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Use of electrochemical techniques to study the Langmuir – Blodgett films of redox active materials

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Abstract. The electrochemical properties of thin films of electroactive materials formed on the surface of an electrode by the Langmuir – Blodgett (LB) technique are reviewed. Great attention has been paid to LB films of the charge-transfer materials which may form electroconductive films. This group includes tetrathiafulvalene, tetracyanoquinodimethane, dithiolate complexes of metals, fullerenes, phthalocyanines, conjugated polymers, *etc*. Also, LB films of other redox materials such as ferrocenes, metal bipyridine complexes, viologens and other electroactive LB films are comprehensively reviewed. Structure – property relationships in the experimental voltammetry of LB films and their agreement with theoretical models are examined. Specially organized structures, formed by the LB technique, for the study of the mechanism of electron transfer are of special attention. Potential applications of electroactive LB films in electrocatalysis, electrochromic displays, information storage devices and molecular electronic devices are envisaged. The bibliography includes 163 references.

I. Introduction

For a description of the Langmuir – Blodgett technique see Refs 1 – 5. For the electrochemical investigations, the LB films (monolayer or multilayer) are transferred onto the surface of an electrode by the conventional vertical dipping or the horizontal touching technique. Indium – tin oxide coated glass (ITO) or gold evaporated onto different supports are usually used as electrodes. Our primary interest in LB films is associated with the LB films of charge-transfer materials, which can give a mixed valence state upon oxidation or reduction. LB films of these materials can exhibit increased electrical conductivity and they may find an application in the molecular electronics (see reviews [6 – 11]). Electrochemical techniques can be considered as a method of synthesis and/or method for converting these materials to the conducting state. Moreover electrochemical methods can perform this conversion in a more controllable manner because the desired level of oxidation or reduction can be achieved by passing a certain quantity of charge. To comply with the principle of electroneutrality, oxidation or reduction is accompanied by the ingress of counter-ions. It is well known from the chemistry of conducting ion-radical salts [7, 9] that a large variety of cations and anions can be inserted in these crystals during electrochemical growth. Similarly applying electrochemical methods to LB films should yield better control of their properties. However, electrochemical doping found only limited application for LB films compared to the vast use of electrocrystallisation to grow conducting crystals and electropolymerisation to produce conjugated polymers.

The electrochemistry of LB films was reviewed by Facci [12] with emphasis on his own work with ferrocene derivatives. Previously we have also discussed the electrochemistry of LB films.[13] In this review the field is described in more detail taking into the consideration the reports (including ours) published in the last few years.

Other electroactive LB films can serve as models to study the dependence of electrochemical properties on the film structure and the conditions of the LB transfer, *vise versa*. For example phthalocyanine LB films were investigated for their electrochromic properties, but these materials can be also electroconductive. Other potential applications for the electroactive LB films include the formation of ultrathin modified electrodes with the high density of electroactive sites and molecular organisation, which might find application as sensors, photoelectrochemical and information storage devices. LB films can serve as models for molecular rectifying properties in biological systems, electrocatalysis, study of biological membranes, *etc*.

The LB technique is able to create molecularly organised films, advantageous in the preparation of molecular electronic devices. Molecular organisation can also provide new insight on electron transfer reactions at interfaces. Self-assembly (SA) technique also produces molecularly organised films and can be considered as a complimentary approach. Generally, only one type of surface can be used in this technique (for example Au or Pt for thiols and glass or Si for chlorosilanes). This limitation creates difficulties in measuring the electrical properties. The SA technique is not universal and is often limited to monolayer formation.

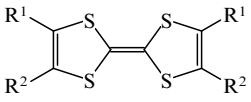
II. Langmuir – Blodgett films of the charge-transfer materials

The formation of conducting LB films falls into five main groups of materials based on amphiphilic analogues of the following

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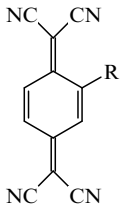
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compounds: tetrathiafulvalene (TTF), tetracyanoquinodimethane (TCNQ), tetrathiotetracene (TTT), dithiolate complexes and fullerenes (**1**–**5**).



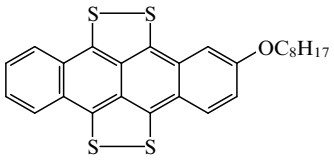
1a–**f**

1a: R^1 = H, R^2 = $COC_{15}H_{31}$;
1b: R^1 = H, R^2 = $COC_{17}H_{35}$;
1c: $R^1 + R^1 = SCH_2CH_2S$,
$R^2 + R^2 = SCH_2CH(C_{18}H_{37})S$;
1d: $R^1 + R^1 = SCH_2CH_2S$,
$R^2 = SC_{18}H_{37}$;
1e: $R^1 + R^1 = SCH_2CH_2S$,
R^2 = H, $CH_2OCOC_{17}H_{35}$;
1f: R^1 = H, R^2 = H, $CH_2OCOC_{17}H_{35}$.

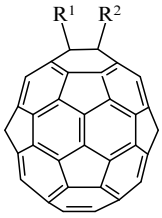


2a,**b**

2a: R = $C_{18}H_{37}$,
2b: R = $C_{12}H_{25}$.

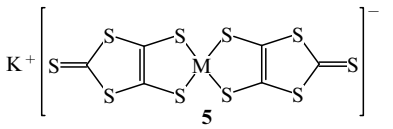


3



4a,**b**

4a: $R^1 + R^2$ = double bond;
4b: R^1 = H, R^2 = Bu^t.



5

M = Ni, Au, Pd.

Chemical oxidation, usually by I_2 vapour, used to be the general method to convert the films to the mixed-valence conducting state. One of its disadvantages is that in these cases the conducting state is not stable as films loose iodine. Several attempts to use electrochemistry can be found in the literature. The electrochemical oxidation during LB film deposition was performed for a TTT derivative **3** [14] using $LiClO_4$ subphase and for a mixture of compound **1d** and behenic acid [15] using 0.002 M KI subphase. The mixed-valence state in LB film was observed spectroscopically in the latter case. Direct electrochemical oxidation of TTF LB films during deposition was suggested.[15] Alternatively, one could suggest that I^- oxidation takes place under these conditions and then I_3^- oxidises TTF chemically. This oxidation on a live electrode (as well as post-deposition oxidation) conserves the ordering in the LB film in contrast to I_2 vapour oxidation which yields a disordered structure.[14] Recently we deposited LB layers of Ni complex **5** with tetrabutylammonium cation onto the electrode with a gap of 30–50 μm under constant current.[16] We were the first to report electrical conductivity (10^{-3} S cm^{-1}) using this approach.

Deposition under constant potential was applied to control the adsorption of malachite green, dissolved in the subphase, into LB films of TCNQ derivative **2b**.[17] The adsorption was assigned to the electrochemical reduction of **2b** and the formation of charge-transfer complex between reduced **2b** and malachite green during LB transfer onto ITO electrodes.

It can be suggested that compact LB films may be oxidised or reduced during the process of electrochemical LB deposition, while a similar electrochemical reaction might be inhibited in the preformed LB films.

Postoxidation of preformed LB films is more widely used. To study the electrochemical properties of LB films voltammetric methods with linear sweep of potential, particularly cyclic voltammetry, are usually employed. The theoretically expected response for the surface electrochemical reaction in this technique is a symmetrical cyclic voltammogram (CV) (without peak separation) and a peak half width of *ca.* 90 mV for the one electron transfer. The best (closer to theoretically expected) stable CV

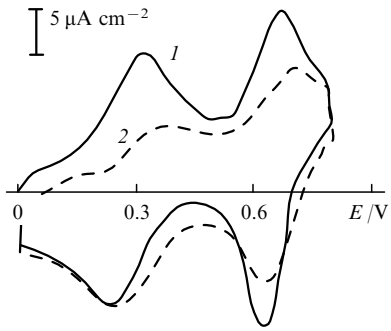


Figure 1. CV of LB film of mixture of **1f** and 23% molar icosanoic acid on ITO glass, 0.2 M $HClO_4$ solution.
Potentials *vs.* SCE; (*1*) monolayer, (*2*) 5 layers, υ = 200 mV s^{-1}.

response between LB films of the TTF derivatives **1** was registered for the derivative **1f** (Fig. 1).† The deviation from the theoretically expected response is manifested in the peak broadening and peak separation. It should be noted that despite the compact structure (the low molecular area [18]), the shape of the CV response for the multilayer film was similar to the response of the monolayer. As expected for the surface electrochemical reaction for both monolayer and multilayer films the peak current was proportional to the scan rate. However, the electroactivity of monolayer films was lower than that calculated from the LB transfer and decreased further in the case of multilayer films (Fig. 1).

It was shown spectroelectrochemically [19,20] that even compact films of TTF derivatives **1a** and **1b** could be oxidised in aqueous electrolyte forming a mixed-valence state. The study of films of **1a** (molecular area close to 0.2 nm^2, corresponding to the cross-section of the alkyl chain) by cyclic voltammetry has shown that the redox process is quite slow and the oxidation is controlled by diffusion of electrolyte ions through a highly hydrophobic film.[19] For several layers, CV response was highly distorted due to hindered diffusion of ions. Similar behaviour for the LB films of fullerene derivative **4b** [21] is shown in Fig. 2. Three diffusion controlled reversible or quasi-reversible reduction steps (Fig. 2 *a*) were observed for monolayer film. The CV response was sug-

† L M Goldenberg, R Andreu, M Saviron, A J Moore, J Garin, M R Bryce, M C Petty, unpublished results.

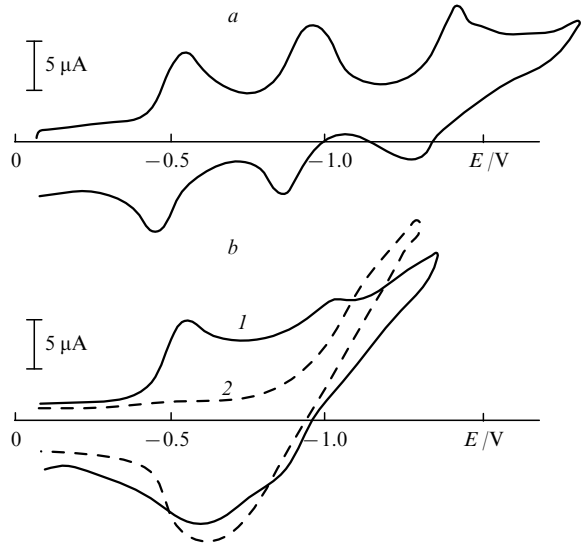


Figure 2. CV of a monolayer film (*a*) and multilayer (*b*) of **4b** on ITO glass in 0.1 M Bu_4NPF_6–acetonitrile.
Potentials *vs.* SCE, υ = 10 mV s^{-1}; (*1*) 3 layers, (*2*) 11 layers.

gested to be limited by the ion diffusion through well ordered hydrophobic film. The CV shape became severely distorted for multilayer films (Fig. 2 *b*).‡

The study of CV response of LB films of other TTF derivatives **1c,e** [18,22] has shown a large influence of the LB film organisation on the electrochemical properties. Films of **1c** have been formed at quite low surface pressure and were not well organised as shown by IR spectroscopy.[22] The films possibly contained a sufficient amount of the defects and short S...S contacts between TTF molecules. As a result CV response was unstable, the oxidation peak was shifted anodically and CV response was not changed in multilayer films (Fig. 3). Unstable CV response with peak splitting was also observed for LB films of material **1e**.[18] The more amphiphilic nature of this material resulted in better film properties. Low electrochemical activity of multilayer films was observed possibly due to a more compact structure.[18] The study of the electroactivity of LB films of a number of TTF derivatives [23–25] resulted in unstable CV responses, often complicated with additional peaks.

Tieke and co-workers were able to observe a well developed

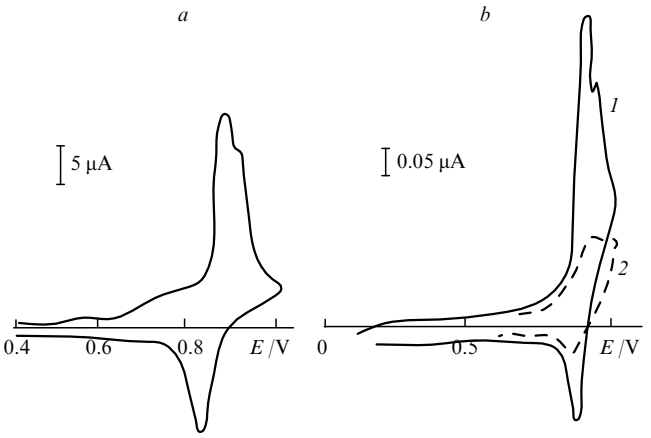


Figure 3. CV of LB film of mixture of **1c** and 20 mol.% stearic acid on ITO glass, saturated KCl solution.[22]
Potentials *vs.* Ag/AgCl; (*a*): 5 layers, $\upsilon = 50$ mV s^{-1}, (*b*): (*1*) — monolayer, $\upsilon = 25$ mV s^{-1}, (*2*) — second scan.

CV response for the multilayer films of **3**.[14,26,27] It is remarkable, that very thick films (80 layers) exhibited the undistorted response,[28] when the films were deposited in the form of radical-cation salt formed on a subphase containing dodecyl sulfate anions. Radical-cation salt formation led to a 70% increase in the molecular area and, possibly, to the formation of the channels for the ion transport. The presence of ions inside LB films may also facilitate the electrochemical reaction.

Nakamura and co-workers [29] measured conductivity up to 10^{-3} S cm^{-1} for LB films of derivative **2a** (15–51 layers) after electrochemical doping at -0.1 V *vs.* SCE. CV of these films demonstrated large peak separation (about 0.4 V) and prepeaks. However, CVs were improved after electroactive compound in the films was diluted by methyl arachidate probably due to a decrease of repulsive interaction between electroactive sites as predicted by theory.[30]

LB films of complexes **5**, deposited by the horizontal lifting method,[31–41] were doped electrochemically. A conductivity as high as 25–50 S cm^{-1} for Au complex with tridecylmethylammonium cation (1 : 1 mixture with icosanoic acid, 20 layers) and in the range of 3×10^{-4}–5 S cm^{-1} for other complexes of Ni and Pd was obtained after the constant current oxidation of the LB films

‡ L M Goldenberg, G Williams, M R Bryce, A P Monkman, M C Petty, A Hirsch, A Soi, unpublished results.

