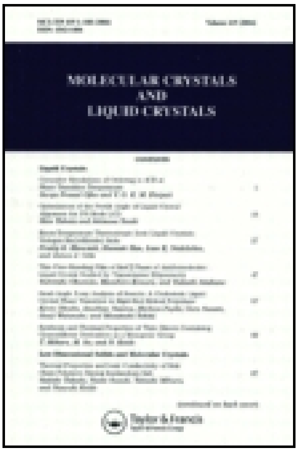

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

General Trends for Obtaining Conducting TCNQ Langmuir-Blodgett Films

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Version of record first published: 22 Sep 2006.

To cite this article: M. Vandevyver, A. Ruaudel-teixier, S. Palacin, J.-P. Bourgoin, A. Barraud, R. Bozio, M. Meneghetti & C. Pecile (1990): General Trends for Obtaining Conducting TCNQ Langmuir-Blodgett Films, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 187:1, 327-334

To link to this article: http://dx.doi.org/10.1080/00268949008036058

Mol. Cryst. Liq. Cryst., 1990, vol. 187, pp. 327–334
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Printed in the United States of America

GENERAL TRENDS FOR OBTAINING CONDUCTING TCNQ LANGMUIR-BLODGETT FILMS

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Abstract Some structure-property relationships for conducting LB films based on semiamphiphilic TCNQ salts with closed shell cations are worked out. Formation of a 3-D ordered structure containing $(TCNQ^-)_2$ dimers on the water subphase followed by a remarkable structural rearrangement of deposited films upon iodination is found to be a necessary requirement for conductivity. Among the studied salts, these processes occur only for those with similar cations.

INTRODUCTION

The Langmuir–Blodgett (LB) method has been proved to be a very convenient one for building up conducting films of molecular thickness. The first successful example of a conducting LB film containing tetracyanoquinodimethane (TCNQ) was reported by Ruaudel–Teixier et al..[1] These authors started from a semiamphiphilic TCNQ ionic salt, namely N–docosyl–pyridinium$^+$ TCNQ$^-$ (NDP–TCNQ) and obtained a conducting film in two successive steps: first, a non–conducting (pristine) film of NDP–TCNQ was built; then, upon controlled exposure to iodine vapor, the TCNQ species was partially oxidized while the film acquired an electrical d.c. conductivity of ca. 0.1 S cm^{-1} parallel to the support.

Based on general criteria for conductivity in organic charge transfer (CT) solids,[2] a film directly obtained from an ionic salt is expected to be non conducting as indeed found for the pristine NDP–TCNQ film. On the same grounds, the finding that partial oxidation of TCNQ results in a mixed valence conducting state is also expected. However, two totally unpredicted features were revealed by extensive structural investigations of the films.[3,4] The pristine films are made up of superimposed single crystal platelets (more than 10 μm wide) remarkably homogeneous in thickness (about 50 Å), just corresponding to a bilayer of NDP–TCNQ. It has been clearly shown that such platelets grow directly on the water subphase during the compression of the film and this has been related to the existence of a plateau on the isothermal compression curve.[5] The second unexpected finding is that the oxidation process triggers a huge molecular reorganization of the TCNQ species.[3,4]

The most significant information concerning the structural properties of the pristine films comes from linear dichroism as well as from ESR experiments.[3] They show unambiguously that the $TCNQ^-$ radicals are in the dimeric $(TCNQ^-)_2$ form with their molecular planes parallel to the plane of the substrate. On the other hand, in the conducting films the TCNQ molecules form stacks along which the electronic conduction occurs and, according to optical and low-angle X-ray scattering data,[4] their molecular planes stand on edge with the long molecular axis perpendicular to the substrate. In summary, besides an expected oxidation process, exposure to iodine induces a remarkable molecular reorganization, notably a tilting of the TCNQ molecular planes from almost parallel to the substrate in the pristine films to perpendicular to it in the conducting ones. LB films which exhibit basically the same behavior have been obtained with TCNQ salts of octadecyl-dimethyl-sulfonium ($ODMS^+$), octadecyl-methyl-ethyl-sulfonium ($OMES^+$), and octadecyl-trimethyl-phosphonium ($OTMP^+$).[6]

