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Chiral molecular patterns of self-assembled ion pairs composed of (*R*,*S*), (*S*)-16-methyloctadecanoic acid and 4,4′-bipyridine†

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Self-assembled monolayers of stearic acid, (*R*,*S*) and (*S*)-16-methyloctadecanoic acid ion-paired with 4,4′-bipyridine have been observed on a solution–graphite interface by a scanning tunneling microscope (STM) and the observed macro-scale molecular patterns have been interpreted in terms of absolute chirality of the constituent molecule.

Scanning tunneling microscopy (STM) has provided molecular images of self-assembled molecules at atomic resolution.[1] Monolayers of self-assembled amphiphiles including fatty acids, alkylated amines, amides and alcohols have been directly imaged at solution–solid interfaces.[2] Recently, determination of absolute configuration of chiral molecules from the STM and AFM images has attracted considerable attention.[3] Determination of the absolute stereochemistry is very important for accessing the biological and toxicological properties of enantiomers. Walba and his group have obtained the STM images of several chiral mesogens aligned on a graphite surface.[4] In this case, the macro-scale chiral structure of the domain has been controlled by the molecular chirality of individual molecules. Flynn's group has observed STM images of (*R*,*S*)-2-bromodecanoic acid aligned on graphite.[5] Although they used a racemic mixture, it was possible to assign the absolute configuration of right handed and left handed molecules from the relative location of the bromine atom, long alkyl chain and hydrogen bonded carboxylic acid. These functional groups provided relative contrast in the image and therefore acted as 'chemical markers'.

In the present paper we have attempted to observe directly the molecular patterns of a chiral and racemic 16-methyloctadecanoic acid (16MeC18) which was synthesized from 2-methylbutanol of known absolute configuration.[6] Such branched fatty acids are found in mammalian tissues and play biologically important roles.[7] In order to confirm the relative position of fatty acid in the observed images, we have attempted to insert 4,4′-bipyridine (bpy) between the carboxy groups as a marker. The observed molecular pattern in the macro-scale order has been correlated with the chirality of the constituent molecule.

For the measurement of STM, sample crystals were dissolved in phenyloctane to near saturation and a drop of solution was applied on the surface of freshly cleaved highly oriented pyrolytic graphite (HOPG). The STM images were obtained in both constant current mode and constant height mode using NanoScope IIIa STM (Digital Instruments). The tunneling tip was a Pt–Ir purchased from Digital Instruments or a tungsten wire which was sharpened by electrochemical etching prior to use. Edges of multilayers were not observed in any STM images, indicating that the observed images are those of monolayers.

Fig. 1 shows the STM image of (*S*)-16MeC18 over a scan area of 12 × 12 nm. Unlike stearic acid, these molecules appear to orient parallel to each other forming a centro-symmetric molecular pattern. An interdigitated geometry, in which the head groups alternately point in opposite directions, has been observed for the molecular alignment of stearic acid and other *n*-alkanoic acids.[8] Steric repulsion between the carboxy group and the branched end group may prevent the molecules from aligning interdigitally. Although a small change in the carbon number of *n*-alkanes and straight chain fatty acids has little effect on the molecular pattern, introduction of a single methyl group on the chain dramatically influences the self-assembled molecular pattern. In Fig. 1, the dark area corresponds to hydrogen bonded carboxy groups associated head-to-head,[8] whereas bright bands can be attributed to the branched alkyl ends. Since most unsubstituted fatty acids do not show such marked contrast in the methylene chain, the alkyl end group in this molecule may locate away from the graphite basal plane.

Stearic acid as well as (*S*)-16MeC18 readily formed 2 : 1 ion pairs with 4,4′-bipyridine (bpy) in octylbenzene solution and generated a stable monolayer on HOPG. Their STM images are given in Figs. 2 and 3, along with their possible molecular alignments. The remarkably bright areas in the image correspond to bpy moieties since areas of higher electronic conductance tend to give brighter images.[9] Therefore a conjugate system like bpy can act as a marker, which provides unusual contrast in the obtained image. Obviously, the bpy moiety is sandwiched by two molecules of fatty acid, as depicted in Figs. 2(b) and 3(b). The molecular axis of the stearic acid appears to incline at an angle of 70° with respect to the bpy array, and that of (*S*)-16MeC18 is inclined as well. It is of note that the bpy salt of stearic acid generates two enantiomeric domains in the macro-scale molecular pattern (Fig. 2(a)). Some achiral molecules are known to form mirror image domains in long-range order when assembled on substrate.[3,4] Thus, sponta-

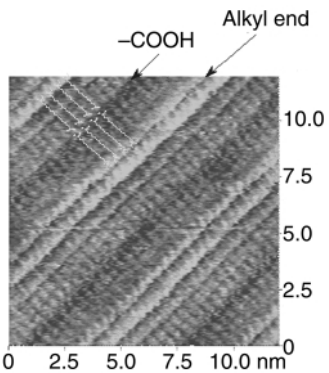

Fig. 1 The STM image of (*S*)-16MeC18 at an interface of phenyloctane and graphite over a scan area of 12 × 12 nm (bias voltage and tunneling current were 1.85 V (tip positive) and 247 pA, respectively).

