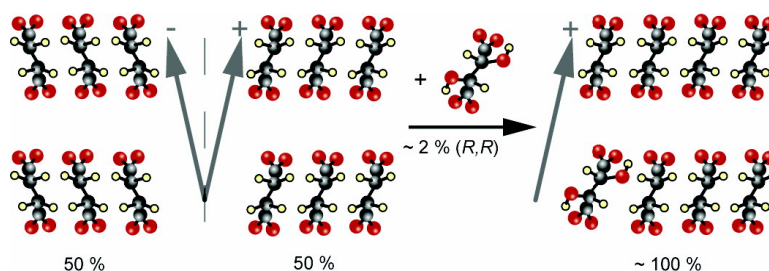


## Induction of Homochirality in Achiral Enantiomorphous Monolayers

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## Induction of Homochirality in Achiral Enantiomorphous Monolayers

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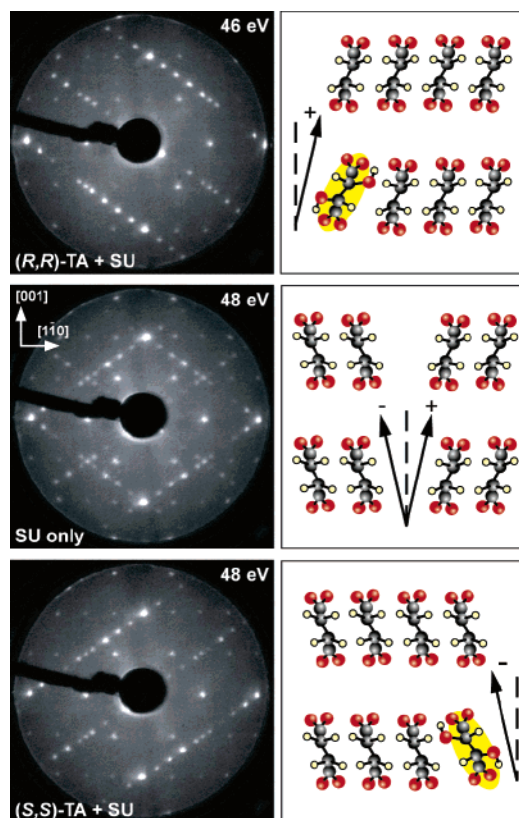
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Achiral molecules can become chiral when adsorbed at surfaces.<sup>1</sup> Either the reduced symmetry of the adsorbate complex or distortions of the molecular frame due to the interaction with the surface are responsible for this induced chirality. In addition, achiral molecules can be organized on regular substrates into mirror domains; i.e., the adsorbate lattice structure destroys the reflection symmetry of the substrate lattice.<sup>2</sup> On average, there are equal left- and right-handed domains in the absence of additional chiral influences, and the surface is globally achiral. A similar orientational chirality effect has been reported for bent-core achiral molecules in smectic liquid crystals.<sup>3</sup> On the other hand, chiral modifiers are used in heterogeneous enantiospecific catalysis to favor one handedness of a prochiral reactant adsorbate complex, but only a few working enantioselective catalysts are available today. Most prominent are the *cinchona*-modified platinum group metal catalysts<sup>4</sup> and the tartaric acid-modified nickel catalysts<sup>5</sup> for asymmetric hydrogenation of functionalized ketones and of  $\beta$ -keto carboxylic acid esters, respectively. However, the mechanism of chirality induction in surface reactions is still poorly understood.<sup>6</sup> Therefore, studies on well-defined model surfaces are a promising approach for getting more insight into these processes.<sup>2</sup> For example, coadsorption studies of an equimolar ratio of methylacetoacetate (MAA) and (*R,R*)-tartaric acid (TA) on Ni(111) showed that only one enantiomeric MAA adsorbate complex was formed.<sup>7</sup>

Here we report that doping of an achiral monolayer with only 2 mol % of chiral modifier is sufficient to generate global homochirality by breaking the reflection symmetry of the whole surface layer. As achiral molecule inducing chiral motifs we used succinic acid (SU, HOOC-CH<sub>2</sub>-CH<sub>2</sub>-COOH). This molecule interacts with the Cu(110) surface through the carboxylate groups and is either singly (monosuccinate) or doubly (bisuccinate) deprotonated,<sup>8,9</sup> as also reported for TA on Cu(110).<sup>10</sup>

Figure 1 shows LEED patterns for SU monolayer lattice structures on Cu(110) after preadsorption of small amounts of (*R,R*)-TA (top) and (*S,S*)-TA (bottom) as well as without any TA involved (middle). This SU-only pattern has previously been reported.<sup>9</sup> Although this LEED pattern has a nonenantiomorphous  $C_{2v}$  symmetry, Humblot et al. showed that it is based on a superposition of two enantiomorphous bisuccinate mirror domains of (90, -11) and (11, -90) periodicity,<sup>11</sup> plus a monosuccinate  $c(4 \times 2)$  lattice.<sup>12</sup>

However, when small amounts of a TA enantiomer were added and the sample was heated to 500 K, only diffraction spots of one enantiomorphous lattice were observable (Figure 1, top and bottom), whereby the opposite TA enantiomer induced the opposite mirror domain pattern. We determined the relative amounts of TA and SU in the monolayers by means of temperature-programmed desorption (TPD). Upon heating, SU and TA decompose in part into carbon dioxide, which desorbs instantaneously. Because SU is thermally more stable on Cu(110) than TA, the TPD signals are well separated and the corresponding signal areas can be used to determine the molecular ratios of both species. Via this quantifica-



