CHEMISTRY LETTERS, pp. 871-874, 1991.

New Langmuir-Blodgett Films Based on Substituted 1,2-Dithiolium-TCNQ Radical Anion Salts

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Based upon the synthesis of 3,4,5-tris(alkylthio)-1,2-dithiolium cation salts, we have realized new Langmuir-Blodgett films. They present either a centrosymmetrical or noncentrosymmetrical bilayer organization depending on the involved molecular association with iodine, tetracyanoquinodimethane or some other radical anion.

The control of the supramolecular organization in the condensed states for obtaining valuable or new physical properties is currently a general aim.[1] Under this general frame to construct a system with suitable arrangement of molecules, the Langmuir-Blodgett (LB) technique is one of the most powerful tools.[2] Recently, it has been a considerable interest in using the LB technique to organize donor and/or acceptor molecules, with the intention to produce conducting or opto-electronic molecular films. A variety of papers have been published on conducting LB films consisting of TCNQ radical anion salts associated with amphiphilic cations,[3-6] alkylammonium-metal(dmit)$_2$ complexes,[7,8] several TTF derivatives[9-12] with different amphiphilic characters. It has been reported in particular, that the 3,5-diaryl-1,2-dithiolium salts associated with diamagnetic anions (ClO_4^-,BF_4^-), as well as with paramagnetic ones ($TCNQ^-$) build up LB films of remarkable quality.[13]

In the present paper, we report the synthesis of 3,4,5-tris(alkylthio)-1,2-dithiolium cation salts, where at least one of the alkylthio substituent is an octadecyl aliphatic chain, and the preliminary results about the observation of a stable floating monolayer and the LB film formation of their iodine and TCNQ salts.

The scheme 1 shows the reactions involved in the synthesis of 3,4,5-(alkylthio)-1,2-dithiolium salts. Compound 1 was obtained as a red solid by the thermal isomerization (140 °C in DMF) of 1,3-dithiole-2-thione-4,5-dithiolate (1)[14,15] obtained from reaction i) (0 °C for 6 h then 12 h at room temperature). When 1 was reacted with n-octadecyl bromide under acetone reflux, a yellow solid was precipitated. Purification by column chromatography (SiO_2, $CHCl_3$/cyclohexane 1:1, R_f=0.6) gave 4,5-bis(octadecylthio)-3-thione-1,2-dithiole 2 (yield 80%, mp 86 °C).

Compound 2 was reacted with methyl iodide under reflux in acetone and the yellow precipitate was recrystallized from acetonitrile to obtain 4,5-bis(octadecylthio)-3-methylthio-1,2-dithiolium iodide 3 (yield 72%, mp 124 °C). 4,5-Bis(methylthio)-3-thione-1,2-dithiole 4 was obtained after reaction of dithiolate 1 with methyl iodide in acetone at 0 °C for 15 minutes. The nonreacted 1 was eliminated by filtration and the reaction product was purified by column chromatography (SiO_2,$CHCl_3$/cyclohexane 1:1, R_f=0.6) (yield 60%, mp 99 °C[15]).

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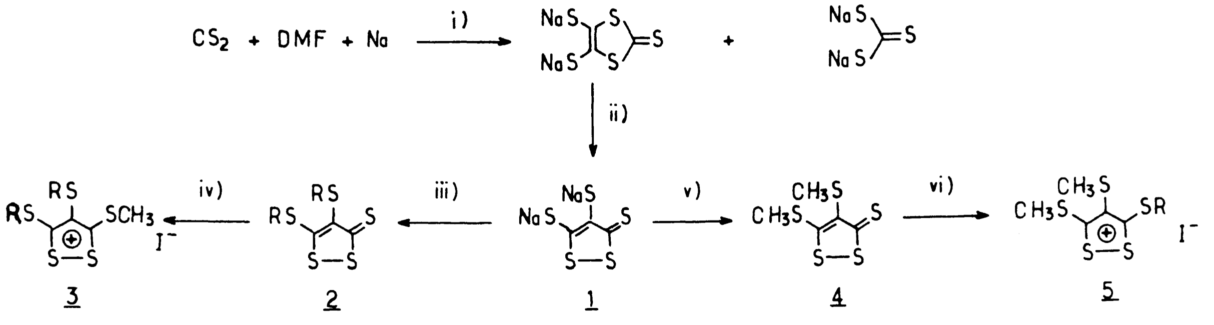


Scheme 1.

