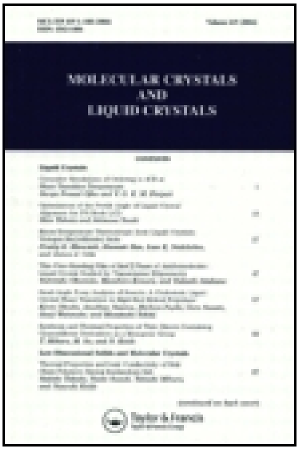

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Molecular Organization of Mixed Monolayers $(C_{18}S)_2$ Dithiolium-TCNQ : Dodecyl-TCNQ at the Air-Water Interface

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MOLECULAR ORGANIZATION OF MIXED MONOLAYERS $(C_{18}S)_2$ DITHIOLIUM-TCNQ : DODECYL-TCNQ AT THE AIR-WATER INTERFACE

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Abstract : Following the homodoping strategy, which consists of mixing two amphiphilic derivatives of the same electroactive compound, one in the neutral state whereas the other is ionic, we have carefully investigated the mixed monolayers by in situ experiments. Using surface pressure isotherms together with surface potential technique but also visible-UV and IR spectroscopies we have characterized the molecular organization. We have shown for the first time that for a given range of mixtures mixed valence clusters likely to be TCNQ-type dimers are formed at the air-water interface.

INTRODUCTION

The homodoping process is a new approach to obtain a conducting film in which a mixed valence system thanks to a controlled ratio between ionic and neutral compounds[1]. The primary question which arises regarding this new strategy concerns the formation of the mixed valence clusters in a layered system. These clusters are the necessary molecular blocks for obtaining conducting mono layers and multilayers. It is therefore of a paramount importance to obtain an understanding of the factors which control the formation of this mixed valence state. The basic point is where the molecular association occurs that is whether in the spreading solution, during formation of the Langmuir film, or during transfer of the monolayer onto a substrate. Therefore to clarify this matter we have carried out a series of in situ experiments at the air-water interface starting with an ionic semi-amphiphilic TCNQ (tetracyanoquinodimethane) salt that we have synthesized and investigated previously[2].

EXPERIMENTAL SYSTEM

Monolayer studies have been performed on the 3 methylthio, 4-5 bis(octadecylthio) 1-2 dithiolium TCNQ (1:1) anion-radical salt (abbreviated as $(C_{18}S)_2$ dithiolium-TCNQ) mixed with the neutral octadecyl TCNQ ($C_{18}TCNQ$). We have prepared the following solutions of these two compounds : $[(C_{18}S)_2$ dithiolium-TCNQ$)]_1$: $(C_{18}TCNQ)_n$ with n = 0, 0.5, 1, 2 and 3 with variations in n allowing us to change in principle the density of electronic charges by volume or surface unit.

In a preliminary experiment the stability of the spreading solutions was monitored with UV spectroscopy ; otherwise the formation of a TCNQ by-product is observed labelled DCTC which is characterized by an absorption band at 480 nm[3]. In addition, we have observed that bulk solutions do not exhibit any of the absorption bands in the UV visible range characteristic of a complexation process[4].

RESULTS

Surface pressure and surface potential isotherms

The surface pressure (π-A) and surface potential (ΔV-A) area isotherms obtained at 20°C±1°C from spreading solutions of the TCNQ compounds with different stoichiometries (1:n) have been examined. The (π-A) isotherms appear to be independent of the compression speed and quite reversible without any apparent plateau for the surface pressure excepted for the (1:3) mixture (figure 1). It appears therefore that these films are mixed homogeneous monolayers when the chemical composition corresponds to n < 3.

