

# Preparation of Chiral Surfaces from Achiral Molecules by Controlled Symmetry Breaking\*\*

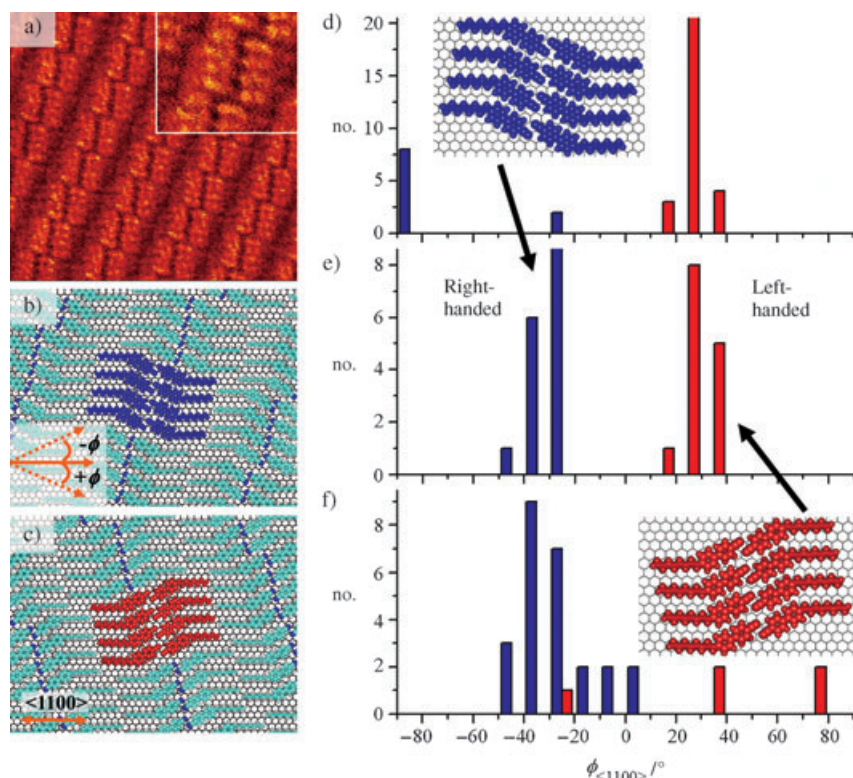
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For over 150 years understanding and controlling chirality has been an important objective in natural science.<sup>[1]</sup> Chirality, the property of an object being nonsuperimposable on its mirror image, affects the performance of many chemical, biochemical, and physical systems, and therefore chiral control has widespread application.<sup>[2]</sup> Surfaces, as with fully three-dimensional objects, can be chiral and such systems have been the focus of much recent attention.<sup>[3]</sup> Herein we report a fundamentally new method for the preparation of chiral organic films which allows control over both the absolute handedness and enantiomeric excess of adsorbed molecules, yet unlike other approaches to the formation of chiral surfaces, our method involves no chiral inputs. Instead, mirror symmetry is broken in a layer of achiral molecules by controlling their arrangement on a single-crystal substrate with a liquid-crystal solvent and a magnetic field.

We studied films of the compound 4-cyano-4'-octylbiphenyl (8CB) on graphite, a room-temperature smectic-A liquid crystal (LC). When placed in contact with graphite, 8CB forms a single polycrystalline monolayer at the interface between the substrate and bulk fluid supernate.<sup>[4]</sup> Molecules in the monolayer organize as shown in Figures 1 a–c, with the long molecular axis in the substrate plane. The unit cell contains eight molecules in registry with the substrate. They are aligned in an antiparallel configuration, which results in a cancellation of dipoles. Registry is driven by an interaction between the alkyl tails and graphite; tails always orient along one of the three graphite  $\langle 1100 \rangle$  directions of a form.<sup>[5]</sup> In three-dimensional space 8CB is achiral, but when the molecule is confined to two dimensions upon adsorption, its conformational mobility is hindered. This breaks the mirror symmetry of the adsorbed molecules; in combination with the graphite substrate the resulting monolayer sur-

face is chiral.<sup>[6]</sup> The two enantiomorphs undergo phase separation into purely left- or right-handed domains measuring a few hundred nanometers in size.