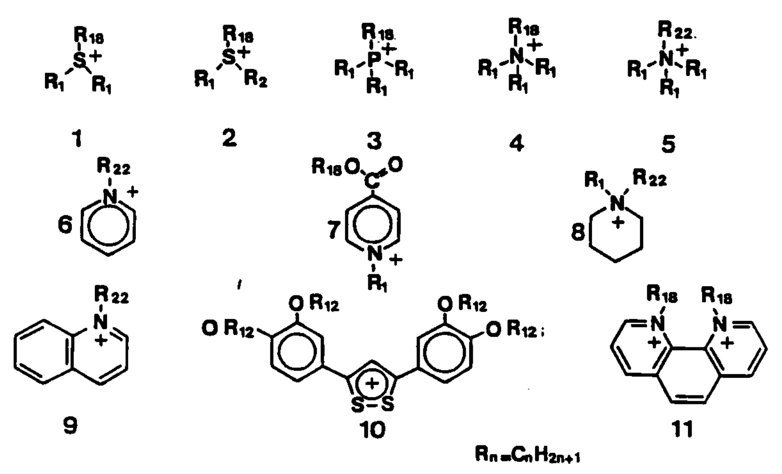
This paper is devoted to a first attempt at clarifying the roles of the formation of $(TCNQ^-)_2$ dimers, and the related crystallization on the water subphase and of the molecular rearrangement upon iodine treatment, through a systematic analysis of related materials. In particular, the relevance and possible interconnection of the two unpredicted features mentioned above will be investigated for LB films containing semiamphiphilic TCNQ salts with cations (see Table I) having polar head groups of different molecular size and shape and either containing a conjugated π-electron system or not. In assessing the electrical conductivity of the films we make use of the correlation between frequency location of the CT absorption peak in the infrared spectra and d.c. conductivity, first demonstrated by Jacobsen et al.[7] and subsequently shown to be applicable to conducting LB films.[3,8] This procedure allows one to get an estimate of the electrical conductivity even for those cases in which macroscopic inhomogeinities, such as grain boundaries, make direct measurement of the d.c. conductivity unreliable. In so doing we put our emphasis on defining at the microscopic level certain structural requirements which must be fulfilled to obtain electrical conductivity. For some cases, dicussed in the following sections, improvements on the macroscopic structural properties must be worked out to enhance the d.c. transport behavior.

EXPERIMENTAL

We have synthesized several new salts with different size and aromaticity for the head group of the cation. The complete set of cations under consideration in the present work is given in Table I. Results for the LB films made up with the TCNQ salts of cations **1** – **3** (and to a lesser extent **4**) and of **10** have already been reported.[6] New results for the salts with cations **4** – **9** and **11** will be shortly reviewed here. Details of the corresponding syntheses will be given elsewhere.

The Langmuir trough is a commercial one (LB 105 ATEMETA) made of special non porous PTFE. The operating process for the cleaning and the

TABLE I Cations[a] of semiamphiphilic TCNQ salts used for preparing LB films.



[a] **1**: Octadecyl–dimethyl–sulfonium$^+$ (ODMS$^+$); **2**: Octadecyl–methyl–ethyl–sulfonium$^+$ (OMES$^+$); **3**: Octadecyl–trimethyl–phosphonium$^+$ (OTMP$^+$); **4**: Octadecyl–trimethyl–ammonium$^+$; **5**: N–docosyl–trimethyl–ammonium$^+$; **6**: N–docosyl–pyridinium$^+$ (NDP$^+$); **7**: N–methyl, 4–octadecyl–carboxylate–pyridinium$^+$; **8**: N–docosyl–piperidinium$^+$; **9**: N–docosyl–quinolinium$^+$; **10**: 3,5–di(phenyl–3,4,di–dodecylether)–dithiolium$^+$; **11**: Dioctadecyl–phenanthrolinium^{++}.

precoating of substrates together with the conditions for film deposition are given in Ref. 3. The transfer is generally performed at surface pressures ranging between 25 and 35 mN/m. The step by step iodination method was performed according to Ref. 9. Most of the structural information on the films comes from linear dichroism spectroscopy in the infrared.[3]

RESULTS

The isothermal compression curves for the TCNQ salts with cations **5** to **11** are given in Fig. 1. Floating films obtained from **1** to **4** are unstable even at very low surface pressure. Considerable improvement was obtained by mixing the salts with octadecylurea.[6] The corresponding compression curves have already been reported (Fig. 2 of Ref. 6) and are not included in Fig. 1.

