

**DIRECT INVESTIGATION OF
MOLECULAR SELF-ORGANIZATION
AT SURFACES**



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The award of the *Prix Latsis Universitaire* is a great honor and it is a pleasure to express my sincere gratitude to the Latsis foundation and family for their generous recognition of scientific research and to the *Commission de Recherche* for the nomination.

Newton a résolu le problème du mouvement dans le système planétaire; c'est magnifique pour vous autres, gens d'esprit et de mathématiques; mais que moi j'eusse appris aux hommes comment s'opère le mouvement qui se communique et se détermine dans les petits corps, j'aurais résolu le problème de la vie et de l'univers le monde des détails reste à chercher.
Napoleon Buonaparte, Campagne d'Egypte, 1799.

Self-organization phenomena are abundant in nature. Many biological systems comprise self-organized architectures, forming by spontaneous association of molecules under equilibrium conditions into stable, structurally well-defined aggregates. For instance, the tobacco mosaic virus consists of about two thousand protein units forming a hydrogen bond stabilized helix attached to a central ribonucleic acid strand. When these components are separated they readily form the entire virus again upon mixing under appropriate conditions. Today, studies on artificial systems are performed where molecular building blocks are developed for self-organization according to the scientists' design criteria. This is a leitmotiv in the field of supramolecular chemistry, where substantial efforts are currently devoted to the development of functional nanostructures. Hydrogen bonding has proven to be particularly useful in this respect, which may also be deduced from the ubiquity of H-bonded architectures in biological systems.

The modern surface techniques open a pathway to the direct elucidation of molecular self-organization and nanostructuring. With molecular building blocks adsorbed at well-defined surfaces, notably the scanning tunneling microscope (STM) can be employed, which proved to be an eminently powerful method giving scientists unprecedented views of the atomic and molecular world at surfaces. This is especially promising when large organic species are employed with specific groups accounting for anisotropic interactions and thus peculiar arrangements. With designed functional molecules the fascinating possibility to monitor and fabricate *supramolecular architectures* at surfaces becomes feasible.

In order to tackle this issue, we performed systematic experiments with various organic species adsorbed at metal surfaces. Especially the rigid rod-like molecule [4-*trans*-2-(4-pyridyl-vinyl) benzoic acid], nicknamed PVBA, comprising functional groups for H-bond formation was investigated. The molecular length is 12.5 Å, i.e., 0.000'001'25 mm (1 Å = 10⁻¹⁰m). The studies revealed that molecular self-organization at surfaces is governed by the subtle balance between intermolecular and molecule-surface interactions which can be tuned via the appropriate choice of substrate material and symmetry. Upon adsorption the molecules experience the potential energy surface of the substrate, which makes certain adsorption geometries energetically favorable. The ease, with which these sites can be changed by either translational or rotational processes, is a key parameter for the arrangement of molecules at surfaces. Similarly important is the strength and nature of the intermolecular interactions which compete with the molecule-substrate interactions. It is the balance of these factors which determine the molecular self-assembly at surfaces.

The STM topographs reproduced in the figure 1 shown below demonstrate what can be achieved by choosing the apt chemical nature and symmetry of a substrate : with the adsorption of PVBA molecules on the (111) oriented surface of silver, well-ordered supramolecular nanostructures can be obtained. The large-scale overview at the left demonstrates the formation of highly regular one-dimensional supramolecular arrangements. This superstructure exists in three rotational domains reflecting the threefold symmetry of the substrate. Mesoscopic ordering is operational at the μm scale, whence the PVBA arrangement can be considered as a *one-dimensional supramolecular nanograting*. High-resolution data such as the image shown in figure 1b reveal that this nanogrid is actually built from PVBA twin chains, each consisting of two coupled molecular rows with an antiparallel orientation.

