

Mesoscopic Correlation of Supramolecular Chirality in One-Dimensional Hydrogen-Bonded Assemblies

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The ordering of 4-[*trans*-2-(pyrid-4-yl-vinyl)] benzoic acid, a two-dimensional chiral species, was studied by scanning tunneling microscopy at noble metal surfaces. Homochiral molecules self-assemble in supramolecular chiral hydrogen-bonded twin chains, which order in nanogratings where the supramolecular chirality is strictly correlated over the entire μm domains without intimate molecular contact. Model simulations indicate that the underlying mesoscopic chiral resolution is associated with twin chains acting as chiroselective templates for transient molecular attachment, which process mediates the gratings' evolution.

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Chirality phenomena associated with molecular species and arrangements in low-dimensional systems have attracted strong interest over the past years [1,2]. Chiral films may exhibit extraordinary optical [3] or electronic [4] properties and form the basis of enantioselective heterogeneous catalysis [5]. At surfaces, chirality can be encountered by adsorption of chiral molecules or be induced through chiral ordering. Moreover, molecules which are achiral in three dimensions may become chiral upon adsorption due to the reduced symmetry. It is a challenging task to determine the structure or elucidate the formation of low-dimensional chiral species. This holds, in particular, when systems are considered where chirality is expressed at the supramolecular level in noncovalent assemblies [6] with their weak bonding and low stability. Chirality in adsorbed supramolecular aggregates requires surface mobility and stereospecific molecular interactions. When these conditions are met, chiral discrimination can lead to the spontaneous resolution of racemic mixture into enantiopure phases.

Here we report direct observations on chiroselective self-assembly of the molecule 4-[*trans*-2-(pyrid-4-yl-vinyl)] benzoic acid (PVBA) at noble metal surfaces. It is demonstrated that chiral correlation can extend over mesoscopic distances without intimate molecular contact. PVBA provides functional endgroups for hydrogen bonding [7]. Its structure formula is depicted in Fig. 1a along with the illustration of the two-dimensional (2D) chiral species designated λ -PVBA and δ -PVBA existing at a surface. For the transformation of the λ into the δ species, a mirror operation is mandatory. We assume that the H atom is free to transfer from one oxygen atom to the other in the adsorbed molecules, a behavior which is well known for related systems [8], so that the two possible orientations of the carboxylic acid moiety are

irrelevant for the symmetry. Small amounts of PVBA were evaporated on the close-packed (111) surfaces of Ag and Au single crystals by organic molecular beam epitaxy

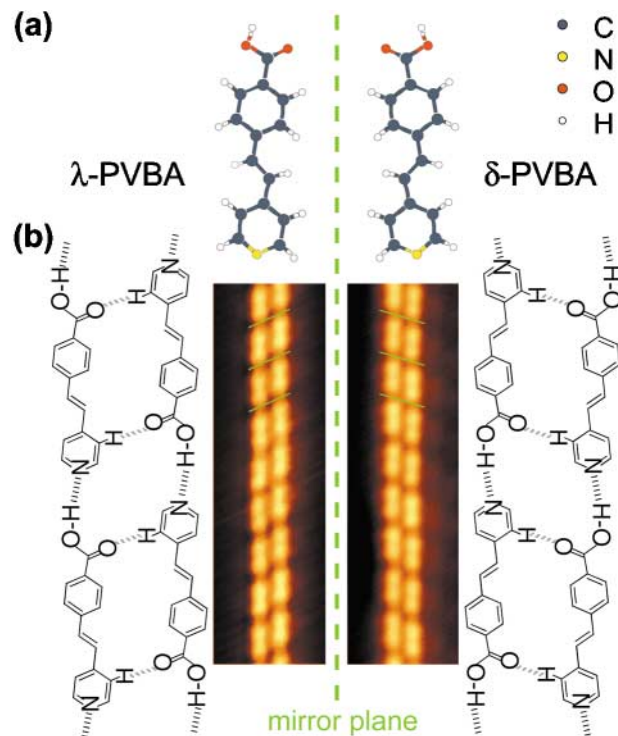


FIG. 1 (color). (a) Chirality of PVBA upon confinement to two dimensions. The respective species are designated λ -PVBA and δ -PVBA; the mirror symmetry is reflected by a dashed line. (b) STM topographs of the two possible supramolecular chiral twin chains from self-assembly of PVBA on Ag(111) (image size: $40 \times 135 \text{ \AA}^2$; adsorption temperature: 300 K, measured at 77 K). The corresponding models for the energetically favored configurations reveal the underlying chiral resolution (hydrogen bonds indicated by dashes).

under ultrahigh vacuum conditions. Because of the stochastic nature of the deposition process, it is expected that a racemic mixture evolves initially at the surface with a homogeneous distribution of both λ and δ species. However, at ambient temperature the surface mobility of adsorbed PVBA is appreciable: The molecules undergo self-assembly and supramolecular twin chains stabilized by formation of hydrogen bonds evolve at the surface [9].