Owing to their better mechanical stability, films of all the other salts can be deposited without any mixing with host amphiphilic molecules. The parts of the curves drawn as full lines in Fig. 1 correspond to well defined highly stable states that allow a well controlled transfer onto a solid substrate. Very homogeneous films from salts with cations **10**[10] and **11** are obtained in this way. They are optically clear without diffusing light defects even for several hundreds superimposed monolayers. On the contrary, for states corresponding to dashed lines (curves 5 to 9 in Fig. 1) the stability is weaker and a good control over the deposition of thick multilayers cannot be obtained. The resulting films are often slightly light diffusing due to macroscopic defects or crystalline mosaic–like

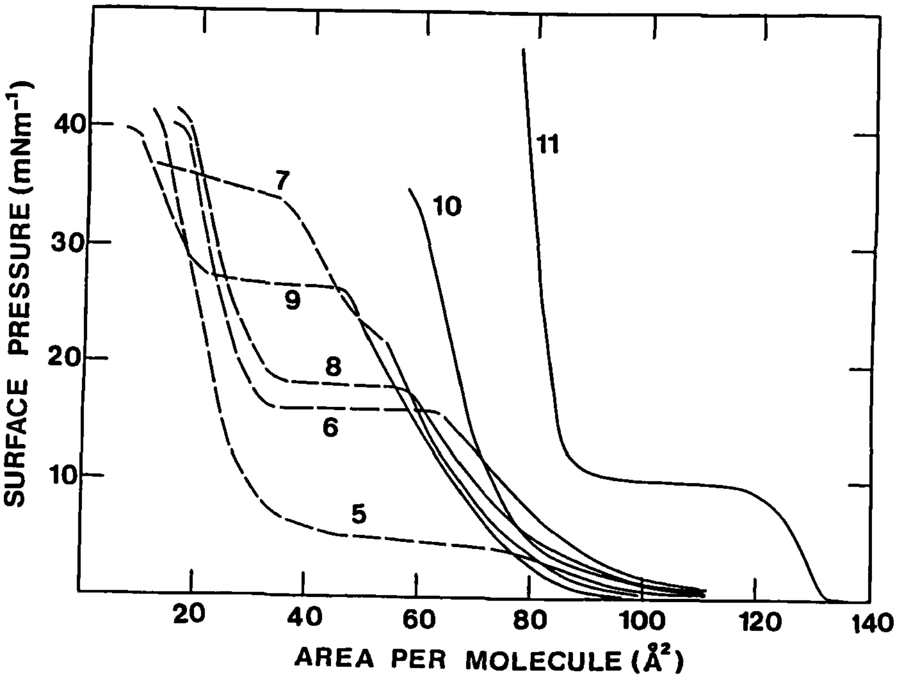


FIGURE 1 Isothermal compression curve for TCNQ salts numbered according to Table I.

structures.

Structural information on the pristine films has been gained through the analysis of their spectroscopic data and in particular, dichroic behavior in the infrared. In the second column of Table II the studied materials are divided into two groups depending on whether their structure is characterized by the presence of $(TCNQ^-)_2$ dimers arranged with their molecular planes almost parallel to the polar planes of the films (i.e. to the substrate) or not. The fact that the films obtained from the salts **1** through **7** exhibit the above structural feature appears to be related to the three-dimensional crystallization of the films at the air/water interface. On the one hand,this phenomenon reduces the stability of the floating films but, on the other hand, it induces a high degree of microscopic order in the transferred films. In fact, optical microscopy shows that the deposited films are composed of very thin needle shaped crystallites or platelets. For the LB films of salts **10**[10] and **11** the dichroic data show that the $TCNQ^-$ anions are close to being on edge with their molecular planes perpendicular to the substrate. In the films of **11** $(TCNQ^-)_2$ dimers are the prevailing species whereas those of **10** contain monomers and dimers in roughly equal amounts.[10] Films of **8** and **9** are characterized by a high degree of disorder. In the latter material this appears to be related to the formation of macroscopic aggregates on the water subphase.

Both d.c. conductivity and infrared spectra are measured after exposure of the films to iodine vapors. The results are summarized in the third and fourth column of Table II respectively. When a conducting mixed-valence

TABLE II Summary of some properties of the studied LB films.

Cation	Flat dimers	IR Conductivity	d.c. Conductivity[a]
1	Yes	Yes	No
2	Yes	Yes	No
3	Yes	Yes	No
4	Yes	Yes	No
5	Yes	Yes	No
6	Yes	Yes	Yes
7	Yes	Yes	Yes
8	No	No	No
9	No	No	No
10	No	No	No
11	No	No	No

[a] For the LB films with cations **1**, **2**, **3**, **4**, and **5** "No" means that a reproducible significant conductivity has not been obtained.

state is attained, upon iodine oxidation of the films, a low lying absorption attributed to a so called A-type CT transition appears in the infrared spectra. In crystalline materials the frequency location of this transition exhibits a semiquantitative correlation with the d.c. conductivity measured at room temperature.[7] This simply indicates that the microscopic (intrinsic) activation energy for conductivity is related to the optical gap. Such a relation is expected and found to hold also for partially ordered materials such as the conducting films.[8] In Table II the films are considered to display infrared conductivity if the A-type CT transition lies below 0.5 eV ($4000\ \mathrm{cm}^{-1}$). Having placed our emphasis on the microscopic structural and electronic requirements for conductivity, the measured d.c. conductivity appears not to be a sensible criterion because of the possible additional resistivity due to grain boundaries and other disorder induced barriers.

