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# Gas–surface interactions with Langmuir–Blodgett films of new derivatives of dibenzo-tetra-aza-dihydro-[14]-annulene

Colin L Honeybourne and Julie O'Donnell

Molecular Electronics and Surface Science Group, Bristol Polytechnic, Frenchay, Bristol BS16 1QY, UK

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**Abstract.** Our new derivatives of the parent macrocyclic ligand dibenzo-[b,i][1,4,8,11]tetra-aza-[4,11]dihydro-[14]-annulene (TTA) can be divided into two classes on the basis of their behaviour concerning the formation of (floating) Langmuir monolayers and solid-supported Langmuir–Blodgett (LB) monolayers and multilayers. Class I consists of molecules that are highly hydrophobic, but do not contain a formal hydrophilic centre whereas the class II molecules are truly amphiphilic. The class I compounds all formed stable Langmuir monolayers at surface pressures of 10–15 mN m<sup>-1</sup> for prolonged periods and, for the C(6) and C(14) compounds, similar stability was also observed at up to 40 mN m<sup>-1</sup>. Although the C(14) material failed to deposit as an LB film, limited multilayer deposition (X or Z-type) was displayed by the other members in class I. In class II, only the di-cumylphenoxy-derivative of the cobalt(II) complex of TAA (CPTAACo, TAA as defined previously) was found to form satisfactory LB multilayers for which a surface pressure in the range 16–20 mN m<sup>-1</sup> was employed. The Langmuir monolayers of the other members of this class were too rigid for LB deposition. Some observations concerning the effect of NO<sub>x</sub> upon an LB film of CPTAACo are described.

## 1. Introduction

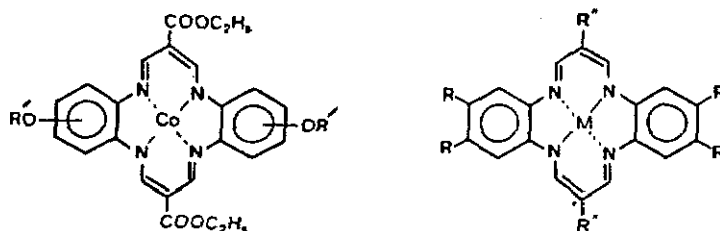
The semiconductive properties of the phthalocyanines (Pcs) were first observed independently by Eley [1] and by Vartanyan [2] in 1948. Since that time, the study of the semiconductive and photoconductive properties of Pcs has become an intensely researched area [3, 4] which has been extended to include the allied macrocyclic ligands porphyrins [5] and tetra-aza-dihydro-dibenzo-[14]-annulenes (TAAs) [6] and a range of dyes, conjugated hydrocarbons and conjugated polymers [7–10]. Recently, Eley has reviewed the past 40 years of development in the theory of electrical conductivity in organic solids [11].

The dark DC conductivity and photoconductivity of conjugated organic solids are both greatly influenced by the presence of dopant gases and vapours—properties which have led to extensive research into the use of thin films of such solids as gas and vapour sensors. For the phthalocyanines in particular, the topic of gas-sensing has recently been reviewed in considerable detail [3], and groups world-wide are continuing to expand the knowledge of organic semiconducting films of phthalocyanines and related materials as sensors for oxidizing gases [12]. The effects of the latter on the conductivity of vacuum sublimed films [5, 6] and LB films [13] of porphyrins have also been reported wherein the in-plane dark DC conductivity of Cu(II)mesoporphyrin IX

diol was found to increase by four orders of magnitude in the presence of 10 ppm of dinitrogen tetroxide in air at 300 K.

In contrast to the phthalocyanines and porphyrins, little work has been reported on Langmuir and LB films of other macrocyclic ligands such as TAA. Deposition of a pure LB film of one amphiphilic TAA has been reported by Tieke and Weymann [14, 15], although their work mainly involved the study of composite films of the TAA derivative with various long-chain acids using a mixed spreading phase. Other workers have been unsuccessful in their efforts to obtain LB films of pure TAA derivatives, and they have also reported very limited success with composite LB films [16].

The principal aim of the work reported herein was to investigate the preparation, characterization and electrical properties of LB films of a range of new TAA derivatives in order to evaluate their applicability to the sensing of oxidizing gases such as dinitrogen tetroxide (NOX) by the dark DC conductive response of a surface cell.