The scanning tunneling microscopy (STM) topographs of twin chains from different areas of the surface reproduced in Fig. 1b show that the constituent molecular rows can have two relative displacements, related by a mirror symmetry. The twin chains thus display supramolecular chirality. To identify the underlying driving forces, we performed molecular dynamics (MD) simulations based on a force field. The model takes into account intermolecular electrostatic and short-range Pauli repulsive interactions, while the presence of the metal substrate is accounted for by an image charge potential [10]. Energetically preferred twin chains consist of exclusively one chiral species as depicted in Fig. 1b. They are stabilized by strong head-to-tail $\text{OH}\cdots\text{N}$ hydrogen bonds between PVBA endgroups. The preferred location of the corresponding OH groups is at the external side of the twin chain. The negatively charged double-bonded O atoms point towards the pyridile moiety of the adjacent molecule, suggestive of weak lateral bonding [9]. The antiparallel arrangement and the shift of the rows account for a twin chain formation energy of ~ 0.2 eV/molecule and corroborate a detailed analysis of high-resolution STM data [9]. In contrast, the energies of racemic chains are found to be higher by a few percent and their structural properties are not in accordance with the STM observations. This implies that there is chiral recognition in the formation of twin chains [11]. Stereochemical considerations let the effect be rationalized: The crooked shape of the molecule promotes optimal sideward bonding of the carboxylic acid group only when it smoothly matches the bending of its antiparallel counterpart, which corresponds to the condition of identical chirality. The findings can be considered as the one-dimensional limit for the spontaneous chiral resolution (i.e., the separation of the two chiral species) in a racemic mixture [12].

The STM data depicted in Fig. 2 reveal, moreover, that the separation is not restricted locally to individual assemblies. The twin chains form nanogratings extending over μm -size domains at Au(111) or Ag(111) surfaces [9], whereby only one handedness is present in a domain. In view of the above analysis, this implies a spontaneous chiral resolution of PVBA at the mesoscopic scale. However, in marked contrast to earlier investigations (e.g., [1,12]), this is not reflected in an intimate contact of the constituent molecules forming a crystal. If we were dealing simply with the 2D analog of the growth of an enantiopure crystal from a chiral seed in a solution, the formation of 2D islands instead of the observed 1D gratings would prevail.

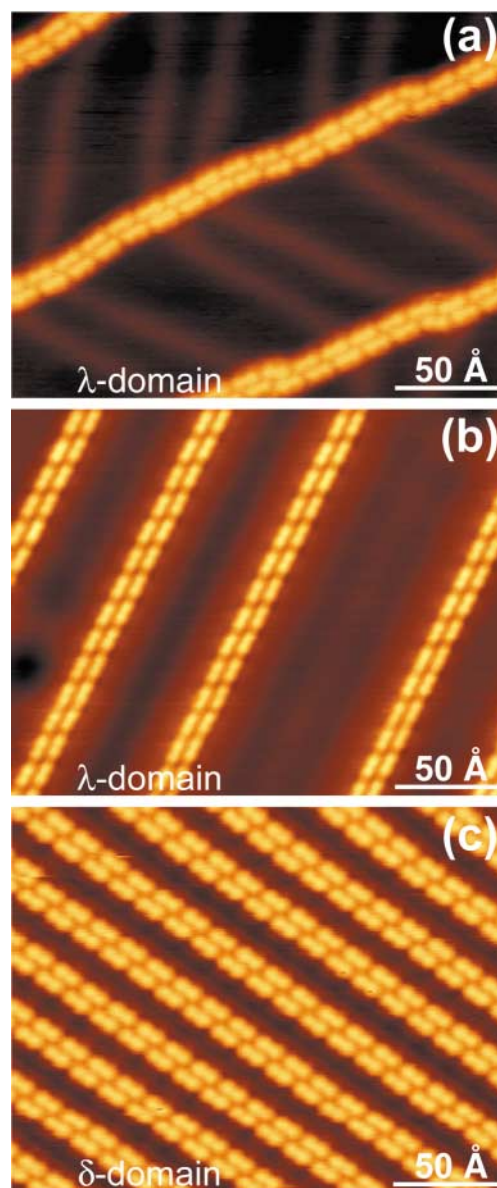


FIG. 2 (color). STM data demonstrating the mesoscopic ordering and spontaneous chiral resolution of PVBA at close-packed noble metal surfaces (adsorption temperature: 300 K, measured at 77 K). Only one supramolecular chirality of the molecular twin chains exists within rotational domains extending in the μm range. At the Au(111) surface shown in (a) a λ domain oriented along substrate elbow defects has formed exhibiting long-range chiral correlation over a distance of ≈ 120 Å (grey double lines are due to the Au surface reconstruction). At Ag(111), the periodicity of the gratings can be tuned by variation of the coverage, which is visualized for both λ and δ domains in (b) and (c), respectively.

