

## Novel Electroactive Langmuir–Blodgett Films based on an Amphiphilic Dibenzotetra-aza[14]annulene Derivative

A. Wegmann, M. Hunziker, and B. Tieke\*

*Ciba-Geigy AG, Research Center, CH-1701 Fribourg, Switzerland*

The preparation of stable monomolecular layers and semiconducting Langmuir–Blodgett films based on a copper(II) dibenzotetra-aza[14]annulene derivative is described; their in-plane conductivity was improved upon exposure to iodine vapour or aqueous potassium tri-iodide solution.

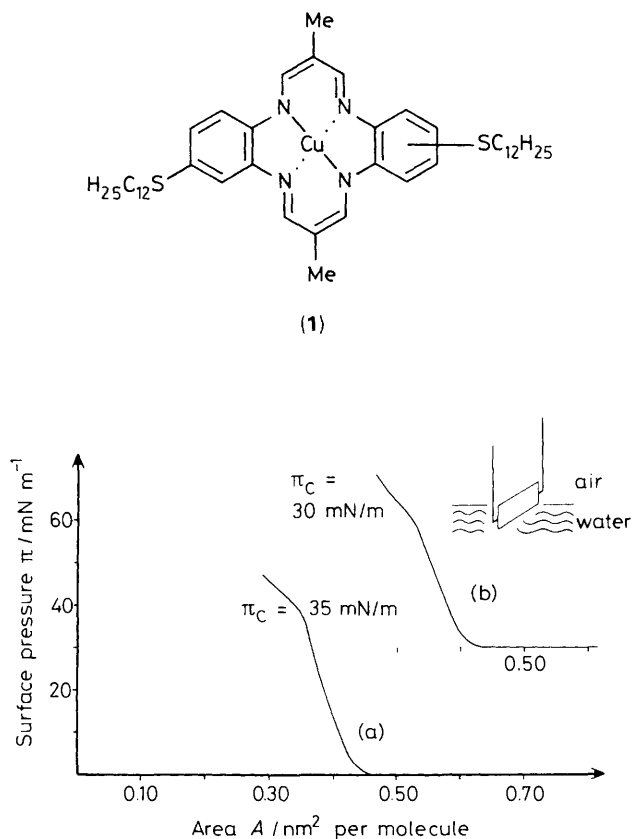
In recent years, the interest in electroactive Langmuir–Blodgett (LB) films exhibiting specific electronic functions such as electrical conduction, redox activity, or piezo- and pyro-electric properties has increased considerably. Among the compounds forming electrically conducting LB films are amphiphilic TCNQ-based (TCNQ = tetracyanoquinodimethane) donor–acceptor complexes,<sup>1,2</sup> tetrathiafulvalene,<sup>3</sup> and tetrathiotetracene<sup>4</sup> derivatives, or substituted metallo-macrocycles such as phthalocyanines<sup>5</sup> and porphyrins.<sup>6</sup> Here we report on a novel donor-type macrocycle (**1**), an amphiphilic dibenzotetra-aza[14]annulene derivative, which exhibits

interesting electrical properties in LB films.

Corresponding non-amphiphilic dibenzotetra-aza[14]annulenes are known to show high electrical conductivity in the crystalline state, when treated with iodine vapour.<sup>7,8</sup> The bisdodecylthio-substituted copper complex (**1**)<sup>†</sup> was synthes-

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<sup>†</sup> *Selected spectral data:* compound (**1**) was characterized by elemental analysis (calc. for C<sub>44</sub>H<sub>66</sub>N<sub>4</sub>S<sub>2</sub>Cu); u.v.,  $\lambda_{\max}$  (CHCl<sub>3</sub>): 440 nm ( $\epsilon = 8400 \text{ m}^2 \text{ mol}^{-1}$ );  $m/z$  cluster at 778 ( $M^+$ ), 609 ( $-C_{12}H_{25}$ ), 577 ( $-SC_{12}H_{25}$ ).