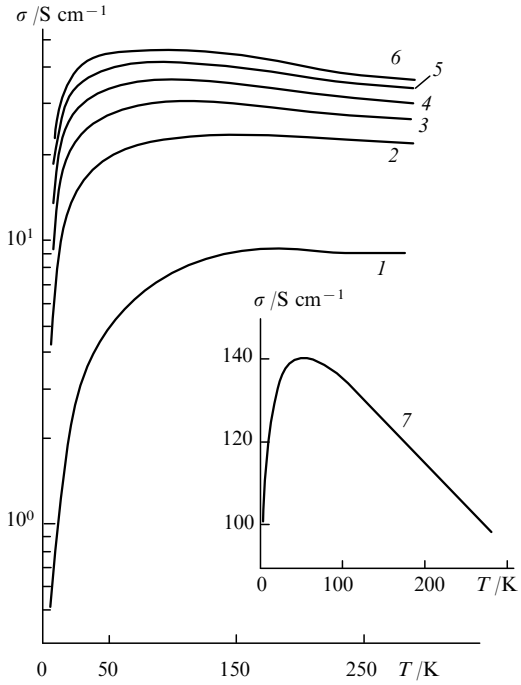


Figure 4. Conductivity as function of temperature for LB films of Au-complex **5** (1 : 1 mixture with icosanoic acid, 20 layers, after the electrochemical doping) under 0 (*1*), 2.7 (*2*), 7 (*3*), 9.5 (*4*), 10.9 (*5*), 11.1 (*6*) and 9.8 (*7*) kbar.[41]

in $LiClO_4$ aqueous electrolyte.[31,32–37] Quasi-metallic character of the conductivity – temperature dependence [31,32,34–37] (Fig. 4) and the increase of the conductivity with pressure [38,41] were registered for Au complex. ESR [33] and thermoelectric power [35–37] measurements also indicated the metallic nature of the films. Very high electrical conductivity of 140 S cm^{-1} was registered at 51 K and 11 kbar.[41]

It was previously shown [37,40,41] that the conductivity was unstable (3-fold decrease in 3 days) and only freshly prepared films showed the metallic conductivity – temperature dependence. In contrast, low-angle X-ray scattering data and thermoelectric power were stable.[40] All these high conductivity values were calculated assuming the layer thickness of 3 nm [31,32,41] despite the AFM study,[39] which revealed plate-like crystallites with a height of about 18 nm. The blurring of the outline of the crystallites was clearly seen after the electrochemical oxidation. The morphological change was accompanied by an increase of the *d*-spacing from 1.9 to 2.7 nm.[35] The value of the *d*-spacing in as-deposited film was ascribed to the interplanar distance of Au complex crystallites as the same value was obtained by X-ray structure analysis of a single crystal.[35,39] This study has been repeated in more detail later [34] and the *d*-spacing of 1.92 nm for as-deposited samples was confirmed. However, this weak pattern was accompanied by stronger peaks corresponding to the *d*-spacing of 4.88 and 4.43 nm. The latter values were ascribed to the icosanoic acid matrix (Y type bilayer). After the electrochemical doping, a new peak corresponding to the *d*-spacing of 3.48 nm appeared. It is unclear how the value of 3.48 nm is correlated to an earlier observed value of 2.7 nm.[35] Using molecular structure simulation, it was suggested [40] that the direction of the longest axis in this complex is almost parallel to the surface of the support. In doped films, molecules of the complex are dimerised along the direction normal to the surface. Molecular resolution with the parallelepiped pattern, specified by 1.06×1.31 nm^2, corresponding to molecular area of complex, was observed in AFM images of the monolayer film.[40] It should be noted, that in this report, AFM was used only for as-deposited samples and possible formation of crystallites was not discussed.[40] Experimentally observed molec-

ular area was 0.28 nm^2 (Ref. 35), which suggests the multilayer or crystallite formation on the water surface.

Recently we studied a similar Ni complex **5** with the octadecylpyridinium cation.[42,43] Both single layer and multilayer films were electroactive with CV peak intensity proportional to the number of layers.[43] LB films were built-up under different conditions resulting in an electrical conductivity difference of a few orders of magnitude.[42] Electrochemistry was found to be useful for determining the difference between these films. The CV response revealed that the same chemical compound was transferred on the solid substrate despite the difference in conducting properties. However, film structure influenced the electroactivity and peak separation (indication of difference in electrochemical kinetics). This suggests that the LB films built-up from the true monolayer (non-conducting films) exhibited slower electrochemical kinetics, because according to schematic structure of the film[42] the molecules of electroactive complex are buried among the hydrophobic chains and are farther from the electrode surface. Electrochemical doping at constant potential of the LB film deposited onto the interdigitated electrode (Fig. 5) exhibited peak shaped current transient (time dependence of current at constant potential). This may be explained by an increase in the effective electrode area due to nucleation of the conducting phase between the fingers of the interdigitated electrode until the film achieves maximum conducting state. The charge consumed in this process corresponds to roughly half of the material being oxidised and consequently to the mixed-valence state. The conductivity value of up to 3×10^{-2} S cm^{-1} was registered either with KCl or $LiClO_4$ electrolytes. The conductivity values and activation energy for these films were similar to ones for the films doped with iodine vapours.[42,43] It should be noted that lower conductivity for these films compared with Au and Pd complexes, studied by Matsumoto group (see above), can be partially explained by using layer thickness measured by profilometry [about 30 nm (Ref. 42)] to calculate the conductivity value, but not the assumed layer thickness of 3 nm.[31,32,41]

The similar approach was applied to obtain conductive LB films from the mixtures of tetrabutylammonium Ni complex **5** and tricosanoic acid.[16] LB films were oxidised at constant potential or constant current in the different electrolyte solutions. In-plane dc conductivity up to 10^{-2} S cm^{-1} was registered after the electrochemical doping in different electrolytes or chemical doping by iodine vapours.[16] It should be mentioned that samples, doped electrochemically in $LiClO_4$ or KI electrolyte or by iodine vapour, were more stable than the samples doped electrochemically in KCl or Bu_4NBr electrolytes. The CV response in all electrolytes studied was similar to the one registered for LB films of the amphiphilic Ni complex.[42] The reversible rapid changes in the visible spectrum were observed under the application of the potential to the LB films (Fig. 6).

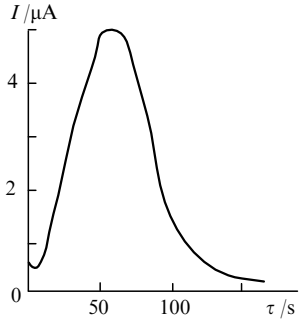


Figure 5. Current transient after application of a potential step for LB film of Ni complex **5** on interdigitated electrode in 3 M KCl solution.[43]

Bard and co-workers[44–46] studied the electrochemical behaviour of LB films of C_{60} **4a**. The first two reduction waves were studied in order to avoid dissolution of films. Most probably these films were not true monolayers. Peak current increased and peak half width decreased with the increase of surface pressure used for film deposition. Peak separation was about 210 mV for lower surface pressure and even at higher surface pressure this value was smaller than that for the cast films.

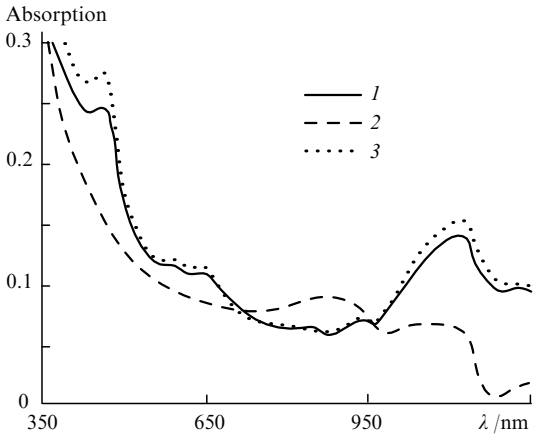


Figure 6. Spectroelectrochemistry upon oxidation of tetrabutylammonium Ni complex **5** (40 mol.% of tricosanoic acid) on ITO electrode, 0.5 M Bu_4NBr aqueous solution.
Potentials *vs.* Ag wire; (*1*) open circuit, (*2*) 1 V, (*3*) −0.3 V.[16]

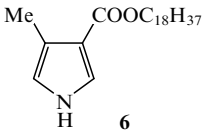
Photoelectrochemical properties of the LB films of C_{60} **4a** and pyrrolidinium derivatives of C_{60} were investigated.[47] The highest photocurrent quantum yield was observed for the derivative with an electron-donating *o*-Me_2NPh group attached to the pyrrolidine ring.

In conclusion, the electrochemical methods can be used for the fabrication of conducting LB films of charge-transfer materials. The electrochemical doping can be realised either during LB film transfer using the subphase as an electrolyte or after LB deposition for already fabricated films. As a result, highly ordered conducting films can be obtained and different counter-ions can be introduced into the LB films. However, further investigations are necessary to elucidate the counter-ion – property relationship. It should be emphasised that very high conductivity of 50 S cm^{-1}, with partially metallic temperature dependence of conductivity, has been obtained using electrochemical technique.

III. Conjugated polymers

The use of electrochemistry for conducting polymer LB films has been very limited despite the number of such polymeric films prepared to date (see review[48]). The successful application of the electrochemical polymerisation for LB films of amphiphilic pyrrole **6**[49–51] is one of the few reported. A short length (several mm) of the electrode covered with LB multilayer film is dipped in $LiClO_4$/acetonitrile electrolyte and a coloured area appears when polymerisation proceeds under an applied potential. Then the covered with polypyrrole part of electrode served as a connecting lead for the rest of the LB film.§ Multilayer polypyrrole films obtained by this method had highly anisotropic conductivity (10^{-1} S cm^{-1} for the direction parallel to electrode surface and 10^{-11} S cm^{-1} for the direction normal to electrode surface). Low angle X-ray scattering also showed that the part of polypyrrole film which was not immersed in the electrolyte solution kept a highly ordered structure. Thus, this method allows synthesis of highly ordered polypyrrole films, which are impossible to obtain by electropolymerisation of the monomer in solution.

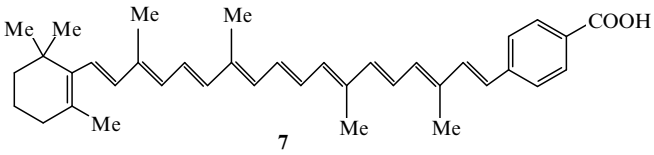
§ It is important that electropolymerisation could not be carried out in aqueous electrolyte, possibly due to hindered diffusion of the water molecules in hydrophobic multilayer films.



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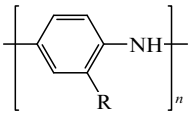
Electrically conducting fine lines of polypyrrole in a matrix of icosanoic acid were fabricated by electrochemical polymerisation during LB film deposition.[52] Pyrrole and icosanoic acid were spread on a $LiClO_4$ subphase and transfer onto ITO electrode was performed by application of 10 V between the moving ITO electrode and the Pt counter electrode. The resulting low conductivity of the film (8×10^{-5} S cm^{-1}) may possibly be ascribed to the fact that the concentration of pyrrole in the matrix is low since most of pyrrole would go into the subphase.

Carotenoids are polyenes and are thus related to the simplest conjugated polymer, polyacetylene. Their importance in photosynthesis and possible involvement as photoreceptors are well known. The photoelectrochemistry of LB films of carotenoid **7** was studied on ITO electrodes.[53] For films up to five layers thick, the photocurrent was linear with the number of layers. This suggests that there is efficient charge and possibly energy transport between monolayers.