† Electronic supplementary information (ESI) is available: colour versions of Figs. 1–4. See http://www.rsc.org/suppdata/cc/b0/b005112h/

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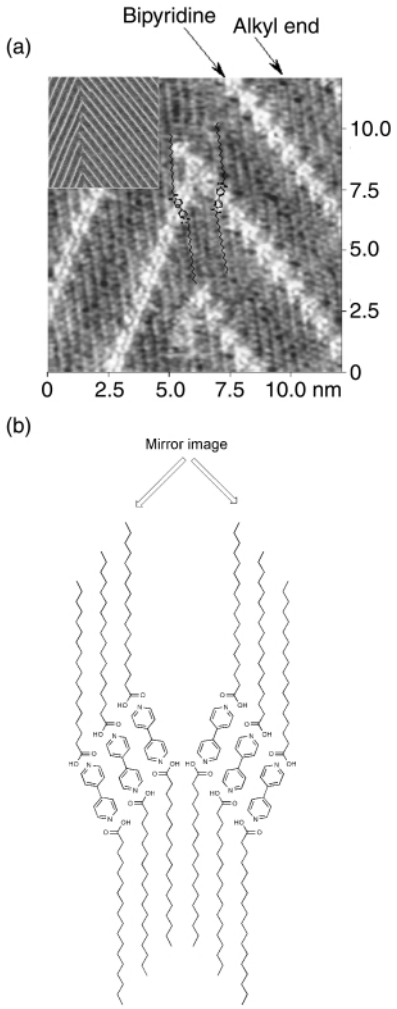

Fig. 2 (a) The STM image of an ion pair composed of stearic acid and 4,4′-bipyridine (2 : 1) over a scan area of 12 × 12 nm (bias voltage and tunneling current were 1.32 V (tip positive) and 234 pA, respectively). A 50 × 50 nm image is inserted in the corner. (b) The schematic drawing of the possible geometry.

neous segregation of achiral bpy salt has taken place upon self-assembly. However, under repeated experiments only a single domain was observed for (*S*)-16MeC18/bpy, as given in Fig.

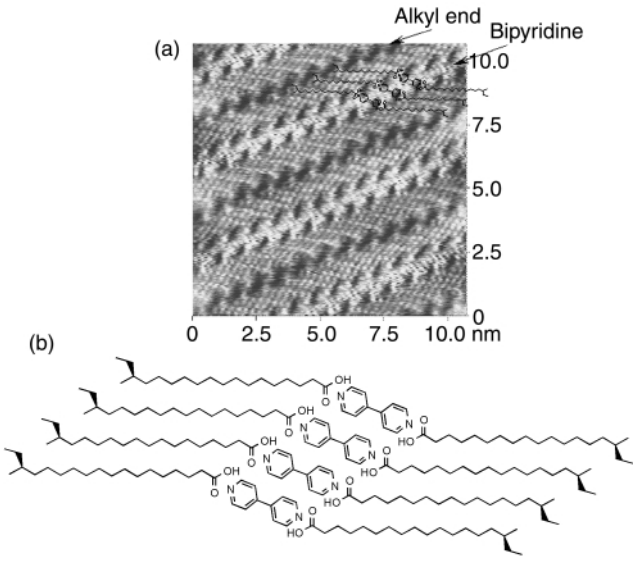

Fig. 3 (a) High resolution STM image of an ion pair composed of (*S*)-16MeC18 and 4,4′-bipyridine (2 : 1) over a scan area of 10.5 × 10.5 nm (bias voltage and tunneling current were 1.85 V (tip positive) and 243 pA, respectively). (b) Proposed molecular alignment of the (*S*)-16MeC18/bpy.

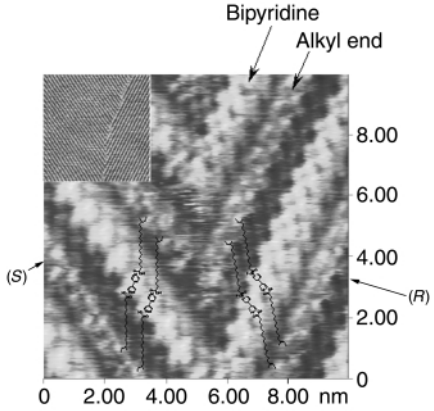

Fig. 4 The STM image of an ion pair composed of (*R*,*S*)-16MeC18 and 4,4′-bipyridine (2 : 1) over a scan area of 10 × 10 nm (bias voltage and tunneling current were 1.80 V (tip positive) and 318 pA, respectively).

3(a). We can clearly see the alkyl chains of the fatty acid as brighter spots. Under careful observation, the alkyl terminal appears to locate out of the straightly stretched alkyl chain. The obtained image is consistent with an (*S*) configuration provided that the bright spot at the alkyl terminal is assigned to the ethyl group, as depicted in Fig. 3(b). Fig. 4 shows the STM image of (*R*,*S*)-16MeC18–bpy over a scan area of 10 × 10 nm, where the racemate mixture appears to segregate into two domains. Thus two different domains of pure enantiomers have grown on the graphite surface from the racemate solution. Since macro-scale morphology of the aligned molecule has been defined by the handedness of the constituent molecule, we can assign the configuration of molecules in each domain by comparison with the macro molecular pattern of (*S*)-16MeC18.

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6 Racemic and (*S*)-16-methyloctadecanoic acids ((*R*,*S*) and (*S*)-16MeC18) were prepared from racemic and (*S*)-2-methyl-1-butyl tosylate as follows. 1-Benzyloxy-14-methylhexadecane was prepared from 2-methyl-1-butyltosylate by Grignard coupling reaction with 12-benzyloxy-1-dodecylmagnesium bromide. After debenzylation of 1-Benzyloxy-14-methylhexadecane and tosylation, the tosylate was reacted with allylmagnesium bromide to produce 17-methyl-1-nonadecene. Then, it was oxidized to 16-methyloctadecanoic acid by $KMnO_4$ in water–CH_2Cl_2 in the presence of tetrabutylammonium bromide as a phase-transfer reagent. The structures of (*R*,*S*)- and (*S*)-16MeC18 were confirmed by their ^{1}H-NMR and high resolution MS spectra.

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