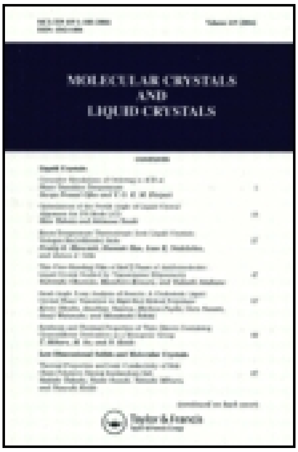

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# Electrical Properties of Multilayer Films Containing a Carotene Derivative

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# ELECTRICAL PROPERTIES OF MULTILAYER FILMS CONTAINING A CAROTENE DERIVATIVE

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Abstract The electrical properties of Langmuir-Blodgett films containing ethyl ß-apo-8'-carotenoate are reported. The incorporation of this derivative of carotene into fatty acid multilayers was found to increase substantially the electrical conductivity measured perpendicular to the substrate plane. An increase in the in-plane conductivity could also be achieved by exposure of the multilayer assembly to iodine vapour.

## INTRODUCTION

The possibility of producing multilayer Langmuir-Blodgett (LB) films with semiconducting or even metallic electrical conductivity is currently receiving much attention.[1-3] In most of the ongoing work, the lateral (in-plane) electrical conductivity is measured. However, there is substantial interest in obtaining conductivity data perpendicular to the film plane. For example, Aviram and Ratner have proposed that organic structures containing appropriate donor and acceptor groups should exhibit diode behaviour.[4] The original suggestion was to incorporate both donor and acceptor moieties in the same molecule; however, this can lead to complex synthetic problems. The LB technique offers an alternative means of arranging the chemical groups at the molecular level. The introduction of specialized LB deposition equipment such as alternate-layer troughs now facilitates the deposition of molecular assemblies containing more than one type of molecule.[5] The conductivity of the resulting multilayers must be measured perpendicular to the plane of the film to study rectification. Although the experiment is, in principle, straightforward, the interpretation of the electrical data may be complicated due to attendant 'oxide' layers on the metallic electrodes and pinholes (and other defects) in the ultrathin organic layers. As a consequence, it is not clear whether the electrical asymmetry observed in some LB layers is the result of a _molecular_ process.[6,7]

Another problem concerns the amphiphilic nature of LB materials that have been developed for conductivity studies. In most cases, molecules such as tetracyanoquinodimethane (TCNQ) and tetrathiafulvalene (TTF) have been made into LB materials by the addition of an aliphatic chain. When built into multilayers, such chains will be aligned at a high angle to the substrate plane and, when a voltage is applied perpendicular to the LB film, they will act as insulators. Consequently, some workers have reported on the incorporation of 'molecular wires' into LB structures in order to increase the conductivity between the polar planes. Polyene molecules based on amphiphilic carotenoids have already been used for this purpose.[8-9] In this work we report on the electrical behaviour of mixed multilayers of ethyl ß-apo-8'-carotenoate and long chain fatty acids.

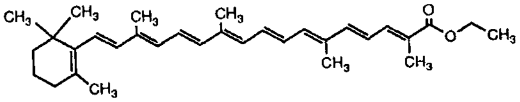
## EXPERIMENTAL

The ethyl ß-apo-8'-carotenoate was obtained from Fluka and used without any further purification. All floating monolayer studies were undertaken in a class 10,000 microelectronics clean room, using a constant-perimeter barrier trough, which has been described previously.[5] The fatty acids (arachidic acid or 22-tricosenoic acid) and carotenoid were dissolved (separately) in chloroform (BDH, Aristar grade) to a concentration of approximately 1 gl$^{-1}$; the molar ratio mixtures were achieved by adding the correct quantity of each solution to a volumetric flask and agitating in an ultrasonic bath. The solution was then spread onto a pure water subphase (obtained by reverse osmosis, deionization and UV sterilization). The subphase was unbuffered and the pH remained between 5.5 and 5.7 during the isotherm measurement and film deposition; the temperature was 18±2° C. Substrates for film deposition consisted of soda glass and quartz microscope slides. For perpendicular conductivity measurements, the glass slides were metallized by the thermal evaporation of aluminium. UV/visible absorption spectra were recorded by a Perkin Elmer λ19 double beam spectrophotometer.