Class I	Class II
C <sub>8</sub> TAACo	CPTAACo
C <sub>6</sub> TAACo	PPTAACo
C <sub>14</sub> TAACo	TMCO <sub>2</sub> TAA
C <sub>8</sub> TAACoCN	

R	R'	R''	M	Code
—	cumylphenyl	—	Co	CPTAACo
—	p-propylphenyl	—	Co	PPTAACo
C <sub>8</sub> H <sub>17</sub>	—	C <sub>8</sub> H <sub>17</sub>	CoCN	C <sub>8</sub> TAACoCN
CH <sub>3</sub>	—	COOC <sub>2</sub> H <sub>5</sub>	H <sub>5</sub>	TMCO <sub>2</sub> TAA
OC <sub>8</sub> H <sub>17</sub>	—	C <sub>8</sub> H <sub>17</sub>	Co	C <sub>8</sub> TAACo
OC <sub>6</sub> H <sub>13</sub>	—	C <sub>6</sub> H <sub>13</sub>	Co	C <sub>6</sub> TAACo
OC <sub>14</sub> H <sub>29</sub>	—	C <sub>16</sub> H <sub>31</sub>	Co	C <sub>14</sub> TAACo

Figure 1. Structures and classes of macrocyclic molecules.

For ease of discussion, the derivatives of TAA have been divided into two classes. Class I consists of molecules having large hydrophobic side-chains but lacking any formal hydrophilic groups, whereas class II consists of truly amphiphilic molecules

with hydrophilic and hydrophobic substituents (figure 1).

### 1.1. Experimental details

All the TAA derivatives were synthesized by the template method as originally described for this class of macrocyclic ligand by Honeybourne [17, 18]. The reactants were cobaltous acetate, an alkyl- or alkoxy-benzene-1,2-diamine and either malonaldehyde (class I) or a 2-malonaldehyde (class II) carrying a hydrophilic substituent. The conversion of cobalt(II) to cobalt(III)CN was achieved by treating the cobalt(II) macrocyclic complex with sodium cyanide in air [19]. The composition and structure of all macrocyclic materials were evaluated by microanalysis, NMR and mass spectrometry [20]. The materials were purified initially by column chromatography: latterly, sublimation in a low-temperature furnace using white-spot nitrogen as the carrier gas was utilized. This produced a mass of brightly-coloured, fine, shiny, prismatic needles.

Full details of the LB technique as utilized in our laboratory are given in other papers by Honeybourne *et al* in this issue [21, 22]. Herein, we simply re-emphasize the need for scrupulous cleanliness of all materials and the working environment, and for a vibration-free table.

The dark DC conductivity of LB films was measured in a surface cell consisting of gold electrodes on glass substrates prepared in the following way. Thin gold films were evaporated onto clean glass substrates [21]. Using a standard photolithographic technique [23], the gold films were then etched to leave inter-digitated electrodes of rectangular geometry. The electrodes were then cleaned in acetone at reflux to remove any remaining photoresist followed by further cleaning in hot chloroform and, latterly, by iso-propyl alcohol. A final treatment with dichlorodimethylsilane provided the required hydrophobic surface. The electrode substrates were then coated with LB films (see later), mounted on 14-pin carriers, and connected electrically using conducting silver paint.

The design and operation of the gas-flow rig for the delivery of between 0.1 and 500 vapour ppm of NOX (see figure 2) has been given elsewhere [6, 16, 20, 23].

## 2. Results and discussion

### 2.1. Deposition of LB films

The class I compounds formed stable Langmuir monolayers at surface pressures between 10 and 15 mN m<sup>-1</sup>. The C(6) and C(14) derivatives also maintained stable films at 30 and 40 mN m<sup>-1</sup> respectively. However, attempted LB film deposition within either of these pressure ranges did not yield the required LB multilayers. Indeed, the C(14) compound did not give even an LB monolayer, although other members of class I did give some initial deposition, albeit at transfer ratios in excess of 100%. This latter is indicative of film collapse and the deposition of fragmented pieces of rigid film.

In the case of class II molecules, surface pressures of between 8 and 25 mN m<sup>-1</sup> were employed. In accord with work by Tredgold on the same sample, TMCO<sub>2</sub>TAA only gave an LB monolayer [24].

CPTAACo gave LB multilayers at surface pressures within the range 16–20 mN m<sup>-1</sup>. However, the deposition process did not proceed easily. Repeated compression of the film, utilized when undertaking the assessment of the uniformity of its deposition by