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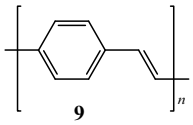
We studied single layer LB films of polyaniline **8** with a thickness of about 6 nm.[54]



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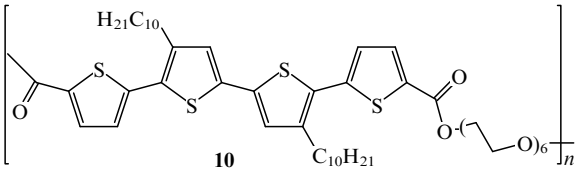
We showed that the use of the LB technique for film formation resulted in the improved electrochemical properties (Fig. 7), comparable with those of the best electrochemically polymerised films (high ratio of first oxidation peak current to plateau current). As expected for the surface electrochemical reaction the peak current was proportional to the scan rate. CV and spectroscopy have shown that LB films are reversibly oxidised (possibly by oxygen) during transfer onto the electrodes. The study of multilayer assemblies of polyaniline[55] resulted in broad peak CV which were similar to those observed by us for spin-coated films (Fig. 7[54]). The distortion of the CV was attributed to slow electron transfer. In the light of a report[56] of very fast redox reaction in polyaniline we believe that hindered ion-diffusion through the thick film, but not slow electrochemical kinetics, is responsible for the observed behaviour. To improve film forming properties LB films were produced from polyaniline doped by amphiphilic acids.[57] A CV response with low peak/plateau current ratio was registered. The films of some substituted polyanilines[57–60] exhibited less resolved CVs compared to the parent polyaniline. Three redox steps, accompanied by an electrochromic effect, could be observed for an alkoxy-substituted polyaniline derivative.[58] A comparison of different film forming techniques (electropolymerisation, spin-coating and LB technique) for poly(*o*-ethoxyaniline) showed that the LB technique was not the best in this case (broad peaks on CV).[60]

A CV response with two broad peaks was observed for poly(*p*-phenylenevinylene) **9** films, which were obtained by vacuum heat treatment of a LB film of the precursor polymer.[61]

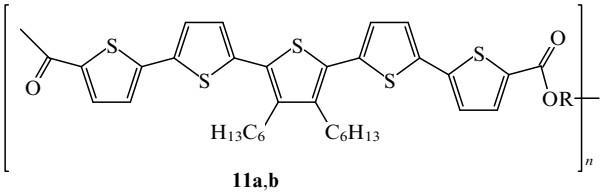


9

Recently we studied electrochemical properties of LB films of substituted polythiophene oligomers **10**, **11** and alkoxy-substituted polythiophene **12**.[62]

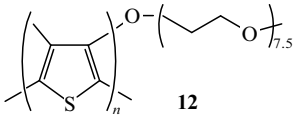


10



11a,**b**

R = $-(CH_2CH_2O)_6-$ (**a**), $-(CH_2)_{10}O-$ (**b**)



12

Oligomers of polythiophene exhibited facile electrochemical behaviour with narrow symmetrical peaks on the CV (Fig. 8). Aggregated films of polythiophene **12**, transferred under special conditions, demonstrated molecular recognition of alkali metal cations (the anodic shift of peak potential upon the addition of metal ions), similar to cast films (Fig. 9).¶

LB films of oligoimides (**13a**–**d**) closely related to conducting polymers have been obtained by Miller *et al.*[63, 64]

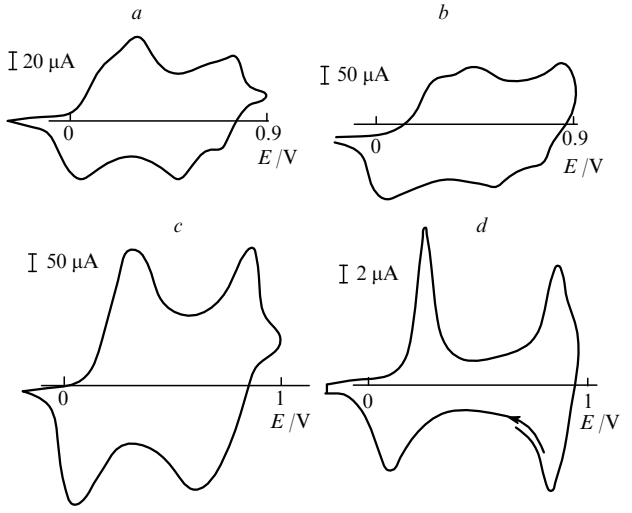


Figure 7. CVs of polyaniline **8** on ITO glass in 1 M HCl, $\upsilon = 50$ mV s^{-1}.[54]
Potentials *vs.* Ag/AgCl; (*a*) dip coated film, (*b*) spin coated film, (*c*) spin coated film after storage in water, (*d*) one layer LB film.

¶ L M Goldenberg, M Leclerc, M C Petty, unpublished results.

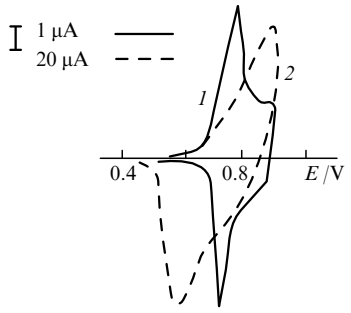


Figure 8. CV of 7-layer LB film of oligomer **10** in 0.2 M Bu_4NBF_4–acetonitrile.
Potentials *vs.* Fc/Fc^+; (*1*) 25 mV s^{-1}, (*2*) 1 V s^{-1}.

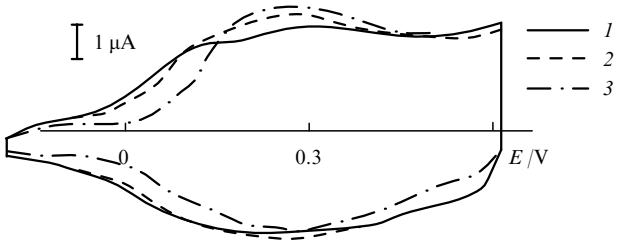
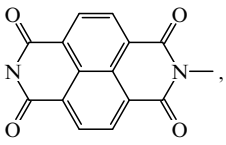
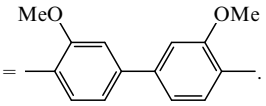


Figure 9. CV of LB films of polythiophene **12** (3 layers) in 0.2 M Bu_4NBF_4–acetonitrile.
Potentials *vs.* Fc/Fc^+, υ = 50 mV s^{-1}; (*1*) without Na^+, (*2*) $[Na^+] = 1.59 \times 10^{-3}$ M, (*3*) $[Na^+] = 7.49 \times 10^{-3}$ M.

13a: HSPh–A–B–A–B–A–B–A–B,
13b: $-O_3SPh$–A–B–A–B–A–$PhSO_3$–,
13c: HO_2CPh–A–B–A–B–A–$PhCO_2H$,
13d: B–A–B–A–B–A–B–A–B–A–B,

where A = , B = .

These imides are able to form *p*-dimers in solution and stacks in electroprecipitated conducting films. The CV of film **13b** shows a reduction peak and two reoxidation peaks (Fig. 10).[63] The films were fully electroactive up to at least 8 layers. Peak current was proportional to scan rate. Even the cathodic peak half width (70–120 mV depending on compound) was rather close to the theoretically expected value (90 mV) for a one-electron surface reaction. Grazing angle IR spectra have shown that the oligomer molecules were oriented with the long axis roughly parallel to electrode surface (tilt angle ~15°), but after electrochemical cycling the tilt angle increases to ~35°. That is similar to the value in isotropically oriented evaporated films and thus electrochemical cycling disrupts the original organisation[63] in contrast to the films of **3**[14] and polypyrrole **6**.[49] The doubling of the reoxidation peak and large peak separation can be explained by thermodynamic stabilisation of the radical-anion in the LB films due to possible formation of dimers or stacks, which oligoimides form in solution.[64] It can also be explained by sufficiently negative interaction energy in a theoretical model.[30] That suggests that reduced LB films of **3a**–**d** could be anisotropic conductors.

Compound **13a** was studied in three possible forms: LB films, an evaporated film and an SA monolayer[63] (Fig. 10 for SA and LB films). The cathodic peak was broader in the evaporated film compared to LB film and SA film. The SA film exhibits only one reoxidation peak, which suggests that interactions between molecules are weaker.

Thus, LB technique allows to fabricate high quality conjugated polymer electrodes. Conducting films with the high

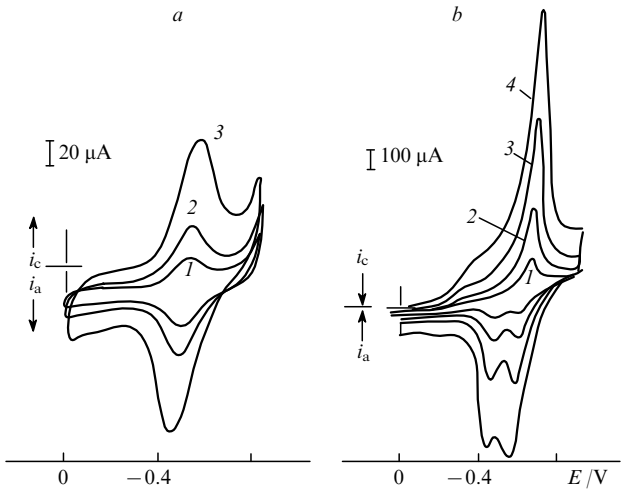


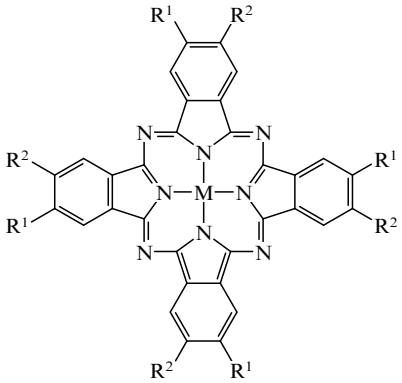
Figure 10. CVs of **13a** films.[63]
Potentials *vs.* SCE; (*a*) SA film at 100 (*1*), 200 (*2*) and 500 (*3*) mV s^{-1} in 0.1 M Ph_4NBF_4–DMF, (*b*) 6 layers LB film at 20 (*1*), 50 (*2*), 100 (*3*) and 200 (*4*) mV s^{-1} in 0.1 M aqueous $BaCl_2$.

anisotropy of the electrical conductivity were obtained. Electropolymerisation on the water surface in an LB trough during the film transfer is of interest. Many of conjugated polymers are used for the fabrication of light emitting diodes. Electrochemical light emitting cells can possess the improved characteristics compared to the conventional light emitting diodes. Recently, LB films of conjugated polymers were employed as emitting layers of the light emitting diodes. The electrochemical properties of the films should be further investigated in order to use them in electrochemical light emitting cells.

IV. Coordination compounds

1. Phthalocyanines and related compounds

The main interest in the electrochemical properties of the phthalocyanines (Pc, **14**)



14

has been related to their electrochromic properties. The LB technique was used as an alternative method to casting for the fabrication of electrochromic films. Electrochromic properties were first reported for LB films of unsubstituted monophthalocyanine;[65] CV with broad peaks corresponding to a transition from green to red form under oxidation and to purple form under reduction was registered. The detailed paper reported the electrochemical study of alkyloxy-substituted diphthalocyanine Lu[66] and LB films showed a one-electron reversible oxidation and a one-electron reversible reduction corresponding to a transition from green to orange and blue forms, respectively. The CV response of multilayers was not distorted and well defined peaks were observed. The electroactivity of films under oxidation

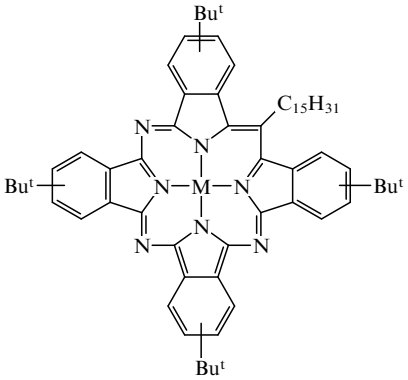
corresponds only to 30% – 50% of the amount of the deposited material and peak currents are neither proportional to scan rate nor to square root of scan rate. The CV for this compound shows a distinctive diffusion tail. Peak separation was highly dependent on the anion of the electrolyte. Thus, the electrochemical response was at least partially controlled by the diffusion of counter-ions.

The electrochemical properties of a variety of phthalocyanine LB films have been studied.[65–82] YPc_2 LB films,[75] mixed with icosanoic acid, showed well developed CV response with peak current proportional to the scan rate. In contrast to the evaporated or cast films, the CV response for LB films was stable upon potential cycling. Three distinct colours (blue, green and red) were observed within the potential range of 1 V. LB films of $PrPc_2$ [79] also showed better resolved and stable CV response compared to the cast films. Four colour changes were attained and the absorbance decreased by only 35% after 10^5 electrochromic cycles.

The electrochemical properties of the LB films formed by Cu and Ni monophthalocyanine substituted with short branched chains were studied.[81] Three surface confined redox transitions (electroactivity of about 30%) were observed in acetonitrile solution; electrochromic effect was noted in a 51 layer film. However, the electrochromic response was not stable, particularly in thicker films, due to desorption of the LB film upon potential cycling.

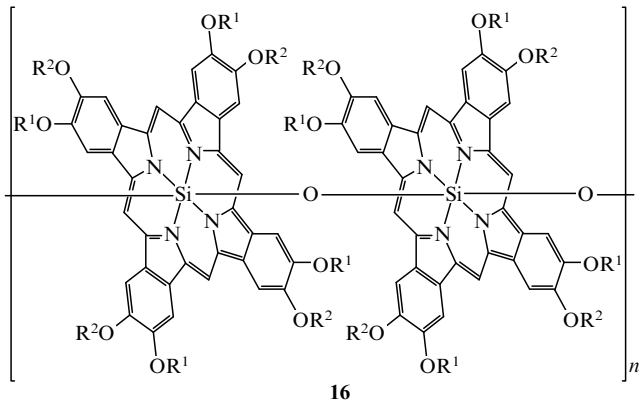
The multilayer assemblies of asymmetrical tetraphenyl substituted $LuPc_2$ exhibited two or three redox steps,[80] accompanied by colour changes from blue to green and from blue to red. The spectral peaks were better resolved and the electrochromism was more stable in the LB films than in the cast films.[80]

The first example of phthalocyanine LB films, in which phthalocyanine molecules were not aggregated, has been studied by Lever and co-workers.[78] Fe bears two long-chain ligands in FePc and these ligands prevent aggregation.[78] The bilayer film was not electroactive in an aqueous electrolyte. This may be due to blocking of the counterion diffusion by the long chains.[78] In contrast, well developed electrochemical response was observed for the randomly oriented cast film, indicating a high level of organisation in the LB films. The same group [77] reported on the assembly of LB films of a new phthalocyanine derivative **15**. A surface electrochemical reaction response with broad peaks was observed at low scan rate for a 10 layer LB film of this amphiphilic Pc.



15

Recently Wegner and co-workers [76] reported on the CV and spectroelectrochemical characterisation of highly ordered LB multilayers of 'hairy-rod' polyphthalocyaninatosiloxanes **16**. The films showed notable stability in aqueous and nonaqueous electrolytes. Up to 100% one-electron oxidation per phthalocyanine ring was achieved at 1 V *vs.* Ag/AgCl.