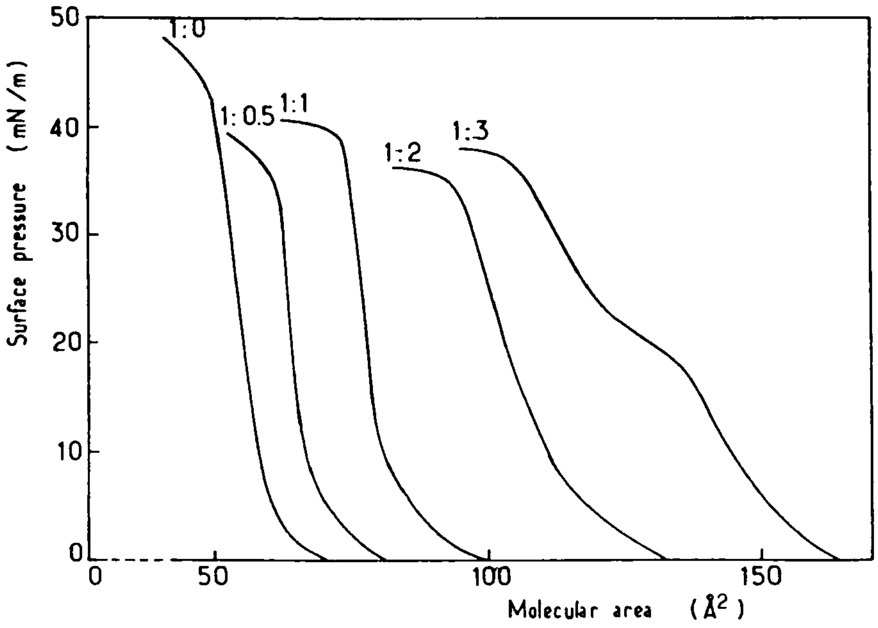

FIGURE 1 : Compression isotherms π(A) obtained at 20°C with a pure water as subphase for different molecular associations of $[(C_{18}S)_2$ dithiolium-TCNQ$]_1$: $(C_{18}TCNQ)_n$ with n = 0, 0.5, 1, 2 and 3

For a constant pressure π = 25 mN/m a molecular area increase of about 24 ± 2 $Å^2$ is observed for the addition of every C_{18}TCNQ, this increase in molecular area is associated with a slight decrease of the collapse pressure. This proves that thermodynamically stable monolayers are realized without multilayer formation.

We have also carried out surface potential measurements using an ionizing Am^{241} electrode situated just above the water surface[5]. The same experiment has been already carried out on pure $(C_{18}S)_2$ TCNQ salt[6] (i.e. with n = 0) ; on the mixed monolayers we observe a similar result for the surface potential area isotherms (see figure 2 for n = 2). A surface potential jump is observed at the gas-liquid phase transition followed by a plateau and a constant increase in potential until the collapse point corresponding to an area of about 100 $Å^2$. It is instructive to evaluate the normal dipole density $\mu_\perp$ associated with ΔV which increases with the surface pressure and reaches a maximum value at the collapse point with about the same order of magnitude as observed for the pure ionic salt (see insert of figure 2).

