breaking crystallization, as observed by Viedma for crystal grinding (Viedma 2005). As a consequence, only one enantiomer will form the solid phase with its chiral surfaces, which, in turn, may be stereocatalytically active and further drive the system to single handedness.

Soai and co-workers have also shown that chiral surfaces have a strong influence on autocatalytic reactions (Sato et al. 2000). It would be therefore interesting to see if the more complex reaction schemes of systems chemistry can be influenced in the same matter, i.e., by chiral surfaces.

Emergence of life and homochirality go hand in hand, but this is certainly a very seldom event. Despite encouraging progress (Eschenmoser 1999; Luther et al. 1998), scientists have not been able to create such complex replicating chemistry that could be considered as a life form (Orgel 2000). Based on statistical grounds, it is questionable that we scientists with our extremely low rate of experiments will be able to compete with the rate of diverse reactions that went on in the prebiotic soup four billion years ago on earth. An experiment that reproduces the emergence of homochirality on Earth—which we consider as the only conclusive one—thus remains very improbable. Hence, there is not much hope that we will

ever find answer to the question of how homochirality evolved from an achiral prebiotic soup.

Conclusions

We have added here another scenario of chiral amplification to those that have been previously discussed as potential symmetry-breaking processes towards homochirality in life. The presented examples included polar as well as nonpolar molecules. We see therefore no limitation of the observed phenomena to special types of molecules. Hence, amino acid derivatives in the racemic prebiotic soup may in principle have formed enantiomorphous surfaces via 2D chirality amplification, that act as heterogeneous catalyst for complex biomolecules.

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