Spontaneous chiral symmetry breaking by achiral molecules in a Langmuir–Blodgett film

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The spontaneous breaking of symmetry is responsible for many physical phenomena, including the mass differences of elementary particles and phase transitions in condensed-matter systems. The breaking of mirror symmetry leads to chirality. In general, chiral effects in condensed-matter systems, such as optical activity, are associated with chiral molecular structures. But several recent observations of domain formation in thin organic films of achiral molecules have suggested that spontaneous separation into regions of differing chirality may occur in these systems. Eckhardt et al., have reported the spontaneous resolution of chiral molecules in Langmuir–Blodgett (LB) films. Here we present images of LB films of calcium arachidate obtained with the atomic force microscope, which suggest that these achiral molecules can separate spontaneously into lattices with chiral packing of opposite handedness. We suggest that this symmetry breaking is driven by the interplay between the packing constraints imposed by the alkane tails and the molecular-area requirements set by the calcium ions.

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In addition to being model systems for the study of molecular interactions that lead to self-assembly, LB films have applications in electronics, nonlinear optics, cell membrane models and biosensors. Although the structure and symmetry of LB films have been studied by a variety of techniques, the atomic force microscope (AFM) has increasingly been used to image molecular structure and defects. The AFM has the advantage of probing only surface topography, and the capability to resolve individual molecules as well as defects such as dislocations and domain boundaries in the surface layer.

Figure 1a shows a typical unenhanced 10 × 10 nm AFM image of the methyl end of trilayers of calcium arachidate (CaA) on mica with the two-dimensional Fourier transform (FT) inset. Although the molecular rows (and some periodicities along the rows) are easily visible in the image, the details of the molecular lattice are much more readily determined from the FT. The six brightest spots in the FT form a skewed hexagonal pattern and correspond to three distinctly different lattice spacings in the film of (A) 0.442 nm, (B) 0.576 nm, and (C) 0.686 nm. The FT has no axis of mirror symmetry; hence the real-space CaA lattice also has no mirror symmetry and is chiral, even though the constituent molecules are achiral. Figure 1b and c are representative FTS of images (not shown) of two different crystalline domains in the same CaA LB film. Figure 1c is similar to the inset in Fig. 1a and has the same progression (clockwise) ABC of lattice spacings. Figure 1b is the mirror image of Fig. 1c and has the same lattice spacings but the progression (clockwise) is ACB; the two FTS cannot be superimposed by any two-dimensional rotation or translation. This shows that the CaA film consists of domains of two distinct lattice structures that are mirror images of each other, that is, that the achiral CaA molecules have undergone a spontaneous chiral symmetry breaking. The crystallinity of the mica substrate had no effect on this ordering as monolayers of CaA showed a smooth and featureless surface without any lattice structure, similar to cadmium arachidate films.

There are several possibilities for chiral symmetry breaking in thin films of achiral molecules: (1) a hexatic phase with the tilt direction between nearest and next-nearest directions (smectic L phase), (2) inequivalent mirror-image molecular packings, and (3) chiral resolution of a racemic mixture of two opposite enantiomers. Case (3) is a particular instance of case (2). Our AFM images of CaA LB films are the first molecular-scale resolution of case (2), a more general example than that reported by Eckhardt et al., who also observed mirror-image lattice structures but ascribed the chirality to a resolution of a racemic mixture of chiral molecules. In fact, our results show that resolution of a racemic mixture can not be safely inferred from the existence of a chiral lattice structure. Although case (1) has been inferred from long-length-scale striped patterns in Langmuir monolayers and thermotropic smectic liquid crystals, a smectic L phase has never been identified at the molecular level in a system where the constituent molecules were achiral.

From the information available from the AFM images and FTS we can propose a lattice structure to explain the origin of the chirality. The additional reflections located within the skewed hexagon pattern show that the unit cell of the lattice consists of more than one molecule. A statistical analysis was used to determine the best fit to the reciprocal lattice vectors (r.l.v.s), b₁, b₂, b₃ (b₁ and b₂ are labelled in Fig. 1b,c). The positions of the r.l.v. are enough to determine the unit cell dimensions, 1.86 ± 0.01 nm × 0.894 ± 0.006 nm with an angle of 71.3 ± 0.5° between them (Fig. 1b,c) for a molecular area of 19.7 ± 0.3 Å², assuming an 8-molecule unit cell. A height profile along the [10] direction (Fig. 2a) shows a regular sawtooth pattern with a repeat every four molecular rows; however, we could not accurately deter-
mine the absolute amplitude. A height profile along the [01] direction (Fig. 2b) shows that the molecular rows alternate up and down (similar to the $2 \times 2$ structure of barium arachidate$^6$).

From the autocorrelation function of the images (see Fig. 3), we can extract the local packing dimensions within the unit cell (0.46 nm $\times$ 0.45 nm with an angle of 79°—see Fig. 4a), confirm the up and down alternation along the rows, and note the increased intensity every fourth row. This leads us to construct a $4 \times 2$ unit cell for the CaA lattice. By analogy with barium arachidate (BaA) films$^5$, the unit cell is constructed by inverting every fourth local cell (in the $3 \times 1$ structure of BaA$^5$ every third local cell is inverted). Combined with the regular height modulation (Fig. 2a), this suggests that there is a stacking fault every four rows in the [01] direction. Figure 4b shows a structural model based on a locally triclinic hydrocarbon packing (Kitaigorodskii's T[1/2 0]), with a stacking fault after four rows that is quantitatively consistent with our data. Asymmetric stacking in molecular films with stacking faults in every fourth row were also reported for monolayers of liquid-crystal-forming alkyldicyanobiphenyl molecules on graphite$^6$.