At Au(111), a grating with ≈ 120 Å periodicity is formed at small coverages (cf. Fig. 2a) due to preferential orientation of the twin chains with the elbow defects of the reconstructed substrate [13]. On Ag(111), regular gratings form whereby the periodicity can be tuned by the amount of the deposited material in the range 25–50 Å (Figs. 2b and 2c). Accordingly, MD results indicate that the twin chains repel each other as a consequence of their external

positive polarity. This favors the formation of a grating over 2D island formation. Nevertheless, long-range electrostatic effects cannot mediate chiroselective interactions inducing the chirality signature from one twin chain to the next over distances in the nanometer range [14].

It is thus concluded that the origin of the chiral resolution is related to the mechanism of the gratings' formation. In order to clarify this issue, metastable configurations were investigated. With deposition of additional PVBA on a grating at Ag(111) held at 160 K, the newly arriving molecules arrange into ramified structures which are attached to the twin chains by coupling of PVBA endgroups (Fig. 3a). Upon gentle annealing at 225 K, the molecular mass transport at the surface is restricted to short distances and new metastable structures evolve, such as the twin chain segment diagonally interconnecting two neighboring molecular rows shown in Fig. 3b. The segment's chirality is different from the original domain. In Fig. 3c, chirality switches at defects in a newly formed twin chain are visualized. These findings substantiate the statement that the molecular beam provides a racemic mixture in the absence of surface mobility. Moreover, it can be seen in Figs. 3b and 3c that the triple chains have formed, where the relative displacement of the previously existing twin chain is continued. Such triple chains are the most typical metastable structure. By contrast, quadruple chains are never observed, which signals that they are energetically unfavorable. Upon annealing of metastable configurations to 300 K, gratings similar to those shown in Fig. 2 are obtained.

The metastable triple chains were analyzed by MD simulations. The energetically preferred configuration reproduced in Fig. 4a is in agreement with the observed displacements of the molecular rows and associated with a cohesive energy per molecule slightly inferior to that of the twin chain. Again exclusively one chiral species must be employed, whereby the double-bonded oxygen atom of the amended lower row must be oriented towards the chain interior to achieve metastability (this implies a reversal of the carboxylic acid moiety with respect to the uppermost row, whence the amended species is designated λ_{rot}). Thus, chiral recognition is similarly operative in the formation of triple chains. This offers a clue to understand the mesoscopic chiral resolution. The metastability of triple chains signals that they act as intermediate species in the evolution of the grating and proliferate the chirality signature as chiral precursors. It is consequently deduced that self-replication of supramolecular chirality takes place in the course of the gratings' evolution. The suggested mechanism is based on the MD results in Figs. 4b and 4c. They depict the transient attachment of a fourth row to a triple chain. The modeling indicates that again the most stable bonding is achieved when the fourth row is formed with the same PVBA chiral species as the template triple chain. However, this configuration readily disrupts upon a flip of the H atom in the third-row benzoic acid moiety, leading to two identical twin chains repelling each other.