**Figure 1.** Homochirality in enantiomorphous succinic acid (SU) monolayers on a copper(110) surface as observed by LEED after doping with tartaric acid (TA) enantiomers. Top: (11, -90) pattern of SU doped with (*R,R*)-TA. Middle: Superposition of (90, -11) and (11, -90) patterns of SU, no TA. Bottom: (90, -11) pattern of SU doped with (*S,S*)-TA. Diffraction spots of  $c(4 \times 2)$  and  $p(4 \times 2)$  structures are also observed in all three patterns. The cartoons in the right column illustrate the situation in real space. The enantiomorphism is manifested by opposite tilt angles of the adsorbate lattices with respect to the [001] substrate lattice direction. While the LEED pattern of the pure SU layer reflects that both enantiomorphous lattices are present on the surface, the TA-doped lattices tilt in only one direction, i.e., the respective opposite enantiomorphous lattice is not observed.

tion, we found that a concentration of 2 mol % of TA in the SU layer was sufficient to prevent formation of one of the enantiomorphous lattices. This amount of TA, in turn, corresponds to an absolute coverage of one molecule per 1000 surface copper atoms. Lower TA concentrations led to both enantiomorphous LEED patterns, but still at different intensities. After selective desorption of TA, an achiral LEED pattern for the SU monolayer structure was observed again.<sup>13</sup>

The SU-TA/Cu(110) homochiral system involves two levels of asymmetrization. First, a chiral distortion of the SU molecular frame takes place and induces long-range enantiomorphism in the SU lattice. Second, the presence of a TA enantiomer energetically favors

one enantiomorph to such an extent that the opposite enantiomorph does not exist on the surface. The local chiral induction can be explained by the similarities of the two molecules and their lateral interactions on the Cu(110) surface. Bitartrate is distorted in a zigzag fashion,<sup>14</sup> and the same is assumed for bisuccinate, although without a stereospecific preference.<sup>9</sup> A TA molecule serves as chiral seed and forces adjacent SU molecules into the same absolute configuration. Consequently, for a given enantiomer, the sign of the adsorbate lattice tilt angle in the TA-doped SU layer is the same as that for the pure bitartrate layer: (*R,R*)-TA favors the formation of the SU (11,−90) lattice, while (*R,R*)-bitartrate forms a (12,−90) lattice, and (*S,S*)-TA induces the SU (90,−11) lattice, while (*S,S*)-bitartrate forms a (90,−12) lattice.<sup>15</sup> Because the adsorbate mesh periodicities are almost identical, the crystallography observed for racemic TA on Cu(110) is quite similar to the one observed for pure SU: bitartrate is self-separated into homochiral (12,−90) and (90,−12) domains, while monotartrate forms a racemic non-enantiomorphous  $c(4 \times 2)$  lattice.<sup>16</sup> Whether the lateral interactions are mediated directly via hydrogen bonds between the molecules or through the substrate, e.g., by a chiral surface reconstruction, cannot be concluded here. A “chiral footprint” reconstruction was observed for the bitartrate/Ni(110) system<sup>17</sup> but ruled out for Cu(110), although a strain in the Cu substrate was put forward to explain the adsorbate mesh structures.<sup>18</sup>

The amount of TA driving the racemic SU layer into a homochiral system is surprisingly small. This raises the question about the effective amplification mechanism. The local chirality induction model, as mentioned above, connects the handedness of TA and the SU domains but does not explain the amplification of orientational order into the long-range structures. We recall that the pure SU layer consists of mirror domains and thus shows also domain boundaries between the two enantiomorphous lattices. The low concentration of TA can only have a global influence if the domain sizes are large enough and/or the existence of domain boundaries at the temperature of chirality induction (~500 K) is energetically unfavorable. SU domains below a critical size would leave enough domains without TA and with random handedness. Scanning tunneling microscopy (STM) images showed on average enantiomorphous SU domain sizes of 20–35 nm.<sup>9</sup> Taking the local coverage of 1/6 SU molecule per Cu atom into account, about  $1500 \pm 1000$  SU molecules are present in a single domain. Since the amplification is then caused by about 30 TA molecules, located within the domains or at the domain boundaries, the transfer of chirality cannot be explained by a local induction mechanism. Most probably, cooperative lateral interactions, in which a small chiral influence has a global consequence, i.e., homochirality in this case, are involved here.

A similar phenomenon, coined as “sergeants-and-soldiers”, has been reported for helical polyisocyanate copolymers of achiral (“soldiers”) and chiral (“sergeants”) units.<sup>19</sup> If only achiral units were used, the polymer helix had equal left- and right-handed domains, leading to zero net optical activity. Small concentrations, however, of chiral units randomly distributed over the helical polymer were sufficient to induce a basically one-handed helix with high optical activity. The same effect was observed for small enantiomeric excess in (*R*)- and (*S*)-copolymers (“majority rule”).<sup>20</sup> Both effects were explained via cooperative interactions causing a magnification of even very small chiral influences,<sup>21</sup> and were quantitatively described via statistical physics by applying a one-dimensional random-field Ising model.<sup>22</sup>

To our knowledge, the TA/SU–Cu(110) system is the first example for a cooperative amplification of chiral ordering on a crystal surface. A few “TA sergeants” force many “SU soldiers”

into the same configuration. A test of this scenario, including an analysis of SU domain sizes as a function of TA concentration in the framework of a two-dimensional quenched chiral field Ising model, is under way. In addition, more theoretical efforts are proposed to evaluate the role of the substrate, not only in long-range chirality transfer in layers of rigid chiral molecules<sup>23</sup> but also in inducing structural modifications between different coadsorbed molecules, as observed here.

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**Supporting Information Available:** Experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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