From a detailed analysis of STM data a model for the twin chains was derived, which reflects the formation of hydrogen bonds. Within the rows, a head-to-tail molecular sequence associated with N···HO coupling prevails. The weak interaction of adjacent rows is similarly attributed to H-bonds, as illustrated by the corresponding model shown in figure 2a. From its inspection moreover the existence of twin chains in two mirror-symmetric configurations can be inferred. The δ-twin

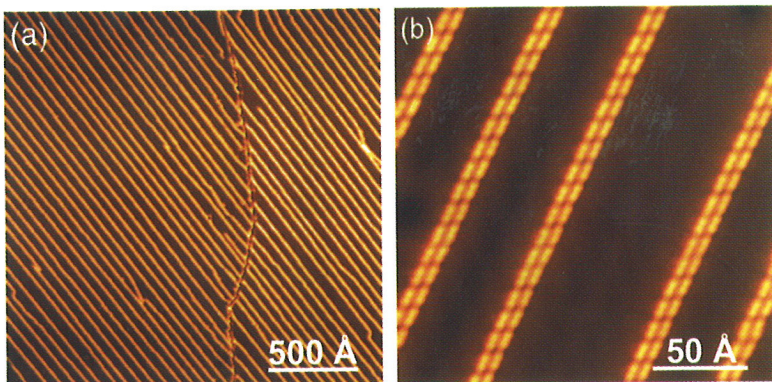


Fig. 1 Fabrication of a nanograting by supramolecular self-organization of [4-*trans*-2-(4-pyridyl-vinyl) benzoic acid] (PVBA) molecules at a Ag(111) surface. **(a)** Large-scale STM topograph demonstrating the mesoscopic ordering of the one-dimensional superstructure in the μm -range. **(b)** In the close-up image of another rotational domain the individual molecules are resolved. They have arranged in twin chains consisting of coupled molecular rows. [J.V. Barth, J. Weckesser, C. Cai, P. Günter, L. Bürgi, O. Jeandupeux and K. Kern, *Angewandte Chemie Int. Ed.* **39**, 1230 (2000)].

chain cannot be transformed into the λ -twin chain by simple translations and rotations in two dimensions. Rather, it must be mirrored at the axis represented by a dashed line. Hence the twin chains are chiral. This is reminiscent of the chirality in naturally occurring supermolecules, such as that of the DNA double helix. With the present system the adsorbed building block PVBA is similarly chiral, as a result from the confinement at the surface and the angled bonding at the central C=C moiety (cf. figure 2b).

For optimal interrow coupling in the twin chain, both molecular rows have to consist of the same chiral species. This implies the operation of chiral recognition in the formation of twin chains. 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, which was first observed by Pasteur in

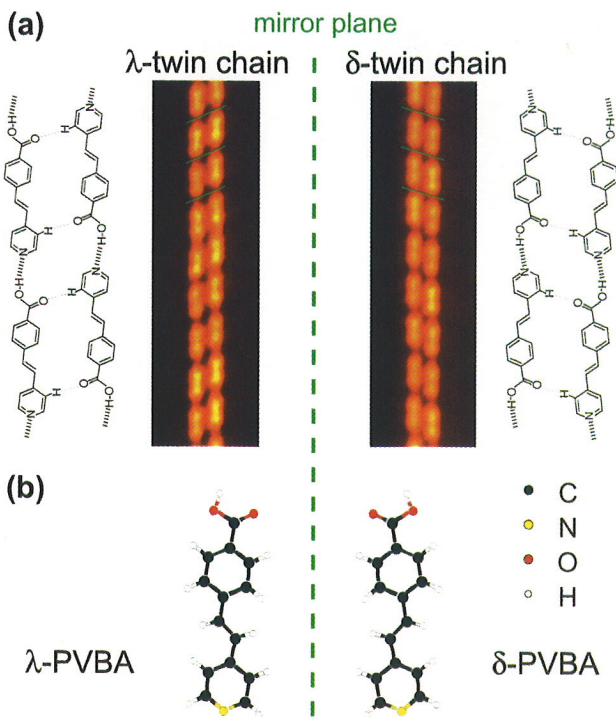


Fig. 2 (a) Models for supramolecular twin chains demonstrating their cohesion mediated by hydrogen bonds (indicated by dashes). Two mirror-symmetric species exist visualized by the corresponding STM topographs. The symmetry axis is indicated by a dashed line. (b) Chirality of the molecular building block when confined to two dimensions.

his famous 19th century experiment. The STM data depicted in figures 1b and 3 reveal moreover that the separation is not restricted locally to individual twin chains. In each nanogrid exclusively one handedness is present, respectively (in figure 1b it is the λ domain). This implies a strict correlation of chirality at the mesoscopic scale. However, in striking contrast to Pasteur's and subsequent studies, this is not reflected in an intimate contact of the constituent molecules forming a regular crystal. If we were dealing simply with the two-dimensional analogue for growth of a chiral crystal from a seed in a solution, the formation of two-dimensional islands instead of the observed one-dimensional gratings would prevail.

