Stereoselective Adsorption on a Gold–Thiol Monolayer with an Enantiopure Surface

Frank Davis, Partha Neogi and Charles J. M. Stirling*

Centre for Molecular Materials, The University of Sheffield, Sheffield, UK S3 7HF

Self-assembled films of (+)-11-toluene-*p*-sulfinylundecanethiol on gold have been shown to adsorb the enantiomeric ethyl lactates from the gas phase; adsorption is totally unselective when the system is not in equilibrium during short exposures at 20 °C but becomes totally selective after extended exposure at 40 °C.

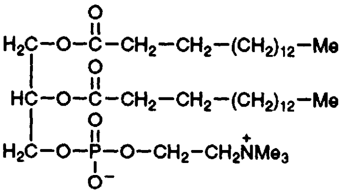
Studies of thin organised films of organic materials prepared by Langmuir–Blodgett (LB) and self-assembly techniques have greatly increased recently.[1] Most work has been carried out on LB films but more recently, the use of gold–thiol monolayers points to the considerable potential for studying the reactivity of such ordered surfaces.[2] Such films have the advantages over LB films of ease of preparation, robustness, and, above all, stability to solvents which enables reactions with both liquid and gas-borne reagents to be investigated. These oriented organic molecules are of great interest in a variety of interface studies relevant to wettability, adhesion, lubrication, microelectronics, electrochemistry and biological membranes. What is surprising in this regard is the dearth of adsorption or reactivity studies on these films.

Some previous work on chiral recognition by enantiopure surfaces has been reported by Heath and Arnett.[3] This demonstrated that chiral recognition in monolayers depends on appropriate stereospecific interactions. Lipid monolayers of L-α-1,2-dipalmitoyl-*syn*-glycero-3-phosphocholine (L-DPPC), **1**, do not usually display chiral interactions because their chiral centres are hidden within hydrocarbon tails. Vodyanoy and coworkers[4] however, have shown that (+) and (−) carvones are evidently able to penetrate phospholipid monolayers and that discrimination between the enantiomers is possible. Chiral recognition in the lateral self condensation of an amphiphilic-(*S*)-serine phenyl ester has been demonstrated by Miyasaka and coworkers.[5]

We now report on chiral recognition by an enantiopure surface. The surface was obtained by self-assembly of the chiral thiol sulfoxide **2** on gold,[6] the sulfoxide being obtained by the route of Scheme 1. The monolayer was obtained by keeping gold-coated mirrors† in a solution of **2** (1 mmol dm^{-3}) in deoxygenated CH_2Cl_2 overnight. After thorough washing with CH_2Cl_2 and drying in high purity argon, the film was examined by polarised (90°) reflectance (75°) absorbance FTIR spectroscopy‡ [Fig. 1(*a*)]. The spectrum was the same as that of bulk sulfoxide **2**. The sessile contact angle of water on the sulfoxide film was 62°.

The coated mirrors (140 cm^2) were dried over anhydrous SiO_2 (4 h) and then exposed to the saturated vapour of (±) ethyl lactate (18 h, 20 °C). The exposed mirrors were then kept *in vacuo* (1 mmHg, 18 h). The FTIR spectrum [Fig. 1(*b*)] of this film then showed additional absorptions due to adsorbed lactate ester, notably at 1747 cm^{-1}, to be compared with that obtained for bulk ester 1736 cm^{-1} (Fig. 1). This frequency change suggests transfer of hydrogen bonding from carbonyl to sulfinyl oxygen. Adsorbed ester was removed from the mirrors by washing with CH_2Cl_2. The washings were carefully concentrated by bulb-to-bulb evaporation to 10 μl and submitted to gas liquid chromatography§ on cyclodextrin B.

On this timescale within experimental error there is no selection of one enantiomer over the other by the enantiopure surface. Closely similar results were obtained with (±) 1-phenylethanol when again there was no evidence of chiral selection on this timescale. There appear to be three possible explanations for this behaviour: (*i*) there is no selection of one enantiomer over another in an equilibrated system. This seems unlikely in view of known energies of such interac-



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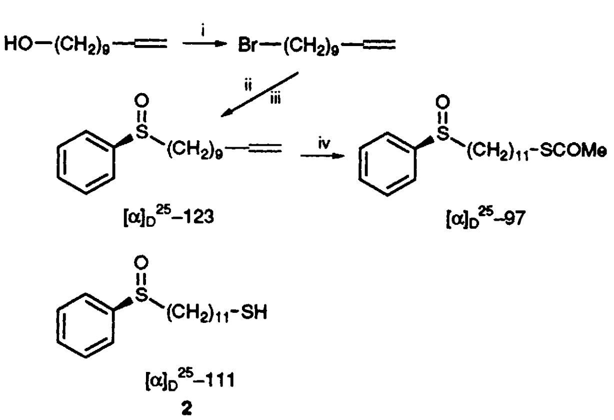