Room temperature electrical conductivity measurements were undertaken in vacuum, in a screened sample chamber containing a desiccant. For in-plane measurements, the multilayers were deposited onto soda glass substrates and electrical contacts were made using air-drying silver paint (electrode length 7 mm; separation 1.5 mm). Current versus voltage measurements were recorded using a two probe technique; by varying the distance between the contacts and monitoring the resistance of the film, it as established that the contact resistances were negligible. In the case of conductivity measurements perpendicular to the film plane, the samples were first transferred to a desiccator where they were stored under vacuum ($\approx 10^{-2}$ mbar) for at least 12 h (experience has shown that this process minimizes the number of short circuited devices). Top electrodes (2 mm diameter Al, 30 nm thick) were then thermally evaporated at $\approx 10^{-6}$ mbar.

## RESULTS AND DISCUSSION

The pressure versus area isotherms for 4:1 and 5:1 molar mixtures of arachidic acid:carotenoid were found to be of a condensed type, similar to those measured for the pure fatty acid and also to those reported previously for mixtures of the carotenoid and methyl arachidate.[9]



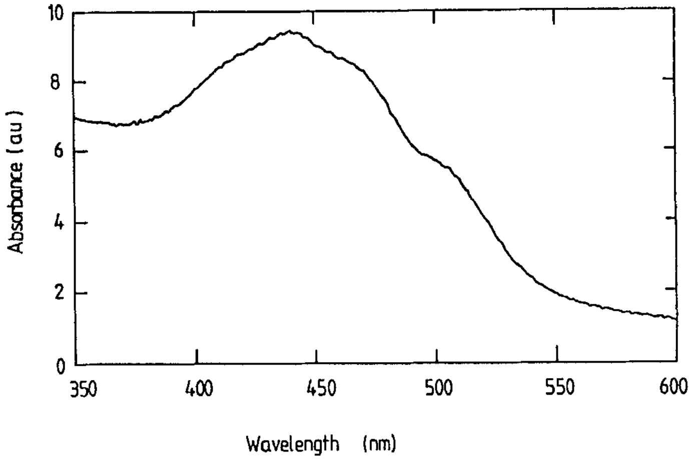


FIGURE 1 Absorption spectrum for 16 LB layers of 3.9:1 molar ratio of 22-tricosenoic acid:carotenoid. The molecular structure of the carotenoid is given.

Excellent Y-type deposition (transfer ratio 1±0.1) was achieved at a dipping pressure of 35 $mNm^{-1}$ and deposition speed of ≈10 mm $min^{-1}$ onto the glass, quartz and aluminized glass substrates. Figure 1 shows the absorption spectrum for a 16 LB layers of a 3.9:1 molar ratio of 22-tricosenoic acid:carotenoid deposited onto quartz. The main absorption at ≈440 nm together with the shoulders at ≈410 nm, ≈470 nm and ≈510 nm are similar to those reported previously.[9]

The in-plane electrical conductivity for 20 LB layers of 5.5:1 molar ratio of arachidic acid:carotenoid deposited onto glass is shown in figure 2. For the as-deposited film, the current versus voltage behaviour was found to reflect the conductivity of the supporting glass substrate. This puts an upper limit on the in-plane conductivity of $\approx 10^{-10}$ $\mathrm{Scm}^{-1}$. After exposure to iodine vapour, the current increases. This conduction is almost certainly due to the presence of the carotenoid, as no similar increase in the in-plane conductivity was observed when pure fatty acid layers were exposed to the iodine. The maximum conductivity value for the doped film is calculated to be $\sigma_0 \approx 2\times10^{-8}$ $\mathrm{Scm}^{-1}$. A similar result has been reported by Wegmann at al. for 1:1 molar ratio films of carotenoid:methyl arachidate.[9] The higher lateral conductivity of $6.4\times10^{-6}$ $\mathrm{Scm}^{-1}$ found by these workers for the iodine doped films may be the result of the higher carotenoid content of their films. The in-plane conductivity was monitored over a 20-day period, with the films kept under vacuum. Over the first 8 days, the conductivity gradually fell to reach a steady value of $0.65\sigma_0$ which was retained for the subsequent 12 days.

