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► **To cite this version:**

Serge Palacin, André Barraud. Highly Ordered Langmuir-Blodgett Films based on Semi-Amphiphilic Phthalocyanines. Chemical Communications, Royal Society of Chemistry, 1989, pp.45-47. 10.1039/c39890000045 . cea-01057203

HAL Id: cea-01057203

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Submitted on 21 Aug 2014

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Highly Ordered Langmuir–Blodgett Films based on Semi-amphiphilic Phthalocyanines

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Semi-amphiphilic phthalocyanines can be built *via* ion exchange at a fatty acid monolayer–water solution interface and be transferred onto solid substrates to give well-ordered Langmuir–Blodgett films.

Semi-amphiphilic compounds are known to be well-suited for building Langmuir–Blodgett (LB) films.¹ Until recently this family of complexes was restricted to metallic fatty acid salts, which can be built either in the expending solution (*'ex-situ'* method) or on the water bath (*'in-situ'*). However, work by Kuhn² and Ruaudel-Teixier³ and the development of conduct-

ing LB films based on charge-transfer complexes has allowed fully organic semi-amphiphilic complexes to be organized as thin films by the LB technique. Using the *'ex-situ'* method, Kuhn and co-workers have shown that J-aggregates can be formed through adsorption of cyanines supporting short chains under a fatty acid monolayer,⁴ but the nature of the

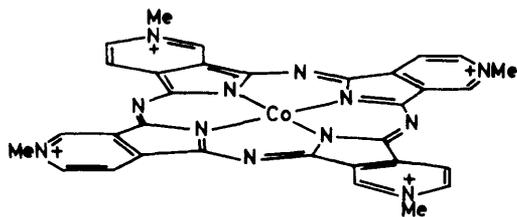


Figure 1. The cobalt tetramethyltetrapyrridino[3,4-*b*:3',4'-*g*:3'',4''-*l*:3''',4'''-*q*]porphyrizinium nucleus (CoS_1).

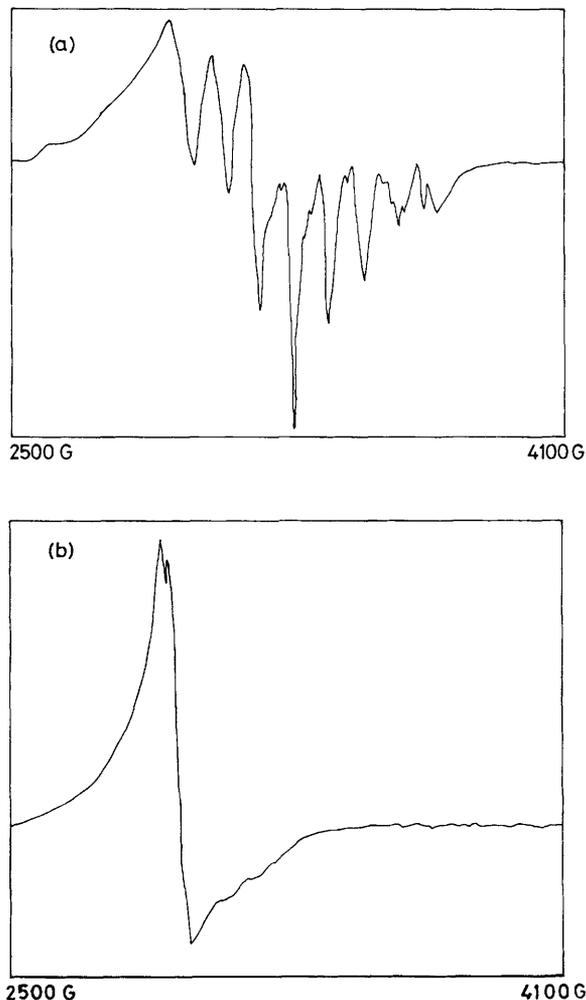


Figure 2. E.s.r. spectra recorded at 300 K of 500 layers of the semi-amphiphilic complex $[\text{CoS}_1, \omega\text{C}_{23}]$ deposited on a quartz slide with (a) 0° and (b) 90° angle between the magnetic field and the normal to the sample. The two spectra are not plotted at the same intensity scale ($1 \text{ G} = 10^{-4} \text{ T}$).

interaction between the amphiphilic and free parts of the semi-amphiphilic compound has not yet been investigated. We have studied the mechanism of this adsorption and the geometry of the ensuing monolayer, using a water-soluble porphyrizine as an example.