Thione 4 was refluxed with n-octadecyl iodide in cyclohexanone for 24 h to obtain, after recrystallization from acetone, brown 4,5-bis(methylthio)-3-octadecylthio-1,2-dithiolium iodide 5 (yield 20%, mp 179 °C).

In a second step, the 1,2-dithiolium iodide 3 was reacted with Li^+TCNQ^- and neutral TCNQ to obtain 1,2-dithiolium-TCNQ (1-1) radical anion salt 3a and 1,2-dithiolium-$(TCNQ)_2$ (1-2) mixed valence radical anion salt 3b respectively.

A summary of the Langmuir experiments carried out on a commercial KSV-5000 trough is presented on the Table 1. The preparation of the Langmuir monolayers is as described previously[10)] with chloroform as a spreading solvent. The compression isotherms (Fig. 1) for salts 3, 3a,and 3b present collapses at surface pressures higher than 30 mN/m and areas per molecule are respectively 43 Å^2 for 3, 58 Å^2 for 3a and 50 Å^2 for 3b. These supposed monolayers were deposited by the classical vertical lifting method onto quartz slides and CaF_2 polished plates, for visible-UV and ESR characterizations respectively.

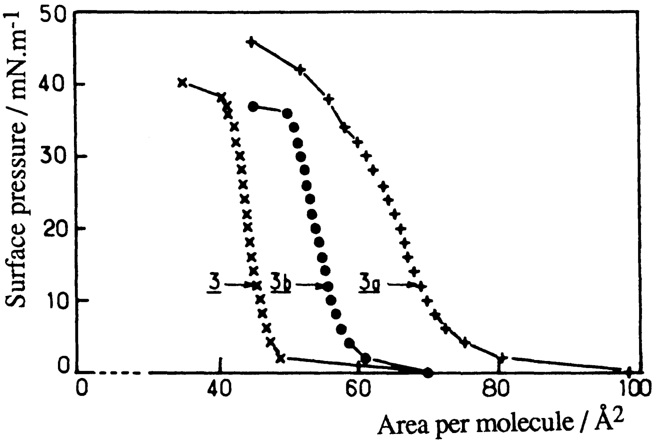


Fig. 1. Compression isotherms obtained at 20 °C with millipore grade pure water used as the subphase.

The LB films were prepared at a surface pressure of 30 mN/m with an effective upward transfer ratio of 1 resulting in a Z-type transfer for 3a and 3b but classical Y-type for 3 as demonstrated by the X-ray diffraction analysis (see Table 1 for the layer spacing d measured with an accuracy ± 1 Å).

The electronic absorption spectra of these compounds were presented on Fig. 2. Concerning powder in diluted KBr pellets, we observed for 3 two intense bands at 26300 and 41800 cm^{-1} whereas for the TCNQ salts new electronic bands were detected at lower frequencies :

- the charge transfer band at 3400 cm^{-1} characteristic of a mixed valence state (so-called Torrance's A band [16)]) for 3b.