The triclinic packing is inherently chiral, leading to both left-handed and right-handed packings that cannot be superimposed (Fig. 4b). The molecules tilt along a direction between nearest and next-nearest neighbours, which also adds to the chirality.) The stacking fault results in a regular sawtooth pattern along the [01] direction with an estimated amplitude of $\sim$0.15-0.2 nm. The overall effect of the stacking fault is to increase the average tilt of the molecules, from the standard T[1/2 0] packing subcell tilt of 19° to a 26° tilt. The 26° tilt is consistent with the measured bilayer thickness of 5.0 nm (the extended length of an arachidic acid molecule is $\sim$5.5-5.6 nm; for a tilt of 26°, the bilayer thickness is $5.6 \times \cos 26^\circ = 5.0$ nm). The observed tilt is also consistent with Fourier transform infrared and near-edge X-ray absorption fine structure (NEXAFS) measurements that show CaA monolayers to be tilted$^{25,26}$.

The stacking fault is necessary because the all trans chains of the alkane portion of the fatty acid can only close-pack at a certain discrete tilt angles, resulting in discrete values for the area per molecule$^1$. These discrete areas per alkane chain are not necessarily consistent with the density preferred by the counterion. Preliminary calculations (D.K.S., C. M. Knobler, R.V., J.A.Z., manuscript in preparation) show that it is energetically favourable for the lattice to incorporate a series of regular stacking faults while maintaining the close-packed triclinic structure with a tilt of 19°, rather than to adopt a less close-packed structure with a homogeneous 26° tilt. As a consequence of these conflicting density requirements, the $4 \times 2$ unit cell of CaA has a locally

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**FIG. 2** a, Height profile along the [10] direction in the CaA LB film (Fig. 1) showing the regular sawtooth pattern with a repeat every four molecular rows, highlighted by the arrows. The amplitude, which was $\sim$1-2 Å, could not be accurately determined due to difficulty in calibrating the z piezoelectric scanner. b, Height profile along the [01] direction showing the molecular rows alternating up and down (similar to the $2 \times 2$ structure of barium arachidate$^6$). The data was smoothed by boxcar averaging.

**FIG. 3** Autocorrelation function of Fig. 1a. Note the alternating vertical displacement of the terminal methylene group in the autocorrelation function, shown by the dark holes in between the bright features along each row of molecules. The stacking fault every four rows is also noticeable as every fourth row is highlighted. From the autocorrelation function, the local cell dimensions, as well as the vertical modulations are readily measured. The chequered nature of the packings is verified.
that is quantitatively consistent with our data. The view is along the chain axis of the molecules. The triclinic structure is inherently chiral and we show the mirror plane (dotted line) and the right- and left-handed structures. The black lines represent the projected hydrocarbon backbone of the chain, the circles represent the radii of the hydrogen atoms. The shaded and unshaded circles represent the hydrogen atoms belonging to the even and odd carbons, respectively. The 4 × 2 unit cell can be constructed by inverting every fourth local cell, corresponding to a regular pattern of stacking faults that causes a jump in the structure both vertically and in the plane (see a). As in the AFM images, lighter (unshaded) molecules are higher, darker (shaded) molecules lower.

triclinic structure (to maximize the van der Waals contact between the alkane chains of the fatty acid), but incorporates a regular stacking fault and the up/down displacement present in the 3 × 1 and 2 × 2 structures, respectively, of BaA films. These defects are necessary to match the alkane packing density with the area per molecule set by the Ca2+ ion. The similarity in lattice structure between Ba2+ and Ca2+ is not surprising as both are alkaline-earth metals and induce similar effects in Langmuir monolayers. From this and our previous work, it is clear that the counterion sets the lateral density or area per molecule of the fatty acid lattice, and that the alkane chains then pack in such a way as to maximize contact. The simplest correlation, which we observe here, is the inverse correspondence between the molecular area of the multilayer films and the Pauling electronegativity of the cations. The local bond angles between the metal and oxygen or type of bond (ionic/covalent) also appear to be important, however, as Ba2+, Ca and Mg (not shown) fatty-acid salts all pack into chiral triclinic 'herringbone' lattices, whereas Cd, Mn and Pb salts pack into rectangular lattices, even though the molecular areas of Ca and Mn salts are very similar.

Spontaneous separation has been observed with AFM in monolayers of racemic mixtures of chiral tetracyclic alcohol in which the symmetry breaking was ascribed to the chirality at the molecular level, similar to three-dimensional resolution of enantiomers by crystallization as shown by Pasteur. In our present experiments with Ca, the chirality is induced by the novel lattice structure forced on the achiral fatty acids by the competing requirements of the calcium ion molecular area (and likely bond angles) and the allowable close-packing arrangements of alkane chains. Future experiments will show if this spontaneous chiral symmetry breaking also leads to long-scale-pattern formation similar to those found in Langmuir monolayers and smectic liquid crystals.

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