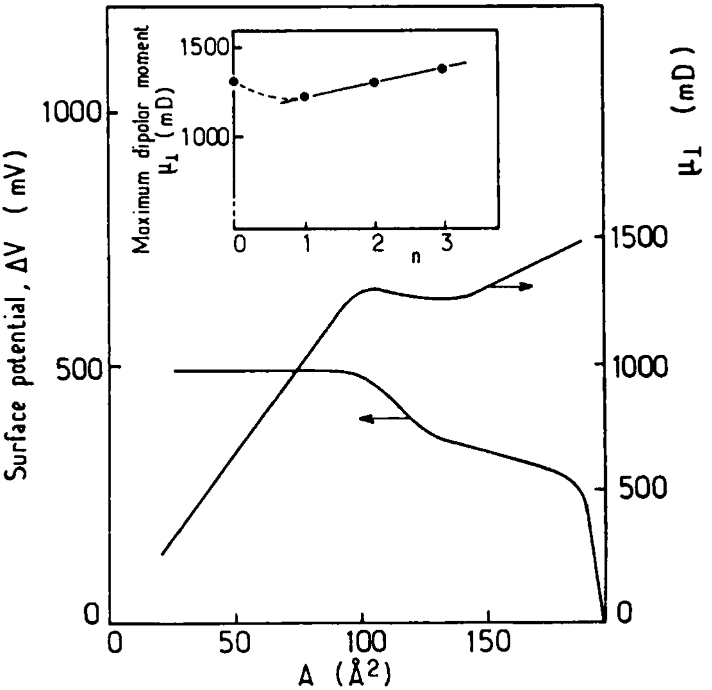

FIGURE 2 : Surface potential (ΔV) molecular area (A) and normal dipole moment ($\mu_\perp$)-molecular area isotherms for the molecular association $[(C_{18}S)_2$ dithiolium-TCNQ$]_1$: $(C_{18}TCNQ)_2$

Since it is not a pure additive effect for the first addition of C_{18} TCNQ molecules we conclude that a molecular reorganization occurs at the air-water interface. This point has been confirmed by transfer onto a substrate which is of a Z-type as for the pristine salt, due to the presence of strong dipole moments in these materials[6].

In situ optical properties

Monolayers have been studied in situ using UV visible and infrared absorption techniques. In the visible-UV range, a home-built UV visible spectrophotometer has been employed to observe strong absorption bands at various surface pressures. We have successively recorded the absorption spectra of pure C_{18}TCNQ monolayer followed by two homodoped mixtures with n = 1 and 2 for different surface pressures (figure 3).

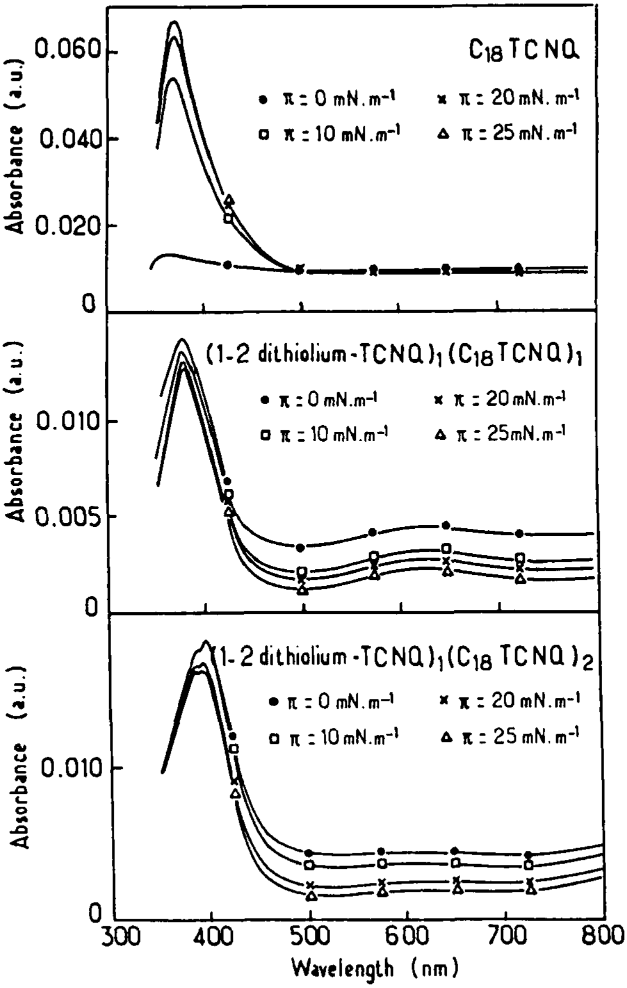

FIGURE 3 : Visible UV surface absorption spectroscopic curves obtained on pure C_{18} TCNQ monolayer and with two different molecular associations at different surface pressures

We routinely observe a strong band at 390 nm which is essentially due to an intramolecular optical transition of C_{18}TCNQ and (C_{18}S) dithiolium and also a new band occurring around 640 nm accompanied with a weaker intensity at 390 nm for the partially ionic monolayers. According to Boyd and Phillips[4] the new electronic transition can be attributed to the presence of a completely ionized TCNQ dimer. However an other possibility has been proposed by Tanaka et coll [7]. These authors have considered that a charge transfer from the highest HOMO to the lowest excited triplet state can occur at 625 nm for a $(\mathrm{TCNQ})_2^{-}$. It appears that at any of the surface pressure we have investigated, we are in presence of TCNQ aggregates as for example dimers. At this point nevertheless we cannot unequivocally define the degree of ionicity of the aggregates.