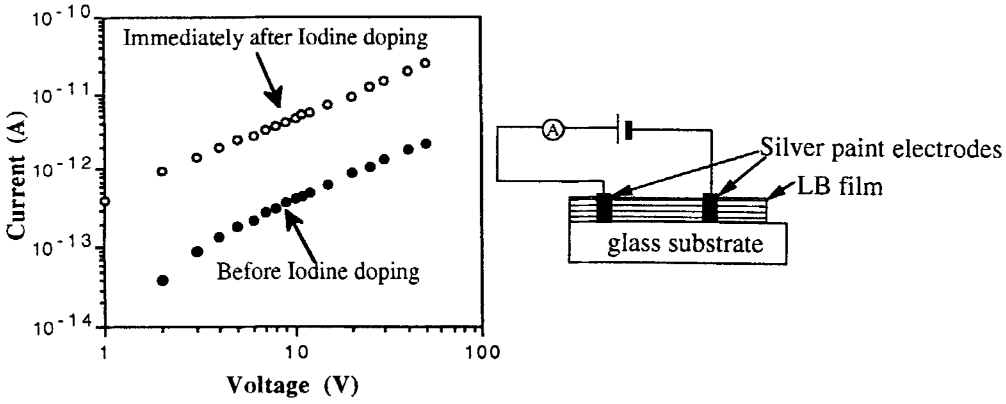


FIGURE 2 Lateral (in-plane) conductivity for 20 LB layers of 5.5:1 molar ratio arachidic acid:carotenoid deposited onto glass. The electrode structure is shown on the right.

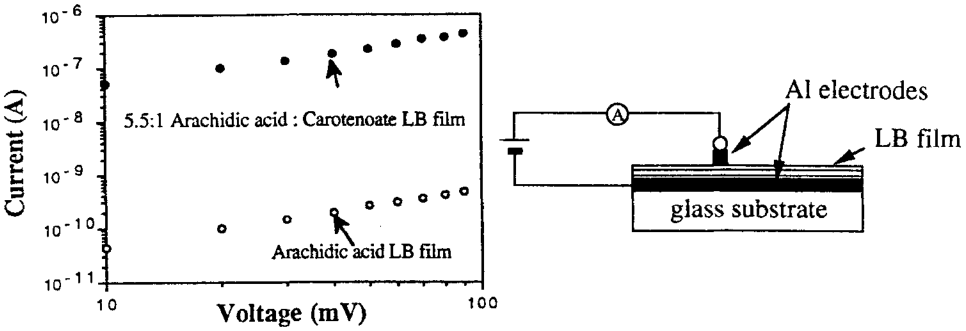


FIGURE 3 Conductivity perpendicular to the substrate plane for 20 LB layers of 5.5:1 molar ratio arachidic acid:carotenoate deposited onto aluminized glass. The electrode structure is shown on the right.

The conductivity data perpendicular to the film plane for 20-layer arachidic acid and 20-layer 5.5:1 molar ratio arachidic acid:carotenoid films are contrasted in figure 3. Similar curves were obtained on reversing the polarity of the applied voltage. The linear dependence of current upon voltage is typical of other LB materials at low electric fields.[10,11] However, the absolute conductivity of $3.3\times10^{-12}$ $\mathrm{Scm}^{-1}$ (obtained using a monolayer thickness of 2.5 nm) for the fatty acid film is considerably larger than the figure of $\approx 2\times10^{-15}$ $\mathrm{Scm}^{-1}$ reported for 17 layers of tricosanoic acid.[11] The higher value is indicative either of an increased number of defects in the fatty acid layer used in the present study or that some of the organic film has been destroyed on evaporation of the metal top contact.

Figure 3 reveals that the perpendicular conductivity for the carotenoid-containing multilayer is significantly larger than that for the fatty acid layer. The measured value of $3.1\times10^{-9}$ $\mathrm{Scm}^{-1}$ corresponds closely with the figure of $1.2\times10^{-9}$ $\mathrm{Scm}^{-1}$ obtained previously for the 1:1 carotenoid:methyl arachidate multilayer structure.[9] An attractive explanation is that the increased conductivity is due to the carotenoid acting as a molecular wire. However, other interpretations are possible. For example, the carotenoid may be disrupting the fatty acid lattice, resulting in an increased number of defects in the organic film.

Exposure to iodine vapour had the effect of removing the aluminium top contact. Even after new Al top electrodes had been evaporated onto the doped films, the number of short circuited devices increased significantly. Thus it was impossible to make direct comparison of the perpendicular conductivity before and after doping.

## CONCLUSIONS

We have demonstrated that the incorporation of ethyl ß-apo-8' carotenoate molecules into fatty acid multilayers produces an increase in the through-plane dc conductivity by about three orders of magnitude. It is possible that the conjugated chain is acting as a molecular wire, providing a conduction path through the insulating hydrocarbon regions in LB multilayers arrays. However, further experimental evidence is required before definite conclusions can be drawn.

## Acknowledgement

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