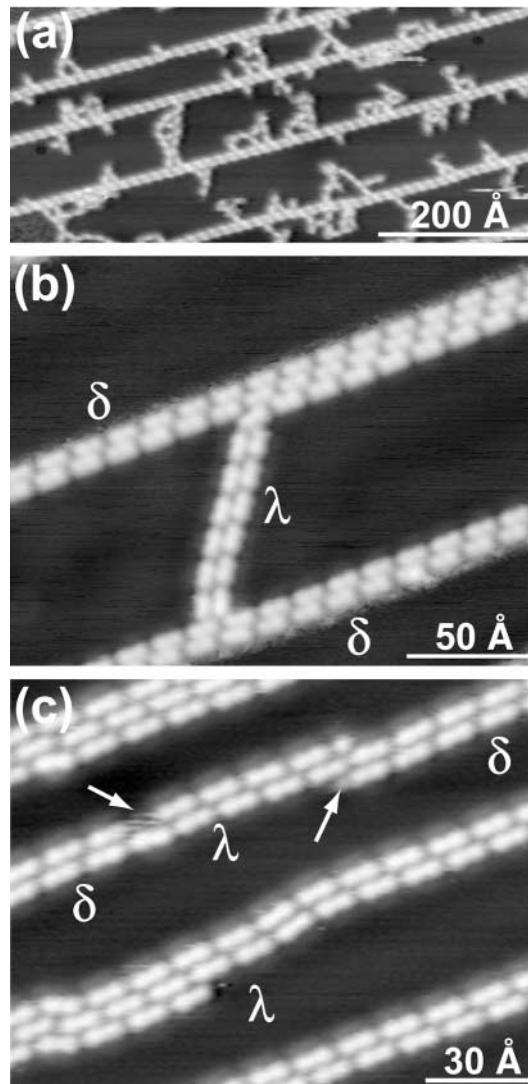


FIG. 3. Metastable structures upon deposition of additional PVBA on Ag(111) decorated by a regular supramolecular grating. In the STM topograph in (a) the situation right after adsorption at 160 K is depicted: ramified molecular branches evolved between the molecular twin chains, where the molecules are coupled via the attractive interactions between the endgroups. Upon gentle annealing at 225 K, the limited surface mass transport leads to metastable configurations, as shown in (b) and (c). The presence of defects and twin chain segments with mixed chirality ascertains the presence of both 2D chiral species in the imaged regions. Chirality switches in (c) are marked by arrows. As a typical feature, triple chains evolve where the relative molecular displacement of the previously existing twin chains is continued.

The corresponding unzipping of twin chains and their repulsive interactions can actually be observed for higher coverages, where due to space limitations 2D islands evolve. This is demonstrated by the STM image reproduced in Fig. 4d, where homochiral twin chains shear off from an island. There is an overall gain in total energy (~ 0.01 eV per chain segment) when the electrostatic repulsion is minimized. The large size of the observed gratings is thus associated with the initial formation of a one-dimensional chiral germ which is replicated over the

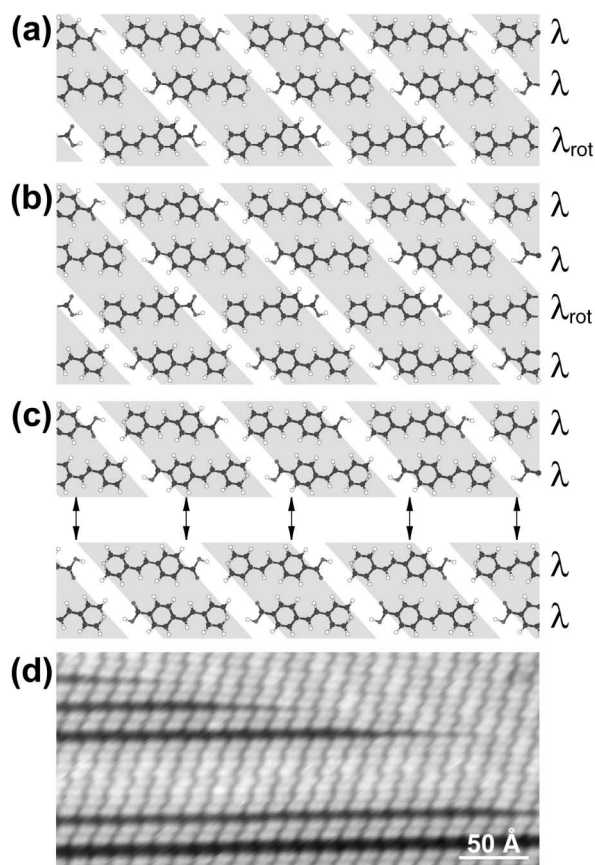


FIG. 4. (a)–(c) Results of molecular dynamics simulations for metastable triple and quadruple chains. The grey shade indicates the molecular groups principally contributing to the tunneling current and allows for a direct comparison of the displacements in the STM images and that in the models. In (a) the energetically preferred metastable triple chain in accordance with the experimentally observed structure (cf. Fig. 3) is shown. It results from the chiroselective attachment of PVBA to a given twin chain. The favored position of the O atom in the carboxylic acid moiety of the amended lower row, designated λ_{rot} , points to the chain interior and is thus reversed with respect to that in the upper row. The suggested mechanism for self-replication of supramolecular chirality is visualized by the MD scenario in (b) and (c). A transient chiroselective attachment of a fourth row (b) followed by a flip of the H atom position in the carboxylic acid moiety of the third row (c) results in two identical twin chains repelling each other. (d) STM image visualizing twin chains zipping off from an island in a space-limited environment at higher coverages.

entire domain. Adsorbed molecules with the inappropriate chirality transport to adjacent domains where they are incorporated.

Our findings demonstrate that novel phenomena may be encountered when 2D chiral species are employed for supramolecular engineering at surfaces. It is interesting to note that, although self-replication of hydrogen-bonded assemblies accounting for large-scale chirality correlation is well-known with biological systems, the restriction to lower dimensionality bears consequences for the replication mechanism. In particular, the 2D confinement of the present 1D supramolecular chiral species is incompatible with semiconservative replication favored in a 3D chiral

twin helix separating into two strands, which act as seeds for two new homochiral helices [15]. Rather, a conservative mechanism is required here, implying the existence of a larger intermediate metastable species.

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