16

$R^1 = Me$, $R^2 = C_8H_{17}$, $C_6H_{12}CH=CH_2$

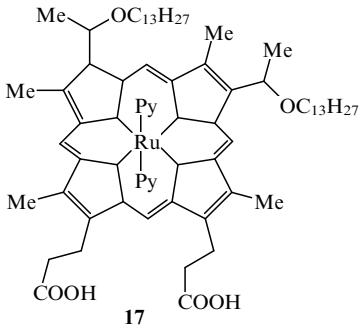
Some of the phthalocyanine LB films showed CVs with peak intensity proportional to the square root of scan rate whose shapes were rather close to a diffusion controlled wave.[72,74] In general, we can state that electrochemistry in Pc LB films is quite facile. Multilayer films can be easily oxidised and reduced and improved electrochemical properties were observed compared to cast films in some cases.[69,70,75] An explanation of relatively facile redox reaction in multilayers is that the phthalocyanine ring is large compared to the alkyl tail projected area and thus even in the solid condensed state enough empty space and channels can be present in LB films to allow ion transport.

Electrochromic devices based on LB films exhibit low response time and improved stability upon potential cycling. Bearing in mind that chemical oxidation can be used for the doping to create electroconducting materials (see review [10]) and the quite facile electrochemistry of these films, electrochemical techniques can be used for producing electroconducting phthalocyanine LB films.

Porphyrin derivatives were studied with an eye to their biological properties as compounds providing electron transfer in such important biological processes as photosynthesis.

Cytochrome *c* was incorporated in an LB film of phospholipid to prevent denaturation on the electrode surface.[83] CV was simulated according to the surface reaction model to yield an estimate of the first-order rate constant of 2 s^{-1}. Such a small value of the rate constant was explained by either a large separation of redox centres from the electrode or nonoptimised orientation of cytochrome *c*.

LB films of Ru hematoporphyrin **17** were studied by CV.[84]



17

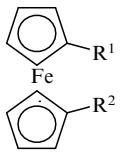
Laviron [85] presented the theoretical treatment for a surface electrochemical reaction in multilayer modified electrodes. Daifuku *et al.*[86] extended this treatment to a monolayer. Ueyama *et al.*[84] suggested a model for Z-type multilayer LB films (when the electroactive heads in all the layers are oriented in the electrode direction). Films were transferred in a solid condensed state with molecular area of 0.83 nm^2. Even at slow scan rates the peak separation for CVs in the monolayer was 90 mV, which was attributed to rearrangement of porphyrin rings during the redox reaction.[84] The plots of peak potential *vs.* ln of scan rate were

linear, starting from about 10 V s^{-1} (irreversible electrochemical reaction), and slopes of these plots gave values of the transfer coefficient of 0.32 and 0.42 for anodic and cathodic reactions respectively. First-order rate constants of 51.1 and 21.1 s^{-1} were obtained for the cathodic and anodic reactions respectively. The simulated and experimental voltammograms for the cathodic wave were not in good agreement, indicating some deviation from the Daifuku model. Two- and three-layer Z-type LB films exhibited complete electroactivity. The peak separation and peak half width increased with an increase of the scan rate. The charge, consumed upon electrochemical cycling, was constant at relatively low scan rates and decreased at high scan rates. This suggests that not all porphyrin rings participated in the electrochemical reaction at higher scan rates. Comparison of experimental and simulated voltammograms[84] yielded a pseudo-first-order rate constant for interlayer electron transfer of 256 and 128 s^{-1} (and the electron diffusion coefficient of 1.6×10^{-11} and 0.8×10^{-11} cm^2 s^{-1}) for anodic and cathodic reactions respectively. At higher scan rates (above 12.8 V s^{-1}) disagreement was observed between simulated and experimental voltammograms, which was attributed to slow counter ion transport. In our opinion even the CV at slow scan rate reveals some diffusional tailing.

Thus, LB films of porphyrins can be a good experimental model for the development of a theory of surface electrochemical reaction.

2. Ferrocene derivatives

Bilewicz and Majda incorporated BuFc **18c** in a passivating $C_{18}H_{37}SH/C_{18}H_{37}OH$ mixed monolayer on a gold electrode[87] and showed that Fc in the matrix was entirely electroactive.



18a–h

18a: $R^1 = R^2 = CONHC_{18}H_{37}$;
18b: R^1 = H, $R^2 = CONHC_{18}H_{37}$;
18c: R^1 = H, R^2 = Bu;
18d: R^1 = H, $R^2 = CH_2\overset{+}{N}Me_2C_{18}H_{37}$;
18e: R^1 = H, $R^2 = C_{15}H_{30}COOH$;
18f: R^1 = H, $R^2 = COCH_2CH_2COFc$ (Fc = $C_5H_5FeC_5H_4$);
18g: R^1 = H, $R^2 = C(O)OCH_2CH_2S-TTF$;
18h: $R^1 = R^2 = C(O)OCH_2CH_2S-TTF$.

A well developed CV with high peak separation about 0.4 V (possibly due to IR drop) was obtained for a densely packed (mean molecular area 0.26 nm^2) eleven layer LB film of an amphiphilic Fc derivative **18b**.[88]

For the Fc derivative **18d** it was shown that the surface pressure used for LB film deposition (and consequently the packing density) did not influence the electrochemical properties.[89] The CV response corresponded to the surface reaction model with a low peak separation (20–30 mV) and a peak current proportional to the scan rate. An electroactivity fraction of around 55%–80% was observed. Possible reasons for such behaviour could be partial monolayer dissolution, incomplete physical contact of Fc sites with the electrode, reorientation of the film after immersion in the electrolyte solution, hindering of counter ion transport by hydrophobic tails and uncertainty in charge calculation due to high background current. The highest electroactivity (about 80%) was obtained for a surface pressure of 22 mN m^{-1} (mean molecular area 0.37 nm^2). The formal potential for LB film was 0.14 V more positive than for the soluble Fc analogue. It was interpreted as the Fc moiety being more strongly adsorbed to the gold surface than the ferricenium moiety and the surface wave may be regarded as an adsorption postwave. An SA monolayer of the same compound showed much narrower peaks

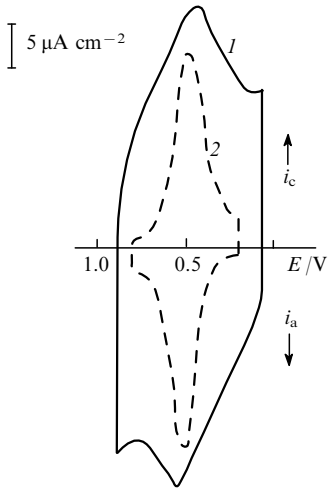
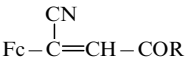


Figure 11. CVs of **18d** monolayer in 1 M H_2SO_4.
Potentials *vs.* SSCE; (*1*) LB monolayer on Au electrode, (*2*) SA on Pt/I electrode.[89]

(Fig. 11). Broadness of CVs for LB monolayers have been attributed to repulsive intermolecular interaction according to theory.[90]

There is a wide variation (0.2–0.55 nm^2) for reported molecular areas for amphiphilic Fc compounds.[91] The cross-sections of the Fc moiety were determined using molecular modelling to be around 0.5 nm^2.[12,91] This value should determine the limiting molecular area for a true monolayer. The staggering of Fc heads is usually suggested [12] in the cases when lower values (0.2–0.3 nm^2) have been registered.

Recently we investigated cyanovinyl Fc derivatives **19**:[92]



19a–c

R = $NHC_{16}H_{33}$ (**a**), $OC_{18}H_{37}$ (**b**), O-cholesteryl (**c**).

The change of the surface pressure–molecular area isotherm with the time that the Langmuir layer was left on the subphase surface before compression is shown in Fig. 12. The monolayer organisation undergoes change from the staggering of Fc heads to the true monolayer. This process can be monitored electrochemi-

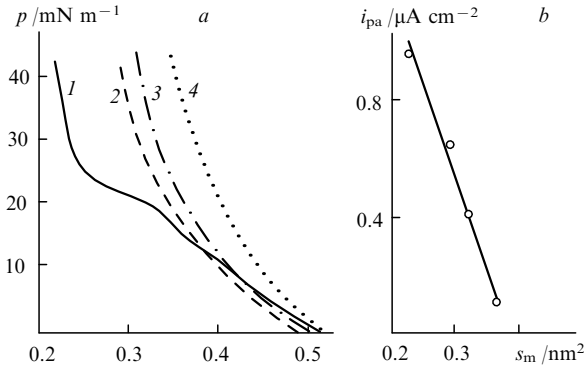
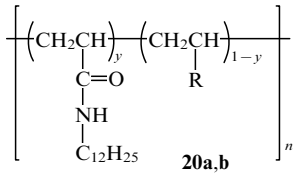


Figure 12. The change of surface pressure *vs.* area per molecule isotherm for compound **19a** with time, monolayer was left on the subphase surface before compression (*a*) and a plot of anodic peak current *vs.* molecular area at the dipping pressure (35 mN m^{-1}) for monolayers transferred onto ITO electrode after the floating film was left on the subphase surface for different lengths of time before compression (*b*); min: (*1*) 10; (*2*) 20; (*3*) 35; (*4*) 120.[92]

cally. At short times two compression regions are observed, of which the second one corresponds to the staggering of Fc heads (the limiting molecular area *ca.* 0.28 nm^2). As the time increases the true monolayer with the limiting molecular area of more than 0.4 nm^2 is formed. The CV response for the films transferred at different times before compression follows the change in the organisation of the Langmuir layer. This results in the linear dependence of the peak current (related to the electroactive coverage) on molecular area, at the surface pressure used for the transfer onto an electrode (the inset in Fig. 12).

Electrochemical properties of mono- and multilayers of amphiphilic polymers with the different content of Fc groups **20** were studied.[93, 94]



20a,**b**

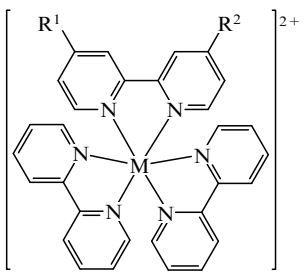
R = Fc (**a**), C(O)CH$_2$Fc (**b**).

The surface wave response with peak currents proportional to the scan rate and low peak separation, but broad peaks (peak half width of 130 – 170 mV) were observed for monolayers of **20b**.[93] The film behaviour depended on the Fc group content in the co-polymer. For polymer films with a molar ratio Fc/polymer repeat unit of 0.41, the LB assembly remains completely electroactive up to at least 5 layers. However, increasing the peak separation indicates kinetic limitations. It was suggested [93] that the interlayer electron transfer process occurs by the electron hopping mechanism. This process is retarded as the number of layers is increased. For the material with an Fc fraction of 0.2 in the co-polymer, the behaviour of multilayer films changes drastically. Clearly, diffusion controlled response has been observed. The diffusion tails, electroactivity (which corresponds only to the inner layer) and non-linear dependence of the peak current on the scan rate were registered. Low-angle X-ray scattering results reveal that *d*-spacing increases by 0.22 nm for the polymer with the lower Fc content. It has been suggested that this increase in the interlayer electron transfer distance could explain the low electroactivity of LB films of the co-polymer with lower Fc fraction.[93] We suggest that, statistically, the decrease in the concentration of electroactive sites even without any structural modifications (the change of the *d*-spacing), could lead to an increase in the distance of the electron hopping. In the case of the polymer with the low Fc content the percolation threshold could be reached.

The reports on the other Fc containing LB films are discussed in the Section VI since these films were predominantly studied in heterolayer structures.

3. Metal bipyridine complexes

Matsuda and co-workers [86, 95, 96] studied LB films of Os and Ru complex **21a**, **b** as experimental model compounds for analysis of a surface electrochemical reaction.



21a: M = Os, R^1 = R^2 = C$_{19}$H$_{39}$;
21b: M = Ru, R^1 = R^2 = C$_{19}$H$_{39}$;
21c: M = Ru, R^1 = Me,
R^2 = CH$_2$NHC$_{19}$H$_{39}$.

21a – c

The theoretical model [97] was extended taking into account the interaction between reactants to explain the deviation from an ideal surface wave. CV shape for a monolayer of the Os(II) complex was close to an ideal surface wave: peak separation was 10 mV, peak current was proportional to scan rate, no diffusion tails were observed and stirring the electrolyte solution did not have any effect on the voltammograms.[86] However, peak half widths were 135 and 125 mV, which are larger than 90 mV for the theoretical wave. The slope of a plot of peak current *vs.* scan rate also shows deviation from the theoretical value. The deviation arises from the interaction between redox sites.

Calculation of the charge consumed under the voltammetric peak showed that the charge decreased with increasing scan rate. Possibly due to electrode roughness and rigidity of monolayer, not all molecules participated in direct electron transfer with electrode at the short time scale. Also some of the material may be oxidised or reduced through lateral electron exchange, which is slower that direct electron transfer. At higher scan rate this process does not contribute to peak current. From the region of the plot of peak potential *vs.* scan rate, where peak potential was proportional to logarithm of scan rate, transfer coefficients were estimated to be 0.46 and 0.55 for anodic and cathodic reaction respectively. The formal first-order rate constant was estimated at *ca.* 100 s^{-1}. Similar treatment was applied to a monolayer of a Ru complex and a mean value of the formal rate constant was estimated as 70 s^{-1} and transfer coefficients were 0.44 and 0.54 for anodic and cathodic reactions respectively.

The same group [95] also studied the electrochemical behaviour of solution redox species on rotating disc electrode (RDE) constructed from monolayers of the same complexes **21**. An Os(II) monolayer of **21a** catalysed the oxidation of Fe^{2+}, which is retarded on a bare SnO_2 electrode (Fig. 13). The apparent rate constant for the electron exchange reaction between Os(III) on the surface and Fe^{2+} in solution was 2.7×10^7 cm^3 mol^{-1} s^{-1} (7.5×10^8 cm^3 mol^{-1} s^{-1} for the Ru complex). A similar electron exchange rate constant for TEMPOL oxidation and Ce (IV) reduction on an Os monolayer were $(2.7-5) \times 10^9$ and 1.5×10^9 cm^3 mol^{-1} s^{-1} respectively.[95] The non-ideality of RDE voltammograms was explained by interaction between the redox sites confined on the electrode surface as an LB monolayer.

It has been shown [96] that the photoexcited state of Ru(III) complex **21b** in LB films, generated upon electrochemical oxidation and irradiation, increases the rate of water oxidation.