8CB is an example of a compound that is achiral in three dimensions but that can form a chiral surface when adsorbed as a two-dimensional film. More generally, any molecule that



**Figure 1.** Monolayers of 8CB on graphite: a) STM image of a right-handed domain ( $20 \times 20 \text{ nm}^2$ ,  $I_{\text{tunn}} = 1.33 \text{ nA}$ ,  $V_b = -1.2 \text{ V}$ ) (The inset is at the scale of the models in parts b) and c) ( $6 \times 6 \text{ nm}^2$ ,  $I_{\text{tunn}} = 0.60 \text{ nA}$ ,  $V_b = -1.87 \text{ V}$ )). b) Model illustration of right-handed and c) left-handed forms, which represent two of the six possible arrangements of molecules in the monolayers; note that the two are mirror images. The remaining four possible configurations are simple rotations by  $\pm 60^\circ$  of the two shown. The chirality and relative orientation illustrated in part b) is the same as the STM images in part a). d)–f) Histograms of molecular headgroup orientations ( $\phi_{\langle 1100 \rangle}$ ) determined by STM for samples prepared with three representative field alignments: d) field at  $-19^\circ$  from  $\langle 1100 \rangle$ ; e) field at  $0^\circ$  (parallel to  $\langle 1100 \rangle$ ); and f) field at  $+19^\circ$  from  $\langle 1100 \rangle$ . The sign convention is shown in the inset of part b). Blue bars indicate right-handed molecules, red bars indicate left-handed molecules. Part e) shows two degenerate molecular configurations that correspond to the two models shown in parts b) and c), with the cyanobiphenyl headgroups oriented at approximately  $\pm 22^\circ$ . More generally, other field orientations break the degeneracy which leads to an excess of one chiral population over the other, as in parts d) and f).  $I_{\text{tunn}}$  = tunneling current;  $V_b$  = bias voltage.

belongs to the  $C_{nh}$ ,  $C_s$ , or  $C_i$  point groups (which are achiral in three dimensions) has the potential to form a chiral surface if restricted to two-dimensional space with the proper orientation.<sup>[7,8]</sup> Furthermore, compounds with other symmetries can form chiral supramolecular patterns even if the individual adsorbates are not themselves chiral.<sup>[9]</sup> This adsorption-induced breakage of chiral symmetry always leads to the formation of pairs of energetically equivalent enantiomorphs or mirror images. Consequently, surfaces covered by multiple microscopic molecular domains are racemic on a macroscopic scale, as left- and right-handed regions form in equal numbers.

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To produce a film with a net excess of one enantiomorph over the other—a prerequisite for many applications of chiral surfaces—a further decrease in symmetry is required. Until now, such homochiral surfaces have always been produced by the introduction of a chiral component of some kind, such as a chiral adsorbate, reactant, or catalyst, or by the cleavage of crystals along high-index faces.<sup>[3]</sup> Herein we introduce a method which, for the first time, allows the preparation of macroscopically homochiral films without any chiral inputs; instead, the chiral symmetry of 8CB films is systematically broken by the use of a LC solvent and a magnetic field to induce a preferred in-plane orientation of adsorbed molecules on an achiral single-crystal substrate. The absolute chirality and enantiomeric excess of the resulting film can be selected and controlled so that surfaces covered by predominately left-handed, right-handed, or a mixture of left- and right-handed molecules can be prepared.

Crystallization of an 8CB monolayer on graphite yields six energetically equivalent configurations, as observed with scanning tunneling microscopy (STM): (three distinguishable orientations)  $\times$  (two enantiomorphs). All six configurations occur with equal frequency; hence in the absence of an external perturbation, 8CB films are racemic.<sup>[5]</sup> Figures 1b and 1c show two of the six possible configurations; the other four are derived from these by a rotation of  $\pm 60^\circ$  in the surface plane.