Upon iodination the films of **4** and **5** display basically the same behavior as those of **1**, **2**, and **3**[6] the changes in their UV-visible spectra strongly suggest the formation of a chemically stable and,likely,stoichiometric ternary conducting compound involving a rather sharp minimum in free energy of the system. Furthermore, all these materials,as well as the films of **7**,display a remarkable molecular reorientation upon iodination similar to that reported in detail for films of **6**.[3] By contrast, for films of **9**, **10**, and **11**, the $TCNQ^-$ species is progressively oxidized to $TCNQ^\circ$ without the emergence of any conducting phase at any step of the oxidation process.

DISCUSSION

The most important empirical notion that the data reported in this paper and summarized in Table II convey is that in the LB films we have investigated the conducting behavior results from a series of phenomena which are strongly correlated with each other. (i) The films of salts **1** to **7** that exhibit infrared conductivity are deposited from floating films that are mechanically unstable owing to the formation of microcrystals at the air/water interface. (ii) Spectroscopic and linear dichroism data show that in these films the polar planes contain $(TCNQ^-)_2$ dimers lying with their molecular planes parallel to the substrate. (iii) Finally, the iodination process induces a remarkable structural rearrangement, notably a large tilting of the TCNQ molecular planes which become almost perpendicular to the substrate. Thus, the entire process leading to the conducting film appears to be dominated by the tendency of salts **1** to **7** to form dimers and to crystallize on the water subphase. The crystalline structures that are formed have room enough in the polar planes for the TCNQ species to rearrange after iodine diffusion and reaction.

The lack of infrared conductivity in the films of **11** likely can be explained as follows. The phenanthrolinium cation bears two positive charges and is associated to two $TCNQ^-$ anions. At the surface pressure used for transferring the films (30 mN/m) the area occupied by a single complex is about 80 Å^2. It is quite consistent with a sandwich type association as shown in Fig. 2a. According to linear dichroism data, the vertical arrangement of the $TCNQ^-$ molecular planes is preserved in the transferred films. The resulting structure of the polar planes is composed of $(TCNQ^-)_2$ dimers lying on edge and effectively isolated from each other by the phenanthrolinium cations (Fig. 2b).

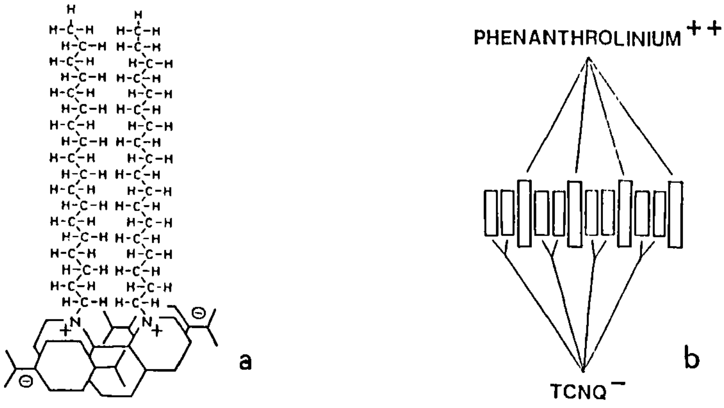


FIGURE 2 Model structures for (a) association of **11** with $TCNQ^-$ anions on the water subphase and (b) polar planes of the transferred films.

Upon iodine exposure, $TCNQ^-$ anions are oxidized but segregated donor and acceptor stacks cannot form and no conducting behavior is observed. A similar explanation can be tentatively proposed for the failure to observe conductivity after iodination of the films of **10**. Also in this case the TCNQ$^-$ anions have their molecular planes on edge in the polar planes of the precursor film but, at variance with the previous case, the UV–visible spectra show that monomers and dimers are present with a concentration ratio close to unity.[10] This is readily understood if we assume that before compression of the floating films each TCNQ$^-$ anion is bound to a dithiolium cation to form an ionic pair. On compressing the films, aggregation of these pairs occurs randomly leading to a mixture of isolated monomers and dimers separated from each other by dithiolium cations. The formation of conducting segregated stacks after iodination is thus prevented. In our proposed explanation, what is common to both the films of **10** and **11** is a weaker tendency to form (TCNQ$^-$)$_2$ dimers and to crystallize on the water subphase compared to the films of **1** to **7**. It is also worth noting that the salts of **10** and **11** yield very stable floating films. The behavior of the films of **8** and **9** is less clear. In particular, the origin of the structural disorder and the nature of the macroscopic aggregates observed for the films of **9** remain to be clarified.