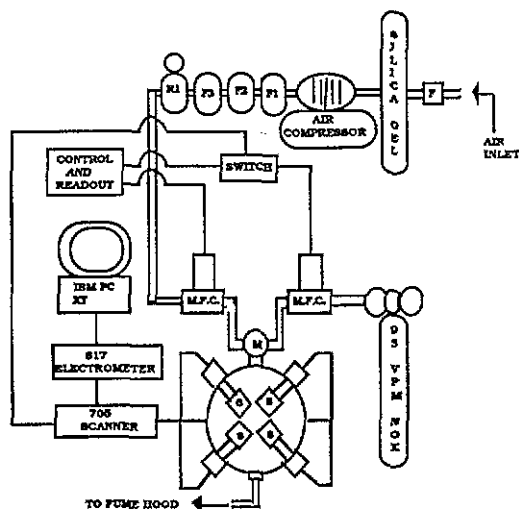


Figure 2. Schema of automated gas-flow rig. M: mixing chamber; M.F.C.: thermal mass flow controller; F: dust filter; S: sensor; F1: IF2 centrifugal pre filter; F2: IC3 aerosol removing coalescing filter; F3: IX1 vapour removing activated carbon filter; R1: IR1 single stage regulator.

measurement of the visible absorbance, produced either erratic deposition, or reduced the transfer ratio to zero. We consider that the repeated compressions (i.e. of the Langmuir monolayer), either caused the film to reorientate into rigid stacks, or forced the side chains to lock together to give a rigid film. The deposited LB film was allowed to 'age' before continuing the dipping sequence also lead to zero transfer ratios. The best results were obtained from a freshly spread and compressed Langmuir monolayer with a continuous dipping sequence. This will now be termed film 'A'. A mixture of  $\text{TMCO}_2\text{TAA}$  with 50 mol% of stearic acid (i.e. a composite spreading phase) did facilitate the deposition of LB multilayers containing this macrocyclic ligand, in agreement with Gaspard and Maillard [25]. This will now be termed film 'B'.

The optimum parameters for the production of A and B were as follows. Film A (pure Co complex), Y-type,  $20 \text{ mN m}^{-1}$ ,  $5 \text{ mm min}^{-1}$ ; film B (composite, 1:1), Z-type,  $25 \text{ mN m}^{-1}$ ,  $5 \text{ mm min}^{-1}$ .

## 2.2. Characterization of LB films

Both sets of films were deposited onto quartz oscillators and produced linear plots of frequency change against number of layers, thereby providing strong evidence for the uniformity of deposition. Further support for the latter is exemplified by the linearity of the plot of optical absorbance against number of layers (see figures 3 and 4).

Further characterization of film 'A' was achieved by the x-ray diffraction of a 50-layer film on silicon (figure 5). Although the baseline is noisy, at least two orders of diffraction are visible, indicative of short-range ordering in the film. The  $d$ -spacings are in the region of 4 nm, which is consistent with Y-type bilayers containing molecules oriented perpendicular to the plane of the substrate. Other workers found it necessary to use a composite spreading phase containing methyl arachidate to obtain a film of an amphiphilic TAA with short-range ordering detectable by the XRD technique [25].

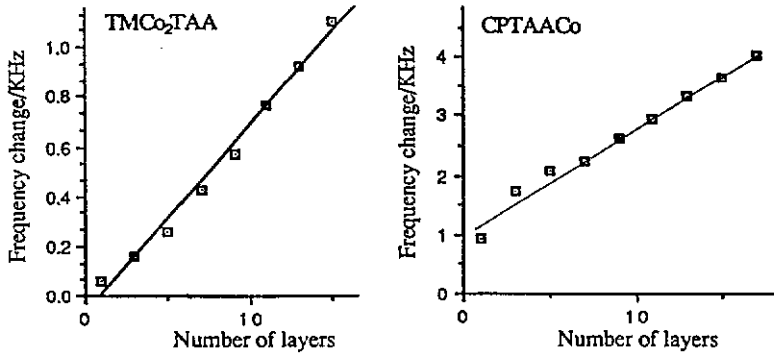


Figure 3. Plots of frequency change against number of layers for CPTAACo and TMC<sub>02</sub>TAA.

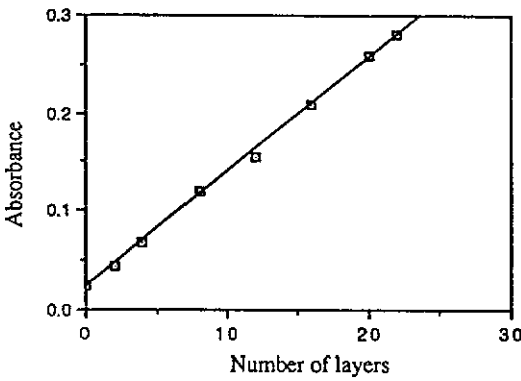


Figure 4. Plot of optical absorbance against number of LB layers for TMC<sub>02</sub>TAA

