

Homochiral monolayers of Cu-Phthalocyanine driven by adsorption induced electronic chirality

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The most efficient route to imprint chirality to surfaces is the adsorption of molecular layers [1]. However, when the molecule is adsorbed on a surface chirality can be induced [2], eliminated [3], or even switched [4]. Hence the molecule-substrate interaction plays a fundamental role in the growth of chiral surfaces.

In the adsorption of Cu-Phthalocyanine (CuPc) on Ag(100), both with four-fold symmetry, the molecule-surface interaction azimuthally rotates the molecule generating a mismatch between the symmetry axes of molecule and substrate and thereby imprinting chirality to the system. Fig. 1 (a) shows scanning tunneling microscopy (STM) images of the two molecular enantiomers. However, in this case the molecule-substrate interaction is not strong enough to induce conformational distortions in the molecule but induces a large charge transfer that imprints chirality to the molecular orbitals. The purely electronic origin of chirality is confirmed by voltage dependent STM topographic and conductance images (Fig. 1 (b)-(e)), where chirality is observed only for negative bias voltage. The energy dependence of the chirality is due to the different contribution of the HOMO/LUMO orbitals, as confirmed by density functional theory (DFT) calculations.

The electronic chirality observed in isolated molecules extends to the nearby surface atoms inducing an asymmetric potential. This breaks the symmetry between otherwise equivalent intermolecular bonding configurations, leading to the growth of one type of cluster for each molecular configuration, as can be seen in Fig. 2. At increasing coverage, the coexistence between the two cluster domains is inhibited by the high energy of domain walls and a single domain is efficiently propagated creating μm -size homochiral layers.

References:

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Figures:

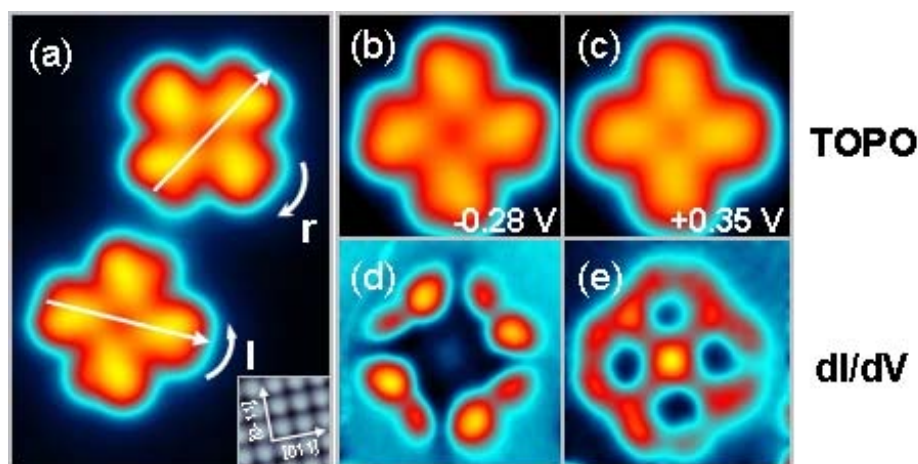


Fig. 1: a) STM image of individual CuPc molecules adsorbed on Ag(100), showing the two type of chiral configurations (*r/l*), rotated $\pm 30^\circ$ with respect to the [011] surface crystallographic direction. b)-e) Topographic and conductance images of a CuPc molecule at -0.28 V (b and d) and +0.35 V (c and e). The electronic chirality, which depends on the molecular resonance where electrons tunnel into at each voltage, is present both in the topographic and conductance images at negative voltage and disappears at positive voltage.

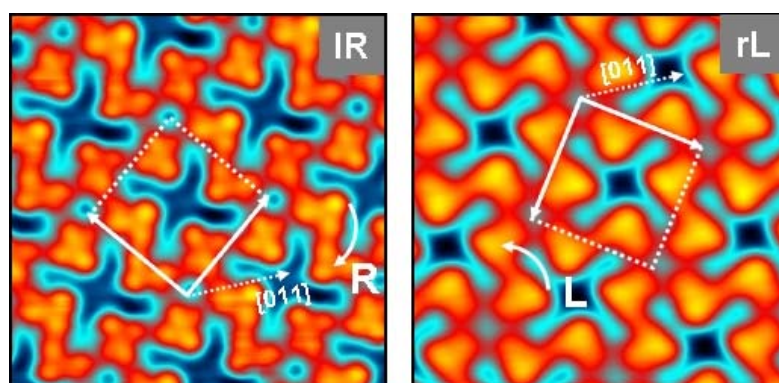


Fig. 2: STM images showing disconnected patches with the two possible chiral assembly configurations of the first CuPc monolayer on Ag(100). Chirality is effectively transferred from molecule to array by a unequivocal assembling relation (*lR/rL*).