According to the above arguments, one key factor in determining the different behavior of the films reported here is the competition between two forms of molecular association on the water subphase: (i) formation of (TCNQ$^-$)$_2$ dimers and subsequent crystallization and (ii) formation of ionic pairs favored by a stronger interaction of the TCNQ$^-$ anions with the cations and/or by steric factors. From Tables I and II and the reported data it is apparent that the first type of aggregation occurs with the smaller cations. Whether the second type of aggregation is favored with the larger cations owing to their size or their extended π-electron conjugation cannot be said with the available data. To confirm our suggested explanation, one key experiment to carry out would be measuring the UV–visible spectra of the floating films as a function of surface pressure. We also note that, with respect to the criteria given above, the behavior of the films of **8** is the least understood.

As for the failure to observe reproducible significant d.c. conductivity for the films of **1** to **5**, i.e. the salts with very small cations, we suggest that this is related to the instability of the floating films and the inhomegeneous nature of the deposited ones. The mechanical properties of the films of **1** to **4** are considerably improved by adding octadecylurea as a matrix forming species but this is likely to introduce microscopic disorder that limits the d.c. transport. Despite this, the microscopic conductivity, as estimated from the frequency location of the A–type CT transition, is higher for these materials than for films of **6** and **7**. This shows that, within the group of films displaying conducting behavior, the level of microscopic conductivity is affected by the nature of the cation.

CONCLUSIONS

Some structure–property relationships have been worked out for conducting LB films based on TCNQ salts. Formation of a three–dimensionally ordered phase containing (TCNQ$^-$)$_2$ dimers with their molecular planes parallel to the substrate has been found to be the primary structural requirement for observing conductivity. Upon treatment with iodine, this type of structure allows the necessary remarkable molecular reorganization of the films to occur. The effect of the size and degree of π–electron conjugation of the cation on the stability of this three–dimensionally ordered phase has been investigated. The two related processes leading to conducting films, namely crystallization at the air/water interface and molecular rearrangement upon iodination, are observed only for the salts with relatively small cations. The same type of crystallization does not occur with cations of larger dimensions and more extended π–electron systems. This is likely due either to a stronger anion–cation association on the water subphase or to steric factors.

It should be pointed out that the arguments presented in this paper are based on empirical correlations between the observed macroscopic behavior of the films and on a very incomplete knowledge of their structural properties. More detailed information on the latter should be made available before attempting to answer some basic questions such as why is a particular arrangement of $(TCNQ^-)_2$ dimers required for switching to a conducting state and what role is played by the dynamical behavior of the films during exposure to iodine. From a more practical point of view, improvements on the macroscopic structural properties of the films with small cations are needed in order to enhance their d.c. conductivity.

ACKNOWLEDGMENTS

We gratefully acknowledge support by EURAM contract MA 1E 0034C (CD).

REFERENCES

1 A. Ruaudel–Teixier, M. Vandevyver, and A. Barraud, Mol. Cryst. Liq. Cryst., **120**, 319 (1985).

2 J.B. Torrance, Acc. Chem. Res., **12**, 79 (19879).

3 J. Richard, M. Vandevyver, P. Lesieur, A. Ruaudel–Teixier, A. Barraud, R. Bozio, and C. Pecile, J. Chem. Phys., **86**, 2428 (1987).

4 B. Belbeoch, M. Roulliay, and M. Tourharie, Thin Solid Films, **134**, 89 (1985).

5 A. Barraud, M. Flörsheimer, H. Möhwald, J. Richard, A. Ruaudel–Teixier, and M. Vandevyver, J. Coll. Interf. Sci., **121**, 491 (1988).

6 M. Vandevyver, J. Richard, A. Barraud, A. Ruaudel–Teixier, M. Lequan, R.M. Lequan, J. Chem. Phys., **87**, 6754 (1987).

7 C.S. Jacobsen, I. Johanssen, and K. Bechgaard, Phys. Rev. Lett., **53**, 194 (1984).

8 J. Richard, PhD Thesis, Universite Paris VI, Paris, 1987.

9 J. Richard, M. Vandevyver, P. Lesieur, A. Barraud, and K. Holczer, J. Phys. D, **19**, 2421 (1986).

10 M. Vandevyver, J. Richard, A. Barraud, M. Veber, C. Jallabert, and H. Strzelecka, J. Chim. Physique, **85**, 385 (1988).