Scheme 1 *Reagents and conditions*: i, PBr_3, dry toluene, reflux 3 h; ii, Mg, Et_2O, 20 °C; iii, (*S*)-menthyl toluene-*p*-sulfinate; iv, Me_3COSH, PhMe, AIBN, *hν*, 15 min; v, 0.1 mol dm^{-3} NaOH–H_2O–MeOH, 48 h, 20 °C

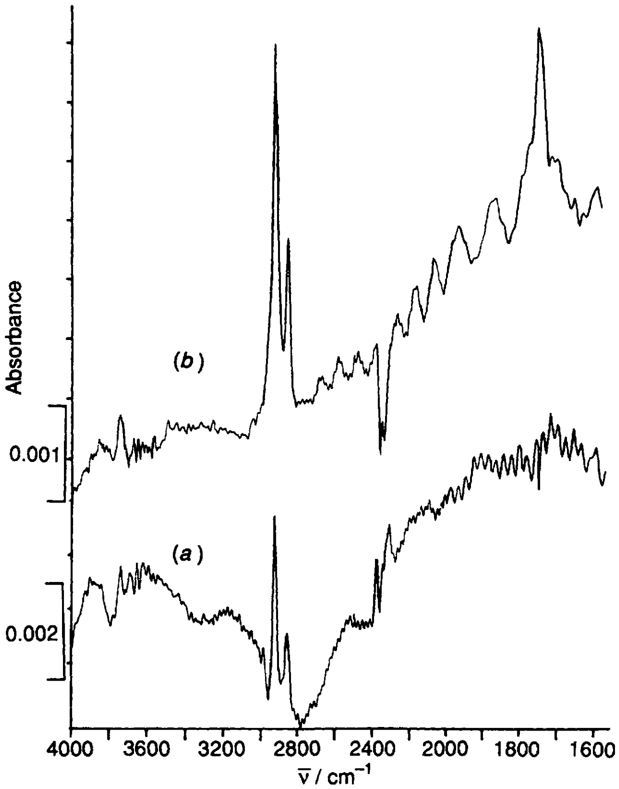

Fig. 1 (*a*) IR spectrum of a gold–thiol monolayer of sulfoxide, **2** and (*b*) monolayer in (*a*) after exposure to the vapour of (±)-ethyl lactate (see text)

tions.[6] (*ii*) Selective adsorption of one enantiomer would, with a bisfunctional adsorbate such as ethyl lactate, produce a new chiral surface upon which the opposite enantiomer might be adsorbed particularly as the free energy of racemates is often less than that of pure enantiomers.[7] This process could possibly be repeated for several layers and hence result in no apparent selection. The lack of selection with the monofunctional 1-phenylethanol is, however, evidence against this possibility, as is the retention of the ester on the surface *in vacuo*. (*iii*) The system is not in equilibrium. The adsorbed molecule may be firmly retained on each collision and hence no selection is seen. The tenacious hold on the adsorbate by the film is seen in the conditions above. In a separate experiment, the film carrying both enantiomers in equal amounts was exposed to the vapour of pure (−)-ethyl lactate under the same conditions. There was substantial growth in the GC peak for the (−)-enantiomer but that of the (+)-enantiomer was unchanged in intensity. Subsequent experiments support this view. When adsorption was carried out at 20 °C for 48 h, there was no selection but at 40 °C for 3 days, the (+):(−) ratio increased to 70:30 and after 10 days, at 40 °C, none of the (−) isomer could be detected. Provided that equilibration is possible, therefore, enantiomeric selection is, within experimental error, complete.

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Footnotes

† Polished glass sheets 7 × 10 cm^2 mm were cleaned with 30% H_2O_2 : H_2SO_4 (1:3) at 100 °C for 1 h, washed with distilled water and dried in a stream of high purity argon. Chromium (5 nm) was deposited first and then gold (100 nm) using an Edwards A360 sputter coater.

‡ Reflectance-absorbance FTIR spectra were measured with a Perkin Elmer 1725X spectrophotometer fitted with an MCT detector, using parallel mirrors mounted to give an incidence angle of *ca.* 75°. The cell compartment was flushed with dry argon; contamination by water and CO_2 do not, however, allow specific compensation for background in the regions 2450–2350 and 3200–3400 cm^{-1}.

§ GC was performed on a 50 m cyclodextrin B capillary column at 93 °C with a helium pressure of 4.5 psi. Under these conditions, (+)-ethyl lactate had a retention time of 5.86 min and the (−)-isomer 6.00 min (−) Propyl lactate used as external standard had a retention time of 9.42 min. Elution curves were deconvoluted to relative peak areas. A problem with adsorption of such very small quantities is accurate quantification. The scale on which the experiments were carried out would produce *ca* 10 µg of adsorbed esters, but calibration of the GC analysis suggests that substantially less than this amount was recovered from the plates. This is probably due to coevaporation in the recovery process, and keeping films with adsorbed lactate *in vacuo* results in slow loss of IR C=O intensity at 1747 cm^{-1}.

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