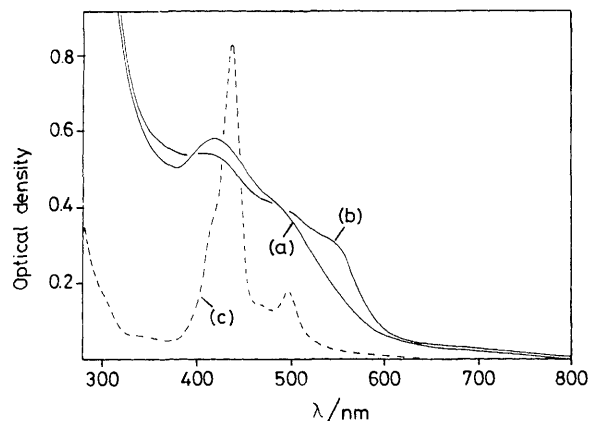


**Figure 1.** Pressure–area isotherms of (a) pure (1) and (b) a mixture of (1) and (2) (molar ratio 2.3:1) on pure water (temp. = 20 °C). Inset: proposed position of (1) at the air–water interface (rectangle = macrocycle; straight lines = alkyl chains).

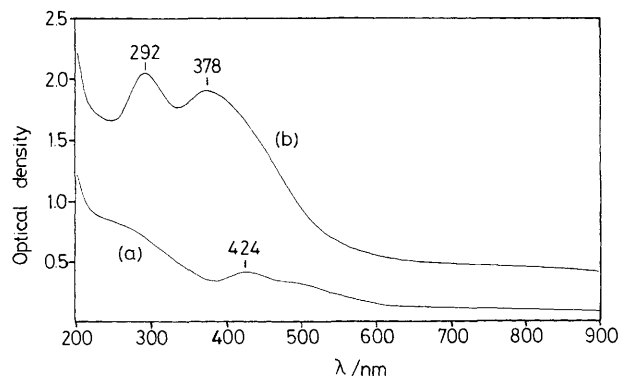
ized from 4-dodecylthio-1,2-phenylenediamine, 3-ethoxy-2-methylacrylaldehyde and copper(II) acetate in dimethylformamide at 120 °C. According to this procedure, (1) was obtained as a microcrystalline mixture of two isomers and was used without further separation for the following experiments.

The macrocycle (1) is readily soluble in various organic solvents which facilitated its spreading from a chloroform solution (spectroscopic grade; concn. 0.5 mg/ml) onto a pure water subphase (Lauda film balance equipped with a film lift FL-1; Milli-Q water). Compound (1) was found to form a stable monomolecular layer at the air–water interface. As shown in Figure 1, curve (a), the collapse pressure is about 35 mN/m (subphase temperature 20 °C; compression rate 1.25 cm/min). From the relatively small collapse area of 0.36 nm<sup>2</sup> per molecule we concluded that the macrocyclic rings are orientated perpendicularly to the water surface forming one-dimensional stacks with the aliphatic groups pointing away from the water, as proposed in the inset of Figure 1. A slightly denser packing of the molecules was achieved, when a mixture of (1) and methyl arachidate (2) (Fluka, puriss.) was spread at the air–water interface [Figure 1, curve (b)]. At a molar ratio of 2.3:1 the mixed monolayer exhibits a collapse area of 0.32 nm<sup>2</sup>/molecule.

Pure monolayers of (1) as well as mixed monolayers of (1) and (2) could be transferred onto various hydrophobic substrates (e.g. glass or quartz silanized with trichlorooctadecylsilane, germanium *etc.*). The spread monolayers were transferred at a constant surface pressure of 15 to 20 mN/m by repetitive dipping of the solid supports perpendicu-



**Figure 2.** U.v.-visible absorption spectra of (a) a pure LB film of (1) and (b) a mixed LB film of (1) and (2) (molar ratio 2.3:1) on glass substrates (film thickness 60 layers). The solution spectrum of (1) is also shown (c).



**Figure 3.** U.v.-visible absorption spectra of a mixed LB film of (1) and (2) (molar ratio 2.3:1) (a) before and (b) after treatment with iodine vapour (film thickness 60 layers; silanized quartz substrate).

larly through the interface. In general, the mixed monolayers could be deposited more easily, and the mixed LB films appeared more homogeneous. Deposition always occurred equally during the down- and up-stroke leading to a head-to-head, tail-to-tail (Y-) type structure of the LB film. In this way, more than 50 layers have been built up without showing any variation in the transfer ratio, or any visible turbidity.