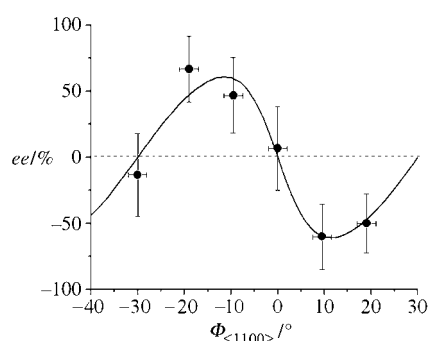
To break the degeneracy among configurations, samples were prepared by applying a magnetic field (1.2 T) parallel to the substrate as a droplet of 8CB was placed on the surface, heated at  $100^\circ\text{C}$  for 2 min, then gradually cooled to room temperature. We call this technique “liquid-crystal imprinting” because orientational order in the bulk LC supernate becomes imprinted on the monolayer, producing a molecular film with macroscopic uniform in-plane alignment.<sup>[10,11c]</sup> Although strong enough to produce well-aligned films, the orientational energy of the magnetic field was small compared with the strength of intermolecular and molecule–substrate interactions. Thus, the arrangement of 8CB molecules within the unit cell, and the registry of molecules with the surface were unaltered from reference samples prepared in the absence of any field. The outcome of applying a magnetic field was therefore to select for some of the six possible configurations as being most favored. Afterward, samples were removed from the field and imaged by STM.<sup>[12]</sup> The STM tip plunged through the thick, nonconducting 8CB-LC supernate covering the sample to image molecules in the polycrystalline monolayer. 30–40 STM images were acquired at widely separated locations (millimeter distances) to observe molecular orientation, with no more than ten measurements taken from any one sample specimen. Naturally occurring single-crystal graphite substrates, which possessed uniform crystallographic orientation over a macroscopic area, were used in all cases.<sup>[13]</sup>

Figures 1d–f present molecular orientational distributions measured by STM for three representative magnetic field directions. The abscissa indicates the angle  $\phi_{(1100)}$  between the 8CB headgroup and the substrate  $\langle 1100 \rangle$  direction, with color indicating molecular chirality (blue = right-handed, red = left-handed).<sup>[14]</sup> The distributions were nonuniform; different

field orientations favored different monolayer configurations. The preferred configuration for a particular field direction was generally observed to be one that oriented the cyanobiphenyl headgroups as nearly parallel to the field as possible, yet maintained registry of the alkyl tails along one of the graphite  $\langle 1100 \rangle$  directions of a form.

A special case is shown in Figure 1e, in which the field was parallel to  $\langle 1100 \rangle$ . In this case, two configurations that correspond to the two shown as models (Figures 1b and 1c), occurred with equal frequency. More generally, one configuration could be made more favored—and the others less favored—by changing the field orientation. This is evident in the data from example experiments in which the magnetic field was rotated by  $-19^\circ$  and  $+19^\circ$  from  $\langle 1100 \rangle$  (Figures 1d and 1f, respectively). The symmetry between configurations was broken, producing a film with a net excess of one enantiomorph over the other.<sup>[15]</sup>

The outcome of this effect is summarized in Figure 2, which shows the overall enantiomeric excess ( $ee = (P_R - P_L) / (P_R + P_L)$ ) for several field orientations measured by STM.



**Figure 2.** Absolute chirality and enantiomeric excess in polycrystalline 8CB monolayers on graphite were both adjustable by preparing samples in a magnetic alignment field oriented along different directions. Each point was determined from 30–40 STM observations on at least three different samples. The solid line is a prediction from the model described in the text.  $\phi_{(1100)}$  = magnetic field orientation with respect to  $\langle 1100 \rangle$ .