The CV characteristic of the surface reaction, with a peak separation of 30 mV, peak current proportional to scan rate, and a peak half width close to 90 mV was obtained for LB monolayer of the Ru complex **21c**.[98] This rather ideal behaviour can possibly be explained by a large (0.5 nm^2) mean molecular area. The ratio of the surface concentration which showed electroactivity in CV decreased with the rise of surface pressure used for LB film transfer.[99] At the surface pressure where the molecular area was 0.60 nm^2, only about 50% of monolayer was electroactive.

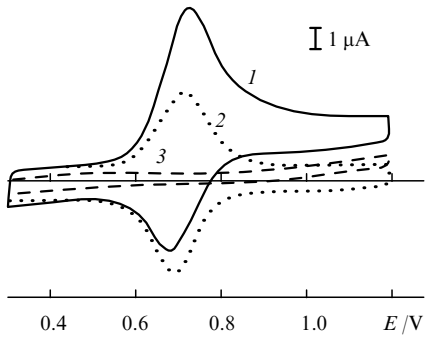


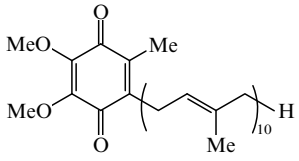
Figure 13. CVs illustrating the catalytic oxidation of Fe^{2+} by monolayer of **21a** on SnO_2 electrode in 0.18 M H_2SO_4.
Potentials *vs.* SCE; υ = 111 mV s^{-1}; (*1*) LB monolayer, (*2*) the same with 0.1 M Fe^{2+}, (*3*) bare SnO_2 electrode with Fe^{2+}.[95]

Electroactive coverage was constant, corresponding to a limiting molecular area in the isotherm surface pressure *vs.* molecular area. An elegant experiment has shown that the monolayer was expanded to the limiting molecular area (owing to repulsive interaction between surfactant molecules) after reimmersion in electrolyte solution. An ITO electrode with a monolayer of **21**c deposited on one half was immersed in electrolyte solution, then dried and another part, where monolayer was not deposited, reimmersed. This part of electrode showed a CV response for the Ru complex. Only the inner monolayer was electroactive in the 2- and 3-layer Y-type LB films. However, a Z-type multilayer, deposited by horizontal lifting technique, showed a CV response which increased with the number of layers.[99]

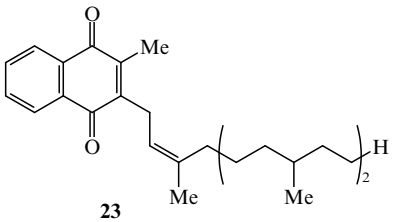
Thus, LB films of metal complexes (Fc, *etc.*) serve as a good model for the study of the relationship between film transfer conditions and electrochemical properties and for the development of a theory of the surface electrochemical reaction.

V. Miscellaneous materials

Amphiphilic quinone derivatives, coenzyme Q **22** and vitamin K_1 **23**, can be incorporated at a low concentration in a mixed $C_{18}H_{37}SH/C_{18}H_{37}OH$ monolayer.[87, 100, 101]



22



23

These quinone derivatives show complete electroactivity with a nice surface wave response and low capacitive background due to the densely packed $C_{18}H_{37}SH/C_{18}H_{37}OH$ monolayer, enabling low quinone concentrations in the monolayer to be detected. At the surface concentration of **22** below 10^{-15} mol cm^{-2} electrochemistry at single molecule 'gate sites' has been registered.[101] These monolayers behave as an array of individually addressed 1 nm diameter disc microelectrodes. An apparent heterogeneous rate constant for the solution redox probe $Ru(NH_3)_6^{3+/2+}$ as high as 80 cm s^{-1} was calculated. Similarly, high values of the rate constant were obtained only using nanodes (microlelectrodes of nm dimensions).[102] This fact proves that ubiquinone molecules in the monolayer film behave as nanodes.

The mediated electroreduction of $Ru(NH_3)_6^{3+}$ and electron tunnelling through ubiquinone were ruled out and a plausible mechanism, where loose conformation of isoprenoid chain in ubiquinone created a channel in LB film, that allows for a direct approach of $Ru(NH_3)_6{}^{3+}$ ions to the electrode surface, was suggested. An additional confirmation of this hypothesis was found in the dependence of ubiquinone electroactivity on the cation size (Fig. 14). Obviously, the electroactivity of ubiquinone is severely hindered, when only a sufficiently large cation (tetrabutylammonium) is available in solution.

The kinetics (rate constant 80 s^{-1})[100] has been obtained from CV according to the Laviron theory [103] and modified theory of Daifuku *et al.*[86] Compound **22** was also transferred onto a Au electrode by the LB technique [104] and the film exhibited a reversible two electron surface reaction in 0.1 M NaOH. The kinetics were slower at the lower pH. It is noteworthy that the electroactivity of the monolayer is complete and the CV response is symmetrical.

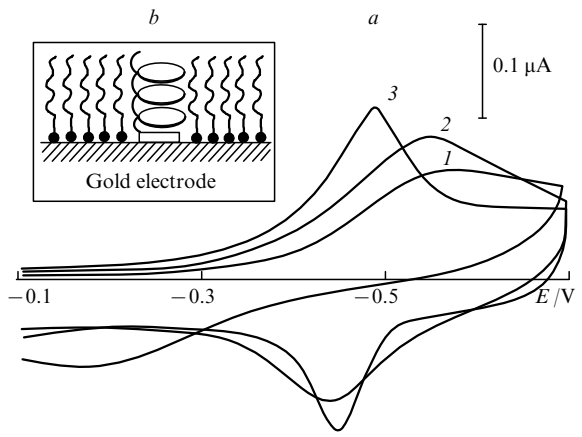
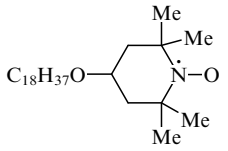


Figure 14. CV of ubiquinone **22** immobilised (1.5 mol.%) in a monolayer of $C_{18}H_{37}SH/C_{18}H_{37}OH$ on a gold surface (*a*) and schematic representation of monolayer (*b*).[101]
Potentials *vs.* SCE: (*1*) 0.4 M Bu_4NOH; (*2*) 0.4 M Bu_4NOH + 0.02 M K_2SO_4; (*3*) 0.4 M Bu_4NOH + 1 M K_2SO_4, υ = 50 mV s^{-1}.

The study of monolayers with the amphiphilic nitroxy radical **24**[105] has shown that both pure monolayers and monolayers highly diluted with icosanoic acid show a defined 'break-in' effect, where electroactivity increases to a maximum upon voltammetric cycling (Fig. 15).



24

Both monolayers show responses with peak current proportional to scan rate, but high peak separations (100 mV) and peak half widths greater than theoretically expected 90 mV. Monolayers of pure material show a less symmetric CV response and two peaks were observed for oxidation, which can be explained by interaction between electroactive sites. More difficult to explain is the dependence of the 'break-in' effect on supporting electrolyte concentration, namely that at higher electrolyte concentration more cycles were necessary to achieve the maximum wave. It was suggested [105] that this phenomenon is similar to the 'salting-out effect' at the interface of aqueous solution and a hydrophobic monolayer.

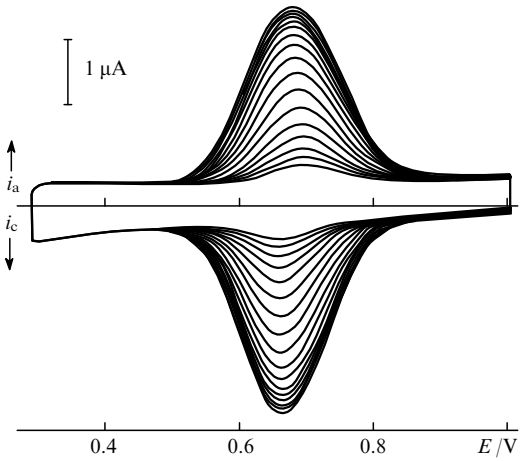
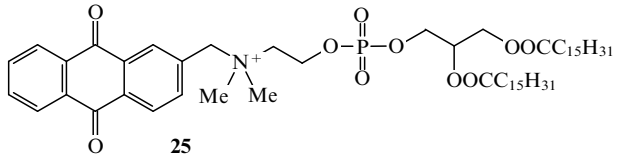


Figure 15. CV of a monolayer film of mixture of **24** and icosanoic acid (1 : 2), 0.18 M H_2SO_4, υ = 100 mV s^{-1}, potentials *vs.* SCE.[105]

Using a phospholipid with attached electroactive anthraquinone moieties **25** authors [106] studied the influence of deposition surface pressure, composition of LB layer, nature of supporting electrolyte and the number of layers.



25

When the monolayers were transferred as a liquid expanded phase a surface wave response was observed and the best shape was observed in the 1 : 1 mixture with dipalmitoylphosphatidylcholine (Fig. 16 *a*). Electroactivity of the films was complete, but the peak half width was considerably higher (80 and 120 mV) than predicted for a two electron surface wave (45 mV). Film transfer in the solid condensed state results in incomplete reoxidation and a postwave after the main reduction peak. This effect was increased in KCl electrolyte (Fig. 16 *b*). Only the inner monolayer was electroactive in Y-type three layer films consisting of either the same molecules or two nonelectroactive layers. This signifies that the two outer monolayers inhibited charge transfer to the inner monolayer (Fig. 16 *c*). All these observations were consistent with hindered ion transport through LB films. The SA films of the same compound **25** [107] showed low peak separation in KCl solution. However, peak splitting appeared upon potential cycling.

Flavin is one of the typical prosthetic groups of electron transfer proteins. Ueyama and co-workers [108] studied a flavin (**26a**) LB monolayer on a gold electrode.

A surfactant molecule was deposited in the solid condensed state with mean molecular area 0.47 nm^2. Peak half widths in voltammograms were much larger than the theoretical value and

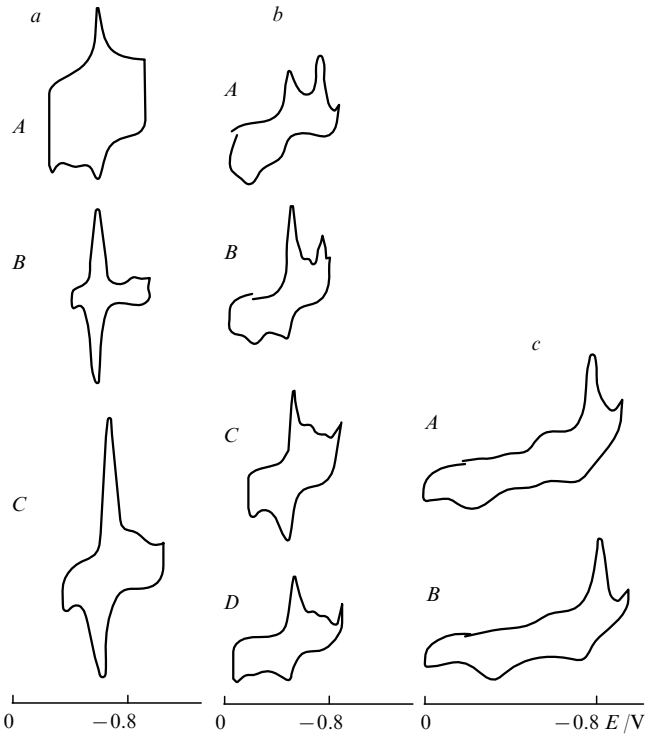
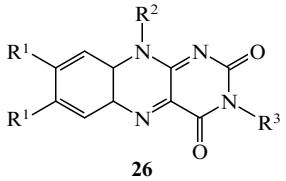


Figure 16. CVs of monolayer of **25**.[106]
Potentials *vs*. SSCE; (*a*) in 0.2 M $NaClO_4$, 50 mV s^{-1}, transferred at 25 mN m^{-1}, molar contents of **25** in monolayer 0.1 (*A*), 0.5 (*B*), 1.0 (*C*); (*b*) in 0.2 M KCl, υ = 200 mV s^{-1}, transferred at 40 mN m^{-1} (*A*), 31 mN m^{-1} (*B*), 25 mN m^{-1} (*C*), 15 mN m^{-1} (*D*); (*c*) in 0.2 M KCl, 200 mV s^{-1}, transferred at 25 mN m^{-1}: (*A*) Y type 3 layer, (*B*) monolayer of **25**, covered with 2 layers of nonoelectroactive surfactant.

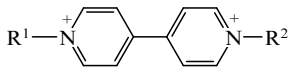


26

26a: R^1 = Me, R^2 = R^3 = C_9H_{19};
26b: R^1 = $CH_2SCH_2CO_2H$, R^2 = R^3 = C_9H_{19}.

the shape of the response was of a diffusion-controlled type. The dependence on scan rate of peak current was also closer to diffusion controlled behaviour than to surface reaction. Thus a first-order rate constant according to the surface reaction model (about 1.5 s^{-1})[86] does not have much validity. In addition electroactivity of the film was not complete even at slow scan rates. Another amphiphilic flavin molecule **26b** [109] showed a better surface wave response for a monolayer film possibly due to higher mean molecular area and consequently more facile ion diffusion.

Bard and co-workers [110] studied amphiphilic viologen **27b** in the form of LB and SA monolayers.



27a – g

27a: R^1 = Et, R^2 = $CH_2CH_2CON(C_{18}H_{37})_2$;
27b: R^1 = Me, R^2 = $C_{16}H_{33}$;
27c: R^1 = Et, R^2 = $C_5H_{10}OPhNNPhOC_{12}H_{25}$;
27d: R^1 = Me, R^2 = $C_{22}H_{45}$;
27e: R^1 = R^2 = $C_{16}H_{33}$;
27f: R^1 = R^2 = $C_{18}H_{37}$;
27g: R^1 = R^2 = $C_{22}H_{45}$.