- several bands around 11000-13000 cm^{-1} which can be both a charge transfer band between ionized states (Torrance's B band [16)]) and intramolecular excitations of $TCNQ^-$ monomers.[17)]

The comparison with the spectra obtained for the LB films gives useful information. For 3b the A band is

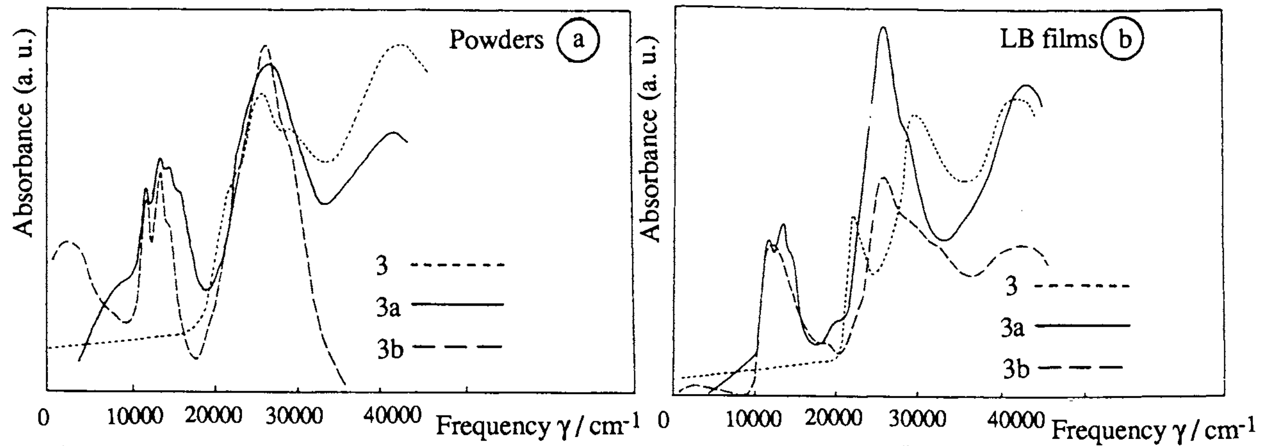


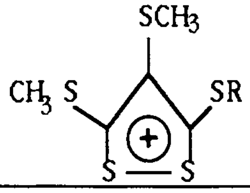
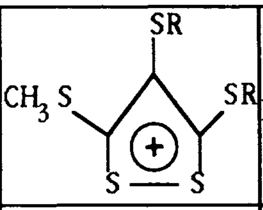
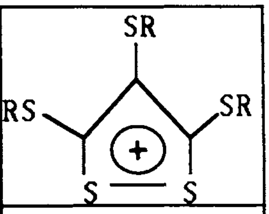
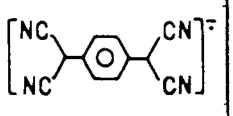
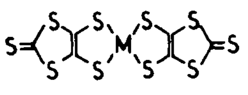
Fig. 2. Electronic absorption spectra of compressed powders (a) and LB films (b) at room temperature.

disappearing but the B band is enlarged, which means that the mixed valence state has been suppressed because, perhaps, of partial solubility of TCNQ in water. Indeed a change of ESR linewidth has been observed confirming this valence state change. For 3a, we observed above 10000 cm^{-1} the same absorption bands as in the polycrystalline compound. Preliminary ESR experiments have showed a characteristic signal of $(TCNQ^-)$; it turns out therefore that we are rather in presence of monomers absorption bands around 11000-13000 cm^{-1}. 17)

Table 1. Summary of molecules and LB films

Hydrophobic character increase →

Hydrophilic character increase ↓

Cation / Anion			
 TCNQ$^{\cdot -}$ a)	c)	LB films Z-type | 3a | 3b stoec. | (1-1) | (1-2) X-Ray (d) | 44 Å | 42 Å	c)
Iodine I$^-$	No Langmuir monolayers π_c - 9 mN/m d)	LB films Y-type from X-Ray d - 56 Å	c)
 [M(dmit)$_2$]$^-$ b)	c)	M - Ni No Langmuir monolayers π_c - 10 mN/m d)	c)

R = $C_{18}H_{37}$. a) Possibility of using $TCNQF_4$ instead of TCNQ. b) M= Ni or Au for the dithiolenes. c) The empty squares indicate that these compounds are under investigation. d) π_c is the pressure collapse.