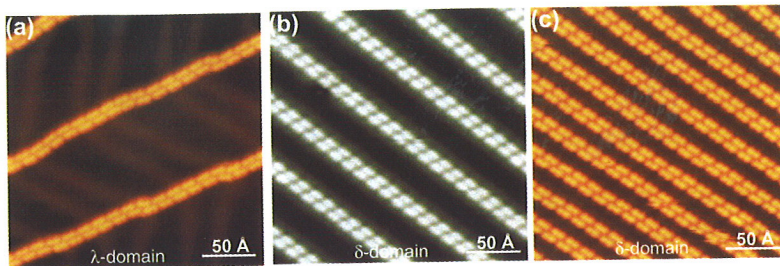


Fig. 3 Mesoscopic correlation of chirality at close-packed noble metal surfaces. Exclusively one twin chain chirality exists within rotational domains extending in the μm -range. With the Au(111) surface shown in (a) a λ domain with chiral correlation over a distance of $\approx 120 \text{ \AA}$ evolved. On Ag(111) the periodicity of the gratings can be tuned by variation of the coverage as shown for the δ domains in (b) and (c). [J. Weckesser, A. De Vita, J.V. Barth, C. Cai and K. Kern, *Physical Review Letters* **87**, 096101 (2001)].

The origin of the chiral correlation is related to the mechanism of the nanogrids' formation. A careful investigation of this issue in conjunction with model simulations revealed that transient triple chains act as an intermediate species in the evolution of a supramolecular grating. As chiral precursors, they proliferate the chirality signature. It thus could be deduced that self-replication of twin chains takes place. The scenario is depicted in figure 4. Firstly a metastable triple chain from one chiral PVBA species forms. For its stability the orientation of the COOH group must be reversed. As the H atom in this moiety can freely transfer from one oxygen atom to the other it is labeled λrot . Subsequently occurs the transient attachment of a fourth row. Again the most stable bonding is achieved when it 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 COOH moiety, leading to two identical twin chains repelling each other. The corresponding unzipping of twin chains and their repulsive interactions can actually be observed for higher coverages, where due to space limitations two-dimensional islands - 5 - evolve. This is demonstrated by the STM image reproduced in figure 4d, where homochiral twin chains shear off from an island. The large size of the observed gratings is thus associated with the initial formation of a one-dimensional chiral germ which selfreplicates whereupon an entire domain with correlated chirality evolves.

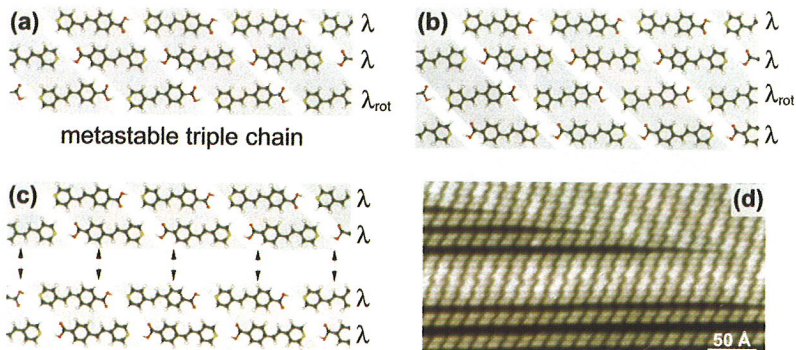


Fig. 4 Model for the self-replication mechanism. (a) Metastable triple chain resulting from the chiroselective attachment of PVBA to a given twin chain. The COOH moiety the amended lower row, designated λ_{rot} , is reversed with respect to that in the uppermost row. The replication process is visualized by the sequence in (b) and (c). A transient chiroselective attachment of a fourth row (b) followed by a flip of the H atom in the third row (c) results in two identical twin chains subject to mutual repulsive interactions. (d) STM image visualizing homochiral twin chains zipping off from an island in a spacelimited environment at higher coverages.

These findings demonstrate that self-organization of functional organic species at surfaces can be studied at the molecular scale whereby intriguing phenomena can be encountered. In general, the self-organization of specifically designed molecules via noncovalent bonding is expected to open novel avenues in nanoscience, which may eventually lead to the deliberate positioning of functional molecular units in supramolecular architectures at surfaces. It is suggested that this approach will be valuable for the future fabrication of nanoscale devices.

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