The value  $P_X$  is the experimental probability of observing a right- or left-handed domain. The enantiomeric excess oscillates between right- and left-handed surfaces with a repeat period of  $60^\circ$ . At the extrema the enantiomeric excess is greater than 60%, meaning that more than 80% of the surface is covered by a single enantiomorph. By simply changing the orientation of the field the absolute chirality and enantiomeric purity of the film can be engineered over a wide range of values.

To explain the trend in Figure 2 we note as discussed in reference [10] that the alignment energy of a molecular monolayer domain deposited from a LC solvent in a magnetic field can be expressed approximately as  $U = A \sin^2 \theta$ , in which  $\theta$  represents the angle between the field and the preferred azimuthal anchoring direction at the film–LC interface, and  $A$  is a constant that depends on the properties of the LC supernate, strength of the magnetic field, domain size, and the anchoring energy. Comparison of STM images and polarizing

optical microscopy observations of the bulk director alignment showed that the preferred anchoring axis was nearly parallel to the cyanobiphenyl headgroup, establishing the reference for measuring  $\theta$ , and in reference [10],  $A$  was measured to be  $25 \text{ kJ mol}^{-1}$ . The probability of observing a given configuration can therefore be estimated by assuming an equilibrium population distribution:

$$P_i = \frac{e^{(-U_i/kT)}}{\sum_{i=1}^6 e^{(-U_i/kT)}}$$

in which  $\sum_{i=1}^6 e^{(-U_i/kT)}$  is the partition function,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. The enantiomeric excess can then be calculated directly from  $P$ , with the predicted (not fitted) result shown by the solid line in Figure 2.

For the system studied herein, the LC solvent and film-forming adsorbate were both the same compound, 8CB. However, LC solvents have been effective in the control of orientational order in thin films composed of a variety of organic compounds, polymers, and small particles, including the unrestricted case in which the identity of the adsorbate building block and LC solvent were not the same.<sup>[10,11]</sup> This method should therefore be applicable to a broad class of surfaces and films, provided a single crystal substrate is used with adsorbates of symmetry  $C_{nh}$ ,  $C_s$ , or  $C_i$ .

More generally, one can view these findings in terms of the classical three-point model for chirality, which states that three unique points, or constraints, are needed to recognize a chiral object. Adsorption defines two effective constraints by inhibiting rotation and breaking mirror symmetry perpendicular to the adsorption plane. The LC-orienting influence provides a third constraint by the restriction of molecules to a single orientation within the confinement plane. The former two constraints break the mirror symmetry of individual molecules, whereas the latter breaks the mirror symmetry of molecular ensembles. This suggests that the symmetry-breaking role played by the LC solvent need not be unique, but could, in principle, be replaced by a different uniaxial influence, such as a laminar-solvent-flow field.

In summary, we report a fundamentally new way to prepare chiral surfaces that allows continuous control over absolute handedness and enantiomeric excess without incorporation of any chiral inputs. Further increases in the maximum enantiomeric excess are likely possible, as are applications of the principle to other systems in which optimization of experimental parameters can be guided by the proposed model. The findings reported herein may be applicable to a variety of fundamental problems and technologies in chiral control, ranging from the formation of chiral surfaces for use in optics, enantioselective adsorption, and chiral separations, to the preparation of orienting films in ferroelectric LC displays.

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- [14] The left- and right-handed designations used herein conform to the convention adopted in most previous studies of 8CB on graphite, but it should be noted these designations are arbitrary and not based on CIP nomenclature rules.
- [15] The spread in the distributions of molecular orientations shown in the histograms arises principally from three factors: 1) measurement error associated with thermal drift during STM imaging and angular alignment of the samples; 2) imperfections on the single crystal substrates; and 3) alternative packing motifs in the 8CB monolayer. 8CB is known to crystallize into a family of closely related polymorphs, of which the STM image and models in Figure 1 are the most common. In some minority structures the cyanobiphenyl heads possess slightly different orientations in the unit cell. (D. L. Patrick, T. P. Beebe, Jr., *Langmuir* **1994**, 10, 298.)