Besides on these LB films of (1-1) TCNQ we also attempted iodine gas oxidation which proceeded towards complete neutral TCNQ molecules whithout any valuable electrical conductivity. A new class of salts has been synthesized which opens several ways to prepare LB films by substituting a third aliphatic chain and by varying their length. We have observed the importance of balance between the hydrophobic and hydrophilic parts for getting a stable monolayer and a specific transfer type (see Table 1). This point is connected with the in situ molecular organization, different for 3a and 3b, currently under investigation by ellipsometry, IR and fluorescence studies.18) A rule of thumb which takes into account the steric effect and the hydrophobic / hydrophilic characters is a necessary objective to build up molecular assemblies with tailored physical properties associated with centrosymmetrical or not bilayer stacking,which could be valuable for non-linear optics.

References

1) See for instance NATO Advanced study institute "Lower Dimensional Systems and Molecular Electronics," ed by R.M.Metzger, Plenum Press (1991).
2) D.Mobius, *Acc.Chem.Res.*, **63**, 14 (1981).
3) A.Ruaudel-Teixier, M.Vandevyver, and A.Barraud, *Mol.Cryst.Liq.Cryst.*, **120**, 319 (1985).
4) J.Richard, M.Vandevyver, P.Lesieur, A.Ruaudel.Teixier, A.Barraud, R.Bozio, and C.Pecile, *J.Chem.Phys.*, **86**, 2428 (1987).
5) M.Matsumoto, T.Nakamura, F.Takei, M.Tanaka, T.Sekiguchi, M.Mizuno, E.Manda, and Y.Kawabata, *Synth.Metals*, **19**, 675 (1987).
6) A.S.Dhindsa, M.R.Bryce, J.P.Lloyd, and M.C.Petty, *Synth.Metals*, **22**, 185 (1987).
7) T.Nakamura, H.Tanaka, K.Kojima, M.Matsumoto, H.Tachibana, M.Tanaka, and Y.Kawabata, *Thin Solid Films*, **179**, 183 (1989).
8) T.Nakamura, M.Matsumoto, H.Tachibana, M.Tanaka, Y.Kawabata, and Y.Miura, *Proceedings, ICSM'90,* Tubingen 2-7 Sept.1990.
9) J.Richard, M.Vandevyver, A.Barraud, J.P.Morand, P.Delhaès, J.F.Jacquinot, and M.Roulliay, *J.Chem.Soc., Chem.Commun.*, 754 (1988).
10) C.Lalanne, P.Delhaès, E.Dupart, C.Garrigou.Lagrange, J.Amiell, J.P.Morand, and B.Desbat, *Thin Solid Films*, **179**, 171 (1989).
11) A.S.Dhindsa, M.R.Bryce, J.P.Lloyd, and M.C.Petty, *Thin Solid Films*, **165**, L97 (1988).
12) M.Vandevyver, M.Roulliay, J.P.Bourgoin, A.Barraud, V.Gionis, V.C.Kakoussis, G.A.Mousdis, J.P.Morand, and O.Noel, *J.Phys.Chem.*, **95**, 246 (1991).
13) M.Vandevyver, J.Richard, A.Barraud, M.Veber, C.Jallabert, and H.Strzelecka, *J.Chim.Phys.*, **85**, 385 (1988).
14) G.Steimecke, H.J.Sieler, R.Kirmse, W.Dietzsch, and E.Hoyer, *Phosphorus Sulfur*, **12**, 237 (1982).
15) G.C.Papavassiliou, *Chem.Scr.*, **25**, 167 (1985) and **27**, 261 (1987).
16) J.B.Torrance, B.A.Scott, and F.B.Kaufman, *Solid State Commun.*, **17**, 1369 (1975).
17) J.B.Torrance, B.A.Scott, B.Welber, F.B.Kaufman, and P.E.Seiden, *Phys.Rev. B*, **19**, 730 (1979).
18) O.Fichet, V.Gionis, P.Delhaès, A.Perrier, D.Ducharme, and R.Leblanc *(work in progress).*

(Received January 17, 1991)