Cobalt tetramethyltetrapyrridino[3,4-*b*:3',4'-*g*:3'',4''-*l*:3''',4'''-*q*]porphyrizinium hydrogenosulphate $[\text{CoS}_1(\text{HSO}_4)_4]$ (Figure 1) was obtained as described by Scott.⁵ ω -Tricosenoic acid (ωC_{23}) was prepared as described by Peterson.⁶ The LB multilayers were built at 20 – 22°C on a fully automatic trough patented by Barraud,⁷ as follows. A

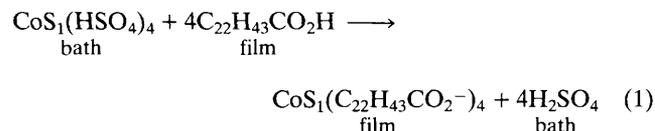
monolayer of ωC_{23} was built on a 10^{-6} M solution of $\text{CoS}_1(\text{HSO}_4)_4$, and after slow compression, the monolayer was transferred onto calcium fluoride or quartz slides at low speed (0.1 cm min^{-1}) under a nitrogen atmosphere.

The compression isotherm of the semi-amphiphilic monolayer on the CoS_1 solution exhibits the same features as pure ω -tricosenoic acid on pure water, indicating that the adsorbed species does not cover the entire surface of the fatty acid monolayer; the lateral interactions between the adsorbed macrocycles are not able to modify the thermodynamic behaviour of the ωC_{23} monolayer.

The u.v.-vis. spectrum (Cary 2390 spectrophotometer) of 100 layers of ωC_{23} built on a $\text{CoS}_1(\text{HSO}_4)_4$ solution shows the typical bands of a cobalt(II) pyridinoporphyrazinium ring; Soret band, 335 nm; Q band, 685 nm, showing that the tetracationic species have been adsorbed by the fatty acid monolayer. The i.r. spectrum of the same sample (Perkin-Elmer 180 spectrometer) shows a broad band centred at 1550 cm^{-1} , as previously observed for mixed layers of a fatty acid and the amphiphilic porphyrizine MS_{18} (the tetraoctadecyl derivative where M is the central metallic ion).⁸ This indicates that some of the fatty acids have been transformed into carboxylate salts; it seems that ion exchange is responsible for adsorption of the cationic macrocycles under the ionizable monolayer.

Figure 2 presents the e.s.r. spectra obtained (ER 200 D Bruker spectrometer) for two orientations of the quartz slide in the permanent magnetic field. The experimental values of g and A (hyperfine coupling constant) calculated from these spectra exactly fit the theoretical values: $g_{\parallel} 2.018$, $A_{\parallel} 93.6 \times 10^{-4} \text{ cm}^{-1}$; $g_{\perp} 2.26$, $A_{\perp} 34.5 \times 10^{-4} \text{ cm}^{-1}$. These spectra indicate that the macrocycles lie flat on the substrate, as in the case of the parent amphiphilic porphyrizines.^{9,10}

Our experiments bring out two major results. (i) The adsorption of ionic species on ionizable monolayers proceeds *via* ion exchange, even in the case of fully organic water soluble molecules. In our case, the reaction between the tetracationic dye in the water bath and the ωC_{23} monolayer leads to a supermolecular assembly composed of the tetramethyl tetrapyridinoporphyrazinium ring and four ω -tricosenoate anions, by mechanism (1). Some extra molecules of



ωC_{23} (four or five according to molecular models) can fill the inner volume of this assembly by standing without any chemical interaction above the central porphyrizinium ring. The exact formula of the supermolecular assembly is therefore uncertain, so the semi-amphiphilic complex will now be called $[\text{CoS}_1, \omega\text{C}_{23}]$. We think that similar ion exchanges are responsible for the behaviour of the cyanine dyes described by Kuhn *et al.*⁴ Lehmann¹¹ has already observed that cationic dyes do not adsorb under neutral or cationic monolayers.