LB films containing (1) exhibit an orange colour with an absorption maximum at 420 nm and shoulders at 500 and 550 nm [Figure 2, spectrum (a)]. The absorption coefficient  $\epsilon$  of the 420 nm maximum is about 31 000 cm<sup>-1</sup>. A corresponding absorption spectrum of (1) in chloroform also shows absorption maxima at about 420 and 500 nm, but the shoulder at 550 nm is absent [spectrum (c)]. We therefore concluded that this absorption originates from an aggregation of the molecules in the LB film, suggesting a well-ordered stacking of the chromophores. The higher intensity of the 550 nm absorption in the mixed film [curve (b)] indicates that the aggregation is favoured by the presence of methyl arachidate.

The in-plane direct-current (d.c.) conductivity  $\sigma$  of the LB films was determined by a two-probe measurement. For this purpose, two gold electrodes (distance 1 mm) were evaporated through a mask onto the film surface and connected to gold wires using platinum paste. As shown in Table 1, the conductivity lies in the semiconductor range. An increase in conductivity up to  $5.3 \times 10^{-4}$  S cm<sup>-1</sup> was observed when the

**Table 1.** D.c. in-plane conductivity ( $\sigma$ ) before and after doping (film thickness 30 layers).

LB film	$\sigma/S\text{ cm}^{-1}$ Undoped	$\sigma/S\text{ cm}^{-1}$ I <sub>2</sub> -Doped	$\sigma/S\text{ cm}^{-1}$ KI <sub>3</sub> -Doped
(1)	$7.4 \times 10^{-6}$	$5.3 \times 10^{-4}$	—
(1) and (2) (Ratio 2.3 : 1)	$6.7 \times 10^{-6}$	$2.7 \times 10^{-4}$	$1.1 \times 10^{-4}$

samples were either exposed to an argon atmosphere saturated with iodine vapour for about one hour, or immersed in an aqueous potassium tri-iodide solution (ICN Biomedicals Inc., concn  $5 \times 10^{-4}$  mol/l) overnight (Table 1).

In air, the  $\sigma$ -values of the doped films dropped gradually and reached identical values to those obtained before doping within several days. Samples doped with iodine vapour lost their conductivity faster than samples doped with potassium tri-iodide solution. The decrease could be reversed when the samples were treated again with iodine vapour or potassium tri-iodide solution. After doping, the LB films are bronze coloured and exhibit a metallic reflection. Two new absorption bands at 292 and 378 nm with absorption coefficients of 122 200 and 109 000  $\text{cm}^{-1}$ , respectively, appeared indicating the formation of a charge-transfer complex between (1) and iodine (Figure 3).

From X-ray diffraction studies, the layer spacing ( $d_{001}$ -value) of the undoped and doped LB films containing (1) and (2) (molar ratio 2.3 : 1) was determined. Undoped films show three orders of 001 reflections and are well ordered. The layer spacing is 3.08 ( $\pm$  0.03) nm. This value is consistent with a Y-type structure of the LB film, where the individual macrocycles form extended stacks parallel to the layer plane. While exposure to iodine vapour damages the LB film considerably, the order is better retained upon treatment with

potassium tri-iodide. In the latter case the resulting  $d_{001}$ -value is 3.17 ( $\pm$  0.05) nm. Transmission electron micrographs of doped LB films confirm these observations. After iodine vapour treatment the surface appears very rough, whereas samples treated with potassium tri-iodide exhibit a smooth surface.

Our studies demonstrate the utility of a substituted dibenzotetra-aza[14]annulene for the formation of LB films as well as the sensitivity of these films to reactive gases and liquids such as, for example, iodine vapour or potassium tri-iodide solution. Current quantitative studies of these reactions probe the utility of the LB films for sensor applications.

The authors thank the Swiss National Science Foundation (NFP 19; Materials for Future Technology) for financial support and Mr J. Pfeiffer for his valuable technical assistance with conductivity measurements.

Received, 31st January 1989; Com. 9/00502A

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