However, using a special in situ infrared technique, the polarization modulation FTIR spectroscopy on surfaces[8] we have been able to obtain more detailed informations. Currently, this differential technique allows us to eliminate both the absorption signals due to air and the water subphase between 3400 and 2000 cm^{-1}. The in-situ IR spectra which have been obtained are presented in figure 4 for an isostoichiometric monolayer (n = 2) at various surface pressures.

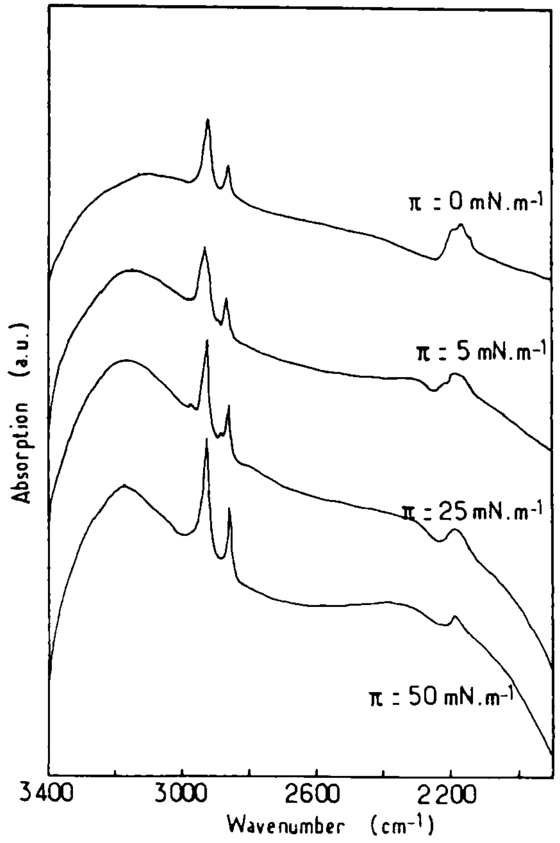

FIGURE 4 : IR surface absorption spectra obtained on the monolayer of $[(C_{18}S)_2$ dithiolium-TCNQ$]_1$: $(C_{18}TCNQ)_2$ at different surface pressures.

In these absorption spectra we observe two new fundamental features :

- Two groups of peaks around 2200 cm^{-1} (at 2181 and 2159 cm^{-1}) and around 2900 cm^{-1} (at 2954, 2918, 2854 cm^{-1}) which are attributed respectively to $C \equiv N$ stretching modes of $TCNQ^{-}$ and the stretching modes of alkyl chains. These experiments indicates that the plane of TCNQ molecules is approximatively orthogonal to the water surface.

- A broad band located around 3200 cm^{-1} with the progressive appearance, when the pressure increase of an absorption shoulder in the vicinity of 2600 cm^{-1}. One of these bands can be assigned to a mixed valence charge transfer band[7] probably the second one because the band at 3200 cm^{-1} could be attributed to water molecules fixed inside the monolayer.

Nevertheless, the most fundamental result is the in-situ detection of a mixed valence C.T. bands with supposed vibronic modes. This result leads us to make the proposal that there is the formation of multimers at the air-water interface.

CONCLUSION

By applying the homodoping strategy we have shown for the first time that mixed valence clusters which are in principle TCNQ type dimers[9] are formed on the floating film. This type of stable monolayer has been obtained for a mixture with $1 \leq n < 3$. Their formation is the necessary initial step for the organization of supramolecular blocks leading to the development of an ultra-thin organized molecular conducting film.

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