(ii) The geometry of the resulting film is, in this case, enforced by the chemical reaction which occurs at the film-bath interface. Indeed, the four pyridinium- ω -tricosenoate salts force the planar macrocycle to be parallel to the interface. The four anionic chains thus play exactly the same role as the four covalently bound aliphatic chains in amphiphilic MS_{18} , stabilizing the geometry of the macrocyclic monolayer by extending into the hydrophobic layer the ionic interactions provided by the four pyridinium rings in the polar plane. In the case of the cyanine dyes, anchoring by only one point (there is only one cationic site in the cyanine molecule) allows some flexibility of the cationic part of the semi-

Table 1. Estimated coverage ratio of fatty acid monolayer by adsorbed porphyrazine for three initial concentrations of $\text{CoS}_1(\text{HSO}_4)_4$ in the water bath.

Initial concentration / 10^{-7} M	U.v.-vis. (± 0.1)	I.r. (± 0.1)
5	0.5	0.6
10	0.6	0.7
50	0.8	0.8

amphiphilic monolayer, allowing lateral interactions in the J-aggregates.

Another important parameter of the chemical adsorption of ionic species under ionizable monolayers is the coverage ratio, which may be directly measured by comparing the reflectance spectra of a pure amphiphilic dye monolayer and the semi-amphiphilic one. However, since reflectance measurements were not available, we compared the spectroscopic properties of the ensuing multilayers. u.v.-vis. absorbance gives the number of porphyrazine rings in the $[\text{CoS}_1, \omega\text{C}_{23}]$ film, while the i.r. absorbance gives the ratio of free fatty acid to carboxylate anion either in the mixed amphiphilic film (when the monolayer is composed of stearic acid and the amphiphilic porphyrazine MS_{18}) or in the $[\text{CoS}_1, \omega\text{C}_{23}]$ film. The results are presented in Table 1, for three initial dye concentrations in the water bath. It appears that coverage of the monolayer by the water-soluble porphyrazines is reasonably high, in spite of the very low concentration in the water bath, and it may be improved by increasing the initial concentration in the water bath.

For cyanine dyes, Lehmann¹¹ claimed that the semi-amphiphilic monolayer obtained by adsorption of water-soluble cyanines under a fatty acid monolayer is homogeneous, *i.e.*, that it exhibits the same thermodynamic behaviour as a pure amphiphilic cyanine monolayer. The lateral interactions between the cyanines, which are enhanced within the semi-amphiphilic monolayer owing to the proximity of the interacting rings, appear to improve the coverage ratio;

the cyanine dyes prefer to build J-aggregates within the semi-amphiphilic monolayer than remain free in the water bath.

For CoS_1 , Table 1 shows that adsorption is not as easy as for cyanines, probably because it affords no energetic gain: the porphyrazinium ring does not tend to interact when the different macrocycles are confined within the same plane. This may be explained by the high charge carried by the porphyrazinium ring, the large distance between the neighbouring aromatic rings in the peculiar geometry of the semi-amphiphilic monolayer, and the disappearance of the mobile anions which are able to screen the repulsive interactions between the neighbouring pyridinium rings. Within the semi-amphiphilic monolayer, the anions are amphiphilic and cannot move easily to decrease the repulsive forces between the different adsorbed macrocycles.

Generalizing this method should produce shorter synthetic routes to new molecular assemblies and should enhance the number of organic compounds suitable for building well-ordered LB films.

Received, 1st July 1988; Com. 8/02625D

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