The LB monolayers with mean molecular area 0.40 nm^2 were completely electroactive. Two definitive reduction and oxidation peaks were observed (Fig. 17), which is in agreement with the theoretical model in the case of sufficiently negative interaction energy.[30] In contrast, a SA monolayer, which was not as closely packed as the LB monolayer and had more random orientation of molecules, showed only a single peak. In simple chemical terms strong pairing of the dication with the radical-cation results in the mixed valence state exhibiting a different reduction potential compared to the parent dication state. A similar explanation can apply to prepeak observations in LB films of derivative **1c**,[22] whose parent compound BEDT – TTF is well known for a strong intermolecular interactions in a mixed valence state, in **2**b LB films,[29] and with oligoimides **13**.[63, 64]

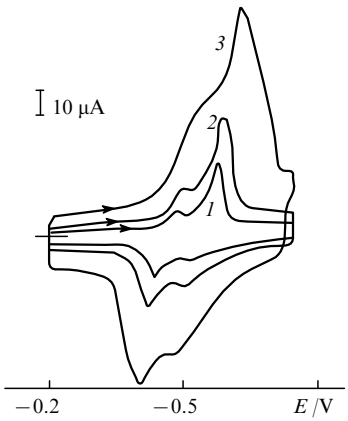


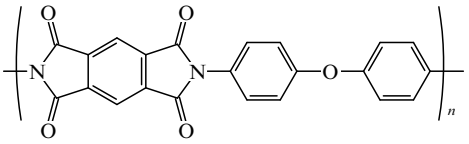
Figure 17. CVs of **27b** monolayer LB films on ITO electrode in 0.2 M $NaClO_4$.[110]
Potentials *vs*. SSCE, scan rate (mV s^{-1}): 100 (*1*), 200 (*2*), 500 (*3*).

The same group studied amphiphilic viologen **27d**, which forms much denser films (molecular area about 0.2 nm^2) and demonstrates more stable electrochemical properties.[111] Better developed splitting of the first reduction peak was observed for these films.[110] However, when viologen was sufficiently diluted with icosanoic acid, the monolayer showed only single peaks in CV indicating the absence of the interaction between viologen sites.

For comparison, LB monolayers formed by symmetrical viologen amphiphiles **27e–g** were studied.[112] Only single redox peaks were observed. The films were loosely packed as was deduced from the higher molecular area, the contact angle measurements and electrochemical experiments with solution redox probes.[112] Thus, the loose structure and, consequently, smaller possibility for intermolecular interactions can account for the single peak behaviour. The reduction potentials for the surface confined viologen in all LB films studied [110–112] were more positive than for the viologen in solution. This was attributed to the stabilisation of the radical-cation form compared to the dication form in the LB films due to the more hydrophobic environment. The effect is probably similar to the one observed for SA monolayers of Fc substituted thiols on Au.[113]

The reduction peak splitting for asymmetrical viologen **27b** depends on the nature of electrolyte.[114] The peak splitting was also observed in the response of SA monolayers. However, only CV of LB monolayers with bulky anions displayed double peaks.

Fujihira and co-workers [115] reported on LB films of polyimides **28**. The films were obtained by the thermal chemical reaction of an LB film of the precursor polymer.



28

A facile electrochemical reaction involving two reduction steps was observed. The electroactivity of the film was proportional to the number of layers (at least up to 30 layers). Unfortunately, the electroactivity decreased upon potential cycling.

The electrochemical technique has been used for detecting methylene green (a water soluble dye) in the LB films, transferred from a mixed monolayer of a phospholipid.[116]

The study of photosensitised electron injection in xanthene dyes, immobilised into LB films of Cd icosanoate, has been reported.[117] The dependencies of current on potential without and with illumination by light of different wavelength (photocurrent spectroscopy) were investigated. Similar studies have been done for LB films of halobacterial violet,[118] where the effective photocurrent depended on the pH and potential. It was suggested that this phenomenon could be used in the fabrication of a luminance sensor. The photochemistry of the xanthene dyes, immobilised into LB films and deposited onto anthracene crystal, was also investigated.[119]

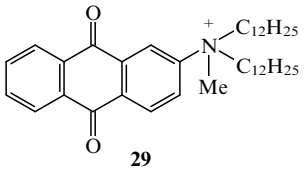
The electrochemical properties of LB films of bacterial photosynthetic membranes were also reported.[120]

LB films discussed in this chapter are interesting objects for the study of surface electrochemical reactions, influence of the conditions of LB film transfer on the electrochemical properties of the coated electrodes and modelling of the properties of biological membranes.

VI. Heterolayers

It was suggested [121–123] that the positively charged viologen amphiphile **27c** forms bilayers with negatively charged poly(1-sulfatoethylene) and other polyelectrolytes. The electroactivity of the films increased with the number of layers, but was not proportional to this number, which means that in a multilayer assembly electrochemistry became more difficult.[121] Peak current became proportional to the square root of the scan rate for films of more than five bilayers which indicates that electrochemistry is limited by diffusion of ions through the LB film.[121, 122] Reduction in the first cycle needed higher overpotential and a stable voltammogram was established after a few scans.[121] Quartz crystal microbalance studies indicate ion transport and morphological changes in the films during the electrochemical process.[121] It was also found that the reduction potential for the viologen **27c** is strongly affected by the structure of polyion. The smaller the molecular area of the complex at low surface pressure the lower the reduction potential.[122] Thus, more compact films required a higher overpotential. For LB films formed with polyacrylic acid [123] the reduction potential was found to depend on the pH of the subphase during LB transfer and the pH of the electrolyte in the CV experiment.

Fujihira and Araki studied a different assembly of LB layer comprised of anthraquinone **29**, viologen **27a** and ferrocene **18a**.[124, 125]



29

Multilayers were constructed from an inactive layer of icosanoic acid and electroactive mixed layers (electroactive surfactant + icosanoic acid). All types of anthraquinone-containing multilayer assemblies were electroactive and the proposed mediator for electron transfer through inactive icosanoic acid layers were either electroactive surfactant molecules penetrating through these layers (which seems quite impossible) or traces of oxygen.[125] The authors estimated a first-order surface reaction rate constant, from peak separations, decreasing with increasing number of inactive layer of icosanoic acid. It seems that electroactivity, as shown by CV,[125] is at least an order of magnitude smaller relative to the amount of deposited materials. In some cases CV response was not higher than the background current.[125]

On reduction of viologen to its neutral state a gradual decrease of peak current was observed until the redox response completely disappeared. This indicates that the viologen surfactant forms a compact hydrophobic structure in the neutral state, so that reoxidation is blocked owing to hindered diffusion of counterions. For the Fc containing multilayer assembly **18a** no peaks of Fc oxidation were seen. A possible explanation of this fact may be found from a study of a viologen multilayer assembly as Fc containing multilayers are neutral. Facci [12] observed blocking of electron transfer from a Fc monolayer divided by one layer of Cd stearate spacer. A more complicated structure **29**/icosanoic acid/**27a** was then constructed.[125] This assembly showed anthraquinone reduction and a first viologen reduction. However, if the potential was held at -1.5 V to reduce the viologen layer to the neutral state, the compact viologen layer hindered the reduction of the inner anthraquinone layer. Electroactivity could be recovered at least partially by reoxidation of the film for 5 min at 0 V.[125]

Ueyama and co-workers [108] studied heterojunction multilayers constructed from amphiphilic flavin **26a** and Ru porphyrin **17**. The theoretical model previously developed for multilayers of one compound [126] was extended to the heterojunction of two monolayers.[108] CVs for flavin, Ru porphyrin and a heterojunction between them are shown in Fig. 18. The shape of the CVs show general agreement with simulated ones. The common features are as follows:

1. Peak potential in the first sweep is similar to Ru porphyrin and no peaks are observed near the flavin peak potential.

2. Anodic peak current in the first sweep is higher than in the subsequent one and charge consumed under the peak corresponds to the sum of the oxidation for flavin and porphyrin.

3. Charge in the second sweep corresponds only to porphyrin oxidation.

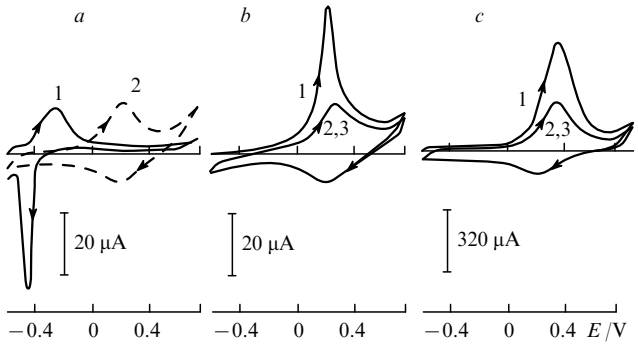


Figure 18. CVs for monolayers of **17**, **26a** (*a*) and *Z* heterolayer (3 layers of **17** + 1 layer of **26a**) (*b*, *c*) electrodes in 0.1 M $NaClO_4$.[108]
Potentials *vs.* Ag/AgCl; (*a*) $\upsilon = 0.05$ V s^{-1}, solid line — **26a**, dashed line — **17**; (*b*) $\upsilon = 0.05$ V s^{-1}; (*c*) $\upsilon = 0.8$ V s^{-1}; indicated numbers of cycle.

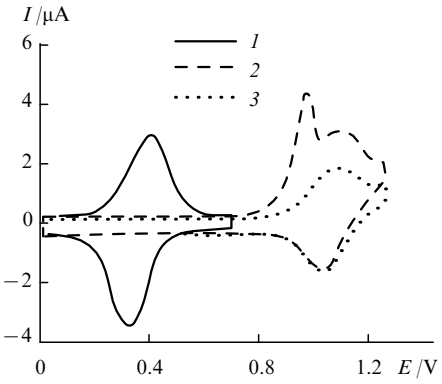
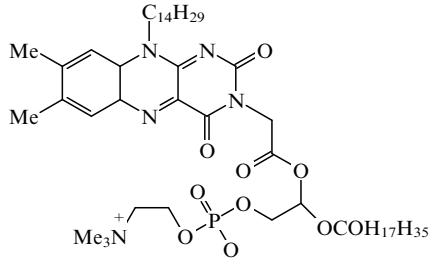


Figure 19. CVs of the LB films of co-polymers on ITO electrode.
Potentials *vs.* SCE, in 0.1 M $NaClO_4$, $\upsilon = 10$ mV s^{-1}; (*1*) 3 layers of copolymer **20b**; (*2*) 3 layers of copolymer **20b** + 2 layers of copolymer **31**, first cycle; (*3*) the same, second cycle.[94]

Theoretically this corresponds to the case where electron transfer in one direction from reduced flavin to oxidised porphyrin is much faster than in the opposite direction. Using simulated and experimental CV the electron transfer diffusion coefficient was estimated as 1.9×10^{-12} cm^2 s^{-1} for the favoured direction and 1.5×10^{-14} cm^2 s^{-1} for the opposite direction. Pseudo-first-order rate constants were estimated as 64 s^{-1} and $\leqslant 0.25$ s^{-1}, respectively.

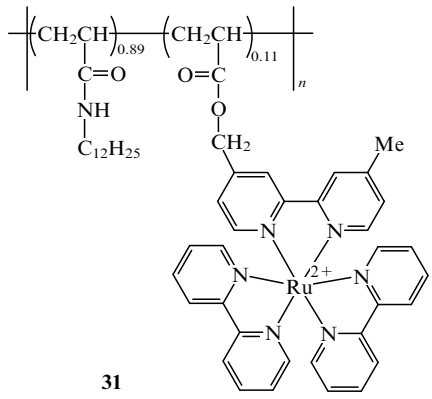
A bilayer of flavolipid **30** — cytochrome *c* showed similar behaviour.[127]



30

In this case electron transfer was much faster from flavolipid to cytochrome.

The electrochemical response of the LB heterolayer, consisting of 3 layers of Ru complex copolymer **31** [94] with an oxidation potential of 1 V *vs.* SCE and 2 layers of Fc co-polymer **20b** with an oxidation potential of 0.35 V *vs.* SCE, is shown in Fig. 19.

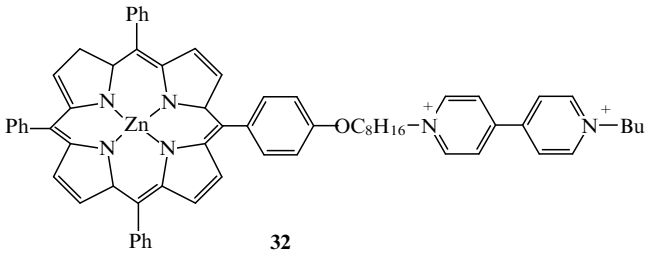


31

In the first cycle, no oxidation current was observed at the Fc redox potential of 0.35 V, because Fc could only be oxidised through the reduced inner layer of Ru complex co-polymer **31**. Fc oxidation appears as a sharp catalytic current at the potential, where Ru(II) is oxidised. Upon repeated cycling, only the redox peaks for the Ru(II)/Ru(III) couple are observed as ferricinium can not be reduced, and the charge is trapped in the outer Fc polymer layers.

It has been suggested earlier [128] that vectorial electron transfer might be obtained, if redox moieties can be placed in a potential gradient along the polymer chain. This idea has partly been substantiated [129, 130] using two differently substituted *p*-benzoquinone species or *p*-benzoquinone and bypyridyl species immobilised on Au surface by the SA technique. Recently, we suggested a novel approach to this idea by LB technique [91] using multiredox centre molecules **18f**–**h**. For this, redox molecules **18f**–**h** were incorporated into an LB array of fatty acid. Direct confirmations of uni-directional electron transfer were not obtained, but electrochemical response of LB arrays differed considerably from that of the randomly oriented cast films suggesting a certain degree of organisation in the LB films. Fig. 20 shows the difference in the CV response for the LB and cast films of the compound **18g**. It is notable that only one peak appears in the LB film of **18g** mixed with fatty acid. An orientation of **18g** with the Fc moiety closer to the electrode surface than the TTF group seems likely.[91] Compound **18f** contains two equivalent Fc redox centres. The experimental observation of the two peaks in CV for the LB films of **18f** mixed with fatty acids led to the conclusion of the ordering of **18f** molecules in an LB array, where two Fc moieties are at a different distance from the electrode surface, and consequently, in a different environment.[91] The peak splitting due to intermolecular interaction [30] was ruled out as the dilution of the LB films with fatty acid did not lead to the disappearance of double peaks.