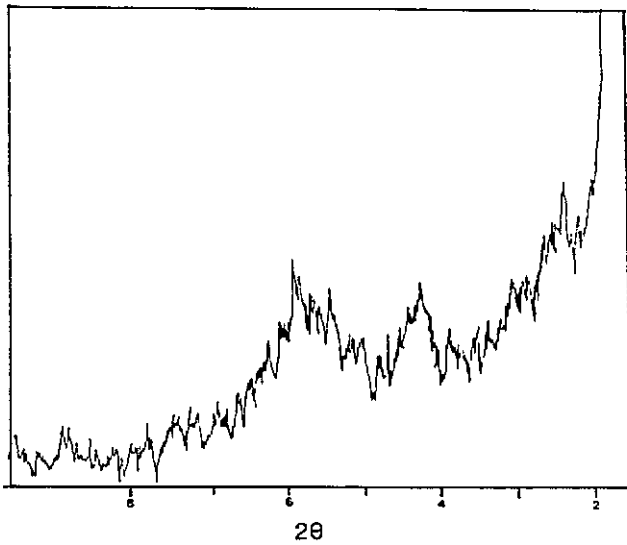


Figure 5. LAXRD pattern for an LB film of CPTAACo.

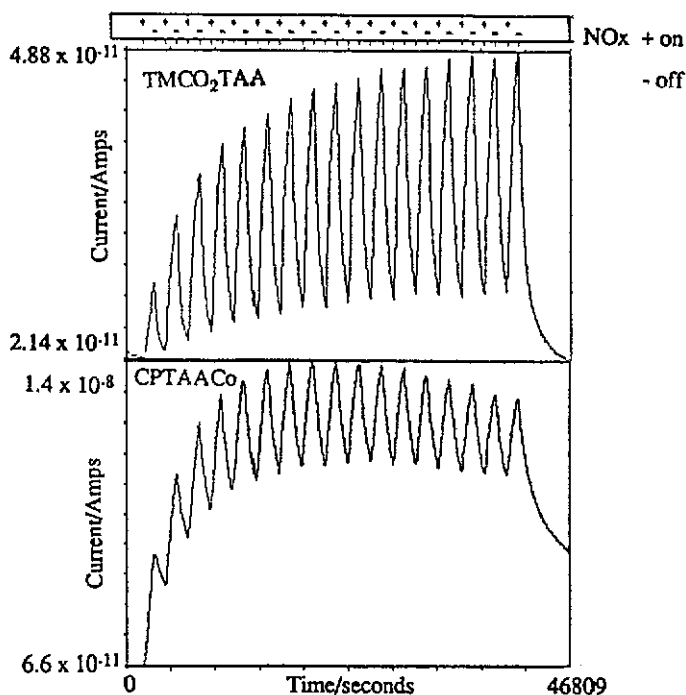


Figure 6. Dark DC surface current of LB-film surface cells of CPTAACo and  $\text{TMCO}_2\text{TAA}$  exposed to 5 ppm of  $\text{NO}_x$ .

### 2.3. Dark DC conductivity of $\text{NO}_x$ -doped LB films

Films A and B comprising various numbers of layers, were exposed to a range of concentrations of  $\text{NO}_x$  in a stream of air. All films gave responses that were both reversible and sufficiently large to have potential as gas-sensing devices. The data (see table 1, figure 6) show that, in accordance with our earlier work [6], the metal-free material is more reversible than the metal complex. We draw attention to the fact that fresh films have to be sensitized before a reproducible response is obtained—this is termed the initialization effect, and occurs during the ejection of dioxygen from various traps by  $\text{NO}_x$  [3]. Exposure of film A to 5 vppm of  $\text{NO}_x$  for 24 h in air lead to the sudden and rapid onset of a decay in the surface current due to irreversible and unfavourable chemical changes.

### 3. Conclusion

The thin LB films described in this paper proffer better sensitivity, better reversibility and simpler gas adsorption behaviour than thicker, vacuum-sublimed films of the same and related materials [6] with regard to the responses of dark DC conductivity on exposure to  $\text{NO}_x$  in air. The free base,  $\text{TMCO}_2\text{TAA}$ , is much more chemically stable in the presence of  $\text{NO}_x$ , and is clearly the most suitable compound from classes I and II for use in gas-sensing devices.

Table 1. Synopsis of response of LB films to NOX, illustrating thickness dependence of the dark DC surface conductivity.

Sample	Film layers	NOX conc. (ppm)	Exposure time (min)	Max. current change $\times 10^{-12}$	Reversal (%)
TMCO <sub>2</sub> TAA 50 mol%	20	2	20	5.3	89
	—	5	20	21	100
	10	2	20	31	100
	—	5	20	990	93
	—	10	20	2400	91
CPTAACo	20	2	20	2000	84
	—	5	20	2300	100
	11	2	20	71	100
	—	5	20	2300	*
	—	10	20	1900	100
	4	2	20	7.1	100
	—	5	20	200	*
	—	10	20	140	100

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