Recently, LB films of amphiphilic diad molecule **32** have been studied.[131]



32

Such porphyrin diads are of interest for modelling of an electron transfer in biological systems. It was shown [131] that a magnetic field in any direction increases the anodic photocurrent at 0 V *vs.* Ag/AgCl and that electron transfer from the porphyrin onto the electrode is mediated by viologen.

Different bilayer assemblies, containing amphiphile **18d** were studied to understand the possibility of long-range electron transfer.[12] In contrast to the results of Fujihira *et al.*[124, 125] less defective

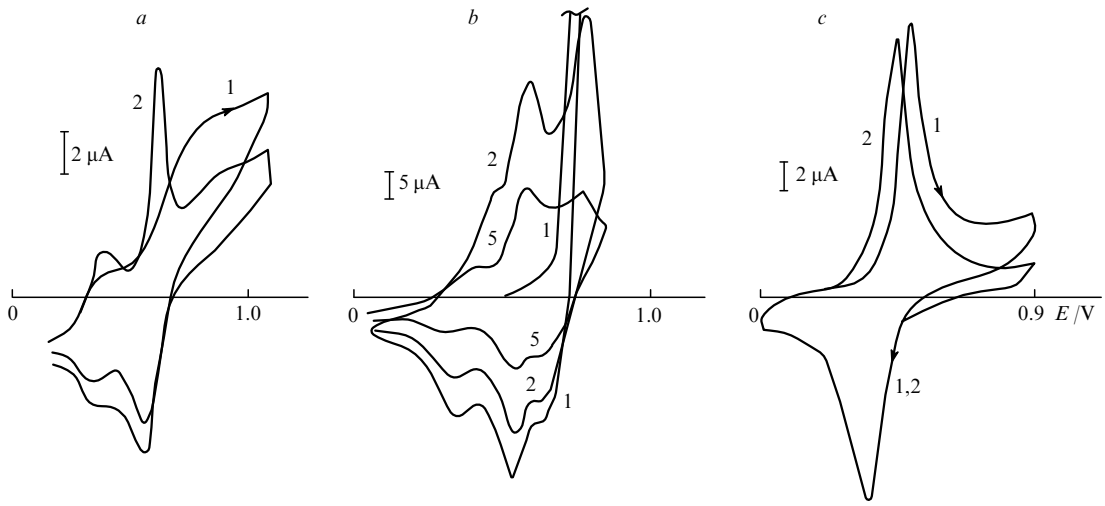


Figure 20. CVs of LB films of **18g** in 0.1 M $HClO_4$, υ = 200 mV s^{-1}.[91]
Potentials *vs.* Ag/AgCl; (*a*) cast film, (*b*) LB film of pure **18g**, (*c*) LB film of **18g** mixed with 20 mol.% of tricosanoic acid, cycle numbers indicated.

films of Cd stearate were employed in this work. When one monolayer of a spacer, cadmium stearate, was deposited between Au and the **18d** monolayer, electron transfer was completely blocked (a distance of about 2.5 nm from the electrode). For a bilayer of a mixture of **18d** and Cd stearate, where the electroactive head of the first layer was oriented away from the gold and adjacent to the electroactive head of the second layer, a CV response was observed, but electroactivity was not higher than 10% and an additional reduction peak appeared. If the second layer in such a bilayer consists only of cadmium stearate electroactivity increased to 60%, which signifies that only the inner layer is electroactive. However, in this case both anodic and cathodic peaks were split. Broadening and splitting of the peaks was explained accordingly.[30] Other possible explanations include different Fc environments or geometric arrangements.

In more recent reports [132, 133] the electron transfer at smaller distances was probed. A SA layer of alkanethiol on gold was employed as a spacer to determine the distance for the long range electron transfer. The advantage is that SA monolayers of alkanethiols on gold have smaller defect concentrations than LB films. The electrochemistry of SA monolayer with attached electroactive groups was investigated in several reports.[134, 135] However, in this case electron transfer could occur through a bond in the alkyl chain. In the case when the LB layer of the amphiphile **18e** [133] was deposited on the top of the SA spacer, only through-space electron tunnelling is possible. Preliminary studies with a monolayer of decanethiol [132] have shown that electrochemistry of **18e** was affected by the composition of the subphase, which was also used as the electrolyte for voltammetry, and the conditions of the film transfer. Two redox couples (0.22 and 0.4 V *vs.* SCE) were observed for pure **18e** on the 0.1 M $NaClO_4$ subphase. The diffusion of **18e** to defect sites in the SA monolayer was ruled out as thiol monolayer completely blocked electrochemical reaction of hexacyanoferrate(III) in solution. It was postulated that because of the mismatch between the molecular areas of the head and tail groups in **18e** a high degree of molecular packing was not possible [132] and the first redox couple is associated with the defects in the LB film, where free counterion transport is allowed. The redox couple at 0.4 V is associated with hindered counterion transport to the Fc sites in a more hydrophobic environment. This corresponds to the report of Creager and co-workers [113] on the increase of the Fc redox potential with increasing hydrophobicity of the environment. White's theoretical treatment [136] can also explain these results. In the case of **18e** diluted by fatty acid no electrochemical response of Fc was seen. The data of the surface pressure – molecular area isotherm and ellipsometry support the idea that the very densely packed bilayer structure with alkyl chains of fatty acid filling in the space in the tail groups of **18e** is formed. Such a compact hydrophobic environment completely blocks counterion permeation to the Fc redox sites and consequently electrochemical reaction is inhibited. On the other hand it was shown that **18e** does not form miscible layers on the $HClO_4$ subphase.[132] These films are not densely packed and electrochemical reaction could be observed. However, even on the $HClO_4$ subphase the electroactivity was not complete and it was necessary to transfer films in the expanded state (with molecular area of 3 nm^2 or even higher, using the horizontal transfer technique). Also if a floating layer was left on the subphase surface for more than 20 min ill-defined CVs were observed. So to ensure a sufficient number of defects in the film for facile counterion transport the floating layer was left on the subphase surface for not more than 5 min. The electron transfer kinetics for SA films of thiols with 10, 12, 14, 15 and 18 carbons were determined according to the Laviron theory.[103] The dependence of first-order rate constant on the length of alkyl chain in thiol was linear with a decay constant of -0.99 per methylene group. The comparison of these data [132] with those obtained for the Fc terminated thiols showed that at a distance of 1.4 nm from the electrode surface, electron transfer was almost two orders of magnitude slower. The largest distance was 2 nm (thiol $C_{18}H_{37}SH$)[133] and it is possible that a complete blocking of the electrochemical reaction was not achieved (compared with the previous results,[12] where this distance was about 2.5 nm).

Using a monolayer of Fc amphiphile **18b** on an interdigitated microarray electrode covered with a monolayer of SA film lateral diffusion in a monolayer has been studied [137] (the transfer on bare electrode was not satisfactory). If all arrays in the interdigitated electrode are connected together the usual surface wave response (Fig. 21 *a*), with some diffusion tailing due to electroactive material diffusing between the arrays were obtained. Generator – collector voltammograms, shown in the same Fig. 21 *b*, were obtained when one set of microelectrodes is made oxidising and another is made reducing with respect to the Fc formal potential. Using appropriate theory and steady state collector voltammogram the authors [137] calculated the lateral diffusion coefficient to be around $(2-4) \times 10^{-8}$ cm^2 s^{-1} depending on the surface pressure used for monolayer deposition. It should be mentioned that the diffusion coefficient decreased when the monolayer became more densely packed. These diffusion coefficients were an order of magnitude smaller than for Langmuir monolayers on a water surface. It was explained as a change of fluidity of Fc molecules and it seems it is only possible because the LB films were studied in a liquid expanded state. In the following work [138] the behaviour of these films was studied in more detail. Since the electrochemical

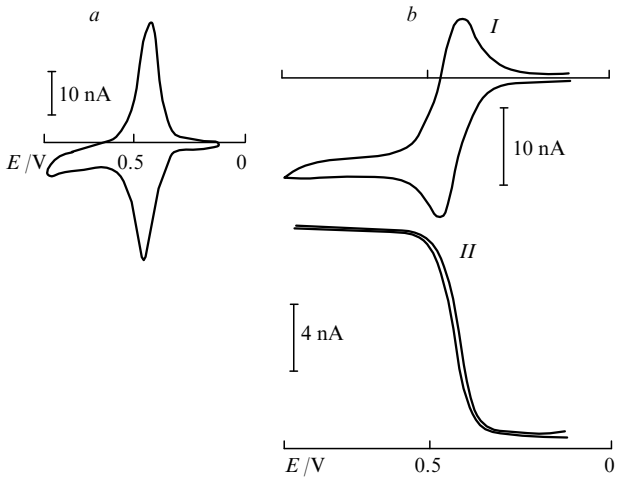


Figure 21. CV (*a*) and generator – collector voltammograms of the same system (*b*) of **18a** on an interdigitated microelectrode array.[137]
(*a*) Potentials *vs*. SCE, with both sets of electrodes driven at the common working electrode potential, 1 M aqueous $LiClO_4$, $\upsilon = 20$ mV s^{-1};
(*b*) generator electrode scanned from 0 to 0.9 V and the collector electrode held at +0.1 V, $\upsilon = 20$ mV s^{-1}, (*I*) generator current – voltage curve, (*II*) collector current recorded at +0.1 V and plotted *vs*. the potential of generator electrode.

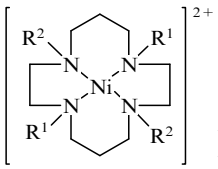
properties were studied using the usual planar electrodes, it implied that electrons are tunnelling over a distance of about 5 nm. This seems impossible in view of the results previously reported.[12] Therefore, it was proposed[138] that electron transfer occurs by lateral diffusion to defect sites in the LB film. However, it is not proven since the voltammetric response possesses the shape of the surface wave response.[138] The voltammetric response seems to be very sensitive to the time the monolayer was left on the subphase surface before compression, the compression rate, the surface pressure for the film transfer and the time monolayer was left after compression. For instance, the films transferred at the high pressure (where the staggering of molecules is supposed) postulated the shoulder on the oxidation peak.

The decrease of the electroactivity in the following cycles was explained by the gradual embedding of Fc head groups in the hydrophobic part of monolayer according to the theoretical treatment of White and co-workers.[136] The electroactive coverage also decreased with the increase of the compression rate and the increase of the time the monolayer was left on the subphase surface before compression. This was ascribed to the two-dimensional reorganisation in the monolayer leading to the burying of Fc head groups in the hydrophobic part of the monolayer. This fact was observed by the AFM (transition from a liquid expanded to a liquid condensed state).[138]

The deposition of ubiquinone **22** on a hydrophobic Au electrode covered with SA monolayer results in only partial electroactivity of ubiquinone. The electroactivity was assigned to the molecules of **22** residing on the defect sites of the SA monolayer.[104] This observation corresponds to the report,[12] where electrochemical reaction was not observed for Fc amphiphile **18d,** when monolayer was deposited onto the top of a passivating monolayer of Cd stearate. Ubiquinone incorporated in a phospholipid bilayer[104] LB film showed distinctive features of diffusion controlled behaviour. This was explained by the diffusion of ubiquinone through the lipid bilayer to the defect sites in the SA monolayer.

VII. Applications

Some of the electroactive LB films showed electrocatalytic properties. A Ni cyclam **33a** LB monolayer on a glassy carbon electrode was active in the electroreduction of CO_2 in aqueous electrolyte at pH 4.5.[139]



33a: $R^1 = R^2 = C_{16}H_{33}$;
33b: $R^1 = H$, $R^2 = C_{22}H_{45}$.

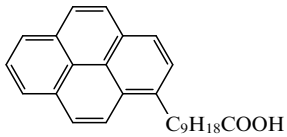
33a,b

Later,[140] these results were found to be irreproducible and LB films of monosubstituted Ni cyclam **33b** have been prepared. The 1 – 3 layer films exhibited complete electroactivity, surface wave response and electrocatalytic reduction of CO_2.

The films containing complexes **21a,b** [95] and bis-Fc[141] catalysed some electrochemical reactions. A monolayer containing a Ru complex **21c** electrocatalysed the oxidation of oxalate anions and generated chemiluminescence.[98]

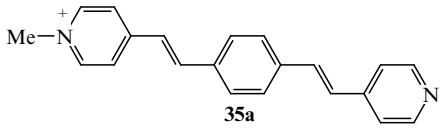
The LB technique was also used for the formation of thin electrocatalytic electrodes loaded with Pt particles.[142] These electrodes had similar activity to smooth Pt electrodes but with a much lower Pt loading level. Catalytic activity in such thin electrodes (~10 nm) cannot be limited by the mass transfer through the film. The electrodes were obtained by LB deposition of the amphiphilic compounds from a H_2PtCl_6 containing subphase with subsequent electrochemical reduction of the incorporated $PtCl_6^{2-}$ anion to Pt metal.

Different approaches for the fabrication of electrochemical diodes have already been discussed above. Using a biomimetic approach of electron transfer in biological systems to model the molecular electronic devices Ueyama and co-workers[108, 109, 126] fabricated multilayer LB assemblies with uni-directional electron transfer. This device can be considered as a molecular photodiode. Similar behaviour is observed in LB films of flavin with cytochrome *c* in solution,[109] LB heterolayers of flavolipid and cytochrome *c*,[127] Fc- and Ru-complex co-polymers,[94] and pyrene **34** and Fc **18a**.[143]

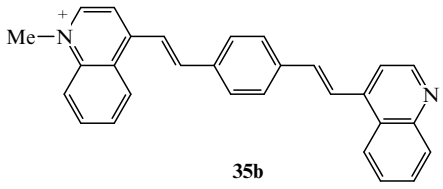


34

Recently[144, 145] LB films of conjugated molecules **35** were used for rectified electron transfer through a LB monolayer to solution redox species.



35a

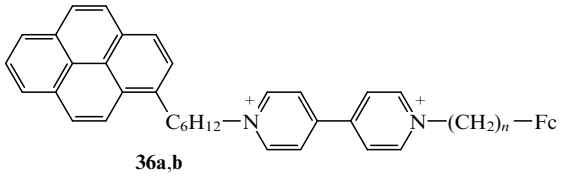


35b

The monolayer of **35a** demonstrated a CV response with high peak separation. This might indicate either slow electrochemical kinetics or a diffusion controlled electrochemical reaction. The electrochemical response of $[Fe(CN)_6]^{3-}$ in solution was blocked by a monolayer of compounds **35**. It should be emphasised that it is not easy to fabricate a passivating monolayer by the LB technique. For instance, Bilewicz and Majda[87] used a monolayer of a mixture of $C_{18}H_{37}SH$ and $C_{18}H_{37}OH$ to achieve good passivating properties on the surface of a gold electrode. This

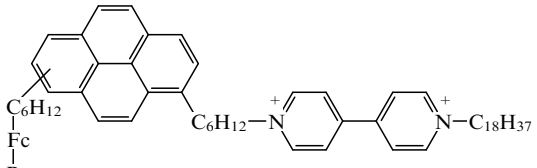
involves SA of thiol by covalent bonds and decreases, thus, the defect concentration in the monolayer. Therefore the passivating properties of the last monolayer were similar to those of monolayers of SA thiols. The hexacyanoferrate(II) reduction was mediated by the monolayer (an increased peak in the CV response) and the re-oxidation was blocked, which was also confirmed by chronocoulometry. It was suggested [144, 145] that these amphiphiles with long conjugation might serve as a 'molecular wire'. However, it remains unclear whether the electron transfer occurs 'through space' or 'through conjugated bonds' in the LB film. Mixed monolayers of the compounds **35** displayed an electrochemical response characteristic of the ultramicroelectrode array.[145]

Electrochemical photodiodes have been fabricated by a LB technique.[146] Using **29** as an electron acceptor (A), **34** as a sensitiser (S) and **18a** as an electron donor (D) and combining the monolayers into the multilayers as A–S–D or D–S–A, the vectorial current was registered.[135] The direction of the observed photocurrent was in good agreement with the energy profile of the film components. Subsequent studies have concentrated on the fabrication of similar devices using a monolayer of a molecule containing all components (intra-molecular photodiode).[146–151] Several triad molecules **36**–**38** were synthesised:



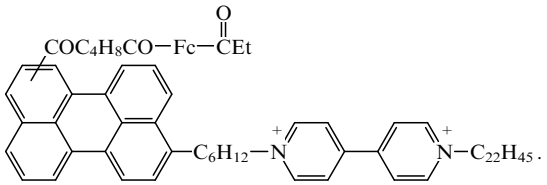
36a,**b**

n = 11 (**a**), 16 (**b**).



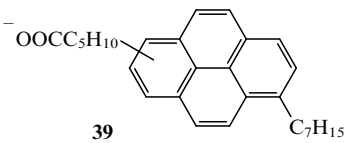
37a,**b**

R = H (**a**), Pr (**b**).



38

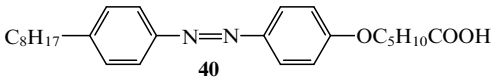
These triad molecules allow the creation of the structure A–S–D as only the viologen (A unit) is hydrophilic within the triad. Due to the two alkyl chains the compound **37b** allows the fabrication of a film with the opposite orientation D–S–A [151] on a hydrophilic support. The direction of the observed photocurrent in all cases considered was in good agreement with the energy diagram of the D, S and A moieties in the film. The highest photoelectric conversion efficiency was registered for photodiodes based on compound **37a**.[148–150] Also, in order to model the transfer of light energy in photosynthesis, monolayer films of a mixture of compounds **38** and **39** were fabricated.[149]



39

In this case compound **39** worked as a light harvesting antenna and the energy transfer from the pyrene moiety of **39** occurred onto the perylene moiety of **38**. The photocurrent was generated after multistep electron transfer through the monolayer.

Japanese group [152–155] proposed an interesting photoelectrochemical 'one-way' process based on the difference between the electrochemical reductions of *trans*- and *cis*-isomers of an azo-compound **40** in LB films.



40

The *cis*-isomer of surfactant azobenzene was much easier to reduce (difference in peak potentials about 400–600 mV depending on pH) than the *trans*-isomer (Fig. 22). However, oxidation of hydrazobenzene yielded only the *trans*-isomer of azobenzene. The *trans*-isomer can be transformed to *cis*-isomer by illumination. This 'one-way' process can be used for high-density information storage either by 'optical writing' (using laser beam) or 'electrochemical writing' (counter electrode probe positioned as in a scanning tunnelling microscope).[152, 153] Information can be read spectroscopically as well. It has been shown later [156] that to further improve storage density the information can be written and read using linearly polarised UV light. Recently, this material has been deposited by the LB method on Au substrates modified with SA thiol monolayers.[157] The electron transfer distance was changed by varying the length of the thiol molecule and the orientation of molecule **40**. The orientation has been changed by choosing the thiol terminal group. When **40** was oriented with the octyl chain adjacent to the hydrophobic end of the alkyl thiol, the total length of 26 carbon atoms completely blocked electron transfer from the azobenzene moiety (Fig. 23). This corresponds to the results of reports.[12, 133] In the case of the hydrophobic end of **40** adjacent to the hydrophilic end of $HOCH_2CH_2SH$ the CV response was not observed. This was explained [157] by the change of the azobenzene electrochemistry from irreversible to reversible. The reduction potential of *cis*-azobenzene becomes more anodic than the reoxidation potential of hydrazobenzene. Owing to this inversion of the redox potentials the reduction of *cis*-azobenzene cannot be observed. This hypothesis was supported by photoelectrochemical studies.[157]

Another azo-derivative **41a** also demonstrated well resolved electrochemical properties. It may be used as a memory material through electrochemical means.[158]

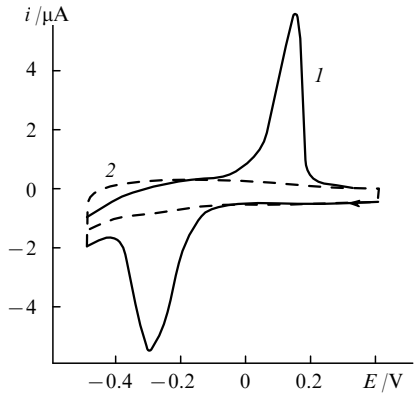


Figure 22. CV curves of monolayer film of compound **40** on an SnO_2 electrode, υ = 20 mV s^{-1}.[153]
Potentials *vs.* Ag/AgCl; (*1*) *trans*, (*2*) *cis*.

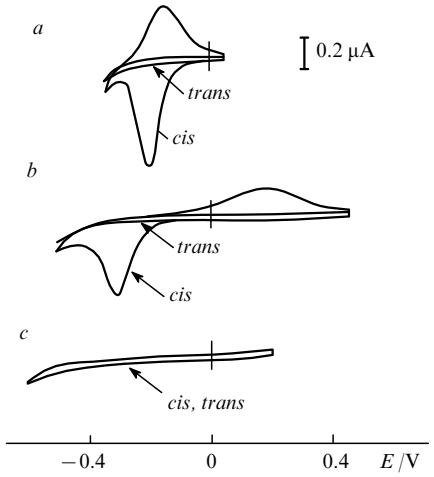
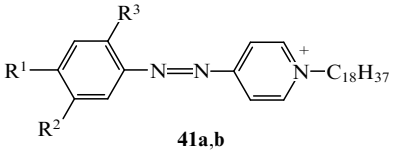


Figure 23. CVs of a monolayer film of **40** transferred onto an SA monolayer of thiol, 0.1 M aqueous $NaClO_4$.[157]
Potentials *vs.* Ag/AgCl, $\upsilon = 20$ mV s^{-1}; (*a*) SA layer of ethanethiol (total length for electron transfer 10 carbon atoms); (*b*) SA layer of octanethiol (total length for electron transfer 16 carbon atoms); (*c*) SA layer of octadecanethiol (total length for electron transfer 26 carbon atoms).



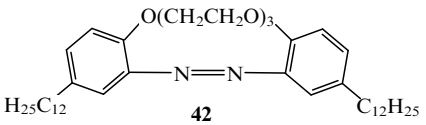
41a,**b**

41a: $R^1 = H$, $R^2 = Me$, $R^3 = OH$;
41b: $R^1 = Me_2N$, $R^2 = R^3 = H$.

Electrochemical properties of the LB films depended on the pH of the subphase and the following illumination of the film. The films transferred from the subphase at pH 3 exist in a *cis*-enol form and undergo the transformation into a *trans*-ketone form upon the illumination with 450 nm light. The last form exists in the LB film transferred from the subphase at pH 6.5. The same group [159] studied photoelectrochemical properties of the LB films of the other azo-derivative **41b**. The occurrence of the photocurrent was attributed to the tautomeric transformation of **41b** upon illumination. In CV this resulted in some change of the peak potentials and decrease of peak separation. It was suggested that these films may be useful for photogenerated information storage and for the fabrication of devices for photoelectric conversion.

A photoalarm based on a photocell using bacteriorhodopsin LB film deposited onto an ITO electrode has been constructed.[160]

Amphiphilic azobenzenecrown derivatives [161] were designed for the molecular recognition of cations. Monolayers of compound **42** were built up on Au or thin layer Hg electrodes.



42

While the CV response of the LB film on a gold electrode was unstable, the thin layer Hg electrode modified by the LB monolayer showed perfectly stable surface wave response. The peak separation was increased when the Li^+ cations in the electrolyte solution (peak separation 20 mV) were substituted by Na^+ or K^+ cations (80 and 400 mV respectively). This was attributed to molecular recognition in the LB monolayer due to complexation with the crown ether. Simultaneously the formal potential did not change significantly. We were the first to register electrochemical molecular recognition on the addition of alkali metal cations to films of polythiophene **12** deposited by the LB technique.† However, the electrochemical behaviour of these films did not show any advantages compared with the cast films of the same polymer.

LB films of polyaniline **8**, obtained as described above,[54, 55] were loaded with glucose oxidase during LB film transfer.[162] These electrodes were used as an amperometric biosensor for glucose at the concentration level of 10^{-2} M.

The electrochemical analysis of trace quantities of water-insoluble electroactive compounds by on-trough voltammetry was described.[163] A specialised microtrough was constructed and water-insoluble compounds were transferred onto ITO or graphite electrodes by the horizontal technique at the low surface pressure. The deposited films were analysed by CV in the same trough. The minimisation of aggregation and the possibility to avoid water-soluble impurities were suggested as potential advantages over the casting of films onto the electrode surface. The application of this technique to the compound **21c** demonstrated linear dependence of CV peak area on the quantity of compound and the possibility of analysing this compound down to 2 pmol. The possibility of the analysis of other non-amphiphilic water insoluble redox active compounds was also demonstrated.

Thus, modified electrodes fabricated by the LB technique can be used in electrocatalysis and electroanalysis. Molecular electronic devices based on electrochemical and photoelectrochemical principles may be constructed.

VIII. Conclusions

LB films exhibit slow redox reactions if they are well ordered and densely packed. This results in a change of mechanism from the surface reaction model to diffusion controlled behaviour. In this case diffusion of the ions through LB film is the limiting process. Hindered voltammetry for multilayer assemblies is usually observed in this case and only the first inner monolayer may be electroactive. When LB films are not as well ordered or the molecule is large, which enables sufficient empty space between the hydrophobic chains, surface reaction response can be obtained. Due to the strong repulsive interaction in highly loaded films this response usually deviates from an ideal surface wave, leading to peak broadening, peak separation, peak doubling and additional peaks. Peak doubling, explained theoretically by sufficiently negative repulsive interaction, can be understood in simple chemical terms as dimerisation of molecules in different redox states in LB films. It is an especially useful explanation when the molecules are known to have strong interaction in crystals and solutions, leading to *p*-dimerisation and stack formation. Such kinds of molecules are often used for conducting charge-transfer complexes and radical-ion salts.

From the theoretical point of view the surface reaction model has been extended for LB monolayer, multilayer and heterolayer films and attempts to calculate *e*-transfer kinetic have been made. First-order *e*-transfer rate constant of $10^0 - 10^2$ s^{-1} and pseudo-first-order rate constant for interlayer transfer of 10^2 s^{-1} have been obtained. An electron diffusion coefficient of $10^{-11} - 10^{-12}$ cm^2 s^{-1} and lateral diffusion coefficients in liquid expended state of 10^{-8} cm^2 s^{-1} have been obtained. Vectorial electron transfer can be achieved in LB films with electron diffusion coefficients two orders of magnitude higher in the appropriate direction.

Electron transfer distance dependence has been probed using LB films electrochemistry. It can be concluded that electron tunnelling is possible over a distance of about 2 – 2.5 nm.

Electrochemical techniques can be used for producing electroconducting LB films of charge-transfer materials and LB films of conducting polymers. The electrochemical doping can be realised either on the trough during LB film transfer or as an electrochemical reaction after film deposition (including electropolymerisation in the LB films). Highly ordered conducting films can be

† L M Goldenberg, M Leclerc, M C.Petty, unpublished results.

obtained. Different counter-ions can be introduced into the films by this technique. However, further investigations are necessary to understand the dependence of the conductivity and other film properties on the structure of the counter-ion. The films with conductivity as high as 50 S cm^{-1} and a partially metallic temperature dependence have been obtained.

Improvement of film quality for electrochromic devices has been achieved. Interesting molecular electronic devices, especially based on a one-way photoelectrochemical process and vectorial electron transfer, can fabricated using LB films. LB films have found an application in electrocatalysis.

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